PREPARATIVE AND SPECTROSCOPIC STUDIES OF SOME PHOSPHORUS (V) CHLORIDE AND BROMIDE DERIVATIVES

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ABSTRACT

Further preparative and Raman spectroscopic investigations of products derived from reactions of phosphorus (III) halides, boron trihalides and halogens have been made. A new compound of empirical formula P_2BCl_{13} has been formulated as $[PCl_4^+{}_2][BCl_4^-][Cl^-]$ and may be considered as the parent of a series involving the $[PCl_nBr_{4-n}^+]$ ($0 \leqslant n \leqslant 4$) cations. The structural implications of the proposed single halide anions and the relationship of the compounds to metastable PCl_5 (Phase III) is discussed; changes which occur on heating have been monitored by Raman and magic angle rotation NMR spectroscopy. A further compound analogous to P_2Cl_9Br has been reported.

The compounds $MePCl_4$, Me_2PCl_3 and Me_3PCl_2 were prepared and Raman and ^{31}P magic angle rotation NMR measurements support ionic formulations containing single halide ions. Complexes of these with Lewis acids were made and the characteristic shifts associated with the presence of single halide ions in the Raman spectra of the phosphonium cations were observed. Mixed chlorobromo cations of these methylphosphoranes were prepared and their Raman spectra partially assigned.

Conventional matrix isolation as well as low temperature sublimation experiments were performed on the vapours above PCl_5, PBr_5 and $MePCl_4$. Monomeric species were observed for both PCl_5 and $MePCl_4$ but decomposition occurred with PBr_5. In these studies Raman spectra were monitored from 15K to ambient temperatures and the conversion of covalent to ionic species was observed.

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DEDICATION

To Barbara Jean and Ronald Stephen

– my parents

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CHAPTER 1

THE PHOSPHORUS (V) HALIDES

1.1 INTRODUCTION

The phosphorus (v) halides exhibit a fascinating variety in their structures amongst both the single halogen and mixed halogen substituted species. Phase changes often produce some significant structural changes and there is also a potentially large number of isomeric possibilities amongst the mixed halogen compounds. This has led to much interest in such systems since the solid state structures of phosphorus pentachloride and pentabromide were first determined in the early 1940's.

1.1.a SINGLE HALOGEN PENTAHALIDES

Phosphorus pentafluoride, pentachloride and pentabromide are well known and their properties well documented (1-7). Also, more recently, a claim for the preparation of the pentaiodide has appeared (8).

Gaseous phosphorus pentafluoride has been shown by electron diffraction (9) to have a trigonal bipyramidal structure (D_{3h} symmetry) and this is supported by vibrational spectroscopy (10) and ^{19}F NMR (11). Further studies have shown that the axial bonds are slightly longer than the equatorial bonds (12-16) and ^{19}F NMR indicates a rapid exchange rate of these non-equivalent fluorine atoms (17). Phosphorus pentafluoride has been observed in the solid state under pressure but nothing is known of its structure (18). The Raman spectrum of condensed PF_5 vapour at 80K has been recorded and a D_{3h} structure is indicated (90). The present work is primarily concerned with phosphorus pentachloride and pentabromide and a more detailed consideration of the pentafluoride will not be given here.

In the gas phase, phosphorus pentachloride exists as a trigonal bipyramidal monomer (D_{3h} symmetry) which is in equilibrium with phosphorus trichloride and chlorine (19-26). This latter dissociation occurs to the extent of 13.5% at 160°C and is negligible at 25°C (27). The structure of this molecule was established by X-ray diffraction (28,29) and electron diffraction (30) with confirmatory evidence from infra-red (31) and Raman spectroscopy (32). The presence of this species is also indicated as phosphorus pentachloride melts (33,34,35,36). Mass spectrometric evidence on the gas phase suggests that there may be some association to give P_2Cl_{10} units which are probably doubly condensed octahedra (37,38).

In the solid state phosphorus pentachloride is a pale yellow crystalline compound which has been shown by single crystal X-ray diffraction to consist of PCl_4^+ and PCl_6^- units disposed in a tetragonal arrangement (39,40,41). The P-Cl bond length is greater in the octahedral anion (2.04Å equatorial, 2.08Å axial) than in the tetrahedral cation (1.96Å). This may account for the preferential fluorination of the anion in some reactions (42) and also the results of radioactive exchange experiments in which exchange with the anion occurs faster than with the cation (43).

The infra-red and Raman spectra of solid phosphorus pentachloride have been much studied (44-46) and provide text book examples of the spectra of isolated tetrahedral PCl_4^+ and octahedral PCl_6^- ions, fully consistent with the X-ray work. The presence of these two species is easily recognised in the solid state ^{31}P NMR spectra (49-51) with two widely separated chemical shifts (+88.3 ppm (PCl_4^+), -299.7 (PCl_6^-) relative to 85% H_3PO_4).

It has been shown by both infra-red (46) and Raman spectroscopy (52) that when phosphorus pentachloride vapour is condensed onto a cold surface at about 80K a solid consisting of the covalent trigonal bipyramidal species is obtained and that on warming this irreversibly transforms to the $PCl_4^+PCl_6^-$ modification. ^{35}Cl NQR (53,54) and heat capacity measurements (55) show similar behaviour.

$PCl_4^+PCl_6^-$ is not, however, the only documented solid state isomer of phosphorus pentachloride. In 1956, Popov et al (56) prepared a sample of phosphorus pentachloride by sublimation whose X-ray diffraction pattern differed from that of the "normal" crystalline form. In a review article Payne reports (3) "Samples of phosphorus (v) chloride obtained from a solvent such as carbon tetrachloride or by sublimation are found to give powder patterns different from those found with material crystallised from nitrobenzene". A Raman spectrum of some sublimed phosphorus pentachloride (57) was found to differ markedly from that of $PCl_4^+PCl_6^-$ with the intensity of the four fundamentals assignable to the PCl_4^+ cation being considerably greater than the three associated with the PCl_6^- anion. Variable temperature Raman studies by Shore (61a) and later D.S.C. observations (61b,61c,156) indicated that this new form of phosphorus pentachloride transformed on heating to the normal and abundantly confirmed $PCl_4^+PCl_6^-$. This behaviour resulted in the new phase acquiring the name "metastable phosphorus pentachloride". More recently in a series of reports by Whalley and co-workers (58-60), the behaviour of normal phosphorus pentachloride (Phase II) under high pressures was investigated by solid state ^{31}P NMR and Raman spectroscopy. The presence of a species $2PCl_4^+PCl_6^-Cl^-$ (Phase III) was inferred as distinct from the normal Phase II modification ($PCl_4^+PCl_6^-$). They speculated that this resulted from the dissociation of a hexachlorophosphate ion in the following manner:-

$$PCl_6^- \longrightarrow PCl_4^+ + 2Cl^-$$

and that this type of complex halide single halide dissociation might be representative of a general class of solid-state reactions. The Raman spectrum of this Phase III modification was the same as that obtained by Baumgartner et al (57) on a sublimed sample of phosphorus pentachloride. Also at ambient temperatures Phase III was observed to convert slowly to Phase II (58-60), the same result as observed by earlier studies on "metastable PCl_5" (61a). Thus it is reasonable to assume that "metastable PCl_5" and Phase III are the same and may be formulated as $2PCl_4^+PCl_6^-Cl^-$.

The behaviour of phosphorus pentachloride in solution is strongly dependent upon the nature of the solvent. In solvents such as benzene, carbon disulphide and carbon tetrachloride it has been shown by infra-red and Raman spectroscopy and also cryoscopy that molecular phosphorus pentachloride of D_{3h} symmetry exists, as in the gas phase (29,31,35,46, 62,63). The presence of the monomer in carbon tetrachloride solution has enabled radioactive tracer experiments to demonstrate the non-equivalence of the apical and equatorial chlorine atoms (64,65). However, in polar solvents such as acetonitrile and nitrobenzene phosphorus pentachloride is electrically conducting (66,67) and although most early workers agreed that the tetrachlorophosphonium cation (PCl_4^+) was present in such solutions the presence of the hexachlorophosphate anion (PCl_6^-) was a source of dispute (48,66,68,69,70). This was resolved by Shore's group (63) who, via Raman spectroscopy and cryoscopy, have provided evidence for two competing equilibria illustrated below and showed that (2) predominated at lower concentrations.

1) $2PCl_5 \rightleftharpoons PCl_4^+ + PCl_6^-$

2) $PCl_5 \rightleftharpoons PCl_4^+ + Cl^-$

Other phosphorus pentachloride/solvent systems of particular interest in this study are anyhydrous liquid hydrogen chloride and arsenic trichloride. In the former, solution Raman studies have shown complete ionization to occur (36) as

$$PCl_5 + HCl \longrightarrow PCl_4^+ + HCl_2^-$$

and this is supported by ^{31}P NMR studies in the same solvent (160).

In the latter the process is more uncertain. Conductivity titrations of such a solution with tetramethylammonium chloride solution have indicated chloride ion transfer to the solvent (71) suggesting the reaction

$$PCl_5 + AsCl_3 \longrightarrow PCl_4^+ \ AsCl_4^-$$

although from a solution of phosphorus pentachloride in arsenic trichloride an adduct P_2Cl_{10}-$5AsCl_3$ may be obtained which is based upon a $PCl_4^+PCl_6^-$ lattice with the $AsCl_3$ as molecules of crystallisation (72).

Structurally phosphorus pentabromide is very different from the pentachloride. In the gas phase there is no evidence for the existence of monomeric PBr_5 molecules; vapour-pressure measurements (73,74) on the species above solid phosphorus pentabromide suggest complete dissociation into phosphorus tribromide and bromine, at least above 305K.

In the solid state, phosphorus pentabromide is an orange-yellow crystalline compound which has been shown by single crystal X-ray diffraction to consist of PBr_4^+ and Br^- units disposed orthorhombically (75-77). The average P-Br bond length is 2.15Å whilst the Br^-....Br non bonding distance is 3.12Å.

Raman spectroscopy has supported this observation with the characteristic four-band spectra of a tetrahedral species (78,79). The solid state ^{31}P NMR spectrum of phosphorus pentabromide produces a single resonance at -104 ppm (relative to 85% H_3PO_4) (164) which again is consistent with the presence of PBr_4^+ as the only phosphorus-containing moiety.

The behaviour of phosphorus pentabromide in solution is more contentious. A molecular weight study in benzene and phosphoryl chloride indicated complete molecular dissociation in the former and electrolytic dissociation in the latter (80). The molecular dissociation in carbon tetrachloride was shown colorimetrically and spectrophotometrically to be close to 90% (81,82) but a further study of this system, together with solutions in carbon disulphide, ethylene chloride and phosphorus tribromide, revealed an even lower percentage of dissociation (83). Transport experiments in acetonitrile showed phosphorus pentabromide to be an electrolytic conductor and PBr_4^+ and PBr_6^- were postulated as the ionic species present (6,84). A review article (3) quoted a report that the ^{31}P NMR spectrum of $PBr_4^+Br^-$ in CS_2 solution indicated the presence of a distinct species (85), although the current Raman study suggests that only PBr_3 and Br_2 are formed. However, more recent ^{31}P NMR studies of phosphorus pentabromide in a wide variety of non polar solvents has not indicated the presence of any ionic species, but only phosphorus tribromide - one of the molecular dissociation products (86).

Phosphorus pentaiodide is not well documented. It was reported in a textbook as being "a dark red prismatic substance" but no details were given (87). More recently a synthesis from phosphorus pentachloride and alkali metal iodides in methyl iodide was reported (8) and some reactions were discussed. No structural date were given but the conclusions drawn from cryoscopy and ^{31}P NMR in methyl iodide suggested an ionic structure $PI_4^+I^-$, similar to $PBr_4^+Br^-$. However, other ^{31}P NMR solution data has indicated a decomposition into phosphorus triiodide and iodine with no evidence for any ionic or molecular phosphorus (V) species (88).

1.1.b MIXED -HALOGEN PENTAHALIDES

The most rigorously investigated mixed-halogen pentahalides of phosphorus are the chlorofluorides (4,5,89). Holmes and co-workers prepared the series of molecular phosphoranes PCl_nF_{5-n} $(n<1<5)$ (91-95) and this and other studies using electron diffraction (9), ^{19}F NMR (96-98), and vibrational spectroscopy (99,100) indicated trigonal bipyramidal structures with fluorine atoms axially disposed where-ever possible. The respective symmetries are therefore PCl_4F (C_{3v}), PCl_3F_2 (D_{3h}),

PCl_2F_3 (C_{2v}) and $PClF_4$ (C_{2v}).

Ionic modifications of the chlorofluorophosphoranes are known and these often result from the molecular forms on standing at ambient temperatures.

The ionic modification of tetrachlorofluorophosphorane was initially formulated as $PCl_4^+F^-$ mainly on the basis of molecular weight determinations (101). Subsequent measurements suggested the presence of a $PCl_4F_2^-$ anion (102), a species independently characterised as the caesium salt (103), and the formulation $PCl_4^+PCl_4F_2^-$ and $PCl_4^+F^-$ though later spectroscopic and analytical data showed the latter to be incorrect (105).

Trichlorodifluorophosphorane has been studied in the ionic form and ^{31}P NMR indicates the formulation $PCl_4^+\ PCl_2F_4^-$ (106).

Dichlorotrifluorophosphorane PCl_2F_3, is known in an ionic form. ^{31}P NMR indicates the presence of both PCl_4^+ and PF_6^- (52) ions and this observation is supported by vibrational spectroscopy (107). The compound $PCl_4^+PF_6^-$ may be prepared by fluorinating phosphorus pentachloride with arsenic trifluoride in arsenic trichloride (42) and the powder X-ray diffraction pattern is identical to that of a sample derived from molecular PCl_2F_3 (99).

There are currently no reported data on an ionic isomer of chlorotetrafluorophosphorane although a compound of stoichiometry P_2Cl_9F has been prepared and electrolytic (37) and mass spectrometric studies (38) suggest the structure $PCl_4^+PCl_5F^-$.

The bromofluorides of phosphorus (V) have not been investigated so thoroughly although all members of the series are known. Tetrabromofluorophosphorane has been prepared and an ionic modification formulated as $PBr_4^+F^-$ (108) but this is by no means certain (6). Tribromidifluorophosphorane is known only in the molecular form (109): a trigonal bipyramidal structure for dibromotrifluorophosphorane is consistent with ^{19}F NMR (97) and vibrational spectra (100) although an ionic form is also known. This has the structure of $PBr_4^+ PF_6^-$ (indicated by ^{31}P NMR (52) and Raman spectroscopy) (110) and is prepared by fluorination of phosphorus pentabromide (112). Bromotetrafluorophosphorane has so far only been reported in a molecular form (98), as indicated by ^{31}P NMR and infra-red spectroscopy.

No evidence is available for the existence of chlorobromofluorides or fluoroiodides of phosphorus (V) in any modification.

The phosphorus (V) chlorobromides have been subject of many investigations over a period of years, but much of the data obtained are inconclusive and only two well-defined compounds are reported:-

$PCl_{4.5}Br_{0.5}$ and $PCl_{4.66}Br_{0.33}$

The yellow crystalline compound $PCl_{4.5}Br_{0.5}$ (hereafter referred to as P_2Cl_9Br) was prepared by the reaction of phosphorus trichloride and bromine in arsenic trichloride (112) and was originally formulated as $PCl_4^+ PCl_5Br^-$ because $PCl_4^+PF_6^-$ was the product of fluorination of phosphorus trichloride and phosphorus pentachloride. A subsequent study showed this to be inaccurate and a formulation $6PCl_4^+ 2PCl_3Br^+ 4PCl_6^- 4Br^-$

was proposed on the basis of ^{31}P NMR, X-ray powder diffraction and vibrational spectroscopy (113). Simple bromination of phosphorus trichloride produced an unstable aggregate analysing as $PCl_3Br_{5.7}$ which was converted by pumping to a yellow powder $PCl_{4.8}Br_{0.4}$. Upon sublimation at 50°C this yielded the compound $PCl_{4.60}Br_{0.33}$, shown by X-ray diffraction to be a unique phase with a face-centred cubic unit cell (58). From these date alone a reasonable formulation of $8PCl_4^+4PCl_6^-4Br^-$ per unit cell was suggested. All other investigations of the phosphorus trichloride/bromine system have given inconsistent results though in general the reaction is thought to produce either some or all of the compounds of the general formula: PCl_4Br, $PCl_3(Br_2)_n$ and $PCl_3Br\ Br(Br_2)_n$ (n = 4 to 10).

In Table 1 a chronological list and summary of these studies is given although much of the work appears to be contradictory and has proved irreproducible.

Attempts to prepare phosphorus (V) chlorobromides by the mutual reaction of the tri and pentabromides and chlorides have also been reported (117,119,122-125). The products are generally the same as those produced by the phosphorus trichloride/bromine system though it was specifically claimed that PBr_4Cl was the product of i) phosphorus pentachloride and excess phosphorus tribromide (117) and ii) phosphorus trichloride and excess phosphorus pentabromide (120). More recently Gabes et al (126) reacted phosphorus pentachloride and phosphorus tribromide in a 4:3 ratio, re-crystallised the product from carbon disulphide, and

TABLE 1

INVESTIGATIONS OF THE PHOSPHORUS TRICHLORIDE/BROMINE SYSTEM

1872 Prinvault	$PCl_3 + Br_2 \longrightarrow PCl_3Br_2$
ref 114	$PCl_3 + Br_2 \longrightarrow PCl_3Br_8$
	$PCl_3Br_8 + PCl_3 \longrightarrow PCl_3Br_4$
	$PCl_3Br_8 \xrightarrow{\Delta} PCl_2Br_7$
	$PCl_2Br_7 + PCl_3 \quad PCl_4Br$
1872 Michaelis	$PCl_3 + Br_2 \xrightarrow{\text{low temp}} PCl_4Br_2$
ref 115	$PCl_3 + Br_2 \longrightarrow PCl_3Br_4$
	$PCl_3Br_2 \xrightarrow{\Delta}$ 2 layers
	lower layer + $PCl_3Br_2 \longrightarrow PCl_3Br_4$
	$PCl_3Br_4 + Br_2 \longrightarrow PCl_3Br_8$
1886 Stern	$PCl_3 + Br_2 \longrightarrow PCl_3Br_2$
ref 116	$PCl_2Br_3 + Br_2 \longrightarrow PCl_2Br_5$
1928 Milobedzki and Krakowieki	$PCl_3 + Br_2 \longrightarrow PCl_3Br_2$
ref 117	$PCl_3 + Br_2 \longrightarrow PCl_4Br$
1930 Milobedzki and Krakowieki	$PCl_3 + Br_2(\text{var}) \longrightarrow PCl_4Br + PCl_2Br_5 +$
	Phase I (brown)
	$PCl_3 + Br_2$ (in vapour) $\longrightarrow$ Phase II (red)
	Phase I + Phase II $\xrightarrow{\text{pump}} PCl_4Br$
	Phase I = $PCl_{3.439}Br_{4.677}$ to PCl_3Br_{20}
	Phase II = Halogen:Phosphorus 7.1 to 8.6:1

TABLE 1 (continued)

1933 Renc ref 119	$PCl_3 + Br_2 \xrightarrow{} PCl_4Br$ $PCl_4Br \xrightarrow{\Delta} PCl_{4.5}Br_{0.5}$
1951 Fialkov and Kuzmenko ref 120	$PCl_3 + Br_2 \xrightarrow{} PCl_3Br_4$ and PCl_3Br_{18}
1952 Fialkov and Kuzmenko ref 121	$PCl_3 + Br_2 \xrightarrow{} PCl_3Br_8$ (not isolated)
1956 Popov, Geske and Baenziger ref 56	$PCl_3 + Br_2 \xrightarrow{} PCl_3Br_{5.7}$ $PCl_3Br_{5.7} \xrightarrow{\text{pumped}} PCl_{4.8}Br_{0.4}$ $PCl_{4.8}Br_{0.4} \xrightarrow{\text{sublimed}} PCl_{4.66}Br_{0.33}$
1957 Kolditz and Feltz ref 112	$PCl_3 + Br_2 \xrightarrow{AsCl_3} P_2Cl_9Br$

gently subjected it to a vacuum until a yellow powder was formed. Analysis was correct for the stoichiometry PBr_4Cl and the Raman spectrum indicated an ionic structure, $PBr_4^+Cl^-$, shown by powder X-ray crystallography to be isomorphous with $PBr_4^+Br^-$.

No pure phosphorus (V) chlorobromides other than P_2Cl_9Br, $PCl_{4.66}Br_{0.33}$ and $PBr_4^+Cl^-$ have been reported and, unlike the chlorofluorides and bromofluorides, no molecular forms have ever been isolated.

A number of phosphorus polyhalides exist; the only single halogen polyhalides being the polybromides. At least two phosphorus polybromides are known:- PBr_7 and PBr_{17} (6,84,127,128), although the structure of the latter has never been fully elucidated. Phosphorus heptabromide has been investigated by single crystal X-ray crystallography (129) and shown to consist of tetrahedral PBr_4^+ ions and almost linear, but unsymmetrical, Br_3^- ions. The higher halogen content polyhalides (PBr_{17}, various products of the PCl_3/Br_2 system etc) most probably contain tetrahedral cations and halogen chain ions or some unionized halogen as an inclusion compound. Compounds such as PCl_6I, PBr_6I, PCl_5BrI and PBr_5ICl are known and consist of PX_4^+ cations with mixed halide anions (6,130,131,132,132a).

1.1.c ANIONIC AND CATIONIC COMPLEXES DERIVED FROM THE PHOSPHORUS PENTAHALIDES

The preceding discussion of the structure of the phosphorus pentahalides has indicated the possibility of halide ion donor/acceptor reactions occurring leading to the formation of either a tetrahedral

PX_4^+ cation or an octahedral PX_6^-. Such behaviour was exhaustively reviewed by Webster (137) in 1966.

Since the discovery of phosphorus pentafluoride in 1875 (138) nothing was reported of it's Lewis basicity until 1973 when the compound $PF_4^+Sb_3F_{16}^-$ was prepared (139) and the ion partially characterized by Raman spectroscopy (140). However the ability of phosphorus pentafluoride to act as a fluoride ion acceptor is well known (137) and the hexafluorophosphates of the alkali metals have been prepared (133-136,136a)

The solid state modifications of phosphorus pentachloride discussed earlier illustrate both chloride ion donation and acceptance. The tetrahedral PCl_4^+ ion probably exists in all of the reported pentavalent addition complexes with a wide variety of anions and these have been discussed extensively elsewhere (1,2,3,137). One system of particular relevance to this study is the complex with boron trichloride which has been formulated as PCl_4^+ BCl_4^- from powder crystallography and other techniques (141-151).

The hexachlorophosphate anion also exists, although it is hydrolytically unstable unlike its fluorine analogue. It has been well characterised as tetraethylammonium and phosphonium hexachlorophosphates by ^{31}P NMR (49-51,152), ^{35}Cl NQR (53,152,153) and vibrational spectroscopy (48). However no alkali-metal hexachlorophosphates have yet been reported and lattice energy calculations have indicated only borderline thermodynamic stability for such compounds (154).

Phosphorus pentabromide exhibits more limited donor-acceptor behaviour than the pentachloride. The tetrabromophosphonium cation is well established in several addition complexes:-

$PBr_4^+Br_3^-$ (110), $PBr_4^+IClBr^-$ (132), $PBr_4^+TaBr_6^-$ (155), $PBr_4^+PF_6^-$ (110) and $PBr_4^+BBr_4^-$ (156,157).

There is no evidence to indicate any acceptor properties of phosphorus pentabromide as the hexabromophosphate anion has yet to be prepared and characterised.

Very little work has been done on the phosphorus pentaiodide system since it's preparation in 1978 (8) but the existence of the tetraiodophosphonium cation was confirmed very recently by the preparation and single crystal X-ray analysis of the compound $PI_4^+AlI_4^-$ (158). The 2:1 adduct of PI_3 with AlI_3 has also been shown to be ionic and of the form $P_2I_5^+AlI_4^-$ (159).

As with the molecular pentahalophosphoranes, the possibility of mixed halogen anions and cations is apparent and some such species have been observed.

The first mixed halogen cation to be characterized was $PFCl_3^+$ in the salt $PFCl_3^+SbCl_6^-$ which was prepared by the reaction of $PFCl_2$, $SbCl_5$ and Cl_2 (161). During the same study some evidence for the $PFBr_3^+$ ion was obtained but product instability prevented a thorough investigation.

The chlorobromophosphonium ions, $PCl_nBr_{4-n}^+$ $(0 \leqslant n \leqslant 4)$, are the most completely investigated class of the mixed halogen cations. The trichlorobromophosphonium ion was first reported by Salthouse and Waddington in the compound $PCl_3Br^+BCl_4^-$ (162) and this and $PCl_3Br^+PF_6^-$ were subsequently vibrationally characterised (163). A study of the $PCl_3/Br_2/BCl_3$ system led to the identification of all the chlorobromophosphonium ions as tetrahaloborate salts by Raman (156) and solid state ^{31}P NMR spectroscopy (164). These species were also detected in anhydrous hydrogen chloride by a ^{31}P NMR solution study (160) on the same system. More recently some of these cations (along with various solvolysed species) have been identified in PCl_3/Br_2 and PBr_3/Cl_2 reaction mixtures in some strongly acidic solvents (165,165a), and also from the reaction of PBr_3 and PBr_5 with chlorosulphonic acid (166,167).

A study of the oxidation of phosphorus trichloride and tribromide by halogens in acetic anyhydride has produced evidence for ionic compound formation containing the following mixed halophosphonium cations:-

PCl_3Br^+, PBr_3Cl^+, PCl_3I^+ and PBr_3I^+ (168)

Chloroiodophosphonium cations and solvolysed species have also been observed by ^{31}P NMR of the reaction between phosphorus triiodide and chlorosulphonic acid (167). The range of mixed halogen anions of pentavalent phosphorus is obviously more restricted given the non-existence of hexabromo and hexaiodophosphates. However mixtures of chlorofluorophosphates $PF_nCl_{6-n}^-$ in solution are quite well known and all the ions except trans $PF_2Cl_4^-$ have been identified by ^{31}P and ^{19}F NMR studies (103,169-172). The $PF_2Cl_4^-$ ion has been obtained in an admixture with the PF_6^- ion as the caesium salt (103) and it's presence in isomeric modifications of tetrachlorofluorophosphorane has been discussed earlier (102). Trichlorodifluorophosphorane has been reported to exist as PCl_4^+ $PF_4Cl_2^-$ in the solid state (106) although the compound P_2Cl_9Br has been shown <u>not</u> to contain the PCl_5Br^- anion (113). More recently some of the compounds Et_4N^+ PF_nCl_{6-n} $(1 \leqslant n/3)$ have been isolated as solids and some azido and thiocyanato derivatives of these were prepared (173) Dillon and co-workers have extensively investigated the substitution of pseudohalogen groups in hexachloro and hexafluorophosphates. The azidochlorophosphates $PCl_{6-n}(N_3)_n^-$ have been identified by solution ^{31}P NMR spectroscopy and the isomers formed when $n = 2, 3, 4$ were deduced by comparison of the observed shifts with those predicted theoretically using the pairwise interaction method (174,175). This involves the summation of interactions between adjacent ligands attached to the central atom and thus there are 12 such interactions in the case of an octahedron. However this method is dependent upon the unambiguous assignment of chemical shifts to parent compounds that encompass all required interactions. The cyanato and thiocyanato derivatives of the hexachlorophosphate ion, $PCl_{6-n}(CN)_n^-$ and $PCl_{6-n}(NCS)_n^-$ have been investigated by ^{31}P NMR spectroscopy; some pure isomers were isolated and others observed in solution (176). Also the series $PF_{6-n}(CN)_n^-$ $(1 \leqslant n \leqslant 4)$ and $PF_3Cl_{3-n}(CN)$ $(1 \leqslant n \leqslant 3)^-$ have been studied by the same method: pairwise interactions were again used to evaluate the structure of isomers formed and some fluxionality was observed in compounds with three or more fluorine atoms at 307.2K (177).

1.1.d METHYL HALOPHOSPHORANES AND THEIR DERIVATIVES

Alkyl and aryl halophosphoranes of the general formula PR_nX_{5-n} resemble the parent halophosphoranes in that several alternative structures are possible:-

(i) trigonal bipyramidal molecules

(ii) $PR_nX_{4-n}{}^+ \; X^-$ as in $PBr_{5(c)}$

(iii) $PR_nX_{4-n}{}^+ \; PR_nX_{6-n}{}^-$ as in PCl_5 Phase II

The present work has involved only the mono, di and trimethylhalophosphoranes Me_nPCl_{5-n} ($1 \leqslant n \leqslant 3$).

This series has not been studied in as much as detail as the unmethylated halophosphoranes. Methyltetrachlorophosphorane ($MePCl_4$) has been investigated in the solid state and in non-ionising solvents by infra-red and Raman spectroscopy. The results indicate an ionic formulation for the solid state:- $MePCl_3{}^+Cl^-$ with the cation having C_{3V} symmetry (57,178) and a molecular structure having C_{2V} symmetry (a trigonal bipyramid with the methyl group equatorially disposed) in benzene, dichloromethane and carbon disulphide (178). The solid state observations are supported by ^{31}P NMR and ^{35}Cl NQR spectroscopy (179).

Dimethyltrichlorophosphorane and trimethyldichlorophosphorane have been shown to be ionic solids by vibrational spectroscopy (57,180) and again magnetic resonance data (179) is consistent with the formulations $Me_2PCl_2{}^+Cl^-$ and $Me_3PCl^+Cl^-$ with the cations having C_{2V} and C_{3V} symmetry respectively. There is little evidence in the literature of a detailed

Raman spectroscopic study of derivatives of the series Me_nPCl_{5-n} ($1 \leqslant n \leqslant 3$). Beattie reports the ionic nature of the $MePCl_4/SbCl_5$ complex as $MePCl_3^+SbCl_6^-$ (178). This compound and the other hexachloroantimonates (V) were subsequently prepared by the reaction of the appropriate methylhalophosphine and antimony pentachloride in a 1:2 ratio and were characterized by infra-red spectroscopy (181,182). Dillon et al have reported the ^{31}P NMR and ^{35}Cl NQR spectra of a number of 1:1 adducts between some methyl and ethylchlorophosphoranes and Lewis acids and deduced ionic structures for these compounds (179). Some methylbromophosphoranes and derivatives have been prepared and identified by ^{31}P NMR spectroscopy but only limited vibrational analysis was performed (183). Only limited acceptor behaviour is exhibited by the methylphosphoranes with only $MePCl_4$ forming compounds with tetraethyl and tetra-n-pentylammonium chloride (183,183a). These may be formulated as $(C_2H_5)_4N^+$ $MePCl_5^-$ and $(C_5H_{11})_4N^+MePCl_5^-$ respectively from ^{31}P NMR and infra-red spectroscopy (183,183a). The introduction of more than one methyl group into the chlorophosphorane has been shown to prevent any observable compound formation and is undoubtedly due mainly to the inductive effects of these groups. This trend is consistent with observations on the respective ethyl (183,183a) and phenylchlorophosphoranes (184).

Dillon and co-workers have extensively investigated the acceptor properties of chlorophosphorus (V) species and some derivatives towards halide ions and uni or bidentate pyridines. They found that mono-methyl and ethyltetrachlorophosphorane (183,183a) and their $SbCl_5$ derivatives were poorer acceptors than PCl_5 (185) or PCl_4^+ (186), similar to behaviour shown by $PhPCl_4$ and $PhPCl_3^+$ (187). Very recently the acceptor compounds of some organophosphorus (V) bromides have been reported (188). The stability of such compounds appears to be less than in analogous chloride systems, especially in the case of anionic species.

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CHAPTER 2

RESULTS AND DISCUSSION A

2. VARIABLE-TEMPERATURE RAMAN SPECTRA OF PHOSPHORUS (V) CHLORIDE AND BROMIDE DEPOSITED AT 15K

2.1.a THE PCl_5 SYSTEM

As noted in Chapter 1, the structure of PCl_5 in the gas phase and in non-polar solvents has been established as a trigonal-bipyramidal (T.B.P.) species with D_{3h} symmetry by vibrational spectroscopy and diffraction studies. The low-temperature infra-red spectrum (1) of PCl_5 vapour condensed onto a cooled plate at 90K is consistent with this T.B.P. structure and on warming this undergoes an irreversible change to the Phase II modification ($PCl_4^+PCl_6^-$). No analogous Raman study has been reported apart from the illustration of a spectrum of (solid) molecular PCl_5 at liquid nitrogen temperature in a review article by Beattie (2).

For a hexatomic molecule of D_{3h} symmetry the predicted 12 normal modes of vibration are distributed as follows:

$$\Gamma_{vib} = 2a_1' \ (R) + 2a_2'' \ (IR) + 3e'(R, IR) + e''(R)$$

where R and IR indicate Raman and infra-red activity. Previous Raman results for molecular (ie T.B.P.) PCl_5 are summarised in Table 2.1.

The present investigation comprised of two main experiments:-

i) Isolation of the PCl_5 vapour in an argon matrix at 15K (this required an average 3½ hours sublimation from 300-310K).

ii) Deposition of the PCl_5 vapour at 15K and subsequent warming to

TABLE 2.1

Raman assignments (cm^{-1}) for molecular PCl_5 obtained prior to this investigation

Carlson(1)	Taylor and Woodward(3)	Wilmshurst and Bernstein(4)	Beattie et al(5)	Beattie et al(6)	Assignment
(C_6H_6/CH_2Cl_2) solution	(CCl_4/C_6H_6) solution	(C_6H_6 solution)	(CH_2Cl_2/C_6H_6) solution	(gas)	
393	395	394	393	392	$\nu_1(a_1')$
-	370	394	282	286	$\nu_2(a_1')$
584	581	585	581	586	$\nu_5(e')$
273	281	338	273	276	$\nu_6(e')$
110(From I.R.)	100	100	100	90	$\nu_7(e')$
280	261	280	261	-	$\nu_8(e'')$

ambient temperature while monitoring theRaman spectrum (this required similar sublimation conditions as in i).

From the matrix isolation experiment a comparatively simple spectrum was obtained and wavenumbers and assignments are presented in Table 2.2. These results are in accord with those of Beattie for gas (6) and non-polar solution (5) phases (Table 2.1.). Small differences in some of the frequencies are undoubtedly due to the presence of the argon matrix. The $\nu_7(e')$ low frequency mode (degen. PCl_5(ax)band) was not readily identifiable in this study because of Rayleigh winging in the spectrum.

The low-temperature sublimation experiments enabled variable-temperature studies to be performed because it allowed slow warming of the sample to ambient temperatures:- a course of action prevented by the argon in the case of the matrix isolation experiments. Some typical spectra (Figs IIa, IIb) and wave numbers (Table 2.3) are presented. The trends observed may be explained as follows: The gas phase (T.B.P.) PCl_5 was stabilized at 15K giving the characteristic spectrum for a D_{3h} molecule in complete agreement with earlier work. On warming to 115-130K a distinct sharpening of the bands occurred and this may be attributed to an ordering of the lattice from the disordered state resulting from the initial vapour deposition. Further warming to about 180K produced more dramatic changes in the spectrum with a decrease in the intensity of the $\nu_1(a_1')$ band at 400 cm^{-1} associated with the T.B.P. PCl_5 molecule and the appearance of bands at 361 and 456 cm^{-1}

TABLE 2.2

Raman wavenumbers/cm^{-1} of PCl_5 vapour co-condensed with Ar at 15K

Assignment			Wavenumbers
$\nu_8(e'')$		PCl_5 (ax) rocking	266 (m)
$\nu_6(e')$	degen	PCl_5 (trig) inplanebend	276 (m)
$\nu_2(a_1')$	sym	PCl_5 (ax) stretch	287 (m)
$\nu_1(a_1')$	sym	PCl_5 (trig) stretch	400 (vs)
$\nu_5(e')$	degen	PCl_5 (trig) stretch	583 (w,br)

TABLE 2.3

Raman wavenumbers/cm^{-1} of PCl_5 vapour deposited at 15K and subsequently warmed

15K	120K	180K	220K
105(w)	98) (m)	99) (m)	
	108)	109)	
		178(w)	178(w)
		242(w)	241(w)
		256(w)	251(w)
267(m)	261(m)	261(m)	
277(m)	275 sh(m)	278) (m)	278) (m)
287(m)	287(s)	282)	282)
		360(m)	360(m)
400(s)	400(s)	400(w)	
		456(m)	456(m)
585(w)	577(w)		
		660(w)	658(w)

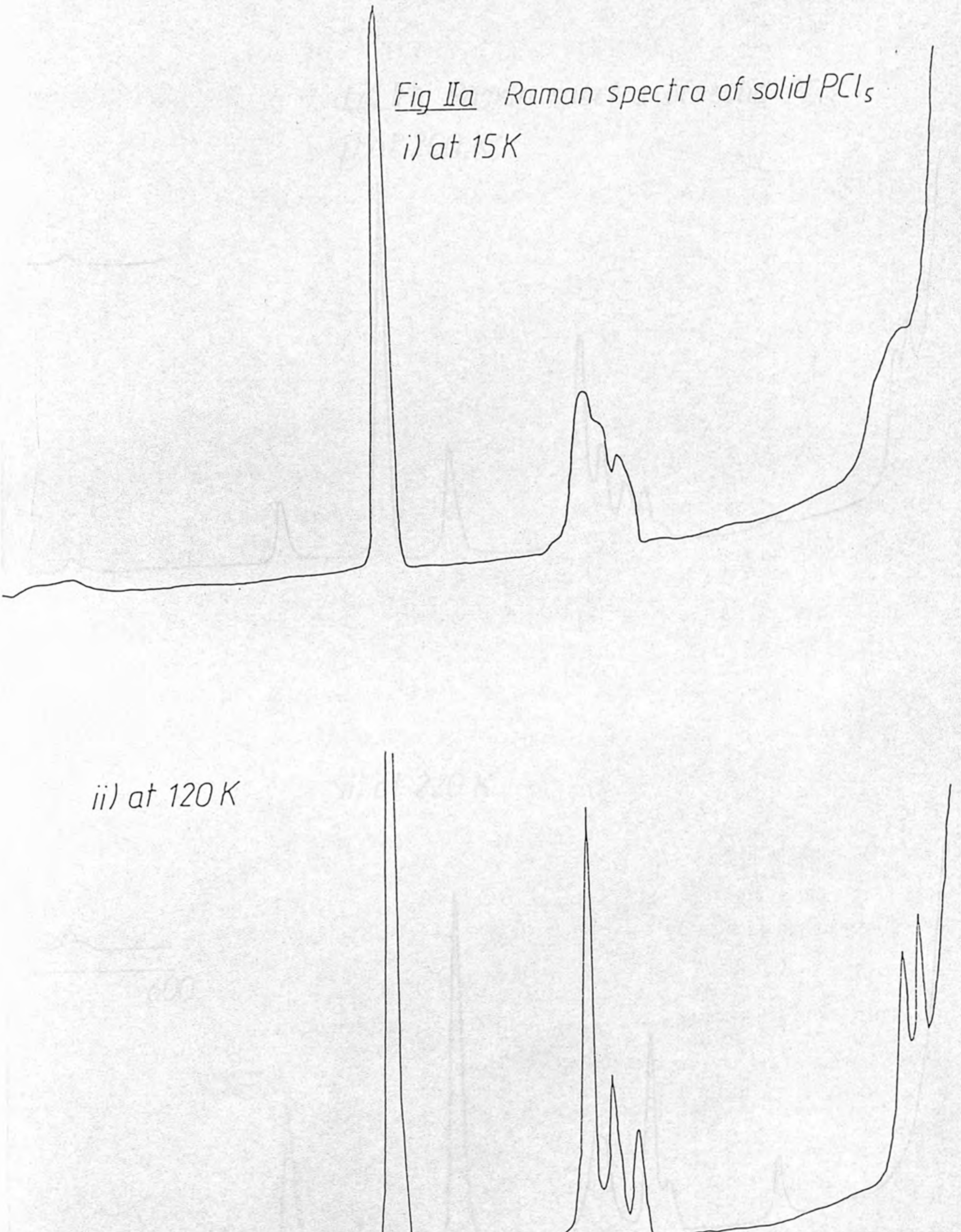
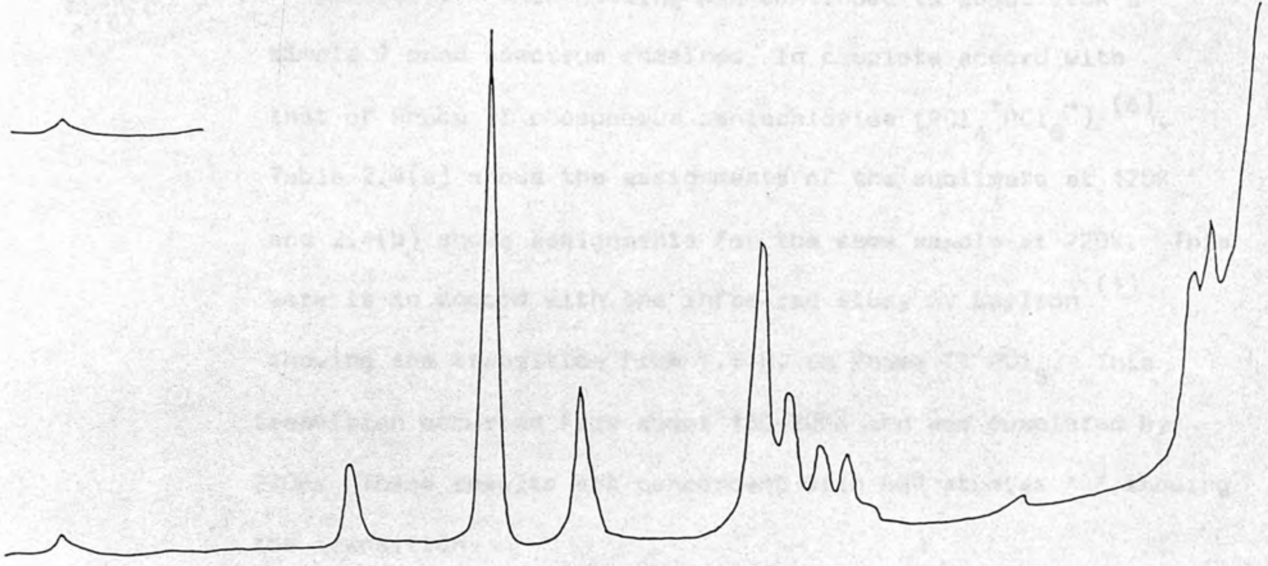


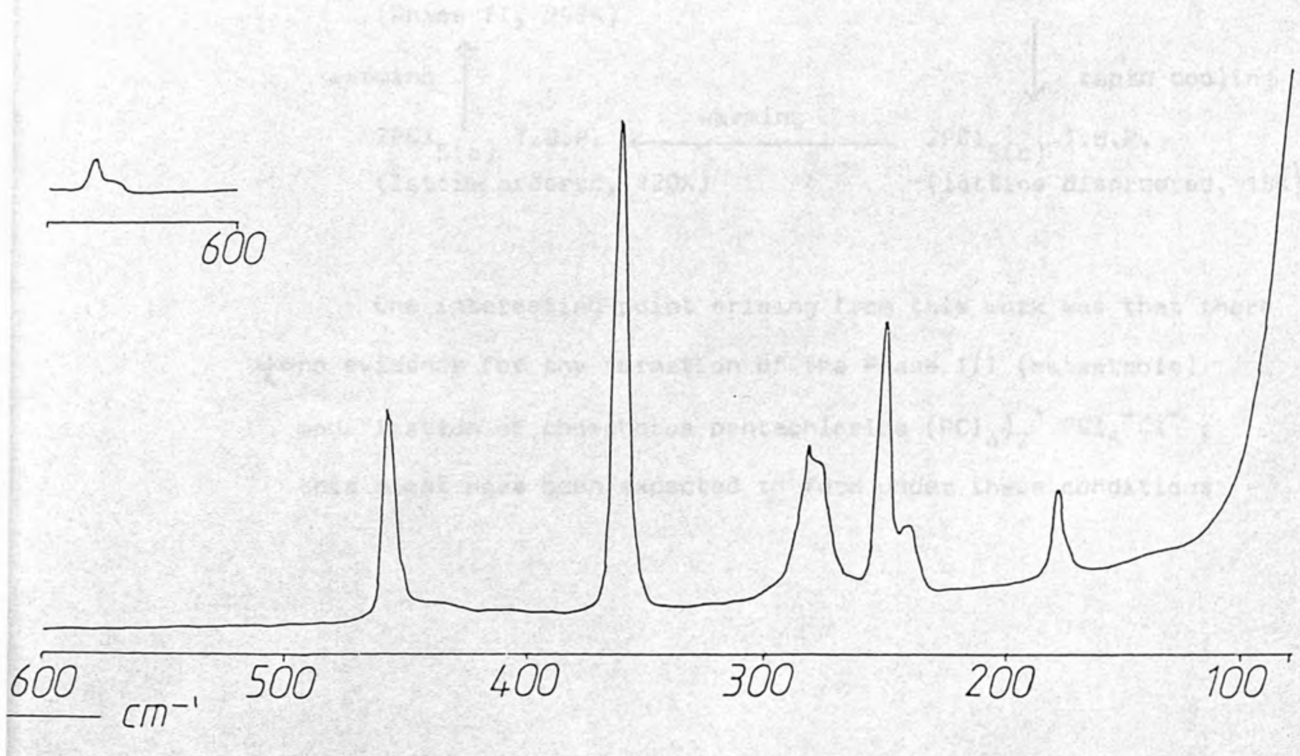
Fig IIa Raman spectra of solid PCl_5

Fig IIb Raman spectra of solid PCl_5

i) at 200 K



ii) at 220 K



characteristic of the PCl_6^- $\nu_1(a_{1g})$ and PCl_4^+ $\nu_1(a)$ modes respectively. When heating was continued to about 220K a simple 7 band spectrum remained, in complete accord with that of Phase II phosphorus pentachloride ($PCl_4^+PCl_6^-$) (6). Table 2.4(a) shows the assignments of the sublimate at 120K and 2.4(b) shows assignments for the same sample at 220K. This work is in accord with the infra-red study by Carlson (1) showing the transition from T.B.P. to Phase II PCl_5. This transition occurred from about 130–200K and was completed by 220K. These results are concordant with NQR studies (7) showing the transition

$$2PCl_5 \longrightarrow PCl_4^+ + PCl_6^-$$

to occur over the temperature range 110–190K. The following scheme summarises the behaviour of phosphorus pentachloride as observed by Raman spectroscopy.

$$\begin{tikzcd}
\begin{array}{c}PCl_4^+PCl_6^-(c)\\ \text{(Phase II, 298K)}\end{array} \arrow[r, shift left] & 2PCl_{5(g)} \arrow[l, shift left] \arrow[r, shift left] & 2PCl_{3(g)} + Cl_{2(g)} \arrow[l, shift left] \arrow[d, "\text{rapid cooling}"] \\
\begin{array}{c}2PCl_{5(c)}\ \text{T.B.P.}\\ \text{(lattice ordered, 120K)}\end{array} \arrow[u, "\text{warming}"] & & \begin{array}{c}2PCl_{5(c)}\ \text{T.B.P.}\\ \text{(lattice disordered, 15K)}\end{array} \arrow[ll, "\text{warming}"']
\end{tikzcd}$$

One interesting point arising from this work was that there was no evidence for the formation of the Phase III (metastable) modification of phosphorus pentachloride $(PCl_4)_2^+\ PCl_6^-Cl^-$; this might have been expected to form under these conditions

TABLE 2.4

Assignments of the PCl_5 variable-temperature study (a) at 120K and (b) at 220K

	(a) 120K (lattice ordered PCl_5)		(b) 220K (lattice ordered $PCl_4^+PCl_6^-$)	
	Assignment	Wavenumber	Assignment	Wavenumber
PCl_5	$\nu_7(e')$	98 108		
			$\nu_2(e)PCl_4^+$	178
			$\nu_5(t_{2g})PCl_6^-$	241
			$\nu_4(t_2)\ PCl_4^+$	251
PCl_5	$\nu_8(e'')$	261		
PCl_5	$\nu_6(e')$	275	$\nu_2(e_g)PCl_6^-$	278 282
PCl_5	$\nu_2(a_1')$	287		
			$\nu_1(a_{1g})PCl_6^-$	361
PCl_5	$\nu_1(a_1')$	400		
			$\nu_1(a_1)PCl_4^+$	456
PCl_5	$\nu_5(e')$	577		
			$\nu_3(t_2)PCl_4$	658

because it had previously been prepared by sublimation methods [8,9].

A check was made on the time dependence of the T.B.P. to Phase II PCl_5 transition by allowing a sublimate to warm to 160K when only small traces of the ionic form was present and holding it at this temperature for several hours. There was no change in the spectrum during this period suggesting temperature, not time, dependence for the transition.

Several variable-temperature Raman studies were performed on the vapour generated from the so called metastable Phase III PCl_5. The results obtained here were not entirely consistent but indicated the expected transition of T.B.P. to Phase II PCl_5 as reported earlier. However, in some cases, this was followed by a further transition to Phase III PCl_5 occurring from 220-240K.

2.1.b THE PBr_5 SYSTEM

In direct contrast to the much studied covalent PCl_5 system, no structural data have been reported on the composition of the vapour phase species above solid PBr_5. All results from vapour pressure measurements indicate complete dissociation in PBr_3 and Br_2 above 305K [10,11]. No conclusive evidence for a T.B.P. PBr_5 molecule in solution has been presented [12]. Experiments analogous to those carried out on the PCl_5 system were performed with the deposition time for the vapour species being 3 hours from about 273K. Results of a matrix isolation study are presented in Table 2.5. These results indicate predominantly the dissociation products, PBr_3 and Br_2, along with some evidence for the tetrabromophosphonium cation and the tribromide anion. The latter products probably arise from incomplete isolation of the PBr_3 and Br_2 by the Ar, allowing some reaction to occur. The presence of PBr_3 and Br_2 was confirmed by examining independently the Raman spectra of authentic samples under identical conditions (see Table 2.6(a) and (b)). The results obtained are in good agreement with literature values (13,14). Confirmation of the bands due to PBr_4^+ and Br_3^- is presented in the discussion of the low temperature sublimation results. Thus, all the observed band can be confidently assigned to either PBr_3 or Br_2 together with some PBr_4^+ and Br_3^-. No bands attributable to a monomeric T.B.P. PBr_5 species are present.

The results of the low temperature sublimation and warm-up experiments were rather different and the results are presented in Table 2.7 and Figs IIc and IId. The trends observed here may be rationalized in the following manner. The spectrum obtained at 15K is not interpretable as resulting solely from the simple dissociation products, PBr_3 and Br_2, or from a T.B.P. PBr_5 molecule. It is also not indentical to the spectrum of the matrix isolated "PBr_5" vapour described earlier, the most noticeable difference being the absence of the characteristic stretching mode at 300 cm^{-1} associated with solid, elemental bromine. However, the

TABLE 2.5

Raman wavenumbers/cm^{-1} of PBr_5 vapours

co-condensed with Ar at 15K

Assignments	Wavenumbers
$\nu_4(e)PBr_3$	123sh(w)
$\nu_4(t_2)PBr_4^+$	140(w)
$\nu_2(a_1)PBr_3$	162(m)
$\nu_1(a_1)PBr_4^+$	233(s)
$\nu_1(\Sigma_g^+)Br_3^-$	268(s)
ν (sym) Br_2	308(s)
$\nu_1(a_1) + \nu_3(e)PBr_3$	384(m,br)
$\nu_3(t_2)PBr_4^+$	490(w,br)

TABLE 2.6

Raman wavenumbers/cm^{-1} of:-

a) PBr_3 vapour condensed at 16K and then warmed

16K	80K	Assignment
119(s)	118(s)	) ν_4(e)PBr_3
	125(s)	)
165(s)	165(s)	$\nu_2(a_1)PBr_3$
385(s,br)	380(s)	$\nu_1(a_1)PBr_3$
	404(m)	ν_3(e)PBr_3

b) Br_2 vapour condensed at 16K

	Assignment
86(vw)	lattice modes
99(vw)	
297) 304)(vs)	ν (Br-Br)

TABLE 2.7

Raman wavenumbers/cm^{-1} of PBr_5 vapour deposited at 15K and subsequently warmed

15K	125K	200K	230K
74(w)	74(w)	73(m)	73(m)
103(vw)	106(vw)		
119(w)	120(w)		
144(m)	143(m)	144(s)	141) 147) (m) 157)
163(m/w)	164(w)		
177(vw)	179(vw)		
247(vs)	243(vs)	233(s,br)	229(vs)
269(vs)	266(m)		
346(vw)	345(vw)		
381(w,br)	380(w,br)		
494(w,br)	487(m,br)	477(m,br)	470) 475) (w) 482)

Fig IIc

Solid PBr$_5$ at i) 15 K

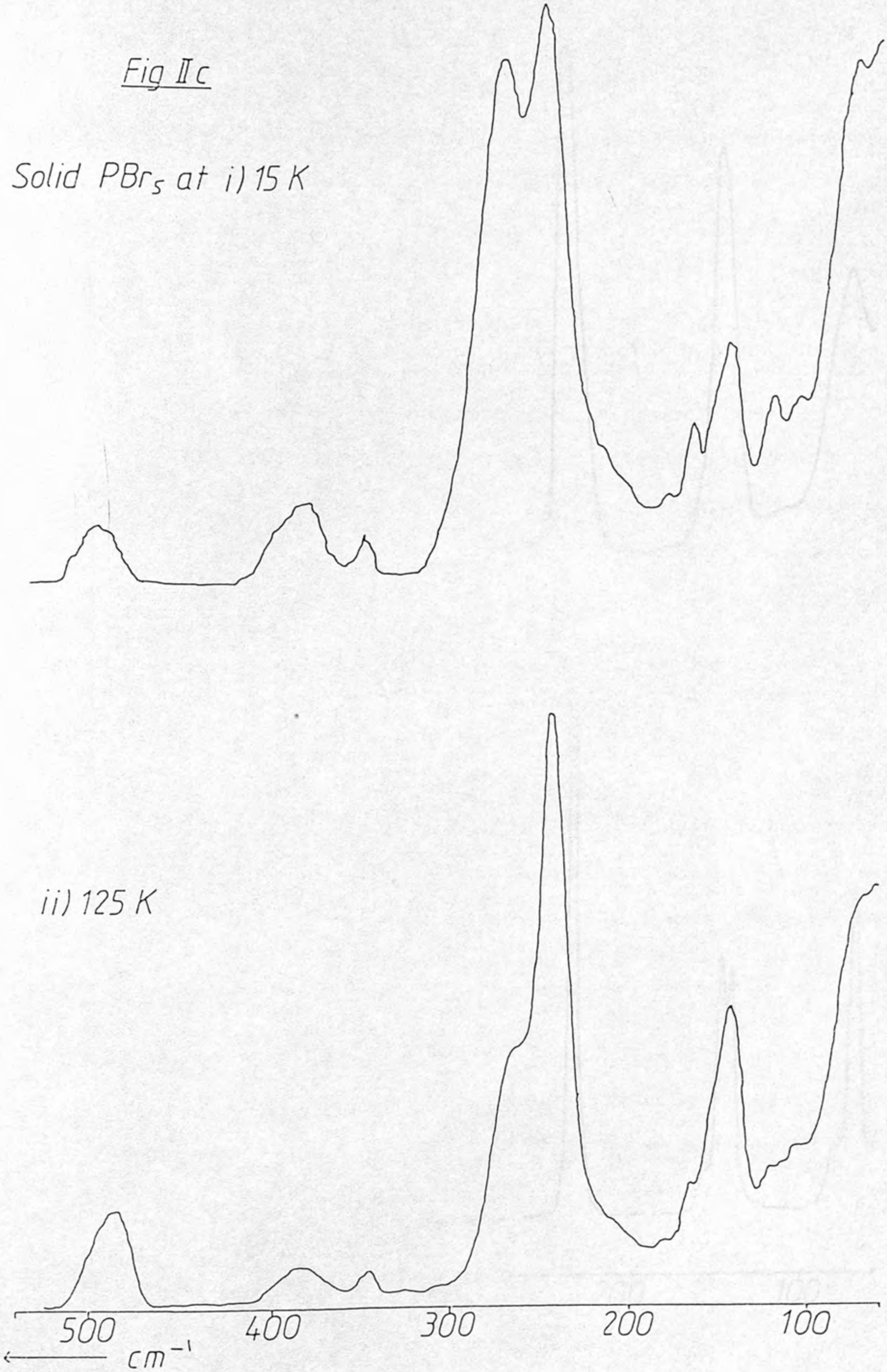
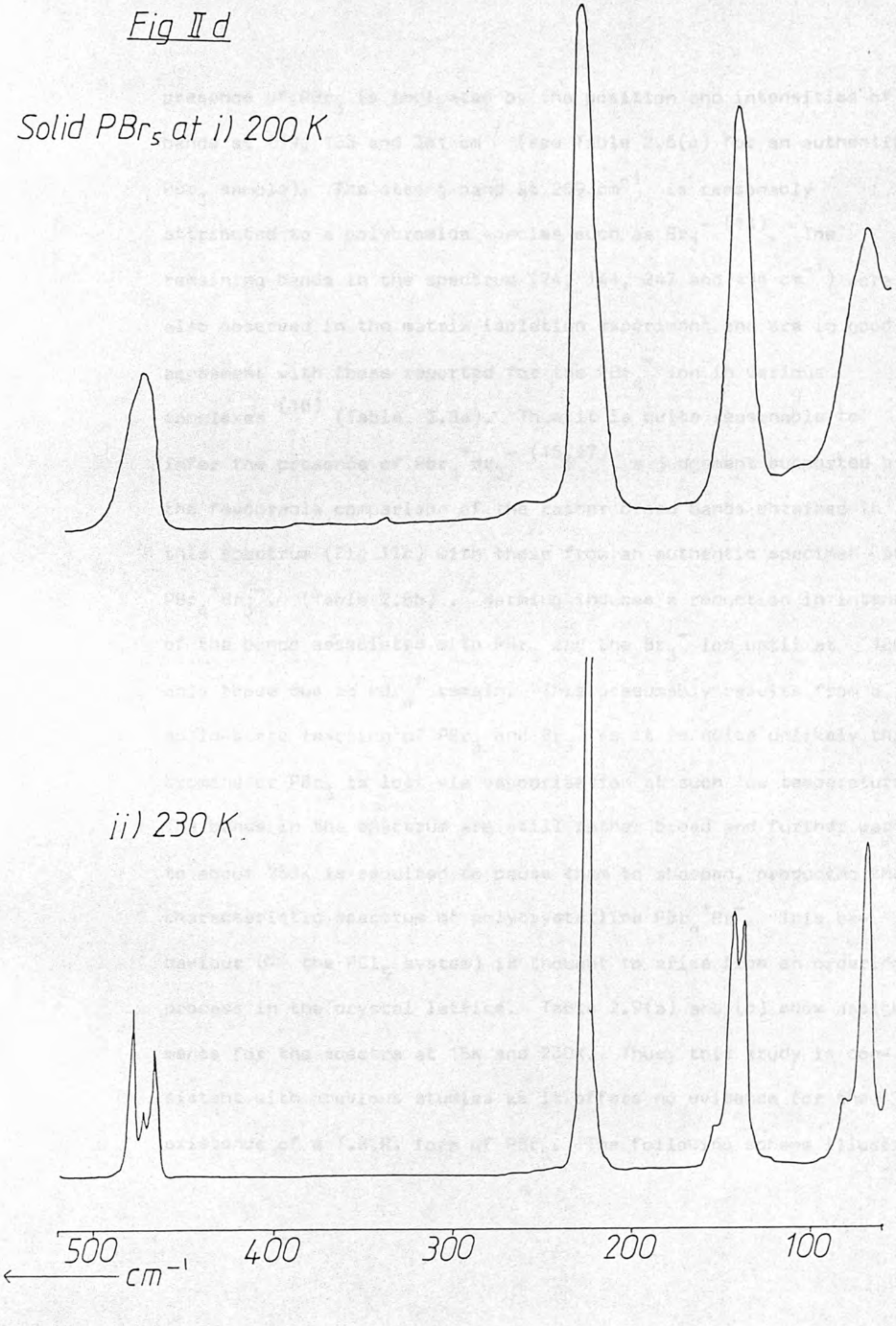


Fig II d

Solid PBr$_5$ at i) 200 K



presence of PBr_3 is indicated by the position and intensities of bands at 119, 163 and 381 cm (see Table 2.6(a) for an authentic PBr_3 sample). The strong band at 269 cm^{-1} is reasonably attributed to a polybromide species such as Br_3^- (13). The remaining bands in the spectrum (74, 144, 247 and 494 cm^{-1}) were also observed in the matrix isolation experiment and are in good agreement with those reported for the PBr_4^+ ion in various complexes (16) (Table 2.8a). Thus it is quite reasonable to infer the presence of $PBr_4^+Br_3^-$ (15,17), a judgement supported by the favourable comparison of the rather broad bands obtained in this spectrum (Fig IIc) with those from an authentic specimen of $PBr_4^+Br_3^-$. (Table 2.8b) . Warming induces a reduction in intensity of the bands associated with PBr_3 and the Br_3^- ion until at 180K only those due to PBr_4^+ remain. This presumably results from a solid-state reaction of PBr_3 and Br_3^- as it is quite unlikely that bromine or PBr_3 is lost via vapourisation at such low temperatures. The bands in the spectrum are still rather broad and further warming to about 230K is required to cause them to sharpen, producing the characteristic spectrum of polycrystalline $PBr_4^+Br^-$. This behaviour (cf the PCl_5 system) is thought to arise from an ordering process in the crystal lattice. Table 2.9(a) and (b) show assignments for the spectra at 15K and 230K. Thus, this study is consistent with previous studies as it offers no evidence for the existence of a T.B.P. form of PBr_5. The following scheme illustrates

TABLE 2.8

Assignment of the Raman spectra of

a) solid $PBr_4^+Br^-$ and b) $PBr_4^+Br_3^-$

a) $PBr_4^+Br^-$ (16)

Assignment	Wavenumber/cm^{-1}
$\nu_2(e)PBr_4^+$	(73 (85
$\nu_4(t_2)PBr_4^+$	(139 (141 (145
$\nu_1(a_1)PBr_4^+$	229
$\nu_3(t_2)PBr_4^+$	(470 (476 (484

b) $PBr_4^+Br_3^-$ (15,17)

Assignment	Wavenumber/cm^{-1}
$\nu_2(e)PBr_4^+$	(67 (69
$\nu_2(\pi)Br_3^-$	(90 (94
$\nu_3(\Sigma^+)Br_3^-$	135
$\nu_4(t_2)PBr_4^+$	(147 (151
$\nu_1(a_1)PBr_4^+$	(228 (231
$\nu_1(\Sigma^+)Br_3^-$	(247 (251
$\nu_3(t_2)PBr_4^+$	(479 (480 (481

TABLE 2.9

Assignment of the PBr_5 variable temperature study at a) 15K and b) 230K

a) 15K (disordered $PBr_4^+Br_3^-$ and PBr_3)		b) 230K (lattice ordered $PBr_4^+Br^-$)	
Assignment	Wavenumber/cm^{-1}	Assignment	Wavenumber/cm^{-1}
$\nu_2(e)PBr_4^+$	74(w)	$\nu_2(e)PBr_4^+$	73(m)
?	103(vw)		
$\nu_4(e)PBr_3$	119(w)	$\nu_4(t_2)PBr_4^+$	(141 (147(m) (157
$\nu_4(t_2)PBr_4^+$	144(m)		
$\nu_2(a_1)PBr_3$	163(m)		
?	177(vw)		
$\nu_1(a_1)PBr_4^+$	247(vs)	$\nu_1(a_1)PBr_4^+$	229(vs)
$\nu_1(\Sigma g^+)Br_3$	269(vs)		
?	246(vw)		
$\nu_1(a_1)+\nu_3(e)PBr_3$	381(w,br)	$\nu_3(t_2)PBr_4^+$	(470 (475(w) (482
$\nu_3(t_2)PBr_4^+$	494(w,br)		

the behaviour of phosphorus pentabromide as observed by Raman spectroscopy.

$$\begin{tikzcd}
\underset{\text{(lattice ordered, 298K)}}{2\mathrm{PBr_4}^+\mathrm{Br}^-(c)} \arrow[r, shift left, harpoon] & 2\mathrm{PBr_3}(g) + 2\mathrm{Br_2}(g) \arrow[l, shift left, harpoon] \arrow[d, "\text{rapid cooling}"] \\
\underset{\text{(lattice disordered, 180K)}}{2\mathrm{PBr_4}^+\mathrm{Br}^-(c)} \arrow[u, "\text{warming}"] & \underset{\text{(lattice disordered, 15K)}}{\mathrm{PBr_4}^+(c) + \mathrm{PBr_3}(c)} \arrow[l, "\text{warming}"']
\end{tikzcd}$$

Overall, this study has served to highlight the structural differences between phosphorus pentachloride and phosphorus pentabromide in the gas phase. It has confirmed the existence of molecular (T.B.P.) PCl_5 and shown that PBr_5 is dissociated in gas phase into PBr_3 and Br_2, indicating that formation of a T.B.P. PBr_5 species must be energetically unfavourable.

2.2 REFERENCES

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CHAPTER 3

RESULTS AND DISCUSSION B

3. Raman Spectra of some Tetrahalophosphonium Compexes

3.1 Effects of "single halide ions" on the Raman Spectra of Tetrahalophosphonium Complexes

In Chapter 1 the existence of compounds containing the tetrachloro and tetrabromophosphonium cations was noted, as were the solid-state structures of the parent pentahalides. These structures were different, with phosphorus pentachloride (Phase II) having the structure $PCl_4^+PCl_6^-$ whereas phosphorus pentabromide exists as $PBr_4^+Br^-$. Both of these compounds contain tetrahedral cations which, according to group theory, should have the following vibrational representation

$\Gamma_{vib} = a_1(R) + e\ (R) + 2t_2\ (R, IR)$ for isolated species

where R and IR indicate Raman and infra-red activity. This has been experimentally confirmed and for clarity in the forthcoming discussion Raman wavenumbers for these two compounds are presented in Table 3.1 and are assigned from previous studies (1,2). It is the behaviour of these 4 Raman active cation modes on complexation that is of interest.

A consideration of various derivatives of phosphorus pentachloride indicates that the PCl_4^+ fundamental frequencies are almost invariant; the Raman wavenumbers are presented for a representative selection in Table 3.2. They may be compared with those of the Phase III "metastable" PCl_5 listed in the same table. As noted in Chapter 1, the formulation $(PCl_4^+)_2PCl_6^-Cl^-$ was presented

TABLE 3.1

RAMAN WAVENUMBERS/cm^{-1} FOR a) PHASE II PHOSPHORUSPENTACHLORIDE AND b) PHOSPHORUS PENTABROMIDE

a) $PCl_4^+PCl_6^-$

Assignment (1)	Wavenumber (2)
$\nu_2(e)$ PCl_4^+	177 (m)
$\nu_5(t_{2g})$ PCl_6^-	240 (w/m)
$\nu_4(t_2)$ PCl_4^+	250 (s)
$\nu_2(e_g)$ PCl_6^-	279 (s)
$\nu_1(a_{1g})$ PCl_6^-	360 (vs)
$\nu_1(a_1)$ PCl_4^+	458 (s)
$\nu_3(t_2)$ PCl_4^+	656 (w)

b) $PBr_4^+Br^-$

Assignment (3)	Wavenumber (2)
$\nu_2(e)$ PBr_4^+	(73 (m) (84 (w)
$\nu_4(t_2)$ PBr_4^+	(140 (m) (146 (m) (156 (w)
$\nu_1(a_1)$ PBr_4^+	229 (vs)
$\nu_3(t_2)$ PBr_4^+	(469 (m) (475 (w) (481 (m)

1) F. J. Ryan; Ph. D. Thesis, University of London, 1972

2) All frequencies obtained in the present study

3) P. Dhamelincourt and M. Crunelle-Cras; Compt. Rendn., 1971, 272B, 124 and references therein

TABLE 3.2

RAMAN WAVENUMBERS/cm^{-1} FOR THE PCl_4^+ ION IN SEVERAL COMPLEXES

a) $PCl_4^+BCl_4^-$ (1)	b) $PCl_4^+SbCl_6^-$ (1)	c) $PCl_4^+AlCl_4^-$ (1)	d) $PCl_4^+PF_6^-$ (2)	e) $PCl_4^+ICl_2^-$ (2)	f) PCl_5(PhaseIII)$^{(1)}$	Assignment
459 (s)	458 (m)	458 (s)	462 (s)	449 (s)	440 (v/s)	$\nu_1(a_1)$ PCl_4^+
180 (w)	obscured	179 (m)	180 (m/w)	192 (w)	187 (w)	$\nu_2(e)$ PCl_4^+
655 (vw)	657 (vw)	657 (w)	656 (w)	646 (w)	638 (m/w)	$\nu_3(t_2)$ PCl_4^+
250 (m)	252 (m)	253 (m/s)	254 (s)	245 (m)	246 (m/s)	$\nu_4(t_2)$ PCl_4^+

1) All requencies obtained in the present study
2) A. Finch, P. N. Gates, F. J. Ryan and F. F. Bentley; J. Chem. Soc. Dalton Trans., 1973, 1863 and references therein

for Phase III PCl_5; hence the main difference between this and the other listed complexes is the presence of a single halide ion. The data in Table 3.2 show that there is a significant frequency decrease in the $\nu_1(a_1)$ mode at $\sim 460cm^{-1}$ and the $\nu_3(t_2)$ mode at 656cm^{-1} of the PCl_4^+ ion when passing from complexes with polyatomic anions (eg. BCl_4^-, $SbCl_6^-$, PCl_6^-) to Phase III PCl_5.

Figure IIIa offers a comparison of the Raman spectra of Phase III and II PCl_5. The low-frequency shift is apparent, as is the reversal of the relative intensities of the bands due to PCl_4^+ and PCl_6^- in the Phase III modification. The implications of this have been discussed elsewhere(5,9) but the change in intensities indicates that there may no longer be a 1:1 correspondence between PCl_4^+ and PCl_6^- ions, so the presence of Cl^- ions is necessary to conform with experimental analysis and to maintain a neutral species.

It is interesting to note that in the case of $PCl_4^+ICl_2^-$ a shift intermediate in comparison with that observed in Phase III PCl_5 is reported (see Table 3.2). Thus there appears to be a trend in the Raman spectra of tetrachlorophosphonium complexes with low frequency shifts when polyatomic anions are replaced with halide or polyhalide anions.

When considering derivatives of phosphorus pentabromide the situation is the reverse of the pentachloride system in that the parent compound contains single halide anion $PBr_4^+Br^-$ instead of

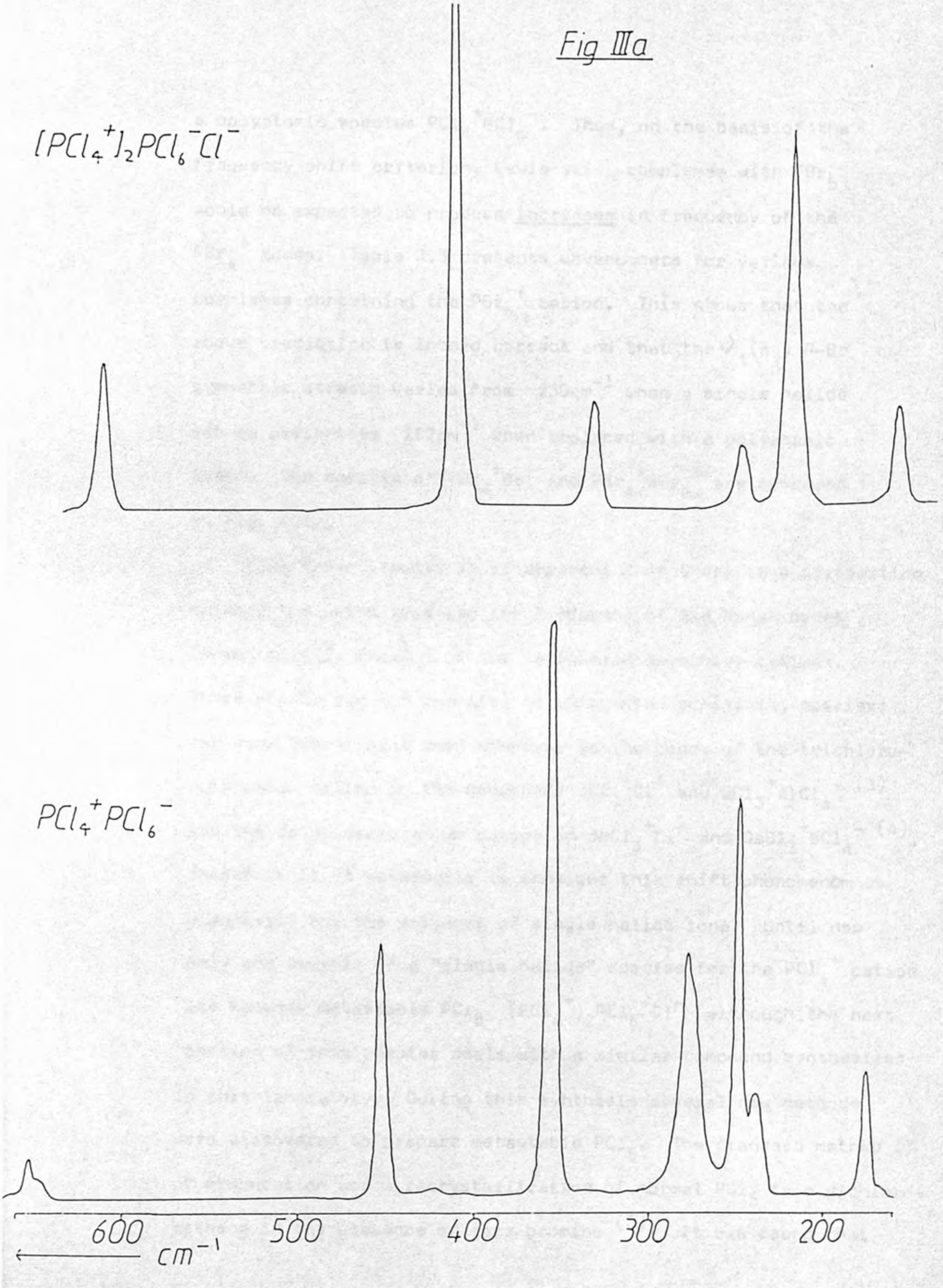

Fig IIIa

a polyatomic species $PCl_4^+PCl_6^-$. Thus, on the basis of the frequency shift criterion, Lewis acid complexes with PBr_5 would be expected to produce increases in frequency of the PBr_4^+ modes. Table 3.3 presents wavenumbers for various complexes containing the PBr_4^+ cation. This shows that the above prediction is indeed correct and that the $\nu_1(a_1)$ P-Br symmetric stretch varies from 230cm^{-1} when a single halide ion is present to 253cm^{-1} when replaced with a polyatomic anion. The spectra of $PBr_4^+Br^-$ and $PBr_4^+BBr_4^-$ are compared in Fig. IIIb.

From these results it is apparent that there is a correlation between the anion type and the frequency of the Raman bands (especially ν_1 and ν_3) of the tetrahalophosphonium cations. These shifts are not peculiar to phosphorus containing species: the same trends have been observed in the cases of the trichlorosulphonium cation in the compounds $SCl_3^+Cl^-$ and $SCl_3^+AlCl_4^-$ (3) and the trichloroselenium cation in $SeCl_3^+Cl^-$ and $SeCl_3^+BCl_4^-$ (4). Therefore it is reasonable to consider this shift phenomenom as diagnostic for the presence of single halide ions. Until now only one example of a "single halide" species for the PCl_4^+ cation was known:- metastable PCl_5 $(PCl_4^+)_2PCl_6^-Cl^-$ although the next section of this chapter deals with a similar compound synthesized in this laboratory. During this synthesis several new methods were discovered to prepare metastable PCl_5. The standard method of preparation was a recrystallization of normal PCl_5 from dichloromethane in the presence of some bromine (5). It was found that

TABLE 3.3

RAMAN WAVENUMBERS/cm^{-1} FOR THE PBr_4^+ ION IN VARIOUS COMPLEXES

a) $PBr_4^+Cl^-$ (1)	b) $PBr_4^+Br_3^-$ (2)	c) $PBr_4^+IBr_2^-$ (3)	d) $PBr_4^+BBr_4^-$ (4)	e) $PBr_4^+TaBr_6^-$ (5)	f) $PBr_4^+PF_6^-$	Assignments
224) 231)	228) 231)	238	253	254	269	$\nu_1(a_1)$ PBr_4^+
72) 74)	67) 69)	60	103) 115)	116	108	$\nu_2(e)$ PBr_4^+
471) 473) 477)	479) 480) 481)	484	497	496) 503)	508) 512)	$\nu_3(t_2)$ PBr_4^+
140) 143 (sh)) 147)	147) 151)	149) 153)	148	148	153	$\nu_4(t_2)$ PBr_4^+

1) W. Gabes, K. Olie and H. Gerding; Rec. Trav. Chim. Pay-Bas., 1972, 91, 1367

2) P. Dhamelincourt and M. Crunelle-Cras; Compt. Rendu., 1971, 272B, 124

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4) All frequencies obtained in the present study

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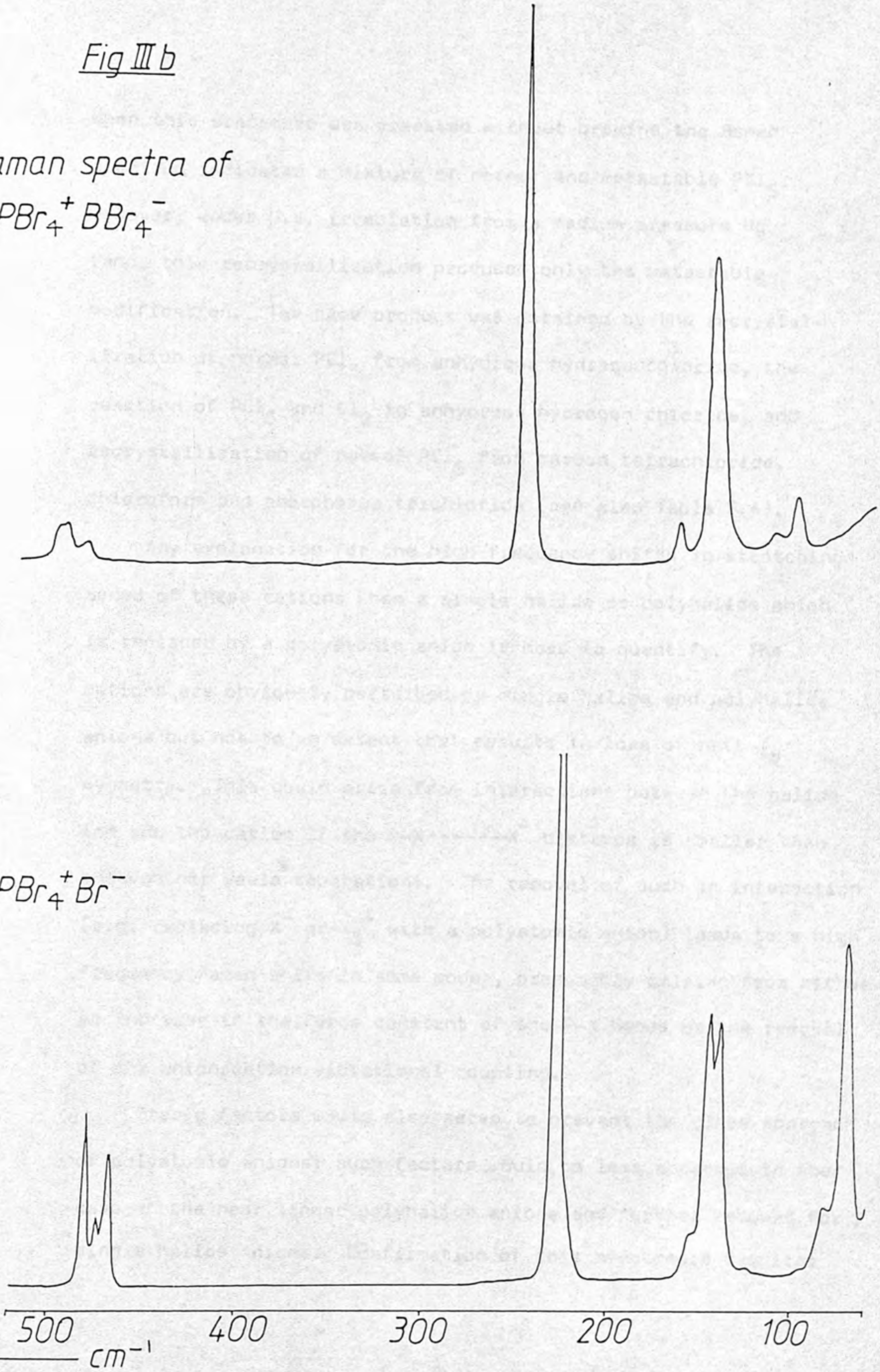
6) P. Dhamelincourt and M. Crunelle-Cras; Compt. Rendu., 1970, 271B, 124

Fig III b

Raman spectra of

i) $PBr_4^+ BBr_4^-$

ii) $PBr_4^+ Br^-$



when this procedure was repeated without bromine the Raman spectrum indicated a mixture of normal and metastable PCl_5. However, under U.V. irradiation from a medium pressure Hg lamp, this recrystallization produced only the metastable modification. The same product was obtained by the recrystallization of normal PCl_5 from anhydrous hydrogenchloride, the reaction of PCl_3 and Cl_2 in anhydrous hydrogen chloride, and recrystallization of normal PCl_5 from carbon tetrachloride, chloroform and phosphorus trichloride (see also Table 3.4).

Any explanation for the high frequency shifts in stretching modes of these cations when a single halide or polyhalide anion is replaced by a polyatomic anion is hard to quantify. The cations are obviously perturbed by single halide and polyhalide anions but not to an extent that results in loss of nett T_d symmetry. This could arise from interactions between the halide ion and the cation if the P-X-------X^- distance is smaller than the van der Waals' separations. The removal of such an interaction (e.g. replacing X^- or X_3^- with a polyatomic anion) leads to a high frequency Raman shift in some modes, presumably arising from either an increase in the force constant of the P-X bonds or the removal of any anion/cation vibrational coupling.

Steric factors would also serve to prevent the close approach of polyatomic anions; such factors would be less apparent in the case of the near linear polyhalide anions and further reduced for single halide anions. Confirmation of this hypothesis requires single crystal X-ray crystallography to give detailed spatial information. Unfortunately, this does not exist for the PCl_5 system. Although the structure of Phase II ($PCl_4^+PCl_6^-$) is well established(6-8), no single crystal X-ray analysis has been reported for Phase III ($(PCl_4^+)_2PCl_6^-Cl^-$. A powder X-ray analysis was performed by Cahay and Whalley(5a) but provides no detailed insight into the structure of Phase III PCl_5. An ionic model of Phase III was proposed by Jenkins et al(9) to enable calculation of various thermochemical properties of phosphorus (V) chloride isomers. This assumed selective ionization of the PCl_6^- ions within the lattice to produce PCl_4^+ and Cl^- ions and an extension of the unit cell to maintain stoichiometry.

During this work attempts were made to grow Phase III crystals of the correct dimensions for Professor S. G. Shore at Ohio State University but they proved to be opaque to X-rays. However there are reported structures for both PBr_5 and PBr_7 which exist as $PBr_4^+Br^-$ (10-12) and $PBr_4^+Br_3^-$ (13) respectively and provide examples of single halide and polyhalide anions (Raman wavenumbers for these two compounds are contained in Table 3.3). Breneman and Willett investigated $PBr_4^+Br_3^-$ (13) and found that the cation was nearly tetrahedral with all angles in the range 107-110° and all bond distances in the range 2.16-2.18Å. The Br_3^- ion was found to be nearly linear but the two bond lengths were significantly different, one being 2.39Å (the single bond distance in Br_2 is 2.28Å) whilst the other was extended to 2.91Å. This indicates polarisation of Br_3^- by the cation and this appears to be confirmed as the extended terminal Br atom was observed to be much closer to the bromine atoms of the surrounding cations than the other two anion atoms. Each elongated end of the Br_3^- was shown to have 4 bromine neighbours within the 3.1-3.4Å range whilst approaches to the other two anion atoms were nearly 3.9Å. The bromine van der Waals radius is 1.95Å and hence significant interaction is indicated. The overall tetrahedral symmetry of the PBr_4^+ cation is not significantly perturbed as each of the bromine atoms is involved in only one "close contact" with the elongated end of the Br_3^- ion. This is wholly consistent with the available Raman data (14) as no bands unassignable to a PBr_4^+ T_d species or the anion appear in the spectrum indicative of no gross distortion of cation symmetry.

The crystal structure of $PBr_4^+Br^-$ was reinvestigated by Gabes and Olie in 1970 (12) and the cation was confirmed to be a nearly regular tetrahedron with all P-Br distances within the range 2.13-2.17Å. This was consistent with earlier work (10,11). Each Br^- ion was found to be surrounded by 4 bromine atoms, each from a different cation, with interaction distances averaging 3.12Å, again less than the van der Waals' separation. Thus there is again quite considerable anion/cation interaction without nett loss of symmetry, facts fully consistent with the Raman spectrum of this compound (14,15).

These data can be used to explain the observed Raman shifts;

the close approach of the halide or polyhalide anion may weaken the P-X bonds in the cation with consequent lower stretching frequencies. Such close contacts are less probable where polyatomic anions are involved and hence significant perturbations of the stretching frequencies are less likely.

At this point it seems worthwhile to speculate on the mechanisms that may be involved in the production of the metastable Phase III PCl_5 and other related compounds. Table 3.4 presents the various methods known to produce Phase III PCl_5 and it is clear from their variety that the processes occurring are, in energetic terms, very finely balanced. Several of these methods require further comment.

The behaviour of PBr_5 and PCl_5 in carbon tetrachloride has long been of interest. In 1930 Krakowiecki (16) reported that when saturated solutions of the phosphorus halides in this solvent were cooled, complex formation occurred and analyses lead to the proposed formulations $PBr_5.2CCl_4$ and $2PCl_5.CCl_4$. The pentabromide complex has been subsequently prepared (17) and the Raman spectrum was recorded during this study. Bands due to the PBr_4^+ cation dominate the spectra $= \nu_1(a_1)$ 228 (vs), $\nu_2(e)$ 74 (m), $\nu_3(t_2)$ 482 (m) and $\nu_4(t_2)$ 145 (m). The position of the ν_1 P-Br symmetric stretch indicates the presence of a single halide ion (cF ν_1 in $PBr_4^+Br^-$ at 229 cm^{-1}) and the degenerate ν_2, ν_3, ν_4 modes do not exhibit the characteristic splittings found in the spectrum of the parent pentabromide. This suggests that the two CCl_4 molecules

TABLE 3.4

KNOWN METHODS OF PREPARATION OF PHASE III "METASTABLE" PCl_5:- $(PCl_4^+)_2\ PCl_6^-Cl^-$

1. Application of pressure to Phase II PCl_5 (a,b,c).
2. Various sublimation techniques (d,e,f,g).
3. Chemical methods.
    - a) Recrystallization of Phase II PCl_5 from Ch_2Cl_2 in the presence of a little Br_2 (h,i,j).
    - b) Recrystallization of Phase II PCl_5 from CH_2Cl_2 in the presence of a little SCl_2 (i).
    - c) Recrystallization of Phase II PCl_5 from CCl_4 (j).
    - d) Recrystallization of Phase II PCl_5 from anhydrous HCl (j).
    - e) Recrystallization of Phase II PCl_5 from $CHCl_3$ (j).
    - f) Reaction of PCl_3 and Cl_2 in anhydrous HCl (j).
    - g) Recrystallization of Phase II PCl_5 from CH_2Cl_2 during continuous U.V. irradiation (j).
    - h) Recrystallization of Phase II PCl_5 from PCl_3 (j).

(a) R. Cahay and E. Whalley; J. Chem. Phys., 1979, 70, 5534

(b) R, Cahay, P. T. T. Wong and E. Whalley; J. Chem. Phys., 1979, 70, 5539

(c) J. A. Ripmeester, P. T. T. Wong, D. W. Davidson and E. Whalley; J. Chem. Phys., 1979, 70, 5545

(d) A. I. Popov, D. H. Geske and N. C. Baenziger; J. Amer. Chem. Soc., 1956; 78, 1793

(e) H. Chihara, M. Nakamura and K. Muskane; Bull. Soc. Chem. Jap., 1967, 40, 50

(f) R. Baumgartner, W. Sawodny and J. Goubeau; Z. Anorg. Allgem. Chem., 1966, 331, 171

(g) S. G. Shore and H. Knachel, personal communication

(h) A. Finch, P. N. Gates, F. J. Ryan and F. F. Bentley; J. Chem. Soc. Dalton Trans, 1973, 1863

(i) A. Finch, P. N. Gates, H. D. B. Jenkins and K. P. Thakur; J. Chem. Soc. Chem. Comm., 1980, 579

(j) Present Study

must be loosely bound to the anion so as to perturb the site symmetry found in phosphorus pentabromide while maintaining total tetrahedral symmetry of the cation. Also, from the position of the ν_1 vibration at 228 cm^{-1}, there is still considerable interaction between the bromide anions and the cationic bromine atoms but no crystallographic study has been performed on this molecule to enable the determination of the nature of these perturbations.

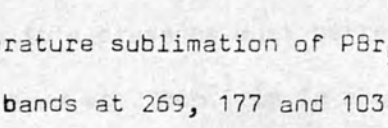
The preparation of the complex $2PCl_5.CCl_4$ has not been repeated despite several attempts (18,19), though recrystallization of Phase II PCl_5 from carbon tetrachloride has been found to produce the metastable modification (20). Studies have shown that in carbon tetrachloride the apparent molecular weight of PCl_5 shows some concentration dependence (21) and, when extrapolated to infinite dilution, Shore's cryoscopic investigations indicate the presence of a dimeric species (18). However, vapour pressure measurements indicated the predominant species to be monomeric (19) and when the cryoscopic measurements noted earlier are corrected for solid solution formation a monomeric formulation in carbon tetrachloride is inferred. Thus it can be seen that the behaviour of PCl_5 in carbon tetrachloride has provided rather conflicting results previously with all physical methods indicating a monomeric molecular species to be present as opposed to the originally reported complex and the fact that metastable PCl_5 is formed upon recrystallization of Phase II PCl_5 in this solvent.

It is interesting at this point to recall (22) that vacuum treatment of an unstable PCl_3/Br_2 reaction product (performed in CCl_4) yielded a yellow powder with unit cell contents $P_{12}Cl_{56}Br_4$ which may be rewritten in simple terms as $P_3Cl_{14}Br$ ie $(PCl_4^+)_2PCl_6^-Br^-$, which is the analogue of metastable PCl_5 but with a bromide substituted for a chloride ion. Under vacuum sublimation this substance produced metastable PCl_5.

Recrystallization of Phase II PCl_5 from dichloromethane produced predominantly unchanged $PCl_4^+PCl_6^-$ though occasionally traces of the metastable modification were obtained. However if the solution was doped with Br_2 the metastable form was invariably produced (5). The behaviour of the bromine has not been discussed in previous reports but a speculative mechanism will be proposed later. It has already been shown that in the presence of a single halide anion, the stretching vibrations of PX_4^+ tetrahedra undergo low frequency shifts and that this phenomenon manifests itself most noticeably on the $\nu_1(a_1)$ P-X symmetric stretch. Thus $\nu_1(a_1)$ P-Cl varies from 458 cm^{-1} in $PCl_4^+PCl_6^-$ to 441 cm^{-1} in $(PCl_4^+)_2PCl_6^-Cl^-$. When PCl_5 is dissolved in bromine, ^{31}P NMR spectroscopy indicates PCl_4^+ as the only phosphorus containing moiety. This is supported by solution Raman spectroscopy; four bands at 179, 250, 452 and 656 cm^{-1} are indicative of this. The symmetric P-Cl stretch is in an intermediate position to those in $PCl_4^+PCl_6^-$ and $(PCl_4^+)_2PCl_6^-Cl^-$

(452 cm^{-1} compared 458 and 441 cm^{-1}). A strong broad (80 cm^{-1}) band centred at 276 cm^{-1} must be associated with the anion and is shifted downfield from the Br-Br stretch in elemental bromine that occurs at 310 cm^{-1}. A saturated solution of Et_4NCl in bromine displays the same strong feature centred on 278 cm^{-1}; thus it is reasonable to surmise that this band arises from a trihalide anion such as Br_2Cl^- or a mixture of a trihalide ion and free Br_2. This is consistent with data in Table 3.2 and 3.3 which shows that the presence of a trihalide species such as IBr_2^- and ICl_2^- causes shifts in the symmetric P-X stretches in PX_4^+ to postions intermediate in comparison with X^- or a polyatomic anion.

The nature of trihalide ions in these systems is worth some discussion at this stage. In PBr_7 the Br_3^- ion has been shown to be asymmetric with the following structure $^{(13,23)}$



with $C_{\infty v}$ symmetry and all three modes showing infra-red and Raman activity (90 + 93, 150 + 154 and 248 + 251 cm^{-1}). An asymmetric structure is also inferred for the Br_3^- ion found in the low temperature sublimation of PBr_5 discussed in the previous chapter with bands at 269, 177 and 103 cm^{-1}. However symmetric Br_3^- ions are known and in the free state exhibit $D_{\infty h}$ symmetry $^{(23,24)}$. Here only the ν_1 symmetric stretching mode is Raman active though the ν_3 antisymmetric stretch may appear with the breakdown of selection rules in the solid state. Symmetrical trihalide ions often occur in crystals with large cations [23] and a symmetric Br_3^- ion was found to occur in the $MePBr_nCl_{3-n}^+$ system discussed later in this thesis and characterized by the intense band at $168cm^{-1}$. As can be seen the ν_1 mode in the asymmetric Br_3^- ion is only about $50cm^{-1}$ lower in frequency than the Br-Br stretch in elemental bromine - thus this mode can be regarded as a slightly perturbed weakened Br-Br stretching mode in a species of the type represented below.

$\left[Br^- \text{.........} Br\text{-}Br\right]$

In the complexes $PCl_4^+ICl_2^-$ and $PBr_4^+IBr_2^-$ the trihalides have a symmetric structure in the former and an asymmetric structure in the latter (25).

The nature of the proposed anion Br_2Cl^- in both the Et_4NCl/Br_2 and PCl_5/Br_2 systems can now be considered. If this anion is regarded as asymmetric then the strong band at $278cm^{-1}$ is in a reasonable position for a slightly perturbed Br-Br stretch as would occur in a species such as

$\left[Cl^- \text{......} Br\text{-}Br\right]$ (c.f. $\left[Br^- \text{.....} Br\text{-}Br\right]$ above).

The Raman spectra displayed no other bands assignable to this anion so it's presence must be regarded as tentative. However, the ν_1 band at $278cm^{-1}$ is in a quite reasonable position for an asymmetric Br_2Cl^- ion, because a similar symmetric species would probably have a symmetric stretch at rather a lower frequency.

In one attempted preparation of metastable PCl_5 by the recrystallization of Phase II PCl_5 from CH_2Cl_2 in the presence of Br_2, rather more Br_2 than usual was used. On crash cooling crystals of metastable PCl_5 were obtained and an unstable yellow solid appeard on further cooling of the filtrate. The Raman spectrum of this solid indicated the presence of PCl_4^+, PCl_6^- and possibly Br_2Cl^- (deduced from the broad band centred at 285cm^{-1} which is undoubtedly shifted to this higher frequency by mixing with the $\nu_2(e_g)$ mode of PCl_6^- at 279^{-1}). The PCl_4^+ $\nu_1(a_1)$ band in this spectrum was rather broad and centred on 449cm^{-1}, a position intermediate to those found in Phase II and metastable PCl_5 (458 and 441cm^{-1}). Examination of the high frequency band in the PCl_4^+ spectrum (ν_3, t_2) shows 3 distinct components, centred on 658, 650 and 640cm^{-1} respectively. Comparison of those values with those for compounds containing the PCl_4^+ cation (Tables 3.1 and 3.2), suggest that they arise from respective association with a polyatomic, trihalide and single halide anion. On standing the solid transformed to metastable PCl_5 - manifested by the decrease in the intensity of the ν_1 (a_{1g}) PCl_6^- mode at 360cm^{-1} and the Br_2Cl^-/PCl_6^- complex of bands centred on 285cm^{-1} with a corresponding increase in intensity of the PCl_4^+ vibrations at 639, 441, 247 and 180cm^{-1}, (all characteristic of the presence of a single halide ion).

In the light of this evidence it is possible that the three components of this mixture were 1) $PCl_4^+PCl_6^-$ 2) $PCl_4^+Br_2Cl^-$

and 3) $(PCl_4^+)_2PCl_6^-Cl^-$, implying that 2) is intermediate in the formation of metastable PCl_5. The following facile scheme could be proposed to represent for these observations

$$6PCl_5 \longrightarrow 3PCl_4^+ + 3PCl_6^-$$

$$PCl_6^- + 2Br_2 \longrightarrow PCl_4^+ + 2Br_2Cl^-$$

$$2Br_2Cl^- \longrightarrow 2Br_2 + 2Cl^-$$

Products: $4PCl_4^+ \; 2PCl_6^- \; 2Cl^- = 2(PCl_4^+)_2 \; PCl_6^-Cl^-$

This scheme appears more reasonable assuming the undoubted instability of the trihalide ion Br_2Cl^- in an environment other than Br_2 which would allow for the decomposition of the intermediate $PCl_4^+Br_2Cl^-$ and also supports Jenkins (9) thermodynamic model for metastable PCl_5 formation by accounting for the selective decomposition of certain PCl_6^- ions into PCl_4^+ and $2Cl^-$ ions. Although this scheme may not account for all preparations leading to the formation of metastable PCl_5, it is supported by Raman evidence as being a plausible mechanism for the $PCl_5/CH_2Cl_2/Br_2$ preparation.

In this study Phase II PCl_5 was recrystallizated from bromine alone. A dark red unstable aggregate was produced and no Raman spectrum could be recorded. However, pumping of this aggregate yielded a pale yellow powder and a Raman spectrum of this was identical to that of Phase III metastable PCl_5.

It is interesting at this point to compare the effects of the various halogens upon recrystallization of Phase II PCl_5

from CH_2Cl_2. Bromine has already been discussed at some length and no data exist for such a process performed in the presence of fluorine. Investigations in this laboratory have shown that the presence of chlorine in the PCl_5/CH_2Cl_2 system does not lead to the formation of the metastable compound (26) and the presence of iodine leads to the formation of $PCl_4^+ICl_2^-$ (25). In terms of the trihalide intermediate discussed earlier for the $PCl_5/CH_2Cl_2/Br_2$ reaction, the interaction of chlorine with PCl_5 is negligible (at least at ambient temperatures where the Cl_3^- ion is known to be unstable). When iodine is present in this system the very stable ICl_2^- salt is formed immediately, possibly because of the greater electropositivity of the iodine atoms. Bromine, therefore, occupies an intermediate position where the Br_2Cl^- ion is of borderline stability. When PCl_5 is recrystallized from liquid Cl_2, the ordinary modification $PCl_4^+PCl_6^-$ is obtained indicating the extreme instability of any intermediate. It should be noted, however that PCl_5 was rather insoluble in chlorine. It would be interesting for future workers to perform a low-temperature sublimation experiment involving the co-condensation of PCl_5 (g) and Cl_2 (g) onto a plate at 15K and the monitoring of its Raman spectrum. This would enable interaction between the two compounds to be observed and facilitate possible warm-up experiments to follow the course of any reactions.

Metastable PCl_5 has been prepared in this study by the recrystallization of Phase II PCl_5 from anhydrous HCl. A previous Raman study of this system has shown the species present to be PCl_4^+ and HCl_2^- (27). Again, when the instability of the anion in a medium other than HCl is considered, a scheme analogous to that suggested for the $PCl_5/CH_2Cl_2/Br_2$ system may be tentatively proposed.

$$3PCl_5 + 3HCl \longrightarrow 3PCl_4^+ + 3HCl_2^-$$

$$PCl_4^+ + 2HCl_2^- \longrightarrow PCl_6^- + 2HCl$$

$$HCl_2^- \longrightarrow HCl + Cl^-$$

Products: $(PCl_4^+)_2PCl_6^-Cl^-$

The evaporation of the HCl on warming this system to ambient would provide a suitable driving force for this reaction scheme.

Thus, using the available data, an attempt has been made to rationalize two systems in which metastable PCl_5 is formed. It would be unreasonable to expect these proposals to explain all methods of preparation listed in Table 3.4 considering their variety and the lack of available structural data.

3.2 The novel compound $(PCl_4^+)_2BCl_4^-Cl^-$

A compound of the title formulation was prepared in these laboratories by the reaction of PCl_3 and BCl_3 in a 2:1 molar ratio with Cl_2 in arsenic trichloride. This is detailed in Section 5.9. The Raman spectrum of this product is presented in Fig. IIIc where it is compared with that of $PCl_4^+BCl_4^-$ obtained in this study. A comparison of the Raman wavenumbers of these two compounds is produced in Table 3.5. The analogy with the $PCl_4^+PCl_6^-$ and $(PCl_4^+)_2PCl_6^-Cl^-$ systems is quite remarkable. The solid state Raman spectrum of the new complex showed a marked increase in the relative intensity in some of the PCl_4^+ fundamental modes so that the weak, but usually observable, anion modes were hardly visible. This indicated that the anion/cation ratio was no longer unity as in $PCl_4^+BCl_4^-$ and elemental analysis suggested a stoichiometry P_2BCl_{13}. Also a low-frequency shift was observed in the PCl_4^+ stretching modes when compared with those in $PCl_4^+BCl_4^-$, consistent with the concept of a single halide anion closely approaching each chlorine atom of the cation, resulting in a weakening of the P-Cl bonds but with no significant distortion of tetrahedral symmetry.

Another similarity with the phosphorus pentachloride system was observed. The low frequency Raman spectrum of $PCl_4^+PCl_6^-$ shows only very weak lattice features at 70, 60 and 40cm^{-1} that cannot be resolved. Similar unresolved features occur at 85, 70 and 65cm^{-1} in the case of $PCl_4^+BCl_4^-$. However, the Raman spectra of <u>both</u> "metastable" species $(PCl_4^+)_2PCl_6^-Cl^-$ and $(PCl_4^+)_2BCl_4^-Cl^-$ possess a medium intensity, well resolved band at 58cm^{-1}. The origin of this band cannot be defined without crystallographic data to enable site and factor group analyses to be performed. However, it is interesting to speculate whether the band arises from the Cl^-/cation interaction and is a weak $Cl_3P^+Cl\text{-----}Cl^-$ stretching mode. This could result from the close approach of

Fig IIIc

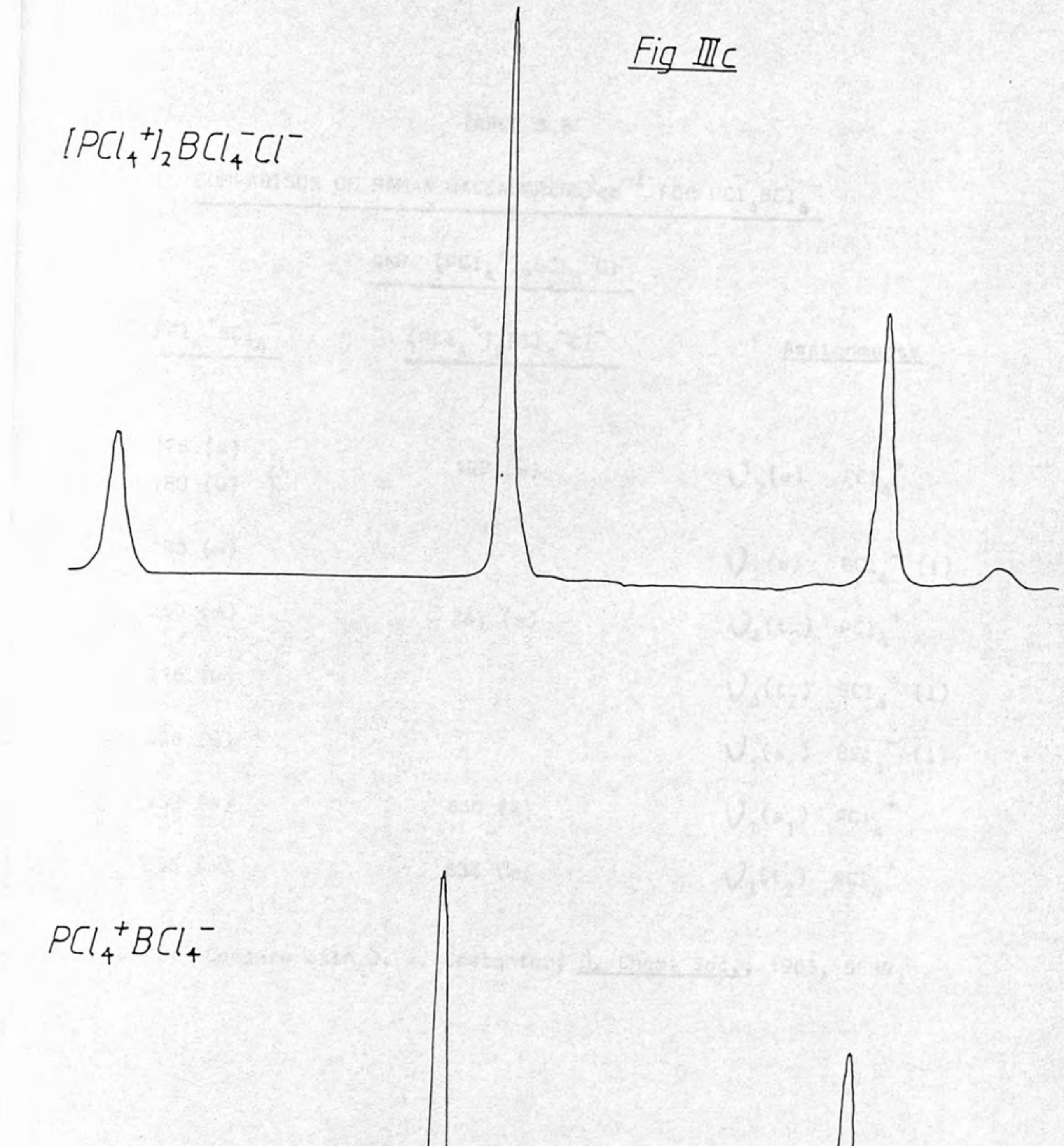


TABLE 3.5

COMPARISON OF RAMAN WAVENUMBERS/cm^{-1} FOR $PCl_4BCl_4^-$ AND $(PCl_4^+)_2BCl_4^-Cl^-$

$PCl_4^+BCl_4^-$	$(PCl_4^+)_2BCl_4^-Cl^-$	Assignments
175 (w)	190 (w)	$\nu_2(e)$ PCl_4^+
180 (w)		
193 (w)		$\nu_2(e)$ BCl_4^- (i)
250 (m)	247 (s)	$\nu_4(t_2)$ PCl_4^+
278 (w)		$\nu_4(t_2)$ BCl_4^- (i)
408 (w)		$\nu_1(a_1)$ BCl_4^- (i)
459 (s)	440 (s)	$\nu_1(a_1)$ PCl_4^+
655 (w)	636 (m)	$\nu_3(t_2)$ PCl_4^+

(i) Compare with J. A. Creighton; J. Chem. Soc., 1965, 6589 of the chloride ions to the cationic chlorine atoms and the subsequent weakening of the P-Cl bonds leading to low frequency vibrational shifts, particularly in the symmetric stretching mode. Normal co-ordinate analysis might provide some insight in to this problem.

Similarly, the intense low frequency band found at 25, 26 and 27cm^{-1} in $PBr_4{}^+Br_3{}^-$ $PBr_4{}^+Br^-$ and $PBr_4{}^+Cl^-$ (42) and assigned as a $PBr_4{}^+$ libration is not observed in the Raman spectrum of $PBr_4{}^+BBr_4{}^-$, a fact which suggests that it may arise from cation/halide anion interaction. However, a more comprehensive study of low frequency vibrations in $PBr_4{}^+$ containing salts would be required to confirm this as a generality.

Attempts to prepare a crystal of this compound for X-ray analysis were not successful: sublimation of the original microcrystalline product in sealed ampoules produced clear crystals whose Raman spectra were identical but handling problems caused by the extremely hygroscopic nature of this substance prevented successful transference to Lindemann tubes. Recrystallization of this compound from benzene and halogenated solvents resulted in a white powder whose Raman spectrum was consistent with that of $PCl_4{}^+BCl_4{}^-$ indicating that decomposition had occurred.

Variable temperature Raman studies were performed on $(PCl_4^+)_2$ $BCl_4{}^-Cl^-$ and some results are presented in Table 3.6. These experiments utilized shortened Raman tubes to prevent sublimation of volatiles during heating. The results indicate that when the sample was warmed to 402K the PCl_4^+ modes (ν_1 and ν_3 in particular) had experienced a high frequency shift from the initial "single halide" to polyatomic positions ($440 \longrightarrow 456$ and $636 \longrightarrow 652cm^{-1}$). Also bands appeared at 190, 270, and $408cm^{-1}$ assignable from earlier work to BCl_4^- (28), and at 280 and $355cm^{-1}$, assignable to the PCl_6^- anion (29,30) (The $\nu_5(t_{2g})$ PCl_6^- band at ~ $240cm^{-1}$ was obscured by the relatively intense $\nu_4(t_2)$ PCl_4^+ band). Upon cooling, the intensity of bands associated with these new features slowly decreased in intensity and a shift back to the "single halide" positions of the PCl_4^+ fundamentals was observed. After cooling for ~ 17 hrs the spectrum had reverted to the original form with only residual traces of the $\nu_1(a_{1g})$ PCl_6^- at $360cm^{-1}$ and $\nu_1(a_1)PCl_4^+$ (polyatomic) bands at $455cm^{-1}$. A possible equilibrium describing this behaviour is

$$(PCl_4^+)_2BCl_4^-Cl^- \rightleftharpoons PCl_4^+BCl_4^- + \tfrac{1}{2}PCl_4^+PCl_6^-$$

Further Raman studies indicated that this transition occurred at 121°C(±3°). Initially, a sample heated to ~ 160°C was thought to have irreversibly decomposed, but the experiment had been performed in a full-length Raman tube and sublimation had occurred. Consequent re-examination of this sample after 7 months showed reversion to the original was well underway.

The reversibility of this transition raises an interesting point of nomenclature. Phase III phosphorus pentachloride $(PCl_4^+)_2PCl_6^-Cl^-$ was named "metastable" because it transformed

TABLE 3.6

RAMAN WAVENUMBERS/cm^{-1} FOR A SAMPLE OF $(PCl_4^+)_2BCl_4^-Cl^-$ AT VARIOUS TEMPERATURES

a) 290K	b) 402K	c) 290K (cooled 2hrs)	d) 290K (cooled 17hrs)	Assignments
190 (w)	175 (w)	178 (w)	190 (w)	$\nu_2(e)$ PCl_4^+(hal + poly) + $\nu_2(e)$ BCl_4^-
	190 (w)	188 (w)		
247 (m)	251 (m)	249 (m)	247 (m)	$\nu_4(t_2)$ PCl_4^+(hal + poly)
	270 (w, br)	275 (w)		$\nu_4(t_2)$ BCl_4^- + $\nu_2(e_g)$ PCl_6^-
	280 (w, sh)			
	355 (m)	356 (w/m)	360 (vvw)	$\nu_1(a_{1g})$ PCl_6^-
	408 (w)	409 (w)		$\nu_1(a_1)$ BCl_4^-
440 (s)		440 (v/s)	440 (v/s)	$\nu_1(a_1)$ PCl_4^+(hal)
	456 (s)	455 (m/s)	455 (vvw)	$\nu_1(a_1)$ PCl_4^+(poly)
636 (m)		635 (m)	636 (m)	$\nu_3(t_2)$ PCl_4^+(hal)
	652 (w)	651 (w, sh)		$\nu_3(t_2)$ PCl_4^+(poly)

irreversibly to Phase II ($PCl_4^+PCl_6^-$) upon heating $^{(1,31)}$. However, the $(PCl_4^+)_2BCl_4^-Cl^-$ transition is reversible hence it would be incorrect to name it "metastable" tetrachlorophosphonium tetrachloroborate ($PCl_4^+BCl_4^-$).

From these results it appeared that a possible method of preparation of this compound would be to heat a 1:0.5 mixture of $PCl_4^+BCl_4^-$ and $PCl_4^+PCl_6^-$. This experiment was performed by heating such a mixture in the variable temperature Raman apparatus and periodically monitoring the spectrum. No compound formation was observed upon cooling such mixtures so the experiment was unsuccessful.

A low-temperature sublimation experiment was performed on $(PCl_4^+)_2BCl_4^-Cl^-$ similar to those described for $PCl_4^+PCl_6^-$ and $PBr_4^+Br^-$ in Chapter 2. The average deposition time was 3½ hours from 50°C. The Raman spectrum at 20K indicated the presence of PCl_4^+ (polyatomic), BCl_4^-, PCl_6^- and PCl_5 (covalent). Warming to ambient under a static vacuum over 12 hours resulted in the loss of PCl_5 (covalent), a process clearly visible by the loss of the characteristic $\nu_1(a_1')$ P-Cl(ax) at 400cm^{-1}, leaving a spectrum that was almost identical to that obtained at 402K in the variable temperature experiment reported earlier (Table 3.6). Further standing for 6 hours resulted in the appearance of a band at 443cm^{-1}, clearly attributable to PCl_4^+ (halide), at the expense of the band at 455cm^{-1} (PCl_4^+ polyatomic). Unfortunately further monitoring was impossible as the sample fell off the cold head, but the indications were that the spectrum was changing to that obtained for ordinary solid $(PCl_4^+)_2BCl_4^-Cl^-$.

Numerous attempts were made to prepare analogues of the compound $(PCl_4^+)_2BCl_4^-Cl^-$ and they are listed in Tables 5.2 and 5.3. They were not successful, indicating a limited stability of such systems. Many of the preparations in arsenic trichloride resulted in products containing arsenic species, undoubtedly similar to those obtained by Beattie et al (29). Those performed in anhydrous hydrogen chloride usually yielded standardtetrachlorophosphonium salts though the reaction of $2PCl_3/BCl_3/Cl_2$ resulted in the formation of the title product, and metastable PCl_5 was formed by either PCl_5 recrystallization or PCl_3/Cl_2 reaction in the same solvent.

It is interesting to note here the claim of Gutmann who (33), during an investigation of the SO_2Cl_2 solvent system, found evidence for 2:1 compound formation between PCl_5 and $SbCl_5$. This was formulated as $(PCl_4^+)_2SbCl_7^{2-}$ but received criticism in a review by Webster (33) who considered a $PCl_5/SbCl_5/SO_2Cl_2$ complex formation to be more likely. As Gutmanns' original formulation may be rewritten as $(PCl_4^+)_2SbCl_6^-Cl^-$ the preparation was repeated during this study. A light brown crystalline substance was isolated but the Raman spectrum was not assignable to this formulation with $SbCl_6^-$ being the only ion immediately assignable from bands at 336, 297 and 184cm^{-1} (29,34). Thus it was apparent that some solvent interaction had occurred though a detailed investigation of the product was beyond the scope of this work.

3.3 Implications of the compound $(PCl_4^+)_2BCl_4^-Cl^-$ to the $PCl_3/BCl_3/Br_2$ system

The $PCl_3/BCl_3/Br_2$ system was extensively investigated by Ryan et al (1,35,36,37) and it is necessary to review his observations prior to further discussion. From such reactions in either anhydrous HCl or CH_2Cl_2 the series of cations $PCl_nBr_{4-n}^+$ ($0 \leq n \leq 4$) were usually obtained in mixtures and identified by static solid-state ^{31}P NMR and Raman spectroscopy. The presence of two different halogen atoms leads to different symmetries for the PCl_3Br^+, $PCl_2Br_2^+$ and $PClBr_3^+$ ions when compared with the tetrahedral parent PX_4^+ species. PCl_3Br^+ and $PClBr_3^+$ exhibit C_{3v} symmetry with the following vibrational representation:

$$vib = 3a_1\ (R,\ IR) + 3e\ (R,\ IR)$$

whereas $PCl_2Br_2^+$ is of C_{2v} symmetry and consequently different vibrational representation.

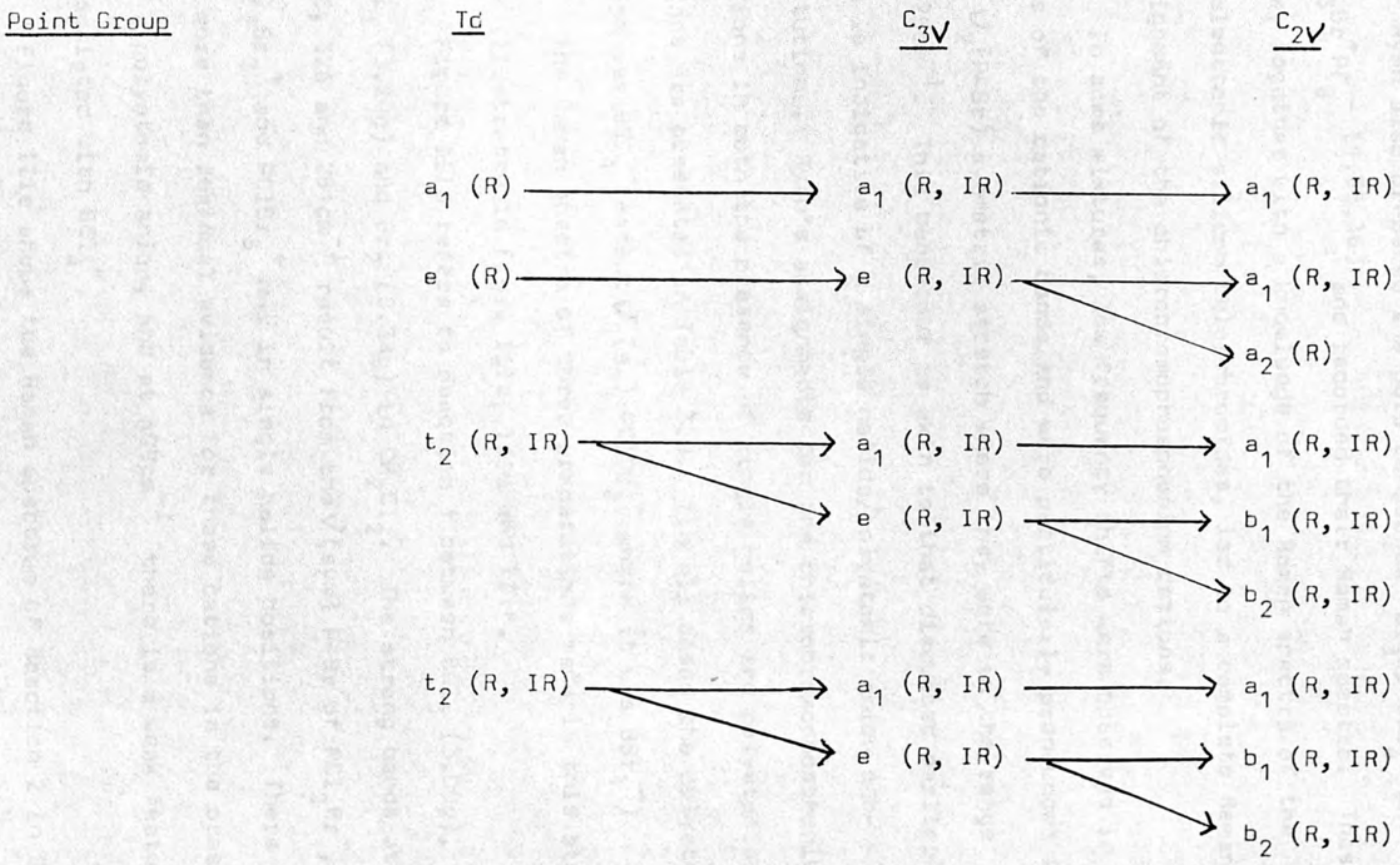
$$\Gamma vib = 4a_1\ (R,\ IR) + a_2\ (R) + 2b_1\ (R,\ IR) + 2b_2\ (R,\ IR)$$

(R and IR indicate Raman and infra-red activity).

This information is more conveniently represented as a correlation table and is presented as such in Table 3.7 where the splitting of degenerate vibrations and activation of infra-red inactive vibrations by the lowering of symmetry is clearly seen.

TABLE 3.7

CORRELATION TABLE FOR T_d, C_{3v} AND C_{2v} SYMMETRIES



Point Group	Td	C_{3v}	C_{2v}
	a_1 (R)	a_1 (R, IR)	a_1 (R, IR)
	e (R)	e (R, IR)	a_1 (R, IR)
			a_2 (R)
	t_2 (R, IR)	a_1 (R, IR)	a_1 (R, IR)
		e (R, IR)	b_1 (R, IR)
			b_2 (R, IR)
	t_2 (R, IR)	a_1 (R, IR)	a_1 (R, IR)
		e (R, IR)	b_1 (R, IR)
			b_2 (R, IR)

Ryan also prepared the pure compounds $PCl_3Br^+BCl_4^-$ and $PCl_3Br^+PF_6^-$ (1,35,36) and recorded their Raman spectra. These data, together with a knowledge of the Raman spectra of the isoelectronic silicon chlorobromides, led to a complete Raman assignment of the chlorobromophosphonium cations.

In some mixtures, low frequency shifts were observed in some of the cationic bands and were particularly pronounced in the ν_2(P-Br) symmetric stretch where they were in the range 14-25cm^{-1}. This behaviour is akin to that discussed earlier and is indicative of a single halide/polyatomic anion substitution. Ryan's assignments for the chlorobromophosphonium cations in both the presence of single halide and polyatomic anions are presented in Table 3.8. (in all cases the polyatomic anion was BCl_4^- except $\nu_3(a_1)$ $PClBr_3^+$ where it was BBr_4^-)

The Raman spectra of three preparations made in this study are illustrated in Figs. IIId, IIIe and IIIf.

Figure IIId refers to Reaction 1 between BCl_3 (3.00g), PCl_3 (3.20g) and Br_2 (2.34g) in CH_2Cl_2. The strong bands at 376, 326 and 281cm^{-1} result from the ν(sym) P-Br of PCl_3Br^+, $PCl_2Br_2^+$ and $PClBr_3^+$ ions in single halide positions. There is no more than residual evidence for these cations in the presence of a polyatomic anion, and at 409cm^{-1} there is a weak feature associated with BCl_4^-.

Figure IIIe shows the Raman spectrum of Reaction 2 in CH_2Cl_2

(3.20g PCl_3, 3.40g BCl_3 and 3.90g Br_2). This is very similar to that obtained for the product of Reaction 1, again showing bands at 376, 327 and 281cm^{-1} resulting from the PCl_3Br^+, $PCl_2Br_2^+$ and $PClBr_3^+$ ions associated with a single halide anion. The only difference in the spectra is the relative intensities of these bands: in Reaction 2 they are more intense for the heavily brominated species when compared with those from Reaction 1, which is not unexpected in view of the reactant ratios. Again, only residual bands corresponding to cations in the polyatomic position are observed and the $\nu_1(a_1)$ BCl_4^- mode at 408cm^{-1} is very weak.

Figure IIIf shows the Raman spectrum of Preparation 4 in anhydrous HCl (6.96g PCl_3, 8.21g Br_2 and 4.86g BCl_3). Each of the chlorobromophosphonium cations has two associated bands arising from ν_{sym} (P-Br): at 392 and 374cm^{-1} for PCl_3Br^+, at 345 and 327cm^{-1} for $PCl_2Br_2^+$ and at 301 and 280cm^{-1} for $PClBr_3^+$. In this spectrum the $\nu_1(a_1)$ BCl_4^- mode at 408cm^{-1} is relatively more intense than the equivalent band in Figs IIId and e. This suggests that this preparation contains a mixture of cations associated with both single halide and polyatomic anions. The ν_2 stretching modes of these three mixtures are compared in Table 3.9.

Thus it is apparent that the $PCl_3/BCl_3/Br_2$ reactions may form cations whose Raman spectra indicate either single halide or polyatomic anions ⊗ or even a mixture of these. (⊗ Reactions where solely polyatomic products were formed are re-

TABLE 3.8

RAMAN WAVENUMBERS/cm^{-1} OF THE CHLOROBROMOPHOSPHONIUM CATIONS IN THE PRESENCE OF BOTH SINGLE HALIDE AND POLYATOMIC ANIONS (all taken from F. J. Ryan, Ph. D. thesis University of London, 1972)

PCl_3Br^+ (C_{3v})			$PCl_2Br_2^+$ (C_{2v})			$PClBr_3^+$ (C_{3v})		
Assignment	Halide	Polyatomic	Assignment	Halide	Polyatomic	Assignment	Halide	Polyatomic
$\nu_1(a_1)$ ν_s(P-Cl)	565 (w)	582 (w)	$\nu_1(a_1)$ ν_s (P-Cl)	584 (w)	600 (w)	$\nu_1(a_1)$ ν (P-Cl)	587 (w)	583 (w)
$\nu_2(a_1)$ ν (P-Br)	376 (vs)	390 (vs)	$\nu_2(a_1)$ ν_s (P-Br)	326 (vs)	348 (vs)	$\nu_2(a_1)$ ν_s (P-Br)	285 (vs)	301 (vs)
$\nu_3(a_1)$ δ (PCl_3)	204 (vs)	213 (vs)	$\nu_3(a_1)$ δ (PCl_2)	191 (s)	198 (s)	$\nu_3(a_1)$ δ (PBr_3)	149 (s)	(151(s))
$\nu_4(e)$ ν_{as}(P-Cl)	628 (w)	647 (vw)	$\nu_4(a_1)$ δ (PBr_2)	132 (w)	128 (w)	$\nu_4(e)$ ν_{as} (P-Br)	500 (m)	503 (w)
$\nu_5(e)$ δ (Br-P-Cl)	230 (m)	233 (s)	$\nu_5(a_2)$ torsion	150 (w)	155 (w)	$\nu_5(e)$ δ (Br-P-Cl)	172 (s)	176 (s)
$\nu_6(e)$ δ (Cl-P-Cl)	161 (w)	155 (s)	$\nu_6(b_1)$ ν_{as}(P-Cl)	616 (w)	632 (w)	$\nu_6(e)$ δ (Br-P-Br)	120 (w)	126 (w)
			$\nu_7(b_1)$ δ (PCl_2)	201 (vs)	207 (s)			
			$\nu_8(b_2)$ ν_{as}(P-Br)	518 (w)	522 (w)			
			$\nu_9(b_2)$ δ (PBr_2)	173 (s)	179 (s)			

Fig III d

Raman spectrum of a PCl_3–BCl_3–Br_2 reaction product (Reaction 1)

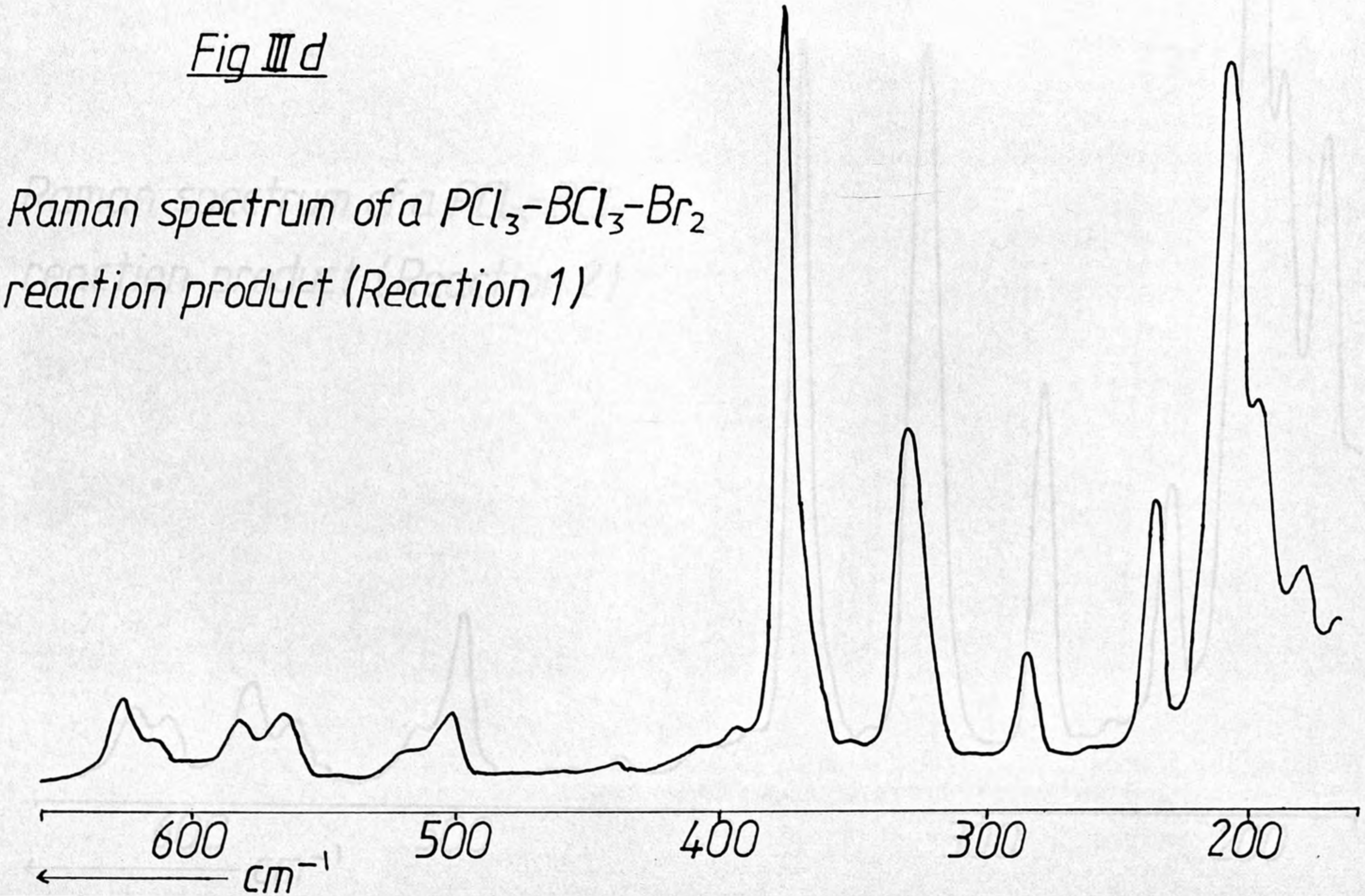


Fig III e

Raman spectrum of a PCl_3–BCl_3–Br_2 reaction product (Reaction 2)

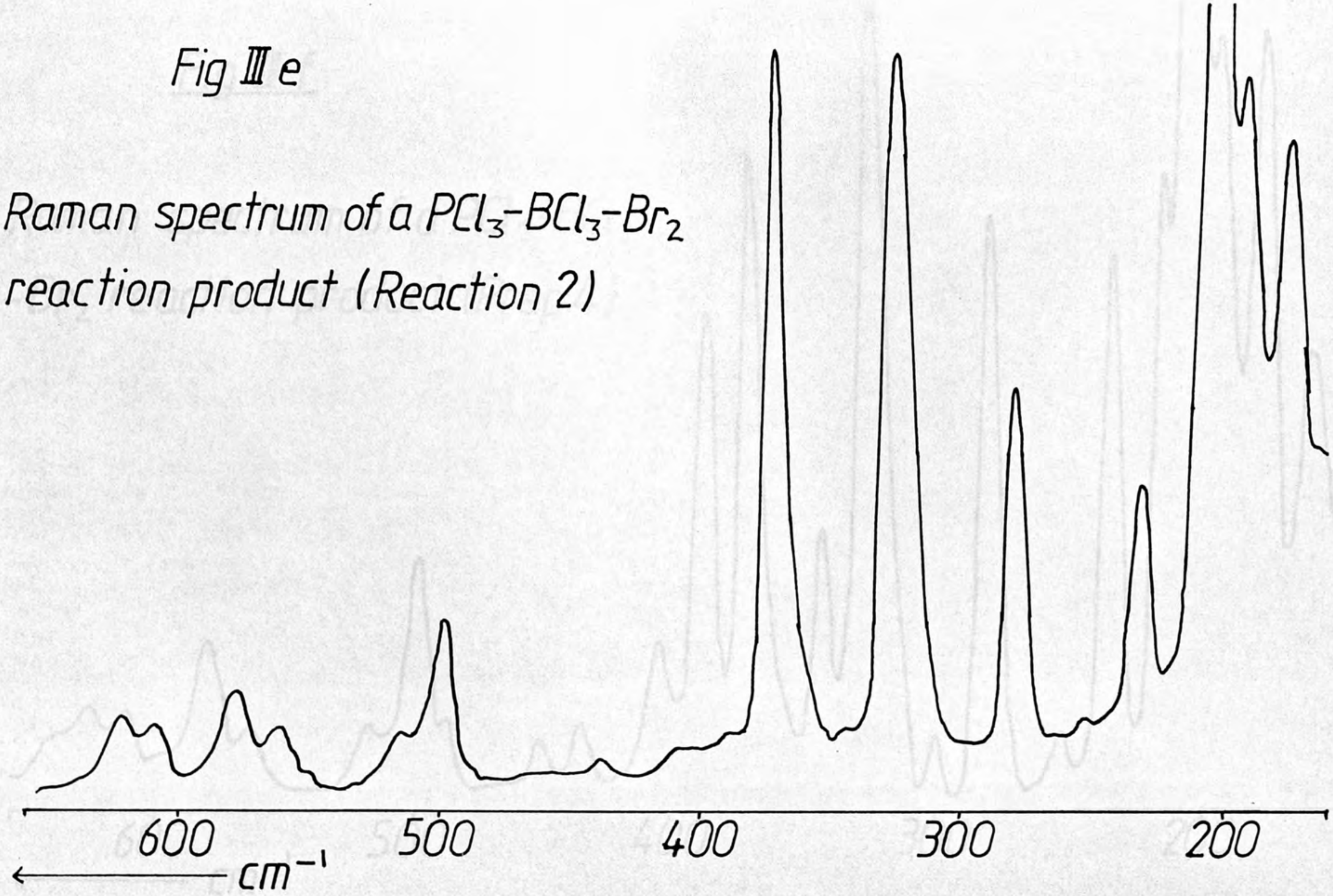


Fig III f

Raman spectrum of a PCl_3-BCl_3 -Br_2 reaction product (Prep 4)

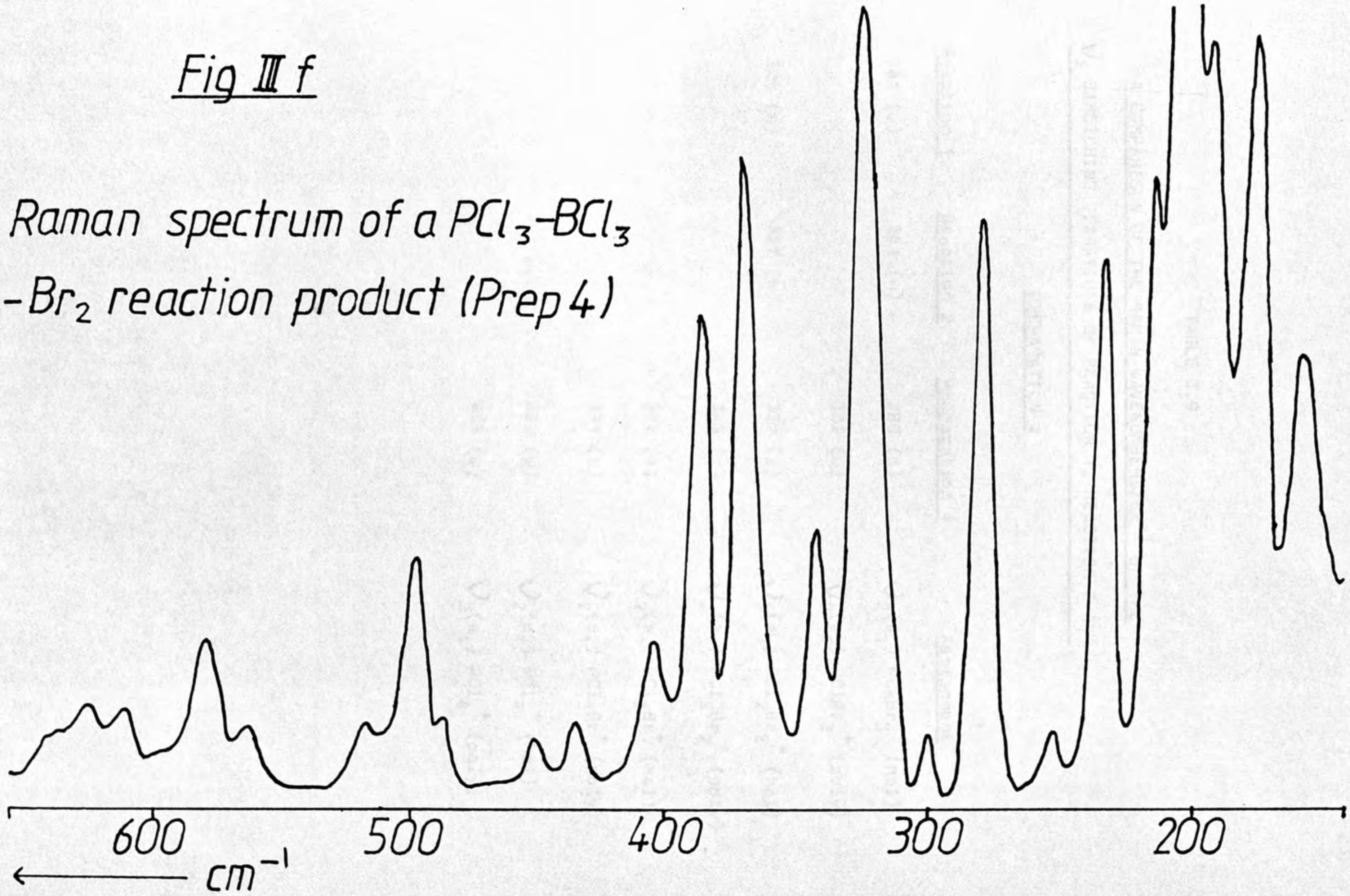


TABLE 3.9

A COMPARISON OF THE RAMAN WAVENUMBERS/cm^{-1} OF THE ν_2 STRETCHING VIBRATIONS OF REACTION 1, REACTION 2 AND PREPARATION 4

Reaction 1	Reaction 2	Preparation 4	Assignment
281 (w)	281 (m)	280 (s)	$\nu_2(a_1)$ $PClBr_3^+$ (hal)
		302 (w)	$\nu_2(a_1)$ $PClBr_3^+$ (poly)
326 (m)	327 (s)	327 (s)	$\nu_2(a_1)$ $PCl_2Br_2^+$ (hal)
		345 (m)	$\nu_2(a_1)$ $PCl_2Br_2^+$ (poly)
376 (s)	376 (s)	374 (s)	$\nu_2(a_1)$ PCl_3Br^+ (hal)
		391 (s)	$\nu_2(a_1)$ PCl_3Br^+ (poly)
440 (vw)	441 (vw)	438 (w)	$\nu_2(a_1)$ PCl_4^+ (hal)
		455 (w)	$\nu_2(a_1)$ PCl_4^+ (poly)

ported in Ryan's thesis) (1).

In view of the isolation of the pure compound $(PCl_4^+)_2BCl_4^-Cl$ (see Chapter 3.2) it is possible to make several inferences concerning the nature of the single halide products from the $PCl_3/BCl_3/Br_2$ system. It is likely that such products are mixtures of compounds with the general formula $P_2X_{13}B$ or more explicitly $(PX_4^+)_2BX_4^-X^-$ where X is Cl or Br. The Raman spectra of single halide products indicate the presence of mixed halide tetrahalophosphonium cations. The nature of X^- is not as obvious but it seems reasonable to assume that it could be either Cl^- or Br^-. (cf $(PCl_4^+)_2BCl_4^-Cl^-$ and $PBr_4^+Br^-$).

Raman spectroscopy is not a satisfactory technique to examine the possibilities of halide scrambling in the tetrahaloborate anions. This results from (a) the inherent weakness of B–X Raman modes in comparison with those of P–X and (b) the proposed formulation $(PX_4^+)_2BX_4^-X^-$ has a 2:1 ratio of phosphorus to boron species as in the case of $(PCl_4^+)_2BCl_4^-Cl^-$ thus further diminishing the relative intensity of any anion modes. ^{11}B M.A.R. NMR was used to investigate such systems and is discussed in Section 3.5.c. This technique revealed that in the case of Preparation 4 BCl_4^- was the only species present and that Reaction 1 contained predominantly BCl_4^- with some traces of BCl_3Br^- and $BCl_2Br_2^-$. Reaction 2 was shown to contain almost exclusively BCl_4^- with only residual BCl_3Br^-.

Thus halide scrambling occurs predominantly at the phosphorus site so the proposed formulation for these single halide mixtures may be modified to $(PCl_nBr_{4-n}^+)_2BCl_4^-X^-$ $(0 \leq n \leq 4)$ where $X = Cl^-$ or Br^-.

In the current study no relatively pure compound containing a chlorobromophosphonium cation was obtained to test the above hypothesis. However, one such compound was reported in the literature: Finch, Gates, Ryan and Bentley (35) noted the preparation of a so-called Compound A produced by a $PCl_3/BCl_3/Br_2$ reaction in CH_2Cl_2 at -50^oC. The Raman fundamentals of this compound showed it to contain the PCl_3Br^+ cation in a single halide position ($\nu_2(a_1) = 376cm^{-1}$) with only slight traces of the $PCl_2Br_2^+$ and $PClBr_3^+$ ions. This was confirmed by static solid-state ^{31}P NMR and similar ^{11}B measurements showed BCl_4^- to be present. Analysis yielded the following results: Cl, 46.9%; Br, 41.5%; P, 8.7% and B, 1.7% and these combined with the empirical formulation P_2BX_{13} lead to the general formula $P_2BCl_9Br_4$. If this is then modified to allow for an artificially high bromide analysis resulting from the heavily brominated impurities, the formulation $P_2BCl_{10}Br_3$ may be proposed for this compound and this may be explicitly expressed as $(PCl_3Br^+)_2BCl_4^-$ Br^- .

This is entirely consistent with the reported Raman spectrum of Compound A when the slight impurities are discounted and is in agreement with the general hypothesis that single halide products as obtained in Reactions 1 and 2 are mixtures of compounds formulated as $(PCl_nBr_{4-n}^+)_2BCl_4^-X^-$ $(0 \leq n \leq 4)$ where $X^- = Cl^-$ or Br^-.

It is interesting to note that the $PCl_3/Br_2/BF_3$ system was previously investigated by Gates et al (26) and Raman spectra of the mixed chlorobromophosphonium cations obtained indicated single halide species were predominantly formed although the BF_4^- anion was also in evidence. Thus it is not unreasonable to assume that the mixtures obtained in this system provide other examples of the $(PCl_nBr_{4-n}^+)_2BF_4^-X^-$ $(0 \leq n \leq 4)$ formulation proposed earlier for some $PCl_3/BCl_3/Br_2$ reaction products.

It is also interesting to note some results reported by Dhamelincourt and co-workers on the Raman spectra of various PBr_5/BBr_3 and $PBr_5/TaBr_5$ fusion mixtures (40,41). Here, where an excess of the phosphorus pentabromide was used, low frequency shifts were observed in the $\nu_1(a_1)$ mode of PBr_4^+ when compared with that observed in the salts $PBr_4^+BBr_4^-$ and $PBr_4^+TaBr_6^-$. The formation of indeterminate species generally formulated as $(PBr_4^+)_n(Br^-)_{n-x}(BBr_4^-)_2$ and $(PBr_4^+)_n(Br^-)_{n-x}(TaBr_6^-)_x$ was proposed to account for these observed shifts and, like the systems under discussion in the current study, single halide ions are present. Unfortunately it appears that no single compound was isolated from these mixtures, hence the absence of analytical and crystallographic data.

Variable temperature Raman studies were performed on Reactions 1 and 2 ($PCl_3/BCl_3/Br_2$ in CH_2Cl_2) and Preparation 4

(PCl_3/BCl_3/Br_2 in HCl) to investigate the relative stabilities of the chlorobromophosphonium cations in the presence of single halide and polyatomic anions. Some of these experiments were performed in Raman tubes long enough to allow some sublimation to occur so both residue and sublimate could be observed. The trends observed were consistent with all samples used and are detailed below.

On warming to approximately 60°C Reactions 1 and 2 showed similar changes with bands at 345, 391 and 456cm^{-1} appearing. These are associated with the $PCl_2Br_2^+$, PCl_3Br^+ and PCl_4^+ ions in the presence of a polyatomic anion. Increasing the temperature resulted in these bands increasing in relative intensity when compared to their single halide counterparts, originally exclusively present. At about 90°C the spectra were dominated by bands at 456, 391 and 352cm^{-1} with bands due to the least brominated forms being most intense. Hardly any trace of the original single halide bands at 376, 327 and 281cm^{-1} remained although the spectra were becoming increasingly feeble. Also the BCl_4^- fundamental at 409cm^{-1} became more intense with heating. Thus two main processes occurred on warming: i) the conversion of single halide to polyatomic species and ii) the increase in proportions of the least brominated species (PCl_4^+, PCl_3Br^+).

On cooling to ambient for about 10 days these residues completely reverted to their original forms, that is with cation bands in the single halide positions though not in their initial intensities. The intensities of these bands obtained on cooling were always in the order PCl_3Br^+ ($376cm^{-1}$) $>$ $PCl_2Br_2^+$ ($327cm^{-1}$) $>$ $PClBr_3^+$ ($281cm^{-1}$).

Sublimates occurring up the heated tube exhibited constant spectra on standing. They were always pure single halide forms with PCl_3Br^+ ($376cm^{-1}$) being the most intense band in the spectrum with lesser amounts of $PCl_2Br_2^+$ ($327cm^{-1}$) and $PClBr_3^+$ ($281cm^{-1}$).

It is quite interesting that in the cases of both Reactions 1 and 2, no evidence was found for anything other than residual PCl_4^+ species in the sublimate and the cooled residue.

The behaviour of Preparation 4 under the same conditions was similar to that recorded for Reactions 1 and 2. This sample contained Raman bands of the chlorobromophosphonium cations relating to both single halide and polyatomic anions and the heating process resulted in an increase in the intensity of the bands at 458, 392, 345 and $301cm^{-1}$ at the expense of those at 441, 374, 327 and $280cm^{-1}$. This can again be explained as a conversion of single halide to polyatomic anions in the lattice. Also the more heavily chlorinated species dominated the spectrum on warming to $95^{\circ}C$ and the band at $409cm^{-1}$ associated with BCl_4^- was relatively more intense. On cooling for 5 days the spectrum had returned to it's original form indicating a mixture of cations associated with single halide and polyatomic anions, and with much less intense PCl_4^+ and PCl_3Br^+ bands than in the heated sample. A sublimate from this sample was the same as those obtained in Reactions 1 and 2; a pure single halide form with PCl_3Br^+, PCl_2Br^+ and $PClBr_3^+$ cations.

Thus this behaviour is consistent with that of $(PCl_4^+)_2$ $BCl_4^-Cl^-$ under variable temperature conditions with the reversible transition of the single halide complex into polyatomic species. In the mixed halide systems there is however, no evidence for the formation of hexahalophosphate anions, only BCl_4^- being observed. This is not entirely unexpected as mixed chlorobromohexahalophosphates are not known.

Preparative sublimations were performed on samples containing a mixture of single halide and polyatomic anions (eg Preparation 4) using the apparatus represented in Fig. V8. Sublimates collected were generally quite pure single halide mixtures whereas the residues were often mixtures weighted towards the dominance of polyatomic species. This is again consistent with the variable temperature Raman studies discussed earlier.

3.4 The compound P_2Cl_9Br and related systems

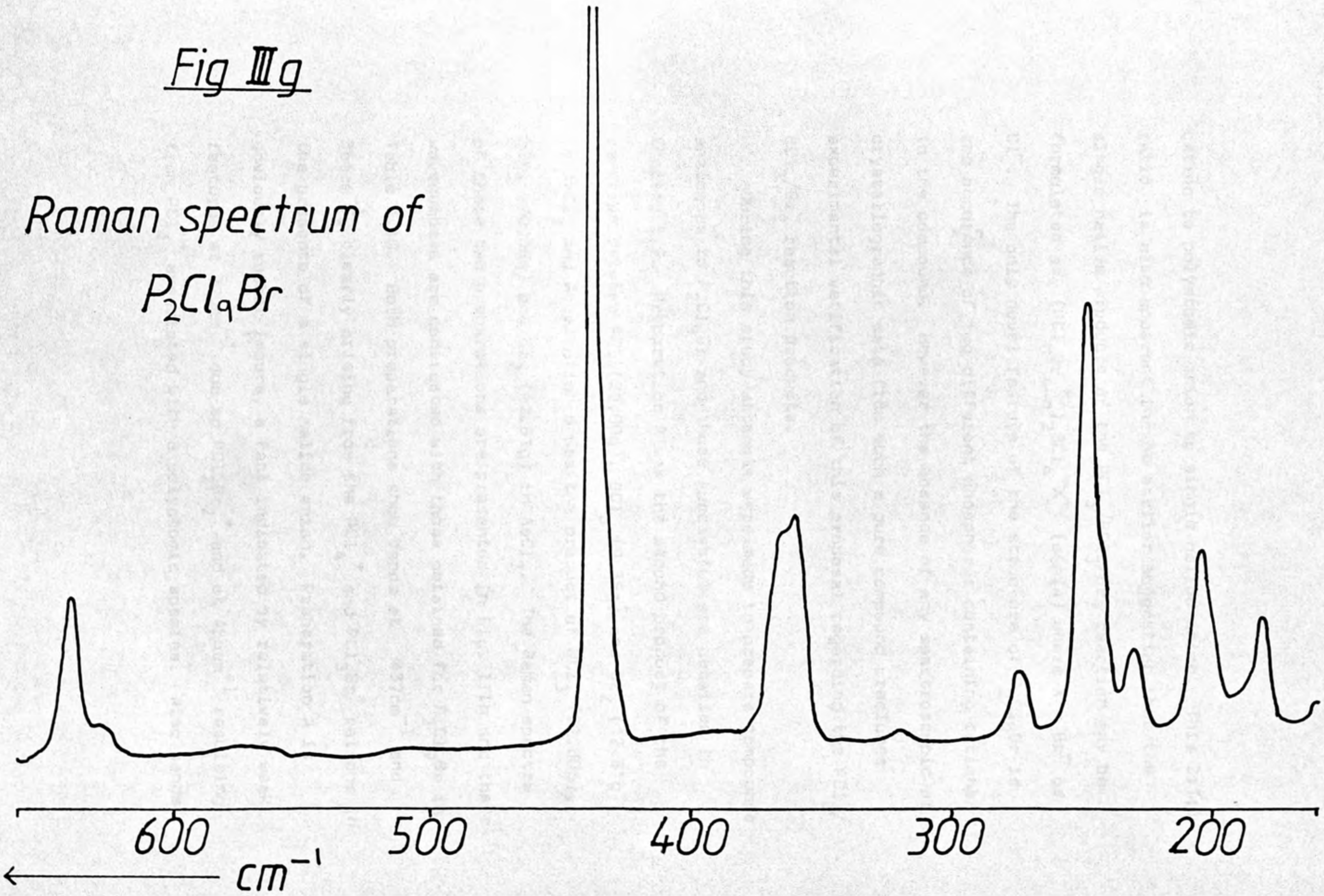
The title compound, a yellow crystalline substance, was first prepared in 1957 by Kolditz and Feltz (38) from the reaction of phosphorus trichloride and bromine in arsenic trichloride. Originally formulated as $PCl_4^+PCl_5Br^-$, this was disproved by vibrational and ^{31}P NMR spectroscopy (39) using the knowledge gained by examination of the $PCl_3/Br_2/BCl_3$

system (1,35,36,37). The Raman spectrum (Fig. IIIg) of this compound showed the presence of the PCl_4^+ and PCl_3Br^+ cations with frequencies in positions indicative of single halide ions in the lattice. The PCl_6^- anion was shown to be present by bands at 358 and 274cm^{-1} and three phosphorus containing species were confirmed by static solid-state ^{31}P NMR with resonances at -295ppm (PCl_6^-), $\sim + 80$ppm (PCl_4^+) and $\sim + 50$ppm (PCl_3Br^+) (all relative to 85% H_3PO_4). This NMR study also suggested a 3:1 ratio of PCl_4^+ to PCl_3Br^+ and a nett formulation $(PCl_4^+)_6(PCl_3Br^+)_2(PCl_6^-)_4Br_4^-$ was proposed for this compound. One reason for arriving at this formulation was based on a powder X-ray diffraction photograph which indicated very similar dimensions to one reported for a compound $PCl_{4.66}Br_{0.33}$ (22). Data for this latter compound led to a proposal that the unit cell consisted of $8PCl_4^+$ ions, $4PCl_6^-$ ions and $4Br^-$ ions. This compound is interesting because this formulation can be reduced to $(PCl_4^+)_2PCl_6^-Br^-$, ie analogous to metastable phosphorus pentachloride $(PCl_4^+)_2PCl_6^-Cl^-$, differing only in the nature of the single halide ion. Unfortunately no Raman data are available for $PCl_{4.66}Br_{0.33}$ which would enable a better comparison to be made.

The formulation for P_2Cl_9Br given earlier reduces to $(PCl_4^+)_3PCl_3Br^+(PCl_6^-)_2(Br^-)_2$ which, in agreement with metastable PCl_5, $PBCl_{13}$ and $PCl_{4.66}Br_{0.33}$ has a 2:1:1 ratio of

Fig IIIg

Raman spectrum of P_2Cl_9Br

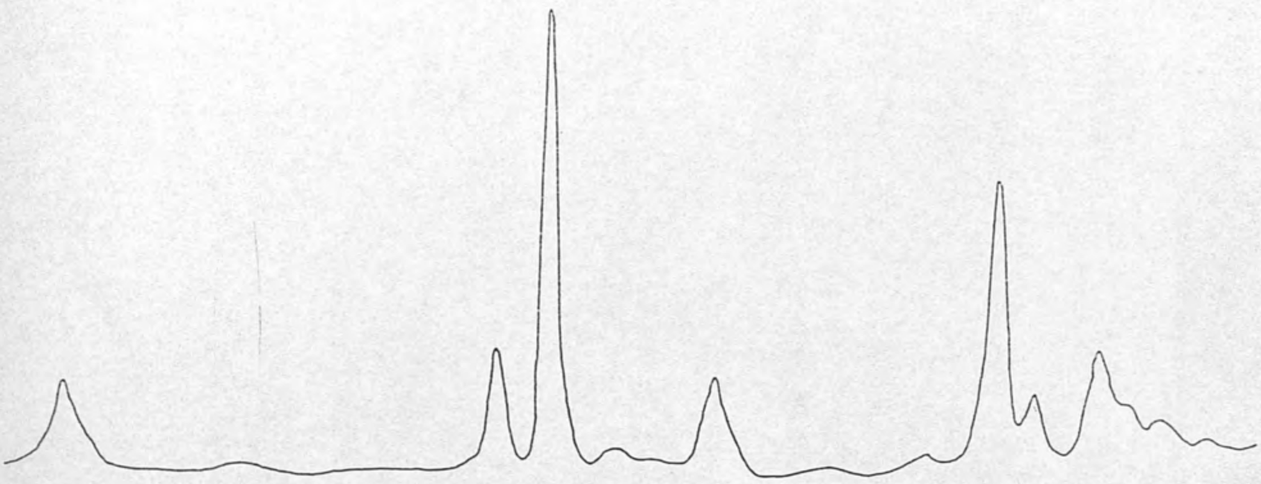


cation to polyatomic anion to single halide anion. This 2:1:1 ratio is also apparent in the earlier suggestion that the single halide products of the $PCl_3/BCl_3/Br_2$ reaction may be formulated as $(PCl_nBr_{4-n}^+)_2BCl_4^-X^-$ $(0 \leq n \leq 4)$ where $X = Br^-$ or Cl^-. The only novel feature of the structure of P_2Cl_9Br is the occurrence of two different phosphorus containing cations in the compound. However the absence of any spectroscopic or crystallographic data from such a pure compound precludes experimental verification of this proposal regarding the $PCl_3/BCl_3/Br_2$ reaction products.

During this study attempts were made to prepare compounds analogous to P_2Cl_9Br and those successful are detailed in Chapter 5.9. Preparation A was the second product of the reaction between PCl_3(22.00g), BCl_3 (9.35g) and Br_2 (12.81g) in $AsCl_3$ and Preparation B was the product of PCl_3 (22.00g), BBr_3 (20.08g) and Br_2 (12.81g) in $AsCl_3$. The Raman spectra of these two preparations are presented in Fig. IIIh and their wavenumbers are contrasted with those obtained for P_2Cl_9Br in Table 3.10. Both preparations show bands at 437cm^{-1} and 366cm^{-1}, clearly arising from the PCl_4^+ and PCl_3Br^+ cations in the presence of a single halide anion. Preparation A is obviously rather impure, a fact indicated by relatively weak features at 220cm^{-1} due to $PCl_2Br_2^+$ and at 456cm^{-1} resulting from PCl_4^+ associated with a polyatomic species. Also bands

Fig IIIh Raman spectra of

i) Prep A [$2PCl_3$-BCl_3-Br_2 in $AsCl_3$]



ii) Prep B [$2PCl_3$-BBr_3-Br_2 in $AsCl_3$]

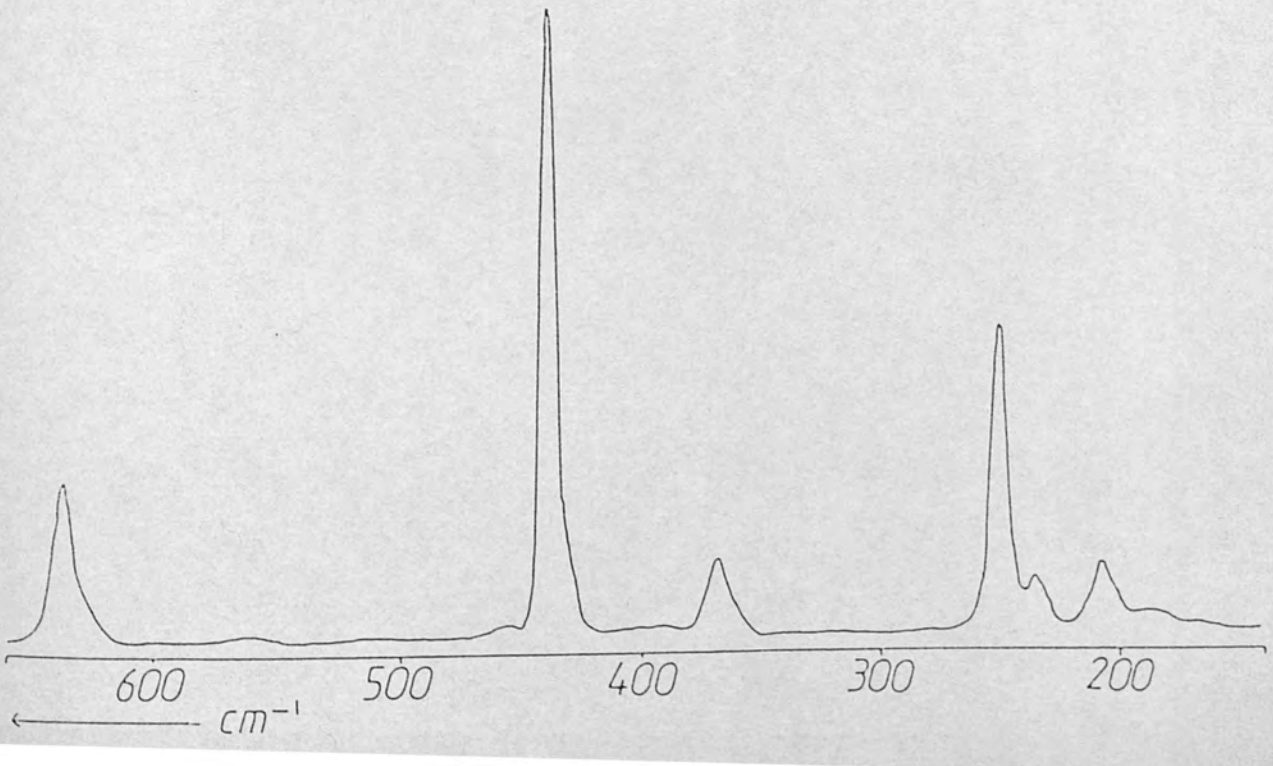


TABLE 3.10

COMPARISON OF THE RAMAN WAVENUMBERS/cm^{-1} OF P_2Cl_9Br AND PREPARATIONS A AND B

P_2Cl_9Br	Preparation A	Preparation B	Assignment
158 (w)	159 (w)	160 (vw)	$\nu_5(e)$ PCl_3Br^+
178 (w)	179 (w)	182 (vw)	$\nu_2(e)$ PCl_4^+
	190 (w)	190 (vw)	$\nu_2(e)$ BCl_4^-
203 (w)	205 (m)	206 (w)	$\nu_3(a_1)$ PCl_3Br^+
229 (w)	231 (w)	233 (w)	$\nu_5(e)$ PCl_3Br^+
245 (m)	246 (m)	247 (m/s)	$\nu_4(t_2)$ PCl_4^+
272 (w)			$\nu_2(e_g)$ PCl_6^-
	277 (vw)		$\nu_4(t_2)$ BCl_4^-
	320 (vw)		$\nu_2(a_1)$ $PCl_2Br_2^+$
359 (m)			$\nu_1(a_{1g})$ PCl_6^-
366 (m)	366 (m)	366 (m/w)	$\nu_2(a_1)$ PCl_3Br^+ (hal)

TABLE 3.10 CONT'D

P_2Cl_9Br	Preparation A	Preparation B	Assignment
	408 (w)		$\nu_1(a_1)$ BCl_4^-
438 (s)	436 (vs)	437 (vs)	$\nu_1(a_1)$ PCl_4^+ (hal)
	456 (w)	458 (vw)	$\nu_1(a_1)$ PCl_4^+ (poly)
570 (vw)	565 (vw)	564 (vw)	$\nu_1(a_1)$ PCl_3Br^+
626 (vw)	625 (w, sh)	624 (w, sh)	$\nu_4(e)$ PCl_3Br^+
636 (w)	635 (w)	635 (w)	$\nu_3(t_2)$ PCl_4^+

at 190 and 408cm^{-1} indicate the presence of the BCl_4^- anion $^{(28)}$. The Raman spectrum of Preparation B is much cleaner, the band due to PCl_4^+ in association with a polyatomic anion is very weak and bands due to BCl_4^- are also weak. The intensities of the PCl_4^+ and PCl_3Br^+ fundamentals at 366 and 438cm^{-1} in these two preparations are similar in ratio to those seen in the Raman spectrum of P_2Cl_9Br. Analytical data questions the purity of Preparation A in that no reasonable forumulation analogous to P_2Cl_9Br can be made; the Cl^- analysis of 63.4% is particularly low. Such data for Preparation B is more promising, which is hardly surprising considering the 96.6 cleaner Raman spectrum. The Cl^- analysis was 75.7% 75.8 and the Br^- analysis was 11.1 10.9% and, assuming no considerable halogen scrambling has occurred on the boron anion, a formulation of

$$(PCl_4^+)_6(PCl_3Br^+)_2(BCl_4^-)_4(Cl^-)_3Br^-$$

could be tentatively proposed. This is consistent with the Raman and analytical data though there is no positive evidence for different single halide anions in the same lattice.

Preparation A showed greater instability than Preparation B in that exposure to the laser beam (514.5nm) resulted in a rapid increase in intensity of the band at 458cm^{-1} due to the PCl_4^+ cation in the presence of a polyatomic anion. Simultaneously, the band at 408cm^{-1} ($\nu_2(a_1)$ BCl_4^-) increased in relative intensity and almost all evidence for cations in the single halide position had vanished after 2 hours exposure to the laser radiation. This same effect was observed on heating Preparation B to about 140°C. Thus it may be reasonable to assume that the products obtained are the same, with Preparation B giving the much purer compound.

A confirmatory test was performed on Preparation B in an attempt to show that it was a discrete compound and not a mixture of P_2Cl_9Br and $PCl_4{}^+BCl_4{}^-$. These last two substances were mixed in a 2:1 ratio and the Raman spectrum examined. The main features differentiating this spectrum from that of Preparation B were in the 350-370cm^{-1} area. The spectrum of the artificial mixture contained a broad band with a maximum at 359 and a shoulder at 366cm^{-1} as seen in that of P_2Cl_9Br (Fig. IIIg). However, the Raman spectrum of Preparation B has a band with a maximum at 366cm^{-1} ($\nu_2(a_1)$ PCl_3Br^+) and no obvious feature at 359cm^{-1}. Hence the absence of $PCl_6{}^-$ from this preparation can be established and thus it is reasonable to assume that it is a compound, possibly with the formulation stated above.

3.5 "Magic Angle Rotation" NMR studies of some solid Phosphorus (V) Halides and derivatives

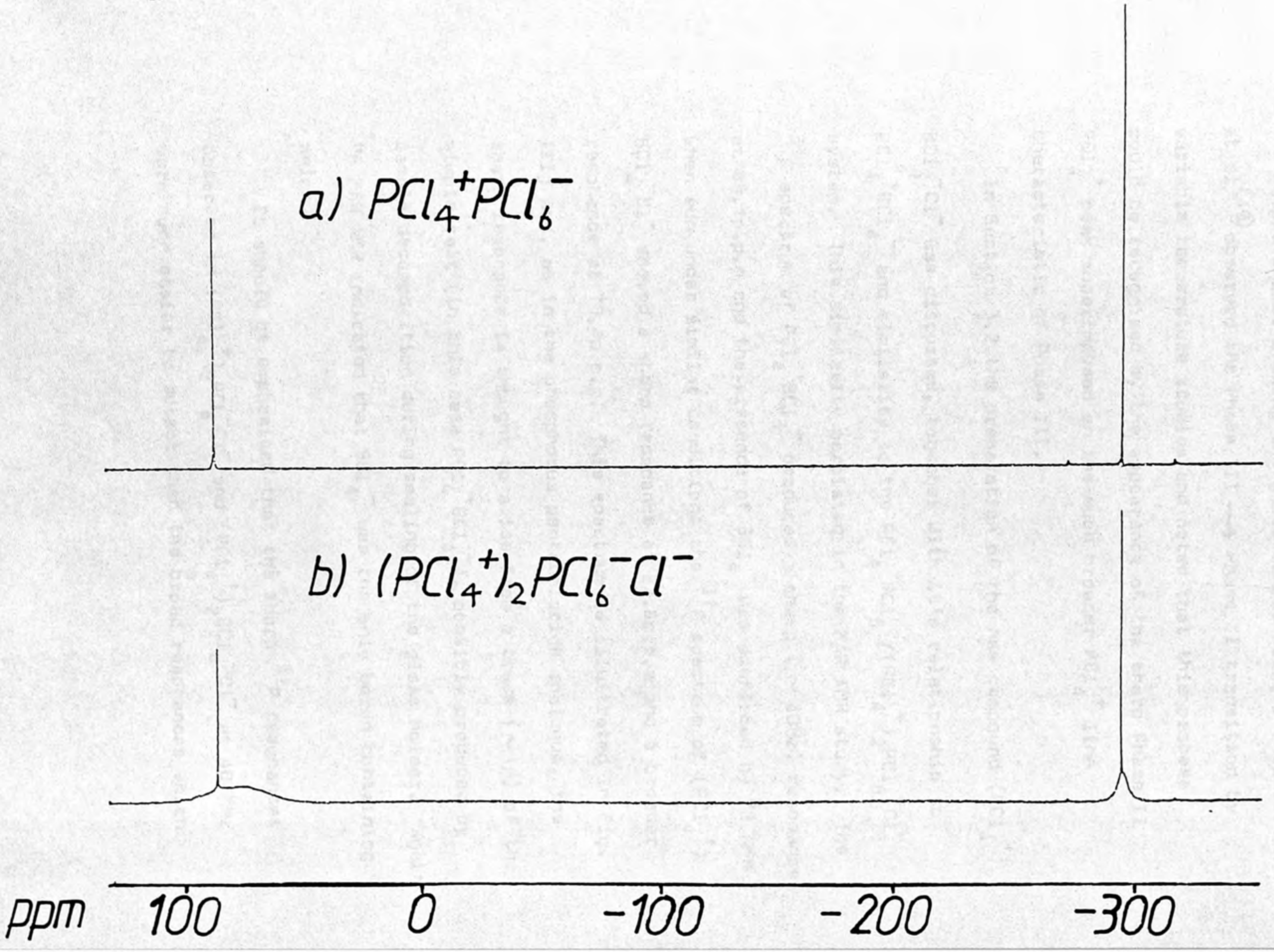
All new spectra reported in this section were run at the University of East Anglia by Mr. A. Root. For ^{31}P NMR studies 85% phosphoric acid was used as a reference with the downfield direction taken as positive; for ^{11}B NMR the reference was trimethyl borate.

3.5.a Complexes containing the PCl_4^+ cation

The ^{31}P NMR of Phase II phosphorus pentachloride ($PCl_4^+PCl_6^-$) has been recorded previously with and without rotation at the magic angle. A static ^{31}P NMR study by Dillon and Waddington (43) revealed two distinct chemical shifts at 88.3 and -299.7p.p.m with a 1:1 area ratio. These were assigned to the PCl_4^+ and PCl_6^- ions respectively. Values of +92 and -289p.p.m were obtained for these resonances by Wieker and Grimmer (44). In pioneering MAR studies by Andrew et al (45-48) the PCl_4^+ and PCl_6^- shifts were observed at 91 p.p.m and -282p.p.m respectively. The present work showed sharp resonances at 86.4 and -295.8p.p.m with an area ratio of almost 1:1 and linewidths of about 34Hz.

There have been few studies on Phase III (metastable) phosphorus pentachloride ($2PCl_4^+PCl_6^-Cl^-$) using ^{31}P NMR spectroscopy. Ripmeester and co-workers (49) investigated the behaviour of solid phosphorus pentachloride under pressure and found that there was a 2:1 ratio in the integrated areas of the PCl_4^+ and PCl_6^- resonances. Also the PCl_4^+ resonance in Phase III was found to be broader than that observed in Phase II due to a larger P-Cl dipolar interaction. The current study revealed two broad resonances at 77.9 and -296.5p.p.m assignable to PCl_4^+ and PCl_6^- in metastable modification and superimposed on these were two very sharp resonances at 86.5 and -295.7p.p.m presumably resulting from residual Phase II phosphorus pentachloride. This spectrum is illustrated in Fig. IIIi; the traces

Fig IIIi ^{31}P M.A.R. NMR spectra of

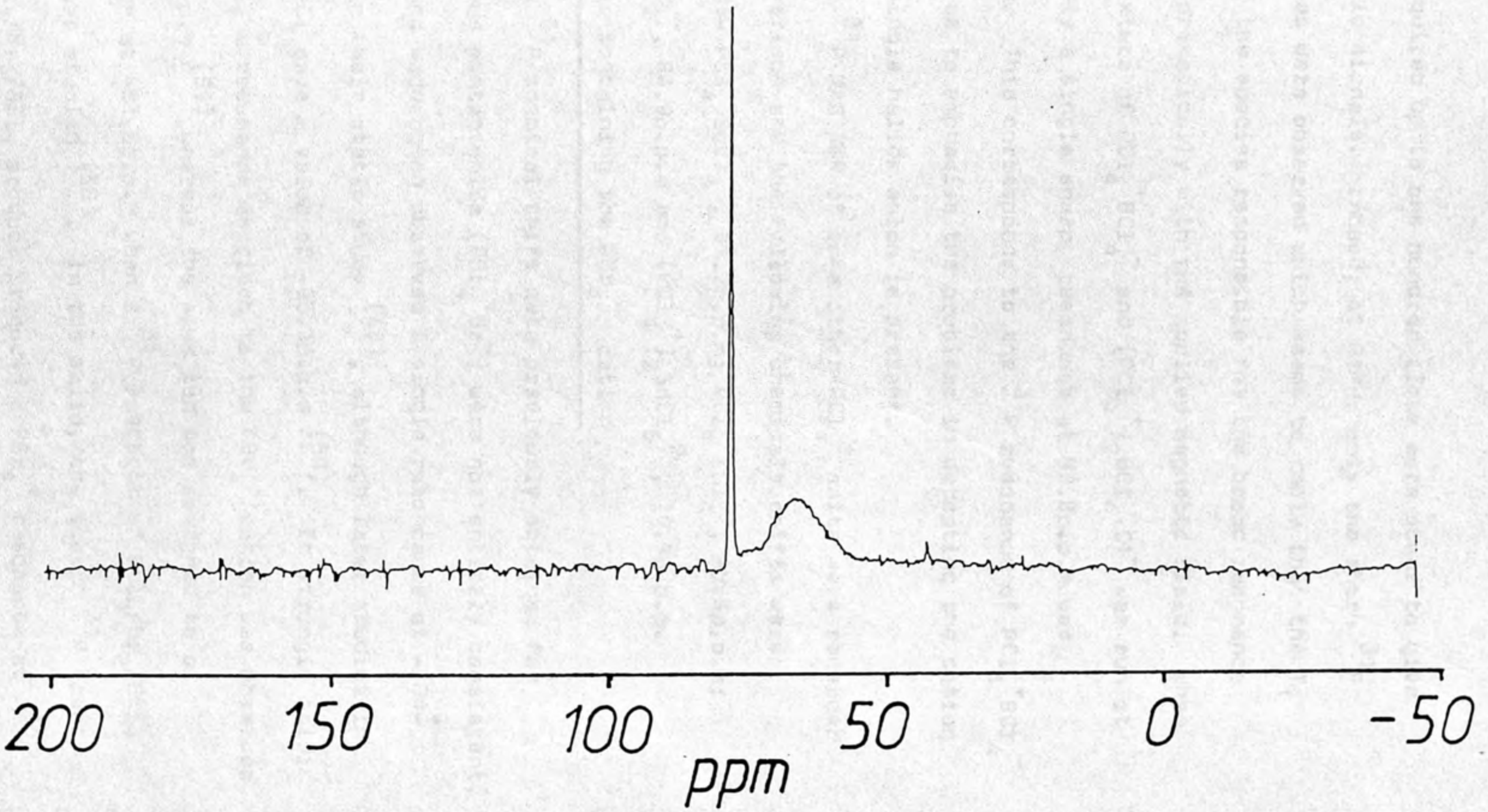


of Phase II are thought to arise from accidental warming of the sample whilst sealing the glass sample holder. Ripmeester et al(49) observed the Phase III ⟶ Phase II transition by variable temperature studies and noted that this process could be recognised by the appearance of the sharp Phase II PCl_4^+ peak superimposed on the much broader PCl_4^+ line characteristic of Phase III.

In Section 3.2 the preparation of the new compound $(PCl_4^+)_2BCl_4^-Cl^-$ was discussed, together with it's relationship to $PCl_4^+BCl_4^-$ and similarity to the $PCl_4^+PCl_6^-/(PCl_4^+)_2PCl_6^-Cl^-$ system. This similarity persisted in the MAR NMR study. The ^{31}P spectrum of $PCl_4^+BCl_4^-$ produced a sharp (~ 40Hz) resonance at 83.1p.p.m and the presence of BCl_4^- was confirmed by ^{11}B NMR When run under similar conditions the ^{31}P spectrum of $(PCl_4^+)BCl_4^-Cl^-$ showed a sharp resonance at 82.8p.p.m and a broader resonance at 70.4p.p.m. This spectrum is illustrated in Fig. IIIj and, as in the phosphorus pentachloride analogue, the sharp resonance is thought to arise from a trace (~1%) of the simple salt (in this case $PCl_4^+BCl_4^-$), possibly produced by sample decomposition during sealing of the glass holder. Again ^{11}B MAR NMR indicated that BCl_4^- was the only boron containing anion.

It should be emphasised that the sharp ^{31}P resonances observed in $(PCl_4^+)_2PCl_6^-Cl^-$ and $(PCl_4^+)_2BCl_4^-Cl^-$ at 40 MHz were much easier to detect than the broad resonances which

<u>Fig IIIj</u> ^{31}P M.A.R. NMR spectrum of $(PCl_4^+)_2BCl_4^-Cl^-$



often required up to one hundred times more scans to give reasonable signals. Indeed, at 81MHz only the sharp ^{31}P resonances were observed which seems to imply that the T_1 value of the species responsible for the broad resonance changes dramatically with the applied magnetic field. When a 1:1 mixture of $PCl_4^+BCl_4^-$ and $(PCl_4^+)_2BCl_4^-Cl^-$ was run at 81MHz only a single sharp resonance at 82.8p.p.m was observed. This corresponds to the ^{31}P resonance of $PCl_4^+BCl_4^-$ and serves to emphasise the problems in detecting the cation when a single halide anion is present.

The ^{31}P MAR NMR of some other PCl_4^+ salts were recorded for comparison and the following chemicals shifts were obtained:- $PCl_4^+SbCl_6^-$, 81.2p.p.m; $PCl_4^+ICl_4^-$, 82.6p.p.m; $PCl_4^+ICl_2^-$, 84.9p.p.m and $(PCl_4^+)_2SnCl_6^{2-}$, 79.9p.p.m.

3.5.b Complexes containing the PBr_4^+ cation

The ^{31}P chemical shift data previously obtained for phosphorus pentabromide ($PBr_4^+Br^-$) were not entirely consistent. Dillon and Waddington observed a single resoncance at -104 ± 1p.p.m in their static study $^{(43)}$, although later studies in liquid HCl gave a value of -95.3p.p.m $^{(50)}$. In strongly acidic solvents, a resonance ascribed to the PBr_4^+ cation was observed at -84p.p.m $^{(51)}$ whereas the same ion was assigned to a resonance at -81.0p.p.m when a ^{31}P spectrum of $PCl_3/Br_2/BCl_3$ in HCl was studied $^{(50)}$. In the solid, the static ^{31}P spectrum of a $PCl_3/Br_2/BCl_3$ product produced a PBr_4^+ resonance at

-68p.p.m (estimated from figure in paper) (37). Other work by Grimmer et al found the ^{31}P chemical shift for $PBr_4^+Br^-$ at -72p.p.m (52) and within the range -68 to -80p.p.m when various adducts were studied (44,52,53). Dillon and Gates also noted the apparently large range of chemical shifts for the PBr_4^+ cation in the solid state as -66p.p.m to -104p.p.m (37). The present study focussed on $PBr_4^+Br^-$ and $PBr_4^+BBr_4^-$, thus providing examples of the cation associated with both a single halide and polyatomic anion. For $PBr_4^+BBr_4^-$ a single sharp ^{31}P resonance was observed at -80.0p.p.m with a line-width of ~ 40Hz and the ^{11}B MAR NMR experiment confirmed BBr_4^- as the main anion with a shift of -30.6p.p.m from BCl_4^- (This is comparable with earlier ^{11}B solution studies (54)). The ^{31}P MAR studies on $PBr_4^+Br^-$ were rather inconclusive and some difficulties were encountered in obtaining spectra (55). In general, single broad resonances (600Hz) were obtained between -80 and -90p.p.m and it was apparent that MAR did not noticeably sharpen these resonances. On one occasion a sharper resonance was obtained at -100p.p.m more consistent with a previous result (43). These results cannot be explained easily; possibly the broad resonances could arise from partial hydrolysis of PBr_4^+ to PBr_3OH^+ due to incomplete sealing of the sample rotor but this does not account for the wide range of PBr_4^+ resonances discussed earlier.

From the observations made in the tetrachlorophosphonium species (Sect. 3.5.a) rather broad resonances would be expected when a single halide anion is present and narrower resonances to occur in the presence of a polyatomic anion. This behaviour is observed in the ^{31}P MAR spectra of methylhalophosphoranes and derivatives and is discussed in Section 4.5.

3.5.c Complexes containing mixtures of $PCl_nBr_{4-n}^+$ cations

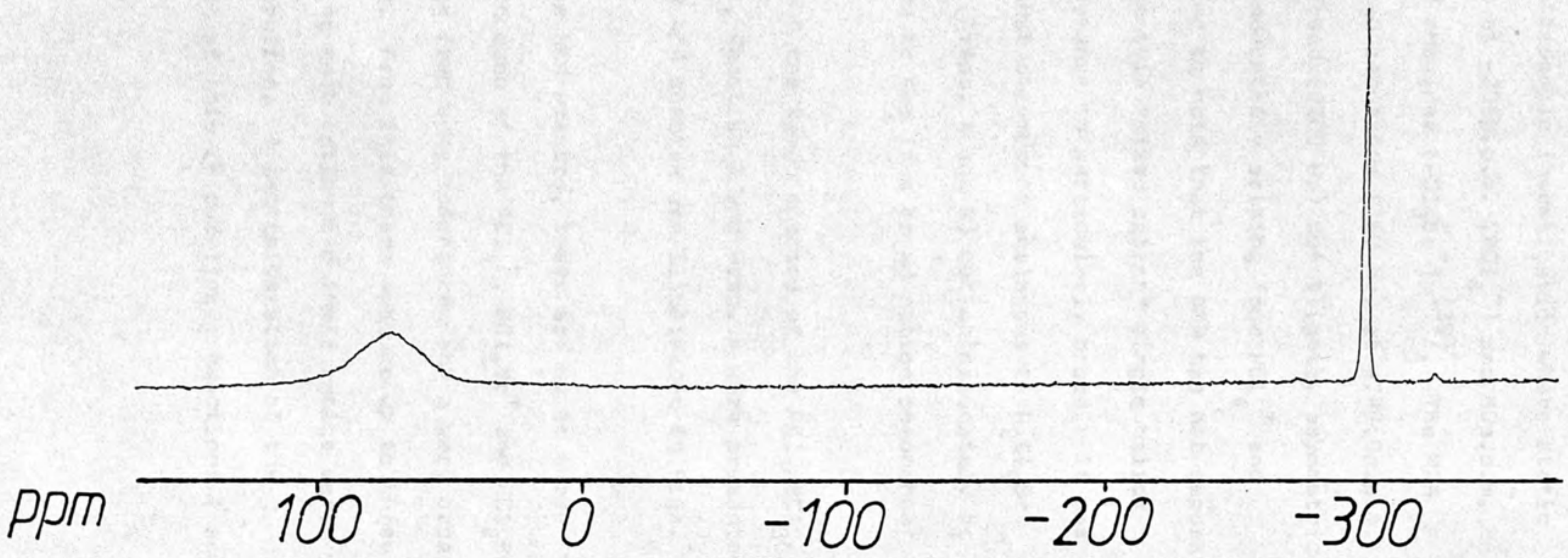
The full range of $PCl_nBr_{4-n}^+$ $(0 \leq n \leq 4)$ ions have been investigated by ^{31}P NMR before, by both the static solid-state (37,53) and solution measurements (50,51,56,57).

In general, the products investigated were prepared by i) $PCl_3/BCl_3/Br_2$ reactions (37,50), ii) PX_5/I_2 reactions (53), iii) the reaction of phosphorus (V) halides with strongly acidic solvents (51), iv) the reaction of phosphorus (III) halides with halogens in strongly acidic solvents (57) and, v) the reaction of phosphorus (III) halides with strongly acid solvents (56). The resonances reported in these studies fall within the following ranges:-

PCl_4^+ (96 to 73p.p.m.), PCl_3Br^+ (50 to 38p.p.m.), $PCl_2Br_2^+$ (12 to 3p.p.m.), $PClBr_3^+$ (-28 to - 35p.p.m.) and PBr_4^+ (-66 to-104p.p.m.)

Discussions earlier in this chapter have indicated the effect of single halide anions upon the Raman spectra of $PCl_3/BCl_3/Br_2$ products and have shown that in some preparations both single halide and polyatomic anion products may result. However, before discussing the present NMR results for that system, the ^{31}P MAR NMR spectrum for the compound P_2Cl_9Br is presented in Fig. IIIk. This compound, first prepared by Kolditz and Feltz (38)

Fig IIIk ^{31}P M.A.R. NMR spectrum of P_2Cl_9Br



has been explicitly formulated as $(PCl_4^+)_6(PCl_3Br^+)_2(PCl_6^-)_4(Br^-)_4$ following a detailed spectroscopic investigation where static ^{31}P NMR showed resonances at -295p.p.m. (PCl_6^-) and 80p.p.m. (PCl_4^+) with a high field shoulder (PCl_3Br^+) (39). The MAR spectrum has a fairly broad resonance (160 Hz) at -298.0p.p.m. due to PCl_6^- and a very broad (2200 Hz) but slightly asymmetric resonance at 70.5p.p.m. undoubtedly arising from PCl_4^+ and PCl_3Br^+. It is interesting to note that the NMR has not separated these cation resonances in this "mixed cation" single halide complex and that this resonance is particularly broad. It was reported in Section 3.4 that a compound analogous to P_2Cl_9Br might have been prepared (Preps. A and B) but unfortunately no NMR measurements were made to see if a broad cation resonance would occur.

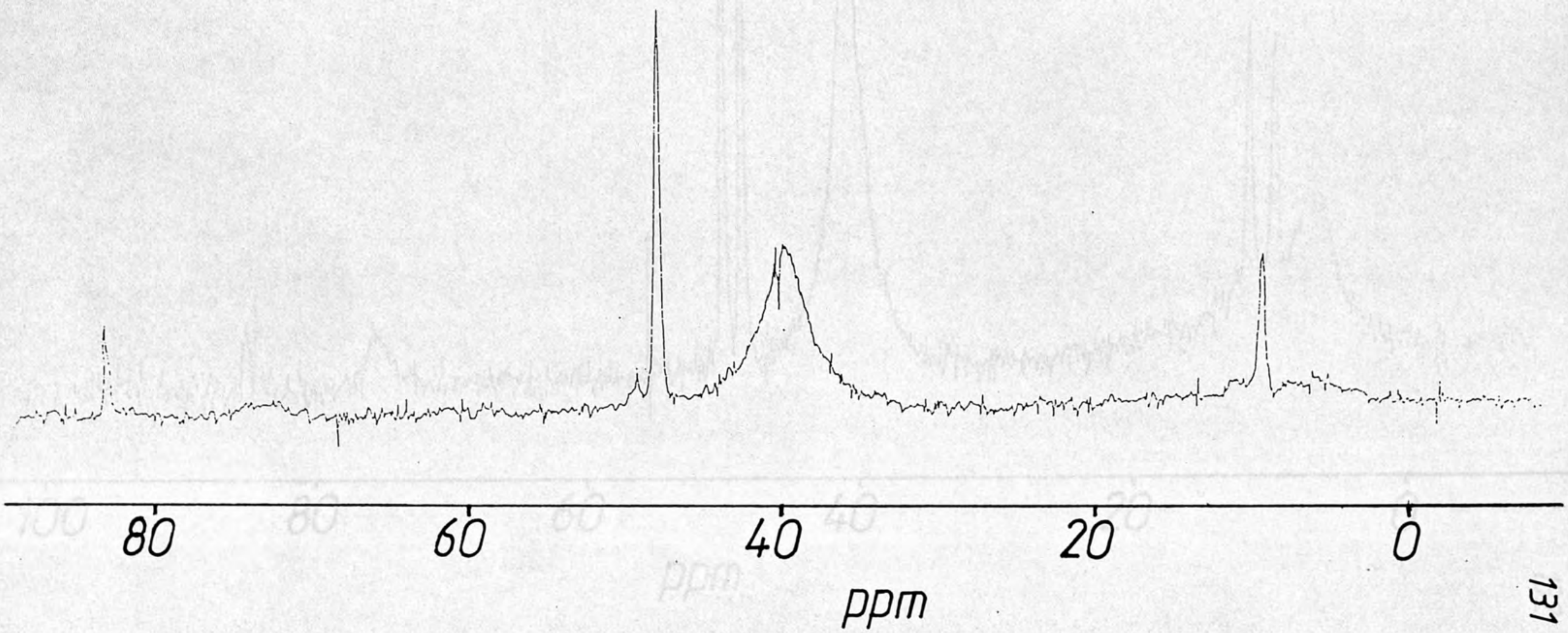
In Figs. IIId, e and f the Raman spectra of the $PCl_3/BCl_3/Br_2$ syntheses, Reaction 1, Reaction 2 and Prep. 4 were presented: the corresponding ^{31}P MAR NMR spectra are illustrated in Figs. IIIl, m and n.

Considering all three NMR spectra, there are up to three resonances associated with each of the PCl_4^+, PCl_3Br^+ and PCl_2Br^+ regions:- two narrow high frequency resonances and a very broad lower frequency resonance. From this there must be up to three different solids containing each cation and their ratios vary from preparation to preparation. A reconsideration of the Raman spectra in the light of this is puzzling. Reactions 1 and

2 are very similar with cationic bands solely in the single halide anion position suggesting formulations of the type $(PX_4^+)_2BX_4^-X^-$ whereas in Prep. 4 cation band positions indicate a mixture of single halide and polyatomic anions. The ^{31}P MAR NMR of Reaction 1 indicates predominantly two resonances per cation; the lower frequency narrow band and the broad band although there are just traces of the higher frequency narrow band. The chemical shifts are as follows: PCl_4^+ (83.6 and 73.4p.p.m.), PCl_3Br^+ (48.2 and 40.0p.p.m.) and $PCl_2Br_2^+$ (9.4 and 5.9p.p.m.). The ^{31}P MAR NMR spectrum of Reaction 2 contains both narrow resonances and the broader, low frequency band with the following chemical shifts: PCl_4^+ (84.8, 84.0 and 75.1 p.p.m.), PCl_3Br^+ (49.7, 48.5 and 40.5 p.p.m.) and $PCl_2Br_2^+$ (11.6, 9.6 and 6.7 p.p.m.). Preparation 4 gave the most complex Raman spectrum but the ^{31}P MAR NMR contained predominantly the two narrow resonances with only traces of the low frequency broad band. The chemical shifts are as follows: PCl_4^+ (84.9 and 84.0 p.p.m.), PCl_3Br^+ (49.8 and 48.4 p.p.m.), $PCl_2Br_2^+$ (11.8 and 9.7 p.p.m.) and $PClBr_3^+$ (-22.8 and -31,6 p.p.m.).

At first sight there seems to be some conflict between the conclusions for Raman and NMR spectra. Data for $(PCl_4^+)_2BCl_4^-Cl^-$, $(PCl_4^+)_2PCl_6^-Cl^-$ and P_2Cl_9Br suggest that sharp cationic resonances are associated with compounds where only polyatomic anions occur whereas broad cationic resonances result where single halide ions are present. It is necessary to re-emphasise here the relatively

Fig IIIl ^{31}P M.A.R. NMR spectrum of a PCl_3–BCl_3–Br_2 product [Reaction 1]



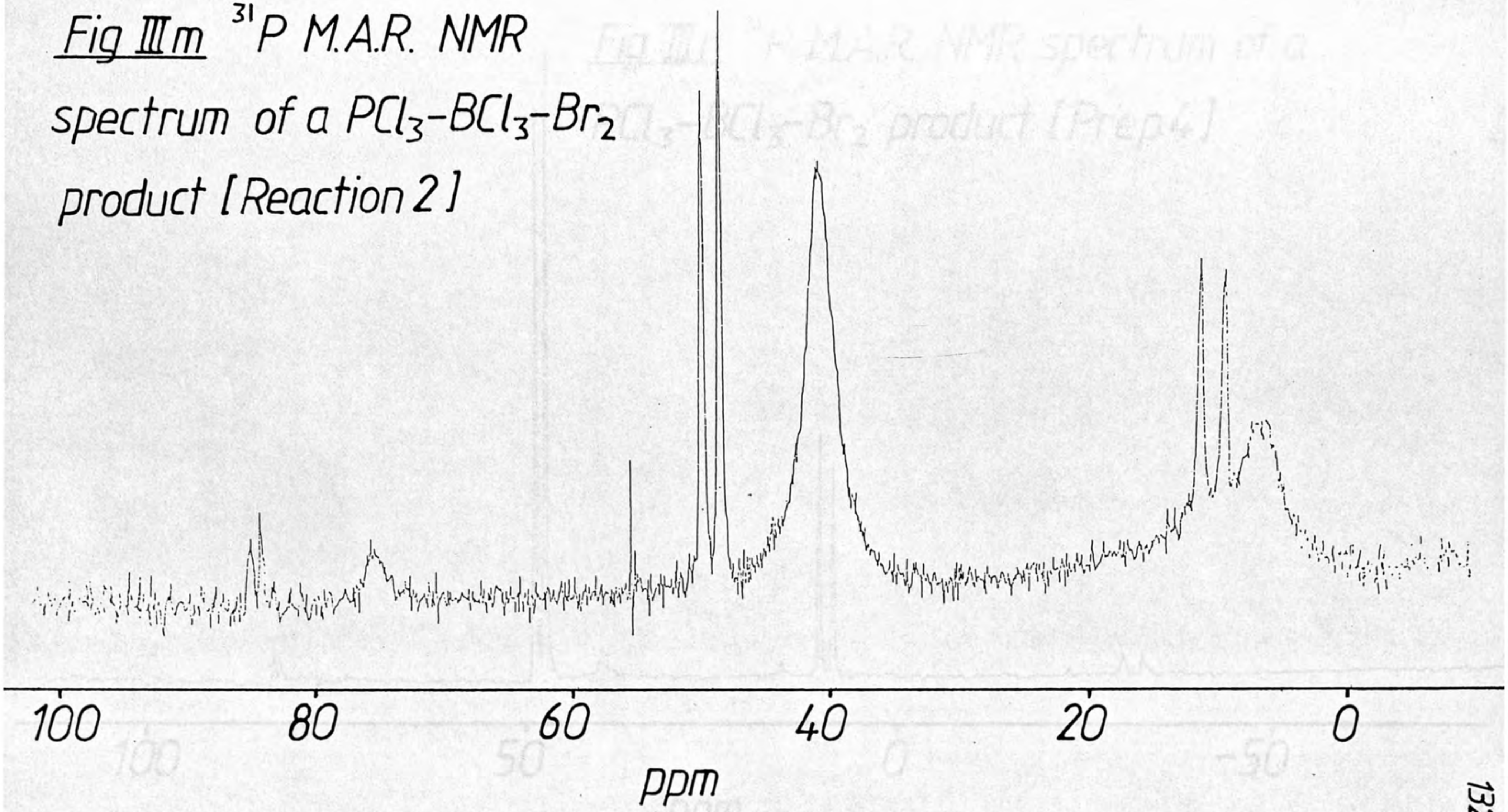


Fig IIIm ^{31}P M.A.R. NMR spectrum of a PCl_3–BCl_3–Br_2 product [Reaction 2]

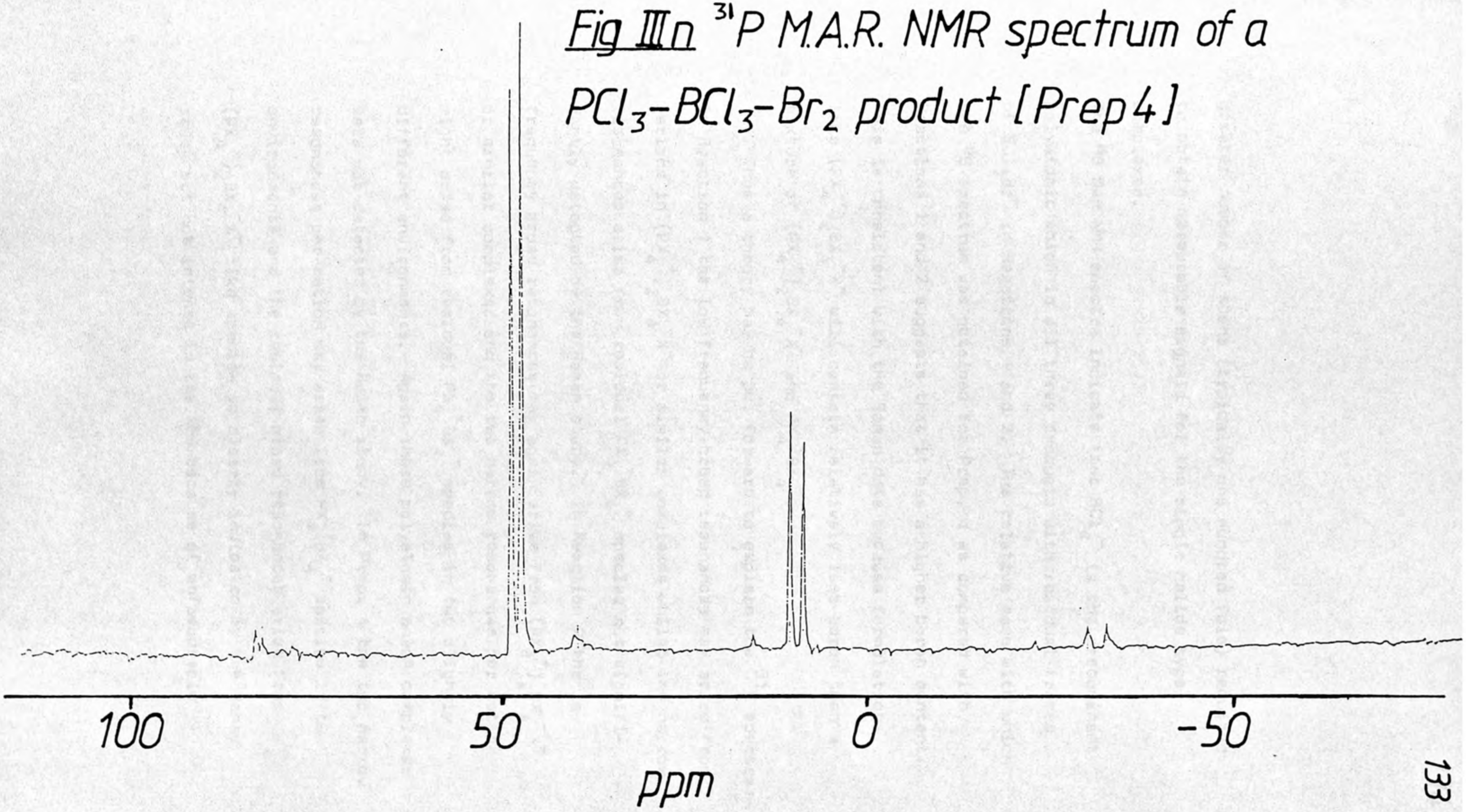


Fig IIIn ^{31}P M.A.R. NMR spectrum of a PCl_3–BCl_3–Br_2 product [Prep 4] greater number of scans (typically one hundred fold) required to obtain measurable signals for the single halide type complexes.

The ^{11}B MAR NMR spectra indicate that BCl_4^- is the predominant polyatomic anion in all three products with residual traces of BCl_3Br^- in Reactions 1 and 2. The relative ease with which the ^{11}B spectrum was obtained for Prep. 4 as compared with Reactions 1 and 2 suggests that it has a higher boron content. This is consistent with the Raman data because formulations like $(PX_4^+)_2BX_4^-X^-$ will contain relatively less boron than a mixture of $(PX_4^+)_2BX_4^-X^-$ and $PX_4^+BX_4^-$.

Thus a theory may be put forward to explain the ^{31}P spectra:- In Reaction 1 the low frequency broad resonances may arise from cations in $(PX_4^+)_2BX_4^-X^-$ or similar complexes whilst the narrow resonances arise from residual $PX_4^+BX_4^-$ species not significantly detected by the Raman study. In Reaction 2 the low frequency broad resonances may again arise from $(PX_4^+)_2BX_4^-X^-$ or similar complexes and the two narrow resonances per cation might arise from residual $PX_4^+BX_4^-$ species in two slightly different environments. Again these polyatomic anion complexes were not detected by the Raman study. In Prep. 4 the two narrow resonances per cation may arise from $PX_4^+BX_4^-$ species in two environments and the residual broad resonances arise from $(PX_4^+)_2BX_4^-X^-$ like species so clearly indicated by the Raman study but not intense in the NMR because of unfavourable conditions.

These ideas reconcile the Raman and NMR spectra quite well and highlight the different sensitivities of the techniques. NMR spectroscopy under the conditions used in this work seems to preferentially detect and resolve ^{31}P resonances from cations associated only with a polyatomic anion. Conversely, Raman spectroscopy readily detects phosphonium cations where there are single halide anions in the lattice. When the Raman spectrum of an equimolar mixture of $PCl_4^+PCl_6^-$ and $(PCl_4^+)_2PCl_6^-Cl^-$ or of $(PCl_4^+)_2BCl_4^-Cl^-$ and $PCl_4^+BCl_4^-$ is run, the bands due to the halide anion form are always more intense than those due to the polyatomic anion complexes. This is probably simply due to the 2:1 cation ratio between the two forms and this could cause preferential Raman detection of such species. It should, however, be noted that no Raman or NMR experiment on the mixed halide products can detect the nature of any X^- species present.

A close examination of the ^{31}P MAR NMR spectra of Reactions 1 and 2 and Prep. 4 reveals that with increasing bromine content of the cation, the larger becomes the separation between the two narrow resonances (0.9 p.p.m. with PCl_4^+ to 2.8 p.p.m. with $PClBr_3^+$. Also the separation between the lowest frequency narrow resonance and the broad resonance decreases with bromine content of the cation (4.9 p.p.m. with PCl_4^+ to 2.9 p.p.m. with $PCl_2Br_2^+$). Thus it appears that a crossover point should occur where the narrow resonances will occur at a lower frequency than the broad resonance. Such a point would be predicted in the $PClBr_3^+$ region but has not been observed though a similar phenomenon was found in the ^{31}P NMR spectra of the methylphosphoranes and their derivatives (Chapter 4.6).

A $PCl_3/BBr_3/Br_2$ reaction was performed in an attempt to observe this crossover point. The Raman spectrum indicated the presence of PBr_4^+ (polyatomic anion), PBr_3Cl^+ (halide anion) and $PCl_2Br_2^+$ (halide anion) as well as BBr_4^-. The ^{11}B MAR NMR indicated the whole range of boron containing anions ($BCl_4^-BBr_4^-$) and was recently reported (58). The ^{31}P MAR NMR spectrum showed broad resonances at 7.6, -28.2 and -64.7 p.p.m. indicating the same cations as the Raman data. The heavier the cationic bromine content, the broader the NMR resonances: the PBr_4^+ resonance is also shifted from that predicted when BX_4^- species are anions although the Raman suggests a polyatomic cation only. This is consistent with the failure to isolate any $(PBr_4^+)_2BX_4^-X^-$ compounds in the course of this work (c.f. reference 41): the only single halide compounds characterized with PBr_4^+ are $PBr_4^+Br^-$ (14) and $PBr_4^+Cl^-$ (42). The broad resonances due to PBr_3Cl^+ and $PBr_2Cl_2^+$ are in reasonable positions for $(PX_4^+)_2BX_4^-X^-$ formulations predicted from Reactions 1, 2 and Prep. 4 although again the possibility of $PX_4^+X^-$ species cannot be dismissed. Despite the fact that the $PCl_3/BBr_3/Br_2$ reaction product does not entirely fit with the idea linking the broad and narrow NMR bands with the Raman data, numerous other $PCl_3/BCl_3/Br_2$ reaction products were studied and do not directly contradict it.

3.5.d Variable temperature M.A.R. NMR studies

Reactions 1 and 2 and Prep. 4 were investigated by V.T. ^{31}P M.A.R. and showed consistent results. Fig. IIIo illustrates the PCl_4^+, PCl_3Br^+ and $PCl_2Br_2^+$ regions of the Prep. 4 ^{31}P spectrum at various temperatures. The changes are quite extraordinary: when the sample was heated to about 60°C there was a loss of the low frequency narrow resonances and a slight increase in intensity of the broad resonances. Further heating to above 90°C caused a more dramatic increase in intensity of the broad resonances especially in the PCl_3Br^+ and $PCl_2Br_2^+$ regions and also the re-appearance of the low frequency narrow resonances whilst the high frequency narrow resonances vanished. Re-cooling to 30°C caused a considerable reduction in intensity of the broad resonances and the re-appearance of the high frequency narrow resonances accompanied by the disappearance of the low frequency narrow resonances. Cooling to ambient from either 60°C or 90°C resulted in the same effect - each cation was characterised by the high frequency narrow resonance and residual broad resonance.

Overall, there appear to be three main processes taking place:- a) The irreversible loss of the low frequency narrow resonance on heating to ~60°C b) The reversible appearance of the low frequency narrow resonance and disappearance of the high frequency sharp resonance on heating to ~ 90°C. This

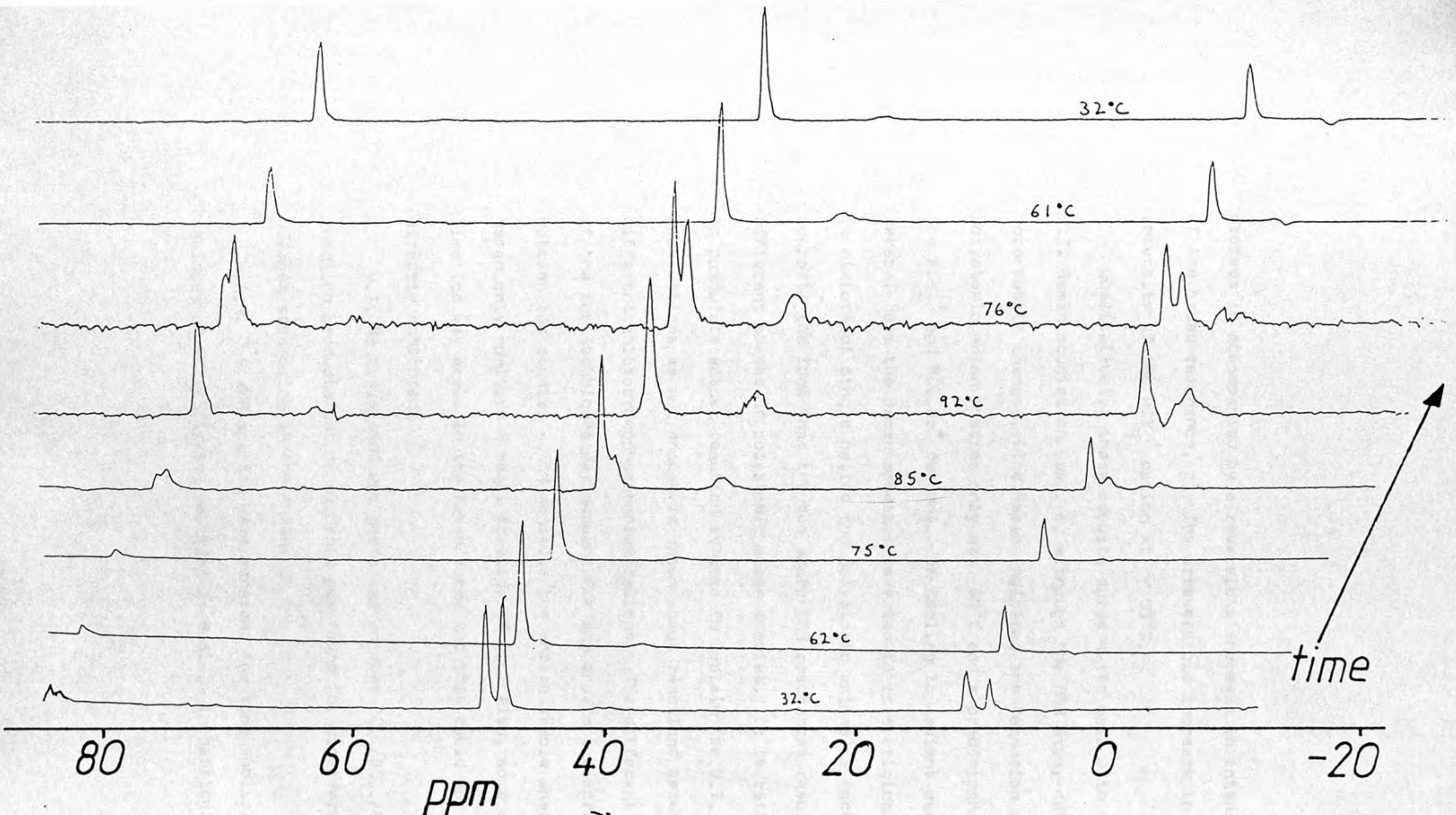


Fig IIIo Variable temperature ^{31}P M.A.R. NMR spectra of a PCl_3–BCl_3–Br_2 product (Prep 4) process is accompanied by a reversible increase in intensity of the broad resonance. c) The irreversible increase in intensity of the PCl_4^+ cation at $\sim 90^{\circ}$C.

Qualitatively, these results agree quite well with the V.T. Raman studies on Prep. 4, although the NMR study detects more subtle changes. The Raman indicated the formation of polyatomic anion species only at 90°C and a predominance of the PCl_4^+ and PCl_3Br^+ cations. On cooling to ambient over several days the Raman spectrum reverted to it's original form (a mixture of single halide and polyatomic anions) a fact which supports the idea that the two sharp NMR resonances result from different phases of polyatomic anion species. It is rather hard to postulate actual reaction schemes to explain the V.T. observations as not enough is known about reactions between different chlorobromophosphonium cations. The different nature of the two techniques may account for any apparent discrepancies between the studies - NMR monitors the entire sample whereas Raman only monitors a small fraction of it. Also, some sublimation may occur in the Raman tubes and this could not be directly monitored.

V.T. ^{11}B M.A.R. NMR was performed on some $PCl_3/BCl_3/Br_2$ reaction products but no evidence was found for considerable halogen scrambling in the anion.

M.A.R. ^{31}P NMR spectra were recorded for some sublimates and residues of $PCl_3/BCl_3/Br_2$ reaction products. In particular, Prep. 4 was investigated. In all cases the sublimates gave broad resonances which suggests that they contain single halide anions and are probably $(PX_4^+)_2BX_4^-X^-$ formulations. This is consistent with the Raman observations discussed in Section 3.3. The residues generally gave sharp resonances (1 per cation) and in some cases contained almost exclusively the PCl_4^+ cation. This suggests that the residues are predominantly polyatomic $PX_4^+BX_4^-$ species, again in fair agreement with the Raman findings. Not enough is known to postulate what reactions are occurring in the sublimation studies but it seems certain that the single halide anion species are more volatile than the polyatomic anion species and are therefore collected as sublimates.

3.6 Summary

The following briefly summarises the main observations reported in Chapter 3.

i) The Raman frequencies of the PCl_4^+ and PBr_4^+ cations were noted with and without the presence of single halide anions. When an X^- anion was replaced by a polyatomic species high frequency shifts of some cationic Raman bands were observed.

ii) An explanation for the Raman shift phenomenom was proposed from the X-ray data available for $PBr_4^+Br^-$ $PBr_4^+Br_3^-$ where there is shown to be considerable anion cation interaction without gross symmetry distortion.

This interaction probably leads to P-Br bond weakening and consequent lower vibrational frequencies.

iii) The behaviour of PCl_5 (Phase II) and PBr_5 in various solvents was discussed. Various methods for the preparation of Phase III PCl_5 were noted and some speculative mechanisms proposed.

iv) The nature of some symmetric and asymmetric trihalides were discussed in view of the mechanism proposed for Phase III PCl_5 formation.

v) The preparation of a new single halide compound $(PCl_4^+)_2BCl_4^-Cl^-$ was noted, Raman spectrum recorded and general comparisons made with $(PCl_4^+)_2PCl_6^-Cl^-$. V.T. Raman indicated a reversible equilibrium between this compound and $PCl_4^+BCl_4^-$ and $PCl_4^+PCl_6^-$.

vi) The compound $(PCl_4^+)_2BCl_4^-Cl^-$ was proposed as being a particular pure example of the single halide anion species containing the $PCl_nBr_{4-n}^+$ ($o \leq n \leq 4$) cations that result from $PCl_3/BCl_3/Br_2$ reactions.

vii) V.T. Raman studies on $PCl_3/BCl_3/Br_2$ reaction products resulted in the formation of polyatomic anion products at high temperatures although the process proved to be reversible on cooling.

viii) The compound P_2Cl_9Br was discussed in relation to single halide anion species and the Raman spectrum of a new BCl_4^- containing analogue was reported. This led to the proposal that there may be more mixed cation single halide anion species present in mixtures.

ix) ^{31}P M.A.R. NMR studies were performed on simple compounds containing the PCl_4^+ and PBr_4^+ cations. Sharp resonances were always found to occur when only a polyatomic anion was present but the presence of single halide anions produced broader resonances that were relatively harder to detect.

x) ^{31}P M.A.R. NMR of some $PCl_3/BCl_3/Br_2$ reaction products showed up to 3 resonances (2 narrow, 1 broad) per cation (for PCl_4^+, PCl_3Br^+, $PCl_2Br_2^+$) and these were explained in terms of two $PX_4^+BX_4^-$ phases and $(PX_4^+)_2BX_4^-X^-$ species.

xi) V.T. ^{31}P M.A.R. NMR studies of some $PCl_3/BCl_3/Br_2$ reaction products were reasonably consistent with the V.T. Raman investigations although some more subtle and as yet unexplained changes were observed. This served to highlight the sensitivity differences of NMR and Raman spectroscopy in studying these systems.

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CHAPTER 4

RESULTS AND DISCUSSION C

4. Preparation and Spectroscopic Studies of some Methylhalophosphoranes and derivatives

4.1 Monomethylhalophosphoranes

4.1.a Methyltetrachlorophosphorane and Methyltetrabromophosphorane and some derivatives

Methyltetrachlorophosphorane had twice been the subject of a detailed Raman spectroscopic investigation prior to the present work(1,2). These studies suggested that in the solid state, the compound was ionic with a cation of C_{3V} symmetry and was formulated as $MePCl_3^+Cl^-$. The vibrational representation for such a cation (assuming the Me group to be a point) would be

$$\Gamma_{vib} = 3a_1\ (R,\ IR) + 3e\ (R,\ IR)$$

where R and IR indicate Raman and infra-red activity. (Work by Beattie indicated that in non-polar solvents this substance was molecular with a trigonal bipyramidal configuration and that the methyl group occupied an equatorial position conferring overall C_{2V} symmetry(2). The results of the current investigation are given later in this chapter). It is important to note here that in all ensuing discussions the Me groups are, in respect to symmetry arguments, regarded as points centred on the carbon atom. This assumption is valid for two main reasons:- i) The relatively small masses of the hydrogen atoms contribute little to the skeletal modes of vibration via coupling phenomena and ii) the C-H modes occur at a sufficiently high frequency not to obscure the other vibrations under observation.

The solid -state Raman spectrum of $MePCl_3^+Cl^-$ is presented in Fig. IVa and the wavenumbers are listed in Table 4.1 where they are compared with those obtained in the earlier studies. The assignments are taken from Beattie's study (2) and the results from this agree well with those obtained earlier except in the case of ν_6. Baumgartner et al (1) assigned ν_6 to a weak band at $153cm^{-1}$; Beattie observed no band here but accepted these findings (2). In the present work no evidence was found for a band in that region of the spectrum but a weak feature was observed at $219cm^{-1}$ and was thus assigned to ν_6. Hence there is agreement with previous vibrational spectra that the formulation for solid methyltetrachlorophosphorane is $MePCl_3^+Cl^-$, a fact confirmed by independent ^{31}P NMR[3] and ^{35}Cl NQR studies (3,4). However, an interesting observation was made during comparison of the Raman spectra of several $MePCl_2/Cl_2$ reaction products. In some cases the ν_2 (a_1) symmetric P-Cl stretch at $477cm^{-1}$ had a high frequency shoulder at $484cm^{-1}$. A similar shoulder was observed in these cases on the $\nu_4(e)$ antisymmetric P-Cl stretch, and a slight high frequency shift ($273 \longrightarrow 275cm^{-1}$) and increase in intensity of the $\nu_5(e)$ Me-P-Cl deformation was also noted. Analysis of such products was in accord with the $MePCl_3^+Cl^-$ formulation and, on pumping, these features were lost and the standard Raman spectrum as illustrated in Fig. IVa remained. Similar behaviour was observed to a greater extent in the Me_2PCl/Cl_2 system and a more detailed discussion is given in Section 4.2.a.

TABLE 4.1

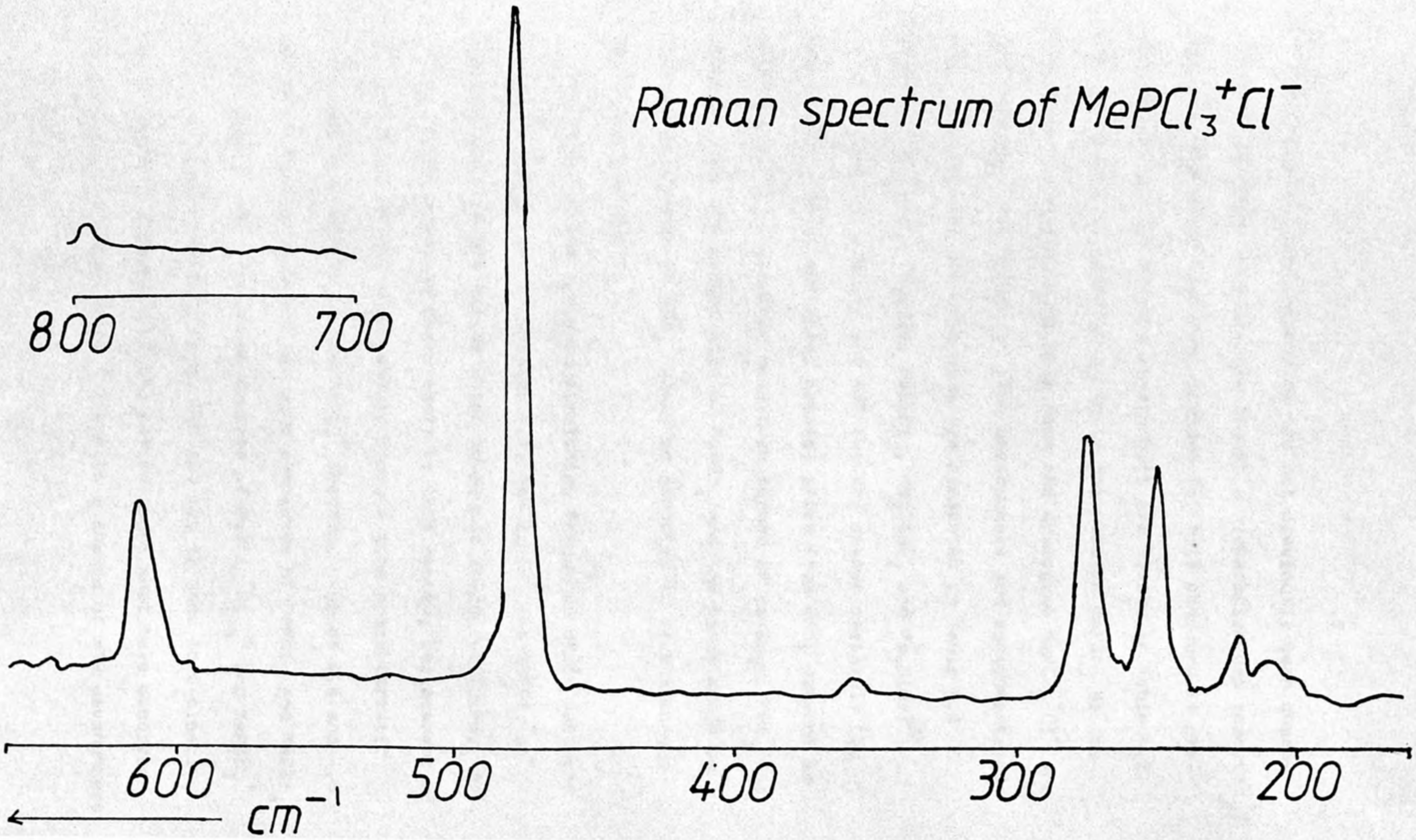
RAMAN WAVENUMBERS/cm^{-1} FOR THE COMPOUND $MePCl_3{}^+Cl^-$

This study	Baumgartner et al[(a)]	Beattie et al[(b)]	Assignments
795 (w)	793 (w)	790 (vw)	$\nu_1(a_1)\nu$ (P-Me)
477 (s)	473 (s)	475 (s)	$\nu_2(a_1)\nu_s$(P-Cl)
248 (m/w)	246 (m/w)	247 (m/w)	$\nu_3(a_1)\delta(PCl_3)$
614 (m)	610 (m)	609 (m)	$\nu_4(e)\nu_{as}$(P-Cl)
273 (m)	276 (m)	274 (m)	$\nu_5(e)\ \delta$ (Me-P-Cl)
219 (w)	153 (vw)	not observed	$\nu_6(e)\ \delta$ (Cl-P-Cl)

(a) R. Baumgartner, W. Sawodny and J. Goubeau; Z. Anorg, Allgem. Chem., 1964, 333, 171.

(b) I. R. Beattie, K. Livingston and (in part) T. Gilson; J. Chem. Soc. "A", 1968, 1.

Fig IVa



Raman spectrum of $MePCl_3^+Cl^-$

Methyltetrabromophosphorane has not previously been characterized by Raman spectroscopy though a preparation was reported by Deng⁽⁵⁾. The Raman spectrum obtained for this compound is presented in Fig. IVb and the wavenumbers are listed in Table 4.2. The assignment is based on an ionic formulation $MePBr_3^+Br^-$ by comparison with data available from the analogous $MePCl_3^+Cl^-$ and the isoelectronic $MeSiBr_3$. (The wavenumbers and assignments of the following silicon compounds are presented in Table 4.3 $MeSiCl_3$, Me_2SiCl_2, Me_3SiCl, $MeSiBr_3$, Me_2SiBr_2 and Me_3SiBr)⁽⁶⁾. Bands at 140 (m) 225 (s) and 490 (w, sh) almost certainly (by comparison with an authentic sample) arise from PBr_5 present as an impurity⁽⁷⁾. This could have been formed if residual PBr_3 was present after the preparation of $MePBr_2$ and the bands would be relatively intense as PBr_4^+ would be expected to be a stronger scatterer than $MePBr_3^+$.

In terms of the cationic stretching frequency shift patterns discussed previously in Chapter 3.1, $MePCl_3^+Cl^-$ and $MePBr_3^+Br^-$ are obviously single halide anion compounds analogous to $PBr_4^+Br^-$. If the trends observed there apply to this system, replacement of X^- with a polyatomic anion should produce some characteristic high frequency shifts in the $MePX_3^+$ spectra. Tables 4.4 and 4.5 present Raman wavenumbers for some complexes of $MePCl_4$ and $MePBr_4$ with Lewis acids. The Raman spectra of $MePCl_3^+BCl_4^-$ and $MePBr_3^+BBr_4^-$ are illustrated in Figs. IVc and IVd to show more clearly the changes in frequency of the cation modes that have occurred on complexation. For $MePCl_3^+$ there is a change of +19 wavenumbers

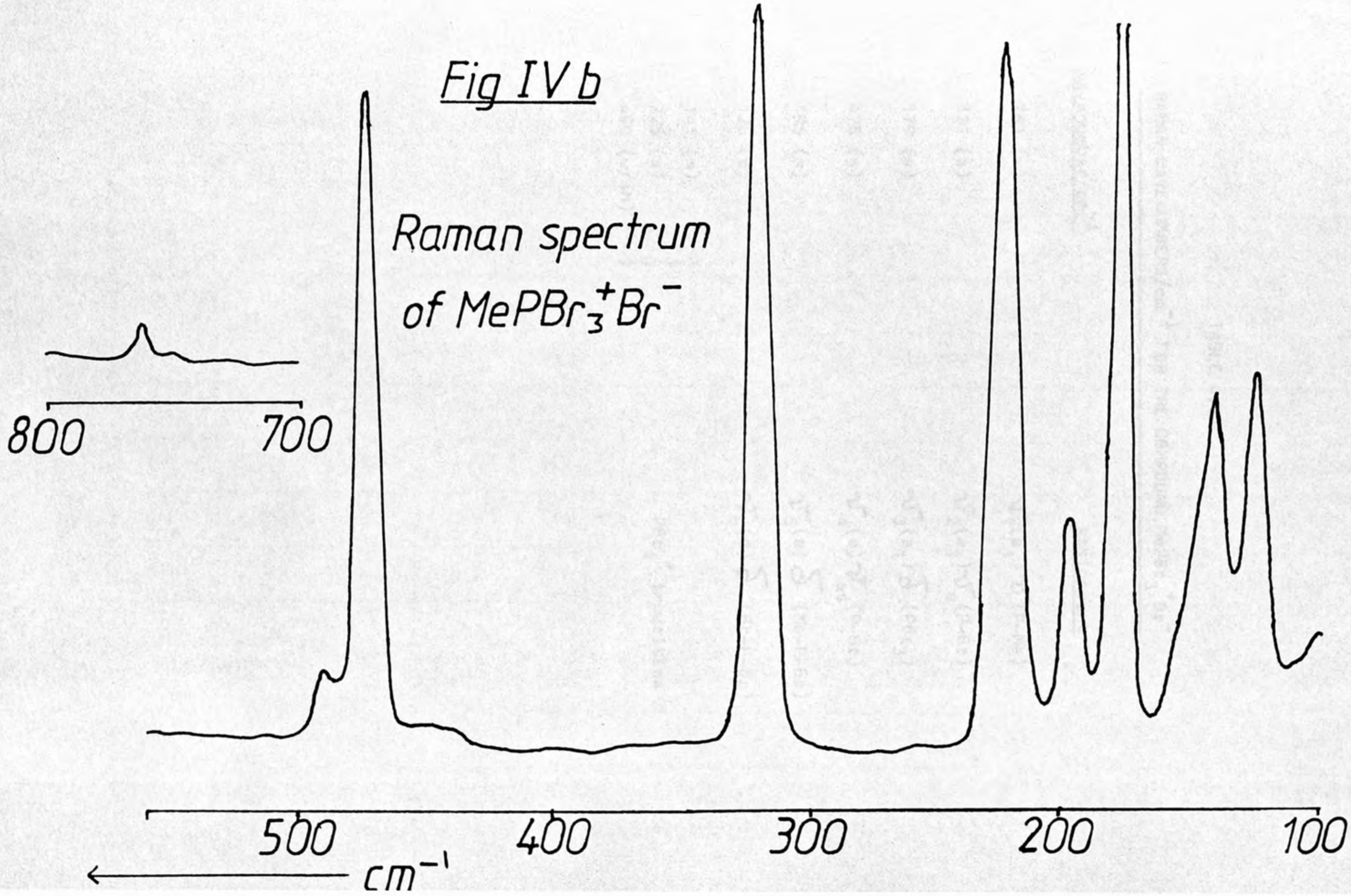


Fig IV b

Raman spectrum of $MePBr_3^+Br^-$

TABLE 4.2

RAMAN WAVENUMBERS/cm^{-1} FOR THE COMPOUND $MePBr_3{}^+Br^-$

Wavenumber/cm^{-1}	Assignment
761 (w)	$\nu_1(a_1)\,\nu(P\text{-}Me)$
321 (s)	$\nu_2(a_1)\,\nu_s(P\text{-}Br)$
179 (s)	$\nu_3(a_1)\,\delta\,(PBr_3)$
475 (s)	$\nu_4(e)\,\nu_{as}(P\text{-}Br)$
196 (m)	$\nu_5(e)\,\delta\,(Me\text{-}P\text{-}Br)$
126 (m)	$\nu_6(e)\,\delta\,(Br\text{-}P\text{-}Br)$
141 (m))	$PBr_4{}^+$ impurities
225 (s))	
490 (w/sh))	

TABLE 4.3

RAMAN WAVENUMBERS/cm^{-1} FOR THE COMPOUNDS $MeSiCl_3$, Me_2SiCl_2, Me_3SiCl, $MeSiBr_3$, Me_2SiBr_2 AND Me_3SiBr

C_{3v} Point Group			C_{2v} Point Group			C_{3v} Point Group		
$MeSiCl_3$	$MeSiBr_3$	Assignment	Me_2SiCl_2	Me_2SiBr_2	Assignment	Me_3SiCl	Me_3SiBr	Assignment
165	98	$\nu_6(e)\delta$ (X-Si-X)	168	118	$\nu_4(a_1)\delta$ (X-Si-X)	188	178	$\nu_6(e)\delta$ (Me-Si-Me)
230	153	$\nu_3(a_1)\delta$ (SiX_3)	180	166	$\nu_5(a_2)\delta$ (Me-Si-Me)	242	213	$\nu_3(a_1)\delta$ ($SiMe_3$)
230	186	$\nu_5(e)\delta$ (X-Si-Me)	225	208	$\nu_9(b_2)\delta$ (X-Si-X)	242	242	$\nu_5(e)\delta$ (X-Si-Me)
450	314	$\nu_2(a_1)\nu_s$(Si-X)	245	208	$\nu_3(a_1)\delta$ (X-Si-Me)	468	374	$\nu_2(a_1)\nu$ (Si-X)
575	453	$\nu_4(e)\nu_{as}$(Si-X)	300	208	$\nu_7(b_1)\delta$ (Me-Si-Me)	637	635	$\nu_1(a_1)\nu_s$(Si-Me)
760	746	$\nu_1(a_1)\nu$ (Si-Me)	462	355	$\nu_2(a_1)\nu_s$(Si-X)	760	758	$\nu_4(e)\nu_{as}$(Si-Me)
			531	426	$\nu_8(b_2)\nu_{as}$(Si-X)			
			689	682	$\nu_1(a_1)\nu_s$(Si-Me)			
			804	682	$\nu_6(b_1)\nu_{as}$(Si-Me)			

All data taken from H. Marata; Science and Industry - Osaka, 1956, 30, 164. (Values given are observed and generally compared well with those calculated via Normal Coordinate Analysis).

Fig IVc

Raman spectrum of $MePCl_3^+BCl_4^-$

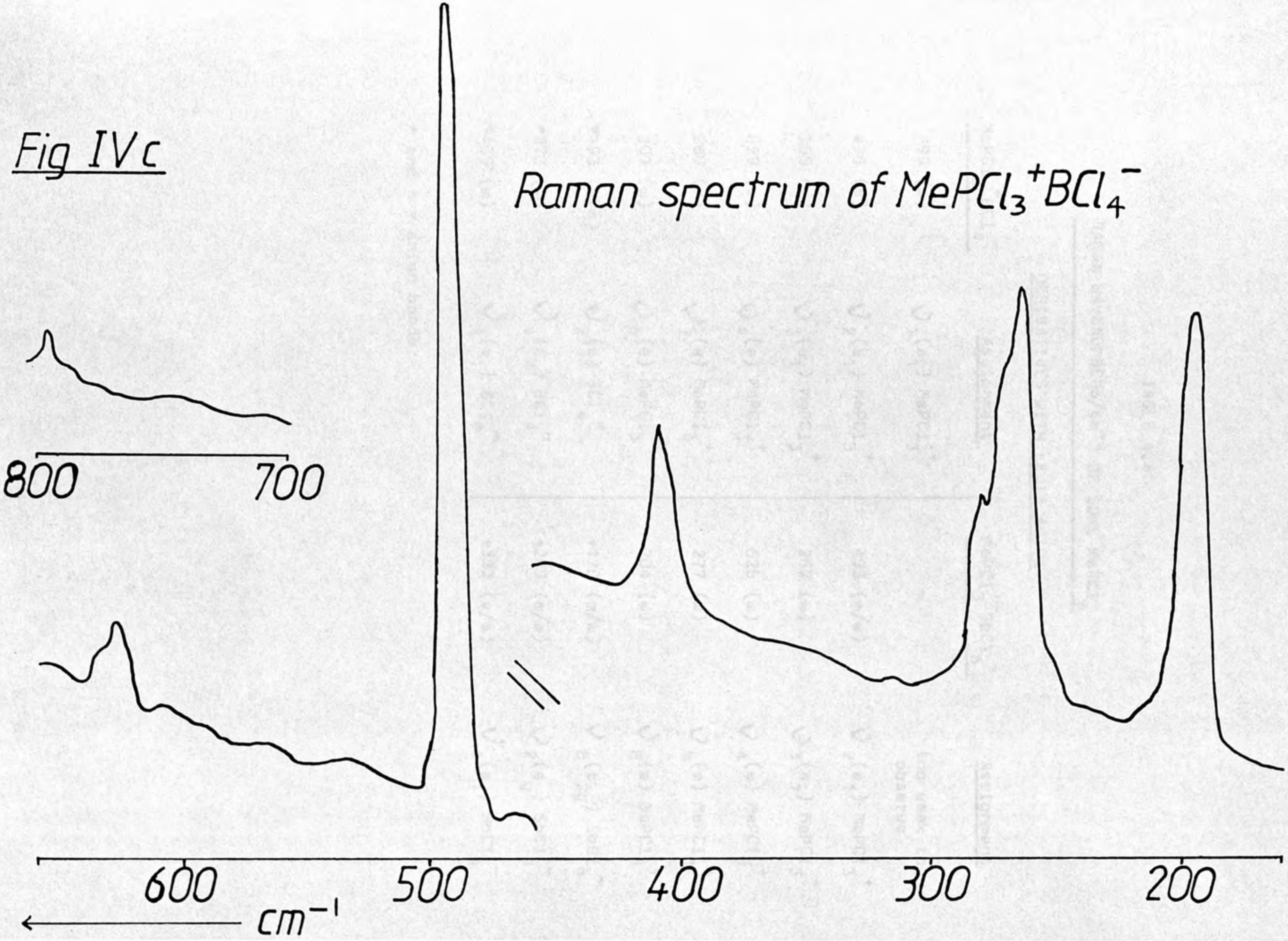
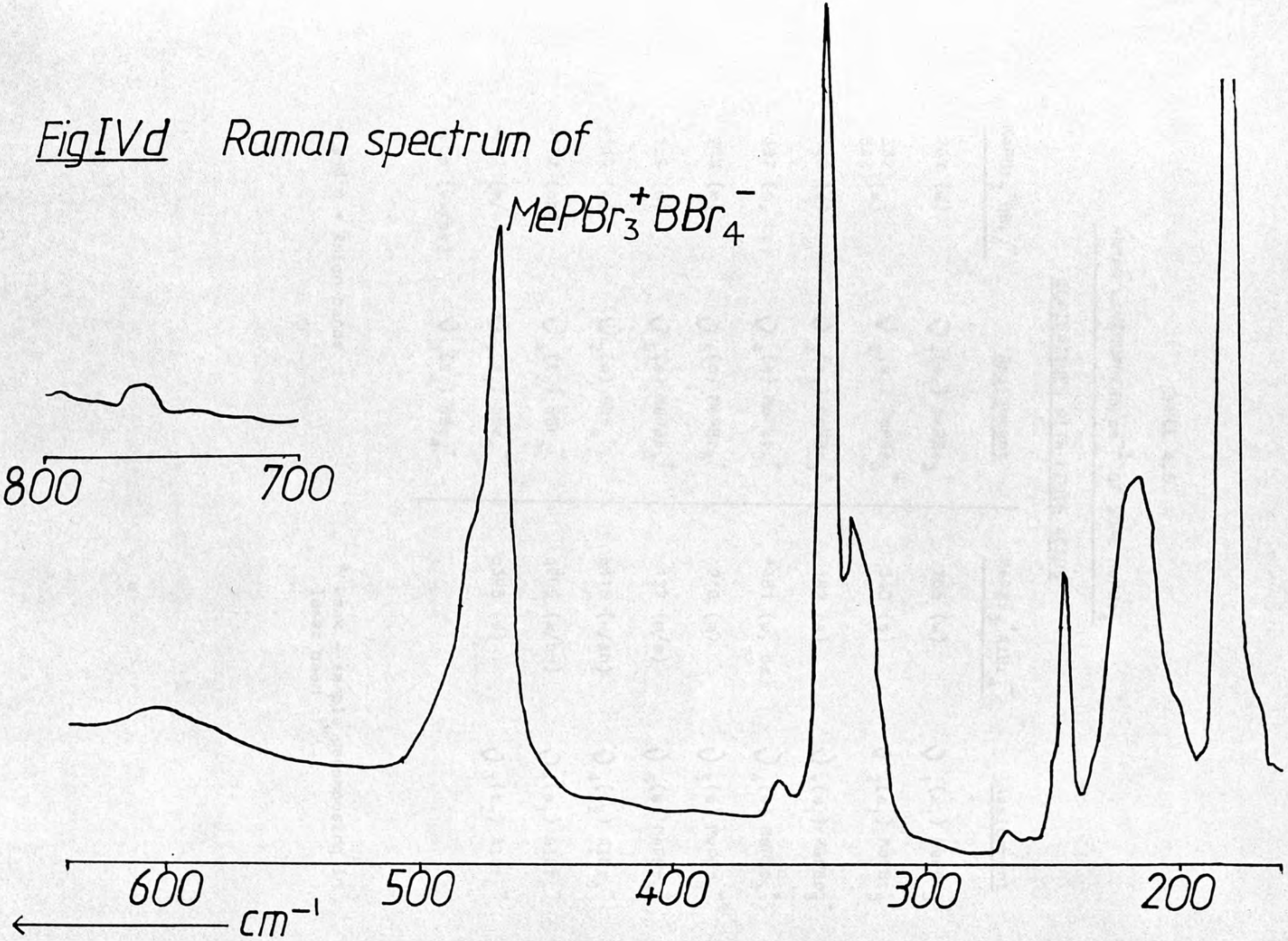


TABLE 4.4

RAMAN WAVENUMBERS/cm^{-1} OF SOME MePCl$_4$ DERIVATIVES WITH LEWIS ACIDS

$\mathrm{MePCl_3^+BCl_4^-}$	Assignment	$\mathrm{MePCl_3^+SbCl_6^-}$	Assignment
799 (w)	$\nu_1(a_1)$ $\mathrm{MePCl_3^+}$	-	too weak to observe
496 (s)	$\nu_2(a_1)$ $\mathrm{MePCl_3^+}$	493 (m/w)	$\nu_2(a_1)$ $\mathrm{MePCl_3^+}$
265 (m)	$\nu_3(a_1)$ $\mathrm{MePCl_3^+}$	267 (w)	$\nu_3(a_1)$ $\mathrm{MePCl_3^+}$
629 (w)	$\nu_4(e)$ $\mathrm{MePCl_3^+}$	625 (w)	$\nu_4(e)$ $\mathrm{MePCl_3^+}$
280 (m)	$\nu_5(e)$ $\mathrm{MePCl_3^+}$	277 (w)	$\nu_5(e)$ $\mathrm{MePCl_3^+}$
207 (w)	$\nu_6(e)$ $\mathrm{MePCl_3^+}$	204 (w)	$\nu_6(e)$ $\mathrm{MePCl_3^+}$
*193 (m/s)	$\nu_2(e)$ $\mathrm{BCl_4^-}$	+170 (m/w)	$\nu_5(t_{2g})$ $\mathrm{SbCl_6^-}$
*273 (m)	$\nu_4(t_2)$ $\mathrm{BCl_4^-}$	+289 (m/w)	$\nu_2(e_g)$ $\mathrm{SbCl_6^-}$
*409 (m)	$\nu_1(a_1)$ $\mathrm{BCl_4^-}$	+333 (v/s)	$\nu_1(a_1)$ $\mathrm{SbCl_6^-}$

* and + = anion bands



<u>Fig IVd</u> Raman spectrum of $MePBr_3^+BBr_4^-$

TABLE 4.5

RAMAN WAVENUMBERS/cm^{-1} OF SOME MePBr$_4$ DERIVATIVES WITH LEWIS ACIDS

$MePBr_3^+BBr_4^-$	Assignment	$MePBr_3^+AlBr_4^-$	Assignment
767 (w)	$\nu_1(a_1)$ $MePBr_3^+$	766 (w)	$\nu_1(a_1)$ $MePBr_3^+$
332) 342) (s)	$\nu_2(a_1)$ $MePBr_3^+$	340 (s)	$\nu_2(a_1)$ $MePBr_3^+$
182 (s)	$\nu_3(a_1)$ $MePBr_3^+$	182 (s)	$\nu_3(a_1)$ $MePBr_3^+$
487 (m, br)	$\nu_4(e)$ $MePBr_3^+$	*481 (w, br)	$\nu_4(e)$ $MePBr_3^+$
219 (m)	$\nu_5(e)$ $MePBr_3^+$	216 (m)	$\nu_5(e)$ $MePBr_3^{-1}$
128 (m)	$\nu_6(e)$ $MePBr_3^+$	127 (m/s)	$\nu_6(e)$ $MePBr_3^+$
+119 (w)	$\nu_2(e)$ BBr_4^-	o115 (w/sh)	$\nu_4(t_2)$ $AlBr_4^-$
+172 (sh)	$\nu_4(t_2)$ BBr_4^-	o209 (w/sh)	$\nu_1(a_1)$ $AlBr_4^-$
+247 (m/w)	$\nu_1(a_1)$ BBr_4^-	o395 (w)	$\nu_3(t_2)$ $AlBr_4^-$
+608 (vw/br)	$\nu_3(t_2)$ BBr_4^-		

+ and o = Anion bands

* weak - sample decomposing in laser beam

(496-477) in the $\nu_2(a_1)$ symmetric P-Cl stretching mode on passing from the single halide "parent" compound to the tetrachlorborate. This anion was confirmed by bands at 193, 273 and 409 cm^{-1} which were in good agreement with literature values$^{(8)}$ and those obtained from a test compound $Et_4N^+BCl_4^-$ during the present work. (The $\nu_3(t_2)$ mode of BCl_4^- at $\sim$ 670 cm^{-1} was too weak to observe in $MePCl_3^+BCl_4^-$). Other cationic bands were shifted in similar ways to those reported for the PCl_5 and PBr_5 systems and the same trends were observed for $MePCl_3^+SbCl_6^-$ where bands at 170, 289 and 331 cm^{-1} were indicative of the hexachloroantimonate anion$^{(9,10)}$. The product from the reaction of $MePCl_4$ and $AlCl_3$ fluoresced considerably during the recording of it's Raman spectrum so no detailed observations were possible, though the structure $MePCl_3^+AlCl_4^-$ has been previously confirmed by ^{31}P NMR and ^{35}Cl NQR spectroscopy$^{(3)}$. The $\nu_2(a_1)$ P-Cl symmetric stretch of the cation would be expected to fall in the 495 cm^{-1} region if the trends discussed earlier are followed.

Similar trends are observed for the $MePBr_3^+$ cation: although the Raman spectra were of lower quality than those of the chloro analogues. Again, the $\nu_2(a_1)$ mode (P-Br symmetric stretch) is affected most by the change in nature of the anion, shifting from 321 cm^{-1} in the case of $MePBr_3^+Br^-$ to about 340 cm^{-1} in complexes with Lewis acids. The Raman spectrum of $MePBr_3^+BBr_4^-$ shows the $\nu_2(a_1)$ cation mode to be split into two components and the anti-symmetric $\nu_4(e)$ mode to be rather broad, although analysis indicates $MePBBr_7$ to be a reasonable stoichiometry. The BBr_4^- anion is confirmed by bands at 119, 172, 247 and 608 cm^{-1} (8). Thus, the observed effects are possibly of crystallographic origin. The $\nu_2(a_1)$ cation mode in $MePBr_3^+AlBr_4^-$, although shifted to a higher frequency by about 20 cm^{-1} from that in $MePBr_3^+Br^-$,

does not exhibit this splitting, though the Raman spectrum obtained was poor owing to sample decompostion. The tetrabromoaluminate bands observed compare favourably with literature values (11).

Thus, for both $MePCl_3^+$ and $MePBr_3^+$, there are two sets of Raman fundamentals dependent upon the nature of the associated anion and are compared in Table 4.6. As in the PCl_5 (Phase II) and PBr_5 systems, substitution of a polyatomic anion for a single halide anion (accomplished by reaction with a Lewis acid) causes characteristic high frequency shifts in some of the cationic mode implying a strengthening of the P-Hal bands. Unfortunately no crystallographic evidence is available to confirm whether the single halide ions interact significantly with the cationic ligands as is the case with $PBr_4^+Br^-$ and $PBr_4^+Br_3^-$ but some interation is implied from the Raman data. The degree of such interaction is not great enough to perturb the symmetry of the cation as no new Raman bands appear in the spectra, hence the behaviour observed is similar in every way to that observed in the PCl_5 and PBr_5 systems. It is interesting to note here that Deng (5) recorded the infra-red spectra of $MePCl_3^+Cl^-$ and some of its salts and, although no assignments were made, high frequency shifts in some bands upon reaction with Lewis acids are apparent. In particular, bands at

TABLE 4.6

COMPARISON OF THE RAMAN WAVENUMBERS/cm^{-1} OF THE $MePCl_3^+$ AND $MePBr_3^+$ CATIONS IN THE PRESENCE OF SINGLE HALIDE AND POLYATOMIC ANIONS

$MePCl_3^+$		Assignment	$MePBr_3^+$	
Single Halide	Polyatomic		Single Halide	Polyatomic
795	799	$\nu_1(a_1)\,\nu\,(P{-}Me)$	761	766
477	496	$\nu_2(a_1)\,\nu_s\,(P{-}X)$	321	340
248	265	$\nu_3(a_1)\,\delta\,(PX_3)$	178	182
614	629	$\nu_4(e)\,\nu_{as}\,(P{-}X)$	475	487
273	280	$\nu_5(e)\,\delta\,(Me{-}P{-}X)$	196	216
219	207	$\nu_6(e)\,\delta\,(X{-}P{-}X)$	126	127

606 and 480 cm^{-1} in the $MePCl_3^+Cl^-$ spectrum shifted to ~ 620 and 490 cm^{-1} respectively upon complexation with $SbCl_5$. These are probably the $\nu_4(e)$ δ_{as}(P-Cl) and $\nu_2(a_1)$ δ_s(P-Cl) modes of the $MePCl_3^+$ cation and similar behaviour in the Raman spectra has already been discussed earlier in this section. Deng briefly reported the Raman spectra of some $MePCl_3^+Cl^-$ derivatives and the characteristic high frequency shifts were observed although they were slightly less than those reported in this study(5).

4.1.b The $MePCl_2/Br_2$ Reaction

This reaction was investigated by Deng(5) who reported obtaining a solid formulated as "$MePCl_2Br_2$" which was shown by ^{31}P NMR spectroscopy to contain a mixture of the $MePCl_nBr_{3-n}^+$ cations. These mixed halide cations have not previously been studied by Raman spectroscopy and this work compares them with the extensively investigated $PCl_nBr_{4-n}^+$ system(12,13,14). Several $MePCl_2/Br_2$ reactions in CH_2Cl_2 were performed and a typical Raman spectrum is illustrated in Fig. IVe (R.4). This spectrum is, not surprisingly, quite complex as there may be up to four cations present if no Me group scrambling has occurred. Assignments were aided by consideration of many products involving different reactant ratios. If all 4 $MePCl_nBr_{4-n}^+$ cations are present in the mixtures a total of 30 Raman active bands may be predicted by symmetry arguments. These arise as follows:- The ions $MePCl_3^+$ and $MePBr_3^+$ are of C_{3v}

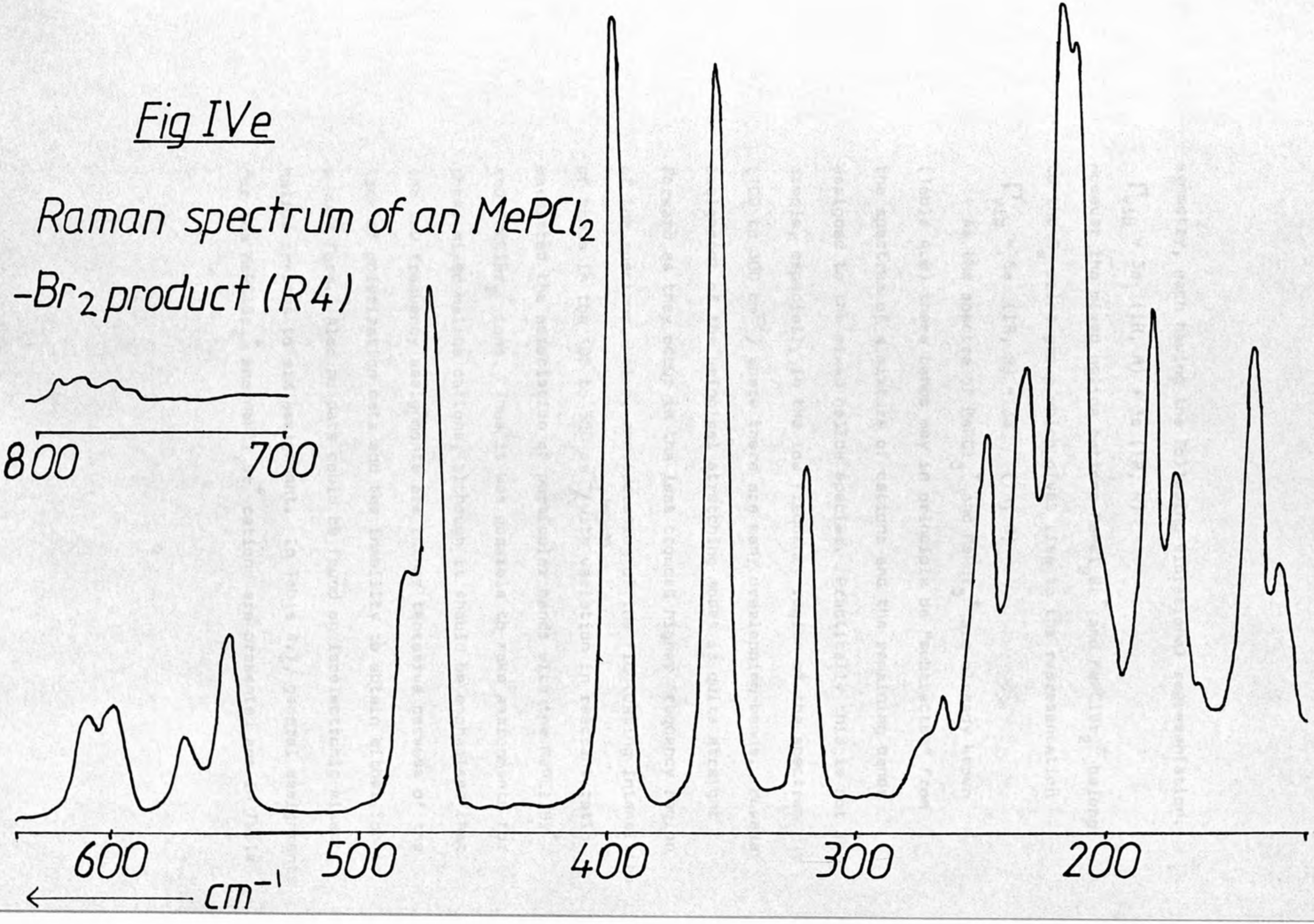


Fig IVe

Raman spectrum of an $MePCl_2$-Br_2 product (R4) symmetry, each having the following vibrational representation.

$$\Gamma_{vib} = 3a_1 \text{ (IR, R)} + 3e \text{ (IR, R)}$$

However the mixed halide cations $MePCl_2Br^+$ and $MePClBr_2^+$ belong to the C_s point group which gives rise to the representation

$$\Gamma_{vib} = 6a \text{ (IR, R)} + 3a \text{ (IR, R)}$$

As the spectra of $MePCl_3^+$ and $MePBr_3^+$ are already known (Table 4.6) these bands may in principle be "subtracted" from the spectrum of a mixture of cations and the remaining bands assigned to the mixed halide species. Practically this is not so simple, especially in the low frequency region of the spectrum (100 to 300 cm^{-1}) where there are many overlapping bands. However assignment of the principal stretching modes is quite straight forward as they occur in the less crowded higher frequency region of the spectrum. Also, consideration of the fluctuating intensities of bands in the 100 to 300 cm^{-1} region with variation in reactant ratio permitted the association of particular bands with the $MePCl_2Br^+$ and $MePClBr_2^+$ ions. Thus it was possible to make assignments for these mixed halide cations, although it should be emphasised that the low frequency assignments are rather tentative because of the lack of polarization data and the inability to obtain either ion in a pure form. Also no data could be found on isoelectronic mixed halide species to aid assignment. In Table 4.7, general assignments for the $MePClBr_2^+$ and $MePCl_2Br^+$ cations are presented and in Table

TABLE 4.7

ASSIGNMENTS OF THE RAMAN WAVENUMBERS/cm^{-1} OF THE $MePCl_2Br^+$ AND $MePClBr_2^+$ CATIONS IN THE PRESENCE OF A SINGLE HALIDE ANION

$MePCl_2Br^+$	Assignment [a]	$MePClBr_2^+$	Assignment
786	$\nu_1(a')\ \nu$ (P-Me)	773	$\nu_1(a')\ \nu$ (P-Me)
601	$\nu_7(a'')\ \nu_{as}\ (PCl_2)$	574	$\nu_2(a')\ \nu$ (P-Cl)
554	$\nu_2(a')\ \nu_s\ (PCl_2)$	482	$\nu_7(a'')\ \nu_{as}\ (PBr_2)$
396	$\nu_3(a')\ \nu$ (P-Br)	356	$\nu_3(a')\ \nu_s\ (PBr_2)$
266	$\nu_4(a')\ \omega\ (PCl_2)$	214	$\nu_4(a')\ \omega\ (PBr_2)$
248	$\nu_5(a')\ \delta\ (PCl_2)$	173	$\nu_5(a')\ \delta\ (PBr_2)$
232	$\nu_6(a')\ \delta$ (Me-P-Br)	163 (?)	$\nu_6(a')\ \delta$ (Me-P-Cl)
220	$\nu_8(a'')\ \gamma\ (PCl_2)$	142	$\nu_8(a'')\ \gamma\ (PBr_2)$
185	$\nu_9(a'')\ \pi$ (Me-P-Br) or $\rho\ (PCl_2)$	129 (?)	$\nu_9(a'')\ \pi$ (Me-P-Cl) or $\rho\ (PBr_2)$

[a] Description of modes based on those listed in "Inorganic Infra-red and Raman Spectra" by S. D. Ross, McGraw-Hill, 1972.

TABLE 4.8

ASSIGNMENTS OF RAMAN WAVENUMBERS/cm^{-1} OF A TYPICAL

$\mathrm{MePCl_2/Br_2}$ REACTION PRODUCT (R4, FIG. IVe)

Wavenumbers/cm^{-11}Fig. IVe (R4)	Assignment
796 (w)	$\nu_1(a_1)\mathrm{MePCl_3}^+$
786 (w)	$\nu_1(a')$ $\mathrm{MePCl_2Br}^+$
773 (w)	$\nu_1(a')$ $\mathrm{MePClBr_2}^+$
762 (w)	$\nu_1(a_1)$ $\mathrm{MePBr_3}^+$
613 (w/m)	$\nu_4(e)$ $\mathrm{MePCl_3}^+$
600 (w/m)	$\nu_7(a'')$ $\mathrm{MePCl_2Br}^+$
573 (w/m)	$\nu_2(a')$ $\mathrm{MePClBr_2}^+$
554 (m)	$\nu_2(a')$ $\mathrm{MePCl_2Br}^+$
482 (m)	$\nu_7(a'')$ $\mathrm{MePClBr_2}^+$
477 (m/sh)	$\nu_4(e)$ $\mathrm{MePBr_3}^+$
473 (s)	$\nu_2(a_1)$ $\mathrm{MePCl_3}^+$
396 (vs)	$\nu_3(a')$ $\mathrm{MePCl_2Br}^+$
356 (vs)	$\nu_3(a')$ $\mathrm{MePClBr_2}^+$
320 (m/s)	$\nu_2(a_1)$ $\mathrm{MePBr_3}^+$
274 (w)	$\nu_5(e)$ $\mathrm{MePCl_3}^+$
265 (w/m)	$\nu_4(a')$ $\mathrm{MePCl_2Br}^+$
248 (m/s)	$\nu_5(a')$ $\mathrm{MePCl_2Br}^+$

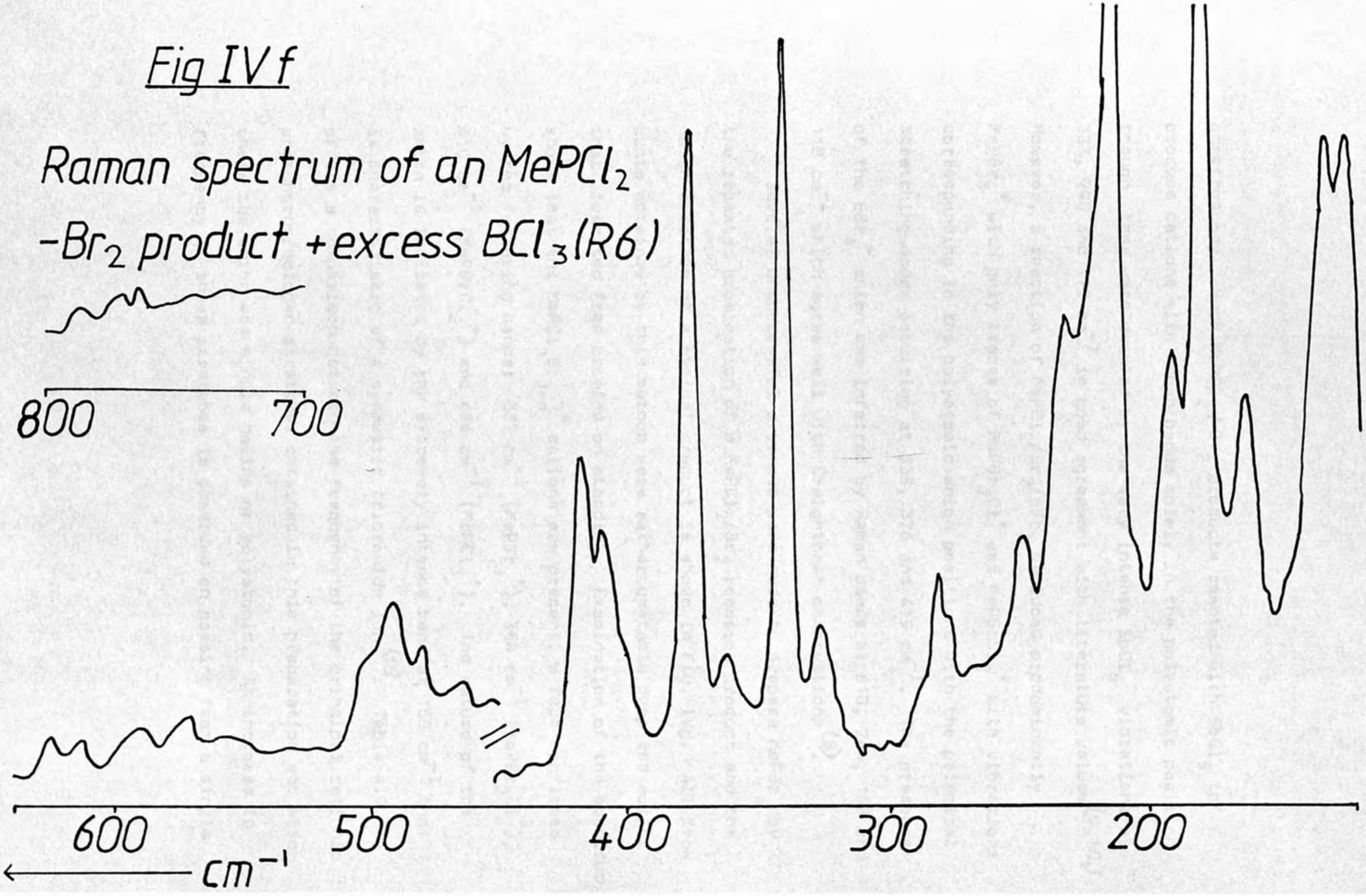
TABLE 4.8 CONT'D

Wavenumbers/cm^{-1} Fig. IVe (R4)	Assignment
233 (m/s)	$\nu_6(a')$ $MePCl_2Br^+$
219 (vs)	$\nu_8(a'')$ $MePCl_2Br^+$
214 (vs)	$\nu_4(a')$ $MePClBr_2^+$
209 (w/sh)	$\nu_6(e)$ $MePCl_3^+$ (?)
198 (w/sh)	$\nu_5(e)$ $MePBr_3^+$
184 (m/s)	$\nu_9(a'')$ $MePCl_2Br^+$
180 (m/sh)	$\nu_3(a_1)$ $MePBr_3^+$
172 (m)	$\nu_5(a')$ $MePClBr_2^+$
164 (w/sh)	$\nu_6(a')$ $MePClBr_2^+$
142 (m/s)	$\nu_8(a'')$ $MePClBr_2^+$
130 (m)	$\nu_9(a'')$ $MePClBr_2^+$
125 (w/sh)	$\nu_6(e)$ $MePBr_3^+$

4.8 the complete assignment of the $MePCl_2/Br_2$ reaction product spectrum (Fig. IVe) is shown. As with the $PCl_nBr_{4-n}{}^+$ systems it is the symmetric P-Br stretches that allow easiest identification of the $MePBr_3{}^+$, $MePBr_2Cl^+$ and $MePBrCl_2{}^+$ cations with relatively strong bands at 320, 356 and 396 cm^{-1} respectively. The frequencies listed in Table 4.8 are for the $MePCl_nBr_{3-n}{}^+$ cations in the presence of single halide ions (ie Cl^- and/or Br^-). Reactions of $MePCl_2/Br_2$ products with Lewis Acids would be expected to cause characteristic shifts in the Raman spectra of the cations present as they become associated with polyatomic anions. This effect was subsequently observed andFig. IVF shows the Raman spectrum of a $MePCl_2/Br_2$ product reacted with an excess of BCl_3. The multitude of bands in the 100 to 300 cm^{-1} area make it hard to define whether any shifts in frequency have occurred when compared with those in the original $MePCl_2/Br_2$ product. However, the P-Br symmetric stretches are significantly affected with increases in frequency of the order of 20 cm^{-1} and this is in accord with results observed for the parent $MePCl_4$ and $MePBr_4$ systems. The new positions of ν_3 (a′) for the $MePCl_2Br^+$ and $MePClBr_2{}^+$ cations are 420 and 376 cm^{-1} respectively. This shift is very apparent in Fig. IVF where there are traces of the original $MePCl_nBr_{3-n}{}^+$ cations associated with single halide anions though they too have been shifted slightly. The presence of $BCl_4{}^-$ as the anion was confirmed by a shoulder at 405 cm^{-1} and bands at 280 and 191 cm^{-1}(8) and solid state ^{11}B NMR

Fig IV f

Raman spectrum of an $MePCl_2$ $-Br_2$ product + excess BCl_3 (R6)



spectroscopy. Such $MePCl_2$ / Br_2 products reacted with $SbCl_5$ to produce cations with Raman bands solely in the polyatomic position though they were dwarfed by the very intense $SbCl_6^-$ vibrations at 333, 290 and 172 cm^{-1} in good agreement with literature values (9,10.) However, a reaction of $MePCl_2/Br_2/BBr_3$ produced predominantly $MePBr_3^+$ with only traces of $MePBr_2Cl^+$ and $MePBrCl_2^+$ with vibrations corresponding to the polyatomic anion positions with the principal stretching modes occurring at 338, 376 and 419 cm^{-1}. The presence of the BBr_4^- anion was inferred by Raman bands at 610, 244, 168 and 118 cm^{-1} which agree well with Creightons' observations (8).

Several unsuccessful attempts were made to prepare $MePBr_4$ by the repeated bromination of a $MePCl_2/Br_2$ reaction product and the Raman spectrum of a typical product is shown in Fig. IVg. All products obtained by this method were rather unstable deep red solids that liberated free bromine on standing. Examination of the spectrum shows that the $MePCl_nBr_{3-n}^+$ cations are present, a fact confirmed by the following bands: 332 cm^{-1} ($MePBr_3^+$), 368 cm^{-1} ($MePBr_2Cl^+$), 410 cm^{-1} ($MePBrCl_2^+$) and 484 cm^{-1} ($MePCl_3^+$). The nature of the anion is indicated by the extremely intense band at 168 cm^{-1} that is characteristic of a symmetric tribromide ion (15). Table 4.9 offers a comparison between the frequency of the principal cationic phosphorus/halogen stretches obtained in this preparation and also where the anion was single halide or polyatomic. An increase in frequency of these stretches is observed on passing from a single

Fig IVg Raman spectrum of an $MePCl_2-Br_2$ product + excess Br_2 [R8]

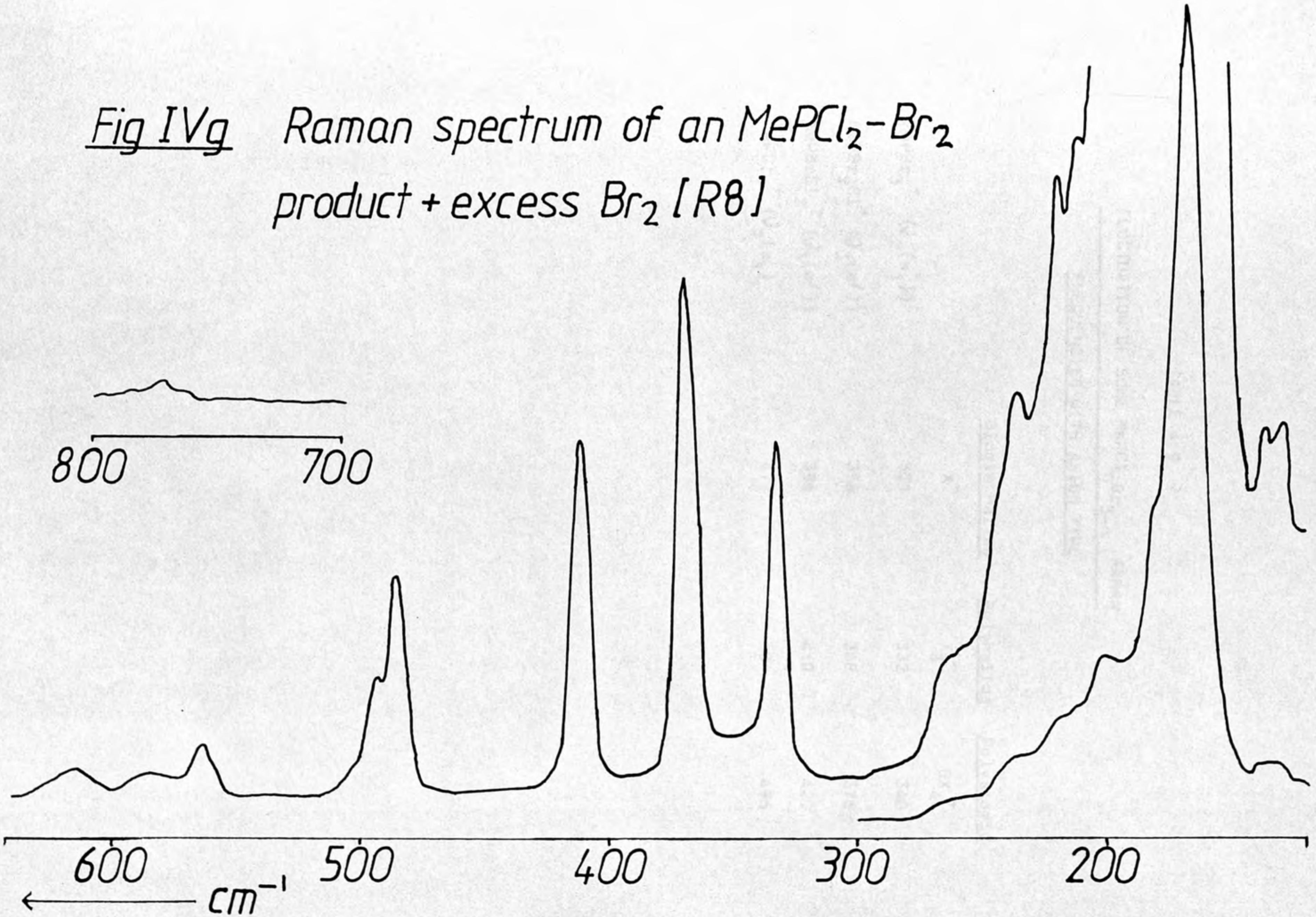


TABLE 4.9

FLUCTUATION OF SOME $MePCl_nBr_{3-n}^+$ RAMAN FREQUENCIES WITH ANION TYPE

	Single Halide X^-	Polyhalide X_3^-	Polyatomic BX_4^-
$MePBr_3^+$ $(\nu_2(a_1))$	321	332	340
$MePBr_2Cl^+$ $(\nu_3(a'))$	356	368	376
$MePBrCl_2^+$ $(\nu_3(a'))$	396	410	420
$MePCl_3^+$ $(\nu_2(a_1)$	477	484	496

halide anion to a polyatomic anion via a polyhalide anion. This is similar to the trends observed in the PBr_4^+ and PCl_4^+ systems and undoubtedly arises from the fact that the smaller single halide anions interact with the cation to a greater extent than the polyatomic anions with the polyhalide anions being an intermediate case. X-ray crystallographic data on this system would prove interesting as it would determine the nature of the anion/cation interaction which, as with the PX_4^+ series, does not perturb the total cation system.

4.2 Dimethylhalophosphoranes

4.2.a Dimethyltrichlorophosphorane and Dimethyltribromophosphorane and some derivatives

The only previous vibrational spectroscopic study of dimethyltrichlorophospharane was reported by Baumgartner et al in 1964 and an ionic formulation was indicated with the cation exhibiting C_{2v} symmetry(1). Such a structure ($Me_2PCl_2^+Cl^-$) was also deduced from solid state NMR and NQR studies(3). The current Raman study produced rather unusual results and these are compared with those obtained by Baumgartner in Table 4.10. The two weak modes reported by Baumgartner at 146 and 168 cm^{-1} were not observed, neither was the band at 364 cm^{-1}: a complex of three bands was, however, observed in the 260-280 cm^{-1} region and these were assigned to various deformation modes. Evidence from several preparations indicated that there are two closely related forms of $Me_2PCl_2^+Cl^-$, designated as

"A" and "B" in Table 4.10 and illustrated in Fig. IVh. (c.f the $MePCl_2/Cl_2$ system). The assignments were made empirically after comparison with $Br_2PCl_2^+$ and the isoelectronic Me_2SiCl_2 (Tables 3.7 and 4.3). The spectra of forms A and B show slight differences in frequency as well as some intensity changes in the 260-280 cm^{-1} region. Analyses for the two forms were consistent and in agreement with the Me_2PCl_3 formulation. Most preparations of $Me_2PCl_2^+Cl^-$ (usually by the chlorination of Me_2PCl) produced mixtures of forms A and B; the Raman spectra were characterized by rather broad bands. However, in it's pure form A was best indentified by the symmetric and antisymmetric P-Cl stretches at 508 and 584 cm^{-1} whereas in form B these modes were shifted to 515 and 603 cm^{-1} respectively. Experiments were performed to establish the relative stabilities of these two forms of $Me_2PCl_2^+Cl^-$. When a mixture of A and B (ie a typical product) was heated to about 110°C it transformed irreversibly to form A, a fact most readily manifested by the increase in bands at 508 and 584 cm^{-1} at the expense of those at 515 and 603 cm^{-1}. When form A only was heated, no change was observed in the Raman spectrum but when a pure sample of Form B was heated to 60°C under a running vacuum it transformed irreversibly to Form A. Also, when a mixture of types A and B was heated to ~ 80-100°C under a running vacuum pure A was formed which proved insensitive to further heating. Thus Form A appears to be the most stable modification of $Me_2PCl_2^+Cl^-$. The exact structure of these

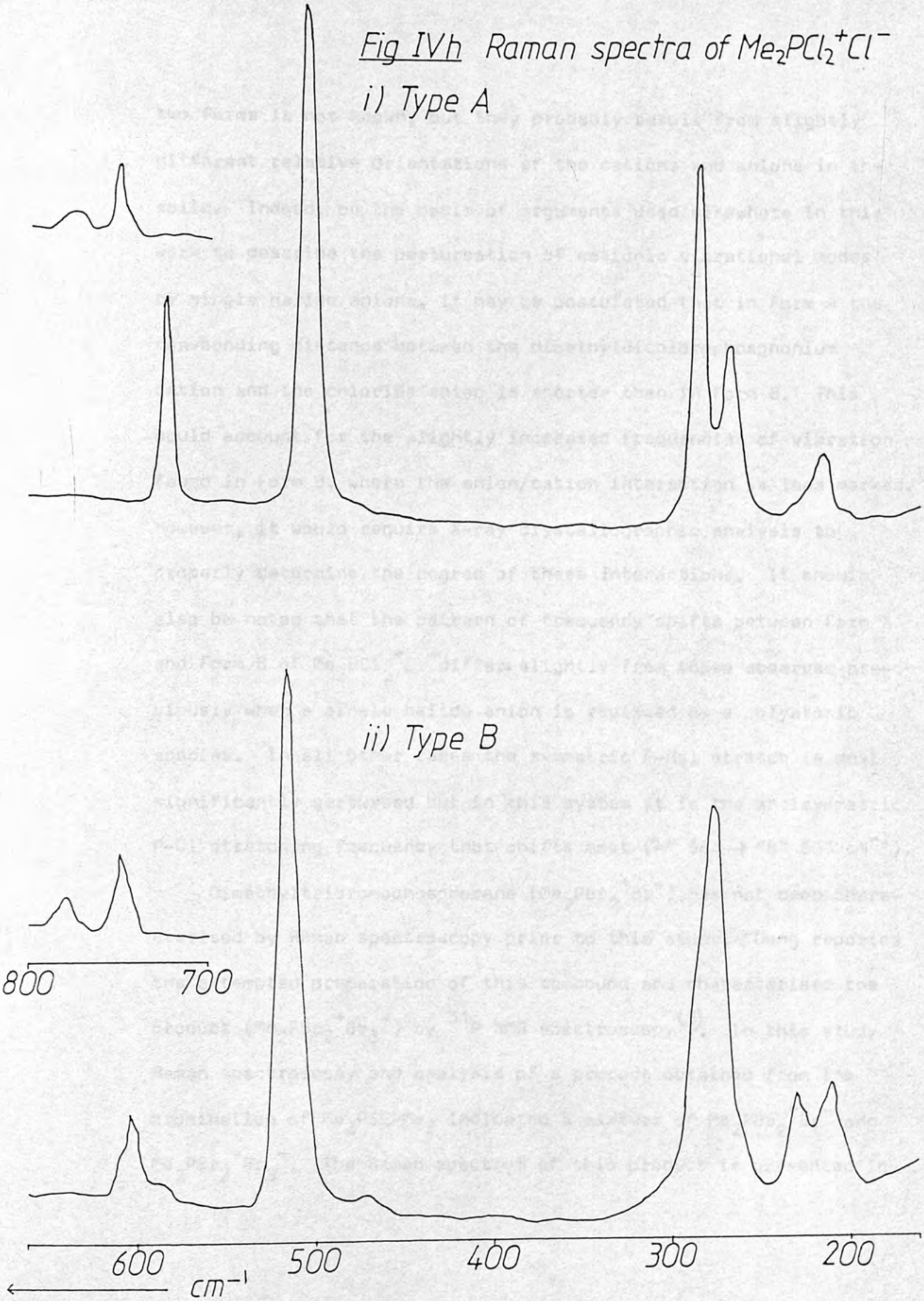
TABLE 4.10

RAMAN WAVENUMBERS/cm^{-1} FOR THE COMPOUND $Me_2PCl_2^+Cl^-$

Baumgartner [(a)]	This Study "A"	This Study "B"	Assignment
146			
168			
	214 (m/w)	210 (m/w)	$\nu_4(a_1)\ \delta(PCl_2)$
212	228 (w)	230 (m/w)	$\nu_5(a_2)$ torsion
281	260 (?)(m/w, sh)	263 (m, sh)	$\nu_9(b_2)\delta(PCl_2)$
	268 (m)	276 (s)	$\nu_3(a_1)\delta(PMe_2)$
	283 (s)	284 (m, sh)	$\nu_7(b_1)\delta(PMe_2)$
364			
496	508 (s)	515 (s)	$\nu_2(a_1)\nu_s(P\text{-}Cl)$
580	584 (m)	603 (m/w)	$\nu_8(b_2)\nu_{as}(P\text{-}Cl)$
743	749 (m/w)	749 (m/w)	$\nu_1(a_1)\nu_s(P\text{-}Me)$
768	776 (w)	779 (w)	$\nu_6(b_1)\nu_{as}(P\text{-}Me)$

(a) R. Baumgartner, W. Sawodny and J. Goubeau; Z. Anorg. Allgem. Chem., 1964, 333, 171.

Fig IVh Raman spectra of $Me_2PCl_2^+Cl^-$



two forms is not known, but they probably result from slightly different relative orientations of the cations and anions in the solid. Indeed, on the basis of arguments used elsewhere in this work to describe the perturbation of cationic vibrational modes by single halide anions, it may be postulated that in Form A the non-bonding distance between the dimethyldichlorophosphonium cation and the chloride anion is shorter than in Form B. This would account for the slightly increased frequencies of vibration found in Form B, where the anion/cation interaction is less marked. However, it would require X-ray crystallographic analysis to properly determine the degree of these interactions. It should also be noted that the pattern of frequency shifts between Form A and Form B of $Me_2PCl_2^+Cl^-$ differs slightly from those observed previously when a single halide anion is replaced by a polyatomic species. In all other cases the symmetric P-Hal stretch is most significantly perturbed but in this system it is the antisymmetric P-Cl stretching frequency that shifts most ("A" 584 → "B" 603 cm^{-1}).

Dimethyltribromophosphorane ($Me_2PBr_2^+Br^-$) has not been characterised by Raman spectroscopy prior to this study. Deng reported the attempted preparation of this compound and characterised the product ($Me_2PBr_2^+Br_3^-$) by ^{31}P NMR spectroscopy(5). In this study Raman spectroscopy and analysis of a product obtained from the bromination of $Me_2PSSPMe_2$ indicated a mixture of $Me_2PBr_2^+Br^-$ and $Me_2PBr_2^+Br_3^-$. The Raman spectrum of this product is presented in

TABLE 4.11

RAMAN WAVENUMBERS/cm^{-1} OF THE $Me_2PSSPMe_2/Br_2$ REACTION PRODUCT

(I) Crude Product ($Me_2PBr_2^+Br^-$ and $Me_2PBr_2^+Br_3^-$)	(II) Crude Product & Further Br_2 (Mainly $Me_2PBr_2^+Br_3^-$)	Assignments
138 (m, sh) 145 (m; sh)	140 (m, sh)	$\nu_4(a_1)\ \delta\ (PBr_2)$
168 (vs)) 170 (sh))	167 (vs)) 170 (sh))	$\nu_1(\Sigma g^+)\ Br_3^-$ $\nu_5(a_2)$ torsion
224 (m/w)	224 (m/w)	$\nu_9(b_2)\delta(PBr_2)$
233 (m/s) 237 (m/s)	236 (m)	$\nu_3(a_1)\delta(P\ Me_2)$
242 (m/s) 247 (m/s)	248 (m)	$\nu_7(b_1)\delta(PMe_2)$
377 (vs) 384 (s)	384 (vs)	$\nu_2(a_1)\nu_s(P{-}Br)$
467 (m) 475 (m/s)	475 (m/s)	$\nu_8(b_2)\nu_{as}(P{-}Br)$
724 (w)	722 (w)	$\nu_1(a_1)\nu_s(P{-}Me)$
772 (w)	771 (w)	$\nu_6(b_1)\nu_{as}(P{-}Me)$

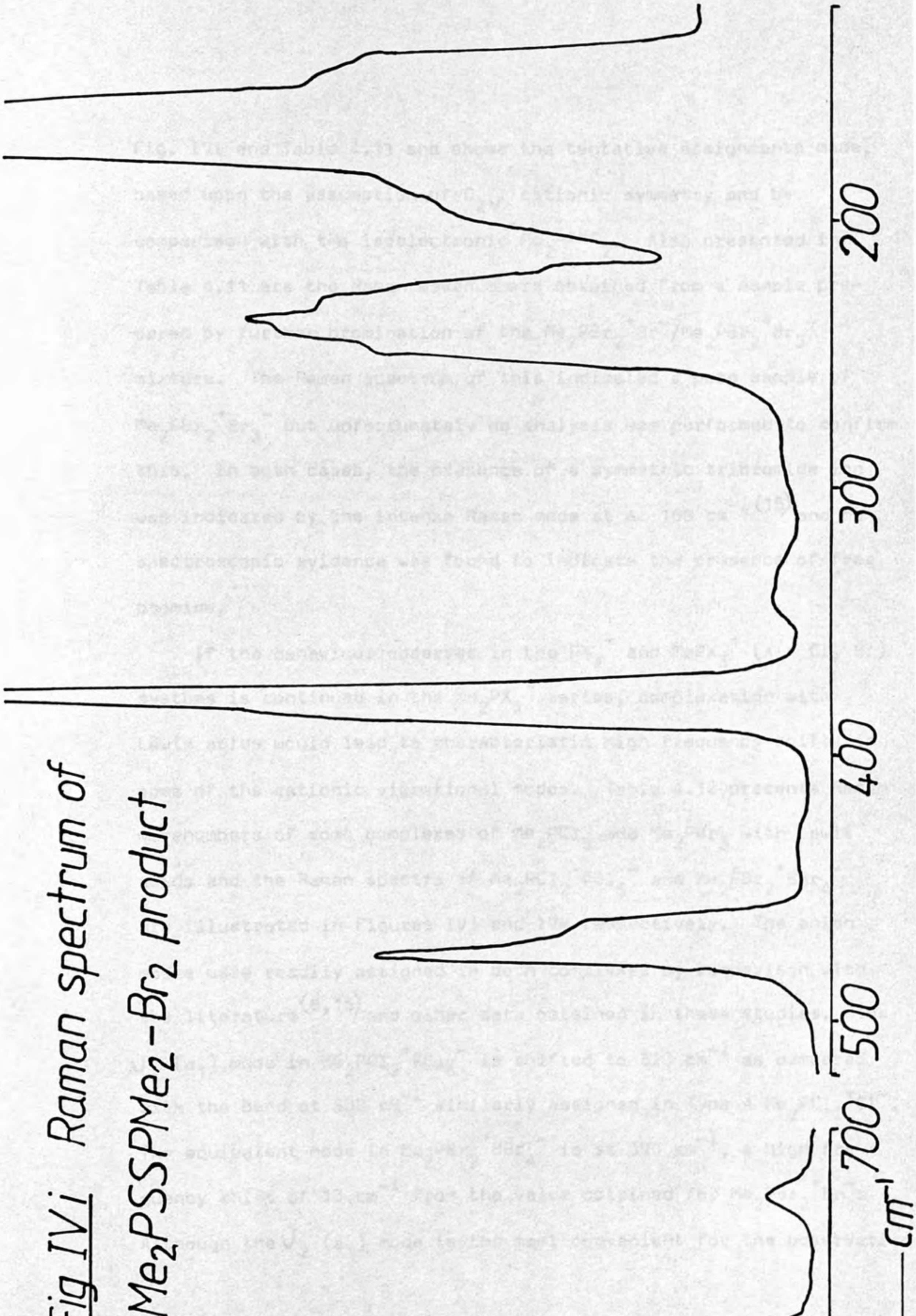


Fig IVi Raman spectrum of an $Me_2PSSPMe_2-Br_2$ product

Fig. IVi and Table 4.11 and shows the tentative assignments made, based upon the assumption of C_{2v} cationic symmetry and by comparison with the isoelectronic Me_2SiBr_2. Also presented in Table 4.11 are the Raman wavenumbers obtained from a sample prepared by further bromination of the $Me_2PBr_2{}^+Br^-/Me_2PBr_2{}^+Br_3{}^-$ mixture. The Raman spectrum of this indicated a pure sample of $Me_2PBr_2{}^+Br_3{}^-$ but unfortunately no analysis was performed to confirm this. In both cases, the presence of a symmetric tribromide ion was indicated by the intense Raman mode at ~ 168 cm^{-1}(15) and no spectroscopic evidence was found to indicate the presence of free bromine.

If the behaviour observed in the $PX_4{}^+$ and $MePX_3{}^+$ (X = Cl, Br) systems is continued in the $Me_2PX_2{}^+$ series, complexation with Lewis acids would lead to characteristic high frequency shifts in some of the cationic vibrational modes. Table 4.12 presents Raman wavenumbers of some complexes of Me_2PCl_3 and Me_2PBr_3 with Lewis acids and the Raman spectra of $Me_2PCl_2{}^+PCl_6{}^-$ and $Me_2PBr_2{}^+BBr_4{}^-$ are illustrated in Figures IVj and IVk respectively. The anion modes were readily assigned in both complexes by comparison with the literature(8,16) and other data obtained in these studies. The ν_2 (a_1) mode in $Me_2PCl_2{}^+PCl_6{}^-$ is shifted to 523 cm^{-1} as compared with the band at 508 cm^{-1} similarly assigned in Type A $Me_2PCl_2{}^+Cl^-$. The equivalent mode in $Me_2PBr_2{}^+BBr_4{}^-$ is at 390 cm^{-1}, a high frequency shift of 13 cm^{-1} from the value obtained for $Me_2PBr_2{}^+Br^-$. Although the ν_2 (a_1) mode is the most convenient for the observation

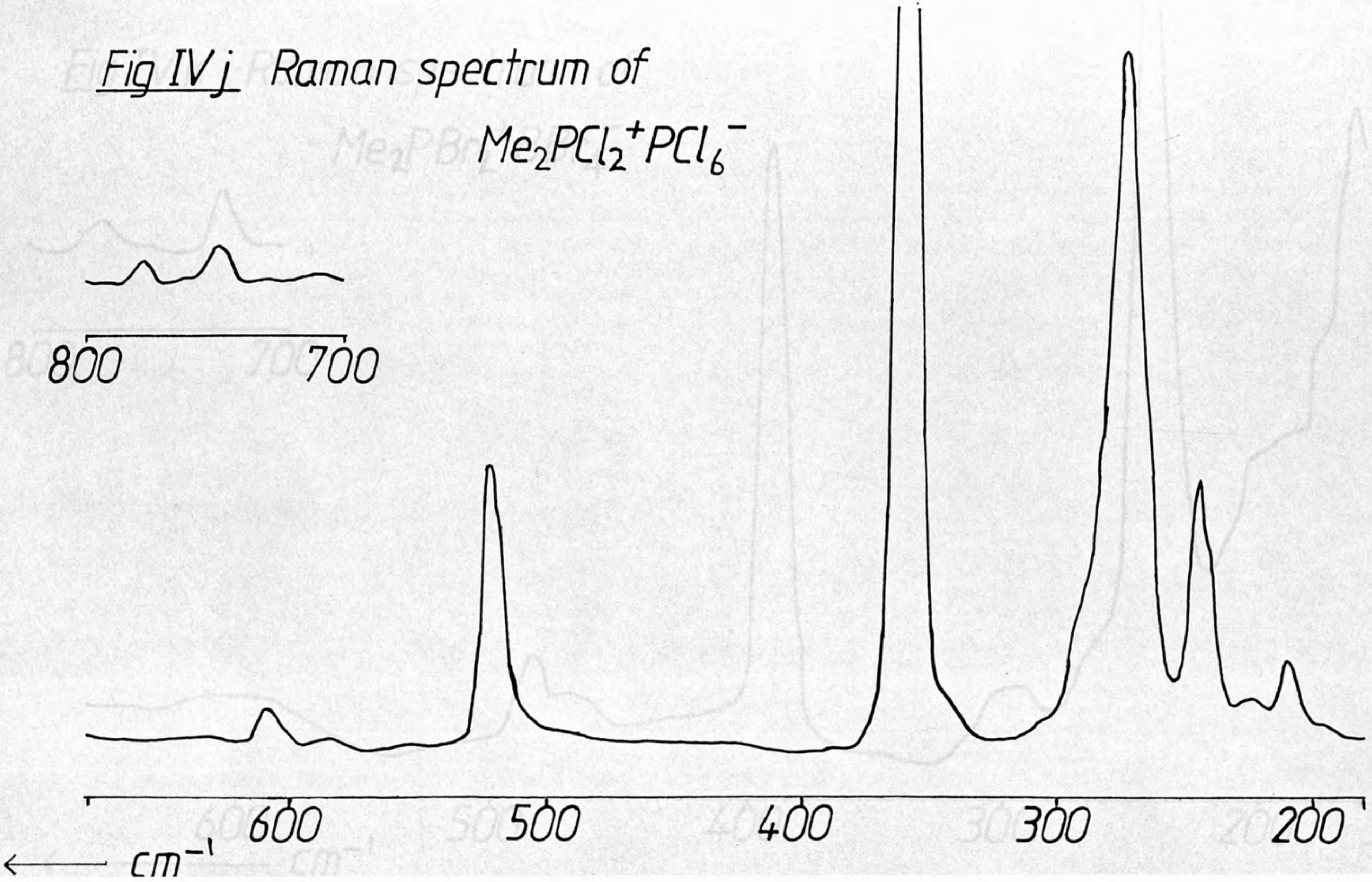


Fig IV j Raman spectrum of $Me_2PCl_2^+PCl_6^-$

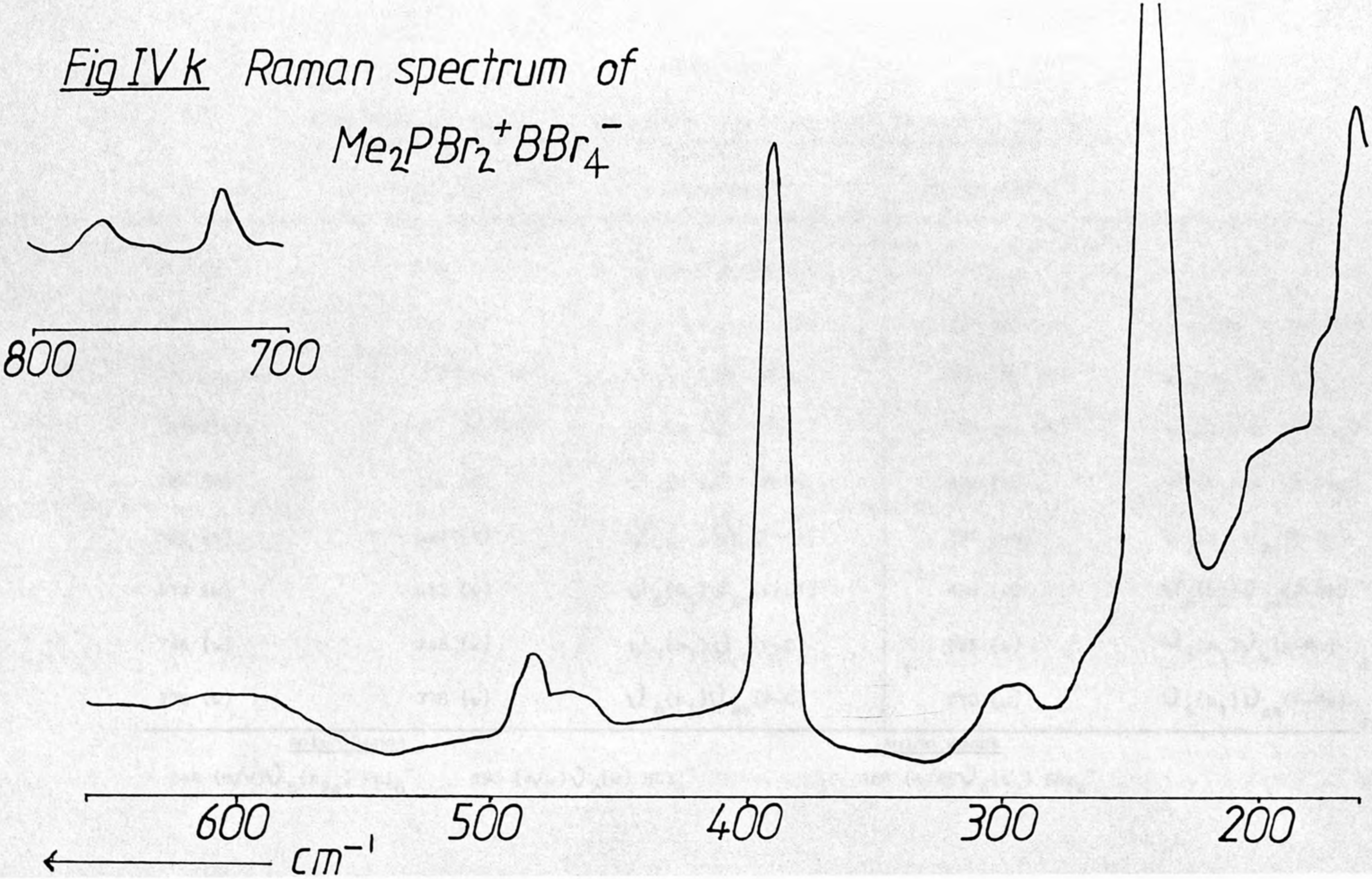


Fig IV k Raman spectrum of $Me_2PBr_2^+BBr_4^-$

TABLE 4.12

RAMAN WAVENUMBERS/cm^{-1} OF SOME LEWIS ACID DERIVATIVES OF Me_2PCl_3 AND Me_2PBr_3

$Me_2PCl_2{}^+PCl_6{}^-$	$Me_2PCl_2{}^+BCl_4{}^-$	Assignments	$Me_2PBr_2{}^+BBr_4{}^-$	Assignment
211 (w)	208 (w)	$\nu_4(a_1)\ \delta\ (PCl_2)$		
225 (w)	224 (w)	$\nu_5(a_2)$ torsion	175 (w)	$\nu_5(a_2)$ torsion
266 (m, sh)	268 (m, sh)	$\nu_9(b_2)\ \delta\ (PCl_2)$	226 (m, sh)	$\nu_9(b_2)\ \delta\ (PBr_2)$
Obscured	271 (m, sh)	$\nu_3(a_1)\ \delta\ (PMe_2)$	238 (m, sh)	$\nu_3(a_1)\ \delta\ (P\ Me_2)$
283 (m)	284 (s)	$\nu_7(b_1)\ \delta\ (P\ Me_2)$	242 (s)	$\nu_7(b_1)\ \delta\ (P\ Me_2)$
523 (s)	520 (s)	$\nu_2(a_1)\ \nu_s\ (P\text{–}Cl)$	391 (vs)	$\nu_2(a_1)\ \nu_s\ (P\text{–}Br)$
612 (w)	612 (w)	$\nu_8(b_2)\ \nu_{as}(P\text{–}C1)$	488 (w)	$\nu_8(b_2)\ \nu_{as}(P\text{–}Br)$
748 (w)	748 (w)	$\nu_1(a_1)\ \nu_s(P\text{–}C)$	725 (w)	$\nu_1(a_1)\ \nu_s(P\text{–}Me)$
778 (w)	778 (w)	$\nu_6(b_1)\ \nu_{as}(P\text{–}C)$	770 (w)	$\nu_6(b_1)\ \nu_{as}(P\text{–}Me)$

Anion Bands

244 (m/w) $\nu_5(t_{2g})\ PCl_6{}^-$ 193 (m/w) $\nu_2(e)\ BCl_4{}^-$

Anion Bands

164 (m/w) $\nu_4(t_2)\ BBr_4{}^-$

TABLE 4.12 CONT'D

Anion Bands		Anion Bands
274 (s) $\nu_2(e_g)$ PCl_6^-	278 (m, sh) $\nu_4(t_2)$ BCl_4^-	247 (m, sh) $\nu_1(a_1)$ BBr_4^-
356 (vs) $\nu_1(a_{1g})$ PCl_6^-	409 (m) $\nu_1(a_1)$ BCl_4^-	601 (w, br) $\nu_3(t_2)$ BBr_4^-
	672 (vw) $\nu_3(t_2)$ BCl_4^-	

of this shift phenomenon, in this system the ν_8 (b_2) antisymmetric P-Hal stretch is most significantly perturbed by the change in anion with shifts of about 20 cm^{-1} in both the $Me_2PCl_2^+$ and $Me_2PBr_2^+$ complexes. A similar pattern of shifts was observed in the complex $Me_2PCl_2^+SbCl_6^-$ (ν_2 at 519 cm^{-1}) but some details of the cation vibrations were rendered unobservable by the relative intensity of the three Raman active $SbCl_6^-$ modes (9,10).

It is interesting to comment upon some results obtained by Deng in his study of dimethyltrichlorophosphorane and some derivatives (5). The Raman data reported for $Me_2PCl_2^+Cl^-$ has a band at 515 cm^{-1}, assignable to the symmetric P-Cl stretch and consistent with that observed in the present mode for Type "B" $Me_2PCl_2^+Cl^-$. Complexation was performed with Lewis acids so as to yield octahedral or square planar anions. The hexachlorophosphate caused a high frequency shift of ν_s (P-Cl) to 520 cm^{-1} which is in reasonable agreement with that reported in Table 4.12. However in the case of the hexachloroantimonate ν_s(P-Cl) is reported at 510 cm^{-1}, fully 11 cm^{-1} less than observed in this study and 5 cm^{-1} less than the equivalent band in the parent $Me_2PCl_2^+Cl^-$. When complexes with a square planar anion (ICl_4^- or $AuCl_4^-$) were formed ν_s (P-Cl) was reported at 515 and 514 cm^{-1} respectively, again barely shifted from that in the parent compound. At first, this behaviour appears to contradict the shift pattern ideas presented in this work but this is not so. The current studies showed that the $Me_2PCl_2^+Cl^-$ (Type "B") reported by Deng is not the only modification of this substance that exists and the Raman spectra (Table 4.10 and Fig. IVh) suggested that in Type "A" $Me_2PCl_2^+Cl^-$ the Cl^- anions interact with the cations to a greater extent than in Type "B". This accounts for the different ν_5 (P-Cl) found for the two forms ("A" = 508 cm^{-1}, "B" = 515 cm^{-1}) and thus, if Deng's observations are based upon Type "A" $Me_2PCl_2^+Cl^-$ there is a high frequency shift when complexes with square planar anions are formed. The shift is smaller than that observed in this study when octahedral and tetrahedral anions were formed but this is not unreasonable as greater anion/cation interaction may be possible with a planar anion.

4.2.b The Me_2PCl/Br_2 Reaction

This reaction was investigated by Deng⁽⁵⁾ and the white solid obtained (formulated as Me_2PClBr_2) was shown by solid state ^{31}P NMR spectroscopy to contain the $Me_2PCl_2^+$, Me_2PClBr^+ and $Me_2PBr_2^+$ cations. The product of this reaction has not previously been investigated by Raman spectroscopy and, assuming that no scrambling occurs amongst the methyl groups a total of 27 Raman active modes may be expected for the three $Me_2PCl_nBr_{2-n}^+$ cations ($0 \leqslant n \leqslant 2$). These may be predicted in the following manner. $Me_2PCl_2^+$ and $Me_2PBr_2^+$ are both of C_{2v} symmetry each having the vibrational representation:-

$$\Gamma_{vib} = 4a_1\ (R,\ IR) + a_2\ (R) + 2b_1\ (R,\ IR) + 2b_2\ (R,\ IR)$$

However the mixed halogencation Me_2PClBr^+ is of C_s symmetry and this point group has the following vibrational representation:-

$\Gamma_{vib} = 6a' \text{ (R, IR)} + 3a'' \text{ (R, IR)}$

R and IR indicate Raman and infra-red activity respectively in both cases. A typical Raman spectrum of a Me_2PCl/Br_2 reaction product is illustrated in Fig. IVI (ASM 39) and is fairly complex, especially in the 200-280 cm^{-1} region where there are obviously several overlapping bands. Interpretation of this is made easier by the fact that the spectra of $Me_2PCl_2^+$ and $Me_2PBr_2^+$ in the single halide positions have already been assigned (Tables 4.10 and 4.11) so "subtraction" of the relevant bands from Fig. IVI should yield the Raman spectrum of $Me_2PClBr^+X^-$.

Table 4.13 presents the deduced assignment for the Me_2PClBr^+ cation in the presence of a single halide anion and Table 4.14 provides the total assignment of bands for the Me_2PCl/Br_2 reaction product illustrated in Fig. IVI. All three $Me_2PCl_nBr_{2-n}^+$ ($0 \leq n \leq 2$) cations are present in this preparation with a predominance of the brominated species. The main stretching modes of Me_2PClBr^+ may be assigned with some confidence; ν (P-C) 735 cm^{-1}, ν (P-Cl) 477 cm^{-1} and ν (P-Br) 417 cm^{-1}, but the deformation modes reported in the 200-280 cm^{-1} region are more tentative. In the mixture it is not possible to assign the $Me_2PCl_2^+$ deformations as they are hidden by more intense Me_2PClBr^+ and $Me_2PBr_2^+$ modes. When a Me_2PCl/Br_2 product was complexed with boron trichloride the characteristic high frequency shifts in the cationic P-Hal stretches were observed along

TABLE 4.13

ASSIGNMENT OF THE RAMAN SPECTRUM OF THE Me_2PClBr^+ CATION IN THE PRESENCE OF A SINGLE HALIDE ANION

Wavenumber/cm^{-1}	Assignment [a]
776 (w)	$\nu_7(a'')\nu_{as}$ (P–Me)
735 (w)	$\nu_1(a')\nu_s$ (P–Me)
564 (w)	$\nu_4(a')\ \omega$ (PMe_2)
470 (m/w)	$\nu_2(a')\ \nu$ (P–Cl)
417 (s)	$\nu_3(a')\ \nu$ (P–Br)
267 (m/w)	$\nu_9(a'')\ \pi$ (Cl–P–Br) or ρ (PC_2)
256 (m/w)	$\nu_6(a')\ \delta$ (Cl–P–Br)
232 (m)	$\nu_8(a'')\ \gamma$ (PMe_2)
206 (w)	$\nu_5(a')\ \delta$ (PMe_2)

[a] Description of modes based on those listed for W_2XYZ species in "Inorganic Infra-red and Raman Spectra" by S. D. Ross, McGraw-Hill, 1972.

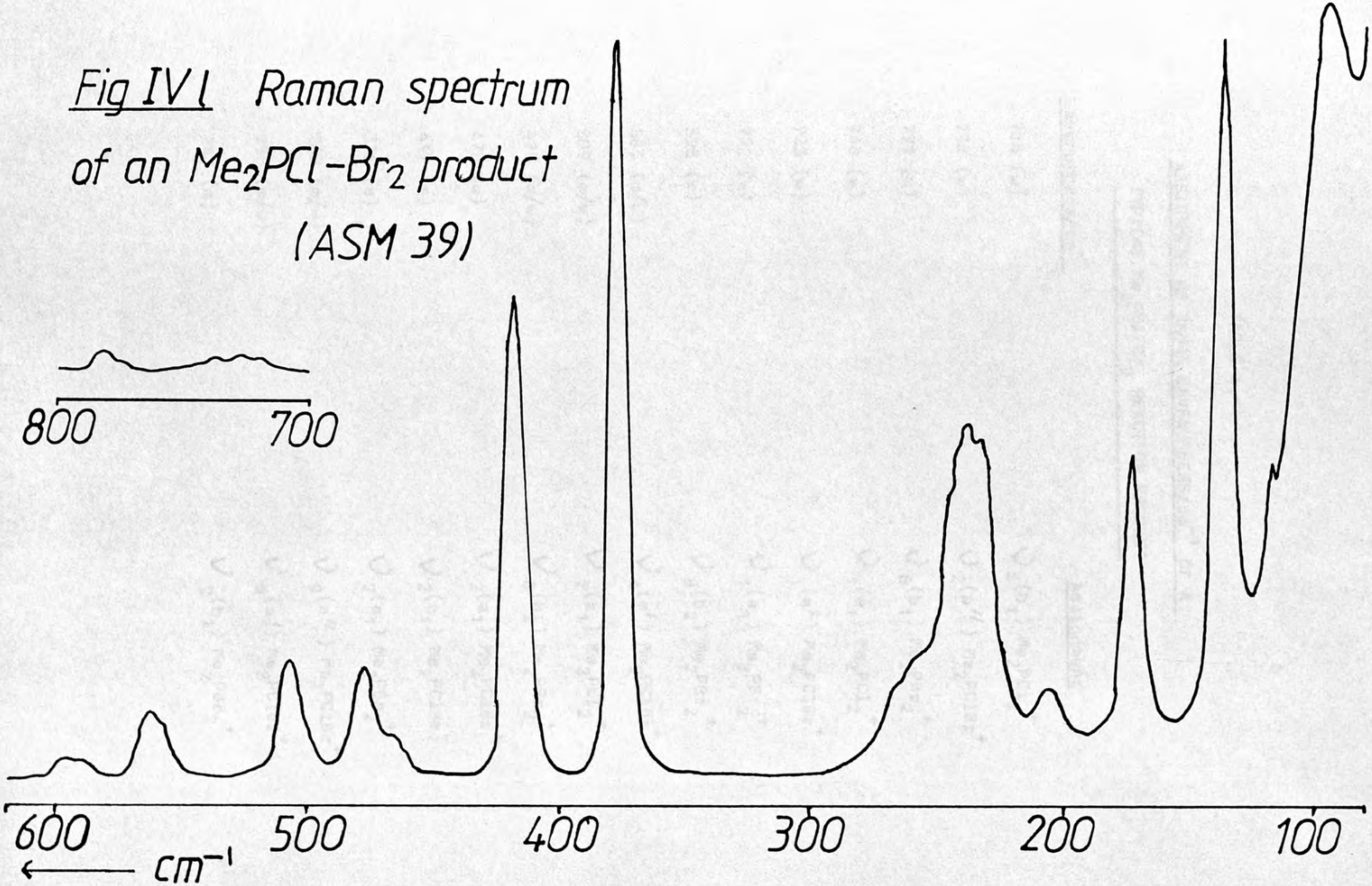


Fig IV1 Raman spectrum of an $Me_2PCl-Br_2$ product (ASM 39)

TABLE 4.14

ASSIGNMENT OF RAMAN WAVENUMBERS/cm^{-1} OF A TYPICAL Me_2PCl/Br_2 REACTION PRODUCT

Wavenumbers/cm^{-1}	Assignment
785 (w)	$\nu_6(b_1)$ $Me_2PCl_2^+$
776 (w)	$\nu_2(a'')$ Me_2PClBr^+
771 (w)	$\nu_6(b_1)$ $Me_2PBr_2^+$
748 (w)	$\nu_1(a_1)$ $Me_2PCl_2^+$
735 (w)	$\nu_1(a')$ Me_2PClBr^+
721 (w)	$\nu_1(a_1)$ $Me_2PBr_2^+$
598 (w)	$\nu_8(b_2)$ $Me_2PBr_2^+$
565 (m/w)	$\nu_4(a')$ Me_2PClBr^+
509 (m/w)	$\nu_2(a_1)$ $Me_2PCl_2^+$
475 (m/w)	$\nu_8(b_2)$ $Me_2PBr_2^+$
470 (w)	$\nu_2(a_1)$ Me_2PClBr^+
417 (s)	$\nu_2(a_1)$ Me_2PClBr^+
376 (s)	$\nu_2(a_1)$ $Me_2PBr_2^+$
268 (m/w)	$\nu_9(a'')$ Me_2PClBr^+
256 (m/w)	$\nu_6(a')$ Me_2PClBr^+
243 (m)	$\nu_2(b_1)$ $Me_2PBr_2^+$

TABLE 4.14 CONT'D

Wavenumbers/cm^{-1}	Assignment
235 (m)	$\nu_3(a_1)$ $Me_2PBr_2^+$
232 (m)	$\nu_8(a'')$ Me_2PClBr^+
224 (w)	$\nu_9(b_2)$ $Me_2PBr_2^+$
206 (w)	$\nu_5(a')$ Me_2PClBr^+
171 (m)	$\nu_5(a_2)$ $Me_2PBr_2^+$
136 (m/s)	$\nu_4(a_1)$ $Me_2PBr_2^+$

TABLE 4.15

FLUCTUATION OF SOME $Me_2PCl_nBr_{2-n}^+$ RAMAN FREQUENCIES WITH ANION TYPE

	Singe Halide X^-	Polyhalide X_3^-	Polyatomic BX_4^-
* $Me_2PCl_2^+$ ($\nu_2(a_1)$)	508	–	520
Me_2PClBr^+ ($\nu_2(a')$)	470	–	483
Me_2PClBr^+($\nu_3(a')$)	417	–	429
$Me_2PBr_2^+$ ($\nu_2(a_1)$)	377	384	391

* Type "A"

with the appearance of the BCl_4^- modes at 190, 275 and 407 cm^{-1}(8). The most important shifts recorded were:- $\nu_2(a_1)$ $Me_2PCl_2^+$ 508 $\rightarrow$ 520 cm^{-1}, $\nu_2(a_1)$ $Me_2PBr_2^+$ 376 $\longrightarrow$ 392 cm^{-1}, $\nu_2(a')$ Me_2PClBr^+ 470 $\rightarrow$ 483 cm^{-1} and $\nu_3(a')$ Me_2PClBr^+ 417 $\longrightarrow$ 429 cm^{-1}. The fluctuation of the principal P-Hal stretches with anion type in the Me_2PClBr^+ $(0\leqslant n\leqslant 2)$ system are presented in Table 4.15. Thus the dimethyldihalophosphonium cation system follows the trends observed for the tetrahalophosphonium and methyltri halophosphonium cation series in that certain modes of vibration are perturbed significantly by single halide anions leading to high frequency shifts upon complexation with Lewis acids.

No evidence was found for methyl group scrambling in this system. Initially one Me_2PCl/Br_2 reaction product gave a Raman spectrum that indicated the presence of some monomethyl derivatives but subsequent investigation suggested that the Me_2PCl used was contaminated with a little $MePCl_2$, thus accounting for the variety of products.

4.3 Trimethylhalophosphoranes

4.3.a Trimethyldichlorophosphorane and Trimethyldibromophosphorane and some derivatives

Trimethyldihalophosphoranes have been investigated by vibrational spectroscopy on two occasions by Goubeau, Baumgartner et al and salt-like $Me_3PX^+X^-$ (X = Cl, Br, I) structures were inferred(1,17). This was supported by ^{31}P NMR and ^{35}Cl NQR studies on the chloro compound and some derivatives(3).

Tetrahedral cations of the type Me_3PX^+ exhibit C_{3v} symmetry and have the following vibrational representation

$\Gamma_{vib} = 3a_1$ (R, IR) + 3e (R, IR)

where R and IR indicate Raman and infra-red activity respectively.

In this study only Me_3PCl_2 and Me_3PBr_2 were examined: the Raman spectra obtained are presented in Figs. IVm and n, and assignments made are compared with those previously obtained in Table 4.16 and 4.17. The assignments are rather arbitary but were made after considering the assignments madefor isoelectronic silicon species (Table 4.3).

The most intense band in the $Me_3PCl^+Cl^-$ spectrum is the P-Cl stretch at 528 cm^{-1}. A low frequency shoulder was consistently observed on this mode and was unaffected by warming, or reduced pressure, indicating it to be a genuine part of the spectrum and not arising from the presence of more than one crystal modification (cf the $Me_2PCl_2^+Cl^-$ system discussed in Section 4.2.a). The symmetric and antisymmetric P-C stretches for $Me_3PCl^+Cl^-$ are readily assigned as the high frequency bands at 694 and 780 cm^{-1} respectively. The equivalent bands in $Me_3PBr^+Br^-$ are found at 683 and 775 cm^{-1} and, once again, the P-Hal stretch is the most intense feature of the spectrum occuring at 413 cm^{-1}. The assignment of the three low frequency bands (ν_6, ν_5 and ν_3) for both compounds is more difficult in the absence of polarization data. The weak, lowest frequency band is in both compounds assigned as ν_6(e) by direct comparison with the spectra of Me_3SiCl and Me_3SiBr (Table 4.3)$^{(6)}$ and occurs at 224 and 212 cm^{-1} for the chloride and bromide respectively. This comparison with isoelectronic species is hindered by the coincidence of ν_3 and ν_5 in Me_3SiCl. In the spectrum of $Me_3PCl^+Cl^-$ these modes are almost coincident with a band of medium/strong intensity at 280 cm^{-1} and a low frequency shoulder 275 cm^{-1} and these are arbitrarily assigned as ν_3 and ν_5 respectively. For Me_3SiBr, ν_3 is reported at 213 cm^{-1} and ν_5 at 242 $cm^{-1}$$^{(6)}$ and the spectrum of $Me_3PBr^+Br^-$ shows an intense band at 248 cm^{-1} and a relatively weak band at 272 cm^{-1}. The symmetric $\nu_3(a_1)$ mode is assigned as an Me-P-Me deformation whereas ν_5(e) is assigned as an Me-P-Br deformation. Thus, if the isoelectronic assignment is followed, the band at 248 cm^{-1} should be ν_3 and that at 272 cm^{-1}, ν_5. However, in terms of relative intensities it is more reasonable to assign the strongest Raman band to the ν_5(e) mode that involves significant motion of the P-Br bond and to assign the weaker 272 cm^{-1} band as the $\nu_3(a_1)$ mode. It is this latter assignment that is given in Table 4.17.

The spectra reported above for $Me_3PCl^+Cl^-$ and $Me_3PBr^+Br^-$ were recorded on samples recrystallized from the appropriate phosphorus trihalide (see experimental section). When samples were not treated in this manner extraneous peaks appeared in the Raman spectra at 468 and 215 cm^{-1}, the former being of medium intensity. The origin

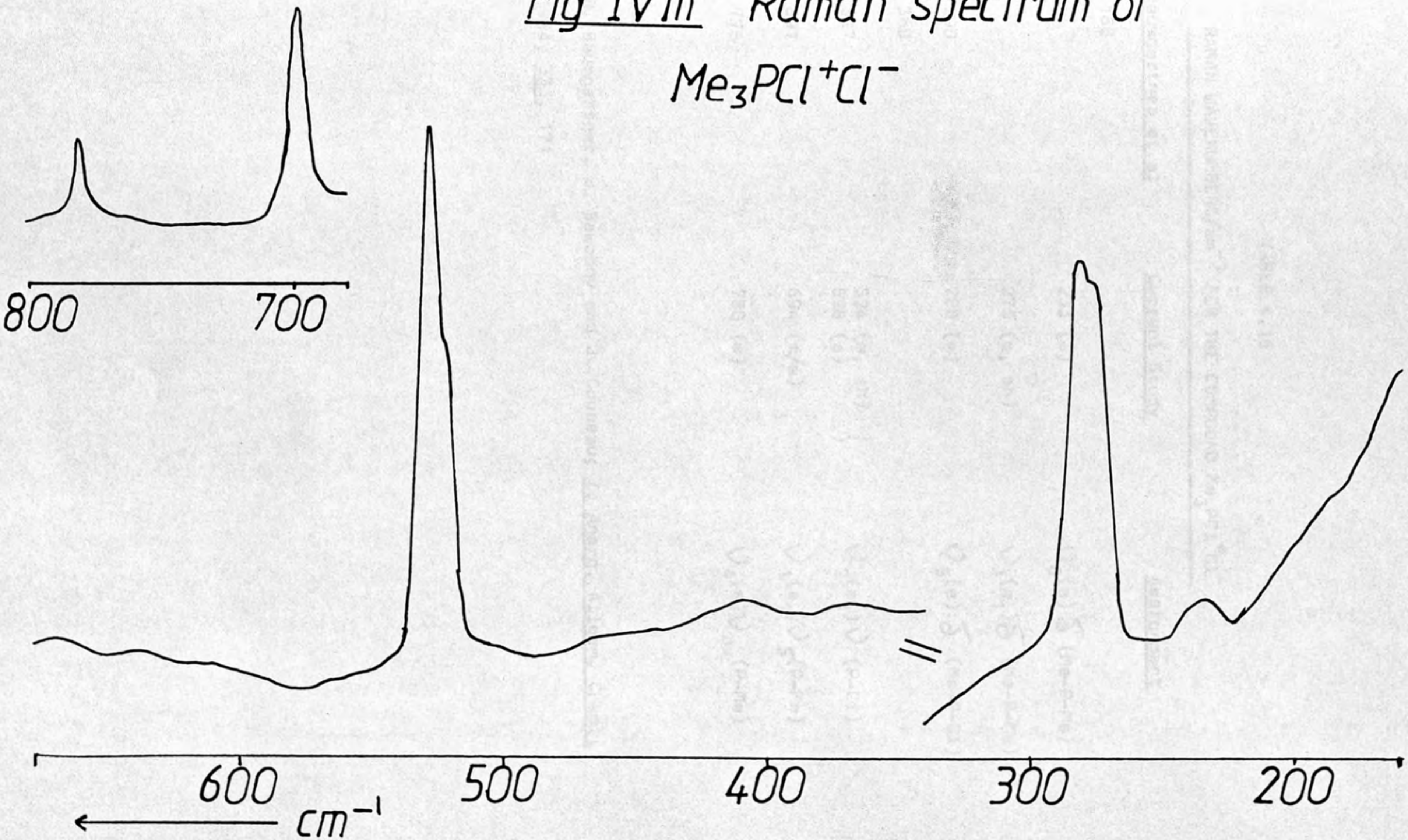


Fig IVm Raman spectrum of $Me_3PCl^+Cl^-$

TABLE 4.16

RAMAN WAVENUMBERS/cm^{-1} FOR THE COMPOUND $Me_3PCl^+Cl^-$

Baumgartner et al	Current Study	Assignment
168		
	233 (w)	$\nu_6(e)\ \delta$ (Me-P-Me)
	275 (m, sh)	$\nu_3(a_1)\ \delta$ (Me-P-Me)
290	280 (m)	$\nu_5(e)\ \delta$ (Me-P-Cl)
368		
527	524 (m, sh)) 528 (s))	$\nu_2(a_1)\ \nu$ (P-Cl)
691	694 (m/w)	$\nu_1(a_1)\ \nu_s$(P-Me)
776	780 (w)	$\nu_4(e)\ \nu_{as}$(P-Me)

R. Baumgartner, W. Sawodny and J. Goubeau; <u>Z. Anorg. Allgem. Chem.</u>, 1964, <u>333</u>, 171

Fig IVn Raman spectrum of $Me_3PBr^+Br^-$

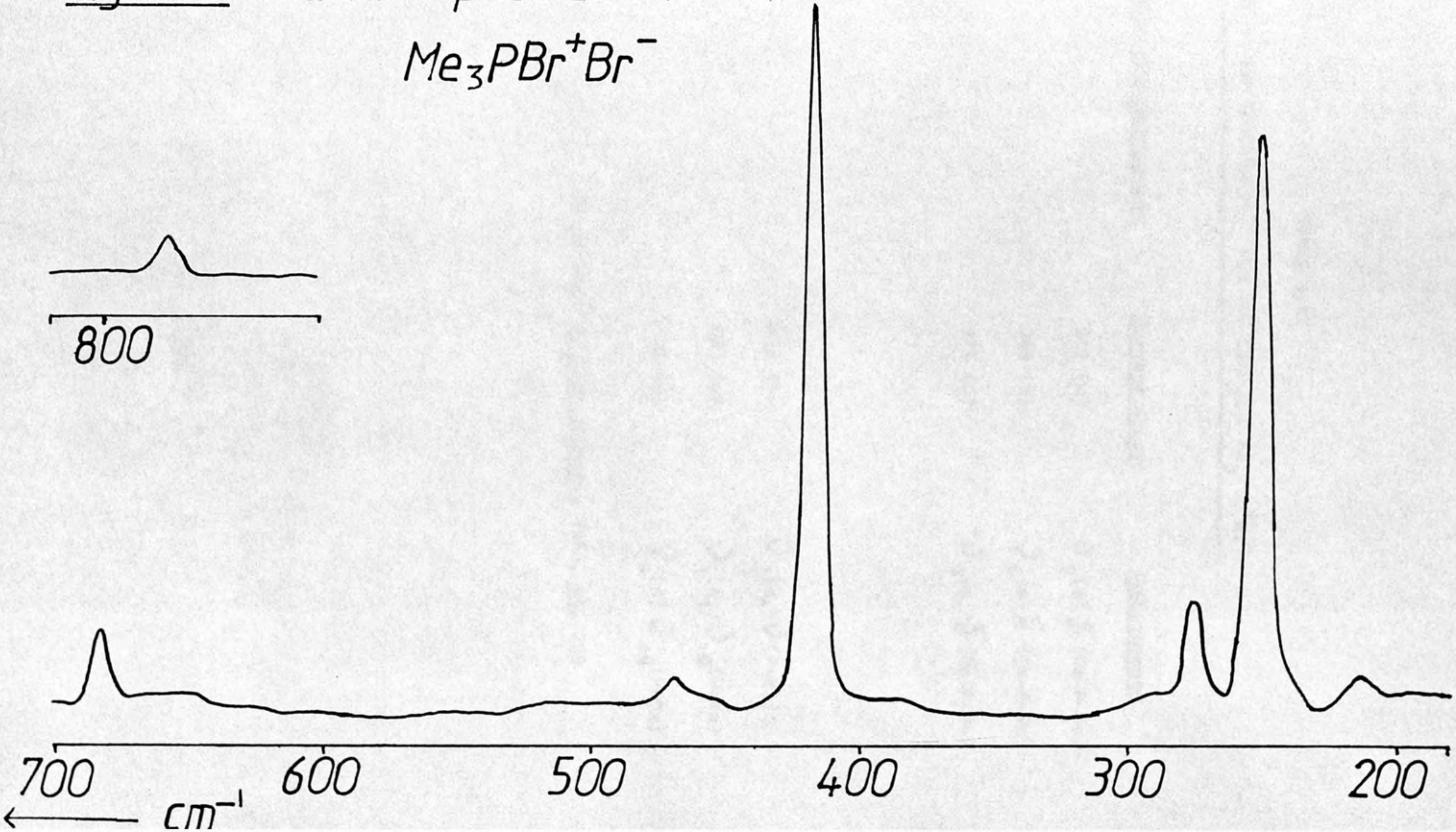


TABLE 4.17

RAMAN WAVENUMBERS/cm^{-1} FOR THE COMPOUND $Me_3PBr^+Br^-$

Goubeau and Baumgartner	Current Study	Assignments
	212 (w)	$\nu_6(e)\ \delta$ (Me-P-Me)
	248 (s)	$\nu_5(e)\ \delta$ (Me-P-Br)
	272 (w)	$\nu_3(a_1)\ \delta$ (Me-P-Me)
302		
323		
334		
398		
415	413 (s)	$\nu_2(a_1)\ \nu$ (P-Br)
674	683 (w)	$\nu_1(a_1)\ \nu_s$(P-Me)
766	775 (w)	$\nu_4(e)\ \nu_{as}$(P-Me)

J. Goubeau and R. Baumgartner; Z. Elektrochem., 1960, 64, 598 of these modes is unknown but as untreated sample gave variable analyses they were not used until purified.

If the patterns observed elsewhere in this work are followed, complexation with Lewis acids should produce high frequency Raman shifts in some cationic modes.

The Raman spectrum of $Me_3PCl^+BCl_4^-$ is illustrated in Fig. IVa and assignments for this and the hexachloroantimonate are presented in Table 4.18. The presence of the anions in these complexes is confirmed by favourable comparison with former Raman studies: all four Raman active modes were observed for the tetrahedral tetrachloroborate anion(8) as were the three Raman active modes for the octahedral hexachlorantimonate anion(9,10).

The $Me_3PCl^+BCl_4^-$ spectrum is particularly clear and high frequency shifts in some cation modes are apparent when compared with $Me_3PCl^+Cl^-$. In particular the $\nu_2(a_1)$ P-Cl stretch is moved by 16 cm^{-1} from 528 cm^{-1} to 544 cm^{-1}. The low frequency shoulder observed on this mode in the parent compound at 524 cm^{-1} is also present in the tetrachloroborate at 539 cm^{-1}. The lower frequency cation deformation modes are also high frequency shifted by ~ 10 cm^{-1} but the ν_1 and ν_4 P-C stretching modes are relatively unaffected by this change in anion. It is interesting to compare the relative intensities of the anion and cation bands - they are quite similar unlike those in $PCl_4^+BCl_4^-$ where cation modes dominate the spectrum (Fig. IIIc). This illustrates the trend in the $Me_nPCl_{4-n}^+$ $(0 \leq n \leq 4)$

Fig IVo Raman spectrum of $Me_3PCl^+BCl_4^-$

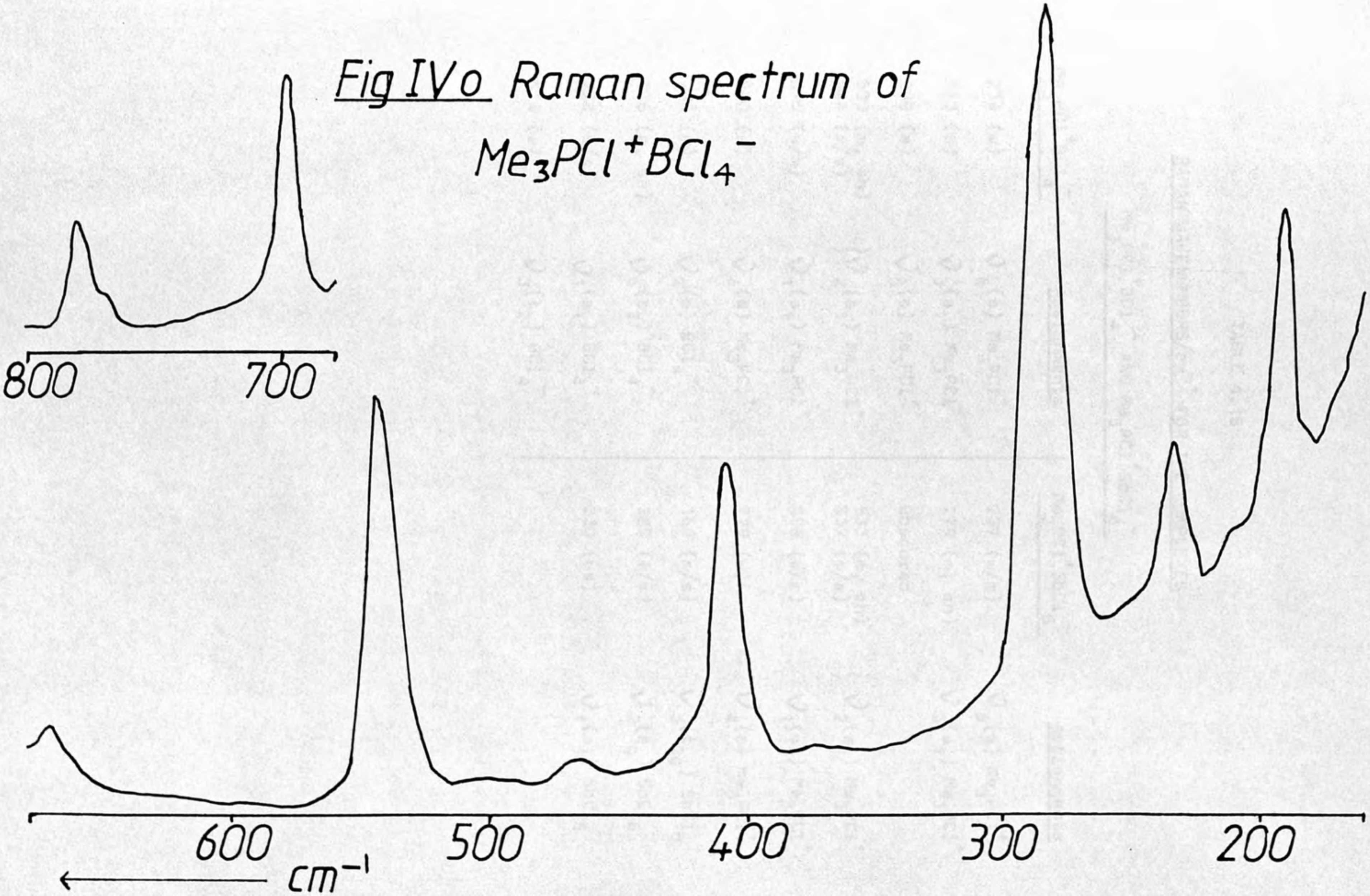


TABLE 4.18

RAMAN WAVENUMBERS/cm^{-1} FOR THE COMPLEXES

$Me_3PCl^+BCl_4^-$ AND $Me_3PCl^+SbCl_6^-$

$Me_3PCl^+BCl_4^-$	Assignments	$Me_3PCl^+SbCl_6^-$	Assignments
234 (w)	$\nu_6(e)$ Me_3PCl^+	237 (w/m)	$\nu_6(e)$ Me_3PCl^+
283 (s)	$\nu_3(a_1)$ Me_3PCl^+	279 (m, sh)	$\nu_3(a_1)$ Me_3PCl^+
290 (s)	$\nu_5(e)$ Me_3PCl^+	Obscured	
539 (m, sh) 544 (m/s)	$\nu_2(a_1)$ Me_3PCl^+	533 (m, sh) 537 (m/s)	$\nu_2(a_1)$ Me_3PCl^+
696 (w/m)	$\nu_1(a_1)$ Me_3PCl^+	696 (w/m)	$\nu_1(a_1)$ Me_3PCl^+
780 (w)	$\nu_4(e)$ Me_3PCl^+	779 (w)	$\nu_4(e)$ Me_3PCl^+
191 (m)	$\nu_2(e)$ BCl_4^-	169 (m/s)	$\nu_5(t_{2g})$ $SbCl_6^-$
276 (m, sh)	$\nu_4(t_2)$ BCl_4^-	289 (m/s)	$\nu_2(e_g)$ $SbCl_6^-$
408 (m/s)	$\nu_1(a_1)$ BCl_4^-	330 (vs)	$\nu_1(a_1)$ $SbCl_6^-$
674 (w)	$\nu_3(t_2)$ BCl_4^-		

cation series that increasing the number of methyl functions decreases the Raman scattering power, as expected.

The hexachlorantimonate shows similar trends to the tetrachloroborate but an additional problem is encountered because of the relatively high intensity of the anion modes. In particular, the $\nu_2(e_g)$ mode of $SbCl_6^-$ at 289 cm^{-1} renders observation of the $\nu_5(e)$ Me_3PCl^+ mode impossible and other cation bands were only seen when the anion bands were run at very high intensity. The $\nu_2(a_1)$ cation mode was shifted to 537 cm^{-1} and the associated low frequency shoulder to 533 cm^{-1}, significantly less than in the tetrachloroborate. All other cation bands were affected as in the tetrachloroborate case but to a lesser degree. Similar trends were also observed in the compound $Me_3PCl^+PCl_6^-$.

Thus with $Me_3PCl^+Cl^-$ there is still significant pertubation of the cation by the single halide anion accounting for the high frequency Raman shifts observed when reacted with Lewis acids to give polyatomic anions.

Attempts were made to prepare the complex $Me_3PBr^+BBr_4^-$ by the reaction of the parent $Me_3PBr^+Br^-$ with boron tribromide. The spectrum obtained is illustrated in Fig. IVp and the wavenumbers are assigned in Table 4.19. Analysis indicated an impure product, a fact readily confirmed by examination of the Raman spectrum. The BBr_4^- anion is indicated by bands at 167, 244 and 590 cm^{-1}, quite consistent with the literature values(8). It appears that the reaction

Fig IVp Raman spectrum of an attempted $Me_3PBr^+BBr_4^-$ preparation

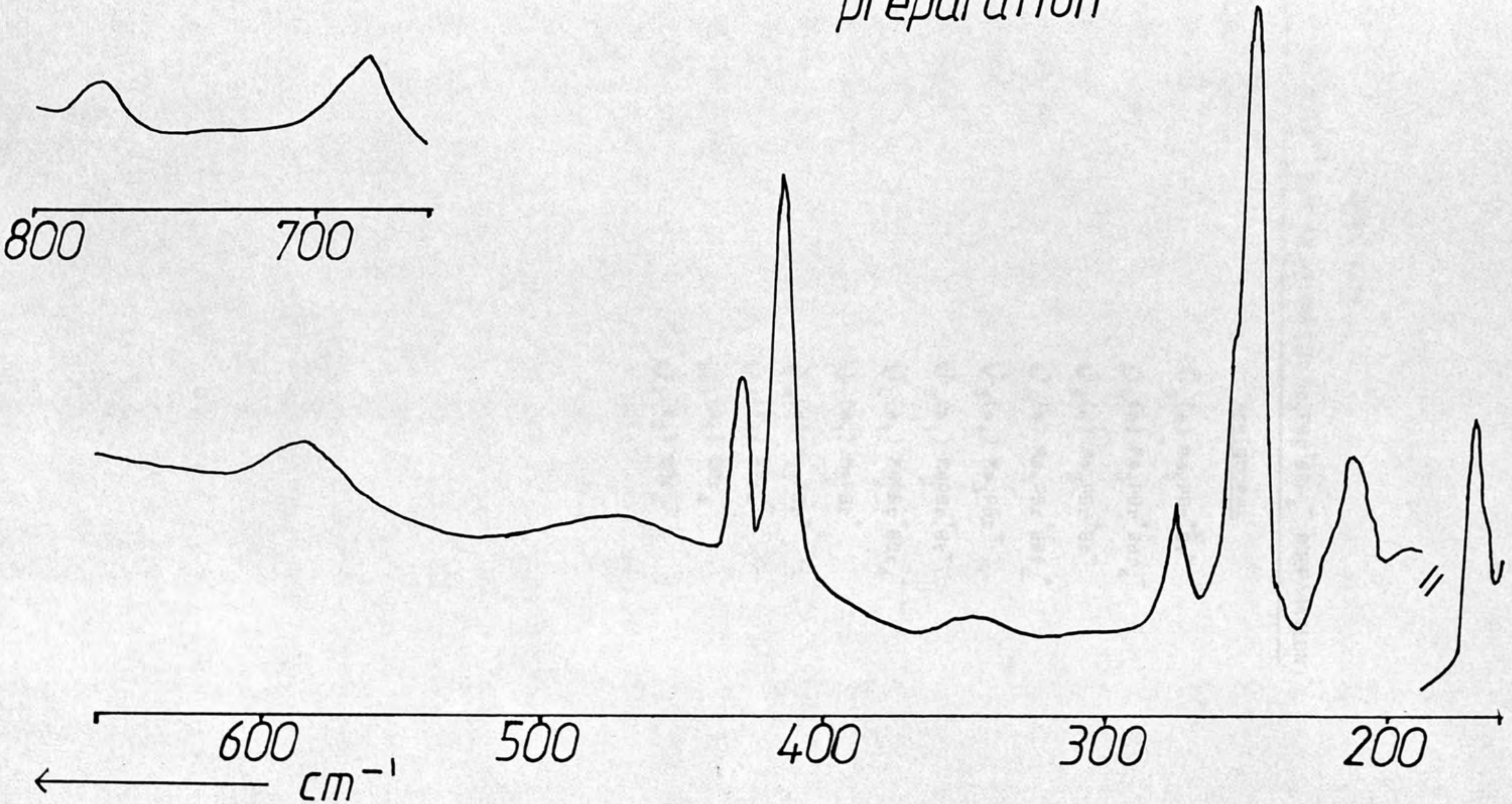


TABLE 4.19

ASSIGNMENT OF WAVENUMBERS/cm^{-1} FOR AN ATTEMPTED $Me_3PBr^+BBr_4^-$ PREPARATION

$Me_3PBr^+BBr_4^-$	Assignment
213 (w)	$\nu_6(e)$ $Me_3PBr^+Br^-$
220 (w, sh)	$\nu_6(e)$ $Me_3PBr^+BBr_4^-$
246 (s)	$\nu_5(e)$ $Me_3PBr^+Br^-$
255 (m, sh)	$\nu_5(e)$ $Me_3PBr^+BBr_4^-$
273 (w)	$\nu_3(a_1)$ Me_3PBr^+
413 (m/s)	$\nu_2(a_1)$ $Me_3PBr^+Br^-$
429 (m)	$\nu_2(a_1)$ $Me_3PBr^+BBr_4^-$
684 (vw, br)	$\nu_1(a_1)$ Me_3PBr^+
778 (vw, br)	$\nu_4(e)$ Me_3PBr^+
167 (m/w)	$\nu_4(t_2)$ BBr_4^-
244 (m/s, sh)	$\nu_1(a_1)$ BBr_4^-
590 (w, br)	$\nu_2(t_2)$ BBr_4^-

product is a mixture of unreacted $Me_3PBr^+Br^-$ and the desired product $Me_3PBr^+BBr_4^-$: this is particularly substantiated by two sets of bands for most of the cationic modes and is most evident when the P-Br stretching mode is examined. Here two bands are observed; one at 414 cm^{-1} corresponding to unreacted $Me_3PBr^+Br^-$ and another at 429 cm^{-1} presumably associated with $Me_3PBr^+BBr_4^-$. Thus the expected high frequency shift is observed and even though it proved impossible to prepare a pure sample of $Me_3PBr^+BBr_4^-$ the mixtures afforded an easy comparison of frequencies.

4.4 Matrix-isolation/low termperature sublimation studies of methylhalophosphoranes

In Chapter 2 of this study matrix isolation and low temperature sublimation experiments on phosphorus pentachloride and pentabromide were described and the merits of the two techniques discussed. An investigation using these techniques was carried out on the methylchlorophosphoranes $MePCl_4$, Me_2PCl_3 and Me_3PCl_2 in an attempt to determine the respective molecular structures.

The only previous study of this nature to use vibrational spectroscopy was by Beattie who deduced that in non-polar solvents $MePCl_4$ was a trigonal bipyramid of nett C_{2v} symmetry (2). More recently Dillon and Deng have reported ^{31}P solution shifts for $MePCl_4$ in a variety of solvents and the results indicate that the compound is predominantly molecular (19). Beattie's Raman results and assignments are presented in Table 4.20 where they are compared with those obtained when $MePCl_4$ vapour was deposited onto a cold-plate at 15K.

The sublimation conditions required to deposit enough sample for Raman spectroscopy was 3 days at 40°C. The low sublimation temperature was used to minimize possible decomposition of the $MePCl_4$ to $MePCl_2$ and Cl_2. The spectrum obtained at 15K is illustrated in Fig. IVq where it is compared with that of the same sample warmed to 260K. The wavenumbers at 15K agree reasonably with those obtained by Beattie and are quite consistent with a species of C_{2V} symmetry with the methyl group occupying an equatorial position. This system possesses the following vibrational representation:

$$\Gamma_{vib} = 5a_1\ (R, IR) + a_2\ (R) + 3b_1\ (R, IR) + 3b_2\ (R, IR)$$

where R and IR refer to Raman and infra-red activity respectively. If the methyl group was axially disposed a nett C_{3V} symmetry would result with the following vibrational representation:

$$\Gamma_{vib} = 4a_1\ (R, IR) + 4e\ (R, IR)$$

Thus there would be less bands expected than are actually observed in the spectrum. The strongest feature is at 451 cm^{-1} and is assigned to the symmetric equatorial P-Cl stretch with the asymmetric equatorial P-Cl stretch appearing as a weak band at 578 cm^{-1}. The weak, high frequency, feature at 752 cm^{-1} can be confidently assigned as the P-C stretching mode. The 240 - 300 cm^{-1} region of the spectrum is rather crowded with several overlapping bands but enough detail is present to show reasonable agreement with Beattie's values which, in turn, coincided well with normal coordinate calculations.

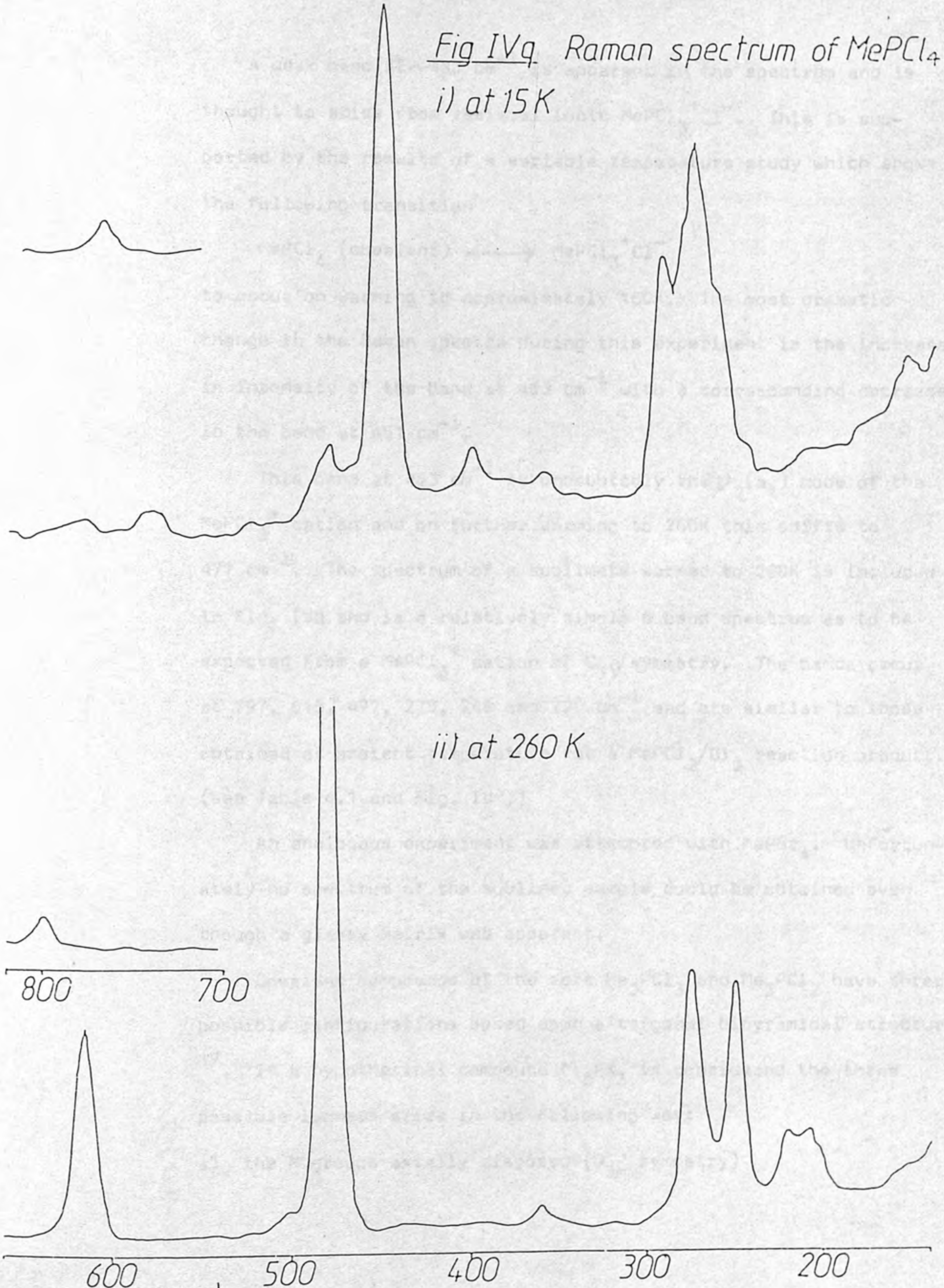
TABLE 4.20

RAMAN ASSIGNMENTS FOR MOLECULAR $MePCl_4$

Beattie (solution study)	Current investigation (low-temperature sublimation) at 15K	Assignments
743 (IR)	752 (w)	$\nu_1(a_1)\,\nu$ (P-C)
567 (IR+R)	578 (w)	$\nu_4(b_1)\nu_{eq}$(P-Cl)
441 (IR+R)	451 (vs)	$\nu_2(a_1)\nu_{eq}$(P-Cl)
382 (IR)	398 (w)	$\nu_5(b_2)\nu_{ax}$(P-Cl)
361 (IR)	360 (vw)	$\nu_6(b_2)\nu_{ax}$(P-Cl)
288 (IR+R)	292 (m)	$\nu_3(a_1)\nu_{ax}$(P-Cl)
278 (IR)	281 (m, sh)	$\nu_{12}(b_2)\delta$ (P-Cl)
271 (R)	274 (s)	$\nu_9(a_2)\delta_{ax}$(P-Cl)
266 (calculated)	265 (m, sh)	$\nu_7(a_1)\delta_{ax}$(P-Cl)
251 (IR+R)	250 (w, sh)	$\nu_{10}(b_1)\delta_{eq}$(P-Cl)
178 (R)	180 (w)	$\nu_8(a_1)\delta$ (P-Cl)
141 (IR)	155 (w)	$\nu_{11}(b_1)\delta_{ax}$(P-Cl)

I. R. Beattie, K. Livingston and (in part) T. Gilson; J. Chem. Soc. "A", 1968, 1.

Fig IVq Raman spectrum of $MePCl_4$



A weak band at ~483 cm^{-1} is apparent in the spectrum and is thought to arise from residual ionic $MePCl_3^+Cl^-$. This is supported by the results of a variable temperature study which shows the following transition

$$MePCl_4 \text{ (covalent)} \longrightarrow MePCl_3^+Cl^-$$

to occur on warming to approximately 160K. The most dramatic change in the Raman spectra during this experiment is the increase in intensity of the band at 483 cm^{-1} with a corresponding decrease in the band at 451 cm^{-1}.

This band at 483 cm^{-1} is undoubtedly the $\nu_2(a_1)$ mode of the $MePCl_3^+$ cation and on further warming to 260K this shifts to 477 cm^{-1}. The spectrum of a sublimate warmed to 260K is included in Fig. IVq and is a relatively simple 6 band spectrum as to be expected from a $MePCl_3^+$ cation of C_{3V} symmetry. The bands occur at 797, 615, 477, 275, 248 and 220 cm^{-1} and are similar to those obtained at ambient temperature for a $MePCl_2/Cl_2$ reaction product. (see Table 4.1 and Fig. IV .)

An analogous experiment was attempted with $MePBr_4$. Unfortunately no spectrum of the sublimed sample could be obtained even though a glassy matrix was apparent.

Covalent compounds of the sort Me_2PCl_3 and Me_3PCl_2 have three possible configurations based upon a trigonal bipyramidal structure 17. If a hypothetical compound M_2PX_3 is considered the three possible isomers arise in the following way:

a) the M groups axially disposed (D_{3h} symmetry)

b) the M groups equatorially disposed (C_{2v} symmetry)

c) one M group axially disposed, one M group equatorially disposed (C_s symmetry)

The vibrational activity of these symmetries is given below with R and IR having the standard meaning.

a) D_{3h} $\Gamma_{vib} = 2a_1'$ (R) + $3e'$ (R, IR) + $2a_2''$ (IR) + $1e''$(R)

b) C_{2v} $\Gamma_{vib} = 5a_1$ (R, IR) + $1a_2$ (R) + $3b_1$ (R, IR) + $3b_2$ (R, IR)

c) C_s $\Gamma_{vib} = 8a'$ (R, IR) + $4a''$ (R, IR)

Thus, in principle, it is possible to differentiate between these configurations by vibrational spectroscopy. However, in practice, this proved impossible with samples of Me_2PCl_3 and Me_3PCl_2 because of the inability to sublime these compounds onto the cold head of the matrix isolation unit. Attempts were made to deposit vapour of these compounds by heating samples to around 250°C in a high temperature Knudsen Furnace, similar to those used by Andrews and Ault to deposit a variety of salt vapours in their matrix isolation studies(18). This method was also unsuccessful usually in charring of the samples and deposition of insufficient vapour to obtain spectra. The possible alternative method of obtaining structural information about monomeric forms of Me_2PCl_3 and Me_3PCl_2 by solution Raman and infra-red spectroscopy also resulted in failure because the compounds were insoluble in many common, inert solvents. This approach may, however, prove successful given a more exhaustive investigation.

4.5 Solid-state NMR studies of Methylhalophosphoranes

Dillon and co-workers have reported the static ^{31}P NMR spectra of $MePCl_4$, Me_2PCl_3, Me_3PCl_2 and addition compounds with some Lewis acids(3). The results indicated ionic structures, consistent with the Raman observations in this and other studies. Deng reported the ^{31}P NMR spectra of various methylhalophosphoranes and derivatives, including mixed halogen species, in strongly acidic media(5,19). There is, however, no reference to any solid state studies on these compounds using the magic angle rotation (MAR) technique to obtain narrow lines. All such spectra reported here were obtained by Mr. A. Root at the University of East Anglia. All ^{31}P chemical shifts were measured relative to 85% phosphoric acid with the downfield direction taken as positive. Where appropriate, ^{11}B NMR spectra were recorded using trimethyl borate as the external standard.

4.5.a $MePX_3^+X^-$ and some derivatives (X = Cl, Br)

Previous static ^{31}P measurements on $MePCl_3^+Cl^-$ are all consistent with one another: Dillon et al report a resonance at 119 ± 2 p.p.m(3,20). whereas Deng gives a chemical shift at 120 p.p.m.(5,19). In the present study a shift at 118.2 p.p.m. was observed with a linewidth of 500 Hz. Slight changes are observed upon complexation with static experimental shifts for $MePCl_3^+$ at 116.5 ± 1, 117 ± 1 and 120.9 p.p.m. respectively for the ICl_2^-, $AlCl_4^-$ and $SbCl_6^-$ salts(3,5,19,20). The MAR ^{31}P spectrum of $MePCl_3^+BCl_4^-$ indicated a shift at 115.8 p.p.m. with a linewidth of 32Hz.

The corresponding bromide cation has not been so thoroughly studied although Deng reports a shift of 30.7 p.p.m. for $MePBr_3^+Br^-$ in oleum(5). The sample sent for ^{31}P MAR studies unfortunately underwent considerable decomposition, the spectrum showing shifts at 26.5 p.p.m. (vw) and 9.2 p.p.m. (vs). The former is assigned to the compound $MePBr_3^+Br^-$ whilst the latter is an impurity, possibly $MePOBr_2$. A static solid state ^{31}P spectrum of $MePBr_3^+BBr_4^-$ shows a resonance at 27.5 p.p.m. which is shifted to 29.1 p.p.m. in oleum(5).

The case of $MePCl_2/Br_2$ reaction products is interesting. Static ^{31}P NMR produced a broad resonance centred at 85.6 p.p.m. but in acidic media bands assignable to all the $MePCl_nBr_{3-n}^+$ cations were observed along with various hydrolysis and oxidation products(5). These data are presented in Table 4.21 where they are compared with results obtained using MAR for samples of $MePCl_2/Br_2$, $MePCl_2/Br_2/BCl_3$ and $MePCl_2/Br_2/BBr_3$. The chemical shifts for the cations are not unexpectedly shifted from their solution values but three other important observations may be made:-

i) Broad resonances are observed when an X^- counter ion is present.

ii) Sharper resonances are observed when a BX_4^- counter ion is present.

iii) The replacement of an X- anion with a BX_4^- species leads to a high frequency shift in resonance.

^{11}B MAR measurements were made on ASM 36 and ASM 42. The presence of predominantly BCl_4^- with only traces of BCl_3Br^- was indicated in the former whilst BBr_4^-, BBr_3Cl^- and $BBr_2Cl_2^-$ were observed in the latter in decreasing amounts. Raman studies also

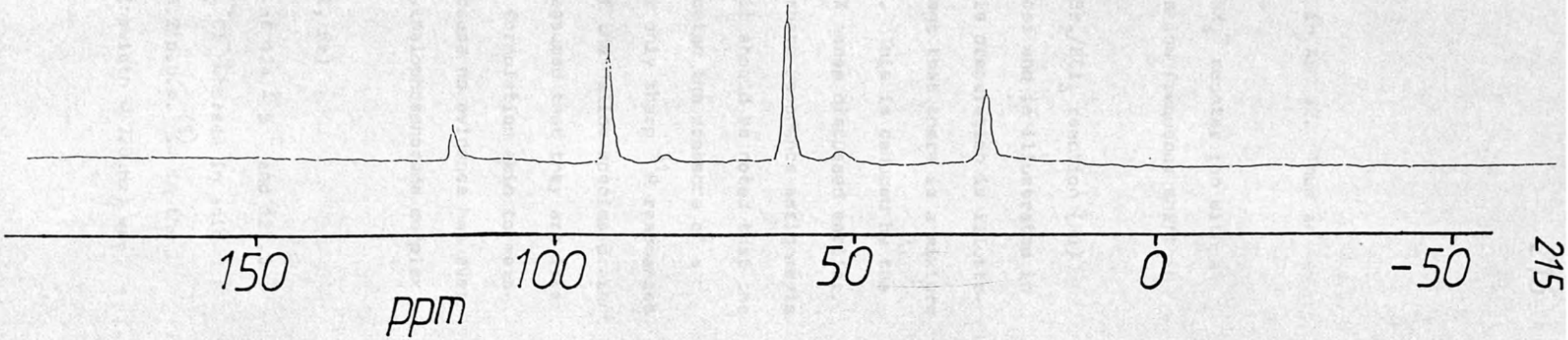
TABLE 4.21

^{31}P NMR SHIFTS (p.p.m.) FOR $MePCl_2/Br_2$ REACTION PRODUCTS

a) $MePCl_2/Br_2$ (oleum)(1)	b) $MePCl_2/Br_2$ (H_2SO_4)(1)	c) $MePCl_2/Br_2$ (MAR-ASM35)	d) $MePCl_2/Br_2$ (MAR-ASM34)	e) $MePCl_2/Br_2/BCl_3$ (MAR-ASM36)	f) $MePCl_2/Br_2/BCl_3$ (MAR-R6)	g) $MePCl_2/Br_2/BBr_3$ (MAR-ASM42)	Assignment
120.9	120.9	105.7 (br)	107.0 (br)	115.3 (sh)	115.3 (sh)	—	$MePCl_3^+$
95.1	95.1	77.0 (br)	80.8 (br)	90.1 (sh)	89.6 (sh) 80.0 (br)	87.2 (sh)	$MePCl_2Br^+$
64.5	64.5	54.0 (br)	54.4 (br)	60.6 (sh)	60.4 (sh) 52 (br)	57.9 (sh)	$MePClBr_2^+$
30.7	30.7	23 (br)	23.6 (br)	27.8 (sh)	27.3 (sh) 22 (br)	25.7 (sh)	$MePBr_3^+$

(1) Values taken from R.M.K. Deng, Ph.D, Thesis, 1980, University of Durham.
Some shifts resulting from hydrolysis and oxidation products omitted.
(br) = broad (sh) = sharp

<u>Fig IVr</u> P M.A.R. NMR spectrum of an $MePCl_2$–Br_2–BCl_3 reaction product (R6)



indicated BCl_4^- in ASM 36 and BBr_4^- in ASM 42. Thus an additional observation may be made:-

iv) The replacement of a chlorine rich BX_4^- counter ion with a bromine rich BX_4^- species leads to a low frequency shift in the ^{31}P resonance.

The ^{31}P MAR NMR of the $MePCl_2/Br_2/BCl_3$ reaction (R6) shows both sharp and broad resonances and is illustrated in Fig IVr. The Raman spectrum of this preparation is illustrated in Fig. IVf where it is apparent that there is a mixture of both BX_4^- and X^- anions present. This is deduced by the shift patterns in some cationic P-X modes discussed earlier. This is consistent with the broad/sharp resonance assignments expressed in points i) to iv) but it should be noted that the Raman spectrum of ASM 36 also indicated the presence of a mixture of anions (BX_4^- and X^-) yet only sharp ^{31}P resonances were observed. The exact nature of the halide species present cannot be exactly defined - it is assumed that they are like $MePCl_nBr_{3-n}{}^+X^-$, rather than of a formulation akin to metastable PCl_5 or $(PCl_4^+)_2BCl_4^-Cl^-$ because no evidence has ever been found to indicate a pure methylhalophosphorane complex of this structure.

4.5.b $Me_2PX_2{}^+X^-$ and some derivatives (X = Cl, Br)

Previous static ^{31}P NMR shift values of 124 ± 5 [3] and 127.5 ± 3 p.p.m.(19) have been reported for $Me_2PCl_2{}^+Cl^-$ whereas in acid solution the resonance was observed at 124.2 p.p.m.(5). In the present study a rather broad resonance (linewidth ~ 220 Hz) was observed under magic angle conditions at 126.8 p.p.m. Unfortunately, a thorough investigation of this compound was not made with particular reference to the Type "A" and Type "B" studied by Raman spectroscopy. Static ^{31}P measurements have also been reported for various Lewis acid complexes of $Me_2PCl_2{}^+Cl^-$ and have the following shift values: 119.3 ($SbCl_6{}^-$)(19), 120.9 ($ICl_4{}^-$)(5), 117.7 ($AuCl_4{}^-$)(19) and 121 ± 1 ($ICl_2{}^-$)(3). The MAR ^{31}P NMR of $Me_2PCl_2{}^+BCl_4{}^-$ showed a sharp resonance at 121.3 p.p.m. (119.5 ± 2 static measurement)(20) whereas in $Me_2PCl_2{}^+PCl_6{}^-$ the cationic resonance was observed at 125.0 p.p.m. as compared with a 124.2 p.p.m. static result(20). No MAR studies were performed on $Me_2PBr_2{}^+Br_3{}^-$ or derivatives though previous static results showed a chemical shift of 72.6 p.p.m. for $Me_2PBr_2{}^+Br_3{}^-$ and 70.9 p.p.m. for $Me_2PBr_2{}^+BBr_4{}^-$(5).

The Me_2PCl/Br_2 and $Me_2PCl/Br_2/BCl_3$ reaction products again provide interesting ^{31}P spectra. Deng has previously studied the Me_2PCl/Br_2 system(5); a static ^{31}P spectrum gave a broad resonance at 112.9 p.p.m. whilst in oleum chemical shifts resulting from the $Me_2PCl_nBr_{2-n}{}^+$ and various solvolysis products were observed. Results obtained in the current study are presented in Table 4.22 and the ^{31}P NMR spectrum of a $Me_2PCl/Br_2/BCl_3$ product (ASM 41) is illustrated in Fig. IV5. It can be seen that sharp resonances occur only after the addition of a Lewis acid to the Me_2PCl/Br_2 reaction, consistent with the results obtained in the analogous $MePCl_2/Br_2$ system. There are, however, two noteworthy differences:-

a) The replacement of an X^- anion with a $BX_4{}^-$ species leads to a

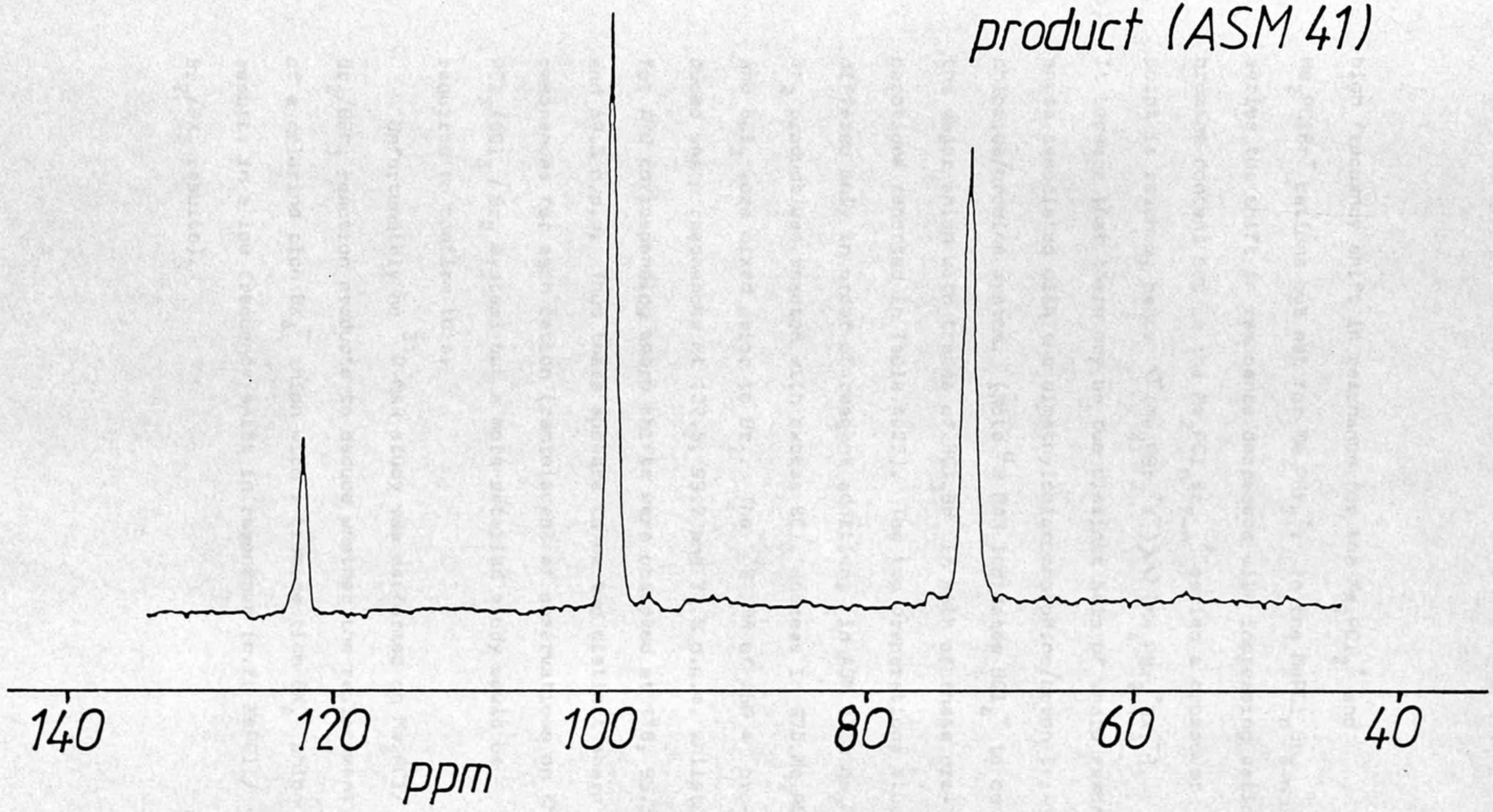
TABLE 4.22

^{31}P NMR SHIFTS (p.p.m.) FOR Me_2PCl/Br_2 REACTION PRODUCTS

a)Me_2PCl/Br_2 (oleum)(1)	b)Me_2PCl/Br_2 (MAR-R25)	c)Me_2PCl/Br_2 (MAR-ASM39)	d)$Me_2PCl/Br_2/BCl_3$ (MAR-ASM41)	e)$Me_2PCl/BCl_3/Br_2$ (MAR-R70)	Assignment
124.2	117 (br)	118 (br)	122.5 (sh)	118.2 (sh)	$Me_2PCl_2^+$
109.6	91 (br)	94 (br)	99.2 (sh)	95.5 (sh)	Me_2PClBr^+
75.8	73 (br)	74.9 (br)	72.5 (sh)	69.3 (sh)	$Me_2PBr_2^+$

(1) Values taken from R.M.K. Deng, Ph.D. Thesis, 1980, University of Durham.
Some shifts resulting from hydrolysis and oxidation products omitted.

Fig IVs ^{31}P M.A.R. NMR spectrum of an $Me_2PCl-Br_2-BCl_3$ reaction product (ASM 41)



high frequency shift in resonance for the $\mathrm{Me_2PCl_2^+}$ and $\mathrm{Me_2PClBr^+}$ cations but not for $\mathrm{Me_2PBr_2^+}$. In the $\mathrm{MePCl_nBr_{3-n}^+}$ series the shift in resonance decreased with increasing cation bromine content but in the $\mathrm{Me_2PCl_nBr_{2-n}^+}$ series a crossover point is reached, hence $\nu(\mathrm{Me_2PBr_2^+X^-}) > \nu(\mathrm{Me_2PBr_2^+BX_4^-})$.

b) It appears that there may be two distinct sets of sharp resonances associated with the dimethylchlorophosphine/boron trichloride/bromine system. (Note ^{11}B MAR indicates $\mathrm{BCl_4^-}$ to be the major anion with traces of $\mathrm{BCl_3Br^-}$ in both of these preparations reported in Table 4.22). The two preparations studied differed only in order of reagent addition; in ASM 41 a $\mathrm{Me_2PCl/Br_2}$ product was reacted with excess $\mathrm{BCl_3}$ whereas in R70 $\mathrm{Me_2PCl}$ and $\mathrm{BCl_3}$ were mixed prior to $\mathrm{Br_2}$. The ^{31}P NMR of ASM 41 produced sharp resonances at 122.5, 99.2 and 72.5 p.p.m. whilst for R70 corresponding sharp shifts were observed at 118, 95.5 and 69.3 p.p.m. Thus there appears to be two distinct sharp resonances for each cation (reminiscent of observations on the $\mathrm{PCl_3/BCl_3/Br_2}$ system) but a more detailed study would be required to confirm this.

Unfortunately no ^{31}P MAR study was performed on $\mathrm{Me_2PCl/Br_2/BBr_3}$ reaction products to deduce whether the replacement of a chlorine rich $\mathrm{BX_4^-}$ anion with a bromine rich $\mathrm{BX_4^-}$ anion results in a low frequency shift in resonance (c.f. $\mathrm{MePCl_2/Br_2/BX_3}$ results).

4.5.c Me$_3$PX$^+$X$^-$ and some derivatives (X = Cl, Br)

Previous static measurements on Me$_3$PCl$^+$Cl$^-$ showed a resonance at 87 ± 4 p.p.m.(3) and the current ^{31}P MAR study resulted in a broad shift centred on 87 p.p.m. For Me$_3$PBr$^+$Br$^-$ a single broad resonance at 71.3 p.p.m. was observed, comparing favourably with earlier static measurements (67.8 p.p.m.)(5). Complexation with Lewis acids seem to indicate a similar crossover to that in the Me$_2$PX$_2^+$ derivatives. The current ^{31}P MAR study of Me$_3$PCl$^+$BCl$_4^-$ showed a chemical shift (narrow line) at 89.2 p.p.m. whilst an earlier static spectrum of Me$_3$PBr$^+$BBr$_4^-$ indicated a ^{31}P resonance at 64.5 p.p.m.(5). Thus a high frequency shift in resonance has occurred upon complexation of the chloride species whereas the opposite has occurred in the case of the bromide.

4.6 Summary

The following summarises the main conclusions reached during the work on methylhalophosphoranes and some derivatives detailed in Sections 4.1 to 4.5.

i) The compounds $MePCl_4$ and $MePBr_4$ are, in the solid state, ionic, with the formulation $MePX_3{}^+X^-$.

The cations exhibit C_{3v} symmetry and show characteristic 6 band Raman spectra spectra. Complexation with Lewis acids results in high frequency Raman shifts in the cation spectra.

ii) The $MePCl_2/Br_2$ reaction yields the following cations: $MePCl_3{}^+$, $MePCl_2Br^+$, $MePClBr_2{}^+$, and $MePBr_3{}^+$.

The mixed halide cations show 9 band Raman spectra, characteristic of C_s point group symmetry, and are affected by complexation with Lewis acids in a similar way to the $MePCl_3{}^+$ and $MePBr_3{}^+$ ions.

iii) Depostion at 15K from the gas phase of $MePCl_4$ gives a trigonal bipyramidal species of C_2 symmetry that changes to the normal room-temperature $MePCl_3{}^+Cl^-$ at about 160K. It was not possible to deduce the gas phase structure of $MePBr_4$ due to experimental difficulties.

iv) Characteristic solid state ^{31}P NMR shifts were obtained for the $MePCl_nBr_{3-n}{}^+$ cations with both single halide and polyatomic anions under magic angle rotation. In general significantly broader ^{31}P resonances were obtained in the presence of single halide anion than when a polyatomic anion was present.

v) The compounds Me_2PCl_3 and Me_2PBr_z (z = 3 or 5) are ionic in the solid ionic with the formulation $Me_2PX_2^+X^-$ (or X_3^-). The cations exhibit C_{2v} symmetry and have 9 Raman active fundamentals. Some Raman evidence suggests the existence of two modifications of $Me_2PCl_2^+Cl^-$. Complexation with Lewis acids results in high frequency shifts in the cation spectra.

vi) The Me_2PCl/Br_2 reation yields the following cations: $Me_2PCl_2^+$, Me_2PClBr^+ and $Me_2PBr_2^+$ with the mixed halogen moiety exhibiting C_s symmetry with 9 Raman active fundamentals.

vii) Under magic angle rotation, solid state ^{31}P NMR spectra were obtained for the $Me_2PCl_nBr_{2-n}^+$ cations and broader resonances were observed when an X^- anion replaced a BX_4^- species.

viii) The compounds Me_3PCl_2 and Me_3PBr_2 in the solid state may be formulated as $Me_3PX^+X^-$ with the cations possessing C_{3v} point group symmetry and showing characteristic 6 band Raman spectra. When reacted with Lewis acids, ionic complexes are formed and some high frequency shifts occur in the cationic Raman spectra.

ix) Solid state ^{31}P NMR resonances were obtained for $Me_3PCl^+Cl^-$, $Me_3PBr^+Br^-$ and some derivatives. Broader resonances were obtained when the counter ion was a single halide anion rather than a polyatomic species.

4.7 References

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CHAPTER 5

EXPERIMENTAL

5.1 Chemicals

In general reagents of the best available commercial grade were used without further purification. However, the following procedures were adopted when necessary:

i) Halogenated solvents were dried over calcium chloride or activated 4Å mesh molecular sieves.

ii) Aluminium trichloride was crushed under dry-box conditions prior to use.

iii) Aluminium tribromide was re-crystallized from hexane and stored in ampoules unless for immediate use.

iv) Tetraethylammonium chloride was re-crystallized from ethanol by the addition of diethyl ether(1), dried in an oven at 50°C for several hours, and stored in a vacuum desiccator over P_2O_5.

v) Boron trichloride (Matheson-Cambrian Gases) was condensed from the lecture bottle into tared ampoules using a salt/ice bath and then stored under refrigeration until use.

vi) Hydrogen chloride was generated as required (see Section 3.3) and dried by passage through a dreschel bottle of concentrated sulphuric acid.

vii) Hydrogen bromide (B.D.H. 99.8%) was used as required from the lecture bottle.

viii) Chlorine (B.O.C. Special Gases) was used directly from the cylinder.

ix) Temperatures of approximately 0°C were maintained by a salt/ice bath and temperatures of -78 to -80°C required the use of a solid CO_2/acetone mixture. Other temperatures were achieved with the use of the appropriate liquid N_2/organic solvent slush bath$^{(2)}$.

x) Methylphosphines were purchased from Strem Chemicals, U.S.A. and used without further purification.

5.2 GENERAL METHODS OF PREPARATION OF PRODUCTS AND HANDLING OF MATERIALS

The compounds described in this work required the use of strictly anhydrous conditions during both preparation and analysis due to their susceptibility to hydrolysis. The alkylhalophosphines used were also susceptible to aerial oxidation (dimethylchlorophosphine spontaneously inflames in air) so all reactions were carried out under an atmosphere of oxygen-free nitrogen (B.O.C.). All products and many of the starting materials were manipulated in a glove-box of nitrogen containing open vessels of P_2O_5 to ensure complete dryness. All glassware used in preparations was dried in an oven at 120°C for at least 3 hours and then permitted to cool, either in a glove-box, or under a gentle stream of nitrogen until required.

All filtrations were carried out in the absence of moisture using the apparatus illustrated in Fig V-1. Nitrogen blown into the upper chamber was sufficient to maintain a dry atmosphere during addition of the reaction mixture and products were dried by suction after sealing the unit. The drying of products at the pump required some caution to ensure that no decomposition occurred, especially when heavily brominated species were involved.

5.3 PREPARATIONS IN ANHYDROUS HYDROGEN CHLORIDE AND HYDROGEN BROMIDE

The addition of concentrated hydrochloric acid (150 cm^3) to concentrated sulphuric acid (300 cm^3) was used to generate hydrogen chloride gas. This was then passed through a drying trap containing concentrated sulphuric acid and a splash trap to prevent any sulphuric acid from being carried over. The system is illustrated in Fig V.2 and full details of the reaction vessel and it's manipulation are given elsewhere (3). The same general system was used for reactions in anhydrous hydrogen bromide except that the gas was condensed directly from the lecture bottle without passage through concentrated sulphuric acid. Also the solid hydrogen bromide was liquefied with an n-butyl acetate/N_2 slush bath (-77°C) (2) whereas a toluene/N_2 slush (-95°C) (2) was used for the liquefaction of solid hydrogen chloride.

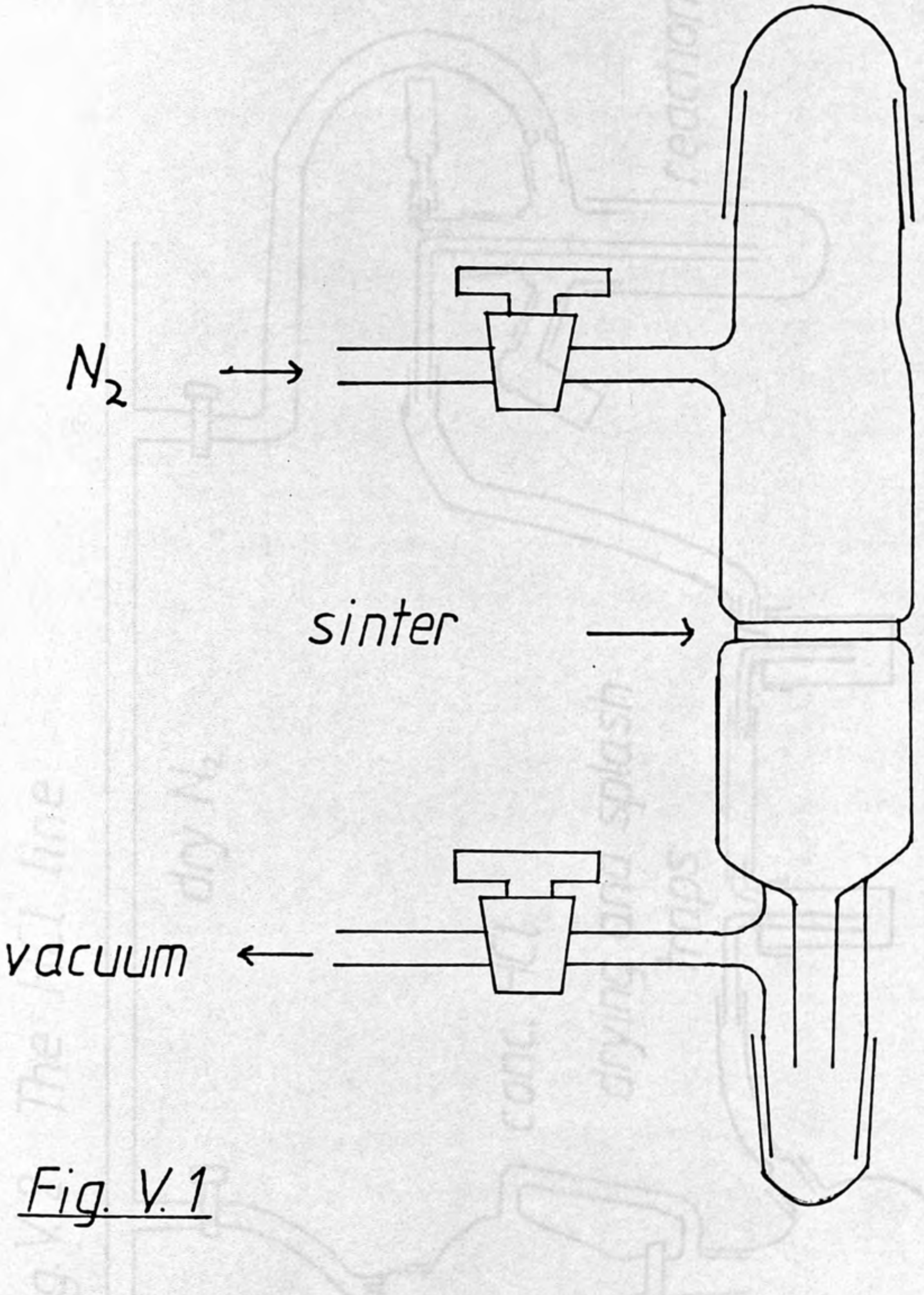
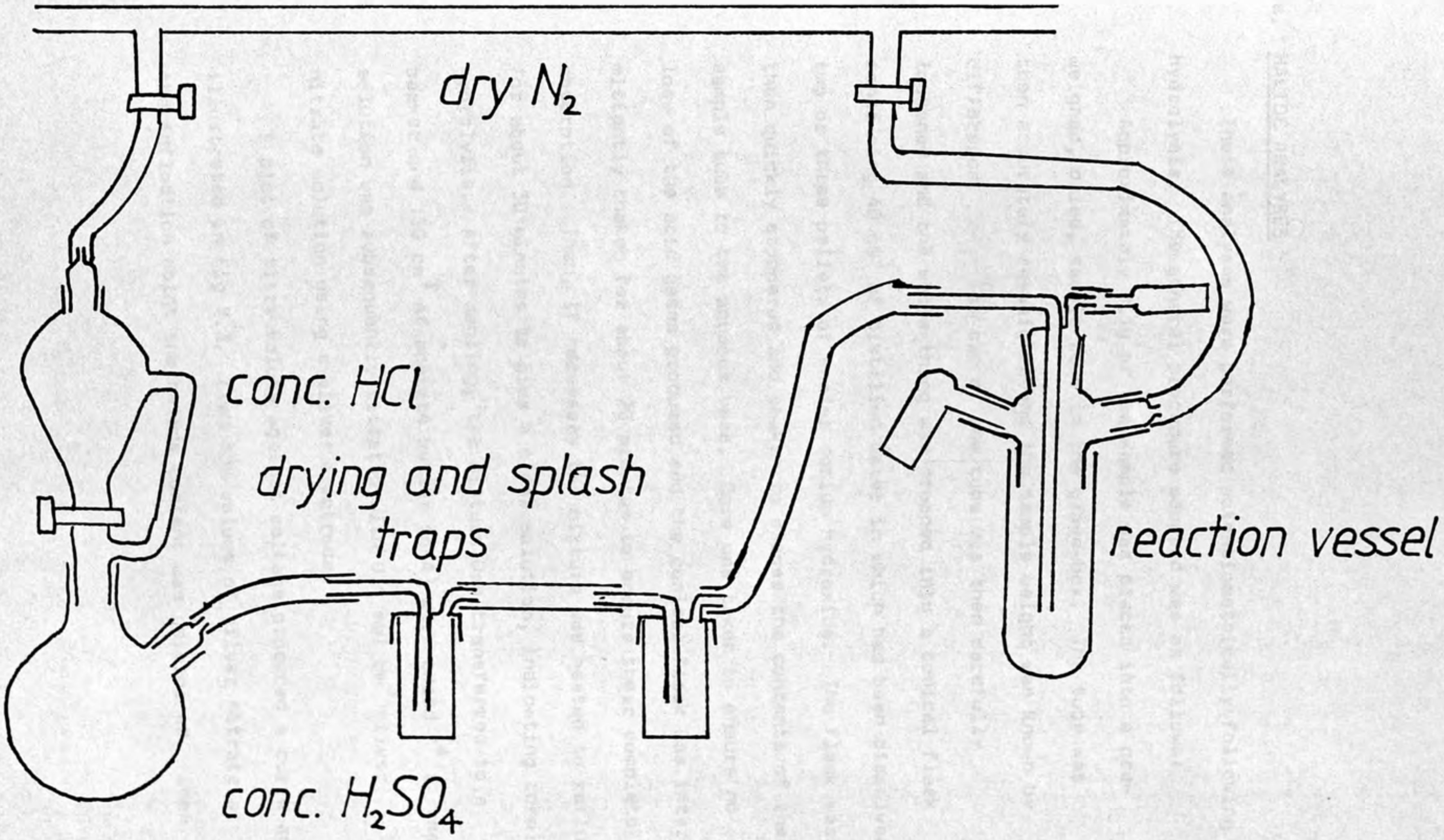


Fig. V.1

Inert atmosphere filtration apparatus.

Fig. V. 2 The HCl line



5.4.a. HALIDE ANALYSES

These analyses were performed potentiometrically following hydrolysis. The general procedure adopted was as follows:

Approximately 0.1g of the sample was placed into a pre-weighed, dried, sample tube in the glove-box. The tube was then accurately re-weighed and the sample weight was known by difference. The cap of the tube was then carefully loosened and the whole thing was dropped into a conical flask containing 40 cm^3 of distilled water in which had been dissolved two or three pellets of Analar sodium hydroxide. The flask was then quickly stoppered and shaken to expose the contents of the sample tube to the aqueous base. Care was taken to ensure no loss of the acid gases produced and the conical flask was intermittently shaken for about 20 minutes to ensure their complete absorption. Then, if necessary the mixture was heated to reflux for about 30 minutes to give a clear solution, indicating complete hydrolysis. After cooling, the mixture was transferred to a beaker and 150 cm^3 of acetate butter (pH4) were added (4): the solution was subsequently titrated with 0.1 mol dm^3 silver nitrate solution using a silver electrode.

A plot of titre volume against voltage produced a curve as illustrated in Fig V.3. From the volume of silver nitrate at the inflection point the halide content was determined. When

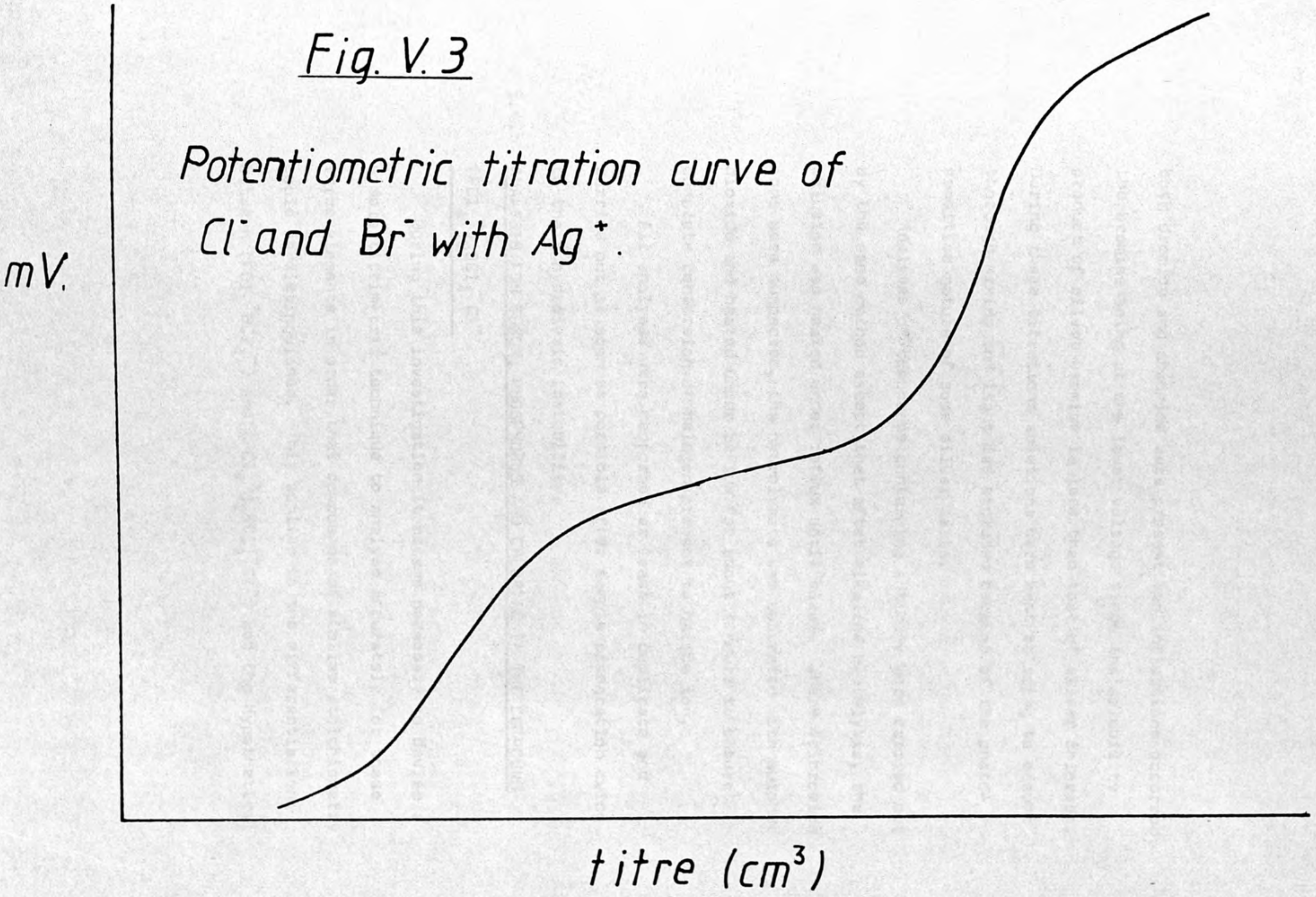


Fig. V.3

Potentiometric titration curve of Cl^- and Br^- with Ag^+.

both bromide and chloride were present two inflections occurred, the bromide being at the lower voltage since the solubility product of silver bromide is less than that of silver chloride. During these titrations solutions were kept stirring to ensure thorough mixing and light was excluded because of the photosensitive nature of some silver salts.

Analyses of compounds containing antimony were carried out by the same method except that after alkaline hydrolysis, the solution was heated under reflux until clear. Where tribromide ions were suspected, the hydrolysate was saturated with sulphur dioxide and heated under reflux for about 4 hours to ensure complete conversion of halogen present to halide ion.

All analyses were performed at least in duplicate and carried out as soon as possible after sample preparation owing to their hydrolytic instability.

5.4.b ANALYSIS FOR BORON, PHOSPHORUS AND CHLORINE IN THE COMPOUND $(PCl_4^+)_2BCl_4^-Cl^-$

During this investigation it became necessary to devise a simple titrimetric technique to analyse accurately for these three elements in order that compounds of similar stoichiometry could be distinguished. This applied to the differentiation between $(PCl_4^+BCl_4^-)$ and$((PCl_4^+)_2BCl_4^-Cl^-)$ and the hypothetical

$(PCl_4^+)_3BCl_4^-2Cl^-$ whose stoichiometries are presented in Table 5.1.

An accurately weighed sample (c.a. 1.25g) was hydrolysed in the manner described earlier and when all the acidic gases were absorbed, the solution was diluted to 250 cm^3 with distilled water. A 25 cm^3 aliquot was then titrated with 0.1 mol dm^3 $AgNO_3$ solution in the usual manner (Ag electrode) to determine the chloride content (V_{C1}). A separate 25 cm^3 aliquot was then titrated with standardized Aristar 0.1 mol dm^3 NaOH solution (glass electrode). Assuming the hydrolysis products to be hydrochloric acid, boric acid and phosphoric acid, the following equation may be written:

$$P_2BCl_{13} + 11H_2O \longrightarrow 13HCl + B(OH)_3 + 2H_3PO_4$$

A typical hydroxide titration curve is illustrated in Fig V.4. The first inflexion corresponds to a superimposition of the HCl and H_3PO_4 ($\rightleftharpoons H^+ + H_2PO_4^-$) end points and yields V_{P+Cl}. V_{Cl} was obtained previously from the $AgNO_3$ titration so Vp may be deduced. When a further volume of hydroxide equal to Vp was added an indistinct inflection corresponding to the second phosphoric acid end point ($H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$) was observed. At this point mannitol was added to the solution to complex with the very weak boric acid and addition of further hydroxide yielded the final end point V_{P+B} (Note: the third

TABLE 5.1

STOICHIOMETRY OF SOME PHOSPHORUS/BORON CHLORIDES

General Formula	%P	%B	%Cl	P:B	Cl:P
$PBCl_8$	9.53	3.32	87.15	1	8
P_2BCl_{13}	11.62	2.02	86.36	2	6.5
P_3BCl_{18}	12.54	1.46	86.00	3	6

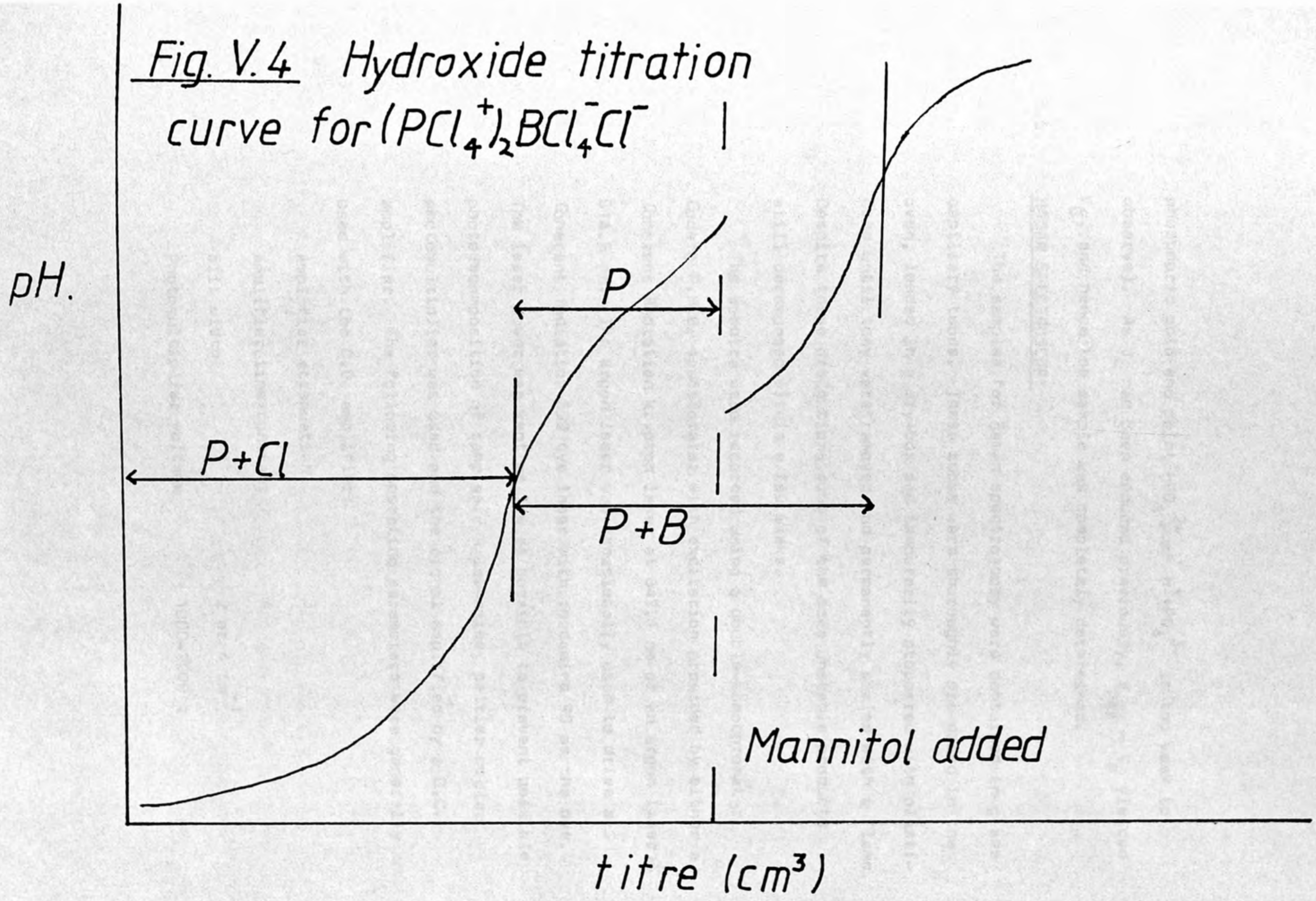


Fig. V.4 Hydroxide titration curve for $(PCl_4^+)_2BCl_4^-Cl^-$

phosphoric acid end point $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ is too weak to observe). As V_P had been deduced previously, $V_{P+B} - V_P$ yielded V_B, and hence the sample was completely determined.

5.5. RAMAN SPECTROSCOPY

The samples for Raman spectroscopy were contained in glass capillary tubes. These tubes were thoroughly pre-dried in the oven, loaded in a dry-box and temporarily stoppered with plasticene until they were removed and permanently sealed with a flame. Despite these precautions some of the more unstable products still decomposed within a few weeks.

The spectra were recorded using a double-monochromator Coderg P.H.O. spectrometer with excitation provided by either a Coherent Radiation krypton laser at 647.1 nm or an argon laser at 514.5 nm. The argon laser was occasionally used to drive a Coherent Radiation 599 dye laser with rhodamine 90 as the dye. The laser power was kept as low as possible to prevent possible photodecomposition of samples. A low-noise, peltier cooled photomultiplier was used and the signal amplified by a D.C. amplifier. The following operating parameters were generally used with the D.C. amplifier:

Amplifier attenuation	3
Amplifier time constant	4
Slit width	2 or 4 cm^{-1}
Photomultiplier voltage	1000-2000 V

Chart speed)
)   20 cm^{-1}/cm
Scan speed)

Variable temperature Raman studies (ambient 150°C) were performed using a modified Coderg cold-cell illustrated in Fig V.5. The bottom of the sample holder was milled so as to ensure a reasonably close fit with the sample tube and the temperature was regulated and monitored using a Beckman T.E.M.I. Temperature Controller. However, even assuming good thermal contact between holder and sample, there are several limiting factors governing the exact sample temperature:-

a) The localized heating of the sample by the incident laser radiation.

b) The temperature gradient between the top and bottom of the sample holder.

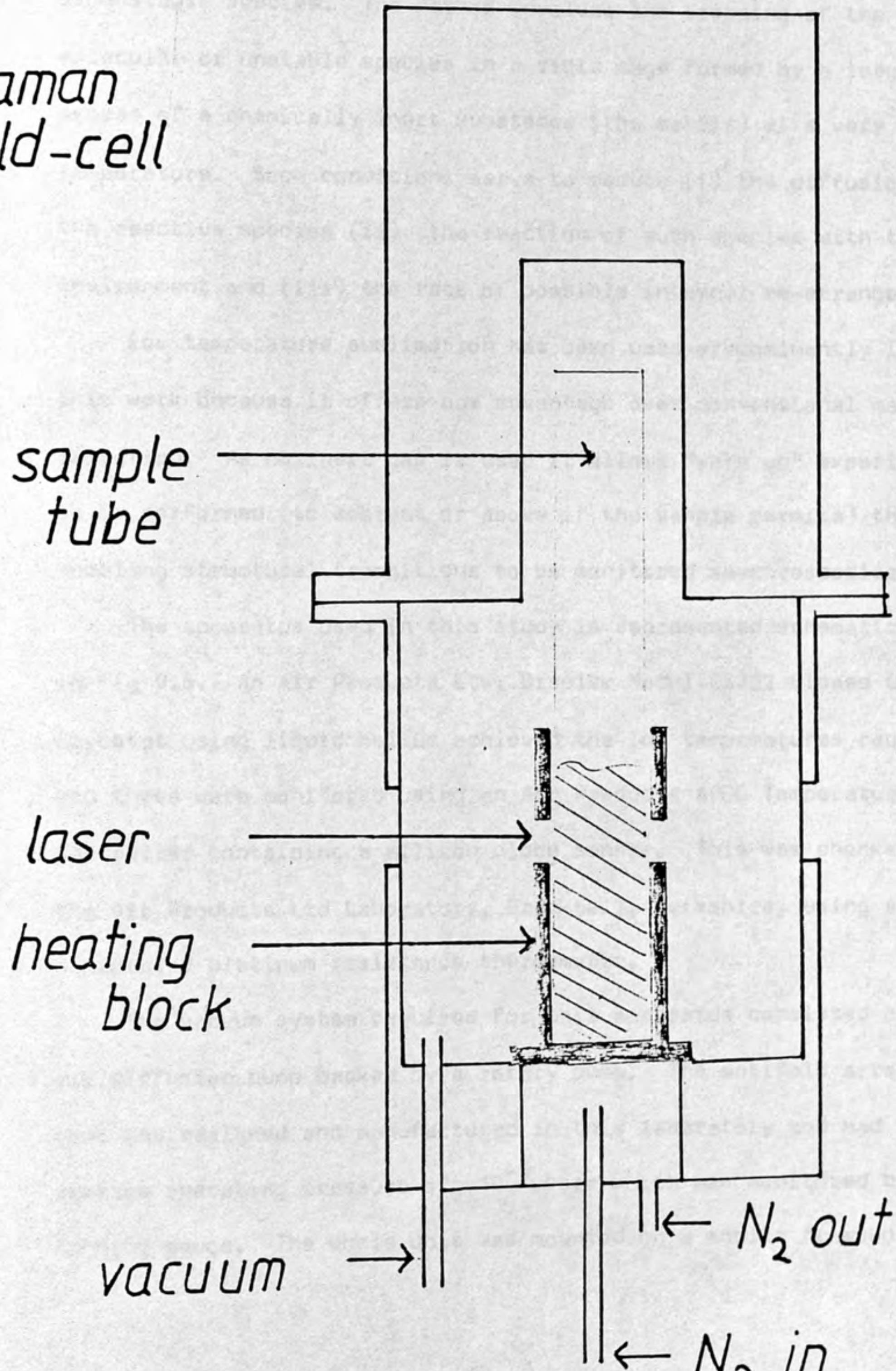
c) The temperature gradient across the sample tube. A check on the temperature at the top of the sample holder was carried out by placing a thermometer on top of the heating block and this indicated the temperature to be accurate within ± 3°C. The samples were usually left for about 20 minutes to allow for temperature equilibration before spectra were recorded.

5.6 MATRIX ISOLATION AND LOW TEMPERATURE SUBLIMATION EQUIPMENT

Matrix isolation is now a well established technique proposed by Pimentel et al in 1954 (5). It was developed to help overcome the difficulties inherent in studying highly reactive, short lived

Fig. V.5

Raman cold-cell



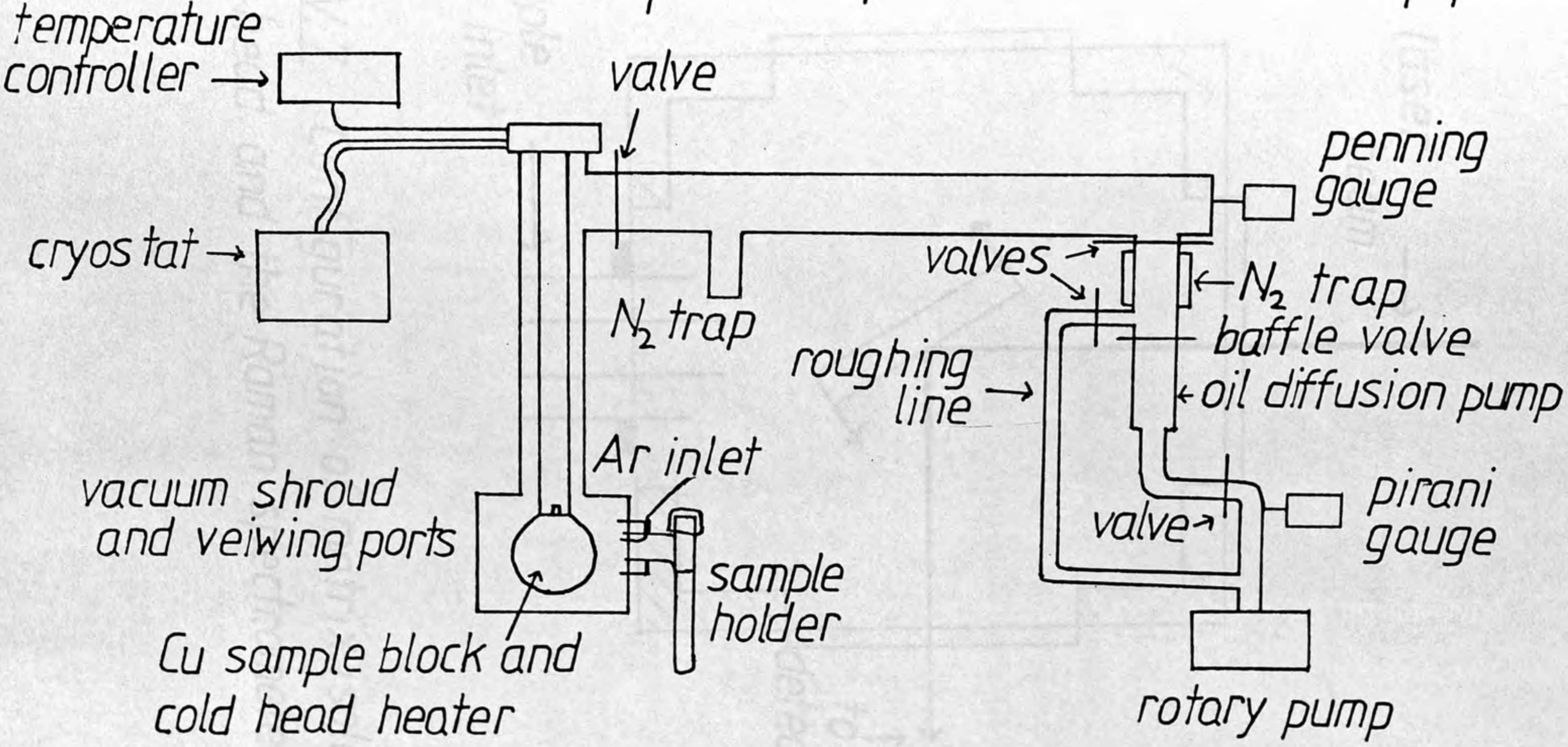
or unstable species. The method involves the trapping of the molecular or unstable species in a rigid cage formed by a large excess of a chemically inert substance (the matrix) at a very low temperature. Such conditions serve to reduce (i) the diffusion of the reactive species (ii) the reaction of such species with their environment and (iii) the rate of possible internal re-arrangements.

Low temperature sublimation has been used predominantly in this work because it offers one advantage over conventional matrix-isolation. As no inert gas is used it allows "warm up" experiments to be performed (to ambient or above if the sample permits) thus enabling structural transitions to be monitored spectroscopically.

The apparatus used in this study is represented schematically in Fig V.6. An Air Products Ltd, Displex Model CS202 Closed Cycle Cryostat using liquid helium achieved the low temperatures required and these were monitored using an Air Products APDG Temperature Controller containing a silicon diode sensor. This was checked at the Air Products Ltd Laboratory, Bracknell, Berkshire, using a calibrated platinum resistance thermometer.

The vacuum system required for this apparatus consisted of an oil diffusion pump backed by a rotary pump. The manifold arrangement was designed and manufactured in this laboratory and had an average operating pressure of 10^{-5} torr which was monitored by a Penning gauge. The whole unit was mounted on a mobile framework

Fig. V.6 Matrix Isolation/Low-temperature sublimation equipment.



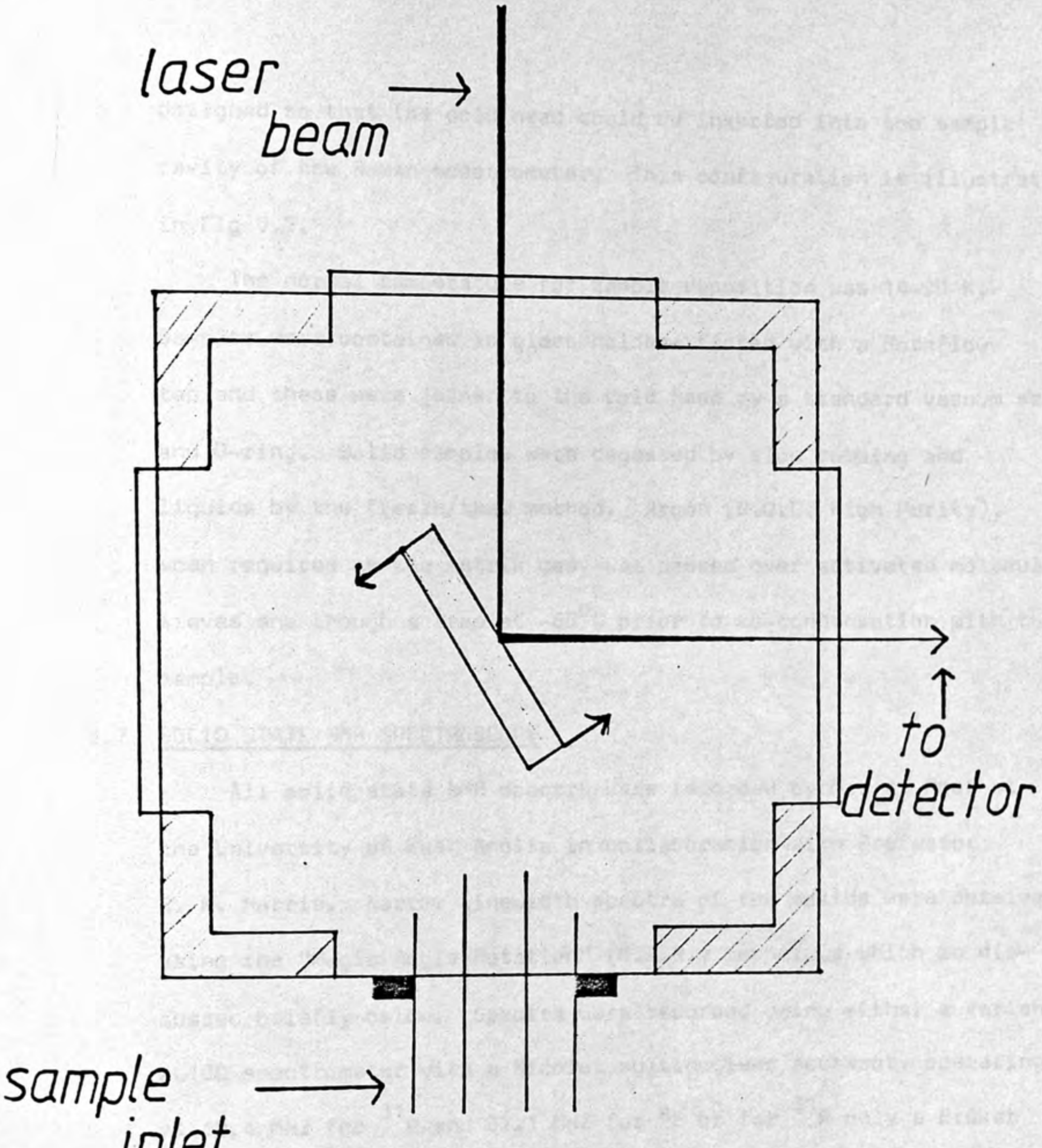


Fig. V. 7 Configuration of matrix isolation cold-head and the Raman spectrometer.

designed so that the cold head could be inserted into the sample cavity of the Raman spectrometer. This configuration is illustrated in Fig V.7.

The normal temperature for sample deposition was 14-20 K. Samples were contained in glass holders fitted with a Rotaflow tap and these were joined to the cold head by a standard vacuum seal and O-ring. Solid samples were degassed by slow pumping and liquids by the freeze/thaw method. Argon (B.O.C. High Purity), when required as the matrix gas, was passed over activated molecular sieves and though a trap at -80°C prior to co-condensation with the sample.

5.7 SOLID STATE NMR SPECTROSCOPY

All solid state NMR spectra were recorded by Mr. A. Root at the University of East Anglia in collaboration with Professor R. K. Harris. Narrow linewidth spectra of the solids were obtained using the "Magic Angle Rotation" (M.A.R.) technique which is discussed briefly below. Spectra were recorded using either a Varian XL100 spectrometer with a Nicolet multinuclear accessory operating at 40.4 MHZ for ^{31}P and 32.1 MHZ for ^{11}B or for ^{31}P only a Bruker CXP200 spectrometer operating at 81 MHZ. Variable temperature studies were performed on some samples.

Until recently, the majority of magnetic resonance measurements on phosphorus (V) compounds similar to those described in this thesis have either been on solutions (eg 6-10) or on static solid state (11,12) samples. The solution state spectra (often measured in strongly acidic media) gave resonances due to halophosphonium cations and various solvolysis, oxidation and halogen exchange products. Dillon and Gates characterised the ions $PCl_nBr_{4-n}^+$ ($0 \leq n \leq 4$) by means of static solid state ^{31}P NMR(13) though the resonance peaks were found to be quite broad. This was not unexpected as dipolar and anisotropic shielding interactions usually dominate spectra in the solid state.

In solids, a geometric factor is involved in the dipolar hamiltonian and is responsible for line broadening whereas in non-viscous liquids this factor is averaged to zero because of isotropic molecular tumbling. In 1958, Andrew, Bradbury and Eades(14,15) used the technique of high-speed rotation of solid specimens to study narrowing effects on dipolar broadened NMR spectra. They observed that their spectra were scaled by a factor of $\frac{1}{2}(3\cos^2\beta-1)$ where β is the angle between the axis of sample rotation and the applied magnetic field. Later Andrew (16) and Lowe (17) independently recognised that if $\beta = 54^\circ\ 44'8''$, $\cos\beta = 1/\sqrt{3}$ and $\frac{1}{2}(3\cos^2\beta - 1) = 0$. Consequently, as in the case of non-viscous liquids, the dipolar interaction is averaged to zero so dipolar broadening is removed. This angle is now known as the "magic angle" and further work on crystalline and amorphous substances indicated that high speed rotation about this axis could remove broadening arising from anisotropic shielding and symmetric electron-coupled nuclear spin interactions. The rate of rotation required to reduce the dipolar interaction to zero has to be greater than the static linewidth in Hertz and the same criterion applies to the removal of broadening due to chemical shift anisotropy.

Thus MAR is readily applicable to investigate both the tetrahalophosphonium cations and the tetrahaloborate anions in the solid state especially as the broadening effect of the dipole-dipole interaction should be reduced under any circumstances by the fast relaxing quadrupolar halogen nuclei. Indeed, very recently, Harris et al (18) have obtained well defined solid state resonances for the anion series $BCl_nBr_{4-n}^-$ ($0 \leqslant n \leqslant 4$) using a sample prepared in this laboratory. More detailed reviews of MAR may be found elsewhere (19,20).

5.8 PREPARATIVE SUBLIMATIONS

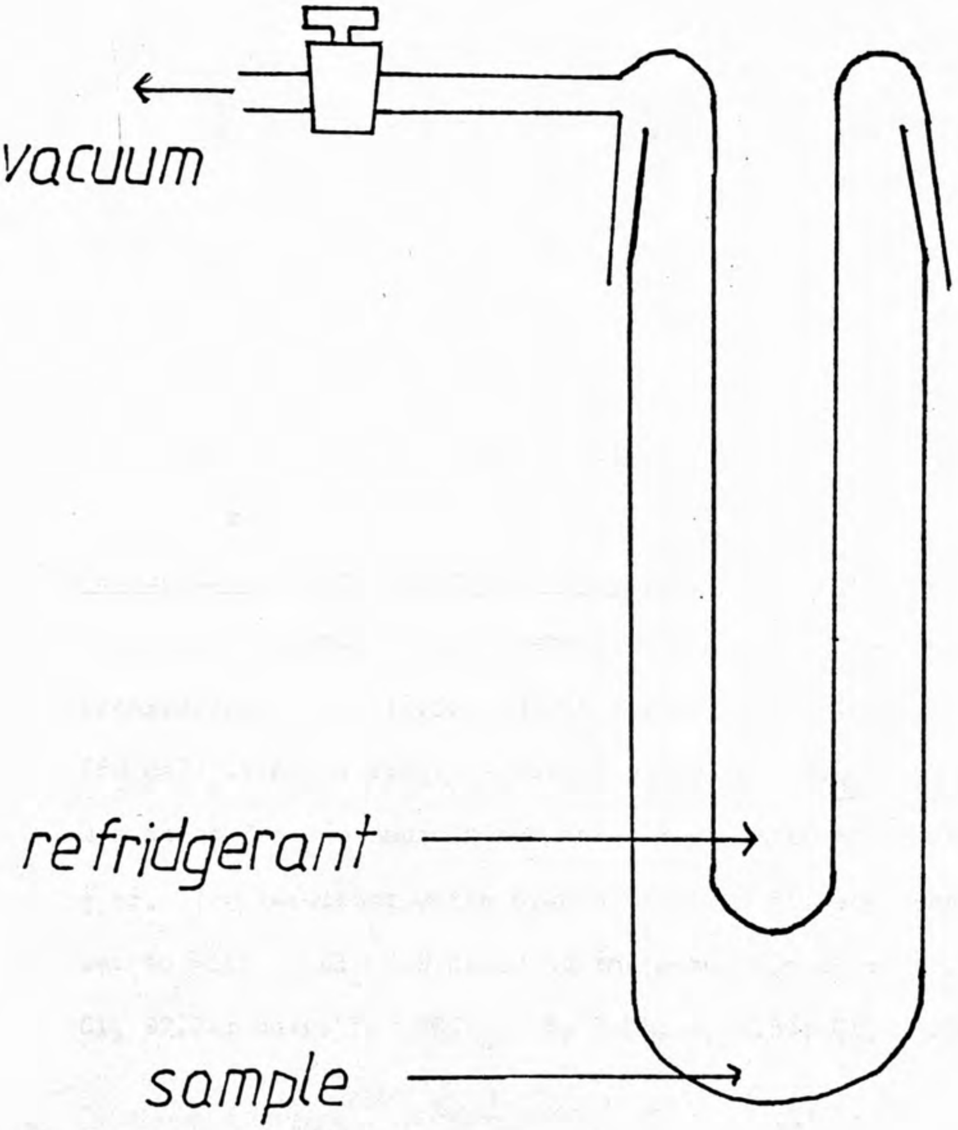
The behaviour of the mixed halophosphonium cations $PCl_nBr_{4-n}^+$ ($0 \leqslant n \leqslant 4$), with both single halide and polyatomic anions, was investigated under preparative sublimation conditions. The apparatus used is illustrated in Fig V.8. The sublimation trap was held at $-78^\circ C$ and the sample temperature was maintained by an oil or water bath. Following sublimation, residues and sublimates were manipulated in the glove-box prior to spectroscopic anyalysis.

5.9 PREPARATION OF COMPOUNDS BASED ON PHOSPHORUS HALIDES.

a) Metastable (Phase III) Phosphorus pentachloride $(PCl_4^+)_2PCl_6^-Cl^-)$

Several methods were used to prepare this compound. The

Fig. V. 8 Preparative sublimation apparatus



standard method adopted was that of Finch et al (21) and a typical preparation is given. Normal PCl_5 (5.00g, 0.024 mol) was dissolved in CH_2Cl_2 (70 cm^3) by continual stirring. Then Br_2 (0.75g, 0.0047 mol) was added to this solution which on standing yielded greenish-white crystals which were filtered under dry N_2 and dried under vacuum. (Found: Cl, 85.1%; Calc. for PCl_5: Cl, 85.1%)

Alternative methods found to yield this compound were:-

i) The reaction of PCl_3 and Cl_2 in anhydrous HCl.

ii) The recrystallization of normal PCl_5 from anhydrous HCl.

iii) The recrystallization of normal PCl_5 from either CCl_4, $CHCl_3$ or PCl_3.

iv) The recrystallization of P_2Cl_9Br from CH_2Cl_2.

v) The recrystallization of normal PCl_5 from CH_2Cl_2 under U.V. irradiation.

b) <u>Tetrachlorophosphonium tetrachloroborate</u> $PCl_4^+BCl_4^-$

A modification of the method of Petro (22) was used for this preparation. PCl_5 (4.00g, 0.019 mol) was dissolved in CH_2Cl_2 (60 cm^3) with stirring. A slight excess of BCl_3 (2.60g, 0.022 mol) was added from an ampoule and the mixture stirred for a further ½ hr. The resultant white precipitate was filtered under dry N_2, washed with CH_2Cl_2 and dried at the pump. (Found: B,3.3%; P, 9.6%; Cl, 87.2%; Calc. for $PBCl_8$: B, 3.3%; P, 9.5%; Cl, 87.2%).

c) Tetrachlorophosphonium hexachloroantimonate $PCl_4{}^+SbCl_6{}^-$

A modification of the method of Beattie and Webster (23) was used. PCl_5(4.01g, 0.0192 mol) was dissolved with stirring in CH_2Cl_2 (60 cm^3). An excess of $SbCl_5$ (7.40g, 0.025 mol, 3.2 cm^3) was added dropwise and the mixture stirred for a further 20 mins. and then filtered under N_2, washed with CH_2Cl_2 and dried at the pump. (Found: Cl, 69.6%;Calc. for $PSbCl_{10}$: Cl, 69.8%)

d) Preparation of the compound P_2Cl_9Br

This was prepared by the method of Kolditz et al (24). PCl_3 (8.25g, 0.06 mol, 5.25 cm^3) was suspended in arsenic trichloride (8 cm^3) and the Br_2 (4.80g, 0.031 mol, 1.55 cm^3) was added dropwise with stirring and cooling in an ice bath. A pale yellow precipitate formed and was filtered under N_2, washed with benzene and dried at the pump. (Found: Cl, 69.4%; Br, 17.2%; Calc. for P_2Cl_9Br: Cl, 69.2%; Br, 17.3%)

e) Tetrachlorophosphonium tetrachloroaluminate $PCl_4{}^+AlCl_4{}^-$

This compound was prepared by a modification of Petro's method (22). PCl_5 (7.65g, 0.0367 mol) was dissolved in CH_2Cl_2 60 cm^3) with stirring. To this was added $AlCl_3$ (4.90g, 0.0367 mol) from a solid addition tube and the mixture stirred for about 2 hrs until no unreacted aluminium trichloride was visible. The grey/white precipitate was then filtered, washed, and dried at the pump in the usual manner. (Found: Cl, 82.3%; Calc. for $PAlCl_8$: Cl, 83.0%)

f) Tetrabromophosphonium tetrabromoborate $PBr_4^+BBr_4^-$

This method was prepared by a modification of that described in Ryan's thesis (3). PBr_5 (5.00g, 0.0116 mol) was dissolved in CH_2Cl_2 (50 cm^3) and to this was added BBr_3 (2.90g, 0.016 mol, 1.1 cm^3) suspended in 15 cm^3 of the same solvent. The resultant yellow precipitate was filtered under N_2, washed with CH_2Cl_2 and dried at the pump. (Found: Br, 93.6%; Calc. for $PBBr_8$: Br, 94.0%)

g) Preparation of the compound $(PCl_4)_2^+BCl_4^-Cl^-$

PCl_3 (15.03g, 0.109 mol) was suspended in arsenic trichloride (35 cm^3) in a three-necked round bottomed flask. BCl_3 (6.43g, 0.0547 mol) was added to this and the mixture stirred for 5 mins. Then, with continued stirring, a gentle stream of chlorine was passed over the surface of the mixture for ½ hr. Initially no reaction appeared to occur during this stage but after 5 mins the solution started fuming and a very exothermic reaction commenced necessitating the addition of more solvent (20 cm^3) and cooling to 0^oC. A white precipitate was formed and the mixture was stirred and cooled for a further 20 mins after the addition of chlorine was complete. The product was filtered under N_2, washed with $AsCl_3$ and pumped until solvent free. (Found: P, 11.7%; B, 2.0%; Cl, 86.1%; Calc. for P_2BCl_{13}: P, 11.6%; B, 2.0%; Cl, 86.4%)

The same product (identified by Raman spectroscopy) was obtained by the reaction of $2PCl_3 + BCl_3 + Cl_2$ in anhydrous HCl and by the same reaction in $SOCl_2$ although this preparation succeeded only once in four attempts.

h) Attempted preparations of compounds analogous to $(PCl_4^+)_2BCl_4^-Cl^-$

Several unsuccessful attempts were made to prepare compounds analogous to $(PCl_4^+)_2BCl_4^-Cl^-$ (see 5.9.F). These attempted preparations are summarised in Table 5.2.

i) Attempted preparations of $(PCl_4^+)_2BCl_4^-Cl^-$ mixed halide analogues

Again most of these preparations were unsuccessful but they are documented in Table 5.3.

j) Unsuccessful attempts at preparing the compound $(PCl_4^+)_2BCl_4^-Cl^-$

Other unsuccessful attempts to synthesise this compound were investigated and will now be generally listed.

1) The addition of BCl_3 to a solution of PCl_5 in CH_2Cl_2 (1:2 molar ratio) with a drop of Br_2 present - ie adding the Lewis acid to a metastable PCl_5 preparation. These reactions always yielded $PCl_4^+BCl_4^-$.
2) The reaction of PCl_3 and BCl_3 (2:1 molar ratio) and Cl_2 in CH_2Cl_2. This always resulted in the production of $PCl_4^+BCl_4^-$.

TABLE 5.2

ATTEMPTED PREPARATION OF $(PCl_4^+)_2BCl_4^-Cl^-$ ANALOGUES

Reactants	Solvent	Conditions + Comments	Species observed in Raman Spectrum
PCl_3(8.20g,0.0598mol,5.25cm^3) $SbCl_5$(8.94g,0.0299mol,3.82cm^3) Cl_2	$AsCl_3$(30cm^3)	0^oC,stirred,bubbled Cl_2 over solution for ½ hr. Exothermic Yellow precipitate (2)	PCl_4^+, $SbCl_6^-$, AsCl Species
PCl_5(5.00g,0.0239mol) $SbCl_5$(3.56g,0.0119mol,1.55cm^3)	$AsCl_3$(25cm^3)	0^oC,stirred, $SbCl_5$ added dropwise. Violent reaction. White precipitate (45)	PCl_4^+, $SbCl_6^-$, AsCl species
PCl_3(8.20g,0.0598mol,5.25cm^3) $AlCl_3$(4.00g,0.0299mol) Cl_2	$AsCl_3$(50cm^3)	Warmed to 50^oC to dissolve $AlCl_3$. Cooled to 0^oC. Stirred,bubbled Cl_2 over solution for ½ hr. Exothermic Yellow precipitate (3)	PCl_4^+, $AlCl_4^-$ AsCl Species

TABLE 5.2 CONT'D

PCl_3(8.20g,0.0598mol,5.25cm^3) ICl_3(6.98g,0.0299mol) Cl_2	$AsCl_3$(40cm^3)	0^{o}C,stirred,violent reaction when ICl_3 added. Cl_2 bubbled over solution for ½ hr. Yellow solid (8)	PCl_4^+, ICl_4^-, AsCl Species
PCl_3(9.42g,0.0686mol,6.00cm^3) $SnCl_4$(8.94g,0.0343mol,4.00cm^3) Cl_2	$AsCl_3$(40cm^3)	0^{o}C,stirred,quite vigorous reaction. Cl_2 bubbled over solution for ⅓ hr. White precipitate (36)	PCl_4^+, $SnCl_5^-$, $SnCl_6^{2-}$ Arsenic Product
$MePCl_2$(2.09g,0.0182mol) BCl_3(1.06g,0.009mol) Cl_2	$AsCl_3$(20cm^3)	0^{o}C,stirred,Cl_2 bubbled over solution for ½ hr. Orange precipitate. Yellow solid isolated on pumping (15)	$MePCl_3^+$, BCl_4^-, Arsenic product

TABLE 5.2 CONT'D

PCl_3(9.42g,0.0686mol,6.00cm^3) $SnCl_4$(8.94g,0.0343mol,4.00cm^3) Cl_2	$SOCl_2$(40cm^3)	0^{o}C,stirred, Cl_2 bubbled over solution for ⅓ hr. Instant white precipitate (39)	PCl_4^+, $SnCl_6^{2-}$, $SnCl_5^-$
PCl_3(4.30g,0.0313mol,2.74cm^3) $SbCl_5$(4.68g,0.0156mol,2.00cm^3) Cl_2	HCl (anhydrous)	Standard method of preparation White solid isolated (27)	PCl_4^+ (n+m/s), PCl_6^-, $SbCl_6^-$
$AlCl_3$(2.50g,0.0187mol) PCl_3(5.14g,0.0375mol,3.27cm^3) Cl_2	HCl (anhydrous)	Standard method of preparation White solid isolated (24)	PCl_4^+, $AlCl_4^-$
PCl_5(6.49g,0.0312mol) $SbCl_5$(4.68g,0.0156mol,2.00cm^3)	HCl (anhydrous)	Standard method of preparation White solid isolated (28)	PCl_4^+ (n+m/s), PCl_6^-, $SbCl_6^-$

TABLE 5.2 CONT'D

PCl_5(4.00g,0.0192mol) $AlCl_3$(1.29g,0.0096mol)	HCl (anhydrous)	Standard method of preparation. White solid isolated (25)	PCl_4^+, $AlCl_4^-$
$MePCl_2$(1.75g,0.0149mol) BCl_3(0.88g,0.0075mol) Cl_2	HCl (anhydrous)	Standard method of preparation. White solid isolated (34)	$MePCl_3^+$, BCl_4^-
PCl_5(2.00g,0.0096mol) ICl(0.80g,0.0048mol)	HCl (anhydrous)	Standard method of preparation. Yellow solid isolated (51)	PCl_4^+, PCl_6^-, ICl_2^-
PBr_3(14.00g,0.0517mol,5.00cm^3) BBr_3(6.48g,0.0258mol,2.50cm^3) Br_2(4.13g,0.0258mol,1.38cm^3)	$AsCl_3$ (50cm^3)	0^oC,stirred,vigorous reaction when Br_2 added. Stirred 1 hr. Orange/Yellow solid isolated. (46)	PCl_4^+, BBr_4^-, Br_3^-, Arsenic product

TABLE 5.2 CONT'D

PBr_3(11.20g,0.0414mol,4.00cm^3) BBr_3(5.18g,0.0207mol,1.97cm^3) Br_2(3.31g,0.0207mol,1.07cm^3)	$SOBr_2$(40cm^3)	0^{o}C,stirred,violent reaction between PBr_3 and BBr_3 Orange precipitate formed which darkened on Br_2 addition.	PBr_4^+, BBr_4^-, other products
PBr_3(11.20g,0.0414mol,4.00cm^3) BBr_3(5.18g,0.0207mol,1.97cm^3) Br_2(3.31g,0.0207mol,1.07cm^3)	HBr (anhydrous)	Standard method of preparation Yellow solid isolated (5)	PBr_4^+, BBr_4^-

(reference no (eg 34) refer to laboratory Raman spectra file)

TABLE 5.3

ATTEMPTED PREPARATIONS OF MIXED HALIDE ANALOGUES OF $(PCl_4^+)_2BCl_4^-Cl^-$

Reactants	Solvent	Conditions + Comments	Species observed in Raman Spectrum
PCl_3(22.00g,0.160mol,14.01cm^3) $AlCl_3$(10.86g,0.080mol) Br_2(12.71g,0.0795mol,4.10cm^3)	$AsCl_3$(20cm^3)	0^{o}C,stirred,violent reaction when Br_2 added. Grey gelatinous solid formed. Unable to dry-dissolve in benzene and filter white solid	PCl_4^+, PCl_3Br^+, $AlCl_4^-$
PCl_3(22.00g,0.160mol,14.01cm^3) $SbCl_5$(23.92g0.080mol,10.22cm^3) Br_2(12.71g,0.0795mol,4.10cm^3)	$AsCl_3$(70cm^3)	0^{o}C,violent reaction when $SbCl_5$ added as well as on Br_2 addition. Red inhomogenous product due to lack of solvent. (47)	PCl_4^+, $SbCl_5Br^-$
PBr_3(21.30g,0.0786mol,7.60cm^3) BCl_3(4.66g,0.0393mol) Br_2(6.28g,0.0393mol,2.09cm^3)	$AsCl_3$(35cm^3)	0^{o}C,stirred,both additions quite violent. Mixture stirred 16 hrs. Initial red gel separated into red Filtrate and pale orange solid. (44)	PCl_4^+, BCl_4^-, Arsenic product

TABLE 5.3 CONT'D

PCl_3(10.40g,0.0758mol,6.63cm^3) BBr_3(9.50g,0.0379mol,3.63cm^3) Cl_2	HCl (anhydrous)	Standard method of preparation. White solid isolated. (22)	PCl_4^+, PCl_3Br^+, BCl_4^-
PCl_3(7.85g,0.0571mol,5.03cm^3) BF_3 Cl_2	HCl (anhydrous)	Standard method of preparation. Fuming white solid isolated. (6)	PCl_4^+
PCl_5(3.85g,0.0185mol) BF_3	HCl (anhydrous)	Standard method of preparation. Fuming white solid isolated. (7)	PCl_4^+

(reference no (eg 47) refer to
Raman Spectra File)

3) The reaction of PCl_5 and BCl_3 (2:1 molar ratio) in CH_2Cl_2 and CCl_4. This always gave $PCl_4{}^+BCl_4{}^-$ as the product.

4) The interaction of a solution of PCl_5 in CH_2Cl_2 with $PCl_4{}^+BCl_4{}^-$ suspended in the same solvent. The Raman spectrum of the solid collected was identical to that of a 1:1 mixture of $PCl_4{}^+PCl_6{}^-$ and $PCl_4{}^+BCl_4{}^-$ indicating that no reaction had occurred.

k) The synthesis of some P_2Cl_9Br analogues

During the attempts to synthesize some mixed halide analogues of $(PCl_4{}^+)_2BCl_4{}^-Cl^-$ two preparations whose Raman spectra bore a marked similarity to that of P_2Cl_9Br were performed. The evidence leading to the proposal of these products as P_2Cl_9Br analogues is discussed in some detail in Chapter 3.c but their preparations are listed below.

Preparation A. PCl_3 (22.00g, 0.160 mol, 14.01 cm^3) was dissolved in $AsCl_3$ (20 cm^3) followed by the addition of BCl_3 (9.35g, 0.0795 mol). The mixture was cooled to 0°C and stirred. A dropping funnel containing Br_2 (12.71g, 0.0795 mol, 4.10 cm^3) was prepared and about one third of this was added dropwise to the mixture, resulting in an inhomogenous pale orange precipitate. This was filtered off and dried at the pump. A Raman spectrum indicated predominantly $PCl_4{}^+BCl_4{}^-$ as well as some partially brominated tetrahalophosphorus cations. The remainder of the bromine was slowly added to the filtrate producing a deep orange precipitate which was filtered under N_2, washed with $AsCl_3$ and dried at the pump. (Found: Cl, 63.4%; Br, 16.6%)

Preparation B. PCl_3 (22.00g, 0.160 mol, 14.0 cm^3) was dissolved in $AsCl_3$ (25 cm^3) and BBr_3 (20.08g, 0.080 mol, 7.66 cm^3) was added. Then, after cooling the mixture to 0^oC, Br_2 (12.71g, 0.0795 mol, 4.1 cm^3) was added dropwise and with stirring, a pale orange precipitate resulted and this was stirred (1 day), filtered under N_2, washed with $AsCl_3$ and dried at the pump. (Found: Cl, 75.6%; Br 10.9%)

1. The preparation of mixed chlorobromophosphonium cations: $PCl_nBr_{4-n}{}^+$ $(1 \leqslant n \leqslant 4)$

These ions were usually prepared by the reaction of PCl_3, BCl_3 and Br_2 in either CH_2Cl_2 or anhydrous HCl though occasionlly other reactants were used. This reaction is thoroughly documented in F. J. Ryans' thesis (3) and the experiments are summarized in Table 5.4. The column headed "product" describes the nature of the anion associated with the chlorobromophosphonium cations and the reasons for this are detailed in Chapter 3. The ratios given are of the relative Raman intensities of the totally symmetric stretching mode (a_1) for each cation.

5.10 Preparation of methylhalophosphoranes and some derivatives

a) Methyltetrachlorophosphorane $MePCl_3{}^+Cl^-$

This compound was prepared by the chlorination of methyldichlorophosphine (25,32). $MePCl_2$ (3.96g, 0.0338 mol) was

TABLE 5.4

PREPARATIONS OF CHLOROBROMOPHOSPHONIUM CATIONS $PCl_n Br_{4-n}^+$

Reactants	Solvent	Conditions + Comments	Species observed in Raman Spectrum
PCl_3(3.20g,0.0233mol,2.05cm^3) BCl_3(3.00g,0.0256mol) Br_2(2.34g,0.0146mol,0.74cm^3)	CH_2Cl_2(50cm^3)	0^{o}C,stirred for $\frac{1}{3}$ hr before white precipitate filtered. (Reaction 1)	Single halide $PCl_3Br^+:PCl_2Br_2^+:PClBr_3^+$ = 10:4.4:1.5
PCl_3(3.20g,0.0233mol,2.05cm^3) BCl_3(3.40g,0.0290mol) Br_2(3.90g,0.0244mol,1.26cm^3)	CH_2Cl_2(50cm^3)	0^{o}C,stirred for $\frac{1}{3}$ hr prior to filtration of buff solid. (Reaction 2)	Single halide $PCl_3Br^+:PCl_2Br_2^+:PClBr_3^+$ = 10:10:5.1
BCl_3(5.05g,0.0430mol) Br_2(7.99g,0.050mol,2.58cm^3) PCl_3(5.90g,0.0429mol,3.78cm^3)	HCl (anhydrous)	Standard method of preparation. White solid pumped for $\frac{1}{2}$ hr. (Prep. 1)	Single halide $PCl_3Br^+:PCl_2Br_2^+:PClBr_3^+$ = 10:6.7:2.4
BCl_3(3.64g,0.031mol) PCl_3(7.20g,0.0524mol,4.61cm^3) Br_2(4.26g,0.0266mol,1.37cm^3)	HCl (anhydrous)	Standard method of preparation. Buff solid pumped for $\frac{1}{3}$ hr. (Prep. 2)	Single halide $PCl_3Br^+:PCl_2Br_2^+:PClBr_3^+$ = 10:4.1:2.8 and some polytomic $PCl_3Br^+:PCl_2Br_2^+:PClBr_3^+$ = 10:1:0.2

TABLE 5.4 CONT'D

BCl_3(2.94g,0.0251mol) PCl_3(3.45g,0.0251mol,2.21cm^3) Br_2(4.80g,0.0300mol,1.55cm^3)	HCl (anhydrous)	Standard method of preparation. Buff solid pumped for $\frac{1}{3}$ hr. (Prep. 3)	Mainly single halide $PCl_3Br^+:PCl_2Br_2^+:PClBr_3^+$ = 10:5.6:2.8
Br_2(8.20g,0.0513mol,2.64cm^3) PCl_3(6.95g,0.0506mol,4.45cm^3) BCl_3(6.95g,0.0593mol)	HCl (anhydrous)	Standard method of preparation. White precipitate pumped for $\frac{1}{4}$ hr. (Prep. 4)	Single halide $PCl_3Br^+:PCl_2Br_2^+:PClBr_3^+$ = 7.6:10:8 Polyatomic $PCl_3Br^+:PCl_2Br_2^+:PClBr_3^+$ = 10:3.6:2.5
Br_2(4.65g,0.0290mol,1.50cm^3) PCl_3(4.08g,0.02397mol,2.61cm^3) BCl_3(4.13g,0.0352mol)	HCl (anhydrous)	Standard method of preparation. Pale yellow solid pumped for $\frac{1}{2}$ hr. (Prep. 5)	Single halide $PCl_3Br^+:PCl_2Br_2^+:PClBr_3^+$ = 10:3.6:2.5 and some polyatomic $PCl_3Br^+:PCl_2Br_2^+:PClBr_3^+$ = 10:1:0.5
PCl_3(8.08g,0.0588mol,5.18cm^3) Br_2(9.26g,0.0579mol,2.99cm^3) BCl_3(6.90g,0.0588mol)	HCl (anhydrous)	Standard method of preparation. Buff precipitate pumped for $\frac{1}{4}$ hr. (Prep. 6)	Mainly single halide $PCl_3Br^+:PCl_2Br_2^+:PClBr_3^+$ = 6.3:10:9.5

TABLE 5.4 CONT'D

BCl_3(2.12g,0.018mol) BBr_3(4.52g,0.018mol,1.71cm^3) PCl_5(7.52g,0.036mol)	CH_2Cl_2(105cm^3)	PCl_5 dissolved separately before boron halides added at 0^{o}C. Stirred 10 mins. Buff solid isolated. (ASM 24)	Predominantly single halide PCl_3Br^+:$PCl_2Br_2^+$:$PClBr_3^+$ = 4.1:9.4:10 traces of polyatomic.
PCl_3(8.20g,0.059mol,5.23cm^3) BCl_3(7.29g,0.062mol) Br_2(4.80g,0.030mol,1.55cm^3)	CH_2Cl_2(60cm^3)	0^{o}C,stirred for ½ hr after Br_2 addition. White solid isolated. (ASM 43)	Single halide PCl_4^+:PCl_3Br^+:$PCl_2Br_2^+$:$PClBr_3^+$ = 3.4:8.2:8.4:10
PCl_3(5.96g,0.0436mol,3.82cm^3) BBr_3(11.67g,0.0466mol,4.45cm^3) Br_2(4.03g,0.0250mol,1.30cm^3)	CH_2Cl_2(50cm^3)	0^{o}C,Br_2 dissolved in CH_2Cl_2 before addition. Stirred for ½ hr. Yellow solid isolated.	Single halide $PCl_2Br_2^+$:$PClBr_3^+$:PBr_4^+ = 0.3:5.3:10
PCl_3(4.19g,0.0305mol,2.60cm^3) BCl_3(3.59g,0.0305mol) Br_2(1.70g,0.0106mol,0.55cm^3)	CH_2Cl_2(60cm^3)	0^{o}C,stirred for 10 mins. White solid isolated. (ASM 30)	Single halide PCl_3Br^+:$PCl_2Br_2^+$:$PClBr_3^+$ = 5:8.4:10 and polyatomic PCl_3Br^+:$PCl_2Br_2^+$:$PClBr_3^+$ = 10:5.3:2

TABLE 5.4 CONT'D

BCl_3(3.26g,0.0278mol) PCl_3(3.40g,0.0247mol,2.18cm^3) Br_2(0.20g,0.0013mol,0.065cm^3)	CH_2Cl_2(50cm^3)	Cooled in refridgerator after Br_2 addition for 2 hrs. White solid isolated. (ASM 28)	Polyatomic only PCl_4^+:PCl_3Br^+ = 10:2.2
BCl_3(7.85g,0.0668mol) PCl_3(9.17g,0.0668mol,5.84cm^3) Br_2(9.00g,0.0500mol,2.99cm^3)	CH_2Cl_2(70cm^3)	0^{o}C,stirred for $\frac{1}{4}$ hr after Br_2 addition. Buff solid isolated. (ASM 52)	Predominantly single halide PCl_3Br^+:$PCl_2Br_2^+$:$PClBr_3^+$ = 5:10:8.3 and some polyatomic PCl_3Br^+:$PCl_2Br_2^+$:$PClBr_3^+$ = 10:10:6
PCl_5) PCl_3) rough preparation PBr_3)	CH_2Cl_2	Yellow solid collected after standing for 2 days. (ASM 55)	Single halide PCl_4^+:PCl_3Br^+:$PCl_2Br_2^+$:$PClBr_3^+$ = 10:5.8:1.9:1.7 (some evidence for PCl_6^-)
PCl_5(4.00g,0.0192mol) PCl_3(5.00g,0.0364mol,3.20cm^3) PBr_3(8.26g,0.0305mol,2.90cm^3)	CH_2Cl_2(60cm^3)	Stirred for 2 days. Orange solid collected. (ASM 56)	Single halide only $PClBr_3^+$:PBr_4^+ = 1.7:10

TABLE 5.4 CONT'D

PCl_3(15.70g,0.114mol,10.00cm^3) PBr_3(29.07g,0.107mol,10.20cm^3) Br_2(4.80g,0.0300mol,1.55cm^3)	No solvent	Phosphorus halides stirred together for 1 day. Cooled 0^oC. Br_2 added dropwise and mixture stirred for ½ hr. Orange solid collected. (ASM 58)	Single halide only $PCl_2Br_2^+$:$PClBr_3^+$:PBr_4^+ = 0.2:3.4:10
PCl_3(8.82g,0.0642mol,5.62cm^3) $AlCl_3$(8.56g,0.0642mol) Br_2(10.27g,0.0642mol,3.31cm^3)	CH_2Cl_2(60cm^3)	Br_2 added dropwise to mixture. Stirred ½ hr. White solid isolated. (ASM 26)	Polyatomic only, PCl_4^+:PCl_3Br^+:$PCl_2Br_2^+$:$PClBr_3^+$ = 1.5:6.4:10:6.5

(reference no (eg ASM 30) refer to
Raman Spectrum File)

dissolved in CH_2Cl_2 (30 cm^3) and the mixture stirred. The reaction vessel was cooled to 0^oC and chlorine was slowly admitted to the mixture via a fine bleed. A fairly vigorous reaction occurred and a white precipitate was formed. When the solvent was discoloured to a pale yellow, the chlorine addition was stopped and the system warmed to ambient. The white powder obtained was filtered under N_2, washed with CH_2Cl_2 and dried at the pump. (Found: Cl, 75.3%; Calc. for $MePCl_4$: Cl, 75.5%)

b) Methyldibromophosphine $MePBr_2$

This was required to prepare $MePBr_4$ and was synthesized by the method of Deng (26). $MePCl_2$ (8.58g, 0.0734 mol) was placed in a two-necked round bottomed flask and PBr_3 (19.88g, 0.0734 mol, 7.1 cm^3) was added. The mixture was stirred for about 1 hour and then fractionally distilled. The fraction at 140^oC ($\pm$ 2^oC) was isolated.

c) Methyltetrabromophosphorane $MePBr_3^+ Br^-$

This was prepared by the method of Deng (26). $MePBr_2$ (2.93g, 0.0142 mol) was dissolved in CH_2Cl_2 (30 cm^3) and the mixture cooled in an ice-bath. Then, dropwise, Br_2 (2.28g, 0.0242 mol, 0.74 cm^3) in CH_2Cl_2 (15 cm^3) was added with stirring. A violent reaction followed, necessitating the addition of a further 20 cm^3 of solvent. A yellow precipitate was formed which was washed, filtered and dried in the usual manner. (Found: Br, 87.1%; Calc. for $MePBr_4$: Br, 87.4%)

d) Methyltrichlorophosphonium tetrachloroborate $MePCl_3^+BCl_4^-$

$MePCl_4$ (1.50g, 0.0079 mol) was suspended in CH_2Cl_2 (30 cm^3) and a slight excess of BCl_3 (1.00g, 0.0085 mol) was added with stirring. After about 1 hr the white precipitate was filtered under N_2, washed with CH_2Cl_2 and dried at the pump. (Found: Cl, 81.2%; Calc. for $MePBCl_7$: Cl, 81.3%)

e) Methyltrichlorophosphonium hexachloroantimonate $MePCl_3^+SbCl_6^-$

The procedure of Schmidt (27) was used in the preparation of this compound. $MePCl_4$ (1.50g, 0.0079 mol) was suspended in CH_2Cl_2 (30 cm^3) and to this mixture $SbCl_5$ (2.40g, 0.0080 mol, 1.03 cm^3) was added dropwise, with stirring. After 1 hr the standard filtering, washing and drying routine yielded a pale yellow solid. (Found: Cl, 65.1%; Calc. for $MePSbCl_9$: Cl, 65.5%)

f) Methyltrichlorophosphonium tetrachloroaluminate $MePCl_3^+AlCl_4^-$

This compound was prepared by the method of Dillon et al (12). $MePCl_4$ (1.00g, 0.0053 mol) was suspended in CH_2Cl_2 (50 cm^3) and $AlCl_3$ (0.71g, 0.0053 mol) was added to this with stirring which was continued for 2 hrs. The white solid formed was then filtered under N_2, washed with CH_2Cl_2 and dried at the pump. (Found: Cl, 77.2%; Calc. for $MePAlCl_7$: Cl, 77.4%)

g) Methyltetrabromophosphonium tetrabromoborate $MePBr_3^+BBr_4^-$

This compound was prepared by the method reported by Deng.(26) $MePBr_4$ (o.65g, 0.0018 mol) was suspended in CH_2Cl_2 (20 cm^3) and BBr_3 (0.45g, 0.0018 mol, 0.17 cm^3) was added with stirring. The buff precipitate formed was filtered, washed and dried in the usual manner. (Found: Br, 90.1%; calc, for $MePBBr_7$: Br, 90.7%)

h) Methyltetrabromophosphonium tetrabromoaluminate $MePBr_3^+AlBr_4^-$

$MePBr_4$ (0.53g, 0.0015 mol) was suspended in CH_2Cl_2 (30 cm^3) and $AlBr_3$ (0.39g, 0.0015 mol) was added with stirring. The resultant yellow-brown precipitate was stirred for 1 day to ensure complete reaction, filtered under N_2, washed with CH_2Cl_2 and dried at the pump. (Found: Br, 87.5%, Calc. for $MePAlBr_7$: Br, 88.3%)

i) The methyldichlorophosphine/bromine reaction

This reaction, originally discussed by Deng (26), was performed several times with various ratios of reactants to prepare mixtures of the methylchlorobromophosphonium cations $MePCl_nBr_{n-3}^+$ ($o \leq n \leq 3$) ie $MePCl_3^+$, $MePCl_2Br^+$, $MePClBr_2^+$ and $MePBr_3^+$ in the hope of assigning the resultant Raman spectra. The experiments are detailed in Table 5.5. The results indicated different product ratios and also shifts in Raman fundamentals were apparent, coincident with the presence of

TABLE 5.5

THE $MePCl_2/Br_2$ REACTION

Reactants	Conditions + Comments	Species observed in Raman Spectrum
$MePCl_2$ (7.19g, 0.0672 mol) Br_2 (10.23g, 0.0671 mol)	$40cm^3$ CH_2Cl_2. 0^oC. Br_2 added drop-wise. Stirred for 1½ hrs. White solid isolated. (R1)	Single halide $MePCl_2Br^+ : MePClBr_2^+ : MePBr_3^+ = 10:7.5:2.3$
R1 (1.10g) Br_2 (0.93g, 0.0058 mol, $0.30cm^3$)	$30cm^3$ CH_2Cl_2. Stirred for 3 hrs. Pale orange solid isolated. (R2)	Single halide $MePCl_2Br^+ : MePClBr_2^+ : MePBr_3^+ = 1.9:6.7:10$ Some polyhalide $MePCl_2Br^+ : MePClBr_2^+ : MePBr_3^+ = 6.6:10:8.3$
R1 (0.80g) Br_2 (0.45g, 0.0028 mol, $0.14cm^3$)	$20cm^3$ CH_2Cl_2. Stirred for 2 days. Yellow solid isolated. (R3)	Single halide $MePClBr_2^+ : MePBr_3^+ = 1.6:10$
$MePCl_2$ (3.68g, 0.0314 mol) Br_2 (3.41g, 0.0213 mol, $1.10cm^3$)	$30cm^3$ CH_2Cl_2. 0^oC. Stirred for 10 mins. White solid isolated. (R4)	Single halide $MePCl_3^+ : MePCl_2Br^+ : MePClBr_2^+ : MePBr_3^+ = 7.1:10:10:4.4$

TABLE 5.5 CONT'D

R1 (4.02g) Br_2 (4.65g, 0.0290 mol, 1.50cm^3	30cm^3 CH_2Cl_2. Stirred for 1 week. Orange product isolated. (R8)	Polyhalide $MePCl_2Br^+ : MePClBr_2^+ : MePBr_3^+$ = 6.4:10:6.6
R1 (1.00g) Br_2 (6.20g, 0.0387 mol, 2.00cm^3)	20cm^3 CH_2Cl_2. Stirred for 2 days. Orange solid isolated. (R9)	Single halide $MePCl_2Br^+ : MePClBr_2^+ : MePBr_3^+$ = 6.9:10:5.2 Polyatomic $MePCl_2Br^+ : MePClBr_2^+ : MePBr_3^+$ = 10:6.9:4 Single halide = Polyhalide
R1 (1.75g) Br_2 (1.08g, 0.0068 mol, 0.35cm^3)	30cm^3 CH_2Cl_2. Stirred for 6 days. Orange solid isolated. (R12)	Single halide $MePCl_2Br^+ : MePClBr_2^+ : MePBr_3^+$ = 3.1:9.4:10 Polyhalide $MePCl_2Br^+ : MePClBr_2^+ : MePBr_3^+$ = 8.7:10:5.5 Polyhalide > Single halide
$MePCl_2$ (3.61g, 0.0309 mol) Br_2 (3.10g, 0.0194 mol, 1.00cm^3)	$MePCl_2$ dissolved in 30cm^3 CH_2Cl_2. Br_2 dissolved in 10cm^3 CH_2Cl_2 and added dropwise when mixture cooled to -80°C. Stirred 10 mins. Yellow isolated. (R37)	Single halide $MePCl_2Br^+ : MePClBr_2^+ : MePBr_3^+$ = 10:5.6:1.3

TABLE 5.5 CONT'D

$MePCl_2$ (3.07g, 0.0262 mol) Br_2 (4.18g, 0.0262 mol, 1.35cm^3)	40cm^3 CH_2Cl_2. Stirred for ½ hr. Orange solid isolated. (ASM 35)	Single halide $MePCl_2Br^+$: $MePClBr_2^+$: $MePBr_3^+$ = 10:8.4:3.2
$MePCl_2$ (4.30g, 0.0367 mol) Br_2 (5.89g, 0.0369 mol, 1.90cm^3)	50cm^3 CH_2Cl_2. Stirred for 1½ hrs. Pale yellow solid isolated. (ASM 34)	single halide $MePCl_2Br^+$: $MePClBr_2^+$: $MePBr_3^+$ = 10:8.6:3.2
ASM 34 (2.13g) Br_2 (4.65g, 0.0290 mol, 1.50cm^3)	25cm^3 CH_2Cl_2. Stirred for 12 hrs. Orange solid isolated. (ASM 44)	Single halide $MePCl_2Br^+$: $MePClBr_2^+$: $MePBR_3^+$ = 4.4:10:9.6

(reference no. (eg ASM 44) refer to laboratory Raman Spectra File)

TABLE 5.6

$MePCl_2/Br_2$ REACTION PRODUCTS WITH LEWIS ACIDS

Reactants	Conditions + Comments	Species observed in Raman Spectrum
R4 (0.90g) BCl_3 (3.50g, 0.0298 mol)	30cm^3 CH_2Cl_2. Stirred for 2 hrs. White product isolated. (R6)	Polyatomic $MePCl_2Br^+$: $MePClBr_2^+$: $MePBr_3^+$ = 4.1:8.5:10 (some halide still present)
R1 (0.87g) $SbCl_5$ (1.60g, 0.0059 mol, 0.69cm^3)	35cm^3 CH_2Cl_2. Stirred for 1 day. Pale orange product isolated. (R7)	$SbCl_6^-$ Polyatomic. (Rather obscured by intense anion spectrum)
$MePCl_2$ (2.01g, 0.0172 mol) Br_2 (2.75g, 0.0172 mol, BCl_3 (5.28g, 0.0450 mol)	$MePCl_2$ dissolved in 35 cm^3 CH_2Cl_2. Br_2 added over ½ hr at 0^{o}C. BCl_3 added and mixture stirred 1 day. White solid isolated. (ASM 36)	Polyatomic. $MePCl_2Br^+$: $MePClBr_2^+$: $MePBr_3^+$: 7.3:10:7.0 Halide $MePCl_2Br^+$: $MePClBr^+$: $MePBr_3^+$ = 6.8:8.6:10 (Polyatomic = Halide)
$MePCl_2$ (1.38g, 0.0118 mol) Br_2 (1.86g, 0.0118 mol, 0.88cm^3) BBr_3 (3.10g, 0.0124 mol, 1.17cm^3)	$MePCl_2$ dissolved in 40cm^3 CH_2Cl_2. Br_2 added over ½ hr at 0^{o}C. BBr_3 added and mixture stirred for 1 day. Buff solid isolated. (ASM 42)	BBr_4^- Polyatomic $MePClBr_2^+$: $MePBr_3^+$ = 0.9:10

(reference no. (eg R7) refer to laboratory
Raman Spectra File)

a polyhalide anion. This behaviour, akin to that observed in unmethylated phosphoranes is discussed in Chapter 5. The ratios given are of the relative Raman intensities of the totally symmetric stretching mode (a_1) for each cation.

j) The reaction of $MePCl_2/Br_2$ products with Lewis acids

These experiments are reported in Table 5.6 and were performed principally to see if any shifts in the Raman spectra could be observed when single halide or polyhalide anion was replaced by a polyatomic species.

5.11 PREPARATION OF SOME DIMETHYLHALOPHOSPHORANES AND SOME DERIVATIVES

a) Dimethyltrichlorophosphorane $Me_2PCl_2{}^+Cl^-$

During the course of this work two methods were used to prepare this compound and an example of each is given.

i) The direct chlorination of Me_2PCl (32) - the phosphine (1.59g, 0.0165 mol) was dissolved in CH_2Cl_2 (25 cm^3) and chlorine gas was bubbled through the solution with stirring. The reaction vessel was cooled in an ice-bath and the chlorine flow continued for ¼ hr. until the solution was saturated. The white precipitate that had formed was stirred for a further ¼ hr, collected by inert atmosphere filtration, washed with CH_2Cl_2 and dried at the pump. (Found: Cl, 63.8%; Calc. for Me_2PCl_3: Cl, 63.5%)

ii) The chlorination of tetramethyldiphosphinedisulphide - this method is the one most frequently reported in the literature. (26,28,29). $Me_2P(S)P(S)Me_2$ (7.65g, 0.0412 mol) was suspended in CCl_4 (120 cm^3) and chlorine gas was bubbled through the suspension until it was saturated. This resulted in the formation of a thick yellow precipitate which was then heated to reflux in the dark for 5 hrs. The solvent was now red and the white precipitate was filtered under N_2, washed with CCl_4 and 30/40 petroleum ether and dried at the pump. (Found: Cl, 63.4%; Calc. for Me_2PCl_3: Cl, 63.5%)

b) Dimethyltribromophosphorane $Me_2PBr_2{}^+Br^-$) - attempted preparation.

The method used in this preparation was the bromination of tetramethydiphosphinedisulphide as reported by Deng.(26) $Me_2P(S)P(S)Me_2$ (8.90g, 0.0480 mol) was suspended in CCl_4 (40 cm^3) and Br_2 (37.20g, 0.233 mol, 12.00 cm^3) dissolved in CCl_4 (30 cm^3) was added dropwise with stirring. The mixture was cooled in an ice/salt bath and a stream of dry N_2 was kept flowing during the addition. The solution turned yellow and continued stirring for 2 hrs. resulted in the solution turning red and the deposition of an orange solid. The filtration process isolated a bright orange solid which was washed with CCl_4 and 30/40 petroleum ether and dried at the pump (Found: Br, 81.1%· calc. for Me_2PBr_3: Br, 79.7%; Calc. for Me_2PBr_5: Br, 86.8%) This analysis suggests a mixture of the tri and pentabromides with the former predominating and this is consistent with the Raman spectrum of this preparation.

c) Dimethyldichlorophosphonium tetrachloroborate $Me_2PCl_2^+BCl_4^-$

This compound was prepared by a modification of Dillon's method (12). Me_2PCl_3 (0.68g, 0.0041 mol) was suspended in CH_2Cl_2 (20 cm^3) and an excess of BCl_3 (1.00g, 0.0085 mol) was added with stirring and cooling to 0^oC. A flaky white precipitate settled out and after stirring for ½ hr. this was filtered, washed and dried in the standard way. (Found: Cl, 74.5%; calc. for Me_2PBCl_6: Cl, 74.7%)

d) Dimethyldichlorophosphonium hexachlorophosphate $Me_2PCl_2^+PCl_6^-$

This compound was prepared by the method of Deng (26). Me_2PCl_3 (0.72g, 0.0043 mol) was suspended in CH_2Cl_2 (20 cm^3) and to this was added PCl_5 (0.89g, 0.0043 mol) dissolved in the same solvent. A white precipitate was produced and was stirred for 1 hr. before being filtered under N_2, washed with CH_2Cl_2 and dried at the pump. (Found: Cl, 75.1%; Calc. for $Me_2P_2Cl_8$: Cl, 75.3%)

e) Dimethyldichlorophosphonium hexachlorantimonate $Me_2PCl_2^+SbCl_6^-$

The method of Schmidt was used to prepare this compound (27). Me_2PCl_3 (0.20g, 0.0012 mol) was suspended in CH_2Cl_2 (10 cm^3) and $SbCl_5$ (0.36g, 0.0012 mol, 0.15 cm^3) was added to this. This mixture was stirred for 10 hrs. and then filtered, washed and dried by the standard method to give a white solid. (Found: Cl, 61.0%; Calc. for Me_2PSbCl_8: Cl, 60.8%)

f) Dimethyldichlorophosphonium tetrachloraluminate $Me_2PCl_2^+AlCl_4^-$

Me_2PCl_3 (0.34g, 0.0020 mol) was suspended in CH_2Cl_2 (15 cm^3) and a suspension of $AlCl_3$ (0.27g, 0.0020 mol) in CH_2Cl_2 (10 cm^3) was added to this. The mixture was stirred for 1 day and the resulting pale yellow solution was evaporated to dryness to yield a sticky buff solid. (Found: Cl, 71.2%; Calc. for Me_2PAlCl_6:· Cl, 70.8%) It proved impossible to record a Raman spectrum of the substance because of fluorescence problems.

g) Dimethlydibromophosphonium tetrabromoborate $Me_2PBr_2^+BBr_4^-$

This preparation was based on the method of Deng $^{(26)}$. Me_2PBr_3 (3.66g, 0.0122 mol) was suspended in CH_2Cl_2 (45 cm^3) and a slight excess of BBr_3 (3.17g, 0.0126 mol, 1.20 cm^3) was added to the mixture. After stirring for 10 hrs, inert atmosphere filtration, washing with CH_2Cl_{21} and pumping isolated a buff solid. (Found: Br, 86.8%; Calc. for Me_2PBBr_6: Br, 87.0%)

h) Dimethyldibromophosphoniumtetrabromoaluminate $Me_2PBr_2^+AlBr_4^-$

Me_2PBr_3 (0.95g, 0.0032 mol) was suspended in CH_2Cl_2 (25 cm^3) and $AlBr_3$ (0.84g, 0.0032 mol) dissolved in the same solvent (20 cm^3) was added to this mixture. A red solution was formed and was pumped until solid was precipitated. The mixture was then filtered as usual to yield a buff solid which was dried at the pump. (Found: Br, 83.9%; Calc. for Me_2PAlBr_6: Br, 84.6%)

i) The dimethylchlorophosphine/bromine reaction

This reaction was discussed in Deng's thesis (26). The possible products of this reaction could contain the parent dimethydichloro- and dimethyldibromophosphonium cations as well as the mixed dimethychlorobromophosphonium cation ie $Me_2PCl_nBr_{2-n}{}^+$ ($0 \leq n \leq 2$). The reaction was performed several times and the results are summarised in Table 5.7. The ratios given are of the relative Raman intensities of the totally symmetric stretching (a_1) for each cation.

j) Reaction of Me_2PCl/Br_2 products with Lewis acids

These reactions was performed to investigate any shifts in the Raman spectra of the dimethyldihalophosphonium cations when they are associated with polyatomic anions. Details are given in Table 5.8 and the results are discussed in Chapter 4.

2.12 PREPARATION OF TRIMETHYLHALOPHOSPHORANES AND SOME DERIVATIVES

a) Trimethyldichlorophosphorane $Me_3PCl^+Cl^-$

Me_3P (1.19g, 0.0156 mol) was dissolved in CH_2Cl_2 (20 cm^3) and chlorine was bubbled through the solution with stirring and cooling to 0^oC. A white precipitate was formed and the chlorine addition was continued until the solvent became discoloured. The solution was then stirred for 1½ hrs and filtered in the usual way yielding a fluffy white solid. The Raman spectrum

TABLE 5.7

THE Me_2PCl/Br_2 REACTION

Reactants	Conditions and Comments	Species observed in Raman Spectrum
Me_2PCl (1.59g, 0.0165 mol) Br_2 (2.48g, 0.0155 mol, 0.80cm^3)	Br_2 dissolved in CH_2Cl_2 (10cm^3). Added dropwise to Me_2PCl in CH_2Cl_2 (15cm^3). Stirred for 5 mins. Creamy white solid isolated. (R25)	Halide $Me_2PCl_2^+$: $MePClBr^+$: $Me_2PBr_2^+$ = 3.4:9.4:10
Me_2PCl (1.34g, 0.0139 mol) Br_2 (2.20g, 0.0138 mol, 0.71cm^3)	Br_2 dissolved in CH_2Cl_2 (10cm^3). Added dropwise to Me_2PCl in CH_2Cl_2 (20cm^3). Stirred for 2 hrs. Buff solid isolated. (ASM 39)	Halide $Me_2PCl_2^+$: $MePClBr^+$: $Me_2PBr_2^+$ = 1.5:6.5:10
Me_2PCl (1.57g, 0.0163 mol) Br_2 (3.10g, 0.0194 mol, 1.00cm^3)	Br_2 added neat and dropwise to Me_2PCl in CH_2Cl_2 (20cm^3). Stirred for 1 day. Bright orange solid isolated. (ASM 40)	Halide $Me_2PCl_2^+$: $MePClBr^+$: $Me_2PBr_2^+$ = 0.1:5:10 (estimated)

(reference no (eg R25) refer to laboratory
Raman Spectrum File)

TABLE 5.8

THE Me_2PCl/Br_2 REACTION PRODUCTS WITH LEWIS ACIDS

Reactants	Conditions and Comments	Species observed in Raman Spectrum
ASM 39 (1.80g) BCl_3 (5.33g, 0.0455 mol)	CH_2Cl_2(40cm^3). Stirred for 2 hrs. Buff solid isolated. (ASM 41)	Predominantely polyatomic. $Me_2PClBr^+ : Me_2PBr_2^+ = 6.7:10$ BCl_4^-
Me_2PCl (1.08g, 0.0112 mol) BCl_3 (1.47g, 0.0125 mol) Br_2 (1.08g, 0.0068 mol, 0.35cm^3)	CH_2Cl_2 (40cm^3). Br_2 added neat to mixture. Stirred for 2 days. Pale orange solid isolated. (R 70)	Predominantly polyatomic. $Me_2PClBr^+ : Me_2PBr_2^+ = 8.5:10$

(reference no (eg R 70) refer to laboratory Raman Spectra File) of this indicated an impure product so the solid was suspended in PCl_3 (20 cm^3) and stirred for 15 hrs. Subsequent filtration and pumping resulted in a white solid. (Found: Cl, 48.2%; Calc. for Me_3PCl_2: Cl, 48.3%)

b) Trimethyldibromophosphorane $Me_3PBr^+Br^-$

An extension of Deng's method was used in this preparation (26). Me_3P (1.06g, 0.0139 mol) was dissolved in CH_2Cl_2 (20 cm^3) and the mixture cooled to 0°C. Then Br_2 (2.22g, 0.0139 mol, 0.72 cm^3) dissolved in CH_2Cl_2 (10 cm^3) was added to this dropwise, resulting in an instant yellow precipitate. This was stirred for 1 hr, and filtered in the usual way. The impure product was then suspended in PBr_3 (20 cm^3), stirred for 12 hrs. and then refiltered and pumped to dryness. (Found: Br, 67.5%; Calc. for Me_3PBr_2: Br, 67.5%)

c) Trimethylchlorophosphonium tetrachloroborate $Me_3PCl^+BCl_4^-$

This compound was prepared by the method of Dillon et al (12). Me_3PCl_2 (0.35g, 0.0024 mol) was suspended in CH_2Cl_2 (20 cm^3) and excess BCl_3 (1.50g, 0.0128 mol) was added to this mixture. A white precipitate formed instantly and was stirred for 10 hrs. before filtering, washing and drying by the usual method. (Found: Cl, 66.3%; Calc. for Me_3PBCl_5: Cl, 67.1%)

d) Trimethylchlorophosphonium hexachlorophosphate $Me_3PCl^+PCl_6^-$

Me_3PCl_2 (0.19g, 0.0013 mol) was suspended in CH_2Cl_2 (20 cm^3) and to this was added PCl_5 (0.27g, 0.0013 mol) dissolved in the same solvent (10 cm^3). The mixture was stirred for 2 days and the fine white precipitate was filtered under N_2, washed with CH_2Cl_2 and dried at the pump. (Found: Cl, 69.6%; Calc. for $Me_3P_2Cl_7$: Cl, 69.8%)

e) <u>Trimethylchlorophosphonium hexachloroantimonate</u> $Me_3PCl^+SbCl_6^-$

This compound was prepared by the method of Schmidt (27, 30,31). Me_3PCl_2 (0.20g, 0.0014 mol) was suspended in CH_2Cl_2 (20 cm^3) and a slight excess of $SbCl_5$ (0.42g, 0.0014 mol, 0.18 cm^3) was added to this with stirring. A pale yellow precipitate formed and was filtered under N_2, washed with CH_2Cl_2 and dried at the pump to yield a white solid. (Found: Cl, 55.6%; Calc. for Me_3PSbCl_7: Cl, 55.7%)

f) <u>Trimethylbromophosphonium tetrabromoborate</u> $Me_3PBr^+BBr_4^-$

This compound was prepared by the method of Deng (26) Me_3PBr_2 (0.45g, 0.0019 mol) was suspended in CH_2Cl_2 (20 cm^3) and a slight excess of BBr_3 (0.53g, 0.0021 mol, 0.20 cm^3) was added with stirring. The mixture was stirred for a further 5 hrs. before the buff precipitate was isolated by the standard filtration, washing and pumping techniques. (Found: Br, 81.4%; Calc. for Me_3PBBr_7: Br, 82.1%)

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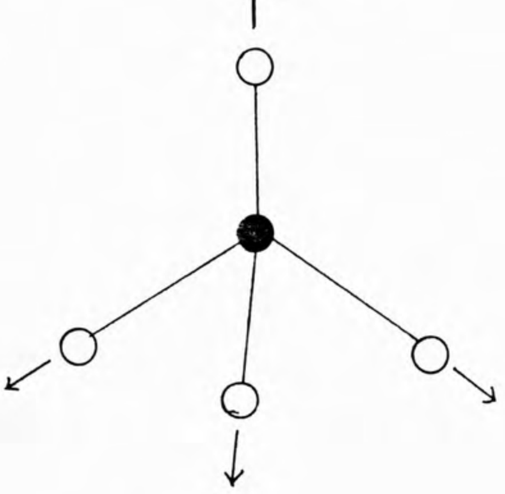
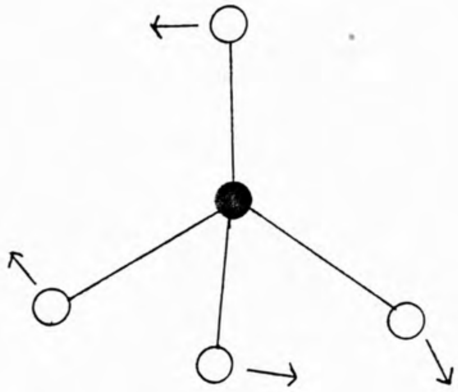
APPENDIX

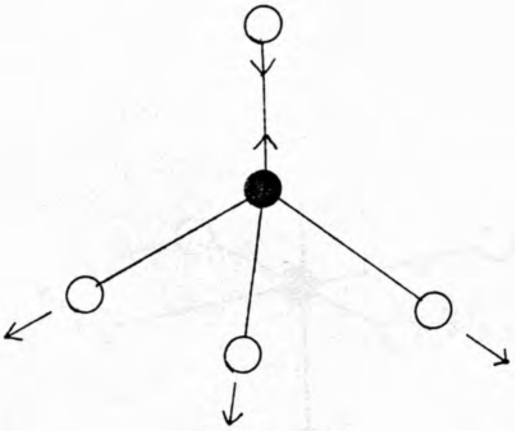
Normal modes of vibration of tetrahedral MX_4 species [T_d]



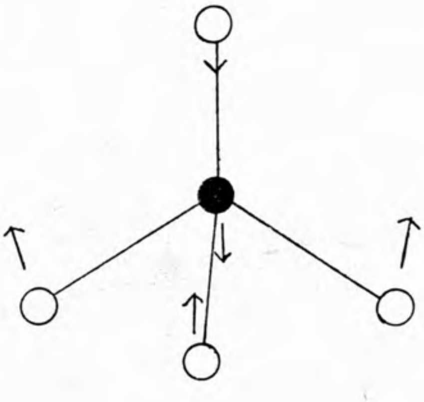
ν_1 A_1



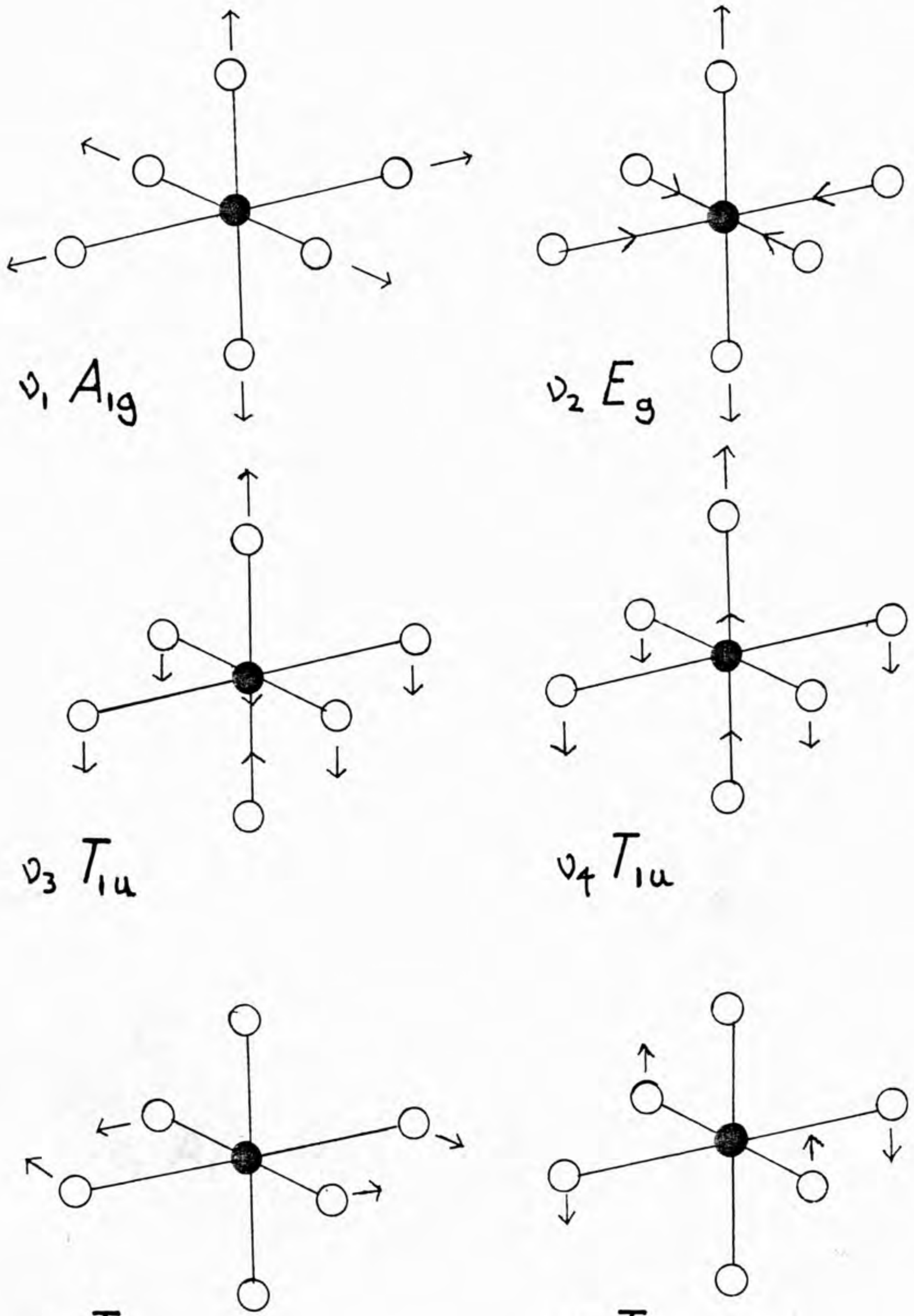
ν_2 E



ν_3 T_2



ν_4 T_2



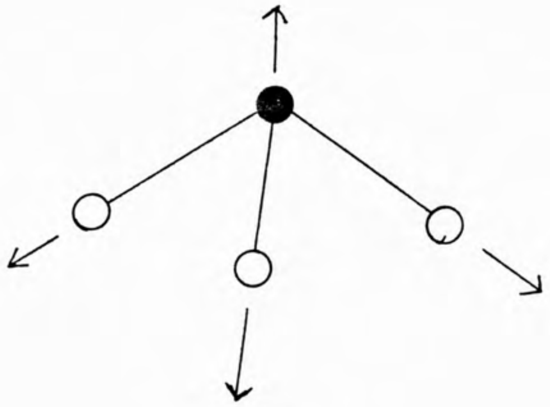
ν_1 A_{1g} ν_2 E_g

ν_3 T_{1u} ν_4 T_{1u}

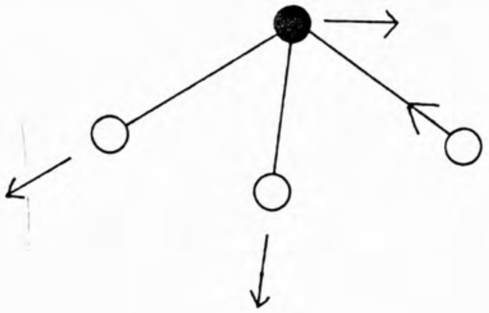
ν_5 T_{2g} ν_6 T_{2u}

Normal modes of vibration of octahedral MX_6 species [O_h]

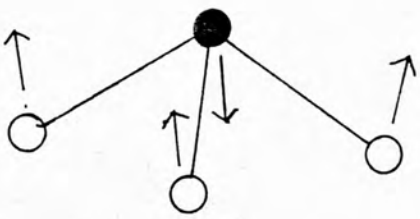
Normal modes of vibration of pyramidal MX_3 species $[C_{3v}]$



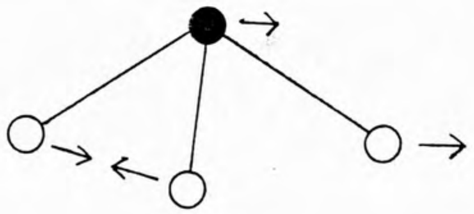
ν_1 A_1



ν_3 E



ν_2 A_1



ν_4 E

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Variable-temperature Raman Spectra of Phosphorus(v) Chloride and Bromide deposited at 15 K

By Arthur Finch, Peter N. Gates, and Alan S. Muir
(*The Bourne Laboratory, Royal Holloway College, University of London, Egham, Surrey* TW20 0EX)

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Summary Variable-temperature (15 K—ambient) Raman spectra of solid PCl_5 and PBr_5 deposited at 15 K from the vapour phase are interpreted in terms of ionic and covalent species.

PHOSPHORUS PENTACHLORIDE exists in a variety of forms: (i) in the solid state as ionic species[1] (*e.g.*, phase II, the normal room-temperature modification, PCl_4^+ PCl_6^- and phase III, the so-called metastable form,[2] $2PCl_4^+PCl_6^-Cl^-$), (ii) in the gas phase as a trigonal-bipyramidal (t.b.p.) species[3,4] and (iii) in solution as either the t.b.p. form or an ionic species depending on the nature of the solvent.[5] The low-temperature infra-red spectrum of PCl_5 condensed from the vapour phase on to a cooled plate at 90 K is consistent with the t.b.p. species; on warming, this irreversibly isomeries to the phase II modification, PCl_4^+ PCl_6^-.[6] The Raman spectrum[7] of a similar low-temperature sample is also consistent with the t.b.p. form.

Phosphorus pentabromide is very different, existing as $PBr_4^+Br^-$ in the solid state,[8,9] but fully dissociated into PBr_3 and Br_2 in a wide variety of solvents.[10] No structural data have been reported on the nature of the vapour-phase species above solid PBr_5, but vapour-pressure measurements[11,12] suggest complete dissociation into PBr_3 and Br_2, at least above 305 K.

In this Communication we present the Raman spectrum of the sublimation products of PBr_5 and contrast this with the very different results obtained for PCl_5.

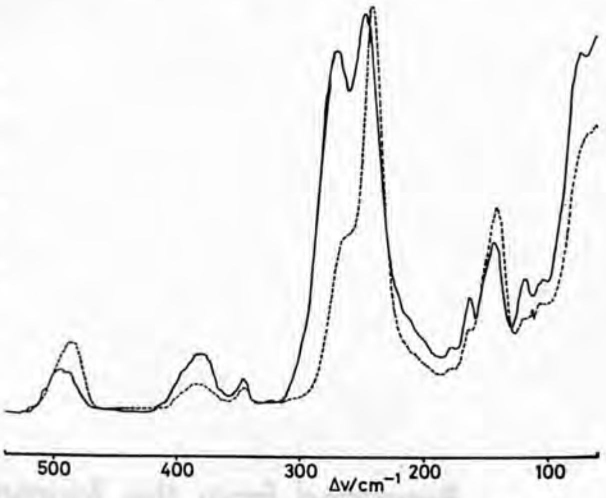

FIGURE 1. Raman spectra of PBr_5 deposited at 15 K (———) and warmed to 125 K (-----).

TABLE. Raman wavenumbers/cm^{-1} of phosphorus pentabromide deposited at 15 K and warmed to 200 K and 230 K.

15 K (disordered $PBr_4^+\,Br_3^-$ and PBr_3)	200 K (disordered $PBr_4^+\,Br^-$)	230 K (lattice-ordered $PBr_4^+\,Br^-$)	Assignment
494 (w,br.)	477 (m,br.)	482 475 } (w) 470	$\nu_3(t_2)$ PBr_4^+
381 (w,br.)			$\nu_1(a_1)$- and $\nu_3(e)$-PBr_3
346 (vw)			?
269 (vs)			$\nu_1(\Sigma_g^+)$ Br_3^-
247 (vs)	233 (s,br.)	229(vs)	$\nu_1(a_1)$ PBr_4^+
177 (vw)			?
163 (m-w)			$\nu_2(a_1)$ PBr_3
144 (m)	144 (s)	141 147 } (m) 157	$\nu_4(t_2)$ PBr_4^+
119 (w)			$\nu_4(e)$ PBr_3
103 (vw)			?
74 (w)	73 (m)	73 (m)	$\nu_2(e)$ PBr_4^+

The Raman spectrum of a sample of PBr_5, sublimed from *ca.* 273 K on to a liquid helium-cooled (Air Products Displex system) copper plate at *ca.* 15 K is shown in Figure 1; wavenumbers are listed in the Table. This spectrum is not interpretable as resulting either from an intact t.b.p. PBr_5 molecule (analogous to the PCl_5 system) or from the simple dissociation products PBr_3 and Br_2. The presence of PBr_3 is confirmed by the positions and intensities of the bands at 119, 163, and 381 cm^{-1}, compared with those from an authentic sample deposited and maintained under the same conditions. However, the characteristic Br–Br stretching mode at 297 cm^{-1} associated with solid-phase elemental Br_2 is *not* observed. The strong band at 269 cm^{-1} is reasonably attributed to a polybromide species such as Br_3^-.[13] Other bands in the spectrum are clearly associated with the PBr_4^+ ion,[14] and we propose the formulation $PBr_4^+Br_3^-$ for this species (see Table for assignments). Comparison of the rather broad bands in this spectrum with those of an authentic sample of $PBr_4^+Br_3^-$[13,15] suggests that the low temperature, vapour-condensed sample consists of randomly orientated crystallites, consistent with the very rapid condensation from the gas phase. On slow warming from 15 K the bands attributed to Br_3^- (269 cm^{-1}) and PBr_3 (119, 163, and 381 cm^{-1}) gradually reduce in intensity (Figure 1) until only the bands due to PBr_4^+ remain. The disappearance of these bands is complete at *ca.* 180 K and presumably results from the solid-phase reaction of PBr_3 and Br_3^-, since vaporisation loss of bromine from the tribromide ion, or of PBr_3 from the solid is unlikely at these low temperatures. At *ca.* 230 K the remaining bands have sharpened to give the characteristic spectrum of polycrystalline PBr_4^+ Br^-, presumably owing to an ordering of the crystal lattice with increasing temperature (Scheme 1 and Figure 2). Preliminary attempts to isolate the vapour-phase products in a matrix of solid argon resulted only in the spectrum of the dissociation products PBr_3 and Br_2 being observed. Hence this work provides no evidence for the existence of the t.b.p. form of PBr_5, consistent with earlier measurements.[10–12]

$$\begin{tikzcd}
2\,\mathrm{PBr_4^+\,Br^-}\,(c) \arrow[rr, harpoon, shift left] & & 2\,\mathrm{PBr_3}\,(g) + 2\,\mathrm{Br_2}\,(g) \arrow[ll, harpoon, shift left] \arrow[dd, "\text{rapid cooling}"] \\
\text{lattice-ordered, 298 K} & & \\
2\,\mathrm{PBr_4^+\,Br^-}\,(c) \arrow[u, "\text{warming}"] & & \mathrm{PBr_4^+\,Br_3^-} + \mathrm{PBr_3}\,(c) \arrow[ll, "\text{warming}"'] \\
\text{lattice-disordered, } ca.\ 180\text{ K} & & \text{lattice-disordered, 15 K}
\end{tikzcd}$$

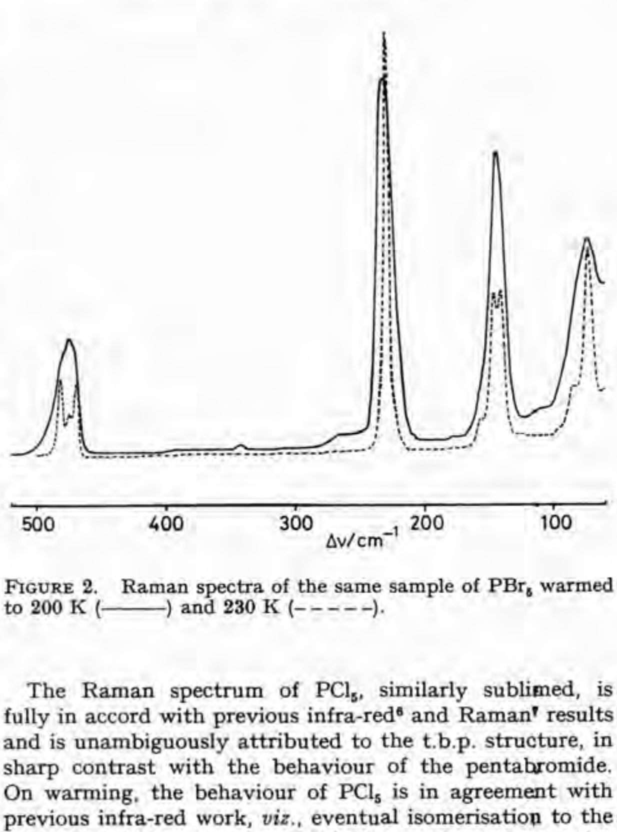

FIGURE 2. Raman spectra of the same sample of PBr_5 warmed to 200 K (———) and 230 K (– – – – –).

The Raman spectrum of PCl_5, similarly sublimed, is fully in accord with previous infra-red[6] and Raman[7] results and is unambiguously attributed to the t.b.p. structure, in sharp contrast with the behaviour of the pentabromide. On warming, the behaviour of PCl_5 is in agreement with previous infra-red work, *viz.*, eventual isomerisation to the ionic phase-II modification, PCl_4^+ PCl_6^-. However, as with the PBr_5 system, a distinct sharpening of the bands occurs at about 130 K, indicative of an ordering of the lattice from the disordered state resulting from the initial vapour deposition (Scheme 2). Interestingly, there is no evidence

$$\begin{tikzcd}
\mathrm{PCl_4^+\,PCl_6^-}\,(c) \arrow[rr, harpoon, shift left] & & {[2\,\mathrm{PCl_5} \rightleftharpoons 2\,\mathrm{PCl_3} + 2\,\mathrm{Cl_2}]}\,(g) \arrow[ll, harpoon, shift left] \arrow[dd, "\text{rapid cooling}"] \\
\text{phase II, 298 K} & & \\
2\,\mathrm{PCl_5}\,(c)\,(\text{t.b.p.}) \arrow[u, "\text{warming}"] & & 2\,\mathrm{PCl_5}\,(c)\,(\text{t.b.p.}) \arrow[ll, "\text{warming}"'] \\
\text{lattice-ordered, } ca.\ 130\text{ K} & & \text{lattice-disordered, 15 K}
\end{tikzcd}$$

for the phase-III modification which might have been expected to form under these conditions.[16] Apparently the production of this phase from vapour deposition procedures is critically dependent on, *inter alia*, apparatus geometry.

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