Journal of Organometallic Chemistry, 70 (1974) 153—227
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Review

VIBRATIONAL SPECTRA OF THE ORGANIC DERIVATIVES OF THE GROUP VB ELEMENTS

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(Received August 22nd, 1973)

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I. INTRODUCTION

Vibrational data have proved very useful in discussions of the structures of organic derivatives of the Group Vb elements. Although summaries have appeared of the vibrational data of these compounds[1,2], they have been far from complete and have been mainly concerned with an analysis of infrared data with little Raman data being included.

In the following review, the infrared and Raman data appearing up to the middle of 1973 are summarized and compared for the organic derivatives of phosphorus, arsenic, antimony and bismuth.

II. NEUTRAL AND CATIONIC ALKYL COMPOUNDS

A. Methyl

Vibrational data have been reported for the $(CH_3)_3M$ derivatives of all of the Group Vb elements. The frequency ranges expected for the modes arising from the methyl groups are summarized in Table 1. The frequency variations of these modes with increasing mass of the central atom[3-7] are illustrated in Figure 1. The $\nu(CH)$ modes are relatively stationary; showing little variation from one metal to another.

Table 1: Vibrational Frequency Ranges (cm^{-1}) Expected for Modes Arising from the Methyl Group[a].

Mode	Frequency Range
ν_a	3050-2850
ν_s	2950-2750
δ_d	1475-1375
δ_s	1350-1100
ρ_r	975-700

a) Throughout this review, the following abbreviations are used to denote the modes of vibrations: ν, stretching; ν_s, symmetric stretching; ν_a, antisymmetric stretching; δ, in-plane bending; π, out-of-plane bending; δ_d, degenerate deformation; δ_s, symmetric deformation; ρ_w, wagging; ρ_r, rocking; ρ_t, twisting. The band intensity is designated by s, strong; m, medium; w, weak; sp, sharp; sh, shoulder; and br, broad. M denotes the Group Vb element. Polarized and depolarized Raman bands are denoted by p and dp, respectively.

The same is true for the δ_d(CH) modes. The δ_s(CH) and ρ_r(CH) modes, however, appear at progressively lower frequencies as the mass of the metal atom increases.

In addition to the various carbon-hydrogen modes, ν(MC) and δ(CMC) modes are expected. The advantage of using both infrared and Raman data for determining structures is illustrated for the $(CH_3)_3M$ compounds. Assuming the methyl groups to be single atoms, the skeletons can form

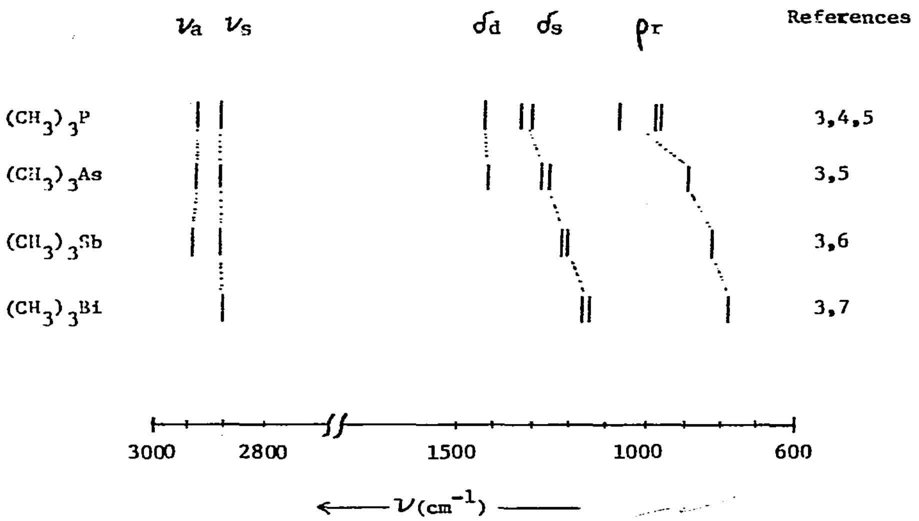


Figure 1: Fundamental methyl mode frequencies of $(CH_3)_3M$ (M=P, As, Sb; Bi).

planar or pyramidal structures. If the skeleton is planar, two ν(MC) modes and one δ(CMC) mode are Raman active and one ν(MC) and two δ(CMC) modes are infrared active. If the skeleton is pyramidal, the two ν(MC) and two δ(CMC) modes are both infrared and Raman active.

It is dangerous, however, to base structural conclusions mainly on the absence of a band for two reasons. The first is that the band of interest may accidentally overlap another band. In $(CH_3)_3Sb$ and $(CH_3)_3Bi$ only one ν(MC) band is observed in the infrared spectrum[8]. If only infrared data were available, one might be tempted to conclude that these two compounds are planar, though they are not. The Raman spectra of these two compounds again show one band in the ν(MC) region. It is therefore concluded that the two ν(MC) modes expected for each compound are accidentally degenerate, due to the relatively heavy mass of the metal atom, which insulates the methyl groups from interacting with one another. As a rule, as the mass of the metal atom increases, the separation of the expected ν(MC) and δ(CMC) modes decreases, till at infinite mass only one ν(MC) and one δ(CMC) peak is observed. The second possible reason for the absence of an expected band might be that its intensity is too low to be detected. For example, the ν_s(MC) mode of a pyramidal $(CH_3)_3M$ skeleton might not be observed in the infrared spectrum for this reason. To describe a situation such as this, in which, though the skeleton is nonplanar, the vibrational spectrum appears to be governed by planar selection rules, the compound is said to be "pseudoplanar". It is difficult to predict the angle required before the symmetric mode becomes observable in the infrared spectrum. This phenomenon appears, in fact, to depend not only on the geometry of the compound but also on the nature of the atoms involved[8]. In addition to data for the trimethyl derivatives, the low frequency infrared and Raman data for $(CH_3)_5Sb$ have been interpreted as showing this compound to have a trigonal bipyramidal skeleton[9].

Vibrational data are also available for several cationic methyl derivatives. The Raman spectra of aqueous solutions of the perchlorate and nitrate salts of $(CH_3)_3Sb^{2+}$ have been interpreted in terms of a planar skeletal structure[10]. Solid state infrared and solution infrared and Raman data have appeared for several halide salts of $(CH_3)_4M^{1+}$ (M=P[4,11,13], As[3];Sb[3,14]). In both the solid state and solution the cations

Table 2: Skeletal Mode Assignments (cm^{-1}) for Methyl Group Vb Derivatives

Compound	Skeletal Symmetry	ν_a(MC)	ν_s(MC)	δ(CMC)	Ref.
$(CH_3)_3P$	C_{3v}	708	653	305 263	3,15,16
$(CD_3)_3P$	C_{3v}	643	596	256 221	16
$(CH_3)_3As$	C_{3v}	583	568	239 223	3,15,16
$(CH_3)_3Sb$	C_{3v}	513	513	188	3,6
$(CD_3)_3Sb$	C_{3v}	472	472	159	17
$(CH_3)_3Bi$	C_{3v}	460	460	171	3,7
$(CH_3)_3Sb^{2+}$	D_{3h}	582	536	166	10
$(CH_3)_4P^{1+}$	T_d	783	649	285 170	11,12
$(CH_3)_4As^{1+}$	T_d	652	590	217	3
$(CH_3)_4Sb^{1+}$	T_d	574	535	178	3
$(CH_3)_5Sb$	D_{3h}	516[a] 456[b]	493[a] 414[b]	239 213[a] 195[b] 108[a]	9

a) Equatorial Mode.

b) Axial Mode.

$(CH_3)_4M^{1+}$ are tetrahedral. Table 2[3,6,7,9-12,15-17] summarizes the low frequency assignments made for neutral and cationic methyl derivatives, while the infrared spectrum of $((CH_3)_4Sb)I$ is illustrated in Figure 2[14].

A limited amount of data are available for compounds with bridging methylene ($-CH_2-$) groups[18-20]. A linear relationship has been found for these compounds between the $\rho_r(CH_2)$

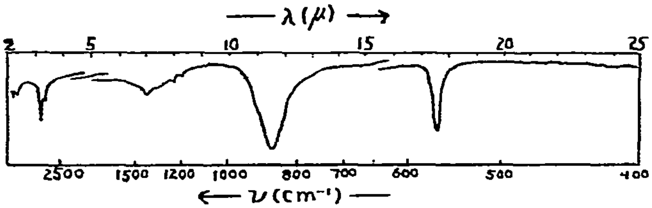


Figure 2: Infrared mull spectrum of $((CH_3)_4Sb)I^{14}$.

mode and the average ν(SbC) frequencies of the Sb_2C group, ν_{av} (ν_{av} = 0.5(ν_a(Sb$_2$C) + ν_s(Sb$_2$C)))^{20}. This relationship is explained in terms of the amount of s-character of the antimony orbitals used in forming antimony-carbon bonds in these compounds. The infrared and Raman spectra of the interesting compound $(CH_3)_3PCH_2$ have been reported and assigned[21]. The ν(PC) mode arising from the methylene-phosphorus bond is assigned at 998 cm^{-1} in the Raman spectrum.

B. Ethyl and Higher Alkyls

The vibrational data for ethyl compounds is not as complete as that discussed for the corresponding methyl derivatives. The vibrational modes expected for the ethyl group include those expected for the carbon-hydrogen bonds of the methyl ($-CH_3$) and methylene ($-CH_2-$) groups. In addition, a methyl torsional mode, carbon-carbon stretching mode and various δ(MCC) modes are expected. In many cases, it has proved difficult to make complete vibrational assignments or establish frequency ranges for the various modes because of one or more of the following reasons: 1) overlapping of the vibrations of the methyl and methylene groups, 2) inter ethyl group coupling (if more than one ethyl group is bonded to a metal atom); 3) intra ethyl group coupling between the modes within a single ethyl group. It is the possibility of intra group coupling which makes previous assignments given for ν(CC) and $\rho_r(CH_3)$ modes somewhat questionable. Recent normal coordinate calculations performed on the series $C_2H_5SiCl_nH_{3-n}$ (n=1-3) have shown severe mixing of the various ethyl modes[22]. For $C_2H_5SiCl_3$, a peak at 1010 cm^{-1} was shown to involve changes of not only the CC bond but also of the HCC, HCH and HCSi angles (and to a lesser extent the SiCC angle); a band at 975 cm^{-1} involved changes in the HCC and SiCH angles and the CC bond and a band at 965 cm^{-1} involved changes of the HCC, SiCH and HCH angles and can only approximately be described as an out of plane $\rho_r(CH_3)$ mode. Bands in the same frequency range have been found in the spectra of $(C_2H_5)_4P^{1+}$ (1044,1003;975 cm^{-1})[11], $(C_2H_5)_3P$ (1041,982;934 cm^{-1})[23] and $(C_2H_5)_3Sb$ (1020,960;935 cm^{-1})[23]. In recognition of the possibility of mixing between the $\rho_r(CH_3)$ and ν(CC) modes, rather than attempting to assign these bands to pure modes, they have been given the designation A, B and C, respectively[11,23]. Besides the three bands already mentioned for $(C_2H_5)_3P$, additional bands have also been observed in this region of the spectrum. It is suggested that they can be due to the analogous A, B and C bands for other possible rotational isomers[23]. Complete vibrational assignments have been made for the highly strained heterocycle phosphiran, $(CH_2)_2PH$[24,25], and its deuterated analogs, phosphiran-1-d_1[24,25] and phosphiran-2,3-d_4[24]. The metal-carbon skeletal assignments made for various ethyl derivatives are given in Table 3[11,23-29]. In Figure 3, the infrared spectrum is illustrated for $(C_2H_5)_5Sb$[30].

Table 3: Skeletal Mode Assignments (cm^{-1}) for Ethyl-Group Vb Derivatives.

Compound	ν_a(MC)	ν_s(MC)	Deformations	Ref.
$(C_2H_5)_3P$	690	619	410-249	23
$(C_2H_5)_3As$	540	570,563		26
$(C_2H_5)_3Sb$	502	502		23,27
$(C_2H_5)_3Bi$	450	450	253, 213, 160, 124	28
$(C_2H_5)_4P^{1+}$	787	590	390-290, 182	11
$(C_2H_5)_4As^{1+}$	613	548	349, 327, 312	29
$(CH_2)_2PH$	657	598		24,25
$(CH_2)_2PD$	643	595		24,25
$(CD_2)_2PH$	597	593		24,25

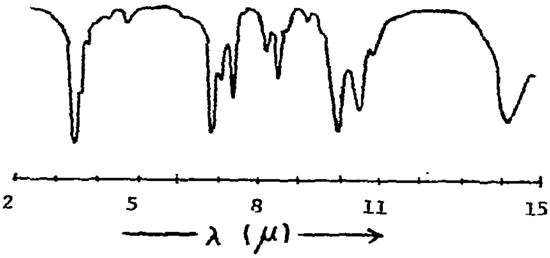


Figure 3: Infrared spectrum of $(C_2H_5)_5Sb^{30}$.

Limited vibrational data have also been presented for the following alkyl derivatives: $(n\text{-}C_4H_9)_3P^{23}$, $(n\text{-}C_3H_7)_3As^{31}$, $(n\text{-}C_4H_9)_3As^{31}$, $(n\text{-}C_5H_{11})_3As^{31}$, $(n\text{-}C_3H_7)_3Sb^{27,32}$, $(i\text{-}C_3H_7)_3Sb^{32}$, $(i\text{-}C_4H_9)_3Sb^{32}$, $(sec\text{-}C_4H_9)_3Sb^{32}$ and $(n\text{-}C_4H_9)_3Sb^{26,27,32}$

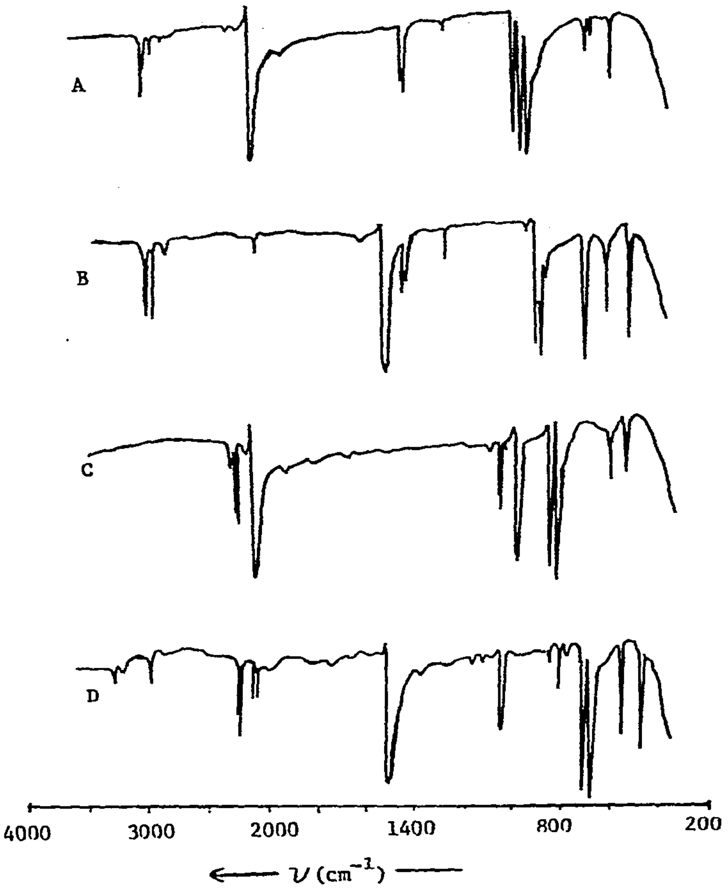


Figure 4: Infrared spectrum of solid films of A) CH_3AsH_2, B) CH_3AsD_2, C) CD_3AsH_2 and D) CD_3AsD_2 at -190°C[33].

III. ALKYL DERIVATIVES

A. Hydrides

The ν(MH) modes of the alkyl Group Vb hydrides give rise to bands of relatively strong intensity in both the infrared and Raman spectra. This is illustrated by the

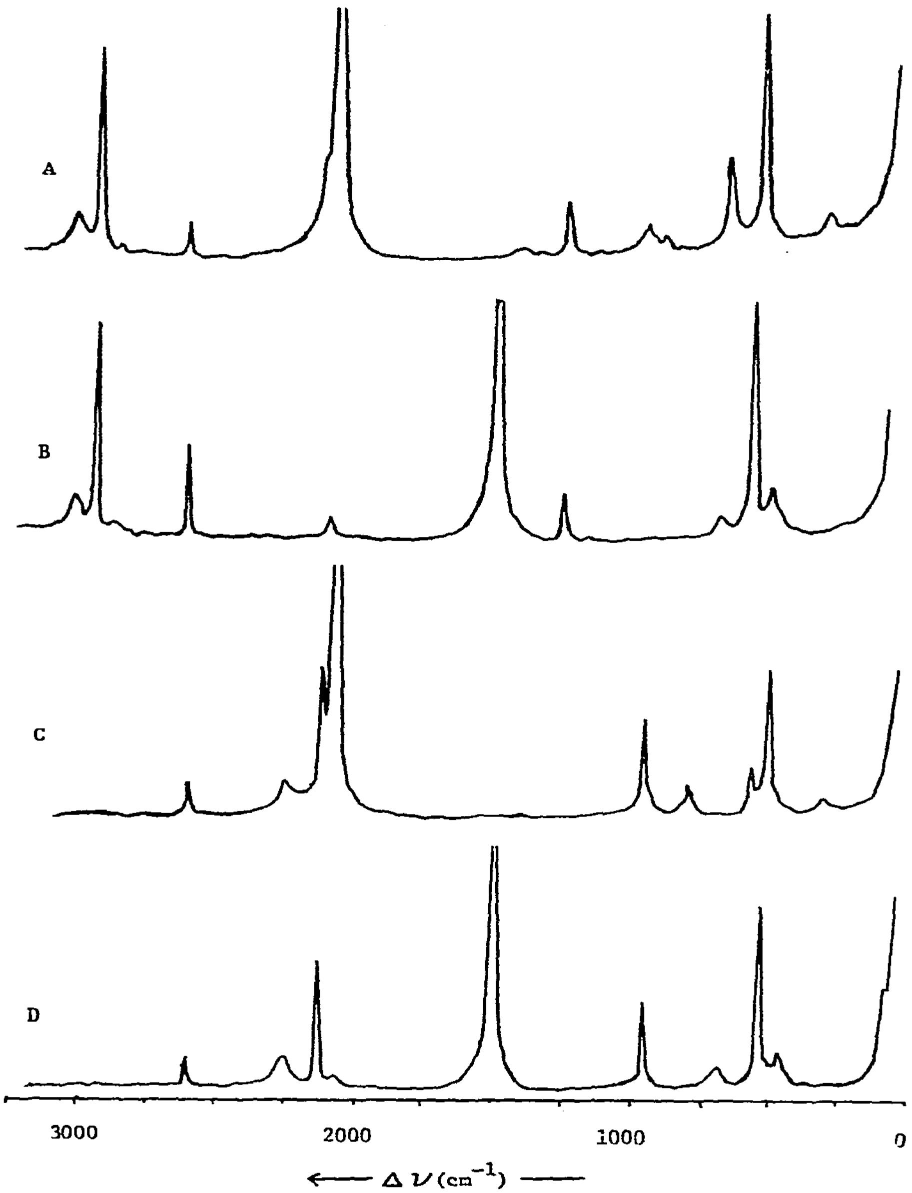


Figure 5: Raman spectrum of liquid A) CH_3AsH_2, B) CH_3AsD_2, C) CD_3AsH_2 and D) CD_3AsD_2 at room temperature[33].

Table 4: Skeletal Stretching Mode Assignments (cm^{-1}) for Trivalent Group Vb Hydrides and Methyl Group Vb Hydrides.

Compound	ν(MH)	ν(MC)	Ref.	Compound	ν(MD)	ν(MC)	Ref.
PH_3	2328 2323	—	35	PD_3	1698 1694	—	35
CH_3PH_2	2309 2305	676	34,36	CH_3PD_2		686	36
$(CH_3)_2PH$	2290	709 665	37				
AsH_3	2123 2116	—	38	AsD_3	1529 1523	—	38
CH_3AsH_2	2102	563	33	CH_3AsD_2	1517	585	33

infrared (Figure 4) and Raman (Figure 5) spectra of CH_3AsH_2 and its deuterated analogs[33]. Although more than one ν(MH) mode is expected for $-MH_2$ skeletons, they have sometimes been observed to be accidentally degenerate. The δ(MH) and δ(MD) modes have been assigned for many compounds but are not as easily identified as the ν(MH) and ν(MD) modes because of the possibility of vibrational coupling. Normal coordinate calculations have shown strong interactions between the $\rho_r(CH_3)$, $\rho_w(PH_2)$ and $\rho_t(PH_2)$ modes of CH_3PH_2[34] and the ν(AsC) and $\rho_w(AsD_2)$ modes of CH_3AsD_2 and CD_3AsD_2[33].

For a given stoichiometry, the ν(MH) frequency decreases within a group as the mass of the metal atom increases. The ν(MH) frequency also decreases as each hydrogen atom is progressively replaced with an alkyl group. The ν(MH), ν(MD) and ν(MC) assignments for the methyl Group Vb hydrides and deuterides are given in Table 4 where they are also compared with the relevant assignments for the corresponding hydrides and deuterides[33-38]. Although phosphiran, $(CH_2)_2PH$, contains a three membered ring, the position of the ν(PH) mode (2291 cm^{-1}) does not appear to be affected by this structural characteristic[24,25] and is not very different from that given for the ν(PH) mode of $(CH_3)_2PH$ (2290 cm^{-1})[37].

Several bands were observed in the ν(PC) region of the Raman spectrum of $(C_2H_5)_2PH$[23,39]. This may indicate the presence of various rotational isomers; six of which are possible[23]. The ν(MH) mode has also been assigned for $(C_2H_5)_2PH$ (2270 cm^{-1})[23,39] $(C_2H_5)_2SbH$ (1835 cm^{-1})[26] and $(n\text{-}C_4H_9)_2SbH$ (1855 cm^{-1})[40]. Additional extensive correlations have been reported for alkyl phosphorus hydrides[41].

B. Halides

The intensity of an infrared active metal-halogen stretching mode increases as the electronegativity of the halogen increases. The intensity of a Raman active metal-halogen stretching mode, however, decreases as the electronegativity of the halogen increases. This is illustrated in Figures 6 and 7 in which the low frequency infrared and Raman spectra, respectively, are illustrated for the series $(CH_3)_3SbX_2$ (X=F,Cl;Br)[42]. It is assumed that the change in relative intensity of the peaks due to the ν(SbC) modes is

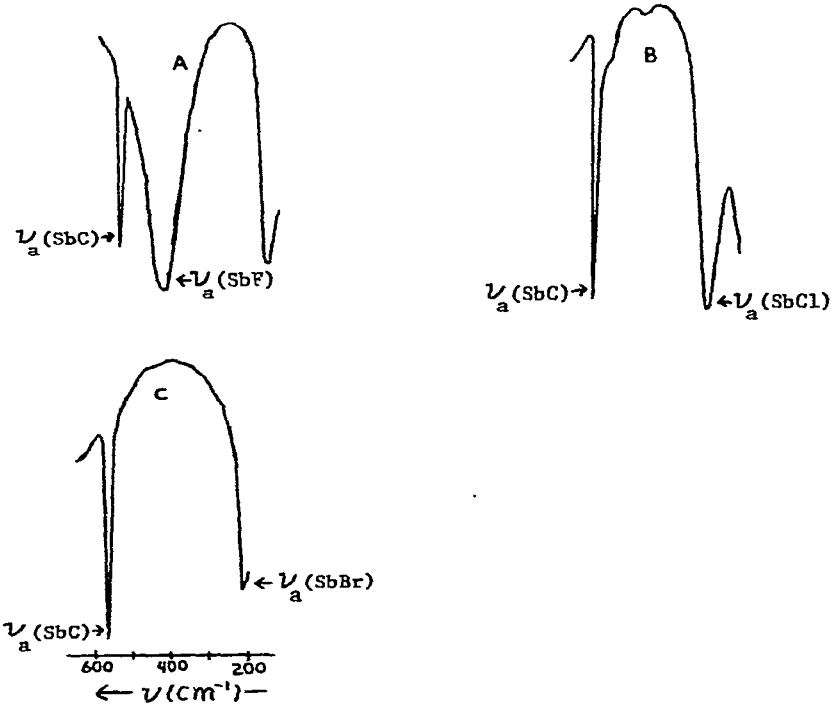


Figure 6: Infrared mull spectra (600-200 cm^{-1}) of A) $(CH_3)_3SbF_2$, B) $(CH_3)_3SbCl_2$ and C) $(CH_3)_3SbBr_2$[42].

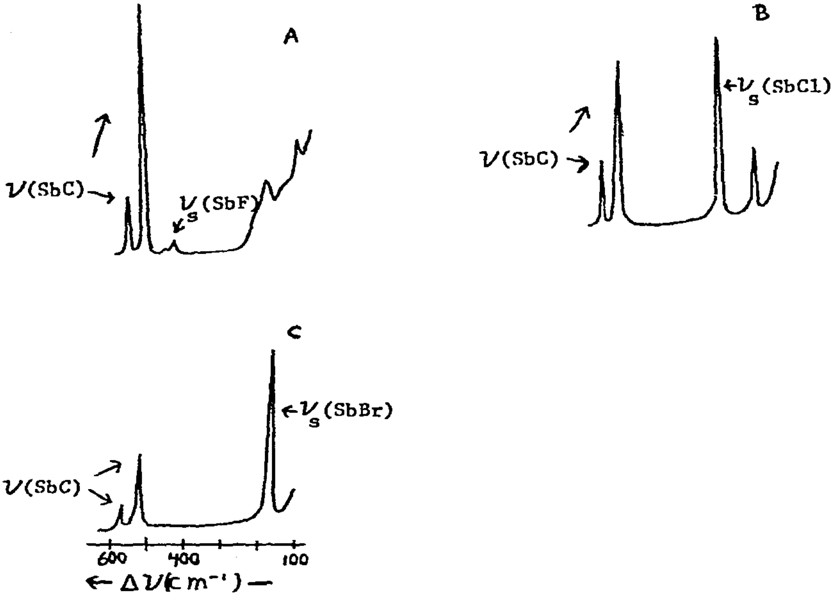


Figure 7: Solid state Raman spectra (600-100 cm^{-1}) of A) $(CH_3)_3SbF_2$, B) $(CH_3)_3SbCl_2$ and C) $(CH_3)_3SbBr_2$[42].

relatively small for these three compounds in either the infrared or Raman spectra. This being the case, the intensity differences between the ν(SbX) modes is very evident, especially in the Raman spectra (Figure 7) in which the ν_s(SbF) mode is very weak in intensity relative to the ν(SbC) modes while the ν_s(SbBr) mode is of relatively strong intensity relative to the ν(SbC) modes and easily observed.

The trivalent alkyl Group Vb halides have pyramidal skeletons. The assignments of the skeletal modes for these compounds are summarized in Table 5[19,23,26,43-55]. Normal coordinate calculations using a generalized valence force field have been reported for the series $(CH_3)_nAsX_{3-n}$ (n=0-3;

Table 5: Skeletal Mode Assignments (cm^{-1}) for Trivalent Alkyl Group Vb Halides

Compound	ν(MC)		ν(MX)		Deformations				Ref.
CH_3PF_2	700		864	806	483	402	335		43
CH_3PFCl	701		797[a]	512[b]					44
CH_3PCl_2	692		487	473	286	237	194		45,46
CH_3PFBr	700		796[a]	413[c]					44
CH_3PBr_2	682								47
CH_3PI_2	675								47
$(CH_3)_2PCl$	710	680	479						48
$C_2H_5PCl_2$	687	671	502	480					23,49
$t\text{-}C_4H_9PF_2$	615		820	814	477	363	288	213	50
$(t\text{-}C_4H_9)_2PF$	615	584	756		485	290	224	202	51
$(t\text{-}C_4H_9)_2PCl$	599	572	508		285	262	179	165	51
CH_3AsCl_2	581		388	364	224	201	160	144	52-54
CH_3AsBr_2	575		278	263	189	134	100		52,54
CH_3AsI_2	563		225	204	176	87			52,54
CD_3AsI_2	520		224	199	162	86			54
$(CH_3)_2AsCl$	581[d]		362		244	211	198		52,53

Table 5 (continued)

$(CH_3)_2AsBr$	582	573		267	236	188	165	52
$(CH_3)_2AsI$	576	567		230	177	95		52,55
$(CH_2)(SbCl_2)_2$			323	297				19
$(n\text{-}C_4H_9)_2SbBr$		507						26

a) phosphorus-fluorine stretching mode.

b) phosphorus-chlorine stretching mode.

c) phosphorus-bromine stretching mode.

d) The $\nu_a(AsC)$ and $\nu_s(AsC)$ modes could not be resulved.

X=Cl,Br)[56]. The arsenic-carbon stretching force constant, K(AsC), increased slightly from $(CH_3)_3As$ to $(CH_3)_2AsX$ to CH_3AsX_2 (X=Cl,Br). It decreased slightly for a given compound when chloride was replaced with bromide. The K(AsX) force constant increased from $(CH_3)_2AsX$ to AsX_3.

The pentavalent alkyl Group Vb halide derivatives can have two types of structures; ionic with tetrahedral $(R_nMX_{4-n})X$ skeletons, or covalent with trigonal bipyramidal (rather than square pyramidal) R_nMX_{5-n} skeletons in which the R groups preferentially occupy equatorial positions. Some compounds can exist with either of these structures, depending on the phase they are in. Therefore, on the basis of infrared and Raman data, CH_3PCl_4 has been reported to have the ionic structure in the solid state but the covalent trigonal bipyramidal structure of C_{2v} symmetry in nonionizing solvents[57]. Also, $(CH_3)_4PF$, which has an ionic solid state structure, exibited bands in the infrared spectrum which might be associated with the molecular compound when the vapor at 10^{-6} torr was condensed on a AgCl disk at -160°C[58]. These bands disappeared on warming the sample. The structures proposed for the known pentavalent alkyl Group Vb halides on the basis of mainly X-ray and vibrational data are summarized in Table 6. Although the data in this Table are far from complete, it appears that the ionic character of these compounds increases 1) as the halide is changed from fluoride to iodide, 2) as the central atom is changed from antimony to phosphorus or 3) as the derivative becomes more highly alkylated. The vibrational assignments made for these and other ionic tetrahedral and covalent trigonal bipyramidal

Table 6: Proposed Skeletal Structures for Known Pentavalent Methyl Group Vb Halide Derivatives.

M	X	CH_3MX_4	$(CH_3)_2MX_3$	$(CH_3)_3MX_2$	$(CH_3)_4MX$
P	I			Tetrahedral	Tetrahedral
	Br			Tetrahedral	Tetrahedral
	Cl	Tetrahedral[a]	Tetrahedral	Tetrahedral	Tetrahedral
	F	Trig-Bipyr.	Trig-Bipyr.	Trig-Bipyr.	Tetrahedral[b]
As	I			Tetrahedral	Tetrahedral
	Br			Tetrahedral	Tetrahedral
	Cl		Trig-Bipyr.	Trig-Bipyr.	Tetrahedral
	F			Trig-Bipyr.	Tetrahedral
Sb	I			Trig-Bipyr.	Tetrahedral
	Br			Trig-Bipyr.	Tetrahedral
	Cl		Trig-Bipyr.	Trig-Bipyr.	Tetrahedral
	F			Trig-Bipyr.	Trig-Bipyr.

a) Though an ionic tetrahedral structure is found in the solid state, a covalent trigonal bipyramidal structure has been found when this compound is dissolved in non-ionizing solvents[57].

b) Though an ionic tetrahedral structure is found in the solid state, a covalent structure has been proposed as a possibility for the vapor state[58].

Table 7: Skeletal Mode Assignments (cm^{-1}) for Ionic, Pentavalent, Tetrahedral Methyl Group Vb Halides.

Compound	ν(MX)	ν(MC)	Deformations	Ref.
$(CH_3PCl_3)Cl$	610 473			13,57
$((CH_3)_2PCl_2)Cl$	580 496	768 743	364 281 168	13
$((CH_3)_3PF)Cl$	668	780 708	476	13
$((CH_3)_3PCl)Cl$	522	773 688	368 302 168	13,59
$((CH_3)_3PBr)Br$	415	766 674	302	59
$((CH_3)_3PI)I$	358	764 666	303	59
$((CH_3)_3AsBr)Br$	299	646 585	281 185	60,61
$((CD_3)_3AsBr)Br$	295	589 540	242 163	60,61
$((CH_3)_3AsI)I$		629 576		61
$((CH_3)_3PCl)SbCl_6$	522	767 684	235	62
$((CH_3)_3AsCl)SbCl_6$	430	649 588	232	62
$((CH_3)_3SbCl)SbCl_6$	382	569 524	230	62

methyl Group Vb halide derivatives are summarized in Table 7[13,57,59-62] and Table 8[42,53,57,60,61,63-68], respectively. Table 7 does not include data for the ionic $((CH_3)_4M)X$ derivatives[3,4,11-14] since they do not possess covalent MX bonds. Data for these compounds are found in Section IIA. In addition to the data summarized above for the methyl derivatives, vibrational assignments have also been presented for the ionic salts $((C_2H_5)_2PX_2)X$ (X=Cl,Br)[13] and the trigonal bipyramidal derivatives $(C_2H_5)_2SbCl_3$ (ν(SbC)=512,483 cm^{-1};ν(SbCl)=329 cm^{-1})[65], $(C_2H_5)_3SbBr_2$ (ν(SbC)=534 cm^{-1})[67], $(n\text{-}C_4H_9)_3SbCl_2$ (ν(SbC)=520,460 cm^{-1})[26] and $(n\text{-}C_4H_9)_3SbBr_2$ (ν(SbC)=512,460 cm^{-1})[26]. An attempt was reported to prepare a trigonal bipyramidal mono(t-butyl)-phosphorus(V) derivative in which, it was hoped, the t-butyl group would occupy an axial rather than equatorial position due to steric factors[57]; due to the compounds instability, however, it could not be characterized.

Normal coordinate calculations reported for $((CH_3)_nPCl_{4-n})Cl$ and $(CH_3)_nSiCl_{4-n}$ (n=0-4) show the K(MC) and K(MCl) force constants of the phosphorus derivatives to be larger than the corresponding force constants of the silicon derivatives[13]. Normal coordinate calculations have also been reported for $(CH_3)_3AsCl_2$, $((CH_3)_3AsBr)Br$ and their deuterated analogs[60], and for $(CH_3)_3SbF_2$[42], $(CH_3)_3SbCl_2$[42,66] and $(CH_3)_3SbBr_2$[42,66]. Vibrational data have also been reported for several organo phosphonic and thiophosphonic fluorides, chlorides and bromides[49,50,69-72].

C. Pseudohalides

The appearance of a strong intensity pseudohalide

Table 8: Skeletal Mode Assignments (cm^{-1}) for Pentavalent Trigonal Bipyramidal Methyl Group Vb Halides.

Compound	$\nu(MX)_{equat.}$		$\nu(MX)_{axial}$		$\nu(MC)$		Deformations						Ref.
CH_3PF_4	1009	932	843	596	725		536	507	412	397	179		63
CH_3PCl_4	567	441	382^{a} 361^{a}	288	743		278	271	251	178	141		57
$(CH_3)_2PF_3$	836		755	540	779	675	496	471	459	401	340	184	64
$(CH_3)_2AsCl_3$	413		315 302	278	581								53
$(CH_3)_2SbCl_3$	342				567	504							65
$(CH_3)_3PF_2$			670	501	778	647	422	392	367	190			64
$(CH_3)_3AsF_2$			525		662								61
$(CH_3)_3AsCl_2$			312	260	642	563							60,61
$(CD_3)_3AsCl_2$			291	258	599	527							60,61
$(CH_3)_3SbF_2$			480	465	590	546	245	220	200	158			42
$(CH_3)_3SbCl_2$			288	266	571	522	210	193	164	118			42,66
$(CH_3)_3SbBr_2$			210	164	565	514	177	148	90				42,66,67
$(CD_3)_3SbBr_2$			207	167	521	473	165	135	88				66,67
$(CH_3)_3SbI_2$					554								67
$(CH_3)_4SbF$			385		568^{b} 508^{c}	530^{b}	250	200	143				68

a) The two bands are attributed to Fermi resonance.
b) Equatorial $\nu(SbC)$ mode.
c) Axial $\nu(SbC)$ mode.

stretching band in the infrared spectrum from ca. 2300-2000 cm^{-1} is evidence for the presence of a pseudohalide ligand. The Raman active pseudohalide stretching modes are less useful since they can give rise to strong or weak intensity peaks. The infrared and Raman spectra of tetramethylantimony azide in the solid state and CH_2Cl_2 solution indicate the presence of partly distorted tetrahedral $(CH_3)_4Sb^{1+}$ cations ($\nu_a(SbC)=575\ cm^{-1}, \nu_s(SbC)=537\ cm^{-1}$) and N_3^{1-} anions ($\nu_a(N_3)=2024\ cm^{-1}, \nu_s(N_3)=1329\ cm^{-1}; \delta(N_3)=631\ cm^{-1}$)[73]. Similar structures have been proposed for $((CH_3)_4Sb)NCS$ with the frequencies of the NCS modes ($\nu(CN)=2064\ cm^{-1}, \nu(CS)=748\ cm^{-1}; \delta(NCS)=475\ cm^{-1}$)[73] similar to those found for KNCS ($\nu(CN)=2053\ cm^{-1}, \nu(CS)=749\ cm^{-1}; \delta(NCS)=484,470\ cm^{-1}$)[74] and for $((CH_3)_4Sb)CN$ in which the $\nu(CN)$ frequency was assigned at 2066 cm^{-1} in the solid state infrared and Raman spectra[73]. Data have also appeared for alkyl derivatives with covalently bonded N_3[75-78], NCO[78] and NCS[42,79] groups. For $(CH_3)_3Sb(NCO)_2$ it is concluded that the NCO group is bonded through the nitrogen atom to give an isofulminate structure[78]. Although the NCS groups in $(CH_3)_3As(NCS)_2$[79] and $(CH_3)_3Sb(NCS)_2$[42,79] are bonded through the nitrogen atom to produce isothiocyanate structures, in $(CH_3)_2BiSCN$ it is proposed that the NCS group bonds through the sulfur atom to give a thiocyanate structure[79]. Selected vibrational assignments for covalent alkyl Group Vb pseudohalide derivatives are presented in Table 9[42,75-79].

D. Oxides, Chalconides, Oxo-Acid Salts and Related Derivatives

In the compounds $(alkyl)_3MO$ (M=P,As;Sb) the MO bond is

Table 9: Selected Vibrational Assignments (cm^{-1}) for Alkyl Group Vb Pseudohalides.

Compound	$\nu_a(XYZ)$	$\nu_s(XYZ)$	$\delta(XYZ)$	$\nu(MN)$	$\nu(MC)$	Ref.
$(CH_3)_2AsN_3$	2081	1257	680	442	602 585	75,76
$(C_2H_5)_2AsN_3$	2082	1256	673	443	574 541	75,76
$(CH_3)_3As(N_3)_2$	2050	1268	665	345	640 594	77
$(CH_3)_3Sb(N_3)_2$	2064	1285	658	358	568 522	77,78
$(CH_3)_3Sb(NCO)_2$	2200		620	325		78
$(CH_3)_3As(NCS)_2$	2040	841	489 475			79
$(CH_3)_3Sb(NCS)_2$	2045	843	492 482	268	585 535	42,79
$(CH_3)_2BiSCN$	2110	795	450 440			79

Table 10: Calculated Frequency Ranges (cm^{-1}) and Observed Frequencies (cm^{-1}) for $(Alkyl)_3MO$ Derivatives.

	$R_3PO^{\underline{a},\underline{b}}$		$R_3AsO^{\underline{a},\underline{c}}$		$R_3SbO^{\underline{d}}$	
	$\nu(P=O)$	$\nu(P-O)$	$\nu(As=O)$	$\nu(As-O)$	$\nu(Sb=O)$	$\nu(Sb-O)$
R	1175	840	965	695	803	550
CH_3	1148		868			
C_2H_5	1166		885		678	
$n-C_3H_7$	1172		888		650	
$n-C_4H_9$	1169		892		650	
$n-C_5H_{11}$					650	

a) Frequency range calculated using MO bond length from Ref.81.

b) Data $(CH_3)_3PO$ from Ref. 81 and Ref. 82; that for $(C_2H_5)_3PO$, $(n-C_3H_7)_3PO$ and $(n-C_4H_9)_3PO$ from Refs. 83, 84 and 85, respectively.

c) Data for $(CH_3)_3AsO$ from Ref. 81; data for other R_3AsO compounds from Ref. 86.

d) Frequency range and assignments for R_3SbO compounds from Ref. 87.

considered to have a bond order greater than one because of donation of the oxygen p electrons into the empty d orbitals of phosphorus , arsenic or antimony. Using Gordy's rule, which relates the force constant of a diatomic system to its bond order, bond length and the electronegativity of the constituent atoms, a force constant can be obtained for an isolated MO bond, assuming the bond order to be either one or two. These data can then be substituted into the harmonic oscillator equation to determine the approximate frequency range that can be expected for the ν(MO) mode. Ranges calculated for the ν(MO) frequencies, together with assignments made for specific alkyl derivatives are compared in Table 10[81-87]. Normal coordinate analyses have been reported for $(CH_3)_3PO$ and $(CH_3)_3AsO$[81]. Using the K(MO) force constants from these calculations and Gordy's rule, the PO and AsO bond orders were calculated to be 1.96 and 1.60, respectively. In Figure 8, the infrared and Raman spectra are illustrated for $(CH_3)_3PO$ and $(CH_3)_3AsO$[81]. In addition to the bands listed in Table 10 and assigned to the ν(SbO) mode in the $(alkyl)_3SbO$ derivatives, additional bands at 478 cm^{-1} for $(C_2H_5)_3SbO$ and 470 cm^{-1} for the other $(alkyl)_3SbO$ derivatives appeared in the infrared spectra of carbon tetrachloride solutions of these compounds, and were attributed to ν(SbO) modes arising from molecular association of the $(alkyl)_3SbO$ molecules[87]. The fact that $(C_2H_5)_3SbO$ is monomeric in chloroform is attributed to an association of the type $(C_2H_5)_3Sb\text{-}O\cdots HCCl_3$ which can not take place in carbon tetrachloride[87]. The ν(MO) frequencies of trialkyl phosphorus , arsenic and antimony oxides have been correlated with an expression involving the total mass of the molecule and the masses and electronegativities of oxygen and phosphorus , arsenic or antimony[88]. The ν_a(SbO) mode of the Sb-O-Sb unit in the covalent compounds $((CH_3)_3SbX)_2O$ (X=Cl,Br;NO_3) and

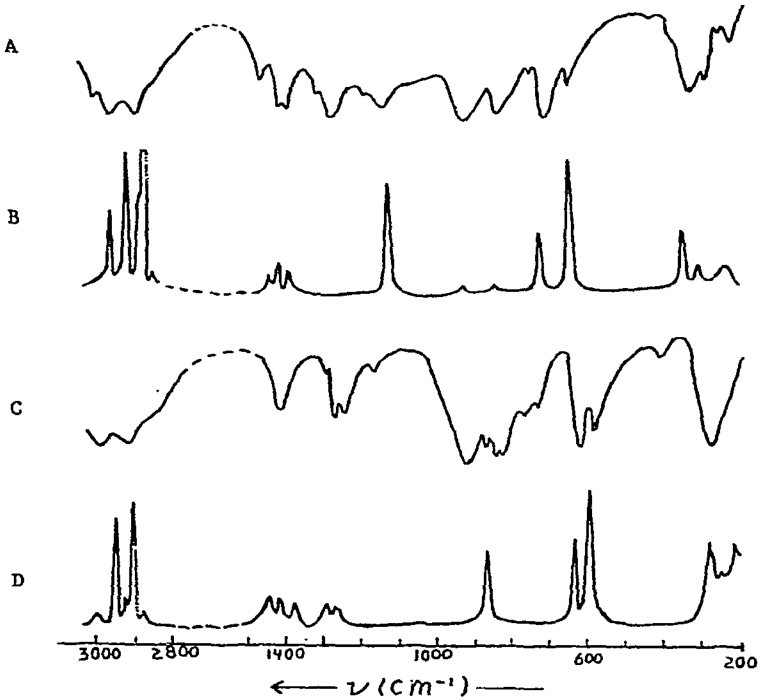


Figure 8: The A) infrared and B) Raman spectra of $(CH_3)_3PO$, and C) infrared and D) Raman spectra of $(CH_3)_3AsO$[81].

$((CH_3)_3Sb)_2OX$ ($X=SO_4, SeO_4, CrO_4; C_2O_4$) has been assigned to an infrared band in the region 790-775 cm^{-1} [14,67,89]. A covalent structure is found for $(CH_3)_3Sb(NO_3)_2$ (with the $\nu(SbO)$ modes assigned at *ca.* 275 cm^{-1} [42]) and $(CH_3)_3SbX$ ($X=SO_4$[67], SeO_4[89]). Although originally formulated as an ionic compound[67], more recently it has been suggested on the basis of infrared data that $((CH_3)_3Sb(ClO_4))_2O$ has a covalent pentacoordinate structure[90].

Complete infrared and Raman analyses have been reported for the aqueous solutions of phosphonic acid, $CH_3PO_3H_2$[91], and

Table 11: Selected Vibrational Assignments (cm^{-1}) of Aqueous Solutions of Methyl Phosphonic Acid, its Mono and Dibasic Anions and the Dimethyl Phosphonic Acid Anion.

Mode	$CH_3PO_3H_2$[a]		$CH_3PO_3H^{1-}$ [a]	$CH_3PO_3{}^{2-}$ [b]	$CD_3PO_3{}^{2-}$ [c]	$(CH_3)_2PO_2{}^{1-}$ [d]
	80% soln.	20% soln.				
$\nu(OH)$	2900 2100		2700 2200	---- ----	---- ----	---- ----
$\delta(OH)$		1250	1250	----	----	----
$\nu(P{=}O)$	1140	1170	----	----	----	----
$\nu_a(PO)$	----	----	1150	1050	1060	1128
$\nu_s(PO)$	----	----	1060	972	969	1040
$\nu(P\text{-}OH)$	1005 950	1005 950	925	---- ----	---- ----	---- ----
$\nu(PC)$	758	760	763	750	720	738 700
$\delta(PO_3)$	492 443	493 446	507 462	522 498	510 495	315[e]
$\rho(PO_3)$	330	325	320	336	320	275[f]

a) Ref. 91.
b) Refs. 91 and 92.
c) Ref. 92.
d) Ref. 93
e) C_2PO_2 twisting mode.
f) C_2PO_2 deformation mode.

its mono[91] and dibasic[91,92] anions, and the dimethyl phosphinic acid anion, $(CH_3)_2PO_2^{1-}$ [93]. Selected vibrational data for these compounds are compared in Table 11[91-93]. In the region from 3000-1500 cm^{-1} of the infrared spectrum, hydrogen bonded compounds with the P(=O)OH grouping give rise, in general, to three characteristic absorptions[94]. For $CH_3PO_3H^{1-}$ only two of these bands have been observed as shoulders on the solvent absorptions[91]. The same two bands are observed in the infrared spectrum of $CH_3PO_3H_2$ with the third observed as a shoulder on the high frequency side of the water absorption at 1640 cm^{-1} [91]. One interpretation of these results is that the bands arise from strong Fermi resonance of the ν(OH) mode and twice the OH bending modes[95]. The ν(P=O) mode in the infrared spectrum of $CH_3PO_3H_2$ shifts to higher frequencies and becomes sharper as the concentration of this compound in water decreases[91]. This change is attributed to hydrogen-bonding effects. In high concentrations the most probable interaction is between $CH_3PO_3H_2$ and other acid molecules; in dilute solutions the most probable type of interaction is between $CH_3PO_3H_2$ and water molecules. Normal coordinate calculations for $CH_3PO_3H_2$, $CH_3PO_3H^{1-}$ and $CH_3PO_3^{2-}$ show the extent of coupling between the internal modes of each of these compounds[96]. The coupling is most severe for the ν(PC), ν(POH) and ν(PO) modes from ca. 1060 to 750 cm^{-1}. It has been suggested[91] that compounds of the type $Na_2(alkylPO_3)$ can be distinguished from $Na((alkyl)_2PO_2)$ type compounds by the fact that the ν_a(PO) and ν_s(PO) modes of the former are observed at ca. 1100 and 1000 cm^{-1}, respectively, while the corresponding modes of the latter are observed at ca. 1150 and 1050, respectively. Infrared data indicate a tetrahedral ionic structure for the compounds $((CH_3)_3AsOH)X$ ($X=NO_3,ClO_4;HSO_4$) and a covalent trigonal bipyramidal structure for $(CH_3)_3AsOHCl$; in the same study, however, the structures of $(CH_3)_3AsOHBr$ and $(CH_3)_3AsODBr$ could not be determined[61]. The infrared spectra of $(CH_3)_4SbOH$ as a mull indicates it to have a covalent trigonal bipyramidal structure with the OH group in an axial position[68]. The $\nu_a(SbC)$ mode ($566\ cm^{-1}$) has been assigned for $(CH_3)_3Sb(OH)_2$[67].

As was true for the corresponding oxygen compounds, the MS bond in the derivatives $(alkyl)_3MS$ ($M=P,As;Sb$) has double bond character due to overlap of the filled sulfur p orbitals with the empty d orbitals of the central atom, M. The assignments given for the $\nu(MS)$ modes of several trialkyl sulfides are summarized in Table 12[31,87,97-99]. The $\nu(MS)$ assignments have been correlated in a linear relationship involving the total mass of the compound and the mass and electronegativity of the central atom, M and the sulfur atom[88]. The crystal structure of $((C_2H_5)_2P(S))_2$ shows it to have a trans structure in which there is a phosphorus-phosphorus bond and the phosphorus atoms are equivalent with two ethyl groups and a sulfur atom bonded to each[100]. The infrared and Raman spectra of this compound have been interpreted in terms of this structure for not only the solid state but also the liquid state and CS_2 and cyclohexane solutions[101]. A similar structure has been proposed for $((CH_3)_2P(S))_2$[102,103]. The solid state infrared spectrum and solution infrared and NMR spectra of $(CH_3)_4As_2S_2$ show it

Table 12: Assignments (cm^{-1}) of ν(MS) Modes for Several Trialkyl Group Vb Sulfides.

R	ν(PS)[a]	ν(AsS)[b]	ν(SbS)[c]
CH_3	567	473	431
C_2H_5	552	476	439
n-C_3H_7	596,583	487,485	439
n-C_4H_9	596	487	440
n-C_5H_{11}	599,588	434	438

a) Data for $(CH_3)_3PS$ from Refs. 98 and 99.; remaining data from Ref. 99.

b) Data from Ref. 31.

c) Data from Refs. 87 and/or 97.

to have a different structure from that of the corresponding phosphorus derivative[104]. In solution, the following equilibrium has been proposed:

$$(CH_3)_2\underset{\underset{S}{\|}}{As}SAs(CH_3)_2 \rightleftharpoons (CH_3)_2AsSSAs(CH_3)_2$$

I II

As the temperature of the solution is raised, the equilibrium is shifted to the right. This is noted in Figure 9 where the solution infrared spectrum is illustrated at three different temperatures. As the temperature is raised, the intensity of the peak assigned to the ν(As=S) mode (488 cm^{-1}) decreases while those assigned to the ν(AsS) modes (399 and 365 cm^{-1})

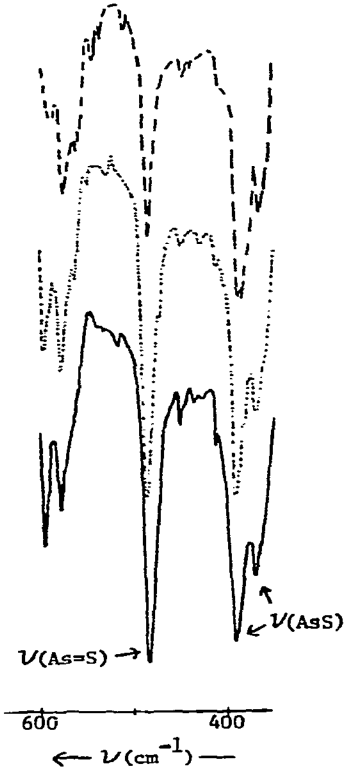


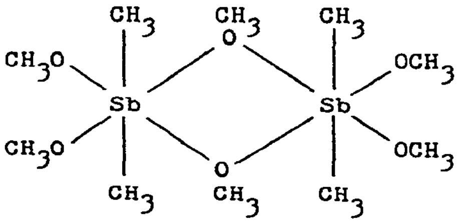
Figure 9: Temperature dependence of the infrared spectrum of $(CH_3)_4As_2S_2$ in carbon tetrachloride and 1,1,2,2, tetrachloroethane at 30°C (——), 60°C (······) and 75°C (---)[104].

increase in intensity. In the solid state it is concluded that species I is present. The ν(AsS) assignment given for CH_3AsS (565 cm^{-1}) together with molecular weight measurements in bromomethane suggest that this compound consists of $(CH_3AsS)_n$ aggregates (where n equals <u>ca</u>. 3.23)[31]. The position of the ν(MX) modes for the derivatives $(alkyl)_3MX$

(M=P,As,Sb;X=Se,Te)[87,88,105,106] have been interpreted in terms of some degree of multiple bonding between the Group Vb element and the selenium or tellurium atoms.

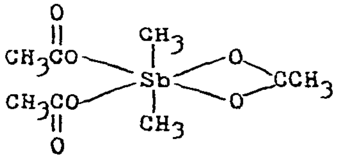
E. Alkoxides, Carboxylates and Chelates

The complex infrared spectrum of $(CH_3)_4POCH_3$ seems to rule out the possibility of an ionic $((CH_3)_4P)OCH_3$ structure[107]. Using vibrational data, covalent trigonal bipyramidal structures have been found for $(CH_3)_4SbOR$ (R=CH_3, C_2H_5, i-C_3H_7; t-C_4H_9)[68]. On the basis of the solid state Raman spectrum and benzene solution NMR spectrum, a dimeric structure with both terminal and bridging methoxy groups has been proposed for $(CH_3)_2Sb(OCH_3)_3$ in both the solid state



and concentrated solutions[108].

Both monodentate and chelating carboxylate groups are found in methyl-antimony carboxylates. The vibrational spectra of the melt and CCl_4 solutions of $(CH_3)_4Sb(OOCCH_3)$ suggest the presence of a monodentate ester like acetate group with a pentacoordinate trigonal bipyramidal structure about the antimony atom[73]. For the same compound in the solid state, however, the acetate group becomes chelating (ν_a(CO)=1590 cm^{-1}, ν_s(CO)=1405 cm^{-1}) to produce a hexacoordinate octahedral structure[73]. Similar results have been reported for tetramethylantimony formate, trifluoroacetate, trichloroacetate, propionate, pivalate and benzoate[73]. The vibrational spectra of $(CH_3)_3Sb(OOCR)_2$ ($R=H,CH_3,C_2H_5,n-C_3H_7;$ C_6H_5) indicate the presence of a trigonal bipyramidal structure with the monodentate carboxylates in the axial positions[14]. From the solid state infrared spectrum of $(CH_3)_3Sb(OOCCH_3)_2$ the ν(C=O) modes were assigned at 1637 and 1600 cm^{-1} and the ν(CO) modes at 1287 and 1274 cm^{-1} [14]. The ν(SbO) modes for $(CH_3)_3Sb(OOCCH_3)_2$both appear at <u>ca</u>. 279 cm^{-1} as confirmed by the fact that this band shifts to 268 cm^{-1} when the acetate groups are deuterated[42]. Molecular weight and conductance measurements, and solid state and $CHCl_3$ and CCl_4 solution infrared data have been reported for several trimethylantimony derivatives of fluoro-, chloro-, bromo- and cyanoacetic acids[109]. They are all pentacoordinate compounds with a linear relationship being found between the ν(CO) frequencies of these compounds and the pK or Taft σ^* constants for the parent acids. Based on infrared and Raman data, an octahedral structure with two monodentate and one chelating acetate groups has been proposed for $(CH_3)_2Sb(OOCCH_3)_3$[108]. Through a comparison with data previously given for the solid



state infrared spectra of $(CH_3)_4Sb(OOCCH_3)$ and $(CH_3)_3Sb(OOCCH_3)_2$, bands at bands at 1640 cm^{-1} (Nujol mull) or 1660 cm^{-1} (benzene solution) in the infrared spectrum of $(CH_3)_2Sb(OOCCH_3)_3$ can be assigned to the ν(C=O) modes of the monodentate ester like acetate groups while bands at 1568 cm^{-1} (Nujol mull) or 1567 cm^{-1} (benzene solution) can be assigned to the ν_a(CO) mode of the bidentate, chelating acetate group. Also, the ν_a(SbO) and ν_s(SbO) modes were assigned at 296 and 261 cm^{-1}, respectively for the monodentate acetate groups, and 245 and 221 cm^{-1}, respectively for the chelating acetate group[108]. In $(CH_3)_3Sb(OSCR)_2$ ($R=CH_3,C_6H_5$) coordination is through the sulfur atoms with the frequencies assigned to the ν(C=O) modes of $(CH_3)_3Sb(OSCCH_3)_2$ in the solid state (1639 and 1634 cm^{-1})[110,111] very similar to those of the corresponding modes in $(CH_3)_3Sb(OOCCH_3)_2$. The ν(SbS) modes for $(CH_3)_3Sb(OSCCH_3)_2$ are assigned at a relatively high frequency (380 cm^{-1}) relative to the assignments of the corresponding ν(SbO) modes (279 cm^{-1}) for $(CH_3)_3Sb(OOCCH_3)_2$. The ν(SbS) mode has also been assigned at <u>ca</u>. 360 cm^{-1} for $(CH_3)_3SbX(OSCC_6H_5)$ and <u>ca</u>. 380 cm^{-1} for $(CH_3)_3SbX(OSCCH_3)$ (X=Cl,Br)[111].

Octahedral coordination is found in the acetylacetonate (Acac) derivatives $R_nSbCl_{4-n}Acac$ ($R=CH_3,C_2H_5;n=1-4$)[112,113] with the proposal that the alkyl groups preferentially occupy positions in the same plane as the acetylacetonate oxygen atoms and that the chloride ligands preferentially occupy the axial positions. Such a structure with the axial chloride ligands bent toward the acetylacetonate group has been found in an X-ray crystallographic study of CH_3SbCl_3Acac[114]. The metal-oxygen bond strength increases and the carbon-oxygen bond strength decreases in these avetylacetonate derivatives as the alkyl groups are replaced with chloride ligands. Spectral data (UV,IR;NMR) show the complexes $R_nSbCl_{4-n}Ox$ ($R=CH_3,C_2H_5,n\text{-}C_3H_7;n=1,2,4;Ox=$oxinate) to have hexacoordinate structures in benzene solution with chelating oxinate groups[115]. The $RSbCl_3Ox$ and R_2SbCl_2Ox complexes also have hexacoordinate structures in 100 % ethanol and chloroform solutions, although there is partial or complete rupture of the antimony-nitrogen bond in polar solvents. The $R_3SbClOx$ complexes apparently have pentacoordinate structures[115].

F. Metal-Metal Bonds and Complexes

The vibrational spectra of $(CH_3)_4P_2$[116] and $(CH_3)_4As_2$[117] show both to exist exclusively in the trans conformation in the solid state and as mixtures of both trans and gauche conformers in the liquid state. As the M-M bond length increases, a greater percentage of the trans conformer is favored. Therefore, while liquid $(CH_3)_4P_2$ consists of a 40:60 percentage mixture of the trans and gauche conformers, respectively, liquid $(CH_3)_4As_2$ consists of a 60:40 percent mixture of the trans and gauche conformers, respectively[116,117]. The vibrational spectra of $(RP)_4$ ($R=C_2H_5,n\text{-}C_3H_7;i\text{-}C_4H_9$) have been interpreted in terms of structures consisting of puckered P_4 rings[118]. The assignments made for the $\nu(MM)$ modes of the above mentioned derivatives, together with those made for $(C_2H_5)_4P_2$ and $(n\text{-}C_4H_9)_4P_2$[119] are summarized in Table 13[116-119]. Vibrational assignments have also been reported for several derivatives of the type $((CH_3)_kM_nM'X_m$ ($M=P,As;M'=$main group element;$X=H,$alkyl,halide;$k=1\text{-}3;n=1\text{-}3;m=1\text{-}4$)[120-124]. The $\nu(MM')$ assignments have been made for several complexes with Group Vb-transition metal bonds[125-129].

Table 13: Assignments of $\nu(MM)$ Frequencies (cm^{-1})

Compound	$\nu(MM)$		Ref.
$(CH_3)_4P_2$	455[a]	429[b]	116
$(CH_3)_4As_2$	271[a]	254[b]	117
$(C_2H_5)_4P_2$	424		119
$(n\text{-}C_4H_9)_4P_2$	419		119
$((C_2H_5)P)_4$	467	404	118
$((n\text{-}C_3H_7)P)_4$	468	409	118
$((i\text{-}C_3H_7)P)_4$	488	405	118
$((i\text{-}C_4H_9)P)_4$	467	391	118

a) Due to <u>trans</u> conformer.

b) Due to <u>gauche</u> conformer.

Among the most interesting of these involved the use of stable nickel isotopes to assign the $\nu(NiP)$ modes of $Ni(P(C_2H_5)_3)_2Cl_2$ and $Ni(P(C_2H_5)_3)_2Br_2$[128,129].

IV. PERHALOGENATED ALKYL DERIVATIVES

Very limited vibrational data have been reported for Group Vb derivatives of perhalogenated alkyl groups. Most of these data are limited to perfluorinated alkyl derivatives. Assignments made for the infrared and Raman spectra of $(CF_3)_3M$ (M=P,As;Sb)[130] are summarized in Table 14. There is a noticable decrease in the frequencies of the various modes for these compounds as the central atom is changed from

Table 14: Vibrational Assignments (cm^{-1}) for $(CF_3)_3M$ (M=P, As, Sb)[a].

Mode	$(CF_3)_3P$	$(CF_3)_3As$	$(CF_3)_3Sb$
$\nu_a(CF)$	1235, 1189	1219, 1177	1194, 1148
$\nu_s(CF)$	1158, 1129	1152, 1114	1129, 1089
$\delta_d(CF)$	573, 559	557, 537	526
$\delta_s(CF)$	747	737	725
$\rho_r(CF)$	270, 250	249, 232	222, 201
$\nu_a(MC)$	470	337	269
$\nu_s(MC)$	450	349	286
$\delta(MC_3)$	169, 109	144, 90	130, 72

a) All data from Ref. 130.

phosphorus to antimony. Normal coordinate calculations for $(CF_3)_3M$ (M=P,As;Sb) indicate that the K(MC) force constants are slightly smaller than those of the corresponding methyl derivatives[130]. These calculations also show several of the modes to be highly coupled, though the coupling decreases as the mass of the central atom increases. In Figure 10, the gas phase infrared and liquid phase Raman spectra are illustrated for $(CF_3)_3As$[130]. The gas phase infrared and liquid phase Raman spectra have been reported and assigned for $(CF_3)_2PH$, $(CF_3)_2AsH$ and their deuterated analogs[131]. Assignments were made on the basis of a normal coordinate analysis in which force constants were transferred from the corresponding $(CF_3)_3P$ and $(CF_3)_3As$ derivatives. The $\nu(PH)$ mode of

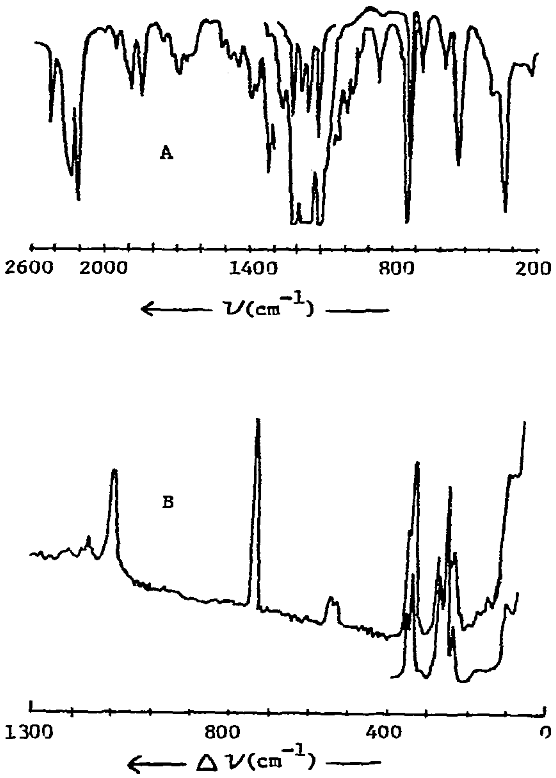


Figure 10: Gaseous phase A) infrared spectrum and liquid phase B) Raman spectrum of $(CF_3)_3As$[130].

$(CF_3)_2PH$ (2358 cm^{-1})[131,132] is higher in frequency by ca. 68 cm^{-1} than the analogous mode in $(CH_3)_2PH$ (2290 cm^{-1})[37]. Also, the $\nu(PH)$ mode of $(CF_3)_2PH$ in the solid state infrared spectrum is split (2372 and 2342 cm^{-1}); this being attributed to the presence of more than one molecule in the unit cell[132]. The infrared spectra (4000-650 cm^{-1}) have been assigned for $(CH_3)_nP(CF_3)_{3-n}$ (n=1-3) and $(CF_3)_nPI_{3-n}$ (n=1,2)[133] while more complete infrared and Raman assignments have been made for CF_3PCl_2[46]. Using infrared and Raman data, the penta-coordinate derivatives CF_3PCl_4[134] and $(CF_3)_2PCl_3$[135] have been interpreted to have trigonal bipyramidal skeletons with the trifluoromethyl groups in axial positions. Although microwave data for CF_3PF_4 are said to favor a trigonal bipyramidal structure in which the trifluoromethyl group occupies an axial position[136], infrared spectra for the gas phase and Raman spectra for the liquid phase indicate that the trifluoromethyl group occupies an equatorial position of a trigonal bipyramidal skeleton[137]. The infrared and Raman spectra of CCl_3PF_4 show the trichloromethyl group to occupy an equatorial position[138]. In Table 15 the vibrational assignments are compared for CH_3PF_4[63], CF_3PF_4[137] and CCl_3PF_4[138].

Two studies have appeared of the vibrational spectra of $(CF_3)_4P_2$. In the first[132] it is concluded that although the compound exists in only the _trans_ form in the solid state, the gaseous and liquid states consist of mixtures of both _trans_ and _gauche_ forms with the _trans_ form predominating. This can be compared to the fact that in liquid $(CH_3)_4P_2$ there was a 40:60 percent mixture of the _trans_ and _gauche_ conformers, respectively[113]. In the second study of $(CF_3)_4P_2$, however, the spectra are interpreted to indicate that only the _trans_ form is present in the liquid and gaseous phases[139]. This study also included an analysis of the vibrational spectrum of $(CF_3)_4As_2$ in which it is again concluded that only the _trans_ conformer is present in the liquid and gaseous phases. Normal coordinate analyses have been carried out for $(CF_3)_4P_2$ and $(CF_3)_4As_2$[139]. The ν(MM)

Table 15: Vibrational Assignments (cm^{-1}) for CH_3PF_4, CF_3PF_4 and CCl_3PF_4.

Mode	Sym.	CH_3PF_4[a]	CF_3PF_4[b]	CCl_3PF_4[c]
ν(CX)	B_1	2963	1162	773
	B_2	2949	1231	757
	A_1	2932	1183	713
δ_a(CX)	B_1	1434	510	328
	B_2		518	368
δ_s(CX)	A_1	1328	754	409
ρ_r(CX)	B_1	985	229	267
	B_2		304	302
ν(PC)	A_1	596[b]	423	569
ν(PF)	B_1	1009	986	985
	B_2	843	892	807
	A_1	932	909	918
	A_1	725[b]	674	665

a) Ref. 63.

b) Ref. 137.

c) Ref. 138.

modes have been assigned at 485 and 204 cm^{-1}, respectively for the trans forms of $(CF_3)_4P_2$[132,139] and $(CF_3)_4As_2$[139]. The ν(PP) mode for the gauche form of $(CF_3)_4P_2$ has been assigned at 406 cm^{-1} by the first group[132] while the second group[139] assigned this band to a ν(PC) mode. The infrared and Raman spectra have also been reported for $(CF_3)_2PPF_2$[140].

Table 16: Selected Vibrational Assignments (cm^{-1}) for Acetylenic-Group Vb Derivatives.

Compound	$\nu(C\equiv C)$	$\nu(MC)$	$\delta(CCC)$	$\delta(MC\equiv C)$	$\delta(MC_3)$	Ref.
$(HC\equiv C)_3P$	2061	615 646		445 424 266		142
$(HC\equiv C)_3As$	2053	526 517		399 379 231		142
$(HC\equiv C)_3Sb$	2033	477 450		341 325 219		142
$(CH_3C\equiv C)_3P$	2193	641 677	565 411 530	283 436 364	77 or 65	143
$(CH_3C\equiv C)_3As$	2192	450 615	446 374 392	266 349 221	71?	143
$(CH_3C\equiv C)_3Sb$	2156	406 454	257 335 191	143 120 101		143
$(CH_3C\equiv C)PF_2$	2193	593				144
$(CH_3C\equiv C)PF_4$	2240	672				144

V. VINYLIC, ACETYLENIC AND CYCLOPENTADIENYL DERIVATIVES

The only vibrational information for vinylic derivatives to be reported has been for $(H_2C{=}CH)_3P$[141]. The most characteristic mode for vinylic derivatives is the $\nu(C{=}C)$ vibration which has been assigned at 1595 cm^{-1} for $(H_2C{=}CH)_3P$.

More extensive and complete vibrational assignments are available for acetylenic derivatives. The complete infrared and Raman spectra and assignments have been reported for $(HC{\equiv}C)_3M$ (M=P,As;Sb)[142] and $(CH_3C{\equiv}C)_3M$ (M=P,As;Sb)[143] in various phases while less complete infrared data have been reported for $(CH_3C{\equiv}C)PF_2$ and $(CH_3C{\equiv}C)PF_4$[144]. Selected assignments for all of the above mentioned derivatives are summarized in Table 16[142,144]. Most of the modes arising from the acetylenic group are fairly insensitive to the nature of the Group Vb element. The frequency of the $\nu(C{\equiv}C)$ mode decreases slightly as the mass of the central atom increases. This mode gives rise to a very strong intensity and characteristic band, especially in the Raman spectrum. This is observed in Figure 11 which illustrates the CCl_4 solution infrared spectrum and solid state Raman spectrum of $(CH_3C{\equiv}C)_3As$[143]. The $\delta(CC{\equiv}C)$ modes (of the $(CH_3C{\equiv}C)_3M$ derivatives) and the $\nu(MC)$ and $\delta(MC{\equiv}C)$ modes are much more mass sensitive; again showing a decrease in frequency as the mass of the central atom increases.

Infrared (3500-150 cm^{-1}) and NMR data for $(C_5H_5)_3As$, $(C_5H_5)_3Sb$ and a yellow and black form of $(C_5H_5)_3Bi$ indicate the presence of different types of structures for these compounds[145]. There is a trend from the monohapto structure for $(C_5H_5)_3As$ to the pentahapto structure for the black form

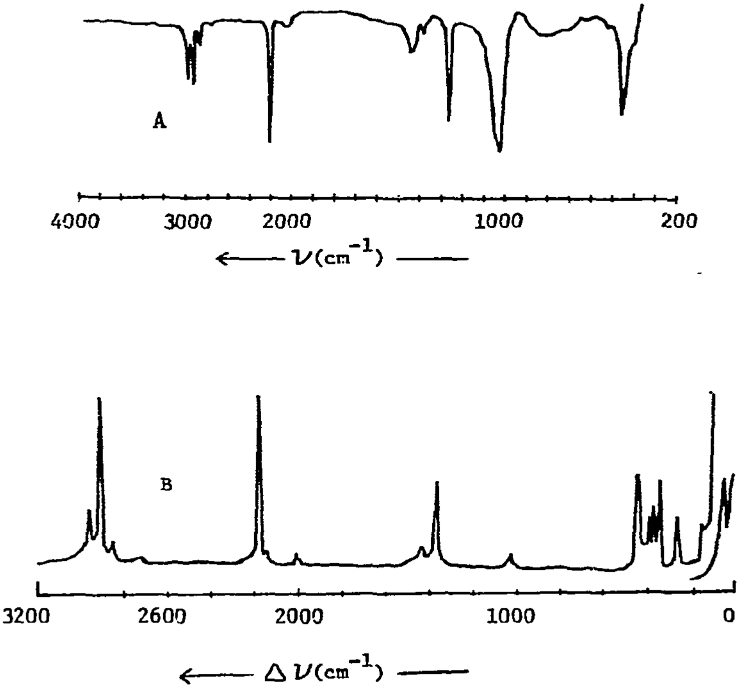


Figure 11: The carbon tetrachloride A) infrared spectrum and solid state B) Raman spectrum of $(CH_3C{\equiv}C)_3As$[143].

of $(C_5H_5)_3Bi$. Intermediate structures, in which there is a rapid interconversion of monohapto and pentahapto rings are proposed for $(C_5H_5)_3Sb$ and the orange form of $(C_5H_5)_3Bi$. The infrared spectrum of the black form of $(C_5H_5)_3Bi$ is very simple as expected for a compound with highly symmetric pentahapto cyclopentadienyl rings. The infrared spectrum of $(C_5H_5)_3As$ is much more complex, again as expected for the lower symmetry monohapto cyclopentadienyl rings. The infrared spectra of $(C_5H_5)_3Sb$ and the orange form of $(C_5H_5)_3Bi$, however, show a complexity which might be attributed to the presence of both monohapto and pentahapto rings.

VI. NEUTRAL AND CATIONIC PHENYL COMPOUNDS

Several structures are found for the phenyl derivatives of the Group Vb elements. There are trivalent derivatives of the type $(C_6H_5)_nMX_{3-n}$ (n=1-3;X=counter anion) in which the central atom has a coordination number of three and a pyramidal skeleton. There are also the pentavalent derivatives, $((C_6H_5)_4M)X$ in which an ionic tetrahedral structure is found or $(C_6H_5)_nMX_{5-n}$ (n=1-5;X=counter anion) in which a covalent trigonal bipyramidal structure is found (except for $(C_6H_5)_5Sb$ which has a square pyramidal skeleton).

In assigning the vibrational spectra for phenyl derivatives, reference is often made to the assignments given by Whiffen for the monosubstituted halobenzenes[146]. Whiffen showed that of the thirty fundamental modes for a monosubstituted phenyl ring, the positions of twenty four are relatively independent of the halogen substituted on the ring. The frequencies of the other six are sensitive to the substituent and were given the term mass- or X-sensitive. Of these X-sensitive modes, those denoted as the q, r and t vibrations contain contributions from the stretching of the phenyl-M bond, while those denoted as y, u and x vibrations involve phenyl-M bending. The X-sensitive modes, however, are not pure phenyl-M stretching or bending modes since they are coupled to some extent with the phenyl ring modes. It is therefore incorrect to assign phenyl-M stretching or bending modes in the same sense as the corresponding methyl-M stretching or bending modes are assigned. It has been stated that when the substituent on the phenyl ring is relatively light in mass (as, for example, a first row element)[147,148]

Table 17: Assignments (cm^{-1}) of the Non Mass-Sensitive Modes for the Triphenyl Derivatives of the Group Vb Elements.

Assignments[a]			$(C_6H_5)_3P$[b,c]	$(C_6H_5)_3As$[b,d,e]	$(C_6H_5)_3Sb$[b,d,f]	$(C_6H_5)_3Bi$[b]
ν(CC)	k	A_1	1582 m	1577 m	1573 m	1567 m
ν(CC)	l	B_1	1569 w 1566 w	1566 sh w	1562 sh	
ν(CC)	m	A_1	1482 s	1480 vs	1477 s	1474 m
ν(CC)	n	B_1	1435 s 1429 s	1431 vs	1429 vs	1428 s
ν(CC)	o	B_1	1337 w 1322 w	1320 w	1329 w	1325 w
δ(CH)	e	B_1	1280 w 1268 w	1270 w	1261 w	
δ(CH)	a	A_1	1179 w	1182 m	1182 mw	1182 vw
δ(CH)	c	B_1	1157 w 1152 w	1152 m	1153 w	1156 vw
δ(CH)	d	B_1	1068 w 1065 w	1066 m	1063 vs	
δ(CH)	b	A_1	1028 m	1026 m	1018 m	1014 m
ring	p	A_1	997 w 993 w	999 ms	997 s	995 m
π(CH)	j	B_2	985 w	985 w	988 vw	
π(CH)	h	A_2	970 w	970 w	970 vw 963 vw	
π(CH)	i	B_2	914 w 905 w	914 vw 909 mw	914 w 907 w	
π(CH)	g	A_2	850 847	848 w 840 w	852 mw 848 mw	
π(CH)	f	B_2	754 746 741	746 w 734 vs	744 w sh 736 vs sh 730 vs	739 vs sh 734 vs
π(CC)	v	B_2	692 vs	693 vs	694 vs	692 vs
δ(CCC)	s	B_1	619 w	614 vw	615 vw	610 vw
π(CC)	w	A_2	398 w	397 vvw	398 vvw	393 vw

Table 17 (continued)

a) For a description of the modes, the terms used to describe them and their symmetry, see Ref. 146.

b) Refs. 150 and 151.

c) Ref. 152.

d) Ref. 149.

e) Ref. 153.

f) Ref. 154.

and/or when interactions are possible between lone-pairs of electrons on the central atom and the pi-electron system of the phenyl ring[148] the major contribution of the stretching of the phenyl-M bond is to the q-type vibration. For heavier elements, however, such as phosphorus, arsenic, antimony and bismuth, it is the t-type vibration which contains the major contribution from the stretching of the phenyl-M bond[148,149].

The above considerations have mainly been with referance to monosubstituted phenyl derivatives. When the substituent is a Group Vb element, more than one phenyl group can be bonded to the central atom. Although each ring would then be expected to give rise to a set of peaks, the inter ring coupling is slight so that there will be accidental degeneracy of a large number of the non mass-sensitive phenyl vibrations. Therefore, the spectra arising from these modes can still be interpreted in terms of the C_6H_5M unit. Splitting or asymmetry noted for these bands in the solid state have been attributed to solid state effects[149]. The assignments made from the solid state infrared spectra of the non mass-sensitive phenyl modes (exclusive of the ν(CH) modes) are summarized in Table 17 for $(C_6H_5)_3M$ (M=P,As,Sb;Bi)[149-154]. Similar assignments have been made for tetraphenyl phosphorus(V)[155], arsenic(V)[156], antimony(V)[149] and bismuth(V)[157] derivatives; pentaphenyl phosphorus[158,159], arsenic[149] and antimony[149], and $Li(Sb(C_6H_5)_6)$[149].

The six mass-sensitive vibrational modes show a greater degree of splitting than the non mass- sensitive modes. This complexity has been attributed to not only solid state effects[151] but more importantly to changes in coordination number and symmetry about the central atom. The low frequency (550-100 cm^{-1}) infrared and Raman spectra of $(C_6H_5)_3M$ (M=P,As,Sb;Bi) have been assigned for the solid state and benzene solution phases[151]. Figure 12 illustrates the infrared and Raman spectra of the benzene solutions for these compounds. Assuming the phenyl groups to be single atoms, the triphenyl derivatives would have skeletons of C_{3v} symmetry and two phenyl-M stretching and two phenyl-M bending modes are expected. Since the t and u modes are predominately phenyl-M stretching and bending modes, respectively, the splitting of these modes into two components is explained[151]. To help confirm the above assignments, approximate normal coordinate calculations were carried out assuming the phenyl groups to be single atoms. Complete vibrational assignments have also been given for $C_6H_4(As(CH_3)_2)_2$ and $C_6H_4(As(CD_3)_2)_2$[153], and $(p\text{-}XC_6H_4)_3As$ and $(m\text{-}XC_6H_4)_3As$ (X=Cl,F)[160], while infrared data have been presented for $(C_6F_5)_3Bi$[161].

The Raman spectra (below 700 cm^{-1}) of several tetraphenyl

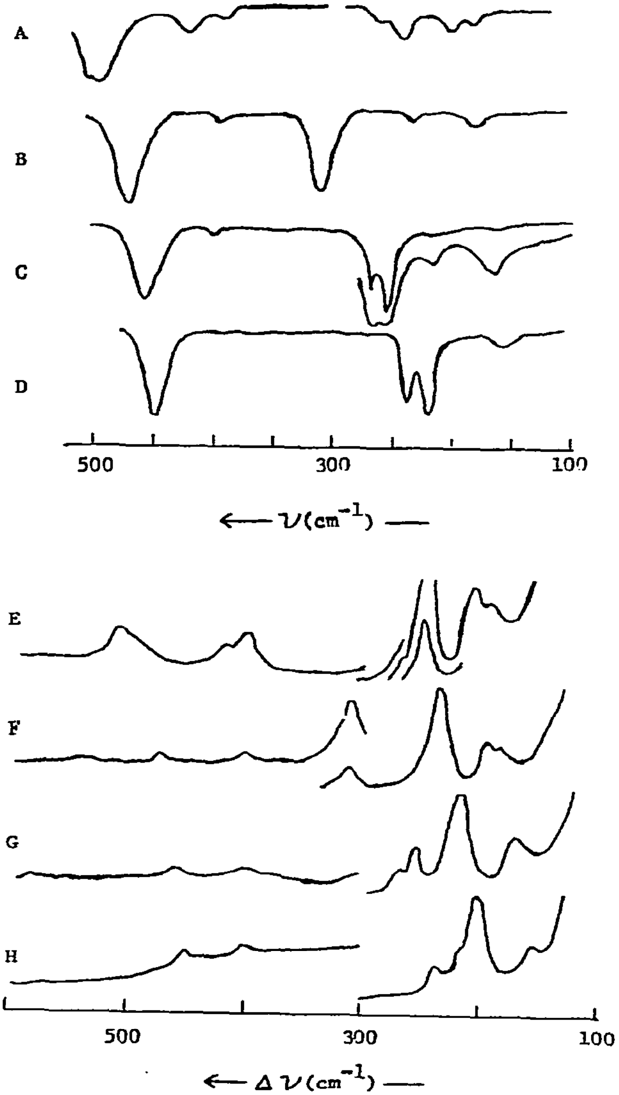


Figure 12: The infrared spectra (A, B, C, D) and Raman spectra (E, F, G, H) of $(C_6H_5)_3P$, $(C_6H_5)_3As$, $(C_6H_5)_3Sb$ and $(C_6H_5)_3Bi$, respectively in benzene[151].

Table 18: Assignments (cm^{-1}) of the X-Sensitive Modes for Phemyl-Group Vb Compounds[a].

Compound	q-Mode	r-Mode		y-Mode		t-Mode		x-Mode		u-Mode		Ref.
	IR	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	
$(C_6H_5)_3P$	1089m			501vs	501w,dp	428m 398w	423w,dp 403w,dp	248m	252vs,p	209m 190w	212m,dp 193sh,dp	151,152
$(C_6H_5)_3As$	1082w 1074m	667vw		474vs	478w,br	313vs	313m,dp	237w	237vs,p	192w 183w	194m,dp 185sh,dp	151,153
$(C_6H_5)_3Sb$	1065m	651w		457vs	460w,br	270s 257vs	272m,p 257m,dp	216w	219vs,p	166m	169m,dp	151,154
$(C_6H_5)_3Bi$	1055m			448vs	450w,br	237s 220s	237m,p 219sh,dp	207sh	203vs,p	157m	155m,dp	150,151
$(C_6H_5)_4P^{1+}$	1105vs	687s	682ms	526vs	529vw	454vw 431w	463w 435w	209m 202m 195mw	197ms,dp	283w 270w	285mw 281mw 257s	155,162
$(C_6H_5)_4As^{1+}$	1079vs	670w	670s		505vw	375w 364s 345vs	370vw 350w		186m	245s	267vw,sh 261ms 245w,sh	149,162
$(C_6H_5)_4Sb^{1+}$	1067s	665s			460mw 446mw		315w 291m			252m 239vs		149,162

a) A description of the X-sensitive modes is given in Ref. 146.

phosphorus(V), arsenic(V) and antimony(V) derivatives have been discussed in detail in order to differentiate between tetracoordinate and pentacoordinate structures[162]. While the solid state phosphorus(V) and arsenic(V) derivatives and $((C_6H_5)_4Sb)ClO_4$ have tetracoordinate skeletons, the antimony(V) derivatives $(C_6H_5)_4SbX$ (X=F,Cl,Br,OH) and $((C_6H_5)_4Sb)_2SO_4$ appear to be pentacoordinate with trigonal bipyramidal skeletons. In Table 18[149-155,162] the assignments are compared for the X-sensitive modes of $(C_6H_5)_3M$ (M=P,As,Sb;Bi) and the tetracoordinate derivatives $(C_6H_5)_4M^{1+}$ (M=P,As;Sb). It has been noted that the two bands observed for the t-mode of $(C_6H_5)_4P^{1+}$ are consistent with the known tetrahedral local symmetry of this cation[162]. It is difficult, however, to draw structural conclusions from the number of components associated with the X-sensitive modes of the $(C_6H_5)_4M^{1+}$ derivatives since the data are all for solid samples and the splitting also might be attributed to solid state effects. While the assignments made for the X-sensitive modes of the $(C_6H_5)_3M$ and $(C_6H_5)_4M^{1+}$ derivatives are fairly consistent, for the triphenyl series the x-modes have been assigned at higher frequencies than the u-modes[151] while for the tetraphenyl derivatives the u-modes have been assigned at the higher frequencies[162].

Although $(C_6H_5)_5P$ and $(C_6H_5)_5As$ have approximate trigonal bipyramidal MC_5 skeletons in the solid state[163], $(C_6H_5)_5Sb$ has been shown to have an approximate square pyramidal MC_5 skeleton in the solid state[164,165]. A detailed study has been reported of the low frequency (below 400 cm^{-1}) solid state and CH_2Cl_2 or CH_2Br_2 solution infrared and Raman spectra.

of both $(C_6H_5)_5As$ and $(C_6H_5)_5Sb$[166]. It is suggested from this study that both compounds retain their solid state structures in solution; indicating that the structure of $(C_6H_5)_5Sb$ in the solid state is not due to packing effects.

VII. PHENYL DERIVATIVES

A. Hydrides, Halides and Pseudohalides

An interpretation[167] has been offered for the infrared and Raman data originally thought[168] to have been for $C_6H_5PF_2$. It is now known to be $C_6H_5PF_4$[169,170] with a more recent vibrational study having been reported for $C_6H_5PF_2$[170]. The frequencies of the non mass-sensitive and q- and r- modes of the trivalent phenyl-Group Vb hydrides and halides are very similar to those discussed in Section VI for phenyl compounds. The metal-hydride and metal-halide stretching mode assignments are summarized for these trivalent derivatives in Table 19[40,48,53,167,168,170-175]. Although the frequencies of the metal-hydride stretching modes are not significantly different from those of the corresponding alkyl derivatives, the frequencies of the metal-halide stretching and the metal-hydride and -halide deformation modes of the phenyl derivatives can be influenced through interactions with the t, y, u, and x mass-sensitive modes which appear in the same frequency region. Interactions of this type have made it difficult to assign the low frequency spectra of these phenyl derivatives and led to some contradictory assignments[167,171,174]. Although the phosphorus(III) and arsenic(III) halide derivatives are monomeric, the structures of the corresponding bismuth(III) derivatives are not as certain. It

Table 19: Metal-Hydride and Metal-Halide Stretching Modes (cm^{-1}) for Trivalent Phenyl-Group Vb Hydrides and Halides:

Compound	ν(MX)	References
$(C_6H_5)_2PH$	2286	171,172
$C_6H_5PH_2$	2293	167,173
$(C_6H_5)_2AsH$	2071	171
$C_6H_5AsH_2$	2089	171
$(C_6H_5)_2SbH$	1855	40
$C_6H_5PF_2$	817 793	170
$(C_6H_5)_2PCl$	500	48,167,174
$C_6H_5PCl_2$	500 495	48,167,174
$C_6H_5PBr_2$	403 374	167,168
$(C_6H_5)_2AsCl$	372	53
$C_6H_5AsCl_2$	393 369	53,174
$(C_6H_5)_2AsBr$	315[a] 291[a]	53
$C_6H_5AsBr_2$	312[a] 290[a] 276[a]	53
$C_6H_5BiBr_2$	120	175
$C_6H_5BiI_2$	90	175

a) The t and ν(AsBr) modes overlap.

has been suggested that in the solid state $C_6H_5BiX_2$ (X=Cl,Br, I) have polymeric structures with bridging halogen ligands[175]. This is offered as a possible explanation for the fact that the bismuth-halogen stretching modes show an increase in frequency of ca. 20-30 cm^{-1} when these compounds form complexes with 1,10-phenanthroline or 2,2'-bipyridine, rather than a frequency decrease which might be expected if the uncomplexed compounds were monomeric.

As was true for the corresponding alkyl derivatives, there appears to be an increasing tendency toward covalence in the pentavalent phenyl-Group Vb halide derivatives as the mass of the central atom increases in a given series or as the mass of the halogen decreases. Therefore, although the vibrational spectra of the known tetraphenyl phosphorus(V)[155,162] and arsenic(V)[149,156,162] halides show them to have tetracoordinate ionic structures, the tetraphenyl antimony(V) halides have covalent trigonal bipyramidal structures in the solid state[149,162,176]. Also, while in methanol $(C_6H_5)_4SbF$ retains this covalent structure, vibrational data indicate that the other tetraphenyl(V) halides dissociate to give tetracoordinate $(C_6H_5)_4Sb^{1+}$ cations[162]. In contrast, a recent pulsed NMR study of the nuclear relaxation of the ^{121}Sb nucleus of $(C_6H_5)_4SbCl$ dissolved in methanol indicates that the coordination number of antimony is not four[177]. This NMR study does, however, support the conclusion of the vibrational study[162] that in an aqueous solution the tetraphenylantimony(V) halides form pentacoordinate $(C_6H_5)_4SbOH_2^{1+}$ cations. Also, as was noted for the corresponding alkyl derivatives, covalence increases as phenyl groups are replaced with halide ligands. Therefore, all of the pentavalent triphenyl-Group Vb dihalides studied have trigonal bipyramidal skeletons with the halides in the axial positions[42,53,149,178-183]. In Table 20[42,53,149,179-181] the metal-halide stretching mode assignments are summarized

Table 20: Metal-Halide Stretching Modes (cm^{-1}) for Pentavalent Phenyl-Group Vb Halides.

Compound	ν(MX)	References
$C_6H_5AsCl_4$	420^{a} 398^{a}	53
$(C_6H_5)_2AsCl_3$	423^{a}	53
$(C_6H_5)_3AsCl_2$ [b]	270	149
$(C_6H_5)_3SbF_2$	509 485	42,179
$(C_6H_5)_4SbF$	400	162,176
$(C_6H_5)_3SbCl_2$	275	42
$(C_6H_5)_4SbCl$	353	162
$(C_6H_5)_3SbBr_2$	188 161	42
$(C_6H_5)_4SbBr$	263^{c}	162
$(C_6H_5)_3BiF_2$	412	180
$(C_6H_5)_3BiCl_2$	240	180,181
$(C_6H_5)_3BiBr_2$	164	181

a) Axial mode.

b) In a more recent study[53] no ν(AsCl) assignments were given because of mixing between these modes and the t-modes which appear in the same frequency region.

c) Assigned to the same mode as the u-modes.

for covalent pentavalent phenyl-Group Vb halides.

Both $(C_6H_5)_2AsN_3$ and several other covalent phenylarsenic(III) azides have been characterized[76]. More data are available for pentavalent phenyl-Group Vb pseudohalide derivatives. Tetraphenyl arsenic(V) tellurocyanate and

Table 21: Selected Vibrational Assignments (cm^{-1}) for Phenyl-Group Vb Pseudohalides.

Compound	ν_a(XYZ)	ν_s(XYZ)	δ(XYZ)	ν(MX)	Ref.
$(C_6H_5)_2AsN_3$	2084	1250		441	76
$(C_6H_5)_3As(NCS)_2$	2000	861	479		79
$(C_6H_5)_3Sb(N_3)_2$	2072	1268	648	348	78
$(C_6H_5)_3Sb(NCO)_2$	2208		633 620	335	78
$(C_6H_5)_3Sb(NCS)_2$	2022	865	495 481	265	42,78,79
$((C_6H_5)_3SbN_3)_2O$	2071	1284	658	319	78
$((C_6H_5)_3SbNCO)_2O$	2209		642 622		78
$((C_6H_5)_3SbNCS)_2O$	2050	854		382	78
$(C_6H_5)_2BiSCN$	2080	764	444 438		79
$(C_6H_5)_3Bi(N_3)_2$	2050	1265		328 303	177
$(C_6H_5)_3Bi(CN)_2$	2135 2128			289 275	177
$((C_6H_5)_3BiNCO)_2O$	2190				178

cyanate dihydrate[156] consist of ionic structures with $(C_6H_5)_4As^{1+}$ cations. The antimony derivatives, $(C_6H_5)_4SbX$ (X=N_3,NCO;NCS), however, have covalent pentacoordinate structures[176]. The triphenyl derivatives, $(C_6H_5)_3SbX_2$ (X=N_3[78], NCO[78];NCS[42,78]), $((C_6H_5)_3SbX)_2O$ (X=N_3,NCO;NCS)[78], $(C_6H_5)_3BiX_2$ (X=N_3[185],NCO[180];CN[185]) and $((C_6H_5)_3BiNCO)_2O$[186] also have covalent structures with the pseudohalide groups occupying axial positions. An X-ray crystallographic study has confirmed this for $((C_6H_5)_3SbN_3)_2O$[187].

B. Oxides, Chalconides, Nitrates and Other Oxo-Acid Salts

Complete vibrational assignments have been made for $(C_6H_5)_3PO$[152], $(C_6H_5)_3AsO$[188,189], $(p\text{-}XC_6H_5)_3AsO$[160] and $(m\text{-}XC_6H_5)_3AsO$[160] (X=F,Cl) with the ν(MO) modes of the former two compounds assigned at 1193 and 880 cm^{-1}, respectively. The assignment of the ν(AsO) mode was made using ^{18}O labeled $(C_6H_5)_3AsO$[189]. Although $(C_6H_5)_3PO$ and $(C_6H_5)_3AsO$ have monomeric solution and solid state structures, this is not true for the corresponding antimony and bismuth compounds. Monomeric $(C_6H_5)_3SbO$ has been reported as the product of heating $(C_6H_5)_4SbOH$ in xylene[190], yet another group reports that heating $(C_6H_5)_4SbOH$ in p-xylene gives a product that does not analyze for $(C_6H_5)_3SbO$, and that the products prepared by other methods which do analyze for triphenylstibine oxide are not monomeric but polymeric[191]. The ν_a(SbO) and ν_s(SbO) assignments given for poly(triphenylstibine oxide) are 744 and 669 cm^{-1}, respectively. Its low solubility in organic solvents and its infrared spectrum have led to the conclusion that triphenylbismuthine oxide also has a polymeric structure consisting of -Bi-O-Bi-O- units; the ν_a(BiO) mode being assigned at 630 cm^{-1} [186]. Assignments have been made for $(C_6H_5)_3MS$ (M=P,As[31];Sb) and $(C_6H_5)_3MSe$ (M=P,As) assuming them to be monomers[150]. The ν(AsS) assignment for C_6H_5AsS (465 cm^{-1}) together with a molecular weight determination in bromoethane indicate that it is a tetramer[31].

Several vibrational studies have been made of pentavalent triphenyl and tetraphenyl Group Vb derivatives of mono- and dibasic inorganic acids. These data have been useful in determining the solid state and solution structures of these compounds. The $(C_6H_5)_3M(NO_3)_2$ (M=As[192],Sb[179];Bi[180]) and $(C_6H_5)_4MNO_3$ (M=Sb[176],Bi[193]) derivatives all have covalent structures with the unidentate nitrate groups in the axial positions. Although the covalent compound $((C_6H_5)_3SbNO_3)_2O$ (ν_a(SbO)=738 cm^{-1}) has been reported, attempts to prepare the corresponding phosphorous and arsenic derivatives have resulted in the formation of the nitric acid adducts $(C_6H_5)_3P{\cdot}HNO_3$ and $(C_6H_5)_3As{\cdot}HNO_3$; infrared assignments have been reported for all three compounds[192]. The infrared data originally reported to have been for $((C_6H_5)_3Sb)_2O(ClO_4)_2$[179] have recently been interpreted as having been for the hydrated species[90]. An investigation of the splitting of the perchlorate bands for solid anhydrous $((C_6H_5)_3Sb)_2O(ClO_4)_2$ has led to the conclusion that this compound has a nonionic structure[90]. Support for this conclusion is the fact that the perchlorate frequencies for $((C_6H_5)_3Sb)_2O(ClO_4)_2$ are in the same region as those of anhydrous $((C_6H_5)_3Bi)_2O(ClO_4)_2$[186] which an X-ray crystallographic study has shown[187] to have a slightly distorted trigonal bipyramidal structure with coordinated perchlorate groups. The splitting of the $\nu_a(ClO_4)$ band of the perchlorate group in $((C_6H_5)_3Sb)_2O(ClO_4)_2$ (140 cm^{-1}), $((C_6H_5)_3Bi)_2O(ClO_4)_2$ (100 cm^{-1}) and $((CH_3)_3Sb)_2O(ClO_4)_2$ (13 cm^{-1}) is interpreted[90] as implying that the strength of the M-$OClO_3$ bond is greatest in $((C_6H_5)_3Sb)_2O(ClO_4)_2$ and weakest in $((CH_3)_3Sb)_2O(ClO_4)_2$. The low frequency Raman spectrum of $((C_6H_5)_4Sb)ClO_4$[162] and the infrared spectrum (4000-250 cm^{-1}) of solid $((C_6H_5)_4Bi)ClO_4$[157] indicate both to have ionic structures. The infrared results for the derivatives $(C_6H_5)_3SbX$ and $((C_6H_5)_3SbX)_2O$ ($X{=}SO_4$[179], SeO_4[89]; CrO_4[89]), and $(C_6H_5)_3BiX$ ($X{=}CO_3, SO_4, SeO_4; CrO_4$)[194] in the solid state indicate them to have nonionic polymeric structures with bridging anion groups and pentacoordination of the antimony and bismuth atoms. The solid state infrared spectra, molecular weight measurements in benzene and conductivity measurements in nitromethane have been reported for $((C_6H_5)_4Sb)_2X$ ($X{=}SO_4, SeO_4; CrO_4$)[176]. These data indicate the presence of covalent pentacoordinate structures both in the solid state and benzene and nitromethane solutions.

C. Alkoxides, Carboxylates and Chelates

In the derivatives $(C_6H_5)_4SbOR$ ($R{=}CH_3, C_2H_5, n\text{-}C_3H_7; i\text{-}C_3H_7$) the alkoxide group occupies an axial position with the $\nu(SbO)$ mode assigned between 335 and 320 cm^{-1}.[195]

The separation of the $\nu_a(CO)$ and $\nu_s(CO)$ frequencies for $(C_6H_5)_3SbX_2$[42,107,179] and $(C_6H_5)_3BiX_2$[180,193] (X=acetate, haloacetate; cyanoacetate) indicate that the carboxylate groups are unidentate. This is also true for the mono-carboxylate derivatives $(C_6H_5)_4Sb(OOCCF_3)$ and $(C_6H_5)_4Sb(OOCCCl_3)$[176]. However, while $(C_6H_5)_4Sb(OOCCH_3)$ has a pentacoordinate structure with a monodentate acetate group in chloroform and bromoform solutions (ν(CO)=1625 and 1370 cm^{-1}), in the solid state the acetate group becomes chelating to give a hexacoordinate structure as indicated by the closeness of the ν(CO) frequencies (1555 and 1395 cm^{-1})[176]. Likewise, while the structures of $(C_6H_5)_3SbC_2O_4$[89], $((C_6H_5)_3SbC_2O_4)_2O$[89] and $(C_6H_5)_3BiC_2O_4$[194] are polymeric with pentacoordinate central atoms and bridging oxalate groups, in $((C_6H_5)_4Sb)_2C_2O_4$ the structure consists of hexacoordinate antimony atoms with a symmetrically bichelating oxalate group[176]. This is indicated by the fact that while $(C_6H_5)_3SbC_2O_4$ shows two strong infrared bands in the $\nu(CO_2)$ region (1740 and 1655 cm^{-1}), $((C_6H_5)_4Sb)_2C_2O_4$ gives one band in this region (1625 cm^{-1}). The solid state infrared data for the compounds $(C_6H_5)_nSbCl_{4-n}Acac$ (n=1-4) show them all to have hexacoordinate structures with chelating acetylacetonate groups[113]. For $(C_6H_5)_2SbCl_2Acac$ there is the possibility of different stereoisomers. An X-ray crystallographic study has shown that in the solid state the chloride ligands are located cis to one another and are coplanar with the acetylacetone group, while the phenyl groups are trans to each other[196]. It was originally proposed[112] that in solution $(C_6H_5)_2SbCl_2Acac$ consists of an equilibrium between the trans dichloro structure with a chelating acetylacetone group and a structure with a nonchelating acetylacetone group. This equilibrium has been questioned[197] and it is now proposed that in solution not only $(C_6H_5)_2SbCl_2Acac$[113,197] but all of the compounds

R_2SbX_2Acac ($R=C_6H_5$, $p-CH_3C_6H_4$; $X=Cl,Br,NCS$)[197] consist of an equilibrium between the structures in which the R groups are in the <u>trans</u> positions and the X groups are in the <u>trans</u> positions. Spectroscopic data (UV,IR;NMR) indicate that the compounds $(C_6H_5)_nSb_{4-n}Ox$ ($n=1-4$) consist of hexacoordinate structures with chelating oxinate groups in benzene. The same structure is found for $C_6H_5SbCl_3Ox$ and $(C_6H_5)_2SbCl_2Ox$ in 100% ethanol or chloroform. If the solvents used are polar, however, complete rupture of the antimony-nitrogen bond or partial rupture of this bond can occur[115]. In the solid state, spectral data indicate $(C_6H_5)_3BiClOx$ and $(C_6H_5)_3BiBrOx$ to have hexacoordinate structures with chelating oxinate groups[181]. Although $(C_6H_5)_3BiClOx$ initially retains this structure when dissolved in CH_2Cl_2 or benzene, over a period of time the bismuth-nitrogen bond is ruptured. The bismuth-nitrogen bond is broken immediately when $(C_6H_5)_3BiClOx$ or $(C_6H_5)_3BiBrOx$ is dissolved in methanol or chloroform and when $(C_6H_5)_3BiBrOx$ is dissolved in benzene or CH_2Cl_2.

D. Lewis Base Adducts, Metal-Metal Bonds and Complexes

Infrared data and conductance measurements have been reported for the following complexes containing neutral oxygen donor Lewis bases: $(C_6H_5)_3SbCl_3L$ (L=DMSO,HMPA)[65], $((C_6H_5)_3SbL)_2O(ClO_4)_2$ (L=DMA,DMSO,DPSO,PyO,$(C_6H_5)_3PO$; $(C_6H_5)_3AsO$)[198], and $((C_6H_5)_3BiL_2)X_2$ and $(((C_6H_5)_3BiL)_2O)X_2$ (L=DMSO,PyO,$(C_6H_5)_3PO$,$(C_6H_5)_3AsO$;X=ClO_4,BF_4,PF_6)[199].

The only phenyl complexes with direct MM interactions to be studied using vibrational spectroscopy are $((C_6H_5)_2P)_2$[103,167] and $(C_6H_5P)_4$[200]. The latter compound contains a puckered four membered P_4 ring and has been reported to exist in the solid state in two different stereochemical forms[201]. The Raman spectra of both forms have been assigned[200]. Although the ν_a(PP) modes were assigned at 488 and 501 cm^{-1} for these two stereoisomers, the ν_s(PP) modes could not be identified due to mixing with other low frequency modes.

Vibrational data have also been reported for several derivatives where $(C_6H_5)_3M$ (M=P,As) act as ligands in coordinating to main group or transition metals or complexes[122,129,152,202-206].

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