VIBRATIONAL SPECTRA OF INTRA- AND INTER-METAL AND SEMIMETAL BONDS

EDWARD MASLOWSKY, JR.

Department of Chemistry, University of Guelph, Guelph, Ontario, Canada

Contents

I. Introduction

The following review is intended as a comprehensive survey of the literature to the end of 1970 dealing with the vibrational spectra of intra- and inter-metal and semimetal bonds. A strict division between metals and nonmetals is difficult to make. There are several borderline or semimetallic elements that exhibit different properties depending on their allotropic state. For example, while white and red phosphorus are both electric insulators and therefore nonmetals, the allotrope black phosphorus has a crystal structure made up of corrugated sheets and behaves like a semimetal. The same is true of the allotropic forms of selenium. Therefore, since it is difficult to define some elements as either metals, semimetals, or nonmetals, this discussion will include the elements boron, silicon, germanium, phosphorus, arsenic, selenium, and tellurium, in addition to the generally accepted metals.

Although very strong low-frequency lines were observed as early as 1930 in the Raman spectra of solid mercurous nitrate dihydrate[1] and calomel,[2] they were not assigned to the Hg–Hg stretching mode. In 1934, Woodward was the first to assign a metal–metal stretching mode (abbreviated as ν(M–M)).[3] He recorded the Raman spectra of 3 N nitric acid solutions of both thallous nitrate and mercurous nitrate. The former solution gave no evidence for the existence of Tl_2^{2+}. The latter solution gave a band at 169 cm^{-1}, which Woodward assigned to the ν(Hg–Hg) mode of Hg_2^{2+}.

Until recently, very little additional vibrational data have been reported for compounds containing metal–metal bonds. Most of the references to be cited have been published after 1960, and a majority of these have appeared in the last 5 years. One reason for the inactivity in this field had been a lack of compounds known to contain metal–metal bonds. Another was the unavailability of suitable instrumentation with which to study these compounds. In recent years, however, many new compounds possessing metal–metal bonds have been prepared. There have been several recent reviews on the preparation and properties of compounds with metal–metal bonds.[4-6] These compounds might be broadly divided into three groups. The first includes homo- and heteronuclear compounds between the nontransition metal elements. The second contains heteronuclear compounds, mainly formed between transition metals and ligands containing nontransition elements (*e.g.*, organophosphorus and organotin ligands). The last includes homonuclear compounds of the transition elements. Also, instrumentation has progressed along with these synthetic developments. Infrared spectrophotometers are now available to study spectra below 600 cm^{-1}, where metal–metal stretching vibrations appear. The advent of the laser source for Raman instruments has made the observation of Raman spectra of many colored compounds much simpler. The situation has changed quite dramatically from the time when Woodward reported Raman data for Hg_2^{2+}. He had to work with photographic plates which were exposed for 2 or 3 hr before suitable data could be obtained.

Raman spectra have proved more useful in the study of metal–metal bonds than infrared spectra, especially for homonuclear compounds in which the ν(M–M) vibration is not infrared active. The ν(M–M) vibrations are observed as relatively intense peaks in the Raman spectra. There is a relatively large change in polarizability during a stretching vibration. The intensity of a Raman line is proportional to the change in polarizability accompanying the vibration. Although ν(M–M') vibrations and some skeletal modes of cluster compounds are infrared active, the bands arising from these vibrations are much weaker and therefore less easily identified than for Raman spectra. Even so, it has been noted that in some cases the ν(M–M') mode can give rise to relatively intense infrared peaks.[7]

Vibrational spectra have proved useful in establishing the structures of polymetallic compounds. In some instances they have been used to rule out the presence of metal–metal

(1) P. Krishnamurty, *Indian J. Phys.*, 5, 1 (1930).
(2) P. Krishnamurty, *ibid.*, 5, 113 (1930).
(3) L. A. Woodward, *Phil. Mag.*, 18, 823 (1934).

(4) M. C. Baird, *Progr. Inorg. Chem.*, 9, 1 (1968).
(5) N. S. Vyazankin, G. A. Razuvaev, and O. A. Kruglaya, *Organometal. Chem. Rev., Sect. A*, 3, 323 (1968).
(6) F. A. Cotton, *Accounts Chem. Res.*, 2, 240 (1969).
(7) N. A. D. Carey and H. C. Clark, *Chem. Commun.*, 292 (1967).

bonds.[8] In addition to structural information, vibrational spectral data might also be used for normal coordinate calculations. Through the use of normal coordinate analyses, metal–metal stretching force constants can be obtained. These are useful in discussing the relative strength of metal–metal bonds. In favorable cases it is also possible to estimate metal–metal bond orders.[9] Spiro's recent review on vibrational spectra and metal–metal bonds[10] gives a thorough discussion of the techniques and available data on force constants and bond order calculations of metal–metal bonds.

This review will show that vibrational data have and will continue to play an increasingly important role in discussions of structure and bonding for compounds with intra- and/or inter-metal and/or semimetal bonds.

II. Group IVa Elements

A. SILICON

Although the ν(Si–Si) mode has been assigned for Si$_2$H$_6$[11] and (CH$_3$)$_6$Si$_2$,[12,13] the assignment of this mode is less certain for the hexahalodisilanes. It was originally assigned at 626 cm^{-1} for Si$_2$Cl$_6$.[14] In a recent report on the vibrational spectra and normal coordinate analysis for the series Si$_2$X$_6$ (X = Cl, Br, I),[15] the ν(Si–Si) mode is assigned from 510 to 624 cm^{-1} although the ν(Si–Si) mode is reported to be mixed with the A$_{1g}$ ν(Si–X) and to a lesser extent with the A$_{1g}$ Si–X bending (δ(SiX$_3$)) mode. The degree of mixing decreases as X changes from Cl to I. The normal coordinate calculations suggest that the Si–Si stretching force constant order is Si$_2$Cl$_6$ > Si$_2$Br$_6$ > Si$_2$I$_6$. This is attributed to the relative tendency of the halogen atom to polarize the silicon atoms and donate p electrons to the empty silicon d orbitals. As this tendency increases, there is an increased interaction of the silicon d orbitals. The approximate Si–Si stretching force constant obtained using these data indicates that the Si–Si bond order of Si$_2$Cl$_6$ is 50% greater than that of Si$_2$H$_6$.[10] Electron impact measurements, however, predict about the same bond dissociation energies for these two compounds.[16] In another recent vibrational study of Si$_2$Cl$_6$, the ν(Si–Si) mode is assigned at 354 cm^{-1},[17] since this band is absent in the Raman spectrum of Cl$_3$SiOSiCl$_3$.[18] No significant mixing, however, is reported between the ν(Si–Si) and A$_{1g}$ ν(Si–Cl) modes. More complete vibrational data are needed for the compounds mentioned above before these data can be used to compare the relative strength of the corresponding Si–Si bonds. Table I summarizes the vibrational band assignments made for Si$_2$H$_6$, (CH$_3$)$_6$Si$_2$, and the hexahalodisilanes.

The ν(Si–Si) mode has been assigned in the range 300–500 cm^{-1} for methylpolysilanes of the type (CH$_3$)$_3$SiSi(CH$_3$)$_2$X

Table I

Vibrational Assignments (cm^{-1}) for the Series Si$_2$X$_6$ (X = H, CH$_3$, Cl, Br, I)

Mode[a]	Sym	H[b]	CH$_3$[c]	Cl		Br[e]	I[e]
ν(Si–Si)	A$_{1g}$	434	404	354[d]	624[e]	562	510
ν_s(SiX$_3$)	A$_{1g}$	2152	638	624	351	223	154
δ_s(SiX$_3$)	A$_{1g}$	909	184	132	127	80	51[f]
ν_s(SiX$_3$)	A$_{2u}$	2154	610	463	460	329	255
δ_s(SiX$_3$)	A$_{2u}$	844	243	242	241	168	116
ν_a(SiX$_3$)	E$_g$	2155	689	589	590	473	398
δ_a(SiX$_3$)	E$_g$	929	249	211	212	139	94
ρ(SiX$_3$)	E$_g$	625	215	124	132	89	53[f]
ν_a(SiX$_3$)	E$_u$	2179	691	604	603	479	388
δ_a(SiX$_3$)	E$_u$	940	243	179	178	114	81
ρ(SiX$_3$)	E$_u$	379		75	74	50	31[f]

[a] ν, stretching; δ, bending; ρ, rocking; s, symmetric; a, asymmetric. [b] Data from ref 11. [c] Data from ref 12 and 13. [d] Data from ref 17. [e] Data from ref 15. [f] Calculated values.

(X = H, OH, Br).[19] The symmetric and asymmetric ν(Si–Si) modes have also been reported from 310 to 375 cm^{-1} and from 444 to 467 cm^{-1}, respectively, for the series ((CH$_3$)$_3$Si)$_3$-SiX (X = H, Cl, Br, NH$_2$).[20]

The vibrational spectra of several compounds of the type (R$_3$Si)$_n$MH$_m$ (R = H, CH$_3$; n = 1–4; m = 0–3) have been reported.[21–34] Table II lists the skeletal modes for the series ((CH$_3$)$_3$Si)$_n$M.[21–24] The danger of drawing structural conclusions on the basis of negative spectral evidence is illustrated for the series (H$_3$Si)$_3$M (M = P, As, Sb). The Si$_3$N skeleton of (H$_3$Si)$_3$N has been shown to be planar rather than pyramidal.[25,35] This is accounted for by invoking (p → d) π bond formation. If the Si$_3$M skeleton is planar, the totally symmetric ν(Si–M) mode is only Raman active while the doubly degenerate ν(Si–M) mode is both Raman and infrared active. In studies of the vibrational spectra of (H$_3$-Si)$_3$P[26,27] and (H$_3$Si)$_3$As,[28] the asymmetric ν(Si–M) mode was observed only in the Raman spectra (at 414 and 346 cm^{-1}, respectively) while the doubly degenerate mode was observed in both the Raman and infrared spectra (at 455 and 362 cm^{-1}, respectively). These data seemed to lead to the conclusion that the Si$_3$M skeletons of these two compounds were planar. In a vibrational study of (H$_3$Si)$_3$Sb the sym-

(8) E. W. Abel, P. J. Hendra, R. A. N. McLean, and M. M. Qurashi, *Inorg. Chim. Acta*, 3, 77 (1969).

(9) C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, 9, 1045 (1970).

(10) T. G. Spiro, *Progr. Inorg. Chem.*, 11, 1 (1970).

(11) G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, 26, 1107 (1957).

(12) M. P. Brown, E. Cartmell, and G. W. A. Fowles, *J. Chem. Soc.*, 506 (1960).

(13) B. Fontal and T. G. Spiro, *Inorg. Chem.*, 10, 9 (1971).

(14) M. Katayama, T. Shimanouchi, Y. Morino, and S. Mizushima, *J. Chem. Phys.*, 18, 506 (1950).

(15) F. Höfler, W. Sawodny, and E. Hengge, *Spectrochim. Acta, Part A*, 26, 819 (1970).

(16) I. M. T. Davidson and I. L. Stephenson, *Chem. Commun.*, 746 (1966).

(17) J. E. Griffiths, *Spectrochim. Acta, Part A*, 25, 965 (1969).

(18) J. E. Griffiths and D. F. Sturman, to be published, cited in ref 17.

(19) U. Stolberg and H. P. Fritz, *Z. Anorg. Allg. Chem.*, 330, 1 (1964).

(20) H. Bürger, *Organometal. Chem. Rev., Sect. A*, 3, 425 (1968).

(21) H. Bürger and U. Goetze, *Angew. Chem., Int. Ed. Engl.*, 8, 140 (1969).

(22) A. G. Lee, *Spectrochim. Acta, Part A*, 25, 1841 (1969).

(23) H. Bürger, U. Goetze, and W. Sawodny, *ibid., Part A*, 26, 671 (1970).

(24) H. Bürger, U. Goetze, and W. Sawodny, *ibid., Part A*, 26, 685 (1970).

(25) E. A. V. Ebsworth, J. R. Hall, M. J. Mackillop, D. C. McKean, N. Sheppard, and L. A. Woodward, *ibid.*, 13, 202 (1958).

(26) G. Davidson, E. A. V. Ebsworth, G. M. Sheldrick, and L. A. Woodward, *Chem. Commun.*, 122 (1965).

(27) G. Davidson, E. A. V. Ebsworth, G. M. Sheldrick, and L. A. Woodward, *Spectrochim. Acta*, 22, 67 (1966).

(28) G. Davidson, L. A. Woodward, E. A. V. Ebsworth, and G. M. Sheldwick, *ibid., Part A*, 23, 2609 (1967).

(29) H. Siebert and J. Eints, *J. Mol. Struct.*, 4, 23 (1969).

(30) E. A. V. Ebsworth, R. Taylor, and L. A. Woodward, *Trans. Faraday Soc.*, 55, 211 (1959).

(31) R. D. Greene, K. M. Mackay, and S. R. Stobart, *J. Chem. Soc. A*, 3250 (1970).

(32) H. R. Linton and E. R. Nixon, *Spectrochim. Acta*, 15, 146 (1959).

(33) J. E. Drake and J. Simpson, *ibid., Part A*, 24, 981 (1968).

(34) J. E. Drake and C. Riddle, *ibid., Part A*, 26, 1697 (1970).

(35) A. K. Hedberg, *J. Amer. Chem. Soc.*, 77, 6491 (1955).

Table II

Skeletal Modes (cm^{-1}) for ((CH$_3$)$_3$Si)$_n$M-Type Compounds[a]

Compound	$\nu_a(Si-M)$	$\nu_s(Si-M)$	$\delta(Si_nM)$	$\delta_a(SiC_3)$	$\delta_s(SiC_3)$	$\rho(SiC_3)$	Ref
((CH$_3$)$_3$Si)$_3$In	311 (m), R	307 (s), R	111 (m), R	224 (w), R	165 (sh), R	157 (vs), R	21
((CH$_3$)$_3$Si)$_3$Tl	286 (sh), R	296, R	112 (m), R	222 (w), R	161 (sh), R	152 (vs), R	22
((CH$_3$)$_3$Si)$_3$P	461 (m), R	380 (vs), R	102 (s), R	225 (m), ir	265 (m), ir	177 (vs), R	23
				232 (s), R	276 (w), ir		
((CH$_3$)$_3$Si)$_3$As	356 (m), R	341 (vs), R	89 (w), R	210 (s), ir	210 (s), R	155 (sh), R	23
				249 (m), ir	249 (m), ir	175 (sh), R	
((CH$_3$)$_3$Si)$_3$Sb	319 (s), ir	318 (vs), R	71 (s), R	229 (s), ir	193 (s), ir	145 (sh), R	23
					187 (vs), R	162 (vs), R	
((CH$_3$)$_3$Si)$_4$Si	457 (m), ir	328 (s), R	101 (w), ir	223 (s), ir	222 (m), R	172 (vs), R	24
					262 (s), ir		
((CH$_3$)$_3$Si)$_4$Ge	360 (vs), ir	319 (vs), R	89 (w), ir	240 (m), ir	202 (w), R	170 (vs), R	24
					213 (vs), ir		
((CH$_3$)$_3$Si)$_4$Sn	328 (vs), ir	311 (vs), R	73 (w), ir	230 (w), ir	180 (sh), R	158 (vs), R	24
					196 (vs), ir		

[a] ν_a, asymmetric stretching; ν_s, symmetric stretching; δ, bending; ρ, rocking; vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; ir, infrared; R, Raman.

metric and degenerate ν(Si–Sb) modes both appear at *ca.* 309 cm^{-1}.[28] Therefore, no conclusion could be made about the structure of this compound. Electron diffraction data, however, have shown that the skeletons of (H$_3$Si)$_3$P[36,37] and (H$_3$Si)$_3$As[38] are pyramidal. There thus appears to be a contradiction between the electron diffraction and vibrational data. One might expect that the slightest change from a planar to a pyramidal structure would cause the symmetric stretching mode to become infrared active with its intensity directly proportional to the degree of nonplanarity. For varying degrees of nonplanarity, however, the intensity of the symmetric mode may not be experimentally detectable. To describe this situation, illustrated by the above-mentioned compounds, in which, though the skeletons are nonplanar, the vibrational spectra seem to obey planar selection rules, the compounds are said to be "pseudoplanar." It is difficult to predict the angle required before the symmetric mode becomes observable in the infrared spectrum. Indeed, this phenomenon appears to be a function not only of the geometry but also of the nature of the atoms involved.[39] In a recent reinvestigation of the vibrational spectrum of (H$_3$Si)$_3$P, the symmetric ν(Si–P) mode is reported to be present in both the infrared (423 cm^{-1}) and Raman (415 cm^{-1}) spectra in support of a pyramidal Si$_3$P skeleton.[29] The vibrational spectrum of (H$_3$Si)$_2$Se shows the Si$_2$Se skeleton to be bent with both ν(Si–Se) modes assigned at *ca.* 388 cm^{-1}.[30] The infrared spectrum of H$_3$SiPH$_2$,[32] infrared and Raman spectrum of H$_3$SiAsH$_2$,[33] and the infrared spectra of their deuterated analogs[34] have been reported. Normal coordinate calculations have also been performed on these compounds.[34] The ν(Si–P) and ν(Si–As) modes for the nondeuterated compounds have been reported at 454 and 357 cm^{-1}, respectively, in these studies.

The ν(Si–Au) mode has tentatively been assigned to a medium-intensity infrared band at 305 cm^{-1} for (C$_6$H$_5$)$_3$PAu-

Si(C$_6$H$_5$)$_3$.[40] In several square-planar platinum complexes, the ν(Si–Pt) mode has been assigned from 326 to 352 cm^{-1}.[40–42] Assignments have been made for the ν(Si–Mn) mode of Cl$_3$-SiMn(CO)$_5$ (219 cm^{-1}) and the ν(Si–Co) modes of (CH$_3$)$_3$-SiCo(CO)$_4$ (295 cm^{-1})[43,44] and Cl$_3$SiCo(CO)$_4$ (303 cm^{-1}).[43] More recently, a complete vibrational analysis and normal coordinate treatment has been reported for Cl$_3$SiCo(CO)$_4$.[45] The results indicate that while a band at 309 cm^{-1} is principally ν(Si–Co) in character, it is also coupled with the ν(Si–Cl) and δ(SiCl$_3$) modes, all of which have the same symmetry.

B. GERMANIUM

The ν(Ge–Ge) mode has been assigned for Ge$_2$H$_6$ (270 cm^{-1}),[46,47] (CH$_3$)$_3$GeGeH$_3$ (270 cm^{-1}),[31] and (CH$_3$)$_6$Ge$_2$ (273 cm^{-1}).[12,13] It has also been tentatively assigned at 228 cm^{-1} in the infrared spectrum of ((C$_6$H$_5$)$_3$Ge)$_3$GeH.[48] Vibrational spectroscopy has shown the Ge$_3$P skeleton of (H$_3$Ge)$_3$P to be pyramidal with the ν(Ge–P) modes assigned at 322 (A$_1$) and 366 (E) cm^{-1}.[49] Similar Raman assignments have been made for the ν(Ge–P) modes of ((CH$_3$)$_3$Ge)$_3$P (320 (A$_1$) and 399 (E) cm^{-1}),[50] ((C$_6$H$_5$)$_3$Ge)$_3$P (311 (A$_1$) and 366 (E) cm^{-1}),[50] and H$_3$GePH$_2$ (363 cm^{-1}).[51] The ν(Ge–As) modes have been reported at 267 cm^{-1} for H$_3$GeAsH$_2$[52] and 258 and 268 cm^{-1}

(36) B. Beagley, A. G. Robinette, and G. M. Sheldrick, *Chem. Commun.*, 601 (1967).

(37) B. Beagley, A. G. Robinette, and G. M. Sheldrick, *J. Chem. Soc., A*, 3002 (1968).

(38) B. Beagley, A. G. Robinette, and G. M. Sheldrick, *ibid., A*, 3006 (1968).

(39) L. A. Woodward in "Raman Spectroscopy," Vol. 2, H. A. Szymanski, Ed., Plenum Press, New York, N. Y., 1970, p 1.

(40) M. C. Baird, *J. Inorg. Nucl. Chem.*, **29**, 367 (1968).

(41) F. Glocking and K. A. Hooton, *J. Chem. Soc. A*, 1066 (1967).

(42) J. E. Bentham and E. A. V. Ebsworth, *ibid., A*, 587 (1971).

(43) O. Kahn and M. Bigorgne, *C. R. Acad. Sci., Ser. C*, **266**, 792 (1968).

(44) J. R. Durig, S. J. Meischen, S. E. Hannum, R. R. Hitch, S. K. Gondal, and C. T. Sears, *Appl. Spectrosc.*, **25**, 182 (1971).

(45) K. L. Watters, J. N. Brittain, and W. M. Risen, Jr., *Inorg. Chem.*, **8**, 1347 (1969).

(46) V. A. Crawford, K. H. Rhee, and M. K. Wilson, *J. Chem. Phys.*, **37**, 2377 (1962).

(47) J. E. Griffiths and G. E. Walrafen, *ibid.*, **40**, 321 (1964).

(48) F. Glockling and K. A. Hooton, *J. Chem. Soc.*, 1849 (1963).

(49) S. Cradock, G. Davidson, E. A. V. Ebsworth, and L. A. Woodward, *Chem. Commun.*, 515 (1965).

(50) G. Engelhardt, P. Reich, and H. Schumann, *Z. Naturforsch. B*, **22**, 352 (1967).

(51) K. M. Mackay, K. J. Sutton, S. R. Stobart, J. E. Drake, and C. Riddle, *Spectrochim. Acta, Part A*, **25**, 925 (1969).

(52) J. E. Drake, C. Riddle, K. M. Mackay, S. R. Stobart, and K. J. Sutton, *ibid., Part A*, **25**, 941 (1969).

for $(H_3Ge)_2AsH$.[53] The $\nu(Ge-Sn)$ mode has been assigned from 225 to 240 cm^{-1} for several organometallic compounds of germanium and tin.[7,54] Some of these assignments, however, have been questioned as a result of recent studies on phenyltin compounds containing Sn–Sn bonds (reference should also be made to the discussion in section II.C on $\nu(Sn-Sn)$ vibrations).[10]

Vibrational data have been reported on $(Ge_2H_5)Mn(CO)_5$, which is the first example of a transition metal derivative of a catenated group IV hydride.[55] The vibrational data are interpreted as indicating some interaction of the $\nu(Ge-Ge)$ and $\nu(Ge-Mn)$ modes, though the evidence seems rather inconclusive. The vibrational spectrum of $(H_3Ge)_2Fe(CO)_4$ supports the existence of the cis configuration for this compound.[56] Also, the symmetric $\nu(Ge-Fe)$ mode is reported to be at a higher frequency than the asymmetric $\nu(Ge-Fe)$ mode. Though to a lesser extent than was found for the corresponding mode of $Cl_3SiCo(CO)_4$, the $\nu(Ge-Co)$ mode in $Cl_3GeCo(CO)_4$ is not a pure vibration but couples with the $\nu(Ge-Cl)$ and $\delta(GeCl_3)$ modes.[45] Table III summarizes

Table III

Germanium–Transition Metal Stretching Frequencies

Compound	Mode	Frequency, cm^{-1}	Ref
$(CH_3)_3GeCr(CO)_3C_5H_5$	Ge–Cr	191 (ir)	57
$H_3GeMn(CO)_5$	Ge–Mn	220 (R)	58
$Cl_3GeMn(CO)_5$	Ge–Mn	228 (R)	43
$(Ge_2H_5)Mn(CO)_5$	Ge–Mn	205 (R)	55
$(H_3Ge)_2Fe(CO)_4$	Ge–Fe	217 (R)	56
		229 (R)	
$H_3GeCo(CO)_4$	Ge–Co	224^a	59
$Cl_3GeCo(CO)_4$	Ge–Co	237 (R)	43, 45
$(CH_3)_3GeMo(CO)_3C_5H_5$	Ge–Mo	184 (R)	57
$(CH_3)_3GeW(CO)_3C_5H_5$	Ge–W	177 (R)	57
$H_3GeRe(CO)_5$	Ge–Re	209 (R)	60
$(Cl_3Ge)_2Pd(C_6H_5NC)_2$	Ge–Pd	240 (ir)	61
$Cl_3GePdCl(C_6H_5CN)P(C_6H_5)_3$	Ge–Pd	228 (ir)	61
$(Cl_3Ge)_2Pd(C_6H_{11}NC)_2$	Ge–Pd	233 (ir)	61
$trans$-$H_3GePtCl(P(C_2H_5)_3)_2$	Ge–Pt	225 (ir)	42
$trans$-$ClH_2GePtCl(P(C_2H_5)_3)_2$	Ge–Pt	252 (ir)	42
$trans$-$ClH_2GePtBr(P(C_2H_5)_3)_2$	Ge–Pt	245 (ir)	42
$trans$-$ClH_2GePtI(P(C_2H_5)_3)_2$	Ge–Pt	244 (ir)	42
$trans$-$BrH_2GePtBrP(C_2H_5)_3)_2$	Ge–Pt	241 (ir)	42
$trans$-$BrH_2GePtI(P(C_2H_5)_3)_2$	Ge–Pt	242 (ir)	42
$trans$-$((C_6H_5)_3Ge)_2Pt(P(C_2H_5)_3)_2$	Ge–Pt	242 (ir)	62
$trans$-$((C_5H_5)_3Ge)_2Pt(P(n-C_3H_7)_3)_2$	Ge–Pt	244 (ir)	62
cis-$((C_6H_5)_3Ge)_2Pt(P(C_6H_5)_3)_2$	Ge–Pt	222 (ir)	62
		224 (ir)	

^{a} Nor designated as infrared or Raman.

the several assignments made for germanium–transition metal stretching modes.[42,43,45,55–62]

C. TIN

Several organotin compounds containing Sn–Sn bonds have been synthesized.[63] The $\nu(Sn-Sn)$ mode has been assigned at 190 cm^{-1} for $(CH_3)_6Sn_2$.[12,13] Assignments of $\nu(Sn-Sn)$ modes have also been made for $(C_6H_5)_6Sn_2$ (208 cm^{-1}) and $((C_6H_5)_3Sn)_4Sn$ (207 cm^{-1}).[64] More recently, on the basis of a Raman study of both and a partial normal coordinate analysis of the former of these two compounds, these bands have been reassigned to an internal mode of the coordinated phenyl ring.[10,65] New $\nu(Sn-Sn)$ assignments have been made at 136 and 140 cm^{-1} for $(C_6H_5)_6Sn_2$ (the splitting being attributed to crystal effects) and at 103 (A$_1$) and 159 (F$_2$) cm^{-1} for $((C_6H_5)_3Sn)_4Sn$. In several other organotin compounds of the type R_3SnMR_3' (M = Sn, Ge; R and R' = C_6H_9, C_4H_9, C_2H_5, CH_3), infrared-active $\nu(Sn-Sn)$ and $\nu(Sn-Ge)$ modes have also been assigned from $ca.$ 200 to 230 cm^{-1}.[7] These assignments, however, have been questioned on the basis of results obtained for $(C_6H_5)_6Sn_2$ and $((C_6H_5)_3Sn)_4Sn$, and a suggestion has been made that they should be reinvestigated using Raman spectroscopy.[10] Assignments have been made for the $\nu(Sn-P)$ modes of $((CH_3)_3Sn)_3P$ (284 (A$_1$) and 351 (E) cm$^{-1})$[50,66] and the $\nu(Sn-As)$ modes of $((CH_3)_3Sn)_3As$ (209 (A$_1$) and 233 (E) cm^{-1}),[66] both of which have pyramidal Sn$_3$M skeletons.[66] Also, $\nu(Sn-P)$ modes for the series $((C_6H_5)_3Sn)_{3-n}P(C_6H_5)_n$ (n = 0–2) have been assigned from 294 to 369 cm^{-1}.[50,67]

Several group IV metal–transition metal compounds have been studied in the carbonyl stretching region.[68] The results of these studies indicated the presence of (d → d) π interaction with the group IV metal acting as a π acceptor. An infrared study of several tin–transition metal compounds in the metal–metal stretching region has been carried out to test this hypothesis.[69] The $\nu(Sn-M)$ bands were easily observed in the infrared spectra. Figure 1 illustrates one of the series of compounds studied. On successively replacing methyl groups with chlorine atoms in the compounds $(CH_3)_3SnMn(CO)_5$ and $(CH_3)_3SnMo(CO)_3C_5H_5$, the $\nu(Sn-M)$ frequency, in general, increases slightly. This is explained in terms of a competition between the increasing mass of the $(CH_3)_{3-x}Cl_xSn$ group and an increasing Sn–M interaction in proceeding from the fully methylated to the fully chlorinated compounds. This conclusion supports that previously reached using the data obtained in the carbonyl stretching region. These findings, however, should be contrasted with the report that the $\nu(CO)$ frequencies are nearly identical for the series $Cl_3MCo(CO)_4$ (M = Si, Ge, Sn), though normal coordinate calculations show that the M–Co stretching force constant decreases in value as M changes from silicon to tin.[45] The Sn–M interaction is also said to increase when R changes from methyl to phenyl for $R_3SnMn(CO)_5$, $R_3SnMo(CO)_3C_5H_5$, and R_3-$SnFe(CO)_2C_5H_5$.[69] This conclusion involves the assumption that the $\nu(Sn-M)$ vibrations are relatively pure. Though, as noted previously, this is a bad assumption for $Cl_3SiCo(CO)_4$

(53) J. E. Drake and C. Riddle, *Inorg. Chim. Acta*, 3, 136, (1969).
(54) H. Schumann and S. Ronecker, *Z. Naturforsch. B*, 22, 452 (1967).
(55) S. R. Stobart, *Chem. Commun.*, 999 (1970).
(56) S. R. Stobart, *Inorg. Nucl. Chem. Lett.*, 7, 219 (1971).
(57) D. J. Cardin, S. A. Keppie, and M. F. Lappert, *ibid.*, 4, 365 (1968).
(58) K. M. Mackay and R. D. George, *ibid.*, 5, 797 (1969).
(59) K. M. Mackay and R. D. George, *ibid.*, 6, 289 (1970).
(60) K. M. Mackay and S. R. Stobart, *ibid.*, 6, 687 (1970).
(61) B. Crociani, T. Boschi, and M. Nicolini, *Inorg. Chim. Acta*, 4, 577 (1970).
(62) U. Belluco, G. Deganello, R. Pietropaolo, and P. Uguagliati, *Inorg. Chim. Acta, Rev.*, 4, 7 (1970).

(63) T. Tanaka, *Organometal. Chem. Rev., Sect. A*, 5, 1 (1970).
(64) H. M. Gager, J. Lewis, and M. J. Ware, *Chem. Commun.*, 616 (1966).
(65) P. A. Bullinger, C. O. Quicksall, and T. G. Spiro, *Inorg. Chem.*, 10, 13 (1971).
(66) R. E. Hester and K. Jones, *Chem. Commun.*, 317 (1966).
(67) H. Schumann, P. Jutzi, A. Roth, P. Schwabe, and E. Schauer, *J. Organometal. Chem.*, 10, 71 (1967).
(68) (a) H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, 5, 1401 (1966); (b) D. J. Patmore and W. A. G. Graham, *ibid.*, 5, 1405 (1966); (c) *ibid.*, 5, 1586 (1966); (d) W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *ibid.*, 5, 2217 (1966).
(69) N. A. D. Carey and H. C. Clark, *ibid.*, 7, 94 (1968).

Table IV

Tin–Transition Metal Stretching Frequencies

Compound	Mode	Frequency, cm⁻¹	Ref	Compound	Mode	Frequency, cm⁻¹	Ref
$(CH_3)_3SnCr(CO)_3C_5H_5$	Sn–Cr	183 (ir)	57	$(CH_3)_2ClSnW(CO)_3C_5H_5$	Sn–W	174 (ir)	69
$(CH_3)_3SnMn(CO)_5$	Sn–Mn	182 (ir)	7, 69	$Cl_3SnRh(norbornadiene)_2$	Sn–Rh	165 (R)	71
$(CH_3)_2ClSnMn(CO)_5$	Sn–Mn	197 (ir)	7, 69	$((CH_3)_4N)_4(Rh_2Cl_2(SnCl_3)_4)$	Sn–Rh	210 (ir)	72
$(CH_3)Cl_2SnMn(CO)_5$	Sn–Mn	201 (ir)	7, 69	$((C_2H_5)_4N)_4(Rh_2Cl_2(SnCl_3)_4)$	Sn–Rh	209 (ir)	72
$Cl_3SnMn(CO)_5$	Sn–Mn	201 (ir)	7, 69	$((C_2H_5)_4N)_4(Rh_2Br_2(SnBr_3)_4)$	Sn–Rh	217 (ir)	72
$(CH_3)_2BrSnMn(CO)_5$	Sn–Mn	191 (ir)	7, 69	$Cl_3SnIr(cycloocta-1,5-diene)_2$	Sn–Ir	165 (R)	71
$Br_3SnMn(CO)_5$	Sn–Mn	182ᵃ	70	$(Cl_3Sn)_2Pd(C_6H_5NC)_2$	Sn–Pd	214 (ir)	61
$(CH_3)_2ISnMn(CO)_5$	Sn–Mn	179 (ir)	7, 69	$(Br_3Sn)_2Pd(C_6H_5NC)_2$	Sn–Pd	156 (ir)	61
$I_3SnMn(CO)_5$	Sn–Mn	154ᵃ	70	$Cl_3SnPdCl(C_6H_5NC)As(C_6H_5)_3$	Sn–Pd	199 (ir) or 212 (ir)	61
$(C_6H_5)_3SnMn(CO)_5$	Sn–Mn	174 (ir)	7, 69				
$Cl_2Sn(Mn(CO)_5)_2$	Sn–Mn	170ᵃ 199ᵃ	70	$(Cl_3Sn)_2Pd(C_6H_{11}NC)_2$	Sn–Pd	208 (ir)	61
				$(Br_3Sn)_2Pd(C_6H_{11}NC)_2$	Sn–Pd	178 (ir)	61
$(CH_3)_3SnFe(CO)_2C_5H_5$	Sn–Fe	185 (ir)	7, 69	$(Cl_3Sn)_2Pd(p-O_2NC_6H_4NC)_2$	Sn–Pd	211 (ir)	61
$Br_3SnFe(CO)_2C_5H_5$	Sn–Fe	198 (ir)	71	$(Br_3Sn)_2Pd(p-O_2NC_6H_4NC)_2$	Sn–Pd	180 (ir)	61
$(C_6H_5)_3SnFe(CO)_2C_5H_5$	Sn–Fe	174 (ir)	7, 69	$(Cl_3Sn)_2Pd(C_6H_5NC)$-	Sn–Pd	213 (ir)	73
$Cl_2Sn(Fe(CO)_2C_5H_5)_2$	Sn–Fe	196 (R) 233 (ir)	71	$(C_6H_5NHCNHC_7H_7)^b$			
				$(Cl_3Sn)_2Pd(C_6H_5)_3)$-	Sn–Pd	121 (ir)	73
$Br_2Sn(Fe(CO)_2C_5H_5)_2$	Sn–Fe	197 (R) 235 (ir)	71	$(C_6H_5NHCNHC_7H_7)^b$		131 (ir)	
						142 (ir)	
$I_2Sn(Fe(CO)_2C_5H_5)_2$	Sn–Fe	198 (R) 232 (ir)	71	$((C_2H_5)_4N)_3(Pt(SnCl_3)_5)$	Sn–Pt	210 (ir)	72
				$((C_2H_5)_4N)_3(Pt(SnBr_3)_5)$	Sn–Pt	193 (ir)	72
$(CH_3)_3SnCo(CO)_4$	Sn–Co	176 (ir)	43, 69			207 (ir)	
$Cl_3SnCo(CO)_4$	Sn–Co	205 (R)	45	$(Cl_3Sn)_2Pt(C_6H_{11}NC)$-	Sn–Pt	194 (ir) or	73
$Br_3SnCo(CO)_4$	Sn–Co	189ᵃ	70	$(C_7H_7NHCNHC_6H_{11})^c$		202 (ir)	
$I_3SnCo(CO)_4$	Sn–Co	159ᵃ	70	$(Cl_3Sn)_2Pt(C_6H_{11}NC)_2$	Sn–Pt	190 (ir)	61
$Cl_2Sn(Co(CO)_4)_2$	Sn–Co	174 (R) 213 (ir)	71	$(Cl_3Sn)_2Pt(p-CH_3OC_6H_4NC)_2$	Sn–Pt	200 (ir) 206 (ir)	61
$Br_2Sn(Co(CO)_4)_2$	Sn–Co	168 (R) 210 (ir)	71				
$I_2Sn(Co(CO)_4)_2$	Sn–Co	190 (ir)	71				
$(CH_3)_3SnMo(CO)_3C_5H_5$	Sn–Mo	172 (ir)	7, 69				
$(CH_3)_2ClSnMo(CO)_3C_5H_5$	Sn–Mo	186 (ir)	69				
$(CH_3)Cl_2SnMo(CO)_3C_5H_5$	Sn–Mo	195 (ir)	69				
$Cl_3SnMo(CO)_3C_5H_5$	Sn–Mo	190 (ir)	69, 71				
$(C_6H_5)_3SnMo(CO)_3C_5H_5$	Sn–Mo	169 (ir)	7, 69				
$(CH_3)_3SnW(CO)_3C_5H_5$	Sn–W	168 (ir)	69				

ᵃ Not designated as Raman or infrared. ᵇ $C_6H_5NHCNHC_7H_7$ = (phenylamino)(p-tolylamino)carbene. ᶜ $C_7H_7NHCNHC_6H_{11}$ = (p-tolylamino)(cyclohexylamino)carbene.

and $Cl_3GeCo(CO)_4$, the $\nu(Sn-Co)$ mode of $Cl_3SnCo(CO)_4$ is fairly pure owing to the relatively heavy mass of the tin atom.[45] Still, heavy ligands such as chlorine and C_6H_5 are expected to couple to some extent with the $\nu(Sn-M)$ mode, and this coupling cannot be ignored when relating shifts of $\nu(Sn-M)$ frequencies to the relative strength of Sn–M bonds. Table IV summarizes the several assignments made for tin–transition metal stretching modes.[7,43,45,57,61,69-73]

D. LEAD

Two infrared and Raman studies of $(CH_3)_6Pb_2$ have appeared.[13,74] In both, a Raman band at 116 cm⁻¹ is assigned to the $\nu(Pb-Pb)$ mode. These studies disagree, however, as to the assignment of the $\delta(C-Pb-C)$ modes. The extent of skeletal mode coupling in the series $(CH_3)_6M_2$ (M = Si, Ge, Sn, Pb) decreases with increasing mass of the metal atom. This is illustrated in Figure 2 for the Raman-active skeletal modes of this series. The $\nu(Pb-Pb)$ mode of $(C_6H_5)_6Pb_2$ has been assigned at ca. 109 cm⁻¹.[65,75]

Much weaker lead–lead interactions than those found in the above-mentioned compounds have recently been proposed to explain the Raman spectra of two hydroxyl lead compounds. In the first, $Pb_6O(OH)_6^{4+}$, the lead atoms form a cluster of three face-sharing tetrahedra[76] as shown in Figure 3. An oxygen atom is found at the center of the central tetrahedron with one hydroxide group located above each of the six exterior faces of the two end tetrahedra. In the light of this structural study, the original Raman study[77] has been

(70) M. J. Ware and A. G. Cram, private communication, cited in ref 10.

(71) D. M. Adams, J. N. Crosby, and R. D. W. Kemmitt, *J. Chem. Soc. A*, 3056 (1968).

(72) D. M. Adams and P. J. Chandler, *Chem. Ind. (London)*, 269 (1965).

(73) F. Bonati, G. Minghetti, T. Boschi, and B. Crociani, *J. Organometal. Chem.*, **25**, 255 (1970).

(74) R. J. H. Clark, A. G. Davies, R. J. Puddephatt, and W. McFarlane, *J. Amer. Chem. Soc.*, **91**, 1334 (1969).

(75) R. J. H. Clark, A. G. Davies, and R. J. Puddephatt, *Inorg. Chem.*, **8**, 457 (1969).

(76) T. G. Spiro, D. H. Templeton, and A. Zalkin, *ibid.*, **8**, 856 (1969).

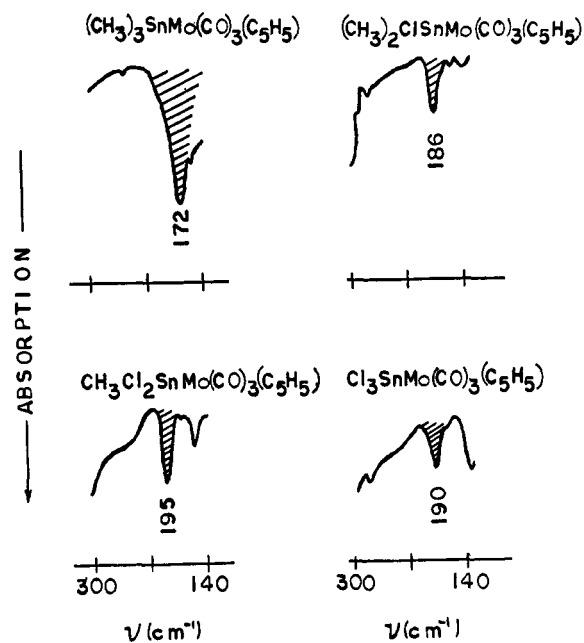(77) V. A. Maroni and T. G. Spiro, *ibid.*, **7**, 188 (1968).

Figure 1. Infrared spectra (140–300 cm⁻¹) of (CH₃)₃₋ₙClₙSnMo-(CO)₃(C₅H₅), where n = 0, 1, 2, or 3.[69] The shaded peaks indicate the Sn–Mo stretching band.
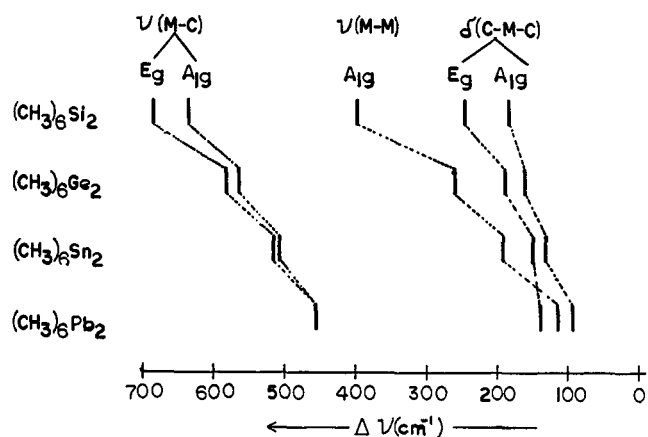
Figure 2. Raman-active skeletal modes for the series (CH₃)₆M₂, where M = Si, Ge, Sn, or Pb.[13]
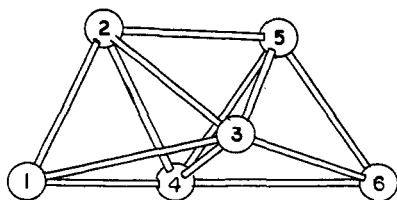
Figure 3. Structure of Pb₆ cluster in Pb₆O(OH)₆⁴⁺.[76]

repeated using a single crystal cooled to −110°.[78] This study includes a normal coordinate analysis. Since there are five different sets of Pb–Pb bonds, a different Pb–Pb stretching force constant is assigned to each in the normal coordinate

calculation. A band at 150 cm⁻¹ is assigned to the ν(Pb–Pb) mode of the shortest Pb–Pb bond (labeled Pb(3)–Pb(4) in Figure 3). This bond has a Pb–Pb stretching force constant of 1.09 mdyn/Å. All 12 modes expected for the cluster are assigned. In the other hydroxyl lead compound, Pb₄(OH)₄⁴⁺, three low-frequency bands in the Raman spectrum have been attributed to the Pb–Pb stretching modes of the Pb₄ tetrahedron on the basis of a normal coordinate calculation.[77] A single Pb–Pb stretching force constant of 1.7 mdyn/Å was used with the cluster modes assigned at 130 (A₁), 87 (F₂), and 60 (E) cm⁻¹. This calculation has been repeated using force fields that did not include the metal–metal interaction force constant.[79] It is found that the force field which included the metal–metal stretching force constant is the only one which gives a consistent explanation of the observed Raman data. It is also concluded that the metal–metal interaction, though relatively weak in nature, is needed to account for the relatively strong Raman intensity of the A₁ cage deformation mode. The only assignment of a lead–transition metal stretching mode has been made for (C₂H₅)₃PbMn(CO)₅ (161 cm⁻¹) in the infrared and Raman spectra.[70]

III. Group Va Elements

A. PHOSPHORUS

Phosphorus vapor consists of various proportions of P₂ and tetrahedral P₄ molecules, with the number of P₂ molecules increasing as the temperature is raised. In a recent Raman study of phosphorus vapor at 500°, only P₄ molecules are detected.[80] In this study, assignments are made for the P₄ molecule at 600 (A₁), 450 (F₂), and 360 (E) cm⁻¹ in agreement with previous assignments.[81,82] At 1000°, P₂ molecules are also detected by the appearance of the ν(P–P) mode at 775 cm⁻¹, this assignment also agreeing with one previously made.[83] Solid phosphorus can exist in many different allotropic and crystalline forms. One of these allotropic forms, white phosphorus, consists of tetrahedral P₄ molecules. Another allotropic form, red phosphorus, behaves like a high polymer. It has been suggested that it is formed from white phosphorus by breaking one P–P bond of the P₄ tetrahedron.[84] There are several possible structures for the repeating unit of red phosphorus. The possible existence of each of these has been considered in a recent infrared and Raman study of solid red phosphorus.[85] The results of this study are consistent with a four-membered puckered ring either with or without a transannular bond. The vibrational spectra of tetraphenyl-cyclotetraphosphine[86] and a series of tetraalkylcyclotetra-phosphines,[87] all of which contain a puckered P₄ ring, have also been assigned. A series of compounds have been reported in which a P₄ molecule is bonded to rhodium.[88] These mole-

(78) T. G. Spiro, V. A. Maroni, and C. O. Quicksall, Inorg. Chem., 8, 2524 (1969).

(79) P. A. Bulliner and T. G. Spiro, Spectrochim. Acta, Part A, 26, 1641 (1970).

(80) G. A. Ozin, Chem. Commun., 1325 (1969).

(81) H. J. Burnstein and J. Powling, J. Chem. Phys., 18, 1018 (1950).

(82) C. S. Venkateswaren, Proc. Indian Acad. Sci., Sect. A, 2, 260 (1935).

(83) G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed, Van Nostrand, New York, N. Y., 1950.

(84) L. Pauling and M. Simonetta, J. Chem. Phys., 20, 29 (1952).

(85) J. R. Durig and J. M. Casper, J. Mol. Struct., 5, 351 (1970).

(86) R. L. Amster, W. A. Henderson, and N. B. Colthup, Can. J. Chem., 42, 2577 (1964).

(87) R. L. Amster, N. B. Colthup, and W. A. Henderson, Spectrochim. Acta, 19, 1841 (1963).

(88) A. P. Ginsberg and W. E. Lindsell, J. Amer. Chem. Soc., 93, 2082 (1971).

cules have the general formula $PhClP_4L_2$ (L = $(C_6H_5)_3P$, $(p-CH_3C_6H_4)_3P$, $(m-CH_3C_6H_4)_3P$, $(C_6H_5)_3As$). The P_4 frequencies in these compounds are from 15 to 90 cm^{-1} lower than the corresponding frequencies in the free P_4 molecule. A structure in which the rhodium is bonded through a face of the P_4 tetrahedron seems to be favored.

Molecules of the type P_2X_4 can have the gauche, trans, or various other configurations between these two extremes. The configuration of a compound can also vary with the molecular state. The infrared spectrum of gaseous P_2H_4 has been interpreted in terms of the gauche configuration.[89] The Raman spectrum of liquid P_2H_4, though interpreted in terms of the gauche configuration,[90] can also be interpreted in terms of the trans configuration.[91] From a Raman and infrared study of solid P_2H_4, however, it is tentatively concluded that the trans form is present with the ν(P–P) mode assigned at 437 cm^{-1}.[92] A comparison of the infrared and Raman spectra of liquid $(CH_3)_4P_2$ shows the presence of the trans and gauche configurations with the gauche structure slightly predominant.[93] The ν(P–P) mode of the trans and gauche forms of $(CH_3)_4P_2$ are assigned at 455 and 429 cm^{-1}, respectively. In the same study, only the trans form of $(CH_3)_4P_2$ is found to be present in the solid state. The series P_2X_4 (X = F, Cl, I) exists in the trans configuration with the ν(P–P) mode assigned at 541,[94] 410,[95] and 316[96] cm^{-1}, respectively. A value of 374 cm^{-1} has been reported for the ν(P–P) mode of $P_2S_6{}^{4-}$.[97] The vibrational spectra of nine diphosphine disulfides of the type R_2SPPSR_2 have been reported with bands at 445 and 510 cm^{-1} tentatively assigned to the ν(P–P) mode of the methyl and n-butyl members of this series, respectively.[98]

Since phosphines can act as π acceptors when bonded to metals, they have been used extensively as ligands in coordination compounds. Many vibrational studies involving the assignment of the ν(P–M) mode have been reported. The assignments have ranged from ca. 150 to 550 cm^{-1} for the different compounds studied. The broadness of this range has been attributed in part to the effect of changing the metal bonded to the phosphorus atom. Even for the same metal, however, the range may be relatively broad. This has been attributed to differences in one or more of the following factors: (1) metal oxidation state; (2) coordination number of the metal atom; (3) type of phosphorus-containing ligand coordinated to the metal; (4) ligand symmetry around the central metal.[99,100] The effect of these factors on ν(P–Ni) frequencies is illustrated in Table V.[101–113]

Several of these ν(P–Ni) assignments were made using the recently developed metal isotope technique.[101,102,114] Figure 4 illustrates spectra obtained using this technique. In this method, a pair of metal complexes is prepared in which only the metal atoms are isotopically substituted. Only the vibrations involving motion of the metal atom are shifted by the metal isotope substitution. This method has been found most useful in assigning stretching as opposed to bending modes since the isotope shifts of the former are in general much larger than those of the latter.

The ν(P–M) modes of several palladium and platinum alkyl- and arylphosphine complexes have been assigned in the range 310–460 cm^{-1}.[41,42,115] The relatively high value of these assignments has been attributed to π back-bonding from palladium or platinum to phosphorus.[99] Recently, however, through use of the metal isotope technique, the ν(P–Pd) modes have been assigned at the relatively low frequencies of 234 (ir) cm^{-1} for $trans$-Pd(P(C_2H_5)$_3$)$_2$Cl$_2$, 155 (R) and 191 (ir) cm^{-1} for $trans$-Pd(P(C_6H_5)$_3$)$_2$Cl$_2$, and 150 (R) and 185 (ir) cm^{-1} for $trans$-Pd(P(C_6H_5)$_3$)$_2$Br$_2$.[102] The results obtained by using the metal isotope technique cast doubt on the reliability of many previous ν(P–Pd) and ν(P–Pt) assignments. Assignments have also been made between 200 and 220 cm^{-1} for the tetrakis PF_3[108] and $P(OC_2H_5)_3$[111] complexes of Pd(0) and Pt(0).

Assignments of ν(P–M) modes have been made for several other metals in addition to nickel, palladium, and platinum. Table VI summarizes some results on metal halide complexes of triphenylphosphine.[99,103,116,117] The failure to observe the ν(P–M) modes in the infrared spectra of triphenylphosphine-iron and -molybdenum carbonyls has been attributed to coupling between the ν(P–M) and ν(M–C) modes.[118] In an infrared study of the series $(LCo(CO)_3)_2$ (L = triaryl- or

(89) E. R. Nixon, *J. Phys. Chem.*, **60**, 1054 (1956).

(90) M. Baudler and L. Schmidt, *Z. Anorg. Allg. Chem.*, **289**, 219 (1957).

(91) M. Baudler and L. Schmidt, *Naturwissenschaften*, **44**, 488 (1957).

(92) S. G. Frankiss, *Inorg. Chem.*, **7**, 1931 (1968).

(93) J. R. Durig and J. S. DiYorio, *ibid.*, **8**, 2796 (1969).

(94) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Amer. Chem. Soc.*, **88**, 3729 (1966).

(95) S. G. Frankiss and F. A. Miller, *Spectrochim. Acta*, **21**, 1235 (1965).

(96) S. G. Frankiss, F. A. Miller, H. Stammreich, and Th. Teixeira Sans, *Chem. Commun.*, 318 (1966); *Spectrochim. Acta, Part A*, **23**, 543 (1967).

(97) H. Bürger and H. Falius, *Z. Anorg. Allg. Chem.*, **363**, 24 (1968).

(98) A. H. Cowley and W. D. White, *Spectrochim. Acta*, **22**, 1431 (1966).

(99) G. B. Deacon and J. H. Green, *Chem. Commun.*, 629 (1966).

(100) A. A. Chalmers, J. Lewis, and R. Whyman, *J. Chem. Soc. A*, 1817 (1967).

(101) K. Nakamoto, K. Shobatake, and B. Hutchinson, *Chem. Commun.*, 1451 (1969).

(102) K. Shobatake and K. Nakamoto, *J. Amer. Chem. Soc.*, **92**, 3332 (1970).

(103) J. Bradbury, K. P. Forest, R. H. Nuttall, and D. W. A. Sharp, *Spectrochim. Acta, Part A*, **23**, 2701 (1967).

(104) J. T. Wang, C. Udovich, K. Nakamoto, A. Quattrochi, and J. R. Ferraro, *Inorg. Chem.*, **9**, 2675 (1970).

(105) M. Bigorgne, A. Loutellier, and M. Pankowski, *J. Organometal. Chem.*, **23**, 201 (1970).

(106) W. F. Edgell and M. P. Dunkle, *Inorg. Chem.*, **4**, 1629 (1965).

(107) A. Loutellier and M. Bigorgne, *Bull. Soc. Chim. Fr.*, 1629 (1965).

(108) H. G. M. Edwards and L. A. Woodward, *Spectrochim. Acta, Part A*, **26**, 897 (1970).

(109) L. A. Woodward and J. R. Hall, *ibid.*, **16**, 654 (1960).

(110) H. G. M. Edwards and L. A. Woodward, *ibid., Part A*, **26**, 1077 (1970).

(111) V. G. Meyers, F. Basolo, and K. Nakamoto, *Inorg. Chem.*, **8**, 1204 (1969).

(112) R. L. Keiter and J. G. Verkade, *ibid.*, **9**, 404 (1970).

(113) A. C. Vandenbroucke, Jr., D. G. Hendricker, R. E. McCarley, and J. G. Verkade, *ibid.*, **7**, 1825 (1968).

(114) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley, New York, N. Y., 1970, p 206.

(115) (a) D. M. Adams and P. J. Chandler, *J. Chem. Soc. A*, 1009 (1967); (b) R. J. Goodfellow, P. L. Goggin, and L. M. Venanzi, *ibid., A*, 1897 (1967); (c) R. J. Goodfellow, P. L. Goggin, and D. A. Duddell, *ibid., A*, 504 (1968); (d) R. J. Goodfellow, J. G. Evans, P. L. Goggin, and D. A. Duddell, *ibid., A*, 1604 (1968); (e) G. Deganello, G. Carturan, and U. Belluco, *ibid., A*, 2873 (1968); (f) D. M. Adams and P. J. Chandler, *ibid., A*, 588 (1969); (g) J. Chatt, G. J. Leigh, and D. M. P. Mingoe, *ibid., A*, 2972 (1969); (h) D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *ibid., A*, 545 (1970); (i) J. Chatt, C. Eaborn, and S. Ibekwe, *ibid., A*, 1343 (1970); (j) M. J. Taylor, A. L. Odell, and H. A. Raethel, *Spectrochim. Acta, Part A*, **24**, 1855 (1968); (k) P. J. D. Park and P. J. Hendra, *ibid., Part A*, **25**, 227 (1969); (l) *ibid., Part A*, **25**, 909 (1969); D. A. Duddell, P. L. Goggin, R. J. Goodfellow, and M. G. Norton, *Chem. Commun.*, 879 (1968); (n) M. Akhtar and H. C. Clark, *J. Organometal. Chem.*, **22**, 233 (1970).

(116) A. Balls, N. N. Greenwood, and B. P. Straughan, *J. Chem. Soc. A*, 753 (1968).

(117) R. Rivest, S. Singh, and C. Abraham, *Can. J. Chem.*, **45**, 3137 (1967).

(118) S. Singh, P. P. Singh, and R. Rivest, *Inorg. Chem.*, **7**, 1236 (1968).

Table V

Nickel–Phosphorus Stretching Frequencies (cm^{-1})

Compound	Structure	$\nu(P\text{–}Ni)$ freq	Ref
$^{58}Ni^{II}(P(C_2H_5)_3)_2Cl_2$	Trans planar	273.4 (ir)	101, 102
$^{58}Ni^{II}(P(C_2H_5)_3)_2Br_2$	Trans planar	265.0 (ir)	102
$^{58}Ni^{II}(P(C_6H_5)_3)_2Cl_2$	Tetrahedral	189.6 (ir), 164.0 (ir)	102, 103
$^{58}Ni^{II}(P(C_6H_5)_3)_2Br_2$	Tetrahedral	196.8 (ir), 189.5 (ir)	104
$^{58}Ni^{II}(P(C_6H_5)_2(C_2H_5))_2Br_2$	Trans planar	243.0 (ir)	104
	Tetrahedral	194.5 (ir), 182.0 (ir)	104
$Ni^{II}(P(C_6H_5)_2(n\text{-}C_3H_7))_2Br_2$	Trans planar	260 (ir)	104
	Tetrahedral	178 (ir), 162 (ir)	104
$Ni^{II}(P(C_6H_5)_2(i\text{-}C_3H_7))_2Br_2$	Trans planar	273 (ir)	104
	Tetrahedral	195 (ir), 170 (ir)	104
$Ni^{II}(P(C_6H_5)_2(i\text{-}C_4H_9))_2Br_2$	Trans planar	261 (ir)	104
	Tetrahedral	190 (ir), 175 (ir)	104
$(Ni^{II}P(C_6H_5)_3Cl_3)^-$	Tetrahedral	177 (ir)	103
$Ni^0(PH_3)(CO)_3$	Tetrahedral	295 (ir)	105
$Ni^0(P(CH_3)_3)(CO)_3$	Tetrahedral	218 (ir)	105
$Ni^0(P(C_6H_5)_3)(CO)_3$	Tetrahedral	192 (R)	106
$Ni^0(PF_3)(CO)_3$	Tetrahedral	262 (ir)	105, 107
$Ni^0(PF_3)_2(CO)_2$	Tetrahedral	209 (ir), 254 (ir)	107
$Ni^0(PF_3)_3(CO)$	Tetrahedral	216 (ir), 253 (ir)	107
$Ni^0(PF_3)_4$	Tetrahedral	217 (ir), 195 (R)	108, 109
$Ni^0(PCl_3)_4$	Tetrahedral	206 (R), 133 (R)	110
$Ni^0(P(OCH_3)_3)(CO)_3$	Tetrahedral	240 (ir)	105
$Ni^0(P(OC_2H_5)_3)_4$	Tetrahedral	335 (ir), 305 (ir), 210 (ir)	111
		299 (ir)	112
$Ni^0(P(OCH)_3(CH_2)_3)_4$	Tetrahedral	162 (ir)	112
$Ni^0(P(OCH_2)_3CCH_3)_4$	Tetrahedral	157 (ir)	112, 113
$Ni^0(P(OCH_2)_3CCH_3)_3(CO)$	Tetrahedral	151 (ir), 157 (ir)	113
$Ni^0(P(OCH_2)_3CCH_3)_2(CO)_2$	Tetrahedral	144 (ir), 155 (ir)	113
$Ni^0(P(OCH_2)_3CCH_3)(CO)_3$	Tetrahedral	143 (ir)	113
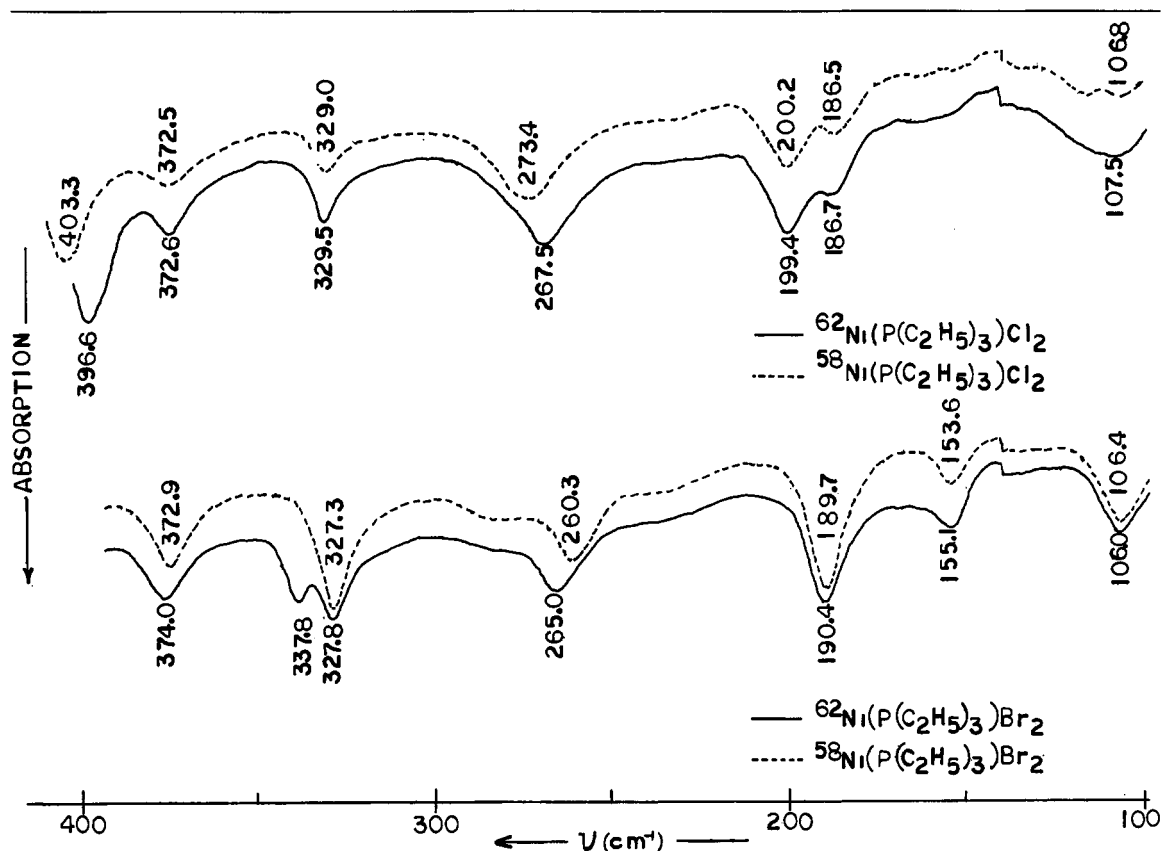
Figure 4. Far-infrared spectra of $^{58}NiX_2(P(C_2H_5)_3)_2$ and $^{62}NiX_2(P(C_2H_5)_3)_2$, where X = Cl and Br.[102]

Table VI

Metal–Phosphorus Stretching Frequencies of (Triphenylphosphine)metal Halide Complexes

Compound	$\nu(P-M)$ mode	Frequency, cm^{-1}	Ref
$Zn(P(C_6H_5)_3)_2Cl_2$	P–Zn	140, 166	99, 103
$(C_2H_5)_4N(Zn(P(C_6H_5)_3)(Cl_3)$	P–Zn	146	103
$Zn(P(C_6H_5)_3)_2Br_2$	P–Zn	128, 138, 156	103
$(C_2H_5)_4N(Zn(P(C_6H_5)_3)Br_3)$	P–Zn	141	103
$(C_6H_5)_4N(Zn(P(C_6H_5)_3)Br_3)$	P–Zn	134	103
$Cd(P(C_6H_5)_3)_2Cl_2$	P–Cd	136	99
$Hg(P(C_6H_5)_3)_2Cl_2$	P–Hg	108, 137	99
$Ga(P(C_6H_5)_3)Br_3$	P–Ga	350	116
$Sn(P(C_6H_5)_3)_2Cl_4$	P–Sn	513	117
$Sn(P(C_6H_5)_3)Cl_4$	P–Sn	529	117
$Co(P(C_3H_5)_3)_2Cl_2$	P–Co	151, 187	103
$(C_2H_5)_4N(Co(P(C_6H_5)_3)Cl_3)$	P–Co	167	103
$Co(P(C_6H_5)_3)_2Br_2$	P–Co	142, 187	103

trialkylphosphine), the $\nu(P-Co)$ mode of A_{2u} symmetry is reported to couple with the $\nu(Co-C)$ and $\delta(Co-C-O)$ modes of the same symmetry.[119] The $\nu(P-Ti)$ and $\nu(Ti-Cl)$ modes are also mixed in the series X_3TiCl_4 (X = H, D, CH_3).[120] The vibrational spectra of $HCo(PF_3)_4$ and $KCo(PF_3)_4$ have shown the former to have C_{3v} symmetry and confirmed the T_d symmetry for the latter.[121] In $HCo(PF_3)_4$, the equatorial $\nu(P-Co)$ modes are assigned to Raman bands at 212 (A_1) and 230 (E) cm^{-1}, and the axial $\nu(P-Co)$ mode is assigned to an infrared band at 235 (A_1) cm^{-1}. For $KCo(PF_3)_4$, the $\nu(P-Co)$ modes are assigned to Raman bands at 230 (A_1) and 250 (F_2) cm^{-1}. The differences observed on comparing the $\nu(P-Co)$ and $\nu(P-F)$ frequencies for these two compounds are attributed to the relative difference in the charge density on the cobalt atom. Similar assignments of the $\nu(P-M)$ mode for the trifluorophosphine complexes $M(PF_3)_5$ (M = Fe, Ru, Os) have also been made (200–250 cm^{-1}).[122] The $\nu(P-Au)$ has been assigned at *ca.* 375 cm^{-1} in the series $((CH_3)_3PAuX)^-$ (X = Cl, Br, I)[115h] and from 350 to 400 cm^{-1} for several other R_3PAuX and R_3PAuX_3 (R = alkyl group; X = halogen or alkyl group) type compounds.[123] For the tetrakis(bicyclic phosphate) complexes of silver and copper the $\nu(P-M)$ modes have been assigned at 112 and 132 cm^{-1}, respectively.[112] The $\nu(P-M)$ modes have also been reported for phosphine complexes of chromium, molybdenum, and tungsten carbonyls (*ca.* 173–210 cm^{-1}),[100] the series $Os(P-(C_6H_5)_3)_2(CO)_2X_2$ (X = Cl, Br, I) (*ca.* 157 cm^{-1}),[124] phosphine complexes of alkyltricarbonyl-π-cyclopentadienylmolybdenum (145–245 cm^{-1}),[125] and several transition metal complexes of polycyclic phosphites.[113]

The above discussion has mainly covered substituted phosphine–transition metal compounds. There are also several vibrational studies of substituted phosphines with nontransition metals. The $\nu(P-B)$ mode has been assigned at 550 cm^{-1} for I_3PBI_3.[126] Because of the relatively heavy mass of iodine,

however, the $\nu(P-B)$ mode is strongly coupled with the $\nu(B-I)$, $\delta(I-B-I)$, and $\delta(P-B-I)$ modes. Assignments of $\nu(P-B)$ modes have also been made for H_3PBH_3 (572 cm^{-1})[127] and its deuterated analogs[128] and for $Na(H_2P(BH_3)_2)$ (560 (A_1) and 643 (B_1) cm^{-1}).[129] The $\nu(P-Ga)$ modes have been reported at 352 and 362 cm^{-1} for H_3PGaBr_3 and $(CH_3)_3PGaBr_3$, respectively.[116] A single-crystal Raman study of $((CH_3)_3P)_2$-$InCl_3$ has produced an unambiguous assignment of the symmetric $\nu(P-In)$ mode (135 cm^{-1}).[130] In a study of the addition compounds of trimethylphosphine with several group IV tetrahalides, the $\nu(P-Si)$ modes have been suggested at 415 (A_{2u}) and 158 (A_g) cm^{-1}, the $\nu(P-Ge)$ modes at 386 (A_{2u}) and 145 (A_g) cm^{-1}, and the $\nu(P-Sn)$ modes at 346 (A_{2u}) and 146 (A_g) cm^{-1} for the series $((CH_3)_3P)_2MCl_4$ (M = Si, Ge, Sn).[131] In all three of these compounds, coupling is observed between the $\nu(P-M)$ modes and various ligand bending modes. This is especially serious for the A_{2u} $\nu(P-M)$ modes. A Raman study of mixtures of phosphorus–arsenic and phosphorus–antimony vapors has been reported.[132] In the former mixture the species P_3As and PAs_3 were detected, while in the latter mixture P_3Sb was the only interatomic system detected. It is concluded that all three species have a tetrahedral structure. This study also includes vibrational assignments and normal coordinate calculations for these compounds. The $\nu(P-Se)$ mode has been reported from 473 to 577 cm^{-1} in a study of several organophosphorus selenium compounds.[133,134] For $(C_2H_5)_3PSe$, however, another group has assigned the $\nu(P-Se)$ mode to a strong Raman band at 422 cm^{-1}.[135] The $\nu(P-Se)$ mode has also been reported from 408 to 414 cm^{-1} for several cobalt, nickel, and zinc complexes of trimethylphosphine-selenide.[136]

B. ARSENIC

Arsenic vapor at 800° consists mainly of tetrahedral As_4 molecules, with a small quantity of As_2 molecules.[137,138] In a Raman study of arsenic vapor at 900° the $\nu(As-As)$ mode of As_2 was detected at 421 cm^{-1}, while the As_4 modes were assigned to bands at 340 (A_1), 250 (F_2), and 200 (E) cm^{-1}.[80] Recently, in an infrared study of condensed arsenic vapor at −196°, the As_4 mode of F_2 symmetry (which is the only one of the three that is infrared active) is assigned at 250 cm^{-1},[139] in agreement with the results of the vapor-phase Raman study.

As with phosphorus, there are many reports of compounds with arsenic–metal bonds. Most of these compounds involve

(119) A. R. Manning, *J. Chem. Soc. A*, 1135 (1968).

(120) I. R. Beattie and R. Collins, *ibid., A*, 2960 (1969).

(121) S. Bénazeth, A. Loutellier, and M. Bigorgne, *J. Organometal. Chem.*, **24**, 479 (1970).

(122) T. Kruck and A. Prasch, *Z. Anorg. Allg. Chem.*, **356**, 118 (1968).

(123) G. D. Coates and C. Parkin, *J. Chem. Soc.*, 421 (1963).

(124) C. W. Bradford, W. van Bronswijk, R. J. H. Clark, and R. S. Nyholm, *ibid., A*, 2889 (1970).

(125) P. J. Craig, *Can. J. Chem.*, **48**, 3089 (1970).

(126) G. W. Chantry, A. Finch, P. N. Gates, and D. Steele, *J. Chem. Soc. A*, 896 (1966).

(127) R. W. Rudolph, R. W. Parry, and C. F. Farran, *Inorg. Chem.*, **5**, 723 (1966).

(128) J. Davis and J. E. Drake, *J. Chem. Soc. A*, 2959 (1970).

(129) E. Mayer and R. E. Hester, *Spectrochim. Acta, Part A*, **25**, 237 (1969).

(130) G. A. Ozin, *J. Chem. Soc. A*, 1307 (1970).

(131) I. R. Beattie and G. A. Ozin, *ibid., A*, 370 (1970).

(132) G. A. Ozin, *ibid., A*, 2307 (1970).

(133) R. A. Chittenden and L. C. Thomas, *Spectrochim. Acta*, **20**, 1679 (1964).

(134) L. C. Thomas and R. A. Chittenden, *Chem. Ind. (London)*, 1913 (1961).

(135) J. R. Durig, J. S. Di Yorio, and D. W. Wertz, *J. Mol. Spectrosc.*, **28**, 444 (1968).

(136) M. A. Brodie, G. A. Rodley, and C. J. Wilkins, *J. Chem. Soc. A*, 2927 (1969).

(137) L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, *J. Chem. Phys.*, **3**, 699 (1935).

(138) Y. Morino, T. Ukaji, and T. Ito, *Bull. Chem. Soc. Jap.*, **3**, 64 (1966).

(139) R. J. Chapwell, Jr., and G. M. Rosenblatt, *J. Mol. Spectrosc.*, **33**, 525 (1970).

palladium or platinum, for which the ν(As–M) mode has, in general, been assigned from ca. 250 to 350 cm^{-1}.[115a–e,h–1,123] More recently, ν(As–Pd) modes have been assigned at the relatively low values of 132 (R) and 180 (ir) cm^{-1} for *trans*-((C_6H_5)$_3$As)$_2$PdCl$_2$ and 130 (R) and 180 (ir) cm^{-1} for *trans*-((C_6H_5)$_3$As)$_2$PdBr$_2$.[102] These assignments were made on the basis of a comparison with the ν(P–Pd) assignments made for *trans*-((C_6H_5)$_3$P)$_2$PdCl$_2$ using the metal isotope technique, and suggest the need for further such studies to obtain more reliable ν(As–M) assignments. Other ν(As–M) assignments have been proposed for ((C_6H_5)$_3$As)$_2$SnCl$_4$ (330 cm^{-1}) and ((C_6H_5)$_3$As)$_2$SnBr$_4$ (334 cm^{-1}),[117] ((C_6H_5)$_3$As)$_2$HgI$_2$ (70 cm^{-1}), ((C_6H_5)$_3$AsHgCl$_2$)$_2$ (138 cm^{-1}) and ((C_6H_5)$_3$AsHgBr$_2$)$_2$ (112 cm^{-1}),[140] and (CH$_3$)$_3$AsAuCl (267 cm^{-1}), (CH$_3$)$_3$AsAuBr (273 cm^{-1}), and (CH$_3$)$_3$AsAuI (269 cm^{-1}).[115h]

C. ANTIMONY AND BISMUTH

Assignments have been made for the ν(Sb–M) modes of ((CH_3)$_3$Sb)$_2$PdCl$_2$ (202 and 210 cm^{-1}), ((CH_3)$_3$Sb)$_2$PtCl$_2$ (203 and 215 cm^{-1}), and ((CH_3)$_3$Sb)$_2$PtBr$_2$ (207 cm^{-1}).[115k] The ν(Sb–Sb), ν(Bi–Bi), and ν(Sb–Bi) modes for Sb$_2$, Bi$_2$, and SbBi have been assigned at 270, 172, and 221 cm^{-1}, respectively.[83] Using these data, the frequencies of several homo- and heteronuclear tetraatomic antimony and/or bismuth compounds have been estimated.[141]

On the basis of the vibrational spectra[142,143] and a normal coordinate analysis,[144] the presence of weak Bi–Bi interactions has been proposed for Bi$_6$(OH)$_{12}$$^{6+}$, with the A$_1$ ν(Bi–Bi) mode assigned at 177 cm^{-1}. Recently, an error has been noted in the original vibrational analysis of Bi$_6$(OH)$_{12}$$^{6+}$, which has resulted in some changes in the assignment.[79] The assignments originally made for the ν(Bi–Bi) modes, however, remained unchanged.

IV. Additional Main Group Elements

A. GROUP IIb

Other than the ν(P–Zn) modes reported in Table VI, only two other vibrational studies have been reported involving a zinc–metal bond. In the first, zinc was dissolved in molten zinc chloride, producing a yellow glass which contained Zn$_2$$^{2+}$. Both this yellow glass and an ether solution of the glass gave a Raman line at 175 cm^{-1} which has been assigned to the ν(Zn–Zn) mode.[145] This assignment gives a value of 0.6 mdyn/Å for the Zn–Zn stretching force constant of Zn$_2$$^{2+}$. In the other study, the symmetric ν(Zn–Co) mode of Zn(Co(CO)$_4$)$_2$ has been assigned at 170 cm^{-1}.[146]

The Raman spectrum of a melt of 0.67 Cd$_2$(AlCl$_4$)$_2$–0.33 Cd(AlCl$_4$)$_4$ exhibited a strong Raman band at 183 cm^{-1}.[147] This has been assigned to the ν(Cd–Cd) mode of Cd$_2$$^{2+}$. Using this frequency, a Cd–Cd stretching force constant of 1.11 mdyn/Å was calculated, which is twice as large as the Zn–Zn stretching force constant of Zn$_2$$^{2+}$. Both the symmetric and

asymmetric ν(Cd–Mn) stretching modes have been assigned for Cd(Mn(CO)$_5$)$_2$ at 162 and 208 cm^{-1}, respectively,[70] while the symmetric ν(Cd–Co) mode of Cd(Co(CO)$_4$)$_2$ has been assigned at 152 cm^{-1}.[148] It has been suggested that CdFe(CO)$_4$ has a cis polymeric structure with a ν(Cd–Fe) frequency of 216 or 226 cm^{-1}.[149]

As noted in the Introduction, the first assignment of a metal–metal stretching mode was made for Hg$_2$$^{2+}$ at 169 cm^{-1}.[3] Since this assignment was made, the ν(Hg–Hg) mode has been assigned for many other compounds with Hg–Hg bonds. Among these is the assignment of the ν(Hg–Hg) mode at 167 cm^{-1} for Hg$_2$Cl$_2$.[150] Although this assignment has been confirmed by other workers,[64,151] the assignment made for the asymmetric ν(Hg–Cl) mode of this compound has been questioned.[152] The ν(Hg–Hg) mode has also been assigned for Hg$_2$F$_2$ (185.9 cm^{-1}),[151] Hg$_2$Br$_2$ (133 cm^{-1}),[64] and Hg$_2$I$_2$ (112.5 cm^{-1})[151] in addition to several other Hg$_2$X$_2$-type compounds.[151] The data on ν(Hg–Hg) stretching assignments have recently been thoroughly reviewed.[10]

The ν(Hg–M) mode has also been assigned for several mercury–transition metal compounds with Hg–M and linear or bent Hg$_2$M or HgM$_2$ bonds. The first vibrational study of such a compound was made on Hg(Co(CO)$_4$)$_2$. The presence of a linear Co–Hg–Co skeleton was indicated by the presence of only the symmetric ν(Hg–Co) mode in the Raman spectrum.[148] This conclusion has been confirmed in a later study.[153] The presence of substantial vibrational interaction between the ν(Hg–X) and ν(Hg–Fe) modes of *cis*-Fe(CO)$_4$(HgX)$_2$ (X = Br, I) makes it unreasonable to assign these modes separately.[149] It is more reasonable to make assignments for the entire Fe(HgX)$_2$ framework. Although a similar interaction is present in *cis*-Fe(CO)$_4$(HgCl)$_2$, it is not as great as in the corresponding bromide and iodide, and the asymmetric ν(Hg–Fe) mode of the chloride has been assigned in the infrared spectrum.[149] A similar situation is present in the series XHgMn(CO)$_5$ (X = Cl, Br, I). Though the ν(Hg–Mn) mode of the chloride has been made, interactions between the ν(Hg–Mn) and ν(Hg–X) modes of the bromide and iodide make it unreasonable to assign the ν(Hg–Mn) modes for these two compounds.[154] Table VII summarizes the ν(Hg–M) assignments made for several compounds.[148,149,154–157]

B. GROUP IIIa

As is true for phosphorus compounds such as P$_2$X$_4$, boron compounds of the type B$_2$X$_4$ can also exist in different configurations. According to electron diffraction studies, gaseous B$_2$Cl$_4$ takes on a staggered configuration of V$_d$ symmetry.[158,159]

(140) G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, **25**, 355 (1969).
(141) F. J. Kohl and K. D. Carlson, *J. Amer. Chem. Soc.*, **90**, 4814 (1968).
(142) A. Olin, *Sv. Kem. Tidskr.*, **73**, 498 (1961).
(143) V. A. Maroni and T. G. Spiro, *J. Amer. Chem. Soc.*, **88**, 1410 (1966).
(144) V. A. Maroni and T. G. Spiro, *Inorg. Chem.*, **7**, 183 (1968).
(145) D. H. Kerridge and S. A. Tariq, *J. Chem. Soc. A*, 1122 (1967).
(146) J. M. Burlitch, *J. Organometal. Chem.*, **9**, P9 (1967).
(147) J. D. Corbett, *Inorg. Chem.*, **1**, 700 (1962).

(148) H. Stammreich, K. Kawai, O. Sala, and P. Krumholz, *J. Chem. Phys.*, **35**, 2175 (1961).
(149) D. M. Adams, D. J. Cook, and R. D. W. Kemmitt, *Nature (London)*, **205**, 589 (1965).
(150) H. Poulet and J. P. Mathieu, *J. Chim. Phys. Physicochim. Biol.*, **60**, 442 (1967).
(151) H. Stammreich and Th. Teixeira Sans, *J. Mol. Struct.*, **1**, 55 (1967–1968).
(152) M. Goldstein, *Spectrochim. Acta*, **22**, 1389 (1966).
(153) D. M. Adams, J. B. Cornell, J. L. Dawes, and R. D. W. Kemmitt, *Inorg. Nucl. Chem. Lett.*, **3**, 437 (1967).
(154) P. N. Brier, A. A. Chalmers, J. Lewis, and S. B. Wild, *J. Chem. Soc. A*, 1889 (1967).
(155) C. W. Bradford, W. van Bronswyk, R. J. H. Clark, and R. S. Nyholm, *ibid.*, *A*, 2456 (1968).
(156) D. M. Adams and A. Squire, *ibid.*, *A*, 2817 (1968).
(157) W. Beck and K. Noack, *J. Organometal. Chem.*, **10**, 307 (1967).
(158) K. Hedberg and R. Ryan, *J. Chem. Phys.*, **41**, 2214 (1964).
(159) R. Ryan and K. Hedberg, *ibid.*, **50**, 4986 (1969).

Table VII

Mercury–Transition Metal Stretching Frequencies

Compound	$\nu(Hg-M)$ mode	Symmetry	Frequency, cm^{-1}	Ref
$ClHgMn(CO)_5$	Hg–Mn	. . .	184 (ir)	154
$BrHgMn(CO)_5$	Br–Hg–Mn[a]	Linear	162 (ir), 195 (ir)	154
$IHgMn(CO)_5$	I–Hg–Mn[a]	Linear	120 (ir), 176 (ir)	154
cis-$Os(CO)_4(HgCl)Cl$	Hg–Os	. . .	155 (R), 172 (R)	155
$Hg(Cr(CO)_3(C_5H_5))_2$	Cr–Hg–Cr (s[b])	Linear	. . .[c]	153
	Cr–Hg–Cr (a[b])	Linear	186 (ir)	153
$Hg(Mn(CO)_5)_2$	Mn–Hg–Mn (s)	Linear	167 (R)	153, 156
	Mn–Hg–Mn (a)	Linear	188 (ir)	153, 154, 156
$Hg(Fe(CO)_2(C_5H_5))_2$	Fe–Hg–Fe (s)	Linear	. . .[c]	153
	Fe–Hg–Fe (a)	Linear	200 (ir)	153
$Hg(Fe(CO)_3NO)_2$	Fe–Hg–Fe (a)	Linear	186 (ir)	157
$Hg(Co(CO)_4)_2$	Co–Hg–Co (s)	Linear	161 (R)	148, 153
	Co–Hg–Co (a)	Linear	196 (ir)	153, 154
$Hg(Mo(CO)_3(C_5H_5))_2$	Mo–Hg–Mo (s)	Linear	. . .[c]	153
	Mo–Hg–Mo (a)	Linear	178 (ir)	153
$Hg(W(CO)_3(C_5H_5))_2$	W–Hg–W (s)	Linear	133 (R)	153
	W–Hg–W (a)	Linear	166 (ir)	153, 154
$(HgFe(CO)_4)_n$[d]	Hg–Fe–Hg	Bent	170 (ir)	157
	Hg–Fe–Hg	Bent	201 (ir)	149, 154, 157
cis-$Fe(CO)_4(HgCl)_2$	Hg–Fe–Hg[e]	Bent	219 (ir)	149, 154
cis-$Ru(CO)_4(HgCl)_2$	Hg–Ru–Hg[e]	Bent	170 (R), 187 (R)	153
cis-$Ru(CO)_4(HgBr)_2$	Hg–Ru–Hg[e]	Bent	157 (R), 175 (R)	153
cis-$Os(CO)_4(HgCl)_2$	Hg–Os–Hg[e]	Bent	156 (R), 169 (R)	153
cis-$Os(CO)_4(HgBr)_2$	Hg–Os–Hg[e]	Bent	140 (R), 156 (R)	153
cis-$Os(CO)_4(HgI)_2$	Hg–Os–Hg[e]	Bent	135 (R), 140 (R)	153

[a] Calculations indicate coupling of the $\nu(Hg-Mn)$ and $\nu(Hg-X)$ modes. [b] s = symmetric stretching mode; a = asymmetric stretching mode. [c] Sample gave poor Raman spectrum; preventing observation of this mode. [d] Polymeric structure with mercury atoms cis to the iron atom. [e] Not assigned as either symmetric or asymmetric stretching mode by the authors.

Infrared[160-163] and Raman[160,161,164] spectra of B_2F_4 and B_2Cl_4 in the vapor and liquid states have also been interpreted in terms of the staggered structure. The presence of two naturally occurring isotopes of boron (^{10}B = 20%, ^{11}B = 80%) can simplify the analysis of the vibrational spectra of boron compounds. From the liquid-state Raman spectra, assignments have been made for the $\nu(B-B)$ mode of both B_2Cl_4 ($\nu(^{10}B-^{10}B)$ = 1177.0 cm^{-1}, $\nu(^{10}B-^{11}B)$ = 1152.8 cm^{-1}, $\nu(^{11}B-^{11}B)$ = 1128.6 cm^{-1}) and B_2F_4 ($\nu(^{10}B-^{10}B)$ = 1456.6 cm^{-1}, $\nu(^{11}B-^{11}B)$ = 1398.2 cm^{-1}).[164] In contrast to the situation in the liquid and vapor states, X-ray diffraction studies have shown that B_2F_4 and B_2Cl_4 are planar in the solid state.[165,166] This is also the conclusion of an infrared study of solid B_2F_4 at $-190°$.[162] In a recent infrared study of B_2F_4 and B_2Cl_4 in a solid argon matrix at liquid hydrogen temperature, it is concluded that both molecules have the staggered configuration of V_d symmetry.[164]

Very little data are available for borohydrides. The infrared and Raman spectra of $B_{12}H_{12}{}^{2-}$ have been shown to be in agreement with the predictions for a regular icosahedral structure.[167] A normally intense infrared band from *ca.*

1000 to 1075 cm^{-1} has been reported to be characteristic of systems with a boron cage structure.[167-171] The absence of such an absorption in the infrared spectrum of $B_4(N(CH_3)_2)_4$ has led to the proposal that this compound might contain a planar four-membered boron ring.[170]

Diborane (B_2H_6) has been shown to have a bridging structure in an electron diffraction study.[172] Since the B–B distance found in the electron diffraction study (1.77 Å) is approximately equal to the sum of the tetrahedral covalent boron radii (1.76 Å), the possible existence of a B–B interaction has been proposed.[173] Using previously reported vibrational data on B_2H_6,[174] a normal coordinate analysis, which included a B–B stretching force constant of 2.72 mdyn/Å, has been reported for this molecule.[175] The magnitude of this force constant is given as confirming the existence of a B–B bond, and Raman bands at 820 cm^{-1} for $^{10}B_2H_6$ and 794 cm^{-1} for $^{11}B_2H_6$ are assigned as predominantly $\nu(B-B)$ in character. Similar assignments are given in another recent vibrational study of diborane.[176] This conclusion, however, may not be a valid one since it has been shown possible to include a metal–metal force constant in normal coordinate calculations

(160) M. J. Linevsky, E. R. Shull, D. E. Mann, and T. Wartik, *J. Amer. Chem. Soc.*, **75**, 3287 (1953).
(161) D. E. Mann and L. Fano, *J. Chem. Phys.*, **26**, 1665 (1957).
(162) J. N. Gayles and J. Self, *ibid.*, **40**, 3530 (1964).
(163) A. Finch, I. Hyams, and D. Stelle, *Spectrochim. Acta*, **21**, 1423 (1965).
(164) L. A. Simon, K. S. Seshadri, R. C. Taylor, and D. White, *J. Chem. Phys.*, **53**, 2416 (1970).
(165) M. Atoji, P. J. Wheatley, and W. N. Lipscomb, *ibid.*, **27**, 196 (1957).
(166) L. Trefonas and W. N. Lipscomb, *ibid.*, **28**, 54 (1958).
(167) E. L. Muetterties, R. E. Merrifield, H. C. Miller, W. H. Knoth, Jr., and J. R. Downing, *J. Amer. Chem. Soc.*, **84**, 2506 (1962).

(168) A. R. Pitochelli and M. F. Hawthorne, *ibid.*, **82**, 3228 (1960).
(169) G. Urry, E. P. Schram, and S. I. Weissman, *ibid.*, **84**, 2654 (1962).
(170) G. Urry, A. G. Garrett, and H. I. Schlesinger, *Inorg. Chem.*, **2**, 396 (1963).
(171) J. L. Boone, *J. Amer. Chem. Soc.*, **86**, 5036 (1964).
(172) K. Hedberg and V. Schomaker, *ibid.*, **73**, 1482 (1951).
(173) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.
(174) R. C. Lord and E. Nielsen, *J. Chem. Phys.*, **19**, 1 (1951).
(175) T. Ogawa and T. Miyazawa, *Spectrochim. Acta*, **20**, 557 (1964).
(176) W. L. Smith and I. M. Mills, *J. Chem. Phys.*, **41**, 1479 (1964).

for which no metal–metal interactions seem possible (reference should be made to the discussion in section V.B on Nb_6-$O_{19}{}^{8-}$ and $Ta_6O_{19}{}^{8-}$).[177] On methylation of B_2H_6, the terminal rather than bridging hydrogens are replaced. The ν(B–B) mode has been assigned for monomethyldiborane (697 cm^{-1}), 1,1-dimethyldiborane (619 cm^{-1}), trimethyldiborane (572 cm^{-1}), and tetramethyldiborane (508 cm^{-1}).[178]

Both electron diffraction[179] and X-ray crystallographic[180] studies have shown that trimethylaluminum, like diborane, has a bridging dimeric structure. The possibility of an Al–Al interaction in $(CH_3)_6Al_2$ has been discussed by several groups.[179–182] A normal coordinate calculation treating all 26 atoms of $(CH_3)_6Al_2$ has recently been reported.[183] An Al–Al stretching force constant of 1.059 mdyn/Å was used in this calculation with a 312-cm^{-1} Raman band assigned as being due primarily to the ν(Al–Al) mode. As was true for diborane, however, it is dangerous to postulate the existence of an Al–Al interaction because an Al–Al stretching force constant appears to be needed in a normal coordinate calculation. A Ga–Ga stretching force constant (1.618 mdyn/Å) has been used in a vibrational analysis of Ga_2Cl_6.[184] Another group of workers has reported the normal coordinate analyses of diborane and the series M_2X_6 (M = Al, Ga, In; X = Cl, Br, I).[185] While this group felt that there probably is a B–B interaction in B_2H_6, a M–M stretching force constant seemed neither necessary nor desirable for the M_2X_6 series. Therefore, the results mentioned above for Ga_2Cl_6 were questioned. It was concluded that, although a relatively large Al–Al stretching force constant has been reported for $(CH_3)_6Al_2$,[183] the Al–Al distance in this compound (2.55 Å)[179] is very close to that reported for the sum of the covalent radii for tetrahedral aluminum (2.25 Å).[173] The metal–metal distance for all of the halides, however, is greater than 3 Å, which points to the unlikely presence of a significant Ga–Ga interaction in Ga_2Cl_6. There has been a recent characterization of the anions $Ga_2X_6{}^{2-}$ (X = Cl, Br, I) which contain a Ga–Ga bond and probably have an ethane-like rather than bridging structure.[186] The ν(Ga–Ga) mode for this series is assigned at 233, 162, and 122 cm^{-1} for the chloride, bromide, and iodide, respectively. The species $Ga_2Cl_6{}^{2-}$ has also been detected by the presence of the ν(Ga–Ga) mode (ca. 235 cm^{-1}) in the Raman spectrum of gallium metal dissolved in molten Ga_2Cl_4.[187] The Raman spectra of both molten In_2Cl_3 and a molten mixture of InCl in a LiCl–KCl eutectic have been reported.[188] In both samples, In$^+$ disproportionates in the presence of free chloride to form an In–In bond between In^0 and In$^{III}Cl_4{}^-$. The ν(In–In) mode is assigned to a strong polarized band at ca. 170 cm^{-1}.

The infrared and Raman spectra have been reported for $Tl_4(OR)_4$ (R = ethyl, n-propyl).[189] The Tl atoms form a tetrahedral cluster. A stretching force constant of 0.26 mdyn/Å was estimated for the Tl–Tl bond with the A_1 ν(Tl–Tl) mode (which also contains a 31% contribution from the δ(Tl–O–C) mode) assigned at 102 cm^{-1}. The vibrational spectrum of $TlAu(CN)_2$ has been analyzed.[190] The data indicate the presence of a T-shaped structure with a weak Tl–Au bond and a linear or near-linear $Au(CN)_2$ group. It is further suggested that the ν(Tl–Au) mode can be assigned either to a Raman band at 124 cm^{-1} or to one of the lower frequency bands at 78 or 67 cm^{-1}.

C. SELENIUM AND TELLURIUM

There have been many reports of compounds containing selenium or tellurium. By heating a potassium iodide crystal in a selenium atmosphere, the $Se_2{}^-$ anion is produced.[191] The Raman spectrum of this sample at liquid-helium temperature showed a band at 328 cm^{-1} which has been assigned to the ν(Se–Se) mode. This frequency is comparable to the value of 392 cm^{-1} for the ν(Se–Se) mode of Se_2.[83] It has been shown that the $Se_4{}^{2+}$ species in $Se_4(HS_2O_7)_2$ has a square-planar structure of D_{4h} symmetry[192] as illustrated in Figure 5. The $Se_4{}^{2+}$ system can be considered as an "aromatic" six π-electron compound. The infrared and Raman spectra have been reported for a number of compounds containing the $Se_4{}^{2+}$ group. The characteristic frequencies of the $Se_4{}^{2+}$ group are at 327 (A_{1g}), 306 (E_u), and 188 (B_{2g}) cm^{-1}, and the Se–Se stretching force constant (Urey–Bradley force field) is 2.2 mdyn/Å.[193] It has been reported that the red solution produced on slowly dissolving tellurium in cold H_2SO_4 or HSO_3F contains $Te_4{}^{2+}$.[194] In view of the similarity observed between the infrared and Raman spectra of $Te_4{}^{2+}$ and $Se_4{}^{2+}$, the square-planar structure has also been proposed for $Te_4{}^{2+}$.[194]

Both S_2Cl_2 and S_2Br_2 have been shown to have neither a cis nor trans structure but a skewed structure between the cis and trans extremes of C_2 symmetry.[195] Vibrational data indicate that a similar structure is present for Se_2Cl_2 and Se_2Br_2.[196,197] The ν(Se–Se) mode for Se_2Cl_2 and Se_2Br_2 has been assigned at 288 and 292 cm^{-1}, respectively.[196–198] In a normal coordinate analysis of these two compounds using a general valence force field, Se–Se stretching force constants of 1.88 mdyn/Å for the chloride and 1.74 mdyn/Å for the bromide have been reported.[199] The vibrational spectra of $(CH_3)_2Se_2$ in the vapor,[200] liquid,[201] and solid[201] states all indicate the presence of the skewed conformation. The ν(Se–Se) mode of $(CH_3)_2Se_2$ has been assigned at 286 cm^{-1},[200,201]

(177) F. J. Farrell, V. A. Maroni, and T. G. Spiro, *Inorg. Chem.*, **8**, 2638 (1969).

(178) J. H. Carpenter, W. J. Jones, R. W. Jotham, and L. H. Long, *Chem. Commun.*, 881 (1968); *Spectrochim. Acta, Part A*, **26**, 1199 (1970).

(179) P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).

(180) R. G. Vranka and E. L. Amma, *J. Amer. Chem. Soc.*, **89**, 3121 (1967).

(181) T. Ogawa, K. Hirota, and T. Miyazawa, *Bull. Chem. Soc. Jap.*, **38**, 1105 (1965).

(182) K. A. Levison and P. G. Perkins, *Discuss. Faraday Soc.*, **47**, 183 (1969).

(183) T. Ogawa, *Spectrochim. Acta*, **24**, 15 (1968).

(184) I. R. Beattie, T. Gilson, and P. Cocking, *J. Chem. Soc. A*, 702 (1967).

(185) D. M. Adams and R. G. Churchill, *ibid.*, *A*, 697 (1970).

(186) C. A. Evans and M. J. Taylor, *Chem. Commun.*, 1201 (1969).

(187) M. J. Taylor, *J. Chem. Soc. A*, 2812 (1970).

(188) J. H. R. Clarke and R. E. Hester, *Inorg. Chem.*, **8**, 1113 (1969).

(189) V. A. Maroni and T. G. Spiro, *ibid.*, **7**, 193 (1968).

(190) H. Stammreich, B. M. Chadwick, and S. G. Frankiss, *J. Mol. Struct.*, **1**, 191 (1967–1968).

(191) W. C. Holton and M. de Wit, *Solid State Commun.*, **7**, 1099 (1969).

(192) I. D. Brown, D. B. Crump, R. J. Gillespie, and D. P. Santry, *Chem. Commun.*, 853 (1968).

(193) R. J. Gillespie and G. P. Pez, *Inorg. Chem.*, **8**, 1229 (1969).

(194) J. Barr, R. J. Gillespie, R. Kapoor, and G. P. Pez, *J. Amer. Chem. Soc.*, **90**, 6855 (1968).

(195) E. Hirota, *Bull. Chem. Soc. Jap.*, **31**, 130 (1958).

(196) P. J. Hendra and P. J. D. Parks, *J. Chem. Soc. A*, 908 (1968).

(197) S. G. Frankiss, *J. Mol. Struct.*, **2**, 271 (1968).

(198) H. Stammreich and R. Forneris, *Spectrochim. Acta*, **8**, 46 (1956).

(199) R. Forneris and C. E. Herrnies, *J. Mol. Struct.*, **5**, 449 (1970).

(200) W. H. Green and A. B. Harvey, *J. Chem. Phys.*, **49**, 3586 (1968).

(201) S. G. Frankiss, *J. Mol. Struct.*, **3**, 89 (1969).

while it has been assigned at 293 cm^{-1} for $(n$-$C_4H_9)_2Se_2$.[202] The ν(Te–Te) mode of $(CH_3)_2Te_2$ has been assigned at 188 cm^{-1} with a normal coordinate analysis indicating that the Te–Te bond is weaker than the Se–Se bond in $(CH_3)_2$-Se_2.[203] The ν(Te–Pt) mode has been assigned from 177 to 197 cm^{-1} for $(R_2Te)_2Pt_2Cl_4$ ($R = C_2H_5$, n-C_3H_7).[115f] Table VIII summarizes several assignments made for ν(Se–M)

Table VIII

Various Selenium–Metal Stretching Frequencies

Compound	ν(Se–M) mode	Frequency, cm^{-1}	Ref
$(CoL_4)(ClO_4)_2{}^a$	Se–Co	201, 237	136
$CoL_2Cl_2{}^a$	Se–Co	227	136
$CoL_2Br_2{}^a$	Se–Co	211, 222	136
$COL_2I_2{}^a$	Se–Co	223, 231	136
$(NiL_4)(ClO_4)_2{}^a$	Se–Ni	250	136
$(ZnL_4)(ClO_4)_2{}^a$	Se–Zn	202	136
$ZnL_2Cl_2{}^a$	Se–Zn	225	136
$ZnL_2Br_2{}^a$	Se–Zn	. . .^{b}	136
$((CH_3)_3Sn)_2Se$	Se–Sn	224, 238	204
$((CH_3)_2Se)_2PdCl_4$	Se–Pd	282	115f
$((n$-$C_3H_7)_2Se)_2PdCl_4$	Se–Pd	290	115f
$(Pd(su)_4)Cl_2{}^c$	Se–Pd	176 (B_{2g}) 182 (A_{1g}) 235, 253 (E_u)	205
$(Pd(su)_4)Br_2{}^c$	Se–Pd	170 (B_{2g}) 186 (A_{1g}) 235, 245 (E_u)	205
$(Pt(su)_4)Cl_2{}^c$	Se–Pt	190 (B_{2g}) 199 (A_{1g}) 214, 231 (E_u)	205
$(Pt(su)_4)Br_2{}^c$	Se–Pt	182 (B_{2g}) 202 (A_{1g}) 215, 227 (E_u)	205
$MoSe_4{}^{2-}$	Se–Mo	255 (A_1) 340 (F_2)	206
$WSe_4{}^{2-}$	Se–W	278 (A_1) 310 (F_2)	206

^{a} L = $(CH_3)_3PSe$. ^{b} Coupling between the ν(Zn–Br) and ν(Se–Zn) modes prevented assignment of the ν(Se–Zn) mode. ^{c} su = $(NH_2)_2CSe$.

modes.[115f,136,204–206]

V. Transition Metal Elements

A. BIMETALLIC AND LINEAR AND BENT TRIMETALLIC SYSTEMS

Most of the vibrational studies of bimetallic transition metal compounds have dealt with metal carbonyl compounds with the general formula $M_2(CO)_{10}$. The structure determined for one of these, $Mn_2(CO)_{10}$, in an X-ray crystal study[207]

(202) K. G. Allum, J. A. Creighton, J. H. S. Green, G. J. Minkoff, and L. J. S. Prince, *Spectrochim. Acta, Part A*, **24**, 927 (1968).
(203) C. W. Sink and A. B. Harvey, *J. Mol. Struct.*, **4**, 203 (1969).
(204) H. Kriegsman, H. Hoffman, and H. Geissler, *Z. Anorg. Allg. Chem.*, **341**, 24 (1965).
(205) P. J. Hendra and Z. Jóvic, *Spectrochim. Acta, Part A*, **24**, 1713 (1968).
(206) A. Müller, B. Krebs, R. Kebabcioglu, M. Stockburger, and O. Glemser, *ibid., Part A*, **24**, 1831 (1968).
(207) (a) L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957); (b) L. F. Dahl and R. E. Rundle, *Acta Crystallgr.*, **16**, 419 (1963).
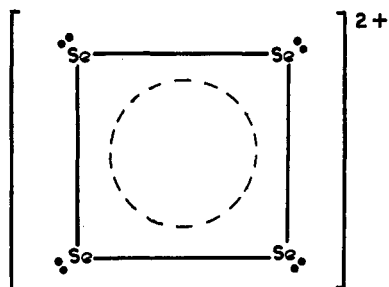
Figure 5. Structure of $Se_4{}^{2+}$ in $Se_4(HS_2O_7)_2$.[192]
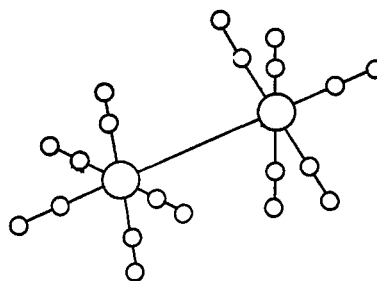
Figure 6. Structure determined for $Mn_2(CO)_{10}$ in the solid state.[207]

is shown in Figure 6. Two of the carbonyl groups and the metal atoms are colinear. The remaining carbonyl groups form two staggered squares with the metal atoms displaced outward from the squares.

The first assignment of the ν(M–M) mode for a $M_2(CO)_{10}$-type compound was made for $Re_2(CO)_{10}$.[208] In this study, the ν(Re–Re) mode was assigned to a strong polarized Raman band at 128 cm^{-1}. At approximately the same time, a second group of workers tentatively assigned the ν(Re–Re) mode of $Re_2(CO)_{10}$ (120 cm^{-1}) and gave a value of 0.8 mdyn/Å as the approximate Re–Re stretching force constant.[209] They noted, however, that the 120-cm^{-1} band might also be due to a δ(Re–C–O) mode. In a third study, a value of 1.6 mdyn/Å was given as the approximate Re–Re stretching force constant of $Re_2(CO)_{10}$.[64] In this calculation, $Re_2(CO)_{10}$ together with $Mn_2(CO)_{10}$ and $MnRe(CO)_{10}$ were treated as diatomic molecules with each atom having a mass of a $M(CO)_5$ unit. This third study also included assignments of the ν(Mn–Mn) mode of $Mn_2(CO)_{10}$ (157 cm^{-1}) and the ν(Mn–Re) mode of $MnRe(CO)_{10}$ (182 cm^{-1}). The values obtained, however, for the Re–Re, Mn–Mn (1.43 mdyn/Å), and Mn–Re (2.3 mdyn/Å) stretching force constants for these three compounds gave an unexpected order for the metal–metal bond strengths. A fourth group compared the vibrational spectra of $Re_2(CO)_{10}$ and $Re(CO)_5I$ and proposed that the ν(Re–Re) and δ(C–Re–C) modes of $Re_2(CO)_{10}$ lie close to one another and are probably in Fermi resonance.[210] Polarized Raman bands at 128 cm^{-1} in $Re_2(CO)_{10}$ and ca. 125 cm^{-1} in $Re(CO)_5I$ were assigned to the A_1 δ(C–Re–C) mode, and another reportedly polarized Raman band of $Re_2(CO)_{10}$ at ca. 100 cm^{-1} which is absent from the Raman spectrum of $Re(CO)_5I$ was assigned to the

(208) J. Lewis, A. R. Manning, J. R. Miller, M. J. Ware, and F. Nyman, *Nature (London)*, **207**, 142 (1965).
(209) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 1328 (1965).
(210) I. J. Hyams, D. Jones, and E. R. Lippincott, *J. Chem. Soc. A*, 1987 (1967).
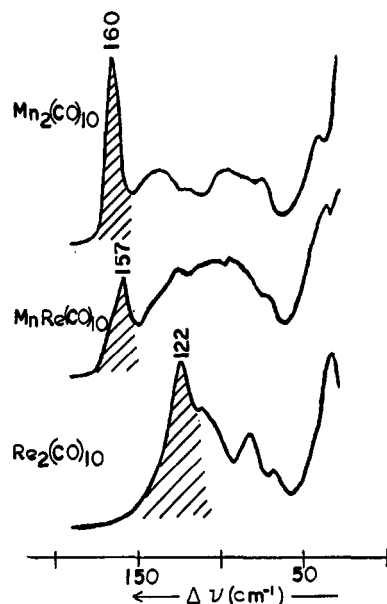
Figure 7. Low-frequency Raman spectra of $Mn_2(CO)_{10}$, MnRe-$(CO)_{10}$, and $Re_2(CO)_{10}$.[211] Shaded peaks indicate metal–metal stretching band.

ν(Re–Re) mode. The ν(Mn–Mn) mode of $Mn_2(CO)_{10}$ has also been assigned at 163 cm^{-1},[156] in close agreement with the original assignment.

More recently two additional vibrational studies on dimetallic carbonyls have appeared which help to explain some of the anomalies thus far obtained for these compounds. In the first the Raman spectra of polycrystalline samples of $Re_2(CO)_{10}$, $Mn(CO)_{10}$, and MnRe$(CO)_{10}$ have been reinvestigated.[211] The Raman spectra between 50 and 250 cm^{-1} (illustrated in Figure 7) have been assigned, and normal coordinate calculations have been performed for these three compounds. The ν(Tc–Tc) mode (communicated by another group[212]) and normal coordinate analysis of $Tc_2(CO)_{10}$ are also included. The assignment of the ν(Mn–Mn) mode of $Mn_2(CO)_{10}$ (160 cm^{-1}) agrees with those previously made.[64,156] The assignment for the ν(Re–Re) mode of $Re_2(CO)_{10}$ (122 cm^{-1}) agrees with all of the previous assignments.[64,208,209] except for the last.[210] The band at $ca.$ 100 cm^{-1} which this last group[210] reported to be polarized, did not, indeed, appear to be polarized. In addition, the normal coordinate analysis indicated that the A_1 δ(C–Re–C) mode of $Re_2(CO)_{10}$ should appear at $ca.$ 57 cm^{-1}, although it was not observed in the Raman spectra of any of the $M_2(CO)_{10}$-type compounds studied. The assignment of the ν(Mn–Re) mode of MnRe-$(CO)_{10}$ (157 cm^{-1}) which has been confirmed in another recent study (154 cm^{-1})[213] differed from the previous assignment.[64] The ν(Tc–Tc) mode of $Tc_2(CO)_{10}$ was assigned at 148 cm^{-1}. In the second study, the Raman spectra of solutions and polycrystalline samples of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ and of an oriented single crystal of $Mn_2(CO)_{10}$ are reported and discussed for both the ν(CO) and low-frequency (below 700 cm^{-1}) regions.[214] The spectra of polycrystalline $Mn_2(CO)_{10}$

and $Re_2(CO)_{10}$ below 700 cm^{-1} are identical when taken at ambient temperature with those previously reported[211] except for the presence of one additional band for each at 25 and 19 cm^{-1}, respectively. On cooling the samples to $ca.$ $-153°$, however, much better spectral resolution was obtained. The presence of lattice modes in this region complicated the assignment of the spectra.

As seen in Table IX, complete normal coordinate analyses

Table IX

Metal–Metal Stretching Force Constants (mdyn/Å) for the Series $M_2(CO)_{10}$ (M = Mn, Re, Tc) and MnRe$(CO)_{10}$

Compound	Force constants[a]		
	NCA^b	$NFRL^c$	$IFRL^d$
$Mn_2(CO)_{10}$	0.59	0.41	1.46
$MnRe(CO)_{10}$	0.81	0.61	1.76
$Re_2(CO)_{10}$	0.82	0.81	1.42
$Tc_2(CO)_{10}$	0.72	0.63	1.53

[a] All frequency assignments taken from ref 211. [b] Values obtained from complete normal coordinate analyses in ref 211. [c] Simple diatomic calculation in which mass of carbonyl groups is neglected; NFRL = neglect of first row ligands. [d] Simple diatomic calculation in which mass of carbonyl groups is included with mass of metal atom; IFRL = include first row ligands.

based on the latest vibrational assignments for several M_2-$(CO)_{10}$ compounds give a more reasonable trend in the metal–metal stretching force constants. For the transition elements, the metal–metal bond strength is expected to decrease on going across the periodic table and increase on going down the periodic table.[215] Table IX also included the metal–metal force constants obtained for these compounds using the two common types of diatomic approximations. In the first, the full mass of the $M(CO)_5$ unit is included in a simple diatomic calculation. The metal–metal stretching force constants obtained using this type of approximation are too high. The second type of approximation involves the neglect of the carbonyl groups in a diatomic calculation. This is a poor approximation when the metal is as light as manganese, since vibrational coupling with the carbonyl modes can be serious in these cases. Since most of the ligands bonded to metals are first row elements, the force constants obtained by using this type of approximation have been referred to as "neglect of first row ligand" or NFRL force constants by Spiro.[10] He has reported values of these force constants for many compounds in his recent review on vibrational spectra and metal–metal bonds. He notes that these approximations could be improved by calculating an "effective mass" which takes into account the effect of coupling but that the procedures for such a calculation[216,217] can be quite involved. The NFRL approximation is most useful when the mass of the ligand bonded to the metal atom is small relative to the mass of the metal atom and therefore is most useful when the ligand is a first row ligand. Therefore, although both approximations have limitations, it has been found that the best model for calculating approximate metal–metal stretching force con-

(211) C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, **8**, 2363 (1969).

(212) R. Levenson and H. B. Gray, private communication, cited in ref 211.

(213) G. O. Evans, W. T. Wozniak, and R. K. Sheline, *Inorg. Chem.*, **9**, 979 (1970).

(214) D. M. Adams, M. A. Hooper, and A. Squire, *J. Chem. Soc. A*, 71 (1971).

(215) J. Lewis, *Pure Appl. Chem.*, **10**, 11 (1965).

(216) E. B. Wilson, J. C. Decius, and R. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955.

(217) W. T. King and B. Crawford, Jr., *J. Mol. Spectrosc.*, **5**, 421 (1960).

stants of compounds with first row ligands is one which neglects the mass of the ligands bonded to the metal atom.[10,45,218]

Assignments have also been made for the ν(Co–Co) mode in $K_8(Co_2(CN)_8)$ (184 cm^{-1}), $K_6(Co_2(CN)_{10})$ (177 cm^{-1}), Co_2-$(CO)_6(P(OC_6H_5)_3)_2$ (172 cm^{-1}), and $(Co_2(CNCH_3)_{10})(ClO_4)_4$ (190 cm^{-1}) and the ν(Ni–Ni) mode in $K_4(Ni_2(CN)_6(CO)_2$ (180 cm^{-1}) and $K_4(Ni_2(CN)_6)$ (190 cm^{-1}).[219]

The symmetric and asymmetric ν(M–M) modes have been reported for the linear trimetallic skeletons in $Mn_2Fe(CO)_{14}$ (ν_1 = 143 cm^{-1}, ν_3 = 214 and 220 cm^{-1}), $Re_2Fe(CO)_{14}$ (ν_1 = 107 cm^{-1}, ν_3 was not reported), and $ReFeMn(CO)_{14}$ (ν_1 = 135 cm^{-1}, ν_3 = 217 and 225 cm^{-1}).[213] The splitting observed in the asymmetric stretching mode is attributed to the existence of two different crystallographic molecules though the absence of splitting for the ν_1 band is not explained. The NFRL force constants reported for these compounds are 0.58 mdyn/Å (Mn–Fe) for $Mn_2Fe(CO)_{14}$, 0.58 mdyn/Å (Re–Fe) for Re_2Fe-$(CO)_{14}$ and 0.58 (Mn–Re) and 0.53 (Re–Fe) mdyn/Å for Mn-$ReFe(CO)_{14}$. In the series $Os_3(CO)_{12}X_2$ (X = Cl, Br, I) the Os_3 skeleton has been reported to be linear[220] with the ν(Os–Os) modes assigned at 116 (A_{1g}) and 163 (A_{2u}) cm^{-1} for the chloride, 100 (A_{1g}) and 157 (A_{2u}) cm^{-1} for the bromide, and 97 (A_{1g}) and 153 (A_{2u}) cm^{-1} for the iodide.[221]

B. CLUSTER COMPOUNDS

Most of the polycrystalline cluster compounds contain either carbonyl or halide ligands which are either bridging or non-bridging or both. Figure 8 illustrates various possible structures for M_3, M_4, and M_6 cluster compounds. As a general principle, the cluster frequencies of a homonuclear metal cluster compound can be shown to be at a certain ratio to one another.[10,77] This rule can prove useful in identifying the cluster frequencies. There must, however, be little interaction of the metal–metal and/or metal–ligand modes. With increasing interactions of this type which are reflected by the presence of coupling or the need of interaction force constants in a normal coordinate calculation, the ratio rule becomes less useful. Table X summarizes the frequency

Table X

Frequency Ratios Expected for Some Common Cluster Symmetries

Structure	Symmetry	Frequency ratio
M_3	D_{3h}	$\nu(A_1')/\nu(E') = \sqrt{2}/1$
M_4	T_d	$\nu(A_1)/\nu(F_2)/\nu(E) = 2/\sqrt{2}/1$
M_6	O_h	$\nu(A_{1g})/\nu(F_{2g})/\nu(F_{1u})/\nu(E_g) = 2/\sqrt{2}/\sqrt{3}/1$

ratios expected for some common types of cluster compounds.

X-Ray studies on $Ru_3(CO)_{12}$[222] and $Os_3(CO)_{12}$[223] have shown both to have the structure illustrated in Figure 8A. For both $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ two cluster modes are expected. In the former compound these modes have been assigned at
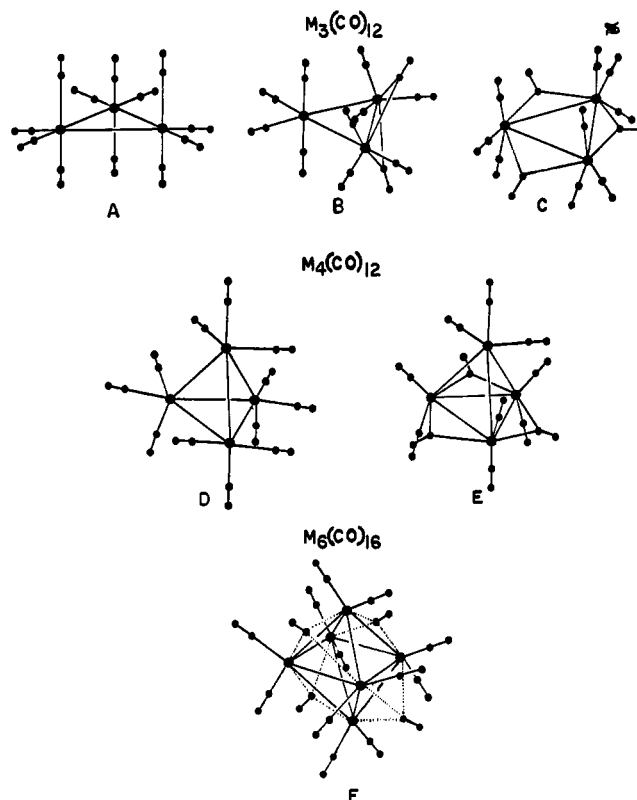

Figure 8. Some of the possible structures for metal–carbonyl cluster compounds with M_3, M_4, and M_6 metal clusters.

186 (A_1') and 152 (E') cm^{-1}, while in the latter compound the assignments are at 161 (A_1') and 120 (E') cm^{-1}.[221] These assignments have been confirmed in a second study which includes complete normal coordinate analyses of these two compounds.[224] These calculations indicate that while the A_1' cluster modes show little mixing with the ligand modes (ca. 20%) the E' cluster modes, which are closer in frequency to the δ(M–C–O) modes, show a greater degree of coupling although they are still mainly stretching in character (63% stretching in $Ru_3(CO)_{12}$ and 57% stretching in $Os_3(CO)_{12}$). The Ru–Ru and Os–Os stretching force constants were reported as 0.82 and 0.91 mdyn/Å, respectively.

The structure of $Fe_3(CO)_{12}$ in the solid state is different from that of the corresponding ruthenium and osmium compounds. An X-ray crystallographic study has shown that $Fe_3(CO)_{12}$ has the structure shown in Figure 8B.[225] Also, though the infrared spectra of $Ru(CO)_{12}$ and $Os_3(CO)_{12}$ in solution and in argon and nitrogen matrices are very similar (though the molecules are somewhat distorted from D_{3h} symmetry in the matrices), this is not true for $Fe_3(CO)_{12}$.[226] On comparing the solid-state infrared spectrum of $Fe_3(CO)_{12}$ with that obtained in solution[225,227] and, more recently, with that obtained in argon and nitrogen matrices,[226,228] it appears that while the solid-state and matrix-isolated molecules have the same structure, the solution-state structure is quite different from that found in the solid state. Figure 8C il-

(218) R. J. H. Clark and B. C. Crosse, *J. Chem. Soc. A*, 224 (1969).
(219) W. P. Griffith and A. J. Wickham, *ibid.*, *A*, 834 (1969).
(220) B. F. G. Johnson, J. Lewis, and P. A. Kilty, *Chem. Commun.*, 180 (1968); *J. Chem. Soc. A*, 2859 (1968).
(221) D. Hartley, P. A. Kilty, and M. J. Ware, *Chem. Commun.*, 493 (1968).
(222) R. Mason and A. I. M. Rae, *J. Chem. Soc. A*, 778 (1968).
(223) E. R. Corey and L. F. Dahl, *Inorg. Chem.*, 1, 521 (1962).

(224) C. O. Quicksall and T. G. Spiro, *ibid.*, 7, 2365 (1968).
(225) C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 91, 1351 (1969).
(226) M. Poliakoff and J. J. Turner, *J. Chem. Soc. A*, 654 (1971).
(227) J. Knight and M. J. Mays, *Chem. Commun.*, 1006 (1970).
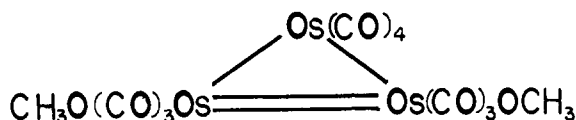(228) M. Poliakoff and J. J. Turner, *ibid.*, 1008 (1970).

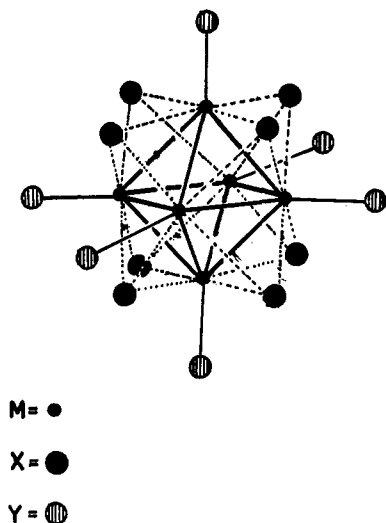**Figure 9.** Structure proposed for $Os_3(CO)_{10}(OCH_3)_2$.[221]

M = ●

X = ⬤

Y = ◍

Figure 10. Structure of a metal–halide cluster ion with the formula $M_6X_8Y_6{}^{2-}$.[237]

lustrates the proposed solution-state structure.[225] These infrared studies have been made in the carbonyl stretching region with no data reported for the ν(M–M) stretching modes.

Though it was originally concluded from vibrational data[221] that $Os_3(CO)_{10}(OCH_3)_2$ has the structure shown in Figure 9, a recent X-ray crystal study has shown that while the Os_3 skeleton does form an isosceles triangle, both methoxide groups bridge the unique Os–Os bond.[228a] This revised structure, however, does not change the original assignment of the ν(Os–Os) modes to three very strong Raman bands (two of which coincide with infrared bands) at 172 (A_1), 136 (A_1), and 119 (B_2) cm^{-1}.[221,228b] Compounds of the general formula $Os_3(CO)_{10}(AuP(C_6H_5)_3)X$ (X = Cl, Br, I, SCN) and Os_3-$(CO)_{10}(AuPR_3)Cl$ (R = $C_6H_4CH_3$) have been prepared and characterized.[124] They all contain an Os_3 triangular arrangement in which the A_1' ν(Os–Os) mode was assigned at ca. 150 cm^{-1} while the E' mode was not observed. The same study also includes vibrational data for the series $Os_3(CO)_{12-x}L_x$ (L = $P(C_6H_5)_3$; x = 1–3) which is also thought to contain an Os_3 skeleton for which the A_1' ν(Os–Os) mode is assigned from 146 to 161 cm^{-1} and the E' mode probably lies near 110 cm^{-1}.

The Ir_4 cluster is present in $Ir_4(CO)_{12}$ (Figure 8D).[229] Three skeletal cluster frequencies are expected. Two of these (A_1 and E) are only Raman active while one of them (F_2) is both infrared and Raman active. These modes were originally assigned at 208 (A_1), 164 (F_2), and 105 (E) cm^{-1}.[230] In addi-

tion to corroborating these assignments, another group has detected a band in the infrared spectrum at 164 cm^{-1} which supports the original assignment of this band to the F_2 mode.[8] The assignment of the E mode, however, has been revised by two different groups.[231,232] Both groups have assigned it to a band at 131 cm^{-1} and reassigned the 105-cm^{-1} band to an iridium–carbon deformation band. The frequency ratio then becomes $\nu(A_1)/\nu(F_2)/\nu(E) = 2.00/1.56/1.27$, which shows a greater deviation from the predicted frequency ratio than the original assignment. A normal coordinate calculation shows little mixing of the Ir_4 cluster modes with the iridium–carbon deformation modes.[232] The discrepancy between the predicted and experimental frequency ratios, however, is explained by the need of substantial metal–metal interaction force constants to fit the calculated to the observed frequencies. It was concluded, therefore, that caution must be exercised in using predictions based on cluster frequency ratios in making band assignments.[232] The structure of Rh_4-$(CO)_{12}$ differs from that of $Ir_4(CO)_{12}$ in that there are three basal bridging carbonyls (Figure 8E).[233] Although one group has assumed a tetrahedral Rh_4 cluster in assigning the cluster modes,[219] a second group has treated it as a M_3M' cluster.[234] The M_3 triangle should then give a frequency ratio of $\nu(A_1)/\nu(E)' = \sqrt{2}/1$ for its cluster modes. This ratio is well satisfied with the assignments of 176 (A_1) and 128 (E) cm^{-1}. Using these assignments, a value of 0.95 mdyn/Å is obtained for the M–M stretching force constant. The two ν(M–M') modes were assigned at 220 and 225 cm^{-1}. This assignment is predicted within 10 cm^{-1} by using a M–M' stretching force constant of 0.35 mdyn/Å. Two compounds with the formula $M_6(CO)_{16}$ (Figure 8F) have been studied using vibrational spectroscopy. One group has assigned bands at 199 (A_1) and 172 (E) cm^{-1} to two of the Rh_6 cluster modes of $Rh_6(CO)_{16}$.[219] Another group has assigned the F_{1u} cluster mode for Rh_6-$(CO)_{16}$ at 165.4 cm^{-1} and the same mode of $Co_6(CO)_{16}$ at 205 cm^{-1}.[235]

The first far-infrared study of metal halide cluster compounds did not involve the assignment of metal–metal stretching modes.[236] The first assignments of ν(M–M) modes for this type of compound were made for the series $Mo_6X_8Y_6{}^{2-}$, where X is a bridging halide ion (Cl, Br) and Y is a terminal halide ion (Cl, Br, I), and $W_6Cl_8Cl_6{}^{2-}$, all of which have the structure of O_h symmetry shown in Figure 10.[237] For systems such as these, the only infrared-active modes are those of F_{1u} symmetry. Though there are five of these, only one is a ν(M–M) mode. This fact together with the possibility of coupling between these modes makes the assignment of the infrared-active ν(M–M) mode relatively difficult. The infrared-active ν(M–M) mode for the series $Mo_6Cl_8Cl_6{}^{2-}$ (Y = Cl, Br, I) is assigned at 220, 232, and 233 cm^{-1}, respectively. For $Mo_6Cl_8Cl_6{}^{2-}$, it is concluded that the ν(Mo–Y) mode (ca. 245 cm^{-1}) interacts with the "natural" ν(Mo–Mo) mode frequency (ca. 230 cm^{-1}), thereby shifting the ν(Mo–Mo) mode

(228a) V. Duckworth and R. Mason, private communication, cited in ref. 228b.
(228b) M. J. Ware, in "Essays in Structural Chemistry," D. A. Long, A. J. Downs, and L. A. K. Staveley, Ed., Macmillan, London, 1971, p 404.
(229) G. R. Wilkes, Diss. Abstr., 26, 5029 (1966).
(230) C. O. Quicksall and T. G. Spiro, Chem. Commun., 839 (1967).

(231) F. Cariati, V. Valenti, and G. Zerbi, Inorg. Chim. Acta, 3, 378 (1969).
(232) C. O. Quicksall and T. G. Spiro, Inorg. Chem., 8, 2011 (1969).
(233) C. H. Wei and L. F. Dahl, J. Amer. Chem. Soc., 88, 1821 (1966).
(234) E. W. Abel and R. A. N. McLean, Inorg. Nucl. Chem. Lett., 5, 381 (1966).
(235) F. Cariati, V. Valenti, and P. Barone, Gazz. Chim. Ital., 99, 1327 (1969).
(236) R. J. H. Clark, D. L. Kepert, R. S. Nyholm, and G. A. Rodley, Spectrochim. Acta, 22, 1697 (1966).
(237) F. A. Cotton, R. M. Wing, and A. Zimmerman, Inorg. Chem., 6, 11 (1967).

to 220 cm^{-1}. It is also concluded that the Mo–Mo stretching force constant, and therefore the metal–metal bonding in the Mo$_6$X$_8$Y$_6$$^{2-}$ species, is not appreciably influenced by changing the Y group. In Mo$_6$Br$_8$Cl$_6$$^{2-}$, mixing of the two infrared-active ν(Mo–Br) modes and the infrared-active ν(Mo–Cl) mode produced a broad band in the region 220–230 cm^{-1} with the ν(Mo–Mo) mode assigned in the region from 240 to 260 cm^{-1}. The ν(Mo–Mo) mode and the two ν(Mo–X) modes of Mo$_6$Br$_8$Br$_6$$^{2-}$ were assigned from 220 to 250 cm^{-1} or to a strong band at $ca.$ 270 cm^{-1}. Bands at 274 cm^{-1} and from 210 to 250 cm^{-1} were assigned to the same modes for Mo$_6$Br$_8$I$_6$$^{2-}$. A weak infrared band at 150 cm^{-1} of W$_6$Cl$_8$Cl$_6$$^{2-}$ was in the region expected for the ν(W–W) mode. Relatively low-frequency infrared-active ν(Mo–Mo) assignments have also been made for Mo$_6$Cl$_8$Cl$_4$ (99 cm^{-1}), Mo$_6$Cl$_8$Br$_4$ (99 cm^{-1}), and Mo$_6$Br$_8$Br$_4$ (85 cm^{-1}) with the Mo–Mo stretching force constant given as 0.3 mdyn/Å for each of these compounds.[238] Infrared spectra have been reported for the series W$_6$X$_8$Y$_{6-n}$$^{n-2}$ (X = Cl, Br, I; Y = F, Cl, Br, I; n = 0, 2).[239] It was not thought possible to assign metal–metal and metal–halogen stretching and bending modes because of mixing and interaction of these modes. Assignments were made, however, for the W$_6$X$_8$$^{4-}$ cluster modes and the W–Y stretching and bending modes by observing spectral changes caused by varying both X and Y. These data are summarized in Table XI. The infrared-active ν(Ta–Ta) mode is assigned at 140

Table XI

Assignment of Infrared Spectra (cm^{-1}) for the Series W$_6$X$_8$Y$_n$ (X = Cl, Br, I; Y = F, Cl, Br, I; n = 4, 6)[239]

	Y = F	Y = Cl	Y = Br	Y = I
W$_6$Cl$_8$ (i^a)		318	319	320
W$_6$Cl$_8$ (i)		284	257	248
W$_6$Cl$_8$ (i)		225	212	210
W–Y (ts^a)		305	170	134
Cl–W–Y (tb^a)		105	76	57
W$_6$Br$_8$ (i)	255	245	256	255
W$_6$Br$_8$ (i)	217	215	214	204
W$_6$Br$_8$ (i)	198	198	186	143
W–Y (ts)	510	294	159	124
Br–W–Y (tb)	158	108	76	63
W$_6$I$_8$ (i)	225	237	237	229
W$_6$I$_8$ (i)	170	219	185	170
W$_6$I$_8$ (i)	157	154	156	158
W–Y (ts)	472	283	138	116
I–W–Y (tb)		114	78	61

^{a} i, internal cluster mode; ts, terminal stretching mode; tb, terminal bending mode.

cm^{-1} in a study of compounds containing the Ta$_6$X$_{12}$ (X = Cl, Br) cluster by one group[240] and at 62 cm^{-1} in Ta$_6$Br$_{12}$Br$_{12}$ and 55 and 57 cm^{-1} in Ta$_6$I$_{12}$I$_2$ by another group.[241] The low-frequency infrared spectra and some assignments have also been reported for the compounds M$_6$X$_{12}$Y$_2$ (M = Ta, Nb;
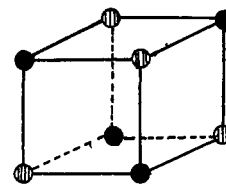

(CO)$_3$ Re = ◍

R–X = ●

Figure 11. Structure proposed for the series (Re(CO)$_3$X)$_4$, where X = SCH$_3$, SC$_6$H$_5$, or SeC$_6$H$_5$.[8]

X = Y = Cl, Br).[242] For the series Nb$_6$Cl$_{12}$$^{n+}$ (n = 2, 3, 4), the infrared-active ν(Nb–Nb) mode has been assigned at 143, 142, and 141 cm^{-1}, respectively.[243] It is suggested that the decrease of 1 cm^{-1} per unit increase in oxidation state of Nb, though small, might indicate a weakening of the metal–metal bond due to removal of electrons from the metal atom cluster.

One expects ten Raman-active modes (3A$_{1g}$ + 3E$_g$ + 4F$_{2g}$) for systems of the type M$_6$X$_8$Y$_6$$^{2-}$ with O$_h$ symmetry. Three of these (one each of A$_{1g}$, E$_g$, and F$_{2g}$ symmetry) are metal–metal cluster modes. From a Raman study of methanol solutions of the compounds Mo$_6$Cl$_8$Y$_6$$^{2-}$ (Y = Cl, Br, I), two of the three A$_{1g}$ modes have been identified by their total polarization with the third A$_{1g}$ mode attributed to bands of undetermined polarization.[244] In this study approximate Mo–Mo stretching force constants are given as 1.6, 1.6, and 1.4 mdyn/Å and the A$_{1g}$ ν(Mo–Mo) modes are assigned at 236, 150, and 117 cm^{-1} for Y = Cl, Br, I, respectively. The A$_{1g}$ ν(Mo–Mo) and ν(Mo–Y) modes, however, are also observed to be completely mixed. In another Raman study, a band at 124 cm^{-1} is assigned to the ν(Mo–Mo) mode of Cs$_2$(Mo$_6$Cl$_8$Cl$_6$).[238] The sample used in this study, however, was in the solid state and no polarization data are reported. Some of the assignments made in the previous studies[241–243] have been questioned recently since it is felt that definite assignments cannot be made without normal coordinate calculations which take into account the mixing of normal vibrations and which are based on more complete vibrational data, including Raman spectra.[245]

In addition to studies on carbonyl and halide cluster compounds, a few investigations have been reported on other types of cluster compounds. On the basis of their vibrational spectra, it has been concluded that the compounds (Re(CO)$_3$X)$_4$ (X = SCH$_3$, SC$_6$H$_5$, SeC$_6$H$_5$) (Figure 11) have structures with bridging tetradentate organothio and organoseleno groups but no formal metal–metal interaction.[8] Normal coordinate analyses have been carried out on the species Nb$_6$O$_{19}$$^{8-}$ and Ta$_6$O$_{19}$$^{8-}$ that have included metal–metal stretching force constants.[177] It is concluded, however, that metal–metal bonding is improbable in these compounds since each metal ion formally has a rare gas configuration (d^0) and a full octahedral coordination shell of oxide ions (Figure

(238) R. Mattes, *Z. Anorg. Allg. Chem.*, **357**, 30 (1968).
(239) R. D. Hogue and R. E. McCarley, *Inorg. Chem.*, **9**, 1354 (1970).
(240) R. E. McCarley, J. Meyer, B. G. Hughes, and J. G. Converse, paper presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, cited in ref 243.
(241) R. Mattes, *Z. Anorg. Allg. Chem.*, **364**, 279 (1969).

(242) P. M. Boorman and B. P. Straughan, *J. Chem. Soc. A*, 1514 (1966).
(243) R. A. Mackay and R. F. Schneider, *Inorg. Chem.*, **7**, 455 (1968).
(244) D. Hartley and M. J. Ware, *Chem. Commun.*, 912 (1967).
(245) P. B. Fleming, J. L. Meyer, W. K. Grindstaff, and R. E. McCarley, *Inorg. Chem.*, **9**, 1769 (1970).
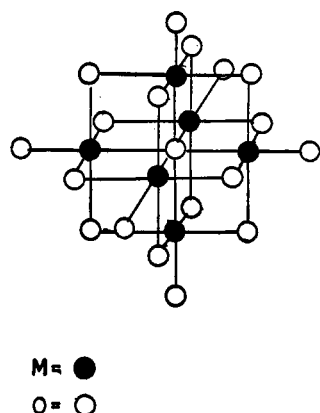
M = ●
O = ○

Figure 12. Structure of the ions $Nb_6O_{19}{}^{8-}$ and $Ta_6O_{19}{}^{8-}$.[177]

12). In addition, the Raman bands of these compounds[246,247] below 300 cm^{-1} are relatively weak in intensity. Raman-active $\nu(M-M)$ modes, however, are expected to be strong in intensity. Therefore, since it is possible to include metal–metal stretching force constants in calculations of vibrational frequencies, even though no metal–metal interaction exists, the importance of Raman intensities must be emphasized in discussions of the vibrational spectra of polymetallic compounds with bridging ligands. The Raman and infrared spectra have been reported for the tetrameric molecules $((CH_3)_3PtX)_4$ (X = OH, Cl, I).[248] This study has included single-crystal Raman studies of the hydroxide and chloride which have provided an unambiguous determination of the symmetry of the observed bands. Since there is only one tetrameric

molecule per unit cell, no lattice vibrations are allowed in either the infrared or Raman spectra. A series of three strong low-frequency Raman bands was observed with frequency ratios close to those expected for a tetrahedron of like atoms. These are assigned to the $\nu(Pt-Pt)$ modes as shown in Table XII. The data in Table XII also show the Pt–Pt stretching

Table XII

Platinum–Platinum Cluster Modes (cm^{-1}), Stretching Force Constants (mdyn/Å), and Bond Orders for the Pt$_4$ Cluster in $((CH_3)_3PtX)_4$ (X = OH, Cl, I)[248]

Symmetric species	X = OH	X = Cl	X = I
A$_1$	137	99	88
F$_2$	97	79	65
E	75	57	48
Pt–Pt stretching force constants	0.79	0.50	0.49
Pt–Pt bond length (Å)	3.42	3.73	4.0
Pt–Pt bond order (no. of electrons/2)	0.118	0.064	∼0

force constant to decrease from the hydroxide to the chloride to the iodide which is the order of increasing Pt–Pt bond distance. From the calculation of absolute Raman intensities, it is concluded that the interactions between the platinum atoms and between the platinum atoms and the bridging ligands are weak and highly ionic.

(246) J. Aveston and J. S. Johnson, *Inorg. Chem.*, **3**, 1051 (1964).
(247) R. S. Tobias, *Can. J. Chem.*, **43**, 1222 (1965).
(248) P. A. Bulliner, V. A. Maroni, and T. G. Spiro, *Inorg. Chem.*, **9**, 1887 (1970).