PREPARATIVE AND SPECTROSCOPIC STUDIES OF SOME SULPHUR HALIDE SPECIES

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ABSTRACT

Raman spectra of trichlorosulphonium tetrachloroaluminate, $SCl_3^+ AlCl_4^-$, and hexachloroantimonate, $SCl_3^+ SbCl_6^-$, are in agreement with previously reported work. Two complexes of the novel tribromosulphonium cation, $SBr_3^+ AlX_4^-$ (X = Cl, Br), have been prepared and Raman spectra assigned on the basis of a pyramidal, C_{3v}, SBr_3^+ ion. Mixing solid trichloro- and tribromosulphonium tetrachloroaluminates produced a solid containing mixed chlorobromosulphonium cations, $SCl_nBr_{3-n}^+ AlCl_4^-$ $(0 \leqslant n < 3)$. Reactions involving sulphur dichloride, bromine and aluminium trichloride or antimony pentachloride yielded solids whose Raman spectra are assigned to mixtures of mixed chlorobromosulphonium tetrachloroaluminates or hexachloroantimonates. No pure compounds involving the ions SCl_2Br^+ or $SClBr_2^+$ were isolated.

The Raman spectrum of sulphur tetrachloride is substantially in agreement with recently published work and can be assigned reasonably on the basis of a structure involving SCl_3^+ and Cl^- ions. However, there are differences from the selenium and tellurium analogues.

Reaction of dimethyl sulphide with chlorine or bromine in the presence of a Lewis acid (aluminium trihalide, tin tetrahalide or antimony pentachloride) yielded a series of complexes of the dimethylhalosulphonium cation, $(CH_3)_2SX^+$ (X=Cl, Br). Analogous complexes of the methyldihalosulphonium cation,

$CH_3SX_2^+$ (X = Cl, Br), were prepared from dimethyl disulphide. Reactions of antimony pentachloride in the presence of bromine yielded complexes of the pentachlorobromoantimonate anion, $SbCl_5Br^-$, in contrast to similar reactions involving sulphur dichloride. Raman spectra are assigned for the methylhalosulphonium ions.

Reactions of dimethyl sulphide and bromine gave two isomeric complexes which, on the basis of the analytical and spectral evidence, were assigned as the charge-transfer species, $(CH_3)_2SBr_2$, or an ionic complex $(CH_3)_2SBr^+Br^-$.

Sulphur dichloride and bromine, sometimes in the presence of chlorine, yielded a series of solids stable only at low temperatures. Analysis of their Raman spectra suggested the presence of mixed chlorobromosulphonium cations associated with various halide or polyhalide anions.

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DEDICATION

To my Father

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LITERATURE

1.1 SULPHUR HALIDES

Sulphur occurs widely in nature both as the element and in the combined state. It is the twelfth most abundant element in the igneous rocks of the earth's crust and occurs as 4 natural isotopes. ^{32}S is the most abundant isotope, accounting for 95•0% of the atoms and ^{34}S for 4•2%, ^{33}S and ^{36}S are present in minor amounts and account for the remaining 0•8% Sulphur of mass number 35 is unstable and decays by β emission with a half life of 87•1 days.

Sulphur is a member of Group VI of the periodic table and has the outer electronic configuration $3s^2 3p^4$. Thus sulphur exhibits an oxidation state of -II in the sulphides of the electropositive metals. However the noble gas configuration can also be attained by the formation of divalent species such as $(CH_3)_2S$, SCl_2, R_3S^+, RS^-. Sulphur can also form species in formal oxidation states other than +II, generally +IV and +VI, eg. SCl_3^+, SF_4, SF_6, SO_3. In these compounds it is thought that sulphur may utilise its d orbitals to form hybrid orbitals especially with electronegative ligands. In general d orbitals are of too high an energy to contribute significantly to bonding. However, in sulphur particularly, these orbitals are reduced in size by promotion of 2 electrons to give sp^3d^2 hybrids. This together with effective removal of electron density (oxidation) from sulphur allows the d orbitals' to contribute to bonding and provides for an increased co-ordination number over the first element of the group[1,2].

However, bonding in many sulphur compounds is still contentious and a number of theories have been proposed. In particular a recent chapter by H.A. Bent [18] discusses a number of these theories with particular reference to molecular orbital models, a detailed discussion of which is outside the scope of this thesis.

Sulphur forms halides with fluorine, chlorine, bromine and iodine although this survey covers mainly the chloro and bromo compounds. In many cases the small and very electronegative fluorine atom produces sulphur fluorides that are often not typical of other sulphur halides, whereas relatively few sulphur iodine species are known.

Sulphur forms hexa-, tetra-, di- and monofluorides[3] together with a disulphur decafluoride[1] and these compounds are all volatile liquids or gases. Sulphur hexafluoride is a colourless gas which is almost totally inert and has been shown to have an octahedral structure.[3] It is probable that the small electronegative fluorine atom provides the ideal ligand to enable the sulphur d orbitals to participate in bonding forming sp^3d^2 hybrids providing considerable overlap with the fluorine orbitals. The strength of these bonds together with the co-ordination saturation of sulphur and the associated steric hindrance account for this halide's inertness which is kinetically derived as its hydrolysis is thermodynamically favourable.

It is of course also possible to describe the bonding of SF_6 in molecular orbital terms and this has been done by Bent,[18] and Rundle.[75]

Sulphur tetra fluoride by comparison is instantly hydrolysed by water. It exists as a distorted tetrahedron in which the sulphur lone pair occupies the equatorial position of a trigonal bipyramid sp^3d hydrid[3]. Sulphur difluoride has been found in the gaseous products derived from the electrical breakdown of the hexafluoride[1,3] and was identified spectroscopically.

However, recently[6] the difluoride has been isolated and observed in various matrices at 14K. The monofluoride, S_2F_2 has been found to exist as two isomers $S{=}SF_2$ and FSSF.[4,5] The latter structure is of C_2 symmetry and is similar to that of the analogous chloride and bromide detailed later although the S-S bond length is somewhat shorter. The reasons for this are in doubt but it would appear that the bonding cannot be described in simple covalent terms[4].

The other members of Group VI, selenium and tellurium, form only tetra- and hexafluorides and in the gaseous state their structures are similar to their sulphur analogues. However in the solid state tellurium tetrafluoride tends to form structures with fluorine bridges[7].

Sulphur forms three chlorides the mono-, S_2Cl_2, the di-, SCl_2, and the tetra-, SCl_4 apart from the dichlorosulphanes, S_nCl_2. Analogous bromides and iodides are also formed in respect of the mono- and dihalides but apart from sulphur monobromide these products are unstable and have been identified only at low temperatures. There are no known tetrabromides or tetraiodides.

Sulphur monochloride was studied in some detail during the late sixties and early seventies.[8,9,10,11,12] A molecule of structure Cl-S-S-Cl can exist in three configurations with different symmetries depending on the relative angle of the two S-Cl bonds when rotated about the S-S bond. If the molecule is planar then the chlorine atoms may either be cis, C_{2v} symmetry, or trans, C_{2h} symmetry. The former symmetry (C_{2v}) will give rise to 6 Raman bands (3 polarised) of which 5 will also be infra-red active. The trans molecule (C_{2h}) is centro-symmetric and will give rise to 3 Raman active bands and 3 different infra-red active bands. However, if the molecule is non-planar (C_2) then there will be 6 Raman bands and 6 coincident infra-red bands.

The published data all show 6 Raman bands, 4 polarised, together with 6 coincident infra-red bands. Sulphur monochloride therefore exists in a non-planar (C_2) configuration with a large barrier to rotation about the S-S bond. It is probable that interaction between the sulphur lone pairs is responsible for this rigidity and determines the S-Cl relative angle at about 83°.[10,11,12,19]

The analogous bromide, S_2Br_2,[32] has also been studied by a number of authors[9,10,11,12] and these more recent references all give similar spectra which is entirely consistent with a C_2 structure as for the monochloride.

Sulphur monoiodide, S_2I_2, has been prepared[33,34] and found to be stable only below -30°C. The infra-red spectrum has been recorded[35] and although the limited data is consistent with a C_2 structure further work is required.

Very little data exists on disulphur dihalides with mixed halogens. However Forneris [12] has observed 4 Raman bands in mixtures of S_2Cl_2 and S_2Br_2 that were not attributable to the starting materials. He has assigned the bands to S_2BrCl with C_s symmetry but did not observe the two sulphur-halogen stretching modes due to the presence of the monochloride and monobromide. The presence of mixed species has also been observed in mixtures of sulphur chlorides and bromine under electron impact in the ion source of a mass spectrometer [36].

Frankiss [10], Forneris[12] and Hendra[11], have also studied the monobromides and monochlorides of selenium. Although there are minor differences in frequencies quoted for some bands, due primarily to experimental difficulties, there is general overall agreement between the three authors. The spectra can be assigned on the basis of C_2 symmetry and are similar to their sulphur analogues with the expected reduction in frequences of the fundamentals as sulphur is replaced by the heavier selenium atom.

No analogous selenium monoiodide has been found in the literature.

Data on the tellurium monohalides is very limited. No chlorides or bromides have been observed but Russian workers have noted the monoiodide in vapour above tellurium-iodine mixtures.[37]

Sulphur dichloride readily dissociates within a few hours to give an equlibrium mixture $2SCl_2 \rightleftharpoons S_2Cl_2+Cl_2$ containing about 85% of the dichloride.[1,13] However fractionation of the equilibrium mixture in the presence of phosphorous penta-or trichloride yields pure dichloride which is stable for weeks at room temperature.[13]

Surprisingly little spectroscopic data has been published on sulphur dichloride, especially Raman data and most is fairly early.[14,15,16] However two recent reports detail the spectra of the dichloride [8,17] and one [17] also provides an excellent assignment of the low temperature Raman spectrum.

Sulphur dichloride would be expected to exist as a bent molecule of C_{2v} symmetry and as such should give rise to three Raman bands (2 polarised) and three infra-red bands. The early Raman data [14] suggested the ν_3 antisymetric stretching mode occurred at 535 cm^{-1}. However it is probable that this band was due to sulphur monochloride formed by decomposition of the dichloride and ν_3 band was observed at about 525 cm^{-1} by Savoie [17] and Frankiss.[8]

The analogous dibromide and diiodide have been recently observed [38] in a solid argon matrix at 14K after passing sulphur monochloride and bromine or iodine through a microwave discharge. Infra-red spectra were recorded but only to 200cm^{-1} and therefore no bending vibrations were observed. The dibromide radical ion has also been observed in mixtures of sulphur chlorides and bromine in the ion source of a mass spectrometer.[36]

Selenium dibromide has been suggested as a product of the decomposition of other bromides in solution [39] or vapour [40,41] but no diiodide apparently exists. The dihalides of tellurium have been observed in the vapour phase [42, 43] and in mass spectra.[44] However, no spectral data are available for these compounds.

Sulphur forms a tetrachloride but there is no evidence for either the tetrabromide or tetraiodide. The tetrachloride, which is formed by chlorination of sulphur dichloride, has been known for some time [20] but is only stable below about -30°C. This has caused experimental problems in the recording of its spectra [21,22] and it is only comparatively recently that good spectra have been obtained.[23, 24]

It might be expected that the structure of SCl_4 would be similar to that of SF_4 [25] ie. a trigonal bipyramid with an equatorial lone pair, giving rise to C_{2v} symmetry. In this case one would expect 9 Raman Bands (4 polarised) and 8 infra-red bands. However, the spectra show only 4 bands and therefore this structure is unlikely. Lachman[26] proposed a regular tetrahedral (T_d symmetry) for SCl_4 but this is considered most unlikely in view of the 6 valence electrons of sulphur. Ionic forms therefore appear the most likely structure for this tetrahalide and two possibilities are $SCl_3^+Cl^-$ or $[SCl_3]^+[SCl_5]^-$. The latter can be discounted in view of the limited number of spectral bands observed.[23] An $SCl_3^+Cl^-$ type of structure would be expected to contain pyramidal SCl_3^+ ions of C_{3v}

symmetry and give rise to 4 Raman bands (2 polarised) and 4 infra-red bands. Vibrational spectra suggest a formulation involving essentially this type of structure.

It is however interesting to note [27] that the reaction of chlorine monofluoride with sulphur tetrachloride yields the covalent sulphur tetrafluoride. This together with the band positions in $SCl_3^+Cl^-$ as against those for trichlorosulphonium salts (Section 1.2) of Lewis acids suggest that the ionic chlorines may not be totally removed from their cations. In fact Feuerhahn[23] suggests that SCl_4 contains some bridging chlorine on the basis of his spectral evidence.

The structures of solid selenium and tellurium tetrahalides have been the subject of some discussion but later authors tend to agree that MCl_3^+ units are present in the chlorides, bromides and tellurium tetraiodide.[28,29]

An x-ray crystal structure has been determined for $TeCl_4$ [30] in which Te_4Cl_{16} units are present. $TeCl_3$ units occupy alternate corners of a cube with bridging chlorine atoms occupying the remaining positions. Therefore each Te atom is surrounded by 3 bonded chlorine atoms and 3 bridging chlorine atoms with significantly longer bond lengths. It is suggested that essentially similar structures exist for the bromide and the selenium analogues.[29,28,31]

1.2 TRIHALOSULPHONIUM CATIONS

Sulphur in a formal oxidation state of +IV forms cationic species SX_3^+ with halogens (X=F, Cl, Br) with a pyramidal structure of C_{3v} symmetry. Bonding in these compounds has been described using a number of approaches including hybridisation[1] and various molecular orbital theories,[31,18] with the former probably the most useful in respect of molecular shape. Sulphur in trihalosulphonium species can be considered to form sp^3 hybrid orbitals so producing three bonds with the halogen and leaving one orbital to be filled by the sulphur lone pair of electrons. However more recently it has been suggested [45] that the bonds are formed by overlap of the p orbitals of sulphur with those of the halogen, leaving the lone pair to occupy the symmetrical 3s orbital. Little x-ray evidence relating to the sulphur halogen bond angles is detailed in the literature but Edwards[87] gives the Cl-S-Cl angle in $SCl_3^+ICl_4^-$ as 101° and Gibler[46] the F-S-F angle in $SF_3^+BF_4^-$ as 97°. Both these angles are significantly less than the 109° predicted by tetrahedral sp^3 hybrid orbitals and is usually explained by assuming interactions with the lone pair of electrons. The use of p orbitals to form bonds would suggest 90° sulphur halogen angles, increased by ligand repulsion. This stereochemically inert lone pair theory has a precedent in the hexahalo anions of selenium and tellurium (section1.4) but there is evidence of the steric activity of the lone pair in trifluorosulphonium ions[46] (see later).

There are many examples of trichlorosulphonium containing complexes and in general these have been prepared from sulphur chloride, chlorine and a Lewis acid. Vibrational spectra have been recorded for a number of complexes with the following anions.

$AlCl_4^-$,[47] $SbCl_6^-$ [21,48] ICl_4^-,[51] $SnCl_6^{2-}$ and AsF_6^-,[48] SO_3Cl^-,[22] $NbCl_6^-$ and $TaCl_6^-$.[49] Recently $SCl_3^+AlCl_4^-$ has been prepared from highly purified materials and the infra-red, Raman and X-ray powder spectra recorded.[50] In most of these references there is general agreement on the assignment of the SCl_3^+ frequencies and it is found that there are only relatively minor shifts in band frequency as the anion is changed. These data are tabulated later (Chapter 2) and are consistent with a pyramidal shape of C_{3v} symmetry for the SCl_3^+ ion. Such a molecule would be expected to give rise to 4 Raman bands (2 polarised) and 4 infra-red bands. However, two of the Raman bands are doubly degenerate (E) modes and in the solid state might be expected to show some splitting. Most of the above workers recorded 6 Raman bands and 4 infra-red bands providing excellent support for the pyramidal ionic structure of these compounds.

A recent U.S. Patent discloses a method of preparation of SCl_3^+ complexes using very short reaction times in the presence of hydrogen fluoride. In general fluorine containing Lewis acids such as BF_3, PF_5 and TaF_5 were used but very few spectroscopic data are quoted.

Trihalosulphonium ions with halogens other than chlorine are relatively rare but SF_3^+ and SBr_3^+ are known. The crystal structure of SF_3^+ has been determined [46] in complexes containing the BF_4^- and AsF_6^- anions after some years of debate regarding the spectroscopic and conductometric evidence. The SF_3^+ ion was found to be pyramidal with C_{3v} symmetry. It was also found that the fluorine ligands of the BF_4^- ion made their closest approach to the effectively positively charged sulphur atom well off the C_3 axis. This would be expected if the sulphur lone pair occupied a spatially directed orbital, such as an sp^3 hybrid, rather than assuming its presence in an s orbital.

Until recently no tribromosulphonium ion was known, but Passmore[54] has reported the preparation and Raman spectra of $SBr_3^+AsF_6^-$ and $SBr_3^+SbF_6^-$. The spectra were assigned on the basis of a pyramidal ion of C_{3v} symmetry. No analogous SI_3^+ salts are known and attempts to prepare them led to the formation of S_7I^+ complexes.[55,56]

The literature contains no references to the existence of trihalosulphonium ions with mixed halogens. However Hulme in a U.S. Patent[53] mentions that long reaction times and higher temperatures lead to the gradual replacement of the chlorine in SCl_3^+ by fluorine to give mixed products SCl_2F^+ and $SClF_2^+$. However, very little evidence as to their existence is given and no spectroscopic data are quoted.

Trihalo complexes are formed by both selenium and tellurium to give trichloro[21,22,43,49,57] and tribromo [58,59] species. In general their structures are thought to be essentially similar to their sulphur analogues, however, the frequencies of some stretching modes vary with the anion.[48,49] It has been suggested that considerable interaction between the ions occurs[49,57] and in some complexes even to the extent that free $SeCl_3^+$ and $TeCl_3^+$ can be excluded[49] from those complexes. None of the explanations of the bonding in these complexes are wholly consistent with all the experimental data and Poulsen[49] concludes that their structure is not understood. The SeI_3^+ ion has been described[52] but it is unstable to light and no Raman data were given.

1.3 METHYLHALOSULPHONIUM CATIONS

The previous section described trihalosulphonium salts, SX_3^+, in complexes with various Lewis acid derived anions. If dialkyl sulphides or dialkyl disulphides are used in place of the sulphur chloride in the reaction with the halogen and the Lewis acid then two series of salts result, R_2SX^+ or RSX_2^+, depending on whether the mono- or disulphide is used.

$$RR'S + X_2 + MX_n \longrightarrow RR'SX^+MX_{n+1}^-$$

$$RSSR + 3X_2 + 2MX_n \longrightarrow 2RSX_2^+MX_{n+1}^-$$

where MX_n is a Lewis acid

X is a halogen

These reactions are part of a general series forming sulphonium salts, the preparations and reactions

$$RR'S + R''X \longrightarrow RR'R''S^+X^-$$

of which have been reviewed.[45,60,67] In the present work we are primarily concerned with the methylsulphonium species.

There are a number of references to the preparation of dimethylhalosulphonium species, $(CH_3)_2SX^+$, with various Lewis acids in series of papers primarily by Meerwein[61] and Böhme[62] (and references therein). However, no spectroscopic data are given in these papers but Warthmann details the infra-red spectra[63] of $(CH_3)_2SCl^+SbCl_6^-$

and of its dimethylaminosulphonium analogue.[64] It has been found that the halogen in these compounds is easily replaced by any reagent with an active hydrogen such as an alcohol,[66] phenol,[65] malononitrile,[65] fluorene[65] or even water.[66]

Methyldihalosulphonium species can be formed from dimethyl disulphide and the Raman and infra-red spectra of the hexachloroantimonate complex have been reported,[68,63] as well as the infra-red spectrum of the dimethylamino anologue.[64] However, there do appear to be some differences between our interpretation of the Raman spectrum of $CH_3SCl_2{}^+SbCl_6{}^-$ and that of Shamir[68] and these will be discussed later. The replacement of the halogen in these compounds using various hydroxylic compounds is again discussed by Warthmann.[66]

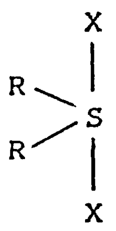
Species of the type SA_2B^+ could be considered to be formed by sulphur using sp^3 hybrid orbitals. The ion would then be pyramidal with a lone pair of electrons in one of the non-bonded orbitals. The low frequency vibrational spectra of these methylhalosulphonium species can be most easily assigned if the methyl groups are considered as point masses and not as groups of four atoms. This assumption is valid since the hydrogens are very light and relatively little coupling occurs between the C-H and S-C stretching motions.[68]

The SA_2B^+ ion can then be considered to be of C_s symmetry and give rise to 6 Raman bands (4 polarised) and 6 infra-red bands. This of course ignores the C-H vibrations which occur at very much higher frequencies and the spectroscopic data of these methylhalosulphonium complexes have been assigned on the above basis where such data were available.

The reaction of dimethyl sulphide with a methyl iodide or bromide yields a solid formulated as trimethylsulphonium halide $(CH_3)_3S^+X^-$. The cation is pyramidal of C_{3v} symmetry and its Raman and infra-red spectra has been assigned on that basis.[69,70]

The above references, with the exception of those relating to the trimethylsulphonium ion, all deal with methylsulphonium complexes in which the anion is a Lewis acid derived species. When attempts are made to produce dimethylsulphonium species with a halide cation the structure of the resulting complex may not be so clearly ionic. The reaction of a sulphide, selenide or telluride with a halogen can result in the formation of three possible products.[71]

$$R_2S + X_2 \longrightarrow R_2SX_2 \quad (S = S, Se, Te)$$



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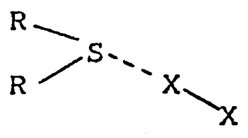
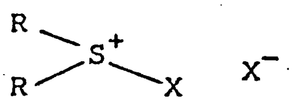


II



III

The charge transfer (II) and ionic (III) structures can be considered to be extreme forms of each other, i.e. a charge-transfer complex with a very strong donor-acceptor interaction becomes very close to an ionic structure. This effect is thought to be responsible for the anomalous increase in conductivity of the thiophene-bromine complex as bromine is added[71] or the high dipole moment of the triethylamine-iodine complex.[72] The proposed formation of the X_3^- species in these cases has been supported by the presence of Raman bands indicative of that species.

Halogens form, with dimethyl compounds of Group VI, basically two types of compound, either an essentially trigonal bipyramid (I) compound or a charge-transfer complex[71,73 74] (II). Baenziger[74] quotes a "rule" which indicates the nature of the Group VI element - halogen interaction and predicts the type of complex formed. The rule states that if the Group VI element has an electronegativity less than that of the complexing halogen, then the resulting configuration of the complex is trigonal bipyramid. This empirical rule is explained by a comparison of the bonding in trihalide anions with that of the X-S-X group. The centre atom of a trihalide is generally the largest, and of lowest electronegativity leading to a greater bonding electron density on the terminal atoms.[75] Therefore complexes with electronegative halogens tend to be essentially trigonal bipyramidal to maintain the Group VI atom at the centre of the three atoms, i.e. chloro complexes tend to be trigonal bipyramidal giving Cl - M - Cl (M=S,Se,Te). Similarly iodine complexes tend to be of the charge-transfer type to maintain the large iodine atom of relatively low electronegativity at the centre of the 3 atom group i.e. M - I - I (M=S,Se,Te).

There is also an element of intermolecular interaction between halogens which is less probable with large Group VI atoms (and bulkier alkyl groups). This, it is said,[74] would tend to favour the formation of a trigonal bipyramidal structure.

Baenziger[74] details x-ray crystallographic data showing a sulphur- chlorine complex to be trigonal bipyramidal whereas two sulphur - iodine complexes have been shown to be of the charge transfer type.[76,77] These complexes support the above rule by displaying structures where the central atom is the largest and of lowest electronegativity. A sulphur - bromine complex should, on the basis of the Baenziger rule, be trigonal bipyramidal although the electronegativity of sulphur is not greatly lower than that of bromine. Lambert[71] however, whilst supporting the electronegativity rule suggests that size plays an important role and that for elements of different rows in the Periodic Table a better prediction is obtained by assuming the larger atom is at the centre of the 3 atom unit. A sulphur - bromine complex should then be a molecular (charge - transfer) complex. Hendra[73] and Allegra[78] found that sulphur - bromine complexes were of the charge - transfer type.

Allegra[78] also suggests that in the thiophan - bromine complex there is such strong charge - transfer interaction that the largest contributor to the structure representation is an ionic form (III).

It is interesting to note that some references,[60,79,80] although generally those only using the dimethyl sulphide - bromine adduct as an intermediate, tend to write the structure in the ionic form. However, the preparative method used would be expected to favour the formation of a charge - transfer complex owing to the use of relatively low dielectric constant solvents (see Chapter 3).

Generally it would appear that dimethyl sulphide complexes with Lewis acids produce ionic compounds as does sulphur dichloride. However, with halogens sulphur dichloride gives rise to ionic complexes, $SX_3^+X^-$, whereas dimethyl sulphide yields non-ionic molecular complexes ($(CH_3)_2S-X-X$ or $(CH_3)_2SX_2$ depending on the halogen). The reason for this difference is not clear but could be due to the inductive effect of the halogen bonded to sulphur tending to reduce the electron density on the sulphur and therefore its ability to form two additional covalent bonds. The formation of molecular complexes is in fact exactly analogous to that existing in the oxidative addition reactions undergone by certain complexes having non-bonding electrons and vacant co-ordination sites. (See also Chapter 3).

The structure of halogen adducts of monomethyl - sulphonium cations would be of interest. However, these do not appear to have been studied in detail although references exist to the preparation and reactions of methylsulphur trichloride.[60,81,82,83] This compound is unstable above about 0°C., decomposing primarily by loss of hydrogen chloride with simultaneous chlorination of the α - carbon atom.[81] The reactions and properties of this compound all suggest an ionic structure although no spectroscopic data can be found.

1.4 HALOSULPHONIUM ANIONS

The formation of MX_3^+ ions can be considered as arising from Lewis base activity of MX_4. However, MX_4 can also be considered as a Lewis acid when MX_5^- or MX_6^{2-} anions would be formed. Considerable work has been done on the anions MX_6^{2-} when M=Se or Te and X = halogen. A valence bond consideration of bonding in MX_6^{2-} would suggest sp^3d^3 hybrid orbitals with a distored octahedral configuration caused by one hybrid orbital being occupied by a lone pair of electrons. It has however, been found by both vibrational spectroscopy[105-111] and x-ray crystallography [112,113] that generally the MX_6^{2-} ions are rigorously regular octrahedral in configuration although with some anomalies for TeX_6^{2-} spectra due to perturbation of their vibrations by low energy unsymmetrical electronically excited states.[111,114] Therefore a situation exists in which MX_6^{2-} ions have 6 valence pairs of electrons plus 1 lone pair but in an octrahedral configuration. This implies that the lone pair cannot exist in a stereochemically directed orbital.

It is possible[1,115] to propose a limited molecular orbital approach to bonding in these ions where linear orbitals are formed from the p orbitals of the central atom and two of the halogens. This leads to 3 mutually perpendicular molecular orbitals to accomodate the 6 bonding electrons in an octrahedral configuration with the lone pair existing in the symmetric s orbital of the central atom.

This theory however, ignores the d orbitals of the central atom whose energy has been shown[1,116] to be a function of the oxidation state and electronic configuration of the central atom (cf SF_6, Chapter 1.) as well as the halogen. It is therefore probable that these d orbitals are of sufficiently low energy to participate in bonding in these MX_6^{2-} complexes. The effects of a number of factors including electronegativity difference, lone electron pair presence in the s orbital and ligand orbital interaction on the d orbitals of a number of elements, including those of Group VI, have been discussed by Urch.[117] He considers these effects in relation to the molecular orbitals of the halide complexes and explains the existence or otherwise of those compounds largely on the basis of the presence of the lone pair in an antibonding molecular orbital.

In general selenium and tellurium form anionic complexes, MX_6^{2-}, with all the halogens and in some cases mixed species $MX_4Y_2^{2-}$ or $MX_2Y_2Z_2^{2-}$ can be formed, probably in the cis configuration.[118]

Urch argues that although the s orbital in selenium and tellurium interacts relatively little with the halogens, the presence of an electron pair screens the p orbitals from the nuclear charge, so increasing their polarisation by the halogen and exposing the d orbitals to a net increase in nuclear charge. This results in a decrease in their radius and increases their participation in forming bonding molecular orbitals.

With sulphur however, the s orbital interaction is stronger and significant s character exists in the bonding molecular orbital. There is therefore less screening of nuclear charge from the p orbitals, therefore less polarisation by the ligands, and so the d orbitals are not so exposed to nuclear charge and they do not participate in forming bonding orbitals, consistent with the non-existence of SX_6^{2-} ions. The very electronegative fluorine however, is capable of producing d orbital contraction in sulphur (Chapter 1.) and non-ionic SF_6 can be formed although it is not thermodynamically stable.

In contrast to this work two papers by Donaldson[140,141] describe the structure of these and related ions by considering the s electron pair as existing in a delocalised low energy solid-state band. The presence of electrons in this band explains the colour of the complexes and also their conductivity. The population of this low energy conductance band can be decreased by reducing the temperature of the complex and it is found that the colour disappears. However, Adams[142] suggests that little delocalisation of the inert pair occurs at ambient pressure, but the energy of this conductance band is lowered by increase of pressure giving greater delocalisation. There is obviously still scope for further work on the bonding in these complexes.

In the case of the MX_5^- complexes selenium and tellurium again form compounds with all the halogens. The structure of these complexes can be relatively easily explained on the basis of sp^3d^2 hybridisation giving rise to an octahedral distribution of electron pairs in which one orbital is occupied by a lone pair of electrons. The ions MX_5^- are therefore square pyramidal of C_{4v} symmetry and this has been confirmed by vibrational spectroscopy[109,118-120,127] and by x-ray crystallography.[121-123] Mixed tellurium species also exist,[118] TeX_4Y^- and $TeX_3Y_2^-$ and for the former the single halogen is in the equatorial position leading to C_s symmetry. For $TeX_3Y_2^-$ the ion is of C_{2v} symmetry with the pair of halogen atoms equatorial and trans. In contrast to the situation with the hexahalo anions sulphur does form a pentahalo anion SF_5^-. As for its analogues this ion is square pyramidal with a localised lone pair in what may be considered as sp^3d^2 hybrid orbitals and this configuration has been confirmed by vibrational spectroscopy.[119,124,125] However, no SX_5^- ions with other halogens are known.

Barefield[126] has isolated the ion SF_6^- in an argon matrix at 10K by photolysis of SF_6 in the presence of sodium or potassium. The ion was identified by infra-red spectroscopy and it was thought to be octahedral with the single electron in the next highest available molecular orbital. No further details were given.

1.5 HALIDE ANIONS

The present work has been mainly concerned with the structure of sulphur containing cations although it has obviously been necessary to identify the associated anions. Most of the anions used are well known and their spectra will be discussed where appropriate. However, the presence of some polyhalide anions will be suggested and the structure of these ions will be discussed in this section.

Halogens readily form the simple anions, X^-, and diatomic molecules, X_2 (X=F,Cl,Br,I) as would be expected for elements of Group VII. Some cationic species can be formed but these ions are only stable in the presence of anions of low basicity or acidic solvents.[2] Spectroscopic data for both the X_2^+ and X_3^+ cations (X=Cl,Br,I) have been given by Gillespie[84,85,86] but detailed discussion is not appropriate here as these species are unlikely to be formed in this work.

The anionic species are formed by reaction of a halide with an interhalogen compound. The anions usually contain three halogen atoms in a linear, but not necessarily symmetric, arrangement although species containing up to seven atoms, often including fluorine, are known.[2]

Considering the trihalide anions, most exist as linear symmetrical molecules with the lower electronegativity, heavier atom at the centre.[75] The bonding in these molecules has been the subject of considerable discussion and initially it was considered that bond hybridisation theory would explain their structures. The centre atom would form sp^3d hybrid orbitals and the three lone pairs would occupy the three equatorial positions of the trigonal bipyramidal orbital configuration giving rise to a linear molecule.[2] However, the energy of these d orbitals is probably too high for effective participation in bonding. The use of sp^3d orbitals would also suggest that most of the charge should exist at the central atom whereas NQR data show much of the charge resides on the end atoms.[89,90]

In the 1950's Pimentel[91] and Rundle[75,99] suggested that the bonding in trihalide ions could be explained by forming three molecular orbitals from the p orbitals of the halogens without the contribution of any higher orbitals. Four electrons may then be considered to take part in bonding by occupying molecular orbitals formed from linear combination of one p orbital from each halogen. This molecular orbital theory has become accepted as providing the best explanation of bonding in these ions and the calculations have since been considerably refined by a number of workers[92,93,95,96] including ab initio calculations[94] which support the charge distribution found experimentally by NQR.

In general the anions in compounds containing a large cation e.g. tetraalkylammonium, tend to be symmetric whereas in those compounds with a small cation e.g. alkali metals, they tend to be asymmetric.[89] However exceptions are known and in one case both symmetric and asymmetric ions co-exist in the same crystal.[97] The asymmetry in these ions is thought to be due to different crystal environments of the terminal atoms and not due to differences in bonding in the anion.[2,90,99]

The spectra of the symmetric and asymmetric ions are different, the former being of $D_{\infty h}$ symmetry and giving rise to one Raman band (Σ_g^+ symmetric stretch) and two infra-red bands (Σ_u^+ anti-symmetric stretch, Π_u doubly degenerate bending) In the asymmetric ion, $C_{\infty v}$ symmetry, all three modes show both Raman and infra-red activity.

It should however, be noted that the selection rules determining Raman and infra-red activity can break down in solids leading to more complex spectra than might be expected from the free ion. If the symmetry of the ion site in the crystal is lower than the point group symmetry of the ion and the electric field created by the other ions is sufficient to perturb the ion in question, then degenerate vibration modes can split. The effect of this lowering of symmetry on the vibrations of the ion can be determined, assuming the crystal structure is known, by the use of correlation tables so enabling band assignments to be made (site group analysis). If, in the crystal unit cell, there is significant interaction between the vibrations of different molecular groups then these bands can also split (factor group splitting). In the spectra of the halide anions these effects are prominent and complicate the spectra as also do band splittings caused by the halogen isotopes. The effects of the three sets of splittings on the spectra of trihalide anions have been described in detail by Gabes[96,98] and will not be repeated.

Table 1.1 summarises the vibrational spectra data for various trihalide anions formed from bromine and chlorine, together with data for the ions Cl_5^- and Br_5^-. The bands are given as ranges rather than specific values due to the various splittings present to varying degrees in the various compounds studied. However, the ranges are sensibly short enough to be of value in assigning spectra.

TABLE 1.1

Halide Anion Frequencies (cm^{-1})

Ion		Symmetry		Reference
		Sym($D_{\infty h}$)	Asym ($C_{\infty v}$)	
Br_3^-	ν_1	162-173	198-221 (287)*	96,98,100
	ν_2	51	79-82	101,102
	ν_3	187-193	140-143 (186)*	
Cl_3^-	ν_1	268		104
	ν_2	(165)		
	ν_3	242		
Br_2Cl^-	ν_1	230		103
	ν_2			
	ν_3	192		
$BrCl_2^-$	ν_1	266-285	293-310	96,98,100
	ν_2	144	144-158	101
	ν_3	212-238	204-235	
Br_5^-	ν_1	250		102
Cl_5^-	ν_1	482		104

* Very asymmetric ion

CHAPTER 2

TRIHALOSULPHONIUM CATIONS

2.1 INTRODUCTION

A survey of the literature on trihalosulphonium cations is given in Chapter 1, Section 1.2 but this work is primarily concerned with the trichloro and tribromo species, SX_3^+, together with the mixed species $SBrCl_2^+$ and SBr_2Cl^+. In each case the associated anion has been derived from the Lewis acids aluminium trihalide or antimony pentachloride.

It is also possible to prepare a compound formulated as sulphur tetrachloride although it is only stable at low temperatures unlike its selenium and tellurium analogues. It is generally thought that SCl_4 exists as the complex $SCl_3^+Cl^-$ [23,24] although there is no doubt that there is significant cation-anion interaction. This interaction has been largely defined for the tellurium (and selenium) tetrahalides by x-ray crystallography[30] and similar structures might, by analogy, be expected for sulphur tetrachloride.

The species SX_3^+ would be expected to exist as a pyramidal ion of C_{3v} symmetry and would possess 4 normal modes of vibration. Two of these vibrations would belong to the singly degenerate A_1 species and two to the doubly degenerate E species. All would be expected to be both infra-red and Raman active and the two A_1 modes would be polarised.

The ion SX_2Y^+ would, by analogy, be pyramidal but of C_s symmetry. The 6 normal modes of vibration would be expected to consist of 4A' and 2A'' species, all of which would be both infra-red and Raman active. The 4 symmetric A' species would again give rise to polarised bands.

The anions generally used in this section of the present work were derived from Lewis acids and the configuration and spectra of these ions are well known. They will be briefly discussed and their spectra tabulated as it is obviously essential to distinguish their bands from those of the cations.

The $SbCl_6^-$ ion is octahedral in configuration with symmetry O_h.[128] It will therefore give rise to two triply degenerate F_{1u} modes active in the infra-red together with A_1,E_g and F_{2g} modes active in the Raman. As the molecule has a centre of symmetry there will be no coincidences, the F_{2u} mode is both Raman and infra-red inactive. The following table (Table 2.1) details the $SbCl_6^-$ Raman frequencies in a number of complexes.

Relatively few complexes containing mixed haloantimonates are known but two papers[136,137] have reported vibrational spectra on such anions. $SbCl_5Br^-$ would be expected to be octahedral of symmetry C_{4v} giving rise to 11 Raman active bands ($4A_1$+4E+$2B_1$+B_2) and 8 infra-red bands. Table 2.2 details the bands and their assignments for $PCl_4^+SbCl_5Br^-$ and $Et_4N^+SbCl_5Br^-$. There appears to be general agreement between the two references regarding the higher frequency modes although

TABLE 2.1

$SbCl_6^-$ RAMAN BANDS (cm^{-1})

Cation	ν_1 (A_1)	ν_2 (Eg)	ν_5 (F_{2g})	Reference
-	337	277	172	128
$AsCl_4^+$	333	291	174	129
Et_4N^+	335	292	176	-
$py\overset{+}{H}$	329	280	170	134
PCl_4^+	331(s)	273(m)	(171)	57
SCl_3^+	332(s)	(282)	176(m)	48
SCl_3^+	328	-	175	21

TABLE 2.2

$SbCl_5Br^-$ RAMAN BANDS (cm^{-1})

PCl_4^+ 136	Et_4N^+ 136	Et_4N^+ 137	Assignment
363(w,sh)		340(sh)	$\nu_8(E)$
332(vs)	332(s)	331(s)	$\nu_1(A_1)$
310(m)	308(m)	304(vs)	$\nu_2(A_1)$
290(m)	289(m)	284(m)	$\nu_5(B_1)$
222(s,br)	223(s,br)	215(vs)	$\nu_3(A_1)$
175(s)	173(m,br)	178(m,w)	def.
156(w)	158(w)	156(m)	$\nu_4(A_1)$
		108(mw)	def.
		85(w)	def.
		80(mw)	def.
		73(w)	def.

there are differences in relative band strengths. Adams[137] observed the low frequency bending and skeletal modes but did not have sufficient evidence to assign them all. Adams[137] also quotes the spectra of the $SbClBr_5^-$, $SbCl_3Br_3^-$ and $SbBr_6^-$ ions but these are not detailed here as they would not be expected to occur in this work and bands characteristic of them were not observed.

The anion derived from aluminium chloride, $AlCl_4^-$, is tetrahedral,[130] symmetry T_d. The ion therefore possesses a totally symmetric A_1 mode, a doubly degenerate E mode and two triply degenerate F_2 modes. All modes will be Raman active but only the two F_2 modes will be infrared active. It is assumed that $AlBr_4^-$ will be similar in configuration. The following table (Table 2.3) details spectral data for $AlBr_4^-$ and $AlCl_4^-$ and it is interesting to note the disagreement in the frequency assignment of the ν_2 band in both complexes. It should be noted that only the ν_1 and ν_3 modes are anything other than weak even in alkylammonium complexes and it is possible that in complexes containing cations that scatter strongly only the ν_1 modes may be observable.

Mixed tetrahaloaluminate anions can in principle be produced pure but in solution equlibration occurs giving mixtures containing all possible ions.[131] However, the bands due to $AlBr_3Cl^-$, $AlBr_2Cl_2^-$ and $AlBrCl_3^-$ have been assigned by Bradley[131] and are summarised in Table 2.4. The ion AlX_3Y^- would still be expected to be tetrahedral although now of C_{3v} symmetry giving rise to

TABLE 2.3

$AlCl_4^-$ AND $AlBr_4^-$ RAMAN BANDS (cm^{-1})

Cation	ν_1 (A_1)	ν_2 (E)	ν_3 (F_2)	ν_4 (F_2)	Reference
$AlCl_4^-$					
$(CH_3)_4N^+$	352(m)	125(m)	488(w)	183(w)	131
–	352	147	490	176	133
SCl_3^+	352(m)	138(m)	480(w)	185(w)	47
$AlBr_4^-$					
$(CH_3)_4N^+$	214(vs)	76(w)	400(m)	119(m)	131
$(CH_3)_4N^+$ $(C_2H_5)_4N^+$	(212(vs)	98(w)	393(m)	114(w)	132

TABLE 2.4

MIXED TETRAHALOALUMINATE RAMAN BANDS (cm^{-1})

(Reference 131)

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
	(A_1)	(A_1)	(A_1)	(E)	(E)	(E)
$AlBrCl_3^-$	440(m)	308(m)	(153)	495	(166)	(115)
$AlBr_3Cl^-$	(478)	247(m)	(132)	400	(134)	(90)

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
	(A_1)	(A_1)	(A_1)	(A_1)	(A_2)	B_1
$AlBr_2Cl_2^-$	465(m)	278(m)	(222)	(126)	(107)	495

ν_7	ν_8	ν_9
(B_1)	(B_2)	(B_2)
(153)	(412)	(142)

Values in parentheses were not directly observed but were calculated.

$3A_1$ modes and 3E modes all Raman and infra-red active. The ion $AlBr_2Cl_2^-$ possesses symmetry C_{2v} and gives rise to $4A_1$ modes, $1A_2$ mode, $2B_1$ modes and $2B_2$ modes, all Raman active and with only the A_2 mode being infra-red inactive. As for the AlX_4^- ions most of the bands are weak in intensity and would be difficult to observe. The ν_2 modes are generally the strongest although it may be possible to observe the ν_1 mode.

It was also thought desirable to record the spectra of starting materials that might contaminate the products. Table 2.5 details the spectrum of antimony pentachloride and it shows good agreement with the literature data.

Table 2.6 details the observed spectra for aluminium bromide and chloride and again good agreement is observed with literature spectra for the dimers.

The spectra of the sulphur halides are detailed elsewhere (Chapter 4).

TABLE 2.5

$SbCl_5$ RAMAN BANDS (cm^{-1})

This work	Ref. 138	Assignment
400(w)	397	$\nu_5(E')$
353(vs)	357	$\nu_1(A_1')$
308(w)	307	$\nu_2(A_1')$
180(m,br)	177	$\nu_6(E')$
170(wsh)	165	$\nu_8(E'')$

TABLE 2.6

$AlCl_3$ AND $AlBr_3$ RAMAN BANDS (cm^{-1})

Al_2Cl_6		Al_2Br_6		Assignment
This work	Ref. 144	This work	Ref. 139	
		225(vw)	226(w)	$\nu_3+\nu_4$?
309(s)	335(sh) 311(s)	211(s)	210(s)	ν_2(Ag)
200(w)	206(w)	143(m)	140(m)	ν_3(Ag)
171(m)	147(w)	115(m)	114(w)	$\nu_{12}(B_{2g})$
		86(w,sh)	85(m)	$\nu_7(B_{1g})$
		80(m)	79	lattice ?
–	95(s)	70(m)	70(m)	ν_4(Ag)

2.2 TRICHLORO AND TRIBROMOSULPHONIUM CATIONS

Doorenbos[47] prepared $SCl_3{}^+AlCl_4{}^-$ by the addition of chlorine to sulphur dichloride to produce the tetrachloride slurried in liquid chlorine. To this was added aluminium chloride and the isolated salt recrystallised from thionyl chloride. This method was used to produce a reference compound of known spectrum but it was later found that a satisfactory compound could be prepared rather more easily using dichloromethane as solvent and not recrystallising the product. This reduced handling and hydrolysis of both the solvent (thionyl chloride) and the complex. However, there is a tendency for short reaction times to leave unreacted aluminium chloride in the product but this is easily detected by its 310cm^{-1} emission.

Only a very limited amount of experimental detail relating to the preparation of $SCl_3{}^+SbCl_6{}^-$ is available.[21,48] Identical spectra were obtained from the reaction of sulphur dichloride with antimony pentachloride at low temperature using dichlormethane, chloroform or liquid chlorine as solvents. Elimination of a solvent and reaction at 10-15°C gave obviously impure products.

The spectra, together with assignments, are detailed in Table 2.7, Figures 2.1 and 2.2 and generally agree well with literature data.[47,48] The four Raman bands expected for an ion of C_{3v} symmetry are observed and both the degenerate E modes are split, presumably as a result of site symmetry effects.

TABLE 2.7

TRICHLOROSULPHONIUM RAMAN SPECTRA (cm^{-1})

$SCl_3^+AlCl_4^-$ (Figure 2.1)	$SCl_3^+SbCl_6^-$ (Figure 2.2)	Assignment
532(m)	536(m))	ν_3(E) SCl_3^+ (S-Cl asym.)
520(m)	523(m))	
498(s)	502(s)	ν_1(A) SCl_3^+ (S-Cl sym.)
480(w,sh)		$\nu_3(F_2)$ $AlCl_4^-$
352(m)		$\nu_1(A_1)$ $AlCl_4^-$
	336(sh))	ν_1(A) $SbCl_6^-$
	329(s))	
	296(w)	ν_2(E) $SbCl_6^-$
	287(m)	
275(m)	276(w)	$\nu_2(A_1)$ SCl_3^+ (def.)
214(m)	217(vw))	ν_4(E) SCl_3^+ (def.)
207(m)	209(w))	
180(vvw)		$\nu_4(F_2)$ $AlCl_4^-$
	176(s))	ν_5(F) $SbCl_6^-$
	168(w,sh))	
136(w,br)		ν_2(E) $AlCl_4^-$

PCl_3[129] 504 (ν_1,A_1), 482 (ν_3,E), 252 (ν_2,A_1), 198 (ν_4,E).

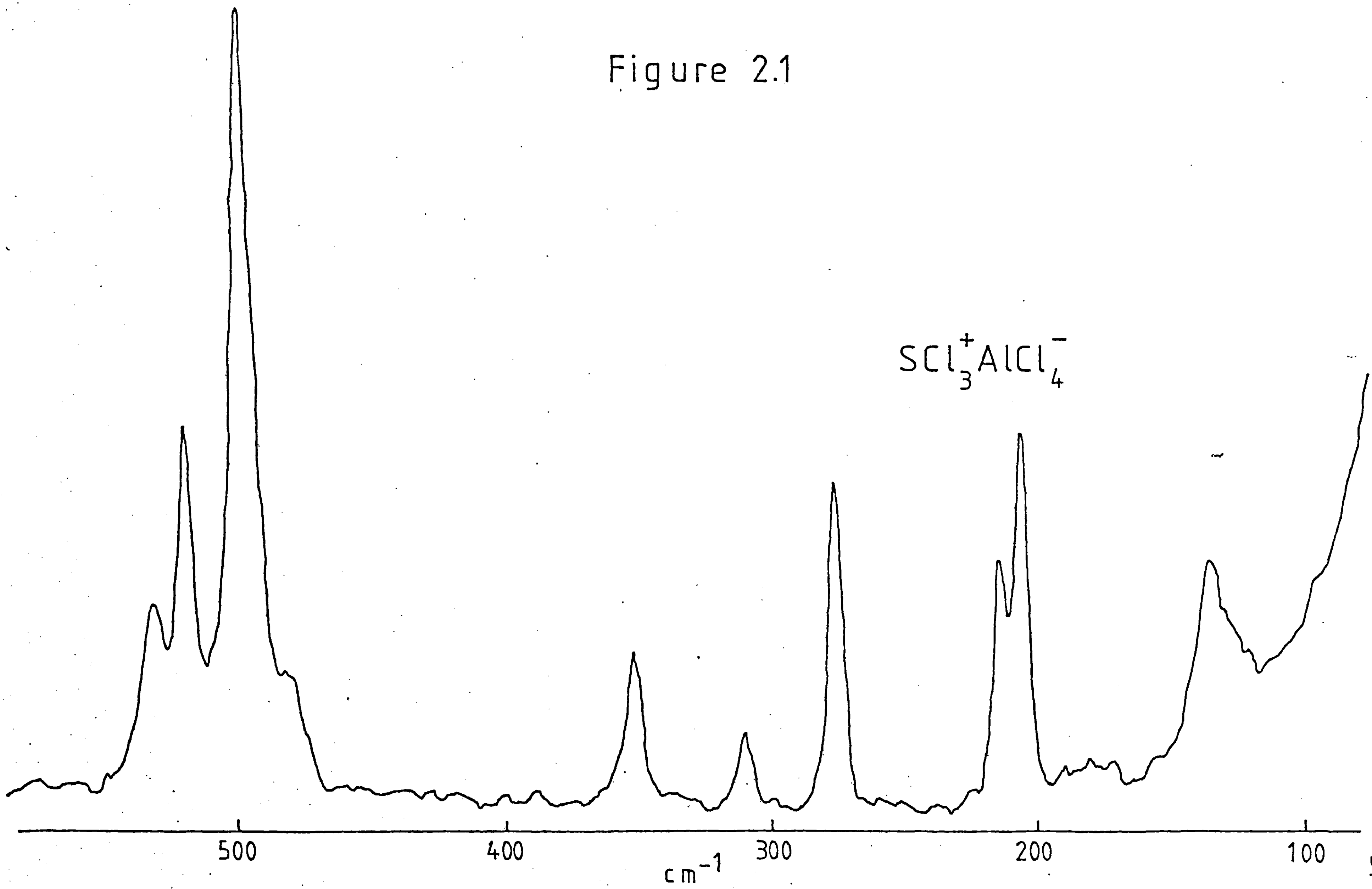


Figure 2.1

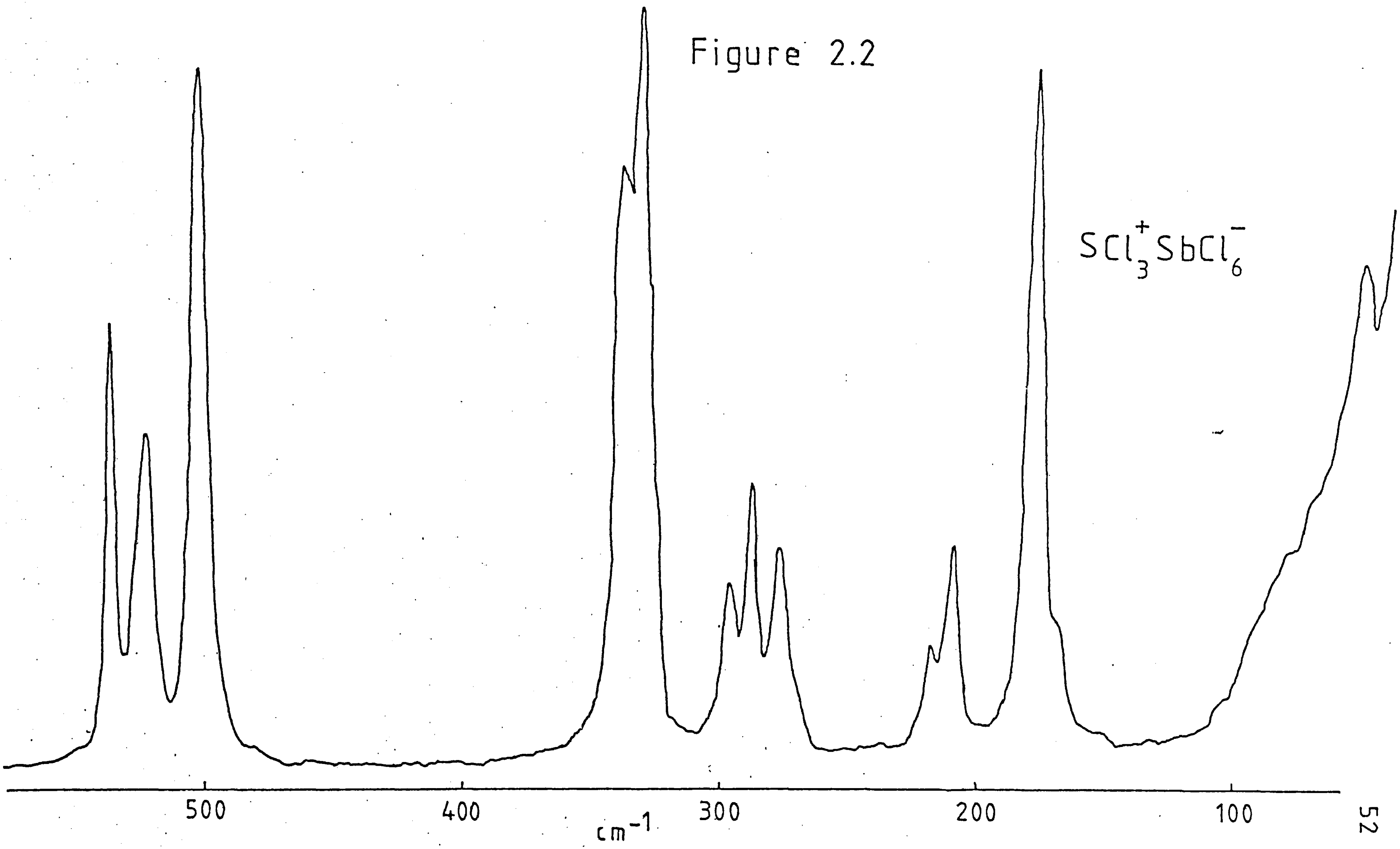


Figure 2.2

The anion bands are in general agreement with the literature values but it is interesting to note that the $SbCl_6^-$ ν_1(A) mode is split and as this is not a degenerate mode presumably factor group splitting is responsible. The F mode is a triply degenerate mode but we observed only a small shoulder on an otherwise symmetrical shaped band. Both these splittings were repeatably observed in a number of spectra and are therefore probably not the result of impurities.

The $AlCl_4^-$ ν_2(E) mode, about which there is some disagreement regarding its frequency, is observed as a broad band at 136cm^{-1} in agreement with Doorenbos.

It was found necessary to prepare pure SBr_3^+ species but this proved very difficult as the products obtained with tetrahaloaluminate anions were extremely hydrolytically unstable. The products degraded even under dry box conditions and flaming of Raman tubes was essential, but not always successful, to reduce hydrolysis even in a small sealed tube.

A number of attempts were made to produce these complexes but only the most successful method is given in the experimental section (Chapter 5). It was found that the complexes were best obtained in dichloromethane although long reaction times at room temperature were necessary for the tetrachloroaluminates whereas for the tetrabromoaluminates a short reaction at low temperature was essential. This is probably a result of the different solubilities of the aluminium halides in the solvent leading to homogeneous reaction even at -80°C for the bromide. However, both $SBr_3^+AlCl_4^-$ and $SBr_3^+AlBr_4^-$ were prepared on more than one occasion and identical spectra recorded. Analysis of the solids for halide gave good agreement with calculated values in view of their hydrolytic instability.

The spectra are given in Figures 2.3 and 2.4 and assignments are detailed in Table 2.8, the frequencies for the SBr_3^+ ion support the C_{3v} symmetry by providing the two high frequency stretching S-Br modes and two low frequency modes similar in pattern to those observed for SCl_3^+. However, whereas both the E modes were split for the SCl_3^+ complexes and in $SBr_3^+AlBr_4^-$ only the deformation mode in $SBr_3^+AlCl_4^-$ was split, there being no evidence of splitting in the S-Br antisymmetric E mode. The frequencies of the S-Br stretching modes are about 150cm^{-1} lower than those of S-Cl as would be expected from the atomic weight change, but the S-Br stretching frequencies in $SBr_3^+AlBr_4^-$ are also some 20-25cm^{-1} lower than in the corresponding $SBr_3^+AlCl_4^-$ complex.

The frequencies given agree with those reported independently by Passmore[54] but he found the high frequency E mode to be split in both his complexes. However, his spectra contain many impurity bands and it is therefore difficult to be certain of assignments.

The anion bands in our spectra are very weak in comparison to the strongly emitting SBr_3^+ ion and therefore only the strongest ν_1 band is readily observed. The other bands also tend to be masked by the SBr_3^+ bands

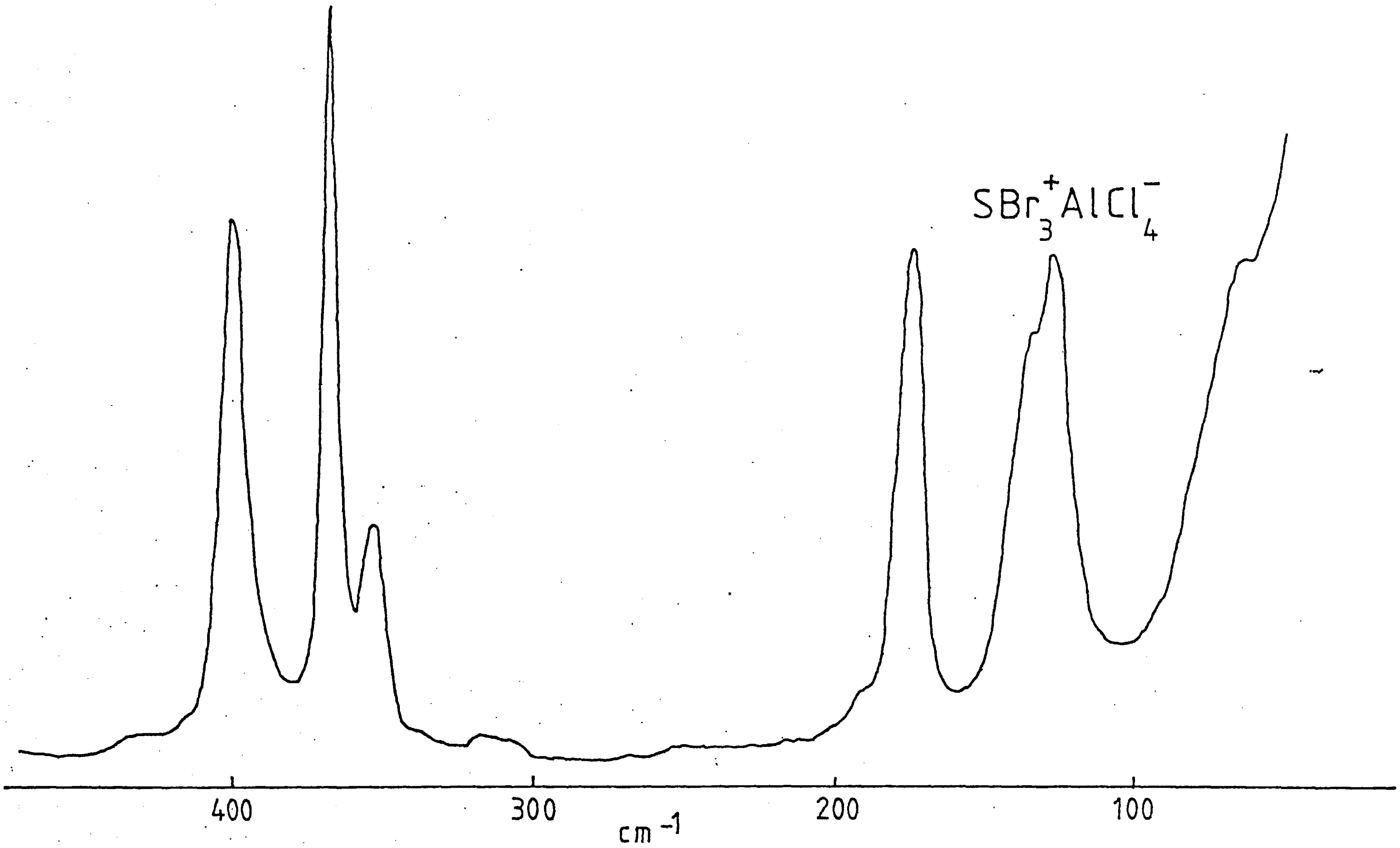
TABLE 2.8

TRIBROMOSULPHONIUM RAMAN SPECTRA (cm^{-1})

$SBr_3^+AlCl_4^-$ (Figure 2.3)	$SBr_3^+AlBr_4^-$ (Figure 2.4)	Assignment
490(vvw)		$\nu_3(F_2)$ $AlCl_4^-$
	400(vw,sh)	$\nu_3(F_2)$ $AlBr_4^-$
401(s)	386(sh) 375(m)	$\nu_3(E)$ SBr_3^+ (S-Br asym)
368(s)	348(s)	$\nu_1(A_1)$ SBr_3^+ (S-Br sym)
354(m)		$\nu_1(A_1)$ $AlCl_4^-$
	211(m)	$\nu_1(A_1)$ $AlBr_4^-$
174(m)	169(m)	$\nu_2(A_1)$ SBr_3^+ (def)
135(w,sh) 126(m)	134(w) 123(m)	$\nu_4(E)$ SBr_3^+ (def)
64(w)	86(vw) 78(w) 58(w) 46(w)	lattice bands

PBr_3 [135] 400 (ν_3,E), 380 (ν_1,A_1), 162 (ν_2,A_1), 116 (ν_4,E).

Figure 2.3



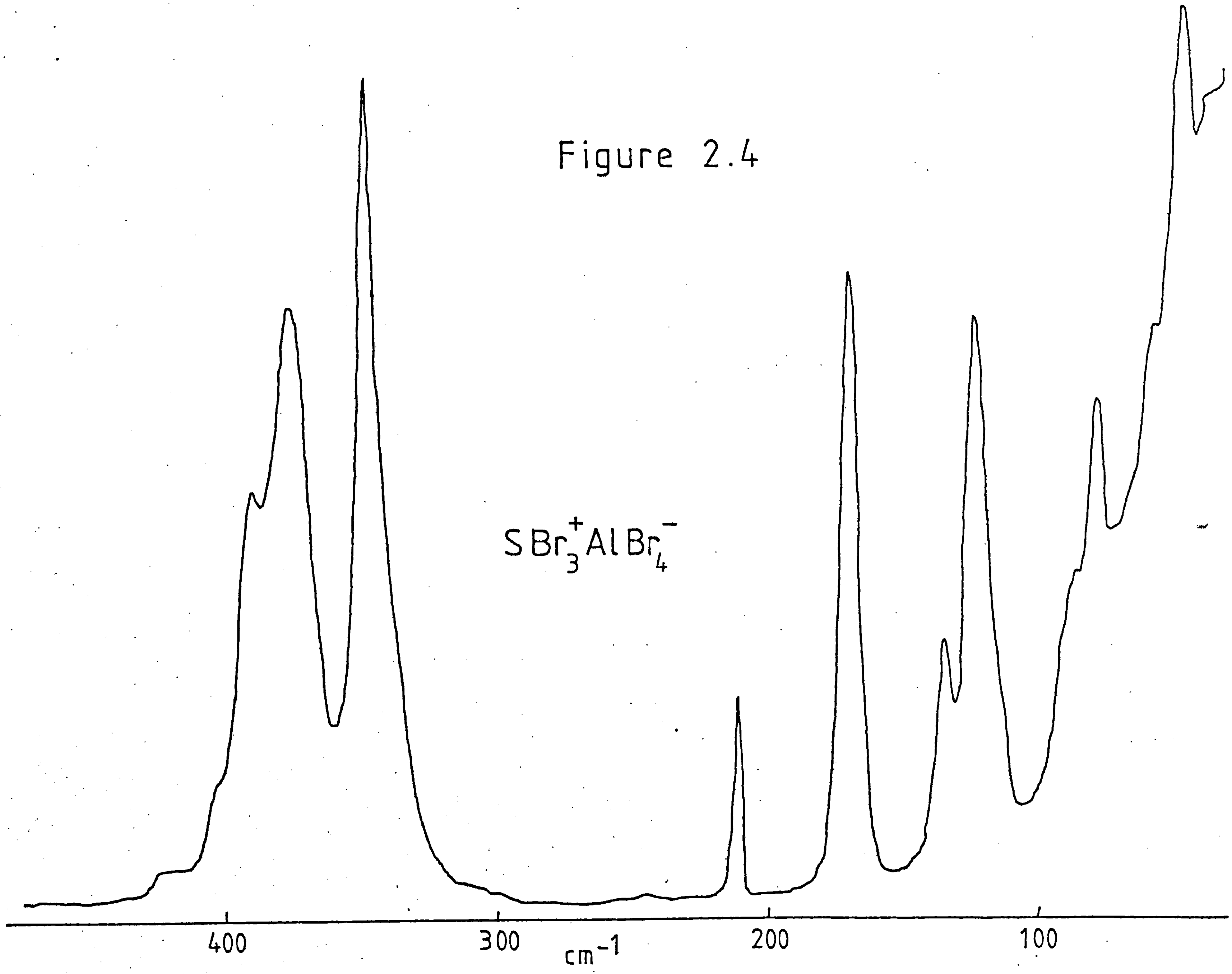


Figure 2.4

$SBr_3^+AlBr_4^-$

although the ν_3 bands are observed very weakly.

It is possible, in theory, to produce a mixed aluminate ion when preparing $SBr_3^+AlCl_4^-$. However, there is no evidence for the presence of a band of any real significance at 308cm^{-1} indicative of $AlCl_3Br^-$ (Table 2.4). The very weak emission in this area seen in the spectrum is most probably due to residual aluminium trichloride. This view is supported by the lack of a 440cm^{-1} band in an area clear of other bands, even though the ν_1 $AlCl_3Br^-$ band is weaker than the ν_2 band. It is therefore considered that the presence of $AlCl_3Br^-$ is unlikely particularly in view of the analytical evidence.

If the formation of the anion is considered as the reaction of aluminium chloride with a halide cation then the Hard and Soft Acid and Base (HSAB) Principle[145,146,147] becomes useful. A soft base is defined as one in which the donor atom is easily polarizable. Such a base is therefore generally large and has a donor atom of low electronegativity. A hard base has its electrons more tightly bonded and tends to be small and not easily polarised. Similarly a soft acid is one in which the acceptor atom is relatively easily polarized and is generally a large cation or metal in low oxidation state. A hard acid is one where the acceptor atom is not easily polarized and is usually a small cation in a high oxidation state or a molecule with incomplete valence shells and electron withdrawing groups. The basic HSAB principle is that hard acids tend to combine with hard bases and soft acids with soft bases.

In the case of the reaction

$AlCl_3+X^- \longrightarrow AlCl_3X^-$ the aluminum chloride may be considered as a hard acid. The acceptor atom is in a high oxidation state, is combined with electron withdrawing groups and is electron deficient. The halide ion in this case is the base and moving from Cl^- to Br^- the ion becomes larger and of lower electronegativity. Therefore Br^- is softer than Cl^-.

Application of the HSAB Principle would therefore suggest that the hard acid - hard base $AlCl_3$-Cl^- reaction would be favoured over the hard acid - softer base $AlCl_3$-Br^- reaction. This appears to be what is found in practice.

A number of attempts were made to prepare further complexes of SBr_3^+ with anions other than tetrahaloaluminate. However, reactions involving antimony pentachloride always resulted in the formation of mixed products containing S-Cl bands presumably as a result of chlorination by $SbCl_5$.

Again the HSAB Principle is useful in that the production of SX_3^+ may be considered as the reaction.

$$SX_2+Y^+ \longrightarrow SX_2Y^+$$

In this case the acceptor atom, the acid, is a halogen cation and both bromine and chlorine cations are within the definition of a soft acid. Sulphur dichloride has two lone pairs of electrons and may be considered as a soft base. Therefore mixed trihalosulphonium cations can be produced and this perhaps explains why the presence of relatively small amounts of bromine or chlorine lead to the formation of mixed sulphonium species (Section 2.3)

A number of other Lewis acids were tried, under a variety of reaction conditions, in an attempt to produce complexes but only the starting materials could be isolated. It was thought desirable to use only bromo species to eliminate the possibility of scrambling and therefore the Lewis acids used were antimony tribromide boron tribromide, indium tribromide, and tin tetrabromide. Table 5.1 (Chapter 5, Experimental) details the preparations and products obtained which in nearly all cases consisted of the recovered Lewis acid. No identifiable complexes were obtained.

2.3 MIXED TRIHALOSULPHONIUM CATIONS

It would be interesting to prepare pure complexes of SCl_2Br^+ and $SClBr_2^+$ as well as the trihalosulphonium cations detailed earlier. A number of attempts were made to prepare pure species but it became obvious that pure products could not be isolated. In order to test the ease with which scrambling occurred among the cations equal quantities of pure solid $SCl_3^+AlCl_4^-$ and $SBr_3^+AlCl_4^-$ were mixed. An immediate colour change occurred and the Raman spectrum was characteristically that of mixed halosulphonium cations and not that of a mixture of the complexes. This reaction was repeated a number of times and mixed cations always resulted although the time for the reaction to occur varied. Therefore a series of products were prepared with different reactant ratios to obtain spectra with differing band intensities. These could then be analysed and the bands attributed to the various species. This procedure was adopted with the tetrahaloaluminates and the hexachloroantimonates.

Initially reactions between sulphur dichloride, bromine and aluminium chloride were attempted in liquid chlorine. However, in every case $SCl_3^+AlCl_4^-$ was isolated and even restricting the chlorine to a molar equivalent still gave a product that was mainly $SCl_3^+AlCl_4^-$.

It was therefore decided to prepare complexes in the absence of chlorine but using a solvent to maintain fluidity and details of the preparation of these products are given in Table 5.2 (Chapter 5, Experimental). It was found that the purest products were obtained from dichloromethane or chloroform at low temperature although later reactions at 20°C gave acceptable products indicating that the preparation of SCl_4 (or SCl_nBr_{4-n}) is not a necessary prerequisite of complex formation. However, again considerable care had to be taken to minimise hydrolysis.

It might be anticipated that the preparation of these compounds in the absence of chlorine would give complexes containing mixed tetrahaloaluminate ions with the species $AlCl_3Br^-$ being formed preferentially at low bromine levels. This species would give rise to bands at $308cm^{-1}$ and $440cm^{-1}$ (See Section 2.1 and Table 2.4) but the spectra are generally free of bands in both these regions, apart from some weak bands at $310cm^{-1}$ attributable to free aluminium chloride. The other arguments relating to the HSAB Principle mentioned earlier (Section 2.2) also apply and it is considered unlikely that any $AlCl_3Br^-$ anions are present.

The spectra obtained from the compounds listed in Table 5.2 were analysed and it became obvious that basically three very different spectra (* in Table 5.2) had been obtained in terms of relative band intensities. These spectra were derived from products with SCl_2: Br_2:$AlCl_3$ reactant ratios of 0·5:1:0·5, 1:1:1 and 2·7:1:1·7 and are illustrated in figures 2.5, 2.6 and 2.7.

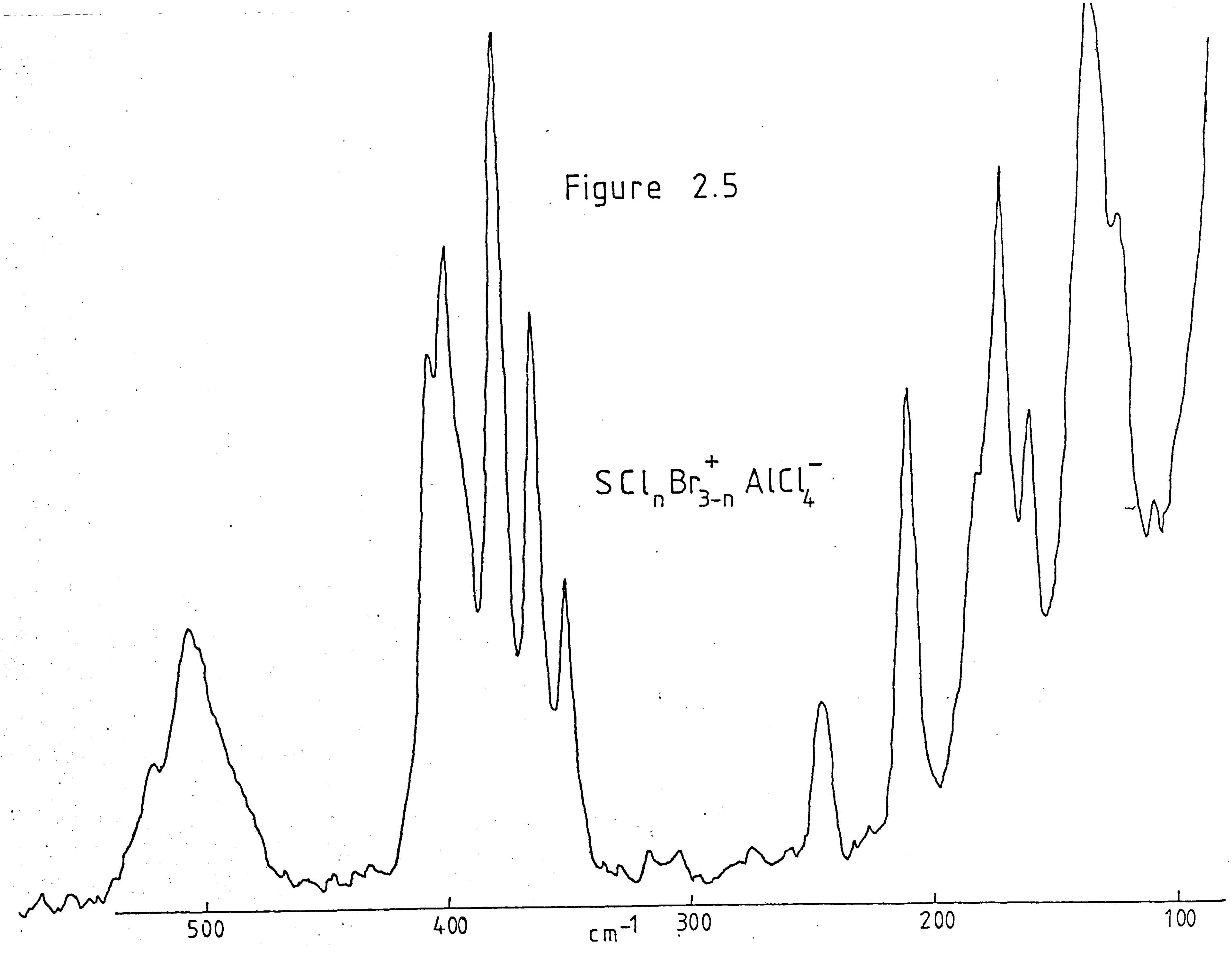


Figure 2.5

$SCl_nBr_{3-n}^+ AlCl_4^-$

Figure 2.6

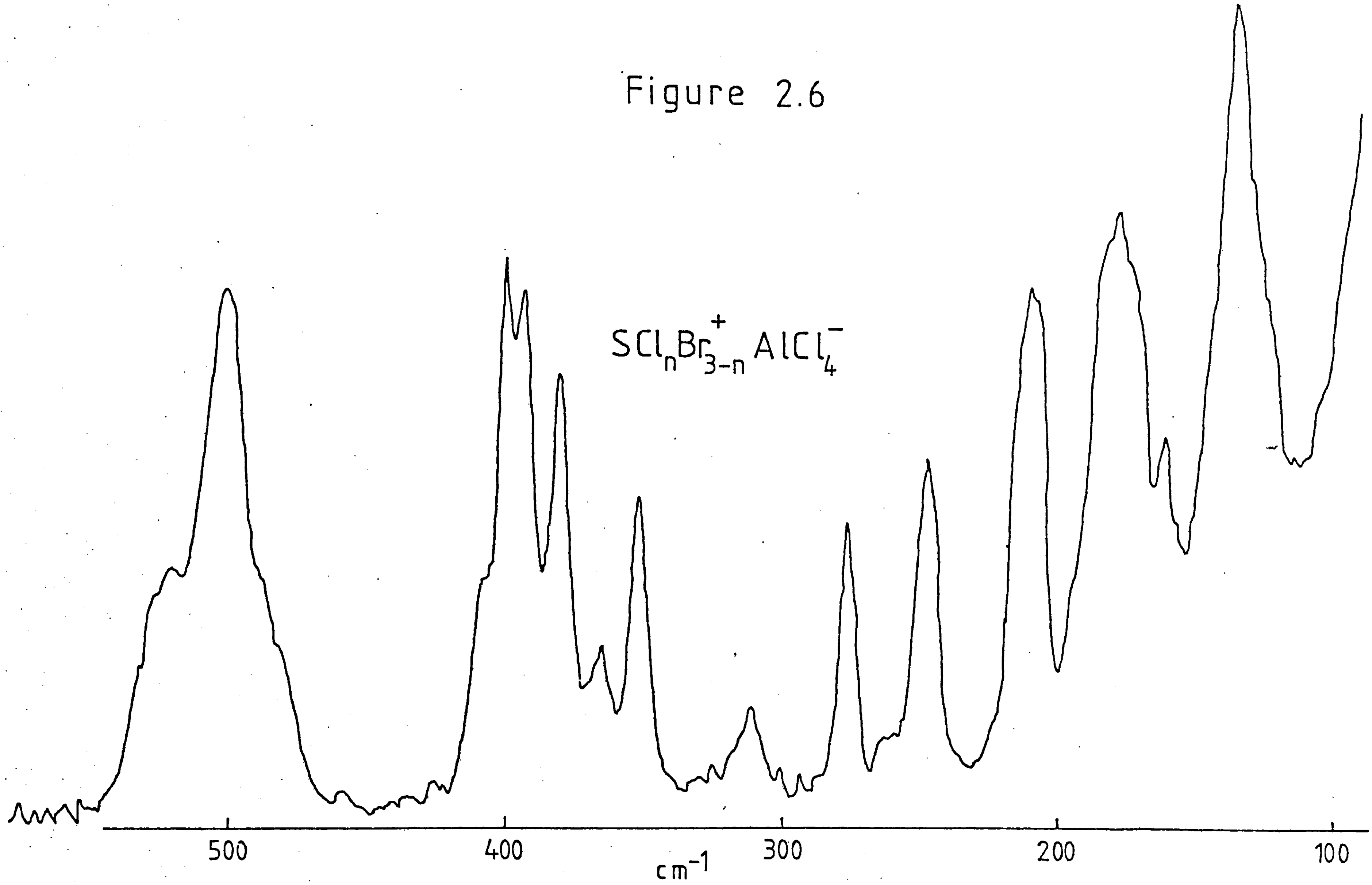
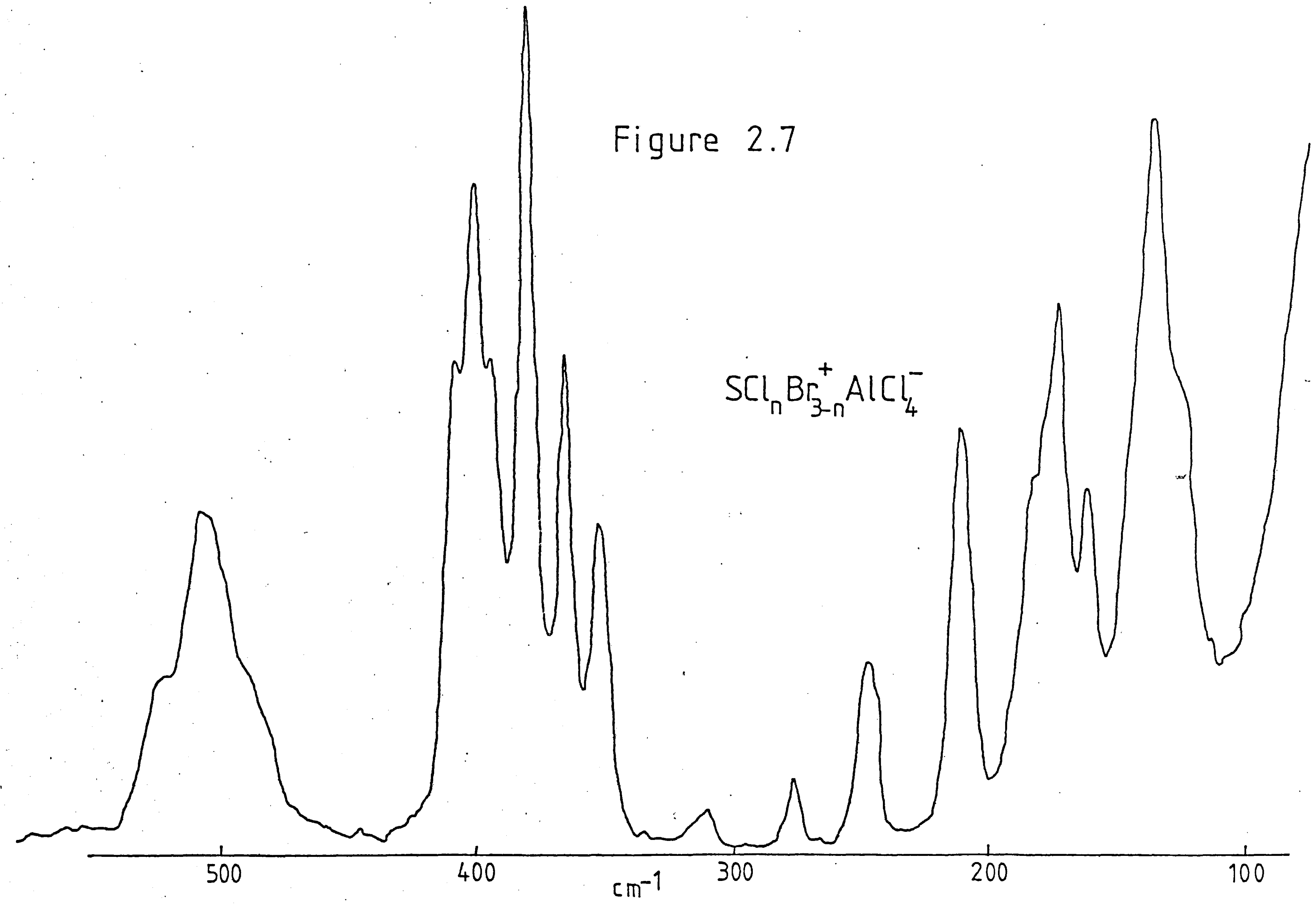


Figure 2.7



An examination of the spectra suggested that three cations were present together with only a small amount of $SCl_3^+AlCl_4^-$ as evidenced by the relatively weak 277cm^{-1} band. It was therefore decided to analyse the spectra carefully in terms of peak height variations. The peak heights were measured and scaled to the $AlCl_4^-$, 352cm^{-1}, peak as a reference. The scaled peak heights of two of the spectra were then compared to those of the third to give two sets of bands each listing series of bands increasing and decreasing together. Four sets of bands were obtained, two from each pair of spectra, and from one spectrum in each pair the bands due to $SBr_3^+AlCl_4^-$ (Table 2.8) were eliminated. The four band sets provided two pairs each containing mostly bands of the same frequency. There were only three bands apparently in the "wrong" set and an examination of these bands in the spectra, together with their numerical ratios, suggested that they could reasonably be placed in the other set. Therefore two of these ambiguous bands were transferred to one set and one band to the other set, thus two sets of bands of identical frequencies were obtained and the table below details each set:-

520	407
506	380
394	210
246	160
181	134

Table 2.9 lists the frequencies of the phosphorus trihalides which are isoelectronic with the trihalosulphonium cations and would be expected to give bands of similar frequencies.

A comparison of the trihalosulphonium sets of frequencies to those of PBr_nCl_{3-n} (Table 2.9) shows that the 520,506,394,246, and 181cm^{-1} set corresponds to those for $PBrCl_2$ and the 407,380,210,160 and 134cm^{-1} set corresponds to those for PBr_2Cl. However, there is a missing high frequency band for the SBr_2Cl^+ set and a missing low frequency band for $SBrCl_2^+$. The spectra were therefore re-examined and evidence could be seen for a band at 490cm^{-1} on the shoulder of the 506cm^{-1} band. The missing low frequency band should occur at about 150cm^{-1} and may be hidden in the rather broad bands at 180cm^{-1} or possibly 134cm^{-1}. Therefore the following frequencies for the mixed halosulphonium cations are suggested:-

SBr_2Cl^+	$SBrCl_2^+$
490cm^{-1}	520cm^{-1}
407cm^{-1}	506cm^{-1}
380cm^{-1}	394cm^{-1}
210cm^{-1}	246cm^{-1}
160cm^{-1}	181cm^{-1}
134cm^{-1}	?

TABLE 2.9

BAND FREQUENCIES OF PX_nY_{3-n} (cm^{-1}) (n=0-3)

	ν_3	ν_1	ν_2	ν_4			Reference
	(E)	(A_1)	(A_1)	(E)			
PBr_3	400	380	162	116			135
PCl_3	482	504	252	198			129
	ν_1	ν_5	ν_2	ν_3	ν_4	ν_6	
	(A')	(A")	(A')	(A')	(A')	(A")	
PBr_2Cl	480	390	390	197	123	153	143
$PBrCl_2$	495	495	400	230	167	149	143

A number of attempts using a variety of reaction conditions were made to produce mixed halosulphonium tetrabromoaluminate species. Initial attempts gave solids in low yield that produced no Raman spectra and were probably hydrolysis products or impurities in the aluminium bromide. It became apparent that hydrolysis of any products formed was very rapid and any exposure to the atmosphere would result in hydrolysis. Later attempts used rigorously dried reactants and nitrogen atmospheres together with "flamed" apparatus but degradation of the products still occurred. A final attempt was made by conducting the preparation in a Raman cold cell tube and removing solvents and excess reactants under vacuum. However, even this method, with absolute minimal exposure to dry nitrogen atmosphere, still resulted in degradation of the product. It was therefore thought that the production of mixtures of species would result in very low melting solids. These would be sensitive to even small smounts of moisture and readily give rise to semi-solids derived from hydrolysis of the complexes mainly to starting materials together with their hydrolysis products.

It would obviously be desirable to produce mixed halosulphonium cations with counter-ions other than a haloaluminate and therefore analogous reactions were carried out using antimony pentachloride as the chloride ion acceptor.

Initially products were produced

from sulphur dichloride and bromine in various ratios using chloroform or liquid hydrogen chloride as solvent. The products are listed in Table 5.3 (Experimental) but basically only two different spectra were obtained. These are illustrated in Figures 2.8 and 2.9 and are spectra of mixtures of compounds. $SCl_3^+SbCl_6^-$ has bands attributable to SCl_3^+at 209/217cm^{-1}, 276cm^{-1}, 502cm^{-1} and 523/536cm^{-1} and generally these bands are largely absent from the spectra. It is therefore unlikely that these products contain significant quantities of $SCl_3^+SbCl_6^-$.

In view of the presence of bromine there is a possibility that the anion $SbCl_5Br^-$ might be produced. However, no bands at 310cm^{-1} and 220cm^{-1} (See Table 2.2) are visible and the presence of $SbCl_5Br^-$ is therefore improbable. It would therefore appear that three products are produced by the reaction of SCl_2,Br_2 and $SbCl_5$, consisting of $SCl_nBr_{3-n}^+SbCl_5^-$ compounds with n=0, 1 or 2.

A number of attempts were made to produce pure $SBr_3^+SbCl_6^-$ by reaction of sulphur monobromide, bromine and antimony pentachloride. Table 5.4 summarises these attempts and it is interesting that the spectra of the products were all virtually identical even though various reactant ratios and conditions were used. However, in all cases the spectra of the products showed the presence of S-Cl bands (Figure 2.10) and pure SBr_3^+ species had not been produced, although it is probable that the products did contain large amounts

Figure 2.8

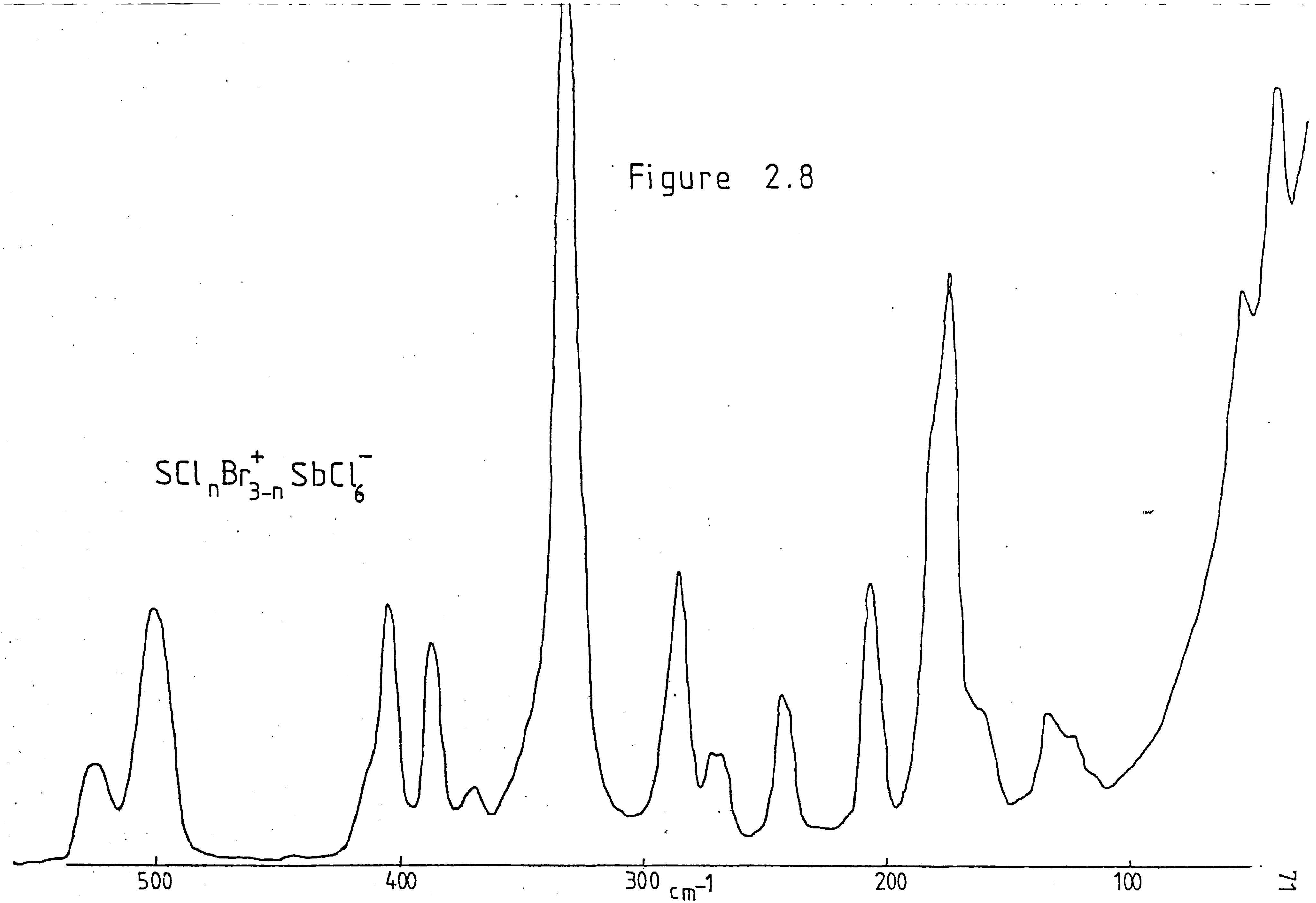
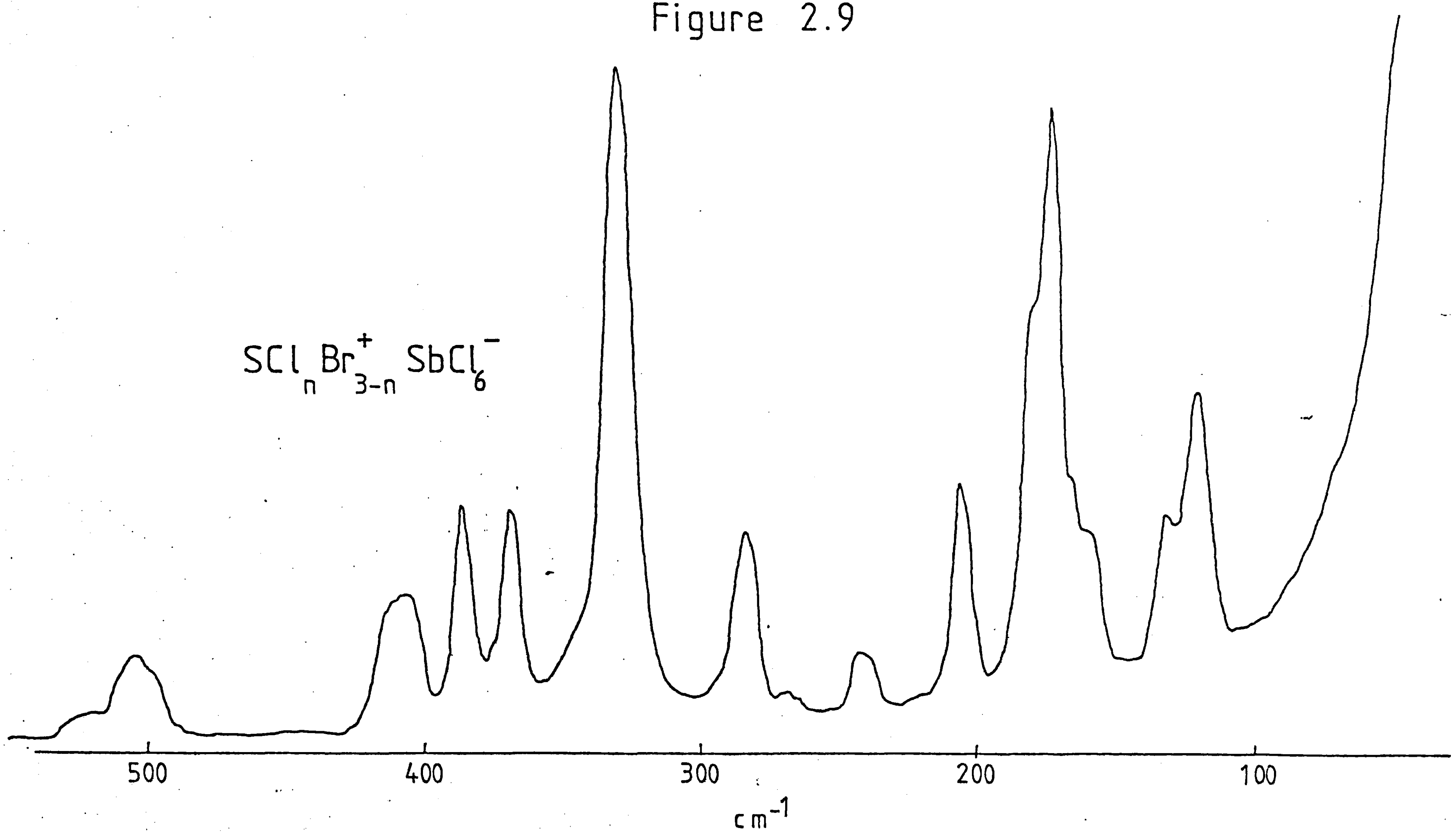


Figure 2.9



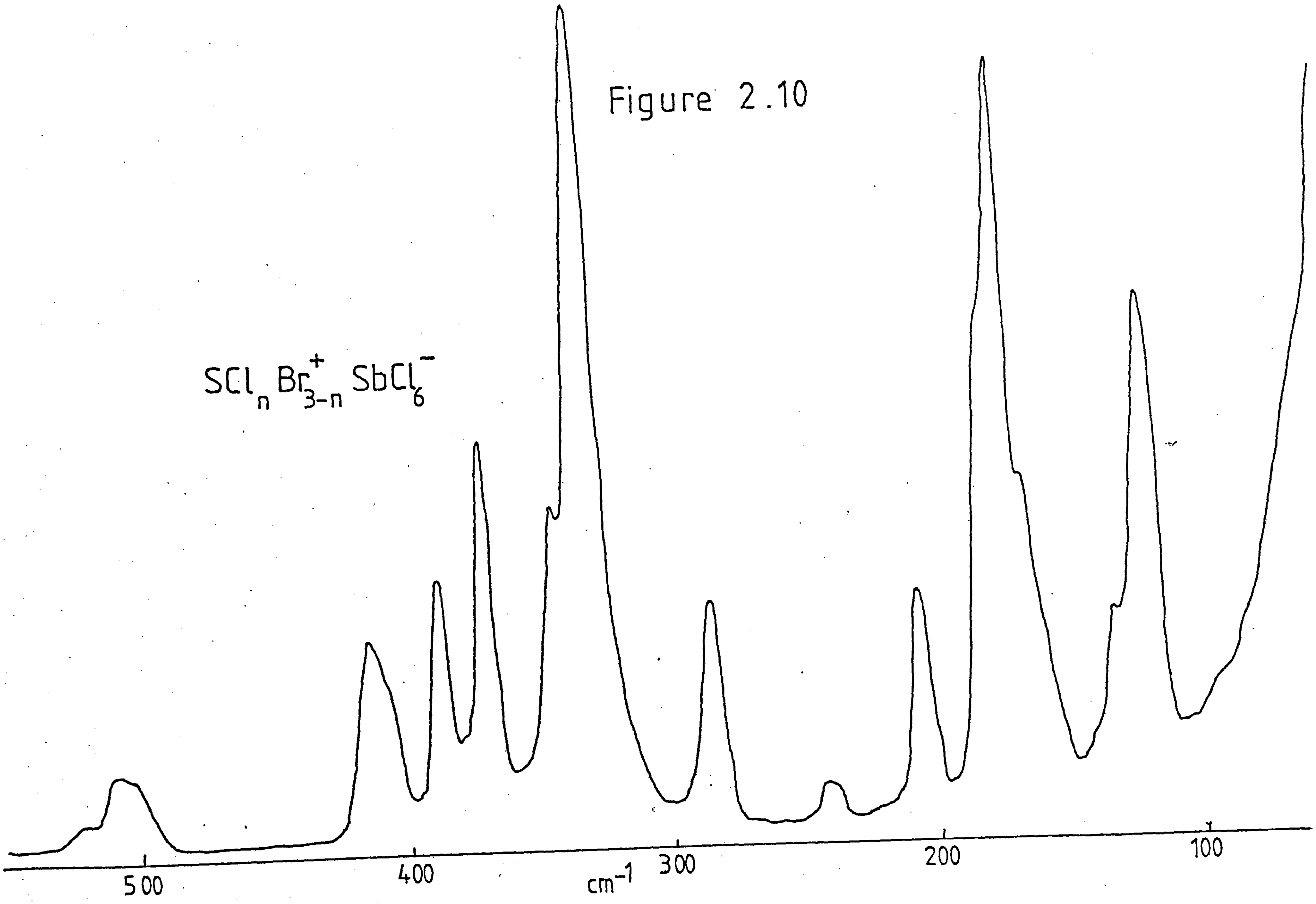


Figure 2.10

of SBr_3^+ species. The absence of $\overset{b}{S}Cl_5Br^-$ was again confirmed by the lack of bands at 310cm^{-1} and 220cm^{-1}.

From both the sets of antimony pentachloride reactions three very different spectra were chosen and the band intensity variations analysed as for the tetrahaloaluminates yielding two sets of bands.

525cm^{-1}	414cm^{-1}
505cm^{-1}	387cm^{-1}
404cm^{-1}	370cm^{-1}
243cm^{-1}	206cm^{-1}
	180cm^{-1}
	(174)cm^{-1}
	(166)cm^{-1}
	160cm^{-1}
	133cm^{-1}
	122cm^{-1}

$SBr_3^+AlCl_4^-$ has been shown (Table 2.8) to give bands at 401, 368, 174, and 126cm^{-1} and very similar bands can be extracted from the larger set of data. This leaves bands at 387, 206, 160 and 133cm^{-1}. Again a comparison of the two sets of data was made with the band frequencies of both the phosphorus halides and the tetrahaloaluminates and the bands assigned to $SBrCl_2^+$ and SBr_2Cl^+ respectively. A reassessment of the spectra was then made and it became obvious that the missing high frequency bands for SBr_2Cl^+ should occur at 505cm^{-1} and 414cm^{-1}. The presence of the strong $SbCl_6^-$ band at 174cm^{-1} masks a number of bands for the halosulphonium ions and some can be observed as shoulders on the $SbCl_6^-$ band. In particular it is possible that shoulders observed at 166cm^{-1} and 180cm^{-1} can be assigned to SBr_2Cl^+ and $SBrCl_2^+$ respectively. Therefore the following frequencies for the mixed halosulphonium cations are suggested.

SBr_2Cl^+	$SBrCl_2^+$
505cm^{-1}	525cm^{-1}
414cm^{-1}	505cm^{-1}
387cm^{-1}	404cm^{-1}
206cm^{-1}	243cm^{-1}
160cm^{-1}	180cm^{-1}
132cm^{-1}	

The band frequencies for each of the ions SBr_2Cl^+ and $SBrCl_2^+$ with the different anions are compared in Table 2.10 and are assigned by a) comparison with their phosphorus halide analogues and b) predictions based on the values of the SCl_3^+ and SBr_3^+ frequencies. There is considerable agreement between the data and this is a powerful argument in favour of the assignments given as most of the band frequencies were obtained independently from a variety of spectra with two different anions. A comparison of the known frequencies of SBr_3^+ and SCl_3^+ with those of

TABLE 2.10

SBr_2Cl^+ AND $SBrCl_2^+$ FREQUENCIES (cm^{-1}) AND ASSIGNMENTS

SBr_2Cl^+

$AlCl_4^-$	$SbCl_6^-$	PBr_2Cl	Assignment
490	505	480	ν_1(A') S-Cl str.
407	414	390	ν_5(A") S-Br asym.
380	387	390	ν_2(A') S-Br sym.
210	206	197	ν_3(A') S-Cl def.
160	160	153	ν_6(A") SBr_2Cl def.
134	132	123	ν_4(A') SBr_2 def.

$SBrCl_2^+$

$AlCl_4^-$	$SbCl_6^-$	$PBrCl_2$	
520	525	495	ν_5(A")S-Cl asym.
506	505	495	ν_1(A') S-Cl sym.
394	404	400	ν_2(A') S-Br str.
246	243	230	ν_3(A') $S-Cl_2$ def.
181	180	167	ν_4(A') S-Br def.
?	?	149	ν_6(A") $SBrCl_2$ def.

the mixed halosulphonium cations and the isoelectronic phosphorus halides is given in Table 2.11. There is a large measure of agreement between the frequencies for the cation vibrations in complexes with various anions together with considerable correlation of trends in the phosphorus halides with those in the sulphonium species. The missing low frequecy band for the $SBrCl_2^+$ ion probably occurs at around $160cm^{-1}$, but tends to be masked by the $SbCl_6^-$ and S-Br bands. It is also unfortunate that we could not obtain pure $SBr_3^+SbCl_6^-$ to substantiate whether or not the high frequency E mode is split. There is some evidence for a shoulder on the $414cm^{-1}$ band (Figure 2.10) and as this product is probably mainly $SBr_3^+SbCl_6^-$ it suggests the band may be split. However, the relative intensity is not the same as that found in $SBr_3^+AlBr_4^-$ where the lower frequency band is the larger. Passmore[54] has reported solid state spectra where the bands appear similar in intensity and it would be reasonable to suppose this band to be split in $SBr_3^+SbCl_6^-$.

TABLE 2.11

$SBr_nCl_{3-n}^+$ FREQUENCIES (cm^{-1}) (n=0-3)

SBr_3^+

$AlBr_4$	$AlCl_4^-$	$SbCl_6^-$	PBr_3
386)	401	414)	400
375)		(407?))	
348	368	370	380
169	174	174	162
134)	135)	133)	116
123)	126)	122)	

SBr_2Cl^+

$AlCl_4^-$	$SbCl_6^-$	PBr_2Cl
490	505	480
407	414	390
380	387	390
210	206	197
160	166	153
134	132	123

$SBrCl_2^+$

$AlCl_4^-$	$SbCl_6^-$	$PBrCl_2$
520	525	495
506	505	495
394	404	400
246	243	230
181	180	167
?	?	149

SCl_3^+

$AlCl_4^-$	$SbCl_6^-$	PCl_3
532)	536)	504
520)	523)	
498	502	482
275	276	252
214)	217)	198
207)	209)	

2.4 SULPHUR TETRACHLORIDE

Earlier difficulties[21,22] in obtaining good spectra of sulphur tetrachloride now appear to have been overcome.[23,24] Figures 2.11 and 2.12 show the spectra produced during the present work on the yellow solid obtained by cooling mixtures of chlorine and sulphur dichloride. These spectra are in excellent agreement with that given by Morishita[24] and differ only in minor detail from that obtained by Feuerhahn.[23]

We also ran the spectrum at various temperatures to determine the decomposition temperature of the solid. Below -50°C the spectrum was typically SCl_4 and no significant changes were observed down to -170°C. However, at -47°C some slight degradation of the spectrum was noted and after 30 minutes at -45°C the solid disappeared and the spectrum indicated a mixture of sulphur dichloride and chlorine. Cooling reproduced the original spectrum which again decomposed at -45°C. We could not obtain SCl_4 at up to -30°C, the often-quoted decomposition temperature. One reference[3] states that acetonitrile can stabilise SCl_4 but this was not substantiated in our experiments when the solid decomposed at about -50°C in the presence of acetonitrile. There was also some indication that the presence of a vast excess of chlorine gave lower decomposition temperatures but this could simply be a solubility effect.

In view of the limited number of bands present in

Figure 2.11

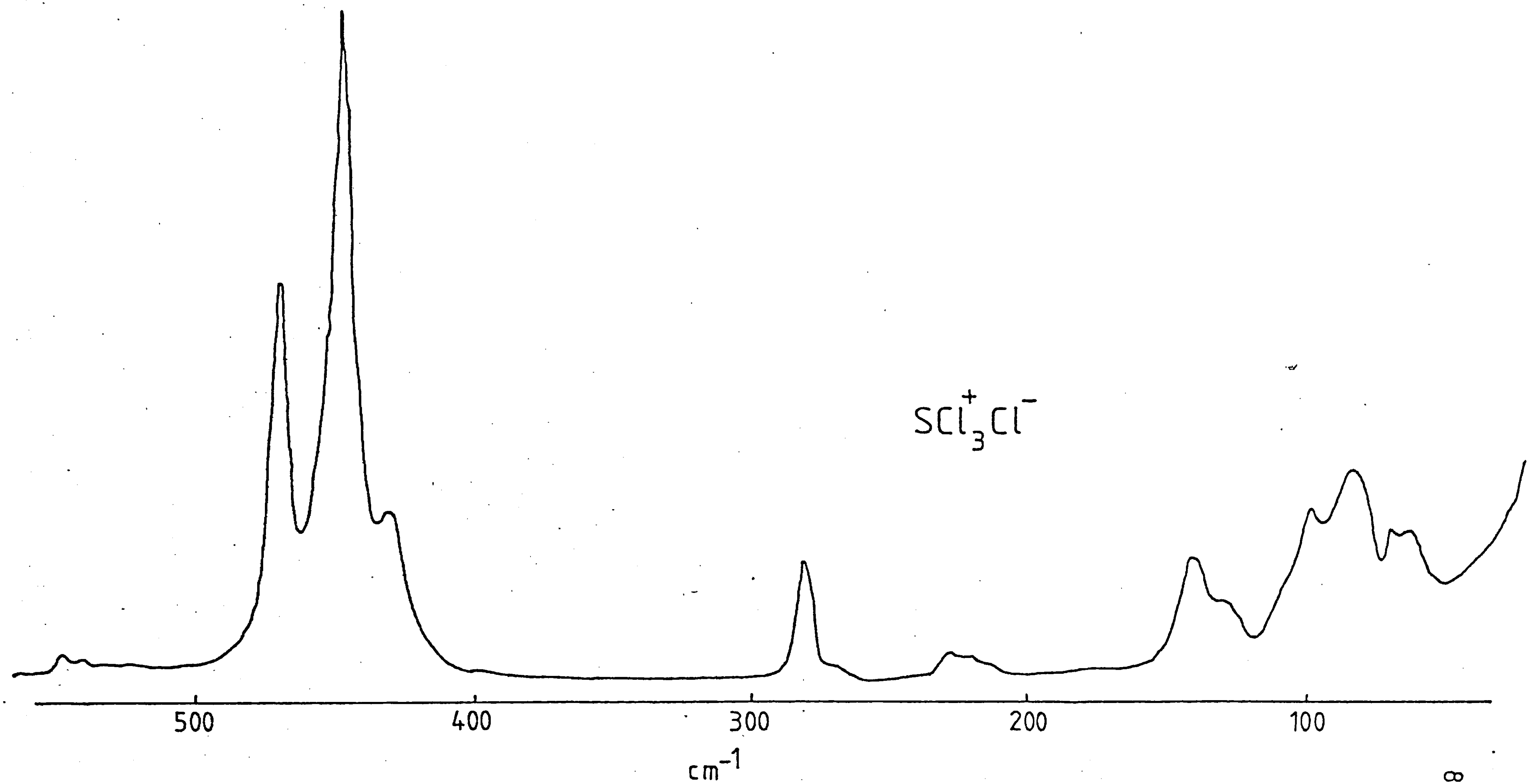
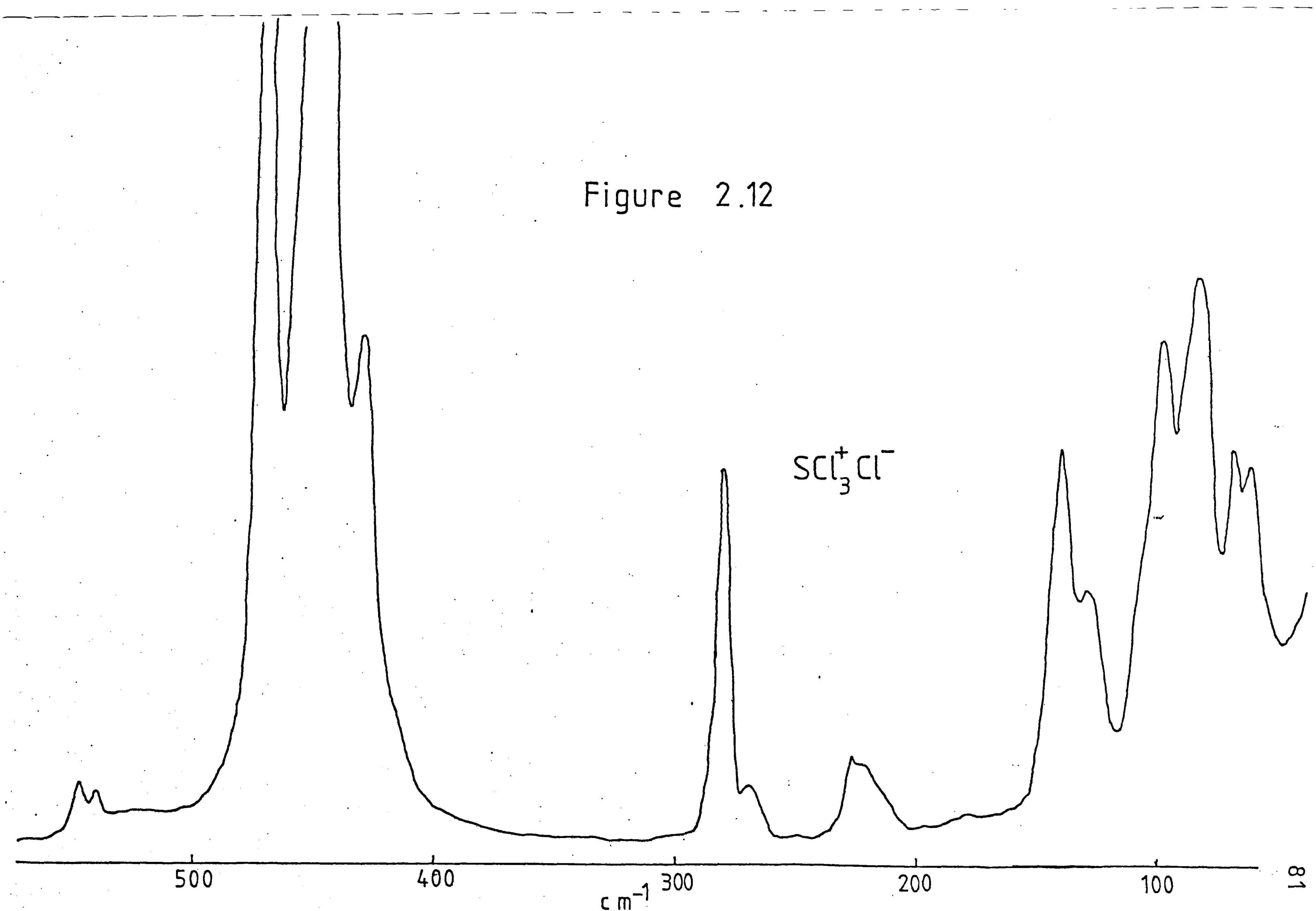


Figure 2.12



the spectrum it is probable that sulphur tetrachloride consists of pyramidal SCl_3^+ ions of C_{3v} symmetry (See Chapter 1, Section 1.2). Feuerhahn (and Morishita) assign the bands as detailed in Table 2.12 which also lists the corresponding frequencies found in this work. There are however, a number of other bands visible in the spectrum of SCl_4 and these have been assigned by Feuerhahn[23] as follows:-

1.	539,532 and 524cm^{-1}	chlorine
2.	512 and 218cm^{-1}	sulphur dichloride
3.	432, 210 and 244cm^{-1}	sulphur monochloride
4.	268cm^{-1}	Cl_3^- anion
5.	140cm^{-1}, 130cm^{-1}	chlorine bridging.

To support these arguments, he has observed corresponding bands in the infra-red. It is however, rather difficult to see how weak bands could be assigned to the presence of S_2Cl_2 when a significant level of free chlorine is also present in view of the equlibrium

$$2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2$$

It is however, accepted that equlibrium may only be attained slowly at low temperatures but the 430cm^{-1} band was always present, even after warming to room temperature. In sulphur monochloride the S-Cl stretching mode is observed in the Raman at 451cm^{-1} at 20°C and 446cm^{-1} at-50°C. The 209cm^{-1} deformation mode is as intense as the 451cm^{-1} band although much sharper. One

TABLE 2.12

RAMAN SPECTRA OF SCl_4 (cm^{-1})

Ref 24	Ref 23	This work (Figure 2.11)	Assignment[23]
470	472	471	ν_1 (A_1) S-Cl sym.
447	450	449	ν_3 (E) S-Cl asym.
(280)	279	280	ν_2 (A_1) def.
(225)	228	230	ν_4 (E) def.

would therefore expect that if S_2Cl_2 were present in SCl_4, a much larger 209cm^{-1} band would also be present. It should be noted that in our spectra we have no bands just below 210cm^{-1} although a weak broad complex exists between 210 and 230cm^{-1} (Figure 2.12).

On the addition of excess chlorine the 449cm^{-1} band becomes broader, hiding the 430cm^{-1} band but the 210-230cm^{-1} complex changes little, again suggesting that S_2Cl_2 is absent as otherwise it would be expected to decrease. The band positions are also slightly in error for S_2Cl_2 although again problems arise due to the possibility of solvent shifts. On balance therefore it is possible that the 430 and 210cm^{-1} bands may not be due to S_2Cl_2. Sulphur dichloride does give a Raman band at 216cm^{-1} together with a complex scattering around 510cm^{-1} at low temperatures, (-50°C) and it is possible that the region between 210 and 230cm^{-1} could contain such a band. The presence of weak bands around 510cm^{-1} in SCl_4 also supports this suggestion. We observed no band at 244cm^{-1}.

Pyramidal SCl_3^+ should exhibit two high frequency stretching modes, a symmetric S-Cl stretch (A_1) and an antisymmetric S-Cl stretch (E). In solids containing the SCl_3^+ cation in combination with Lewis acid-derived anions the strongest band is the A_1 at about 500cm^{-1}. The antisymmetric modes (E) are observed at about 520cm^{-1} and 530cm^{-1} and both are weaker than the A_1 band although the difference in intensity is not great in the $SbCl_6^-$

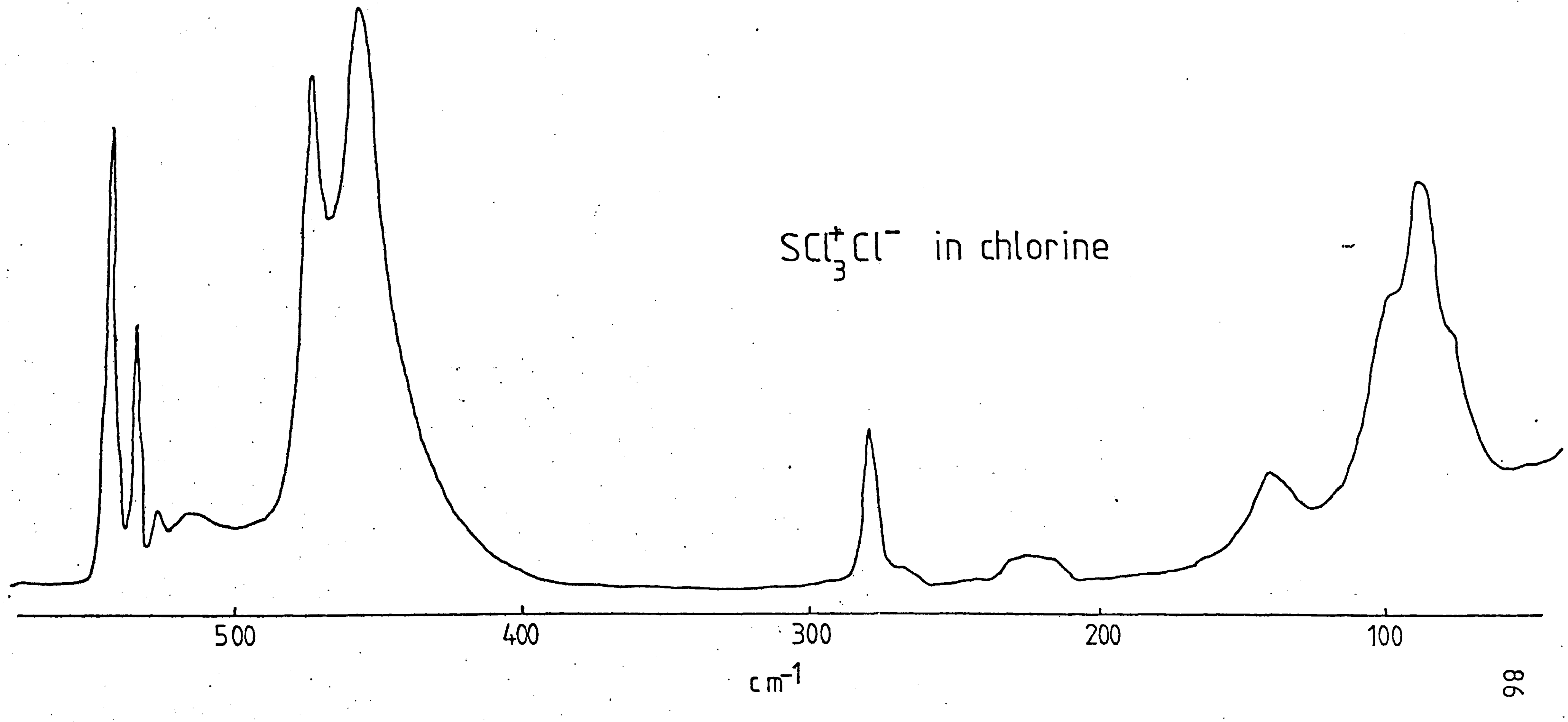
complex. The relative intensity of these two bands differs in the two complexes examined (Figures 2.1 and 2.2) It would be attractive to suggest that the bands at 449 and 430cm^{-1} be attributed to the E mode. However, for a C_{3v} ion the A_1 mode should be stronger than the E mode in the Raman but weaker in the infra-red.[29] The infra-red spectrum given in the paper by Feuerhahn[23] shows the lower frequency band to be possibly the weaker and therefore to be the A_1 mode. It is however, interesting to note that in the analogous selenium and tellurium tetrachlorides the higher frequency band is very much the stronger and is assigned to the A_1 mode.[29]

The bands at around 540cm^{-1} are due to excess chlorine and are very characteristic because of the isotope splitting pattern. Feuerhahn[23] attributes the weak band at 268cm^{-1} to the Cl_3^- anion. Unlike Feuerhahn we found no significant increase in the 268cm^{-1} band strength in the presence of excess chlorine (Figure 2.13) but certainly one would expect a Cl_3^- ion, if present, to be symmetric due to the cation size and exhibit a Raman band at 268cm^{-1} (Chapter 1, Section 1.5, and Evans.[104])

Feuerhahn[23] suggests that bands at 140 and 130cm^{-1} can be assigned to chlorine bridges and such bands would be expected in the low frequency region.

It might be predicted that a comparison of the spectrum of SCl_4 with its selenium and tellurium analogues could resolve the above doubts. The infra-red and Raman spectra of $SeCl_4$ and $TeCl_4$ have been described and

Figure 2.13



$SCl_3^+Cl^-$ in chlorine

assigned by Ponsioen[29] and George[28] using crystal structures derived from x-ray data by Buss.[30] The spectra of $SeCl_4$ and $TeCl_4$ are, however, very different to those obtained for SCl_4. The high frequency stretching modes are split into a complex of some 7 or 8 bands with a very strong band of highest frequency. These have been assigned by Ponsioen[29] on the basis of site symmetry effects. The $TeCl_3^+$ ion, of C_{3v} point group, would be expected to exhibit A_1 and E stretching modes. However, in the unit cell the ion does not exist at a symmetrical site so lowering its symmetry to C_1. $TeCl_4$ also has been shown[30] to exist as Te_4Cl_{16} units which are only loosely coupled. The symmetry of the unit is C_2 and because of the loose coupling factor-group splitting can be neglected. The A_1 symmetric stretch would therefore be expected to give rise to two A modes and two B modes and the E, antisymmetric stretch, to four A modes and four B modes. Some of these modes give rise to bands of very similar frequencies and are not resolved but Ponsioen gives a complete assignment of the stretching vibrations.

The deformation modes and chlorine bridging vibrations occur in the complex of bands between $120cm^{-1}$ and $210cm^{-1}$ which were not assigned completely. However, bands at $200cm^{-1}$ and $130cm^{-1}$ were ascribed to the chlorine bridging vibrations in $TeCl_4$. In view of the differences in the spectra a direct comparison should be only tentative but bands in these regions are present in SCl_4.

There is one major similarity between the spectra of SCl_4 and its selenium and tellurium analogues and this concerns the large drop (~50cm^{-1}) in stretching frequencies between MCl_3^+ in Lewis acid complexes such as $MCl_3^+AlCl_4^-$ and MCl_3^+ in MCl_4. In the tellurium compounds this is paralleled by an increase in Te-Cl bond length in the $TeCl_3$ groups. This suggests that in SCl_4, whose stretching frequencies are some 50cm^{-1} lower than in $SCl_3^+AlCl_4^-$, the S-Cl bond length is significantly longer than in the Lewis acid complexes. It is therefore probable that chlorine bridging occurs in SCl_4.

George[28] suggests that in $SeCl_4$ the vibrational spectra do not exclude the presence of $SeCl_6^{2-}$ anions. The presence of SCl_6^{2-} in SCl_4 is considered unlikely as no other compounds containing SCl_6^{2-} are known to exist. An octahedral SCl_6^{2-} would be expected to exhibit bands at about 400 and 350cm^{-1} by comparison of the stretching frequencies of MCl_3^+ and MCl_6^{2-} (M=Se,Te). These areas are free of bands in SCl_4.

In summary the spectrum of SCl_4 can be assigned reasonably on the basis of $SCl_3^+Cl^-$ but there are problems in relation to some of the minor bands. The spectrum differs considerably from those of the selenium and tellurium analogues and the solid must therefore differ in structure from these selenium and tellurium compounds. The structure of SCl_4 is not amenable to solution by x-ray diffraction at the present time owing to the difficulties in growing single crystals of a hygroscopic compound that decomposes above -40°C. Similarly Raman polarisation data would resolve any doubts regarding the assignment of the stretching modes but decomposition of the compound when dissolved in many solvents precludes obtaining this data. There is obviously scope for further work on this compound.

CHAPTER 3

METHYLHALOSULPHONIUM CATIONS

3.1 INTRODUCTION

In Chapter 1 (Section 1.3) the literature relating to alkylhalosulphonium cations was reviewed, but in this work we are primarily concerned with the methylhalosulphonium species where the halogen is either chlorine or bromine. The general reactions considered are those between a mono- or disulphide and the halogen in the presence of a Lewis acid:

$$(CH_3)_2S + X_2 + MX_n \longrightarrow (CH_3)_2SX^+MX_{n+1}^-$$

$$CH_3SSCH_3 + 3X_2 + 2MX_n \longrightarrow 2CH_3SX_2{}^+MX_{n+1}^-$$

However, the reaction between a sulphide and a halogen is also considered in the absence of a conventional Lewis acid.

$$\begin{tikzcd} (CH_3)_2S + X_2 \arrow[r] \arrow[dr] & (CH_3)_2S\ {-}{-}{-}X_2 \\ & (CH_3)_2SX^+X^- \end{tikzcd}$$

Such a reaction might be expected to produce, by analogy with sulphur dichloride, an ionic complex. However, a molecular adduct could also be produced and the work of Baenziger[74] and others[71,73] in this respect is interesting.

An ion of the type $(CH_3)_2SX^+$ or $CH_3SX_2{}^+$ would be pyramidal with a sulphur lone pair of electrons occupying one sp^3 hybrid orbital. As described earlier the low frequency spectrum is most easily assigned by considering the methyl groups as point masses. The pyramidal ion is of C_s symmetry and the 6 normal modes of vibration would be expected to consist of 4A' and 2A" species, all of which would be both infra-red and Raman active. The vibrations of the methyl group occur as bands at about $3000cm^{-1}$ and $1400-1000cm^{-1}$ consisting of C-H stretching and deformation modes respectively. These bands have been ignored in this work as they contribute little to a knowledge of the complexes' structure and work has therefore been concentrated on the skeletal vibrations.

As in the work on the trihalosulphonium cations (Chapter 2) a knowledge of the bands associated with any anion used is necessary. A number of these ($SbCl_6^-$,$SbCl_5Br^-$ and AlX_4^-) have been listed (Chapter 2, Section 2.1). The only additional anions used in this section are the hexahalostannates and the Raman active frequencies of the bands associated with these ions are listed in Tables 3.1 and 3.2. The hexahalostannates, SnX_6^{2-}, would be expected to be octahedral in configuration and of O_h symmetry. The six normal modes of vibration would be the same as for $SbCl_6^-$ namely A_1,E_g,F_{2g} active in the Raman, F_{1u} active in the infra-red together with an inactive F_{2u} mode. It is interesting to note that the ν_5 (F_{2g}) mode appears to vary considerably in intensity depending on the cation and this has been

TABLE 3.1

RAMAN ACTIVE VIBRATIONAL FREQUENCIES (cm^{-1}) of $SnCl_6^{2-}$ and $SnBr_6^{2-}$

	ν_1 (A_{1g})	ν_2 (E_g)	ν_5 (F_{2g})	Reference
$SnCl_6^{2-}$	309(vs)	232(w)	159(vs)	148[1]
$SnCl_6^{2-}$	307(m)	242(m)	159(w)	159[2]
$SnBr_6^{2-}$	182(vs)	135(m)	101(s)	148[1]

1. Et_4N^+ salts
2. SCl_3^+ salt

TABLE 3.2

RAMAN ACTIVE VIBRATIONAL FREQUENCIES (cm^{-1}) of $SnCl_4Br_2{}^{2-}$ and $SnCl_2Br_4{}^{2-}$ 148

	M-Cl str.	M-Br str.	def.
$SnCl_4Br_2{}^{2-}$	304(vs)	204(s)	157(m)
	287(w)	180(m,br)	144(w,sh)
	264(m)		
	254(mw)		
$SnCl_2Br_4{}^{2-}$	298(s)	200(vs)	153(vw,sh)
	288(sh)	187(s)	
	260(m)		

Et_4N^+ salts

found to occur in the work reported in this Chapter.

The ion $SnX_4Y_2^{2-}$ could exist in either a cis configuration of C_{2v} symmetry or a trans configuration of D_{4h} symmetry. The latter configuration is centro-symmetric and should therefore give rise to no coincidences of Raman and infra-red bands. Clark[148] has described the infra-red and Raman spectra of these ions and although they were not completely assigned, largely because of experimental difficulties restricting the low frequency bands observed, a number of coincidences were found. It is therefore probable that $SnX_4Y_2^{2-}$ exists in the cis configuration (Table 3.2).

3.2 DIMETHYLHALOSULPHONIUM CATIONS

Initial work concentrated on the chloro compounds and although a number of references[60,61,62] refer to their preparation only infra-red spectroscopic data[63] have been reported. Details of the preparation of dimethylchlorosulphonium hexachloroantimonate, tetrachloroaluminate and the hexachlorostannate are given in the experimental section (Chapter 5). Essentially similar methods to those in the literature were used except that it was found preferable to use dichloromethane as solvent and low temperatures. The products (except the antimonate) were analysed for chloride and in view of the hydrolytic instability of the compounds the values are in satisfactory agreement with the calculated values. The spectra of the compounds are given in Table 3.3 and in Figures 3.1, 3.2 and 3.3. An ion of the type $(CH_3)_2SCl^+$ would be expected to be pyramidal of C_s symmetry and give rise to 6 Raman and 6 infra-red bands. The ion would also be isoelectronic with $(CH_3)_2PCl$ and an essentially similar spectrum would be expected. Table 3.4 summarises the low frequency Raman spectrum of liquid $(CH_3)_2PCl$ together with the assignment of the bands. The liquid data is quoted as, in the crystalline state, a dimer is formed giving rise to a large increase in the number of bands which would not be relevant for a comparison with

TABLE 3.3

DIMETHYLCHLOROSULPHONIUM RAMAN SPECTRA (cm^{-1})

$SbCl_6^-$ (Figure 3.1)	$AlCl_4^-$ (Figure 3.2)	$SnCl_6^{2-}$ (Figure 3.3)	Assignment
709(vw)	710(w)	713(w)	C-S asym. str.
666(w)	668(m)	672(m)	C-S sym. str.
529(m)	526(s)	524(s)	S-Cl str.
522(w,sh)		520(w,sh)	
	310(vw)		$AlCl_3$
	352(s)		$AlCl_4^-$
332(s)			$SbCl_6^-$
		308(m)	$SnCl_6^{2-}$
284(br,m)			$SbCl_6^-$
274(w,sh)	272(m)	278(w)	$(CH_3)_2S$ def.
250(w)	252(m)	255(w)	S-Cl def.
		233(m)	$SnCl_6^{2-}$
177(m)	182(m)	180(vvw)	$(CH_3)_2SCl$ def.
172(m)			$SbCl_6^-$
		162(m) 156(sh)	$SnCl_6^{2-}$
	125(m)		$AlCl_4^-$

Figure 3.1

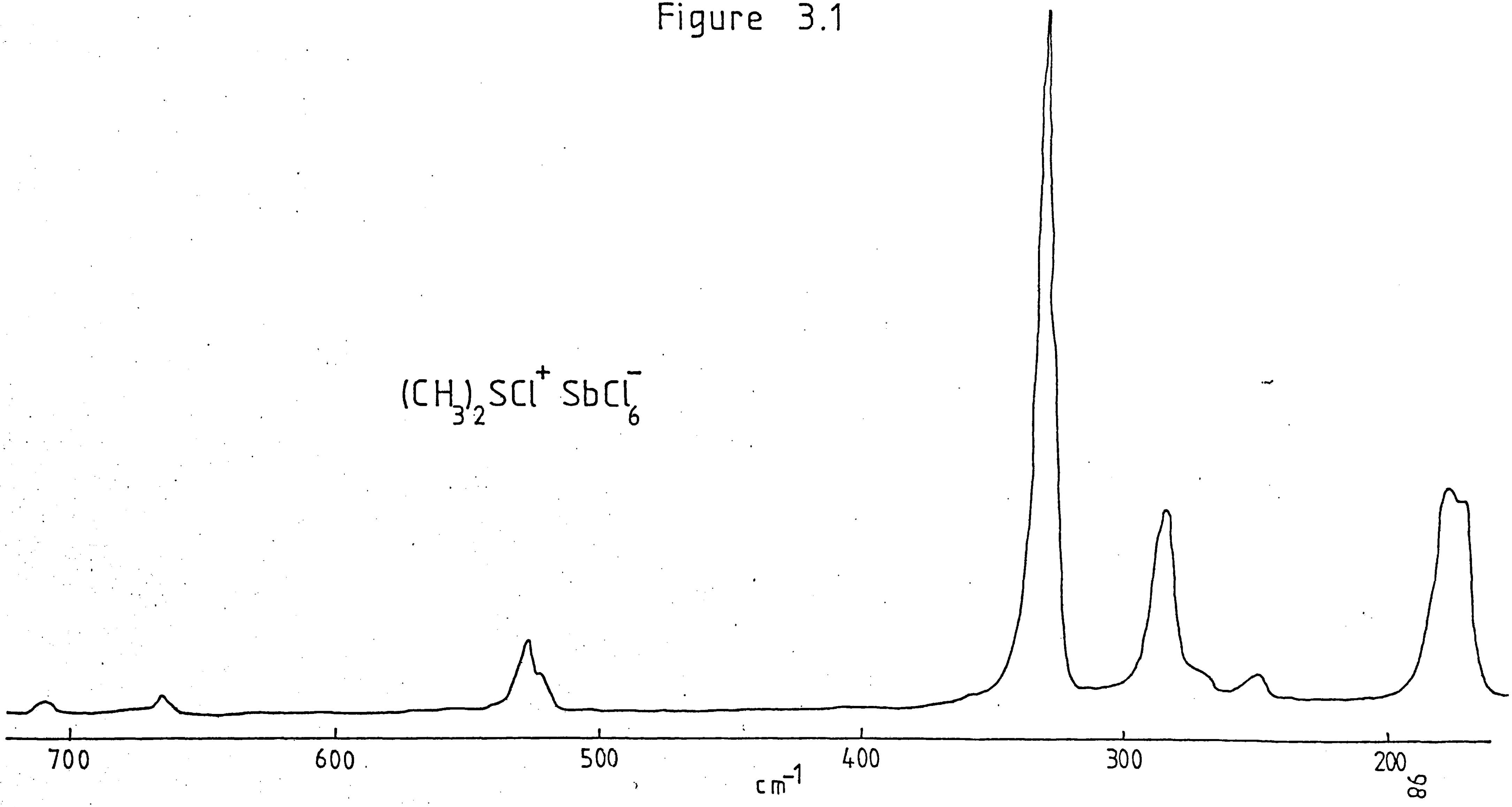
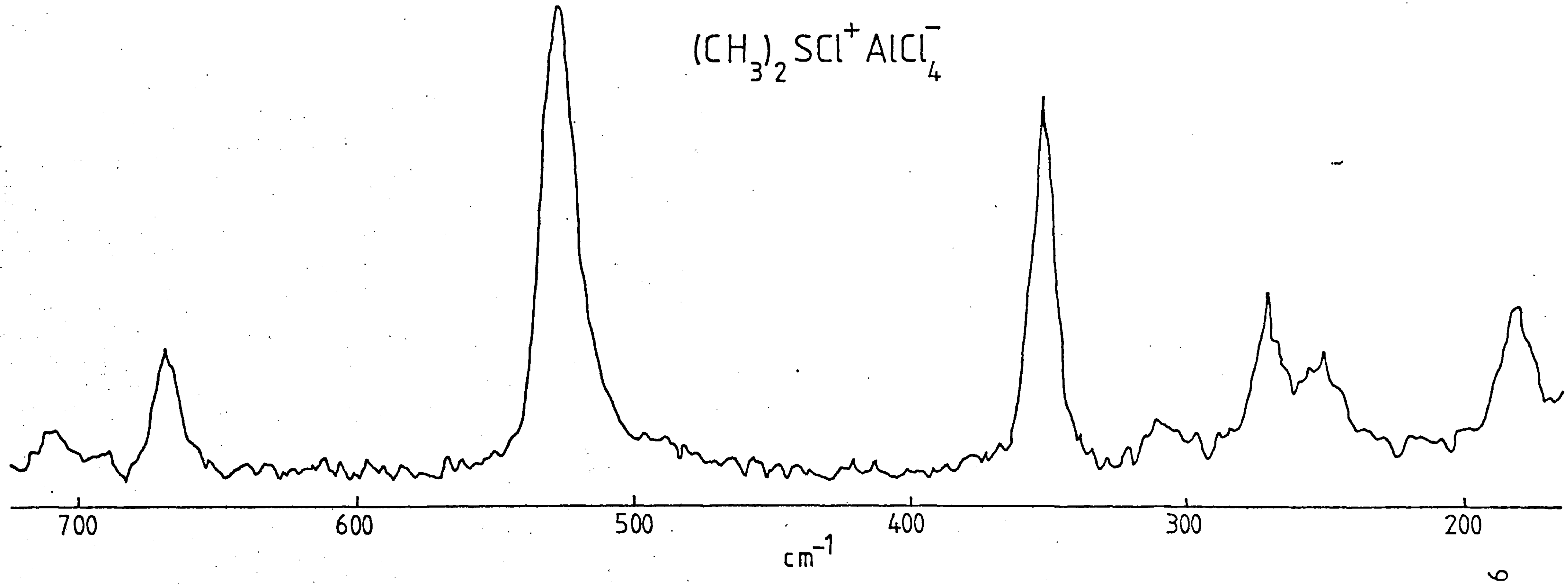


Figure 3.2



$(CH_3)_2SCl^+AlCl_4^-$

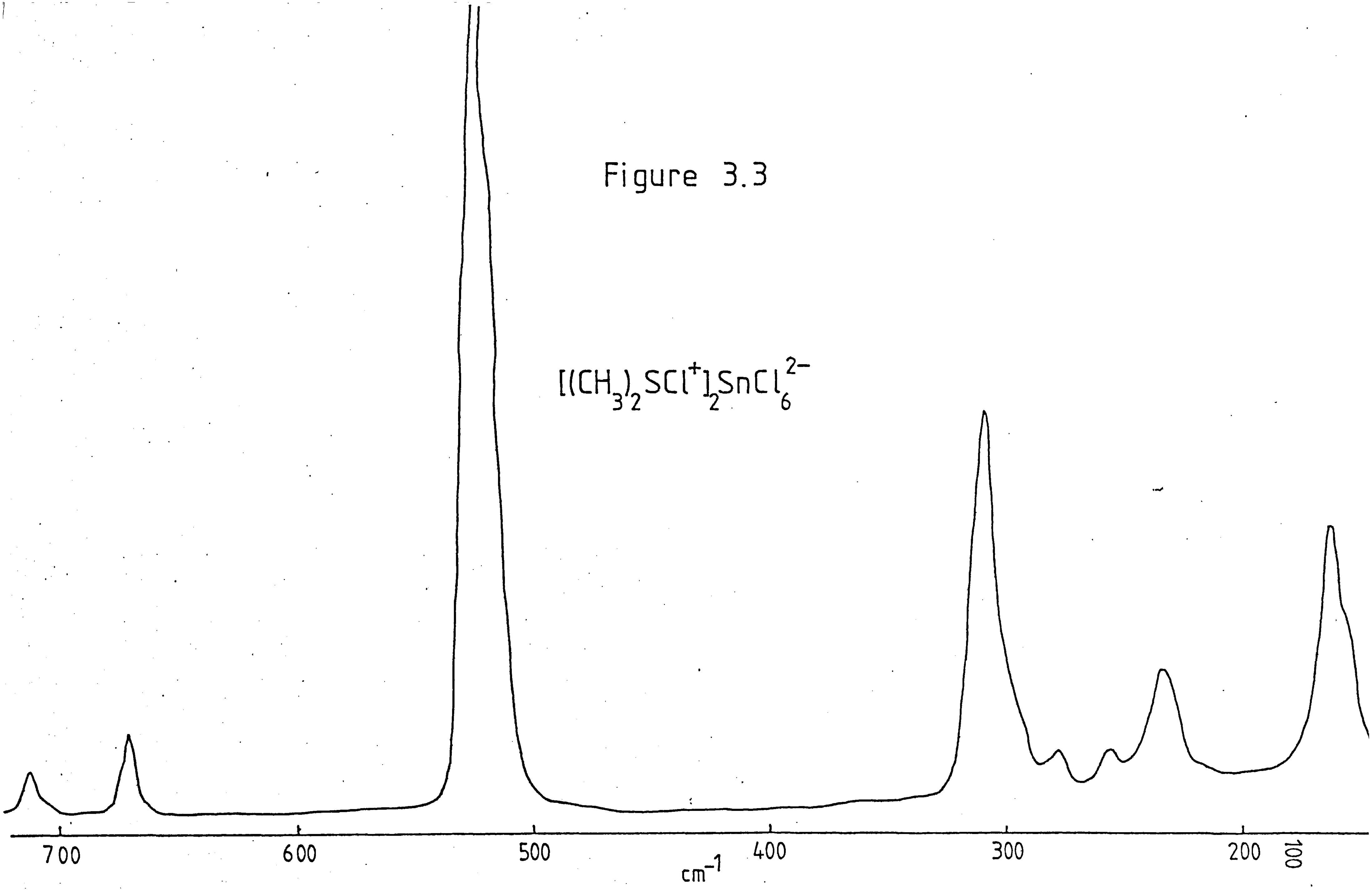


Figure 3.3

$[(CH_3)_2SCl^+]_2SnCl_6^{2-}$

TABLE 3.4

$(CH_3)_2PCl$ RAMAN BANDS $(cm^{-1})^{149}$

Liquid	Assignment
703(m)	CH_3-P asym. str.
674(s)	CH_3-P sym. str.
462(s)	P-Cl str.
301(m)	$(CH_3)_2P$ def.
247(m)	P-Cl sym. def.
233(w)	$(CH_3)_2PCl$ def.

$(CH_3)_2SCl^+$.

From the data given in Table 3.3 the bands due to the anions can readily be extracted with the use of quoted data (Tables 3.1, 2.1 and 2.3). There is also evidence of a very weak band at 310cm^{-1} in $(CH_3)_2SCl^+AlCl_4^-$ indicative of unreacted aluminium chloride. For both the hexachloro cations the low frequency F_{2g} mode may be (see later) split into a partially resolved doublet and the higher frequency E mode, although not obviously split, does show evidence of a shoulder in the case of the hexachloroantimonate, the high frequency strong band (A_1) is readily visible. The $AlCl_4^-$ ion shows the strong bands at 352cm^{-1} and 125cm^{-1} but the much weaker bands expected at 488cm^{-1} and 183cm^{-1} are not observed. There is however, a band in the spectrum of $(CH_3)_2SCl^+AlCl_4^-$ at 182cm^{-1} but this is relatively strong and is much stronger than would be expected for an $AlCl_4^-$ band (cf Figure 2.1, $SCl_3^+AlCl_4^-$).

The remaining bands are due to $(CH_3)_2SCl^+$ and similar bands are observed in each of the three spectra. The strong band at about 526cm^{-1} can be assigned primarily to the S-Cl stretching mode and shows evidence of possible splitting. As this is not a degenerate mode this is presumably due to factor group splitting described earlier. The two weak high frequency bands, about 710 and 668cm^{-1}, can be assigned to the symmetric and antisymmetric $(CH_3)_2S$ stretching modes. Both these bands are at essentially similar frequencies to the analogous bands in $(CH_3)_2PCl$. The bands at about $272cm^{-1}$ and $252cm^{-1}$, observed in each spectrum, can be assigned to two of the three expected deformation modes. By a comparison with the $(CH_3)_2PCl$ $(CH_3)_2P$ deformation at $301cm^{-1}$ and the $(CH_3)_2S$ in $(CH_3)_3S^+$ at $317cm^{-1}$ [70] it is suggested that the $272cm^{-1}$ band be assigned to this mode. The $252cm^{-1}$ band can be considered as an S-Cl symmetric deformation by comparison with the equivalent modes in $(CH_3)_2PCl$, $247cm^{-1}$ and PBr_2Cl, $197cm^{-1}$. The third deformation mode, the $(CH_3)_2SCl$ antisymmetric deformation occurs at $233cm^{-1}$ in $(CH_3)_2PCl$ and the most likely candidate is the band at $182cm^{-1}$. This relatively weak band is masked by the strong anion bands in this region for the $SbCl_6^-$ and $SnCl_6^{2-}$ complexes but is too strong in the $AlCl_4^-$ spectrum to be an $AlCl_4^-$ band. There is slight evidence for a band at $180cm^{-1}$ on the shoulder of the anion band in the $SnCl_6^{2-}$ spectrum but this is only really visible in an expanded spectrum. There is also evidence that the low frequency $SbCl_6^-$ band in these complexes may not be split (see below) and therefore the $177cm^{-1}$ band should be assigned to the $(CH_3)_2SCl^+$ deformation mode.

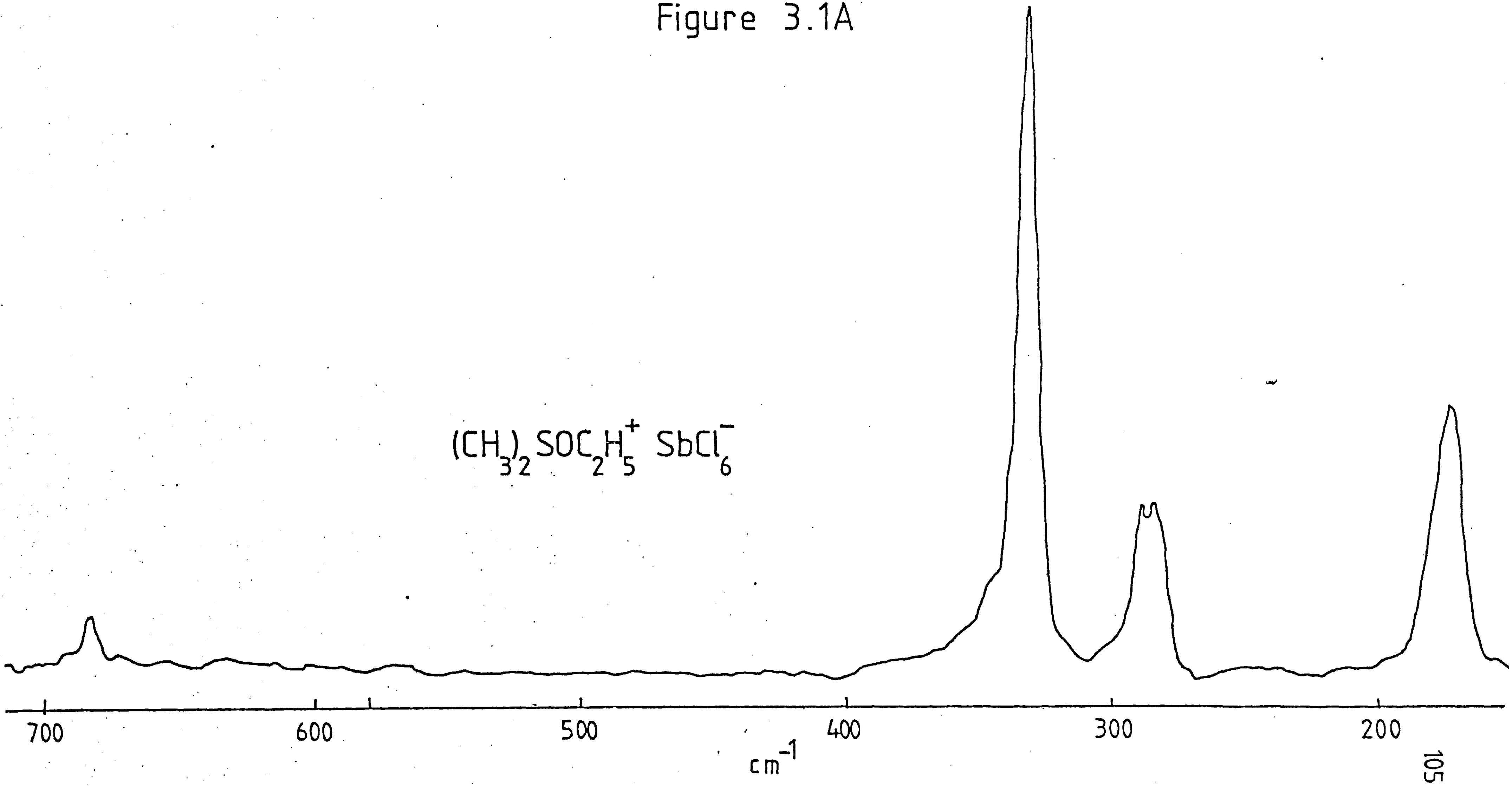
As an aid to the identification of the compound and the interpretation of the spectrum the product $(CH_3)_2SCl^+SbCl_6^-$ was warmed with absolute ethanol.

After removal of excess ethanol the brown viscous mass was recrystallized from a dichloroethane/ dichloromethane mixture to yield a white solid. The spectrum of this solid is given in Figure 3.1A and the bands listed below:-

$(CH_3)_2SOC_2H_5^+ SbCl_6^-$	Assignment
765(vw)	S-O str.
732(vw)	CH_3-S asym. str.
684(w)	CH_3-S sym. str.
331(s)	$SbCl_6^-$
290(m)	
284(m)	
173(m)	

If the alkoxy group has replaced the labile chlorine on the sulphur a compound formulated as $(CH_3)_2SOC_2H_5^+SbCl_6^-$ would be formed.[61,66] In such a complex the bands associated with S-Cl would be expected to be replaced by others associated with the $S\text{-}OC_2H_5$ group which would be expected to be very much weaker than the S-Cl bands and shifted to higher frequencies. There would of course be complications as a simple interpretation of the spectrum in terms of C_s symmetry would probably not then be valid. The high frequency infra-red spectra of these coupounds have been separately analysed by Warthmann[61,66] however, no data below $330cm^{-1}$ are available. The Raman spectrum detailed above shows no band at $529cm^{-1}$

Figure 3.1A



expected for an S-Cl stretching vibration. Also absent are bands at 274cm^{-1} and 250cm^{-1} assigned (Table 3.3) to the deformation modes of $(CH_3)_2SCl^+$. It is interesting that the low frequency $SbCl_6^-$ band is visible as a single band at 173cm^{-1} in this compound. It is therefore probable that the two bands seen in this area in $(CH_3)_2SCl^+SbCl_6^-$ should be assigned to $SbCl_6^-$ and the $(CH_3)_2SCl^+$ deformation. This is of course not definitive proof as crystal structure changes could lead to different splittings of the degenerate $SbCl_6^-$ mode in each compound but does provide support for the assignment of the $(CH_3)_2SCl^+$ deformation mode to a band in this area i.e. 177cm^{-1}. The spectrum of this compound therefore provides additional support for the assignment of the bands as indicated in Table 3.3.

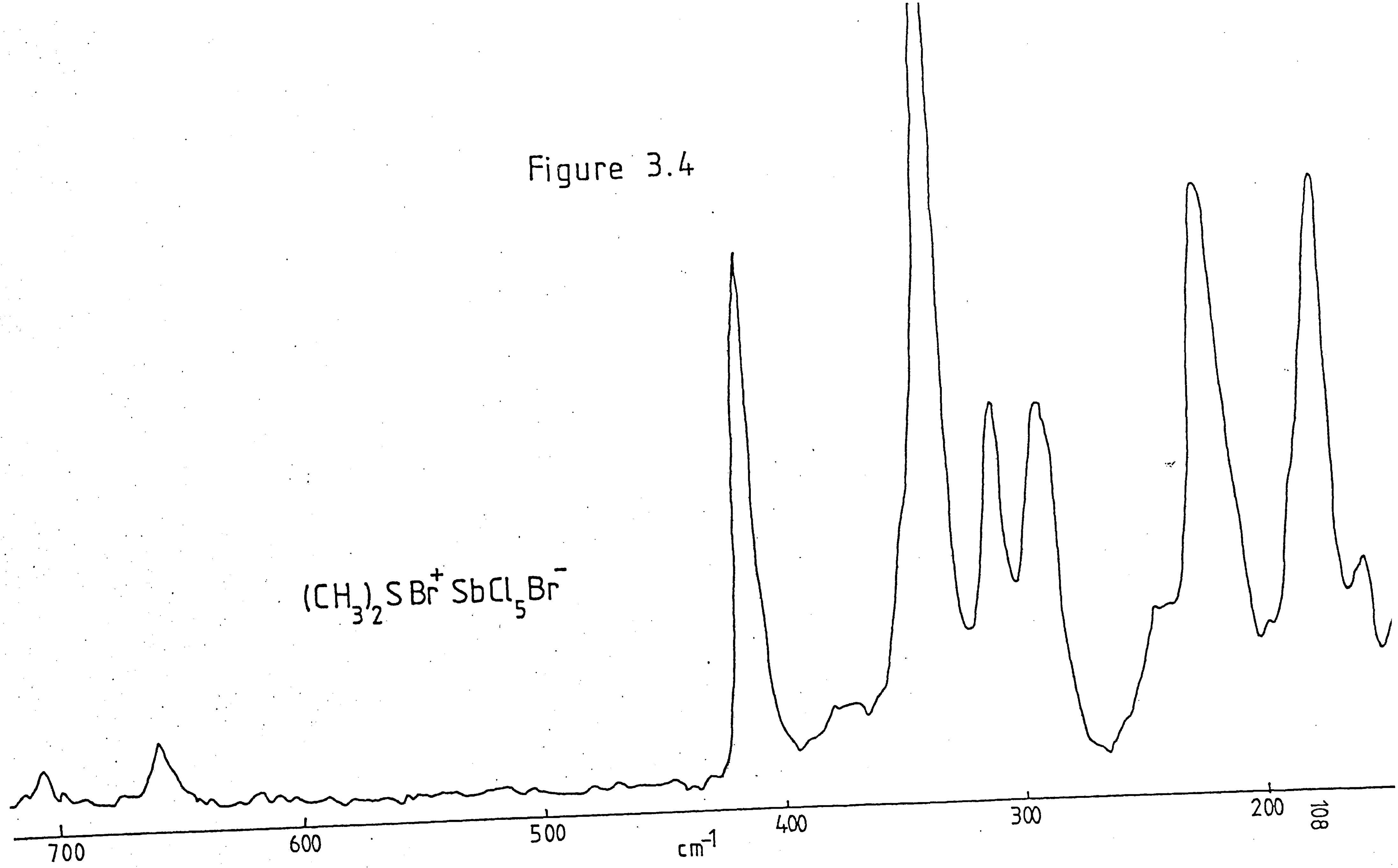
The work on the bromo analogues of the dimethylchlorosulphonium compounds was complicated by the hydrolytic instability of the complexes prepared. Most of these compounds are here reported for the first time. A reference does exist [62] to the preparation of an aluminum bromide adduct of dimethyl sulphide formulated as $(CH_3)_2SAlBr_3$ but no spectral details are quoted.

An attempt to prepare the hexachloroantimonate of the dimethylbromosulphonium cation failed. The product actually produced was the pentachlorobromoantimonate and no evidence in the spectrum exists for the presence of any S-Cl bonds because of the lack of bands at about 500cm^{-1} (Figure 3.4 and Table 3.7). The analytical data were also in excellent agreement for a product formulated as $(CH_3)_2SBr^+SbCl_5Br^-$. The lack of any S-Cl containing complex is at first sight surprising especially in the presence of a powerful chlorinating agent such as antimony pentachloride. In Chapter 2 it was noted that the reaction of sulphur monobromide, bromine and antimony pentachloride always yielded some S-Cl compounds and the difference in products when the sulphur halide is substituted by dimethyl sulphide is marked. Application of the Hard and Soft Acid and Base Principle to these reactions in fact supports the experimental findings. The reaction can be considered as follows:-

$$(CH_3)_2S + Br^+ \longrightarrow (CH_3)_2SBr^+$$

The "acid" is the bromo cation and can be considered as a soft acid. The dimethylsulphide base is also considered soft and therefore it is not surprising that the complex is formed. However it is really a competitive reaction between Cl^+ and Br^+ for the dimethylsulphide that shows why no S-Cl complexes are formed. The +I inductive effect of the methyl groups in dimethyl sulphide would suggest that it would be a softer base than the sulphur halide. The bromo cation would also be considered a softer base than the chloro cation and therefore on the basis of the HSAB Principle

Figure 3.4



the formation of $(CH_3)_2SBr^+$ should be favoured over $(CH_3)_2SCl^+$. This appears to be what is found in practice.

The preparation of the tetrabromoaluminate complex proved very difficult and full details are given in the experimental section (Chapter 5). The most successful products were those that produced a two phase system on addition of the aluminium bromide, which was solidified by cooling and a buff product obtained.

Two products were analysed but in each case the bromine level was slightly low and a small amount of chlorine was found in a product thought to contain only bromine. It was originally thought that this might have been due to contaminated analytical solutions or to impure aluminium bromide. On obtaining the same result, although at different chlorine levels, a second time the blanks were found to be zero, so the aluminium bromide was also analysed. This analysis showed the aluminium bromide to be essentially pure with no evidence for any chlorine. Although neither the bromine nor the dimethyl sulphide were analysed no problems were found with their use in other products and they were considered to be pure. The only other chloro compound used for the preparation of these products was the solvent, dichloromethane, It is not known how this solvent can enter into the reaction, it appears not to in other similar reactions (Section 3.3).

These reactions appear particularly sensitive to solvent effects and over a period the best solvents for production of the present products were discovered by trial and error. In general they are chloro compounds and there would appear to be little point in substituting dichloromethane for another chlorinated solvent. An attempt was however made to use hexane, but no product was obtained. The hexane was therefore removed and substituted by acetonitrile but the only product obtained was the dimethyl sulphide/bromine adduct.

It should however, be noted that the spectra show no evidence for the presence of any S-Cl bands at about 520cm^{-1} but they may not be observable at the low levels indicated by the analyses.

In spite of the unsatisfactory analysis of these products the spectra (Figures 3.5, 3.6 and Table 3.5) did show some bands expected for $SBr_3{}^+AlBr_4{}^-$. However, a comparison of the two spectra shows that the 404/407cm^{-1} band varies in intensity and this variation was found in all the spectra produced. This suggests the product is a mixture and the presence of unreacted aluminium bromide can be seen as the 210cm^{-1} band. The high frequency bands(708cm^{-1}, 666cm^{-1}) may be assigned to C-S symmetric and antisymmetric stretching modes but cannot be due to free dimethyl sulphide as these bands occur at 743 and 692cm^{-1} in this compound.[150]

The band at 407cm^{-1} is probably an S-Br

TABLE 3.5

TETRAHALOALUMINATE SPECTRA

Figure 3.5	Figure 3.6	Figure 3.7	Assignment
710(vw)	708(w)	710(vvw)	$(CH_3)_2S$ asym.
663(w)	666(w)	662(w)	$(CH_3)_2S$ sym.
404(m)	407(s)	410(w)	S-Br
374(s)	373(s)		
		378(vs)	
365(s)	365(s)		
		369(vs)	
		306(w)	$AlCl_3$
	292(w)		
241(w,sh)	240(w,sh)		
230(m,br)	230(m,br)	228(m)	
212(m)	210(s)		$AlBr_3$
116(w)	116(w)		
		83(m)	
		70(m)	

Figure 3.5

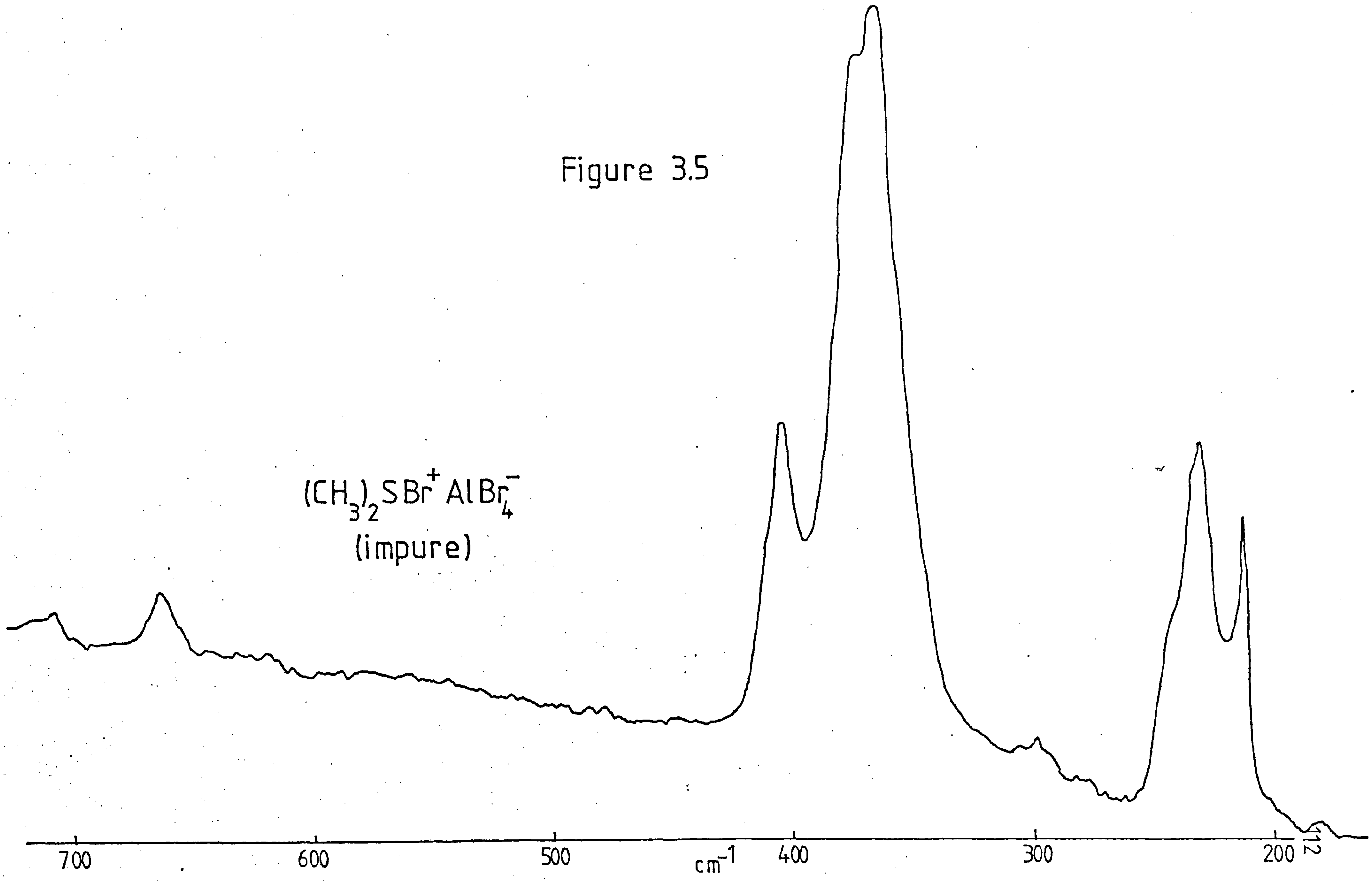
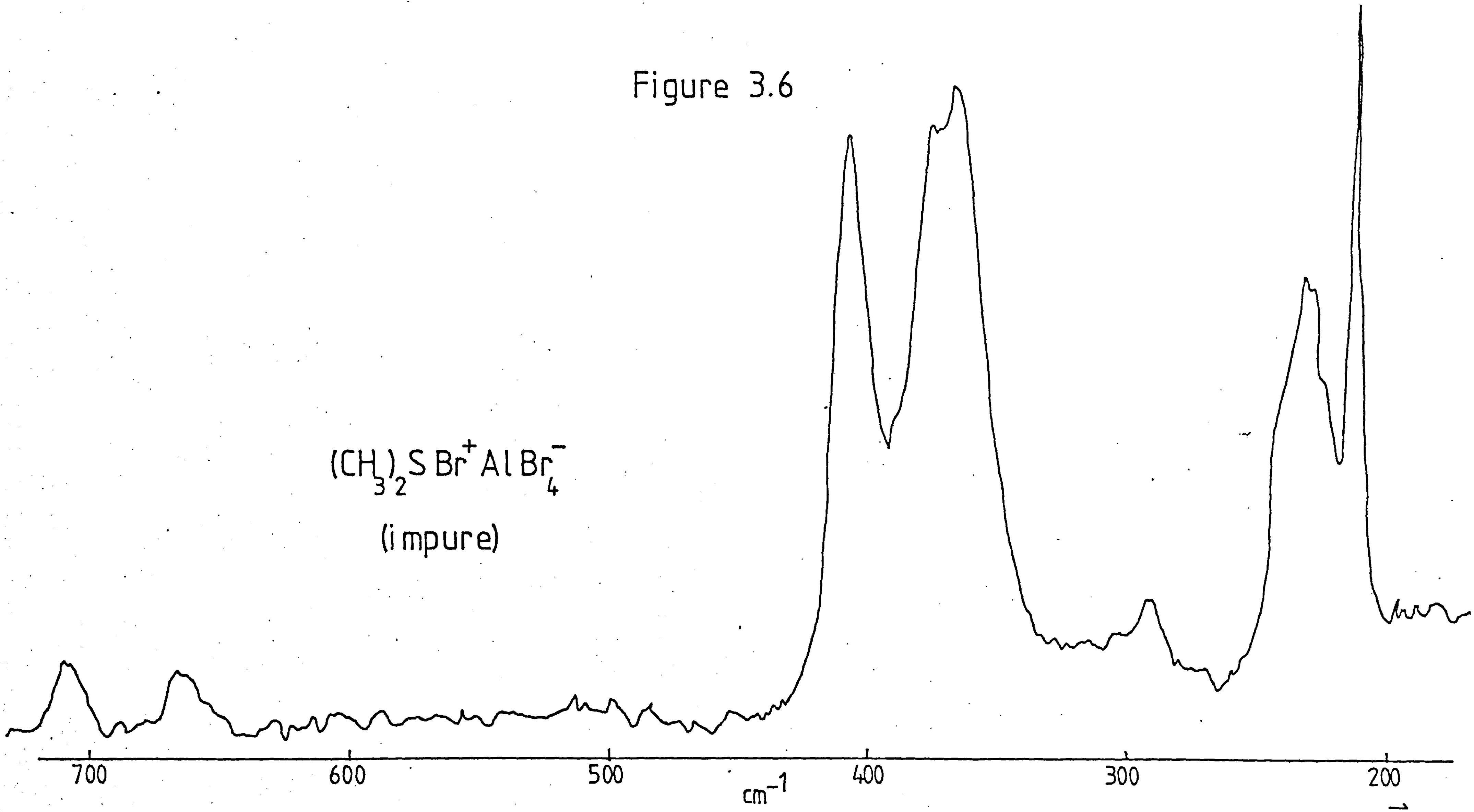


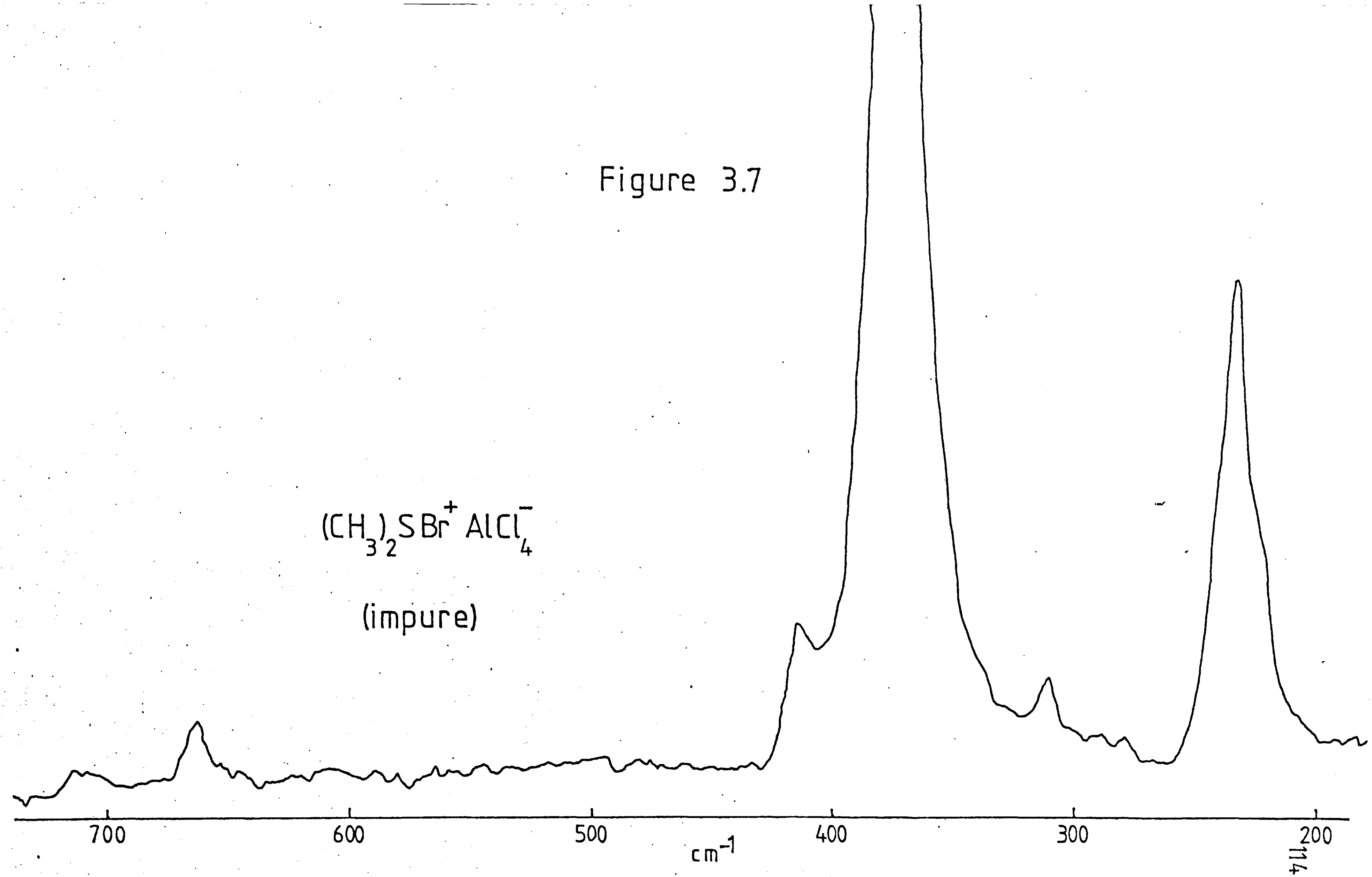
Figure 3.6



$(CH_3)_2SBr^+AlBr_4^-$

(impure)

Figure 3.7



$(CH_3)_2SBr^+ AlCl_4^-$

(impure)

stretching mode on the basis of its strength and position (Table 3.5). The broad band around 370cm^{-1} consisted of two unresolved bands at 373cm^{-1} and 365cm^{-1}. The former may be associated with the 407cm^{-1} band (See Figure 3.9, and discussion on $SnBr_6^{2-}$ products) although when the higher frequency band is weak (Figure 3.5) there still appears to be a strong band at the low frequency . These spectra obviously do not resolve whether or not these bands are associated. However, this leaves the broad bands at about 365cm^{-1} and 230cm^{-1} unassigned. The former is a very intense band and from its position it has to be assigned to an S-Br stretching mode. In $SCl_3^+Cl^-$ the S-Cl stretching modes were reduced in frequency by some 50cm^{-1} when the anion changed from a Lewis acid derivative to Cl^-. It is suggested that a similar drop for S-Br from 413cm^{-1} in $SBr_3^+SbCl_5Br^-$ would lead to an S-Br frequency of about 360cm^{-1} for S-Br in $SBr_3^+Br^-$. This is very close to the observed and unassigned high frequency mode in the spectra under discussion.

In section 3.4 the preparation of the hitherto unknown $(CH_3)_2SBr^+Br^-$ will be suggested and it was found that intense bands at 346cm^{-1} and 232cm^{-1} were observed in the Raman. These correspond in frequency with both the unassigned bands in these spectra although it should be noted that the bands under discussion are much broader than those observed in the spectra of Section 3.4, and the high frequency band occurs some 20cm^{-1} lower in frequency.

The preparative method used, i.e. the separation of a separate layer and freezing, could also lend support to the existence of $(CH_3)_2SBr^+Br^-$ because the authentic product (Section 3.4) was prepared in an ionizing solvent. It is possible that the separate layer in these preparations could consist of a concentrated solution of aluminium bromide in dichloromethane. Such a solvent would be expected to promote production of an ionic compound.

Overall it is suggested that most of the products prepared by the reaction of dimethyl sulphide, bromine and aluminium bromide contain free aluminium bromide, $(CH_3)_2SBr^+Br^-$ as well as $(CH_3)_2SBr^+AlBr_4^-$.

One product was prepared from dimethyl sulphide, bromine and aluminium chloride in an exactly analogus manner to that used for the aluminium bromide products. However, no second phase separated and the preparation appeared to proceed normally. The spectrum is given in Figure 3.7 and it shows a remarkable similarity to that found for the aluminium bromide products. The analysis of this product shows very poor agreement with the calculated values for $(CH_3)_2SBr^+AlCl_4^-$ although much better agreement with $(CH_3)_2SBr^+AlCl_3Br^-$. However, the latter is discounted because although a weak $310cm^{-1}$ band is present in the spectrum in the correct position for $AlCl_3Br^-$ it is very weak. No other products have shown mixed tetrahaloaluminates and they would not be expected on the HSAB Principle. The remainder of the spectrum is also inconsistent with such a proposal.

It is suggested that the product consists of a mixture of $(CH_3)_2SBr^+AlCl_4^-$ and $(CH_3)_2SBr^+Br^-$ as for the analogous products discussed above. A 60%:40% mixture of these two products would give a halide analysis very close to that actually found.

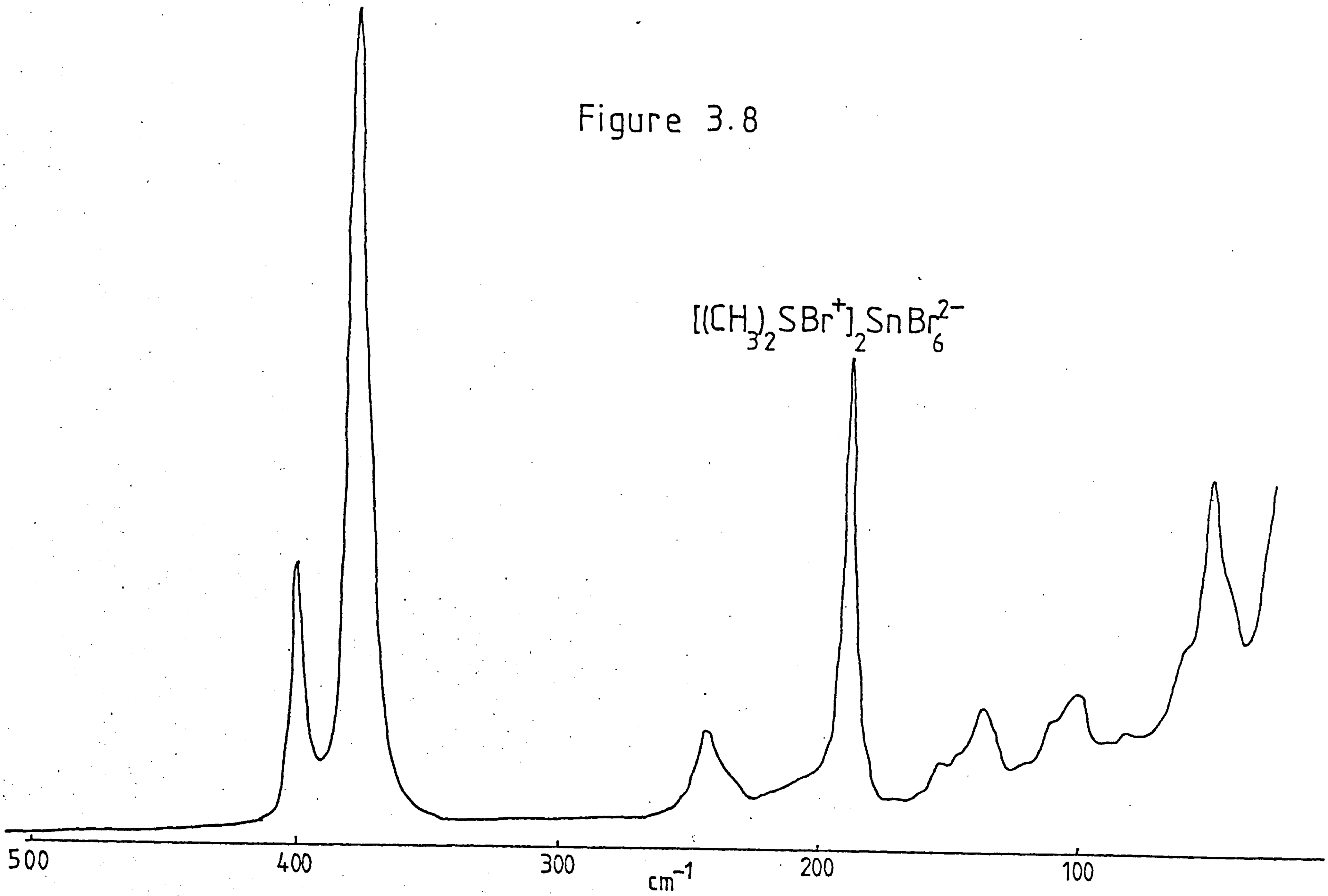
Found:	Br 44.9% Cl 27·4%
Calculated:	
60% $(CH_3)_2SBr^+$ $AlCl_4^-$) 40% $(CH_3)_2SBr^+Br^-$)	Br 44·3% Cl 27·4%

The spectrum is also not inconsistent with this mixture although it is recognised that the anion bands are hidden by the broad strong 370cm^{-1} band. The weak 310cm^{-1} band in this case could be attributed to free aluminium chloride as has been found for other products.

The preparation of the hexabromostannate (Chapter 5, Section 5.6) using the normal procedure gave a yellow solid whose spectrum (Figure 3.8 and Table 3.7) was consistent with the formulation $[(CH_3)_2SBr^+]_2$ $SnBr_6^{2-}$. However, the S-Br band is split by 23cm^{-1}, which is fairly large, and this mode is not degenerate.

The preparation was therefore repeated but with both a higher and a lower bromine level to see if the

Figure 3.8



same compound was produced. These spectra were however very different, and different from that given in Figure 3.8. It was thought that these differences could have been due to the reaction time which had been reduced somewhat due to the apparent lack of reaction throughout the reaction period. A preparation was therefore run exactly as for the successful product but with a reaction time of less than 30 minutes. This product produced an abnormal spectrum. A repeat but using a two hour reaction time and 1 hour addition time yielded a product that gave an identical spectrum to that first obtained.

The spectrum obtained (Figure 3.9) from the first reaction with high bromine level (Table 3.6) shows bands at 406 and 376cm^{-1} possibly indicative of $[SBr_3^+]_2\ SnBr_6^{2-}$ although the frequencies are a little higher than in the pure product and are reversed in intensity. The other band present in this area (368cm^{-1}) must also be assigned to S-Br in view of its position and intensity. It is noticeable that only two bands in the 700cm^{-1} region are visible indicating only one type of $(CH_3)_2S$- grouping and no free $(CH_3)_2S$ as the frequencies are too low ($(CH_3)_2S$ 743cm^{-1} + 692cm^{-1}).

The very strong broad band at about 280cm^{-1} is probably due to bromine associated in a molecular complex with dimethyl sulphide. (See Section 3.4).

The anions that must be associated with the cations are difficult to detect from the spectra. The

TABLE 3.6

HEXABROMOSTANNATE RAMAN SPECTRA (cm^{-1})

Figure 3.9	Figure 3.10	Assignment
	730(vvw)	$(CH_3)_2S$ asym.
710(vw)	707(vw)	$(CH_3)_2S$ asym.
	680(w)	$(CH_3)_2S$ sym.
664(w)	661(w)	$(CH_3)_2S$ sym.
406(s)		S-Br
	394(s)	
376(s)		
	370(br)	
368(s)		
280(vvs)		$(CH_3)_2S:Br_2$
	275(m)	
244(w)	241(w)	
208(w)		
	192(m)	$(CH_3)_2S:SnBr_4$
183(s)		
	153(w)	$(CH_3)_2S:SnBr_4$
140(s)		
106(w)	108(w)	

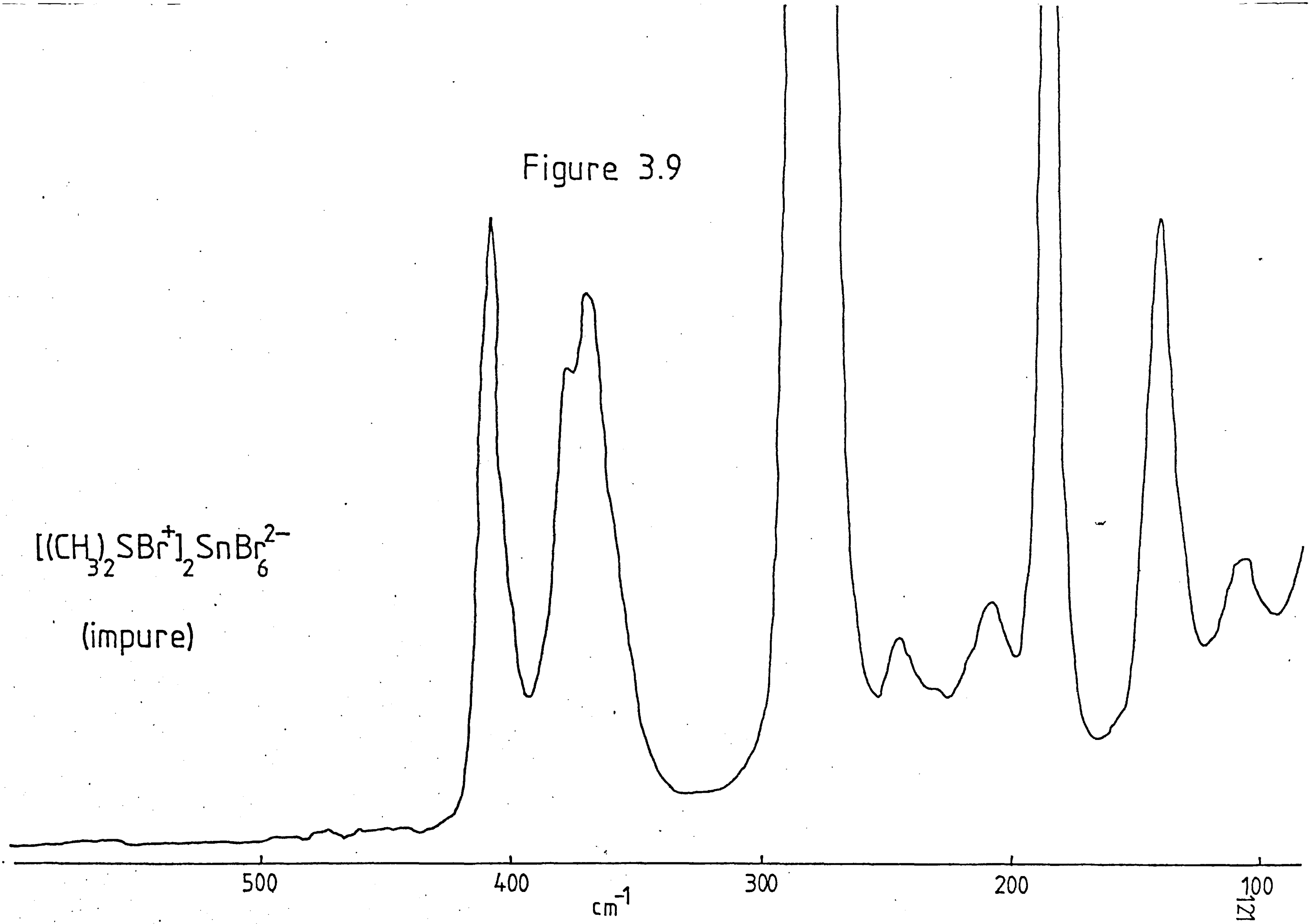
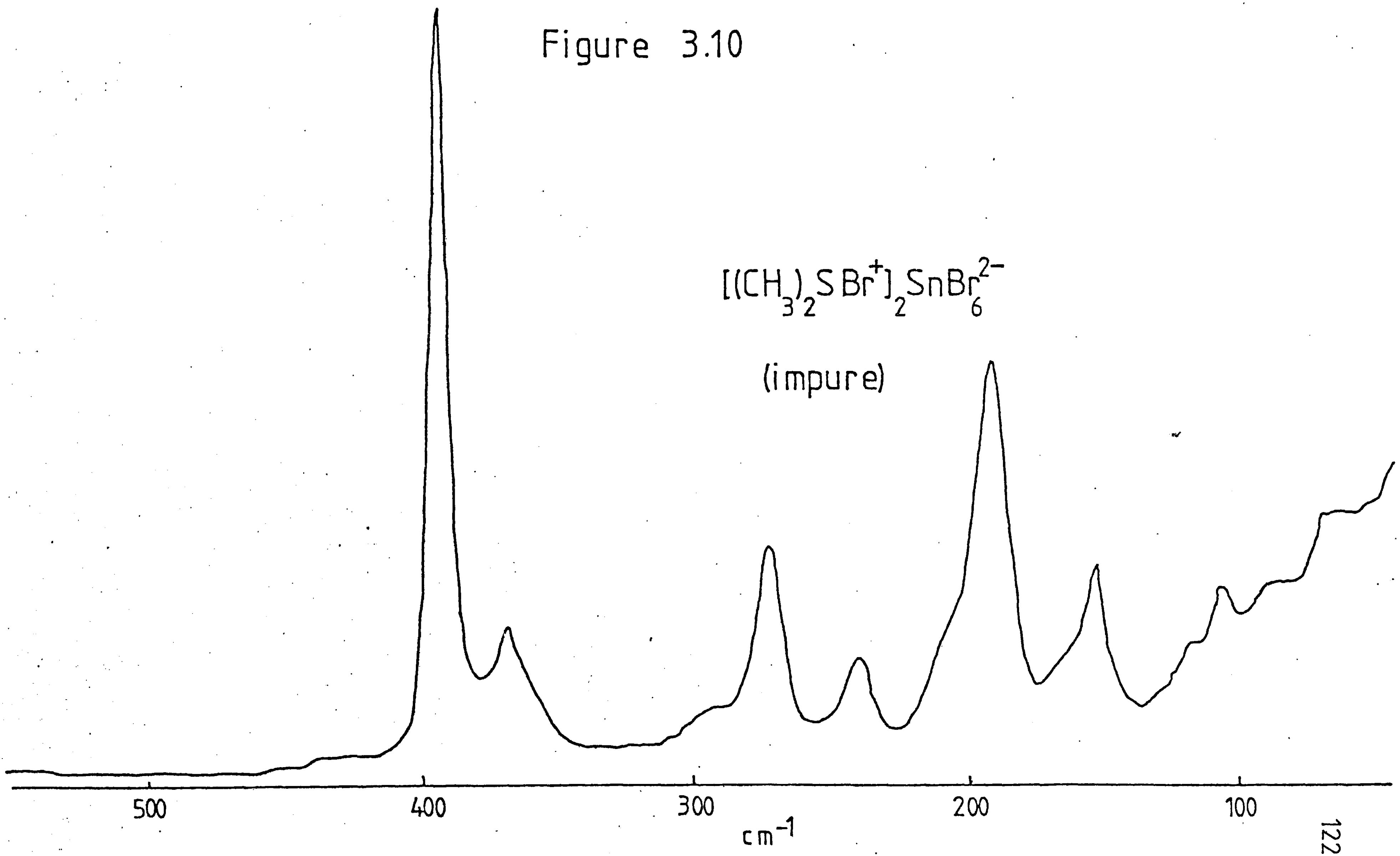


Figure 3.9

$[(CH_3)_2SBr^+]_2SnBr_6^{2-}$

(impure)

Figure 3.10



$[(CH_3)_2SBr^+]_2SnBr_6^{2-}$

(impure)

product of Figure 3.9 was washed with solvent and a new spectrum run. This showed decreased bands at 406, 376 and 183cm^{-1} indicating that these are associated. The 406/378 doublet could be due to S-Br in $[(CH_3)_2SBr^+]_2SnBr_6^{2-}$ (cf figure 3.8) although the intensities are reversed. It is possible that they are due to S-Br in $(CH_3)_2SBr^+Br_3^-$, the Br_3^- band occurring at 183cm^{-1} (Table 1.1, Chapter 1). It is then possible that the 368cm^{-1} band could be S-Br associated with a Br^- anion which would not be seen in these spectra. However, the S-Br frequency in $(CH_3)_2SBr^+Br^-$ occurs at 347cm^{-1} (Section 3.4) some 20cm^{-1} lower than in that spectrum given in Figure 3.9 There is also a strong band at 232cm^{-1} in $(CH_3)_2SBr^+Br^-$ which is absent in this spectrum.

The S-Br bands in these spectra show a remarkable resemblance to those in the tetrahaloaluminates discussed earlier (Figures 3.6 and 3.7). However, the band at 230cm^{-1} present in the aluminate spectra appears to be absent in the later spectra although the broad complex at 200-260cm^{-1} may hide the relatively weak 230cm^{-1} band. Equally the strong 183cm^{-1} band is absent in the aluminate spectra. It is largely on this very tentative evidence that the 407/373cm^{-1} bands are attributed in one case to $(CH_3)_2SBr^+AlBr_4^-$ and the other to $(CH_3)_2SBr^+Br_3^-$.

The spectrum given by the rapid reaction of the reactants that produced the product $[(CH_3)_2SBr^+]_2SnBr_62-$

was very noisy and showed a broad complex band centred on 368cm^{-1} with weak bands at 181/187, 240cm^{-1} and 398cm^{-1}. It is possible that this complex is primarily due to S-Br associated with various anions, probably bromine derived, before the reaction to form the hexabromo species could occur.

The spectrum formed in the presence of a limited quantity of bromine shows (Figure 3.10) a complex of high frequency bands indicating at least two types of $(CH_3)_2S$- species. There is evidence of a $(CH_3)_2S:SnBr_4$ molecular complex from the broad bands at about 190cm^{-1} and 152cm^{-1}, which accounts for one set of $(CH_3)_2S$- bands. The other is presumbaly associated with the strong S-Br band observed at 394cm^{-1}. The anion associated with this cation is unknown. If it were Br^- one would expect the S-Br frequency to be rather lower. A Br_3^- anion is unlikely in view of the low bromine level. It is possible that $SnBr_5^-$ exists as the anion but there is no strong band at 202cm^{-1} expected for such an anion.[109] The hexabromostannate, $SnBr_6^{2-}$, could exist as its characteristic frequencies are hidden by other bands. However, the S-Br band would then be expected at 400/377cm^{-1}. It is however suggested that possibly due to the presence of the $(CH_3)_2:SnBr_4$ complex a different crystal structure is present leading to only the single S-Br frequency expected. In theory only a single S-Br band should be expected for $(CH_3)_2SBr^+$ and it is probably a result of factor group splitting in the case of the pure product that gives the doublet.

Obviously further work on these spectra, which probably contain mixtures of species, would be necessary before they could be completely assigned.

An attempt was made to prepare complexes using the Lewis acids antimony tribromide, titanium tetrabromide and boron tribromide. However in all cases no products were obtained.

From these bromo spectra two products can be taken as providing spectra of pure complexes i.e. $(CH_3)_2SBr^+SbCl_5Br^-$ and $[(CH_3)_2SBr^+]_2\ SnBr_6^{2-}$. From the spectrum of $(CH_3)_2SBr^+AlBr_4^-$ it is possible to abstract bands that are probably due to the $(CH_3)_2SBr^+$ ion. These spectra are tabulated in Table 3.7.

It would have been helpful to compare these spectra with those of the anologous isoelectronic phosphorus compound, $(CH_3)_2PBr$. However, no low frequency Raman or infra-red spectra appear to have been recorded in the literature.

By analogy with the chloro compound described earlier, $(CH_3)_2SBr^+$ would be expected to be of C_s symmetry giving 6 Raman bands. From the data in Table 3.7 the anion bands can be extracted using data quoted in Tables 2.2, 2.3 and 3.1. Similar bands can then be observed in each of the spectra and may be assigned to $(CH_3)_2SBr^+$. The two high frequency bands are readily assigned to the C-S symmetric and

TABLE 3.7

DIMETHYLBROMOSULPHONIUM RAMAN SPECTRA (cm^{-1})

$SbCl_5Br^-$ (Figure 3.4)	$SnBr_6^{2-}$ (Figure 3.8)	$AlBr_4^{-*}$ (Figure 3.6)	Assignment
706(vw)	710(vw)	708(vw)	C-S asym. str.
660(w)	665(w)	666(w)	C-S sym. str.
413(s)	400(m)	407(s)	S-Br str.
	377(vs)	373(s)	
334(vs))			)
308(m))			) $SbCl_5Br^-$
290(m))			)
240(sh)	242(m)	240(sh)	$(CH_3)_2S$ def.
222(m)			$SbCl_5Br^-$
185(sh)			S-Br def.
	187(s)		$SnBr_6^{2-}$
174(m))			)
156(w))			) $SbCl_5Br^-$
	154(vw)		
143(w)	144(wsh)		$(CH_3)_2SBr$ def.
	136(m)		$SnBr_6^{2-}$
	111(sh)		
	100(w)		$SnBr_6^{2-}$
	81(vvw)		
	48(m)		

* bands abstracted from Figure 3.6

antisymmetric stretching modes and are very similar to those observed in the chloro compound. The S-Br stretching mode is seen as a strong emission at around 400cm^{-1}. In the case of the $SbCl_5Br^-$ spectrum this mode occurs as a single band at 413cm^{-1} whereas in the $SnBr_6^{2-}$ spectrum a doublet occurs at 400cm^{-1} and 377cm^{-1}. This spectrum is repeatable and therefore the S-Br emission has to be assigned to these two bands even though the split is relatively large and this mode would not be expected to be degenerate. Presumably this split must be due to factor group splitting and was also observed for the S-Cl band in $(CH_3)_2SCl^+$ (Table 3.3) The large split is supported by the $AlBr_4^-$ spectra where similar bands can be seen. It is interesting in this respect to compare the split S-Br band in $[(CH_3)_2SBr^+]_2\ SnBr_6^{2-}$ with the similar band in $[(CH_3)_2SBr^+]_2\ SnCl_6^{2-}$, discussed later, where it occurs as a singlet at about 415cm^{-1}.

The $(CH_3)_2S$ deformation mode occurs at about 272cm^{-1} in $(CH_3)_2SCl^+$ and a similar band is observed at about 242cm^{-1} in the spectra detailed in Table 3.7 which can be assigned to that mode reduced in frequency by some S-Br coupling.

The other deformation modes are difficult to assign owing to the many low frequency anion bands and the poor $AlBr_4^-$ spectrum. There is a weak band in the $SbCl_5Br^-$ spectrum at 143cm^{-1} which corresponds to bands at 154 and 144cm^{-1} in the $SnBr_6^{2-}$ spectrum.

The antisymmetric deformation mode occurs in $PBrCl_2$ at $149cm^{-1}$ and it is likely that the $143cm^{-1}$ band can be assigned to this mode in $(CH_3)_2SBr^+$. This vibration should be the lowest frequency in these spectra and for the $SbCl_5Br^-$ spectrum no bands occur below $143cm^{-1}$ with the exception of a very weak, doubtful, shoulder at $120cm^{-1}$ and a lattice band at $64cm^{-1}$. This supports the assignment of the $143cm^{-1}$ band to the $(CH_3)_2SBr$ antisymmetric deformation mode. The higher frequency S-Br deformation occurs at $167cm^{-1}$ in $PBrCl_2$ and about $180cm^{-1}$ in $SBrCl_2^+$ (Table 2.10) but there are no obvious bands in this area in the spectra summarised in Table 3.7. However, the $174cm^{-1}$ $SbCl_5Br^-$ band has a shoulder on the high frequency side at $185cm^{-1}$. In the $SnBr_6^{2-}$ spectrum this region is obscured by the anion band but it is neverthless suggested that the S-Br deformation mode be assigned to the $185cm^{-1}$ band.

In each of the above cases attempts were made to eliminate as far as possible the formation of mixed halo species giving rise to complex spectra. However, two products were prepared using tin tetrabromide with chlorine, or vice versa. The preparative details are given in Chapter 5 (Section 5.6) with the spectra illustrated in figures 3.11 and 3.12 and the frequencies listed in Table 3.8.

The reaction with tin tetrabromide was carried out in liquid chlorine and necessitated a slow reaction. The product obtained gave a Raman spectrum that obviously

TABLE 3.8

MIXED DIMETHYLHALOSULPHONIUM HEXAHALOSTANNATE

RAMAN SPECTRA (cm^{-1})

Figure 3.11	Figure 3.12	Assignment
712(w)	709(w)	C-S asym. str.
673(w)	665(w)	C-S sym. str.
525(s)		S-Cl str.
520(sh)		
415(s)		S-Br str.
410(sh)		
	401(s)	
	394(vs)	
	382(s)	
	312(w)	
310(m)		$SnCl_6^{2-}$
	289(w)	
280(w)		$(CH_3)_2S$ def.
	270(w)	
257(w)		S-Cl def.
	244(m)	
233(m)		$SnCl_6^{2-}$
	204(w)	
	194(w)	
163(m)		$SnCl_6^{2-}$
	153(m)	

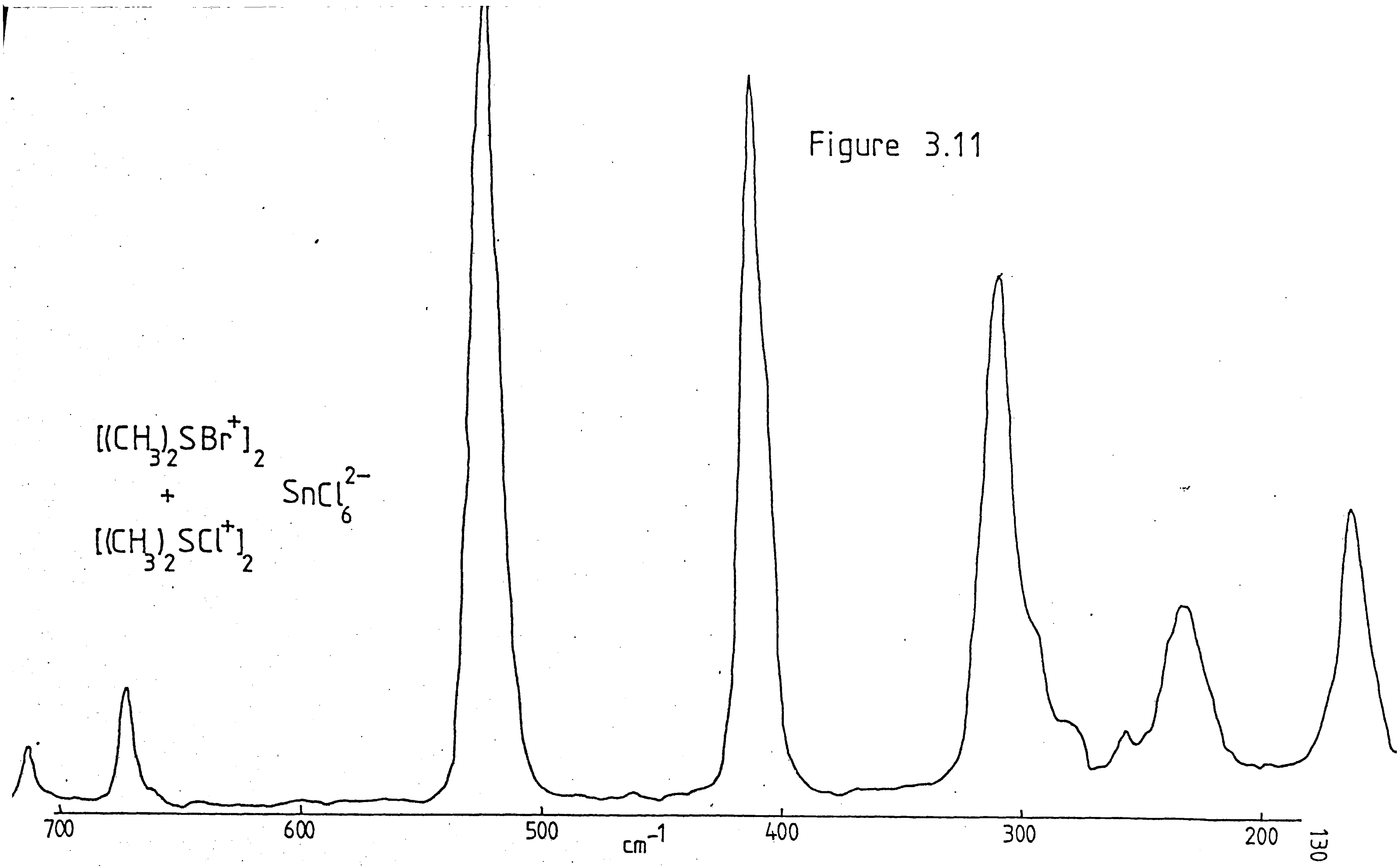


Figure 3.11

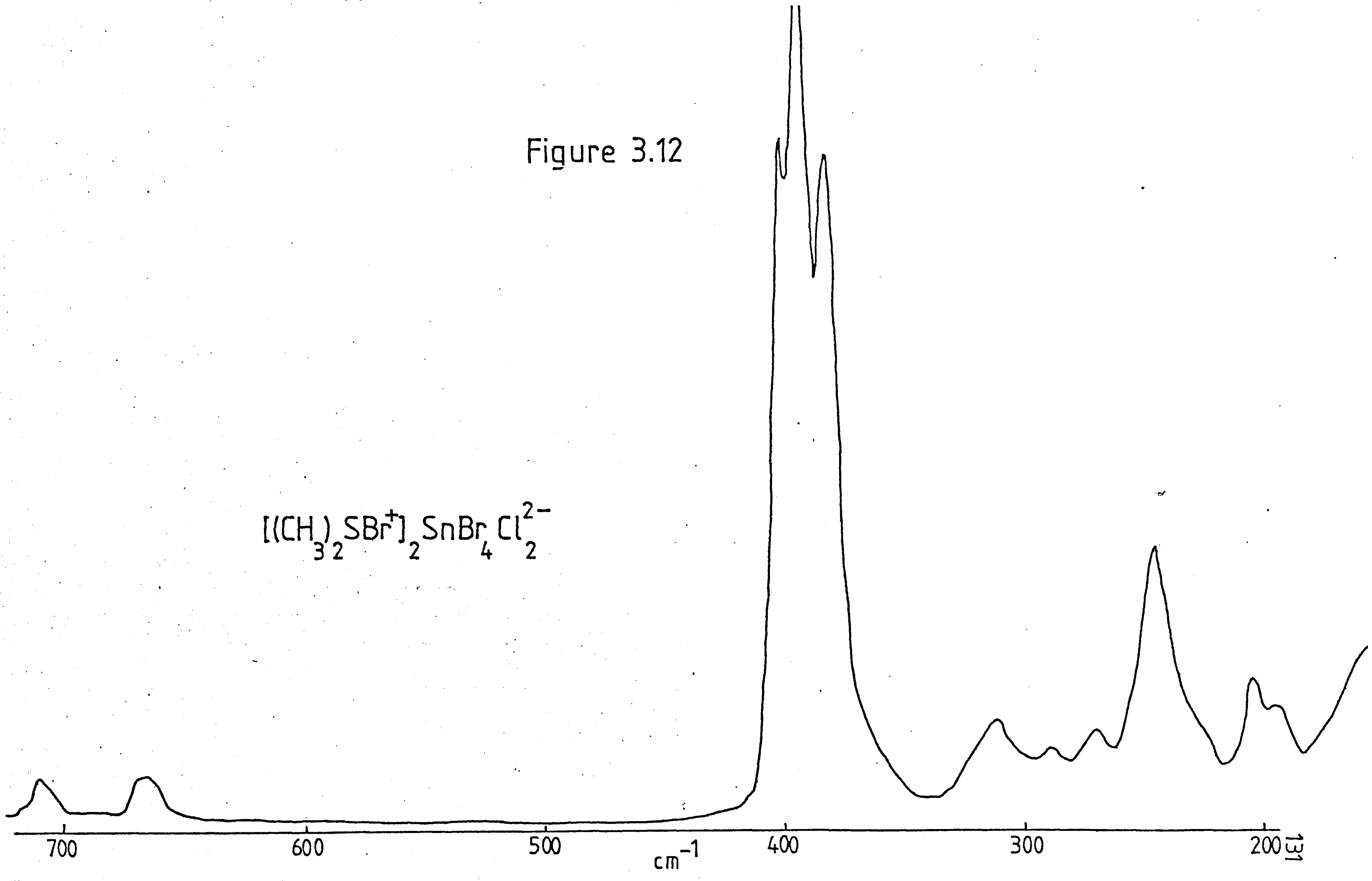


Figure 3.12

$[(CH_3)_2SBr^+]_2SnBr_4Cl_2^{2-}$

contained both S-Br and S-Cl groups. In this case the S-Cl bands occurred at 525cm^{-1}, with evidence of splitting, as for the $[(CH_3)_2SCl^+]_2\ SnCl_6^{2-}$ spectrum given earlier (Table 3.3). However, the S-Br band occurs as a band at 415cm^{-1}, with evidence of a shoulder, quite unlike the S-Br bands in $[(CH_3)_2SBr^+]_2SnBr_6^{2-}$ (Table 3.7). The band is in fact virtually identical with that found in $(CH_3)_2SBr^+SbCl_5Br^-$ (Table 3.7) and provides some confirmation of the correct assignment of the band in the $SnBr_6^{2-}$ spectrum, in view of the similar preparative procedures, the shift and splitting being due to crystal effects operating in the $SnBr_6^{2-}$ product. A full x-ray crystal structure on these two products would be interesting.

The spectrum (Figure 3.11) of this mixture below 350cm^{-1} is virtually identical in all respects with that of $[(CH_3)_2SCl^+]_2SnCl_6^{2-}$ and it would therefore appear that the only anion present in significant quantity is $SnCl_6^{2-}$. It is probable that the vast excess of chlorine present in the system together with the "softness" of dimethyl sulphide compared to Sn^{4+} would tend to lead to $[(CH_3)_2SBr^+]_2SnCl_6^{2-}$. However the excess of chlorine would also ensure the formation of some chlorosulphonium species.

The analysis of this product is in good agreement with it being a mixture of 21•5% bromo- and 78•5% chlorosulphonium species. It appears that the anion is $SnCl_6^{2-}$. The spectrum is in full agreement with this

Table 3.2 summarises literature data on mixed hexahalostannates although the spectra were not completely assigned because of experimental problems in the recording of the spectra. However, the data quoted suggests that the anion in this work could be $SnCl_4Br_2{}^{2-}$ but the evidence is not strong and, in particular, the band intensities do not show a good correlation with those quoted. It is, of course, difficult to see what other anions could be present particularly as the analytical evidence shows reasonable agreement for $[(CH_3)_2SBr^+]_2SnCl_4Br_2{}^{2-}$. For the other possible anions $Br_3{}^-$, $Br_5{}^-$, $SnBr_5{}^-$, or $SnCl_5{}^-$, strong bands at 165cm^{-1}, 250cm^{-1}, 202cm^{-1}, or 338cm^{-1} would be expected, the first two being considered unlikely in view of the lack of a large bromine excess. Although bands do exist at these frequencies they are weak and not as expected from those anions. A bromide anion would be expected to lead to a low S-Br frequency of about 346cm^{-1} (section 3.4).

It is therefore considered likely that this product is a mixture containing probably two anions although it is possible that crystal effects could mean that only one anion is present. It is likely that these anions contain mixed hexahalostannate species.

3.3 MONOMETHYLHALOSULPHONIUM CATIONS

The reaction of antimony pentachloride with dimethyl disulphide was studied by Warthmann and infra-red[63] and Raman[68] spectra reported. Dichloromethylsulphonium hexachloroantimonate was prepared using the known methods as described in Chapter 5 (Section 5.7). The analysis of the product was in reasonable agreement with the calculated values.

The low frequency Raman spectum is given in Figure 3.13 and Table 3.9 and is in good agreement with that of Shamir[68] except that we did not observe the band at 462cm^{-1}. In Table 3.10 are listed the low frequency bands of CH_3PCl_2 which is isoelectronic with $CH_3SCl_2^+$ and would be expected to show the same 6 Raman bands of an ion with C_s symmetry.

The three high frequency bands are readily assigned (Table 3.10) but assignment of the deformation modes is complicated by the presence of the bands due to the anion and here we differ with Shamir. He assigns bands at 287, 285 and 263 cm^{-1} to the E_{1g} mode of $SbCl_6^-$. However this mode is only doubly degenerate and in any case a split of some 22cm^{-1} would be excessively large for the splitting of a degenerate mode in the solid state. In previous hexachloroantimonate spectra (Figures 2.2 and 3.1) this splitting has been much less and the band centred at about 290cm^{-1} or 284cm^{-1}. It is therefore considered that in this case the bands at

TABLE 3.9

METHYLDICHLOROSULPHONIUM RAMAN SPECTRA (cm^{-1})

$CH_3SCl_2^+SbCl_6^-$

This Work	Shamir[68]	Assignment
670(vw)	666	S-C str.
536(w)	535	S-Cl asym. str.
512(m)	513	S-Cl sym. str.
	462	
333(s)	333	$SbCl_6^-$
290(m)	287	$SbCl_6^-$
286(m)	285	
260(w)	263*	CH_3-S def.
212(m)	213	SCl_2 def.
180(sh)	176*	CH_3SCl_2 def.
173(m)	173	$SbCl_6^-$

* Shamir 263cm^{-1} $SbCl_6^-$ E_{1g}
176cm^{-1} $SbCl_6^-$ F_{2g}

Figure 3.13

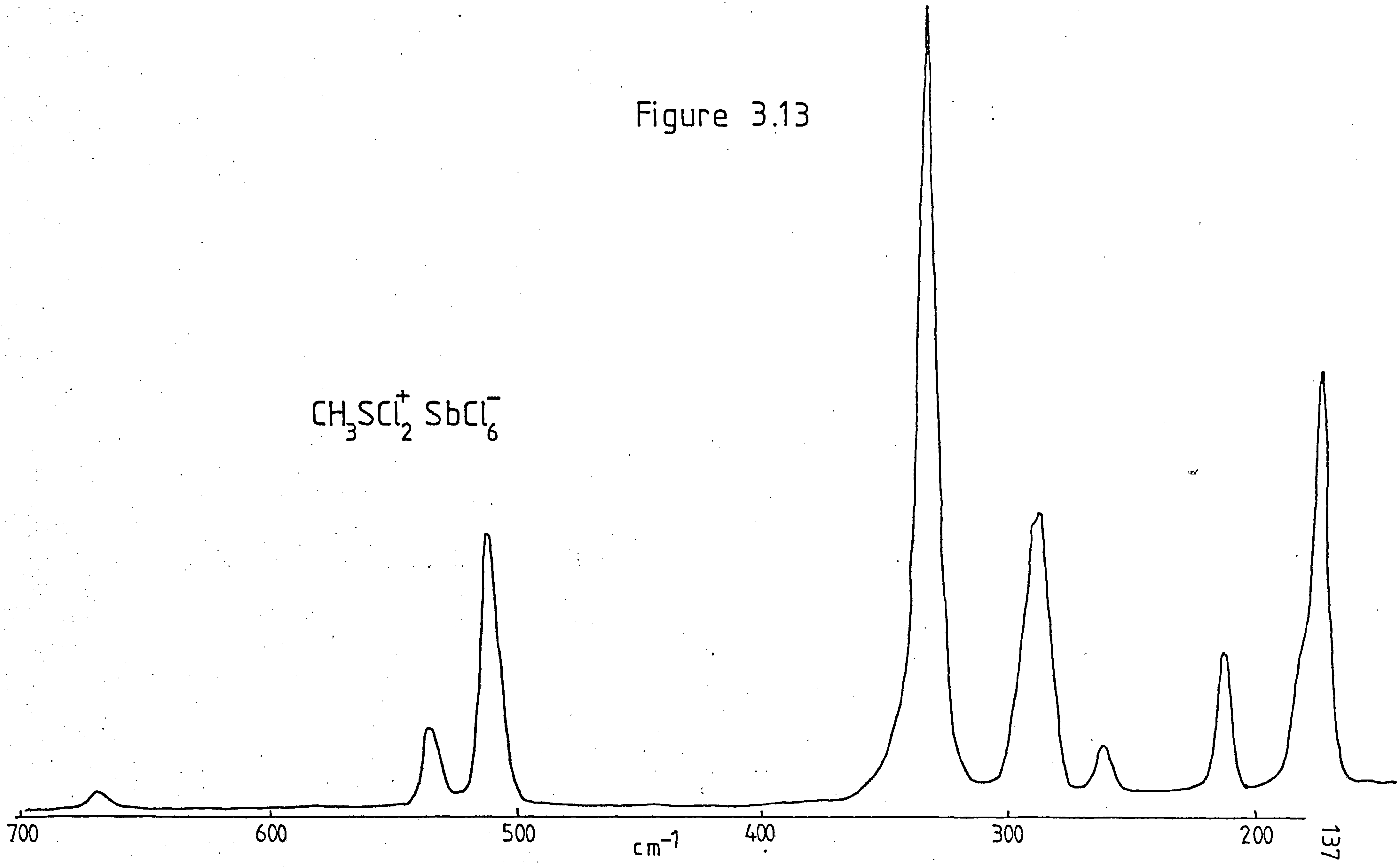


TABLE 3.10

CH_3PCl_2 RAMAN BANDS (cm^{-1})

Griffith[151]	Geiseler[152]	Assignment
692	690	P–C str.
487	492	P–Cl_2 asym. str.
473	470	PCl_2 sym. str.
286	288	PCH_3 def.
237	240	PCl_2 sym. def.
194	194	CH_3PCl_2 def.

290/286cm^{-1} only should be assigned to $SbCl_6^-$. Shamir reports solution data to support his view but possibly the resolution was insufficient to distinguish the weak 260cm^{-1} band from the single $SbCl_6^-$ 284cm^{-1} band observed in the liquid.

In CH_3PCl_2 (Table 3.10) the CH_3P deformation occurs at 288cm^{-1} and it is possible that in $CH_3SCl_2^+$ this mode can be assigned to the 260cm^{-1} band. The SCl_2 deformation can then be assigned to the 212cm^{-1} band which occurs at 240cm^{-1} in the CH_3PCl_2 and 230cm^{-1} in $PBrCl_2$. The assignment of the antisymmetric deformation is difficult as no immediately obvious band presents itself. It is possible that the 180cm^{-1} shoulder on the F_{2g} $SbCl_6^-$ 173cm^{-1} band could be assigned to that mode. Shamir assigns this shoulder to the $SbCl_6^-$ anion but in the spectra of Figures 2.2 and 3.1 the split is towards the low frequency side.

It is just possible that the 212cm^{-1} band should be assigned to the CH_3SCl_2 deformation although this would put it at a higher frequency than the analogous mode in $(CH_3)_2SCl^+$ (Table 3.3) which is unlikely. However, in this event the SCl_2 deformation would be assigned to the 260cm^{-1} band and the CH_3S deformation to a band hidden under the $SbCl_6^-$ band at 290cm^{-1}. This would perhaps place the band frequencies in closer agreement with those of CH_3PCl_2 but this assignment is considered less likely particularly as there is not especially good agreement between the spectra of $(CH_3)_2PCl$ and $(CH_3)_2SCl^+$. Shamir appears to totally ignore two of the deformation modes but does assign the SCl_2 deformation to the $213cm^{-1}$ band.

An attempt was made to prepare $CH_3SCl_2^+AlCl_4^-$ using the usual technique. However, the product appeared so hydrolytically unstable that deliquescence occurred even in the dry conditions of the filter. No further attempts were made primarily because one of the $AlCl_4^-$ bands occurs at $185cm^{-1}$ and would cause doubts regarding the assignment of any band in this area.

Similar to the bromo analogues of dimethylchlorosulphonium cations the bromo analogues of methyldichlorosulphonium cations also proved to be unstable, although in this case bromine was evolved by the product on standing. Again these compounds have not been reported in the literature and the spectral assignments are complicated by the lack of data on the isoelectronic phosphorus compound.

As for the dimethylsulphonium complexes the reaction in the presence of antimony pentachloride gave a complex containing the anion $SbCl_5Br^-$ not $SbCl_6^-$. The experimental details are given in Chapter 5 (Section 5.8) and the first attempt at preparing the product gave a complex whose analysis was not in good agreement with the calculated values although duplicate agreement was excellent. A second attempt yielded a product of virtually identical spectrum but whose analysis was different to that of the first and again not in agreement with the calculated value. In each case the bromine analysis was significantly below that calculated for $CH_3SBr_2^+SbCl_5Br^-$ although above that for $CH_3SBr_2^+SbCl_6^-$. There is no evidence from either spectrum that any S-Cl is present due to the lack of bands around $500cm^{-1}$. The presence of some $SbCl_6^-$ products cannot be excluded from the spectroscopic evidence because of the overlap of its bands with those of $SbCl_5Br^-$. However, it is thought that a more likely explanation for the low bromine analysis is that the compound evolves a red vapour, probably bromine, on standing. The drying of the solid by suction would tend to remove a variable amount of bromine so giving the differing analysis, although with only a small duplicate variation. It is thought that this instability is due to hydrolysis even though extreme care was taken to reduce water contamination as far as possible. The products did however, give good spectra which is perhaps not surprising as the complex would be at least 80% pure based on the analysis and the loss of bromine would not be particularly visible in the Raman spectrum (Figure 3.14 and Table 3.11).

The preparation of the tetrabromoaluminate salt proceeded relatively easily using recrystallised aluminium bromide and as described in Chapter 5 the analysis of the product for bromine was in excellent agreement with that calculated for $CH_3SBr_2^+AlBr_4^-$.

TABLE 3.11

METHYLDIBROMOSULPHONIUM RAMAN SPECTRA (cm^{-1})

$SbCl_5Br^-$ (Figure 3.14)	$AlBr_4^-$ Figure 3.15)	Assignment
664(w)	660(w)	C-S str.
424(m)	409(m)	S-Br asym. str.
	385(vw,sh)	$AlBr_4^-$
389(s)	369(s)	S-Br sym.str.
334(s)		$SbCl_5Br^-$
309(m)		
286(m)		
244(m)	244(m)	CH_3-S def.
224(m)		$SbCl_5Br^-$
	225(w)	CH_3SBr_2 def. (?)
	211(m)	$AlBr_4^-$
175(m)		$SbCl_5Br^-$
160(w)		
135(m)	135(m)	SBr_2 def.
	117(w)	$AlBr_4^-$
	81(m)	

Figure 3.14

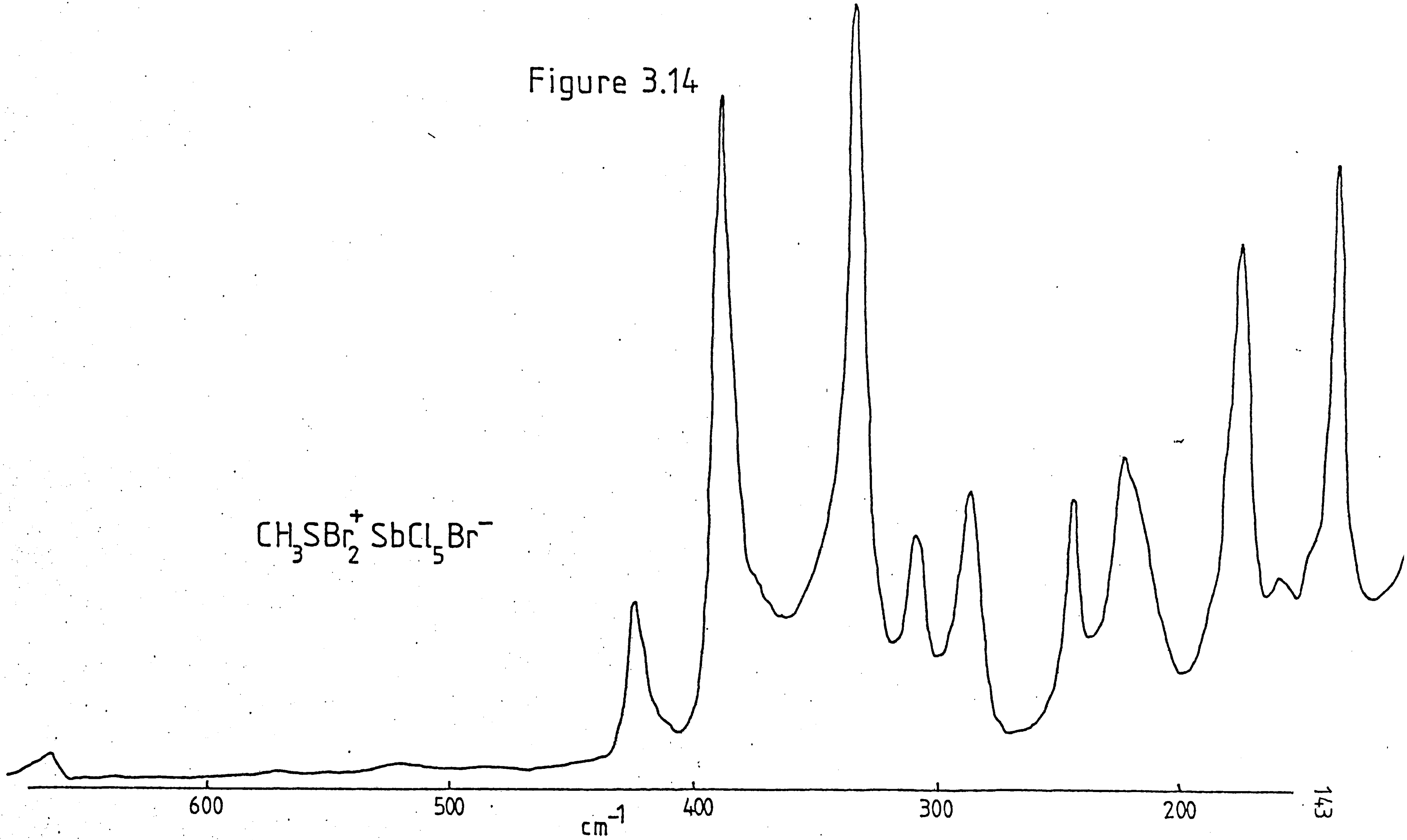
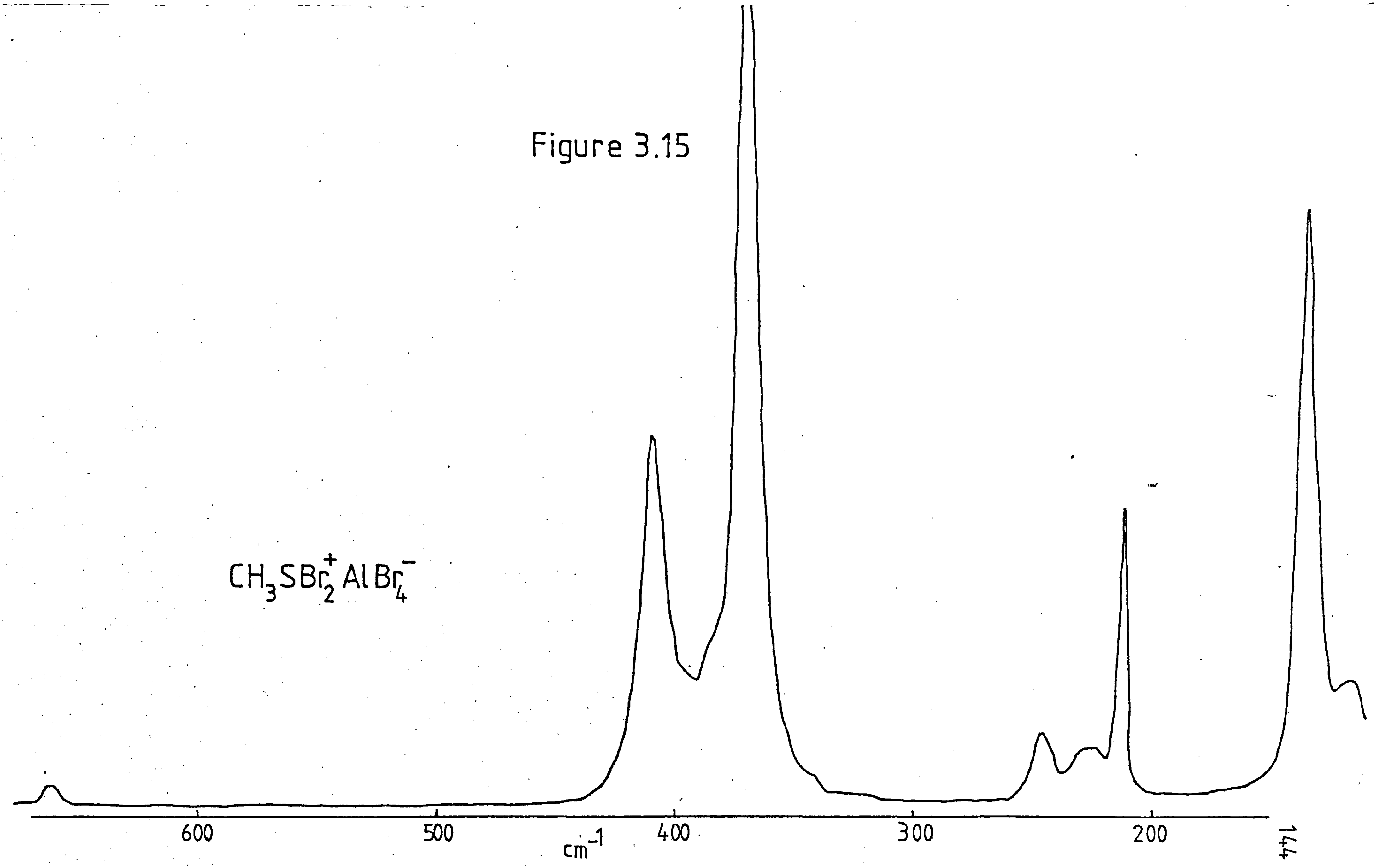


Figure 3.15



$CH_3SBr_2^+AlBr_4^-$

The spectrum is shown in Figure 3.15 and the bands listed in Table 3.11.

The preparation of the hexabromostannate is described in Chapter 5. The product, however, was soluble in the solvent and was only precipitated by cooling to -80°C, it evolved a red vapour on standing, so it was therefore thought that analysis would be of doubtful value. The spectrum (Figure 3.16) shows a strong band at $296 cm^{-1}$ which is due to either free bromine or, more probably, associated bromine possibly with the dimethyl disulphide. Although the band is the strongest in the spectrum it probably does not represent a very large quantity of product as this bromine band is so strong. The S-Br bands visible in the other spectra at about $410 cm^{-1}$ and $370 cm^{-1}$ (in $CH_3SBr_2^+AlBr_4^-$) are not obviously visible as the characteristic doublet. In this area only a single broad asymmetric and relatively weak band is visible. This must be assigned to an S-Br vibration and possibly both symmetric and antisymmetric vibrations are contained within the envelope. The CH_3-S vibration is visible as the normal single band at about $680 cm^{-1}$ suggesting the presence of only one CH_3-S species. The anion bands ($SnBr_6^{2-}$) are observed at $181 cm^{-1}$, $140 cm^{-1}$ and $102 cm^{-1}$ very much as expected. Weak bands at $314 cm^{-1}$ and $480 cm^{-1}$ are due to unknown species. The band at $222 cm^{-1}$ could be a deformation mode of $CH_3SBr_2^+$ or possibly a $SnBr_4$ band. In the latter case

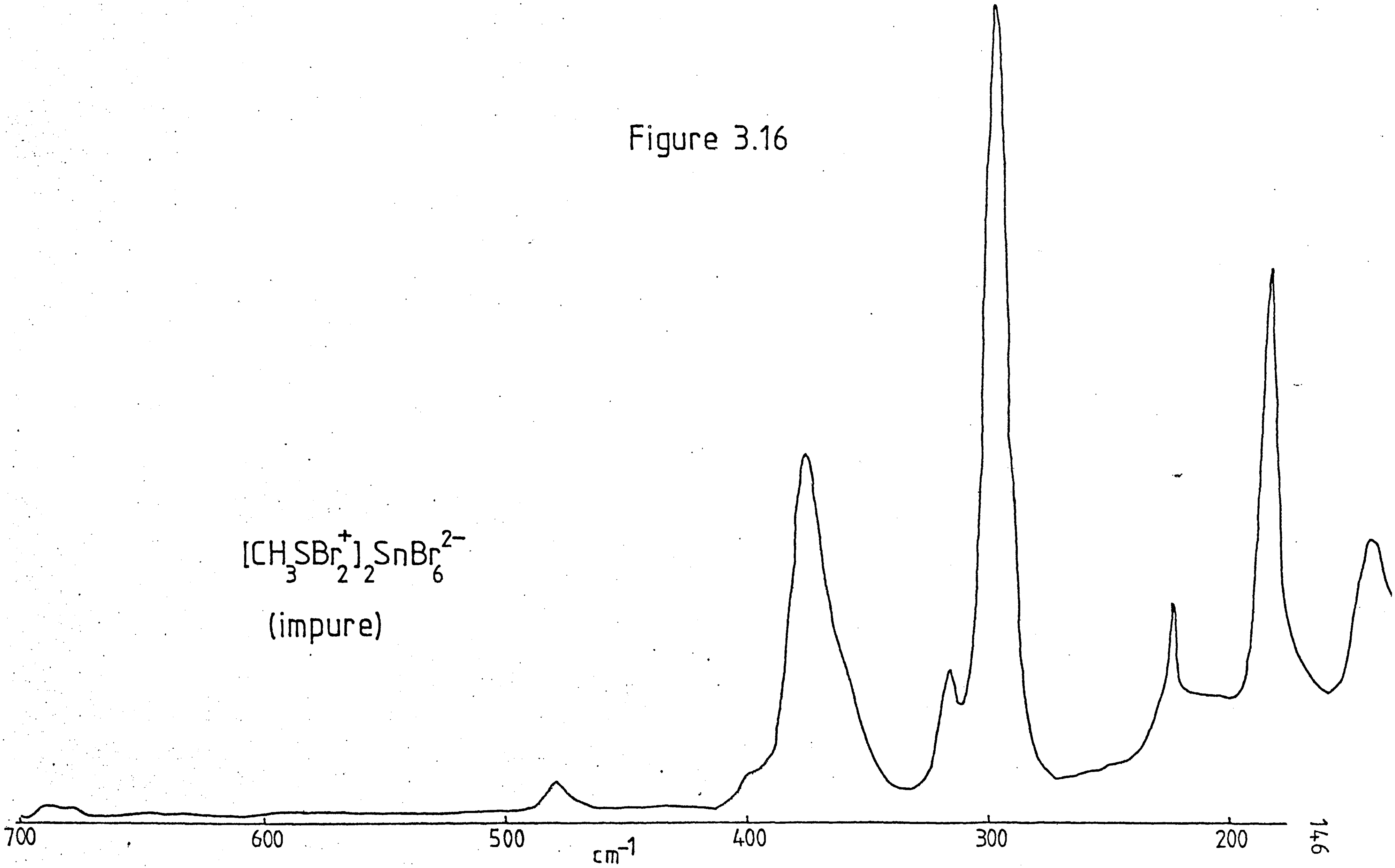


Figure 3.16

$[CH_3SBr_2^+]_2SnBr_6^{2-}$

(impure)

however, one would also expect to see the weaker band at 88cm^{-1} which appears to be absent. However, some scatter from the laser line occurs in this region and as the band would be expected to be weak, it may not be visible. The deformation mode visible in the other spectra at about 244cm^{-1} appears to be absent and as this spectrum is not entirely satisfactory in view of the above doubts and the broad S-Br band it has not been included in Table 3.11.

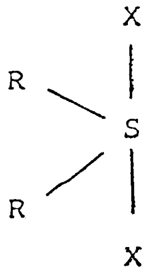
The spectra of $CH_3SBr_2{}^+SbCl_5Br^-$ and $CH_3SBr_2{}^+AlBr_4{}^-$ are collated in Table 3.11. The anion bands are readily assigned using data in Tables 2.2 and 2.3 together with a comparison with other spectra containing these ions. The remaining bands generally occur at very similar frequencies in both spectra and can be assigned to $CH_3SBr_2{}^+$. The single C-S and two S-Br high frequency stretching modes are readily assigned. The CH_3-S deformation mode occurs at about 260cm^{-1} in $CH_3SCl_2{}^+$ (Table 3.9), the bands at 244cm^{-1} can be assigned to this mode with the drop in frequency being due to the heavier halogen contributing to the vibration. The strong band at 135cm^{-1} is assigned to the SBr_2 deformation which occurs at 123cm^{-1} in $PClBr_2$. The remaining deformation occurs at 153cm^{-1} in $PClBr_2$ and the replacement of Cl by CH_3 might be expected to increase the frequency a little. In any case the frequency would be expected to be lower than that in CH_3SCl_2 assigned at 180cm^{-1} (Table 3.9). However, the only band not assigned in the spectra of Table 3.11 occurs at $225cm^{-1}$ in the $AlBr_4^-$ spectrum. In the $SbCl_5Br^-$ spectrum this region is complicated by the presence of an anion band. This frequency is very high for the $CH_3SBr_2^+$ antisymmetric deformation. There is a weak shoulder in the $SbCl_5Br^-$ spectrum at about $142cm^{-1}$ in the region expected for the deformation mode. However, no such band is visible in the $AlBr_4^-$ spectrum although a weak band does occur at $117cm^{-1}$ which is possibly due to $AlBr_4^-$. Overall it is considered that the CH_3SBr_2 antisymmetric deformation be assigned to the $225cm^{-1}$ band.

3.4 DIMETHYL SULPHIDE-BROMINE REACTIONS

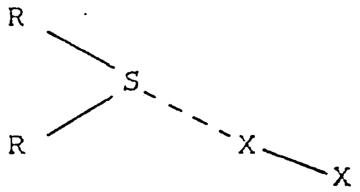
In Chapter 1 (Section 1.3) the literature relating to the reaction of halogens with sulphides was reviewed. From **reactions** of the type

$R_2S+X_2 \longrightarrow R_2SX_2$ (X=Cl,Br,I),

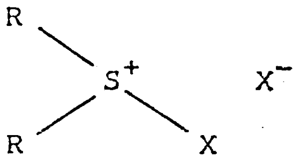
three types of complex could be envisaged:-



I



II



III

I a covalent compound in which the sulphur atom is at the centre of a trigonal bipyramid (tetrasubstituted).

II a charge - transfer molecular complex

III an ionic compound

It was found that the type of complex formed depended on the electronegativities of the halogen and group VI element[74,75] as well as their size.[71] On the basis of the criteria suggested by Baenziger[74] and Lambert[71] the reaction between bromine and dimethyl sulphide would be predicted to form a charge transfer type complex (II) rather than a covalent compound (I). This ensures that the least electronegative and/or larger atom is at the centre of the group of three atoms.

For the reaction between dimethyl sulphide and bromine these criteria predict that the complex formed will be of the charge transfer type. This structure has been confirmed by Hendra[73] on the basis of infra-red spectroscopy. It should be noted that some earlier references[60,79,80] to this compound formulated it as being ionic mainly by analogy with the Lewis acid adducts.

The dimethyl sulphide - bromine charge - transfer complex was produced (Chapter 5) using dichloromethane as solvent and was identical to that produced by Hendra[73] in carbon tetrachloride. The spectrum is given in Figure 3.17 and the bands listed in Table 3.12. The strong bands at 284/295cm^{-1} are characteristic[72] of complexed bromine and are shifted to a lower frequency than in bromine itself. However the covalent compound would be expected to give rise to S-Br bands in the region of 400cm^{-1}. In $SCl_3^+Cl^-$ the S-Cl bands are some 70cm^{-1} below those in the analogous Lewis acid complex (Chapter 2). In a complex formulated with an ionic structure a frequency of about 330cm^{-1} might be expected for the S-Br band and it is most unlikely that it would drop to below 300cm^{-1}. The high frequency C-S stretching modes at 700/672cm^{-1} are at intermediate frequencies to those in dimethyl sulphide and the dimethylhalosulphonium cations. The remaining strong

TABLE 3.12

RAMAN SPECTRA OF $(CH_3)_2S/Br_2$ PRODUCTS

$(CH_3)_2SBr_2$ (Figure 3.17)	$(CH_3)_2SBr^+Br^-$ (Figure 3.18)	Assignment
720(vw)	720(vw)	C–S asym.str.
672(w)	671(w)	C–S sym. str.
418(vw,br)		
	346(s)	S–Br str.
295(s)	296(sh)	Br_2 complexed.
284(vs)	286(m)	
	232(s)	S–Br def.
215(m)	204(vw,sh)	S---Br_2
204(sh)		
150(m)	148(vw)	
104(w)	105(w)	
80(sh)		
	84(m)	
68(m)		
	64(m)	
50(m)	50(m)	
42(sh)	46(m)	
39(s)		

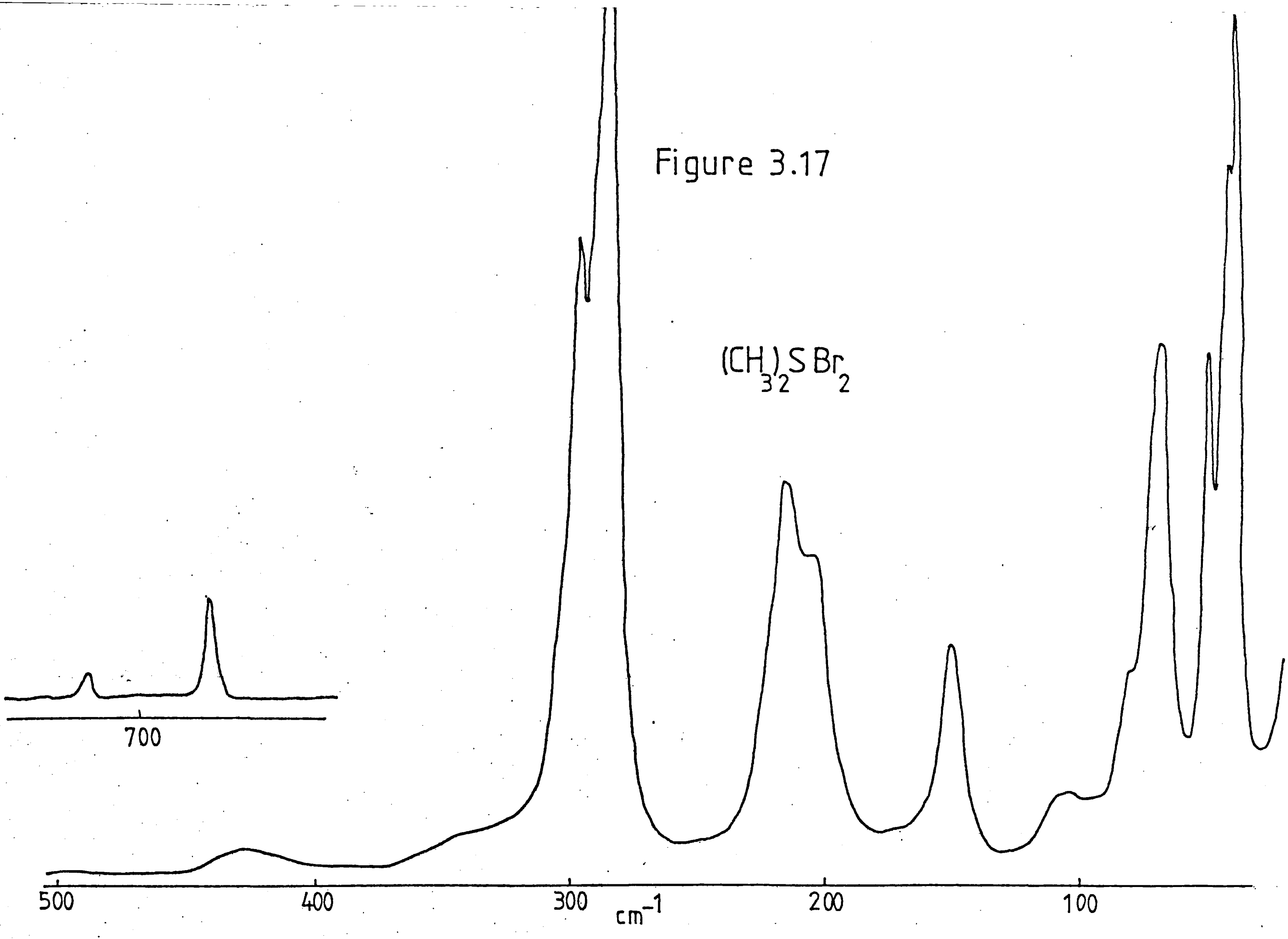


Figure 3.17

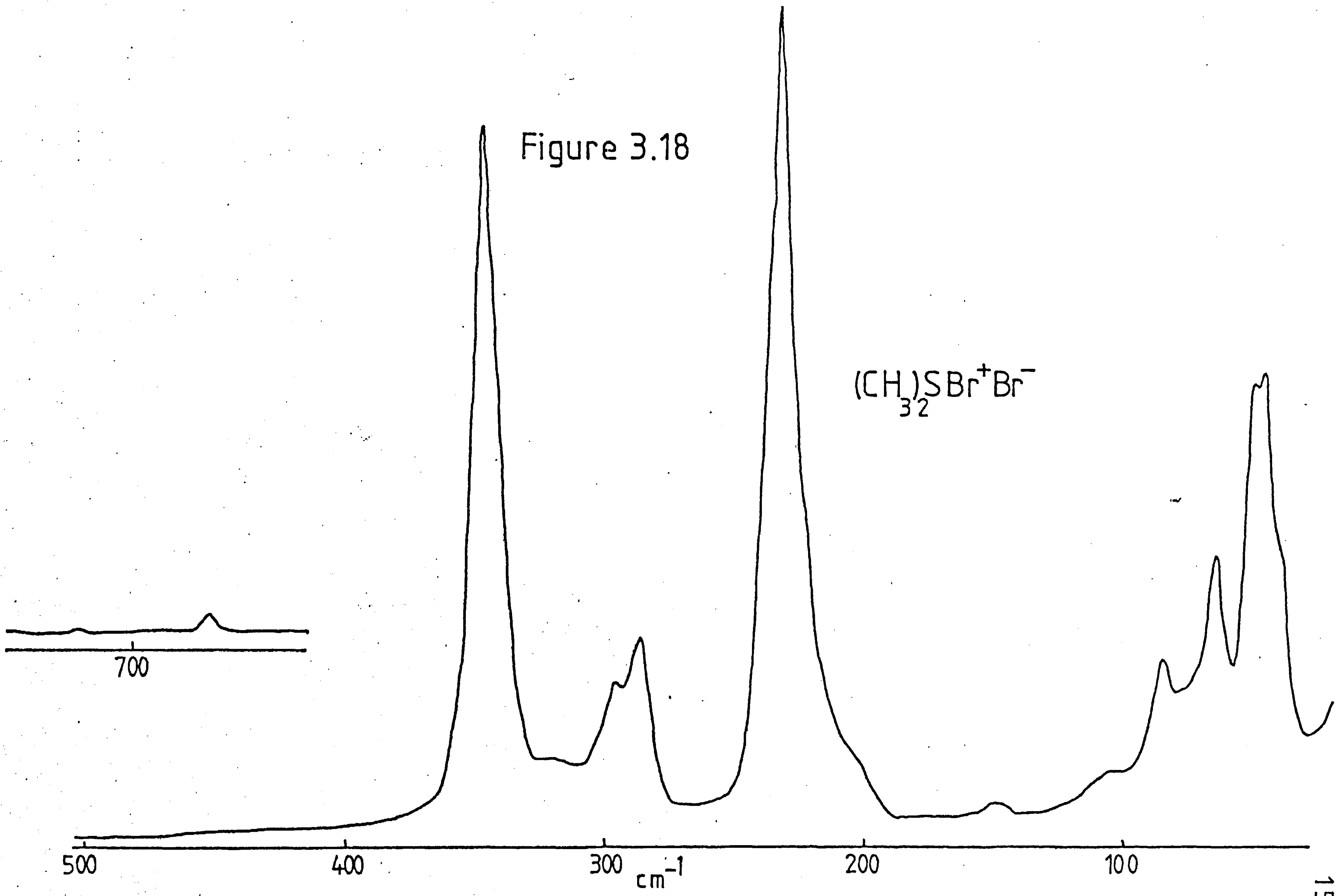


Figure 3.18

bands at 204/215cm^{-1} are presumably associated with the weak S-----Br mode in view of their strength. The very weak broad band observed at 418cm^{-1} is of unknown origin. The Raman spectra reported here, and which Hendra was unable to obtain owing to thermal decomposition, therefore support the charge-transfer type structure for this complex.

If the reaction between bromine and dimethyl sulphide is conducted in thionyl chloride, a solid is formed whose spectrum is very different to that obtained in dichloromethane. The spectrum is shown in Figure 3.18 and the bands compared with those of the charge transfer complex in Table 3.12. The product obviously contains some charge - transfer complex as evidenced by the 296/286cm^{-1} bands. The two weak high frequency bands can be assigned to the CH_3-S stretching modes. The strong band at 346cm^{-1} must be assigned to an S-Br stretching mode in view of its strength. It is however, some 50-70cm^{-1} below the equivalent modes in $(CH_3)_2SBr^+AlBr_4^-$ or $(CH_3)_2SBr^+SbCl_5Br^-$ (Table 3.7) but this would be expected as the S-Cl modes in $SCl_3^+Cl^-$ are some 30-70cm^{-1} below those in $SCl_3^+AlCl_4^-$ (Tables 2.7 and 2.12).

A strong band is observed at 232cm^{-1} and in view of its strength it must be assigned to an S-Br mode. In $(CH_3)_2SBr^+$ the S-Br deformation probably occurs at about 185cm^{-1}. It is possible that the 232cm^{-1} band could be assigned to this mode, however, it is very much stronger than expected for reasons that are unknown. The remaining deformation occurs at 154cm^{-1} in the Lewis acid complexes. However, although a band exists at 148cm^{-1} in this spectrum this may be due to contaminating $(CH_3)_2SBr_2$, similarly the shoulder at 204cm^{-1} could be due to the charge - transfer complex as well as the deformation sought. The $(CH_3)_2S$ deformation mode seen at 240cm^{-1} in the $(CH_3)_2SBr^+AlBr_4^-$ spectrum and expected in a similar position for $(CH_3)_2SBr^+Br^-$ would be hidden by the other bands in the spectrum.

The very low frequency bands are similar in both compounds and are probably lattice bands.

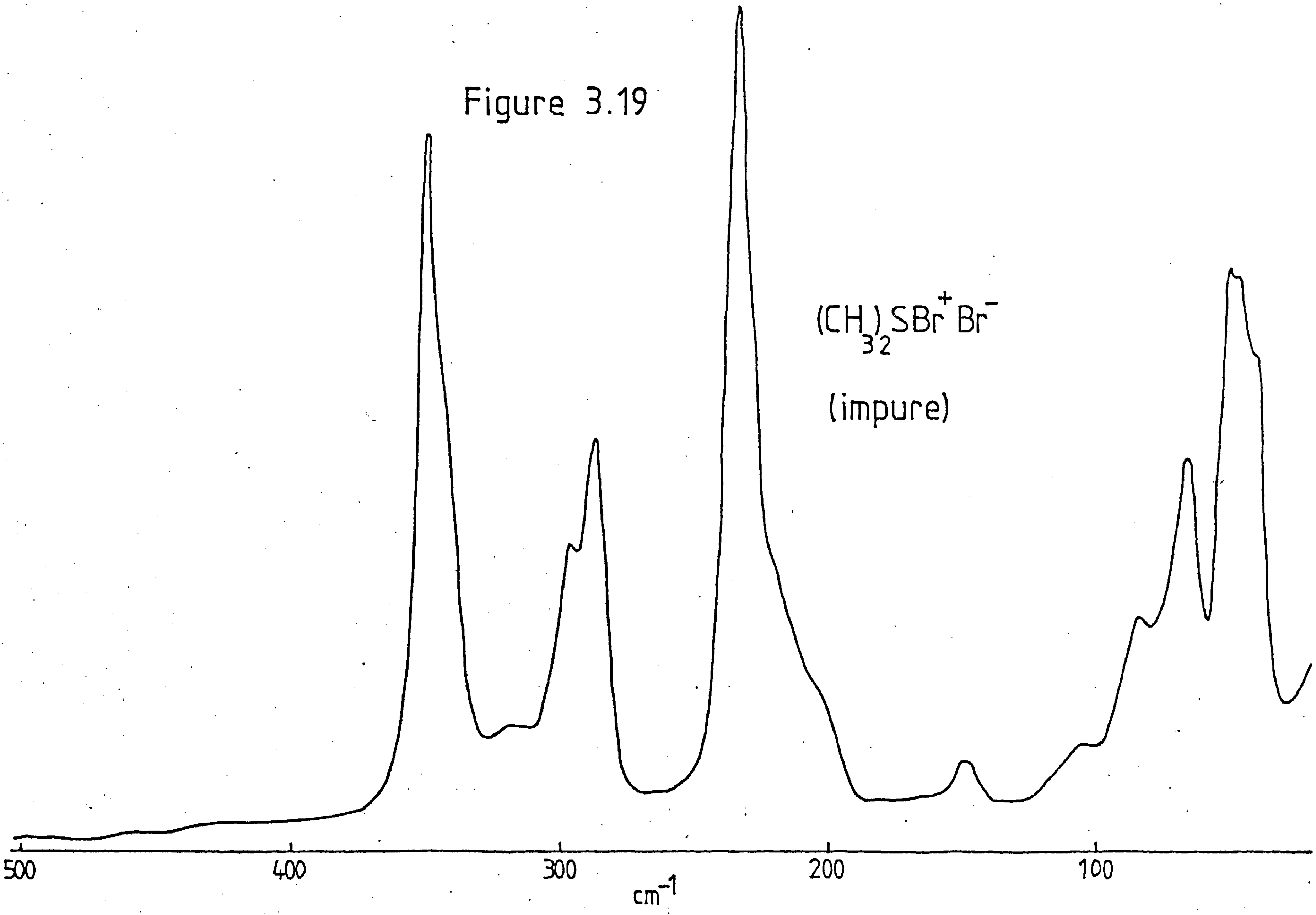
It became obvious during the handling of this compound that degradation occurred especially as it was proving impossible to prepare the pure ionic complex The band at 284cm^{-1} can be assigned to the complex $(CH_3)_2SBr_2$ and the band at 346cm^{-1} to the ionic complex $(CH_3)_2SBr^+Br^-$. Therefore a ratio of the peak heights of these two bands can be used as a measure of any change in composition of the product. This ratio is quoted in Table 5.7 which summarises a number of attempts to produce the ionic compound. A low value suggests a low level of ionic compound and vice versa. The best method of preparation is detailed in section 5.9c and the minimum amount of charge - transfer complex was produced by working in thionyl chloride at 0°C by adding dimethyl sulphide to bromine, the reverse of the normal procedure.

An earlier reaction yielded a product which was not quite so pure (347/286 ratio 1.88 against 4.16) but on which a number of experiments were performed to increase purity and determine stability. After the spectrum of the initial product (A) had been recorded, the solid was subsequently stirred with dichloromethane for 1 hour. The undissolved solid was removed (B) and its spectrum recorded together with that of a solid (C) precipitated by cooling the filtrate. These three spectra were recorded after 2 weeks at room temperature and again 1 week later. The following table summarises the changes in the 347/286 band ratio for these spectra:-

	A	B	C
immediate	1·88	1·34	1·98
after 2 weeks	0	0·75	1·38
after 3 weeks	-	-	1·43

These data show that the product reprecipitated from solvent was marginally the purest and degraded more slowly to the charge transfer adduct than either of the other solids. In fact the initial product was completely degraded before the second spectrum was recorded. This change in spectrum was simply from an obviously mixed product (Figure 3.19) to one identical

Figure 3.19



to that of the prepared charge transfer complex (Figure 3.20 cf Figure 3.17) No additional bands were formed, apart from a weak shoulder at 160cm^{-1}, and the high frequency CH_3-S stretching bands remained as single emissions.

In addition to this work the best product (Figure 3.18) was stored for 2 weeks at 0°C before re-recording the spectrum. The solid was then heated at 50-60°C for 20 minutes and the spectrum re-run, this was repeated.

The measured 347/286 band ratios were as follows:

initial	4.16
2 weeks at 0°C.	5.14
20 mins 50-60°C.	3.81
40 mins 50-60°C.	0

This shows that storage of the compound at 0°C. did not increase the proportion of charge transfer adduct but warming the solid rapidly degraded it totally.

It is therefore apparent that two compounds are present one of which is readily converted into the other, the charge transfer molecular complex. From the predictions of Baenziger and Lambert the charge transfer molecular complex should be the stable form. In the other examples studied the covalent compound was considered as the other possibility but the spectrum (Figure 3.18) does not contain enough bands for such a

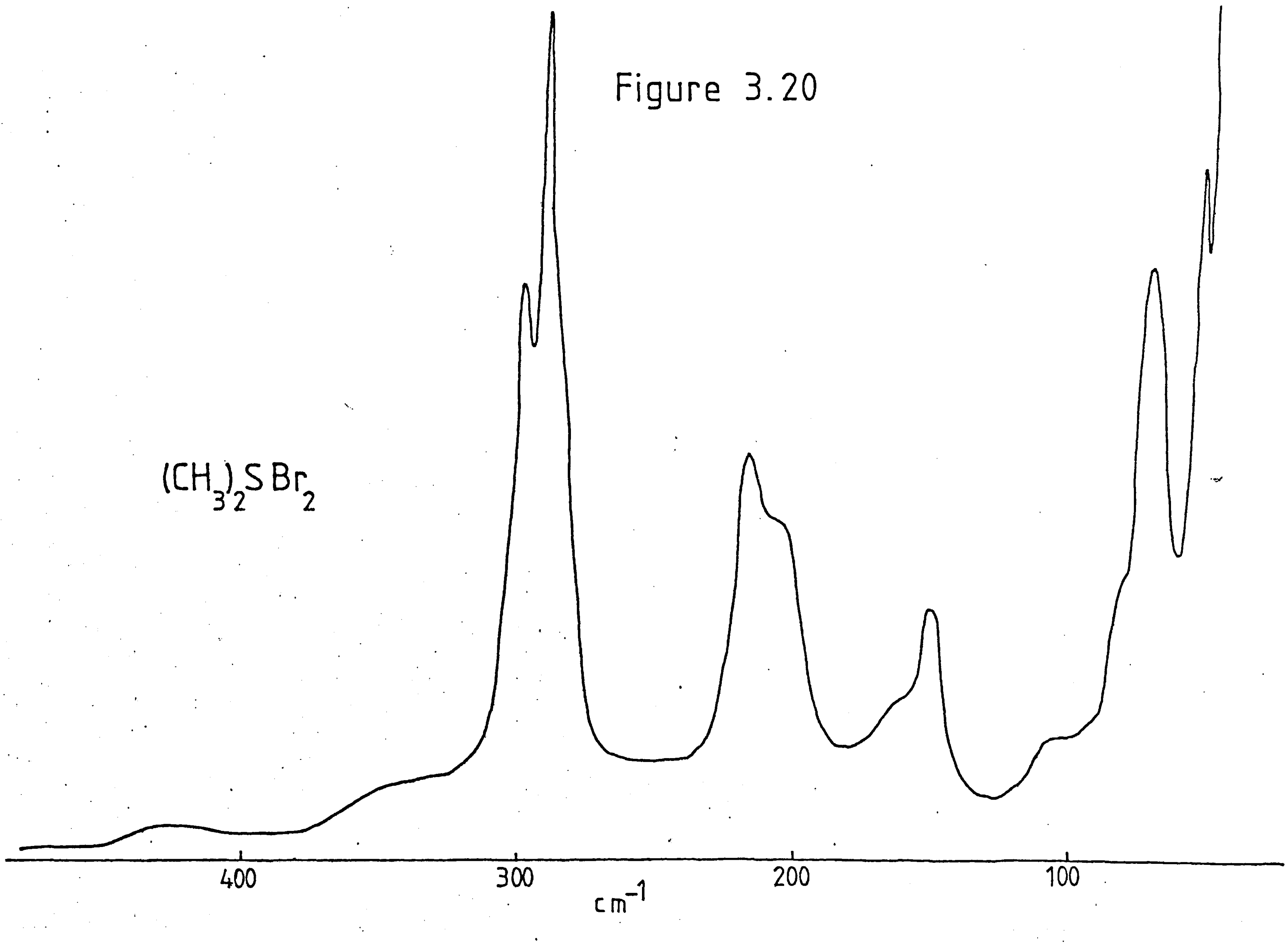


Figure 3.20

trigonal bipyramidal (distorted tetrahedron) type structure. An ionic formulation can be considered as an extreme form of the charge transfer complex and it is therefore reasonable to suggest that the two products are these extreme forms.

The analytical data shows that bromine analyses for the two products were almost identical and very close to that calculated for $(CH_3)_2SBr_2$. The analysis of both the ionic and charge transfer forms are of course identical and cannot be used to distinguish these compounds. However, it does suggest that the compounds have the same composition. The ionic compound was produced in thionyl chloride and it was thought that some chlorine may have been incorporated into the complex even though no evidence for S-Cl was observed in the spectra. The analysis shows that about 2.3% chlorine was present and suggests that some halogen interchange occurred. However, no evidence for the presence of thionyl bromide could be found in spectra of bromine/thionyl chloride mixtures even when stored for 2 weeks.

Since this is the first claim for the existence of a compound formulated as $(CH_3)_2SBr^+Br^-$ it was thought desirable to attempt to obtain far infra-red spectra on both the ionic and charge transfer compounds. Hendra[73] has reported the infra-red spectrum of $(CH_3)_2SBr_2$ and details only a single strong band at 285cm^{-1}. Our data are in agreement with this finding. The spectra of the ionic complex were complicated because the act of making the nujol mull and/or the high temperature generated by the infra-red source tended to decompose the compound and the spectrum was one of the charge - transfer complex. However there was evidence in some spectra of other bands indicating the presence of another compound, presumably the ionic form. The following table summarises the spectra from 450cm^{-1} to 200cm^{-1} but some variability was found due to the inter conversion in the spectrometer.

$(CH_3)_2SBr^+Br^-$ (cm^{-1})	$(CH_3)_2SBr_2$ (cm^{-1})	Assignment
	349 (w)	S-Br str.
	288 (sh)	)
282(S,br)		) Br_2
	277 (s)	)
	245 (m)	S-Br def
	221 (m)	

The main bands present correlate reasonably with those found in the Raman spectrum (Table 3.12) and support both the assignments and the interconversion of the products. It is less satisfactory however, that the spectrum of the ionic form cannot be exactly reproduced each time and further work is necessary using cooled cells.

Two products were produced using higher bromine levels than stoichiometric (i.e. 1:1.5 and 1:2). The first with only a bromine excess of 50% (Table 5.7) yielded a product whose spectrum (Figure 3.21, Table 3.13) is similar to that of $(CH_3)_2SBr^+Br^-$ (Figure 3.18) but with an extra band at 256cm^{-1} and a shoulder at 326cm^{-1}. There was no evidence of bands at 296/286cm^{-1}.

An even higher bromine excess (Chapter 5, Section 5.9a) gave a product whose spectrum (Figure 3.22, Table 3.13) shows apparently little evidence for the presence of $(CH_3)_2SBr^+Br^-$. However, the 255cm^{-1} band is exceptionally strong so making all other bands appear weak. In a spectrum of increased intensity bands at 326cm^{-1} and 230cm^{-1} are present as well as the CH_3–S symmetric and antisymmetric stretching modes. The analysis of this product indicated a bromine level of 82•6% which is close to that calculated for $(CH_3)_2SBr^+Br_3^-$ (83.8%). However, the Br_3^- anion gives rise to Raman bands at about 165cm^{-1} and 190cm^{-1} (Chapter 1). These bands are missing in these spectra. The Br_5^- anion gives a strong band at 250cm^{-1} and it is possible that the spectrum is that of $(CH_3)_2SBr^+Br_5^-$. This compound should possess 88•6% bromine but a mixture of this compound and 36•4% of the simple bromide would give the bromine analysis actually found. The spectrum illustrated in Figure 3.22 is consistent with that expected for such a mixture. It would of course be satisfying if the other deformation modes of $(CH_3)_2SBr^+$ could be observed but these would be hidden by the other spectral bands. No additional bands were observed in a much intensified spectrum obtained on

TABLE 3.13

RAMAN SPECTRA OF $(CH_3)_2S/Br_2$ PRODUCTS

$(CH_3)_2S/Br_2$ 1:1.5 (Figure 3.21)	$(CH_3)_2S/Br_2$ 1:2 (Figure 3.22)	Assignment
715(vvw)	715(vvw)	CH_3-S asym. str.
664(vw)	667(vvw)	CH_3-S sym. str.
346(vs)		S-Br str.
326(sh)	326(m,br)	S-Br str.
256(s)	255(s)	Br_5^-
232(vs)	230(w,sh)	S-Br def.
105(w)	106(w)	lattice
83(w)	81(w)	
62(w)		
50(m)		
	47(vw)	
46(m)		
	36(vw)	
	23(vw)	

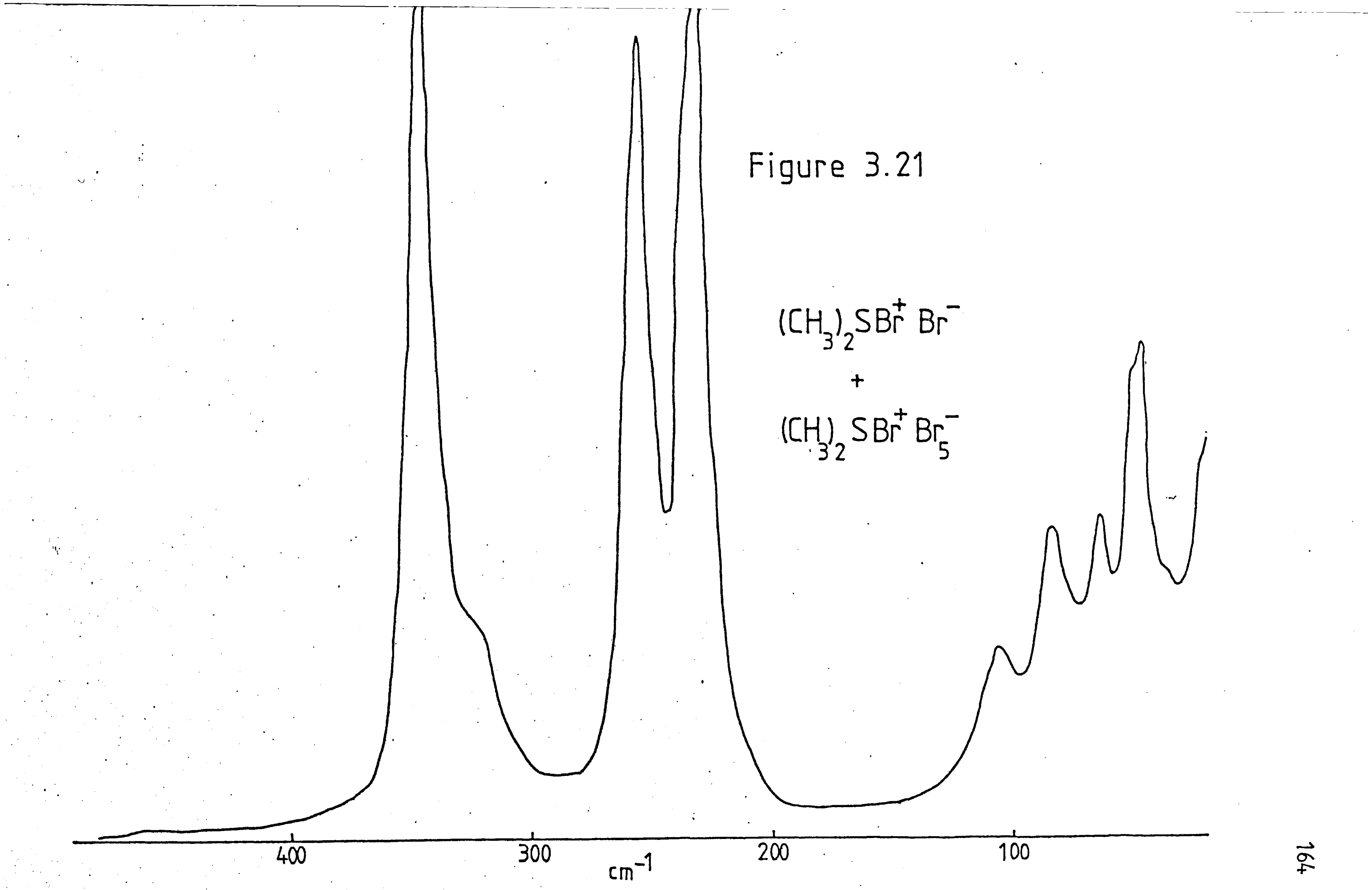


Figure 3.21

$(CH_3)_2SBr^+ Br^-$
+
$(CH_3)_2SBr^+ Br_5^-$

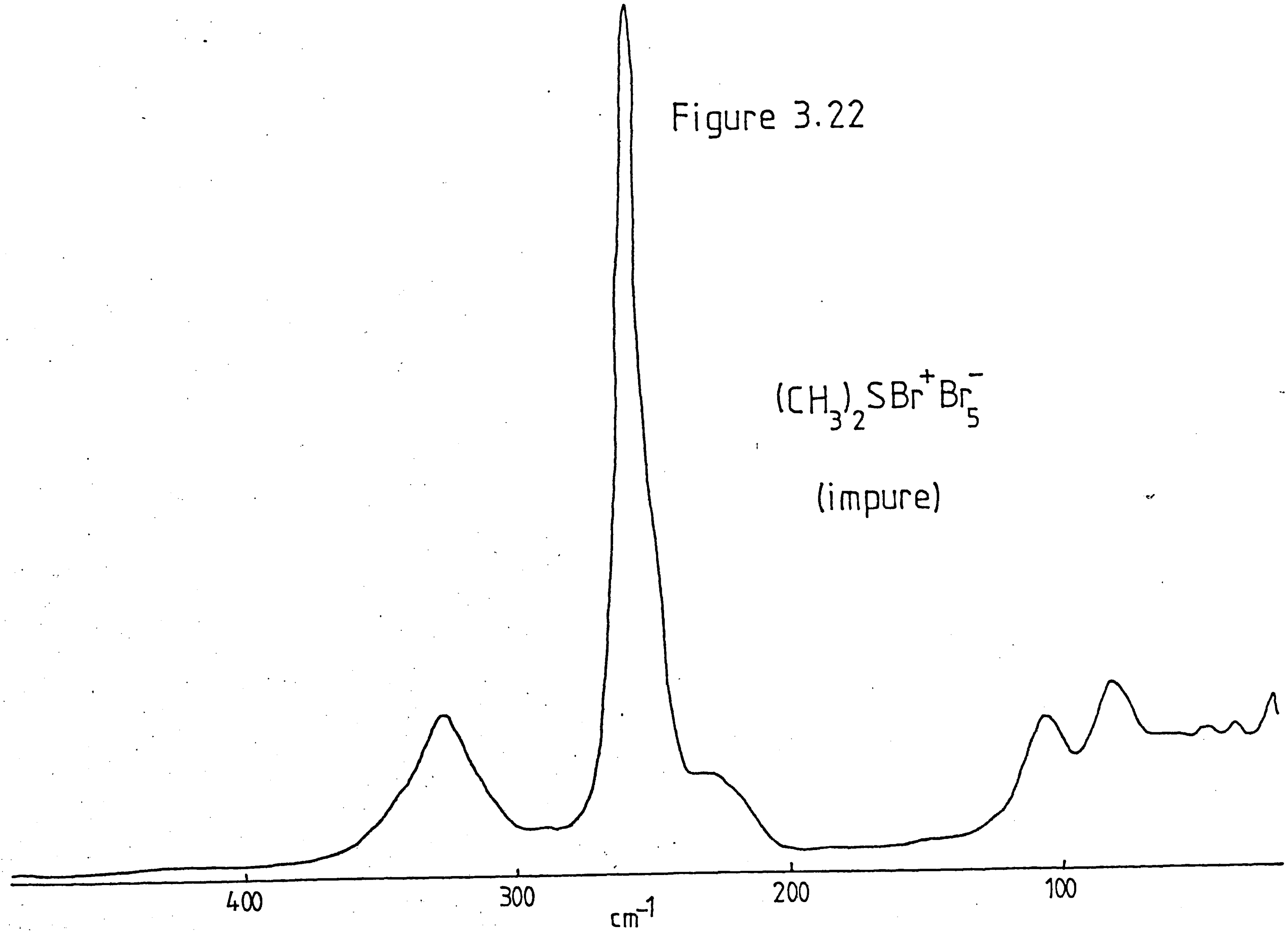


Figure 3.22

$(CH_3)_2SBr^+Br_5^-$

(impure)

this product.

The attempted preparation of the chlorine adduct with dimethyl sulphide is described in Chapter 5 (Section 5.10). However, the solid formed at low temperature in liquid chlorine appeared to decompose below room temperature. A second attempt resulted in the same decomposition occurring and further attempts to produce these complexes were abandoned. It would be interesting to repeat this preparation using a cold cell to maintain the product at low temperature whilst the spectrum is run. However no analysis would be possible for such an experiment.

An attempt was also made to see if the equivalent monomethylsulphonium products could be made. However, no reaction appeared to occur between dimethyl disulphide and bromine in dichloromethane even under reflux. Cooling the mixture resulted in the precipitation of solid bromine only. Further work was not attempted but in view of later preparations in thionyl chloride further investigations would be interesting.

CHAPTER 4

THE REACTION OF SULPHUR DICHLORIDE AND HALOGENS

4.1 INTRODUCTION

Reaction of sulphur dichloride with bromine, and/or chlorine might be expected to lead to relatively simple products readily analyzable by Raman spectroscopy. It was hoped that this reaction, particularly at low temperatures, would lead to the formation of previously unreported compounds. However, it rapidly became apparent that although excellent spectra could be obtained their assignment would be difficult. This was especially so for the sulphur dichloride/bromine spectra when only a very limited number of bands were observed. It should be emphasised that the spectra of a number of reactant mixes were recorded over temperatures of -180°C to 20°C to provide many spectra for analysis but only a few representative examples are illustrated. The chief difficulty was the inability to handle the products above about -80°C so that no analyses or purification attempts were possible. It was therefore decided to attempt to produce solid, analyzable compounds that were stable at room temperature. From data on such complexes it was hoped to infer information regarding the composition of the sulphur dichloride/halogen products. These Lewis acid complexes have been discussed in Chapter 2 and that information is used in the analysis of spectra obtained during this section of the work.

In this chapter a number of references will be made to spectra of the starting materials. The spectra of these compounds have been studied in the literature and as there is substantial agreement between the data any discussion apart from that already given in Chapter 1 is superfluous. However, most of the quoted data was obtained at ambient temperature whereas all this work was conducted at low temperatures, therefore the following tables and spectra list frequencies of these compounds at about -150°C. For the halogen spectra only the stretching modes are illustrated.

TABLE 4.1

SULPHUR HALIDE RAMAN BANDS (cm^{-1}) AT -150°C

SCl_2 (Figure 4.1)	S_2Cl_2 (Figure 4.2)	S_2Br_2 (Figure 4.3)	Assignment[10,11,17]
	548(m)	537(w)	S-S sym. str.
525(m)) 518(m))	451(m)	365(sh)	S-X asym. str.
507(vs)) 500(s))	436(s)	354(s)	S-X sym. str.
216(m)	246(m)	204(m)	S-S-X asym. def.
	218(m)	175(m)	S-S-X sym. def.
	212(m)		
	120(m)	76(m)	torsion

many lattice bands.

Figure 4.1

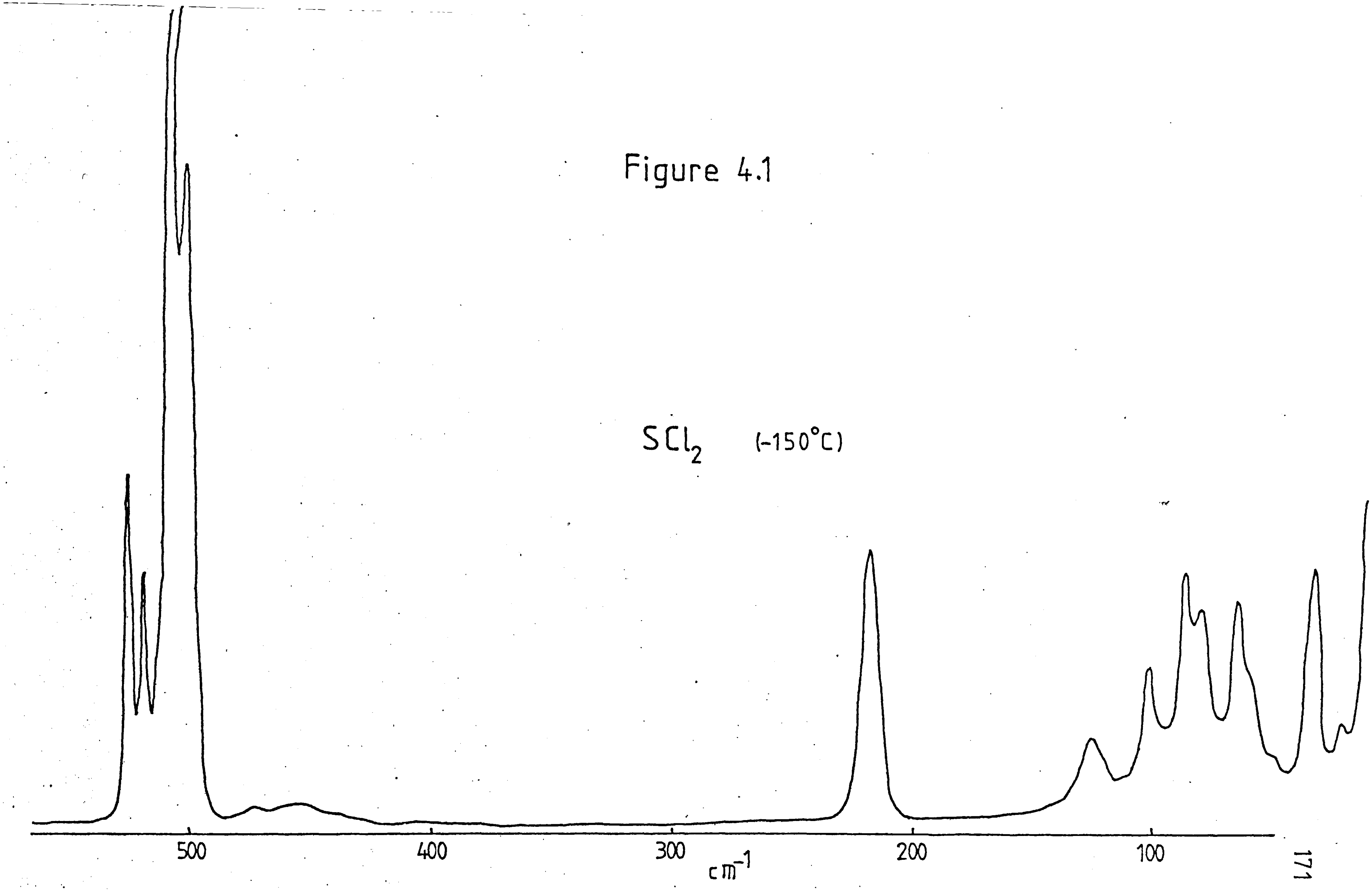


Figure 4.2

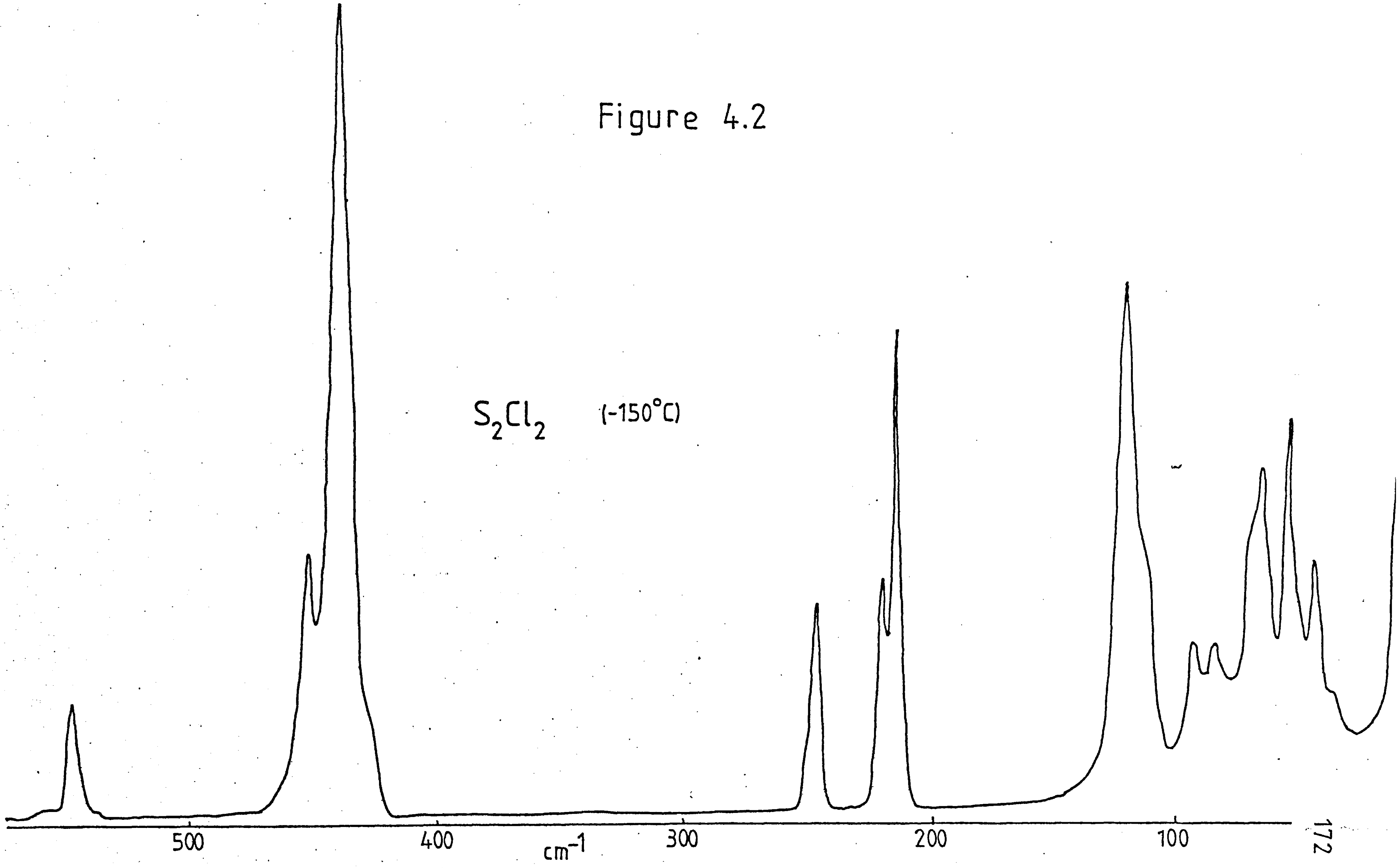


Figure 4.3

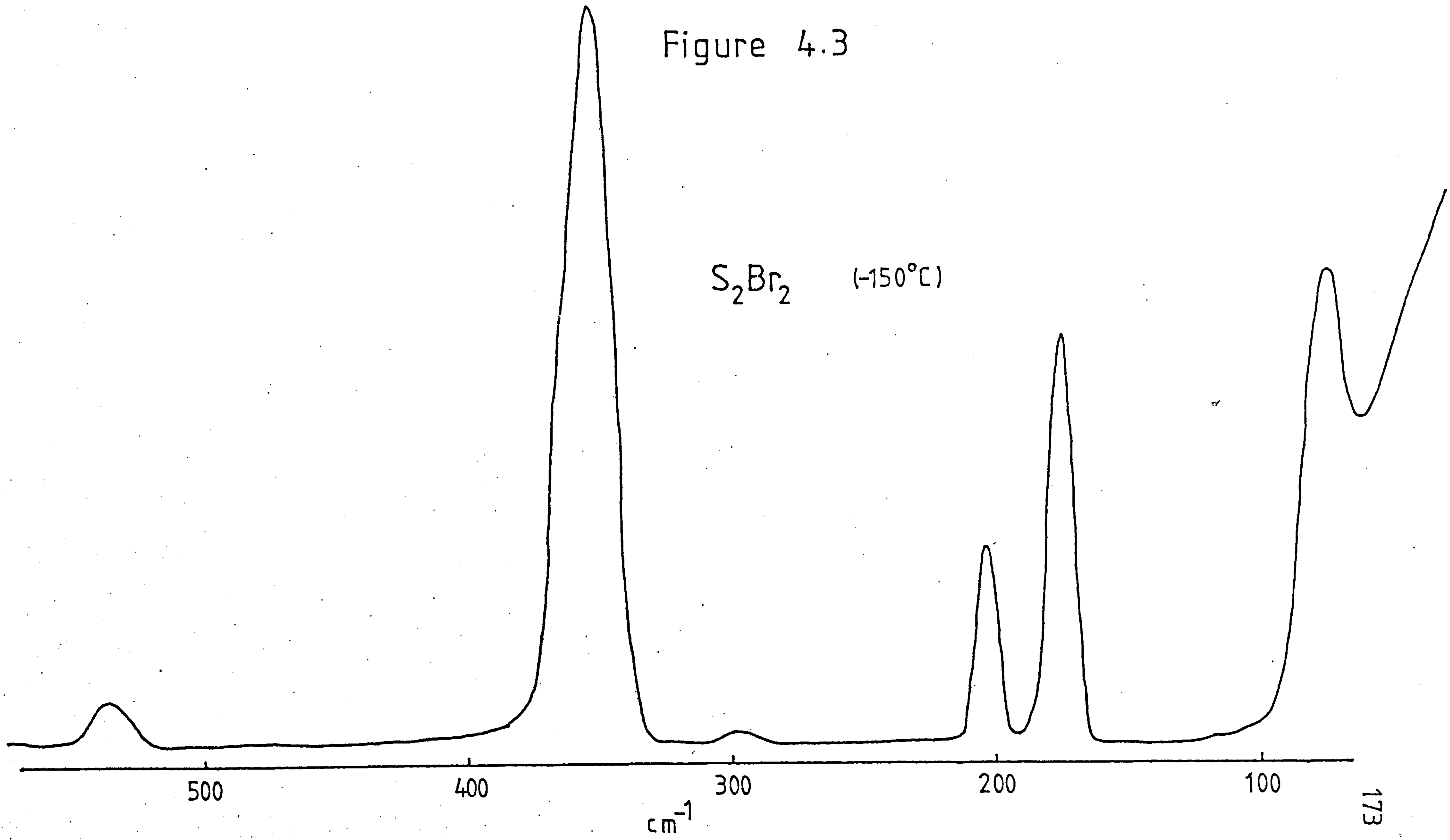


TABLE 4.2

HALOGEN RAMAN BANDS (cm^{-1}) AT −150°C (Figure 4.4)

Cl_2	Br_2	BrCl *	Assignment
541(s)	305(sh)	426(s)	str.
533(m)	298(s)	419(s)	
527(w)			
103(w)	92(w)	105(m)	lattice bands
89(m)	78(w)	89(s)	
80(w)	71(w)	72(sh)	
	54(w)		

* Bands due to Br_2 & Cl_2 also present

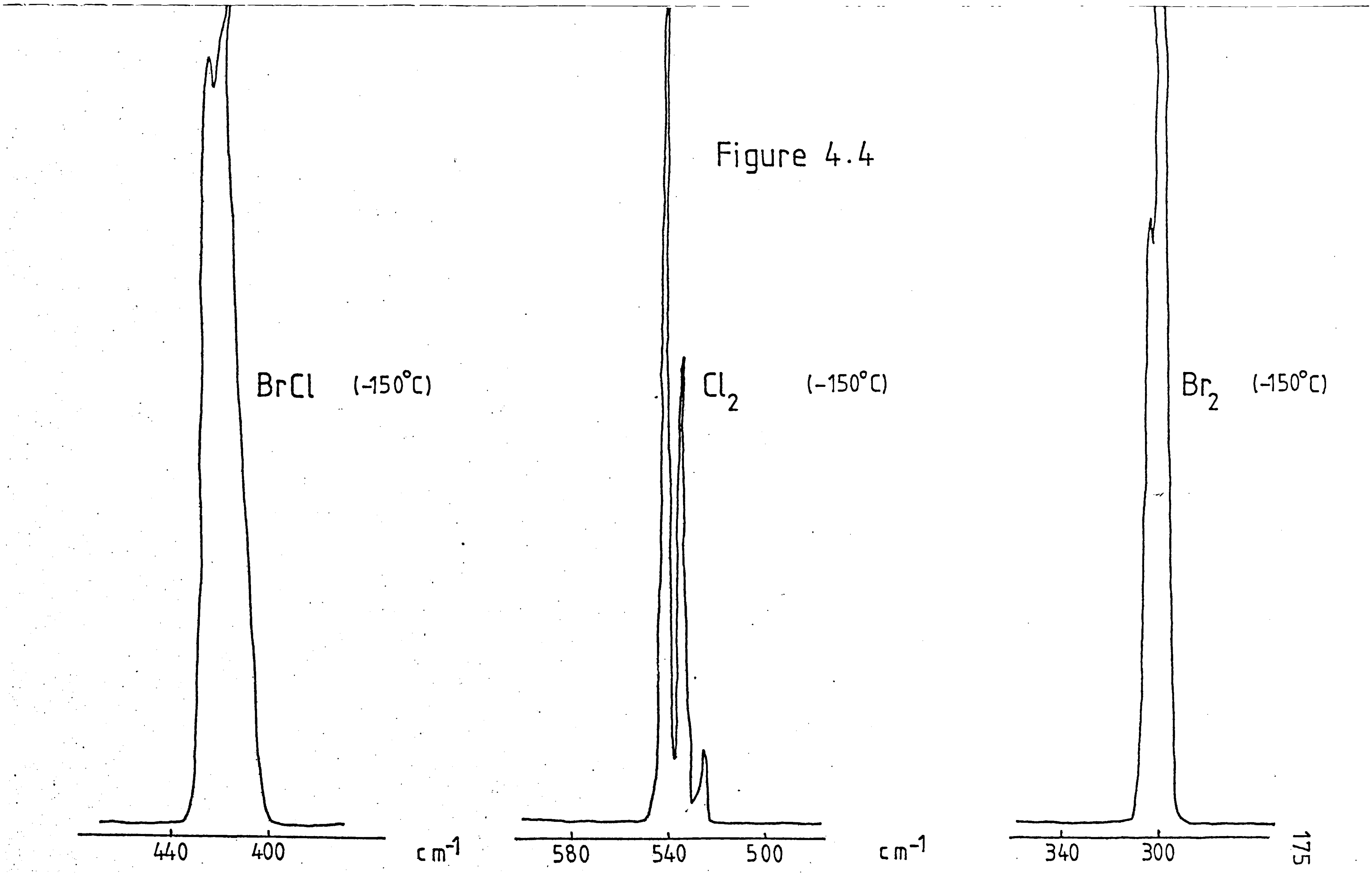


Figure 4.4

4.2 THE REACTION OF SULPHUR DICHLORIDE AND BROMINE

The reaction between sulphur dichloride and bromine gave spectra that above about -80°C could be assigned to mixtures of sulphur dichloride and bromine with other components such as bromine chloride or sulphur monobromide. However on cooling to -150°C and cycling over about 30°C a spectrum was obtained consisting essentially of three bands. A series of products was prepared using various reactant ratios and these are detailed in Chapter 5 (Section 5.11). Figures 4.5, 4.6, and 4.7 illustrate three of the spectra which are representative of all those obtained and Table 4.3 lists the band frequencies.

Basically the spectra show three major bands, a strong 268cm^{-1} band, a moderate, broad 350cm^{-1} band and a weaker 513cm^{-1} band. These bands are present in all the spectra together with a number of weak bands below 200cm^{-1}. On increasing the bromine proportion a band at 298cm^{-1} appears together with a much weaker 414cm^{-1} band. Bromine at -150°C gives a band at 298cm^{-1} (together with a shoulder at 305cm^{-1}) and bromine chloride a band at 419cm^{-1} again at -150°C. It is possible that the 414cm^{-1} band observed could be due to BrCl shifted 3cm^{-1} by the other components of the mixture. A very low bromine proportion gave a spectrum consisting of broad bands at -150°C which were not improved by cycling. These bands were

TABLE 4.3

RAMAN SPECTRA OF SCl_2, Br_2 MIXTURES

Figure 4.5	Figure 4.6	Figure 4.7	Assignment
522(vw)	522(vw)	522(vw)	S-Cl str.
513(w)	512(w)	512(w)	
		414(vw)	
350(m,br)	350(m,br)	358(w,br)	S-Br str.
		303(sh)	solid bromine
296(w)		296(m)	
268(s)	268(s)	272(s)	Cl_3^-
217(w)	218(w)	217(w)	deformation modes
163(w)	160(w)		
142(w)	138(w)	138(w)	
109(w)	108(w)		
86(vw)	86(vw)	90(vw)	
		76(w)	lattice bands
68(w)	65(w)	65(w)	
46(w)	46(w)	46(w)	
		28(w)	
23(m)	23(m)	23(w)	

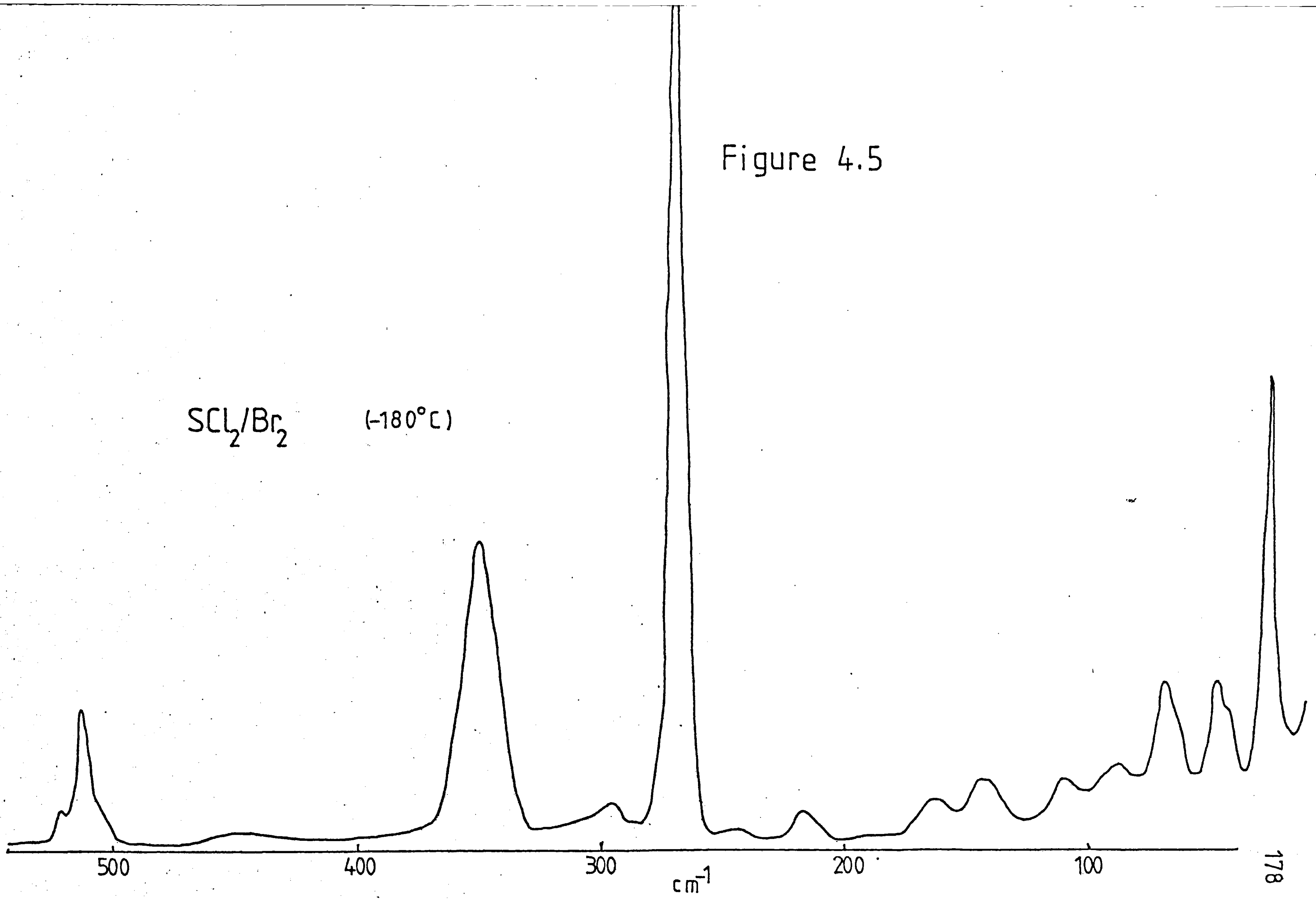


Figure 4.5

Figure 4.6

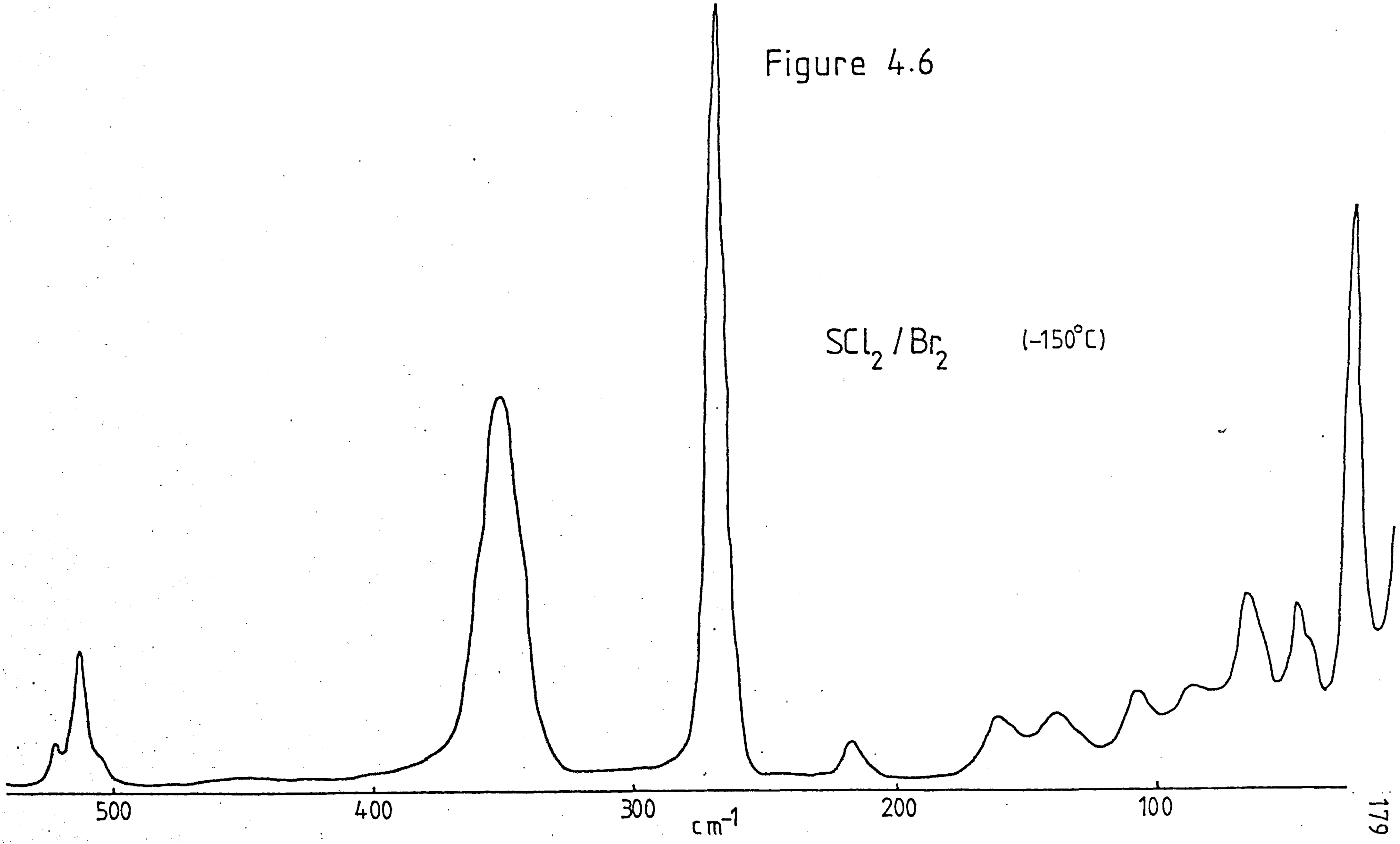
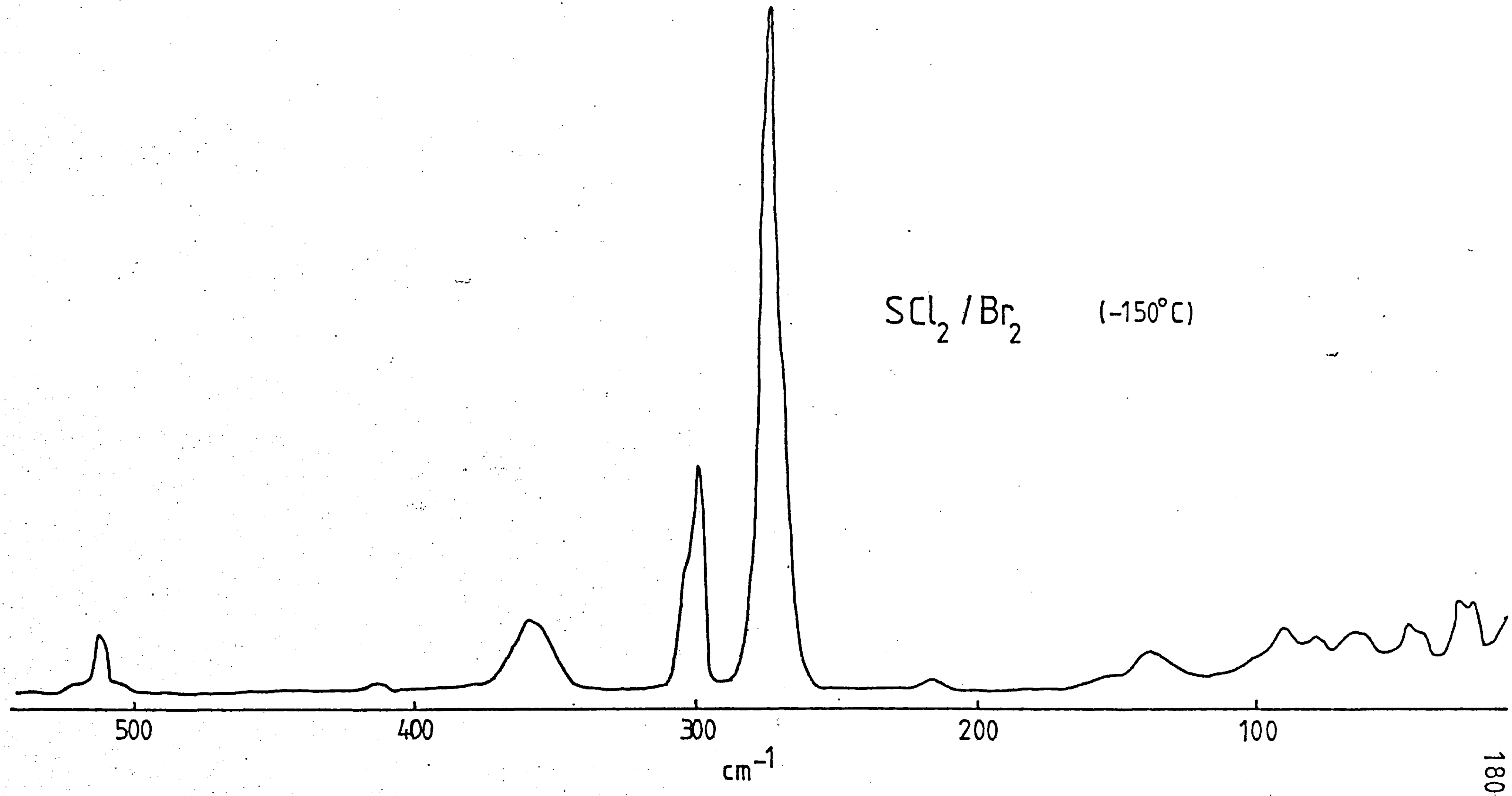


Figure 4.7



attributable to starting materials together with BrCl and S_2Br_2 although a broad band at $283cm^{-1}$ is also present which cannot immediately be assigned.

The three major bands were analysed to see if their intensities were always in the same ratio indicating that they might belong to the same molecule. The following table summarises the intensities of the major bands normalised to that at $268cm^{-1}$ of 100.

$SCl_2:Br_2$		$268cm^{-1}:350cm^{-1}:512cm^{-1}$
2:1	(Fig. 4.5)	100:33•3:15•6
2:1 (+Cl_2)	(Fig. 4.6)	100:50•0:17•7
1:1	(Fig. 4.7)	100:10•7: 8•2
2:1		100:28•7:12•6
1:2		100:43•6:18•8

There is obviously considerable variation in the intensity of the $350cm^{-1}$ band relative to the $268cm^{-1}$ band and it is therefore probable that these two bands are associated with different molecules or ion pairs. There is also some variation in the $268:512cm^{-1}$ band ratios but it is not certain that this is due to the presence of different molecules as the $512cm^{-1}$ band is relatively weak and errors are therefore high. Similarly the small variation in the $350:512cm^{-1}$ intensity ratio may be due to the same cause.

The reaction of sulphur dichloride and bromine in a 2:1 ratio could proceed as follows:-

$$
\begin{aligned}
2SCl_2 + Br_2 &\longrightarrow S_2Cl_2 + Br_2 + Cl_2 \text{ (or } 2BrCl) \\
&\longrightarrow S_2ClBr + BrCl + Cl_2 \\
&\longrightarrow 2SClBr + Cl_2 \\
&\longrightarrow SBr_2 + SCl_2 + Cl_2 \\
&\longrightarrow SCl_nBr_{3-n}^{+}\ X_m^{-} + SX_2
\end{aligned}
$$

m= 1 or 3

n= 0 - 3

x= Cl, Br

The formation of the various non-ionic species can be discounted for various reasons detailed during the following discussion of the spectra.

The band at 512cm^{-1} is in the region expected for an S-Cl vibration and it could be due to some unreacted sulphur dichloride. Figure 4.8 shows a highly intensified spectrum (very similar to Figure 4.6); the band at 512cm^{-1} is now seen to consist of a strong emission at 512cm^{-1} with a very weak shoulder at 504cm^{-1} and a further band at 520cm^{-1}. Sulphur dichloride at -150°C shows a complex of 4 bands in this region (Figure 4.1) at 525, 518, 507 and 500cm^{-1}. It is possible that the 512cm^{-1} band complex could be due to SCl_2 with

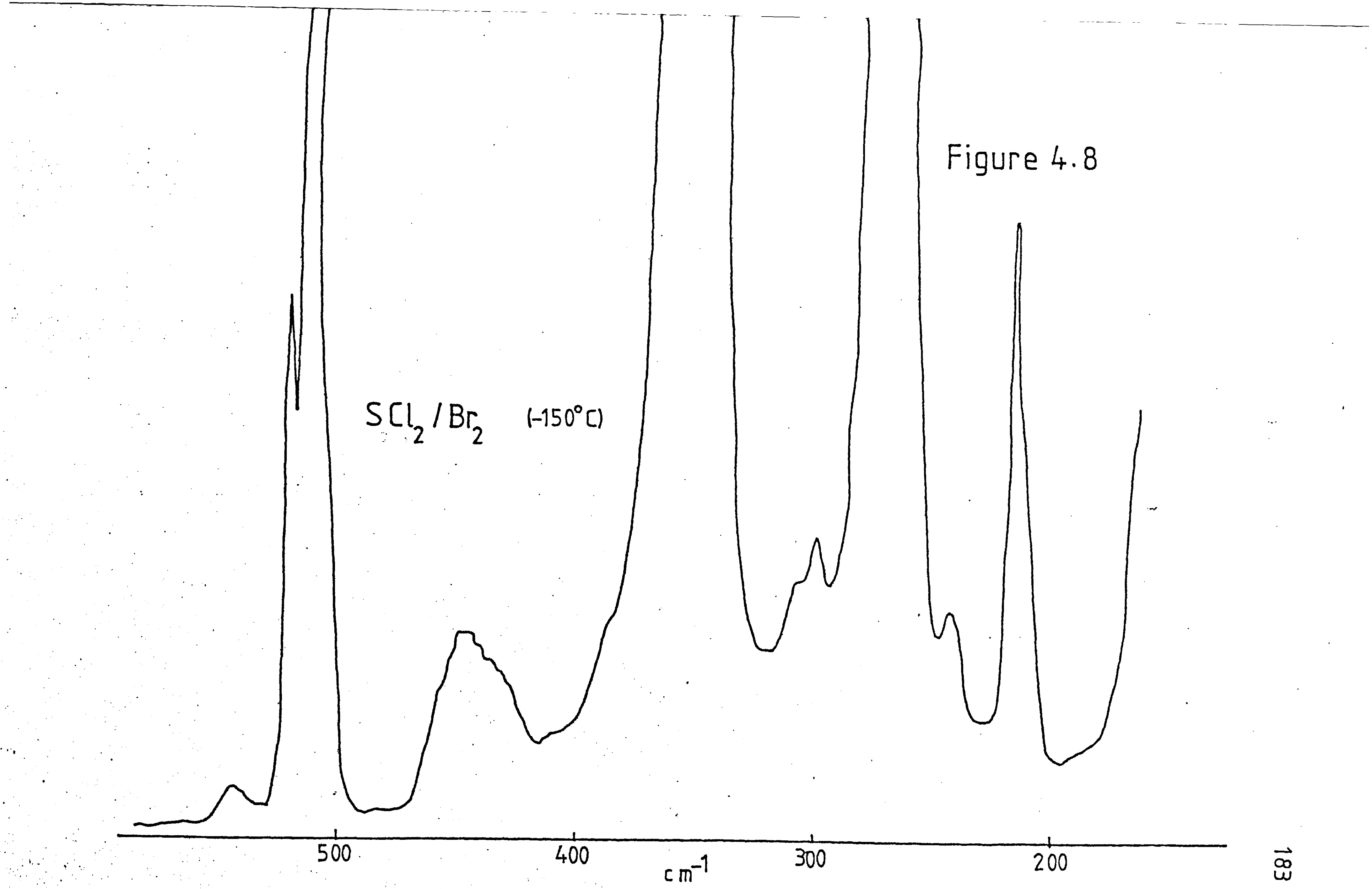


Figure 4.8

the frequencies and band shapes altered by the presence of the major components of the mixture but this is considered unlikely and it is probable that the 512cm^{-1} band is not solely due to SCl_2.

Chlorine at -150°C shows three bands, due to the various isotopic combinations at 541, 533 and 527cm^{-1}. (Figure 4.4) Again it is considered unlikely that the 512cm^{-1} band can be attributed to chlorine in view of band frequencies and shapes.

The weak band at 542cm^{-1} seen in Figure 4.8 may be due to chlorine but itis also in a region associated with S-S vibrations in sulphur monohalides. However, for both the monobromide and monochloride, deformation modes at 212cm^{-1} and 175cm^{-1} should also be visible. No 175cm^{-1} band is present and that at 215cm^{-1} is far too strong relative to the 542cm^{-1} band for it to be due to S_2Cl_2. The 212cm^{-1} deformation expected for S_2Cl_2 may be hidden by the 215cm^{-1} vibration and it is also possible that the S-Cl stretching modes are visible as incompletely resolved bands on the broad but weak 450cm^{-1} band. These assignments, must be regarded as tentative: however, these bands are extremely weak and must arise from compounds constituting only a small proportion of the mixture.

Table 4.4 lists sulphur-halogen stretching frequencies of various sulphur and/or halogen compounds available in the literature. Only the S-Cl bands of sulphur dichloride and the halosulphonium cations occur

TABLE 4.4

FREQUENCIES OF COMPOUNDS OF SULPHUR, CHLORINE AND BROMINE

Compound	Stretching Frequencies			Reference
	S-Cl		S-Br	
SCl_2	525,507			this work
SBr_2			405,418	38
S_2Cl_2	451,436			this work
$SSCl_2$	401,372			154,155
S_2Br_2			356,365	this work, 12
$SSBr_2$			317,311	154
S_2ClBr	427		371	12
$SCl_nBr_{3-n}^+$	532-490		414-348	this work
BrCl		424,419		this work
S_2		716		156
Radicals				
SCl	617			157
SBr			518	157
SSCl	404			158
SSBr			346	158
Anions				
Cl_3^-		268		)
Br_3^-		162-173		)
$BrCl_2^-$		266-285		) Table 1.1
Br_2Cl^-		230		)
Cl_5^-		482		)
Br_5^-		250		)
Cations				
Br_2^+		360		85
Cl_2^+		645		84
Br_3^+		290		85
Cl_3^+		535-493		85,86

in the region of 512cm^{-1} and it is possible that halosulphonium ions could account for the 512cm^{-1} band.

No data are available in the literature for SClBr but it might be expected to possess an S-Cl vibration at a lower frequency than in SCl_2. The 512cm^{-1} band may therefore be due to SCl in SClBr but then the S-Br frequency would have to be assigned to the 350cm^{-1} band. This would be surprising as the S-Br frequency of SBr_2 occurs at 405cm^{-1} and the substitution of a bromine by a chlorine would be expected to raise the frequency somewhat, as in S_2ClBr where S-Br occurs at 371cm^{-1}, whereas in S_2Br_2 it occurs at 365cm^{-1}. Also the deformation mode would have to be assigned to 269cm^{-1} which is the strongest band in the spectrum. This would be unusual in itself but 269cm^{-1} is probably too high a frequency for a band that occurs at 216cm^{-1} in SCl_2. Therefore it is considered unlikely that the spectra under discussion can be assigned to SClBr.

The 350cm^{-1} band is in the region expected for S-Br and in fact the band is at the same frequency and is of the same shape as the S-Br band in S_2Br_2. However in S_2Br_2 a deformation mode is observed at 175cm^{-1} of approximately half the 350cm^{-1} band intensity. There is no 175cm^{-1} band of such strength in the spectra under discussion and therefore the 350cm^{-1} band cannot be assigned to S_2Br_2. Table 4.4 shows that, apart from radicals discussed later and Br_2^+, the only other bands in the 350cm^{-1} region occur in the halosulphonium cations. The existence of the Br_2^+ cation in this work is most unlikely as it is only stable in super acid solvent systems. It is however noticeable that 350cm^{-1} is at the lower end of the range of frequencies observed in the Lewis acid complexes of the halosulphonium cations. This to some extent supports the view that the 512cm^{-1} band is also due to halosulphonium cations and the ratio of intensities of these two bands is similar to that observed in the authentic halosulphonium cations discussed in Chapter 2.

The fact that no strong bands are present in these spectra at around 400cm^{-1}– 420cm^{-1} also effectively precludes the possibility of any significant amounts of SBr_2 being present.[38]

It has already been noted that the 268cm^{-1} band is probably not associated directly with the other major bands and it is therefore possible that this band is attributable to the anion associated with a halosulphonium cation. In any case it would be most unusual to observe an S-Br (or S-Cl) stretching band at such a low frequency. Even charge transfer co-ordinated bromine normally gives rise to bands above about 280cm^{-1} and it is unlikely, although not impossible that this band is associated with such a complex. As a general rule the bromine charge-transfer bands are not sharp single bands as is observed with the 268cm^{-1}

band and it is considered that no such complex is responsible for these spectra. Table 4.4 shows that three ions could give rise to bands at about 270cm^{-1} i.e. Cl_3^-,$BrCl_2^-$ and Br_3^+ although the latter is most unlikely as it is only stable in strongly acidic solution. It is possible that either Cl_3^- or $BrCl_2^-$ could be attributed to the 268cm^{-1} band although Gabes [96,98] observes at least 4 bands for the $BrCl_2^-$ ion due to isotope and factor group splittings. The Cl_3^- ion was observed by Evans[104] as a single, very strong, although rather broad emission. It is also noticeable that excess bromine varies the frequency of this band by some 4cm^{-1}, this has also been observed in other spectra and is therefore reproducible.

The only other possible ions not listed in Table 4.4 are those of the type SX_6^{2-} and SX_5^- which are unknown for halogens other than fluorine. However, it is unlikely that the spectra under discussion could contain these species as the SX_6^{2-} ion would be expected to give 3 strong Raman bands indicative of an octahedral ion and the SX_5^- ion 9 bands for a square pyramidal ion. These spectra possess insufficient bands to be consistent with such ions.

In a series of recent papers Feuerhahn[36,154,157,158] discusses the reaction of bromine with sulphur dichloride (and monochloride), by matrix isolation infra-red spectroscopy and mass spectrometry. However, in all cases the mixture of reactants is ionized by passage through a microwave discharge, by U.V. photolysis, or by electron impact in a mass spectrometer. Under these conditions a number of new species were observed, many being free radicals but the major products were SBr^+ and $SBr_2^{+\cdot}$, only limited amounts of sulphur-chlorine species were formed. In the systems discussed by Feuerhahn considerable amounts of energy would be provided by the ionizing systems employed. Although a laser is used to record the Raman spectra reported here there is no evidence of any change in the spectra on irradiation and the reaction products would probably have been formed before the sample was irradiated. The systems used in this work were not subjected to ionization and it is not clear how relevant Feuerhahn's conclusions are to the mixtures described here however, the radicals SBr and SCl possess vibrational frequencies (518cm^{-1} and 617cm^{-1}, Table 4.4) higher than the bands observed in these spectra although the frequency for the species SBr_2^+ was not given. Feuerhahn does not indicate the production of any particularly unexpected species although it is interesting to note that sulphur-bromine species were favoured.

Hence, from the spectroscopic evidence it would appear probable that these spectra are attributable to mixed halosulphonium cations associated with a trihalide anion. On the basis of the two bands at about 512cm^{-1} together with a single 350cm^{-1} band it would appear that the spectra are consistent with a cation SCl_2Br^+. Assignment of the anion is more tentative. The single emission at 268–272cm^{-1} suggests a Cl_3^- anion, although this is hardly consistent with the restricted amount of chlorine in the reaction mixture. Spectra to be discussed later where chlorine is present also show a band in the 270cm^{-1} region, and some spectra show a band at 279cm^{-1} which may be attributable to $BrCl_2^-$. It is therefore considered more likely that this band is due to Cl_3^- than $BrCl_2^-$. The deformation modes that would be expected for $SCl_nBr_{3-n}^+$ could be assigned to the weak bands below 220cm^{-1} and their pattern is very similar to that observed in similar ions discussed in Chapter 2.

Overall these spectra are most satisfactorily assigned to $SCl_2Br^+Cl_3^-$ although obviously some minor components are also present.

4.3 THE REACTION OF SULPHUR DICHLORIDE, BROMINE AND CHLORINE

The reaction between sulphur dichloride, bromine and chlorine gave spectra that at room temperature consisted of bands assignable to the starting materials together with bromine chloride, BrCl. On cooling to -150°C a spectrum typical of a glass was usually obtained. However, if the tube containing the products was cycled at low temperature then a spectrum was obtained which showed sharp, resolved bands. As a general rule these spectra remained stable as the temperature was varied until at about -50°C they degraded to a liquid showing bands mainly due to the starting materials. On re-cooling and cycling the original spectrum was usually obtained although on a few occasions some bands were not resolved.

A number of different reactant ratios were used but the addition of chlorine had to be performed using vacuum line techniques. Normally little attempt was made to regulate the quantity of chlorine added although the tube was weighed after the addition and sealing to obtain the weight added. In one case a previously calibrated tube was used to add a specific chlorine volume to the other reactants.

In most cases chlorine was added to the other reactants as this was most convenient on a vacuum line. However, in one case the chlorine was added to the sulphur dichloride followed by the bromine but as no particularly different spectrum was obtained this procedure was not repeated.

Details of all the products made are given in Chapter 5, Section 5.12 (Table 5.9), although only a few representative spectra are illustrated.

The spectra all show bands in the following regions:-

A.	520-540cm^{-1}	solid chlorine
B.	430-490cm^{-1}	S-Cl stretching
C.	340-370cm^{-1}	S-Br stretching
D.	260-280cm^{-1}	anion bands
E.	230cm^{-1}	deformation and lattice bands

It is noticeable that the S-Cl and S-Br stretching modes are some 20-50cm^{-1} lower in frequency than those in most of the other spectra discussed in this work.

The spectra are all very complex and exhibit a number of bands. It is therefore unlikely that they could be assigned to any simple sulphur halide species such as sulphur chlorobromide, sulphur dibromide or disulphur chlorobromide. The only bands not attributable to sulphur-halogen vibrations are those in the 270cm^{-1} region; they must therefore be due to vibrations of other species, presumably halide anions. The only anions that show Raman bands in this region are Cl_3^- and $BrCl_2^-$(268cm^{-1} and 266-285cm^{-1}, Chapter 1, Table 1.1). It is also possible for Br_3^- to exhibit a band in this region but it would only arise in a very asymmetric anion usually associated with a small cation.[96,98] It seems unlikely that the Br_3^- ion would be formed in mixtures containing relatively large amounts of chlorine.

It is therefore probable that the spectra are due to ionic species of the type $SCl_nBr_{3-n}^+ X_m$

where n = 0-3

m = 1 or 3

X = Cl^-, Br^-, Br_2Cl^- or Cl_2Br^-

This is exactly analogous to the situation that occurred when mixtures of sulphur dichloride and bromine (and chlorine) formed complexes with Lewis acids as discussed in Chapter 2. Such cations would be expected to show S-Cl and S-Br bands lower in frequency than in their Lewis acid analogues, cf $SCl_3^+Cl^-$ described in Chapter 2. In the case of the Lewis acid mixed halosulphonium species the S-Br bands were always much stronger than in the spectra discussed in this section. The reason for this difference is not clear but may simply be due to the relatively restricted amount of bromine present in these reaction mixtures.

Basically two types of spectra were obtained and they can be broadly classified as follows:-

1. TYPE I SPECTRA. (Figures 4.9 and 4.10)

   a. minimal chlorine bands at 520-540cm^{-1}
   b. broad complex 430-490cm^{-1}
   c. 2 broad bands at 345 and 370cm^{-1}
   d. band at 434cm^{-1}
   e. band at 271cm^{-1}

2. TYPE II SPECTRA (Figures 4.11, 4.12 and 4.13)

   a. large chlorine bands at 520-540cm^{-1}
   b. narrow complex at 490-500cm^{-1}
   c. single broad band at 355cm^{-1}
   d. minimal band at 434cm^{-1}
   e. band at 279cm^{-1}

There is no immediately obvious correlation between reactant ratio and spectra type and indeed it is possible to obtain spectra that are a combination of the above types. These spectra exhibit bands at 271cm^{-1} and 279cm^{-1} of equal intensity. It was also possible to obtain the two types of spectra from one reactant mix showing that considerable interchange between the complexes can occur. It was however, generally observed that rapid cooling of the reactants and minimal cycling gave the Type II spectra. If cooling was slower, and the cycling more prolonged, then the Type I spectra were produced. This was especially noticeable if temperatures as high as -80°C were reached or the mixture was held at this temperature. This suggests that the complex(es) giving the Type II spectra are less stable than those giving the Type I spectra.

Typical Type I spectra are illustrated in Figures 4.9 and 4.10 (Table 4.5). The spectra show only a relatively weak band at 271cm^{-1} together with a shoulder at 279cm^{-1} and as both the Cl_3^- and $BrCl_2^-$ anions exhibit very strong bands (cf spectra of Section 4.2) it is likely that only relatively small amounts of complexes containing these anions are present in these mixtures. Therefore it is considered that the most likely anions to be present in these spectra are Cl^- and Br^-. On the basis of the elements present it is probable that SBr_2Cl^+ and $SBrCl_2^+$ ions are present in varying amounts. There is no evidence for $SCl_3^+Cl^-$ (471cm^{-1} and 479cm^{-1}) or for SBr_3^+ (375-414cm^{-1}) the presence of $SBr_3^+Br^-$ is unlikely in view of the high chlorine levels present.

The assignment of the bands to the individual ions is difficult and to some extent arbitrary without the help of pure complexes whose analysis is known. On the evidence of the work described earlier they are likely to be very difficult to prepare and their analysis would always be in doubt because only the overall degraded mixture could be analysed. However, some attempt can be made to assign the bands but the assignments must be regarded as tentative.

TABLE 4.5

RAMAN SPECTRA OF SCl_2, Br_2, Cl_2 MIXTURES (cm^{-1})

Figure 4.9	Figure 4.10	Assignments
542(vvw)	542(w)	solid chlorine
534(vvw)	534(w)	
490(sh)	490(sh)	S-Cl str.
479(s)	482(m)	
	475(m)	
466(s)	466(s)	
	461(sh)	
435(m)	434(m)	
368(br)	370(sh)	S-Br str.
	362(br)	
342(br)	343(br)	
279(w,sh)	279(w,sh)	$BrCl_2^-$
272(m)	271(m)	Cl_3^-
264(w)	264(w)	def.
218(w,br)	220 (w,br)	
155(w,sh)	155(w)	
146(br)	146(br)	
94(m)	96(m)	

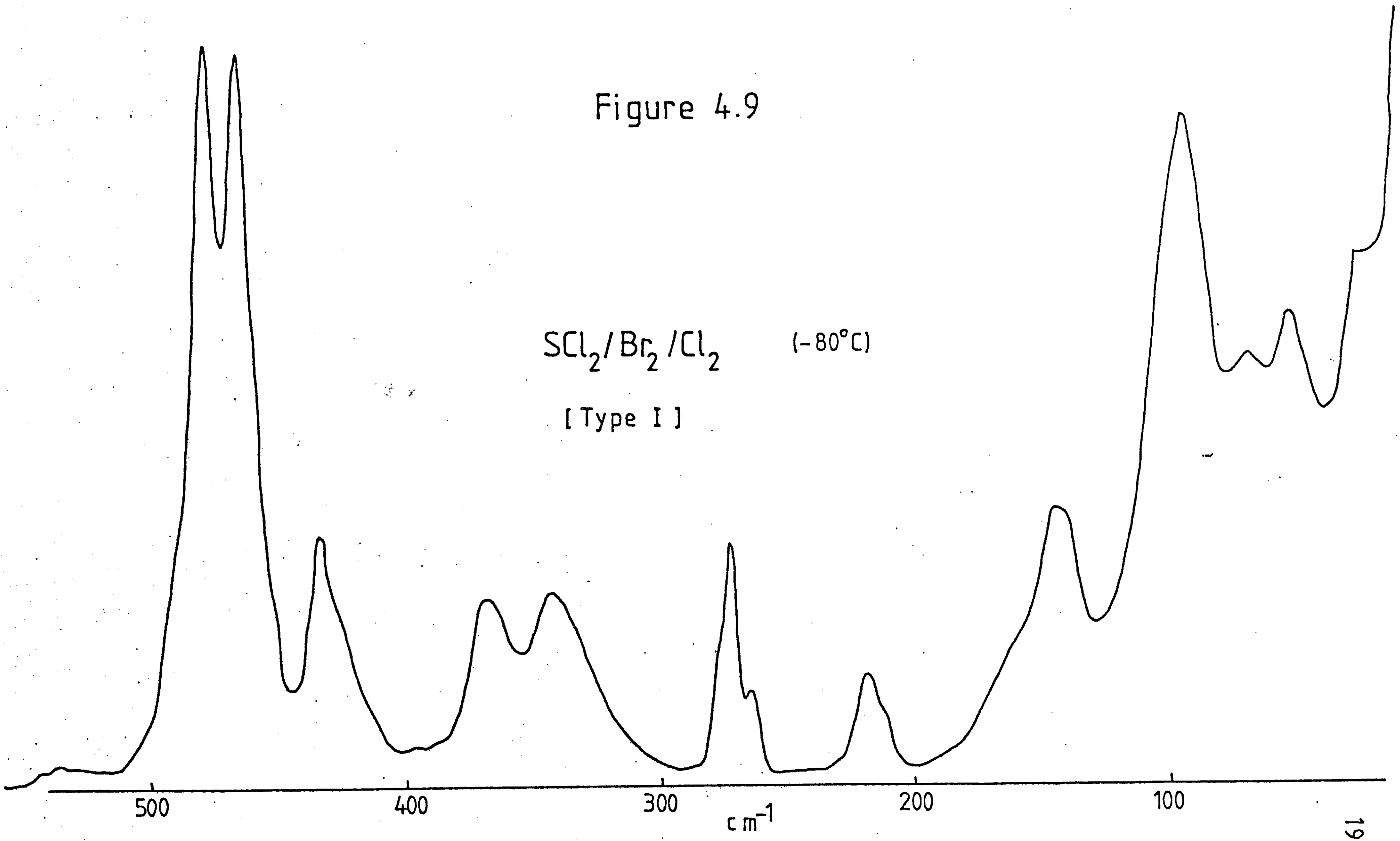
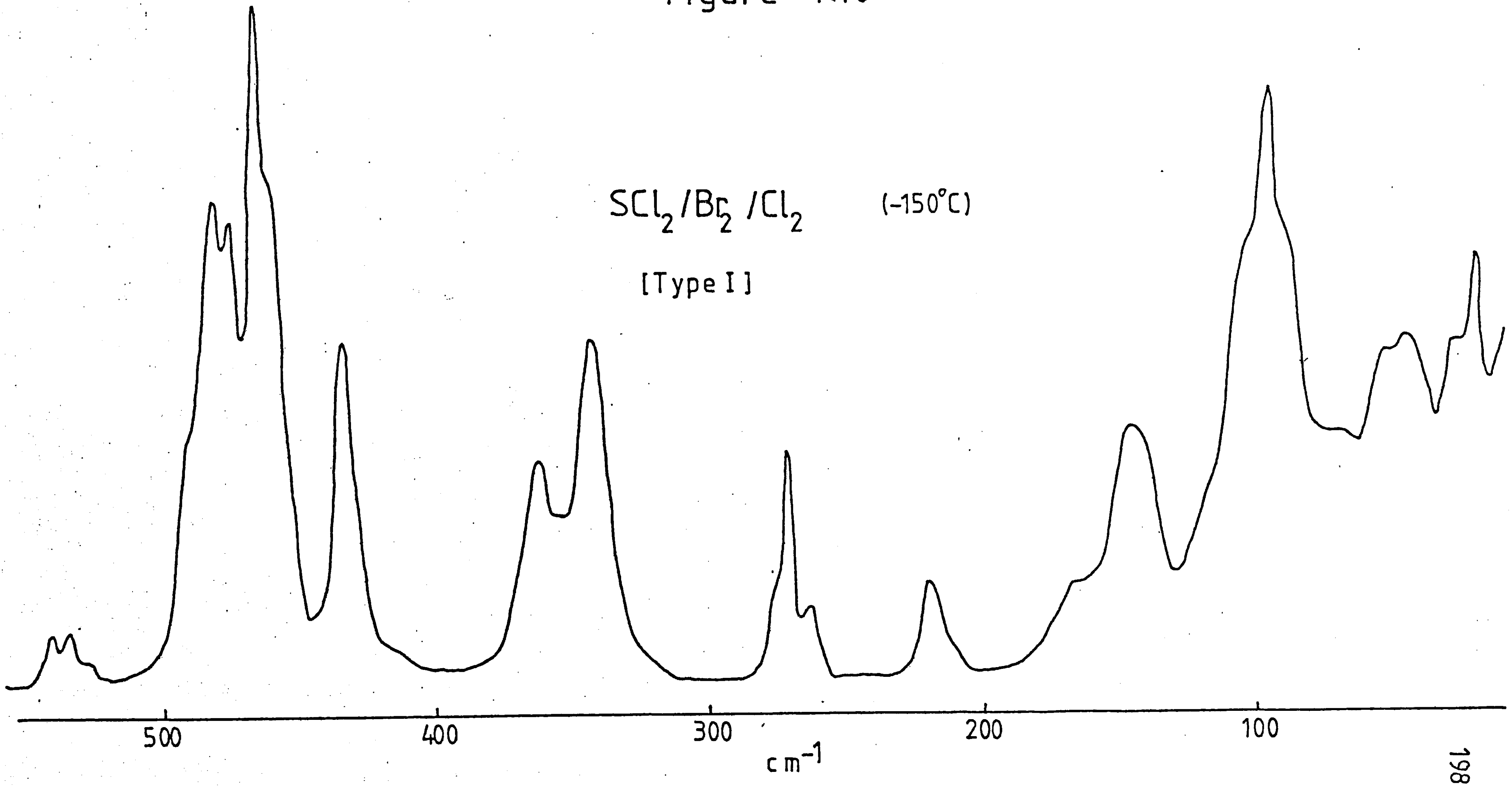


Figure 4.9

$SCl_2/Br_2/Cl_2$ (−80°C)

[Type I]

Figure 4.10



$SCl_2/Br_2/Cl_2$ (-150°C)

[Type I]

Table 2.11 (Chapter 2) lists the frequencies found in Lewis acid complexes for mixed halosulphonium cations. The lowest S-Cl frequency is found in the cation SBr_2Cl^+ and it is known that the Cl^- anion reduces such frequencies significantly. It is therefore probable that the 435cm^{-1} band can be assigned to $SBr_2Cl^+Cl^-$.

This band is in the region of that given by BrCl but the frequencies given by BrCl at -150°C are 426cm^{-1} and 419cm^{-1}, the band being split due to the chlorine and bromine isotopes. At -100°C these frequencies rise by some 5cm^{-1} but never rise to 435cm^{-1}. The BrCl bands also tend to be very sharp and its probable existence is indicated by the shape of the 435cm^{-1} band. However, it is considered that an S-Cl stretching mode is present in this region.

A comparison of the spectra given in Figures 4.9 and 4.10 would suggest that the 479 and 466cm^{-1} bands observed in Figure 4.9 give rise to split bands in the better resolved spectrum of Figure 4.10 presumably due to the more efficient annealing. This product was kept at -70°C for 1 week to obtain this spectrum and it is therefore considered that at the low temperatures involved some evidence of intermolecular interactions is seen causing factor group splitting. The assignment of these two bands in isolation is difficult but a comparison with the Type II spectra suggests reasonable assignments.

Typical Type II spectra are illustrated in Figures 4.11, 4.12 and 4.13 (Table 4.6). There is little evidence of significant emission at 271cm^{-1} and the 279cm^{-1} band is visible as a single peak. However as discussed earlier both Cl_3^- and $BrCl_2^-$ give very strong Raman emissions so it is likely that these anions are present in relatively small amounts.

The bands at 485 and 490cm^{-1} in Figure 4.11 (and also Figure 4.12) are only resolved at -170°C and at slightly higher temperatures (-110°C) only one band at 485cm^{-1} is observed, (Figure 4.14). It is therefore probable that the splitting is due to crystal effects, as observed in the Type I spectra. This spectrum therefore has the bands expected for the cation SBr_2Cl^+ with only a few weak bands not attributable to either the expected stretching or deformation modes for this cation.

It is noticeable that these S-Cl bands (485/490cm^{-1}) occur at higher frequencies than in the Type I spectra where they are only visible as weak shoulders on the 479cm^{-1} band.

From both the Type I and Type II spectra there are bands at the following frequencies in the S-Cl stretching region.

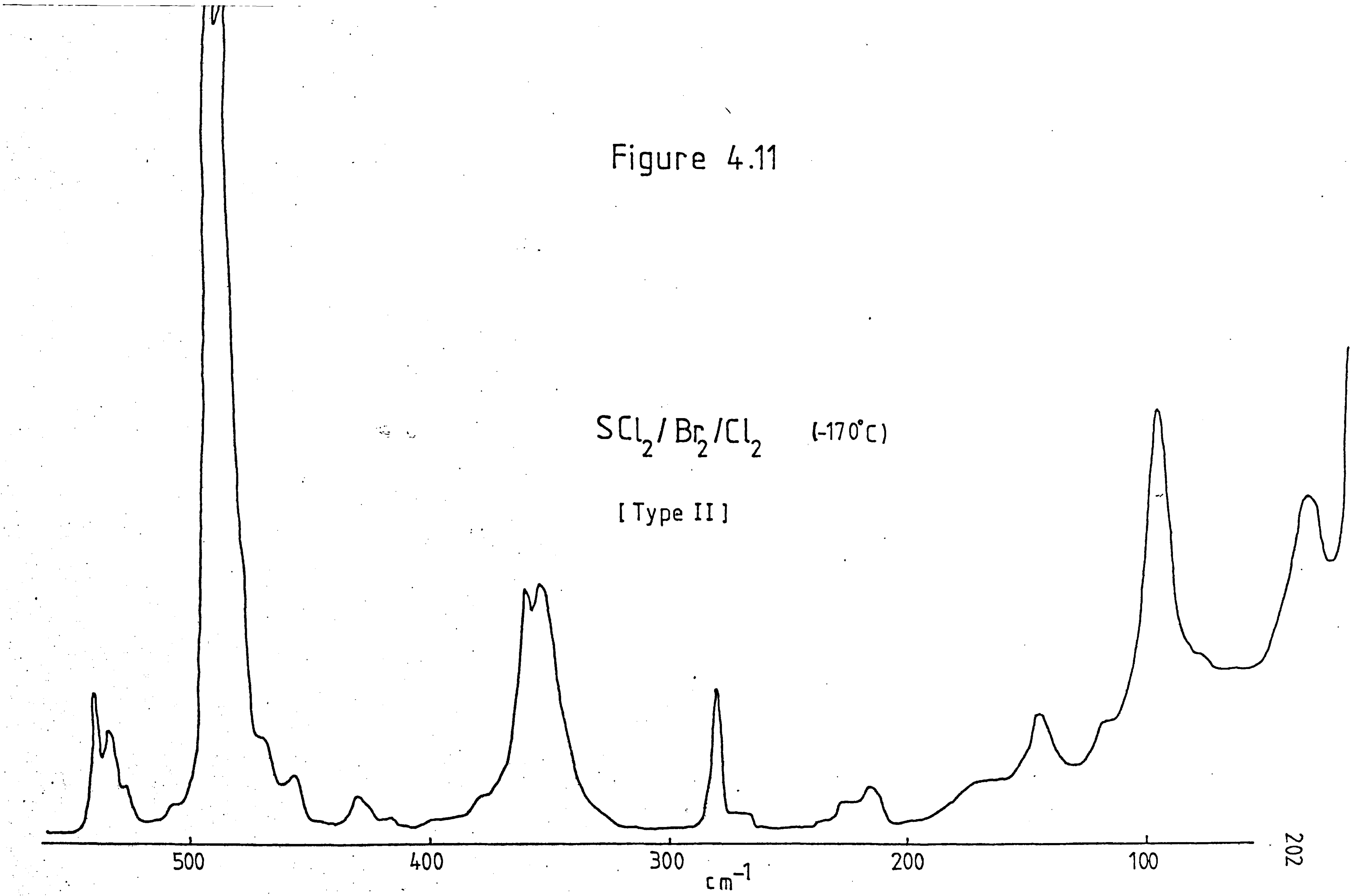
434cm^{-1}		Type I
466cm^{-1}	(466/461cm^{-1})	Type I
479cm^{-1}	(482/475cm^{-1})	Type I and II
485cm^{-1}	(485/490cm^{-1})	Type II

TABLE 4.6

RAMAN SPECTRA OF SCl_2, Br_2 AND Cl_2 MIXTURES (cm^{-1})

Figure 4.11	Figure 4.12	Figure 4.13	Assignment
540(m)			solid chlorine
534(m)	535(br)		
529(w)			
		520(w)	S-Cl str.
490(s)	489(s)		
		488(s)	
485(s)	486(sh)		
	478(s)	479(s)	
470(w)			
457(w)	460(w)	460(w)	
430(w)			
	416(w)	416(m)	BrCl
360(br)	359(br)		S-Br str.
352(br)		350(br)	
		309(w)	Br_2
279(m)	279(m)	279(m)	$BrCl_2^-$
225(sh)	225(sh)	225(sh)	deformation modes
214(w)	213(w)	213(w)	
170(vw)	170(vw)	170(vw)	
143(w)	140(w)	140(w)	
92(m)	94(m)	92(m)	

Figure 4.11



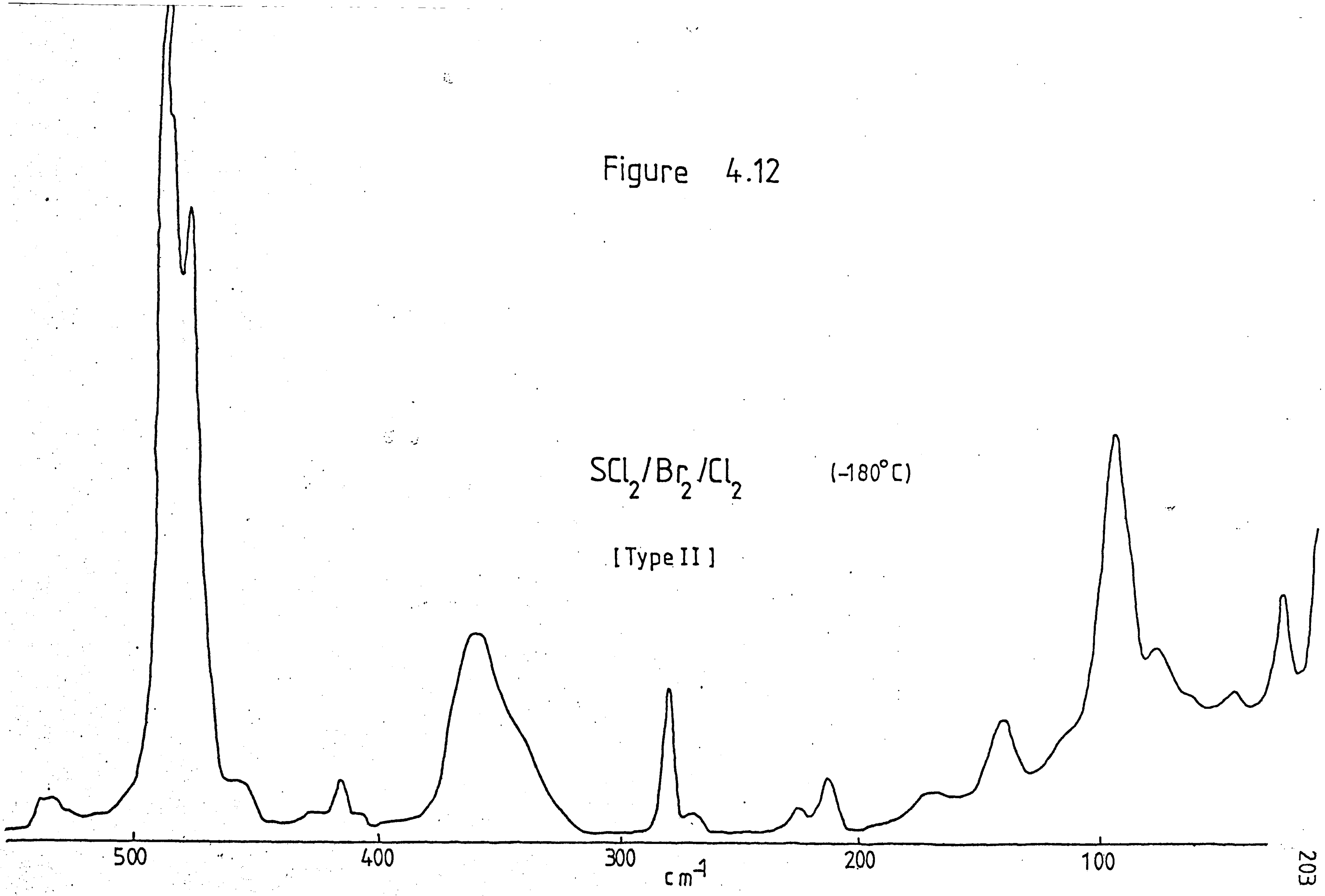


Figure 4.12

$SCl_2/Br_2/Cl_2$ (−180°C)

[Type II]

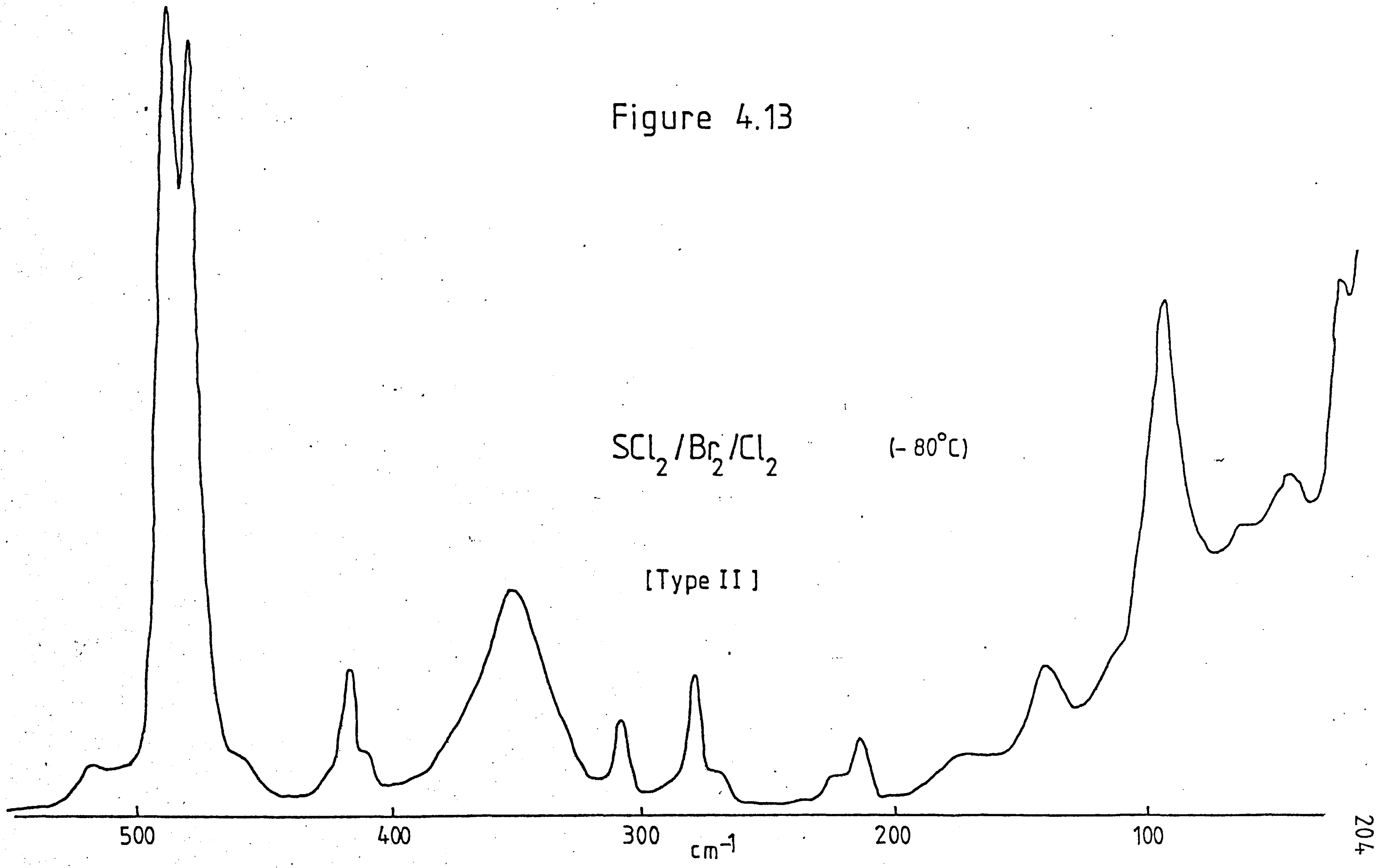


Figure 4.13

$SCl_2/Br_2/Cl_2$ (- 80°C)

[Type II]

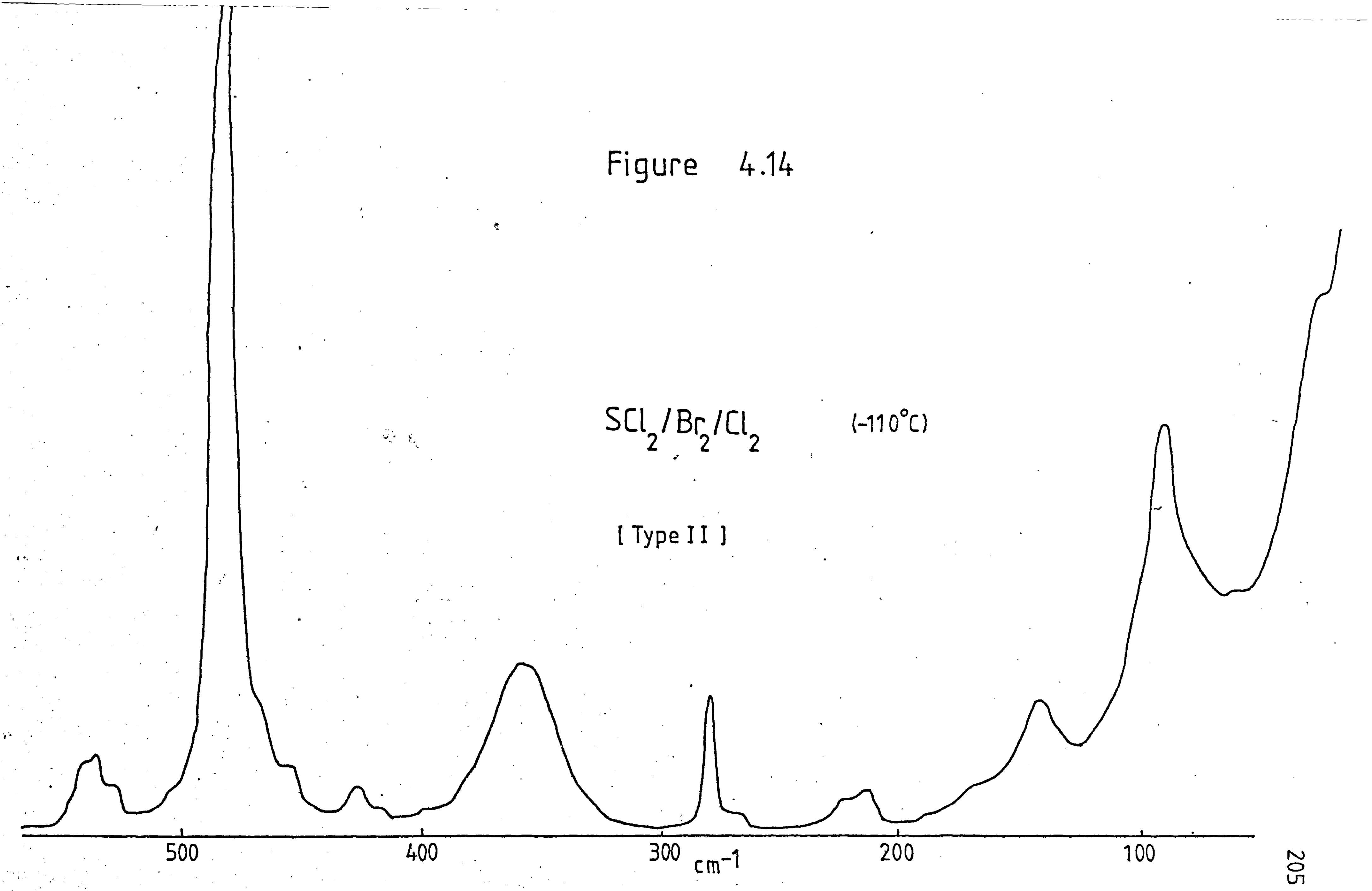


Figure 4.14

$SCl_2/Br_2/Cl_2$ (-110°C)

[Type II]

The cations $SClBr_2^+$ and SCl_2Br^+ would be expected to show either one or two S-Cl bands respectively in the high frequency region. However, in the case of SCl_2Br^+ one S-Cl mode is symmetric and one antisymmetric, and it is generally true that the antisymmetric mode is weaker than the symmetric mode. Therefore it is possible that only the symmetric mode will be observed in these spectra with the weaker mode being obscured by the stronger modes. The bands, particularly in the Type I spectra, are fairly broad and could quite easily overlay relatively weak antisymmetric modes.

The four strong modes can therefore be assigned to four halosulphonium cations and it is suggested that two types of each possible cation, $SBrCl_2^+$ and SBr_2Cl^+, are present. As discussed earlier there are only a limited number of possible anions that are compatible with the spectra under discussion. Table 4.4 and the earlier discussion shows that only bands due to the anions Cl_3^- and $BrCl_2^-$ can be observed in the spectra. The only other anions that can reasonably be present are Cl^- and Br^- and it is suggested that both of these exist in these products. It is recognised that the Br^- ions would have to exist in a system containing high chlorine levels and it is probable that this explains the relative instability of the Type II spectra. The initial product formed possibly contains the Br^- anion but on prolonged cycling this is replaced by the Cl^- anion. The existence of the Br^- anion cannot of course be observed directly by Raman spectroscopy but its presence can be inferred from the frequencies observed for the cations. The S-Cl modes occur for Lewis acid complexes at about 505-525cm^{-1}. In $SCl_3^+Cl^-$ these modes drop in frequency to 449-471cm^{-1} and in the trihalide complex discussed earlier it occurs at 512-522cm^{-1}. The frequencies under discussion occur at about 480cm^{-1} and it is suggested that a Br^- anion would be compatible with such a frequency. This immediately suggests that the bridging halogens are less strongly bound for Br^- than for Cl^- consistent with the larger size and lower electronegativity of Br^-.

It would therefore be reasonable to assign the S-Cl stretching bands as follows:-

434cm^{-1}	$SClBr_2^+$ Cl^-
466cm^{-1}	SCl_2Br^+ Cl^-
479cm^{-1}	$SClBr_2^+$ Br^-
485cm^{-1}	SCl_2Br^+ Br^-

The SBr_2Cl^+ S-Cl frequencies would be expected to be lower than their $SBrCl_2^+$ analogues and, due to its smaller size, the Cl^- anion would be expected to cause a larger drop in frequency than the Br^- anion.

The assignment of the S-Br frequencies cannot be readily accomplished as the bands in this region, 340-370cm^{-1}, are broad and obviously contain a number of unresolved bands. Any assignment of these broad bands would therefore be entirely arbitrary.

The cations under discussion would be expected to give rise to three deformation modes and these would be expected below about 240cm^{-1} based on the data obtained for mixed halosulphonium cations listed in Table 2.11. These spectra show a number of weak bands below 230cm^{-1} and these appear to be grouped into three regions i.e. 210-230cm^{-1}, 140-170cm^{-1} and about 95cm^{-1}. These regions are similar to those areas in which the deformation modes for the mixed halosulphonium cations were observed (Table 2.11). There is evidence from the $SCl_3^+Cl^-$ and SCl_3^+ $AlCl_4^-$ spectra that the deformation modes are not moved in frequency significantly by the anion change and it it therefore reasonable to suggest that similar deformation frequencies to those in Table 2.11 would again be observed. However, in view of the mixed nature of the products it would be difficult to assign each of the bands to specific ions.

One of the differences between the Type I and Type II spectra is the change from a 271cm^{-1} band to one at 279cm^{-1}. If the Type II unstable spectrum contained the $BrCl_2^-$ anion then, in the presence of chlorine, it might be expected that gradual reaction to yield the Cl_3^- anion might occur. This is perhaps not too surprising as the HSAB Principle suggests that there is a tendancy for like ligands to group together,[145,153] therefore favouring Cl_3^- over $BrCl_2^-$. If the 279cm^{-1} band is assigned to $BrCl_2^-$ and the 271cm^{-1} band to Cl_3^- then this is what is observed on cycling. The frequency of 271cm^{-1} for Cl_3^- is also very close to that (268cm^{-1}) observed by Evans.[104] Gabes [96,98] details a number of frequencies for the $BrCl_2^-$ ion caused by the chlorine isotopes and also factor group splitting. The ratio of the two strongest isotope split bands is 1.5:1 as expected for a 3:1 ratio of ^{35}Cl to ^{37}Cl. This is split not observed in the weak 279cm^{-1} bands in our spectra but the frequency difference is only 3cm^{-1} which may not be observable in these weak bands. The band is however, asymmetric. The large factor group splitting observed by Gabes of some 10cm^{-1} is not seen in these spectra but it may be that the cation is sufficiently large, or the system sufficiently dilute, to reduce such splitting.

The spectra given in Figures 4.12 and 4.13 each show bands at 416cm^{-1} whose assignment is not certain. An S-Br stretching mode occurs in this region for Lewis acid complexes but the anion that would lead to such a high frequency in these spectra, where S-Br occurs around 350cm^{-1}, is unknown. The compound BrCl gives rise to a band at 419cm^{-1} (shoulder 426cm^{-1}) at -150°C and it is possible that the presence of the other components of the mixture could shift the band by 3cm^{-1} as was proposed in the previous section.

It is therefore proposed that the spectra under discussion can be assigned to mixed halosulphonium cations associated primarily with halide anions.

4.4 SUMMARY

The following notes summarise the main conclusions reached during the work on the sulphur dichloride and bromine mixtures, optionally with chlorine, discussed in Section 4.2 and 4.3.

A. Sulphur dichloride and bromine mixtures.

1. The Raman spectra of mixtures of sulphur dichloride and bromine at -150°C gave three major bands at 268, 350 and 513cm^{-1}.

2. The spectrum is probably not attributable to the various covalent species that could be formed from the reactants such as S_2ClBr, SBr_2 or SClBr.

3. The spectra are consistent with the presence of a mixed halosulphonium cation associated with a trihalide anion, probably $SCl_2Br^+Cl_3^-$.

4. The 513cm^{-1} band consists of two emissions attributable to the two S-Cl stretching modes reduced in frequency slightly by the anion. The S-Br mode can be assigned to the broad 350cm^{-1} band and the very strong band at 268cm^{-1} to the Cl_3^- anion.

B. Sulphur dichloride, bromine and chlorine mixtures.

1. Low temperature Raman spectra of various mixtures of sulphur dichloride, bromine and chlorine gave bands as follows:-

520-540cm^{-1}	chlorine
430-490cm^{-1}	S-Cl stretching modes
340-370cm^{-1}	S-Br stretching modes
260-280cm^{-1}	anion
$<$230cm^{-1}	deformation modes

2. Two basic types of spectra were obtained:-

Type I

a. minimal chlorine bands at 520-540cm^{-1}

b. broad complex at 430-490cm^{-1}

c. two broad bands at 345 and 370cm^{-1}

d. band at 434cm^{-1}

e. band at 271cm^{-1}

Type II

a. large chlorine bands at 520-540cm^{-1}

b. narrow complex at 490-500cm^{-1}

c. broad band at 355cm^{-1}

d. minimal band at 434cm^{-1}

e. band at 279cm^{-1}

It was also possible to obtain spectra that were obviously combinations of the two basic spectra.

3. The anion bands at 271cm^{-1} (Cl_3^-) and 279cm^{-1} ($BrCl_2^-$) are relatively small indicating that the major anions present are probably Cl^- and/or Br^-.

4. The following S-Cl stretching vibrations were observed in the spectra and tentative assignments are given below:-

434cm^{-1}	(Type I)	$SClBr_2^+Cl^-$
466cm^{-1}	(Type I)	$SCl_2Br^+Cl^-$
479cm^{-1}	(Type I and II)	$SClBr_2^+Br^-$
485cm^{-1}	(Type II)	$SCl_2Br^+Br^-$

The presence of the halide anion lowers the stretching frequency from its normal value of 500-520cm^{-1} as was found for the S-Cl frequencies of $SCl_3^+Cl^-$ compared to SCl_3^+ $AlCl_4^-$. The antisymmetric modes are generally less intense than the symmetric modes and it is thought that when these are present they are overlaid by the stronger symmetric bands.

5. The S-Br stretching frequencies were observed as broad bands in the 340-370cm^{-1} region and no individual assignments are possible.

CHAPTER 5

EXPERIMENTAL

5.1 INTRODUCTION

A number of general points can be made with respect to the preparation and analysis of the compounds reported in this work. These general observations are made under the following headings:-

A. Preparation of Products and Starting Materials.

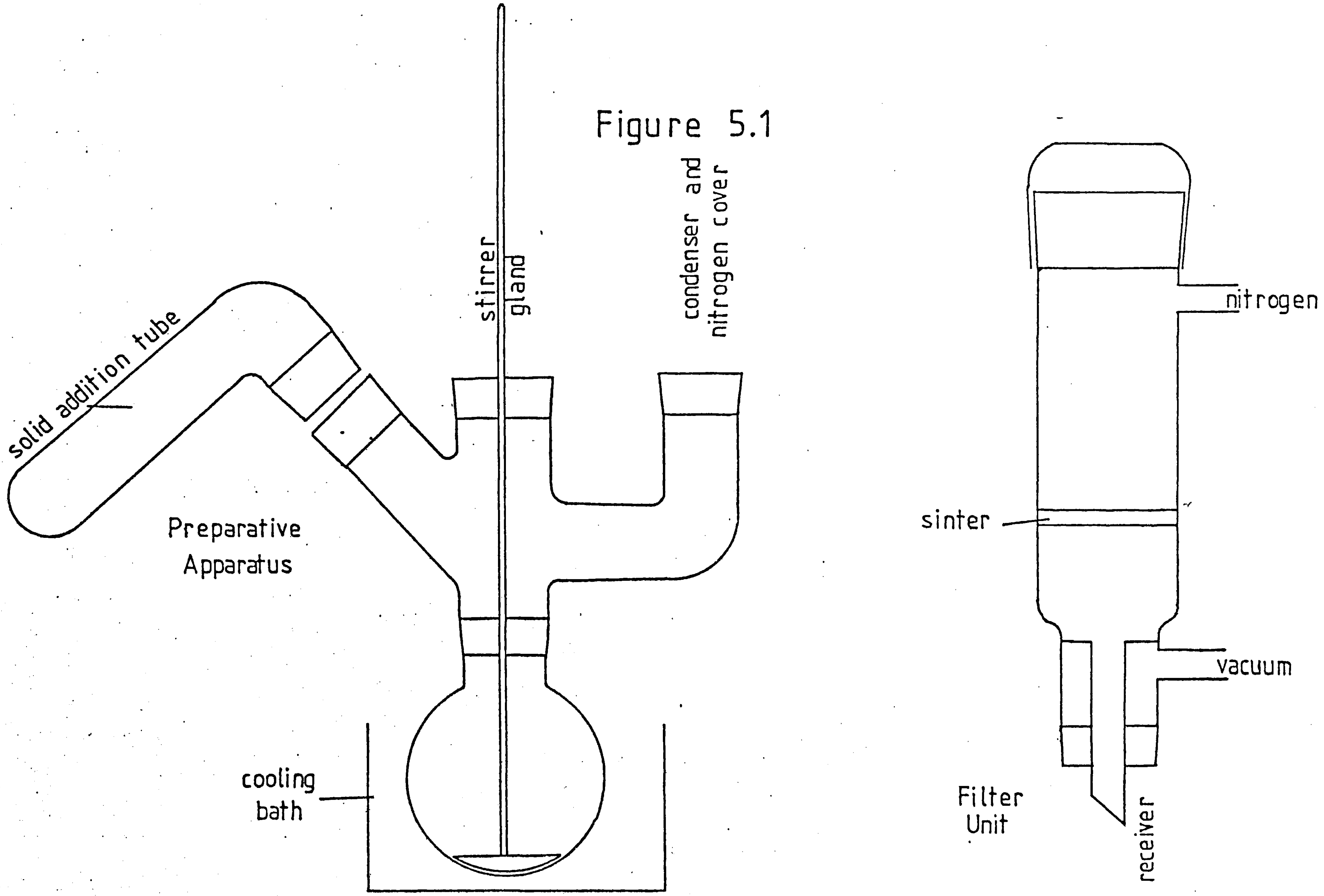
B. Halide Analysis.

C. Raman Spectroscopy.

A. Preparation of Products and Starting Materials

The preparation of all the compounds described in this work required dry conditions to prevent their hydrolysis during both preparation and analyses. All reactions were therefore performed under dry nitrogen using the apparatus illustrated in Figure 5.1. In many reactions it was necessary to add a solid to the reaction mix yet retain the dry conditions. The method used is also shown in Figure 5.1 and consists of an L - shaped tube which, when twisted, deposited solid into the reaction. Careful manipulation enabled portionwise additions to be made. The solid was also weighed under dry conditions by filling the tube in a dry-box and sealing with a suitable cap. The filtration of the reaction mixture to recover the product again had to be performed in the absence of moisture. The filtration unit illustrated in Figure 5.1

Figure 5.1



Preparative Apparatus

Filter Unit

was used and normally nitrogen blown into the upper section maintained a sufficiently dry atmosphere during addition of the reaction mixture to prevent hydrolysis. The product was normally dried by suction after sealing the unit. However, care was taken to ensure that product degradation did not occur by keeping this vacuum period as short as possible. Further manipulation of the product was done in a dry box.

The following general conditions were used:-

1. Temperature of -78° to -80°C were maintained by cardice/acetone mixture, other temperatures were maintained by ice or liquid nitrogen slush baths.
2. Solvents were dried over molecular sieves.
3. Aluminium chloride was crushed under dry-box conditions before use.
4. Aluminium bromide was recrystallised from hexane before use. Invariably a second phase was present, and the upper layer was decanted and allowed to crystallise. The solid was handled in a dry-box and stored in ampoules unless for immediate use.
5. Sulphur dichloride was purified initially by rapid distillation under 250mmHg pressure followed by atmospheric pressure fractionation. It was found necessary to repeat the

fractionation twice more to obtain a stable boiling point of 58°C. The receiver, column and still pot all contained phosphorus pentachloride as stabiliser. The product was stored at -20°C. This purification was essentially that given by Rosser[13] and Lautenschlaeger.[160]

6. Sulphur monochloride was purified by fractionation from sulphur and charcoal using the method of Ariyan and Wiles.[161] However, although a number of attempts were made, in each case it was obvious that the compound was degrading during the fractionation probably to sulphur dichloride.

However, it was found that fractionation under vacuum (b.p 32°C/19mm Hg) gave a pure product with no obvious degradation. The product was a yellow colour and was stored at -20°C.

A later reference to purification of sulphur monochloride, also by Wiles and Ariyan[162] was found, that indicated that decomposition occurred on fractionation at atmospheric pressure. They suggested distillation at a temperature of less than 60°C.

7. Sulphur monobromide was prepared using

the method described by Ospenson[32] from the monochloride by halogen exchange with aqueous hydrobromic acid at 5°C. After separation and drying the fraction boiling at 58-60°C/0·1mm Hg was retained and stored at -20°C.

8. Other reagents were used as received.
9. For reactions involving chlorine normal vacuum line techniques were used.

B. Halide Analysis

The analysis of the products detailed in this work for halide was performed potentiometically after hydrolysis. Essentially the following procedure was adopted.

The sample (~0·1g) was put into a pre-weighed sample tube using a dry-box and the tube re-weighed. The cap of the tube was then loosened and the whole dropped into potassium hydroxide (about 1g) in water (25ml) contained in a conical flask. The flask was then stoppered and shaken to expose the contents of the sample tube to the aqueous base.

As many of these compounds were extremely hydrolytically unstable, the sample was often weighed for analysis and hydrolysed up to this point within as short a period as possible of the samples' preparation. Often the sealed conical flask was left for 1 week before continuing the analysis.

The conical flask, after shaking intermittently for about 15 minutes to ensure absorption of acidic gases, was then heated to boiling under a reflux condenser for about 30 minutes. This period was sufficient to yield a clear solution and indicate complete hydrolysis of even the hexachloroantimonate. After cooling the mixture was acidified to phenolphthalein with acetic acid and 150ml of pH4 buffer added. This halide solution was then titrated with 0·1M silver nitrate using a silver electrode.

A plot of titre against indicated voltage produced a curve as indicated in Figure 5.2. The volume of silver nitrate solution to each inflection was used to determine the bromide and chloride levels, the bromide being the inflection occurring at the lower voltage. Normally a blank was also run but was usually only 0·2ml.

In those cases where a trihalide was suspected any halogen formed on hydrolysis was reduced to halide by using saturated aqueous sulphur dioxide. The excess gas was removed prior to titration by boiling the solution until the vapours were not acidic. The solution was then titrated as usual after dilution with pH4 buffer.

Analyses were always performed in duplicate and often triplicate in view of the products' instability. Blanks were run as necessary and analytical grade reagents were used throughout.

C. Raman Spectroscopy

The hydrolytic instability of the products necessitated thorough pre-drying of the capillary tubes

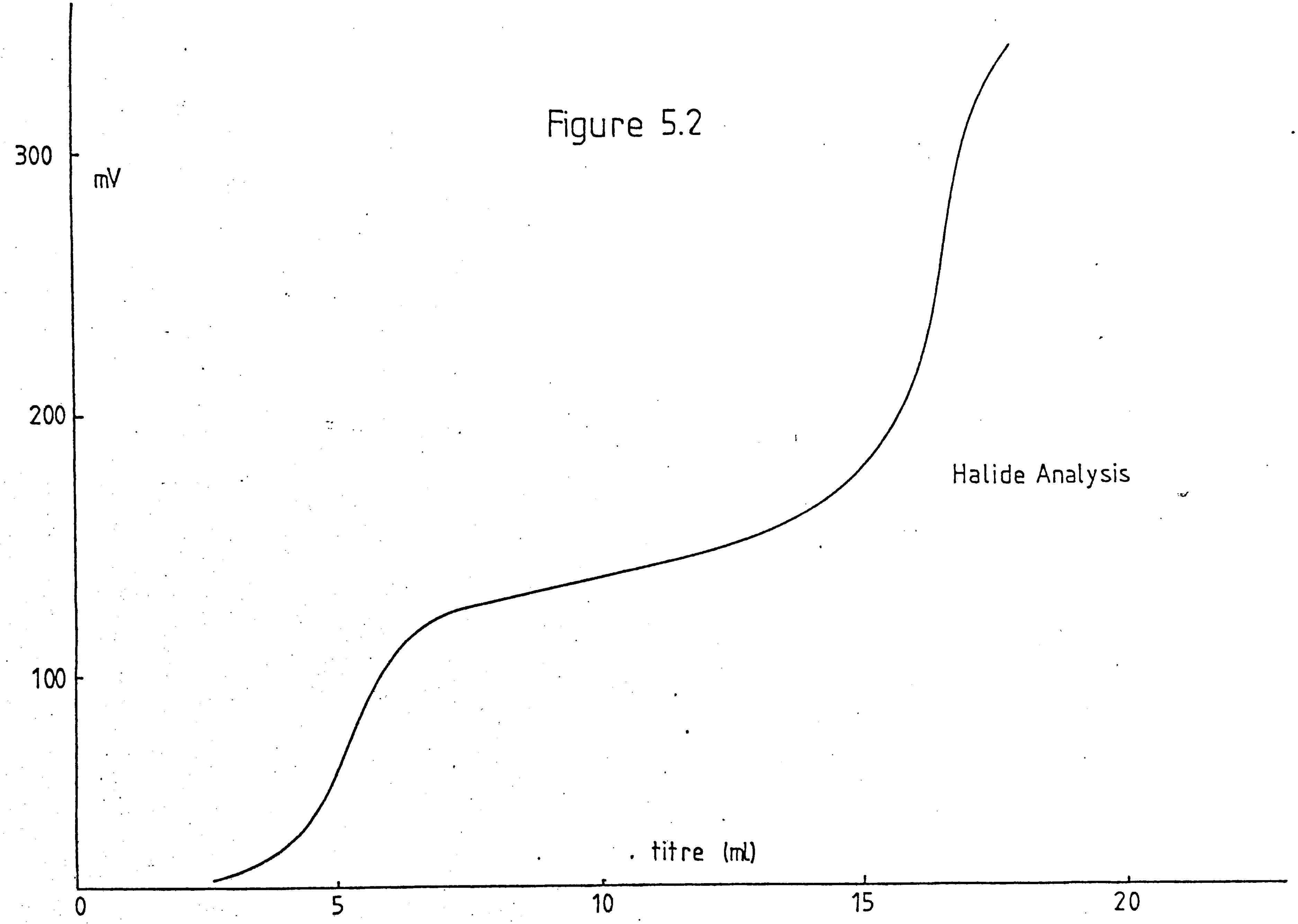
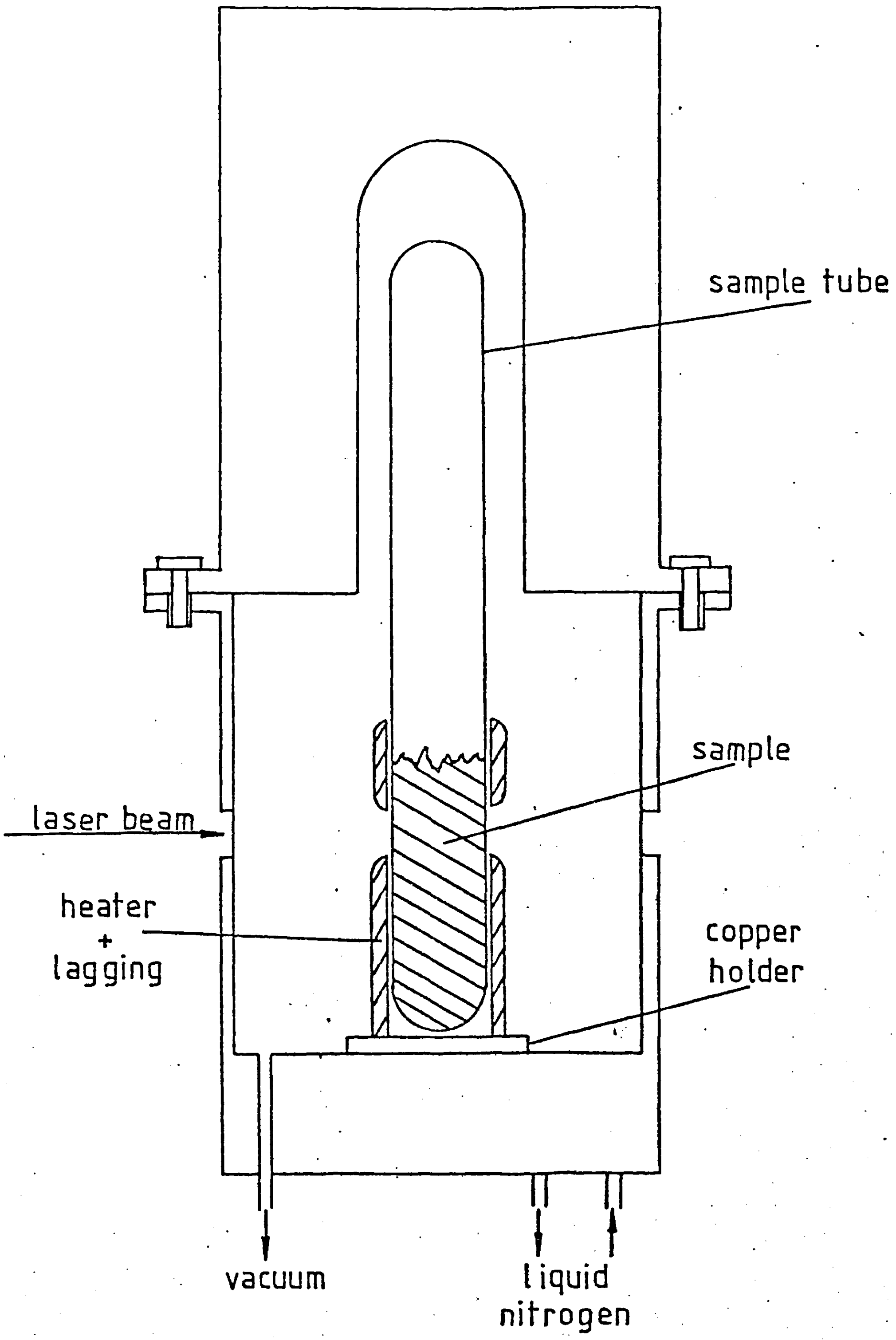


Figure 5.2

used to contain the sample. The tubes were filled in a dry-box and sealed but even so the most unstable products decomposed in a matter of weeks. Samples whose spectra were to be recorded at low temperatures were sealed into a wider tube (~ 4mm dia) choosen to fit the cold cell holder as closely as possible. Often this tube was attached to a vacuum line as most products studied in this way contained free chlorine. To prevent condensation and freezing of water vapour onto the tube at low temperatures the whole unit was enclosed in an evacuated holder. The sample holder was cooled with liquid nitrogen and to maintain higher temperatures a small heater controlled by a thermocouple was used. It was obviously necessary to regulate carefully the liquid nitrogen flow through the holder to prevent over cooling but temperatures stable over long periods to within ±5°C could be obtained. Even though the sample tube was enclosed in an outer tightly fitting copper holder, with holes for the laser beam, it was necessary to allow a minimum of 30 minutes for the sample temperature to stabilise to that of the holder prior to recording the spectra. A diagramatic illustration of the modified Coderg cold cell is given in Figure 5.3.

The spectra were recorded using a double monochromator Coderg PHO spectrometer with excitation by a Coherent Radiation krypton or argon/krypton laser at 647·1nm. Usually the laser power was restricted

Figure 5.3



Raman Cold Cell Unit

to about 150mW to avoid decomposition of the sample and for this reason blue exitation was avoided.

A special low noise, Peltier cooled, red sensitive photomultiplier was used. Amplification was usually using a DC amplifier but for the weakly scattering samples a photon counting technique was used. In general the following operating parameters were used (DC amplification).

Amplifier time constant		3
Amplifier attenuation		5
Slit width		2cm^{-1}
Photomultiplier voltage		800-1700V
Chart speed	2.5cm/min	20cm^{-1}/cm
Scan speed	50cm^{-1}/min	

5.2 PREPARATION OF TRIHALOSULPHONIUM CATIONS

$SCl_3^+ AlCl_4^-$ (Figure 2.1)

a) Chlorine was passed into sulphur dichloride (10•4g, 0•1 mole) at -78°C to produce a slurry of sulphur tetrachloride in liquid chlorine. After 1 hour crushed aluminium trichloride (13•2g, 0•99 mole) was added and the mixture stirred for 1 hour at -78°C. The mixture was allowed to warm to room temperature and left for 6 days to yield an off-white solid. This solid was recrystallised from thionyl chloride (50ml), the solid washed with carbon tetrachloride and dried over phosphorus pentoxide.

Yield 10•8g, 35•5% mp 102-4° (lit. 118-20°)

b) Sulphur dichloride (4.12g, 0•04 mole) was dissolved in dichloromethane (20ml) and cooled to -78°C. Chlorine was added to produce a yellow solid slurry to which was added portion-wise crushed aluminium chloride (5.34g, 0•04 mole) and the mixture stirred for 2 hours at -78°C. The mixture was warmed to room temperature, the solid filtered off and dried by suction to yield a white solid.

Yield 7•8g, 63•7%

$SCl_3^+ SbCl_6^-$ (Figure 2.2)

Sulphur dichloride (5•15g, 0•05 mole) was cooled to -78°C and chlorine passed in to give a red solution containing some yellow solid. After 1 hour at -78°C, antimony pentachloride (14•95g, 0•05 mole) was added dropwise to give a yellow solid. The mixture was stirred at -78°C for 2 hours and then allowed to warm to room temperature to boil off chlorine. An off-white solid was obtained by warming slightly under vacuum.

Yield 19•5g, 82•3%

Very similar products were obtained by dissolving the sulphur dichloride in either chloroform or dichloromethane and adding antimony pentachloride at low temperature. No chlorine was used giving low yields.

The reaction of sulphur dichloride and antimony pentachloride at 10–15°C without solvent gave rise to impure products.

$SBr_3^+ AlCl_4^-$ (Figure 2.3)

Sulphur monobromide (4•48g, 0•02 mole) was dissolved in dichloromethane (20ml) and bromine (9•6g, 0•06 mole) added. Aluminium trichloride (4•81g, 0•036 mole) was then added portion-wise and the mixture stirred at room temperature for 2 hours and then stood for 7 days. The mixture was cooled to -70°C and the precipitated solid filtered off and dried by suction to give a yellow solid.

It was essential to handle the product in a dry-box and glass-ware, including Raman tubes, had to be flamed before use. Hydrolysis of the analytical samples was performed immediately after product isolation.

Yield 7•3g, 41•3% (low yield due to handling losses in prevention of hydrolysis).

Analysis:-

Br (found)	56·1 56·9	56·5%	Cl (found)	32·1 32·1	32·1%

$SBr_3^+ AlCl_4^-$ Br (calc) 54·4% Cl (calc) 32·2%

It was found that no reaction occurred at −78°C and that a reaction time significantly longer than 2 hours at room temperature was necessary as a spectrum run after this time showed little or no product.

$SBr_3^+ AlBr_4^-$ (Figure 2.4)

Sulphur monobromide (4·48g, 0·02 mole) was dissolved in dichloromethane (20ml) and bromine (9·6g, 0·06 mole) added. The mixture was cooled to −78°C and crushed aluminium bromide (10·68g, 0·04 mole) added portion-wise. The mixture was then stirred at −78°C for 30 minutes and filtered. The solid was dried by suction with absolute minimum exposure to air but even after flaming apparatus some degradation occurred at the apparatus walls. Samples of the orange solid were hydrolysed for analysis immediately after isolation. The solid degraded in a sealed Raman tube over a period of days, presumably by hydrolysis.

Yield 11·5g, 46·4% (low yield due to handling losses in prevention of hydrolysis).

Analysis:-

Br (found) 89·97)
)
89·24) 89·9%
)
90·63)

$SBr_3^+ \; AlBr_4^-$ Br (calc) 90·5%

Initial attempts were made to prepare this product using chloroform as solvent but no product was isolated after reaction at room temperature. Reaction at −70°C was successful but dichloromethane was a preferable solvent due to its lower freezing point. Aluminium bromide was soluble at reaction temperature in either solvent and restricted reaction time reduced hydrolysis. However considerable practice was required in handling the product to prevent hydrolysis and formation of sludges.

SBr_3^+ with other Anions

In general the solvent and sulphur monobromide were mixed, cooled if desired and the Lewis acid added. Reaction times and temperatures were varied as detailed in Table 5.1 but as the reaction mixture was often homogeneous it was usually cooled to attempt to precipitate the product. Any solid isolated was removed, dried and subjected to spectroscopic examination.

TABLE 5.1

ATTEMPTED PREPARATION OF $SBr_3^+ MBr_n^-$

Reactant (moles)					Reaction Conditions			Product
S_2Br_2	Br_2	Lewis acid		Solvent	Addition	Reaction	Comments [1]	
0·01	0·06	$SbBr_3$	0·02	$CHCl_3$	20°C	$\frac{1}{4}$ hr @ -60°C		$SbBr_3$
0·01	0·06	$SbBr_3$	0·02	CH_2Cl_2	20°C	1 hr@ 20°C		$SbBr_3$
0·01	0·06	$SbBr_3$	0·02	CH_2Cl_2	20°C	48 hr @ 20°C		$SbBr_3$
0·01	0·06	$SbBr_3$	0·02	CH_2Cl_2	20°C	$2\frac{1}{2}$ hr @ 42°C		$SbBr_3$
0·01	0·06	$SbBr_3$	0·02	CH_2Cl_2	20°C	$\frac{1}{4}$hr @ -78°C	S_2Br_2 added to $Br_2/SbBr_3$	$SbBr_3$
0·008	0·038	$SbBr_3$	0·015	CH_2Cl_2	-78°C	$\frac{1}{2}$hr @ -78°C	recryst $SbBr_3$	$SbBr_3$
0·02	0·06	BBr_3	0·04	$CHCl_3$	-60°C	2 hr @ -60°C		no solid
0·001	0·002	BBr_3	0·002	none	20°C	-50°C to -170°C	Raman cold cell used	S_2Br_2, Br_2, BBr_3
0·02	0·006	BBr_3	0·04	CH_2Cl_2	-70°C	7 days @ 20°C		no solid
(0·05)	0·05	BBr_3	0·05	$CHCl_3$	-70°C	2 hrs @ -70°C	SCl_2 used in place of S_2Br_2	no solid
0·01	0·03	$InBr_3$	0·02	CH_2Cl_2	-78°C	$\frac{3}{4}$hr @ -78°C		$InBr_3$
0·04	0·04	$SnBr_4$	0·02	CH_2Cl_2	-78°C	1 hr @ -78°C	some solid present after 4 months	$SnBr_4$(+?)

[1] Reaction cooled to precipitate any solid

5.3 PREPARATION OF MIXED TRIHALOSULPHONIUM CATIONS

a) Tetrachloroaluminates. (Figures 2.5, 2.6, 2.7)

This preparation is representative of that used for the preparation of all the complexes detailed in Table 5.2

Sulphur dichloride (5•15g, 0•05 mole) was dissolved in chloroform (30ml) and bromine (8•0g, 0•05 mole) added. The mixture was cooled to −60°C and crushed aluminium chloride (6•68g, 0•05 mole) added portion wise. The whole was then stirred at −60°C for 2 hours, warmed to room temperature, the solid filtered off and dried by suction.

b) Hexachloroantimonates. (Figures 2.8, 2.9, 2.10)

Products were prepared using either chloroform or liquid hydrogen chloride as solvent. The following descriptions are representative of these preparations which yielded basically two products of different Raman spectra. The preparations are detailed in Table 5.3.

Sulphur dichloride (5•15g, 0•05 mole) was dissolved in chloroform (40ml) and bromine (24•0g, 0•15 mole) added. The mixture was cooled to about −65°C and antimony pentachloride (14•95g, 0•05 mole), dissolved in chloroform (20ml), added slowly. The reactants were stirred for 2 hours at −65°C and the solid filtered off after warming the reaction mixture to room temperature. The solid was dried by suction.

Hydrogen chloride was generated from concentrated hydrochloric and sulphuric acids and, after drying, was collected in a liquid nitrogen cooled flask. When about 30ml had been obtained the solvent was warmed to -95°C and bromine (8•0g, 0•05 mole) added dropwise to give a red solution containing a yellow solid. Sulphur dichloride (5•15g, 0•05 mole) was then added followed, after 30 minutes, by antimony pentachloride (14•95g, 0•05 mole). An orange precipitate was formed, the mixture stirred for 1½ hours and allowed to warm to room temperature. The solid was slurried in chloroform, filtered and dried by suction. The solid changed from orange to yellow on drying.

Attempts were made to prepare $SBr_3^+SbCl_6^-$ by the reaction of sulphur monobromide, bromine and antimony pentachloride. However, products containing S-Cl bands were always obtained and Table 5.4 details these preparations. The following description is representative of all those detailed.

Sulphur monobromide (4•48g, 0•02 mole) was dissolved in dichloromethane (30ml) and bromine (12•8g, 0•08 mole) added. The mixture was stirred and antimony pentachloride (11.96g, 0•04 mole) in dichloromethane (10ml) added and after 1½ hours the mixture was cooled to -78°C. The precipitated solid was filtered off and dried by suction.

Sometimes the addition of the reactants was performed at low temperature to try to minimise chlorination. Cooling was essential even after reaction at 20°C due to solubility of the product.

Analysis:-

Br (found) 34·60)) 34·2% 33·82) — Cl (found) 41·35)) 41·6% 41·94)

$SBr_3^+SbCl_6^-$ Br (calc) 39·5%, Cl (calc) 35·1%

$SBr_2Cl^+SbCl_6^-$ Br (calc) 28·4%, Cl (calc) 44·2%

TABLE 5.2

PREPARATION OF $SCl_nBr_{3-n}^+\ AlCl_4^-$

Reactant (moles)				Conditions	Appearance	Spectrum
SCl_2	Br_2	$AlCl_3$	Solvent			
0·1	0·22	0·11	CH_2Cl_2	2 hrs. @ –78°C	yellow	mixed
0·05	0·22	0·05	CH_2Cl_2	2 hrs @ –78°C	–	$AlCl_3$
0·05	0·05	0·05	CH_2Cl_2	2 hrs @ –78°C	yellow	mixed + $AlCl_3$
0·05	0·05	0·05	pentane	2 hrs @ –78°C	–	$AlCl_3$
0·05	0·05	0·05	CH_3CN CH_2Cl_2 }	2 hrs @ –50°C, solvents evapd. off	white	weak
0·05	0·05	0·05	$CHCl_3$	2 hrs @ –60°C	brown/yellow	mixed *
0·08	0·03	0·05	$CHCl_3$	2 hrs @ –60°C	yellow	mixed *
0·05	0·1	0·05	$CHCl_3$	2 hrs @ –60°C	yellow	mixed
0·1	0·22	0·11	CH_2Cl_2	2 hrs @ –78°C + 2 hrs @ 20°C	yellow	mixed*
0·05	0·1	0·05	CH_2Cl_2	14 days @ 20°C	yellow	mixed

* spectra analysed for band intensities. (Figures 2.5, 2.6, 2.7)

TABLE 5.3

PREPARATION OF $SCl_nBr_{3-n}{}^+SbCl_6{}^-$

Reactants (moles)				Conditions	Appearance	Spectrum
SCl_2	Br_2	$SbCl_5$	Solvent			
0•05	0•05	0•05	$CHCl_3$	2 hrs @ -65°C	yellow	mixed, A
0•05	0•15	0•05	$CHCl_3$	2 hrs @ -65°C	yellow	mixed, B*
0•03	0•13	0•03	$CHCl_3$	2 hrs @ -65°C	yellow	mixed, B
0•05	0•03	0•05	$CHCl_3$	2 hrs @ -65°C	yellow	mixed, A*
0•05	0•05	0•05	liq HCl	1½ hrs @ -95°C, addition Br_2, SCl_2,$SbCl_5$	-	mixed, B
0•05	0•15	0•05	liq HCl	1½ hrs @ -95°C, addition Br_2, SCl_2,$SbCl_5$	yellow	mixed, B
0•05	0•05	0•05	liq HCl	1½ hrs @ -95°C, addition $SbCl_5$, SCl_2,Br_2	yellow	mixed, B
0•03	0•13	0•03	$CHCl_3$	15 mins @ 20°C	-	mixed, A

* Spectra analysed for band intensities, (Figures 2.8, 2.9)

TABLE 5.4

PREPARATION OF $SCl_nBr_{3-n}^+SbCl_6^-$

Reactants (moles)				Conditions	Appearance	Spectrum
S_2Br_2	Br_2	$SbCl_5$	Solvent			
0·02	0·06	0·04	$CHCl_3$	2 hrs @ −65°C	yellow	mixed
0·02	0·08	0·04	$CHCl_3$	2 hrs @ −70°C	yellow	mixed
0·02	0·06	0·04	CH_2Cl_2	45 mins @ 20°C	–	mixed
0·02	0·08	0·04	CH_2Cl_2	1½ hrs @ 20°C	yellow	mixed *
0·02	0·12	0·04	CH_2Cl_2	1½ hrs @ 20°C	yellow	mixed
0·02	0·08	0·04	CH_2Cl_2	15 mins @ −80°C	–	mixed
0·02	0·08	0·04	$CHCl_3$	15 mins @ −65°C	–	mixed
0·0005	0·0015	0·001	CH_2Cl_2	Reaction in Raman cold cell tube.	–	mixed + reactants
0·02	0·08	0·04	CH_2Cl_2	1½ hrs @ 20°C, solid analysed	–	mixed
0·02	0·08	0·04	cyclo-hexane	15 mins @ 20°C, solid filtered at 0°C	yellow/grey	poor
0·02	0·08	0·04	petrol	15 mins @ 0°C, reactants not soluble	red	poor
0·02	0·06	0·04	CH_2Cl_2	2 hrs @ −78°C	–	mixed
0·02	0·08	0·01	CH_2Cl_2	5 mins @ −78°C	bromine vapour	–

* Spectrum analysed for band intensities (Figure 2.10)

5.4 PREPARATION OF SULPHUR TETRACHLORIDE

Using a vacuum line sulphur dichloride (~0·3g) contained in a wide Raman cold cell tube was cooled in liquid nitrogen and the tube evacuated. Chlorine was also condensed into a cold tube and then allowed to distil into the sulphur dichloride tube held at low temperature. The volume ratio of chlorine to sulphur dichloride was about 2:1. The tube was then sealed and allowed to warm to room temperature to give a homogeneous liquid. On cooling to -70°C a yellow solid formed. The Raman spectra were obtained at various temperatures down to -150°C using the cold cell.

Initially the tube was cooled to -150°C and the spectrum obtained when the temperature had stabilised. Spectra were run at up to -80°C with virtually no change and the tube was then held at -70°C for 1 week. Further spectra were obtained at temperatures commencing at -80°C. Minor changes were visible in the spectra at -47°C and after about 30 minutes at -45°C the solid disappeared leaving a homogeneous liquid whose Raman spectrum was that of the reactants. Cooling reformed the solid which again disappeared at -45°C.

A similar tube was prepared containing a vast excess of chlorine as well as one containing acetonitrile in an attempt to stabilise the solid. However decomposition occurred at lower temperatures.

5.5 PREPARATION OF DIMETHYLCHLOROSULPHONIUM CATIONS

a) $(CH_3)_2SCl^+SbCl_6^-$, (Figure 3.1)

Dimethylsulphide (5•4g, 0•087 mole) was dissolved in dichloromethane (50ml) and cooled to -78°C. Antimony pentachloride (23•0g, 0•077 mole) in dichloromethane (50ml) was then added dropwise over 1½ hours to give a yellow solid after the production of a red colour. The mixture was stirred for ½ hour and chlorine (8•5g, 0•12 mole) bubbled in over ½ hour. After stirring for a further ½ hour the mixture was warmed to 40°C and the white solid filtered off, washed with solvent and dried by suction.

Yield 23•7g, 71•2%

b) $(CH_3)_2SCl^+ AlCl_4^-$ (Figure 3.2)

Dimethylsulphide (2•48g, 0•04 mole) was dissolved in dichloromethane and cooled to -78°C. Chlorine (21•5g, 0•6 mole) was added to form a yellow solid followed by aluminium chloride (5•34g, 0•04 mole) and the mixture stirred at -78°C for 4 hours. The mixture was then warmed to room temperature to boil off excess chlorine when the mixture formed two phases. It was therefore cooled to -78°C to reform the solid which was filtered off cold, and dried by suction. The white solid tended to decompose on standing, presumably by hydrolysis.

Analysis

Cl (found) 65•34)
) 65•2%
64•95)

$(CH_3)_2SCl^+\ AlCl_4^-$ Cl (calc) 66•6%

c) $[(CH_3)_2SCl^+]_2\ SnCl_6^{\ 2-}$ (Figure 3.3)

Chlorine (cylinder weight loss 15•7g) was collected at -78°C and a solution of dimethylsulphide (2•48g, 0•04 mole) in dichloromethane (20ml) added slowly to form a precipitate. A solution of tin tetrachloride (5•22g, 0•02 mole) in dichloromethane (10ml) was then added followed by further solvent (40ml) to maintain fluidity. The mixture was stirred for 2 hours at -78°C and then warmed to 20°C over 1 hour. The solid was removed by filtration and dried by suction to yield an off-white solid.

Yield 10•1g, 95•8%

Analysis

Cl (found) 54•77)
) 54•9%
55•07)

$[(CH_3)_2SCl]_2\ SnCl_6^{\ 2-}$ Cl (calc) 53•9%

5.6 PREPARATION OF DIMETHYLBROMOSULPHONIUM CATIONS

a) $(CH_3)_2SBr^+SbCl_5Br^-$ (Figure 3.4)

Dimethylsulphide (2·05g, 0·033 mole) was dissolved in dichloromethane (20ml) and bromine (5·28g, 0·033 mole) in dichloromethane (10ml) added dropwise to give a red precipitate. Antimony pentachloride (9·88g, 0·033 mole) in dichloromethane (10ml) was then added dropwise at room temperature. The precipitate changed from red to orange, the mixture was stirred for 2 hours, and the solid filtered off and dried by suction.

Yield 13·88g, 80·7%

Analysis

Cl (found) 33·89) 34·00) 33·9%

Br (found) 30·79) 30·83) 30·8%

$(CH_3)_2SBr^+SbCl_5Br^-$ Cl (calc) 34·0% Br (calc) 30·7%

b) $(CH_3)_2SBr^+ AlBr_4^-$ (Figures 3.5, 3.6)

The preparation of this compound proved very difficult. The following descriptions of two preparations were the most successful. The other attempts are detailed in Table 5.5 together with notes on the spectra.

Dimethyl sulphide (1·83g, 0·03 mole) was dissolved in dichloromethane (20ml) and bromine (4·7g, 0·029 mole) in dichloromethane (10 ml) added to produce a yellow precipitate. This mixture was cooled to -78°C and aluminium bromide (7·9g, 0·029 mole) added over 15 minutes. This mixture was stirred for 3½ hours at -78°C but as the mixture then appeared still to have aluminium bromide present it was allowed to warm to 0° - -20°C when the aluminium bromide appeared to react. However, when the mixture was at about 0°C it suddenly became very viscous and the precipitate changed from yellow to buff in colour. The mixture was immediately cooled to-78°C and the solid filtered off and dried by suction to yield anorange solid. Due to the extreme hydrolytic instability of this compound even in a glove box no yields or analysis were recorded.

In an earlier attempt the reaction mixture was not cooled and the reaction was performed at room temperature. On addition of the aluminium bromide the precipitate "liquefied" giving a two phase system. After 2 hours this mixture was cooled to -80°C when the lower layer solidified. The solid was filtered off and dried by suction to yield buff crystals. Some darkening occurred at the filter walls and the solid turned yellow on exposure to air.

Yield 16·2g, 83·0%

Analysis:

Cl (found)	1·65 1·76	1·7%	Br (found)	71·13 71·22	71·2%

$(CH_3)_2SBr^+ AlBr_4^-$ Cl (calc) 0 %, Br (calc) 81·8%

This preparation was repeated (Table 5.5) exactly as above and the product analysed

Analysis

CL (found) 2·81) Br (found) 77·18)
) 3.1%) 77·0%
3·43) 76·91)

In view of the above analytical results it was considered likely that the aluminium bromide contained some chloride. It was therefore analysed with the following results:

Analysis

Cl(found) 0, Br (found) 89·45)
) 89·6%
89·65)

$AlBr_3$,Cl (calc) 0, Br (calc) 89·9%

The solutions were also checked and the blank results indicated the absence of chloride.

It should be noted that after this product had been prepared and analysed the high power argon laser failed and the spectrum was recorded with the low power helium laser. The spectrum was unsatisfactory but was essentially similar to that of Figures 3.5 and 3.6. The product had degraded even in the Raman tube when the spectrum was recorded with the repaired argon laser.

c) $(CH_3)_2SBr^+AlCl_4^-$ (Figure 3.7)

Dimethyl sulphide (1·24g, 0·02 mole) was dissolved in dichloromethane (20ml) and bromine (6·4g, 0·04 mole)in dichloromethane (10ml) added over

15 minutes at 20°C. To this mixture was added aluminium chloride (2·67g, 0·02 mole) and stirred for 3 hours at 20°C. The mixture was then cooled to −80°C and the solid filtered off and dried by suction to give a yellow solid.

Analysis:

Br (found) 27·17)
) 27·5%,
27·73)

Cl (found) 44·90)
) 44·9%
44·88)

$(CH_3)_2SBr^+ \ AlCl_4^-$ Cl (calc) 45·7%, Br (calc) 25·7%

d) $\underline{[(CH_3)_2SBr^+]_2 \ SnBr_6^{\ 2-}}$ (Figures 3.8, 3.9, 3.10)

Dimethyl sulphide (2·48g, 0·04 mole) was dissolved in dichloromethane (20ml) and bromine (6·4g, 0·04 mole) in dichloromethane (10ml) added at 20°C to yield a yellow solid. To this suspension was added a solution of tin tetrabromide (8·78g, 0·02 mole) in dichloromethane (10ml). The mixture was stirred for 30 minutes, the solid removed by filtration and dried by suction to yield a yellow solid.

Yield 16·6g, 94·0%

Analysis:

Br (found) 72·02)
) 72·2%
72·40)

$[(CH_3)_2SBr^+]_2 \ SnBr_6^{\ 2-}$ Br (calc) 72·5%

It was found that to obtain a spectrum of $[(CH_3)_2S\overset{+}{Br}]_2\ SnBr_6^{\ 2-}$ a long reaction time was necessary. A time significantly less than 30 minutes yielded a mixed product.

Reactions were also performed using different reactant ratios as well as the preparation of the simple adducts of the reactants. Table 5.6 details these products.

e) Attempted mixed products $[(CH_3)_2S\overset{+}{Br}]_2[SnCl_4Br_2]^{2-}$, $[(CH_3)_2SCl^+]_2[SnBr_4Cl_2]^{2-}$

Throughout the above preparations endeavours were made to reduce the possibility of scrambling giving complex spectra by using only one halogen. Two products were made with mixed halogens as detailed below.

$[(CH_3)_2SBr^+]_2[SnCl_4Br_2]^{2-}$ (Figure 3.12)

Dimethyl sulphide (2•48g, 0•04 mole) was dissolved in dichloromethane (20ml) and bromine (6•4g, 0•04 mole) in dichloromethane (10ml) added to form an orange precipitate. At about 15°C a solution of tin tetrachloride (5•22g, 0•02 mole) in dichloromethane (10ml) was added when the precipitate changed colour to white. The solid was filtered off and dried by suction to yield a white solid.

Yield 15•6g, (110%)

Analysis:

Br (found)	42•97	43•2%	Cl (found)	17•84	17•9%
	43•34			17.97	

$[(CH_3)_2SBr^+]_2[SnCl_4Br_2]^{2-}$

Br (calc) 45•4% Cl (calc) 20•1%

$[(CH_3)_2\ SCl^+]_2[SnBr_4Cl_2]^{2-}$

Chlorine (cylinder weight loss 18·0g, 0·25 moles) was collected at -70°C and a solution of dimethyl sulphide (2·48g, 0·04 mole) in dichloromethane (20ml) added slowly to form a solid. To this mixture was added a solution of tin tetrabromide (8·8g, 0·02 mole) in dichloromethane (10ml) at -70°C. Additional solvent (20ml) had to be added part way through the addition to maintain fluidity and the mixture was stirred for 2 hours at -70°C. The mixture was warmed to room temperature over 45 minutes to boil off the excess chlorine and the solid removed by filtration and dried by suction to give a yellow solid.

Analysis:-

Br (found)	5·66	5·6%	(Cl found)	52·47	52·8%
	5·58			53·07	

$[(CH_3)_2SCl^+]_2\ SnCl_6^{\ 2-}$

Cl (calc) 53·9%

$[(CH_3)_2SBr^+]_2\ SnCl_6^{\ 2-}$

Br (calc) 26·0%, Cl (calc) 34·6%

A mixture of 21·5% bromo and 78·5% chloro complexes would give

Br (calc) 5·6%, Cl (calc) 49·8%

TABLE 5.5

PREPARATION OF $(CH_3)_2SBr^+ AlBr_4^-$

Reactants (moles)				Reaction Conditions			Yield (%)	Spectrum
$(CH_3)_2S$	Br_2	$AlBr_3$[1]	Solvent	Addition	Reaction	Comments		
0·03	0·03	0·03	C_6H_{14}	20°C	1½ hrs @ 20°C	decanted C_6H_{14}, no reaction		
			CH_3CN	-	1 hr @ 20°C	yellow solid	28·3	$(CH_3)_2SBr_2$
0·04	0·04	0·04	CH_2Cl_2	20°C	2 hrs @ 20°C	lower layer solidified at -80°C	83·8	poor, noisy
0·04	0·04	0·04	CH_2Cl_2	-78°C	2 hrs @ -78°C		NR	$(CH_3)_2SBr^+AlBr_4^-$ + $(CH_3)_2SBr_2$ + D
0·04	0·04	0·04	CH_2Cl_2	0°C	2 hrs @ 0°C		-	$AlBr_3$
0·04	0·04	0·04	CH_2Cl_2	20°C	2 hrs @ 20°C	lower layer solidified at -80°C	NR	He laser,[2] mixed product.
0·04	0·04	0·004	CH_2Cl_2	20°C	weeks @ 20°C	no reaction catalytic level $AlBr_3$	-	-
0·026	0·026	0·025	CH_2Cl_2	20°C	2½ hrs @ 20°C	lower layer solidified at -80°C	NR	largely D
0·026	0·026	0·025	CH_2Cl_2	-50°C	4 hrs @ -60°C		NR	$(CH_3)_2SBr_2$ + D

1. $AlBr_3$ recrystallised from hexane. 2. See experimental for analyses. D Unknown possibly $(CH_3)_2SBr^+Br^-$

TABLE 5.6

PREPARATION OF $[(CH_3)_2SBr^+]_2\ SnBr_6^{\ 2-}$

Reactants (moles)				Reaction Conditions			Yield (%)	Spectrum
$(CH_3)_2S$	Br_2	$SnBr_4$	Solvent	Addition	Reaction	Comments		
0•04	0•06	0•02	CH_2Cl_2	20°C	½ hr @ 20°C	2 phase system $(CH_3)_2SBr_2$	90•0	$[(CH_3)_2SBr_2^+]$ $[SnBr_6]^{2-}$ + Br_2 + D
0•02	-	0•02	CH_2Cl_2	20°C	2 hrs @ 20°C	cooled to -80°C ⟶ solid	11•3	$(CH_3)_2S{:}SnBr_4$
-	0•02	0•02	CH_2Cl_2	20°C	1 hr @ 20°C	Cooled to -80°C ⟶ solid Br_2	-	-
0•04	0•02	0•02	CH_2Cl_2	20°C	½ hr @ 20°C	yellow solid	97•5 [1]	) spectra) identical
0•04	0•02	0•02	CH_2Cl_2	20°C	2 hrs @ 20°C	yellow solid	N.R.	)

[1] Based on $[(CH_3)_2SBr^+]_2\ SnBr_6^{\ 2-}$

5.7 PREPARATION OF DICHLOROMETHYLSULPHONIUM CATIONS

a) $CH_3SCl_2{}^+SbCl_6{}^-$ (Figure 3.13)

Antimony pentachloride (29•95g, 0•1 mole) was dissolved in dichloromethane (20ml) and dimethyl disulphide (1•88g, 0•02 mole) in dichloromethane (20ml) added dropwise at 0°C. A red-brown colour developed and a precipitate formed. The mixture was refluxed for 50 minutes when the solid turned white. It was filtered-off, washed with solvent and dried by suction to give a white solid.

Yield 13•4g, 74•0%

Analysis:

Cl (found) 62•00, 62•13) 62•1%

$CH_3SCl_2{}^+SbCl_6{}^-$

Cl (calc) 62•7%

b) $CH_3SCl_2{}^+ AlCl_4{}^-$

An attempt to produce this complex using the usual reaction conditions failed when the product "liquified" during drying.

5.8 PREPARATION OF DIBROMOMETHYLSULPHONIUM CATIONS

a) $CH_3SBr_2^+SbCl_5Br^-$ (Figure 3.14)

Dimethyl disulphide (1•88g, 0•02 mole) was dissolved in dichloromethane (20ml) and bromine (9•6g, 0•06 mole) added. This mixture was cooled to 0 °C and antimony pentachloride (11•98g, 0•04 mole) in dichloromethane (10ml) added. An orange precipitate formed and the mixture was stirred for 1 hour and filtered. The solid was dried by suction and it was noted that on standing it evolved bromine.

Yield 30•3g, 86•1%

Analysis:

Prepn. 1 Cl (found) 27•65) Br (found) 32•61)
) 27•7%) 32•8%
27•66) 32•96)

Prepn. 2 Cl (found) 33•97) Br (found) 33•90)
) 33•9%) 33•7%
33•92) 33•57)

$CH_3SBr_2^+SbCl_5Br^-$

Cl (calc) 30•3% Br (calc) 40•9%

$CH_3SBr_2^+SbCl_6^-$

Cl (calc) 39•3%, Br (calc) 29•5%

b) $CH_3SBr_2^+ AlBr_4^-$ (Figure 3.15)

Dimethyl disulphide (1•88g, 0•02 mole) was dissolved in dichloromethane (20ml) and bromine

(9•6g, 0•06 mole) added. Aluminium bromide (10•4g, 0•04 mole) was then added and after 20 minutes a solid precipitated and further solvent (20ml) had to be added to maintain fluidity. After 2½ hours the solid was removed by filtration and dried by suction to give a yellow solid.

Yield 13•9g, 64•7%

Analysis:

Br (found) 86•01)
) 86•0%
85•91)

$CH_3SBr_2^+ \ AlBr_4^-$

Br (calc) 86•6%

c) $\underline{[CH_3SBr_2^+] \ SnBr_6^{2-}}$ (Figure 3.16)

Dimethyl disulphide (1•88g, 0•02 mole) was dissolved in dichloromethane (20ml) and bromine (9•6g, 0•06 mole) in dichloromethane (10ml) added to give a red solution. Tin tetrabromide (8•78g, 0•02 mole) in dichloromethane (10ml) was then added and the solution stirred for 1½ hours. On cooling to -80°C a red precipitate formed which was removed by filtration and dried by suction. The red solid evolved bromine vapour.

Yield 10•97g, 54•1%

5.9 REACTION OF DIMETHYL SULPHIDE AND BROMINE

A number of attempts were made to produce the ionic form $(CH_3)_2SBr^+Br^-$ as against the molecular complex $(CH_3)_2SBr_2$. The following preparations detail the best preparative procedures for both of these complexes and also $(CH_3)_2SBr^+Br_5^-$. The other less successful preparations are detailed in Table 5.7.

a) $(CH_3)_2SBr_2$ (Figure 3.17)

Dimethyl sulphide (2·48g, 0·04 mole) was dissolved in dichloromethane (20ml) and bromine (6·4, 0·04 mole) in dichloromethane (10ml) added dropwise over 1 hour. A yellow solid was produced and the mixture stirred for 2 hours before filtration. The solid was dried by suction to yield a yellow solid.

Yield 7·38g, 83·1%

Analysis:

Br (found) 71·84)
71·89) 71·9%
71·83)

$(CH_3)_2SBr_2$

Br (calc) 72·1%

b) $(CH_3)_2SBr^+Br^-$ (Figure 3.18)

Bromine (3·2g, 0·02 mole) was dissolved in thionyl chloride (3·0g) and cooled to 0°C. Dimethyl sulphide (1·24g, 0·02 mole) was added dropwise to yield an orange solid. Dichloromethane (10ml) was then added and the solid removed by filtration and dried by suction. The product was stored at 0°C.

Yield 3·5g, 83·1%

Analysis:

Br (found)	72·28	72.1%	Cl (found)	2·16	2·3%
	71·75			2·26	
	72·02			2·46	

$(CH_3)_2SBr^+Br^-$

Br (calc) 72·1%

Ratio $346/_{286}$ = 4·16

The above preparation was repeated except that bromine (6·6g, 0·04 mole) was used and a red solid obtained.

Analysis:

Br (found)	82·44	82·6%
	82·87	

$(CH_3)_2SBr^+Br_3^-$

Br (calc) 83·8%

$(CH_3)_2SBr^+Br_5^-$

Br (calc) 88·6%

63·6% $(CH_3)_2SBr^+Br_5^-$ + 36·4% $(CH_3)_2SBr^+Br^-$

Br (calc) 82·6%

TABLE 5.7

REACTION OF $(CH_3)_2S$ AND Br_2

Reactant (moles)				Conditions			Spectrum	347/286
$(CH_3)_2S$	Br_2	Solvent	Amount	Addition	Reaction	Comments		
0·04	0·04	$AsCl_3$	40ml	½ hr @ 20°C	1 hr @ 20°C	cooled, no product	-	
0·02	0·02	$SOCl_2$	20ml	20°C	-	cooled, no product	-	
0·02	0·02	$SOCl_2$	3·0g	½ hr @ 10°C	-	CH_2Cl_2(15ml), filtered solid stirred with CH_2Cl_2, filtered	$(CH_3)_2SBr_2$ + $(CH_3)_2SBr^+Br^-$ in different ratios	1·88 1·34 1·98
0·02	0·02	$SOCl_2$	10·0g	10°C	1½hrs @20°C	cooled, no solid added CCl_4, no solid	-	
0·02	0·02	$SOCl_2$	10·0g	-80°C	3 hrs @ -80°C	added CH_2Cl_2, filtered	$(CH_3)_2SBr_2$	0
0·02	0·02	$SOCl_2$	10·0g	0°C	3 hrs @ 0°C	added CH_2Cl_2, filtered	$(CH_3)_2SBr_2$	0
0·02	0·02	$SOCl_2$	3·0g	0°C	3 hrs @ 0°C	added CH_2Cl_2, filtered	$(CH_3)_2SBr_2$+$(CH_3)_2SBr^+Br^-$	0·4
0·02*	0·03	$SOCl_2$	3·0g	0°C	0°C	CH_2Cl_2(10ml), filtered	$(CH_3)_2SBr^+Br^-$+ $(CH_3)_2SBr^+Br_5^-$	
0·02*	0·022	$SOCl_2$	3·0g	0°C	0°C	as above	$(CH_3)_2SBr_2$ + $(CH_3)_2SBr^+Br^-$	1·64
0·02*	0·019	$SOCl_2$	3·0g	0°C	0°C	as above	$(CH_3)_2SBr_2$ + $(CH_3)_2SBr^+Br^-$	0·99

* Bromine dissolved in solvent, dimethyl sulphide added. Other reactions - bromine added to sulphide in solvent.

5·10 REACTION OF DIMETHYL SULPHIDE AND CHLORINE

An attempt was made to duplicate the preparations detailed above (Section 5·9) but the product proved unstable.

Chlorine (cylinder weight loss 15·4g) was collected at −78°C and a solution of dimethyl sulphide (2·48g, 0·04 mole) in dichloromethane (20ml) added slowly. A precipitate formed. The mixture was stirred at −78°C for 2 hours and then warmed to room temperature prior to filtration. However, at about −40°C the solid disappeared so the liquid was cooled to −78°C to regain the solid. This solid was filtered off in the cold but during drying as the temperature rose the solid liquified.

This preparation was repeated with the same result and it is therefore possible that the solid complex is only stable below −20°C.

5.11 THE REACTION OF SULPHUR DICHLORIDE AND BROMINE

The general method used was to mix the sulphur dichloride and bromine by weighing into a Raman cold cell tube. No reaction appeared to occur. The tube was then cooled and sealed using a blow torch. The tube was allowed to warm to room temperature prior to the spectrum being recorded at various temperatures between 20°C and -180°C. It was found that good spectra were obtained if the tube was cycled over about ±30°C to anneal the solid. Spectra recorded above about -80°C were liquid and showed evidence of a mixture of starting compounds together with bromine chloride and possibly sulphur dibromide.

Table 5.8 details the reactions and the spectra obtained.

TABLE 5.8

REACTION OF SCl_2 AND BROMINE

Reactants (moles)			Conditions	Spectrum
SCl_2	Br_2	Cl_2		
0•002	0•001	-	mixed at r.t.	Figure 4.5
0•002	0•001	0•001	Cl_2 added at −180°C	Figure 4.6
0•002	0•002	-	mixed at r.t.	Figure 4.7
0•002	0•001	-	mixed at r.t.	as Figure 4.5
0•001	0•002	-	mixed at r.t.	As Figure 4.7 but very strong 299cm^{-1} band, band at 412cm^{-1}
0•003	0•001	-	mixed at r.t.	Broad bands 517, 370, 283, 212

5.12 REACTION OF SULPHUR DICHLORIDE, BROMINE AND CHLORINE

The general method used was to mix sulphur dichloride and bromine in a Raman cold cell tube. This was then attached to a vacuum line and the liquids frozen in liquid nitrogen before the tube was evacuated. Chlorine was condensed into a transfer tube, frozen and evacuated. Chlorine was then transferred to the sulphur dichloride/ bromine mixture by warming the chlorine and cooling the reaction tube. Finally the tube was sealed using a blow-torch. The volume ratio of chlorine to other reactants was noted and in a number of cases the chlorine was also estimated by weighing the tube portions after sealing.

The tube was then warmed to room temperature to give a homogeneous liquid which was then cooled in the Raman cold cell prior to recording the spectrum. It was found that considerable cycling at low temperatures was necessary to obtain a spectrum that did not change. However, repeatable spectra could also be obtained with minimal cycling. The spectra obtained immediately after cooling contained broad ill-defined bands. The spectra recorded at room temperature showed reactant bands together with BrCl and some broad bands.

In one reaction,chlorine was condensed onto sulphur dichloride followed by the bromine.

The reactions are detailed in Table 5.9.

TABLE 5.9

REACTION OF SCl_2, Br_2 AND Cl_2

Reactants (moles)			Cl_2 Vol	Conditions	Spectrum
SCl_2	Br_2	Cl_2			
0·002	0·001	-	1:1	Cl_2 added at -180°C	initially as Fig 4.12, 1 week r.t. Fig. 4.9
0·002	0·001	0·001	-	Cl_2 added at -180°C	cf Section 5.11
0·002	0·001	excess	-	Cl_2 added at -180°C	Fig. 4.10
0·002	0·001	0·003	1:1	Cl_2 added to SCl_2,Br_2 added	initially as Fig. 4.12, then as Fig. 4.9
0·002	0·001	0·001	1:·5	Cl_2 added at -180°C	Fig. 4.13
0·002	0·001	0·01	excess	Cl_2 added at -180°C	as Fig. 4.11
0·002	0·001	0·007	1:1	Cl_2 added at -180°C	initially Fig. 4.14, then Fig. 4.11
0·002	0·001	0·0015	-	Cl_2 added at -180°C	SCl_2,Br_2 + broad bands
0·001	0·001	0·005	1:2	Cl_2 added at -180°C	initially as Fig. 4.14, then as Fig. 4.11
0·003	0·001	0·004	1:1	Cl_2 added at -180°C	essentially as Fig. 4.14
0·002	0·001		1:3	Cl_2 added at -180°C	as Fig. 4.11

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Preparation and Raman Spectra of Tribromosulphonium and Mixed Chloro-bromo-sulphonium Cationic Complexes†

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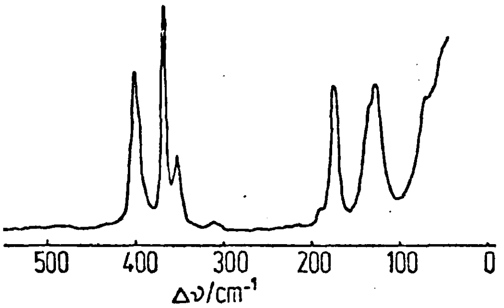
Sulphur tetrachloride, SCl_4, is stable only below about –40 °C but various stable salts of the trichlorosulphonium ion, SCl_3^+, are well known.[1–4] A recent report[5] describes the preparation and characterisation by Raman spectroscopy of the salts $SBr_3^+MF_6^-$ (M = As, Sb), derivatives of the unknown sulphur tetrabromide. We report here the preparation of two further complexes of this type, $SBr_3^+AlX_4^-$ (X = Cl, Br). No mixed chloro-bromo-sulphonium cationic species $SCl_nBr_{3-n}^+$ (n = 1,2) have been described previously; we have now characterised some salts of this type by Raman spectroscopy.

Synthesis of *pure* compounds containing chloro-bromo-sulphonium cations is apparently extremely difficult. We have carried out a variety of reactions involving a sulphur halide (SCl_2, S_2Cl_2, or S_2Br_2), a halogen (Br_2 or Cl_2), and a Lewis acid ($AlCl_3$, $AlBr_3$, or $SbCl_5$) and, in most cases where both chlorine- and bromine-containing species are used, a mixture of products results. An exception is the product from S_2Br_2, Br_2, and $AlCl_3$ (in 1 : 3 : 2 molar ratio, respectively) for which both the analytical composition and Raman spectrum (see Figure) are consistent with the formulation $SBr_3^+AlCl_4^-$. A pure product was also obtained from S_2Br_2, Br_2, and $AlBr_3$.



Raman spectrum of $SBr_3^+AlCl_4^-$

The Raman spectrum of this yellow, highly hygroscopic compound may be interpreted readily in terms of an ionic formulation, $SBr_3^+AlBr_4^-$. The ν_1 (A_1) band of $AlBr_4^-$ is clearly seen at 212 cm^{-1}, although other emissions characteristic of this anion[6] appear only as weak bands at 425, 400sh, 119, and 76 cm^{-1}; the remaining four very strong bands at 374, 347, 170, and 124 cm^{-1} are entirely consistent with a C_{3v} SBr_3^+ species, showing a close correspondence with those for the isoelectronic PBr_3 and also with those observed for SBr_3^+ $AlCl_4^-$ (above) and SBr_3^+ MF_6^- [5] (see Table 1). In both compounds the anion scattering was weak relative to that of SBr_3^+.

All other reactions studied yielded yellow or pale yellow solid products, of non-stoicheiometric analytical composition, and exhibiting complex Raman spectra indicating a mixture of species. A careful analysis of the intensity variations in the Raman spectra of the products of about 20 such reactions shows that there are usually three separate cationic species present, including SBr_3^+. There was no evidence from spectra of the presence of any mixed bromo-chloro-aluminate anions[6] or the $SbCl_5Br^-$ ion.[7] Scattering from the $AlCl_4^-$ was weaker than from the sulphonium cations, the only band with significant intensity being due to the ν_1(A) mode at 354 cm^{-1}. However, scattering from $SbCl_6^-$ appeared with intensity similar to that from the cations.

Repeated attempts to prepare pure salts of SCl_2Br^+ and $SClBr_2^+$ failed, presumably owing to the ease which scrambling occurred among the cations, as evidenced by the appearance of Raman bands due to these species when *solid* SCl_3^+ $AlCl_4^-$ and SBr_3^+ $AlCl_4^-$ were mixed. However, with knowledge of band positions for the SBr_3^+ species and by consideration of (*a*) the intensity variations and (*b*) the band positions of the isoelectronic PCl_2Br and $PClBr_2$ species,[9] vibrational assignments for SCl_2Br^+ and $SClBr_2$ have been made based on C_s point group symmetry (Tables 2 and 3).

Experimental

Owing to the moisture sensitivity of the products, all manipulations were carried out under dry nitrogen.

Analyses were carried out by initial hydrolysis of the compounds and potentiometric titration with 0.1 mol dm^{-3} $AgNO_3$ for chloride and bromide.

Raman spectra were obtained using a Coderg PHO spectrometer with excitation at 647.1 nm from a Coherent Radiation krypton laser; solid samples were sealed in melting point capillary tubes.

$SBr_3^+AlCl_4^-$. Solid aluminium trichloride (4.81 g, 0.036 mol) was added slowly (3 h) with stirring to sulphur monobromide (4.48 g, 0.02 mol) and bromine (9.6 g, 0.06 mol) in dichloromethane (20 cm^3) at room temperature. On cooling to –80 °C a very hygroscopic yellow solid was precipitated. This was filtered cold and dried by suction. (Found: Br, 56.5; Cl, 32.1. $AlBr_3Cl_4S$ requires Br, 54.5; Cl, 32.2%).

$SBr_3^+AlBr_4^-$. A similar procedure to that above using solid aluminium tribromide (10.68 g, 0.04 mol), sulphur monobromide (4.48 g, 0.02 mol), and bromine (9.6 g, 0.06 mol) yielded a bright yellow solid. (Found: Br, 89.94. $AlBr_7S$ requires Br, 90.47%).

Mixed complexes containing the ions $SCl_nBr_{3-n}^+$ (n = 1,2). A variety of preparations were carried out using various reactant ratios, solvents, and conditions with aluminium trichloride or antimony pentachloride as the halide acceptor. Mixtures of products resulted in all attempts. The following reaction is typical: solid aluminium trichloride (6.68 g, 0.05 mol) was added slowly with stirring to a mixture of sulphur dichloride (5.15 g, 0.05 mol) and bromine (8.0 g, 0.05 mol) in chloroform (30 cm^3) at –65 °C. The pale yellow solid was filtered off at room temperature.

In a further experiment, solid $SBr_3^+AlCl_4^-$ and $SCl_3^+AlCl_4^-$ were mixed, producing an immediate colour change. Apart from the bands due to these pure species, the Raman spectrum also showed strong emissions at the same frequencies as those assigned to the ions SCl_2Br^+ and $SClBr_2^+$.

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†This is a Short Paper as defined in the Instructions for Authors [*J. Chem. Research (S)*, 1977, Issue 2, p. iv]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Solid state Raman bands (cm^{-1}) in SBr_3^+ complexes

$SBr_3^+AlCl_4^-$ ^{a}	$SBr_3^+AlBr_4^-$ ^{a}	$SBr_3^+SbCl_6^-$ ^{b}	$SBr_3^+AsF_6^-$ ^{c}	$SBr_3^+SbF_6^-$ ^{c}	PBr_3 ^{d}	Assignment
401s	386m 374s	414s	429 414	421 411	400(ν_3, E)	ν_3 (E)SBr_3^+
368s	347s	370s	375	379	380(ν_1, A_1)	ν_1 (A_1)SBr_3^+
354m						ν_1 (A_1)$AlCl_4^-$
		343sh 332s				ν_1(A_{1g})$SbCl_6^-$
		285m				ν_2 (E_g)$SbCl_6^-$
	212w					ν_1 (A_1)$AlBr_4^-$
174s	170m	174s ^{e} 166w	175	175	162(ν_2, A_1)	ν_2 (A_1)SBr_3^+
135sh 126s	134w 124m	133w 122w	128	128	116(ν_4, E)	ν_4 (E)SBr_3^+
64vw, sh	79w 58w, sh 46w					Lattice bands

[a] Isolated as pure compounds; anion emissions other than ν_1 modes are very weak.
[b] Bands due to $SBr_3^+SbCl_6^-$ abstracted from spectrum of mixture of products.
[c] Ref. 5.
[d] Raman, liquid, ref. 8.
[e] Bands due to ν_5 (T_{2g}) of $SbCl_6^-$ and ν_2 (A_1) of SBr_3^+.

Table 2 Fundamental vibrational Raman bands (cm^{-1}) of the ion SCl_2Br^+ ^{a}

$SCl_2Br^+AlCl_4^-$ ^{b}	$SCl_2Br^+SbCl_6^-$ ^{b}	$PBrCl_2$ ^{c}	Assignments
520mw	525mw	495(ν_5, A")	ν_5 (A"), a sym. SCl_2 str.
506m	505m	495(ν_1, A')	ν_1 (A'), sym. SCl_2 str.
394s	404s	400(ν_2, A')	ν_2 (A'), SBr str.
246ms	243ms	230(ν_3, A')	ν_3 (A'), sym. SCl_2 def.
181m	180sh^{d}	167(ν_4, A')	ν_4 (A'), sym. SBr def.
		149(ν_6, A")	ν_6 (A"), a sym. SCl_2Br def.

[a] Anion bands omitted.
[b] SCl_2Br^+ bands abstracted from spectrum of mixture of products.
[c] Ref. 9.
[d] Partially masked by $SbCl_6^-$ band.

Table 3 Fundamental vibrational Raman bands (cm^{-1}) of the ion $SClBr_2^+$ ^{a}

$SClBr_2^+AlCl_4^-$ ^{b}	$SClBr_2^+SbCl_6^-$ ^{b}	PBr_2Cl ^{c}	Assignment
490m	505m	480(ν_1, A')	ν_1 (A'), sym. SCl str.
407ms	414ms	390(ν_5, A")	ν_5 (A"), a sym. SBr_2 str.
380vs	387s	390(ν_2, A')	ν_2 (A'), sym. SBr str.
210s	206s	197(ν_3, A')	ν_3 (A'), sym. SCl def.
160m	166m, sh	153(ν_6, A")	ν_6 (A"), a sym. $SClBr_2$ def.
134s	132m	123(ν_4, A')	ν_4 (A'), sym. SBr_2 def.

[a] Anion bands omitted.
[b] $SClBr_2^+$ bands abstracted from spectrum of mixture of products.
[c] Ref. 9.

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