Coordination Chemistry Reviews
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

RAMAN SPECTROSCOPIC STUDIES IN COORDINATION CHEMISTRY

RONALD E. HESTER

Chemistry Department, University of York (England)

(Received May 8th, 1967)

CONTENTS

A. Introduction
B. Donor–acceptor complexes
C. Ammine complexes
D. Aquo- and hydroxo-complexes
E. Halogeno complexes
F. Oxyanion complexes
G. Cyano-complexes
H. Carbonyl complexes
I. Miscellaneous ligands
  (i) Cyclopentadienyl and benzene π-complexes
  (ii) Others

A. INTRODUCTION

While it is hardly possible to find a chemistry research laboratory today which is not equipped with sophisticated equipment for the determination of infrared absorption spectra, it still is true that only a small minority of laboratories have Raman spectrometers. The importance of a vibrational spectrum to the coordination chemist interested in structural work need not be stressed, but it remains a fact that most chemists have to content themselves with only a partial picture of the vibrational characteristics of the complexes in which they are interested. The reasons for the relatively slow development of commercially viable Raman spectrometers have principally been involved with the development of special light sources, and only very recently has a commercial instrument comparable in price with medium quality infrared spectrometers become available. However, interest in Raman spectra appears to be growing rapidly at the present time, and this seems an appropriate point at which to survey the work already in the literature of coordination chemistry. In view of the relative unfamiliarity of the Raman effect and the means for its exploitation, it will be profitable to outline these briefly here, before discussing specific chemical systems.

In passing through a clear transparent liquid, a beam of visible light is scattered by the molecules of the liquid to an extent of about 10^{-3} per cent. If monochromatic incident light is used, it is found that the bulk of the light scattered is of the same frequency, and that its intensity is proportional to the fourth power of its frequency. This is Rayleigh scattering. However, about a thousand times weaker than the Rayleigh scattered line, additional lines occur with changed frequencies, characteristic of the scattering molecules. This extremely weak light scattering with frequency change, which can be observed with solids and gases as well as with liquids, and is not dependent on a particular incident light frequency, is known as Raman[1] scattering. The frequency shifts observed in Raman spectra are due to rotational and vibrational transitions occurring in the scattering molecules.

As early as 1939, sufficient data had accumulated to justify the writing of a large book on "The Raman Effect and its Chemical Applications"[2], by Hibben. However, the technical difficulties associated with Raman spectroscopy, coupled with its demand for a large sample size (several cc. of liquid have usually been required), have retarded its extensive exploitation until recent years. With modern laser sources of excitation, it is now possible to deal with liquid samples in the microlitre range, and this, together with the availability of several commercial Raman spectrometers*, has caused a surge of interest in the technique. The principal advantages of this method over conventional infrared absorption spectroscopy as a means of studying molecular vibrations in coordination complexes are found in the ready accessibility of frequencies as low as 50 cm^{-1}, the line polarisation characteristics, and the near-ideality of water as a solvent. Availability of low frequencies allows the study of skeletal modes of vibration. Raman line polarisation data enable assignments to particular normal modes of vibration to be made with much greater certainty than is possible for infrared absorptions. Water is certainly the most common solvent for coordination compounds.

It is the principal aim of this review to discuss applications of Raman Spectroscopy in the general area of coordination chemistry during the past few years. The bulk of this work has been concerned with molecular structure determinations, but many studies of complex solution equilibria, involving determination of association constants and other thermodynamic parameters, also have been made. Basic information on the nature of chemical bonding has been derived from both Raman frequency and intensity data, and some results are available on solvent effects and kinetics of very fast reactions. Probably the main restriction to the

---

* Available in Europe and the Americas are the Cary Model 81, with Hg arc or He–Ne laser sources; the Hilger and Watts E612, with Hg arc source; and most recently the Perkin–Elmer LR-1 with He–Ne laser source.

widespread use of Raman spectra in studies of coordination complexes has been the unsuitability of conventional mercury arc excitation sources for coloured compounds. It is essential that the exciting frequency is well-removed from any absorption band of the molecule under investigation. However, the introduction of the red He/Ne laser source has relieved some of these problems, and several workers have developed more versatile sources, producing a selection of monochromatic exciting radiations covering most of the visible and near ultra-violet regions of the spectrum[3]. Some of these developments in technique will be discussed further, particularly where they are important to applications involving coordination complexes.

For detailed treatments of the theory and practice of Raman spectroscopy, and for a more widely based survey of chemical systems studied by the method, the reader is referred to the several books[4] and general review articles already in the literature[5]. In order to avoid substantial repetition of information already contained in these published surveys, this review is concentrated on those papers dealing with coordination chemistry which have been published in the 1960s.

B. DONOR–ACCEPTOR COMPLEXES

All coordination compounds may be classified as donor–acceptor complexes. However attention is concentrated in this first section upon combinations of typical donors such as NH_3, PCl_3, H_2O, POX_3, etc., with typical acceptors such as the hydrides, halides, and alkyls of the elements B, Al, and Sn. Complexes involving groups of ligand atoms or molecules all coordinating into a common metal atom centre will be dealt with in the subsequent sections.

There has been a considerable volume of spectroscopic work published on donor–acceptor complexes, but most of it has been involved with UV, visible, and infrared absorption[6]. Compared with infrared spectra, the Raman spectra of the usual solvents commonly present more "window" regions for the study of dissolved complex frequencies. Kinell and co-workers[7] have made use of this fact in determining the relative donor strengths of the $POCl_3$ and $(CH_3)_3PO$ molecules. Addition of $SbCl_5$ to a mixture of these two phosphine-oxides, dissolved in 1,2-dichloroethane, resulted in preferential formation of the complex $(CH_3)_3PO \cdot SbCl_5$, as shown by drastic changes in the $(CH_3)_3PO$ spectrum, while the $POCl_3$ spectrum remained unperturbed. Similar work by Dembitskii and co-workers[8] has produced evidence for complexes between stannic chloride, $SnCl_4$, and a large number of carbonyl donors: the methyl and ethyl esters of formic, acetic, and benzoic acids; methyl propionate, ethyl propionate, $CH_2ClCOOCH_3$, $CH_2ClCOOC_2H_5$, $CCl_3COOC_2H_5$, and methyl butanoate. With this latter donor, complex formation caused the 1735 cm^{-1} Raman band to broaden and shift to lower frequency, while the intensity of the 1630 cm^{-1} $>C=O$ band was seen to increase with addition of $SnCl_4$ up to 33–4% by volume. The band intensities have been used to determine complex formation equilibrium constants in this case.

This use of Raman intensities for the determination of complex formation constants depends upon the intensity of a Raman line being directly proportional to the molar concentration of the molecular species responsible for the Raman scattering[9]. Michel and Duyckaerts[10] have used this in determining dissociation constants from the carbonyl bond stretching band intensities of ethyl benzoate and acetophenone complexed with antimony trichloride. For the system $C_6H_5COOC_2H_5 + SbCl_3$ the K value for the 1:1 complex is 1.26 ± 0.18 mole l^{-1}. $C_6H_5COCH_3 + SbCl_3$ gave the K values $(4.1 \pm 0.8) \times 10^{-2}$ mole^2 l^{-2} for the system in CCl_4 solution, and $0.3_7 \pm 0.06$ mole l^{-1} in diethyl ether. These authors established, through Job[11] plots of their carbonyl band intensities, the following stoichiometries of complexes between ethyl acetate and As and Sb trichlorides: $AsCl_3 \cdot CH_3COOC_2H_5$, $3AsCl_3 \cdot CH_3COOC_2H_5$, and $SbCl_3 \cdot CH_3COOC_2H_5$. Also, judging the Raman intensity of a $>C=O$ group to be enhanced by coordination to an acceptor molecule, they found the following relative acceptor strengths: $PCl_3 < AsCl_3 < SbCl_3$—the reverse of the order expected from electronegativity considerations alone. The $C_2H_5COOC_2H_5 + SnCl_4$ system has further been studied by Leclere and Duyckaerts[12]. Here they found a 2:1 (donor–acceptor) stoichiometry for the Lewis acid–base complex, from using Job's continuous variation method with the $>C=O$ Raman band intensities. The dissociation constant of this complex was found to be 0.12 ± 0.02 mole^2 l^{-2}, though the authors recognised some difficulty in its determination due to the influence of internal field effects on the Raman intensities, and made some refractive index corrections for this.

The stereochemistry of 1:1 and 1:2 adducts of $SnCl_4$ with a large variety

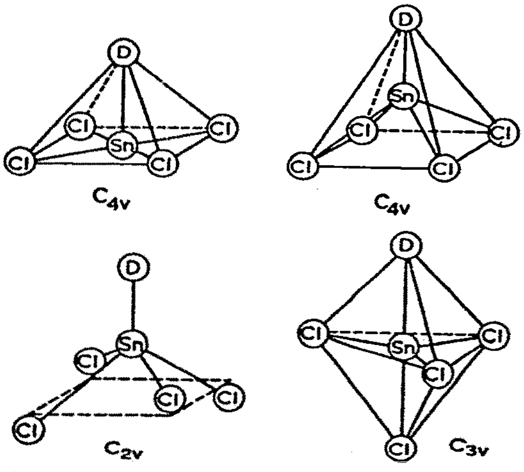


Fig. 1. Possible structures for ($SnCl_4 \cdot$ 1 Donor molecule) complexes[13].

TABLE 1

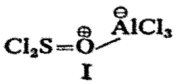
RAMAN FREQUENCIES OF Sn-DONOR VIBRATIONS IN cm^{-1}

Donor	*$SnCl_4 \cdot 1$ Donor*	*$SnCl_4 \cdot 2$ Donors*
H_2O	—	156
D_2O	—	156
$(C_2H_5)_2O$	168	168
$(n\text{-}C_4H_9)_2O$	165	—
CH_3OH	—	168
C_2H_5OH	165	167
$n\text{-}C_3H_7OH$	161	—
$C_5H_{11}OH$	154	—
CH_3CN	174	172
C_2H_5CN	168	158
C_3H_7CN	168	155
$POCl_3$	145	—

of donor molecules has been the subject of several thorough Raman spectroscopic investigations. Brune and Zeil[13] have reported the solution Raman spectra of $SnCl_4$ adducts with water, a number of alcohols, ethers, nitriles, and with $POCl_3$, which they were able to analyse in terms of complex molecules containing 5- and 6-coordinate tin atoms. Of the four possible structures for 1:1 adducts shown in Fig. 1, only the one having C_{2V} symmetry fits the vibrational analysis made by Brune and Zeil. Similarly, they have interpreted the Raman spectra of the ($SnCl_4$. 2 Donor molecules) complexes on the basis of a *trans*-D_{4h}-model. The highly polarised Raman lines assigned to fundamental modes involving primarily the Sn-donor bonds are summarised in Table 1 for both types of adduct. These may be taken as a measure of the relative strengths of the coordinate bonds in these complexes, though this procedure is a dubious one, due to the unknown extent to which other vibrational modes of the molecules may be coupled in with the fundamental Sn-donor vibrations. The *trans*-D_{4h}-assignment has been disputed by Beattie and co-workers[14] in the case of the $SnCl_4 \cdot 2CH_3CN$ and $SnCl_4 \cdot 2C_2H_5CN$ adducts. They have taken the combined evidence of Raman and infrared spectra as indicating *cis*-C_{2V}-structures for these adducts, and for the $SnCl_4 \cdot 2(CH_3)_2CO$ adduct. Beattie and Rule[15] also have used Raman spectra to characterise as *trans*-adducts the compounds of $SnCl_4$ with two molecules of $(CH_2)_4O$, $(CH_2)_4S$, $(C_2H_5)_2S$, and $N(CH_3)_3$.

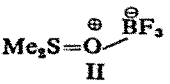
The donor properties of $POCl_3$ have been shown in the earlier work quoted to be unexceptional. However, a considerable amount of spectroscopic work has been done with this donor. Wartenberg and Goubeau[16] have prepared a variety of $POCl_3$ and $POBr_3$ adducts of group III acceptor molecules: $Cl_3B \cdot OPCl_3$, $Cl_3B \cdot OPBr_3$, $Br_3B \cdot OPCl_3$, $Br_3B \cdot OPBr_3$, $Cl_3Al \cdot 2OPCl_3$, $Cl_3Al \cdot OPCl_3$, $Br_3Al \cdot OPCl_3$, $Cl_3Al \cdot OPBr_3$, $Br_3Al \cdot OPBr_3$, $Cl_3Ga \cdot OPCl_3$, $Cl_3In \cdot OPCl_3$, $Cl_3Tl \cdot 2OPCl_3$. Raman and infrared spectra of these complexes have been assigned, and strong negative P-O frequency shifts interpreted as showing that in all cases the addition occurs through the oxygen atom of the phosphorus-oxyhalides. Greatly simplified calculations on a P-O-B model gave force constants for the $Cl_3B \cdot OPCl_3$ molecule of the order of $f_{BO} = 2.0$ and $f_{PO} = 8.0$ mdyn/Å, corresponding to bond orders of 0.4 for BO and 1.7 for PO. These are evidently only very approximate values.

The results obtained with $POCl_3$ as a donor may interestingly be compared with those of $SOCl_2$, which similarly could function as an oxygen-donor or as a sulfur-donor, and is also a useful non-aqueous inorganic solvent. Long and Bailey[17] have studied the Raman spectra of solutions of $AlCl_3$ in $SOCl_2$, in the concentration range 0.11 to 0.73 mole $AlCl_3$ per mole of $SOCl_2$. The 1:1 complex $SOCl_2 \cdot AlCl_3$ was isolated and characterised as structure I below, by analogy with structure II,



$Cl_2S=\overset{\oplus}{O}-\overset{\ominus}{Al}Cl_3$

I



$Me_2S=\overset{\oplus}{O}-\overset{\ominus}{B}F_3$

II

which was earlier established by Lappert and Smith[18]. In $SOCl_2 \cdot AlCl_3$ the only Raman line observed in the S-O stretching region was at 1108 cm^{-1}, which is 121 cm^{-1} lower than in pure $SOCl_2$, while in $Me_2SO \cdot BF_3$ the S-O stretching frequency was lowered by 129 cm^{-1} from the Me_2SO value. Surprisingly, a second 1:2 complex of formula $SOCl_2 \cdot 2AlCl_3$ was also identified through the Raman spectra of the solutions. In this, this $SOCl_2$ frequency was lowered only 101 cm^{-1} from the $SOCl_2$ value, excluding the possibility of two Al atoms being attached to the one O atom in $SOCl_2$. The second $AlCl_3$ molecule is evidently only loosely attached to the stable $SOCl_2 \cdot AlCl_3$ adduct.

The best-known and perhaps the most thoroughly investigated donor–acceptor complexes are those involving the coordinate link $\geqslant B \leftarrow N \leqslant$. A wide range of such complexes have been investigated by Raman and infrared spectroscopic methods by Sawodny and Goubeau[19]. Normal coordinate analyses were made, and force constants determined, using the Wilson FG Matrix Method[20], for the molecules $X_3Z \leftarrow NR_3$, with Z = B, Al; X = H, CH_3, F, Cl, Br; R = H, CH_3. The polarised Raman lines which have been assigned as fundamental Z-N

TABLE 2

VIBRATIONAL FUNDAMENTALS AND DERIVED FORCE CONSTANTS FOR THE Z–N BONDS IN $X_3Z \rightarrow NR_3$ ADDUCTS[19]

	BH_3–NH_3	BH_3–ND_3	BH_3–NMe_3	BD_3–NH_3	BD_3–ND_3	BD_3–NMe_3
ν(Z–N), cm^{-1}	776	754	668	737	708	651
f_{ZN}, mdyn/Å	2.95		2.29			
	BMe_3–NH_3	BMe_3–ND_3	BMe_3–NMe_3	BF_3–NH_3	BF_3–ND_3	BF_3–NMe_3
ν(Z–N), cm^{-1}	683	687	681	738	710	695
f_{ZN}, mdyn/Å	2.54		3.16	3.11		3.35
	BCl_3–NMe_3	BBr_3–NMe_3	AlH_3–NMe_3	$AlCl_3$–NMe_3	$AlCl_3$–NH_3	
ν(Z–N), cm^{-1}	745	727	525	565	579	
f_{ZN}, mdyn/Å	3.07	3.08	2.32	2.25	1.91	

stretching modes are summarised in Table 2, together with the derived Z-N bond force constants. It is seen that the frequency which mainly represents the B-N vibration occurs in the region 650 to 780 cm^{-1}, and the corresponding Al-N frequency is about 550 cm^{-1}. Force constants determined from the frequencies reported are in the range 2.3 to 3.4 mdyn/Å for the B-N bonds, and between 1.9 and 2.3 mdyn/Å for the Al-N bond. Sawodny and Goubeau estimate that these values correspond to bond orders in the region 0.59 to 0.86 in both cases. This work evidently supercedes the earlier analysis of the $BF_3 \cdot NH_3$ spectrum by Goubeau and Mitschelen[21], wherein the 738 cm^{-1} line, given as 735 cm^{-1} in this earlier work, was assigned to the symmetric BF_3 stretching mode. The later analysis gives this mode a frequency of 982 cm^{-1}. It is of interest that this is almost 100 cm^{-1} higher than the corresponding mode in the non-complexed BF_3 molecule, since it is fairly well established that the B-F bonds in this latter molecule have a significant degree of π-character. Goubeau and Bues[22] have determined the B-F bond force constant in BF_3 as 6.86 mdyn/Å, compared with the value of 5.28 mdyn/Å for the simple σ-bonds in the BF_4^- ion. A similar Raman and infrared study of the $BF_3 \cdot NH_3$ and $BF_3 \cdot ND_3$ molecules has been made by Babushkin and coworkers[23], from which they conclude that the B-N bond is strong and predominately covalent in nature. The magnitudes of the B-N bond force constants listed in Table 2 are usefully compared with the value of 7.50 mdyn/Å determined by Becher and Goubeau[24] from the Raman spectra of the borazines Me_2BNH_2, Me_2BNHMe, and Me_2BNMe_2, all of which evidently contain a B=N double bond. The B–N mode in these molecules occurs in the 1447 to 1530 cm^{-1} region.

The normal coordinate calculations made on $BF_3 \cdot NH_3$ by Taylor[25] have shown very clearly the dangers inherent in making deductions about bond strengths from the frequencies of vibrational lines assigned rather arbitrarily to particular bonds in this type of molecule. The B–F and B–N stretching motions are strongly mixed here, giving two modes better described as in- and out-of-phase symmetric NBF_3 stretchings. Amster and Taylor[26] have reported infrared and Raman spectra of the 1:1 complexes of $N(CH_3)_3$ with BF_3, BCl_3, and BBr_3, including some ^{10}B isotopically enriched samples, and made full vibrational assignments of their observed frequencies on the basis of isotopic shifts and frequency trends within the series. However, in the absence of normal coordinate analyses they made no conclusions about the nature of the B–N dative bonds in these complexes. The modes most closely resembling B–N vibrations gave lines at 692 and 689 cm^{-1} in the BF_3 and BBr_3 complexes, respectively, (*cf.* 695 and 727 cm^{-1} from Table 2) but the corresponding frequency from the BCl_3 complex occurs at 746 cm^{-1}. This is very close to the uncoupled B–N frequency obtained by Taylor and Cluff[27] from a study of several isotopic varieties of $BH_3 \cdot NH_3$.

Related Raman spectral studies by Taylor[28] of the simple BH_3CO and BD_3CO compounds have been accompanied by normal coordinate calculations, allowing complete assignments of all the fundamental modes and calculation of some molecular force constants. These compounds were studied as liquids at $-80°$, and yielded bond force constants of 17.99 mdyn/Å for the C–O bond (*cf.* free CO, 18.53 mdyn/Å), and 2.775 mdyn/Å for the B–C bond.

C. AMMINE COMPLEXES

Compared with infrared studies, relatively few complex ammines have been investigated by Raman spectroscopy. However, Raman spectra have proved particularly valuable in making band assignments in the low frequency region, as is illustrated by the work of Mathieu, *et al.*[29]. The hexammines of Rh^{3+}, Co^{3+}, Cr^{3+}, Zn^{2+}, Cd^{2+} and Ni^{2+} were studied by these authors, who used a modified Urey–Bradley force field to calculate the frequencies of the vibrational fundamentals as an aid to making their normal mode assignments. Their spectra and assignments for the rhodium complex $[Rh(NH_3)_6]Cl_3$ are given in Table 3, where they are compared with results of a similar study by Griffith[30]. The infrared frequencies were obtained from mulled solids, while the Raman spectra were obtained from aqueous solutions. The assignments are made on the basis of regular octahedral geometry, and follow the conventional O_h point group pattern. Griffith's assignments were made with the aid of deuterium isotope shifts obtained from the $[Rh(ND_3)_6]Cl_3$ molecule. Corresponding values for the frequencies of the skeletal totally symmetric MN_6 stretching modes are given as 370 cm^{-1} for $[Ni(NH_3)_6]^{2+}$, and 418 cm^{-1} and 340 cm^{-1} for the Zn^{II} and Cd^{II} complexes, respectively. However, there is some doubt whether these latter values are meaningful, since hexammines of Zn and Cd probably dissociate in aqueous solution. A marked influence on the spectra was observed by changing the nature of the anion in the series of

TABLE 3

VIBRATIONAL SPECTRA OF $[Rh(NH_3)_6]Cl_3$

Frequency (cm^{-1})				
Ref. 29	*Ref. 30*	*Activity*	*Type*	*Approx. description**
3230	3200	IR	T_{1u}	ν(N–H)
3140	—	R, IR	T_{1u}	ν(N–H)
1550	1618	IR	T_{1u}	$\delta(NH_3)$, asym.
1330	1352	R	E_g	$\delta(NH_3)$, sym.
1318	1318	IR	T_{1u}	$\delta(NH_3)$, sym.
830	845	IR	T_{1u}	$\rho(NH_3)$
515	514	R	A_{1g}	$\nu(RhN_6)$, sym.
480	483	R	E_g	$\nu(RhN_6)$, asym.
470	472	IR	T_{1u}	$\nu(RhN_6)$, asym.
310	302, 287	IR	T_{1u}	$\delta(RhN_6)$
240	240	R	T_{2g}	$\delta(RhN_6)$

* ν = stretch, δ = deformation, ρ = rock.

hexammine complexes studied by Mathieu, *et al.*[29]. In particular, the N—H stretching frequencies were lowered by the following anions in the order PF_6^-, BF_4^-, SiF_6^{2-}, ClO_4^-, F^-, Cl^-, Br^-, I^-. The magnitude of the effect appears to parallel the order of anion polarisabilities.

In addition to the ruthenium hexammine, Griffith[30] obtained Raman spectra of the normal and fully deuterated hexammines of iridium and ruthenium. In all cases his intensity ratios for the three Raman active MN_6 skeletal fundamentals were $\nu_1 : \nu_2 : \nu_5 \sim 10:4:2$, and his observed isotope shifts were all very close to the value $\nu_H/\nu_D = 0.922$. The intensity pattern is normal for XY_6 molecules of O_h symmetry, and the normal/isotopic frequency ratios approximate closely the value $(17/20)^{\frac{1}{2}}$ predicted from a treatment based on NH_3 and ND_3 point masses. These facts support the assignments made, which further include the bands listed in Table 4.

TABLE 4

SKELETAL FREQUENCIES* OF $M(NH_3)_6^{+3}$ AND $M(ND_3)_6^{+3}$ CATIONS, M = Ru, Ir, Rh

	$\nu_1(A_{1g})$ *R, pol.*	$\nu_2(E_g)$ *R, depol.*	$\nu_3(T_{1u})$ *IR*	$\nu_4(T_{1u})$ *IR*	$\nu_5(T_{2g})$ *R, depol.*
$Ru(NH_3)_6^{3+}$	500	475	463	283, 263	248
$Ru(ND_3)_6^{3+}$	466	430	417	—	228
$Ir(NH_3)_6^{3+}$	527	500	475	279, 264	262
$Ir(ND_3)_6^{3+}$	498	471	440	255, 235	245
$Rh(NH_3)_6^{3+}$	514	483	472	302, 287	240
$Rh(ND_3)_6^{3+}$	489	455	433	278, 256	220

* frequencies in cm^{-1}, pol. = polarised, depol. = depolarised.

The availability of red He—Ne laser excitation has recently enabled Haas and Hall[31] to determine the most intense bond-stretching fundamental frequencies in the Raman spectrum of the coloured hexammine $Co(NH_3)_6^{3+}$. An aqueous solution of $[Co(NH_3)_6]Cl_3$ shows broad absorption bands at 4750 and 3390 Å. The 6328 Å line of the laser is thus well-removed from these absorption bands. Lines at 495 cm^{-1} (pol.) and 440 cm^{-1} (depol.) were assigned as the A_{1g} and E_g fundamentals. Comparing these frequencies with those of the rhodium hexammine, and with the corresponding frequencies of 569 and 545 cm^{-1} reported by Clegg and Hall[32] for $Pt(NH_3)_6^{4+}$, it is seen that there is an upward trend in both frequencies from Co to Rh to Pt. Haas and Hall very qualitatively correlate this trend with a corresponding increase in pK_a values for these complex ions.

A Raman study[32] of the mixed complexes $[Pt(CH_3)_3(NH_3)_3]Cl$ and $[Pt(CH_3)_3(ND_3)_3]Cl$ has yielded Pt—N stretching vibrations at 390 cm^{-1} and 364 cm^{-1}, respectively. The authors conclude that the Pt—N bonds evidently are significantly weakened by the three methyl groups, though they make no calculations of the extent of Pt—C and Pt—N vibrational coupling. The Pt—C stretch is assigned as 584 cm^{-1}. Mixed ammine-chloride complexes have been studied by

Mathieu and co-workers[33]. They have assigned a line at 528 cm^{-1} to the Pt$-$NA_{1g} mode in $[Pt(NH_3)_4Cl_2]^{2+}$, and compare this with the value of 524 cm^{-1} found for the simple tetramine $[Pt(NH_3)_4]^{2+}$. A full normal coordinate analysis of the mixed complex was performed to assist the assignment of modes.

Ethylenediamine complexes of a large number of metal ions have been subjected to infrared vibrational analyses, but very few analogous investigations of Raman spectra have been made. Krishnan and Plane[34] have found that the spectra of tris-complexes of ethylenediamine (*en*) with Zn^{II} and Cd^{II}, can be analysed satisfactorily in terms of the expected hexacoordinate metal, bidentate chelating ligand, D_3 symmetry model. Their results with Hg^{II} are less certain, the tris-complex readily dissociating in aqueous solution to the bis-complex in this case. For the bis-complexes $[Zn(en)_2]^{2+}$, $[Cd(en)_2]^{2+}$, $[Hg(en)_2]^{2+}$, metal–nitrogen stretching frequencies were determined as 450, 435 and 450 cm^{-1} respectively. These may be compared with the corresponding values for the metal–nitrogen frequencies of the tetrammine complexes of Zn^{2+}, Cd^{2+}, and Hg^{2+}: 427, 350, and 410 cm^{-1}, respectively[35]. The increased chelate frequencies in each case are attributed to stronger metal–nitrogen binding with $H_2NCH_2CH_2NH_2$ than with simple NH_3 ligands. A much earlier Raman study of *en* complexes with the metals, Zn, Pt, Rh, Ir, and Ni, was made by Mathieu[36], but there evidently is some disagreement between this and the later work[35].

D. AQUO- AND HYDROXO-COMPLEXES

Aqueous solutions are notoriously difficult to study by infrared absorption spectroscopy. The extremely strong absorption by the solvent water leaves only very few "window" regions for the study of solute vibrational modes. However, liquid water is a weak Raman scatterer. Only the broad band in the 3500 cm^{-1} O$-$H stretching region is sufficiently strong to seriously obscure solute bands. Since most molecules have most of their molecular vibrations at lower frequencies than this, water is an extremely good solvent for Raman spectroscopy.

Complexes of water itself with simple solute ions have been subjected to study by several workers. Several of these investigations have been concerned primarily with the structure of liquid water itself, and with the modifications resulting from the presence of dissolved electrolytes[37–44]. These will not be discussed here.

As early as 1950, Mathieu[45] was able to characterize zinc-water vibrational modes through the appearance of a Raman band in the 370–390 cm^{-1} region of the spectra both from crystals containing the $[Zn(H_2O)_6]^{2+}$ cation, and from aqueous solutions of zinc salts. A similar Cu$-$OH$_2$ band was found in the region 390–435 cm^{-1}. Lafont[46], and da Silveira and co-workers[47], further characterised Mg$-$OH$_2$ and Al$-$OH$_2$ vibrational modes in Mg^{2+} and Al^{3+} ion hydrates.

From both H_2O and D_2O solution spectra, the latter authors were able to assign Raman bands at 350 cm^{-1} and 525 cm^{-1} to the totally symmetric vibrational modes of the hexaquo Mg^{2+} and Al^{3+} ions, respectively. Other bands at 315 and 240 cm^{-1} for $Mg(H_2O)_6{}^{2+}$, and at 450 and 340 cm^{-1} for $Al(H_2O)_6{}^{3+}$, were assigned to doubly and triply degenerate vibrations. Lafont and Vinh[48] have given the $Mg(H_2O)_6$ symmetric stretch as 380 cm^{-1}. The *ca.* 390 cm^{-1} $Zn–OH_2$ band was also recognised by Irish, *et al.*[49]. One of the more extensive investigations of totally symmetric vibrational modes of cation hydration spheres was made by Hester and Plane[50]. Some of their results are summarized in Table 5. All lines listed were found to be highly polarized, and were obtained from aqueous solutions of the salts listed. Spiro[51] has found an aquo-Tl^{3+} band at around 445–455 cm^{-1}, which is eliminated by addition of two chloride ions to Tl^{3+} in aqueous solution. The $Be(H_2O)_4{}^{2+}$ vibrations have been studied by Grigor'ev and co-workers[52], who have gone as far as determining the Be–O bond force constant to be 3.04 mdyn/Å in this complex.

TABLE 5

RAMAN LINES CHARACTERIZING METAL-WATER VIBRATIONAL MODES IN HYDRATED CATIONS[50]

Salt	*Raman line, cm^{-1}*
$Cu(NO_3)_2$	440
$Zn(NO_3)_2$	390
$Hg(NO_3)_2$	380
$Hg(NO_3)_2$	370
$In(NO_3)_3$	410 and 460 overlapping bands
$CuSO_4$	440
$MgSO_4$	360
$ZnSO_4$	400
$Ga_2(SO_4)_3$	475, shoulder on $SO_4{}^{2-}$ line
$In_2(SO_4)_3$	350–550
Tl_2SO_4	470
$Cu(ClO_4)_2$	440
$Hg(ClO_4)_2$	380
$In(ClO_4)_3$	*ca.* 420, shoulder on $ClO_4{}^-$ line
$Mg(ClO_4)_2$	360

The Raman spectra of methyl mercuric salts in aqueous solution commonly show lines due to the aquo-complex $CH_3Hg–OH_2{}^+$. This species has been studied by Goggin and Woodward[53], who found the Hg–O stretching frequency to be 463 cm^{-1}. This is 48 cm^{-1} lower than the corresponding mode in the hydroxo-complex $CH_3Hg–OH$, also studied by Goggin and Woodward[54]. The frequencies of these lines may be used as an indication of the Hg–O bond strengths, but their intensities are also significant. A similar study of the aqueous solutions of dimethyl thallic hydroxide has failed to detect any Tl–O Raman line[54], though the perturbation of the $(CH_3)_2Tl^+$ ion spectrum shows evidence of at least intimate ion-pair formation with OH^-. Woodward and co-workers[55] established much earlier that very low or zero intensity is associated with ion-pair bonds, as found in the Tl^+OH^- species, so that it can be assumed that all complexes discussed here as having been characterised by their Raman spectra are essentially covalent in nature. Clegg and Hall[56] have shown that the aquated $(CH_3)_3Pt^+$ cation in aqueous solution does give a new polarized Raman line, at about 357 cm^{-1}, assignable to the Pt–OH_2 stretching vibration. Evidently this hydration, like that discussed previously for CH_3Hg^+ and simple metal ions, involves more than mere electrostatic ion-dipole forces.

Organo-metallic hydroxo-complexes similar to those discussed above have been investigated by Raman spectroscopic and e.m.f. methods by Tobias and co-workers[57]. These authors have studied the stoichiometry, geometry, bond strengths, and acid dissociation constants of the $(CH_3)_2M^{2+}(aq)$ ions, with M = Ge^{IV}, Sn^{IV}, and Pb^{IV}. They have shown the $(CH_3)_2Sn(aq)$ ion to possess a linear C–M–C skeleton when fully hydrated in aqueous solution, and assume four water molecules to be coordinated in the inner spheres of each of these ions. By way of contrast, the $(CH_3)_2Ge(OH)_2$ molecule has been shown to be tetrahedral in aqueous solution. In strongly alkaline solutions, the $(CH_3)_2Sn(OH)_4{}^{2-}$ tetrahydroxy-anion was formed and found to have a tin–oxygen stretching frequency at 555 cm^{-1}. This is virtually identical with the $Sn(OH)_6{}^{2-}$ totally symmetric stretching mode, which occurs at 556 cm^{-1} in aqueous solutions.

Simpler hydroxo-complexes which have been characterised by Raman measurements are the aluminate, $Al(OH)_4{}^-$, and zincate, $Zn(OH)_4{}^{2-}$, ions. Lippincott and co-workers[58] found Raman lines from strongly alkaline zinc-containing solutions which they assigned as $\nu_1(A_1)$ at 470 cm^{-1}, $\nu_3(T_2)$ at 420 cm^{-1}, and $\nu_2(E)$ coincident with $\nu_4(T_2)$ at 300 cm^{-1}, for a tetrahedral (T_d symmetry) $Zn(OH)_4{}^{2-}$ ion. They performed a normal coordinate analysis, using a simple valence force field, with these frequencies. They determined f_{Zn-O} as 2.21 mdyn/Å. The $Al(OH)_4{}^-$ ion was similarly assigned to the T_d point group, with frequencies $\nu_1 = 615\ cm^{-1}$, $\nu_3 = 720\ cm^{-1}$, and ν_2 and $\nu_4 = 310\ cm^{-1}$. 3.79 mdyn/Å was the corresponding f_{Al-O} determined. Fordyce and Baum[59], whilst pointing out that Lippincott's spectra were also consistent with D_{4h} symmetry, square planar structures, confirmed the tetrahedral nature of $Zn(OH)_4{}^{2-}$ and redetermined its frequencies as $\nu_1(A_1) = 484\ cm^{-1}$, $\nu_2(E) = 285\ cm^{-1}$, $\nu_3(T_2) = 430\ cm^{-1}$, and $\nu_4(T_2) = 322\ cm^{-1}$. These authors also claimed to show that the $Zn(OH)_4{}^{2-}$ ion was the predominant species in their solutions, which covered OH/ZnO mole ratios from 8 to 16. However, further work on the related aluminate ion by Carreira and co-workers[60] has produced results which the authors interpret as favouring the existence of a linear $AlO_2{}^-$ ion in solutions above pH 12.5. They observed only a single, highly polarized, line at 628 cm^{-1} from these solutions. The derived Al–O stretching force constant is 3.95 mdyn/Å. At lower pH their spectra became more complicated, showing lines at 830 cm^{-1}, 625 cm^{-1}, and 540 cm^{-1}. These were interpreted as eliminating the possibility of a tetrahedral $Al(OH)_4{}^-$ ion, and indicating either a square planar (D_{4h}) ion, or a polymeric structure in which the Al is octahedrally coordinated.

Aqueous solutions of the OH^-/GeO_2 system have been investigated by Walrafen[61]. From a study of the changing intensities of just three Raman lines, at 529, 667, and 765 cm^{-1}, as the solution composition was changed, Walrafen proposed the existence in aqueous KOH solutions of GeO_2 of the species $H_2GeO_4{}^{2-}$ and $Ge_2O_5{}^{2-}$. More complicated systems still have been studied by Aveston[62], who used a comparison of crystal and solution spectra to establish the presence of the dodecatungstate ion, $W_{12}O_{41}{}^{10-}$, in aqueous solutions of sodium paratungstate, $Na_{10}W_{12}O_{41} \cdot 28H_2O$. Similar studies of $K_{14}Nb_{12}O_{37} \cdot 27H_2O$ and $K_8Ta_6O_{19} \cdot 16H_2O$[63], and of the octahedral cage complex ion[64], $Bi_6(OH)_{12}{}^{6+}$, have been made.

E. HALOGENO-COMPLEXES

Raman spectroscopy has been used to study a large number of halogeno-complexes of metal ions, many of them in aqueous solution. Some of the results which have been obtained are summarized in Table 6. A similar, though briefer, listing has been given by Irish[65]. Spectra reported in the Table have mostly been obtained from aqueous solutions of the complexes, though non-aqueous solution, solid state and molten salt spectra also are included.

Most of the tetrahalogeno-complexes have been found to have T_d symmetry, though a few are recorded in the Table with D_{4h} symmetry. This latter square planar configuration has been found for the interhalogen anion $ICl_4{}^-$, with Raman-active frequencies $\nu_1(A_{1g}) = 288$, $\nu_3(B_{1g}) = 128$, $\nu_5(B_{2g}) = 261$ cm^{-1} as well as for the $PtCl_4{}^{2-}$, $AuCl_4{}^{2-}$, and $AuBr_4{}^{2-}$ complexes[77]. Controversy over the geometry of the $ZnX_4{}^{2-}$ complexes appears to have been resolved in favour of the tetrahedral configuration[85]. Determination of the stoichiometries of the several zinc halide complexes has usually been by the Job method[86].

Probably the most extensively studied halogeno-complex system has been the chloro–zinc one. In addition to the aqueous solution and solid state work, several publications have appeared dealing with the spectra and structure of molten $ZnCl_2$ and $ZnCl_2/MCl$ (M = alkali metal) mixtures. An interesting factor here is the evident retention of highly polymeric $(ZnCl_2)_n$ species in the melt, which appear to have a chain-like form and persist in the liquid, well beyond the melting point[83,84]. In the related aqueous bromo–zinc system, Yellin and Plane[86] have been able to determine stepwise association constants from their Raman data as follows:

$$\frac{(ZnBr^+)}{(Zn^{2+})(Br^-)} = 0.3, \qquad \frac{(ZnBr_2)}{(ZnBr^+)(Br^-)} = 1, \qquad \frac{(ZnBr_4{}^{2-})}{(ZnBr_2)(Br^-)^2} = 0.2.$$

TABLE 6

RAMAN SPECTRA OF HALOGENO-COMPLEXES

Complex	*Symmetry*	*Fundamental frequencies, cm^{-1}*					*References*
		ν_1	ν_2	ν_3	ν_4	ν_5	
Group IIIA							
$AlCl_4^-$	T_d	349	146	575	180		66, 67
$GaCl_4^-$	T_d	346	114	386	149		68
$GaBr_4^-$	T_d	210	71	278	102		68
GaI_4^-	T_d	145	52	222	73		69
$InCl_4^-$	T_d	321	89	337	112		70
$InBr_4^-$	T_d	197	55	239	79		71
InI_4^-	T_d	139	42	185	58		69
$TlCl_4^-$	T_d	312	60	296	78		72
$TlBr_4^-$	T_d	182	58	196	58		72
TlI_4^-	T_d	133		156			72
$TlCl_6^{3-}$	O_h	280	262			155	72
$TlBr_6^{3-}$	O_h	161	153			95	72
Group IVA							
GeF_6^{2-}	O_h	627	454			318	73
$SnCl_6^{2-}$	O_h	311	229			158	74, 75
$PbCl_6^{2-}$	O_h	285	215			137	76
$SnBr_6^{2-}$	O_h	185	138			95	74
Group IB							
$AuCl_4^{2-}$	D_{4h}	347		171		324	77, 97
$AuBr_4^{2-}$	D_{4h}	212		102		196	77
Group IIB							
$ZnCl^+$	$C_{\infty v}$	>305					78, 79
$ZnCl_2$	$D_{\infty h}$	305					78–83
$ZnCl_3^-$	C_{3v}	290					82, 83
$ZnCl_4^{2-}$	T_d	288	116	298	130		80–85
$ZnBr^+$	$C_{\infty v}$	205					86
$ZnBr_2$	C_{2v}	186					80, 82, 86
$ZnBr_4^{2-}$	T_d	178	80	212	89		78, 80, 82, 85, 86
ZnI^+	$C_{\infty v}$	163					80
ZnI_2		140					80
ZnI_4^{2-}	T_d	130	60	172	70		78, 80, 85
$CdBr_4^{2-}$	T_d	166	53	183	62		86, 87
CdI_4^{2-}	T_d	117	36	145	44		80
Hg_2Cl_2	$D_{\infty h}$	270	167	260	42	110	88, 89
$HgCl_2$	$D_{\infty h}$	320					80, 90–92
$HgCl_3^-$	C_{3v}	276		261	103		87, 90, 92–94
$HgCl_4^{2-}$	T_d	264		255	111		87, 90, 92–94
$HgBr_4^{2-}$	T_d	170					87, 90
HgI_4^{2-}	T_d	117					87, 90
Groups IVB and VB							
TiF_6^{2-}	O_h	619				277	95
ZrF_6^{2-}	O_h	588					95
HfF_6^{2-}	O_h	593				234	95
$ZrCl_6^{2-}$	O_h	329	237			293	95
TaF_6^{2-}	O_h	691				279	95
$TaCl_6^{2-}$	O_h	312				330	95
Group VIII							
$PtCl_4^{2-}$	D_{4h}	335		164		304	77, 97
$PtCl_6^{2-}$	O_h	344	320			162	96, 98
$PdCl_6^{2-}$	O_h	317	292			164	96, 98
$PtBr_6^{2-}$	O_h	207	190			97	96, 98

For the formation of the $CdBr_4^{2-}$ complex, they found

$$\frac{(CdBr_4^{2-})}{(Cd^{2+})(B_p^-)^4} > 1,$$

from a study of the concentration dependence of the 166 cm^{-1} polarised Raman line.

Among the spectra of octahedral halogeno-complexes, those of the $PdCl_6^{2-}$, $PtCl_6^{2-}$ and $PtBr_6^{2-}$ complexes are remarkable for their abnormal line intensity patterns[96,98]. Most commonly, MX_6^{2-} complexes show a relative intensity pattern $I_{\nu 1} \gg I_{\nu 2}, I_{\nu 3}$. The three complexes mentioned above show large deviations from this normal pattern, which have been ascribed to effects arising from some $(d\text{–}d)\pi$-bonding in these ions.

The listing of Raman spectra of halogeno-complexes given in Table 6 is by no means exhaustive. Some other systems for which Raman results are available are as follows: molten $MgCl_2$–KCl, showing $MgCl_6^{4-}$ and $MgCl_3^-$ spectra[99]; Hg^{II} monohalide (Cl, Br, I) complexes, showing $(Hg\text{–}I\text{–}Hg)^{3+}$ and $(H_2O\text{–}Hg\text{–}X)^+$ species[100]; the square pyramidal (C_{4v}) TeF_5^- ion[101]; $SbFCl_4$[102]; IOF_5[103]; ReF_7[104]; VF_5[104]; CH_3Hg–X, with X = Cl, Br, I[105]; $(CH_3)_nGeCl_{(4-n)}$[106]; CH_3SnX_3, X = Cl, Br[107]; $C_4H_4Ge_2Cl_4$[108]; $C_6H_5MX_3$ with X = Cl, Br and M = Sn, Ge[109]; $Hg(CN)_2X^-$, X = Br, I[110].

F. OXYANION COMPLEXES

Complexes of simple and well-defined oxyanions such as NO_3^-, SO_4^{2-}, PO_4^{3-} and ClO_4^- are dealt with in this section. More Raman work has been done with nitrate complexes of metal ions than with any of the other simple oxyanions, and much of this work has been concerned with complex formation in aqueous solutions. A comparative study of interionic association in aqueous solutions of metal nitrates, sulfates, and perchlorates, by Hester and Plane[111], revealed quite clearly that the tendency toward metal complexation decreases rapidly in the order $NO_3^- > SO_4^{2-} > ClO_4^-$. The magnitude of the perturbation of the oxyanion spectra was used as an indication of the strength of complex formation. Later theoretical work has fully confirmed the validity of this procedure[112,113]. With the free nitrate D_{3h} symmetry lowered to C_{2v} by association with metal ion through an oxygen atom, the frequency difference $\nu_4(B_1)-\nu_1(A_1)$ was used for complexed nitrate ions as a measure of the nitrate perturbation; the following order of complex strengths was observed: $Th^{4+} > In^{3+} > Cu^{2+} > Hg^{2+} > Ce^{3+} > Ca^{2+} > Zn^{2+}, Al^{3+}, Ag^+ > Na^+, K^+, NH_4^+$. Fig. 2 summarises the basis for this experimental criterion of binding strength in metal-nitrate complexes.

Detailed studies of specific metal-nitrate systems in aqueous solution have established complex stoichiometries, and thermodynamic constants for complex

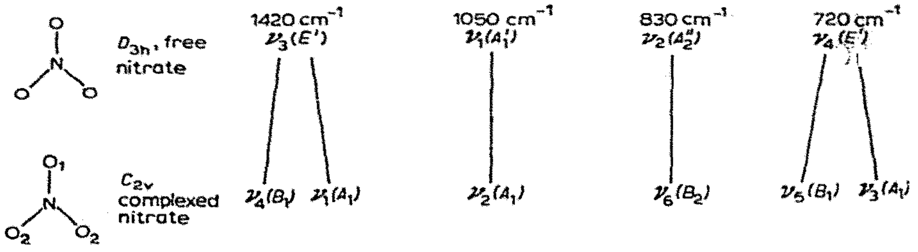


Fig. 2. Perturbation of NO_3^- vibrational modes by complex formation, $MONO_2$.

formation. An example is the Ca^{2+}–NO_3^- system, for which a 1:1 complex has been identified in aqueous solution[114,115]. The formation constant for this $CaNO_3^+$ complex was found[114] to range from 0.12 to 0.17 in solutions covering the range of ionic strengths 10 to 40. The formation constant is temperature independant over the range 26° to 94°, indicating a zero enthalpy of association for Ca^{2+} and NO_3^- ions in water, or approximately equal tendencies for NO_3^- and H_2O to complex with Ca^{2+} ions. Other metal-nitrate systems which have been studied in detail by Raman spectroscopic methods are In^{3+}–NO_3^- in water, for which a metal-nitrate vibrational mode has been characterized[116,117] at 270 cm^{-1}; Zn^{2+}–NO_3^- in water, showing the presence of contact ion pairs[118]; Ce^{4+}–NO_3^- in water, showing evidence for bidentate nitrate ion complexation[119]; CH_3Hg^+–NO_3^- in water and in benzene solution[53,120], showing an Hg-ONO_2 vibration at 292 cm^{-1}; Hg^{2+}–NO_3^- in water/acetone mixtures[121]; Th^{4+}–NO_3^- and rare earth metal nitrates as tri-n-butyl phosphate complexes[122,123]; Ag^+–NO_3^- in acetonitrile solution[124].

In addition to the aqueous solution work, a number of studies have been made of nitrate ion complexation in molten anhydrous salts. Much of this is reported in a review by Wait and Janz[125]. Later work has shown a contact ion pair model to be satisfactory for explaining the observed Raman spectra from melts containing alkali and alkaline earth metal nitrates, $AgNO_3$, and $TlNO_3$[126–128]. Metal-nitrate complexes in molten alkali metal nitrate solvents appear to resemble very closely those formed in aqueous solutions[129].

As mentioned earlier, sulfate complexes with metal ions have been shown to be much less common than nitrate complexes[111]. The metal-sulfate association, which is well-known from conductimetric studies of aqueous solutions, is evidently of the solvent-separated type in most cases, *e.g.* $Mg^{2+}(H_2O)_nSO_4^{2-}$. An exception is the aqueous In^{3+}–SO_4^{2-} system, wherein direct complexation has been found[116], and an In–OSO_3 vibrational mode identified at 255 cm^{-1}. A 1:2 complex appears most likely here, *viz.* $In(SO_4)_2^-$. Even in molten anhydrous sulfates of Li^+ and Na^+, the SO_4^{2-} ion retains its T_d symmetry[130].

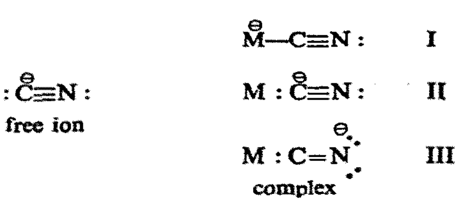
Raman evidence for complex formation with other oxyanions is scarce. Steger and Simon[131] have reported spectra of a series of crystalline tetrametaphosphates, including $Al_4(P_4O_{12})_3$, $Cu_2P_4O_{12}$, and $Mg_2P_4O_{12}$. Brintzinger and Plane[132] have characterised Zn^{II} and Be^{II} bisdiphosphate complexes in aqueous solution through their Raman spectra. The nitrite complexes $Rh(NO_2)_6{}^{3-}$, $Ir(NO_2)_6{}^{3-}$, and $Pt(NO_2)_4{}^{2-}$ have been studied by Mathieu and co-workers[133]. The MN_6 structures appear to be regular octahedral, and the PtN_4 has square planar, D_{4h} geometry.

G. CYANO-COMPLEXES

C–N stretching modes in both simple and complex cyanides give strong sharp bands in both Raman and infrared spectra in the 2040–2210 cm^{-1} region. At much lower frequencies, usually around 280–500 cm^{-1}, metal–carbon stretching bands can be observed. Raman spectra are particularly useful for assigning these metal–carbon bands, since symmetrical stretching of M–C bonds in complex cyanides gives rise to highly polarised bands. A knowledge of the totally symmetrical C–N and M–C stretching vibrations also enables simple calculations of the C–N and M–C bond force constants to be made. These in turn provide information on the changing character of the bonds as the nature of the central metal atom is changed in a series of metal-cyanide complexes.

Table 7 contains Raman frequencies for these totally symmetric vibrations, together with the force constants derived from them, for a wide selection of cyano-complexes. It is immediately obvious from inspection of this table that the C–N vibrational frequency is invariably increased by complex formation. It is tempting to take this as implying an increase in the C–N bond strength in all cases. However, this would be an oversimplification, neglecting the fact that other modes of vibration within the complex molecules can couple with the symmetrical C–N stretching, and affect the frequency the normal mode which we have called the C–N vibration. Indeed, at least for the case of $Cu(CN)_4{}^{3-}$, a force constant calculation has been made[139] which shows the C–N bond to be weaker in the complexed than in the free ion form. This has been interpreted as evidence for a strong contribution from ionic structure III of Fig. 3 in the bonding of the $Cu(CN)_4{}^{3-}$ complex[148].

All available evidence from vibrational spectra of cyano-metal complexes suggests that the metal–carbon bonds are weak, in keeping with the requirement



$$:\overset{\ominus}{C}{\equiv}N: \qquad \overset{\ominus}{M}{-}C{\equiv}N: \quad \text{I} \qquad M:\overset{\ominus}{C}{\equiv}N: \quad \text{II} \qquad M:C{=}\overset{\ominus}{N}\!: \quad \text{III}$$

Fig. 3. Bonding in cyano-complexes.

TABLE 7

C–N AND M–C TOTALLY SYMMETRIC STRETCHING VIBRATIONS IN METAL CYANIDE COMPLEXES

Species	*Symmetry*	*Frequencies in cm^{-1}*		*Force consts. in mdyn/Å*		*References*
		$\nu_s(C–N)$	$\nu_s(M–C)$	F_{CN}	F_{MC}	
Free CN^-		2079		16.5		134, 135
Group IB						
$Cu(CN)_2^-$	$D_{\infty h}$	2106				136–138
$Cu(CN)_3^{2-}$	C_{3v}?	2094				136, 137
$Cu(CN)_4^{3-}$	T_d	2094	288	16.3	1.3	134, 136, 137, 139–142
$Ag(CN)_2^-$	$D_{\infty h}$	2141	360			136, 143
$Ag(CN)_3^{2-}$	C_{3v}?	2108				136
$Ag(CN)_4^{3-}$	T_d	2097				134, 136
$Au(CN)_2^-$	$D_{\infty h}$	2164	448		2.7	143–145
$Au(CN)_4^-$	D_{4h}	2209	461	17.4	3.0	144
Group IIB						
$Zn(CN)_4^{2-}$	T_d	2157	347	17.2	1.3	134, 136
$Cd(CN)_3^-$	C_{3v}	2140	339			146
$Cd(CN)_4^{2-}$	T_d	2145	327	17.1	1.3	134, 136
$Hg(CN)_2$	$D_{\infty h}$	2190	412	17.3	2.7	135, 136, 147
$Hg(CN)_3^-$	C_{3v}	2160	358			136, 146
$Hg(CN)_4^{2-}$	T_d	2148	335	17.1	1.5	134–136, 147, 148
CH_3HgCN	C_{3v}	2180	386	17.5	2.1	149
Other transition elements						
$Mo(CN)_8^{4-}$	D_{4d}	2135	394			150
$Os(CN)_6^{4-}$	O_h	2109	465			151
$Rh(CN)_6^{3-}$	O_h	2166	445	16.8	2.4	152
$Ir(CN)_6^{3-}$	O_h	2167	463	16.7	2.7	152
$Cr(CN)_6^{3-}$	O_h	2137				153
$Fe(CN)_6^{3-}$	O_h	2136				153, 154
$Fe(CN)_6^{4-}$	O_h	2090	505			134, 153, 155–157
$Co(CN)_6^{3-}$	O_h	2150	408	16.7	2.1	134, 152, 153, 155, 157, 158
$Ni(CN)_4^{2-}$	D_{4h}?	2159	294			153
$Pt(CN)_4^{2-}$	D_{4h}	2168	320			155
$Pd(CN)_4^{2-}$	D_{4h}	2159	294			155

of essential electrical neutrality for the central metal atom[159]. Fig. 3 suggests how accumulation of negative charge on a central metal atom in a cyano-complex can be avoided by polarisation of the M–C σ-bonding electrons toward the C atom. The low values of the M–C force constants, and low intensities of M–C Raman bands, may be taken as evidence for the absence of appreciable π-electron participation in the M–C bonds[134,148]. This may be contrasted with the situation in the isoelectronic CO complexes discussed in the following section.

The C–N bonds in most of the complexes listed in Table 7 clearly are stronger than in the free cyanide ion, however. This testifies to the importance of structure I of Fig. 3, since donation of electrons, NC → M, reduces the screening of the carbon nucleus, thus increasing its effective positive charge, and tightening the C–N bond[135]. Any contribution to the bonding from back-donation of metal *d*-electrons would result in $M \rightleftharpoons C = \overset{\ominus}{N}$: types of structure, with weakening of the C–N bonds. The predominance of high F_{CN} values may therefore be taken as further evidence for "σ-only" bonding in most of the cyano-metal complexes. Where the M–C bonding is seen to be stronger than usual (*e.g.* in the gold complexes[143]), it seems probable that some M–C π-bonding is involved, though this is not even here a very significant factor in the bonding[144]. Within each of the series [$Cu(CN)_4{}^{3-}$, $Cu(CN)_3{}^{2-}$, $Cu(CN)_2{}^{-}$], [$Ag(CN)_4{}^{3-}$, $Ag(CN)_3{}^{2-}$, $Ag(CN)_2{}^{-}$], [$Hg(CN)_4{}^{2-}$, $Hg(CN)_3{}^{-}$, $Hg(CN)_2$], and [$Cd(CN)_4{}^{2-}$, $Cd(CN)_3{}^{-}$] there is seen to be a decrease in the M–C bond strength, judged as above, as the number of CN ligands per metal atom increases. This also may be rationalised in terms of weakening of M–C σ-bonds in order to retain essential electrical neutrality of the metal.

Chantry and Plane[134] have shown that additional information bearing on the problem of the nature of metal-ligand bonding can be obtained from a careful study of Raman band intensities. Raman intensities are determined by the derivatives of molecular polarisability with respect to elongations of the various bond lengths, and in Table 8 are listed a number of cyano-complexes for which these quantities have been determined. The complexes listed are seen to fall into two sets: one for which the derived C-N bond polarisabilities $\bar{\alpha}'_{CN}$, lie between the free CN^- and the CH_3CN values; another for which the CN-band intensities, and hence the $\bar{\alpha}'_{CN}$ values, are abnormally large. The first set of values is consistent with partial σ-bonding in the M–C skeletons, and the extremely low intensities of the $\nu_2(A_1)$ M–C stretching bands has been attributed to the large amount of s-character in the carbon σ-orbital used for M–C bonding[134]. However, the abnormally high values for the Cu^{II}, Ag^{I}, and Fe^{II} complexes evidently represent a breakdown of the theory of localised bond polarisabilities, and have not been satisfactorily explained.

TABLE 8

BOND POLARISABILITY DERIVATIVES FOR SOME CYANO-COMPLEXES[134]

Species	*A_1 freq. (cm^{-1})*	*Rel. Intensity/CN^-*	*Derived bond polarisability, $\bar{\alpha}'_{CN}$ ($Å^2$)*
CN^-	2079	1.00	1.71
$Zn(CN)_4{}^{2-}$	2143	1.55	2.12
$Cd(CN)_4{}^{2-}$	2145	1.60	2.16
$Hg(CN)_4{}^{3-}$	2148	1.60	2.16
	340	0.013	
$Co(CN)_6{}^{3-}$	2152	1.68	2.21
	404	0.015	
CH_3CN	2248	1.85	2.61
$Cu(CN)_4{}^{2-}$	2094	2.78	2.84
$Ag(CN)_4{}^{3-}$	2097	3.15	3.03
$Fe(CN)_6{}^{4-}$	2094	3.48	3.18

In addition to the pure cyano-complexes discussed so far, a number of mixed cyano-halogeno-complexes have been investigated by the Raman method. The $Au(CN)_2Cl_2^-$ complex has been shown to exist in the trans-planar, D_{2h} structure[160,161], with $F_{CN} = 17.3$ and $F_{AuC} = 3.0$ mdyn/Å. The $Pt(CN)_4Cl_2$ complex has very similar bonding, with $F_{CN} = 17.3$ and $F_{PtC} = 2.8$ mdyn/Å[162], and evidently resembles $Au(CN)_4^{3-}$ rather closely in having metal–carbon bonds with strong σ-character, but little π-character[144]. Cooney and Hall[163] have found both the C–N and the Hg–C frequencies are lowered by addition of halogen to $Hg(CN)_2$ in aqueous solution, in the order $F < Cl < Br < I$.

Summarising the extensive infrared and Raman evidence, Jones[164] has formulated a set of general rules to describe the nature of the chemical bonding in cyano-complexes. These are as follows:

1. M–C π-bonding increases with the number of d_ε electrons on the metal.
2. M–C π-bonding decreases with increase in effective nuclear charge of the metal.
3. M–C σ-bonding increases with increase in effective charge of the metal.
4. The C–N force constant decreases as M–C π-bonding increases.
5. The C–N force constant increases as M–C σ-bonding increases.

The reader should investigate these rules with the aid of the data given in Table 7.

H. CARBONYL COMPLEXES

The CO molecule is isoelectronic with the CN^- ion, and much of the interest in its complexes arises from the possibility of multiple bonding in the M–C skeletons of its complexes with transition metals. Table 9 contains the frequencies of totally symmetrical C–O and M–C stretching modes which have been observed in the Raman spectra of a number of metal-carbonyl complexes, together with the bond force constants which have been derived from these frequencies by normal coordinate analyses. In direct contrast with the behaviour shown by the cyano-complexes listed in Table 7, complexing of CO with metals is seen to result in lowering of the C–O stretching frequency, and weakening of the C–O bond.

The arguments presented in the previous section lead to the conclusion that metal–carbon π-bonding, arising from back-donation of metal d-electrons, is much more important in the transition metal carbonyl complexes than in the cyano-complexes. The contribution to bonding from structures of the form $M\rightleftharpoons C=O$ resulting in lowering of the C–O bond order from the triply bonded free CO, is apparently very significant. In the $H_3B \leftarrow CO$ molecule, included in Table 9 for comparison purposes, there is no possibility of B–C π-bonding. The C–O force constant is seen to increase slightly from the free CO, in keeping with the predictions and observations made for the analogous σ-bonded cyano-complexes in the previous section.

At first sight, the M–C force constants given in Table 9 appear to be remarkably small for multiple bonds. Indeed, many of the M–C bonds seem weaker even

TABLE 9

C–O AND M–C TOTALLY SYMMETRIC STRETCHING VIBRATIONS IN METAL CARBONYL COMPLEXES

Species	*Symmetry*	*Frequencies in* cm^{-1}		*Force consts. in mdyn/Å*		*References*
		$\nu_s(C\text{–}O)$	$\nu_s(M\text{–}C)$	F_{CO}	F_{MC}	
Free CO		2143		18.5		165
H_3BCO	C_{3v}	2166	707	18.9	2.6	165–167, 28
$Cr(CO)_6$	O_h	2118	390	17.9	2.0	168–170
$Mo(CO)_6$	O_h	2124	392	18.1	1.8	168–170
$W(CO)_6$	O_h	2124	420	17.7	2.1	168–170
$Fe(CO)_5$*	D_{3h} axial	1984	492	16.1	3.0	171–177
	eq.	2114	414	17.1	1.9	171–177
$Fe(CO)_4^{2-}$	T_d	1788	464	11.4	4.1	178
$HFe(CO)_4^-$	C_{3v}	1895	451			178
$Co(CO)_4^-$	T_d	1918	439	13.2	3.5	178, 179
$Ni(CO)_4$	T_d	2128	380	16.3	2.5	180–184
$Hg[Co(CO)_4]_2$	D_{3d}	2030	416			185
$Cd[Co(CO)_4]_2$	D_{3d}	1984	429			185

* The trigonal bipyramidal structure contains distinct axial and equatorial CO groups.

than the "σ-only" B–C bond in $H_3B \leftarrow CO$. However, this is an unfair comparison, for there is no reason why an Ni–C single bond, say, should have a force constant equal to a B–C single bond. In the absence of "standard" M–C single bond force constant values, the absolute magnitude of the F_{MC} values of Table 9, as also for Table 7, must be interpreted with great care. Nevertheless, the relative C–O and M–C frequencies and force constants do indicate some interesting trends. For example, it may be seen quite unambiguously that the metal–carbon bond strengths for the hexacarbonyls of Cr, Mo, and W increase in the order Mo–C < Cr–C < W–C. This unpredictable order is also judged to be the order of importance of M–C π-bonding[169]. For these octahedral molecules, only four of the vibrational fundamentals are infrared active, while six more are observable in the Raman effect, thus underlining the importance of the Raman data in obtaining structural analyses of these complexes.

Raman spectra similarly have been essential in establishing the trigonal bipyramidal geometry of the $Fe(CO)_5$ complex, and eliminating the C_{4v}, square pyramidal, possibility[173]. The data reported for this complex show that the axial CO groups are bonded more strongly to the Fe atom than are the equatorial groups. The Fe–C bonds are unusually strong, and apparently have more π-character than the M–C bonds in any other neutral complex investigated. The related $Fe(CO)_4^-$ anionic complex has a still more strongly π-bonded Fe–C skeleton. Even in the $Co(CO)_4^-$ complex, a metal–carbon bond order of 1.87 has been determined from the spectroscopic data[179]. The Ni–C bond order has similarly been calculated as 1.67 in the $Ni(CO)_4$ complex.

Polynuclear metal carbonyls have not been extensively investigated by Raman spectroscopy, though this provides the best means for detecting and characterising the metal–metal bonds which often are present in such species. The Re–Re stretching frequency of 120 cm^{-1} has been measured, and used to calculate a bond force constant F(Re–Re) = 0.8 mdyn/Å[186]. The highly symmetrical $M[Co(CO)_4]_2$ complexes, with M = Cd and Hg, have been shown to possess 3-fold principal molecular symmetry axes containing all the atoms O–C–Co–M–Co–C–O, wherein symmetrical Co–M–Co stretching modes give rise to the Raman frequencies 152 cm^{-1} (Cd) and 161 cm^{-1} (Hg). Metal–metal bond force constants have been determined as 2.33 (Cd) and 2.61 (Hg) mdyn/Å.

The spectral effects of partial substitution of CO groups on $Ni(CO)_4$ by a wide range of other ligands have been studied by Bigorgne and Zelwer[187]. Fig. 4 shows how the polarised Raman line characterising the symmetric C–O stretching varies with degree of substitution and with the nature of the ligand. The lowering of the CO frequency, which is observed in every case, implies increased Ni–C π-bonding. This, in turn, implies a competition between the ligands for the nickel *d*-electrons, with CO easily the winner in each of the molecules studied. These ligands may therefore be ordered on the basis of their π-acceptor strengths as follows: $CO > PF_3 > PCl_3 > P(OPh)_3 > P(OMe)_3 > PPh_3 > PMe_3$. Substitution of all four CO groups by PF_3 ligands has been achieved by Woodward and Hall[165], who report the totally symmetric Ni-P stretching frequency as 195 cm^{-1}, corresponding to a force constant of 2.71 mdyn/Å. This is a little higher than the corresponding value for Ni–C in $Ni(CO)_4$, but, in the light of the evidence of Fig. 4, probably should not be interpreted as implying greater π-character in $Ni–PF_3$ than in Ni–CO bonds. Further Raman work with partially substituted metal carbonyls has been done by Pailblanc and Bigorgne[188], and Cotton and Kraihanzel[189] have presented approximate methods for analysis of mixed ligand complex spectra.

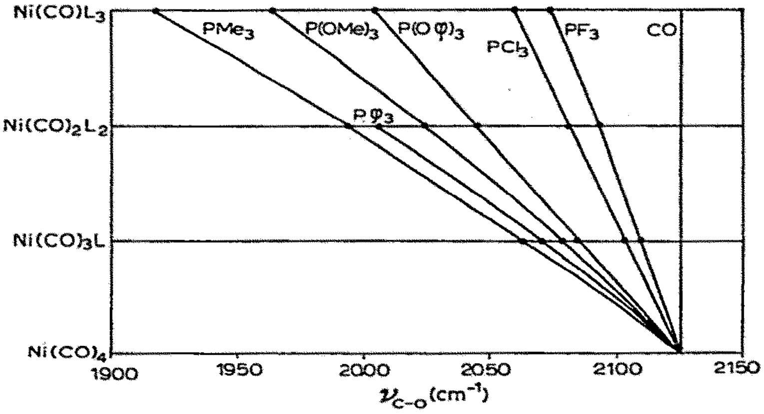


Fig. 4. Variation of C–O frequency with ligand substitution in $Ni(CO)_nL_{4-n}$ complexes (Adapted from ref. 187).

Hester and Nixon[190] have recently shown that substitution of $PF(CF_3)_2$ ligands for CO's in $Mo(CO)_6$ results in an increase of the bond strength in the remaining CO's, which implies that this perfluoromethyl substituted phosphine is an even better π-acceptor than CO.

I. MISCELLANEOUS LIGANDS

(i) Cyclopentadienyl and benzene π-complexes

Although this review journal does not normally deal with organo-metallic compounds, it is worth devoting a little space here to the metal-ligand bonds in this interesting class of coordination complexes. Very little Raman work has been published in this area, mainly because of the unsuitability of conventional radiation sources for use with coloured compounds. However, where the 4358 Å line of the mercury arc has proved unsuitable, good spectra have been obtained using the green line at 5461 Å, the 5876 Å and 6678 Å helium lines, or lines from other sources[4]. Argon ion and He/Ne c.w. gas lasers also can be used with some coloured compounds.

Ferrocene was the first π-cyclopentadienyl compound to be studied in detail by Raman spectroscopy. Lippincott and Nelson[191] used Hg 5461 Å, Hg 5770–5790 Å doublet, and Na 5890–5895 Å doublet excitation in obtaining the spectra of ferrocene, ferrocene-*d*-10, and ruthenocene. Symmetrical Cp–M–Cp stretching frequencies were assigned at 303 cm^{-1} and 330 cm^{-1} for $Fe(C_5H_5)_2$ and $Ru(C_5H_5)_2$, respectively. Subsequent determination of the $Mg(C_5H_5)_2$ Raman spectrum showed this to be similar to the ferrocene and ruthenocene spectra, but the coordinate bond symmetric stretching frequency was identified at 191 cm^{-1}, showing much weaker metal-ring bonding in this complex. However, the Raman results show that the Mg–Cp bonds clearly are still essentially covalent in nature[192]. Analogous metal-ring vibrational frequencies have been assigned at 350 cm^{-1} for the $(C_5H_5)Mn(CO)_3$ complex[193]; at 270 cm^{-1} for the dibenzene chromium sandwich, $(C_6H_6)_2Cr$; and at 279 cm^{-1} for the $(C_6H_6)_2Cr^+$ cation[194]. Fritz[195] has reported normal coordinate analyses of a few of these complexes, which indicate the following order of metal-ring bond strengths: $Cp_2Ru > Cp_2Fe > Cp_2Mg > Cp_2Ni$, and $(C_6H_6)_2Cr > (C_6H_6)_2Cr^+$. The force constants are Cp_2Ru, 3.20; Cp_2Fe, 3.11; Cp_2Mg, 1.83; Cp_2Ni, 1.68; $(C_6H_6)_2Cr$, 2.89; $(C_6H_6)_2Cr^+$, 2.78 mdyn/Å.

(ii) Others

No very extensive set of Raman data has been compiled for any other single class of coordination complex. A few representative examples only of the many and varied remaining types of complex will be presented here.

Form a study of thiocyanate ion complexes with a range of metal ions in aqueous solution, including Zn^{II}, Cd^{II}, Hg^{II}, Ag^{I}, Pt^{IV}, Cr^{III}, Ni^{II}, and Mg^{II}, Tramer[196] has shown that a clear distinction can be made between X–NCS, Y–SCN, and X–NCS–Y types of complex formation. The vibrational spectra show that Y–SCN complex formation results in an increase in the C–N bond strength, and a decrease in the C–S bond strength, while X–NCS attachment produces little change in the C–N bond, but increases the C–S bond strength. Bridging thiocyanates, such as in the mixed complex $ZnHg(NCS)_4$, with Zn–NCS–Hg links, show intermediate behaviour. Related work by Forster and Horrocks[197] on the tetrahedral pseudohalogeno-complexes of zinc, $Zn(NCO)_4{}^{2-}$, $Zn(NCS)_4{}^{2-}$, and $Zn(NCSe)_4{}^{2-}$, has confirmed Tramer's conclusions, showing that Zn–N–C–X binding results in a big increase in the C–X bond strength, though the C–N bond is little affected. The A_1 Raman lines arising from Zn–N symmetric stretching occur at 330 cm^{-1} and 255 cm^{-1} for $Zn(NCO)_4{}^{2-}$ and $Zn(NCS)_4{}^{2-}$, respectively, giving force constants of 1.8 and 1.7 mdyn/Å. These are significantly higher than the corresponding M–C bond force constant in the $Zn(CN)_4{}^{2-}$ complex, given as 1.3 mdyn/Å in Table 7.

Complexes of metal ions with chelating ligands usually give extremely complicated vibrational spectra which are difficult to interpret sufficiently well to provide meaningful metal-ligand bond strengths. However, making use of the Raman line polarisation characteristics, and by intercomparison of spectra of the closely related tris-chelate oxalate and acetylacetonate complexes of Al^{III}, Ga^{III}, and In^{III}, Hester and Plane[198] have been able to assign lines to totally symmetrical metal–oxygen stretching modes in these complexes. Their results, particularly the unusually high intensities associated with metal-oxygen modes in the tris-acetylacetonates, indicate appreciable electron delocalisation and pseudo-aromatic character in the metal-chelate rings, as indicated in Fig. 5. Additional evidence for this type of metal-oxygen π-bonding in analogous compounds is provided by n.m.r. results[199]. Characterisation of the simpler trisoxolato complexes has been assisted by Gaufres and Mathieu's[200] work on the $K_3[Al(Ox)_3]3H_2O$ complex.

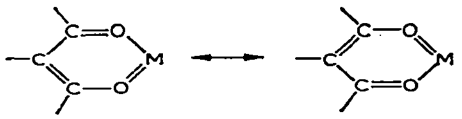


Fig. 5. Electron delocalisation in Al, Ga, and In trisacetylacetonates.

Krishnan and Plane[34] similarly have measured the Raman spectra of complexes of ethylenediamine with Zn^{II}, Cd^{II}, and Hg^{II}, and have assigned M–N symmetric stretching modes in the tris-complexes at 423 (Zn), 400 (Cd), and 422 (Hg) cm^{-1}. Much earlier, Mathieu[36] reported spectra of Zn, Pt, Rh, Ir, and Ni complexes of $H_2N(CH_2)_2NH_2$. Another potential chelating ligand is the glycinate ion. Complexes of this ligand with Zn^{II}, Cd^{II}, and Be^{II} have been studied by Krishnan and Plane[201], who have found that although $H_2N \cdot CH_2 \cdot CO_2^-$ does behave as a bidentate ligand with Zn^{II} and Cd^{II} in aqueous solutions at around pH 7, at lower pH values the nitrogen end of the ligand becomes protonated and breaks away from the metal centre, leaving only the carbonyl oxygen binding the metal.

Metal–metal bonding has been mentioned earlier, in section H, for the binuclear carbonyl[187] $Re_2(CO)_{10}$, and the $Cd[Co(CO)_4]_2$ and $Hg[Co(CO)_4]_2$ complexes. The Re_2 compound also has been studied by Lewis and co-workers[202], who report a Re–Re bond stretching frequency of 128 cm^{-1}. The Raman spectra of a number of other compounds containing Mn–Mn, Mn–Re, Mn–Sn, Sn–Sn, Hg–Hg, and Cd–Cd bonds have been summarised by Gager, Lewis, and Ware[203]. They point out that these symmetrical vibrations, all of which occur in the range 120–210 cm^{-1}, typically give rise to strong sharp polarised Raman lines, but are either absent of very weak and difficult to detect in far infrared absorption spectra[204].

REFERENCES

1 C. V. RAMAN, *Indian J. Phys.*, 2 (1928) 387; C. V. RAMAN AND K. S. KRISHNAN, *ibid.*, 2 (1928) 399; C. V. RAMAN AND K. S. KRISHNAN, *Nature*, 121 (1928) 501.

2 J. H. HIBBEN, *The Raman Effect and its Chemical Applications*, Reinhold Publishing Corp., New York, 1939.

3 H. STAMMREICH, *Phys. Rev.*, 78 (1950 79; *Spectrochim. Acta*, 8 (1956) 41; *Pure Appl. Chem.*, 4 (1962) 97.
E. R. LIPPINCOTT, F. X. POWELL, J. A. CREIGHTON AND D. G. JONES, *Develop. Appl. Spectry.*, 3 (1963) 106; F. X. POWELL, O. FLETCHER, E. R. LIPPINCOTT, *Rev. Sci. Instr.*, 34 (1963) 36; F. X. POWELL, *Spectrochim. Acta*, 12 (1958) 88; N. S. HAM AND A. WALSH, *J. Chem. Phys.*, 36 (1962) 1096.

4 HIBBEN, see ref. 2; TA-YOU WU, *Vibrational spectra and structure of Polyatomic Molecules*, Peking University Press, 1939; K. KOHLRAUSCH, *Der Smekel-Raman Effekt*, Julius Springer, Berlin, 1938; G. HERTZBERG, *Molecular Spectra and Molecular Structure, Vol. II, Infrared and Raman Spectra*, Van Nostrand, 1945; J. BRANDMULLER AND H. MOSER, *Einfuhrung in die Ramanspektroskopie*, Steinkopf, Darmstadt, 1962; H. SIEBERT, *Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie*, Springer-Verlag, Berlin, 1966; H. A. SZYMANSKI (ed), *Raman Spectroscopy*, Plenium Press, 1967.

5 L. A. WOODWARD, *Quart. Revs.*, 10 (1956) 185; D. A. LONG, *Annual Reports of the Chemical Society*, 60 (1963) 120; R. N. JONES AND M. K. JONES, *Anal. Chem.*, 38 (1966) 393R; R. S. TOBIAS, *J. Chem. Educ.*, 44 (1967) 2.

6 G. BRIEGLEB, *Elektronen–Donator–Acceptor-Komplexe*, Springer Verlag, Berlin, 1961.

7 O. KINELL, I. LINDQVUIST AND M. ZACKRISSON, *Acta Chem. Scand.*, 13 (1959) 190.

8 A. D. DEMBITSKII AND T. N. SUMAROKOVA, *Opt. i Spektroskopiya*, 12 (1962) 369; *ibid.*, 12 (1962) 484; A. D. DEMBITSKII, T. N. SUMAROKOVA AND M. I. USANOVICH, *ibid.*, 15 (1963) 48.

9 R. E. HESTER, *Raman Intensities and the Nature of the Chemical Bond*, Ch. 4 in Raman Spectroscopy, ed. H. A. SZYMANSKI, Plenium Press, 1967.

10 G. MICHEL ET G. DUYCKAERTS, *Spectrochim. Acta*, 21 (1965) 279.

11 P. JOB, *Ann. Chim. (Paris)*, 9 (1926) 113.

12 G. LECLERE ET G. DUYCKAERTS, *Spectrochim. Acta*, 22 (1966) 403.

13 H. A. Brune and W. Zeil, *Z. Phys. Chem. (Frankfurt)*, 32 (1962) 384.
14 I. R. Beattie and L. Rule, *J. Chem. Soc. (London)*, (1964) 3267; I. R. Beattie, G. P. McQuillan, L. Rule and M. Webster, *ibid.*, (1963) 1514.
15 I. R. Beattie and L. Rule, *J. Chem. Soc. (London)*, (1965) 2995.
16 E. W. Wartenberg and J. Goubeau, *Z. Anorg. Allgem. Chem.*, 329 (1964) 269.
17 D. A. Long and R. T. Bailey, *Trans. Faraday Soc.*, 59 (1963) 594.
18 M. F. Lappert and J. K. Smith, *J. Chem. Soc. (London)*, (1961) 3224.
19 W. Sawodny and J. Goubeau, *Z. Physik. Chem.*, NF 44 (1965) 227.
20 C. B. Wilson, J. C. Decius and P. C. Cross, *Molecular Vibrations*, McGraw-hill, New York, 1955.
21 J. Goubeau and H. Mitschelen, *Z. Physik. Chem. (Frankfurt)*, 14 (1958) 61.
22 J. Goubeau and W. Bues, *Z. Anorg. Allgem. Chem.*, 268 (1952) 221.
23 A. A. Babushkin, I. F. Kovalev and Emel'yanova, *Opt. i Spektroskopiya*, 4 (1958) 468.
24 H. J. Becher and J. Goubeau, *Z. Anorg. Allgem. Chem.*, 268 (1952) 133.
25 R. C. Taylor, *Advan. Chem. Ser.*, No. 42, Boron–Nitrogen Chemistry, Ch. 6, The American Chemical Society, 1964.
26 R. L. Amster and R. C. Taylor, *Spectrochim. Acta*, 20 (1964) 1487.
27 R. C. Taylor and C. L. Cluff, *Nature*, 182 (1958) 390.
28 R. C. Taylor, *J. Chem. Phys.*, 26 (1957) 1131; *ibid*, 27 (1957) 979.
29 J. M. Terrasse, H. Poulet and J. P. Mathieu, *Spectrochim. Acta*, 20 (1964) 305.
30 W. P. Griffith, *J. Chem. Soc. (A)*, (1966) 899.
31 T. E. Haas and J. R. Hall, *Spectrochim. Acta*, 22 (1966) 988.
32 D. E. Clegg and J. R. Hall, *Spectrochim. Acta*, 23A (1967) 263.
33 H. Poulet, P. Delorme and J. P. Mathieu, *Spectrochim. Acta*, 20 (1964) 1855.
34 K. Krishnan and R. A. Plane, *Inorg. Chem.*, 5 (1966) 852.
35 R. A. Plane, *Proc. Intern. Conf. Coordin. Chem., 8th, Vienna*, 1964, p. 17.
36 J. P. Mathieu, *J. Phys. Radium*, 8 (1937) 169.
37 W. R. Busing and D. F. Hornig, *J. Phys. Chem.*, 65 (1961) 284.
38 J. W. Schultz and D. F. Hornig, *J. Phys. Chem.*, 65 (1961) 2131.
39 G. E. Walrafen, *J. Chem. Phys.*, 36 (1962) 1035.
40 R. E. Weston, *Spectrochim. Acta*, 18 (1962) 1257.
41 G. E. Walrafen, *J. Chem. Phys.*, 40 (1964) 3249.
42 T. T. Wall and D. F. Hornig, *J. Chem. Phys.*, 43 (1965) 2079; *J. Chem. Phys.*, 45 (1966) 3424.
43 W. A. Senior and W. K. Thompson, *Nature*, 205 (1965) 170.
44 G. E. Walrafen, *J. Chem. Phys.*, 44 (1966) 1546.
45 J. P. Mathieu, *Compt. Rend.*, 231 (1950) 896.
46 R. L. Lafont, *Compt. Rend.*, 244 (1957) 1481.
47 A. da Silveira, M. A. Marques and N. M. Marques, *Compt. Rend.*, 252 (1961) 3983.
48 R. Lafont and L. D. Vinh, *Compt. Rend.*, 262 (1966) 49.
49 D. E. Irish, B. McCarroll and T. F. Young, *J. Chem. Phys.*, 39 (1963) 3436.
50 R. E. Hester and R. A. Plane, *Inorg. Chem.*, 3 (1964) 768.
51 T. G. Spiro, *Inorg. Chem.*, 4 (1965) 731.
52 A. I. Grigor'ev, V. A. Strachev and A. V. Novoselova, *Dokl. Akad. Nauk. SSSR*, 160 (1965) 383.
53 P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, 58 (1962) 1495.
54 P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, 56 (1960) 1591.
55 J. H. B. George, J. A. Rolfe and L. A. Woodward, *Trans. Faraday Soc.*, 49 (1953) 375.
56 D. E. Clegg and J. R. Hall, *Spectrochim. Acta*, 21 (1965) 357.
57 R. S. Tobias and C. E. Freidline, *Inorg. Chem.*, 4 (1965) 215; R. S. Tobias and S. Hutcheson, *J. Organometal. Chem.*, 6 (1966) 535.
58 E. R. Lippincott, J. A. Psellas and M. C. Tobin, *J. Chem. Phys.*, 20 (1952) 536.
59 J. S. Fordyce and R. L. Baum, *J. Chem. Phys.*, 43 (1965) 843.
60 L. A. Carreira, V. A. Maroni, J. W. Swain, Jr, and R. C. Plumb, *J. Chem. Phys.*, 45 (1966) 2216.
61 G. E. Walrafen, *J. Chem. Phys.*, 42 (1965) 485.

62 J. Aveston, *Inorg. Chem.*, 3 (1964) 981.
63 R. S. Tobias, *Can. J. Chem.*, 43 (1965) 1222.
64 V. A. Maroni and T. G. Spiro, *J. Am. Chem. Soc.*, 88 (1966) 1410.
65 D. E. Irish, *Raman Spectroscopy*, Ed. H. A. Szymansi, Plenium Press, 1967, Ch. 7.
66 H. Gerding and H. Hautgraaf, *Rec. Trav. Chim.*, 72 (1953) 21.
67 K. Balasubrahmanyam and L. Nanis, *J. Chem. Phys.*, 42 (1965) 676.
68 L. A. Woodward and A. A. Nord, *J. Chem. Soc.*, (1956) 3721; (1955) 2655.
69 L. A. Woodward and G. H. Singer, *J. Chem. Soc.*, (1958) 716.
70 L. A. Woodward and M. J. Taylor, *J. Chem. Soc.*, (1960) 4473.
71 L. A. Woodward and P. T. Bill, *J. Chem. Soc.*, (1955) 1699.
72 T. G. Spiro, *Inorg. Chem.*, 4 (1965) 731; 6 (1967) 569.
73 J. E. Griffiths and D. E. Irish, *Inorg. Chem.*, 3 (1964) 1134.
74 L. A. Woodward and L. E. Anderson, *J. Chem. Soc.*, (1957) 1284.
75 J. Hiraishi, I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 20 (1964) 819.
76 J. A. Creighton and L. A. Woodward, *Trans. Faraday Soc.*, 58 (1962) 1077.
77 H. Stammreich and R. Forneris, *Spectrochim. Acta*, 16 (1960) 363.
78 D. E. Irish, B. McCarroll and T. F. Young, *J. Chem. Phys.*, 39 (1963) 3436.
79 D. E. Irish and T. F. Young, *J. Chem. Phys.*, 43 (1965) 1765.
80 M. L. Delwaulle, *Compt. Rend.*, 240 (1955) 2132; *Bull. Soc. Chim. France*, (1955) 1294.
81 Z. Zecki and J. Mankowski, *Rozcnicki Chem.*, 36 (1962) 375.
82 D. F. C. Morris, E. L. Short and D. N. Waters, *J. Inorg. Nucl. Chem.*, 25 (1963) 975.
83 R. B. Ellis, *J. Electrochem. Soc.*, 113 (1966) 485.
84 J. R. Moyer, J. C. Evans and G. Y. S. Lo, *J. Electrochem. Soc.*, 113 (1966) 158.
85 C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, 5 (1966) 2232.
86 W. Yellin and R. A. Plane, *J. Am. Chem. Soc.*, 83 (1961) 2448.
87 J. A. Rolfe, D. E. Sheppard and L. A. Woodward, *Trans. Faraday Soc.*, 50 (1954) 1275.
88 H. Poulet and J. P. Mathieu, *J. Chim. Phys.*, 60 (1963) 442.
89 M. Goldstein, *Spectrochim. Acta*, 22 (1966) 1389.
90 E. L. Short, D. N. Waters and D. F. C. Morris, *J. Inorg. Nucl. Chem.*, 26 (1964) 902.
91 H. Braune and G. Engelbrecht, *Z. Phys. Chem. (Frankfurt)*, 10 (1930) 1; 11 (1931) 409; 19 (1932) 303.
92 Z. Zecki, *Spectrochim. Acta*, 18 (1962) 1165.
93 G. B. Deacon, J. H. S. Green and W. Kynaston, *Austral. J. Chem.*, 19 (1966) 1603.
94 G. J. Janz and D. W. James, *J. Chem. Phys.*, 38 (1963) 902, 905.
95 W. R. Griffith and T. D. Wicknis, *J. Chem. Soc. (A)*, (1967) 675.
96 L. A. Woodward and J. A. Creighton, *Spectrochim. Acta*, 17 (1961) 594.
97 P. J. Hendra, *Nature*, 212 (1966) 179.
98 L. A. Woodward and M. J. Ware, *Spectrochim. Acta*, 19 (1963) 775.
99 K. Balasubrahmanyam, *J. Chem. Phys.*, 44 (1966) 3270.
100 J. H. R. Clarke and L. A. Woodward, *Trans. Faraday Soc.*, 61 (1965) 207.
101 N. N. Greenwood, A. C. Serma and B. P. Straughan, *J. Chem. Soc. (A)*, (1966) 1446.
102 K. Dehnicke and J. Weidlein, *Chem. Ber.*, 98 (1965) 1087.
103 D. F. Smith and G. M. Begun, *J. Chem. Phys.*, 43 (1965) 2001.
104 H. H. Claasen and H. Selig, *J. Chem. Phys.*, 43 (1965) 103.
105 P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, 62 (1966) 1423.
106 D. F. van der Vondel and G. P. van der Kelen, *Bull. Soc. Chim. Belges*, 74 (1965) 453.
107 H. Kreigsmann and S. Pauly, *Z. Anorg. Allgem. Chem.*, 330 (1964) 275.
108 E. G. Gal'pern and R. S. Mayants, *Zh. Strukt. Khim.*, 6 (1965) 785.
109 J. R. Durig, C. W. Sink and S. F. Bush, *J. Chem. Phys.*, 45 (1966) 66.
110 R. P. J. Cooney and J. R. Hall, *J. Inorg. Nucl. Chem.*, 28 (1966) 1679.
111 R. E. Hester and R. A. Plane, *Inorg. Chem.*, 3 (1964) 769.
112 R. E. Hester and H. Brintzinger, *Inorg. Chem.*, 5 (1966) 980.
113 R. E. Hester and W. E. L. Grossman, *Inorg. Chem.*, 5 (1966) 1308.
114 R. E. Hester and R. A. Plane, *J. Chem. Phys.*, 40 (1964) 411.
115 D. E. Irish and G. E. Walrafen, *J. Chem. Phys.*, 46 (1967) 378.
116 R. E. Hester, R. A. Plane and G. E. Walrafen, *J. Chem. Phys.*, 38 (1963) 249.

117 J. P. Mathieu and M. Lounsbury, *Disc. Faraday Soc.*, 9 (1950) 196.
118 R. E. Hester and R. A. Plane, *J. Chem. Phys.*, 45 (1966) 4588.
119 J. T. Miller and D. E. Irish, *Can. J. Chem.*, 45 (1967) 147.
120 J. H. R. Clarke and L. A. Woodward, *Trans. Faraday. Soc.*, 62 (1966) 3022.
121 R. R. Miano and R. A. Plane, *Inorg. Chem.*, 3 (1964) 987.
122 J. R. Ferraro, A. Walker and C. Cristallini, *Inorg. Nucl. Chem. Letters*, 1 (1965) 25.
123 J. R. Ferraro, C. Cristallini and I. Fox, *J. Inorg. Nucl. Chem.*, 29 (1967) 139.
124 C. B. Baddeil, M. J. Tait and G. J. Janz, *J. Phys. Chem.*, 69 (1965) 3634.
125 S. C. Wait and G. J. Janz, *Quart. Revs. (London)*, 17 (1963) 225.
126 G. J. Janz and T. R. Kozlowski, *J. Chem. Phys.*, 40 (1964) 1699.
127 S. C. Wait, Jr., A. T. Ward and G. J. Janz, *J. Chem. Phys.*, 45 (1966) 133.
128 M. A. Ponyatenko and I. V. Radchenko, *Ukr. Fiz. Zh.*, 9 (1964) 1233; 11 (1966) 317.
129 R. E. Hester and K. Krishnan, *J. Chem. Phys.*, 46 (1967) 3405.
130 G. E. Walrafen, *J. Chem. Phys.*, 43 (1965) 479.
131 E. Steger and A. Simon, *Z. Anorg. Allgem. Chem.*, 294 (1958) 1.
132 H. Brintzinger and R. A. Plane, *Inorg. Chem.*, 6 (1967) 623.
133 M. Le Postollec, J. P. Mathieu and H. Poulet, *J. Chim. Phys.*, 60 (1963) 1319.
134 G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, 35 (1961) 1027.
135 L. A. Woodward and H. F. Owen, *J. Chem. Soc.*, (1959) 1055.
136 G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, 33 (1960) 736.
137 M. J. Reisfield and L. H. Jones, *J. Mol. Spectry.*, 18 (1965) 222.
138 G. Moreau, H. Poulet and J. P. Mathieu, *Bull. Soc. Franc. Mineral Crist.*, 88 (1965) 6.
139 L. H. Jones, *J. Chem. Phys.*, 29 (1958) 463.
140 P. Chiorboli, *J. Inorg. Nucl. Chem.*, 8 (1958) 133.
141 H. Poulet and J. P. Mathieu, *Spectrochim. Acta*, 15 (1959) 932.
142 P. Chiorboli and C. Testa, *Ann. Chim. (Rome)*, 47 (1957) 639.
143 L. H. Jones, *Spectrochim. Acta*, 19 (1963) 1675.
144 L. H. Jones and J. M. Smith, *J. Chem. Phys.*, 41 (1964) 2507.
145 L. H. Jones, *J. Chem. Phys.*, 43 (1965) 594.
146 W. P. Griffith, *J. Chem. Soc.*, (1964) 4070.
147 H. Poulet and J. P. Mathieu, *Compt. Rend.*, 248 (1959) 2079.
148 L. H. Jones, *Spectrochim. Acta*, 17 (1961) 188.
149 J. R. Hall and J. C. Mills, *J. Organometal. Chem.*, 6 (1966) 445.
150 H. Stammreich and O. Sala, *Z. Elektrochem.*, 64 (1960) 741; *ibid.*, 65 (1961) 149.
151 J. P. Mathieu and H. Poulet, *Spectrochim. Acta*, 19 (1963) 1966; *Compt. Rend.*, 248 (1959) 2315.
152 L. H. Jones, *J. Chem. Phys.*, 41 (1964) 856.
153 I. Damaschun, *Z. Physik. Chem.*, B16 (1932) 81.
154 J. Deveze and M. Krauzman, *Compt. Rend.*, 263B (1966) 864.
155 J. P. Mathieu and S. J. Cornevin, *J. Chim. Phys.*, 36 (1939) 271, 308.
156 G. B. Bonino and O. Salvetti, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, 20 (1956) 150.
157 P. Chiorboli and F. Cappellina, *Ann. Chim. (Rome)*, 46 (1956) 875; P. Chiorboli, F. Cappellina and E. Tedeschi, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, 22 (1957) 44.
158 L. H. Jones, *J. Chem. Phys.*, 36 (1962) 1209.
159 L. Pauling, *J. Chem. Soc.*, (1948) 1461.
160 L. H. Jones, *Inorg. Chem.*, 4 (1965) 369.
161 J. M. Smith, L. H. Jones, I. K. Kressin and R. A. Penneman, *Inorg. Chem.*, 4 (1965) 369.
162 L. H. Jones and J. M. Smith, *Inorg. Chem.*, 4 (1965) 1677.
163 R. P. J. Cooney and J. R. Hall, *J. Inorg. Nucl. Chem.*, 28 (1966) 1679.
164 L. H. Jones, *Inorg. Chem.*, 2 (1963) 777.
165 L. A. Woodward and J. R. Hall, *Spectrochim. Acta*, 16 (1960) 654.
166 G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, 26 (1957) 1118.
167 S. Sundaram and F. F. Cleveland, *J. Chem. Phys.*, 32 (1960) 166.
168 A. Danti and F. A. Cotton, *J. Chem. Phys.*, 28 (1958) 736.

169 L. H. Jones, *Spectrochim. Acta*, 19 (1963) 329.
170 R. L. Amster, R. B. Hannan and M. C. Tobin, *Spectrochim Acta*, 19 (1963) 1489.
171 C. W. F. T. Pistorius and P. C. Haarhoff, *J. Chem. Phys.*, 31 (1959) 1439.
172 L. H. Jones and R. S. McDowell, *Spectrochim. Acta*, 20 (1964) 248.
173 H. Stammreich, O. Sala and Y. Tavares, *J. Chem. Phys.*, 30 (1959) 856.
174 F. T. King and E. R. Lippincott, *J. Am. Chem. Soc.*, 78 (1956) 4192.
175 W. G. Fateley and E. R. Lippincott, *Spectrochim. Acta*, 10 (1957) 8.
176 H. Murata and K. Kawai, *J. Chem. Phys.*, 28 (1958) 516.
177 W. F. Edgell, W. E. Wilson and R. Summitt, *Spectrochim. Acta*, 19 (1963) 863.
178 H. Stammreich, K. Kawai, Y. Tavares, P. Krumholtz, J. Behmoires and S. Bril., *J. Chem. Phys.*, 32 (1960) 1482.
179 R. A. Friedel, I. Wender, S. L. Shufler and H. W. Sternberg, *J. Am. Chem. Soc.*, 77 (1955) 3951.
180 H. Stammreich, K. Kawai, O. Sala, P. Krumholtz, *J. Chem. Phys.*, 35 (1961) 2168.
181 M. Bigorgne, *Compt. Rend.*, 251 (1960) 355.
182 B. L. Crawford and P. C. Cross, *J. Chem. Phys.*, 6 (1938) 525.
183 G. Bouquet and M. Bigorgne, *Compt. Rend.*, 261 (1965) 2865.
184 L. H. Jones and R. S. McDowell, *J. Chem. Phys.*, 46 (1967) 1536.
185 H. Stammreich, K. Kawai and O. Sala, *J. Chem. Phys.*, 35 (1961) 2175.
186 F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 4 (1965) 1328.
187 M. Bigorgne and A. Zelwer, *Bull. Soc. Chim. France*, (1960) 1986.
188 R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, (1962) 1301.
189 F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, 84 (1962) 4432; *Inorg. Chem.*, 2 (1963) 533.
190 R. E. Hester and J. Nixon, unpublished results.
191 E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, 10 (1958) 307.
192 E. R. Lippincott, J. Xavier and D. Steele, *J. Am. Chem. Soc.*, 83 (1961) 2262.
193 I. Hyams, R. T. Bailey and E. R. Lippincott, *Spectrochim. Acta*, 23A (1967) 273.
194 H. P. Fritz, W. Lüttke, H. Stammreich and R. Forneris, *Spectrochim. Acta*, 17 (1961) 1068.
195 H. P. Fritz, *Adv. Organometallic Chem.*, 1 (1964) 239.
196 A. Tramer, *J. Chim. Phys.*, 59, (1962) 232; *Compt. Rend.*, 250 (1960) 3150.
197 D. Forster and W. de W. Horrocks, Jr., *Inorg. Chem.*, 6 (1967) 339.
198 R. E. Hester and R. A. Plane, *Inorg. Chem.*, 3 (1964) 513.
199 R. E. Hester, *Chem. Ind. (London)*, (1963) 33.
200 R. Gaufres and J. P. Mathieu, *Compt. Rend.*, 248 (1959) 81.
201 K. Krishnan and R. A. Plane, *Inorg. Chem.*, 6 (1967) 55.
202 J. Lewis, A. R. Manning, J. R. Miller, M. J. Ware and F. Nyman, *Nature*, 207 (1965) 142.
203 H. M. Gager, J. Lewis and M. J. Ware, *Chem. Comms.*, (1966) 616.
204 N. A. D. Carey and H. C. Clark, *Chem. Comms.*, (1967) 292.