409. *The Far-infrared Spectra* (190—460 cm.$^{-1}$) *of Tetraethylammonium Salts of Some Complex Chlorides and Bromides.*

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The preparation and far-infrared spectra (190—460 cm.$^{-1}$) of anhydrous complex chlorides (and some complex bromides) of 30 metallic elements are described. Metal–chlorine stretching frequencies were found in the range 228—377 cm.$^{-1}$ and are discussed in terms of the bonding within the complexes. The use of thionyl chloride as solvent in the preparation of complex chlorides is described.

OWING to the common occurrence of chloride and bromide ions as ligands in metal complexes, metal–chlorine and metal–bromine stretching frequencies are of interest both analytically and for the structural information that they can provide. Nevertheless, published infrared and Raman data for regular octahedral and tetrahedral complex halides are very incomplete, except for the fluorides which have received extensive attention.[1]

Using a new and simple method we have prepared the anhydrous tetraethylammonium salts of complex chlorides derived from most of the metallic elements. They are nearly all mononuclear and of regular octahedral or tetrahedral symmetry. Their infrared-active stretching frequencies occur in the range 228—377 cm.$^{-1}$.

Spectroscopic Results.—Owing to the presence of a centre of symmetry in species of regular octahedral disposition, there is a mutual-exclusion rule between normal vibrational modes allowed in the infrared and in the Raman spectra. The two techniques give different but complementary information. For a regular XY_6 species the only infrared-active modes (f_{1u} symmetry class) are ν_3 (stretching) and ν_4 (bending). The known vibrational values for regular octahedral complex chlorides and bromides have been collected by Adams and Gebbie,[2] who also report new results for the stretching and bending modes for these classes of compound.

All four fundamental vibrational frequencies of a regular tetrahedral species XY_4 are permitted in the Raman effect. Only the two f_2 modes (one stretching and one bending) are permitted in the infrared spectrum. A good collection of vibrational data for neutral and charged tetrahedral $M(Hal)_4$ species has been made by Godnev and Aleksandrovskaya.[3] As regards the tetrahedral ions for which we now report infrared results, a comprehensive Raman study of $[GaCl_4]^-$ is available[4] and there are less satisfactory accounts[5,6] of $[AlCl_4]^-$ and $[ZnCl_4]^{2-}$.

Preparation of Complex Chlorides.—Complex halides of many metals are hygroscopic; rigorously dry conditions and solvents are required for their preparation. Alcohol has generally been used but thionyl chloride has especially suitable solvent properties.[7] The latter is a good dehydrating reagent[8] and therefore allows the use of hydrated metal chlorides as starting materials. It is an ionising medium which permits the preparation of ionic complexes and has been used by Gutmann for conductance titrations between vanadium tetrachloride and quaternary ammonium salts.[9] Sandhu, Chakkal, and Sandhu[10] prepared the octahedral complex chlorides of titanium(IV), tin(IV), and zirconium(IV) in thionyl chloride.

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[1] Peacock and Sharp, *J.*, 1959, 2762, and references therein.
[2] Adams and Gebbie, *Spectrochim. Acta*, in the press.
[3] Godnev and Aleksandrovskaya, *Optics and Spectroscopy*, 1961, **10**, 14.
[4] Woodward and Nord, *J.*, 1956, 3721.
[5] Gerding and Hautgraaf, *Rec. Trav. chim.*, 1953, **72**, 21.
[6] Delwaulle, *Compt. rend.*, 1955, **240**, 2132.
[7] Gutmann, *Quart. Rev.*, 1956, **10**, 451.
[8] Freeman and Smith, *J. Inorg. Nuclear Chem.*, 1958, **7**, 224, 287.
[9] Gutmann, *Monatsh.*, 1954, **85**, 286.
[10] Sandhu, Chakkal, and Sandhu, *J. Indian Chem. Soc.*, 1960, **37**, 329.

Most of the complex chlorides prepared for this study were isolated from thionyl chloride by one of the following two procedures. Tetraethylammonium chloride tetrahydrate in small excess and the metal chloride or its hydrate were boiled with thionyl chloride. Tetraethylammonium chloride is very soluble in this solvent, and metal chlorides normally dissolve in it without difficulty. After filtration the chromium complex crystallised from the hot solution, while some others (Al, Fe, Ga, Nb, Pt, Sn, Ta, W) were obtained as well-defined crystals on refrigeration. For the more soluble complexes (Cd, Co, Cu, Hg, In, Mg, Mn, Ni, Pb, Ru, Th, Ti, U, Zn, Zr), thionyl chloride was removed from the clear solution at 15 mm. and acetic anhydride was added to the ill-defined residue. Pure products were precipitated at once, and were washed with small volumes of acetic anhydride which serves to destroy traces of thionyl chloride and to remove the excess of tetraethylammonium chloride. Before being dried *in vacuo* the crystals may be handled in moist air since both thionyl chloride and acetic anhydride act as protective coverings. The utility of the method is illustrated by the preparation of the salt $[NEt_4]_2[MgCl_4]$. This is the first example of a complex chloride of magnesium and it is excessively hygroscopic. Palladium gave an ill-defined product; rhodium, calcium, and strontium chloride failed to react. Molybdenum pentachloride afforded an oxyhalide complex. The yields were uniformly high, but ruthenium and thorium chloride dissolved only with difficulty.

Near its boiling point, thionyl chloride commences to decompose according to the scheme: $12SOCl_2 \longrightarrow 3S_2Cl_2 + 6SO_2 + 9Cl_2$. For this reason the solvent behaves as an oxidising medium and the complexes obtained had the metal in the highest common oxidation state. Lead dichloride, palladium dichloride, and ruthenium trichloride gave octahedral $[M^{IV}Cl_6]^{2-}$ ions and ferrous chloride gave $[Fe^{III}Cl_4]^-$. It is therefore remarkable that tungsten hexachloride dissolves in the thionyl chloride–tetraethylammonium chloride solution with effervescence and in this case reduction occurs with formation of the salt $[NEt_4]^+[W^VCl_6]^-$.

The binuclear ions $[M_2{}^{III}Cl_9]^{3-}$ were obtained from chromium(III) and vanadium(III) chloride, instead of the expected mononuclear complex chlorides. Similar compounds have been obtained previously from melts and have two octahedra joined by a face containing three bridging chlorine atoms.[11]

Complex bromides may be prepared in a similar manner, by using thionyl bromide as solvent, but pure products are difficult to obtain owing to the low thermal stability of thionyl bromide which leads to much deposition of elementary sulphur. However, tetrahedral complexes of manganese(II), iron(III), and cobalt(II) are presented as examples of the use of this solvent.

Only the salts $[NEt_4]_2[MgCl_4]$ and $[NEt_4][WCl_6]$ are new types of compound, but in other cases the tetraethylammonium salt may not have been prepared previously.

Discussion.—A quantitative discussion of our results is not admissible since in the infrared region we are limited, by the selection rules, to observations of antisymmetric stretching frequencies. Directly comparable bond-stretching force constants cannot be calculated from these, as is possible with Raman data on totally symmetric stretching modes. Unfortunately, no direct relation exists between infrared- and Raman-active frequencies for a given species: examples are known in which the infrared-active stretching frequency in XY_4 and XY_6 species is either above or below the Raman-active stretching frequency. Nevertheless, for a series of ions (XY_6 and XY_4) of similar mass, trends in ν_3 will probably follow those in ν_1. With these reservations in mind we shall discuss our new results (Table 1).

The complexes belong to four main classes (parts *a*, *b*, *c*, and *d* of Table 1), within which isomorphism was demonstrated by means of *X*-ray powder photography. In three cases inversion of intensity between pairs of lines, indicative of distortion, was apparent in these photographs. These were the copper salt, which is expected to undergo Jahn–Teller

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[11] Wessel and Ijdo, *Acta Cryst.*, 1957, **10**, 466.

distortion, and the thorium and the mercury salt. Also in the infrared spectra of the above three salts, the ν_3 bands appeared with badly distorted shapes.

The three complex bromides (Table 1*e*) all gave split ν_3 absorption bands, and $[FeBr_4]^-$ gave a broad, square-topped peak indicative of two closely spaced bands of equal intensity. These may all be sufficiently distorted in the solid state to resolve the triply degenerate ν_3 band.

(*a*) *Octahedral complexes of quinque- and quadri-valent metals.* The M^{IV} and M^{V} complexes form two isomorphous series. Among the octahedral complexes of quadrivalent metals (Table 1*a*) those of the platinum metals and rhenium (class *b* [12]) have much higher ν_3 values than those of class *a*. The effect of nuclear mass on the latter elements is evident in the Group IV metal complexes which show steadily decreasing ν_3's with increasing mass. The ion $[GeCl_6]^{2-}$ seems anomalous in this respect. However, its *X*-ray powder photograph showed that it is not isomorphous with the other $[MCl_6]^{2-}$ complexes, as might be expected in view of the small ionic radius of Ge^{4+}.

TABLE 1.

Infrared-active metal–halogen absorption frequencies (cm.$^{-1}$) of some tetraethylammonium salts.

(*a*) $M^{IV}Cl_6^{2-}$:	Ti	V	Cr	Mn	Fe	Co	Ni——	——Ge	
	330 302(sh)	—	—	—	—	—	—	293 205 *	
	Zr	Nb	Mo	Tc	Ru	Rh	Pd——	——Sn	
	293	—	—	—	332	—	336·5	294	
	Hf	Ta	W	Re	Os	Ir	Pt——	——Pb	
	—	—	—	300 314	304·5 318·5(sh)	316 324	330	265	
	Th	U							
	263	260							
(*b*) $M^{V}Cl_6$:	Nb	Ta	W						
	333	330	329						
(*c*) $M^{II}Cl_4^{2-}$:	Mg	Mn	Fe	Co	Ni	Cu	Zn	Cd	Hg
	344	281	276	295	283	267	271	260	228
(*d*) $M^{III}Cl_4^{-}$:	Al	Fe	Ga						
	(606) (545)	377	373 342†(vw)						
(*e*) $M^{II}Br_4^{2-}$:	Mn	Fe	Co			(*f*) $M^{III}Br_4^{-}$:		Fe	
	210 221	212 219	228 233					289	
(*g*) Miscellaneous:	$InCl_5^{2-}$	$Cr_2Cl_9^{3-}$	$V_2Cl_9^{3-}$						
	267 281(sh)	341(vs) 322(m)	335(vs) 296(m)						

* Bending frequency. † Raman frequency (see text). ( ) Doubtful assignment (see text).
sh = Shoulder.

Remarkably similar values of ν_3 are found for those complex chlorides where the central metal ions have similar radii, the same charge, and a spherically symmetrical electronic arrangement, but widely different masses. Thus the frequencies are closely similar for Nb^{V} (d^0) and Ta^{V} (d^0). The value for Zr^{IV} (d^0) is similar to that for Sn^{IV} (d^{10}), and ν_3 for Pb^{IV} (d^{10}) close to that of Th^{IV} (d^0). Even W^{V} (d^1) has ν_3 very similar to those of Nb^{V} and Ta^{V}, and ν_3 for U^{IV} (d^2) resembles those of Pb^{IV} and Th^{IV}.

Among the platinum elements the high bond strength due to ligand-field stabilisation leads to high ν_3 frequencies. Thus, the elements from rhenium to platinum form a series

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[12] Ahrland, Chatt, and Davies, *Quart. Rev.*, 1958, **12**, 265.

with steadily increasing ν_3, despite the increase in atomic mass and the steady diminution of the lanthanide effect upon the ionic radius. As a result of this stabilisation the platinum complex has as high a ν_3 frequency (330 cm.$^{-1}$) as titanium.

We have also observed the deformation frequency (ν_4) of $[GeCl_6]^{2-}$, thereby fully determining the infrared spectrum of this ion. Our value of 260 cm.$^{-1}$ for $[UCl_6]^{2-}$ is closely comparable with that of 258 cm.$^{-1}$ deduced by Sutton, Young, and Gruen [13] from the electronic spectrum of $Cs_2[UCl_6]$.

(*b*) *Tetrahedral complexes of bi- and ter-valent metals.* The M^{II} and M^{III} complexes form two isomorphous series, neither as extensive as the octahedral. The light transition elements form a series of ions $[MCl_4]^{2-}$ (M = Mn to Zn). Within experimental error there is a small general decrease in ν_3 along the series, with the exception of $[CoCl_4]^{2-}$ which has a significantly higher value of ν_3 than any of its neighbours. This may be associated with a higher bond strength since, having a d^7 configuration, Co^{2+} has the highest ligand-field stabilisation energy of the series. This observation is supported by the correspondingly high metal–bromine stretch of $[CoBr_4]^{2-}$ (Table 1*e*). A clear decrease in ν_3 with increasing atomic number is found on passing down Group II from magnesium to mercury. This follows the increase in metal ionic radius and atomic number, but not the order of the M^{2+} to M^{3+} ionisation potentials. There is no correspondence between our values of ν_3 for the manganese to zinc complex chlorides and the Irving–Williams order of stability constants.[14]

The isomorphous trio $[MCl_4]^-$ (M = Al, Ga, Fe) has high ν_3 frequencies compared with those of the bivalent tetrahedral series. There is clearly a large increase in bond strength for the Fe^{3+} over the Fe^{2+} complex chlorides and bromides. A similar phenomenon is observed in many isoelectronic series: *e.g.*, ν_3 for $GeCl_4^-$, $[GaCl_4]$, $[ZnCl_4]^{2-}$ decreases, being 453, 373, and 271 cm.$^{-1}$.

Our spectrum of $[GaCl_4]^-$ agrees with the Raman spectrum determined by Woodward and Nord. We find ν_3 at 373vs cm.$^{-1}$, whereas the Raman value is 386 cm.$^{-1}$ (weak and diffuse). Part of this small discrepancy may be due to the difference in state. The intense Raman-active (infrared-inactive) ν_1 frequency was found at 346 cm.$^{-1}$. We observed a very weak band at 342 cm.$^{-1}$ which may be the ν_1 frequency weakly permitted by virtue of a solid-state distortion.

Delwaulle,[6] in a Raman study of $ZnCl_4^{2-}$, was unable to find ν_3 but observed ν_1 at 282 cm.$^{-1}$. We find ν_3 as a moderately sharp and very intense band at 271 cm.$^{-1}$.

Our study of the salt $[NEt_4][AlCl_4]$ revealed a moderately intense band at 242 cm.$^{-1}$ and a broad doublet at 606 and 545 cm.$^{-1}$. Gerding and Hautgraaf,[5] from a Raman study of a melt of aluminium chloride plus sodium chloride, found ν_3 at 575 cm.$^{-1}$ as a very diffuse band. They did not find absorption at 242 cm.$^{-1}$ but recorded two lower-frequency bands. This species obviously requires further study.

(*c*) *Binuclear ions.* Both $Cr_2Cl_9^{2-}$ and $V_2Cl_9^{3-}$ gave a two-band spectrum, the lower-frequency absorption being the weaker. We assign the higher-frequency band to metal–terminal chlorine stretching and the lower-frequency band to vibrations involving the bridging chlorine atoms. The band observed by Jonassen and Cantor [15] at 961 cm.$^{-1}$ in the infrared spectrum of the salt $K_3W_2Cl_9$ and assigned by them to ν(W–Cl), is probably a second overtone of the true ν(W–Cl).

The structure of the salt $[NEt_4]_2[InCl_5]$ is not known but ν(In–Cl) appeared in the infrared spectrum at 267 cm.$^{-1}$ with a shoulder at 281 cm.$^{-1}$.

EXPERIMENTAL

The *complexes* are listed in Table 2. They were characterised by elementary analysis and assigned to four main classes by examination of their *X*-ray powder photographs. For the

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[13] Sutton, Young, and Gruen, *J. Chem. Phys.*, 1960, **33**, 1140.
[14] Irving and Williams, *J.*, 1953, 3192.
[15] Jonassen and Cantor, *Rec. Trav. chim.*, 1956, **75**, 609.

TABLE 2.

Complexes prepared.

Anion	Colour	Found (%)					Required (%)					Prep.	Magnetic moment (B.M.; 20°)	Ref.	Starting material
		C	H	Br	Cl	N	C	H	Br	Cl	N				
$[AlCl_4]^-$	None				47·2	4·59				47·4	4·68	A			$AlCl_3$
$[CdCl_4]^{2-}$	None				27·4	5·41				27·5	5·44	B			$CdCl_2,2·5H_2O$
$[CoBr_4]^{2-}$	Pale blue			50·1		4·45			50·0		4·38	B	4·80[19]	19	$CoBr_2,5H_2O$
$[CoCl_4]^{2-}$	Blue				30·7	5·84				30·7	6·07	B	4·47	17	$CoCl_2,6H_2O$
$[Cr_2Cl_9]^{3-}$	Violet	35·6	7·63		39·0	5·18	35·4	7·43		39·2	5·16	A			$CrCl_3,6H_2O$
$[CuCl_4]^{2-}$	Yellow				30·3	6·18				30·4	6·01	B	2·01	17	$CuCl_2,2H_2O$
$[FeBr_4]^{2-}$	Pale green			50·1					50·3			Lit.	5·46[18]	18	$FeBr_2$
$[FeBr_4]^-$	Brown			63·1		2·79			63·2		2·76	A		18	$FeBr_3$
$[FeCl_4]^{2-}$	Pale green				30·9					30·9		Lit.	5·40[18]	18	$FeCl_2$
$[FeCl_4]^-$	Pale green	29·3	6·14		42·6	4·17	29·0	6·14		43·2	4·27	A	5·94	18	$FeCl_2,4H_2O$ or $FeCl_3$
$[GaCl_4]^-$	None				41·5	4·09				41·5	4·09	A			$GaCl_3$
$[GeCl_6]^{2-}$	None				38·9	5·23				38·2	5·13	Text			$GeCl_4$
$[HgCl_4]^{2-}$	None				23·2	4·75				23·6	4·64	B			$HgCl_2$
$[InCl_5]^{2-}$	None				32·4	5·08				32·0	5·07	B		26	$InCl_3$
$[IrCl_6]^{2-}$	Red					4·17					4·21	C	1·75		K_2IrCl_6
$[MgCl_4]^{2-}$	None				33·0	6·52				33·2	6·56	B			$MgCl_2,6H_2O$
$[MnBr_4]^{2-}$	Pale green			50·5		4·35			50·3		4·41	B	5·97[17]	17	$MnBr_2,4H_2O$
$[MnCl_4]^{2-}$	Pale green				30·9	6·03				31·0	6·12	B	5·94[17]	17	$MnCl_2,4H_2O$
$[NbCl_6]^-$	Yellow				48·8	3·17				48·8	3·11	A		23	$NbCl_5$
$[NiCl_4]^{2-}$	Green				30·4	6·06				30·7	6·07	B	3·87[17]	17	$NiCl_2,6H_2O$
$[OsCl_6]^{2-}$	Orange					4·16					4·22	C	1·52		$(NH_4)_2OsCl_6$
$[PbCl_6]^{2-}$	Yellow				30·9	4·11				31·2	4·12	B			$PbCl_2$
$[PdCl_6]^{2-}$	Red					4·68					4·83	C			$(NH_4)_2PdCl_6$
$[PtCl_6]^{2-}$	Orange	28·5	6·07			4·24	28·7	6·03			4·19	A		20	$PtCl_2$
$[ReCl_6]^{2-}$	Pale green					4·22					4·25	C	3·61		K_2ReCl_6
$[RuCl_6]^{2-}$	Red-brown	33·8	7·05		37·0	5·19	33·4	7·02		37·0	4·87	B			$RuCl_3,4H_2O$
$[SnCl_6]^{2-}$	None				36·1	4·63				35·9	4·73	A		25	$SnCl_4$
$[TaCl_6]^-$	None				40·6	2·82				40·6.	2·67	A		23	$TaCl_5$
$[ThCl_6]^{2-}$	None				30·0	3·95				30·1	3·97	B			$ThCl_4,10H_2O$
$[TiCl_6]^{2-}$	Yellow				40·8	5·18				40·6	5·37	B		22	$TiCl_4$
$[UCl_6]^{2-}$	Pale green				29·4	3·92				29·9	3·94	B	1·71	24	UCl_4
$[V_2Cl_9]^{3-}$	Maroon	35·8	7·62		39·3	5·15	35·4	7·43		40·1	5·17	Text			VCl_3
$[WCl_6]^-$	Black (green streak)	18·2	3·92		40·2	2·80	18·2	3·83		40·3	2·66	A	~0·8		WCl_6
$[ZnCl_4]^{2-}$	None				30·2	5·93				30·3	5·99	B			$ZnCl_2$
$[ZrCl_6]^{2-}$	None				37·4	4·81				37·6	4·96	B		21, 22	$ZrCl_4$

[17] Gill and Nyholm, *J.*, 1959, 3997. [18] Gill, *J.*, 1961, 3512. [19] Chiswell and Livingstone, *J.*, 1960, 97. [20] Khomenko, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1951, 806. [21] Gutmann and Himml, *Z. anorg. Chem.*, 1956, **287**, 199. [22] Gutmann and Tannenberger, *Monatsh.*, 1957, **88**, 292. [23] Gutmann and Mairinger, *ibid.*, 1958, **89**, 724. [24] Ferraro, *J. Inorg. Nucl. Chem.*, 1957, **4**, 283. [25] Gutbier, Kunze, and Guhring, *Z. anorg. Chem.*, 1923, **128**, 169. [26] Ekeley and Potratz, *J. Amer. Chem. Soc.*, 1936, **58**, 907.

paramagnetic ions the room-temperature magnetic moment was recorded as routine. Sample procedures for preparation of the complexes are given below. A few examples were prepared by reaction of alkali-metal salts of complex chlorides with tetraethylammonium chloride in aqueous solution (method C) or by methods recorded in the literature.

Method A.—Tetraethylammonium hexachlorotungstate(V). Freshly sublimed tungsten hexachloride (1·0 g.) was added to thionyl chloride (20 ml.) containing tetraethylammonium chloride tetrahydrate (1·1 g.) and, on warming, it dissolved with effervescence. The deep brown solution was concentrated to 10 ml. and on refrigeration the *product* crystallised as lustrous black needles which were washed with several small portions of cold thionyl chloride and dried *in vacuo* (yield 0·56 g.).

Method B.—Bis(tetraethylammonium) tetrachloromagnesate(II). Magnesium chloride hexahydrate (0·5 g.) and tetraethylammonium chloride tetrahydrate (1·0 g.) were boiled with thionyl chloride (20 ml.) until dissolution was complete. After filtration the thionyl chloride was removed at 15 mm. and acetic anhydride (10 ml.) was added to the residue. The *product* was precipitated as a microcrystalline solid, and was washed twice with small portions of acetic anhydride at the centrifuge. After drying *in vacuo* at 56°/0·1 mm. the complex was very hygroscopic (yield 0·95 g.).

Bis(tetraethylammonium) hexachlorogermanate(IV).—Tetraethylammonium chloride tetrahydrate (0·5 g.) was dissolved in thionyl chloride (10 ml.). A large excess (0·7 g.) of germanium tetrachloride was then added, followed by sufficient ether to precipitate the *complex*. Crystallisation was completed by refrigeration after which the very hygroscopic salt $[NEt_4]_2[GeCl_6]$ (0·2 g.) was collected at the centrifuge and dried *in vacuo*.

Tris(tetraethylammonium) nonachlorodivanadate(III).—Vanadium trichloride (1·0 g.) was ground to a fine powder beneath thionyl chloride (30 ml.). Tetraethylammonium chloride tetrahydrate (1·0 g.) was then added and the deep red mixture was left for 24 hr. with intermittent agitation. The solution was filtered and stripped at 15 mm. until the *product* commenced to crystallise. Ether–thionyl chloride (2 : 1) was then added to complete the crystallisation. The deep red complex was collected at the centrifuge, washed twice with ether–thionyl chloride, and dried *in vacuo* at 56°/0·1 mm.

Spectra.—The infrared spectra of all the halide complexes were recorded at $-10°$ for Nujol mulls supported on polythene plates ("Alkathene," grade 7; 1 mm. thick). The spectrometer used was the fully evacuated grating instrument described in ref. 16.

The band shape varied considerably amongst the complexes studied. In $[GaCl_4]^-$, ν(Ga–Cl) was very sharp ($\Delta\nu_{\frac{1}{2}}$ 12 cm.$^{-1}$), whereas other complexes had broad, asymmetric, or split absorption bands. These effects are probably due to solid-state interactions. For asymmetric bands the frequency of the absorption maximum is reported. For bands with an unresolved shoulder the prominent absorption maximum has been recorded.

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[16] Adams, *Spectrochim. Acta*, 1962, **18**, 1039.