SPECTROSCOPIC INVESTIGATION
OF SOME
METAL VI CARBONYL PHOSPHINE
COMPLEXES

THESIS

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DAVID W. MILNE B.Sc.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

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SUMMARY

Preparation of metal carbonyl phosphine complexes of type $LM(CO)_5$ and trans $L_2M(CO)_4$ M = Cr, Mo and W; L = $P(OMe)_3$, $P(OEt)_3$, $P(OPr^i)_3$, PPr^i_3 and PBu^n_3 has been studied in a systematic way. Direct solventless reaction has been found applicable for preparation of the trans disubstituted derivatives, especially those of tungsten which are difficult to obtain in other ways. Chromatography was used for separation and purification of the complexes.

The ultraviolet spectra of the phosphine complexes have been recorded both at room temperature and low temperature. The low temperature spectra were obtained using a sample cooled by liquid nitrogen in a dewar. The observed change in the spectral outline on sample cooling has been successfully related to the forbidden/allowed character of the electronic transition involved. Using this experimental evidence, the spectra of the metal complexes have been partially assigned for the energies approximately 35,000 - 25,000 cm^{-1} where transition energies may represent either d-d or charge transfer type transitions and the extinction coefficients at room temperature have values intermediate between accepted d-d and charge transfer values. Thus the lowest energy charge transfer transition has been assigned for thirty complexes, in only three of which it has been previously reported and these on the basis of spectra recorded at room temperature only.

Some representative examples of the ultraviolet spectra having

several overlapped, partially resolved bands were analysed using a combination of Gaussian curves. This technique has become more popular recently and has been applied to complex spectra of derivatives of the type studied here. The spectral outlines were not all suitable for curve analysis since in cases where the degree of overlap is very high, it is not possible to make a plausible assessment of the number of peaks involved, this information being essential for the analysis. Comparative critical studies have been carried out on the Gaussian analyses obtained, taking account of the subjective factors of the operator's decisions concerning the number of peaks and their relative intensities. This has been used in assessing both the validity and usefulness of the peak information revealed by such analyses.

Nuclear magnetic resonance spectra of the complexes have been recorded for proton and carbon-13 resonance. The proton spectra of the trans disubstituted phosphite derivatives have been related to the phenomenon of virtual coupling which is seen for protons on the α-carbon of the ligand substituent only. Analogous phosphine derivatives are seen to have second order splitting patterns which would require further analysis, probably by computer simulation, to be discussed in relation to the phosphite spectra. The carbon-13 spectral parameters are reported for these complexes for the first time. Chemical shifts of the carbon in the carbonyl groups and in the ligands along with coupling constants for phosphorus-carbon and tungsten-carbon coupling are given. Their discussion is limited by the undeveloped nature of chemical shift and coupling theory as they apply to carbon-13 magnetic resonance.

The mass spectra of a limited number of the complexes are reported and a short discussion of the possible fragmentation patterns is given. These patterns are derived by analogy with previously reported patterns of similar complexes. The spectra of two monosubstituted complexes are compared with those of the corresponding trans disubstituted derivatives and the differences in relative intensities and m/e fragments observed are discussed.

Infrared spectra of the complexes have been recorded in the stretching carbonyl region on solutions of very high concentration and formally forbidden peaks have been observed and assigned for mono- and trans disubstituted phosphite derivatives while only for the monosubstituted phosphine derivatives have such peaks been assigned. The δMCO and νMC absorptions have been recorded although, as in previous studies, fewer peaks are observed than are required by group theory.

Metal phosphorus bonding is discussed taking account of the U.V., I.R. and N.M.R. studies reported here along with recent developments in relevant molecular orbital theory and other reported results concerning bonding in similar complexes. An assessment has been made of the value of relating spectroscopic results directly to variations in the metal-ligand bonds, especially the metal-phosphorus bond.

A short appendix deals with preparation of trifluorophosphine derivatives of $M_2(CO)_{10}$ M = Mn, Re.

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CHAPTER 1

INTRODUCTION

INTRODUCTION

Organometallic chemistry, in common with many other fields of scientific study has experienced unprecedented growth in the last decade. There are some particular aspects of it, however, which cause the study of organometallic complexes to have a special attraction not present in many areas of chemistry today. The name organometallic conveys the essential attribute which is the interdisciplinary nature of the field. Inorganic and organic techniques are combined with physical and spectroscopic analytical methods in an attempt to construct and consolidate a theoretical approach to organometallic compounds. The requirement for new concepts and semi-empirical explanations gives rise to originality and ingenuity which inspires interest and enthusiasm and is indeed the source of the dynamism which has been maintained over the past ten years.

The scope of organometallic chemistry is so wide as to have made inevitable the concentration of effort in some broadly specialised paths. One such is concerned with the development of the chemistry of transition metal carbonyls and their derivatives. Some of the transition groups have been more predominant than others in this development due to the relative ease with which their complexes may be synthesised, manipulated chemically and treated in a chosen theoretical framework. Thus the group VIII metals nickel, palladium and platinum have been used extensively in metal complex chemistry[1-3] as a basis for evolving theoretical work concerned with square planar complexes of type MX_nY_{4-n} where X and Y are a variety of ligands. Complexes of these group VIII metals have been known for many years, are comparatively readily available and are most commonly characteristic of square planar molecules. Similarly, group VI metal complexes are typically derived from an octahedral structure and their hexacarbonyl derivatives have been particularly useful in developing theoretical considerations of octahedral complexes and their symmetrically related derivatives.

Initially, interest was centred on the group VI hexacarbonyls due to the occurence of the metal in low oxidation state, the octahedral symmetry of the molecule and, later, the range of relatively stable complexes readily derived from such simple precursors. Blanchard[4] in 1937 noted that if ligands such as carbonyl contribute two electrons to a metal in complex, the total number of electrons surrounding the metal usually equals that of a closed shell configuration. This is termed the "effective atomic number" rule. This empirical rule may be extended to other ligands and has been used to develop and correlate the types and stoichiometries of possible complexes of transition metals with many different ligands. The application of rules such as this in conjunction with symmetry and molecular orbital theories induced intense interest in the group VI metal hexacarbonyls $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ and their derivatives.

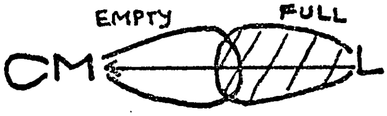
Early preparations of the metal VI hexacarbonyls[5, 6] have been supplanted by techniques developed at the beginning of the 1960's[7] and later[8]. Substitution of carbonyl groups in the metal hexacarbonyls by amine ligands was found to be readily observed.[6,9,10] Phosphine complexes of both nickel[1] and manganese[11] were known before such complexes of the group VI metal carbonyls were successfully prepared in 1959.[12,13] The preparation of group VI metal carbonyl phosphine complexes developed fairly rapidly although the number of monodentate phosphine ligands involved was limited at first. Comprehensive reviews have appeared [14,15] giving accounts of preparative techniques, thermal, photochemical and indirect methods being covered along with tabulation of the complexes prepared. The most recent of these reviews was published in 1966 since when synthetic work has tended to assume the role of a necessary precursor to other research aspects such as spectroscopic investigations of the complexes.

Much of the early interest in the phosphine derivatives of the hexacarbonyls was concentrated on preparative techniques and the nature of the bond between the metal and the phosphorus atoms. Synthesis of the complexes has now less intrinsic interest and the general study of bonding has assumed the dominant role in metal carbonyl chemistry. The treatment of bonding is discussed in some detail below, but is is interesting to note that the occurrence of metal carbonyl phosphine complexes may be understood using the hard and soft acid-base theory of Pearson.[16] Carbonyl and phosphine are both soft bases which are expected to co-ordinate with the metal (0) atom which is a soft acid in these complexes. The classification of the metal atom is based on work by Ahrland, Chatt and Davies carried out in 1958.[17]

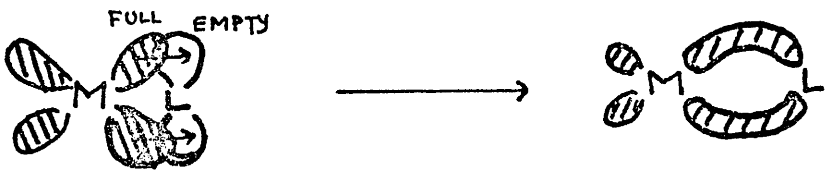
Early investigations of transition metal carbonyl complexes showed clearly that some new theoretical concepts would be necessary to explain many of their most common aspects. The stability of many of the complexes could not readily be explained by existing theories. This was particularly true of metal complexes in which the metal existed in a low oxidation state or the ligands where weak basic donors such as carbonyl or phosphorus trifluoride which showed no ability to bond to non-transition metals. Some of the physical measurements available also indicated anomalies in bonding and general electronic structure. For example, the carbon oxygen stretching frequencies observed in the infrared spectra of metal carbonyl complexes and their derivatives were seen to have values consistently less than that for free carbon monoxide (typically 2000cm^{-1} for the former compared to 2133cm^{-1} [18] for CO). Abnormally short bond lengths were also observed in some complexes. However, the most important factor concerning the development of transition metal chemistry at this time was the appreciation that the metals involved all had partially filled d-orbitals and the ligands in many cases possessed vacant orbitals capable of accepting the metal d-electrons. Indeed, L.E. Orgel probably the most significant single contributor to early transition metal complex bonding theory was quoted then as saying that "the peculiar interest of the transition metals is generally agreed to be connected with their ability to form compounds in which the outermost set of stable d-orbitals is only partially filled".

This observation coupled with qualitative molecular orbital theory produced the most elegant and useful concept of mutual reinforcement of σ- and π-orbital overlap in a single bond.

Bonding in metal carbonyls where the metal has a low oxidation number may be represented as a single synergic effect involving σ- and π- overlap. In the present study, the metal ligand bonds are all of a similar nature. Each ligand donates a pair of electrons to the metal atom, carbon monoxide donating the electron pair in a σ-orbital of the carbon and phosphines donating the electron pair of a hybrid orbital on the phosphorus atom. In either case, the bond may be represented



The donation of electron pairs from each of the ligand molecules must cause charge build up on the metal atom which would be expected to cause instability by charge repulsion. The fact that such instability is not observed has been explained[19] by proposing a method of transferring the charge from the metal back to the ligands. This is termed "backbonding" and is accounted for by donation of electrons from the π-bonding orbitals on the metal to empty π-antibonding orbitals on the ligand.



Carbon monoxide is a very weak base and thus the ligand metal bond is expected to be weak in this case. Formation of carbonyl complexes may be attributed to the backbonding mechanism which allows formation of a strong metal carbon bond. The failure of metals having no d-orbital electrons to form carbonyl complexes may be instanced as evidence of the backbonding requirement. Phosphines, however, are potentially strong σ-donors although they also possess low lying empty 3d orbitals which may accept π- electrons from the metal. In this respect, phosphines differ from amines which have no such low lying π- acceptor orbitals. The greater stability of phosphine complexes as compared to analogous amine complexes may possibly be due in part to the participation of π- accepting orbitals only in the phosphine complexes. In general, ligands of class B type[17] bond to group VI metals most easily.

The existence of the metal carbonyls and their derivatives is thus attributed to the stabilisation of the ligand-metal σ-bonding structure by charge distribution into a π-overlap system. Such stabilisation need not involve each of the metal ligand bonds as may be seen on considering amine complexed and it may vary according to the nature of the ligand involved. At this stage, more recent developments which have introduced complications must be considered. There is by no means concensus on the relative roles of σ- and π- overlap in metal phosphine bonding of metal carbonyl derivatives. Indeed, one of the most lively aspects of the chemistry of metal carbonyl phosphine derivatives in the 1960's was the basic disagreement between those who consider π- bonding as an important aspect of metal-phosphine bonding and those others who relegate π-bonding to an entirely insignificant position in any bonding theory. I will be discussing the relation of my results to the postulates of both σ- and π-bonding in some detail, but it is of interest to consider the development of the various approaches.

Generally, there is acceptance of theidea that π-bonding is involved to some extent in the bonding of derivatives of metal carbonyls including the metal phosphine bond. The explanation of strong metal-carbonyl bonding requires this to be so and ligands of type PR_3 have analagous π-bonding abilities which are difficult to discount. Some treatments[19,20] seem to discound the existence of π-bonding altogether but more frequently the controversy is concerned with the ability to correlate accepted π-bonding ability with observed physical measurements such as the carbonyl stretching frequency values or derived properties such as force constant parameters. Thus, even very early in the development of bonding theory, π- bonding ability was related to infrared frequency values in the carbonyl stretching region.[12,21,22] Other instances where π-bonding has been used as an explanation of observed effects include the well known trans effect in platinum (II) chemistry[23] and the relative thermodynamic stabilities of cis- and trans-isomers of type $PtIIX_2Y_2$, square planar complexes with X and Y various ligands[24]. Support for the theory involving σ-bonding only has come from studies of nuclear magnetic resonance phosphorus 31-proton coupling constants in various metal phosphine complexes[3,25,26] along with theoretical work by Zumdahl and Drago[27]. Other nuclear magnetic resonance studies have, however, been interpreted in terms of possible π-bonding correlations[28]. Also of importance to the σ-bonding approach is the polarisation theory invoked to explain the trans influence of hydride in various complexes[29]. Some infrared spectral work has also been interpreted as relating to the σ-bonding theory only[30].

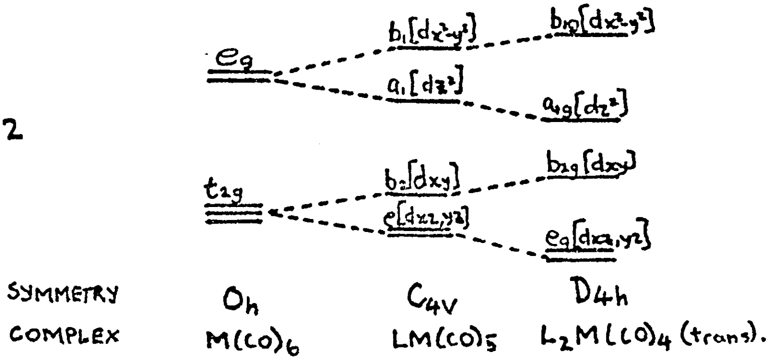
Recent work has produced conflicting evidence without any clear indication that one orother theory is necessarily superior. It has been shown[31,32] that carbonyl stretching frequencies may be related directly to the substituents on the phosphorous atom of a phosphine substituted nickel complex. This relation involves the inductive effect (σ^*) of the groups on the phosphorous atom and thus provides evidence for the bonding theory. Other studies involving infrared frequencies have provided results supporting this substituent relation [19,33]. Evidence supporting the involvement of π-bonding has been put forward by Graham[34] who used Cotton and Kraihanzel's approach[21] to obtain σ- and π- parameters for a variety of ligands deriving these parameters from force constant parameters. This is a questionable extreme, relying as it does on a direct application of approximations to a σ-π bonding system which suffer from inaccuracies outlined by Cotton and Kraihanzel themselves[21] and expanded by Jones[35]. These approximations along with further aspects of theories concerned with force constants will be discussed below.

As more information, experimental and theoretical, is collated, ideas concerning metal phosphine bonding in metal carbonyl phosphine complexes develop and alter. The most recent approaches to this problem have involved X-ray photoelectron spectroscopy as a probe to determine "2p" orbital electron densities in a series of phosphorus complexes[36], molecular orbital calculations on a series of manganese complexes with carbonyl and cyanide ligands[37] and investigation of the absolute raman intensities of the group VI metal hexacarbonyls[38]. Thus metal phosphine bonding remains an active and fertile field of study in organometallic chemistry. While the problems are by no means resolved, the weight of evidence suggests that π- bonding should be considered as a parameter in any theoretical approach and such bonding will be considered in the treatment of the spectroscopic results reported in this work.

The bonding in metal carbonyl derivatives may be represented by a molecular orbital energy level diagram which gives the orbitals derived from the interaction of atomic orbitals localised on the metal atom and molecular orbitals localised on the ligands. This approach was first applied to complexes by Van Vleck[39,40] and is a satisfactory compromise between crystal field theory which allows no metal-ligand orbital interaction and pure molecular orbital theory which is impossibly complex for such systems. Several approaches to the molecular orbital diagram of group VI metal hexacarbonyls have been developed in the past few years[41-43] in which metal nd, (n+1)s and (n+1)p orbitals are combined with σ- and π- bonding and antibonding orbitals of carbonyl to give some form of the energy level diagram shown in figure 1.1. The high octahedral symmetry of these hexacarbonyls and the relatively small number of ligand molecular orbitals involved has made semi-empirical calculations of the molecular energy levels feasible. When the symmetry of the complex is lower than octahedral and ligand molecular orbitals derived from more than one type of ligand are involved, it is not possible to construct a comprehensive energy level diagram because the required parameters are not available. It is, however, possible by taking account of some qualitative features of the molecular orbital diagram for the hexacarbonyl and, considering the effect of reducing symmetry on specific orbitals in the diagram, to correlate some of the observed data with a qualitatively satisfying model. Further, using an approximate molecular orbital approach, the relative ordering of the ligand molecular orbitals involved in the charge transfer electronic absorption spectra in region 25,000-45,000cm^{-1} has been calculated[44] and will be discussed later.

The effect of symmetry lowering on the relative ordering of the d-orbitals splitting in a strong field (see below) is shown in figure 1.2.

Figure 1.2



From this it may be seen that the D_{4h} trans $L_2M(CO)_4$ and C_{4v} $LM(CO)_5$ orbital orderings are qualitatively similar with the filled, triply degenerate t_{2g} orbitals in O_h symmetry splitting to give one singly and one doubly degenerate orbitals in each case. Thus it is expected that the electronic transition spectra characteristic of electron transitions from the t_{2g} level in O_h symmetry will have analogous spectra which are significantly more complex in the case of the less symmetric derivatives. As the unfilled Eg levels are no longer degenerate and ligand molecular orbitals are necessarily split, it is clear that the number of electronic transitions possible must be very much larger in the derivatives. The splitting of the d-orbitals of a metal in a complex is determined by the relative strengths of the perturbations involved. Thus, both carbonyl and phosphine ligands exert a strong field (i.e. are high in the spectrochemical series[45]) and will provide a field sufficiently large to overcome interaction between terms (i.e. levels derived from interelectronic repulsion) of the same configuration. This approach, however, presupposes that the energy levels of the d-electrons may be represented by considering a perturbed one electron scheme as basis. While this is a reasonable approximation for the first transition series, metals in higher transition series must be treated with more caution. In these cases, magnetic spin-orbital coupling forces may be stronger than the interelectronic repulsion forces which form the basis for the one electron perturbation or Russell-Saunders[46] scheme. When attempting to interpret and assign spectral bands in complexes such as the group VI metal carbonyl phosphine derivatives, it is thus necessary to consider the field of the ligands involved, the most appropriate energy level scheme as derived from the relative forces experienced by the metal and the effect of the symmetry group of the molecule on possible energy levels. Selection rules (discussed below) may be used to determine whether a transition between two levels is allowed or forbidden.

Much of the work on metal VI carbonyl derivatives has centred on obtaining their spectroscopic parameters and correlating these with an appropriate theoretical approach. The present work is concerned with several spectroscopic investigations of group VI metal hexacarbonyl derivatives of type $LM(CO)_5$ and trans $L_2M(CO)_4$ M is Cr, Mo or W and L is a phosphorus (III) ligand . The infrared, ultraviolet, nuclear magnetic resonance and mass spectra of these derivatives have been recorded and the various parameters employed in a discussion of metal-ligand bonding. The studies of mass spectra, ultraviolet and nuclear magnetic resonance spectra are treated separately whereas the infrared spectroscopic techniques were employed throughout the entire work. The nature of the former investigations is therefore best introduced in the chapters dealing with these studies. The basic concepts and techniques involved in infrared spectral studies of metal carbonyl derivatives have been more thoroughly treated and as they are used extensively it is appropriate to give a short summary of their development to this point.

The basis of theoretical treatments of the infrared spectra of metal carbonyl derivatives is the application of the powerful methods of group theory and molecular symmetry to the structures of the complexes involved. A molecule may possess certain symmetric properties which can be expressed in terms of the corresponding symmetry elements. The symmetry elements belonging to any molecular structure allow it to be classified into one of a finite number of symmetry point groups. Such symmetry groups may be treated using formal group theory[47] as their elements also form a group in the strict mathematical sense. The development of group theory as a powerful aid to the analysis of molecular vibrations is comprehensively treated by Wilson, Decius and Cross[48] while Cotton in an excellent treatment[49] has considered the development and application of group theory to the more qualitative aspects of chemical spectroscopy. Most group theoretical work concerning the interpretation and assignment of infrared spectra of metal carbonyl derivatives has comprised a qualitative interpretation of the number of bands expected from vibrations of the carbonyl groups in the appropriate symmetry. Studies concerning vibrations other than those of carbonyl groups or other skeletal deformations of any kind have been less frequent due to complications such as the abundance of peaks from various sources in the regions concerned or the lack of appropriate techniques for obtaining such spectra.

The use of observed carbonyl stretching frequencies to correlate with a specific structure involves a comparison of the number of such observed peaks with the number expected for various symmetry groups. Thus substituted carbonyl derivatives may be considered as belonging to a molecular symmetry group and from the character table of that group may be obtained the number and activities of the modes of vibration associated with the carbonyl groups. The molecular point group of a derivative may be chosen in two ways which may be illustrated with reference to the monosubstituted case $LM(CO)_5$ derived from the octahedral $M(CO)_6$. If L is considered as a radially symmetric ligand, the molecule belongs to the C_{4v} group while if L is assumed to be spacially asymmetric and the symmetry of the entire molecule is then considered, $LM(CO)_5$ belongs to a symmetry group lowered with respect of C_{4v} and determined by the symmetry of the ligand. The possibility of symmetry lowering and other effects causing formally forbidden modes to be observed in a spectrum make it essential that structure correlations based on, for example, the carbonyl stretching region only, take account of these anomalies. Many observations of formally forbidden peaks have been reported for complexes of the type $M(CO)_{6-n}L_n$ M = Cr, Mo, W L is a P(III) ligand, n = 1-4 [21,50,51] and recently the origin of such peaks has been discussed [52,53]. Such treatments are complicated by other considerations such as the possible appearance of bands belonging to ^{13}CO substituted species[54] and the effects of solvent.[55,56] Correlation of infrared spectra with complex structure has been widely used in the present work to characterise the mono and trans disubstituted derivatives. Formally forbidden bands are observed for each of these configurations and are discussed in relation to current ideas on their origins.

Prior to 1962 the study of infrared spectra of metal carbonyl derivatives was predominantly qualitative in nature, mainly used to monitor reactions or to identify a complex. Work by Orgel[57] and Cotton and Kraihanzel[21] saw the development of a semiquantitative approach to the carbonyl stretching frequency region. Orgel used the relative intensities of the infrared bands to assist in their assignments to the normal modes involved in the vibrations and Cotton and Kraihanzel developed a relatively simple model for analysing and assigning carbonyl stretching frequencies of complexes derived from octahedral molecules (i.e. of type $MX_{6-n}L_n$). The latter work allowed an approximate calculation of the force constant parameters involved in carbonyl stretching by substituting observed spectral frequencies in approximate secular equations obtained by standard vibrational analysis[48].

The work of Cotton and Kraihanzel involved two main simplifying approximations. First, the observed frequencies in the infrared spectrum were used without correcting for the anharmonicity of the vibration concerned, and secondly, the carbonyl frequencies were considered to be pure, that is non interacting with any other skeletal deformation. It was further assumed that orbitals involved in σ-bonding could not mix with π-bonding orbitals (this from their respective symmetries) and this "factoring out" of π-bonding led to the formulation of five conditions concerning carbonyl force constants, stretch-stretch interaction constants and π- accepting ability of the ligands. Use of these conditions reduced the number of force constants involved to the three shown in figure 1.3 k_1, k_2 and k_i.

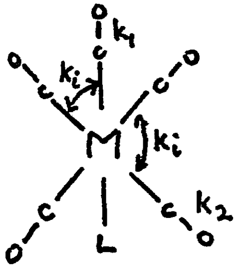


Figure 1.3

Assuming that the coupling between carbonyl groups is non mechanical to obtain a simplified G matrix and using combinations of the force constants k_1, k_2 and k_i to construct the F matrix allowed evaluation of the factored secular equations. Further, using the approximation $k_i = k_c = k_{t/2}$ (derived from orbital sharing arguments. k_c, k_t are interaction constants between two carbonyls cis and trans to each other respectively) approximate secular equations which are shown in table 1.1 were obtained. These secular equations are useful in that they provide a simple means of calculating approximate force constant parameter values for k_1, k_2 and k_i from observed carbonyl stretching frequencies. The equations may also be used to check assignments by calculating force constant parameters using all but one of the carbonyl frequencies and using these force constant parameters to calculate the remaining frequency. These correlations may, however, be misleading and it has been found necessary to employ other methods for assigning spectral peaks with certainty.

TABLE 1.1

COMPLEX	MOLECULAR SYMMETRY	SYMMETRY SPECIES OF CO STRETCHING MODE	APPROXIMATE SECULAR EQUATIONS
$LM(CO)_5$	C_{4v}	A_1^1 A_1^2	$\begin{vmatrix} \mu k_1 - \lambda & 2\mu k_i \\ 2\mu k_i & (k_2 + 4k_i) - \lambda \end{vmatrix} = 0$
		B_1	$\lambda = \mu k_2$
		E	$\lambda = \mu(k_2 - 2k_i)$
$L_2M(CO)_4$	D_{4h}	A_{1g}	$\lambda = \mu(k + 4k_i)$
		B_{1g}	$\lambda = \mu k$
		E_u	$\lambda = \mu(k - 2k_i)$

k in dyne cm.

μ is the reciprocal of the reduced mass of CO = 0.14583.

$\lambda = (5.8890 \times 10^{-2})\nu^2$, ν in cm^{-1}.

This treatment of Cotton and Kraihanzel has been used extensively to calculate approximate force constant parameters from carbonyl stretching frequencies,[58-60] and from these parameters, observed trends in physical and spectroscopic properties have been accorded plausible explanations. While the use of Cotton-Kraihanzel parameters was widely accepted, it was recognised that the inherent approximations in the method caused it to be less than ideal. Thus, certain workers reported anomalous results in calculating force constant parameters on the Cotton-Kraihanzel model which they attributed to its approximations.[51,61,62] Later, specific studies of the relation of Cotton-Kraihanzel force constant parameters to the values of these parameters as calculated on a more rigorous basis were undertaken by Jones[63] for $M(CO)_6$ and by Bower and Stiddard[64] for $M(CO)_6$ and $L_2M(CO)_4$ M = Cr, Mo, W in each case. A modified treatment of the carbonyl stretching frequencies of monosubstituted $LM(CO)_5$ complexes M = Cr, Mo, W when all four of the stretching modes $(2a_1 + b_1 + e)$ are observed was proposed by Stone and coworkers[65]. This involved the use of carbonyl stretch-stretch interaction relationships derived from bonding relations but the values of parameters obtained were not improved using this technique. The method of ref. 65 gives $k_1 > k_2$ for $M(CO)_6$ M = Cr, Mo, W[132] and is thus in error. Recent reports of improved force constant calculations[66,67] using this approach are therefore misleading and provide a good example of the care required in using approximate methods. The use of approximate force constant parameters has long been justified as a practical semi quantitative approach which may, when employed with care, rationalise some observed properties of simple metal carbonyl derivatives. This remains a fair assessment of these approximate methods provided that the approximations are accounted for in any argument employed.

The spectroscopic studies undertaken in this work were considered justified by the confusion of thought concerning the electronic structure of the metal carbonyl derivatives treated. The paucity of data available for the ultraviolet spectra of these complexes gave an impetus to record these and the search for relationships between the electronic transitions and bonding characteristics of the metal ligand and metal carbonyl bonds was the primary reason for doing so. The infrared spectra of the complexes have been recorded more accurately than previously and consideration of formally forbidden peaks along with general frequency trends correlated with the electronic transitions to clarify the bonding properties being discussed. Nuclear magnetic resonance data obtained for the proton and C-13 nuclei are also reported and their relevance to bonding discussed. A survey of the preparative techniques previously employed is given and a systematic approach is adopted to simplifying such preparations.

CHAPTER 2

SYNTHESIS OF METAL CARBONYL PHOSPHINE DERIVATIVES

SYNTHESIS OF METAL CARBONYL PHOSPHINE DERIVATIVES

Introduction

Synthesis of phosphine derivatives of chromium, molybdenum and tungsten hexacarbonyls may be effected by three main types of reaction. The first of these involves direct reaction, replacing one or more carbonyls by phosphine groups using either thermal or photochemical energy. Preparative photochemistry has been studied principally by Strohmeier and his co-workers for an extensive series of both amine[68] and phosphine[69] complexes. The mechanisms and other properties of these reactions have also been studied.[70,71,68] Thermal reaction has been used more extensively to obtain monodentate phosphine complexes[72-74] probably because it is a more adaptable technique required for the diverse reactivities shown by different phosphines. These direct techniques have been popular as straightforward methods of obtaining structurally and chemically interesting substituted carbonyl derivatives from stable, readily available reactants. It has been observed that substitution of carbonyl by phosphine in the metal VI hexacarbonyls becomes progressively more difficult as the degree of substitution increases. Direct methods are therefore primarily used as pathways to derivatives having low degrees of substitution.

The remaining two methods of complex formation are of the indirect type, involving an intermediate which reacts with the phosphine to give the required compound. The intermediate may be a neutral complex of the type $M(CO)_nL_{6-n}$ M = Cr, Mo, W e.g. $M(CO)_n(MeCN)_{6-n}$ n = 3, 4, 5[75] which will lose the relatively weakly co-ordinated acetonitrile ligand to accommodate the strongly bonding phosphine ligand. Alternately, the intermediate may be anionic of the type $Cr(CO)_5^{2-}$ or $Cr(CO)_5I^-$.[76,77] These indirect pathways are better suited to preparation of complexes otherwise difficult to obtain including highly substituted complexes and those with ligands which are difficult to co-ordinate directly. The complexes considered in this study are monosubstituted and trans-disubstituted phosphine carbonyls $M(CO)_5L$ and trans-$L_2M(CO)_4$ where M is chromium, molybdenum or tungsten and L is trimethyl phosphite, triethyl phosphite, triisopropyl phosphite, triisopropyl phosphine, trinbutyl phosphine and trisdimethyl aminophosphine. It was considered that the most convenient approach to the preparation of these derivatives was by direct thermal reaction of the metal hexacarbonyl with the phosphine ligand and conditions were adjusted as was found necessary. A recent paper[78] reports the use of sodium borohydride as a catalyst in reactions of Group VI metal carbonyls with some phosphines. While this technique reduces the time and elaboration required to form trisubstituted phosphine derivatives and allows co-ordination of some otherwise unfavourable bidentate ligands, in view of my results, it does not represent an advance in the mode of formation of mono- and disubstituted complexes. Direct reaction under controlled conditions is more rapid and allows control of the substitution product obtained, which is not the case in the catalysed reaction. This use of a catalyst in such reactions is, however, interesting in that it is the first time such a solution has been used to overcome preparative difficulties in this type of preparation. The development of catalysis may become more important as the required conditions for reaction are less disruptive than is normally the case, allowing possible formation of derivatives which might otherwise decompose.

Direct thermal reaction between metal VI hexacarbonyls and phosphines has been developing for more than ten years although until now, no truly systematic study of optimum conditions for such reactions seems to have been carried out. Poilblanc and Bigorgne[79,72] in 1961 reported the first preparation of metal VI carbonyl complexes containing tertiary phosphites other than triphenyl phosphite.[13] Their work in this field was confined, however, to such complexes of molybdenum only, although triethyl phosphine derivatives of tungsten and chromium were reported at this time also. Complexes of group VI metal carbonyls with both triphenyl phosphine and triphenyl phosphite have been known since 1959[13] and such complexes were found to be stable and easily made. An early study by Magee and co-workers[73] developed a useful technique for preparation of monosubstituted and trans-disubstituted phosphine derivatives of metal VI hexacarbonyls. This involved refluxing the hexacarbonyl and phosphine in diglyme for a certain time, the product being determined by the reactant molar ratios and in some cases the time of reaction and the nature of the ligand. Preparations using solvents of different boiling points as reflux agents have been developed mainly by Piolblanc and Bigorgne and in a recent paper[80] they report the preparation of $M(CO)_{6-n} P(OCH_3)_{3\ n}$ $n = 1-4$ M = Cr, Mo, W.

The superiority of direct reaction for the preparation of the types of complex with which we were dealing was well established. However, it was found that the reproducibility of results was fairly poor with complications such as oxidation of the metals in solution causing unexpected difficulties. While triphenyl phosphine and triphenyl phosphite ligands tended to react rapidly and form stable complexes, this was not found to be the case for some of the phosphines in this work. As preparations of this kind are a necessary prelude to spectroscopic and other studies of these complexes and have only limited intrinsic interest, it was considered desirable to investigate such reactions in an attempt to produce a routine technique which would eliminate previous drawbacks. The relatively small number of complexes of this type appearing in the literature seemed to support this line of work.

Preparation of trisdimethyl aminophosphine derivatives of chromium, molybdenum and tungsten carbonyls have been reported[81] using ethylcyclohexane as a reflux medium. This method is not improved for this ligand by altering the conditions, while for reactions involving trimethyl, triethyl and triisopropyl phosphite, triisopropyl and tributyl phosphine such solvents, while allowing formation of the complexes, do not provide optimal conditions. Thus, for example, hydrocarbon solvents when used for tributyl phosphine reactions allow rapid formation of both the monosubstituted and trans-disubstituted complexes causing extensive separation and purification problems. These and other problems have been successfully eliminated by a systematic study the results of which are now reported and discussed.

Discussion

Considering first the preparation of monosubstituted complexes $LM(CO)_5$, one essential condition for reaction is that there should be a slight excess of the hexacarbonyl. A molar ratio $M(CO)_6 : PR_3$ of approximately 1.1 : 1.0 is found to be ideal. If the molar ratio is such that the phosphine is in excess even as little as about ten per cent, there is a marked tendency for rapid formation of the disubstituted species. It is noted that in diglyme, formation of phosphite disubstituted complexes is more rapid than formation of analagous phosphine complexes in a reaction mixture containing excess ligand. Even with an excess of the hexacarbonyl, prolonged heating will cause formation of some disubstituted complex. It is possible to offer an explanation of this behaviour on the basis of previous studies of force constant interpretation.[60] Thus the carbonyl stretching force constants are greater for monosubstituted phosphite complexes than phosphine complexes suggesting weaker metal carbonyl bonds in the former case which could be displaced more readily by excess ligand. However, such arguments are tenuously based on approximate treatments and as other factors such as steric effects must be considered it is probable that the rationalisation of the observed reactions is a combination of these effects.

The other major factor in these reactions involves the choice of solvent. As has been seen, different workers have made use of a variety of solvents sometimes to provide a specific reaction condition (e.g. a particular temperature of reflux) although more often simply as a convenient reaction medium. Solvents such as methylcyclohexane and high boiling petroleum ether fractions were tried with varying success and only marginal reproducibility. In these solvents, the monosubstituted triisopropyl phosphine and trinbutyl phosphine derivatives were seen to form along with their corresponding disubstituted derivatives. As none of the separation techniques investigated allowed separation of these mixtures into their components, such hydrocarbon solvents were found to be of little use.

The use of bismethoxydimethyl ether (diglyme) as a solvent for the reactions of metal VI carbonyls with phosphines was first reported in 1961.[82] Earlier[83] the mode of action of diglyme in such reactions had been postulated as being the formation of an intermediate DIGLYME.M(CO)_3 which subsequently reacted to give elimination of diglyme and co-ordination of a ligand. The solid DIGLYME.$M(CO)_3$ was obtained and characterised by elemental analysis and infrared carbonyl stretching frequencies. The use of diglyme as solvent allowed consistent production of the monosubstituted derivatives required and the contrast between its role as a facile reaction medium with the less useful hydrocarbon solvents lends support to the suggested mechanism involving the diglyme intermediate. Further support for such a mode of reaction may be supplied by the formation of acetonitrile derivatives obtained by direct reflux of the hexacarbonyl in acetonitrile[75] and used as intermediates in metal VI carbonyl phosphine complex formation.[80] There is an interesting point of contrast between the diglyme mechanism and that involving acetonitrile. Derivatives of acetonitrile may be monosubstituted, disubstituted or trisubstituted and previous work has required careful control of reaction conditions to obtain the correct derivative.[84] The metal tricarbonyl diglyme complex is the only one known for diglyme and thus when the ligand of the reaction co-ordinates to the metal, the diglyme will be removed completely leaving a monosubstituted or disubstituted derivative according to the molar ratios involved. The trisacetonitrile complex $(CH_3CN)_3M(CO)_3$ will form complexes of the type $(CH_3CN)_2ML(CO)_3$ which will tend to decompose rather than form $LM(CO)_5$. (All the acetonitrile derivatives are seen to decompose readily). This problem has been overcome using a very convenient technique.[85] Formation of the trisacetonitrile derivative is followed by addition of an amount of the hexacarbonyl sufficient to cause formation of the required substituted derivative.

$$M(CO)_6 + Me\ CN\ (excess) \xrightarrow{reflux} (Me\ CN)_3M(CO)_3 \qquad (1)$$

Then $$(Me\ CN)_3M(CO)_3 + 2M(CO)_6 \xrightarrow[acetone]{reflux} 3(Me\ CN)M(CO)_5 \qquad (2)$$

or $$2(Me\ CN)_3M(CO)_3 + M(CO)_6 \xrightarrow[acetone]{reflux} 3(Me\ CN)_2M(CO)_4 \qquad (3)$$

Refluxing in acetone for thirty minutes followed by injection of the required molar quantity of phosphine ligand allows formation of the monosubstituted (case 2) or disubstituted (case 3) derivative.

Thus preparation of monosubstituted phosphine derivatives of group VI metal hexacarbonyls is best effected by refluxing a mixture of the hexacarbonyl and the phosphine in diglyme, the reaction possibly proceeding by the diglyme metal tricarbonyl intermediate. The reaction may be monitored either by following the evolution of gas as collected in an oil filled burette or by observing the infrared spectrum of the reaction mixture as the reaction proceeds. The gas evolution method has two major disadvantages in reactions of this type. It does not allow the reactions to be carried out under a nitrogen atmosphere and formation of disubstituted derivatives invalidates volume calculations based on mono substituted derivative production only. Therefore the reactions were monitored by considering the infrared spectrum in the carbonyl stretching frequency region as reaction proceeded. Reaction times were not an important factor in the preparation of the phosphite complexes but the preparations involving triisopropyl phosphine and trinbutyl phosphine had to be stopped before production of the disubstituted derivatives was observed, again owing to the difficulty of separating the two products. Production of disubstituted phosphite complexes was seen to be more rapid than analogous phosphine complexes. Thus it was necessary to allow formation of disubstituted phosphites in the preparations of the monosubstituted derivatives in order to obtain a reasonable yield of the required product. This made it necessary to separate the two derivatives before purifying the monosubstituted complex.

A most convenient technique for separating derivatives having different degrees of substitution or different configurations in this work was found to be column chromatography using silica or alumina absorbant in the basic state and eluting with a variety of solvents, principally very non-polar hydrocarbons. All the monosubstituted phosphite complexes could be obtained pure by passing the residue from the reaction mixture through a silica column (30cm x 2cm) using low boiling petroleum ether as elutant. The monosubstituted phosphine complexes could not be separated easily from the corresponding disubstituted derivatives by chromatography on a silica column. Repeated use of an alumina column eventually allows almost complete separation although the time required and volume of elutant used are entirely unrealistic. However, a sample of the crude monosubstituted phosphine derivative, when free of any disubstituted contaminant, may be purified by chromatography on an alumina column again using petroleum ether as elutant. This was found useful for purifying the trinbutyl phosphine derivatives which could not be purified by any of the normal methods. After chromatography, the petroleum ether was removed at a rotary evaporator and the residue filtered through a sinter. The phosphite complexes were all liquids at room temperature and could be distilled at vacuum (0.01-0.03 mm) to give completely pure complexes, excess phosphite being removed as a lower boiling fraction. The triisopropyl phosphine complexes were solid and could be purified by recrystallisation from a cooled chloroform ethanol mixture but the trinbutyl phosphine complexes were all found to be liquids which decomposed at high temperatures without distilling. These latter derivatives were purified by chromatography as already stated but could not be obtained completely pure, possible contaminants being uncomplexed phosphine and residual solvent.

Preparation of the disubstituted complexes has, until now, been very similar to preparation of the monosubstituted complexes. Thus, generally a molar ratio of $M(CO)_6:PR_3$ 1:2 is refluxed for a certain time in a solvent and the product extracted by a variety of techniques. Investigation showed this approach to have some considerable disadvantages if conditions were not chosen with some care. The use of hydrocarbon solvents such as methylcyclohexane gave rise to tediously long preparation times (of the order of one week or more) and low yields of the product. Diglyme was found to shorten the reaction time and for chromium and molybdenum hexacarbonyl reactions could be used very conveniently. The high temperature of reflux (160°C), did however, tend to induce oxidation in the system and the familiar green (chromium) or blue (molybdenum) colouration indicated this clearly. This oxidation caused difficulty in purifying the products and seemed to lower the product yield substantially. In the case of tungsten hexacarbonyl, only phosphine complexes could be obtained readily by this technique, phosphite ligands being either only moderately reactive giving very low yields or in one case (triethyl phosphite) being totally unreactive under these conditions. Such difficulties have been experienced by other workers[80]. It is interesting to note that from some kinetic work Angelici and Graham[86] deduced that reactions such as those being considered proceed by two mechanisms in the presence of a large concentration of the ligand. Thus the rate of the reaction $M(CO)_6 + L \longrightarrow M(CO)_5L + CO$ is

$$\text{Rate} = k_1 [M(CO)_6] + k_2 [M(CO)_6][L]$$

k_1 is the rate constant for an SN_1 reaction involving loss of carbonyl as the rate determining step and k_2 refers to an SN_2 reaction possibly involving a carbon atom as the nucleophilic centre. The value of k_2 is greater for phosphines than for phosphites and the formation of phosphine disubstituted complexes of tungsten and not analagous disubstituted phosphite derivatives is therefore probably due to a more rapid substitution process which occurs before oxidation of the metal can take place. Such oxidation is observed extensively in the reaction mixtures of refluxing tungsten hexacarbonyl with phosphite ligands. Further evidence concerning the competition between ligand substitution and metal oxidation will be discussed later and is derived from the preparation developed for trans-disubstituted phosphite derivatives of tungsten hexacarbonyl.

Various approaches were investigated as alternatives to direct preparation of the tungsten phosphite disubstituted derivatives. The acetonitrile complex intermediate was found to give very low yields and required about four days to complete the reaction. Irradiation by ultraviolet light again required an extended reaction period and in the case of trimethyl phosphite and triethyl phosphite tended to produce the trisubstituted derivatives. Also, the tungsten hexacarbonyl remained approximately fifty per cent unreacted. However, direct reaction of tungsten hexacarbonyl in the refluxing phosphite [trimethyl phosphite (110°C) triethyl phosphite (150°C) triisopropyl phosphite (170°C), approximate reflux temperatures in brackets] in the absence of solvent for a period of six hours gave a high yield (about 80%) of the trans disubstituted complex along with a small amount of the monosubstituted and trisubstituted derivatives. Cooling to 0°C caused crystallisation of the trans-disubstituted product preferentially and filtration followed by recrystallisation gave the pure product. There was no indication of any oxidation products over the six hour reaction period and indeed, on further refluxing for twenty four hours, no oxidation was observed. It seems probable that the concentration of phosphite available to the hexacarbonyl is so much greater than any oxygen concentration that the disubstituted complex will be formed preferentially. When solvent is introduced, the concentration of ligand is reduced, possibly to the point where oxidation will be the predominant reaction rather than ligand substitution. This is not to say that the oxygen concentration is higher than the ligand concentration, merely that oxidation is the more probable process when ligand concentration is low.

Further investigation of direct solventless reactions showed that the reaction $M(CO)_6 + L$ (excess) $\longrightarrow$ trans $L_2M(CO)_4$ is applicable for M = Cr, Mo or W and L = $P(OMe)_3$ $P(OEt)_3$ $P(OPr^i)_3$ $PBu^n{}_3PPr^i{}_3$ with the metal reactivities in order Mo > Cr > W. It is difficult to put the phosphines in order of reactivity as the trimethyl phosphite and triethyl phosphite give a mixture of mono-, trans di- and trisubstituted derivatives as stated earlier, triisopropyl phosphite forms mono- and trans di- substituted derivatives while the triisopropyl phosphine and trinbutyl phosphine react to give a mixture of the cis- and trans-disubstituted complexes in all cases. It is necessary in the cases of cis- trans mixtures to separate the complexes by chromatography, the trans disubstituted complex being eluted first (alumina column, petroleum ether elutant as for monosubstituted complex separation) and on continued elution, the cis disubstituted derivative coming off the column. It is informative to consider the configurations obtained in these reactions. Thus we have formed the trans configuration predominantly in all cases (cis amount normally less than 5%) while thermodynamically, the cis-disubstituted complex is expected to be the more stable[14]. The trisdimethylamino phosphine derivatives $L_2M(CO)_4$ M = Cr, Mo or W all show trans configuration when formed by direct reaction in solvent[81]. The configuration of these derivatives has in most cases been determined from the form of their infrared spectrum in the carbonyl stretching region. For example in the case of disubstituted derivatives the trans configuration has symmetry group D_{4h} (L considered to be radially symmetric) and should have one active infrared frequency in the carbonyl stretching region. The cis derivative has C_{2v} symmetry and is expected to have four such peaks. Occurence of formally forbidden peaks in the carbonyl region caused by effects such as lowering of symmetry by the phosphine ligand and splitting of the E modes in some cases to be discussed later, caused some difficulty in the straightforward application of this technique. However, use of combination spectra and proton nuclear magnetic resonance spectra allowed definite characterisation of the configuration involved.

Poilblanc and Bigorgne[87] reported for molybdenum disubstituted complexes that heating either the cis or the trans derivative for an extended period gave rise to the formation of an equilibrium mixture having isomer ratio trans:cis of 4:1. Thus, we expect that the trans-disubstituted will be predominantly formed in any reaction involving heat over a period of hours and this has been found to be the case in this work. From very accurate spectra of highly concentrated solutions of the purified trans disubstituted complexes obtained, a very small amount of the cis disubstituted complex is always seen (less than two per cent). It seems probable that even at room temperature there is some equilibration set up in the trans disubstituted complex in solution giving a mixture having isomer ratio trans:cis of approximately 50:1. The infrared spectrum in the stretching carbonyl region obtained for the solid trans derivative (on a potassium bromide disc) is not sufficiently resolved to allow an estimation of any possible trans:cis ratio. It is therefore not possible to say whether the trans-cis equilibration is a property of the solid sample or of its solution.

The possibility that the observed cis derivative is merely impurity from the reaction must also be considered. The relative intensities of the highest energy carbonyl stretching peaks A_1 and $A_1^{(2)}$ assigned to the cis and trans complexes respectively have the same ratio within experimental error for samples of each of the disubstituted derivatives obtained from different reactions. This could be taken as evidence that some consistent factor such as trans-cis equilibrium is being observed although it could also be attributed to the fact that reaction conditions are very similar for each of these preparations which might be expected to produce similar ratios of trans:cis isomers. A more telling argument is that the liquid monosubstituted derivative also produced in these reactions may be removed completely by normal purification procedures and as the cis-disubstituted complexes are liquid in at least some of the cases considered[80] we should expect any such impurity to be removed similarly. It is seen that this is not true which supports the suggestion that some regenerated material rather than residual impurity is the source of the observed cis contaminant.

From the evidence obtained we are now able to propose a consistently reliable technique for preparation of products of the type $LM(CO)_5$ and trans $L_2M(CO)_4$ where M = Cr, Mo or W and L = $P(OMe)_3$, $P(OEt)_3$, $P(OPr^i)_3$, PPr^i_3 or PBu^n_3 and it seems probable that such preparations may be extended to other phosphines in the PR_3 group where R is an alkyl or alkoxy group. In summary, monosubstituted complexes may best be prepared by refluxing the metal VI hexacarbonyl and the phosphine in 1.1:1.0 molar ratio in diglyme. Trans disubstituted complexes of chromium and molybdenum hexacarbonyl may be prepared by refluxing a 2:1 molar ratio of phosphine to hexacarbonyl in diglyme or alternatively by direct reaction of the two in the absence of solvent. The former method is the more efficient with a shorter reaction time and greater yield of the product and is therefore preferable. Preparation of trans-disubstituted complexes of tungsten carbonyl may be effected by direct reaction of the phosphine and the hexacarbonyl at about 130°C. Such direct solventless reactions have been reported for some amine derivative preparations[60] and in view of the advance in the synthesis of phosphine disubstituted tungsten carbonyl complexes obtained by extending such a technique I feel that it is perhaps an appropriate time for a thorough appraisal of preparative techniques in metal carbonyl phosphine chemistry. The appearance of Chatt's paper[78] on catalysed reactions is a welcome development in this direction. Much time is inevitably wasted and studies, such as the spectroscopic investigations undertaken here, delayed when no standard preparative techniques have been developed.

EXPERIMENTAL

Purification Procedures

Diglyme was allowed to stand over sodium hydroxide and then distilled under reduced pressure from sodium wire. Methylcyclohexane and Analar petroleum ether were distilled from sodium wire before use. Acetonitrile was first dried with calcium chloride then distilled from phosphorous pentoxide. The phosphines were obtained commercially and were distilled on a vacuum line before use. The metal hexacarbonyls, obtained commercially, were used as supplied.

Instrumentation

Reactions were monitored by infrared spectra taken on a Perkin Elmer 457 spectrophotometer calibrated by reference to polystyrene peaks. Accurate spectra ($\pm 0.2 cm^{-1}$) were obtained for the purified products on a Perkin Elmer 225 spectrophotometer, calibrated by reference to saturated water vapour peaks.

Analysis

Analysis of complexes was carried out by Beller Labs., Gottingen, West Germany and were found to be correct for carbon/hydrogen to within 1% for solid samples and 5% for liquids.

Preparation of Complexes

Monosubstituted Derivatives

Pentacarbonyl Chromium Trimethyl Phosphite

Chromium hexacarbonyl (1.99g; 9.1 m. mole) was heated to reflux temperature (160°C) in diglyme under a stream of dry nitrogen. When the diglyme was refluxing smoothly, trimethyl phosphite (1.04g; 8.4 m. mole) was injected by syringe. The mixture was refluxed for thirty minutes, infrared spectra of aliquots being taken every ten minutes. Peaks in the carbonyl stretching region characteristic of both monosubstituted ~ 2070, 1960cm^{-1} and disubstituted ~ 1905cm^{-1} derivatives were seen. After thirty minutes, the reaction mixture was allowed to cool and the diglyme removed by distillation under reduced pressure (30°C/0.1mm). The liquid residue was taken up in 40-60° petroleum ether (5ml) and chromatographed on a silica column (30cm x 2cm) using 40-60° petroleum ether as elutant. 100ml samples were collected and the first five of these were found to contain only the monosubstituted complex. Continued elution with petroleum ether gave lesser amounts of the monosubstituted complex. Removal of the petroleum ether using a rotary evaporator left a clear liquid which was distilled at vacuum. Unreacted trimethyl phosphite was recovered in the first fraction distilled and a pure sample of the monosubstituted complex $Cr(CO)_5P(OMe)_3$ was obtained as a clear liquid.

BP 96°C/ 3mm Analysis Calc. C 30.4 H 2.85 Found C 30.71 H 2.74 Yield ~50%

Preparations of $M(CO)_5L$ with M = Cr, Mo, W and L = $P(OMe)_3$, $P(OEt)_3$ and $P(OPr^i)_3$ are entirely analagous with that given above. The following complexes were also prepared as above, relevant differences being given as required. All reactions were carried out in an atmosphere of dry nitrogen.

Pentacarbonyl Molybdenum Trimethyl Phosphite

Molybdenum hexacarbonyl (2.16g; 8.2 m. mole) and trimethyl phosphite (0.99g; 8.0 m. mole) were reacted. Reflux for twenty minutes, infrared spectrum showed monosubstituted and disubstituted complexes formed. The crude material was obtained and purified as in the chromium preparation giving $Mo(CO)_5\ P(OMe)_3$. The complex is a clear liquid.

B.P. 68°C/0.25 Analysis Calc. C 26.7 H 2.5 Found C 27.78 H 2.64 Yield~60%

Pentacarbonyl Tungsten Trimethyl Phosphite

Tungsten hexacarbonyl (2.43g; 6.9 m. mole) and trimethyl phosphite (0.82g; 6.6 m. mole) were refluxed for ninety minutes. The infrared spectrum as previously, indicated mono- and disubstituted complex formation. Purification as before gave $W(CO)_5P(OMe)_3$ as a clear liquid.

B.P. 98°C/ 3mm Analysis Calc. C 21.4 H 2.01 Found C 21.41 H 2.18 Yield~40%

Pentacarbonyl Chromium Triethyl Phosphite

Chromium hexacarbonyl (2.04g; 9.3 m. mole) and triethyl phosphite (1.48g; 8.9 m. mole) were refluxed for thirty minutes. Infrared monitoring and work up were as in the trimethyl phosphite reactions. The complex was obtained pure as a clear liquid $Cr(CO)_5P(OEt)_3$.

B.P. 76°C/0.1mm Analysis Calc. C 36.9 H 4.19 Found C 38.18 H 4.50 Yield~50%

Pentacarbonyl Molybdenum Triethyl Phosphite

Molybdenum hexacarbonyl (1.94g; 7.3 m. mole) and triethyl phosphite (1.14g; 6.9 m. mole) were reacted. Reflux for twenty minutes gave a mixture of the monosubstituted and disubstituted complexes which on purification gave a clear liquid which is $Mo(CO)_5P(OEt)_3$.

B.P. 80°C/0.1mm Analysis Calc. C 32.8 H 3.74 Found C 33.47 H 3.79 Yield~50%

Pentacarbonyl Tungsten Triethyl Phosphite

Tungsten hexacarbonyl (2.21g; 6.3 m. mole) and triethyl phosphite (1.02g; 6.1 m. mole) were refluxed for thirty minutes and the reaction mixture worked up as previously. Distillation of the crude product gave a clear liquid $W(CO)_5P(OEt)_3$.

B.P. 114°C/1mm Yield~50% M.W. (calc.) 490 m/e (parent) 490

Pentacarbonyl Chromium Triisopropyl Phosphite

Chromium hexacarbonyl (1.80g; 8.2 m. mole) and triisopropyl phosphite (1.71g; 8.2 m. mole) were reacted for twenty minutes and the crude product obtained as in the trimethyl phosphite case. Distillation allowed removal of excess triisopropyl phosphite and gave a pure sample of $Cr(CO)_5P(OPr^i)_3$ which was a slightly yellow liquid.

B.P. 104°C/ 3mm Analysis Calc. C 42.0 H 5.26 Found C 44.01 H 5.74 Yield~50%

Pentacarbonyl Molybdenum Triisopropyl Phosphite

Molybdenum hexacarbonyl (2.07g; 7.7 m. mole) and triisopropyl phosphite (1.54g; 7.4 m. mole) reacted for fifteen minutes and worked up as before gave a crude product which, when distilled, produced a liquid with blue colouration. The purified material was $Mo(CO)_5P(OPr^i)_3$.

The blue colour became more intense over a period of time and is seen to occur even in a sealed tube. It is probably due to the presence of molybdenum IV or VI in the complex.

B.P. 100°C/0.25mm Analysis Calc. C 36.95 H 4.31 Found C 37.9 H 4.74 Yield~60%

Pentacarbonyl Tungsten Triisopropyl Phosphite

Tungsten hexacarbonyl (2.01g; 5.7 m. mole) and triisopropyl phosphite (1.14g; 5.5 m. mole) were refluxed for twenty minutes. Removal of diglyme, chromatography and distillation of the crude product gave a clear liquid $W(CO)_5P(OPr^i)_3$. B.P. 120°C/ 3mm Yield~50%

M.W. (calc.) 532 m/e (parent) 532

Pentacarbonyl Chromium Triisopropyl Phosphine

Chromium hexacarbonyl (1.86g; 8.5 m. mole) was refluxed with trisopropyl phosphine (1.30g; 8.1 m. mole) in diglyme for sixty minutes. The infrared spectrum of the mixture was followed very closely and the reaction was stopped before formation of the disubstituted complex was seen. The diglyme was removed by distillation under vacuum and a white solid residue was seen to be left. This solid was taken up in a little petroleum ether (5ml) and chromatographed on an alumina column using petroleum ether as elutant. The petroleum ether was removed at vacuum and the solid dried by suction. Alternatively, the crude solid could be recrystallised from a chloroform-ethanol mixture cooled to 0°C to give pure $Cr(CO)_5PPr^i_3$.

M.P. 130-135°C dec. Analysis Calc. C 47.7 H 5.98 Found C 47.73 H 5.82

Yield~ 30%

Pentacarbonyl Molybdenum Triisopropyl Phosphine

Molybdenum hexacarbonyl (1.97g; 7.5 m. mole) and triisopropyl phosphine (1.19g; 7.5 m. mole) were refluxed for thirty minutes and the diglyme removed. The resulting solid was purified as above to give a white solid $Mo(CO)_5PPr^i_3$.

M.P. 140-150°C dec. Analysis Calc. C 42.4 H 5.3 Found C 42.4 H 5.60

Yield ~ 40%

Pentacarbonyl Tungsten Triisopropyl Phosphine

Tungsten hexacarbonyl (2.33g; 6.6 m. mole) and triisopropyl phosphine (1.02g; 6.4 m. mole) were refluxed for forty five minutes and the reaction solution worked up as before. A white solid residue was again obtained and this recrystallised to give pure $W(CO)_5PPr_3$.

M.P. 150-160° dec. Yield ~ 60% M.W. (calc.) 484 m/e (parent) 484

Pentacarbonyl Chromium Trinbutyl Phosphine

Chromium hexacarbonyl (1.90g; 8.7 m. mole) and trinbutyl phosphine (1.69g; 8.4 m. mole) were refluxed in diglyme for two hours. Infrared monitoring indicated formation of the monosubstituted derivative only over this period and reaction was ceased before the disubstituted derivative appeared. Removal of the diglyme by distillation gave a brown liquid residue which was chromatographed twice on an alumina column using petroleum ether as elutant. Removal of the petroleum ether gave a light yellow liquid which is almost pure $W(CO)_5PBu^n_3$. Attempts to purify the liquid by distillation under reduced pressure normally caused extensive decomposition and a darkening of the complex. No phosphine ligand was seen to distill off. Analysis Calc. C 51.8 H 6.86 Found C 54.55 H.6.94 Yield∼50%

Pentacarbonyl Molybdenum Trinbutyl Phosphine

Molybdenum hexacarbonyl (1.93g; 7.3 m. mole) and trinbutyl phosphine (1.40g; 6.9 m. mole) were refluxed for one hour. The reaction mixture was treated as in the chromium preparation and again the complex decomposed on attempted distillation. Analysis Calc. C 46.6 H.6.19 Found C 46.99 H.6.16 Yield∼50% M.W. (calc.) 438 m/e (parent) 438

Pentacarbonyl Tungsten Trinbutyl Phosphine

Tungsten hexacarbonyl (2.16g; 6.1 m. mole) and trinbutyl phosphine (1.18g; 5.9 m. mole) were refluxed for two hours and the reaction mixture worked up and purified as above. The complex $W(CO)_5PBu^n{}_3$ is a light yellow liquid. Yield∼50% M.W. 526 m/e 526

Acetonitrile Reactions

The following monosubstituted complexes were also prepared by the method employing acetonitrile derivatives as intermediates.

Pentacarbonyl Chromium Triethyl Phosphite

Chromium hexacarbonyl (2.04g; 9.3 m. mole) and acetonitrile (40ml) were refluxed for forty hours. The acetonitrile was distilled from the reaction flask under nitrogen and more chromium hexacarbonyl

(4.13g; 18.8 m. mole) was added along with acetone (30ml). This mixture was refluxed for thirty minutes after which, triethyl phosphite (4.83g; 29.1 m. mole) was added and reflux continued for nineteen hours. The reaction mixture was cooled, filtered, the acetone removed at the vacuum and the residue taken up in pentane (30ml). The pentane solution was filtered, reduced to about five ml. and chromatographed on a silica column. A sample of pure $Cr(CO)_5P(OEt)_3$ was obtained by eluting with petroleum ether as previously. Yield ~ 30%

Pentacarbonyl Molybdenum Trimethyl Phosphite

Molybdenum hexacarbonyl (2.37; 9.0 m. mole)and acetonitrile (40ml) were refluxed under nitrogen for four hours. The acetonitrile was distilled off and molybdenum hexacarbonyl (4.41g; 16.8 m. mole) and acetone (30ml) were added. This mixture was refluxed for thirty minutes and trimethyl phosphite (3.54g; 28.5 m. mole) was added. This was refluxed for nineteen hours and worked up and purified as in the chromium preparation above. Yield ~40%

Pentacarbonyl Molybdenum Triethyl Phosphite

The preparation is exactly analagous to the molybdenum trimethyl phosphite case, starting with molybdenum hexacarbonyl (2.01g; 7.6 m. mole), adding (4.23g; 16.0 m. mole) and reacting with triethyl phosphite (4.68g; 28.2 m. mole). The purification procedure gives the complex. Yield ~ 50%

Pentacarbonyl Molybdenum Triisopropyl Phosphite

Preparation as for other molybdenum complexes above starting with molybdenum hexacarbonyl (2.04g; 7.7 m. mole), adding (4.10g; 15.5 m. mole) and reacting with triisopropyl phosphite (5.30g; 25.5 m. mole). Work up and purification gave $Mo(CO)_5P(OPr^i)_3$ in Yield ~50%.

Trisdimethylamino Phosphine Complexes

Monosubstituted Tdp complexes were prepared according to the method of King[81] using methylcyclohexane as refluxing solvent. The complexes were all white solids obtained pure by sublimation and having properties corresponding to those reported by King.

Disubstituted Complexes

Chromium and Molybdenum Complexes

All reactions are carried out under an atmosphere of nitrogen.

Tetracarbonyl Chromium Bis Trimethyl Phosphite

Chromium hexacarbonyl (2.04g; 9.3 m. mole) and trimethyl phosphite (2.25g; 18.2 m. mole) were refluxed in diglyme for three hours. The diglyme was reduced in volume by distillation at vacuum and the cooled mixture put in an ice box. A mass of white solid was seen to form in the solution and rapid filtration gave a white solid which may be recrystallised from a chloroform ethanol mixture on cooling to 0°C. The solid is trans $Cr(CO)_4[P(OMe)_3]_2$.

M.P. 83-4°C. Analysis Calc. C 29.1 H 4.37 Found C 29.31 H 4.30 Yield ~ 60%

Tetracarbonyl Molybdenum Bis Trimethyl Phosphite

Molybdenum hexacarbonyl (2.27g; 8.6 m. mole) and trimethyl phosphite (2.16g; 17.4 m. mole) were refluxed in diglyme for two hours. The reaction mixture was treated as in the chromium case and a white solid which is trans-$Mo(CO)_4[P(OMe)_3]_2$ wasobtained on recrystallisation.

M.P. 92-3°C Analysis Calc. C 26.4 H 3.96 Found C 26.40 H 4.10 Yield ~ 50%

Tetracarbonyl chromium Bis Triethyl Phosphite

Chromium hexacarbonyl (2.16g; 9.8 m. mole) and triethyl phosphite (3.36g; 20.3 m. mole) were refluxed in diglyme for ten hours. Work up was as before, again giving a white solid which is trans-$Cr(CO)_4[P(OEt)_3]_2$.

M.P. 68-9°C Analysis Calc. C 39.5 H 6.05 Found C 39.35 H 6.10 Yield ~ 30%

Tetracarbonyl Molybdenum Bis Triethyl Phosphite

Molybdenum hexacarbonyl (2.21g; 8.4 m. mole) and triethyl phosphite (2.84g; 17.2 m. mole) were refluxed for ten hours in diglyme. It was found that this reaction was unusually susceptible to oxidation and it consequently gave very low yields. Use of a nitrogen leak bubbling through the reaction mixture and maintaining the diglyme at 130° rather than at reflux temperature improved the yield although the final mixture always had a deep blue colouration. Removal of diglyme

at the vacuum and chromatography of the residue on a silica column with petroleum ether/benzene as elutant allowed separation of the pure complex trans-$Mo(CO)_4[P(OEt)_3]_2$. Removal of the ether/benzene mixture gave a solid residue which may be recrystallised as above.
M.P. 74-5°C Analysis Calc. C 35.6 H 5.57 Found C 35.61 H 5.63 Yield ~10%

Tetracarbonyl Chromium Bis Triisopropyl Phosphite

Chromium hexacarbonyl (1.88g; 8.5 m. mole) and triisopropyl phosphite (3.82g; 18.2 m. mole) were refluxed in diglyme for six hours. Work up was straightforward as for trimethyl phosphite derivatives. The pure complex is white solid $Cr(CO)_4[P(OPr^i)_3]_2$.
M.P. 98-9°C Analysis Calc. C 45.3 H 7.21 Found C 45.16 H.7.32 Yield ~ 40%

Tetracarbonyl molybdenum Bis Triisopropyl Phosphite

Molybdenum hexacarbonyl (2.13g; 8.1 m. mole) and triisopropyl phosphite (3.41g; 16.4 m. mole) were refluxed for six hours in diglyme. Purification of the complex was as for the chromium analogue.
M.P. 96-7°C Analysis Calc. C 42.3 H 6.72 Found C 42.41 H 6.82 Yield ~ 40%

Tetracarbonyl Chromium Bis Triethyl Phosphine

Chromium hexacarbonyl (2.12g; 9.7 m. mole) and triethyl phosphine (2.38g; 20.0 m. mole) were refluxed in diglyme for forty eight hours. The yellow solution was reduced to about 5ml by distillation and cooling to 0°C gave large yellow crystals of disubstituted $Cr(CO)_4[PEt_3]_2$. The crystals (anything up to 100mg) formed best from a solution of hexane.

M.P. 63-4°C Analysis Calc. C 49.0 H 7.5 Found C 48.86 H 7.50 Yield ~30%

Tetracarbonyl Chromium Bis Triisopropyl Phosphine

Chromium hexacarbonyl (2.01g; 9.2 m. mole) and triisopropyl phosphite (3.02g; 18.8 m. mole) were refluxed in diglyme for ten hours. The reaction mixture was distilled at vacuum and the liquid residue taken up in petroleum ether (10ml). This was chromatographed on an alumina column to separate the trans disubstituted derivate from the cis configuration which appears in the infrared spectrum of the crude product. This separation procedure was found to be necessary for all the phosphine complexes as relatively large amounts of the cis complex are seen for both triisopropyl and trinbutyl phosphines. After eluting with petroleum ether, this was removed at vacuum and the oily product recrystallised from ethanol-chloroform at 0°C. $Cr(CO)_4[P^iPr_3]_2$ is a yellow solid.

M.P. 123-4°C Analysis Calc. C 54.7 H 8.70 Found C 54.63 H 8.73 Yield ~30%

Tetracarbonyl Molybdenum Bis Triisopropyl Phosphine

Molybdenum hexacarbonyl (2.20g; 8.3 m. mole) and triisopropyl phosphine (2.75g; 17.2 m. mole) were refluxed in diglyme for ten hours. Work up and purification was as for chromium complex. Complex is green.

M.P. 151-2 dec. Analysis Calc. C 50.0 H 7.98 Found C 50.18 H.8.04

Tetracarbonyl Chromium Bis Trinbutyl Phosphine

Chromium hexacarbonyl (1.83g; 8.4 m. mole) and trinbutyl phosphine (3.46g; 17.2 m. mole) were refluxed in diglyme for twelve hours and the reaction mixture treated as in the triisopropyl phosphine preparations. A green-yellow complex $Cr(CO)_4[PBu^n_3]_2$ was obtained.

M.Ipreparations. A green-yellow complex $Cr(CO)_4[PBu^n_3]_2$ was obtained d~30%

Tetracarbonyl Molybdenum Bis Trinbutyl Phosphine

Molybdenum hexacarbonyl (1.94g; 7.4 m. mole) and trinbutyl phosphine (3.03g; 15.0 m. mole) were refluxed in diglyme for twelve hours and the pure complex obtained as in the analagous chromium case above. It is a yellow solid $Mo(CO)_4[P^nBu_3]_2$.

M.P. 41-2°C Analysis Calc. C 55.0 H 8.82 Found C 54.95 H 8.75 Yield ~ 30%

Tungsten Complexes

Tetracarbonyl Tungsten Bis Trimethyl Phosphite

Tungsten hexacarbonyl (2.29g; 6.5 m. mole) was heated with trimethyl phosphite (10ml) to reflux temperature for five hours. The mixture was cooled to 0°C and the resultant white crystals filtered off and purified by sublimation (100°C/0.1mm).

M.P. 96-7°C Analysis Calc. C 22.06 H 3.30 Found C 22.11 H 3.32 Yield ~ 80%

Tetracarbonyl Tungsten Bis Triethyl Phosphite

Tungsten hexacarbonyl (2.42g; 6.9 m. mole) was heated to reflux temperature in triethyl phosphite (10ml). Refluxing for five hours followed by cooling to 0°C gave white crystals of $W(CO)_4[P(OEt)_3]_2$. These were purified by recrystallisation from n-hexane.

Tetracarbonyl Tungsten Bis Triisopropyl Phosphite

Tungsten hexacarbonyl (2.29g; 6.5 m. mole) and triisopropyl phosphite (10ml) were refluxed together for seven hours. Treatment of the reaction mexture as in the other tungsten preparations gave white crystals of $W(CO)_4[P(OPr^i)_3]_2$. Recrystallising from n-hexane gave the pure product.

M.P. 95-6°C Analysis Calc C 37.0 H 5.89 Found 37.04 H 5.79 Yield $\sim$80%

Tetracarbonyl Tungsten Bis Triisopropyl Phosphine

Tungsten hexacarbonyl (2.37; 6.2 m. mole) and triisopropyl phosphine (2.08g; 13.0 m. mole) were refluxed in diglyme for forty eight hours. The diglyme was removed at vacuum and the residue chromatographed on an alumina column using petroleum ether as elutant. The petroleum ether was removed at vacuum and the residue recrystallised from chloroform-ethanol at 0°C. $W(CO)_4(PPr^i_3)_2$ is a green-yellow solid.

M.P. 180-1°C Analysis Calc. C 42.9 H 6.82 Found C 42.88 H 6.87 Yield $\sim$20%

Tetracarbonyl Tungsten Bis Trinbutyl Phosphine

Tungsten hexacarbonyl (2.26g; 6.4 m. mole) and trinbutyl phosphine (2.68g; 13.3 m. mole) were refluxed in diglyme for forty eight hours. The mixture was worked up as in the analagous trisopropyl phosphine-tungsten preparation. Pure $W(CO)_4\{PBu^n_3\}_2$ is a yellow solid.

M.P. 44-5°C Analysis Calc. C 48.0 H 7.71 Found C 48.22 H 7.81 Yield $\sim$30%

Disubstituted Tdp complexes were prepared by the method of King[81].

Purification was by sublimation.

The preparations reported above are for optimum conditions as determined during this study. Other molar ratios, solvents or reflux times may give the same products but generally in lower yield and less successfully.

CHAPTER 3

ELECTRONIC SPECTRA

ELECTRONIC SPECTRA

Introduction

The rapid advance in the preparative chemistry of transition metal carbonyl derivatives has been paralleled by expansion and development of associated spectroscopic techniques. In some cases, spectroscopy forms an integral part of the synthetic procedure as in the use of infrared spectra to monitor product formation. Other spectroscopic investigations are prompted by a desire to clarify and develop theoretical considerations of known complexes. The application of electronic absorption spectroscopy is predominantly in the latter sphere.

Until comparatively recently (c. 1965), ultraviolet and visible spectroscopic work in the field of transition metal chemistry was mainly confined to studies of d→d electronic transitions, these studies providing valuable empirical compatability with crystal field theory and thus assisting in structural investigations. The tardy emergence of electronic absorption spectroscopy in the field of metal carbonyl chemistry may be attributed to three main factors. Spectra obtained in the ultraviolet and visible region are generally broad and asymmetric and in the case of metal VI hexacarbonyls and their derivatives, the d→d and lower charge transfer transitions may occur in the same region of the spectrum and with comparable extinction coefficients. Further, to interpret the spectra and to use the data thus obtained in a meaningful way, it is necessary to construct a plausible energy level diagram for the metal complex system being studied.

Considering first the shape of the peaks generally obtained in an absorption spectrum of a metal carbonyl complex. As electronic transitions take place between two electronic levels of a molecule, each of which possesses vibrational levels, which even at room temperature must be populated by electrons in accordance with Boltzmann's Law, the observed spectrum must represent a range of energy transitions involving each of these vibrational energy states. Thus, the spectra show broad bands rather than the sharp peaks characteristic of single energy transitions. Considerable overlap of peaks in such spectra is therefore to be expected and consequently, few of the observed bands are totally symmetric. This effect may merely cause distortion of a band outline or, in the case of greater overlap, one or more of the peaks in a spectrum may only be discernible as shoulders on the energy "tail" of a more intense peak. In this latter case, some difficulty may be experienced in determining both the frequency (ν_{max}) and the true intensity of such peaks.

Several approaches have been adopted to the problem of analysing complex spectra in terms of a combination of curve areas involving standard distribution curves such as the Gaussian type and their derivatives.[88] An early example of the use of Gaussian curves in analysing a spectrum is provided by the treatment of some arsenic derivatives by Cullen and Hochstrasser.[89] Since then, Gaussian analysis has been widely used as a tool for simplifying spectral outlines. For example, Alexander and Gray employed it in a study of the electronic spectra of some hexacyanometalate complexes,[90] while Gray and Beach used the technique to analyse the electronic spectra of the metal VI hexacarbonyls[41] which are the parent carbonyls of the complexes being studied in this work.

The use of first and second derivative functions has also been employed to analyse complex bands including those in electronic absorption spectra.[91,92] It has been shown[93] from infrared studies that absorption band characteristics vary with slit width, tending towards a Lorenzian curve form for narrow slit widths and containing more Gaussian character at larger slit settings. Slit width, however, has little effect on the shape of a band in the electronic spectral region, Franck-Condon rules being the determining factor in these cases.

Generally, analysis of a spectrum involves an unquantifiable, subjective factor which may be very important when postulating the number of peaks which compose a curve. This aspect of curve analysis will be considered further when the spectra of the metal carbonyl derivatives are being discussed. Meanwhile, it may be stated that the advantages of obtaining separate assignable peaks must be tempered by inaccuracies deriving from inexperience of the researcher or incorrect initial assumptions.

The second important difficulty in interpreting electronic spectra is the necessity for a suitable theoretical interpretation of the observed transitions. One of the principle reasons for the decline in popularity of the valence bond theory was the difficulty experienced in adapting it to interpret electronic transition spectra. Molecular orbital theory has been developed as the most effective theoretical approach to many aspects of transition metal complex chemistry and has been used extensively in the interpretation of electronic absorption spectra.[41,44,94-96] Much of the work in molecular orbital theory is necessarily qualitative and approximate. The complexity of energy level diagrams of all but the most symmetric molecules, coupled with the unavailability of necessary experimental data has required the development of a semi-empirical approach to energy level calculations on transition metal complexes. Early development of molecular orbital theories involving semi-empirical parameters followed two main pathways. Parisier, Pople and Parr[97,98] evolved a molecular orbital approach designed specifically to relate electronic spectra and electronic structure in unsaturated organic molecules. Wolfsberg and Helmholz[99] devised a semi-empirical theory suitable for transition metal complexes, which they used to correlate energy levels and electronic spectra of $MnO_4^=$ and $CrO_4^=$. Their method has since been widely used in transition metal chemistry[100-102] and similar more quantitative methods have also been employed.[103] It should be noted that the energy difference between two one electron levels does not obey the relation $E = h\nu$ although the energy spectra is the necessity for a suitable theoretical interpretation of the observed transitions. One of the principle reasons for the decline in popularity of the valence bond theory was the difficulty experienced in adapting it to interpret electronic transition spectra. Molecular orbital theory has been developed as the most effective theoretical approach to many aspects of transition metal complex chemistry and has been used extensively in the interpretation of electronic absorption spectra.[41,44,94-96] Much of the work in molecular orbital theory is necessarily qualitative and approximate. The complexity of energy level diagrams of all but the most symmetric molecules, coupled with the unavailability of necessary experimental data has required the development of a semi-empirical approach to energy level calculations on transition metal complexes. Early development of molecular orbital theories involving semi-empirical parameters followed two main pathways. Parisier, Pople and Parr[97,98] evolved a molecular orbital approach designed specifically to relate electronic spectra and electronic structure in unsaturated organic molecules. Wolfsberg and Helmholz[99] devised a semi-empirical theory suitable for transition metal complexes, which they used to correlate energy levels and electronic spectra of $MnO_4^=$ and $CrO_4^=$. Their method has since been widely used in transition metal chemistry[100-102] and similar more quantitative methods have also been employed.[103] It should be noted that the energy difference between two one electron levels does not obey the relation $E = h\nu$ although the energy difference between states does. However, in a series of similar complexes, one electron transitions are all assumed to have similar nature and to be analogous to transitions between states.

Despite the extensive work in the field of semi-quantitative molecular orbital theory, its application remains constrained by the symmetry of the complex considered. Thus, of the types of complexes treated in this work, none has been successfully treated by semi-empirical methods although the more symmetric parent hexacarbonyls have been investigated thoroughly.[41,104-106]

A further difficulty in interpreting the electronic spectra of metal VI hexacarbonyls and their derivatives is the occurrence of d⟶d bands and charge transfer peaks in the same region of a spectrum having comparable extinction coefficients at room temperature. This has caused considerable difficulty in assigning the peaks in these regions, as the normal classification of electronic absorption peaks by intensity considerations is no longer valid. The assignment of very strong ($\varepsilon \sim 5000$) or very weak ($\varepsilon \sim$ 1-100) peaks in absorption spectra is reasonably familiar and straightforward.[96,107] Peaks of intermediate extinction coefficient ($\varepsilon \sim$500-5000) present a more difficult problem. Early work tended to assign any peak in this region as a weak charge transfer transition.[108] More recently, certain quite intense bands have been assigned by various authors as d⟶d transitions[109,110] and consequently it is no longer sufficient to quote the extinction coefficient of a peak, obtained at room temperature, as conclusive proof of a spectral assignment. Little work has been done on considering electronic absorption spectra in this region of intermediate intensity and such studies have tended to concentrate on square pyramidal cobalt II,[111] trigonal bipyramidal nickel II[112] and other similar complexes. The ligand field separations in these complexes have been evaluated and the observed energies of the transitions have been correlated in some cases with the calculated ligand field energies. Such correlations have supported the assignment of intermediate intensity bands as d → d rather than charge transfer transitions. These developments may be extended to transition metal carbonyl complexes and used as a basis for improving assignments in their electronic absorption spectra in regions of intermediate extinction coefficient values.

The monosubstituted and trans disubstituted phosphine derivatives of group VI metal carbonyls all have fairly complex electronic absorption spectra,[44] some peaks of which have caused controversy concerning their assignments. For example, Walker[44] has assigned a peak in the region 26,500cm^{-1} - 30,000cm^{-1} in complexes $LM(CO)_5$ and trans $L_2M(CO)_4$ (M = Cr, Mo, W; L various phosphines) as the charge transfer peak analogous to the peak of $M(CO)_6$ (M = Cr, Mo, W) at 35,000cm^{-1}. However, Darensbourg and Brown[74] from infrared intensity work and considering the electronic absorption spectra of a limited number of molybdenum complexes, have concluded that the hexacarbonyl peak at 35,000cm^{-1} has its analogue at approximately

34,500cm^{-1} in the phosphine complexes.

Until now, studies of electronic absorption spectra of phosphine substituted group VI metal carbonyls have been reported at room temperature only. It seemed clear that considerably more information could be obtained from a study of electronic transition spectra taken at different temperatures. Therefore, in an attempt to clarify the assignment of bands in the room temperature spectra of phosphine complexes of chromium, molybdenum and tungsten carbonyls, an investigation of their electronic absorption spectra at liquid nitrogen temperatures was undertaken. Further, the data obtained could be collated and would then be available for correlation with other spectroscopic data. Such a study could also be expected to contribute to the discussion of possible π-bonding participation in the metal carbon and metal phosphorus bonds in metal carbonyl derivatives and the effect of the phosphine substitutions on such bonding.

LOW TEMPERATURE SPECTRA AND SELECTION RULES

Electronic absorption spectra of metal VI hexacarbonyl complexes and their phosphine derivatives represent electronic transitions of various types. These may be considered under two distinct headings. Transitions may occur between orbitals essentially localised on the metal atom giving rise to formally (Laporte) forbidden energy bands. These are termed Ligand Field transitions as they are best understood by the application of the principles of Ligand Field theory to the splitting of the metal orbitals in the given environment. They are also known as d$\rightarrow$d transitions. The other main class of transition observed involves removal of an electron from one localised molecular orbital to another molecular orbital localised on a different centre of the molecule. Such transitions are known as charge transfer bands and may be classified by reference to the location of the initial and final levels involved. Thus, in the complexes studied, charge transfer transitions from metal orbitals to suitable combinations of the π-antibonding (π^*) orbitals of the carbonyl groups are considered while charge transfer from the ligands into the metal orbitals is not discussed. The energy of the t_{2u} π-bonding (π^b) molecular orbital of $M(CO)_5$ (M = Cr, Mo, W) obtained by reference to the ionisation potential of carbon monoxide suggests that the lowest energy ligand to metal charge transfer in such complexes is greater than 60,000cm^{-1}.[113] As we expect such transitions to have similar energy values in the phosphine complexes, such bands are outwith the energy range considered.

Studies of the electronic spectra of metal VI hexacarbonyls[41] and their derivatives[44] have shown that metal-ligand charge transfer and ligand field bands may occur in the same energy region of the spectra. This is the 35,000-25,000cm^{-1} region which is the section of the spectrum of most interest in this work. A study of the spectra obtained at low temperature and comparison of these with room temperature spectra may allow an assignment of the peaks to the appropriate type of transition involved. It is therefore necessary to consider the selection rules applicable to each type of transition and consequent effects of temperature lowering on spectra obtained according to these selection rules.

The two classes of electronic transition ($d \rightarrow d$ and charge transfer) have different selection rules. Considering only electric dipole transitions, such transitions are observed to give peaks of high or low intensity according as the dipole moment operator transforms as one component of translation x, y, z or not[127]. A pure electronic transition may occur if an electric dipole transition may take place according to the required selection rules. Thus the transition associated with an electric dipole moment will be allowed only if the matrix element $Q = \int \psi_a M \psi_b d\tau$ is non zero where Q is the transition moment, M the dipole moment operator and ψ_a, ψ_b are the wave functions of the initial and final states respectively. For the condition above to be satisfied, the representation of the integrand $\psi_a M \psi_b$ must be totally symmetric for at least one of the orientations of M. Thus the selection rule is such that the representation of $\psi_a \psi_b$ must transform as one of the translation vectors T_x, T_y or T_z. Transitions between states of the same parity are therefore forbidden (Laporte's rule).

In a purely centrosymmetric environment this rule would give charge transfer transitions as allowed and d→d transitions as forbidden although the spin selection rule which states that only transitions between states having the same spin value are allowed must also be considered. However, both charge transfer and d→d bands are assigned in spectra of centrosymmetric molecules such as $M(CO)_6$ (M = Cr, Mo, W) and in the types of complex studied in this work, various types of symmetry species are involved. The Laporte rule implies that a charge transfer transition may be orbitally allowed while d→d transitions may be forbidden or partially allowed according to the symmetry of the molecular environment. In centrosymmetric environments such as that for trans $L_2M(CO)_4$ (approximately), the interaction of vibrational states with electronic states may give rise to "vibronic" bands which have non zero transition moments due to vibration having symmetry representation of odd parity being included in the representation of $\psi_a M \psi_b$. Transitions between two "d" levels in a non centrosymmetric environment are also partially allowed because the d orbitals no longer have a symmetric reference system with a symmetry centre. Thus we expect d→d transitions to be observed despite the Laporte rule, centrosymmetric molecules giving d→d bands of lower intensity than those of non centrosymmetric molecules.

The development of these selection rules in terms of the transition moment may be related to the intensity of the peaks observed in a spectrum by considering the expression for the oscillator strengths, f, of the transitions involved. These may be directly expressed in terms of the transition moment as both f and Q may be related to the dipole strength D. This gives

$$f = \text{const.}\,\nu.\,\langle\psi_a|M|\psi_b\rangle^2 \qquad 3.1$$

where ν is the frequency of the transition. These and other relationships which allow the use of experimentally observed parameters in theoretically important relationships will be discussed more fully later. As f is proportional to the area under the transition curve (for a plot of extinction coefficient against frequency) it is seen from equation 3.1 that when the transition moment is zero, the area under the corresponding curve is also zero and the extent to which the transition is allowed determines the area under its spectral peak.

While the above treatment gives the strictly formal selection rules, the approximations employed do not necessarily reflect the true physical situation. Thus, for example, a formally forbidden electronic transition may have its selection rule relaxed by interaction of a vibrational wave function with the electronic wave function of one or both of the initial or final states concerned. Effects of this type must be considered in any attempt to assign the spectral peaks obtained for complexes as in this work where the environment may affect the ideal selection rules.

The Laporte selection rule requires d$\rightarrow$d transitions to be orbitally forbidden while such transitions may be observed in the spectra of most metal carbonyl derivatives and have been assigned by Beach and Gray[41] for the metal VI hexacarbonyls. Relaxation of the selection rule may be the result of several possible mechanisms. For a molecule with no centre of symmetry, there can be no transition designated even-even as it is not meaningful to refer to even or odd symmetry species in such an environment. This is applicable to complexes such as the mono substituted $LM(CO)_5$ which belong to the non centrosymmetric group C_{4v}. In complexes such as trans $L_2M(CO)_4$, symmetry D_{4h}, where the centre of symmetry allows the d-orbitals to be classified as even with respect to inversion, the appearance of d$\rightarrow$d bands must be due to some other mechanism. Two possibilities have to be considered, the first of which attributes d$\rightarrow$d band intensity to some permanent removal of the centre of symmetry by small distortions of the molecule or a lowering of the symmetry by asymmetric ligands. Thus, while trans $L_2M(CO)_4$ is ideally of D_{4h} symmetry, if L is not radially symmetric or the bond lengths or angles are distorted, the centre of symmetry may be effectively removed. This would allow relaxation of the Laporte selection rule. The more common explanation accepted for the appearance of d→d bands in the spectra of centrosymmetric complexes invokes temporary removal of the centre of symmetry by an odd vibration. This is the mechanism of vibronic coupling whereby the molecule absorbs a quantum of radiation corresponding to the energy of an odd parity vibration which promotes the molecule to an excited state which is no longer centrosymmetric. The Laporte rule is therefore invalid and the d→d transitions may then be observed. The intensities of these observed bands which arise from formally forbidden transitions may be accounted for qualitatively by symmetry mixing of the even d-orbitals with odd orbitals which transform similarly in the symmetry group concerned, thus removing their even character. This is more important for non-centrosymmetric molecules and molecular orbital formation between ligand p and metal d-orbitals is probably the most important factor in centrosymmetric cases. It is generally true that d→d transitions are more intense for molecules with no centre of symmetry although 'intensity stealing' from charge transfer transitions close in energy may increase the intensity of the d→d bands. The interaction of d→d and charge transfer transitions in this way is inversely proportional to their energy separation as may be shown by perturbation theory.

In principle, it is possible by experimental techniques to assign a peak as due to a charge transfer or d→d transition although would allow relaxation of the Laporte selection rule. The more common explanation accepted for the appearance of d→d bands in the spectra of centrosymmetric complexes invokes temporary removal of the centre of symmetry by an odd vibration. This is the mechanism of vibronic coupling whereby the molecule absorbs a quantum of radiation corresponding to the energy of an odd parity vibration which promotes the molecule to an excited state which is no longer centrosymmetric. The Laporte rule is therefore invalid and the d→d transitions may then be observed. The intensities of these observed bands which arise from formally forbidden transitions may be accounted for qualitatively by symmetry mixing of the even d-orbitals with odd orbitals which transform similarly in the symmetry group concerned, thus removing their even character. This is more important for non-centrosymmetric molecules and molecular orbital formation between ligand p and metal d-orbitals is probably the most important factor in centrosymmetric cases. It is generally true that d→d transitions are more intense for molecules with no centre of symmetry although 'intensity stealing' from charge transfer transitions close in energy may increase the intensity of the d→d bands. The interaction of d→d and charge transfer transitions in this way is inversely proportional to their energy separation as may be shown by perturbation theory.

In principle, it is possible by experimental techniques to assign a peak as due to a charge transfer or d→d transition although it is rarely possible to say which specific transition is involved. Three main approaches to this problem of classifying transitions as seen in ultraviolet spectra have been developed, each of which is dependent for its efficacy on the orbital selection rule. The first of these methods involves the examination of the spectrum of a cooled sample in an attempt to observe resolution of the vibronic structure of the bands. An allowed transition shows a $v'(0) \leftarrow v''(0)$ origin followed by a progression in the toally symmetric mode. Orbitally forbidden bands, however, must show only a very weak line at $v'(0) \leftarrow v''(0)$ followed by a totally symmetric mode superimposed on a quantum of an odd vibration. Thus, if the vibronic structure of a band may be seen, it may be possible to distinguish ligand field transitions ($d \rightarrow d$) from charge transfer transitions. A more recent technique which may be applied to this type of work is the recording of the fluorescence spectrum for the state involved. This fluorescence will almost exactly correspond to the absorption of radiation while being in the opposite sense, i.e. the former is an emission spectrum. A forbidden transition will exhibit a gap in a superimposed plot of the absorption and emission spectra due to the forbidden $v'(0) \leftarrow v''(0)$ transition while orbitally allowed transitions will have spectra overlapping at the position of the first vibronic component. The third approach is the study of the variation of oscillator strength or, more generally, of maximum extinction coefficient and half band width with respect to changing temperature. It is expected that on cooling a complex in solution, its electronic absorption spectrum will alter in form in a manner which may be correlated with the types of transition involved. It is, therefore, necessary to consider the effects of cooling a sample on the forbidden and allowed bands which appear in its spectrum.

A charge transfer transition as has been stated is orbitally allowed and at room temperature, such a transition is composed of an origin line v'(0) ⟵ v"(0) along with transitions involving other vibrational states v'(1) ⟵ v"(1), v'(2) ⟵ v"(2), etc. This applies to transitions in which the internuclear distances remain constant. The extent of the vibrational structure will depend on the amount by which the ground state and excited state internuclear distances differ. If there is a considerable change, a transition of type v'(2) ⟵ v"(0) or v'(3) ⟵ v"(0) will be more probable than v'(0) ⟵ v"(0) according to the Franck-Condon theory which states that intense vibrational transitions occur when ground and excited states have high probability functions at the same internuclear distance. It is possible for more than one vibrational mode to be excited, causing several corresponding vibrational transitions. Thus, while an allowed electronic transition consists of a vibrational progression (e.g. 3'-0", 2'-0", 1'-0", 0'-0") arising from a totally symmetric mode only, it is possible for any normal mode to give a vibrational sequence (e.g. 1'-1", 2'-2", 3'-3"). This range of possible transitions (progressions extending to energies higher than 0'-0", sequences to lower energies) gives rise to the characteristic broad bands observed in electronic absorption spectra. (Other effects such as spin orbit coupling may also cause band broadening.)

At room temperature, a certain (small) number of the vibrational states v"(1), v"(2), etc. of the electronic level will be occupied according to Boltzmann's distribution law and this allows the 1'-1", 2'-2" transitions to appear in the room temperature spectrum. Cooling the sample will cause an alteration of the Boltzmann population, the v"(0) state being occupied preferentially to v"(1), v"(2), etc. states. This will cause the v'(0) ⟵ v"(0) transition (or in the case of changing internuclear distance, the corresponding transition of highest probability) to gain intensity while the v'(1) ⟵ v"(1) and similar transitions will lose intensity. The peak appearing in the spectrum will therefore tend to sharpen up, losing its lower energy tail, and gain intensity at its frequency maximum on cooling. The area under the transition curve which is proportional to the oscillator strength, f, must however, remain constant. The value of f, as is stated below, may be related to the effective number of electrons involved in a transition and is hence unchanged by temperature variation since only the vibrational states involved alter on cooling while the effective number of electrons undergoing the electronic transition is unaffected.

A ligand field or d ⟶ d transition which is formally forbidden will have no v'(0) ⟵ v"(0) transition and at room temperature will consist of transitions of the type $v'(0) \leftarrow v''(1)$, $v'(1) \leftarrow v''(2)$, etc. which give a broad band in the spectrum. The vibrational levels will correspond to one or more perturbing vibrations which are responsible for removing the strict Laporte selection rule. Cooling the sample will again cause the population of the $v''(0)$ ground vibrational state preferentially, in this case favouring the strictly forbidden $v'(0) \leftarrow v''(0)$ transition. The oscillator strength of a vibronic transition decreases as the population of the perturbing vibrational state decreases on cooling, according to the hyperbolic cotangent law[114,115]

$$f(T) = f(0) \coth (h\nu/2kT) \qquad 3.2$$

where $f(0)$ is the oscillator strength at 0°K and ν is the frequency of the perturbing vibration. Further, as the energy of the $v'(0) \leftarrow v''(1)$ transition is lower than that of the $v'(1) \leftarrow v''(0)$ transition, cooling the sample will tend to cause a shift of the vibronic band to higher energies due to the increased probability of the higher energy transition at low temperatures. This relationship has been known for many years and was first used by Holmes and McClure[116] to distinguish between charge transfer and d $\rightarrow$ d peaks. They derived equation 3.2 as applied to forbidden transitions by modifying a treatment of Sulzer and Wieland[117] for allowed transitions having Gaussian shaped bands. A recent study of the variation of oscillator strength with temperature change[118] used this relationship to study some fairly intense formally forbidden bands in the spectra of

$IrBr_6^=$ and $SnBr_6^=$.

A decrease in the f value of a forbidden transition is thus well understood but unlike the allowed transitions, the behaviour of the extinction coefficient and half band width of its spectral curve are not readily predictable for temperature changes. The value of νmax for any transition may remain constant on cooling the sample while the decreased spread of the transitions involved gives a lower f value at low temperatures. At room temperature vibrational levels v"(1), v"(2) etc. are populated and allow the occurrence of sequences based on $v'(1) \leftarrow v''(0)$ 2'-1", 3'-2" and, to lower frequencies $v'(0) \leftarrow v''(1)$ 1'-2", 2'-3". While cooling the sample causes $v'(0) \leftarrow v''(1)$ to be less probable, $v'(1) \leftarrow v''(0)$ must become correspondingly more probable. The intensity gained by the latter transition may counterbalance the loss of intensity of the former as indicated by the absorption spectrum and hence ν max may not decrease on cooling but is certainly expected to show a shift towards higher frequencies. The lower probability of vibrational states v"(1), v"(2) etc. being occupied also reduces the sequences observed and as a result causes sharpening of the band.

From equation 3.2 it may be seen that the ratio f(T)/f(0) is dependent on the value of the perturbing vibrational frequency in any vibronic band. Thus, it is possible to evaluate f(300)/f(0) for any intensity producing normal mode as has been done in the study of McCaffery and coworkers.[118] Some examples are given in table 3.1.

TABLE 3.1 (REF. 118)

FREQUENCY OF PERTURBING VIBRATION (cm^{-1})	f(300)/f(0-10)	f(300)/f(90)
700	1.07	1.07
500	1.20	1.18
300	1.62	1.59
200	2.24	2.07
100	4.25	3.00
80	5.28	3.02
40	10.5	3.30

It is evident that the intensity of a vibronic band in a room temperature spectrum may vary according to the specific frequency involved in its perturbation and when discussing a series of complexes involving metals and ligands of very different masses, it is necessary to take account of the change in energy values of analagous vibrations in such a series. There is, however, no reason to assume that vibronic interaction arises from the perturbation of an electronic level by one single vibration. Two or more vibrations may be involved producing a complex relationship between oscillator strengths at different temperatures. For this reason, it is not usually possible to determine which skeletal deformations combine with any electronic state to give a vibronic transition. Using the more general properties of charge transfer and d→d transitions at different temperatures does, however, allow meaningful assignments to be made for peaks which, on the evidence of their intensities at room temperature, could be of either type.

ENERGY LEVEL DIAGRAM

Ideally, the assignment of observed peaks in a spectrum would be carried out using a quantitative molecular orbital diagram. Such a diagram may not be constructed for complexes at present. As an aid to assigning electronic transitions a qualitative approach must suffice at present. Complexes of the type $M(CO)_5L$ and $M(CO)_4L_2$ may be considered to be of sufficiently high symmetry (C_{4v} and D_{4h} respectively) to allow construction of a qualitative molecular orbital energy level diagram as an aid to interpretation of their electronic spectra. While a very good semiquantitative energy level diagram has appeared[41] for $M(CO)_6$ (M = Cr, Mo, W), no such approach has been found possible for even their simplest substituted octahedral complexes. A satisfactory qualitative approach may be developed to treat the relevant region of the electronic spectrum as has been employed in a previous study of some phosphine substituted metal VI hexacarbonyls[44]. The validity and reliability of this qualitative scheme may be checked by the more positive assignments of spectral peaks using the extra information from spectra obtained at low temperature.

A brief account of the derivation of the energy level schemes for monosubstituted and trans disubstituted phosphine metal VI carbonyl derivatives will now be given. The procedure is similar for both complex structures and involves a derivation of the molecular orbitals from the combination of metal valence orbitals and π- antibonding

(π^*) orbitals of the carbonyl groups. The reference axes and ligand numbering system is the same in both cases and is shown in figure 3.1 for the $LM(CO)_5$ complexes.

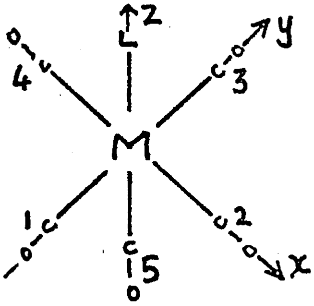


Figure 3.1

In $L_2M(CO)_4$ species, the second L group is in position 5, i.e. in the trans position.

It is necessary to classify both the metal valence orbitals and carbonyl π^* orbitals according to the symmetry elements of the group concerned. Symmetry elements for the C_{4v} species are a C_4 and two C_2 axes coincident with the z axis, two σ_v planes in the xz and yz planes and two σ_d planes bisecting the σ_v planes and containing the z axis. The D_{4h} species has, in addition, four C_2 axes formed by the intersection of the σ_v and σ_d planes with the xy plane and also a σ_h plane in the xy plane. The orbital basis set used comprises metal nd and (n + 1)p orbitals along with the π^* orbitals on each of the carbonyl groups. The procedure for constructing the metal-ligand combinations possible is to obtain the transformation properties of the various carbonyl π^* combinations and combine these with metal orbitals of suitable symmetry.

Thus, considering first the monosubstituted case $LM(CO)_5$, three distinct classes of carbonyl π^* orbitals may be identified and classified in C_{4v} symmetry. The π^* orbitals located on CO(1 - 4) in the xy plane transform as $(a_2 + b_2 + e)$; those on CO(1 - 4) but perpendicular to the xy plane (i.e. π_z^*) transform as $(a_1 + b_1 + e)$; and the π^* orbitals located on CO(5) transform as (e). Each of these transformations is an irreducible representation belonging to symmetry group C_{4v}. In this group, metal p_x, p_y, d_{xz}, d_{yz} orbitals transform as (e) and therefore may combine with all three π^* groups; p_z and d_{z^2} orbitals transform as (a_1) and d_{xy} transforms as (b_2) allowing overlap with $\pi^*(z)$ CO(1 - 4) in the case of the former pair and with $\pi^*(x, y)$ CO(1 - 4) in the latter case. The a_2 ligand combination cannot interact with any metal orbital as no orbital has suitable symmetry and interaction of the metal $d_{x^2-y^2}$ orbital (b_1 transformation) with the ligand $\pi^*(z)$ CO(1 - 4) b_1 combination gives net zero overlap as there is cancellation of two equal interactions having opposite signs.

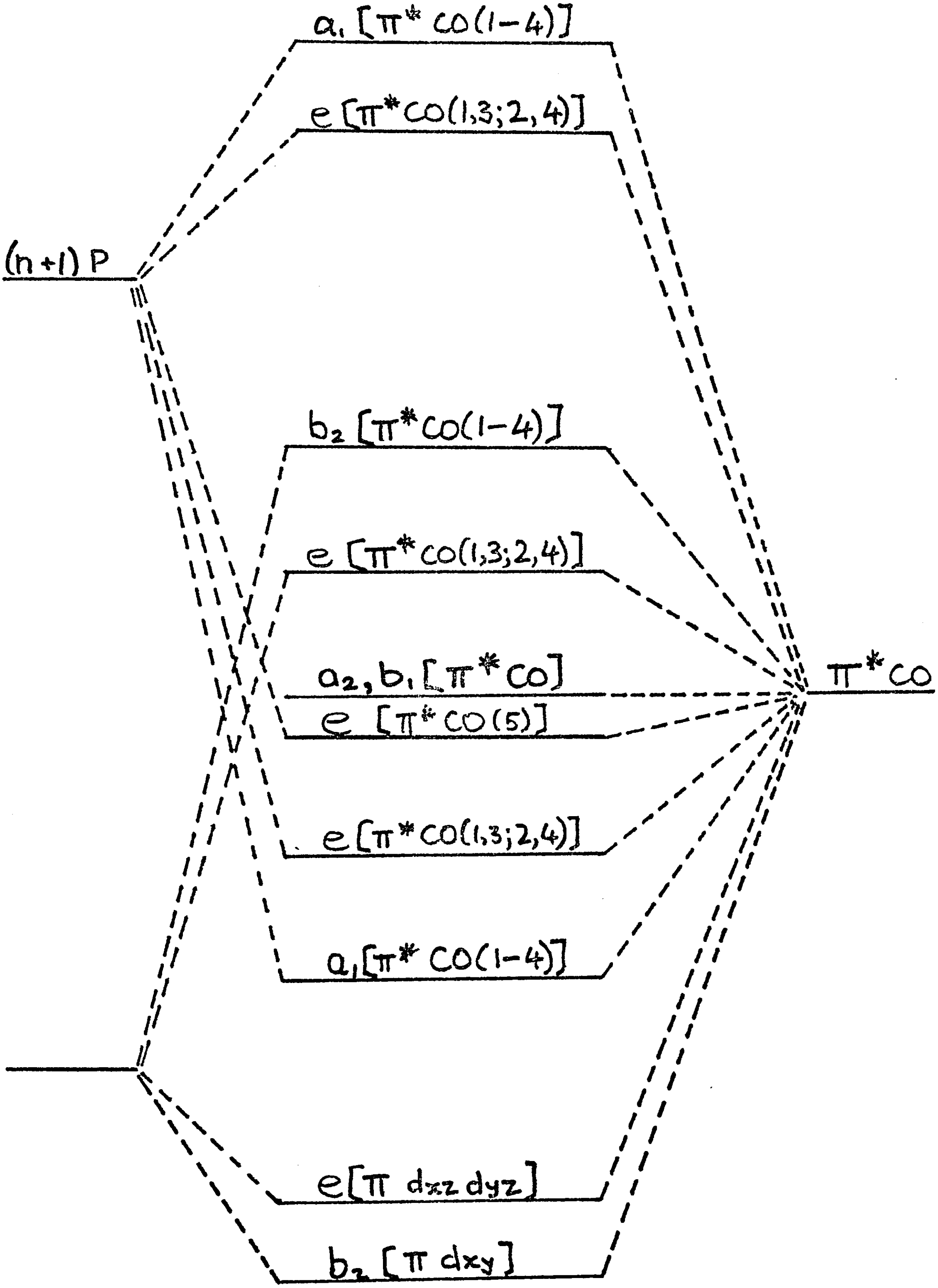
Having obtained the possible metal-ligand combinations allowed by symmetry, a simple energy level diagram may be constructed for these combinations. The molecular orbitals are formed by overlap of a metal orbital with a combination of the ligand orbitals which gives one more stable bonding molecular orbital and one less stable antibonding orbital. The energies of these molecular orbitals may be found by application of second order perturbation theory which gives

$$\text{Energy } E_i = H_{ii} + \sum_{j=i} \frac{H_{ij}^2}{H_{ii} - H_{jj}} \qquad 3.3$$

where H_{ii} is the coulomb energy of the i^{th} orbital uncorrected for overlap and $H_{ij} = N.p.\beta$ where β is the resonance integral between orbitals i and j, p is the number of overlapping orbital pairs and N is a normalising factor. Taking the coulomb energies to have order $(n + 1)p > \pi^*(CO) > nd$ in agreement with the semiquantitative treatment of the metal VI hexacarbonyls allows evaluation of the second order energies using equation 3.3. Taking account of metal-p-ligand orbital interaction and arranging the orbital energies in increasing order gives the qualitative energy level diagram for metal-carbonyl π * orbital interaction as shown in figure 3.2. An analogous procedure to that outlined above may be used to construct a similar energy level diagram for trans disubstituted complexes in D_{4h} symmetry. The resultant energy level diagram is shown in figure 3.3.

We must now consider the general aspects expected for the electronic absorption spectra of the metal carbonyl phosphine derivatives. Both d-d and charge transfer transitions are expected in the spectral region considered (45,000 - 25,000 cm^{-1}). As phosphines occur below carbonyl in the spectrochemical series, it is expected that the lower ligand field in the derivatives will cause the d→d bands to be at lower energies than in the metal VI hexacarbonyls. Metal to ligand transitions occur around 34,000 cm^{-1} in the hexacarbonyls and these are expected to be at lower energies in the case of the derivatives. Using the molecular orbital diagrams in figures 3.2 and 3.3, possible charge transfer transitions may be indicated. The orbital selection rule

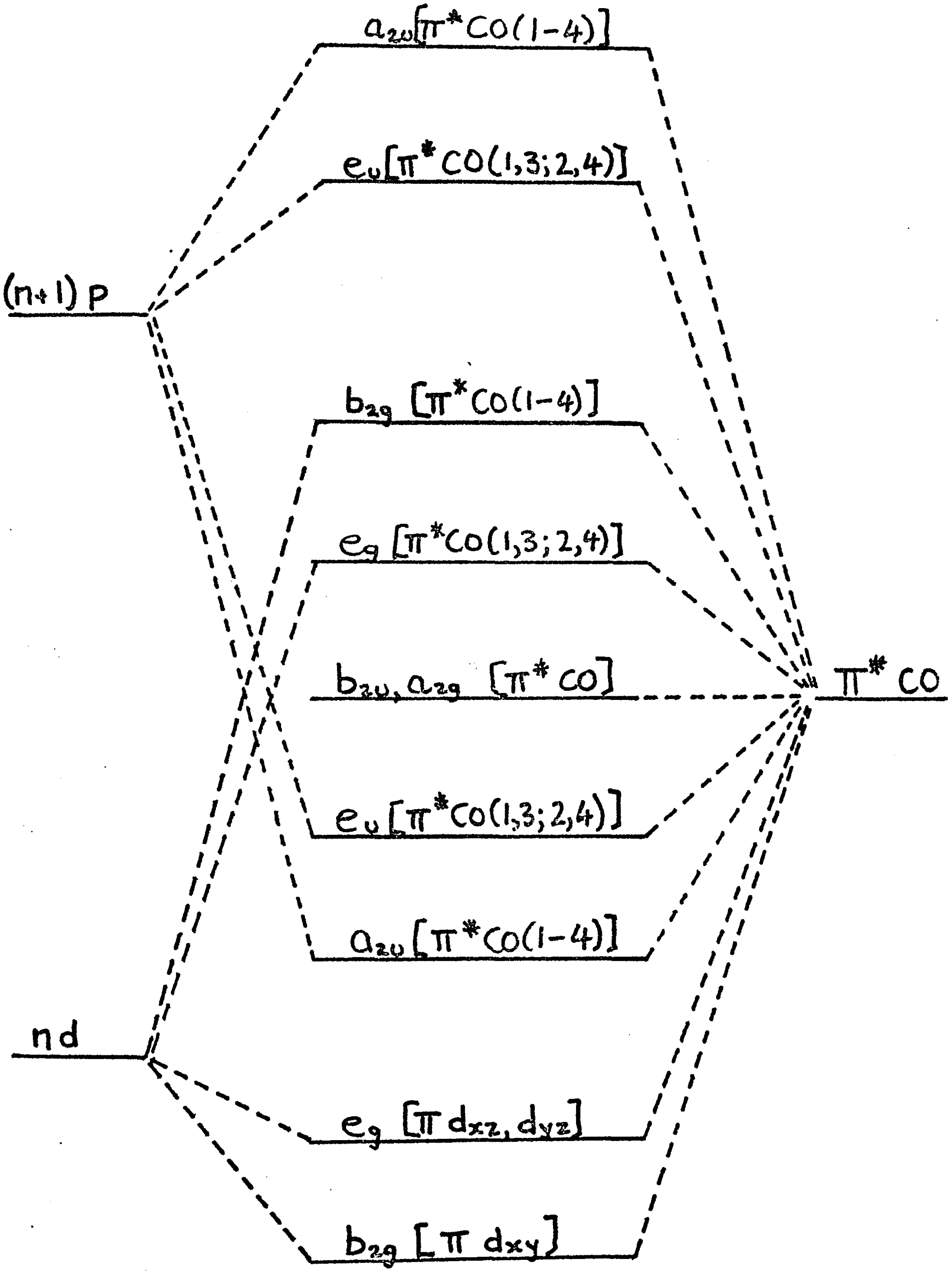
$LM(CO)_5$ METAL-CARBONYL π^* INTERACTION MOLECULAR ORBITAL DIAGRAM



The a_1, b_1 d[σ^*] orbital positions are unknown.

Figure 3.2

$L_2M(CO)_4$ METAL-CARBONYL π^* INTERACTION MOLECULAR ORBITAL DIAGRAM



The a_{1g}, b_{1g} d[σ^*] orbital positions are unknown.

Figure 3.3

(see above) based on the symmetries of the initial and final wave functions gives the selections shown in tables 3.2 and 3.3 for mono and trans disubstituted derivatives respectively. It may be seen from this that the lowest energy charge transfer transition in both mono and trans disubstituted complexes is to a ligand combination of carbonyls in the xy plane. Thus, we expect a corresponding charge transfer band for both derivatives on the model. Previous work[44] on some phosphine substituted complexes suggested that this first charge transfer band is present in the spectra of both derivatives, supporting the molecular orbital diagrams given. The position of this band was further related to possible π-bonding effects of the phosphine substituent. This study extends and modifies these results and gives clarification of the assignment of spectral bands in the 30,000 cm^{-1} region as either charge transfer or d-d transitions.

TABLE 3.2

$LM(CO)_5$ CHARGE TRANSFER TRANSITIONS

DONOR LEVEL	ACCEPTOR LEVEL	CONDITION
$e[\pi d_{xz}d_{yz}]$	$a_1[\pi^* CO(1 - 4)]$	Allowed
$e[\pi d_{xz}d_{yz}]$	$e[\pi^* CO(1, 3; 2, 4)]$	Allowed
$e[\pi d_{xz}d_{yz}]$	$e[\pi^* CO(5)]$	Allowed
$e[\pi d_{xz}d_{yz}]$	$a_2, b_1[\pi^* CO]$	Allowed
$e[\pi d_{xz}d_{yz}]$	$e[\pi^* CO(1, 3; 2, 4)]$	Allowed
$e[\pi d_{xz}d_{yz}]$	$b_2[\pi^* CO(1 - 4)]$	Allowed
$b_2[\pi d_{xy}]$	$a_1[\pi^* CO(1 - 4)]$	Forbidden
$b_2[\pi d_{xy}]$	$e[\pi^* CO(1, 3; 2, 4)]$	Allowed
$b_2[\pi d_{xy}]$	$e[\pi^* CO(5)]$	Allowed
$b_2[\pi d_{xy}]$	$a_2, b_1[\pi^* CO]$	Forbidden
$b_2[\pi d_{xy}]$	$e[\pi^* CO(1, 3; 2, 4)]$	Allowed
$b_2[\pi d_{xy}]$	$b_2[\pi^* CO(1 - 4)]$	Allowed

TABLE 3.3

TRANS $L_2M(CO)_4$ CHARGE TRANSFER TRANSITIONS

DONOR LEVEL		CONDITION
$e_g[\pi\ d_{xz}d_{yz}]$	$a_{2u}[\pi^*CO(1-4)]$	Allowed
$e_g[\pi\ d_{xz}d_{yz}]$	$e_u[\pi^*CO(1,3;2,4)]$	Allowed
$e_g[\pi\ d_{xz}d_{yz}]$	$b_{2u}, a_{2g}[\pi^*CO]$	Allowed
$e_g[\pi\ d_{xz}d_{yz}]$	$e_g[\pi^*CO(1,3;2,4)]$	Forbidden
$e_g[\pi\ d_{xz}d_{yz}]$	$b_{2g}[\pi^*CO(1-4)]$	Allowed
$b_{2g}[\pi\ d_{xy}]$	$a_{2u}[\pi^*CO(1-4)]$	Forbidden
$b_{2g}[\pi\ d_{xy}]$	$e_u[\pi^*CO(1,3;2,4)]$	Allowed
$b_{2g}[\pi\ d_{xy}]$	$b_{2u}, a_{2g}[\pi^*CO]$	Forbidden
$b_{2g}[\pi\ d_{xy}]$	$e_g[\pi^*CO(1,3;2,4)]$	Forbidden
$b_{2g}[\pi\ d_{xy}]$	$b_{2g}[\pi^*CO(1-4)]$	Allowed

EXPERIMENTAL

The electronic spectra were recorded on Pye Unicam SP 700C Ultraviolet and Visible Spectrophotometer giving a linear energy scale abscissa (cm^{-1}), ordinate in absorbance units. These spectral outlines were measured and the absorbance noted at regular energy intervals, normally each 500 cm^{-1} and each 200 cm^{-1} in the regions of peak maxima. The extinction coefficients at each of these points was then calculated and a graph of extinction coefficient (ε 1 cm^{-1} mole^{-1}) against energy (ν cm^{-1}) was drawn. The extinction coefficient obtained for low temperature spectra were corrected as in previous studies[133] by multiplying each ε value by the appropriate constant (0.812) for the temperature -180°C.

The cell was an R.I.I.C. FH - 01 screw sealed metal cell, fitted with quartz windows and a teflon spacer. This was supported by a stainless steel refrigerant vessel which fitted into an outer jacket having sodium chloride windows. The sample was injected by syringe into the cell and the outer jacket and cell holder fitted together. The unit was then evacuated to approximately 10^{-2}mm. Hg and after five minutes, the refrigerant vessel was filled with liquid nitrogen, the vessel having a "piston like" object called a "mushroom" with a polyurethane base. It was necessary to coat the cell with silicon grease to prevent loss of solution under vacuum. When the liquid nitrogen had ceased to boil off rapidly, the mushroom was removed and the cooling process continued. After approximately one hour cooling, the sample reached a temperature of approximately -100°C (measured by a copper-constantin thermocouple) when the low temperature spectrum was recorded. There was a tendency for condensation to form over the cooled cell and this was removed using a blow dryer. It was found that the vacuum tight property of the cell was sensitive to many of the physical conditions involved in the procedure. Thus, cooling the cell without the mushroom, or too quickly, changing the spacer (i.e. dismantling the cell) or returning the cell to room temperature too quickly all caused the cell to leak considerably. The most serious of these conditions was the dismantling of the cell which caused severe leakage over a long period. It was decided for this reason that a 0.01 cm. spacer should be used at all times, using concentration variation to scan peaks having widely differing extinction coefficients. The result of cell leakage was formation of one or more bubbles in the sample which caused light scattering, thus preventing the recording of the spectrum. It was sometimes possible to heat the cell slightly by hot air when a bubble formed, thus lowering the viscosity of the solution and allowing the bubble to float to the top of the cell. This procedure, while eliminating light scattering, gave spectra of solutions with misleading concentrations and thus any loss of solution was considered unsatisfactory whether a spectrum was obtained or not.

The choice of solvent was principally determined by the requirements of the low temperature technique. A solvent in which the complexes were soluble and which formed a clear glass at -180°C was required and two mixed solvents were found to be suitable. A methylcyclohexane - isopentane mixture and ether - isopentane - ethanol (E.P.A.) mixture each form a glass at low temperatures and as methylcyclohexane - isopentane is the less polar, it was chosen to minimise any possible complex - solvent interaction. The solvent was purified by washing with a mixture of concentrated sulphuric and nitric acids, followed by washing with water, drying over calcium sulphate and distillation from sodium wire. A ratio of 3:2 methylcyclohexane - isopentane was used although other ratios also give glasses at low temperatures. Most of the complexes were found to be soluble in this hydrocarbon solvent, but the trimethylphosphite derivatives were only slightly soluble at low temperature (particularly the trans disubstituted complexes). As the other low temperature solvent, E.P.A. showed similar solubility results, the trimethylphosphite complexes were recorded at optimum concentrations in methylcyclohexane - isopentane, this giving satisfactory spectral results.

RESULTS AND DISCUSSION

The electronic absorption spectra of mono and trans disubstituted phosphine complexes of the group VI metal carbonyls $LM(CO)_5$ and $L_2M(CO)_4$ were recorded at room temperature (295°K mean) and in a cell cooled by liquid nitrogen (93°K mean). The frequency of the observed peaks (in cm^{-1}) and the extinction coefficients (ε l cm^{-1} $mole^{-1}$) have been tabulated for monosubstituted complexes in Table 3.4 and for trans disubstituted complexes in Table 3.5 at the end of this chapter. The phosphine ligands considered in this study are Tdp, trimethylphosphite, triethylphosphite, triisopropylphosphite, triisopropylphosphine and trinbutylphosphine. The spectra obtained as plots of optical density against wavenumber (ν cm^{-1}) have been replotted as graphs of extinction coefficient against wavenumber and are shown in Appendix 3.1

The only major study of the ultraviolet spectra metal VI phosphine carbonyl complexes previously undertaken was that of Walker[44] who obtained the spectra of mono and trans disubstituted complexes for ligands Tdp, triphenylphosphine, triphenylphosphite and tricyclohexylphosphine at room temperature only. He also presented the spectra of the trans disubstituted trinbutylphosphine derivatives. The present study extends this previous work to ligands of various bonding abilities which form complexes having spectra uncomplicated by ligand absorptions.

The form of the spectra obtained has been found to depend much more on the nature of both the ligand and the metal ion concerned than has been found to be the case in other studies of analogous complexes of amine[121] and phosphine[44,74] complexes. The spectra of the monosubstituted complexes show less dependence on the ligand or metal involved than do the trans disubstituted spectra. Thus, at room temperature, phosphine and phosphite monosubstituted complexes of chromium, molybdenum and tungsten have similar spectral outlines although spectra obtained at low temperatures indicate that the peak in the 29,000 cm^{-1} region gains intensity on cooling in trialkylphosphine and Tdp complexes and loses intensity in trialkylphosphite complexes. It is also noted that monosubstituted complexes of chromium have spectra which are somewhat less resolved in the 36,000 - 26,000 cm^{-1} region than spectra of molybdenum and tungsten complexes. This effect has been reported previously.[44] The general features of the spectrum of a monosubstituted complex $LM(CO)_5$ at room temperature and low temperature are shown in figures 3.4 and 3.5 for phosphine and phosphite ligands respectively.

The trans disubstituted complexes gave spectra having one of four spectral outlines, dependent on which metal-ligand combination was present. Molybdenum and tungsten complexes are completely analogous and differ considerably from the chromium complexes while in each of these cases, phosphine complexes show a spectral outline very different from that of corresponding phosphite complexes. Examples of these spectra are given in figure 3.6a - d along with their observed

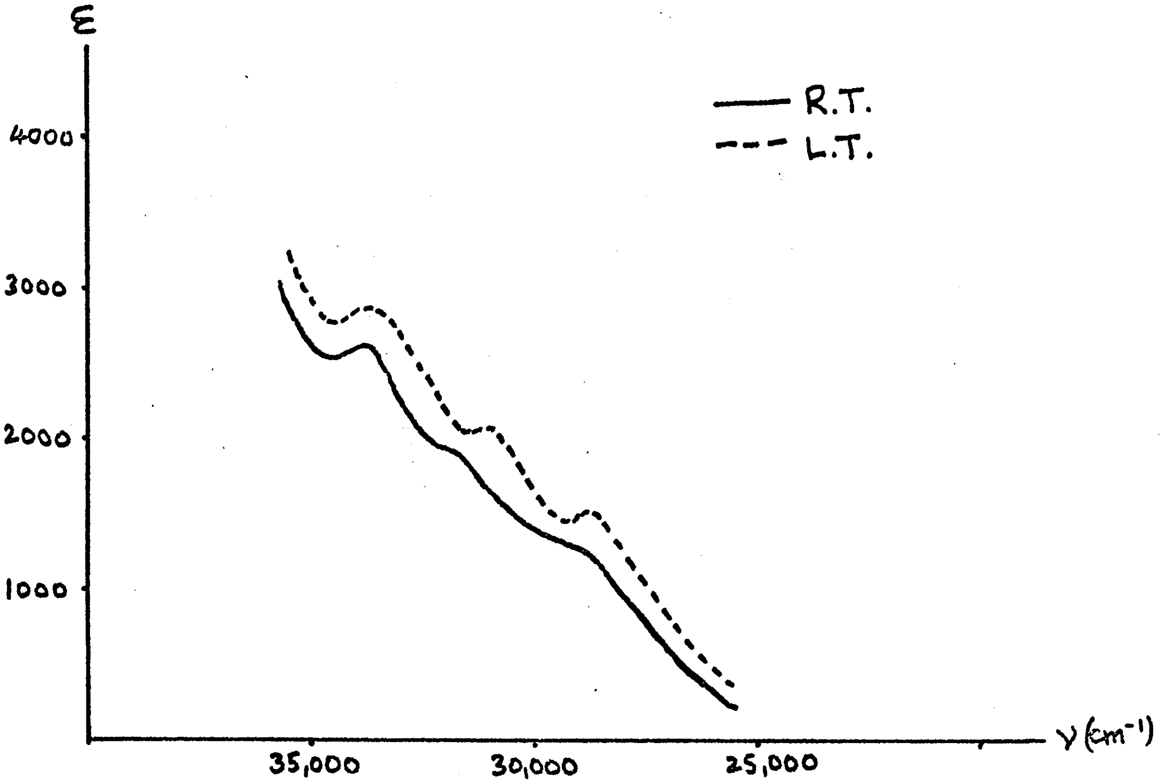


FIGURE 3.4

$PPr^i_3Mo(CO)_5$

Spectral Outline of Monosubstituted Phosphine Complexes. Example.

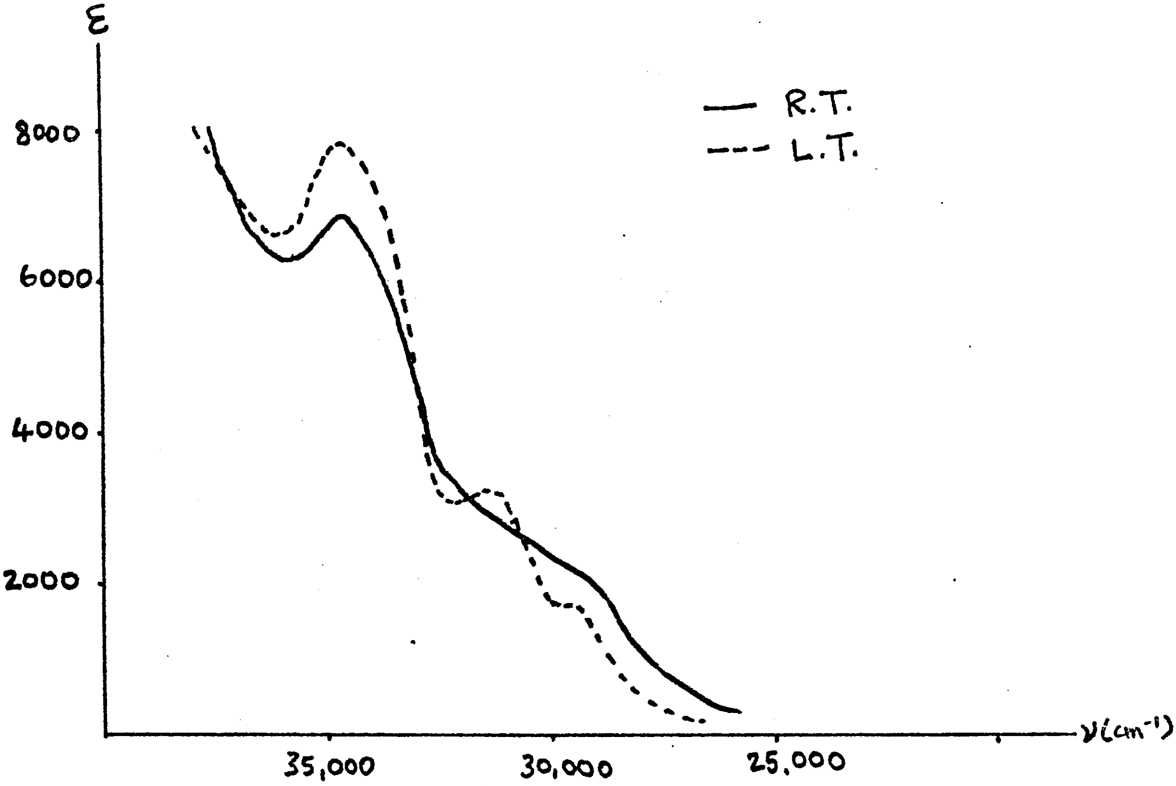


FIGURE 3.5

$P(OEt)_3Mo(CO)_5$

Spectral Outline of Monosubstituted Phosphite Complexes. Example.

FIGURE 3.6

Spectral Outlines of trans Disubstituted Complexes. Examples.

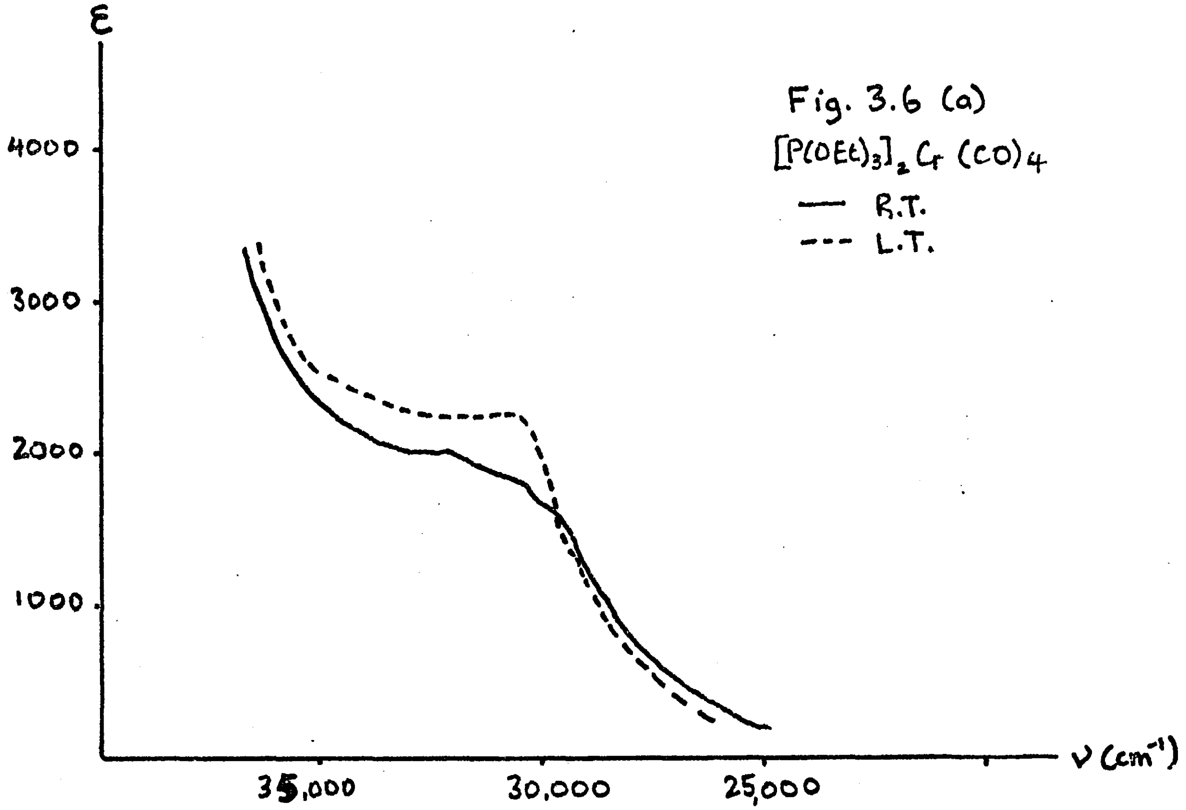


Fig. 3.6 (a)

$[P(OEt)_3]_2Cr(CO)_4$

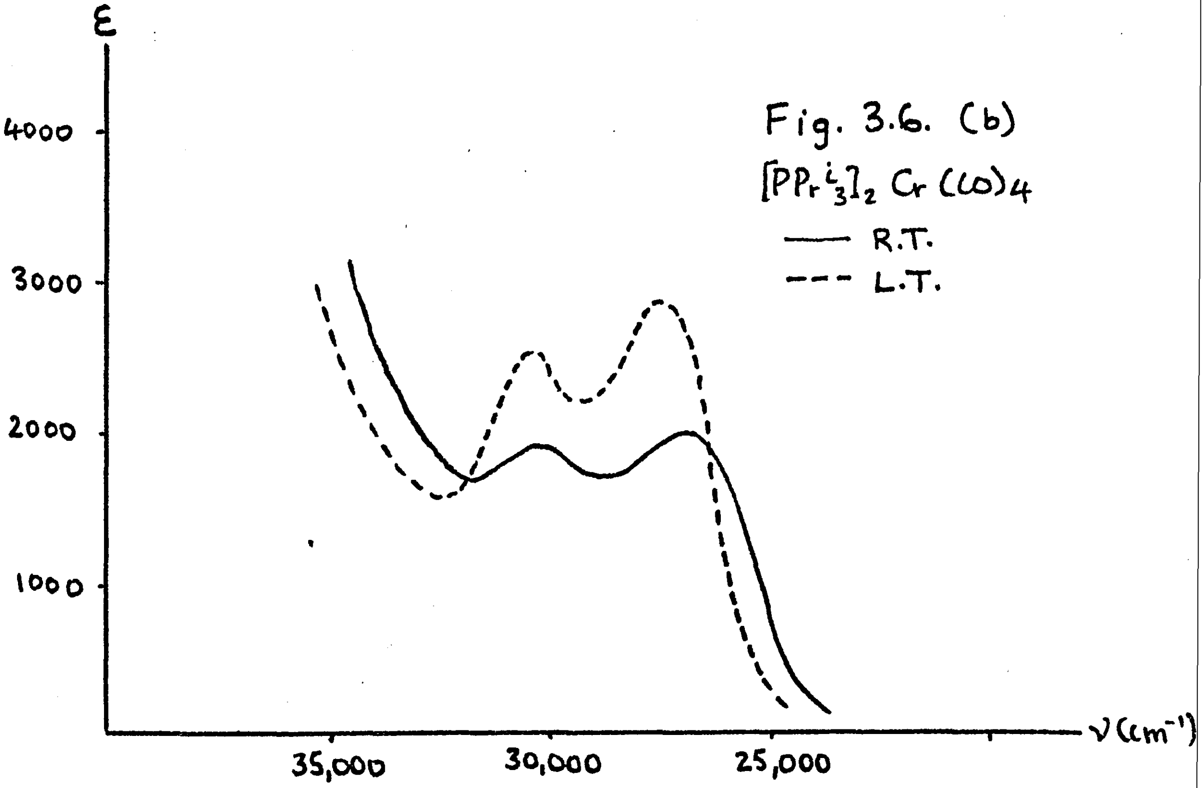


Fig. 3.6. (b)

$[PPr^i_3]_2Cr(CO)_4$

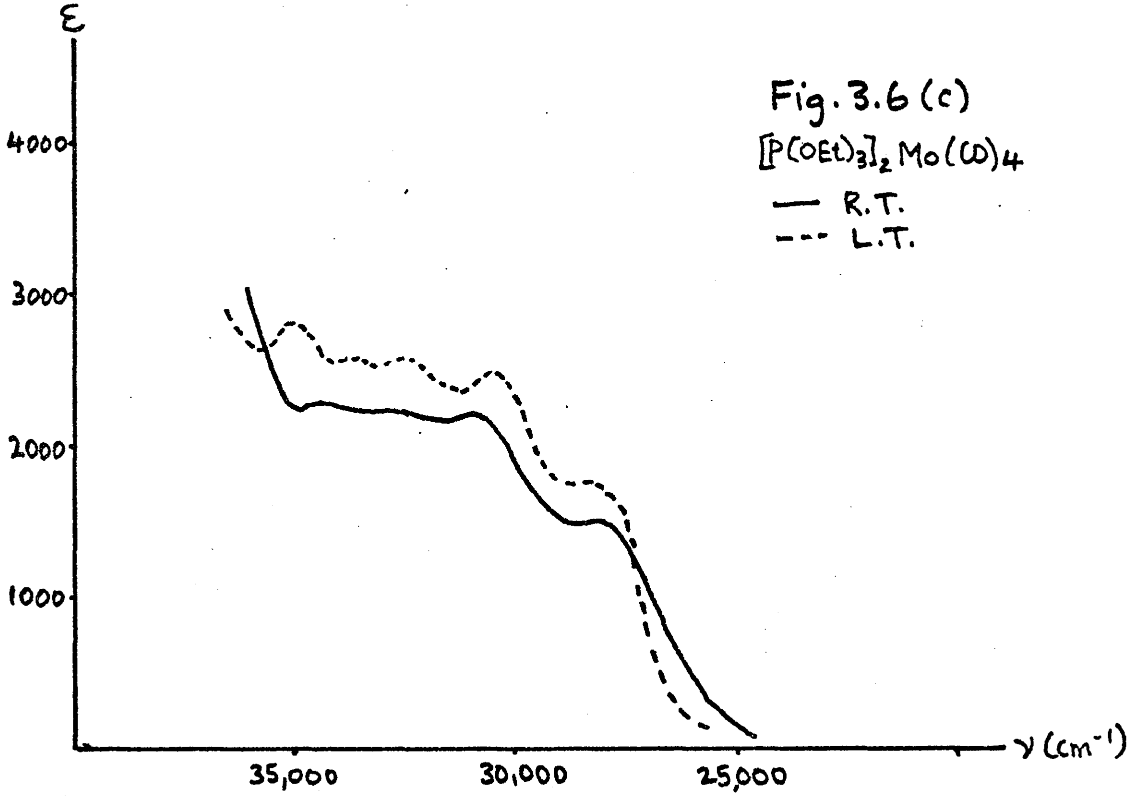


Fig. 3.6 (c)

$[P(OEt)_3]_2Mo(CO)_4$

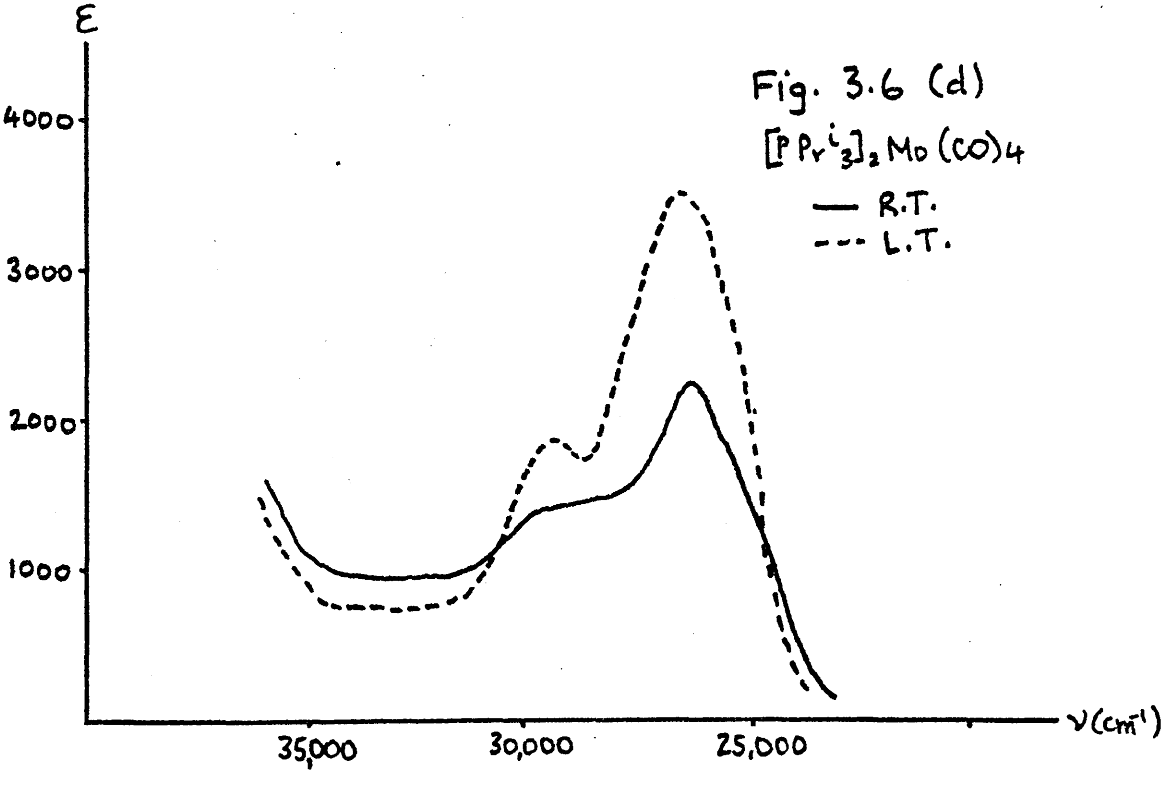


Fig. 3.6 (d)

$[PPr^i_3]_2Mo(CO)_4$

behaviour on cooling the sample.

It may be seen from the diagrams that many of the peaks occur as shoulders and certainly none of them occurs as a separate transition band. It was therefore considered that curve analysis using some combination of Gaussian distributions might profitably be employed to separate the spectrum into a series of individual transition bands. It was clear from the graphs of ν versus ε that some of the spectral forms would be more readily analysed in this way than others. Thus, the monosubstituted complexes and the trans disubstituted phosphite complexes of chromium which all have spectra showing complex overlapping in the 36,000 - 26,000 cm^{-1} region were expected to be less readily analysable than spectra of the trans disubstituted phosphine complexes with their more resolved peaks. An investigation of the use of Gaussian curves for analysing these types of electronic absorption spectra in general was therefore undertaken and some examples of curve analysis applies to the spectra of specific complexes are discussed below.

A hypothetical curve based on spectra of the trans disubstituted phosphine complexes of chromium hexacarbonyl $Cr(CO)_4(R_3P)_2$ was drawn and this outline reconstructed by means of overlapping Gaussian bands. The technique involves first choosing the number of Gaussian curves required to construct the spectral outline and by varying their relative intensities, reproducing the observed intensities at each point along the spectral outline. This is a process of trial and error and has no unique solution as may be seen from figure 3.7a - c which indicates

FIGURE 3.7(a)-(c)

Examples of Gaussian Analyses of a Single Curve Outline

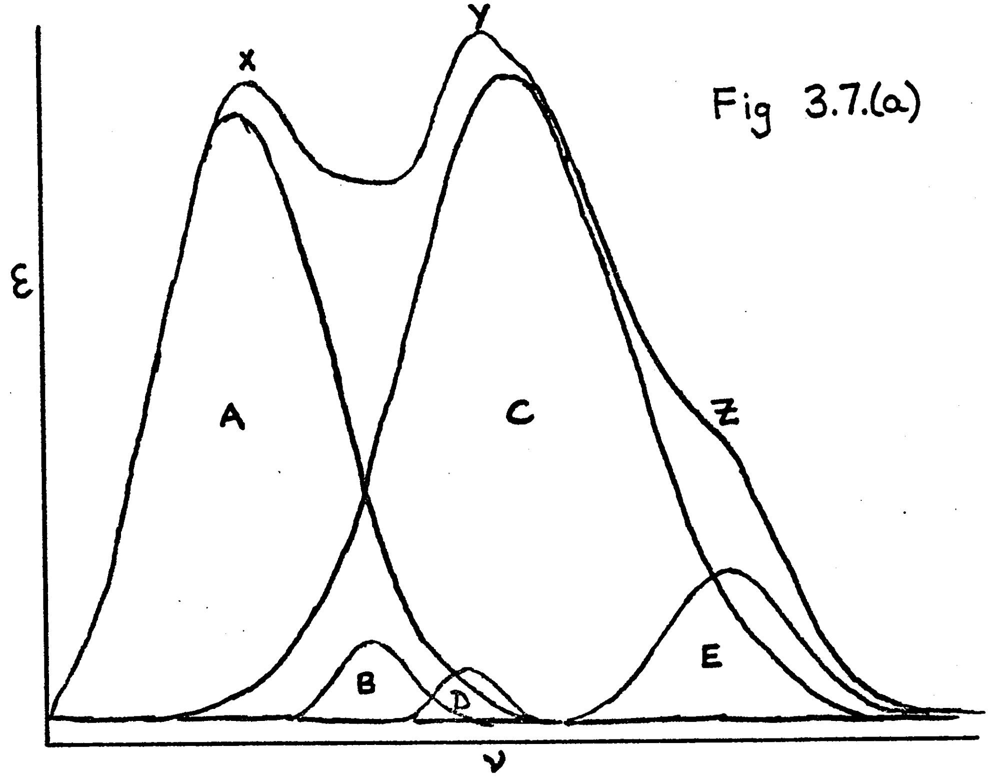


Fig 3.7.(a)

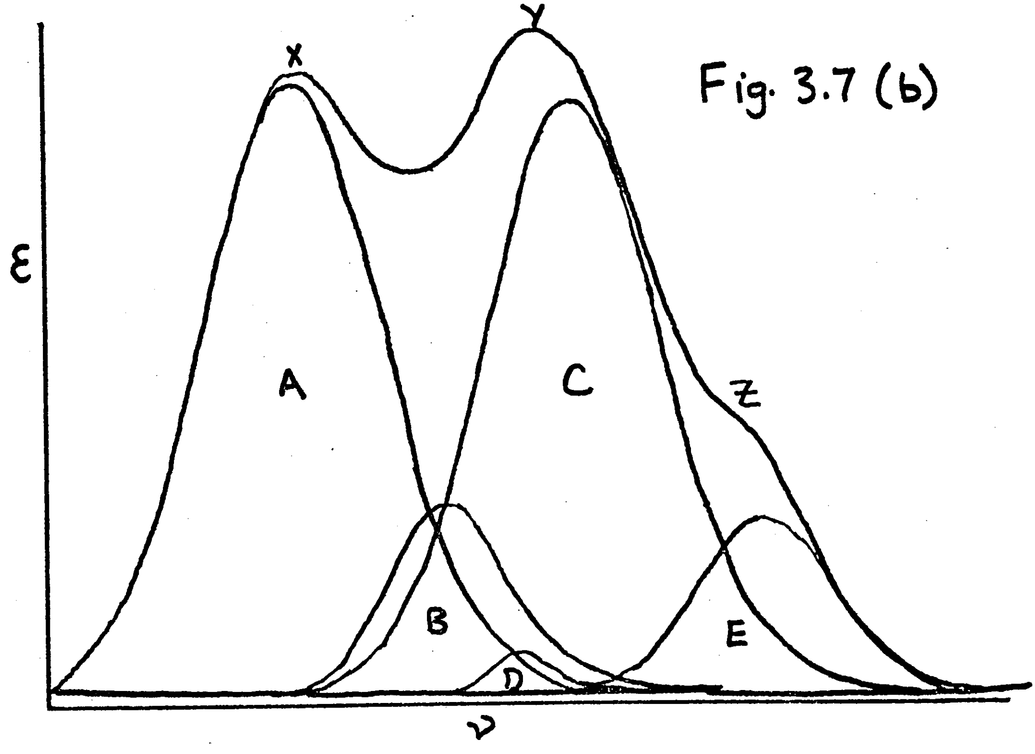


Fig. 3.7 (b)

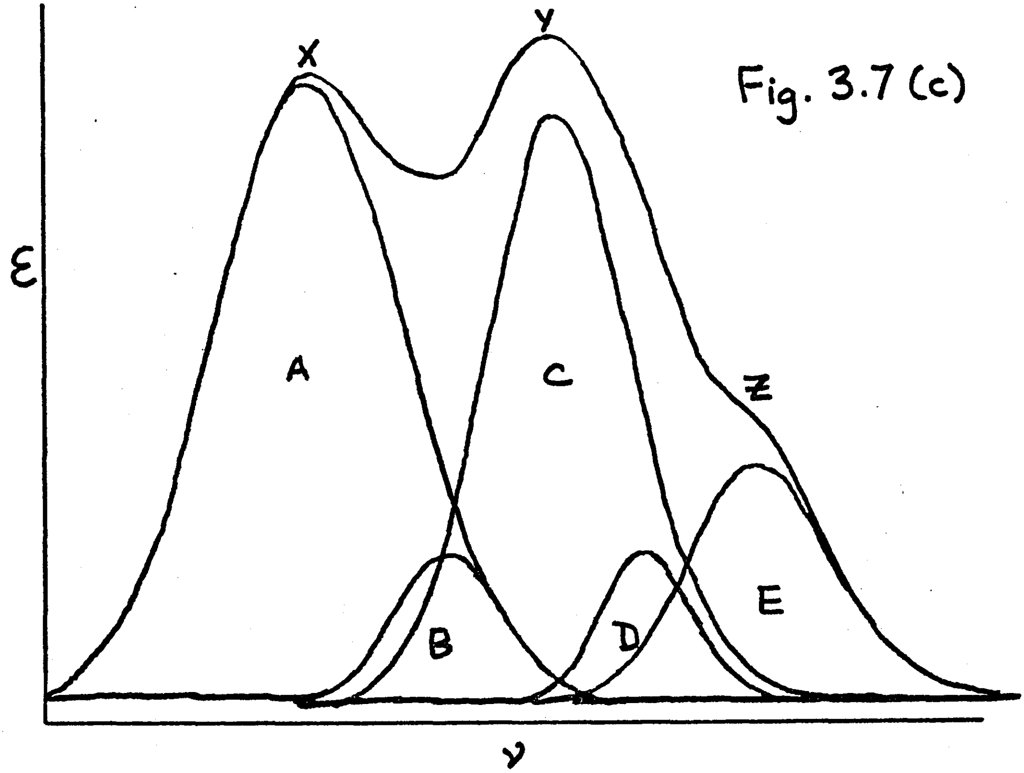


FIGURE 3.7

the results of three such analyses on a single curve. It might be argued that the analyses largely agree in that they each show two prominant peaks A and C along with three lesser bands, one of which, E, is always the largest of these latter. While this is true, it is precisely the two smaller peaks, B and D, which are the most important products of such a Gaussian analysis. The form of the spectrum with maxima at X and Y and a pronounced shoulder at Z clearly suggests that absorption maxima corresponding to some transitions are associated with the areas under these points in the curve. Indeed, such factors are employed as a basis for the curve analysis. The purpose of the Gaussian analysis is to reveal absorption maxima which are hidden in the spectral outline because of their lower intensities. Thus while the analysis has been seen to resolve these absorptions, the disparate intensities of the peaks B and D would seem to indicate that this technique has severe limitations when used to analyse spectra of such complexity. One further consideration is the use of such spectral analyses in comparing spectra obtained at different temperatures. As the analysis of these spectra is designed to clarify assignments of observed peaks to electronic transitions by considering their intensity behaviour on cooling the sample, difficulties in determining the intensity of peaks similar to B and D in the example make meaningful comparisons of intensity changes effectively impossible. For example, the intensity of peak B is seen to increase twofold on comparing figure 3.7a with figure 3.7b both of which represent analyses of one spectrum taken at room temperature.

Another criticism pertaining to Gaussian analysis is that concerning the number of peaks chosen as representing the curve shape. This is an important consideration when analysing spectra involving a high degree of band overlap as is found in many of the spectra being examined in this work. Essentially, the problem is one of circularity of argument. To make a plausible guess at the number of transitions (and hence the number of Gaussian peaks) which combine to produce a spectrum, it is necessary to have a reasonably detailed knowledge of the allowed transitions and their relative ordering in any one energy region. However, it is this data concerning possible electronic transitions which we are attempting to obtain from the spectrum by Gaussian analysis. Hence by choosing to construct a curve from, say, five Gaussian peaks as in the example above, we have introduced an arbitrary factor with little evidence for its justification. Thus, any intensity results subsequently obtained must be considered as limited in application by this essential ad hoc assumption.

It was therefore considered that application of Gaussian analysis to the complex spectra obtained for most of the metal carbonyl derivatives would be impracticable. The inability to estimate the number of transitions involved coupled with the complication of considerable energy "tail" overlaps made it impossible to analyse such spectra with any confidence. Some of the spectra, however, were considered to have band outlines with sufficient resolution to allow as reasonable an estimate of the number of peaks involved as had been obtained in other reported work.[41] Furthermore, Gaussian analysis had been attempted previously on one such spectrum without success[44] using a computer analysis of spectral details known as the "Bird-Sanders" curve analysis Programme while the general technique of Gaussian analysis has been growing in popularity as more complex spectral curves are studies. Consequently, an attempt was made to obtain Gaussian curve analyses of the absorption spectra of these complexes, the results of which are tabulated in Table 3.6 and shown diagramatically in Figure 3.9i - vii. Also shown in Table 3.6 is an analysis of the observed behaviour of the curve parameters on cooling the sample, in terms of percentage changes.

The spectra treated in this Gaussian analysis work were those of complexes $Tdp_2Cr(CO)_4$, $(PEt_3)_2Cr(CO)_4$, $[P(OMe)_3]_2Cr(CO)_4$, $Tdp_2Mo(CO)_4$ and $TdpMo(CO)_5$. The plots of extinction coefficient against frequency obtained for the spectra of these complexes were subjected to analysis by a mechanical curve analyser which combined a series of curves to give the best reproduction of the spectral outline. Before considering the parameters obtained for the complexes studies, it is necessary to consider the quantitative approximations employed in the theoretical approach.

The extinction coefficient, ε, of a point on the absorption spectrum of a solution is obtained from the well known Beer - Bouguer - Lambert relationship for solutions assuming only solute molecules absorb

$$D = \log I_0/I = \varepsilon . c . l.$$

where D is the optical density, I_0 and I are the intensities of the incident and transmitted light respectively, c is the molar concentration of the solution and l the path length in cm. A graph of ε versus ν (frequency cm^{-1}) when analysed into Gaussian curves may be treated as a series of single curves each possessing the characteristic properties ε max and $\Delta\nu$ where ε max is the maximum value of the extinction coefficient of that curve and $\Delta\nu$ is its half band width (i.e. the energy width in cm^{-1} at $\varepsilon = \frac{1}{2}\,\varepsilon$ max). This is shown in figure 3.8.

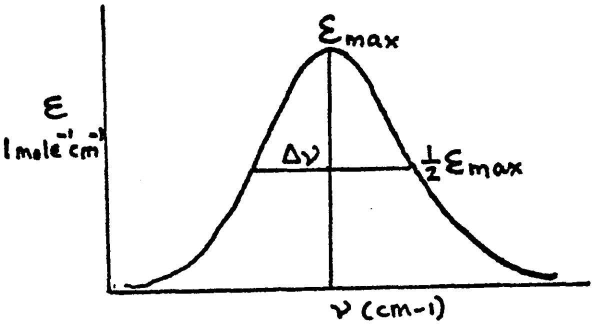


Figure 3.8

Using these properties of the curves it is possible, using simple relationships derived from a quantum mechanical analysis of the problem, to compute values for many of the important properties of the transitions being considered. Thus the area under one such curve may be shown to be[122,123]

$$A = \int_0^\infty \varepsilon . d\nu = \text{const.}\ \varepsilon_{max}\ \Delta\nu$$

$$A = \int_0^\infty \varepsilon . d\nu = \text{const.}\ \varepsilon_{max}\ \Delta\nu$$

Work by Kuhn and Braun using an appropriate Gaussian distribution gave $A = 1.0645\ \varepsilon_{max}\ \Delta\nu$.[124] The oscillator strength f of a transition is a very important property which in classical electromagnetic theory was associated with the excitation of specific electrons by an electromagnetic field. The f value of any transition was taken as a measure of the effective number of electrons involved in any spectral band and quantum mechanics allows an expression of f which has the same theoretical significance as in classical theory. It has been shown[125,126] that

$$f = mc^2/n\pi e^2 \int k.d\nu$$

where e and m are the charge and mass of the electron respectively, c is the speed of light, n the number of solute molecules per cc. and k the absorption coefficient (gaseous). This, when the constant term is evaluated and the expression converted to apply to solution spectra involving ε rather than k gives, assuming the initial and final states to be degenerate

$$f = 4.32 \times 10^{-9} \int \varepsilon \, d\nu = 4.32 \times 10^{-9} \times A$$

This allows practical values of f to be obtained and as f is characteristic of the effective number of electrons taking part in a transition (i.e. of the relative allowed or forbidden character of a transition) it is an interesting parameter in a study such as this. Further characteristics of the transitions which may be derived are the dipole strength and Einstein coefficients of absorption and emission.

The dipole strength D_{nm} for a transition from level n to level m where $E_n < E_m$ is defined as $D_{nm}/G = Q_{nm}^2$ where $Q_{nm} = \int \psi_n^* \sum_i x_i \psi_m d\tau$ the transition moments and $Q_{nm}^2 = Q_{nmx}^2 + Q_{nmy}^2 + Q_{nmz}^2$. G represents

FIGURE 3.9(i)

$Tdp_2Cr(CO)_4$

Gaussian Analysis of Room Temperature

Electronic Absorption Spectrum

35,000-25,000cm^{-1}

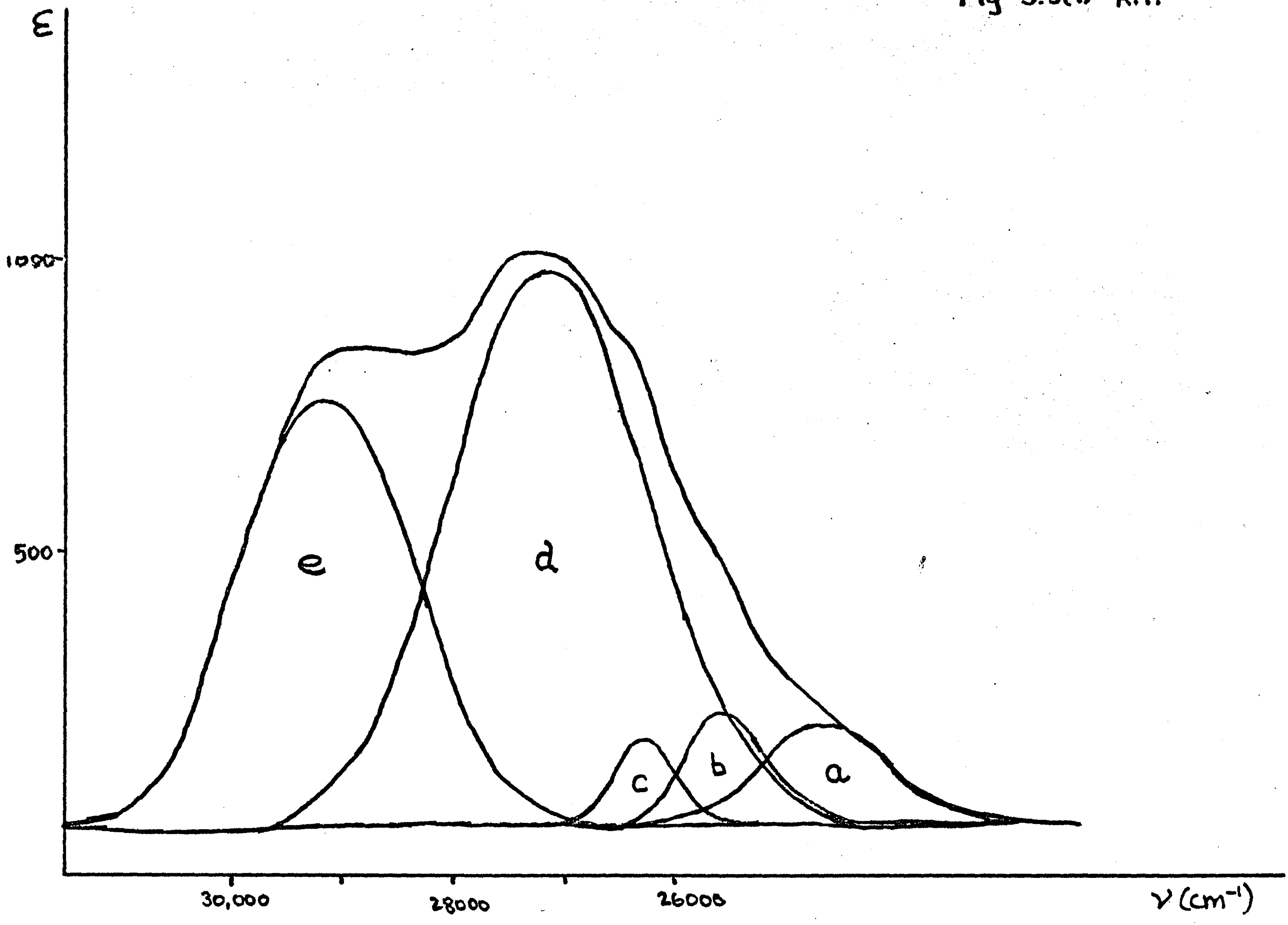


Fig 3.9(i) R.T.

FIGURE 3.9(i)

$Tdp_2Cr(CO)_4$

Gaussian Analysis of Low Temperature
Electronic Absorption Spectrum
35,000-25,000cm^{-1}

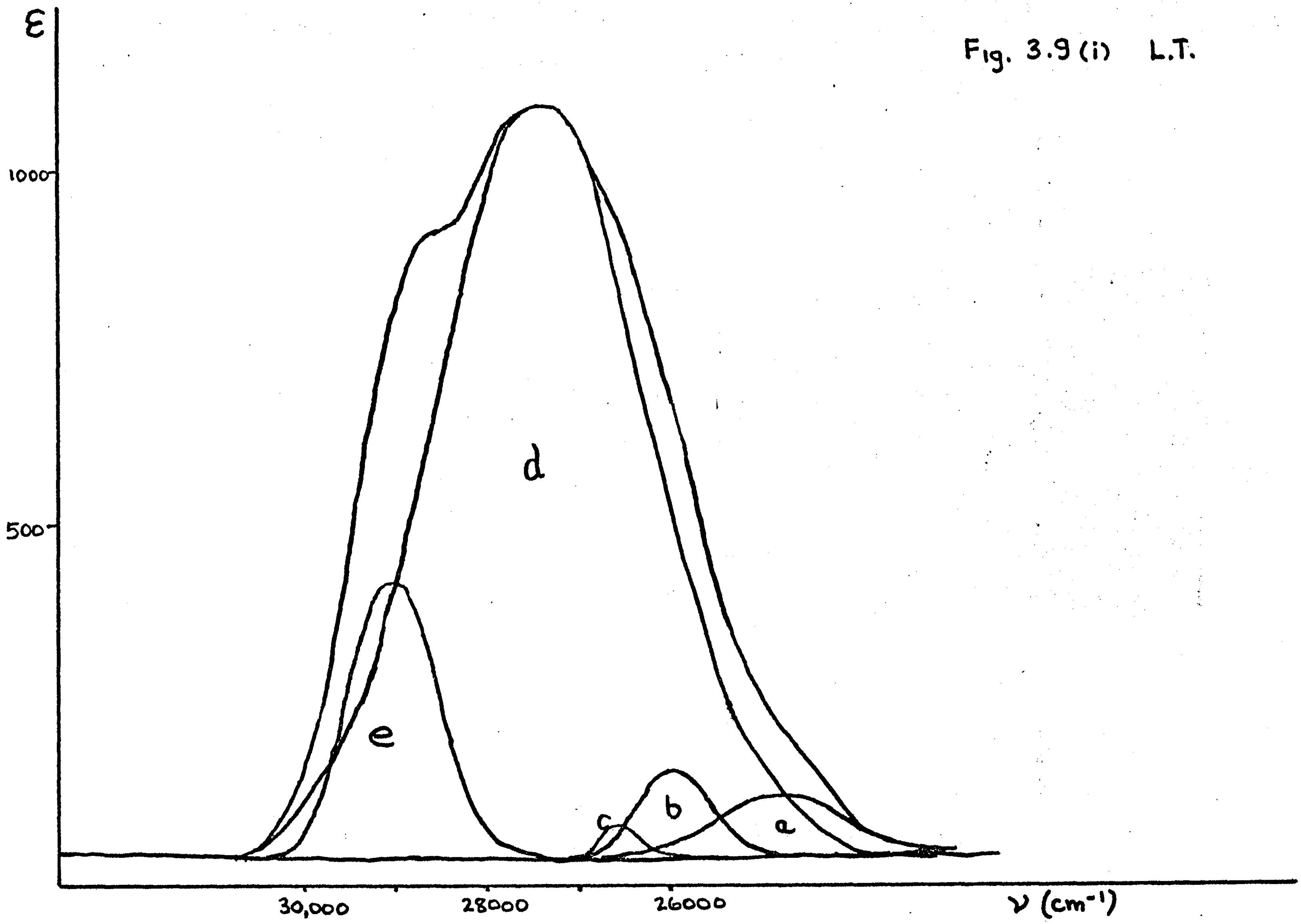


Fig. 3.9 (i) L.T.

FIGURE 3.9(ii)

$Tdp_2Cr(CO)_4$

Gaussian Analysis of Room Temperature

Electronic Absorption Spectrum

45,000-35,000cm^{-1}

Fig. 3.9.(ii) R.T.

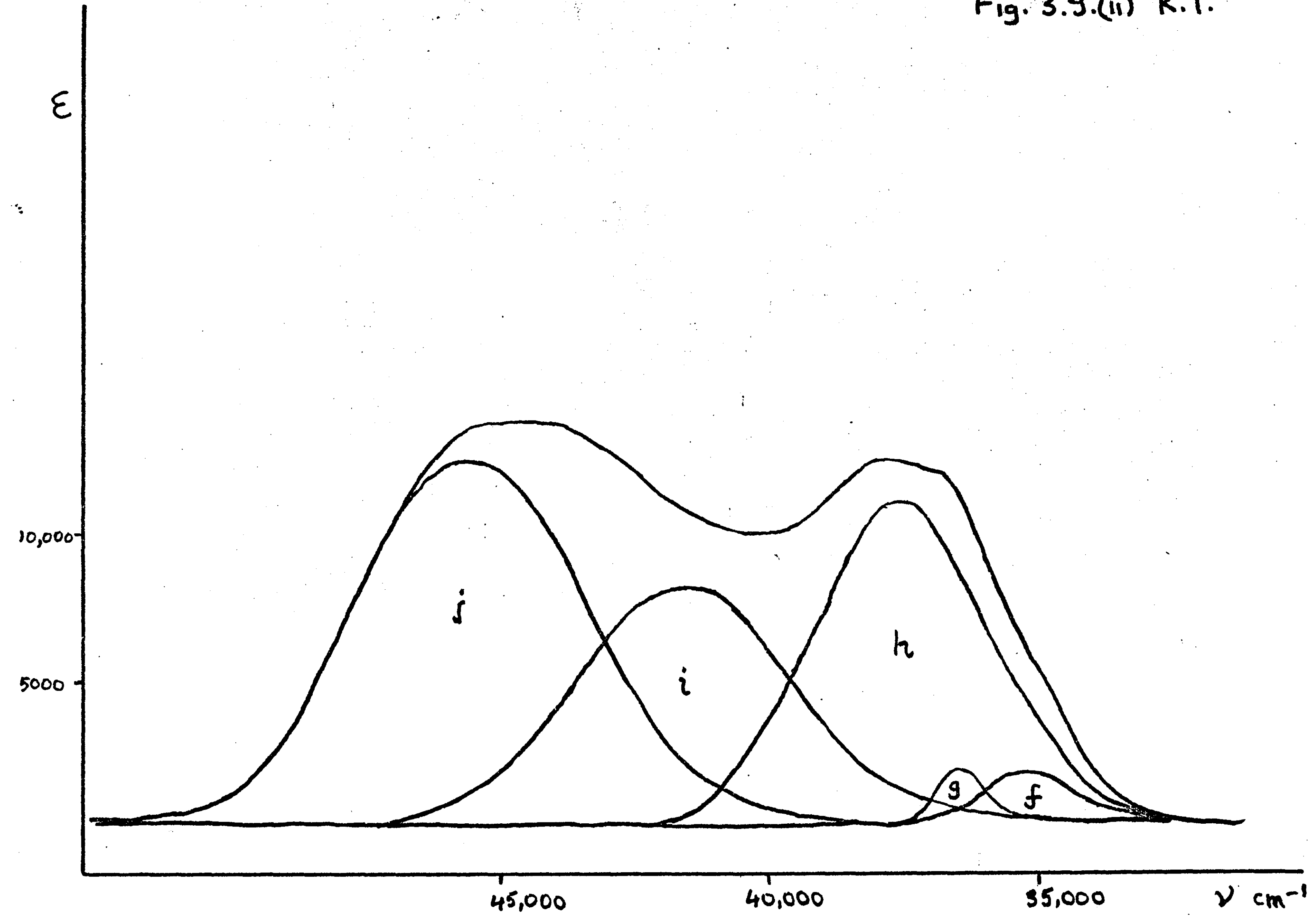


FIGURE 3.9(ii)

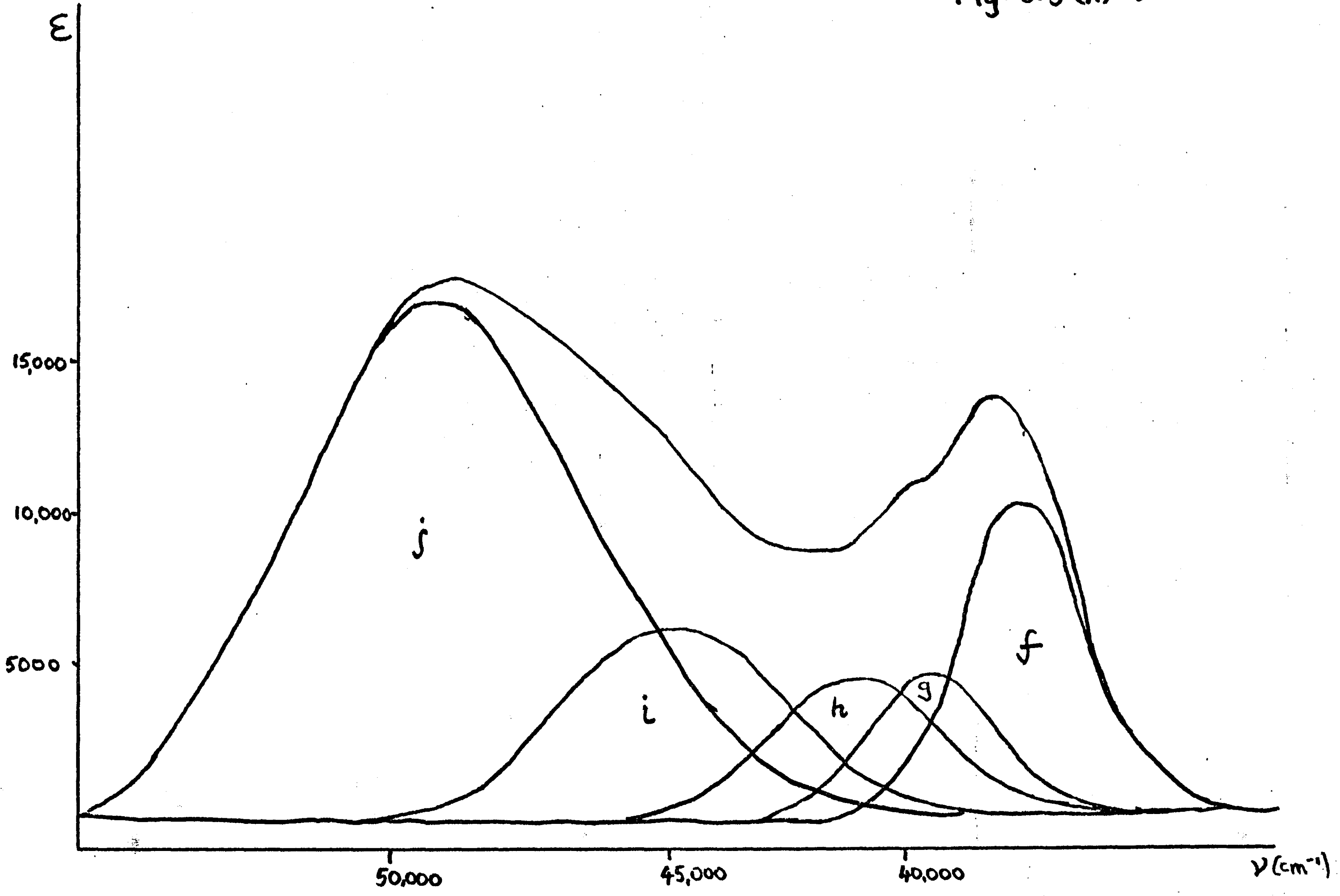
$Tdp_2Cr(CO)_4$

Gaussian Analysis of Low Temperature

Electronic Absorption Spectrum

45,000-35,000cm^{-1}

Fig. 3.9 (ii) L.T.



the degeneracy of the final state. The Einstein coefficients are characteristic of the molecule and represent the probability of absorption (B_{nm}) and emission (A_{mn}) of electromagnetic radiation. They may be related to the dipole strength D_{nm}, as the probability of a transition taking place is related to the transition moment Q_{nm}.

The spectra of $Tdp_2Cr(CO)_4$ and $(PEt_3)_2Cr(CO)_4$ were analysed from 48,000 - 25,000 cm^{-1} by considering regions 48,000 - 35,000 cm^{-1} and 35,000 - 25,000 cm^{-1} separately. $Tdp_2Mo(CO)_4$ and $Tdp(Mo(CO)_5$ were analysed from 35,000 - 25,000 cm^{-1} only and $P(OMe)_3\ _2Cr(CO)_4$ from 48,000 - 35,000 cm^{-1}. In the latter case, the form of the spectrum below 35,000 cm^{-1} did not allow meaningful analysis. The discussion of the spectra will deal mainly with the 35,000 - 25,000 cm^{-1} region which is the electronic absorption region in which it is expected that curves having low extinction coefficient occur and may be revealed by Gaussian analysis. Such weak peaks were observed to be resolved and a discussion of the parameters obtained for these curves is now given. The peaks are identified by letters which are shown on the diagrams in the figures 3.9(i) - (vii).

$Tdp_2Cr(CO)_4$: Gaussian analysis

The spectrum is shown in figure 3.9 (i) and (ii) and the parameters listed in table 3.6 (i) and (ii). The spectrum obtained at room temperature comprises two intense peaks (d and e) between 30,000 and 27,000 cm^{-1} and three very weak peaks (a, b and c) at lower energies. On cooling the sample, peaks a, b and c lose intensity and show lower oscillator strengths. These and all other changes are shown in table 3.6, both percentage and direction of the change being given. The f values of a, b and c at room temperature are characteristic of vibronic d-d transitions in these complexes ($\sim 10^{-3}$) although the possibility of forbidden charge transfer bands giving rise to vibronic bands with similar f-values cannot be discounted. The observed behaviour on cooling supports the assignment of a, b and c as d-d transitions. It is of interest to note that while ε_{max} is roughly halved in each case, the halfband width varies in its behaviour from peak to peak. Thus, it is halved for peak c while remaining approximately constant for peaks a and b. This variation of behaviour may be attributed to the effect of cooling on d-d transitions as described above when temperature effects were considered. The increase of ν_{max} on cooling expected for d-d bands is also seen and in comparison with the ν_{max} shift of peak d is large (850 cm^{-1} approximately for the former cases, 300 cm^{-1} for the latter). Peak d is assigned below as a charge transfer transition and the relative variations in ν_{max} on cooling for peaks (a, b, c) and peak d support the assignment of (a, b, c) as d-d transitions.

Peak d increases its extinction coefficient slightly on cooling, retaining its original halfband width. The oscillator strength remains approximately constant supporting assignment of peak d as a charge transfer band. The peak e is seen to decrease considerably in both intensity and halfband width on cooling and consequently the f-value is much reduced. However, consideration of the spectral outline treated by Gaussian analysis indicates that only the outline up to about 32,000 cm^{-1} is considered. Analysis of the spectrum above 32,000 cm^{-1} (figure 3.9(ii), table 3.6(ii)) shows the area between 40,000 and 30,000 cm^{-1} as one comprising a strong wide absorption h at room temperature with weaker peaks g and f at lower energies which overlap the peak e in the region of 31,000 cm^{-1} due to a long energy "tail". On cooling, the spectrum sharpens up at 35,000 cm^{-1} causing less overlap with peak e. The apparent loss of intensity observed for peak e on cooling may therefore have been caused by this sharpening of a higher energy peak. Much of the intensity of peak e at room temperature is derived from the energy tail of peak h and it is therefore not possible to use the results of the Gaussian analysis in this region. The great difference in form of peaks h, g and f seen on cooling the sample is probably attributable to the failure to consider the remainder of the spectrum. Thus we may support the assignment of peak d as a charge transfer transition and peaks a, b and c as d-d transitions using this Gaussian model while little may be said about the intermediate region 36,000 - 33,000 cm^{-1} where the overlap has not been effectively resolved. However, it may be seen that a summation of the oscillator strengths below 35,000 cm^{-1} shows a decrease on cooling while above 35,000 cm^{-1} this sum shows an increase. As the behaviour of a sum of oscillator strengths on cooling depends on the relative changes in each of the individual transitions, this observation allows us to say that the transitions above 35,000 cm^{-1} are predominantly charge transfer while those below 35,000 cm^{-1} contain a significant amount of d-d character.

$Tdp_2Mo(CO)_4$: Gaussian analysis

Details of this spectrum are given in figure 3.9(iii) and table 3.6(iii). The spectral outline is similar to that of $Tdp_2Cr(CO)_4$ although, as the overlap effects differ, Gaussian analysis is more applicable in the 35,000 - 25,000 cm^{-1} region in which we are interested. There is less overlap from higher energy peaks and the Gaussian peaks at room temperature may be compared with those appearing for the cooled sample to give a more meaningful correlation in this case.

The spectra obtained at both room temperature and low temperature are seen to comprise four Gaussian peaks. There is one intense peak c at about 28,500 cm^{-1} with a medium intensity peak d to higher energy and another b to lower energy. There is also a peak a in the 25,000 cm^{-1} region. Cooling the sample causes little change in the halfband widths of any of the peaks but the extinction coefficients of d and a decrease considerably while that of b increases slightly and of c decreases slightly. The oscillator strength of peak a ($\sim 10^{-3}$) combined with its observed behaviour on cooling the sample suggest that it represents a d-d transition. The value of ν_{max} for a is seen to shift to higher energy by about 350 cm^{-1} on cooling which must be compared with very much smaller shifts observed for b, c

FIGURE 3.9(iii)

$Tdp_2Mo(CO)_4$

Gaussian Analysis of Room Temperature

Electronic Absorption Spectrum

35,000-25,000cm^{-1}

Fig. 3.9(iii) R.T.

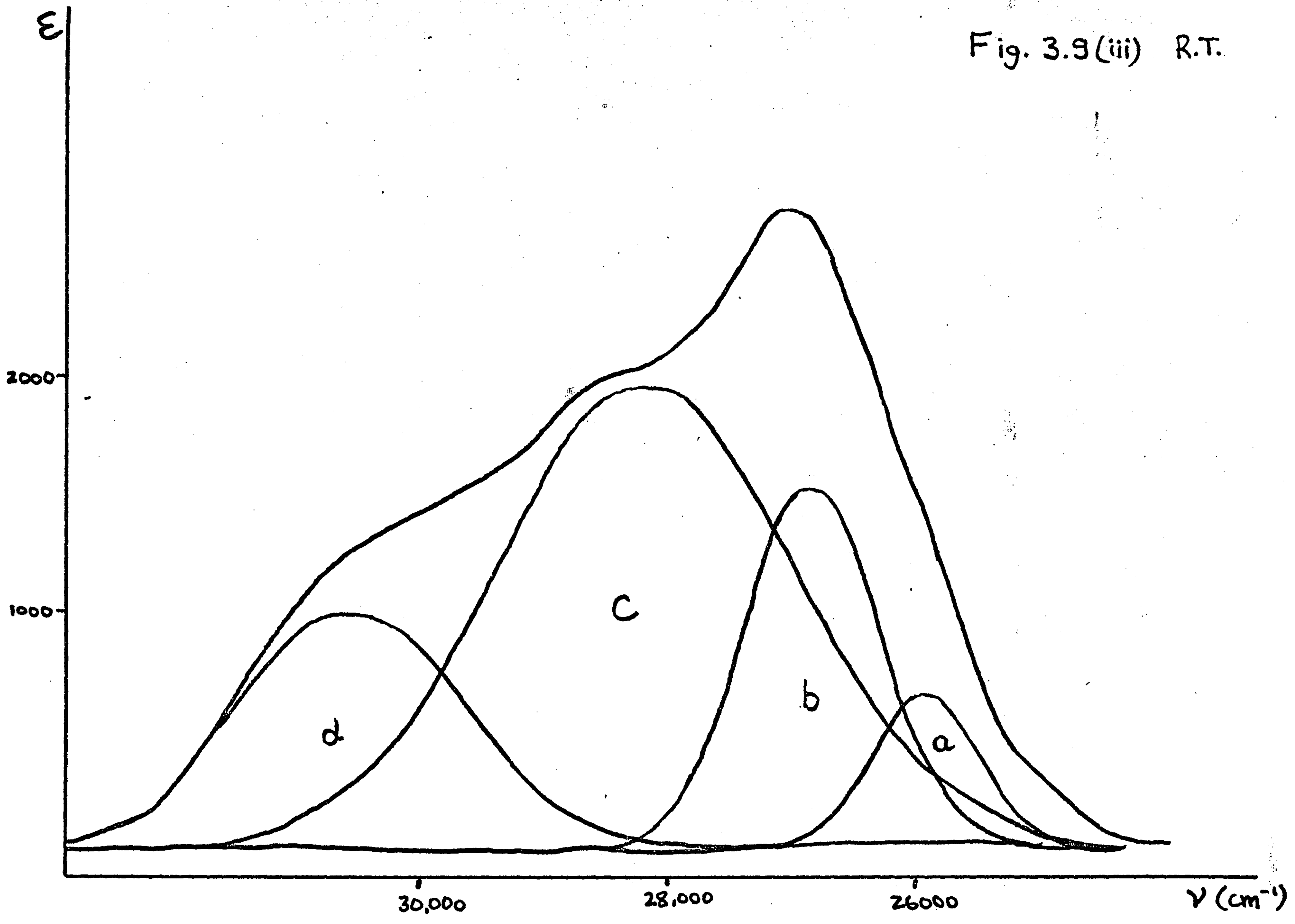


FIGURE 3.9(iii)

$Tdp_2Mo(CO)_4$

Gaussian Analysis of Low Temperature

Electronic Absorption Spectrum

35,000-25,000cm^{-1}

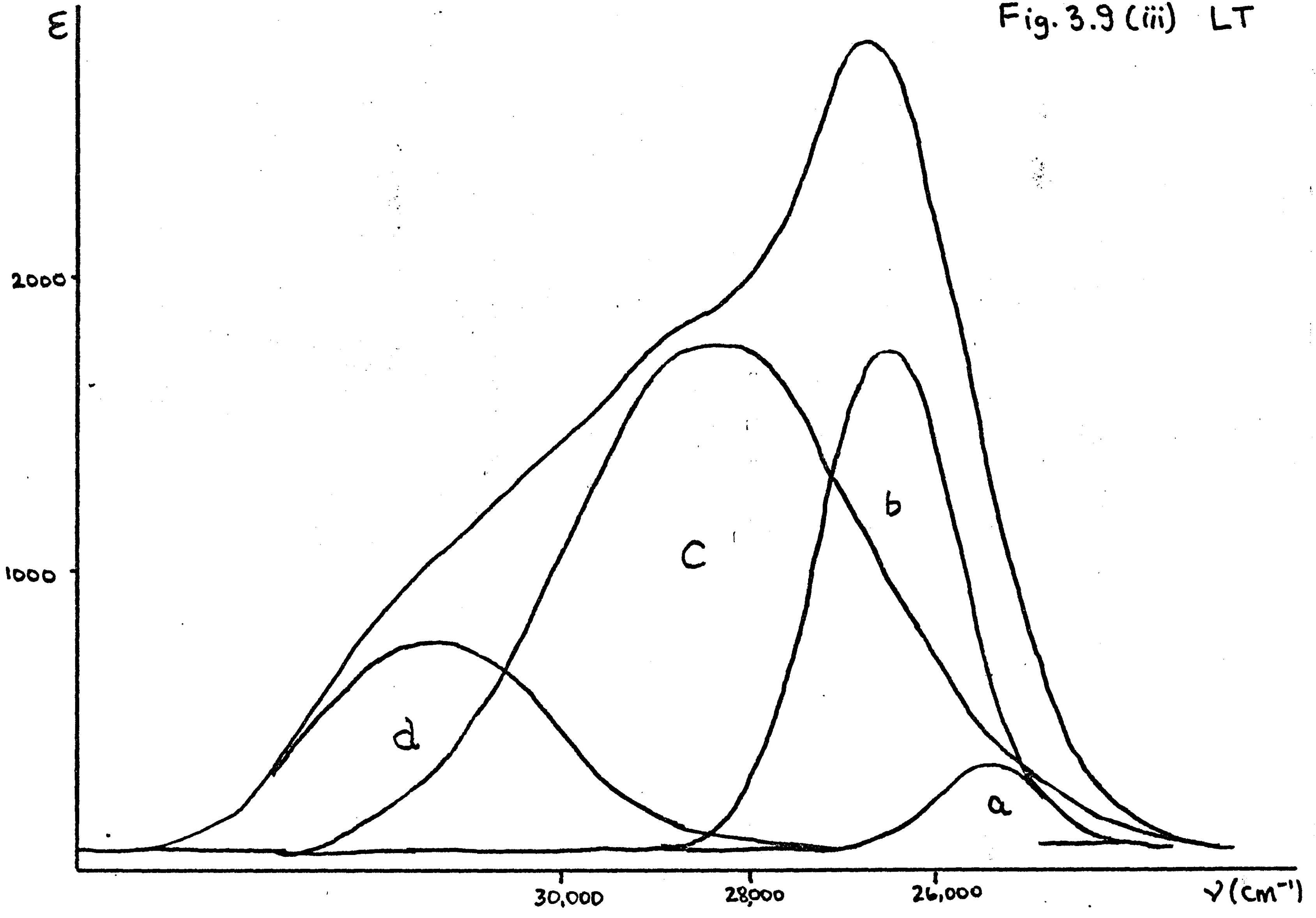


Fig. 3.9 (iii) LT

and d (100, 100 and 50 cm^{-1} respectively). This would be expected if a is a d-d transition and the other peaks are charge transfer transitions.

The oscillator strengths of peaks b and c are relatively high ($\sim 10^{-2}$) and remain fairly constant on cooling and are therefore assigned to charge transfer transitions. Peak d has a high oscillator strength at room temperature which is seen to decrease on cooling by approximately 30% of its original value. This compares with a decrease of 66% by peak a and it is probable that the behaviour of peak d is being affected by the energy tail of peaks at higher energies. Unfortunately, the spectrum at energies greater than 35,000 cm^{-1} has not been analysed but from the form of the spectrum (Appendix 3.1(xxx)) it is clear that overlapping must occur in the region of peak d. Thus the behaviour of peak d may be taken as analogous to that of peak e in the complex $Tdp_2Cr(CO)_4$ i.e. sharpening of the peak at approximately 40,000 cm^{-1} causes apparent loss of intensity on cooling.

A comparison of the analysis of spectra of complexes $Tdp_2Cr(CO)_4$ and $Tdp_2Mo(CO)_4$ allows correlation of certain peaks. Thus it is reasonable to correlate peaks d and e in the chromium complex with peaks b and c in the molybdenum complex with d and b respectively being the lowest energy charge transfer $e_g[\pi\, d_{xz}d_{yz}] \longrightarrow a_{2u}[\pi^*CO(1-4)]$ on the energy level diagram outlined above. Peaks e and c are assigned as the next charge transfer band $e_g[\pi\, d_{xz}d_{yz}] \longrightarrow e_u[\pi^*CO(1,3;\ 2,4)]$ while peaks at higher energies in both complexes (f, g, etc.) are assigned as charge transfer transitions although the donor-acceptor levels cannot be given. The relative energy ordering of the transitions depends on the coulomb and interaction energies of the orbitals and only the first two transitions may be defined for trans disubstituted complexes. It is more difficult to correlate the lower energy peaks (a, b, c) in $Tdp_2Cr(CO)_4$ and the single peak a in $Tdp_2Mo(CO)_4$ because the analysis is less reliable for these peaks and factors such as spin-orbit coupling must be considered. Peaks a in each complex show corresponding behaviour on cooling and occur at similar regions in the respective spectra. Thus peak a in the chromium derivative corresponds to a shoulder on the extreme end of the low energy tail of peak d while peaks b and c have ν_{max} closer to that of the charge transfer peak d. The position of the peak a in $Tdp_2Mo(CO)_4$ at 25,450 cm^{-1} also suggests that the corresponding peak in the chromium complex will be at a lower energy than this as the d-level splittings will be greater in the molybdenum complex. However, as the d-d transition energies depend on the ordering and energies of at least four levels in complexes with D_{4h} symmetry (see figure 1.2) it is not possible to compare two such environments with any confidence. Gaussian analysis is therefore indicative but inconclusive in the low energy region that the peaks a in both $Tdp_2Cr(CO)_4$ and $Tdp_2Mo(CO)_4$ represent d-d transitions and it is interesting to note that the ratio f(300)/f(90) for peaks a is 2.5 and 2.9 for the chromium and molybdenum complexes respectively. This result would be expected for d-d transitions arising from an analogous vibronic effect in two similar complexes. In both complexes, the region below 35,000 cm^{-1} is seen to have a lower value for the summation of oscillator strengths at low temperature than at room temperature. This is taken as evidence of some d-d character in this region, although the main peaks are assigned to charge transfer transitions.

TdpMo(CO)$_5$: Gaussian analysis

The monosubstituted complexes in general have spectra showing a high degree of overlap in the 35,000 - 25,000 cm^{-1} region. Consequently, Gaussian analysis is difficult and this complex is the only monosubstituted derivative treated in this way. Although overlap is significant, resolution of the main peaks is fairly clear from the spectral outline allowing the analysis to be effected. For details of the spectral parameters and outline see Appendix 3.1(xii) figure 3.9(vi) and table 3.6(vi).

Five Gaussian peaks are combined to reproduce the spectral outline at both room temperature and low temperature and as the spectra obtained for different temperatures show a reasonable correspondence, it is possible to correlate the Gaussian analyses. There are three intense peaks _e_, _c_ and _b_ at energies 33,850, 30,850 and 28,350 cm^{-1} respectively at room temperature and two very weak peaks one, _d_, buried in peak _c_ and another, _a_, occurring on the low energy tail of peak _b_. Cooling the sample gives a similar spectrum having three intense and

FIGURE 3.9(vi)

TdpMo(CO)$_5$

Gaussian Analysis of Room Temperature

Electronic Absorption Spectrum

35,000-25,000cm^{-1}

Fig. 3.9 (vi) R.T.

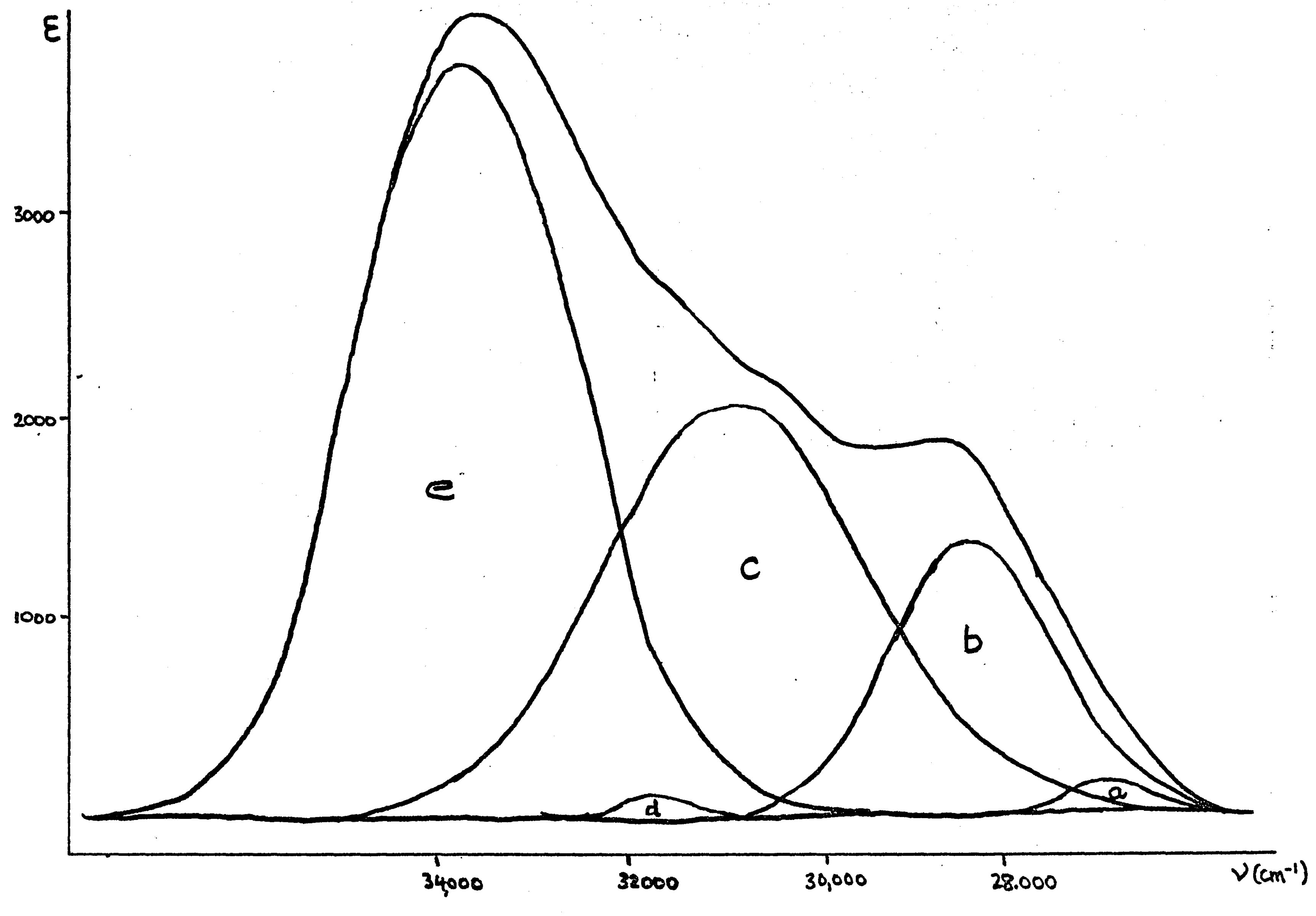


FIGURE 3.9(vi)

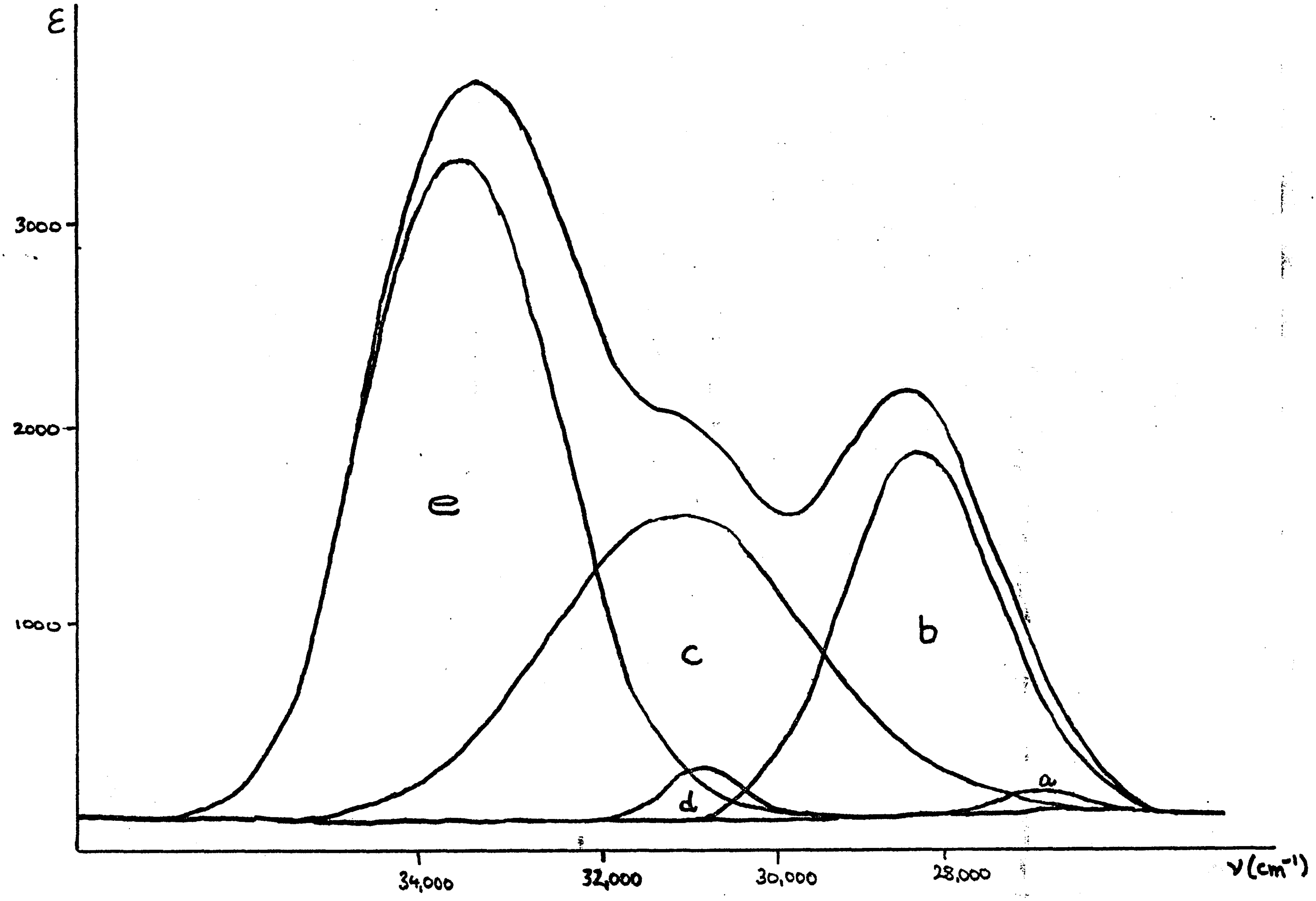
$TdpMo(CO)_5$

Gaussian Analysis of Low Temperature

Electronic Absorption Spectrum

35,000-25,000cm^{-1}

Fig. 3.9 (vi) L.T.



two weak peaks although peaks d and c are seen to alter their relative positions in the two analyses. The positions for peak d at room temperature and low temperature respectively are 31,800 and 30,950 cm^{-1} and for peak c are 30,850 and 31,150 cm^{-1}, the other parameters for these peaks being consistent with their assignment to these particular frequency values. This is probably an anomaly of the analysis as the peak d is a very weak peak arising from a shoulder in the observed spectral outline at the position of peak c. The significance of peak d will not be discussed in view of its anomalous position coupled with its low intensity although this should have little effect on the discussion of the parameters of peak c except, of course, its ν_{max} position.

Peak a has a very low oscillator strength at room temperature ($\sim 10^{-3}$) and while it remains approximately constant on cooling the sample, this is principally due to an increased spread in the transition as the ε_{max} decreases. This leads to the assignment of peak a as a d-d transition and again, a larger shift in ν_{max} is observed for this peak than for peaks b, c and e which are assigned as charge transfer bands (see below). Comparison of peak a in this complex with peak a in $Tdp_2Mo(CO)_4$ shows the former to occur at higher energy than the latter (26,900 and 25,450 cm^{-1} respectively). This is expected as the phosphine exerts a lower ligand field than carbonyl, causing decrease in the d-d transition energies as the degree of substitution increases.

The peak b has a high oscillator strength at room temperature ($\sim 10^{-2}$) and cooling causes sharpening of the peak and an increase in

ε_{max}. The f-value increases from 0.014 to 0.018 which is consistent with assignment as the first charge transfer band $e[\pi\, d_{xz} d_{yz}] \longrightarrow a_1[\pi^* CO(1\text{-}4)]$. Comparing this peak with the first charge transfer assigned for $Tdp_2Mo(CO)_4$ shows that it occurs at slightly higher energy in the monosubstituted complex (28,350 versus 26,750 cm^{-1}). This may be correlated with the smaller π-bonding effect in phosphine-metal bonds as compared to carbonyl metal bonds. These observations support the requirement of the energy level diagrams of figures 3.2 and 3.3 for the first charge transfer transition to be to the radial carbonyls in both mono- and disubstituted complexes. This was previously observed by Walker(44) on the basis of spectral outlines of room temperature spectra. The ε_{max} of the peaks assigned as the first charge transfer transition in both mono- and disubstituted derivatives are comparable and this was quoted as evidence for the assignment as d-d peaks were expected to be more intense in the noncentrosymmetric monosubstituted complexes. However, consideration of possible vibronic effects which have produced d-d peaks with ε_{max} significantly higher than those quoted (up to 3,000 l $mole^{-1}$ cm^{-1} versus 1,500 l $mole^{-1}$ cm^{-1}) and general caution concerning assignments from room temperature spectra only had questioned the validity of these assignments which are confirmed by the present work. Evidence from both the spectral outline and Gaussian analyses of spectra taken at room temperature and low temperature clearly indicates that peak <u>b</u> of both $Tdp_2Mo(CO)_4$ and $TdpMo(CO)_5$ is charge transfer in nature.

The remaining two peaks of TdpMo$(CO)_5$ to be considered c and e each show a slight fall in oscillator strength on cooling the sample, the extinction coefficient decreasing in each case and the halfband width decreasing for e while remaining approximately constant for peak c. It is expected that the intensity of peak e will be affected by the energy tail of higher energy peaks although it has a high oscillator strength at room temperature (0.05) which remains high at low temperature (0.04). Each of the peaks c and e can be assigned as charge transfer transitions on the basis of their high f-values as the decrease in oscillator strength on cooling is insufficient to support a d-d assignment for peaks of such high extinction coefficient (3,780 for e, 2,090 for c) and high oscillator strengths. It is interesting to compare the spectra of the mono- and trans disubstituted Tdp derivatives in the region of 34,000 cm^{-1} where their spectra differ considerably. The trans disubstituted complexes have relatively low extinction coefficients in this region which principally comprises overlap of the charge transfer peaks on each side while monosubstituted complexes have high extinction coefficients at approximately 34,000 cm^{-1} due to an intense peak which occurs as a shoulder on the higher energy charge transfer peak. This result is general for both Tdp and phosphine complexes of chromium, molybdenum and tungsten carbonyl derivatives, the phosphite complexes showing rather complicated behaviour which will be discussed later. However, considering the molecular orbital energy level diagrams in figures 3.2 and 3.3 and the information in tables 3.2 and 3.3 it is seen that the monosubstituted complex has more allowed transitions than the trans disubstituted complex and further that the molecular orbital $e\pi^*CO(5)$ involving the axial carbonyl occurs at energies above the $(p_x,p_y - \pi^*)$ interaction level $e\pi^*CO(1,3;\ 2,4)$. This implies that metal ligand charge transfer transitions into this $e\pi^*CO(5)$ orbital will occur at energies fairly close to those of the lower charge transfer bands in monosubstituted complexes while trans disubstituted complexes which have no such orbital will have no transitions of corresponding energy. This would cause the spectral outlines to differ in the manner observed.

$(PEt_3)_2Cr(CO)_4$: Gaussian analysis

The spectral characteristics of this complex are given in figure 3.9(iv), (v) and table 3.6(iv), (v). The spectrum below 35,000 cm^{-1} showed the best resolved outline treated by Gaussian analysis. As previously, however, the region of the spectrum at about 34,000 cm^{-1} is analysed without reference to possible energy tail overlaps and consequently, results in this region must be considered unreliable. The spectrum at lower energies is straightforward, the room temperature spectrum showing two strong peaks d and b occurring at 30,750 and 27,350 cm^{-1} respectively and another fairly intense peak e at 33,650 cm^{-1} in the "overlap region". Cooling the sample gives a spectrum in which the two peaks b and d remain the dominant features while peak e is seen to decrease significantly. Two further peaks c

FIGURE 3.9(iv)

$(PEt_3)_2Cr(CO)_4$

Gaussian Analysis of Room Temperature

Electronic Absorption Spectrum

35,000-25,000cm^{-1}

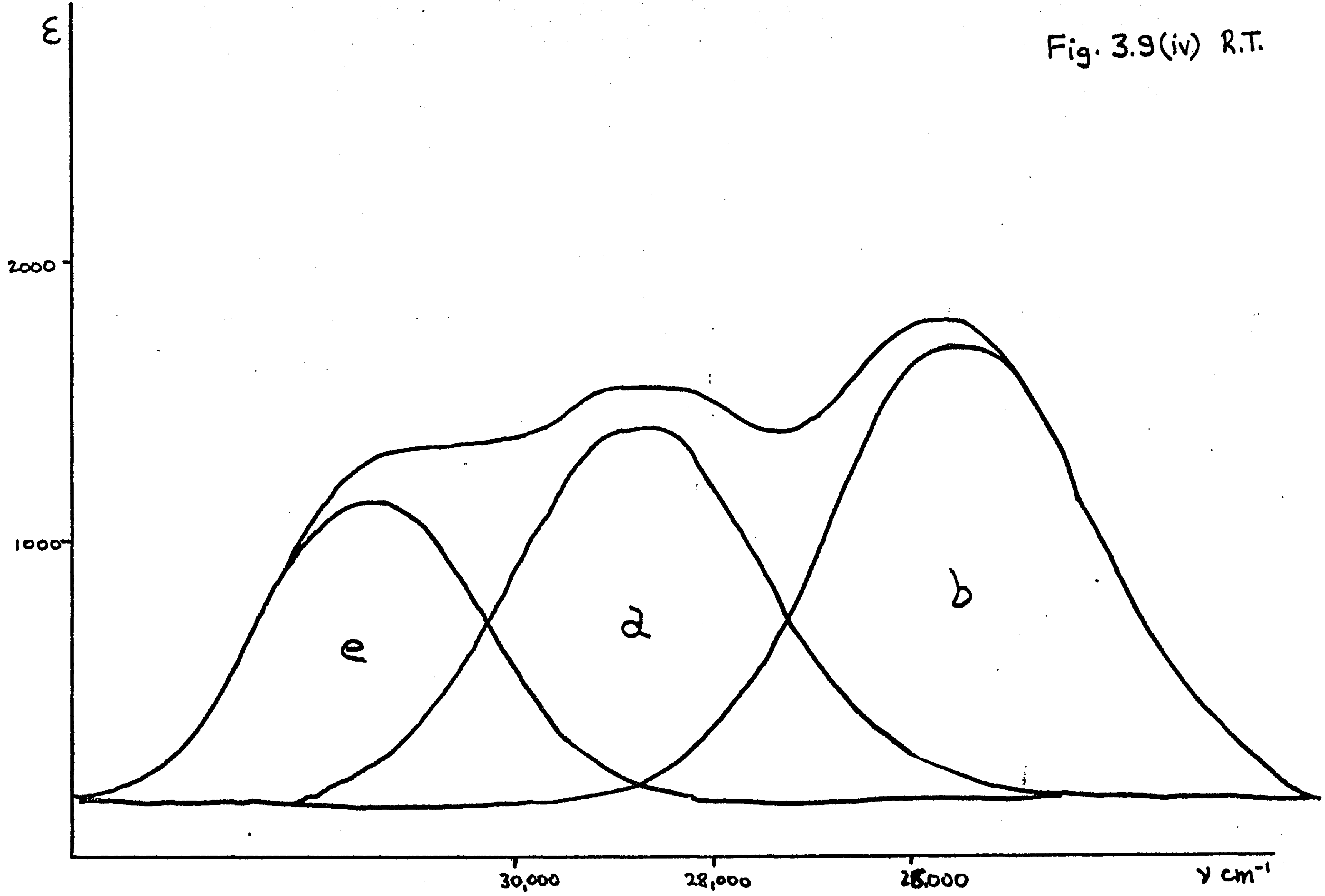


Fig. 3.9(iv) R.T.

FIGURE 3.9(iv)

$(PEt_3)_2Cr(CO)_4$

Gaussian Analysis of Low Temperature

Electronic Absorption Spectrum

35,000-25,000cm^{-1}

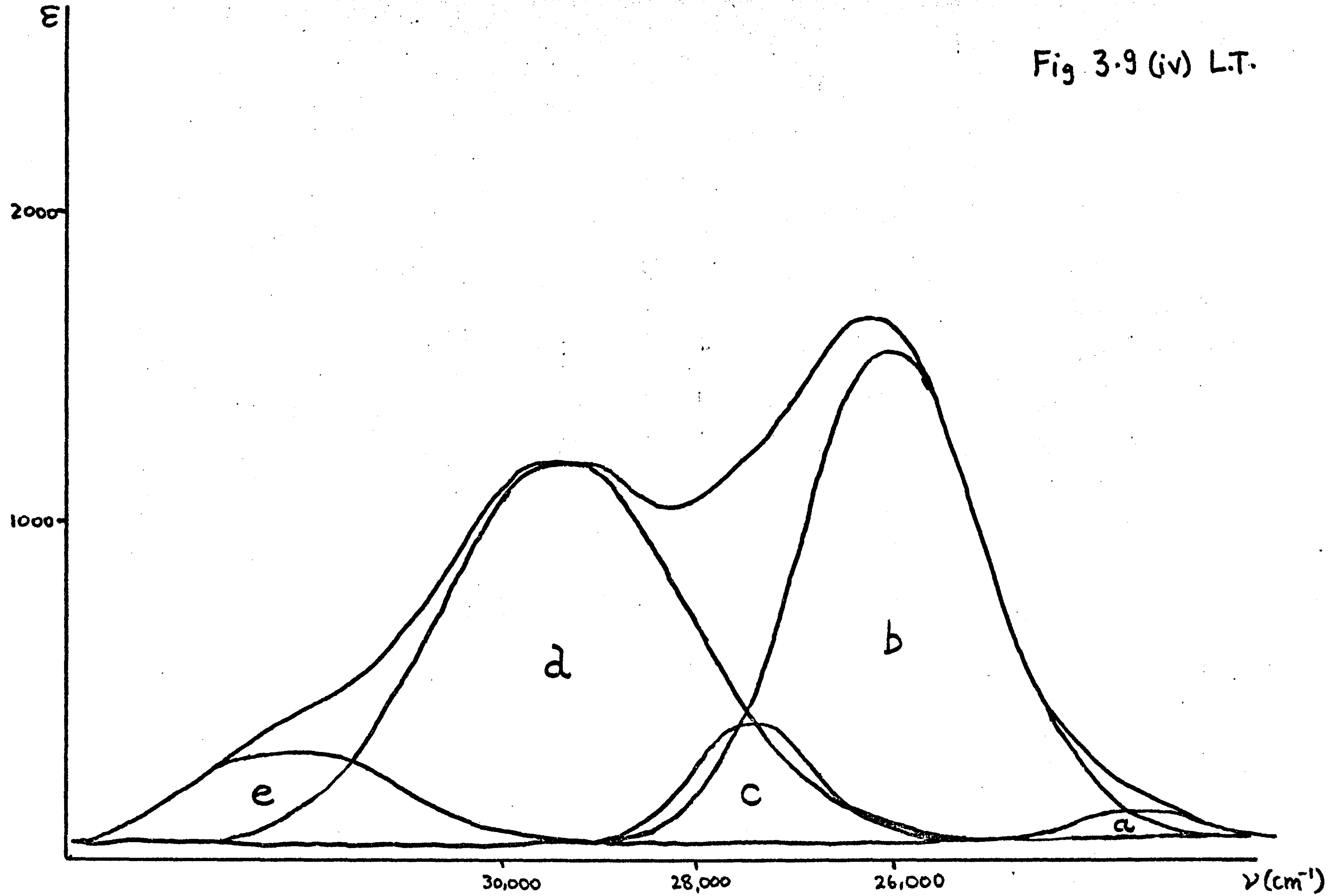


Fig 3.9 (iv) L.T.

FIGURE 3.9(v)

$(PEt_3)_2Cr(CO)_4$

Gaussian Analysis of Room Temperature

Electronic Absorption Spectrum

45,000-35,000cm^{-1}

Fig. 3.9 (v) R.T.

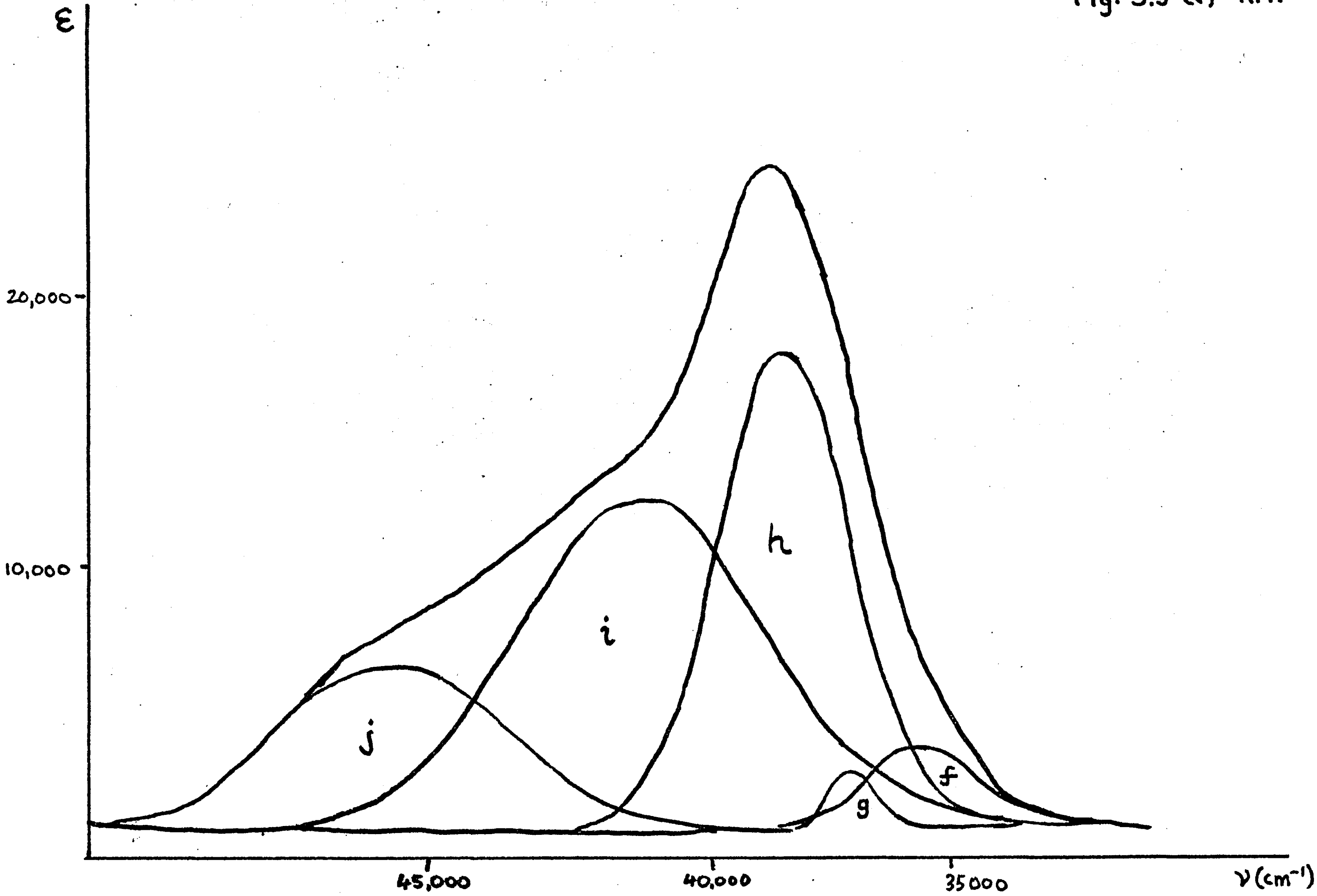


FIGURE 3.9(v)

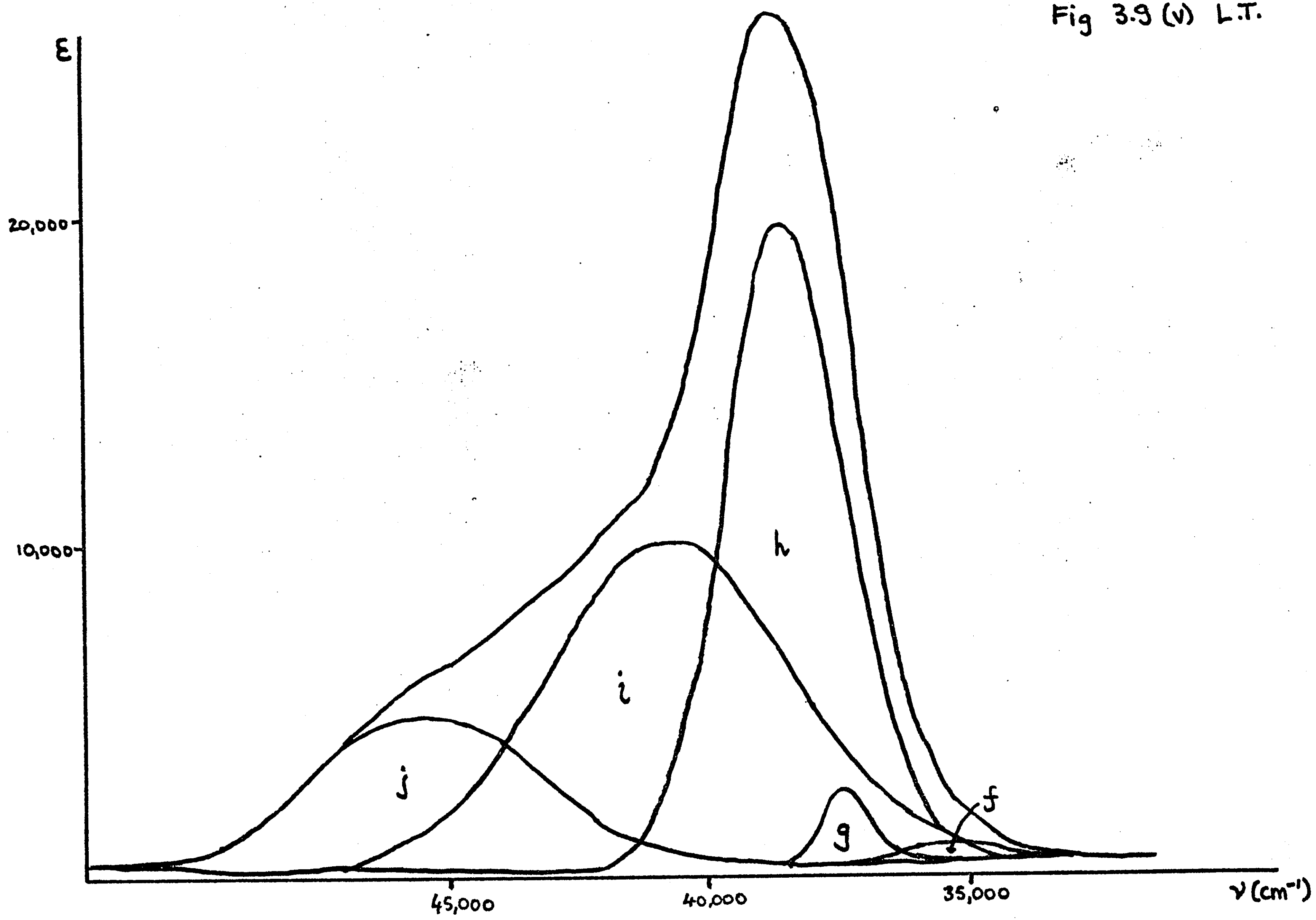
$(PEt_3)_2Cr(CO)_4$

Gaussian Analysis of Low Temperature

Electronic Absorption Spectrum

45,000-35,000cm^{-1}

Fig 3.9 (v) L.T.



and a are observed at 28,800 and 24,500 cm^{-1} respectively which have no corresponding peaks in the room temperature spectrum.

The peak e is clearly affected by overlap as may be seen from the spectrum analysed at higher energies. Thus the spectral outline at room temperature shows considerable overlap of peaks h and f into the region of peak e while at low temperature, the effect of cooling is to reduce the overlap significantly. It is therefore expected that the peak e will lose intensity on cooling and no assignment can be made on this basis. It should be noted that the spectrum of this complex provides a further example of relatively low extinction coefficient, for trans disubstituted complexes in the intermediate spectral region around 34,000 cm^{-1}. The parameters derived from the spectrum of this complex and their observed behaviour on cooling show some unexpected results. Thus peaks b and d both show a decrease in oscillator strength on cooling, sufficiently large in the case of peak b to suggest assignment as a d-d transition despite the large oscillator strength (0.028). The decrease in f-value for peak d is reasonably slight and due entirely to a small decrease in ε_{max}. The position of ν_{max} remains approximately constant suggesting a charge transfer transition although no sharpening of the band is seen. Peak b shows a decrease of 10% in ε_{max} and a decrease of 30% in the halfband width which gives a 40% decrease in f-value on cooling. Comparison of the spectra with those of the disubstituted Tdp derivatives discussed above and other disubstituted chromium phosphine derivatives suggests that the two partly resolved peaks in the spectrum at frequencies 30,750 and 27,400 cm^{-1} (30,800 and 27,450 cm^{-1} at low temperature) are charge transfer bands. The complexes $(PPr^{i}_{3})_{2}Cr(CO)_{4}$ and $(PBu^{n}_{3})_{2}Cr(CO)_{4}$ clearly show two analogous peaks which increase in extinction coefficient on cooling and show general charge transfer character. Further, if the first charge transfer in the triethylphosphine complex is at 30,750 cm^{-1} (i.e. peak *d*) it would be difficult to explain why it is shifted from the lowest energy charge transfers assigned for the triisopropylphosphine and trinbutylphosphine complexes - 27,000 and 27,200 cm^{-1} respectively. It is significant that peak *b* of the triethylphosphine derivative has ν_{max} at 27,400 cm^{-1} which might be expected for this complex on the basis of analogy with these other similar complexes. Comparing the room temperature and low temperature spectral analyses of $(PEt_{3})_{2}Cr(CO)_{4}$, it seems unlikely that peaks *c* and *a* should be seen only at low temperature as is observed, since peak *a* correlates with the d-d transition in the Tdp complexes having a similar f-value to these (8×10^{-4}) and peak *c* is sufficiently intense at low temperature to be expected to occur at room temperature also. It would appear that a peak in a position similar to peak *c* should be included in the Gaussian analysis of the room temperature spectrum and possibly a peak corresponding to peak *a* should be included. This would have the effect of decreasing the values of the oscillator strengths of peaks *b* and *d* at room temperature by reducing their halfband widths.

These considerations underline the necessity to treat Gaussian analyses with care, principally using it as an additional technique while always taking account of the general trends in analogous complexes as derived from their spectral outlines at room temperature and low temperature.

$[P(OMe)_3]_2Cr(CO)_4$: Gaussian analysis

This complex has an unresolved outline below 35,000 cm^{-1} which could not be analysed by Gaussian peaks. As this derivative is expected to have a structure similar to that of the disubstituted Tdp and triethylphosphine complexes discussed above and to be electronically similar, the curve below 35,000 cm^{-1} is considered as comprising two charge transfer peaks comparable to those observed in the more resolved spectra of these other complexes, possibly along with other, weaker peaks the origin of which is less understood and which therefore cannot be discussed. The spectral outline and other data for this complex are to be found in Appendix 3.1(xix), figure 3.9 and table 3.6(vii). The unresolved nature of this spectrum is attributed to a small energy difference between the two lowest charge transfer peaks which produces sufficient overlap to eliminate peak resolution. This and other similar spectra will be discussed in fuller detail when the spectral outlines of all the complexes studied are compared and partly assigned below. The region of the spectrum of this complex analysed by Gaussian peaks extends from 35,000 cm^{-1} to 50,000 cm^{-1} and is probably unreliable at higher energies due to solvent absorption effects.

FIGURE 3.9(vii)

$[P(OMe)_3]_2Cr(CO)_4$

Gaussian Analysis of Room Temperature

Electronic Absorption Spectrum

45,000-35,000cm^{-1}

Fig. 3.9 (vii) RT

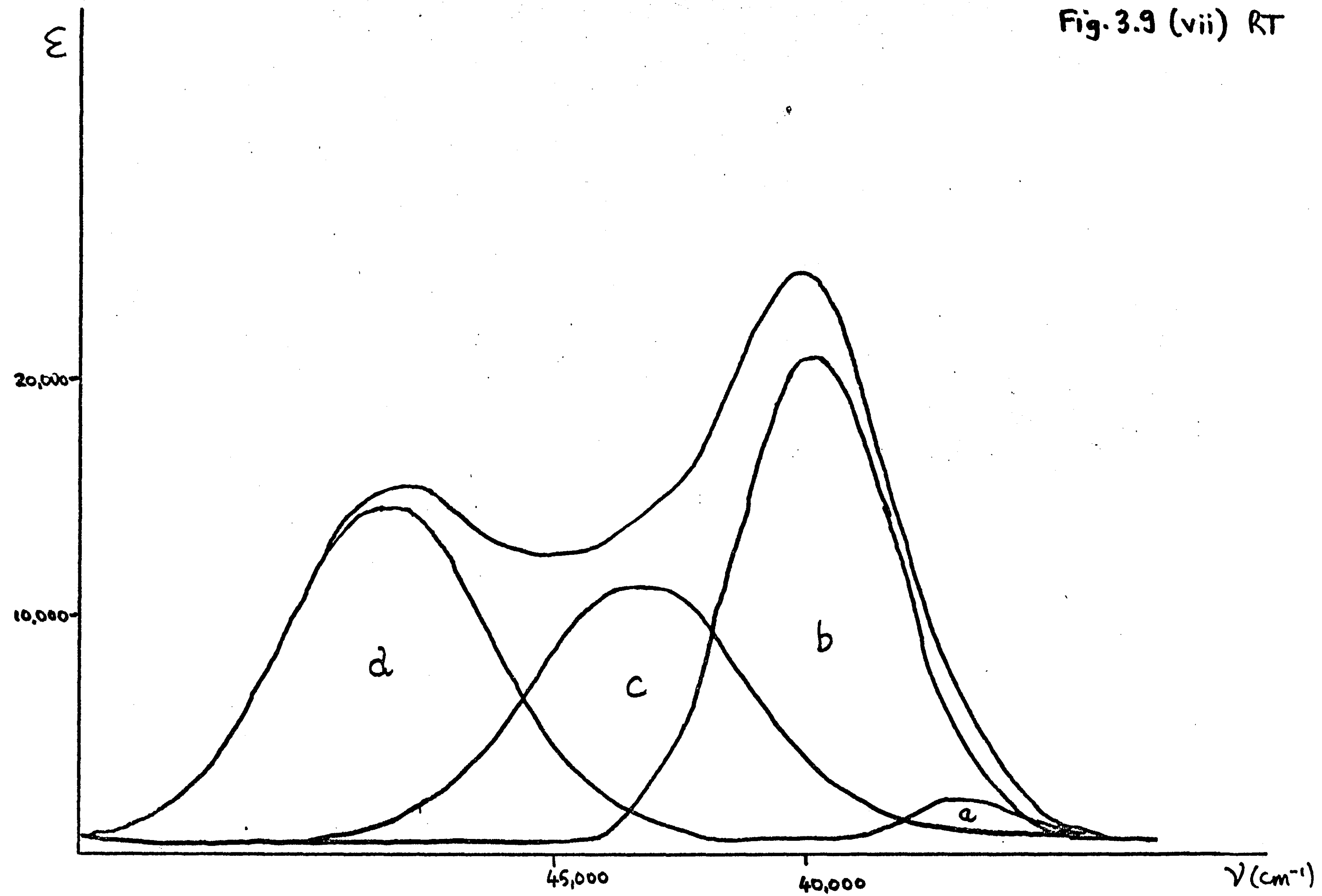


FIGURE 3.9(vii)

$[P(OMe)_3]_2Cr(CO)_4$

Gaussian Analysis of Low Temperature

Electronic Absorption Spectrum

45,000-35,000cm^{-1}

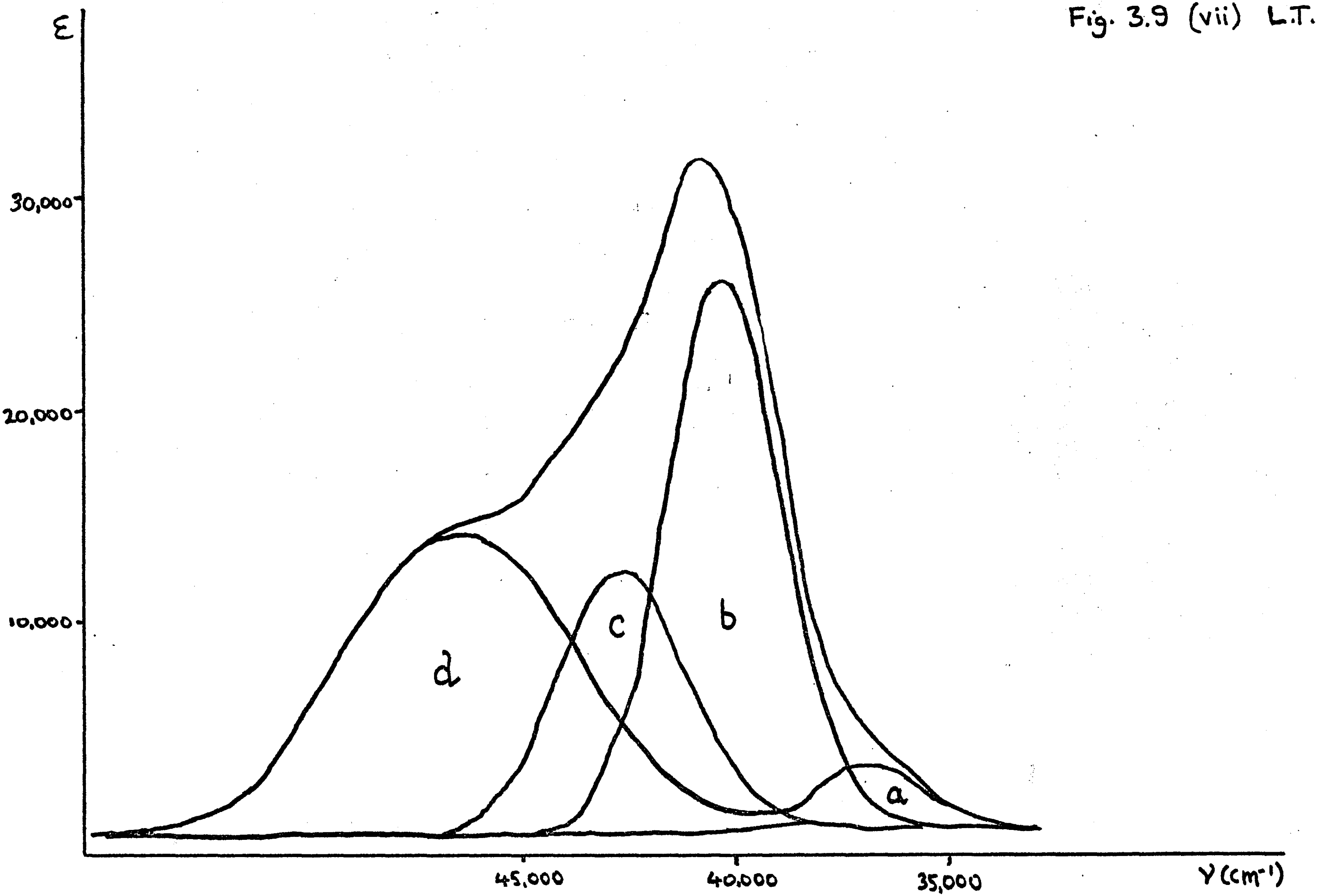


Fig. 3.9 (vii) L.T.

Peak a at 36,600 cm^{-1} has a high oscillator strength which increases slightly on cooling indicating a charge transfer transition as expected in this region. Peak b has an ε_{max} value of 25,100 l cm^{-1} $mole^{-1}$ at room temperature and an oscillator strength of 0.48. It is certainly a charge transfer band although the Gaussian peak behaviour on cooling shows a decrease in ε_{max} and halfband width and consequently in f-value. This may best be explained as the result of using Gaussian distributions without reference to overlap effects of higher energy peaks or solvent absorption. It is important when discussing a Gaussian analysis of any spectral region to know the spectral outline at higher energies if such an outline overlaps the region being discussed. Thus it is possible to derive more consistent results for energies intermediate between charge transfer and d-d spectral regions than it is in the charge transfer region bounded to higher energies by a region of unknown overlap effect.

Conclusions

From the study of Gaussian analysis as applied to the above complex spectra some important results may be derived. These analyses require careful study and may be misleading if obtained for only one complex of a possible series. They can be used to uncover peaks masked by more intense bands although very often the quantitative values obtained for intensity and oscillator strengths are too small to be compared meaningfully at different temperatures. From the spectra analysed, assignments have been derived and are compared with results

TABLE 3.7

COMPLEX	ASSIGNMENT	REF. 44 (c)		THIS WORK (d)							
				GAUSSIAN				NON GAUSSIAN			
				R.T.		L.T.		R.T.		L.T.	
		ν	ε	ν	ε	ν	ε	ν	ε	ν	ε
$Tdp_2Cr(CO)_4$	d → d	24,700	370	25,150	200	25,000	90	24,200	190	(b)	(b)
	First C.T.	27,600	1350	27,250	1050	27,550	1080	27,450	1080	27,600	1120
	Second C.T.	29,400	1130	29,600	(a)	29,100	(a)	29,500	890	29,000	920
$Tdp_2Mo(CO)_4$	d → d	24,600	460	25,450	670	25,800	280	24,420	420	24,430	240
	First C.T.	27,200	2430	26,750	1540	26,850	1640	27,000	2800	27,100	2800
	Second C.T.	30,200	2000	28,500	1940	28,600	1680	29,260	2060	29,580	1800
$TdpMo(CO)_5$	d → d	25,600	580	26,900	200	27,300	150	(b)	(b)	(b)	(b)
	First C.T.	29,200	2330	28,350	1390	28,600	1920	28,900	1900	28,950	2400
	Second C.T.	31,650	3000	30,850	2090	31,150	1620	31,450	2650	31,000	2150

(a) Overlap effects give misleading figures.

(b) Peak not observed.

(c) Beckmann DK.2A Spectrophotometer (λ mμ vs. Absorbance). Cyclohexane Solvent.

(d) Pye Unicam SP 700C Spectrophotometer (ν cm^{-1} vs. Absorbance). Methylcyclohexane : Isopentane 3:2 mixture.

obtained in this study by considering only spectral outlines at room temperature and low temperature without Gaussian analysis and also with results obtained previously[44] from spectra taken at room temperature only. The values are listed in table 3.7. Results obtained from a treatment of the spectral curves without Gaussian analyses are consistent for studies A and B taking account of the difference in conditions and instrumentation. It is seen, however, that Gaussian analyses give ν_{max} values generally higher than those obtained directly from spectra, although both d-d transitions quoted show the reverse effect. This is a consequence of the band overlap and it is generally true that overlap of two peaks of approximately equal intensity will cause the lower to have an apparent ν_{max} value higher than its true value due to the intensity produced by the overlap of the low energy and high energy tails of the higher and lower bands respectively. Overlap of a very small band with one of higher intensity will give no such effect and may cause the apparent ν_{max} to be lower than its true value as seen in the table.

ROOM TEMPERATURE AND LOW TEMPERATURE SPECTRA OF THE COMPLEXES

The study of the technique of Gaussian analysis was undertaken as a feasibility study for its possible use with spectra recorded for complexes $LM(CO)_5$ and trans $L_2M(CO)_4$ M = Cr, Mo, W; L = $P(OMe)_3$, $P(OEt)_3$, $P(OPr^i)_3$, PPr^i_3, PBu^n_3. The results obtained and the critique of the approach in general combined with the form of the spectra obtained for these latter complexes suggested that in the majority of cases, Gaussian analysis would be either impossible to apply or meaningless as a result of overlap, approximations used and the other factors discussed above. However, study of the spectral outlines obtained indicated that some assignments could be made without the use of Gaussian analysis by observing the effect on the spectral outline of changing the sample temperature and by comparing and relating the spectra obtained for the entire series using a standard approach to electronic absorption spectra. The spectral outlines are reproduced in Appendix 3.1 and values for ε_{max} and ν_{max} given in tables 3.4 and 3.5. It should be noted that the values of ε_{max} and ν_{max} given are obtained directly from a plot of ε versus ν, no correction being made for peak overlap. As overlap is approximately equal in comparable spectra and is accounted for qualitatively as far as possible, any interpretations and assignments should be consistent in the series. The general outlines of the spectral curves have been given under certain categories in figures 3.4, 3.5 and 3.6 and the spectra of the complexes are now discussed in relation to these outlines.

Monosubstituted Complexes

The only previous report of the electronic spectra of Group VI metal carbonyl monosubstituted complexes containing the ligands discussed here was in a paper by Darensbourg and Brown[74] who presented the spectra of $P(OMe)_3Mo(CO)_5$ and $P(OEt)_3Mo(CO)_5$ at room temperature only. The spectra of the other monosubstituted complexes in this work are reported for the first time at both room temperature and low temperature. These spectra may best be discussed in two main groups, treating complexes with phosphite and phosphine ligands separately. It may be seen from the spectral outlines that chromium complexes in each group generally have less resolved spectra than corresponding molybdenum or tungsten complexes. Normally, however, the resolution is sufficient to allow discussion of these chromium spectra and comparison with more resolved analogous spectra supports the relevance of such discussions.

The spectra of the phosphite derivatives in the region of intermediate intensity 35,000 - 25,000 cm^{-1} have the general form shown in figure 3.5 for $P(OEt)_3Mo(CO)_5$. Thus, there is a peak at energies just below 35,000 cm^{-1}, peak C, which shows an increase in extinction coefficient on cooling the sample along with sharpening of the peak. This band is observed as a partly resolved peak in molybdenum and tungsten complexes and as an unresolved shoulder in chromium complexes. In the former case, the effect of cooling is to increase the resolution of the peak and as the peaks at higher energies are expected to sharpen and thus contribute less to the intensity of peak C at low temperature, the increase in ε_{max} of peak C leads to its assignment as a charge transfer transition. For chromium complexes, the intensity variation on cooling is less obvious due to the greater overlap but the uncorrected extinction coefficient increases in all cases on cooling giving a more clearly resolved shoulder and this suggests assignment as the charge transfer peak analogous to the resolved peak C in molybdenum and tungsten complexes.

The behaviour of ν_{max} on cooling as used above in Gaussian analysis to support a d-d (increase in ν_{max} on cooling) or a charge transfer (ν_{max} constant on cooling) assignment is less useful for studies of plain spectral outlines as changes in overlap effects are probably more effective in altering the apparent ν_{max} value than are vibrational band effects. Thus although the peaks assigned as charge transfer transitions, such as peaks C discussed above, show little change in their ν_{max} values, this is also seen to be the case for peaks assigned as d-d transitions (see below). From table 3.4 it may be seen that the peak at 34,450 cm^{-1} in the spectrum of $P(OMe)_3Cr(CO)_5$ appears to move significantly to lower energy on sample cooling (33,500 cm^{-1}). It is generally true that complexes (both mono- and trans disubstituted) of trimethylphosphite are much less soluble in the hydrocarbon solvent used for low temperature spectral studies (methylcyclohexane/isopentane) than are complexes of the other phosphites used. The solubility of these trimethylphosphite complexes in other solvents forming glasses at liquid nitrogen temperatures (e.g. ether/isopentane/ethanol) is found to be similar to that in the hydrocarbon glass and hence spectra of these complexes taken at low temperatures are found to be affected by scattering caused by the tendency of the complex to crystallise out of the glass. The solubility of the complexes increases in order $Cr < W < Mo$ and the anomalous position of the peak C in $P(OMe)_3Cr(CO)_5$ at low temperature may be due to the effect of an increase in absorption by scattering which causes a distortion of the spectral outline.

This problem of low solubility of the complexes in the low temperature glass coupled with the general difficulty of obtaining reliable, reproducible spectra led to the investigation of an approach to the use of optimum concentrations in running low temperature spectra. As the technique used to obtain the spectra is time consuming, it is of value to obtain the maximum amount of information from any one complex concentration. The use of a single path length (0.01 cm) is found to be most convenient as it eliminates the necessity to dismantle the cell to replace the spacer between the plates (see discussion of experimental procedure above for the importance of this). The spectrum of a single complex was thus obtained at various concentrations using a single path length (0.01 cm) and graphs of ε versus ν drawn for each concentration. Comparison of these graphed outlines indicates a difficulty inherent in discussing the type of spectral outlines being studied. If the concentration is low, the extinction coefficient of peaks appearing as shoulders may be insufficient to produce a detectable shoulder. However, as the concentration is increased in an attempt to observe these shoulders, the more intense peaks on which the shoulders are seen also gain intensity and if the concentration is too high, the gradient of the plot ($\varepsilon - \nu$) may be sufficiently high to cause difficulty in distinguishing a weak shoulder from spurious noise or from irregularities arising from experimental error in the position of the points. It is found that there is a relatively small concentration range in which peaks of intermediate intensity occurring in energy region 35,000 - 25,000 cm^{-1}, may be observed satisfactorily. This concentration range is 1.25 - 1.75 x 10^{-2}M for monosubstituted and 2.2 - 3.0 x 10^{-2}M for disubstituted complexes. The values of ε_{max} and ν_{max} given for the peaks have been obtained on the basis of close examination of spectra taken at various concentrations both as directly plotted on the spectrophotometer and as graphed in the form ε versus ν. The effect of cooling is helpful in detecting the charge transfer bands but less useful for detecting very low intensity d-d bands as it tends to conceal them even more effectively. When the peaks have been observed the spectral assignments are, of course, based on the effects observed on cooling the sample including the decrease in extinction coefficient seen for the d-d peaks. Thus the spectrum of $P(OMe)_3Cr(CO)_5$ shown in Appendix 3.1(i) is the optimum plot obtained, lower concentrations giving less resolution and higher concentrations causing complete precipitation of the complex in the low temperature glass.

The peaks D which occur at energies between 31,000 and 31,800 cm^{-1} are seen at room temperature as partly resolved spectral shoulders in tungsten complexes, as unresolved but observable shoulders in molybdenum complexes while the spectra of chromium complexes have a less simple structure in this energy region. Cooling the sample produced greater resolution of the spectra in each case, with the extinction coefficient either increasing or remaining constant. It is not possible to comment on any change in half band width on cooling the sample as this peak is not sufficiently resolved at either room temperature or low temperature to allow such a comparison. It is therefore on the basis of the change in extinction coefficient that this peak is assigned as a charge transfer transition. However, as the charge transfer peak, C, is seen to sharpen on cooling, the contribution of its low energy tail to the intensity of peak D should decrease on cooling and hence the increase in ε_{max} for peak D indicated definite charge transfer behaviour. It is interesting to note that the increase in ε_{max} on cooling expressed as a percentage of the ε_{max} at room temperature is greater for peak D than for peak C. This is so because the overlap of the very high intensity peaks above

35,000 cm^{-1} with peak C is relatively greater than overlap of peak C with peak D. Thus the apparent increase in ε_{max} on cooling will be greater for the peak with less overlap because less of the ε_{max} increase will be absorbed to replace the overlap intensity in that case. This is an important consideration when assigning the peaks lower in energy than peak D as, theoretically, it could be argued that some charge transfer peaks might lose intensity on cooling due to a decrease in overlap intensity of a greater magnitude than the increase of intensity arising from the cooling effect. The observed behaviour of ε_{max} for the peaks C and D each of which involves significant overlap supports the unambiguous assignment of peaks showing a decrease in ε_{max} on cooling as d-d peaks (see below).

The number of peaks observed at energies lower than that of peak D varies in monosubstituted phosphite complex spectra generally, two peaks appearing for tungsten complexes and only one peak for chromium and molybdenum complexes. The peak E is seen to occur at energies around 29,300 cm^{-1} and in each case, the ε_{max} value decreases significantly on cooling. This peak is assigned as a d-d transition and its high intensity is attributed to the effect of the noncentrosymmetric environment of the metal combined with the nonradial symmetry of the phsophite ligand which will be discussed later in relation to the appearance of formally forbidden modes in the infrared spectrum of phosphite complexes. In the energy region below 27,500 cm^{-1}, no transitions are observed for chromium or molybdenum complexes while each of the tungsten derivatives is seen to have a very weak peak F in this region. The intensities of these very weak F peaks (<600) as compared to the intensities of the higher d-d bands (>1600) in the same complexes suggest that they may represent spin forbidden, orbitally forbidden triplet transitions, this assignment being supported by the detection of such peaks in the spectra of tungsten complexes only. Beach and Gray[41] found bands of a similar nature for the molybdenum and tungsten hexacarbonyls which they assigned as triplet d-d transitions, the intensity of the band in tungsten hexacarbonyl being greater than that in molybdenum hexacarbonyl. The spectrum of chromium hexacarbonyl showed no such transition. Cooling the sample causes a decrease in the ε_{max} of peak F for the triethylphosphite and triisopropylphosphite complexes while the trimethylphosphite complex has no corresponding peak in its low temperature spectrum. This apparent loss of peak F on cooling is attributed to an increase in the ν_{max} value as discussed for d-d transitions previously. If the value of ν_{max} increases sufficiently, the peak may become masked by the higher energy peaks and thus appear to be lost although it must be said that the peak F of the triethylphosphite complex increases its ν_{max} by 600 cm^{-1} on cooling and remains resolved. Thus the peak F of the trimethylphosphite complex may simply have an extinction coefficient which is too low to be observed in the low temperature spectrum.

The spectral peaks in monosubstituted phosphite complexes having intermediate intensity values are therefore assigned as the above discussion indicates. Peaks A and B are high energy metal-ligand charge transfer transitions reported for completeness. Peaks C and D are metal-ligand charge transfer bands, peak D being the lowest energy charge transfer $e(d_{xz}d_{yz}) \longrightarrow a_1[\pi^*CO(1-4)]$. Peak E is a spin allowed d-d transition and peak F, observed only in tungsten complex spectra maybe a spin forbidden d-d transition.

If the spectra of monosubstituted complexes involving the phosphine ligands triisopropylphosphine, trinbutylphosphine and Tdp are studied, the observed bands may be discussed as in the phosphite complexes. A typical spectral outline is shown in figure 3.4 for $PPr^i_3Mo(CO)_5$. Although the spectral outline obtained for each of the phosphine complexes is similar to the general spectral shape of the phosphite complexes at room temperature, the low temperature spectra are seen to vary in the region at approximately 29,000 cm^{-1}. As discussed above, the peak E of phosphite complex spectra ($\sim$29,300 cm^{-1}) is assigned as a d-d transition and is seen to decrease in intensity on cooling. The peak D in the spectra of phosphine complexes occurs between 28,400 and 29,100 cm^{-1}, gains intensity on cooling the sample and is seen to sharpen up suggesting assignment of this peak as the charge transfer transition analogous to that represented by peak D in phosphite complex spectra (at $\sim$31,500 cm^{-1}). No peaks are observed to lower energies of peak D in the phosphine complexes of chromium or molybdenum and no d-d bands are assigned in the spectra of these complexes as the peaks at higher energies all show charge transfer character. The tungsten derivatives, however, are seen to have a peak E of very low intensity at 26,000 cm^{-1} in the room temperature spectrum of $PPr^{i}_{3}W(CO)_5$ and at 25,900 cm^{-1} in $PBu^{n}_{3}W(CO)_5$. The spectrum of the triisopropylphosphine complex at low temperature could not be obtained as the complex precipitated out of the glass at low temperature but the trinbutylphosphine complex showed a decrease in the intensity of peak E on cooling, accompanied by increase in ν_{max} from 25,900 cm^{-1} to 26,300 cm^{-1}. The Tdp complexes of chromium, molybdenum and tungsten each show a weak d-d transition while the triisopropylphosphine derivative of chromium has a very weak shoulder at 26,950 cm^{-1} observed at room temperature only. The appearance of d-d bands primarily in tungstenphosphine complexes only (excluding Tdp complexes) as compared to their occurrence in the spectra of chromium, molybdenum and tungstenphosphite derivatives and the much smaller extinction coefficients in the former case may be attributed to the greater radial symmetry of phosphines as compared to phosphites. Further evidence for this difference as the origin of the different ε_{max} values is derived from the relative intensities of the formally forbidden b_1 mode occurring in the infrared spectra of these complexes. This mode is observed by relaxation of the strict symmetry selection rules governing vibrational transitions and its intensity depends on the extent to which the symmetry of the $LM(CO)_5$ molecule differs from the ideal C_{4v} group. On this basis, phosphites are significantly less "symmetrical" than phosphines (i.e. the five carbonyl groups experience a lower symmetrical environment in the phosphite complexes. See below for further discussion) as the relative intensities of the b_1 modes are in the approximate ratio 4 to 1, phosphite to phosphine. The lower value of the energy of the d-d transitions in phosphine complexes is expected as a result of the lower ligand field of the phosphines as compared to the phosphite ligands. The appearance of a d-d transition in $PPr^i_3Cr(CO)_5$ is contrary to the above argument although its infrared spectrum has an anomalous shape in the $E + A_1^2$ energy region which may be due to lowered symmetry. This is discussed later along with other aspects of the infrared spectra of these complexes. The fact that Tdp complexes each show d-d bands is in accordance with observation of b_1 modes of higher intensity in their infrared spectra than those in the spectra of trialkylphosphine derivatives.

Peaks D in the phosphine complexes are assigned as the lowest energy charge transfer transitions and the peaks C and D' to higher energies also behave as charge transfer transitions on cooling. The lowest energy charge transfer transition is found at lower energies for complexes involving phosphine ligands compared to those with phosphite ligands and the importance of this along with its relation to the bonding between the metal and phosphorus atoms will be discussed later. The position of these lowest energy charge transfer peaks has been related to the π- bonding ability of the ligand[44] and on that basis phosphines are less π-bonding than phosphites and hence the first charge transfer band occurs at lower energy for the phosphine complexes. Thus it was found that phosphine ligands triphenylphosphine, tricyclohexylphosphine, triphenylphosphite and Tdp when arranged in order of charge transfer energy lowering ability for monosubstituted complexes $LM(CO)_5$ (M = Cr, Mo, W) had the same order as that for carbonyl frequency lowering ability. This order was found to be the same for the chromium, molybdenum and tungsten complexes. If this technique is applied to ligands studied in the present work, it is found that the order of the ligands in charge transfer energy lowering ability differs for chromium, molybdenum and tungsten complexes and shows no obvious relation to the order of their ability to lower the carbonyl stretching frequencies in the monosubstituted complexes. It is, however, true that phosphines show a greater ability to lower both the first charge transfer band energies and the carbonyl stretching frequencies than phosphites. This holds for the ligands considered in this work and those in Ref. 44 and such an ordering is observed for each of the group VI metal complexes. From these results, it may be deduced that while phosphorus (III) ligands which have basic differences in their electronic structures (e.g. phosphines and phosphites) may be seen to have consistent differing effects on properties such as the carbonyl stretching frequencies or the position of the lowest energy charge transfer peaks of the monosubstituted complexes of group VI metal carbonyls, such differences are not necessarily sensitive enough to allow relative ordering of similar ligands (e.g. two phosphites). The relevance of these results to bonding theories and ideas applied to the metal VI carbonyl derivatives containing phosphorus (III) ligands will be developed more fully in a later chapter.

Disubstituted Complexes

The spectra obtained for trans disubstituted complexes vary in spectral outline according to the metal and ligand involved. These outlines are shown in figure 3.6a, b, c and d for $[P(OEt)_3]_2Cr(CO)_4$, $(PPr^i_3)_2Cr(CO)_4$, $[P(OEt)_3]_2Mo(CO)_4$ and $(PPr^i_3)_2Mo(CO)4$ respectively. Tetracarbonyl chromium diphosphite derivatives show very poorly resolved spectral outlines in energy region 35,000 - 25,000 cm^{-1}. Cooling the sample gives sharpening of the peak at lowest energy as indicated by an increase in the gradient of the curve at low energies on cooling. The extinction coefficient remains approximately constant in the entire region and comparing these results with the spectral properties discussed below for the other trans disubstituted complexes leads to assignment of at least one charge transfer peak in this energy region. It is not possible to give even a qualitative analysis of the peaks under the spectral outlines using only the spectra obtained without such comparisons, as the poor resolution prevents an estimate of the number of peaks in the outline. Comparison

in the entire region and comparing these results with the spectral

of these spectra with the outlines obtained for analogous molybdenum and tungsten phosphite complexes suggests that more than one peak occurs for the chromium complexes in the energy region 35,000 - 25,000 cm^{-1} but this cannot be stated unequivocally on the evidence available. (See below for a tentative correlation between resolved and unresolved spectra of this type.)

Disubstituted complexes of molybdenum and tungsten carbonyl phosphites have spectra which are more fully resolved than those of the analogous chromium complexes and these former spectra may be discussed in relation to the spectra of the corresponding monosubstituted complexes. They may subsequently be compared with the unresolved spectra of the disubstituted chromium complexes. The spectra at room temperature show three peaks in the region 35,000 - 25,000 cm^{-1}, one at about 34,500 cm^{-1}, a peak of similar intensity at about 31,000 cm^{-1} and a low energy shoulder around 28,500 cm^{-1} in each case. In each of the spectra, the outline between 28,000 and 29,000 cm^{-1} is parallel to the ν axis (i.e. ε constant) which gives the shoulder at 28,500 cm^{-1} an artificially angular shape. This effect must be due to the overlap of the two lowest energy peaks although it is a very unusual spectral outline and may possibly be a result of a peak coincident with the valley between the two lowest energy charge transfer peaks. Any such peak would be charge transfer in nature but the present analysis is insufficient to allow definite detection or assignment. Cooling the sample causes an increase in ε_{max} for each of the peaks while it is difficult to observe the effects of cooling on the band width due to the high degree of overlap involved. None of the peaks is sufficiently well resolved to show pronounced sharpening on cooling but the increased resolution on cooling is indicative of a decrease in half band width in addition to the increase in ε_{max}. In the spectra of the molybdenum complexes, there is evidence of a fourth peak appearing at 33,300 cm^{-1} at low temperature only. This is not seen in tungsten complexes although the more resolved peaks in the low temperature spectra of both molybdenum and tungsten complexes are more asymmetric than the peaks at room temperature. The peak at 28,500 cm^{-1} is assigned as the lowest energy charge transfer band and occurs at lower energies than the corresponding band in monosubstituted phosphite complexes. These first charge transfer bands are correlated with the charge transfer transition in the metal VI hexacarbonyls occurring at approximately 34,500 cm^{-1}. A progressive lowering of this transition energy is thus observed as phosphite ligands replace the carbonyl groups. The assignment of the peak at 28,500 cm^{-1} in the trans disubstituted phosphite derivatives is based on the increase of ε_{max} and sharpening of the peak at low temperature as shown by a smaller "tail" to low energies for the shoulder at 28,500 cm^{-1}. Further, comparison of the ε_{max} values of the peaks at 28,500 and 31,500 cm^{-1} in trans di- and monosubstituted complexes respectively show that these peaks have comparable extinction coefficients. This is expected for charge transfer bands while d-d bands are expected to be more intense for monosubstituted complexes.

The peak at 29,300 cm^{-1} in monosubstituted phosphite complexes which is assigned as a d-d transition may be correlated with a very much weaker peak observed for only the more soluble tungsten disubstituted derivatives. $[P(OPr^i)_3]_2W(CO)_4$ has a peak at 26,000 cm^{-1} in its room temperature spectrum with $\varepsilon_{max} = 350$ which is apparently lost at low temperature, the extinction coefficient at 26,000 cm^{-1} decreasing to 200. This peak is assigned as a d-d transition, but the complexity of the d-orbital splitting and ordering in third series transition metal atoms prevents a meaningful discussion of the origin of this transition or its relation to the d-d transitions assigned in monosubstituted complexes.

The peaks occurring at energies above the lowest charge transfer band in these complexes exhibit charge transfer behaviour on cooling the sample although there may be d-d transitions buried in these peaks. It is not feasible, on the basis of the spectra obtained, to assign these higher energy peaks to specific charge transfer transitions as such assignments would require a suitable spectral analysis and a more quantitative molecular orbital diagram than is available at present. The comparison of spectra of these molybdenum and tungsten disubstituted phosphite derivatives with analogous chromium complexes suggests that the energy difference between the first two charge transfer peaks (i.e. of lowest energies) is less in the chromium case causing a higher degree of overlap and less resolution. In the complexes $[P(OEt)_3]_2Cr(CO)_4$, $[P(OPr^i)_3]_2Cr(CO)_4$, a poorly resolved shoulder may be detected on the low energy side of the 30,500 peak which may be correlated with the shoulder at 28,500 cm^{-1} in complexes of molybdenum and tungsten. From these considerations, the lowest energy charge transfer peak in trans disubstituted chromium phosphite complexes is assigned in the region of 29,500 cm^{-1} although it should be added that the large overlap effect of two peaks of comparable intensity may lead to an increase in the apparent ε_{max} value of the lower energy peak as discussed for Gaussian peaks and therefore this assignment may be artificially high.

The spectral outlines obtained for disubstituted phosphine complexes may also be treated in two groups, the chromium complexes taken separately from the molybdenum and tungsten complexes. The chromium complexes have relatively well resolved spectra in the 35,000 - 25,000 cm^{-1} region showing two intense peaks at approximately 30,500 and 27,500 cm^{-1} for PEt_3, PPr^i_3, PBu^n_3. In the latter two cases, each of these peaks gains intensity and sharpens on cooling leading to their assignment as charge transfer transitions with the lower energy peak being the first charge transfer band corresponding to the peak E in the monosubstituted phosphine derivatives. The triethylphosphine derivative which shows charge transfer behaviour on cooling for the lower energy peak, while the higher energy peak appears to lose intensity has been discussed above in the Gaussian analysis section. The position and intensity of the peak assigned as the first charge transfer band are seen to correlate with those of the monosubstituted derivatives in the same manner as was observed in the phosphite complexes. Thus the energy of the first charge transfer band decreases on progressive substitution of carbonyl by phosphine and the intensity is comparable in each derivative. As expected, the disubstituted phosphine complexes have the lowest charge transfer at energies less than those of the similar phosphite derivatives. Molybdenum and tungsten phosphine complexes have spectral outlines very similar to those of the chromium complexes although there is a region of very low intensity at 34,000 - 32,000 cm^{-1} in the latter which is less pronounced in the chromium case. The spectra of the molybdenum and tungsten complexes show the lowest energy charge transfer peak well resolved at about 26,500 cm^{-1} along with a very wide shoulder to higher energies which also exhibits an increase in intensity on sample cooling and generally is more fully resolved at low temperatures. These peaks may be correlated with the charge transfer bands observed for the chromium disubstituted phosphine derivatives and a comparison of the energies and intensities of the lowest charge transfer peak with those of the corresponding peak in the monosubstituted phosphine complexes shows the expected lowering in energy for the disubstituted complex and comparable intensity values for each derivative as observed previously.

Thus the electronic absorption spectra of mono- and trans disubstituted metal VI carbonyl phosphorus (III) complexes have been studied and classified on the basis of spectra obtained at room temperature and low temperature and particularly, the lowest energy charge transfer band in each complex has been assigned with greater certainty than was previously possible. It has been found possible to use sample cooling as a convenient technique for improving assignments in spectral regions where d-d and charge transfer transition energies may overlap and the intensity at room temperature is of an intermediate value. This study supports the molecular orbital diagrams developed for metal-carbonyl π-antibonding (π *) orbital interaction as applie$\overset{d}{\text{s}}$ to the charge transfer bands in the spectrum, the lowest charge transfer assigned for the mono- and trans disubstituted complexes being from the metal orbitals into the same combination of the orbitals on the radial carbonyl groups.

TABLE 3.4

Electronic Spectra of Monosubstituted Complexes. Table.

TABLE 3.4 : MONOSUBSTITUTED COMPLEXES

SOLVENT : METHYLCYCLOHEXANE : ISOPENTANE 3:2 by volume

COMPLEX		ROOM TEMPERATURE			LOW TEMPERATURE		
		λmax	νmax	εmax	λmax	νmax	εmax
$P(OMe)_3Cr(CO)_5$(b)	A	234	43,700	38,000			
	B	250	40,000	sh			
	C	290	34,450	5,600	299	33,500	5,400
	*D	322	31,050	2,400	320	31,200	3,200
	E	343	29,200	1,300		(a)	
$P(OEt)_3Cr(CO)_5$	A	228	43,900	30,000	224	44,700	32,000
	B	249	40,200	24,000	244	41,000	27,500
	C	287	34,850	5,850	287	34,900	5,500
	D'	321	31,150	1,800	318	31,450	2,000
	*D	331	30,250	1,350	330	30,350	1,350
	(c)E	342	29,300	1,100	342	29,300	560
$P(OPr^i)_3Cr(CO)_5$	A	229	43,750	24,000			
	B	251	39,800	21,500			
	C	286	34,950	5,450	285	35,000	5,400
	D'	318	31,400	2,100	317	31,550	2,150
	*D	334	29,900	1,500	328	30,450	1,600
	(c)E	351	28,500	720	351	28,500	120

* Lowest energy charge transfer band.
(a) Precipitation of complex prevents spectral observation.
(b) Low solubility gives unknown scattering effects.
(c) No peak seen at low temperature. λ_{max}, ν_{max} and ε_{max} if quoted are for comparison with R.T. data.

TABLE 3.4 (Contd.)

COMPLEX		ROOM TEMPERATURE			LOW TEMPERATURE		
		λmax	νmax	εmax	λmax	νmax	εmax
$PPr^i_3Cr(CO)_5$ (b)	A	233	42,950	26,500			
	B	256	39,000	21,500			
	C	302	33,100	1,700	301	33,200	1,600
	D'	326	30,700	1,100	317	31,500	1,200
	*D	348	28,700	1,000	337	29,700	1,250
	E	371	26,950	420		(a)	
$PBu^n_3Cr(CO)_5$	A	226	44,100	25,700			
	B	251	39,800	29,000			
	C	296	33,750	3,400	296	33,800	3,600
	(c)D'	318	31,400	2,000	318	31,400	2,300
	*D	344	29,050	1,700	338	29,600	2,200
$TdpCr(CO)_5$	A	218	45,800	43,000	216	46,400	54,000
	B	253	39,600	25,000	250	40,000	34,000
	C	295	33,850	2,600	295	33,900	2,700
	D'	318	31,200	1,300	320	31,400	1,400
	*D	341	29,300	1,200	337	29,700	1,400

TABLE 3.4 (Contd.)

COMPLEX		ROOM TEMPERATURE			LOW TEMPERATURE		
		λ_{max}	ν_{max}	ε_{max}	λ_{max}	ν_{max}	ε_{max}
$P(OMe)_3Mo(CO)_5$(b)	A	233	42,900	49,000			
	B	256	39,100	21,500			
	C	288	34,700	7,900	290	34,500	11,000
	*D	315	31,750	2,800	315	31,800	3,300
	E	338	29,600	1,800	339	29,450	1,500
$P(OEt)_3Mo(CO)_5$	A	233	42,900	47,000	232	43,000	50,000
	B	255	39,200	32,000	245	39,300	36,000
	C	288	34,650	6,800	288	34,650	8,000
	*D	314	31,800	3,000	315	31,750	3,100
	E	342	29,300	1,900	339	29,450	1,400
$P(OPr^i)_3Mo(CO)_5$	A	234	42,750	53,000	233	42,900	56,000
	B	255	39,200	30,000	252	39,700	37,000
	C	290	34,500	6,000	290	34,500	7,000
	*D	318	31,500	2,600	317	31,600	2,800
	E	343	29,150	1,500	340	29,400	1,300

TABLE 3.4 (Contd.)

COMPLEX		ROOM TEMPERATURE			LOW TEMPERATURE		
		λmax	νmax	εmax	λmax	νmax	εmax
$PPr^{i}_{3}Mo(CO)_{5}$	A'	213	46,900	27,000			
	A	234	42,700	23,000			
	B	254	39,400	32,500			
	C	296	33,850	2,500	296	33,850	2,800
	D'	313	31,900	1,850	320	31,300	1,900
	*D	346	28,900	1,200	345	29,000	1,500
$PBu^{n}_{3}Mo(CO)_{5}$	A	234	42,800	31,000			
	B	254	39,400	35,000			
	C	297	33,650	3,800	298	33,600	4,900
	D'	323	31,000	2,400	322	31,050	2,900
	*D	346	28,850	1,950	348	28,750	2,400
$TdpMo(CO)_{5}$	A	228	43,800	38,400			
	B	255	39,200	28,600			
	C	292	34,200	4,100	292	34,250	4,400
	D'	318	31,450	2,650	322	31,000	2,150
	*D	346	28,900	1,900	346	28,950	2,400

TABLE 3.4 (Contd.)

COMPLEX		ROOM TEMPERATURE			LOW TEMPERATURE		
		λ_{max}	ν_{max}	ε_{max}	λ_{max}	ν_{max}	ε_{max}
$P(OMe)_3W(CO)_5$ (b)	A	229	43,600	62,000			
	B	254	39,350	19,000			
	C	287	34,800	6,800	287	34,800	9,000
	*D	320	31,250	2,800	312	32,050	4,000
	E	343	29,150	1,700	342	29,350	1,800
	F	372	26,900	360		(c)	
$P(OEt)_3W(CO)_5$	A	230	43,500	69,000			
	B	254	39,350	18,000			
	C	288	34,700	6,200	287	34,800	6,800
	*D	319	31,450	2,800	313	31,950	2,900
	E	343	29,150	1,700	341	29,300	1,300
	F	369	27,100	450	365	27,550	350
$P(OPr^i)_3W(CO)_5$	A	231	43,350	52,000			
	B	254	39,350	17,000			
	C	288	34,650	5,500	288	34,650	5,000
	*D	319	31,300	2,700	313	31,950	2,700
	E	344	29,100	1,600	339	29,450	1,300
	F	372	26,900	550	370	27,000	350

TABLE 3.4 (Contd.)

COMPLEX		ROOM	TEMPERATURE		LOW	TEMPERATURE	
		λmax	νmax	εmax	λmax	νmax	εmax
$PPr^i_3W(CO)_5$	A	231	43,250	24,000			
	B	250	39,900	20,000			
	C	292	34,250	2,500	293	34,100	4,300
	D'	325	30,800	2,100	324	30,600	2,800
	*D	352	28,400	1,700	351	28,450	2,200
	E	376	26,600	320		(c)	
$PBu^n_3W(CO)_5$	A	231	43,250	38,600			
	B	251	39,850	29,500			
	C	290	34,400	3,000	288	34,700	3,700
	D'	325	30,800	2,100	325	30,700	2,900
	*D	351	28,450	1,700	350	28,500	2,400
	E	386	25,900	350	380	26,300	250
$TdpW(CO)_5$	A	227	44,100	73,000	226	44,250	78,000
	B	250	40,000	45,000	250	39,900	46,000
	C	290	34,400	4,050	294	34,000	5,200
	D'	327	30,650	2,900	325	30,800	3,650
	*D	348	28,700	2,250	348	28,750	2,850

TABLE 3.5

Electronic Spectra of trans Disubstituted Complexes. Table.

TABLE 3.5 : TRANS DISUBSTITUTED COMPLEXES

SOLVENT : METHYLCYCLOHEXANE : ISOPENTANE 3:2 by volume

COMPLEX		ROOM TEMPERATURE			LOW TEMPERATURE	
	λmax	νmax	εmax	λmax	νmax	εmax
$[P(OMe)_3]_2Cr(CO)_4$(b)	249	40,150	32,000			
	* 337	29,700	1,650	336	29,750	1,650
$[P(OEt)_3]_2Cr(CO)_4$	250	40,000	33,000			
	309	32,350	2,000		(c)	
	329	30,400	1,700	328	30,500	2,200
	* 339	29,500	1,500	339	29,500	1,400
$[P(OPr^i)_3]_2Cr(CO)_4$	252	39,700	34,000			
	329	30,400	1,650	330	30,250	2,100
	* 341	29,300	1,550	340	29,400	1,800
$(PEt_3)_2Cr(CO)_4$	227	44,000	15,000			
	258	38,700	30,000			
	325	30,750	1,620	325	30,800	1,500
	* 365	27,400	1,950	364	27,450	2,000
	408	24,450	220		(c)	
$(PPr^i_3)_2Cr(CO)_4$	260	38,400	24,000			
	329	30,350	1,850	328	30,450	2,400
	* 370	26,950	2,000	364	27,500	2,800

TABLE 3.5 (Contd.)

COMPLEX	ROOM TEMPERATURE			LOW TEMPERATURE		
	λ_{max}	ν_{max}	ε_{max}	λ_{max}	ν_{max}	ε_{max}
$(PBu^n_3)_2Cr(CO)_4$	260	38,500	30,000			
	327	30,600	2,000	325	30,800	2,300
	* 367	27,250	2,300	364	27,500	3,200
$Tdp_2Cr(CO)_4$	265	37,700	13,000	266	37,600	18,000
	308	32,400	1,300	308	32,450	2,000
	339	29,500	890	345	29,000	920
	* 364	27,450	1,080	362	27,600	1,120
	414	24,200	200		(c)	
$[P(OMe)_3]_2Mo(CO)_4$(b)	220	45,500	25,000			
	250	39,900	70,000			
	290	34,400	2,700		(a)	
	318	31,400	2,950			
	* 346	28,900	2,250			
$[P(OEt)_3]_2Mo(CO)_4$	251	39,800	73,000			
	290	34,500	2,350	290	35,000	3,000
	303	33,000	2,300	298	33,500	2,750
				308	32,500	2,550
	322	31,100	2,300	329	30,400	2,550
	* 356	28,100	1,650	352	28,400	1,850

TABLE 3.5 (Contd.)

COMPLEX	ROOM TEMPERATURE			LOW TEMPERATURE		
	λ_{max}	ν_{max}	ε_{max}	λ_{max}	ν_{max}	ε_{max}
$[P(OPr^i)_3]_2Mo(CO)_4$	252	39,600	77,000			
	286	35,000	2,050	283	35,350	3,000
		(c)		300	33,250	2,600
	324	30,900	2,050	327	30,600	2,900
	* 354	28,250	1,700	348	28,700	2,300
$(PPr^i_3)_2Mo(CO)_4$	220	45,400	23,000			
	260	38,450	60,000			
	337	29,700	1,350	337	29,650	1,850
	* 379	26,400	2,200	375	26,700	3,500
$(PBu^n_3)_2Mo(CO)_4$	258	38,750	63,000			
	338	29,600	1,500	332	30,150	1,500
	* 376	26,600	2,200	374	26,750	2,700
$Tdp_2Mo(CO)_4$	261	38,300	35,000			
	298	33,500	1,900	300	33,400	1,800
	342	29,260	2,050	338	29,580	1,800
	* 370	27,000	2,800	369	27,100	2,800
	410	24,420	420	410	24,430	240

TABLE 3.5 (Contd.)

COMPLEX	ROOM TEMPERATURE			LOW TEMPERATURE		
	λmax	νmax	εmax	λmax	νmax	εmax
$[P(OMe)_3]_2W(CO)_4$(b)	247	40,800	81,000			
	290	34,400	2,550		(a)	
	320	31,300	2,250			
	* 350	28,600	1,400			
$[P(OEt)_3]_2W(CO)_4$	248	40,700	78,000			
	291	34,300	2,900	287	34,800	3,100
	323	31,000	2,800	327	30,600	3,000
	* 350	28,600	1,900	348	28,700	1,900
$[P(OPr^i)_3]_2W(CO)_4$	248	40,600	74,000			
	296	33,700	1,800	290	34,450	2,300
	329	30,400	2,200	327	30,600	2,700
	* 356	28,100	1,600	351	28,500	1,900
$(PPr^i_3)_2W(CO)_4$	254	39,300	67,000			
	339	29,500	1,600	337	29,600	2,100
	* 380	26,300	2,100	376	26,600	3,100

TABLE 3.5 (Contd.)

COMPLEX	ROOM TEMPERATURE			LOW TEMPERATURE		
	λ_{max}	ν_{max}	ε_{max}	λ_{max}	ν_{max}	ε_{max}
$(PBu^n_3)_2W(CO)_4$	252	39,600	76,000			
	335	29,900	1,500	337	29,700	2,000
	357	28,000	1,800	358	27,900	2,400
	* 379	26,400	2,200	379	26,350	3,400
$Tdp_2W(CO)_4$[44]	255	39,200	50,500			
	300	33,350	1,550			
	338	29,600	2,400			
	* 370	27,000	3,200			

TABLE 3.6

NOTES

h	width at half height (cm^{-1})
A	area under curve ($l\ mole^{-1}\ cm^{-1}$)
f	oscillator strength (dimensionless)
D_{nm}	dipole strength (A^2)
B_{nm}	Einstein coefficient of absorption ($sec\ g^{-1}$)
A_{mn}	Einstein coefficient of emission (sec^{-1})
ε_{max}	maximum extinction coefficient ($l\ mole^{-1}\ cm^{-1}$)
ν_{max}	frequency (cm^{-1})
λ_{max}	wavelength (A)
Δ	% change from R.T. value to L.T. value

TABLE 3.6

(i) $Tdp_2Cr(CO)_4$ 35,000 - 23,000 cm^{-1}

Peak	e			d			c			b			a		
Temp.	R.T.	L.T.	Δ	R.T.	L.T.	Δ	R.T.	L.T.	Δ	R.T.	L.T.	Δ	R.T.	L.T.	Δ
h	2,190	1,100	-50	2,440	2,560	+ 5	780	470	-40	970	880	-10	1,630	1,530	- 6
ε_{max}	810	390	-50	1,050	1,080	+ 3	170	50	-70	220	130	-41	200	90	-55
$Ax10^{-6}$	1.88	0.47	-78	2.73	2.95	+ 8	0.14	0.025	-82	0.23	0.12	-48	0.35	0.14	-63
f	0.008	0.002	-78	0.012	0.013	+ 8	0.0006	.00011	-82	0.001	0.0005	-50	0.0015	0.0006	-60
D_{nm}	0.025	0.0064	-80	0.040	0.045	+ 8	0.0021	.00038	-81	0.036	0.018	-50	0.058	0.022	-62
$B_{nm}x10^{-8}$	0.36	0.093	-72	0.58	0.62	+ 7	0.03	0.0055	-84	0.52	0.26	-50	0.84	0.32	-62
$A_{nm}x10^{-8}$	0.049	0.011	-80	0.058	0.065	+12	0.0027	.00052	-78	0.042	0.023	-46	0.060	0.025	-58
ν_{max}	29,600	29,100		27,250	27,550		26,200	26,750		25,300	26,150		24,150	25,000	
λ_{max}	3,380	3,440		3,670	3,630		3,820	3,740		3,950	3,820		4,140	4,000	

TABLE 3.6

(ii) $Tdp_2Cr(CO)_4$ 50,000 - 34,000 cm^{-1}

Peak		j			i		h	f		g	h	f	g
Temp.	R.T.	L.T.	Δ	R.T.	L.T.	Δ	R.T.	L.T.	Δ	R.T.	L.T.	R.T.	L.T.
h	5,880	7,280	+24	5,400	5,760	+ 7	4,380	3,000	-32	1,200	4,380	2,200	3,260
ε_{max}	13,400	17,900	+34	8,900	6,600	-26	12,100	10,900	-10	1,900	4,800	1,900	5,000
$Ax10^{-6}$	84	138	+64	51.2	40.6	-22	56.4	35.0	-56	2.4	22.0	4.4	17.2
f	0.36	0.60	+86	0.22	0.17	-23	0.24	0.15	-38	0.010	0.094	0.02	0.074
D_{nm}	0.71	1.50	+112	0.48	0.36	-25	0.59	0.37	-38	0.026	0.22	0.050	0.17
$B_{nm}x10^{-8}$	10.3	21.7	+110	6.95	5.20	-25	8.55	5.35	-38	0.38	3.18	0.72	2.45
$A_{mn}x10^{-8}$	5.4	13.5	+150	2.66	2.35	-12	2.35	1.40	-40	0.094	1.09	0.16	0.74
ν_{max}	47,130	49,950		42,600	44,900		38,000	37,400		36,750	40,900	35,200	39,300
λ_{max}	2,120	2,000		2,350	2,230		2,630	2,670		2,720	2,450	2,840	2,550

TABLE 3.6

(iii) $Tdp_2Mo(CO)_4$ 35,000 - 23,000 cm^{-1}

Peak	d			c			b			a		
Temp.	R.T.	L.T.	Δ	R.T.	L.T.	Δ	R.T.	L.T.	Δ	R.T.	L.T.	Δ
h	2,900	2,940	+ 1	3,810	3,810	0	1,750	1,750	0	1,400	1,440	+ 3
ε_{max}	980	680	-30	1,940	1,680	-13	1,540	1,640	+ 7	670	280	-58
$Ax10^{-6}$	3.03	2.14	-30	7.87	6.80	-14	2.87	3.04	+ 6	1.00	0.34	-66
f	0.013	0.0092	-29	0.034	0.029	-15	0.012	0.013	+ 6	0.0043	0.0015	-66
D_{nm}	0.038	0.027	-29	0.11	0.095	-14	0.043	0.045	+ 5	0.016	0.0053	-69
$B_{nm}x10^{-8}$	0.55	0.39	-29	1.60	1.38	-14	0.62	0.65	+ 5	0.23	0.077	-65
$A_{nm}x10^{-8}$	0.087	0.062	-29	0.18	0.17	- 5	0.059	0.063	+ 7	0.014	0.0066	-50
ν_{max}	31,700	31,650		28,500	28,600		26,750	26,850		25,450	25,800	
λ_{max}	3,150	3,160		3,510	3,500		3,740	3,730		3,930	3,880	

TABLE 3.6

(iv) $(PEt_3)_2Cr(CO)_4$ 35,000 - 23,000 cm^{-1}

Peak	e			d			c	b			a
Temp.	R.T.	L.T.	Δ	R.T.	L.T.	Δ	L.T.	R.T.	L.T.	Δ	L.T.
h	2,940	2,690	- 9	3,130	3,190	+ 2	1,560	3,310	2,320	-27	1,750
ε_{max}	1,200	300	-75	1,500	1,210	-20	380	1,820	1,560	-14	110
$A x 10^{-6}$	3.76	0.87	-77	5.00	4.10	-18	0.63	6.42	3.86	-40	0.20
f	0.016	0.0039	-75	0.022	0.018	-18	0.0027	0.028	0.017	-39	0.0008
D_{nm}	0.045	0.010	-78	0.065	0.053	-18	0.0089	0.094	0.056	-40	0.033
$B_{nm} x 10^{-8}$	0.65	0.15	-61	0.94	0.77	-18	0.13	1.36	0.81	-40	0.48
$A_{nm} x 10^{-8}$	0.12	0.028	-75	0.14	0.11	-21	0.0017	0.14	0.083	-43	0.035
ν_{max}	33,650	33,750		30,750	30,850		28,800	27,350	27,350		24,500
λ_{max}	2,970	2,960		3,250	3,240		3,470	3,660	3,660		4,080

TABLE 3.6

(v) $(PEt_3)_2Cr(CO)_4$ 50,000 - 30,000 cm^{-1}

Peak	j			i			h			g			f		
Temp.	R.T.	L.T.	Δ	R.T.	L.T.	Δ	R.T.	L.T.	Δ	R.T.	L.T.	Δ	R.T.	L.T.	Δ
h	5,760	5,740	- 1	6,200	6,100	- 2	3,200	3,000	- 6	1,250	1,260	+ 1	1,760	1,760	0
ε_{max}	6,400	4,700	-27	13,100	10,200	-23	19,100	21,700	+14	2,300	2,400	+ 5	3,100	600	-80
$Ax10^{-6}$	39.2	28.8	-27	86.6	66.6	-23	65.0	69.2	+ 6	3.08	3.26	+ 5	9.12	1.80	-80
f	0.18	0.12	-33	0.38	0.28	-26	0.28	0.30	+ 7	0.013	0.014	+15	0.036	0.008	-78
D_{nm}	0.33	0.25	-24	0.84	0.65	-23	0.68	0.72	+ 6	0.033	0.035	+ 6	0.10	0.021	-79
$B_{nm}x10^{-8}$	4.8	3.62	-25	12.2	9.4	-23	9.85	1.04	+ 1	0.48	0.51	+ 6	1.45	0.31	-86
$A_{mn}x10^{-8}$	2.42	1.80	-26	4.28	3.21	-25	2.76	2.96	+ 7	0.12	0.13	+ 8	0.32	0.064	-80
ν_{max}	46,750	46,300		41,300	40,950		38,300	38,500		36,850	37,250		35,300	34,850	
λ_{max}	2,140	2,160		2,420	2,440		2,610	2,600		2,710	2,690		2,830	2,870	

TABLE 3.6

(vi) $TdpMo(CO)_5$ 35,000 - 23,000 cm^{-1}

Peak	e			d			c			b			a		
Temp.	R.T.	L.T.	Δ	R.T.	L.T.	Δ	R.T.	L.T.	Δ	R.T.	L.T.	Δ	R.T.	L.T.	Δ
h	2,880	2,500	-13	750	820	+ 9	3,310	3,310	0	2,180	2,000	- 8	1,070	1,380	+29
ε_{max}	3,780	3,470	- 8	110	300	+170	2,090	1,620	-23	1,390	1,920	+38	200	150	-25
$Ax10^{-6}$	11.6	9.29	-20	0.09	0.26	+190	7.35	5.70	-23	3.23	4.10	+27	0.23	0.24	+ 4
f	0.05	0.04	-20	0.0004	0.0012	+190	0.031	0.024	-23	0.014	0.018	+27	.00099	0.0010	+ 4
D_{nm}	0.14	0.11	-22	0.0011	0.0033	+200	0.095	0.073	-23	0.046	0.057	+24	0.0034	0.0035	+ 3
$B_{nm}x10^{-8}$	2.03	1.60	-21	0.016	0.048	+200	1.38	1.06	-23	0.67	0.83	+24	0.049	0.051	+ 4
$A_{nm}x10^{-8}$	0.4	0.29	-28	0.0026	0.0071	+170	0.20	0.16	-20	0.075	0.096	+28	0.0048	0.0052	+ 8
ν_{max}	33,850	33,550		31,800	30,950		30,850	31,150		28,350	28,600		26,900	27,300	
λ_{max}	2,960	2,980		3,150	3,230		3,240	3,210		3,530	3,500		3,720	3,660	

TABLE 3.6

(vii) $[P(OMe)_3]_2Cr(CO)_4$ 50,000 - 30,000 cm^{-1}

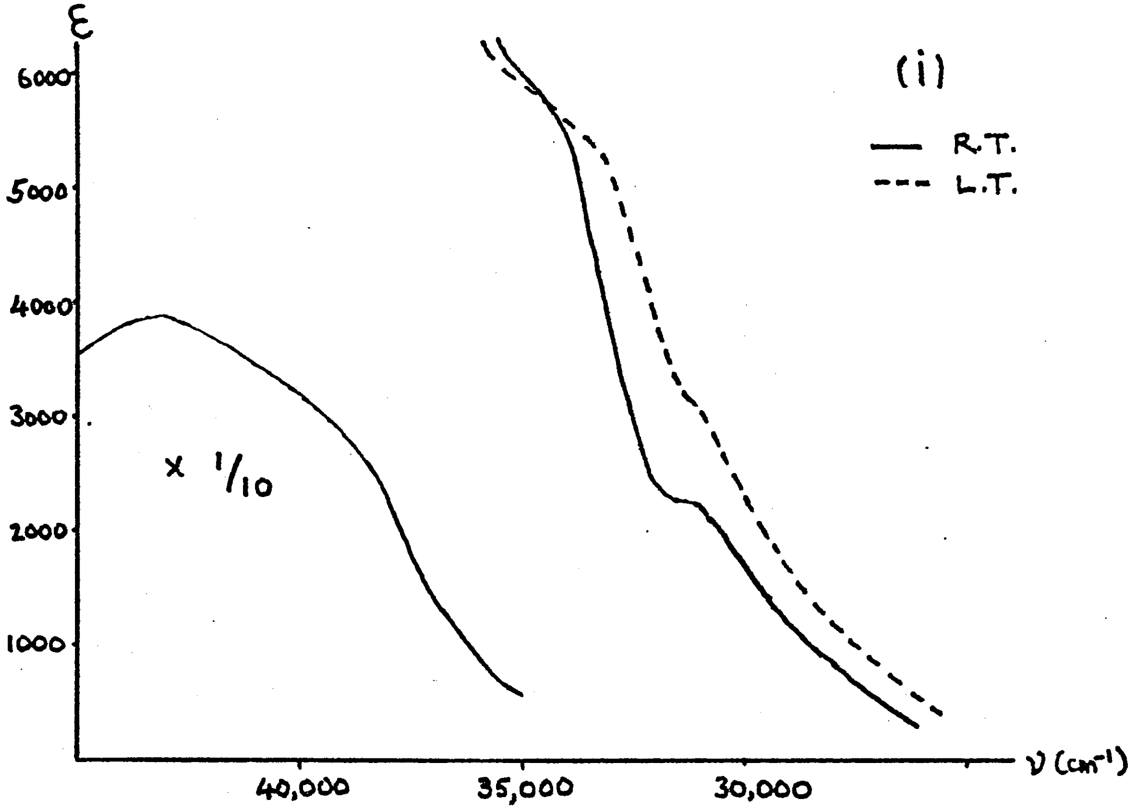
Peak		d			c			b			a	
Temp.	R.T.	L.T.	Δ	R.T.	L.T.	Δ	R.T.	L.T.	Δ	R.T.	L.T.	Δ
h	5,260	5,880	+12	5,500	3,320	-40	4,000	2,940	-27	2,880	2,760	- 4
ε_{max}	17,200	11,900	-31	13,200	10,000	-25	25,100	21,600	-14	2,100	2,500	+19
$Ax10^{-6}$	97.0	73.5	-24	77.3	35.7	-54	107	67.3	-38	6.50	7.49	+15
f	0.42	0.32	-24	0.32	0.16	-54	0.48	0.30	-38	0.28	0.32	+15
D_{nm}	0.79	0.64	-19	0.71	0.34	-52	1.06	0.67	-38	0.071	0.082	+15
$B_{nm}x10^{-8}$	11.4	9.3	-18	10.3	4.94	-53	15.4	9.7	-37	1.03	1.19	+16
$A_{nm}x10^{-8}$	6.8	4.3	-37	4.26	1.80	-58	4.9	3.02	-39	0.25	0.29	+16
ν_{max}	49,100	45,300		43,650	41,800		39,950	39,700		36,600	36,400	
λ_{max}	2,040	2,210		2,290	2,390		2,500	2,520		2,730	2,750	

APPENDIX 3.1

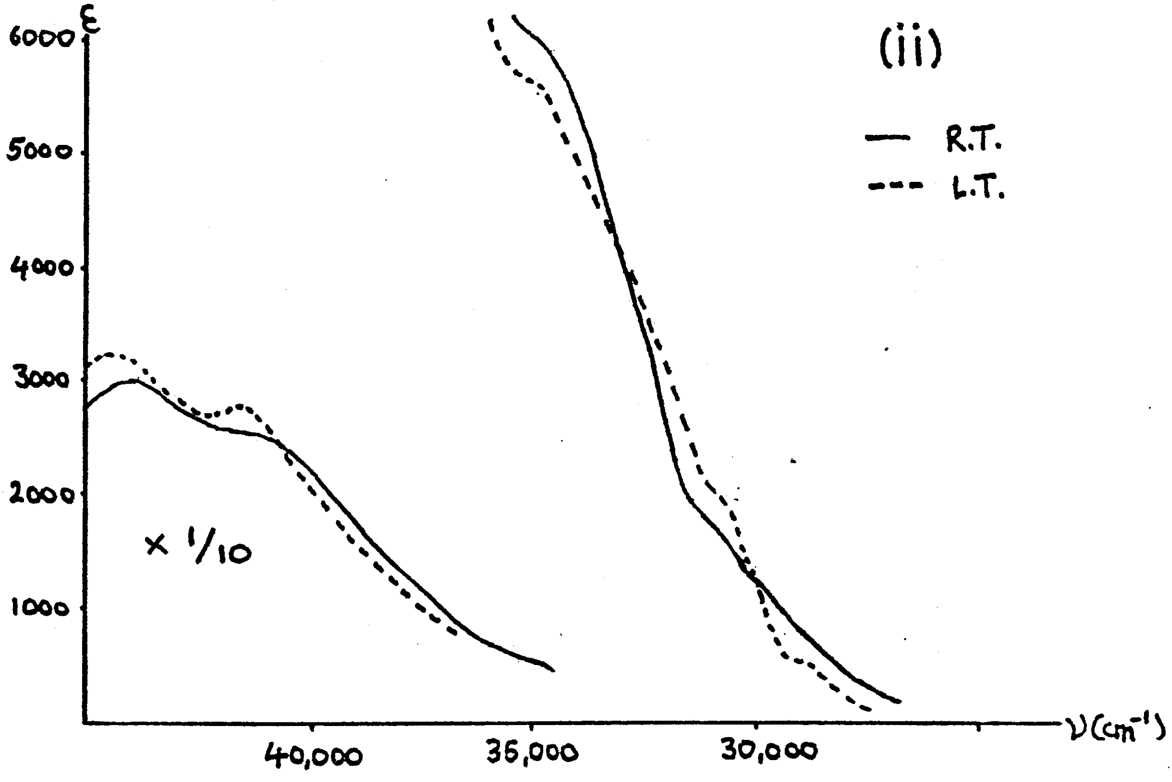
Electronic Spectra of Monosubstituted and trans Disubstituted Complexes. Diagrams.

APPENDIX 3.1

SPECTRUM NUMBER	SPECTRUM
(i)	$P(OMe)_3Cr(CO)_5$
(ii)	$P(OEt)_3Cr(CO)_5$
(iii)	$P(OPr^i)_3Cr(CO)_5$
(iv)	$PPr^i_3Cr(CO)_5$
(v)	$PBu^n_3Cr(CO)_5$
(vi)	$TdpCr(CO)_5$
(vii)	$P(OMe)_3Mo(CO)_5$
(viii)	$P(OEt)_3Mo(CO)_5$
(ix)	$P(OPr^i)_3Mo(CO)_5$
(x)	$PPr^i_3Mo(CO)_5$
(xi)	$PBu^n_3Mo(CO)_5$
(xii)	$TdpMo(CO)_5$
(xiii)	$P(OMe)_3W(CO)_5$
(xiv)	$P(OEt)_3W(CO)_5$
(xv)	$P(OPr^i)_3W(CO)_5$
(xvi)	$PPr^i_3W(CO)_5$
(xvii)	$PBu^n_3W(CO)_5$
(xviii)	$TdpW(CO)_5$
(xix)	$[P(OMe)_3]_2Cr(CO)_4$
(xx)	$[P(OEt)_3]_2Cr(CO)_4$
(xxi)	$[P(OPr^i)_3]_2Cr(CO)_4$
(xxii)	$(PPr^i_3)_2Cr(CO)_4$
(xxiii)	$(PBu^i_3)_2Cr(CO)_4$
(xxiv)	$Tdp_2Cr(CO)_4$
(xxv)	$[P(OMe)_3]_2Mo(CO)_4$
(xxvi)	$[P(OEt)_3]_2Mo(CO)_4$
(xxvii)	$[P(OPr^i)_3]_2Mo(CO)_4$
(xxviii)	$(PPr^i_3)_2Mo(CO)_4$
(xxix)	$(PBu^n_3)_2Mo(CO)_4$
(xxx)	$Tdp_2Mo(CO)_4$
(xxx)	$[P(OMe)_3]_2W(CO)_4$
(xxxii)	$[P(OEt)_3]_2W(CO)_4$
(xxxiii)	$[P(OPr^i)_3]_2W(CO)_4$
(xxxiv)	$(PPr^i_3)_2W(CO)_4$
(xxxv)	$(PBu^n_3)_2W(CO)_4$
(xxxvi)	$Tdp_2W(CO)_4$
(xxxvii)	$(PEt_3)_2Cr(CO)_4$



ε
6000
5000
4000
3000
2000
1000
(i)
R.T.
L.T.
× 1/10
40,000
35,000
30,000
ν (cm⁻¹)



ε
6000
5000
4000
3000
2000
1000
(ii)
R.T.
L.T.
× 1/10
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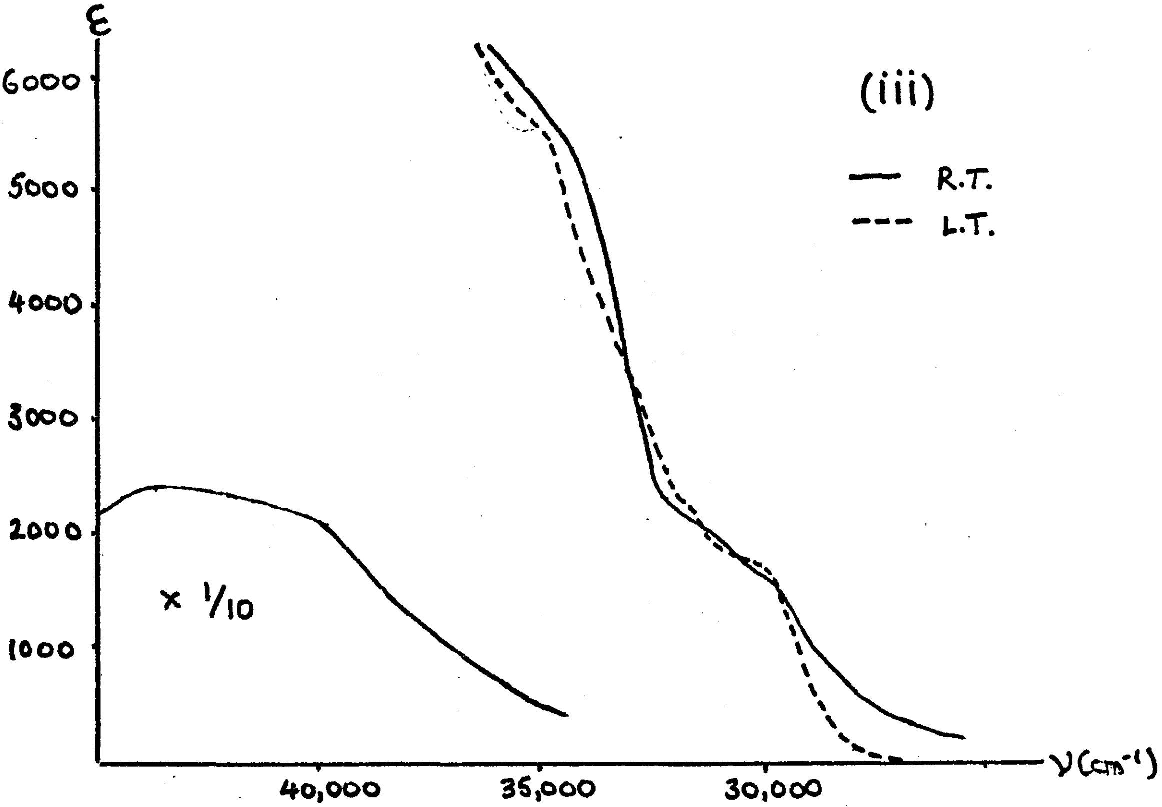
35,000
30,000
ν (cm⁻¹)


ε
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3000
2000
1000
(iii)
R.T.
L.T.
× 1/10
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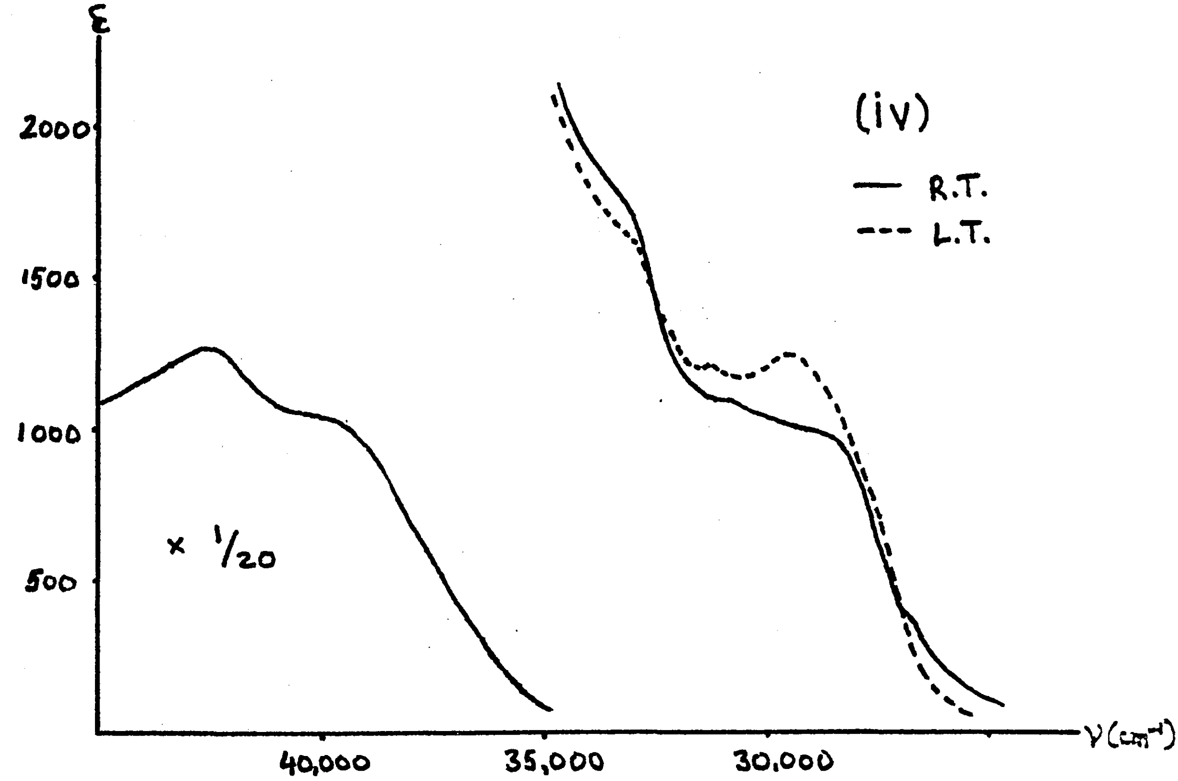
35,000
30,000
ν (cm⁻¹)


ε
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1500
1000
500
(iv)
R.T.
L.T.
× 1/20
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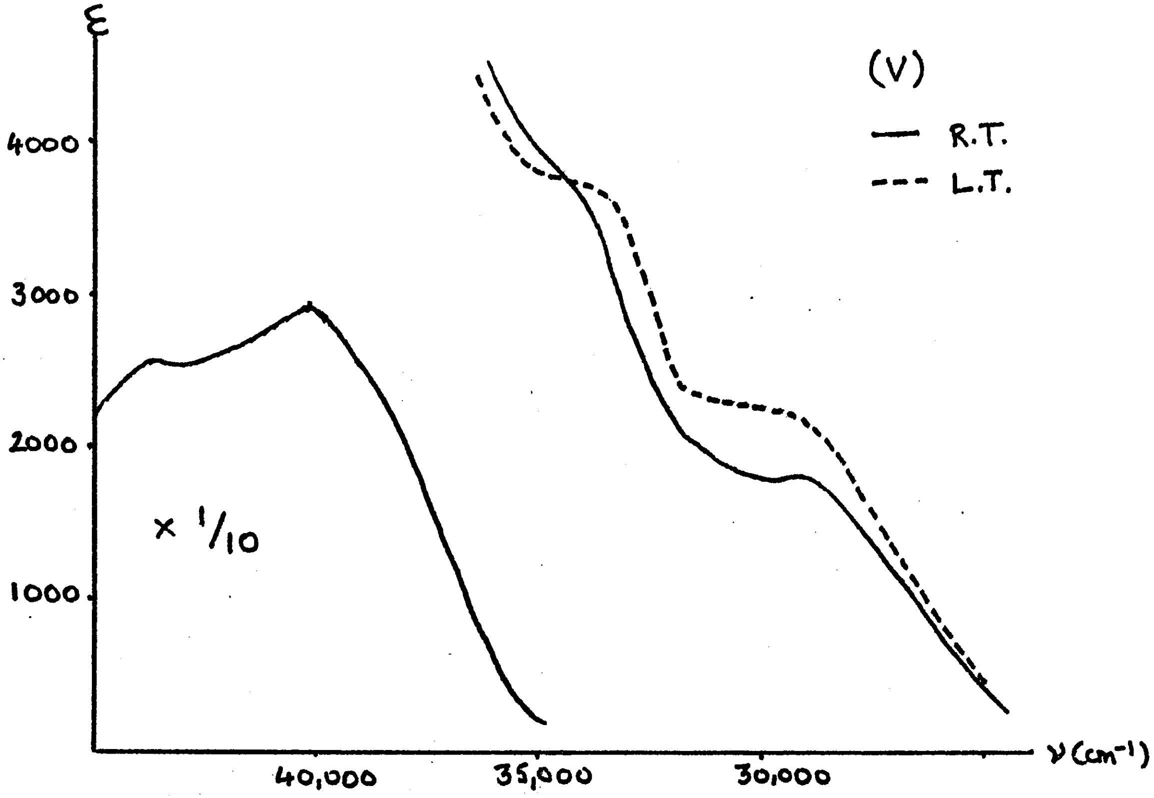
35,000
30,000
ν (cm⁻¹)


ε
(V)
R.T.
L.T.
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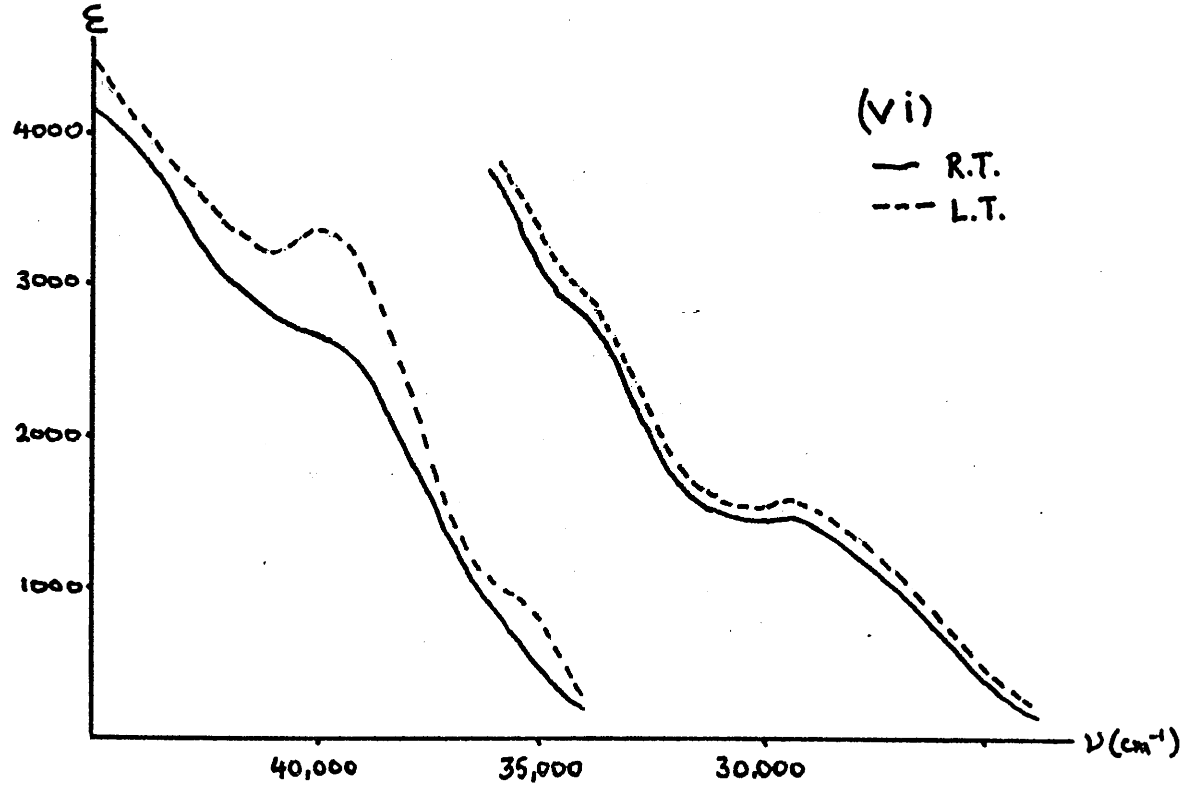
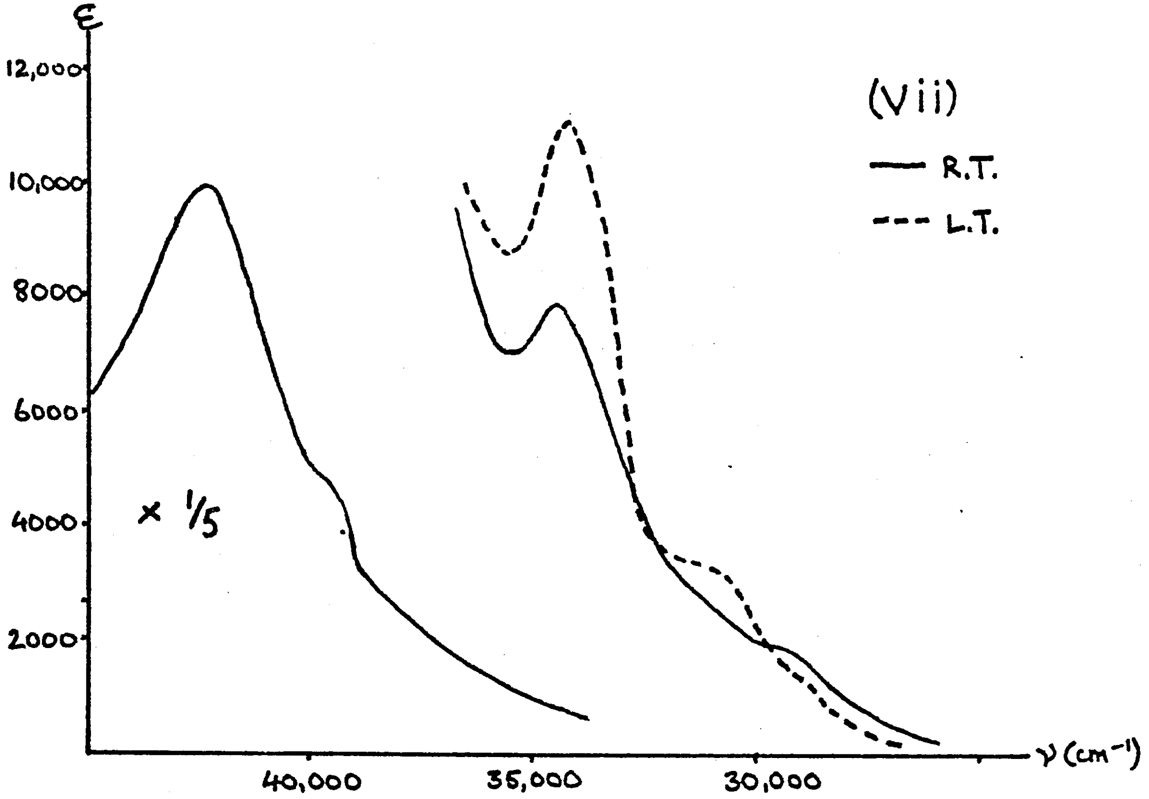
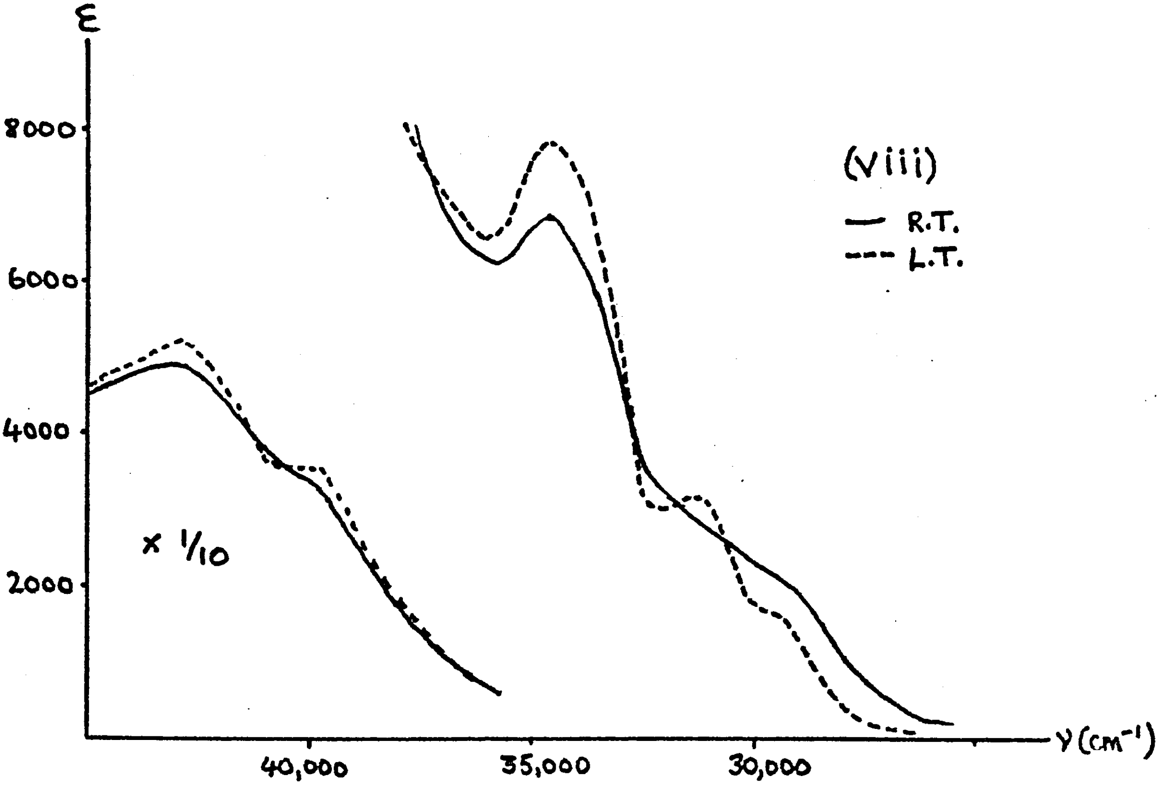
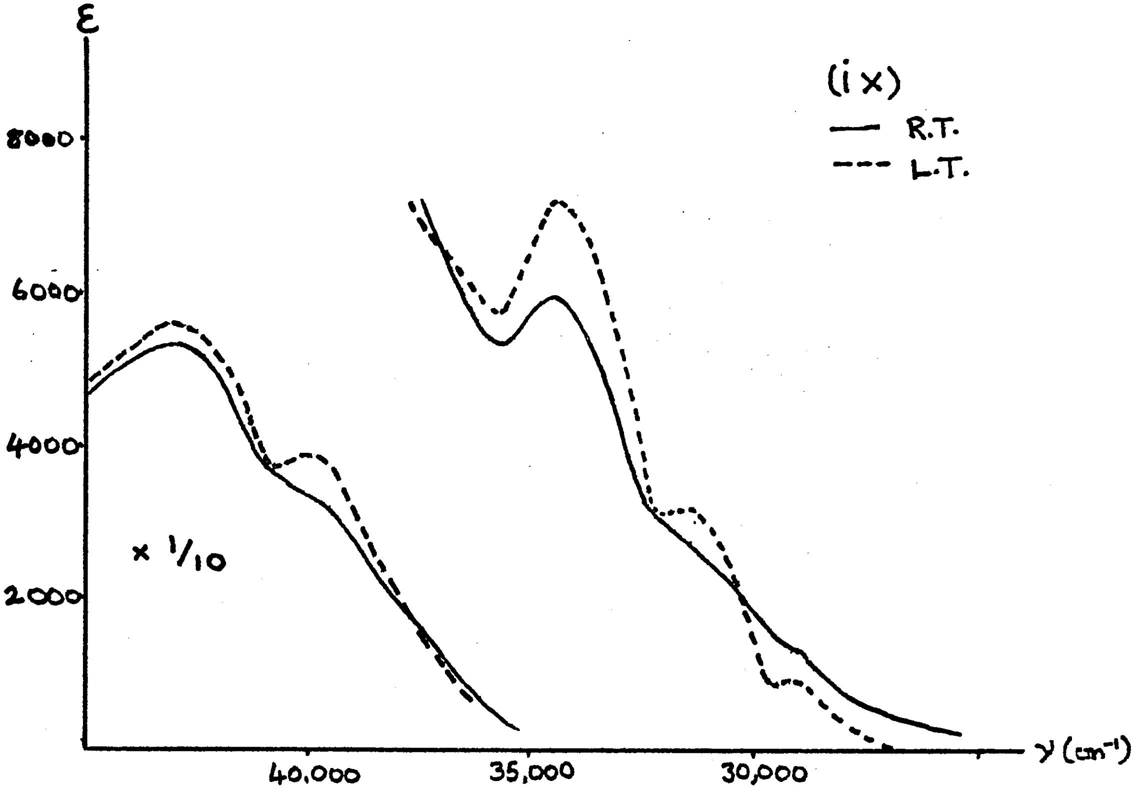
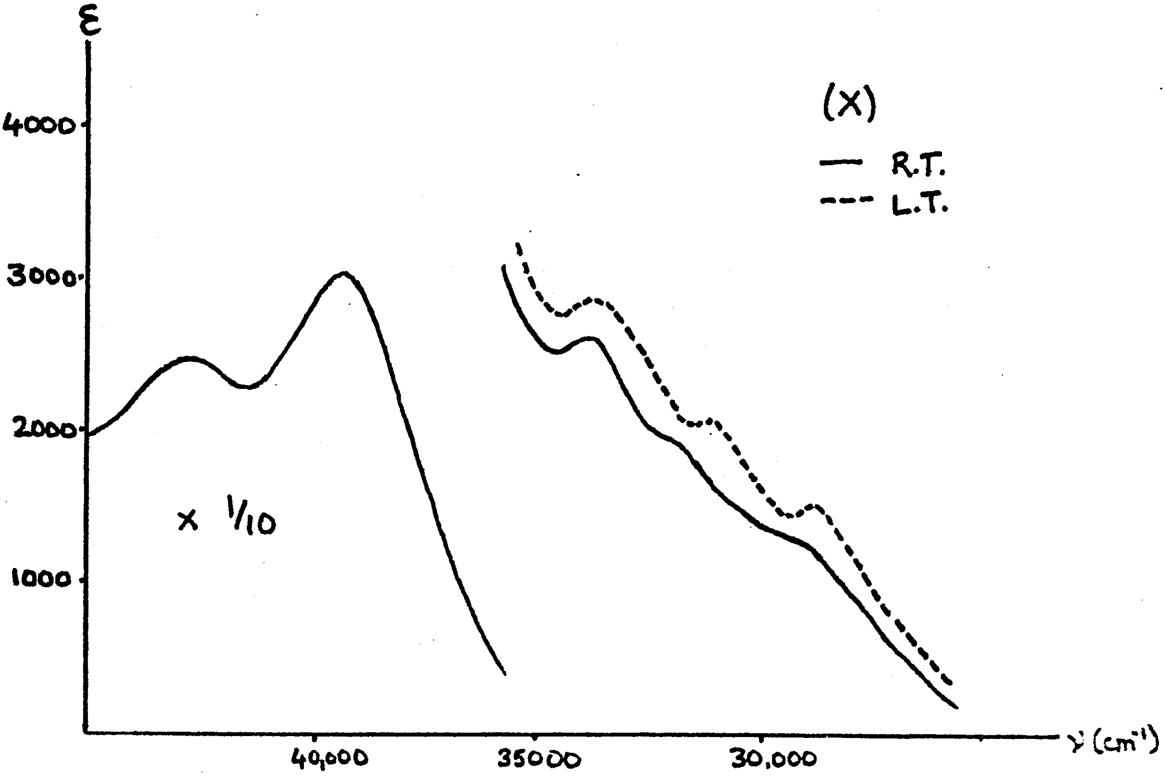
3000
2000
1000
× 1/10
40,000
35,000
30,000
ν (cm⁻¹)


ε
(Vi)
R.T.
L.T.
4000
3000
2000
1000
40,000
35,000
30,000
ν (cm⁻¹)


ε
12,000
10,000
8000
6000
4000
2000
× 1/5
(Vii)
— R.T.
--- L.T.
40,000
35,000
30,000
ν (cm⁻¹)


ε
8000
6000
4000
2000
× 1/10
(Viii)
— R.T.
--- L.T.
40,000
35,000
30,000
ν (cm⁻¹)


ε
(ix)
— R.T.
--- L.T.
8000
6000
4000
2000
× 1/10
40,000
35,000
30,000
ν (cm⁻¹)


ε
(X)
— R.T.
--- L.T.
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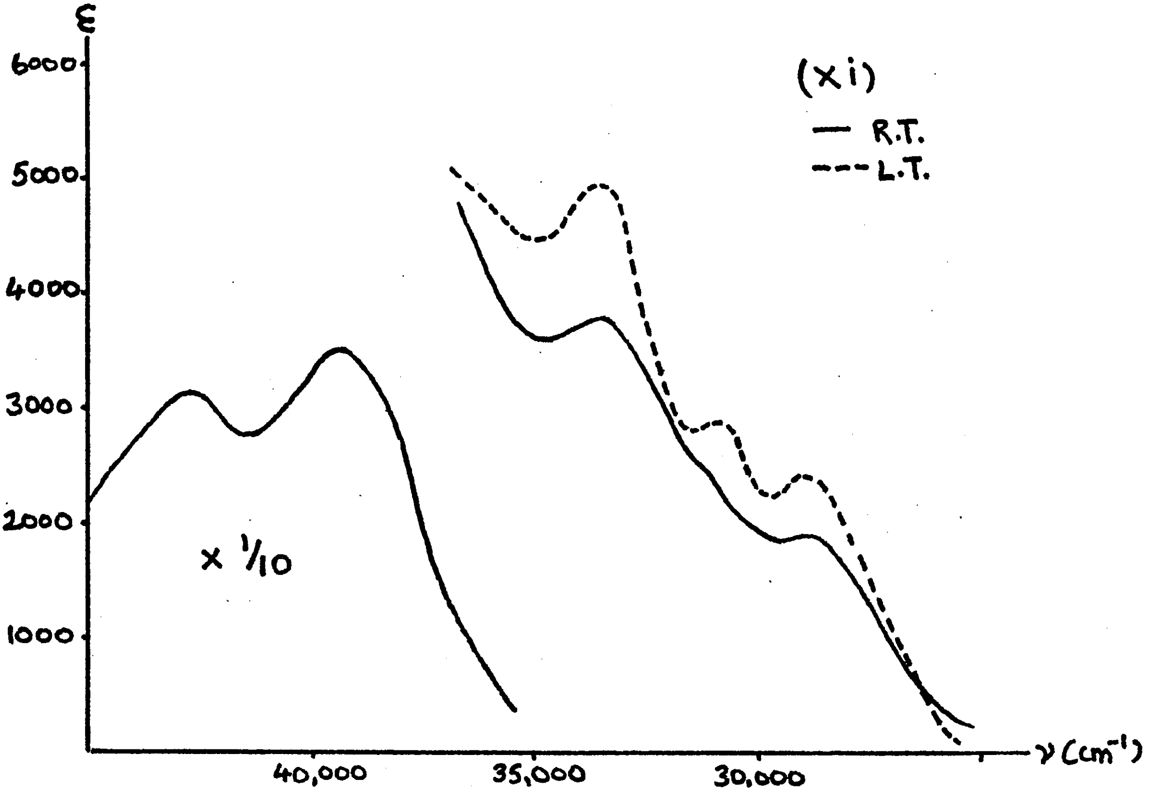
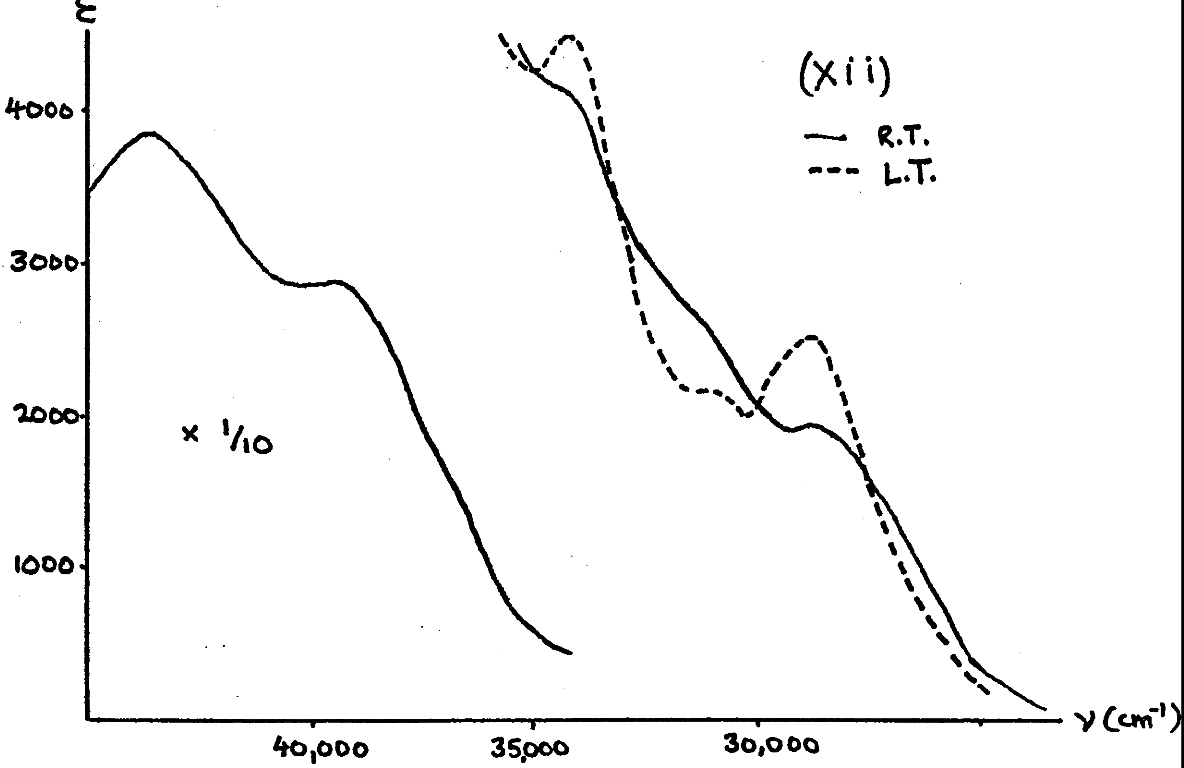
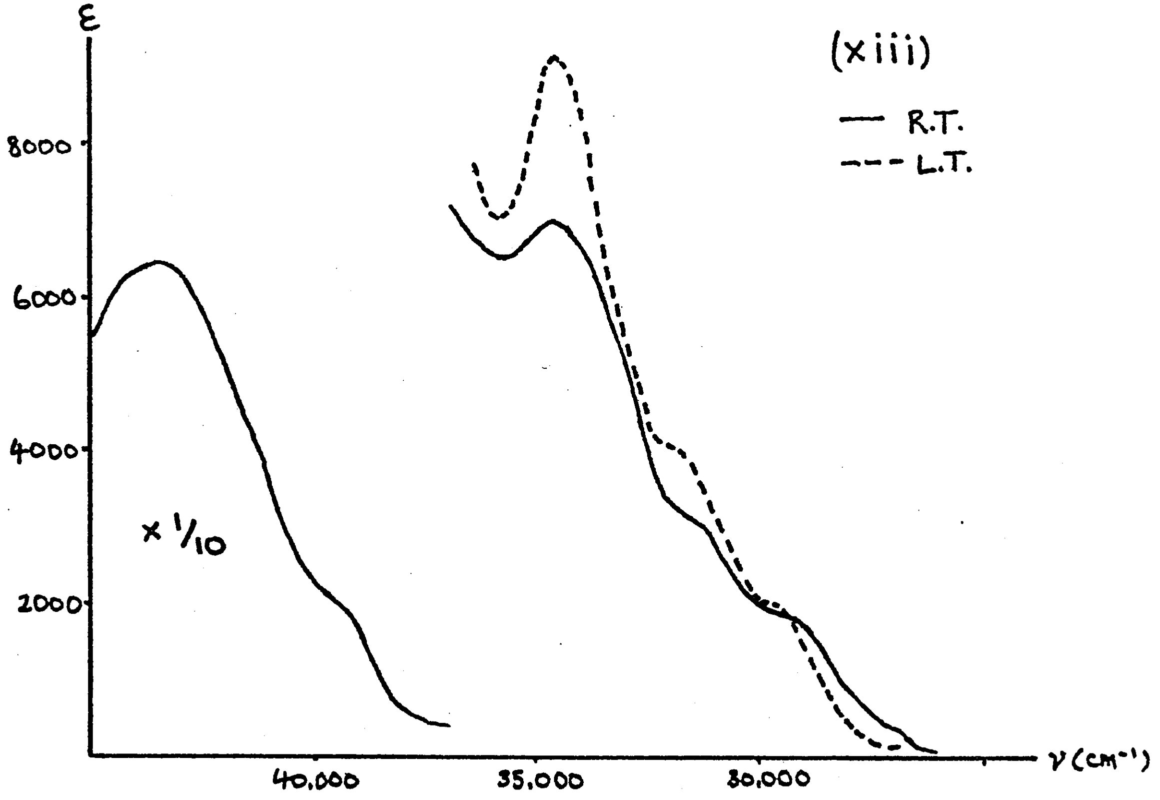
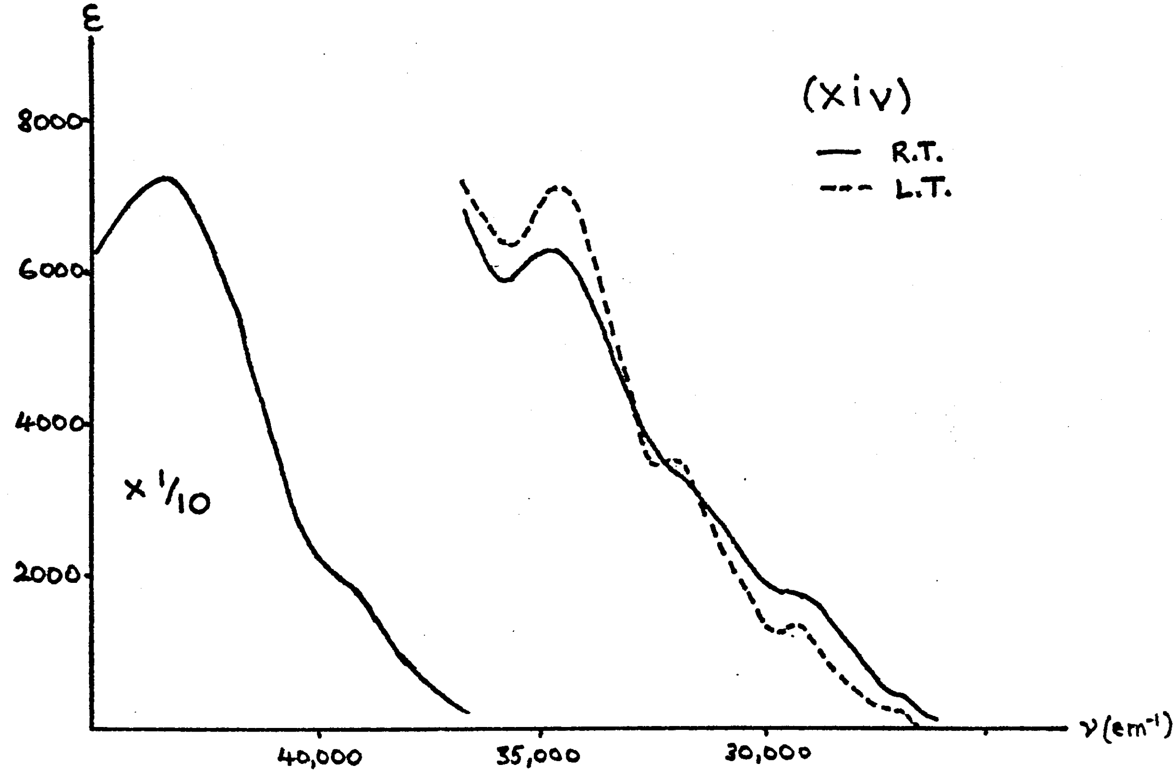
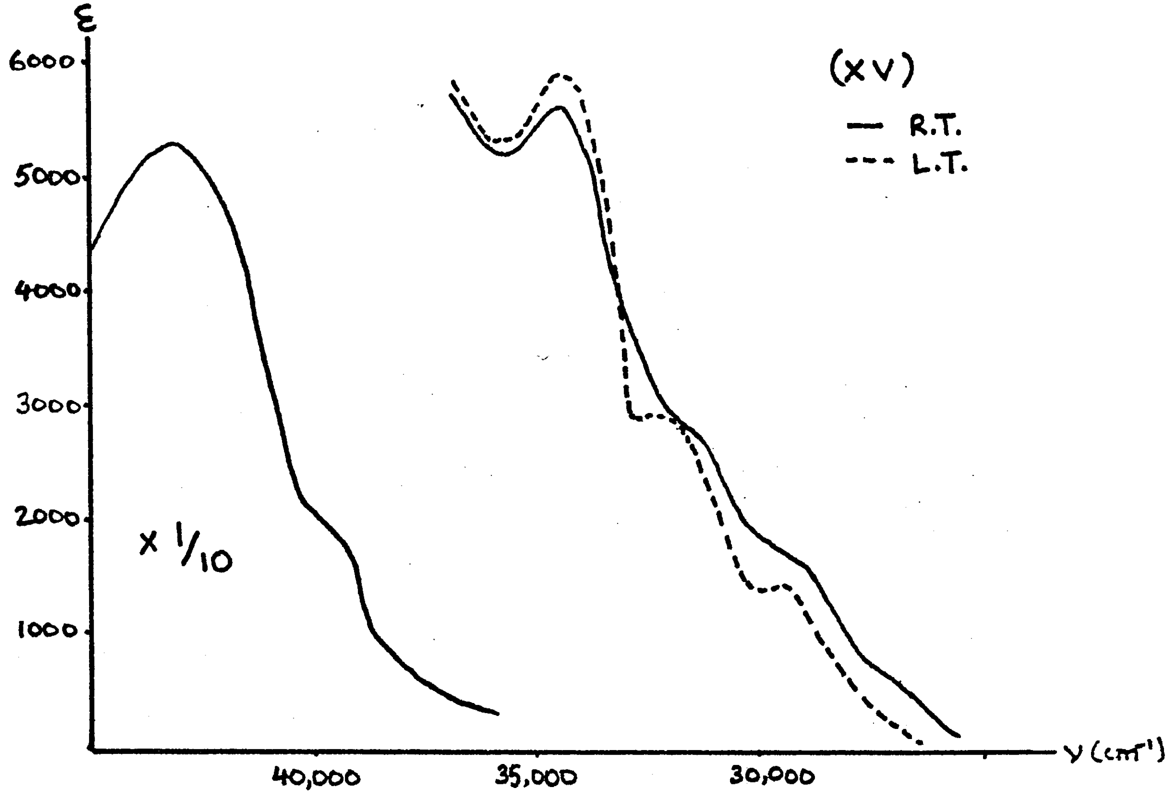
3000
2000
1000
× 1/10
40,000
35000
30,000
ν (cm⁻¹)

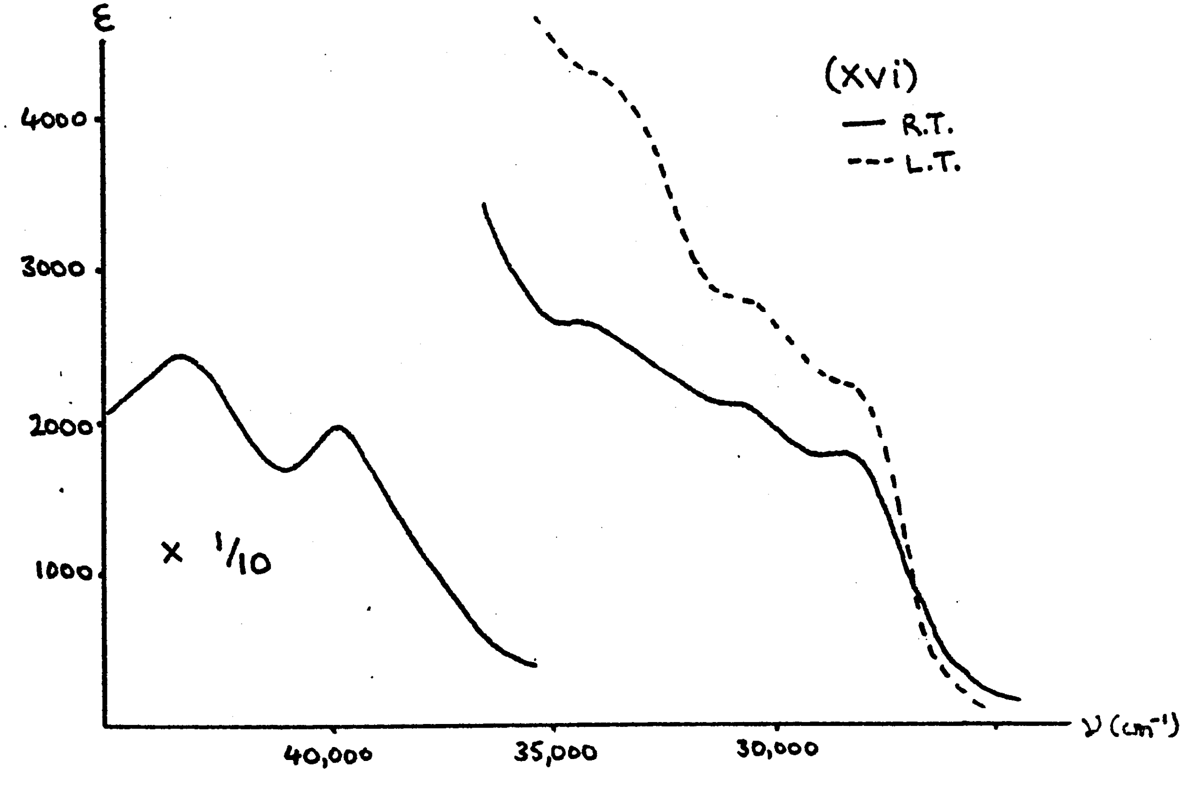

ε
6000
5000
4000
3000
2000
1000
(xi)
— R.T.
--- L.T.
× 1/10
40,000
35,000
30,000
ν (cm⁻¹)

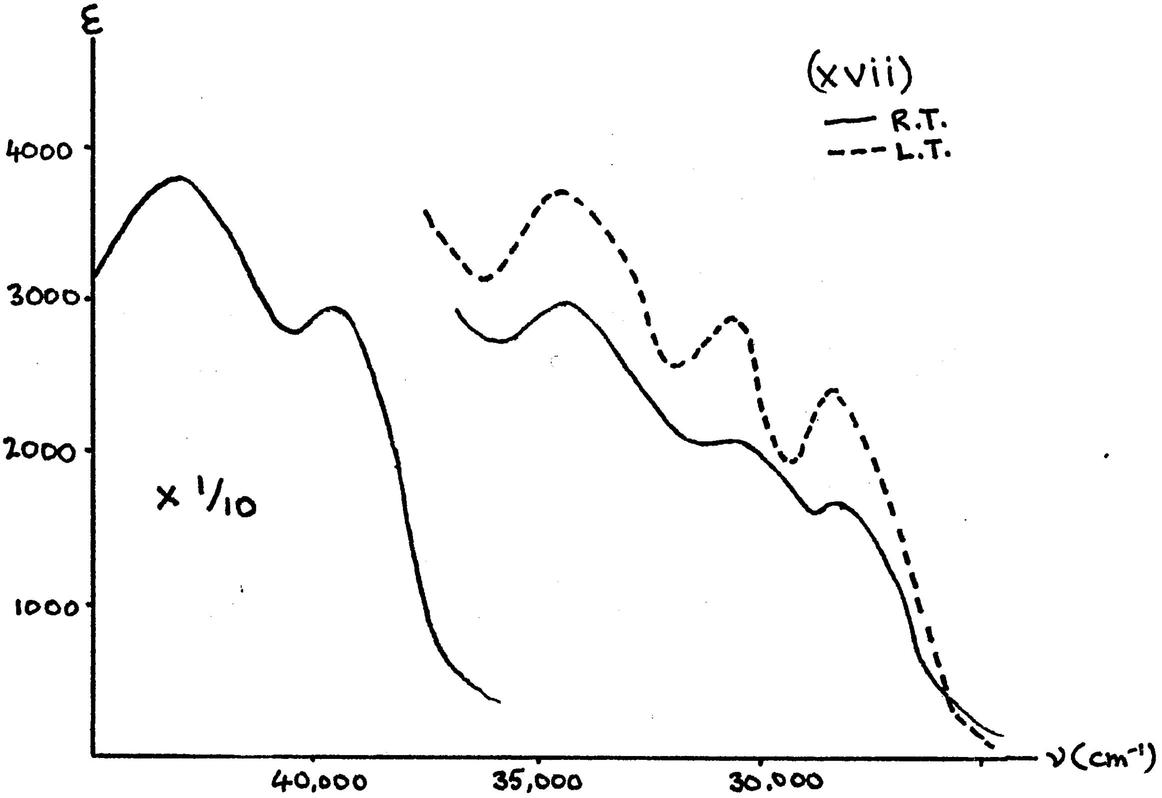

ε
4000
3000
2000
1000
(xii)
— R.T.
--- L.T.
× 1/10
40,000
35,000
30,000
ν (cm⁻¹)

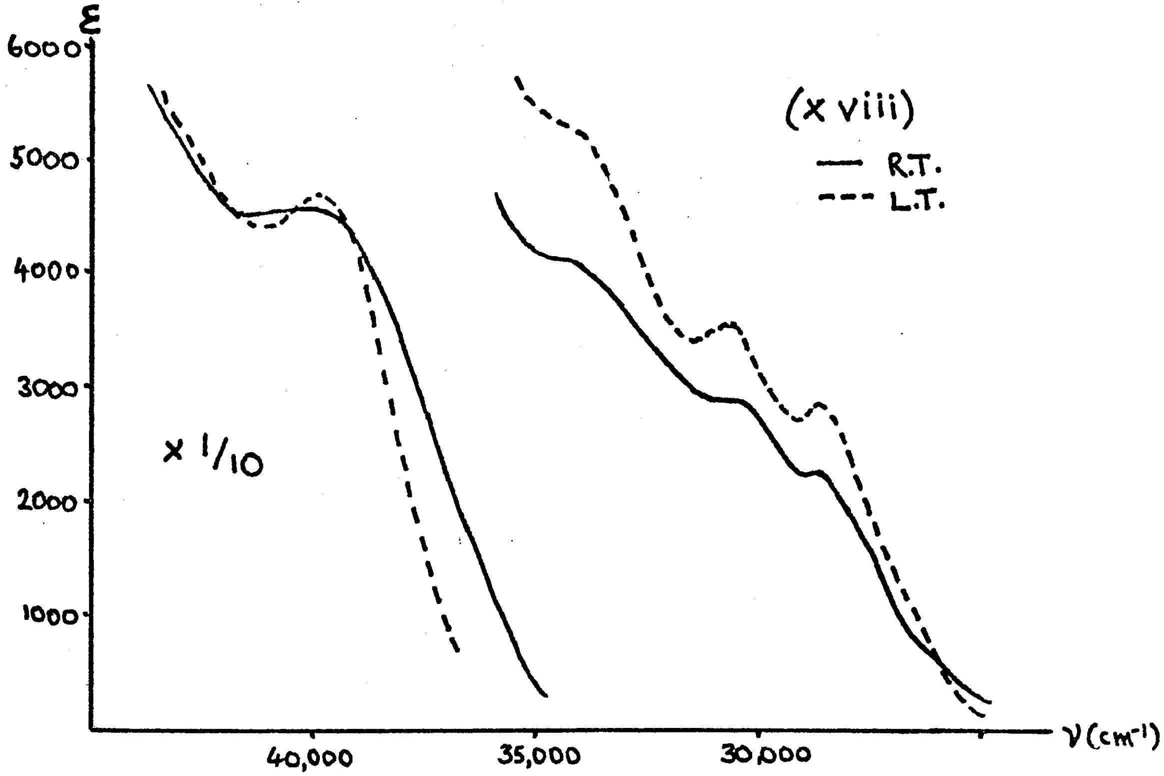

ε
(xiii)
— R.T.
--- L.T.
8000
6000
4000
2000
× 1/10
40,000
35,000
30,000
ν (cm⁻¹)

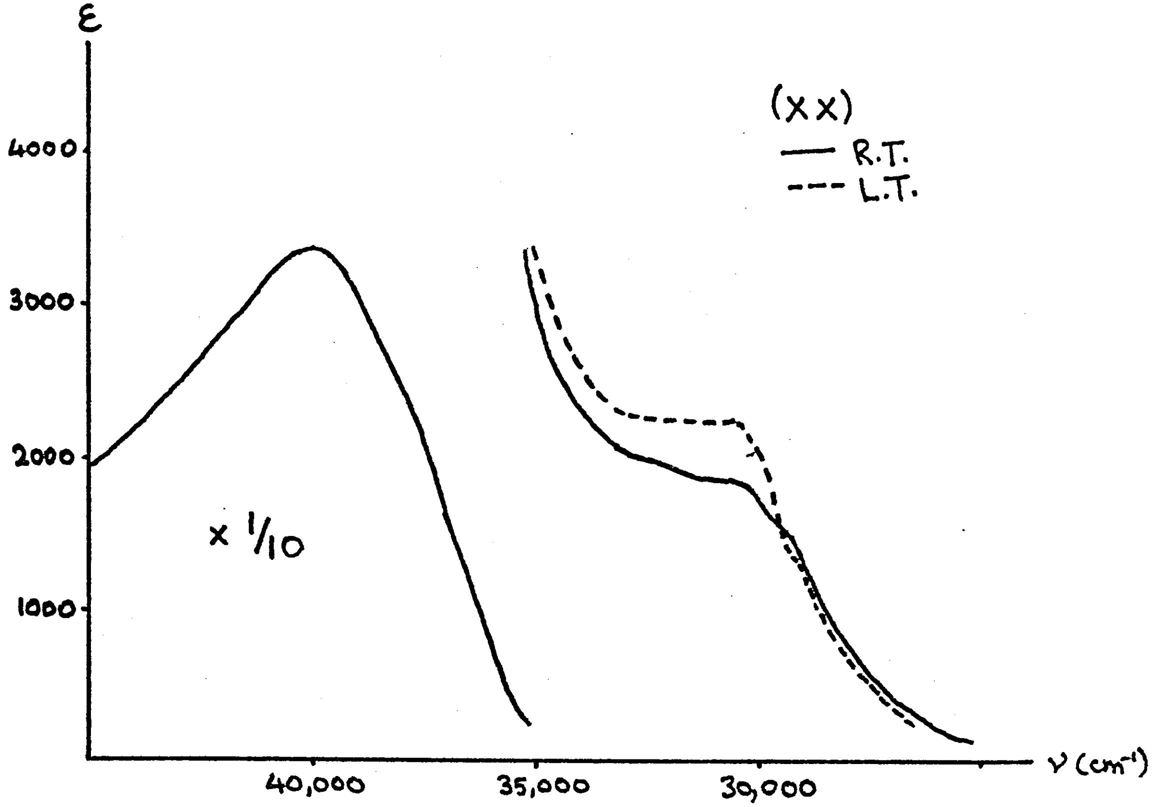

ε
(xiv)
— R.T.
--- L.T.
8000
6000
4000
2000
× 1/10
40,000
35,000
30,000
ν (cm⁻¹)

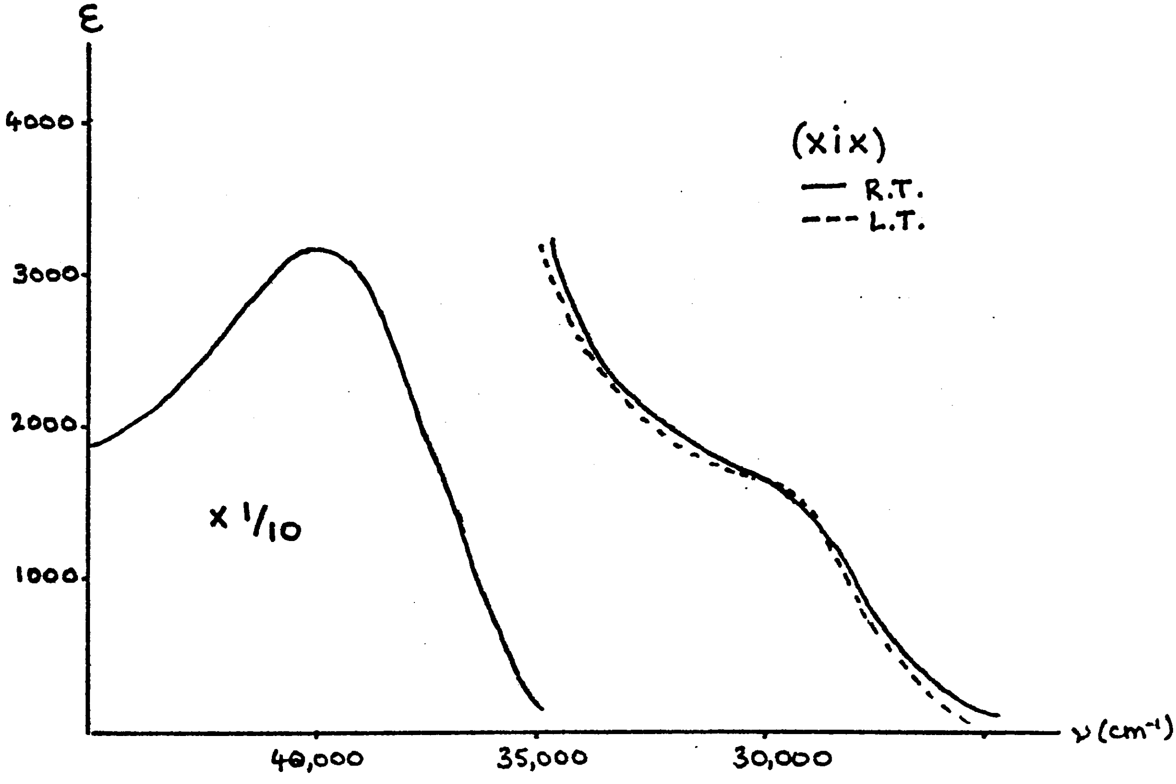

ε
6000
5000
4000
3000
2000
1000
(XV)
— R.T.
--- L.T.
x 1/10
40,000
35,000
30,000
ν (cm⁻¹)

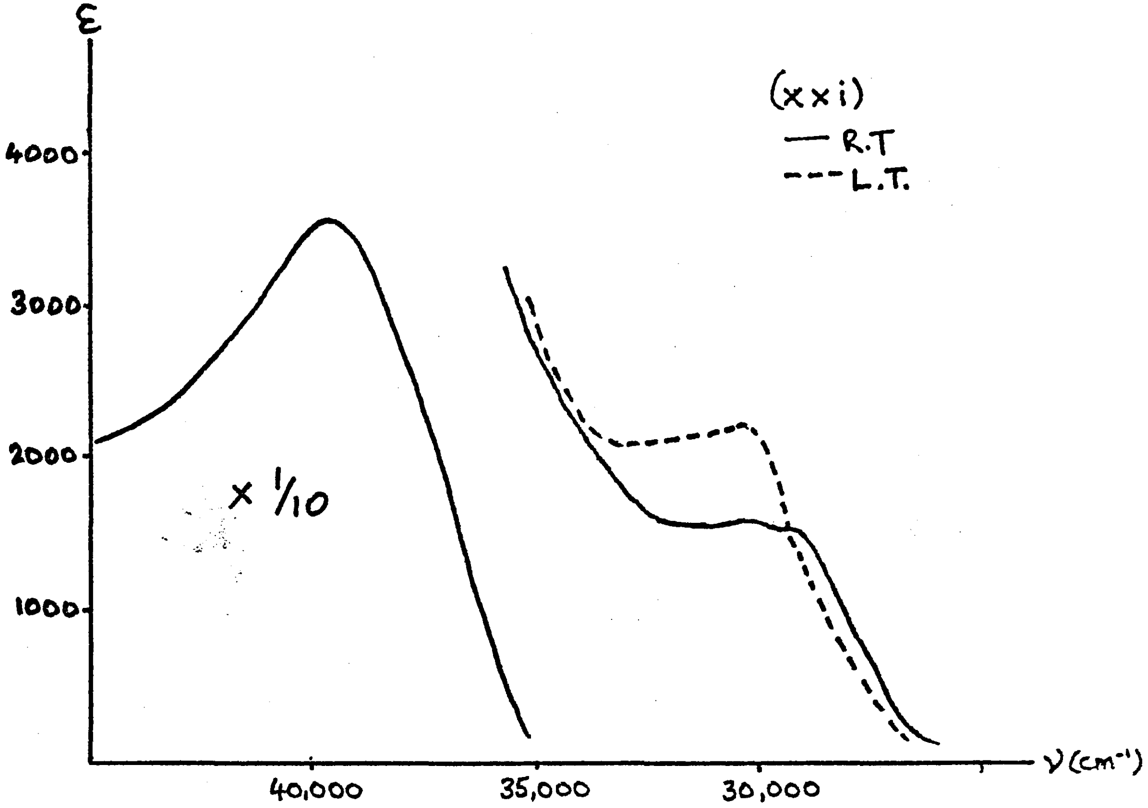

ε
4000
3000
2000
1000
(XVi)
— R.T.
--- L.T.
x 1/10
40,000
35,000
30,000
ν (cm⁻¹)

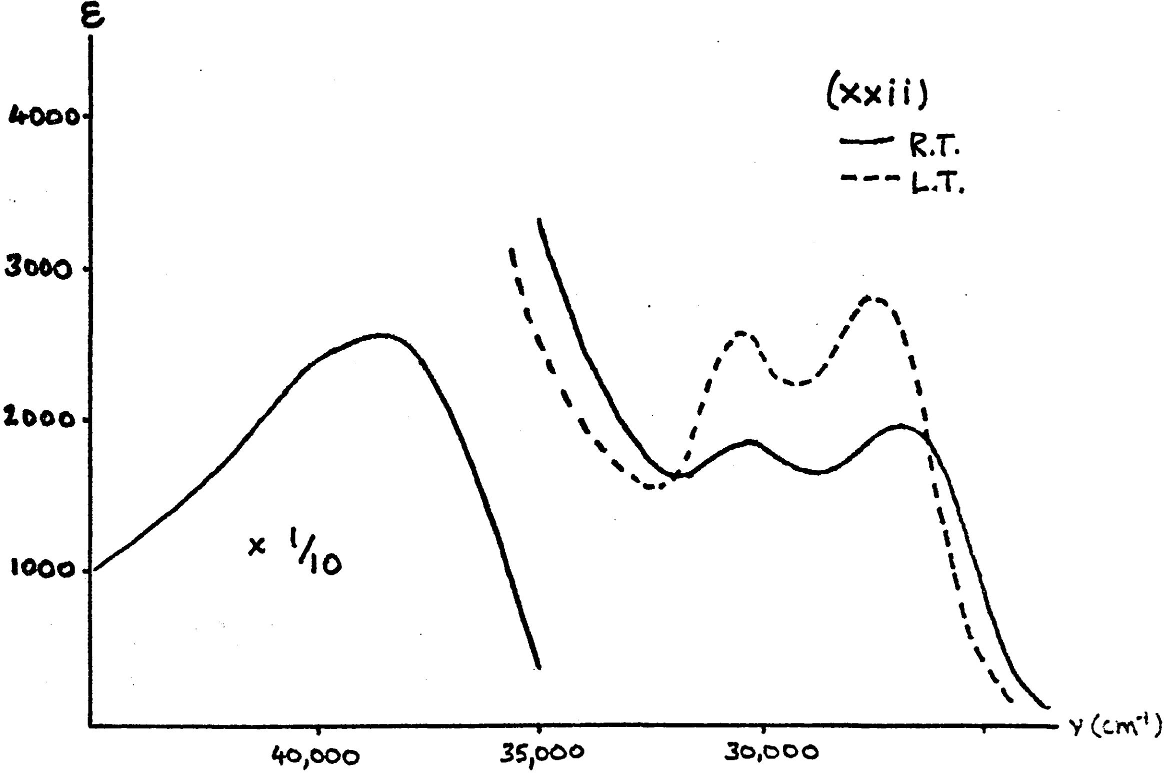

ε
(xvii)
— R.T.
--- L.T.
4000
3000
2000
1000
× 1/10
40,000
35,000
30,000
ν (cm^{-1})

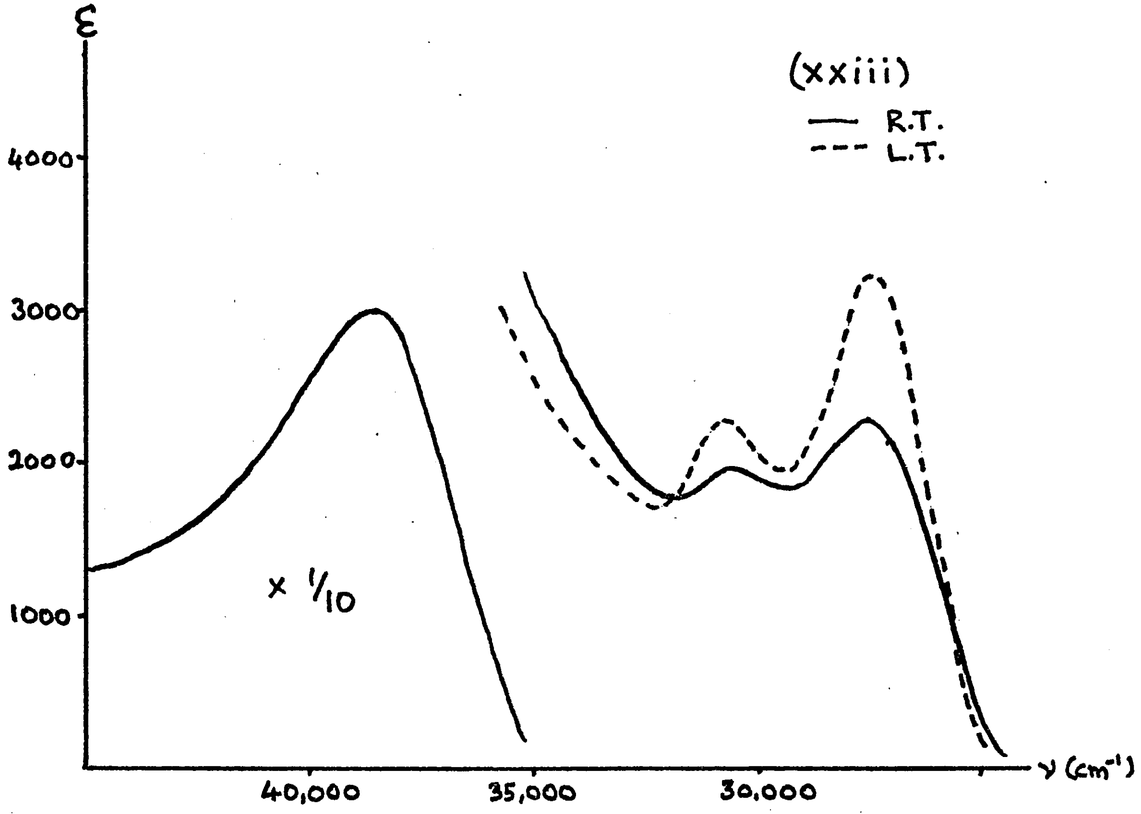

ε
6000
(x viii)
— R.T.
--- L.T.
5000
4000
3000
2000
1000
× 1/10
40,000
35,000
30,000
ν (cm^{-1})

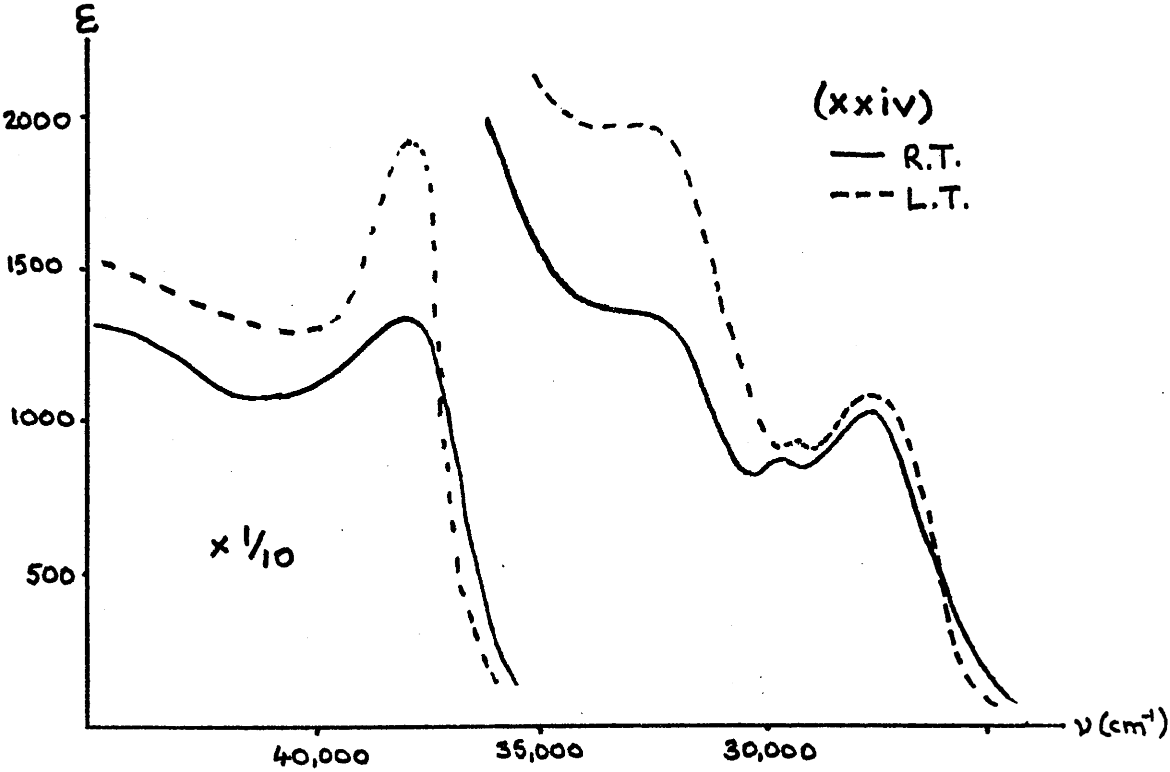

ε
4000
3000
2000
1000
(xx)
R.T.
L.T.
x 1/10
40,000
35,000
30,000
ν (cm⁻¹)

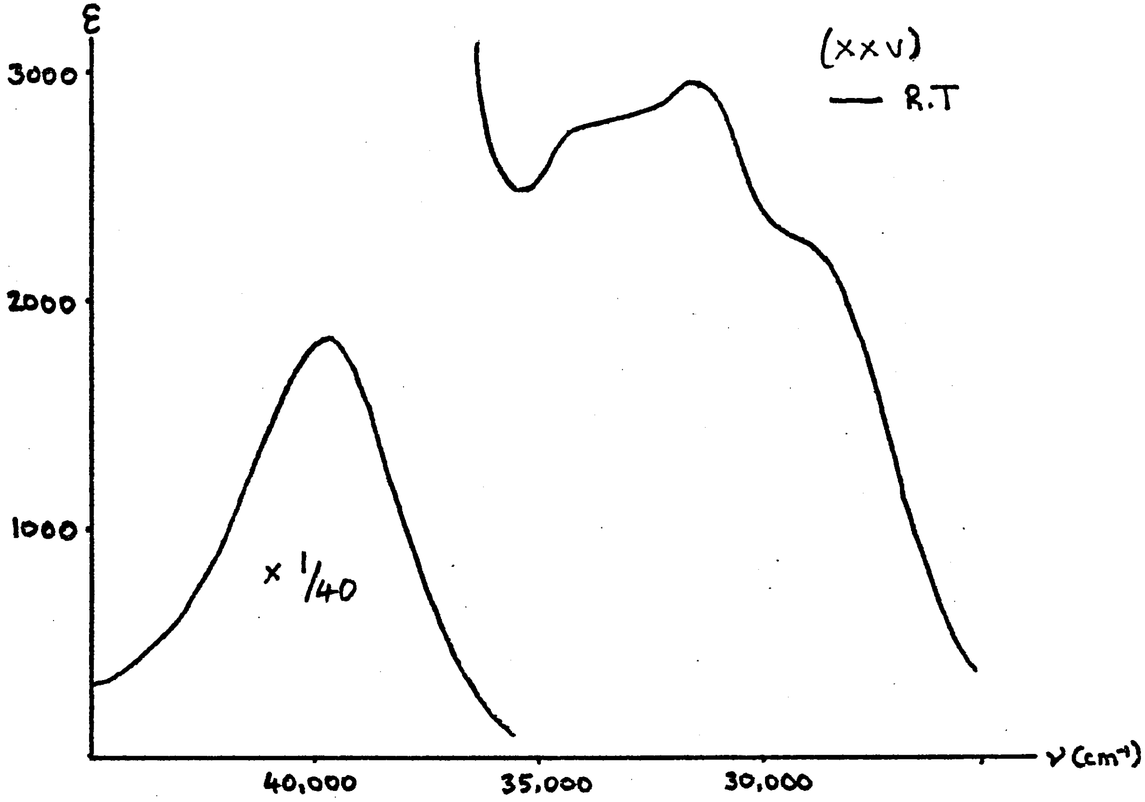

ε
4000
3000
2000
1000
(xix)
R.T.
L.T.
x 1/10
40,000
35,000
30,000
ν (cm⁻¹)

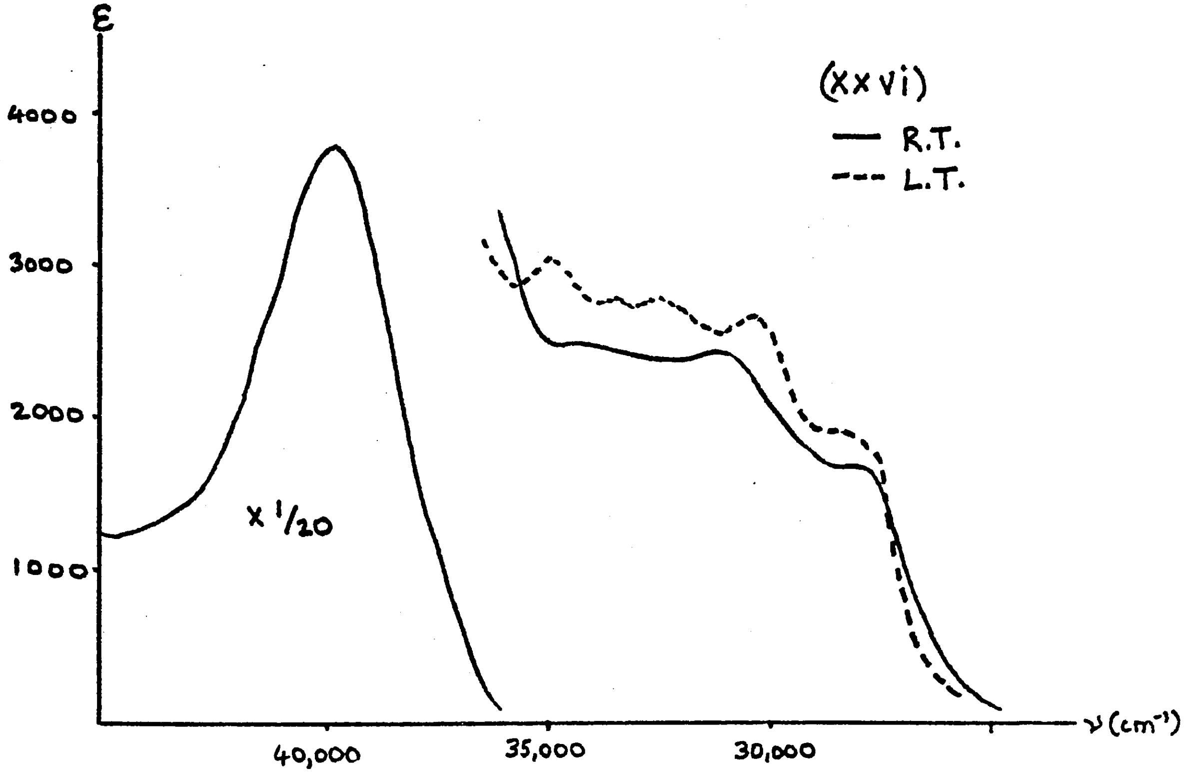

ε
4000
3000
2000
1000
(xxi)
R.T
L.T.
× 1/10
40,000
35,000
30,000
ν (cm⁻¹)

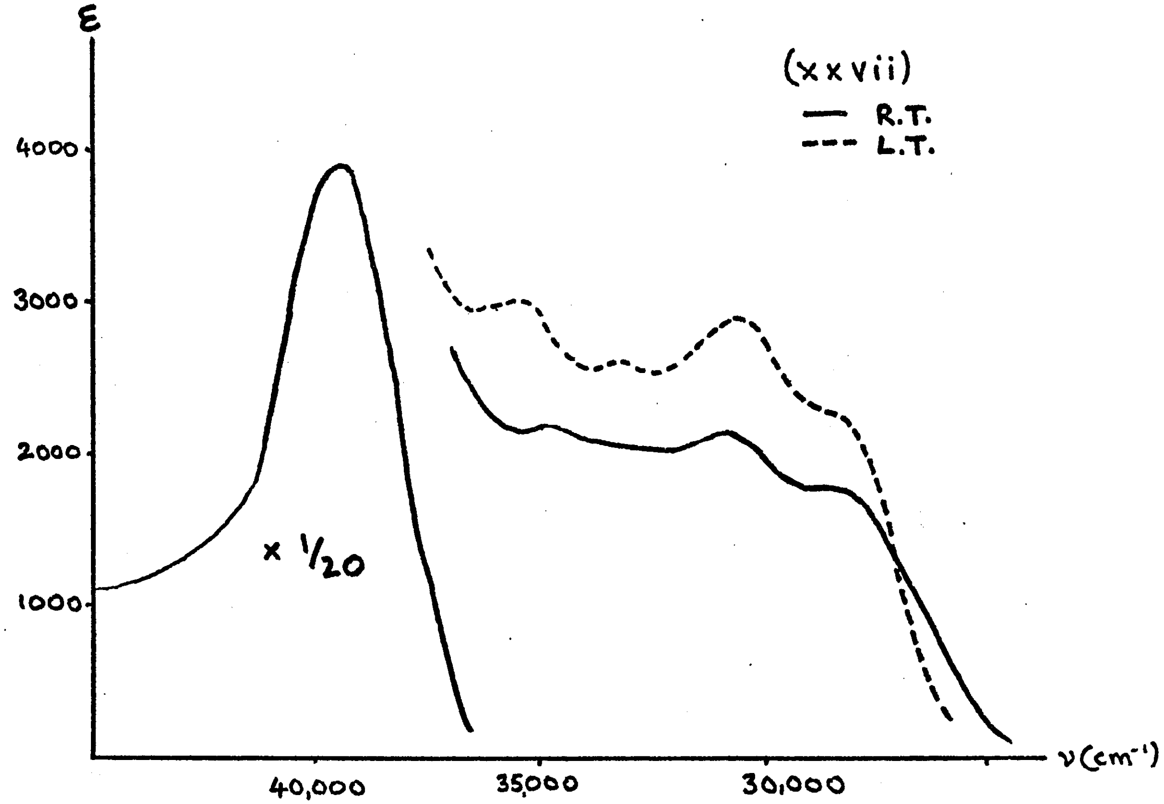

ε
4000
3000
2000
1000
(xxii)
R.T.
L.T.
× 1/10
40,000
35,000
30,000
ν (cm⁻¹)


ε
(xxiii)
R.T.
L.T.
4000
3000
2000
1000
× 1/10
40,000
35,000
30,000
ν (cm⁻¹)


ε
(xxiv)
R.T.
L.T.
2000
1500
1000
500
× 1/10
40,000
35,000
30,000
ν (cm⁻¹)


ε
3000
2000
1000
(XXV)
— R.T
× 1/40
40,000
35,000
30,000
ν (cm⁻¹)


ε
4000
3000
2000
1000
(XXVi)
— R.T.
--- L.T.
× 1/20
40,000
35,000
30,000
ν (cm⁻¹)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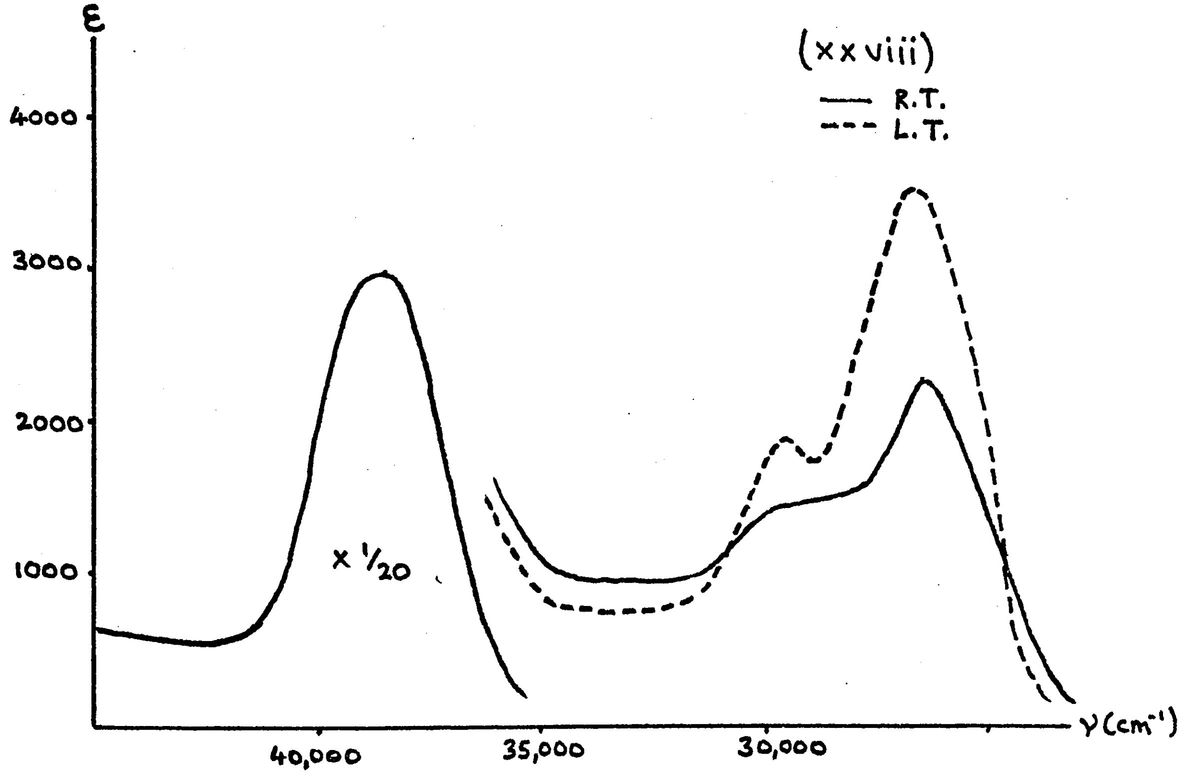
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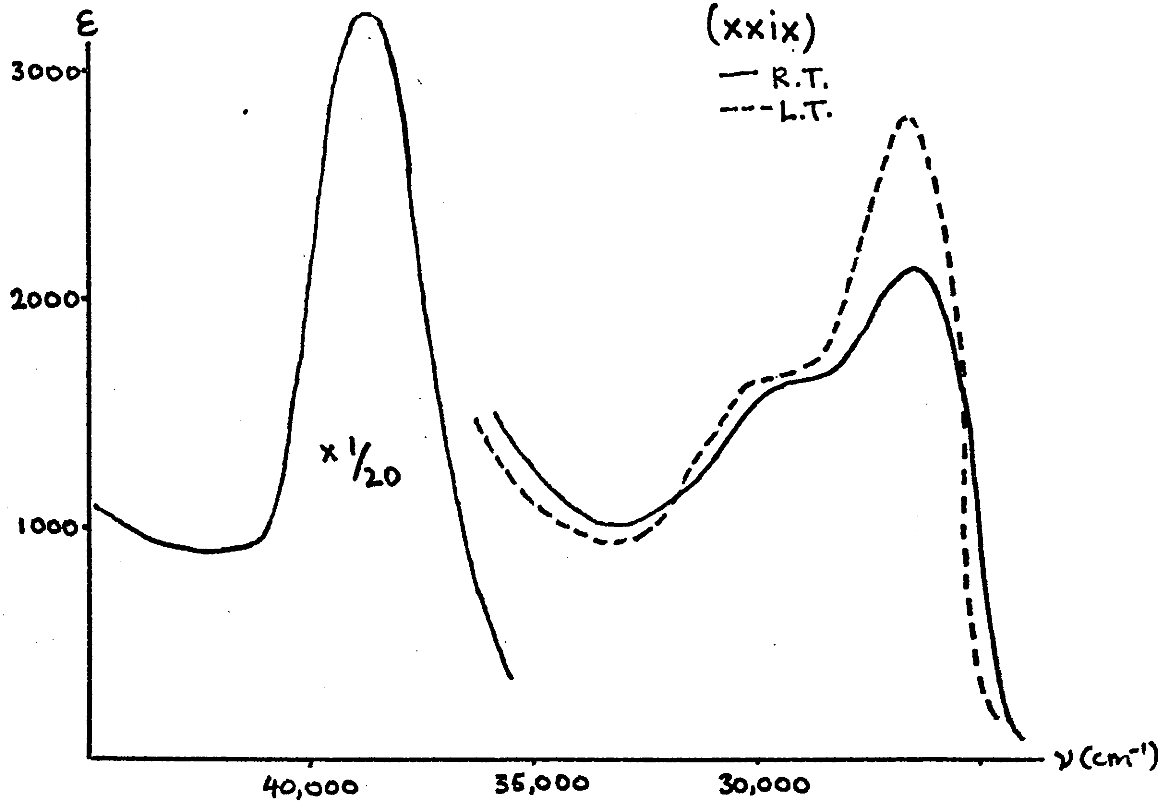
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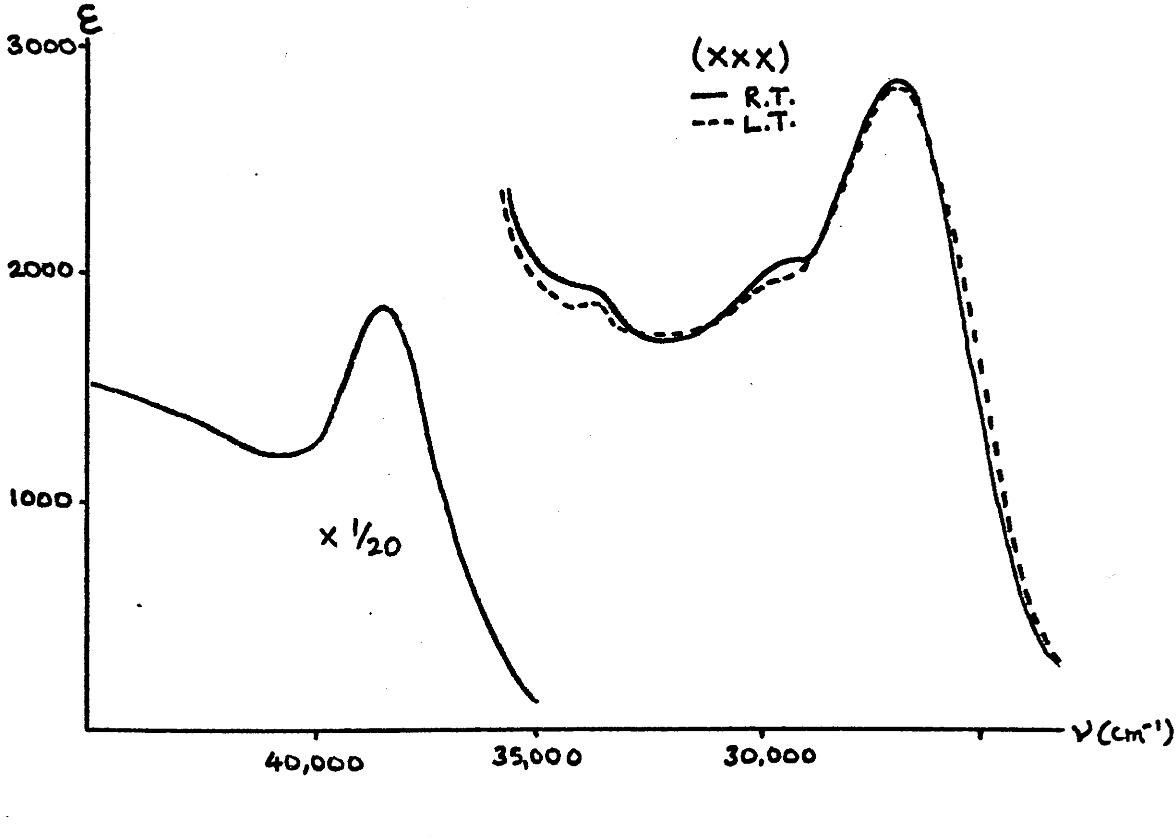
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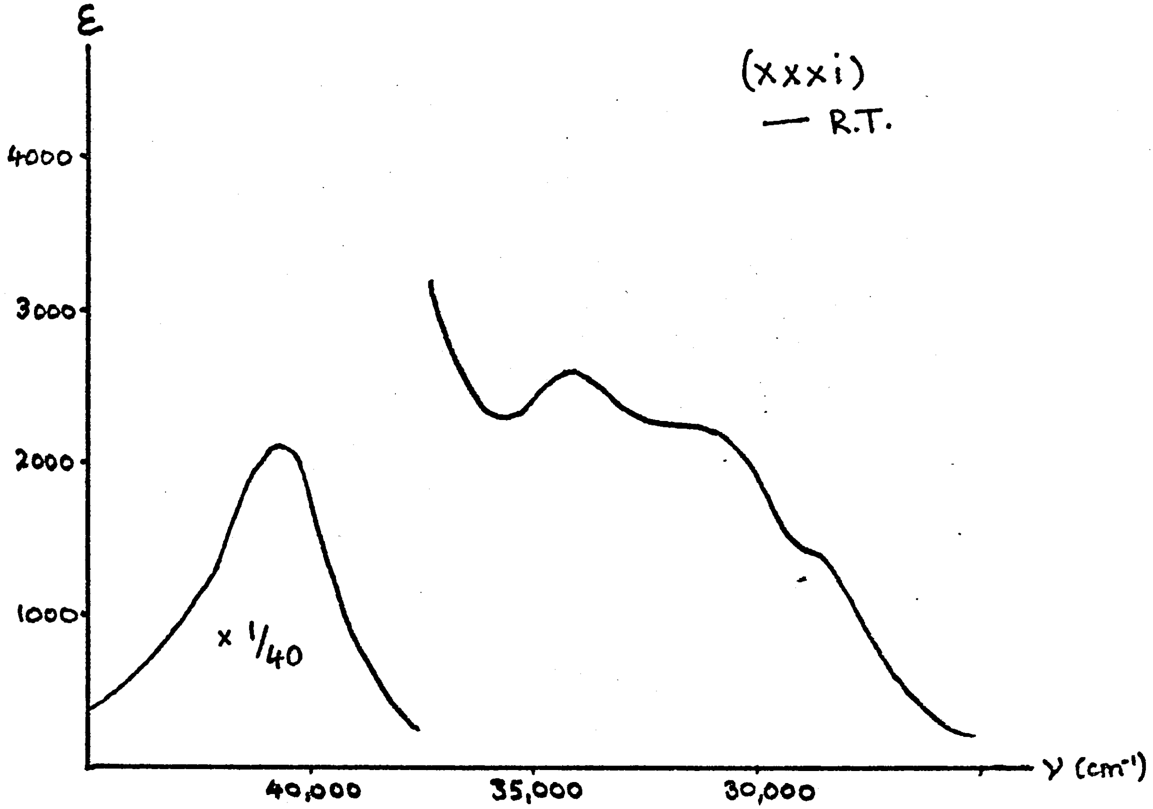
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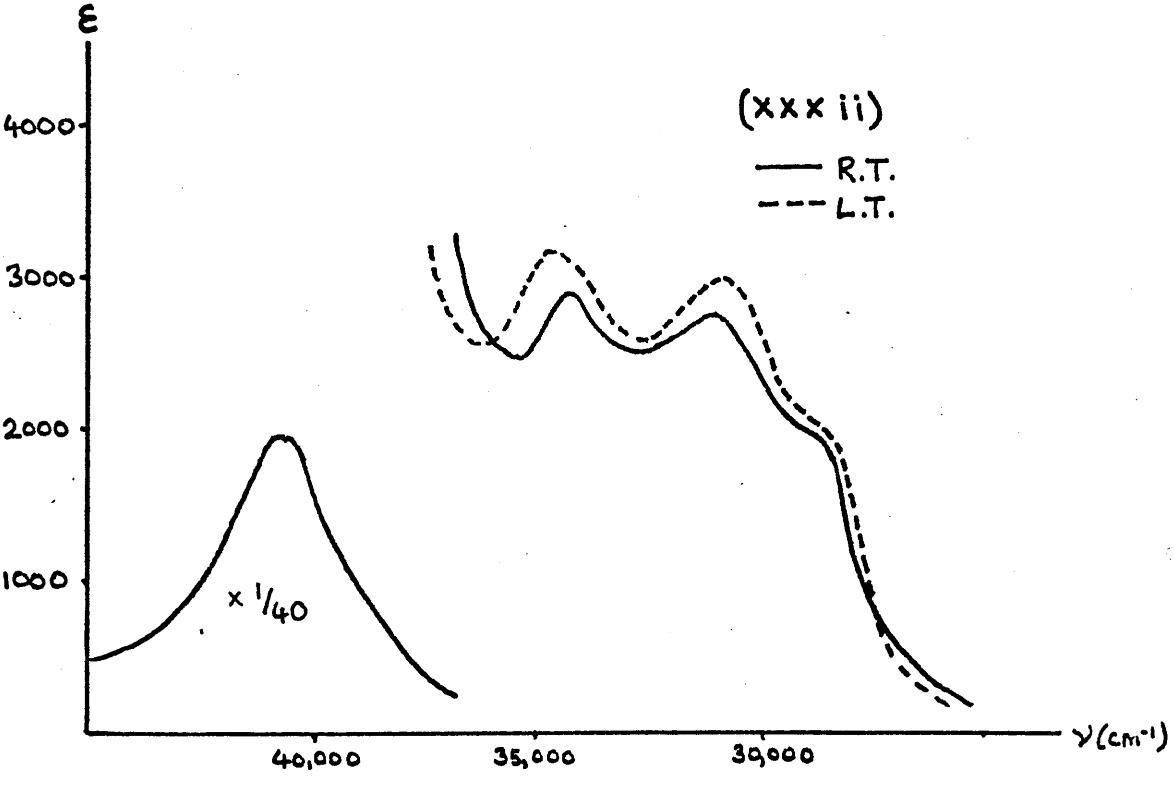
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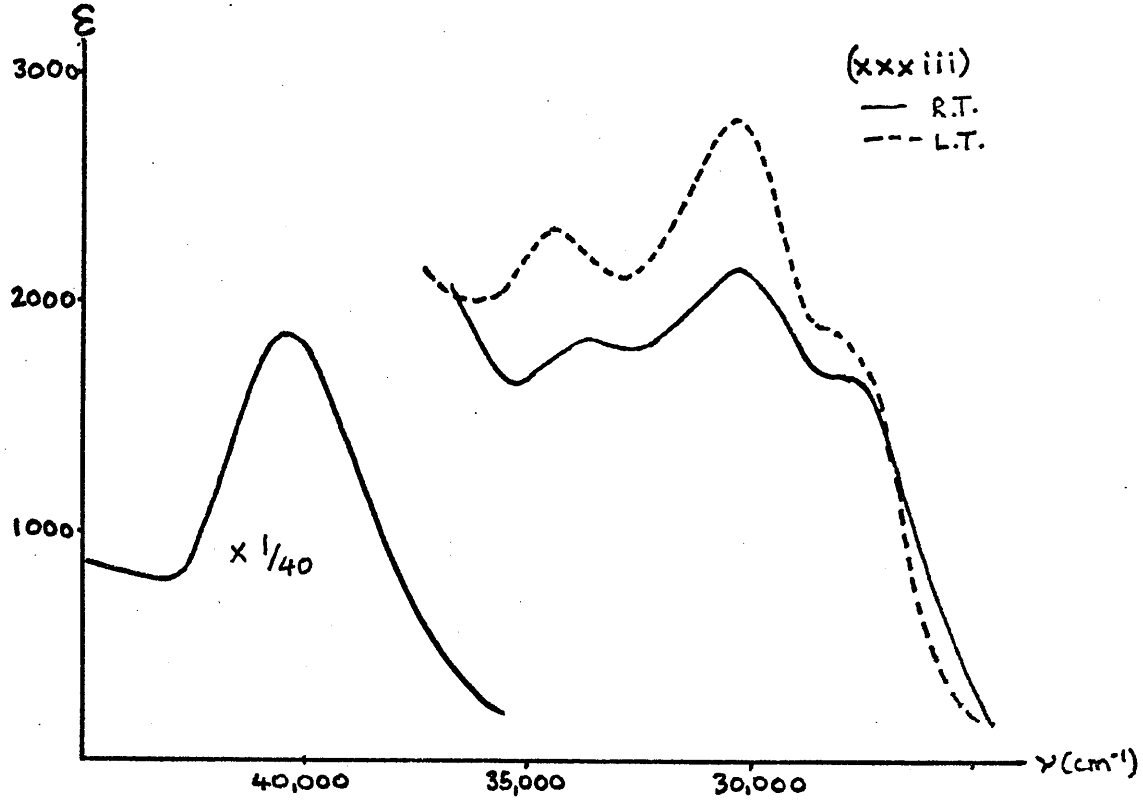
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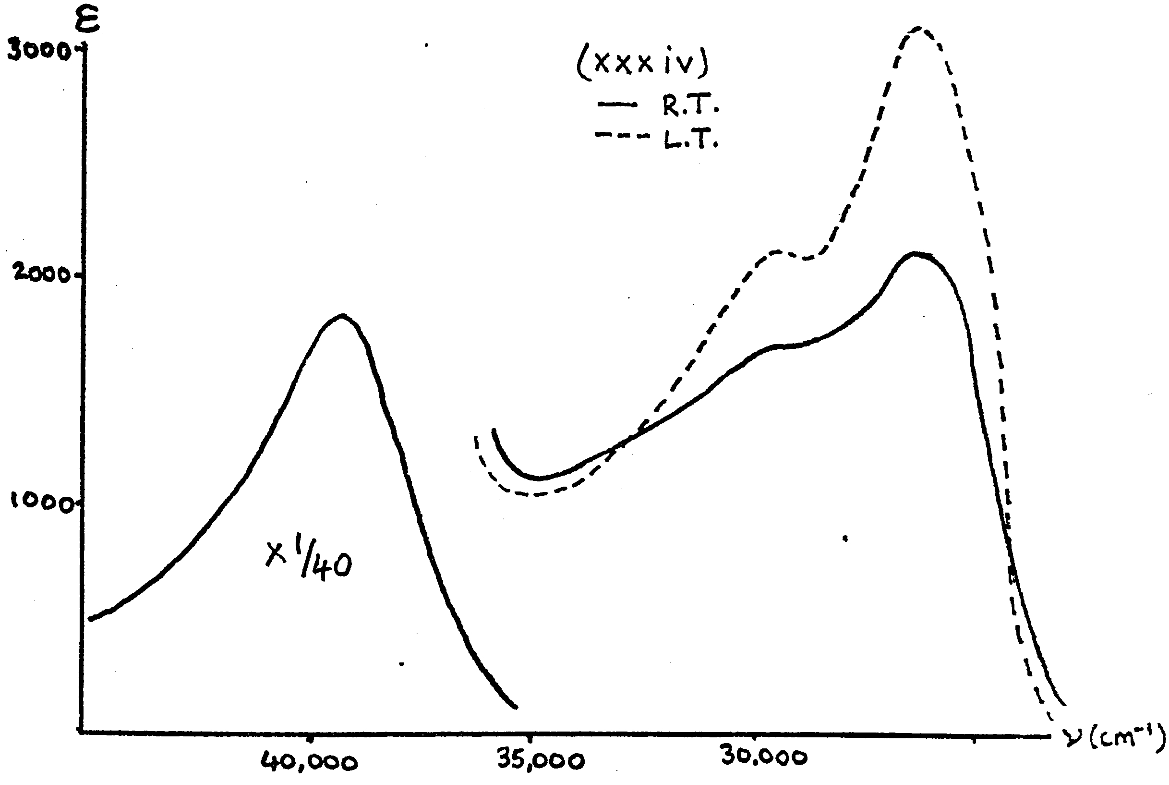
ν (cm⁻¹)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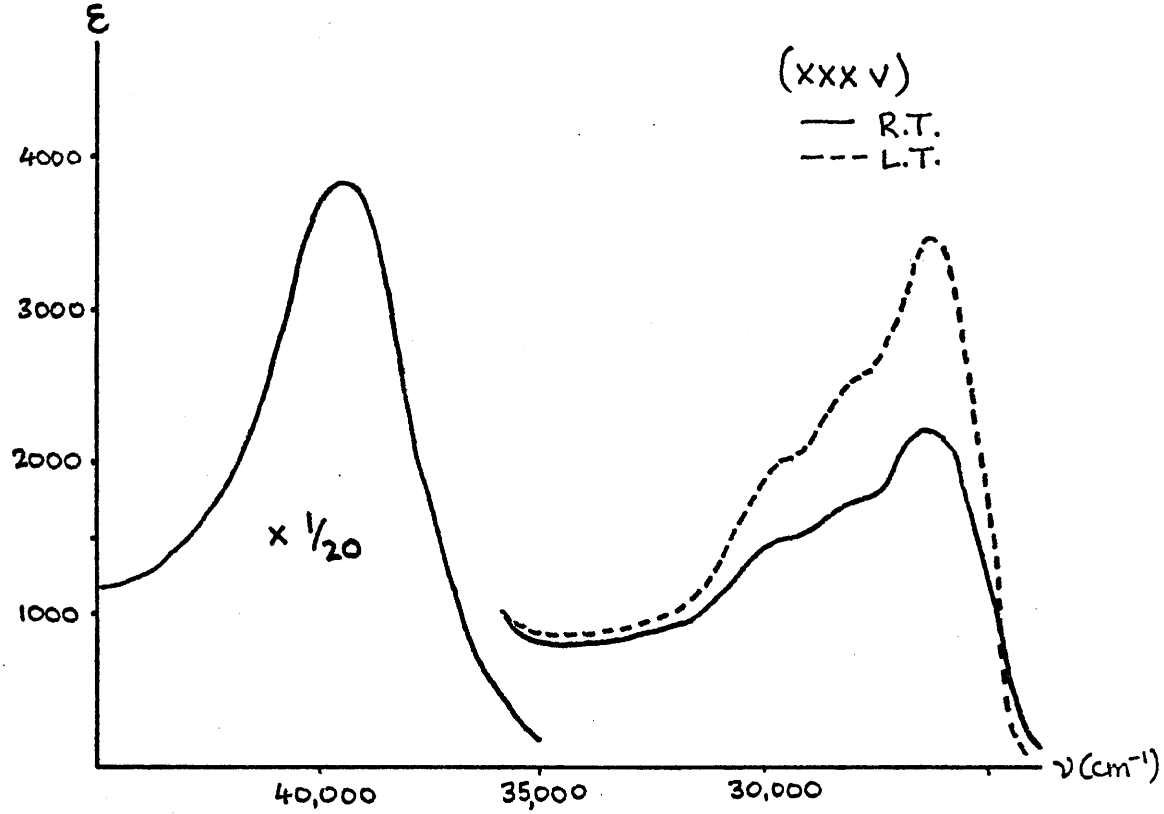
ν (cm⁻¹)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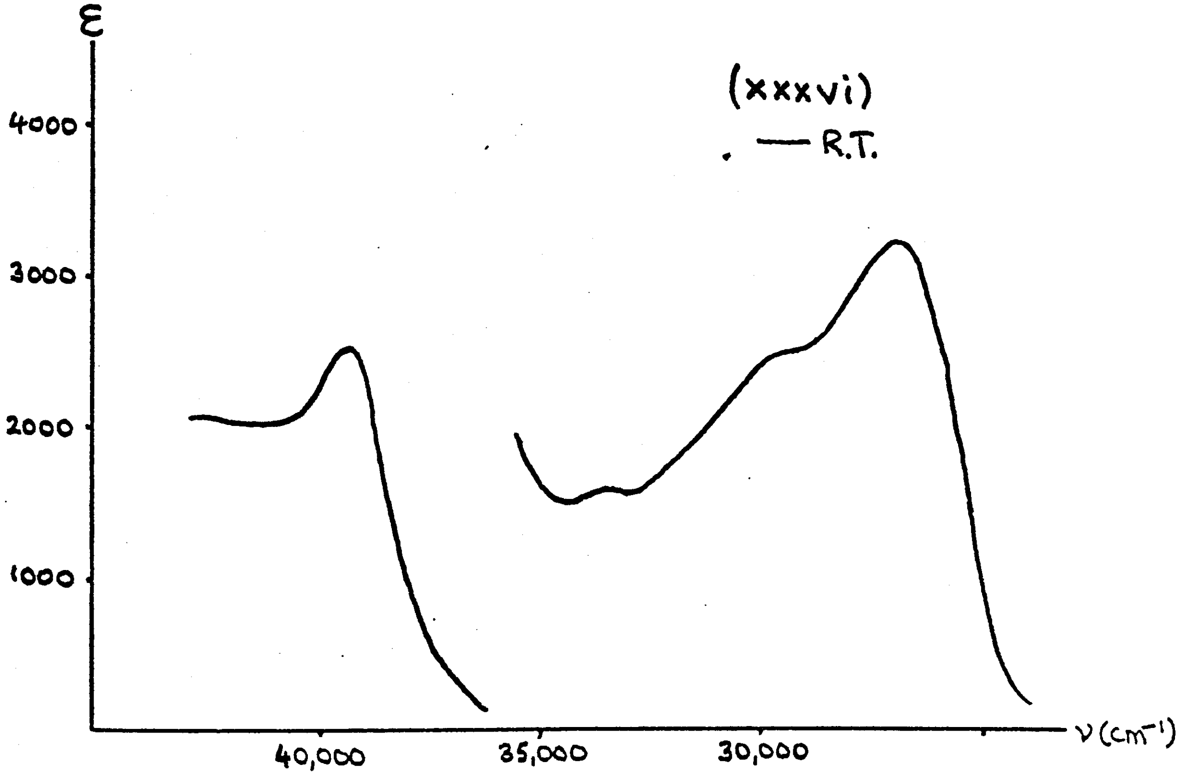
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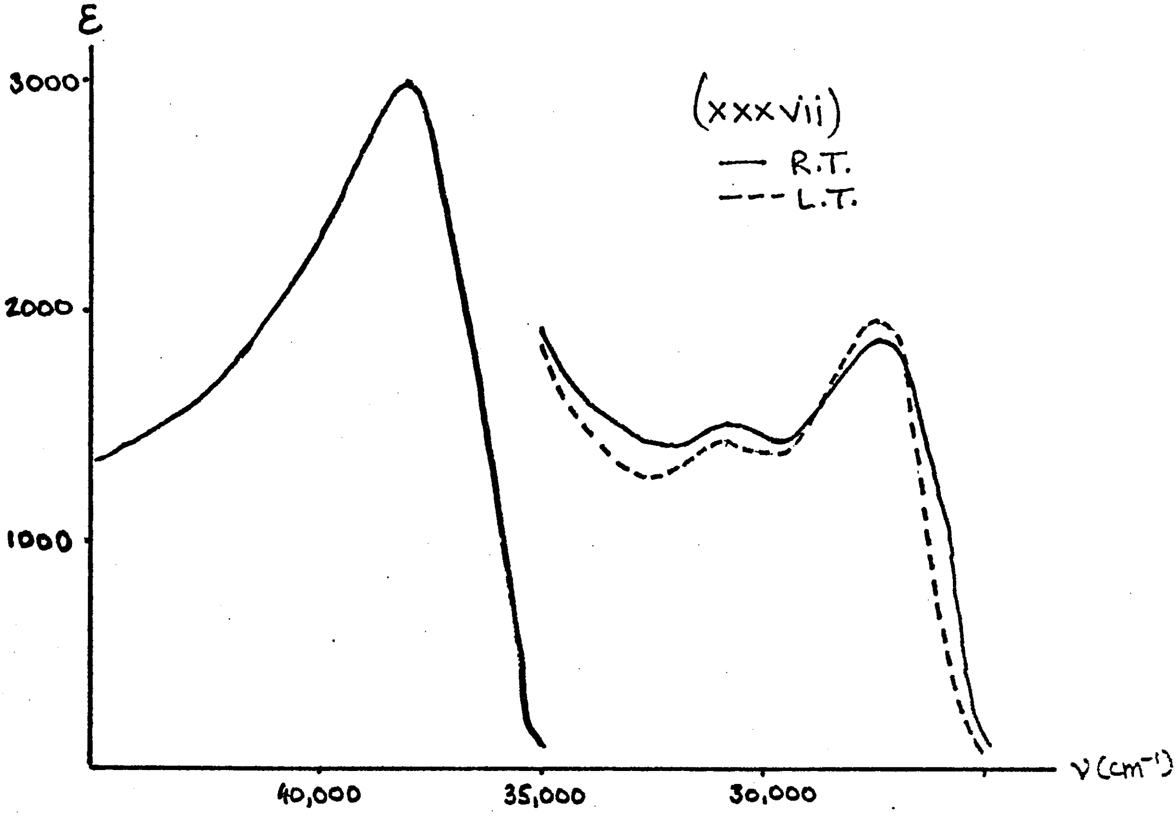
ν (cm⁻¹)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— R.T.
--- L.T.
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ν (cm⁻¹)

CHAPTER 4

NUCLEAR MAGNETIC RESONANCE SPECTRA AND MASS SPECTRA

NUCLEAR MAGNETIC RESONANCE SPECTRA

Introduction

The study of nuclear magnetic resonance spectra of substituted metal carbonyl derivatives of the type discussed here has been concentrated in two principal directions. These concern the ^{1}H and ^{31}P resonance spectra respectively. The ^{31}P studies were referred to in the general introduction and an attempt has been made to relate the $^{31}P - ^{183}W$ coupling constant to the position of the E mode in the infrared spectra of complexes of type $LW(CO)_5$ where L is a variety of phosphorus (III) ligands.[28] Further studies on cis and trans disubstituted group VI metal carbonyls[127] and complexes $L_nM(CO)_{6-n}$ where L = $P(OMe)_3$, PMe_3; M = Cr, Mo or W; n = 1 - 4[80] have been carried out and the phosphorus-31 N.M.R. parameters discussed in relation to the bonding properties of these complexes. The results and discussions are complex and inconclusive and no phosphorus-31 resonance results have been obtained in this work. While this is principally due to the extensive work already reported in this field, the low solubility of many of the complexes in this work made them unsuitable for observing the phosphorus resonance as its signal strength is much less than that of a proton resonance and very highly concentrated solutions are required in the former case.

The other principal study of nuclear magnetic resonance results concerning metal carbonyl phosphine complexes is of proton magnetic resonance spectra and the phenomenon of 'virtual coupling' in these spectra. This effect has been observed for complexes with two phosphorus atoms in trans positions[128], and is due to spin information transmitted via the metal atom. The effect has been reported for transdisubstituted Tdp complexes of chromium, molybdenum and tungsten carbonyls by King[81] and for analogous complexes of the ligand $P(OCH_2)_3CCH_3$ by Verkade and coworkers.[129] They each observed a splitting pattern for the methyl and methylene protons respectively which is identical to that expected for two equivalent phosphorus atoms coupled to the protons. The magnitude of the virtual coupling may be related to J_{PP}. Mann[157] and Ogilvie, Jenkins and Verkade[131] have reported studies on these coupling effects using equations developed by Harris[130] and the nomenclature of Haigh.[158]

The proton magnetic resonance spectra of the complexes $LM(CO)_5$ and trans $L_2M(CO)_4$ where M = Cr, Mo or W and L = $P(OMe)_3$, $P(OEt)_3$, $P(OPr^i)_3$, PPr^i_3, PBu^n_3 have been recorded and measured and the parameters are listed in Table 4.1. The parameter values and spectral patterns are discussed in relation to reported values and spectra of similar complexes. One more recent development in NMR work on metal carbonyl derivatives is the use of ^{13}C resonance techniques and parameters for some of the complexes studied in this work are given in table 4.2 along with recently reported values for some closely related complexes. Theoretical interpretation of ^{13}C spectral work is presently being developed and an introduction to

TABLE 4.1

^1H N.M.R. PARAMETERS

All spectra are recorded in $CDCl_3$ using tetramethylsilane as internal reference.

	COMPOUND	CHEMICAL SHIFTS (τ)	
		α H	β H
A.	$P(OMe)_3$	6.51d (11.7)	
	$P(OMe)_3Cr(CO)_5$	6.37d (11.2)	
	$P(OMe)_3Mo(CO)_5$	6.39d (11.6)	
	$P(OMe)_3LW(CO)_5$	6.35d (11.7)	
	$[P(OMe)_3]_2Cr(CO)_4$	6.35d (11.4)	
	$[P(OMe)_3]_2Mo(CO)_4$	6.39t (11.8)	
	$[P(OMe)_3]_2W(CO)_4$	6.42t (11.9)	
B.	$P(OEt)_3$	6.12q (7.7)	8.73t (7.6)
	$P(OEt)_3Cr(CO)_5$	5.98q (7.5)	8.68t (7.0)
	$P(OEt)_3Mo(CO)_5$	6.01q (7.6)	8.68t (6.9)
	$P(OEt)_3W(CO)_5$	5.92q (7.5)	8.68t (7.5)
	$[P(OEt)_3]_2Cr(CO)_4$	6.00q (7.0)	8.70t (7.0)
	$[P(OEt)_3]_2Mo(CO)_4$	6.02* (3.6)	8.68t (7.2)
	$[P(OEt)_3]_2W(CO)_4$	6.04* (3.7)	8.68t (7.3)

TABLE 4.1 (Contd.)

	COMPOUND	CHEMICAL SHIFTS (τ)		
		α H		β H
C.	$P(OPr^i)_3$	5.58s	(7.0)	8.78d (5.8)
	$P(OPr^i)_3Cr(CO)_5$	5.34s	*	8.69d (5.7)
	$P(OPr^i)_3Mo(CO)_5$	5.55s	(6.1)	8.70d (6.3)
	$P(OPr^i)_3W(CO)_5$	5.45s	*	8.69d (6.5)
	$[P(OPr^i)_3]_2Cr(CO)_4$	5.38s	*	8.69d (5.3)
	$[P(OPr^i)_3]_2Mo(CO)_4$	5.41s	(6.0)	8.72d (6.5)
	$[P(OPr^i)_3]_2W(CO)_4$	5.45s	(6.0)	8.71d (6.2)
D.†	PPr^i_3	8.27	*	8.96d,d
	$PPr^i_3Cr(CO)_5$	8.2	*	8.74d,d
	$PPr^i_3Mo(CO)_5$	7.8	*	8.77d,d
	$PPr^i_3W(CO)_5$	7.8	*	8.78d,d
	$(PPr^i_3)_2Cr(W)_4$	7.6	*	8.70d,d
	$(PPr^i_3)_2Mo(CO)_4$	7.8	*	8.75d,d
	$(PPr^i_3)_2W(CO)_4$	7.7	*	8.73d,d

TABLE 4.1 (Contd.)

	COMPOUND	CHEMICAL SHIFTS (τ)			
E.†	PBu^n_3				
	$PBu^n_3Cr(CO)_5$	8.47	*	9.08	*
	$PBu^n_3Mo(CO)_5$	8.45	(~10)*	9.04	(~5)*
	$PBu^n_3W(CO)_5$	8.56	*	9.09	*
	$(PBu^n_3)_2Cr(CO)_4$	8.47	(~11)*	9.08	(~4)*
	$(PBu^n_3)_2Mo(CO)_4$	8.45	*	9.08	*
	$(PBu^n_3)_2W(CO)_4$	8.50	(~ 7)*	9.06	(~5)*

† Second order spectra

Figures in brackets are peak separation in cps. (adjacent peaks)

Splitting patterns: d doublet; d,d doublet of doublets; t triplet;
q quintet; s septet.

* Complex signal. Multiplicity or peak separation doubtful.

its importance in studies such as this will be given along with the discussion of the parameters obtained.

^{1}H N.M.R. RESULTS

The spectra were obtained on a Perkin Elmer R.10 60 Mc/s spectrometer using deuterochloroform as solvent and tetramethylsilane as internal reference. The observed parameters are given in Table 4.1 grouped according to the ligand.

Trimethylphosphite derivatives

As is seen from table 4.1A, the ligand, each of the monosubstituted derivatives and the trans disubstituted chromium complex show a doublet, the molybdenum and tungsten disubstituted complexes each having a triplet pattern. The ligand doublet arises from spin-spin coupling $^{31}P - {}^{1}H$ of the phosphorus-31 with the three equivalent methyl protons. Co-ordination of the $P(OMe)_3$ ligand to a group VI metal carbonyl causes the N.M.R. signal to shift downfield (i.e. to lower τ values) while the spin-spin coupling pattern remains unchanged. Environment effects on coupling constants are discussed below in relation to similar previous observations. The spin-spin coupling patters of the trans disbustituted complexes differs in the chromium case from that in the molybdenum or tungsten cases. The latter complexes have an apparent triplet pattern, approximate intensity ratio 1:1.5:1, the two outer peaks having a lower half band width than the central peak in each case. The disubstituted chromium derivative shows essentially a doublet pattern although there is a small asymmetric peak between the outer bands.

These spin-spin coupling patterns may be understood using standard coupling theory and possible secondary phosphorus coupling effects transmitted through the metal atom in the disubstituted cases. As has been stated above the occurrence of a doublet in these spectra is readily understood by phsophorus hydrogen coupling theory which the apparent triplet patters arise from complex overlapping of resonance lines. The observed patterns for trans disubstituted complexes imply that phosphorus-phosphorus coupling is small for the P-Cr-P system and fairly high for the P-Mo-P and P-W-P systems. This was previously observed to be so in trans disubstituted Tdp complexes.

The shift downfield from tetramethylsilane is seen to be greater for the complexes than for the trimethylphosphite ligand while generally the shifts for monosubstituted complexes are very similar to those for the trans disubstituted derivatives. This downfield shift on complexing may possibly be related to the magnitude of the positive charge on the phosphorus atom. Hendrickson and coworkers[138] noted that formation of a quaternary salt from a neutral phosphine gave a downfield shift of α-protons in substituents on the phosphorus atom while formation of a phosphine oxide (OPR_3) produced a similar effect on the α- and β-protons, the magnitude of the shift being less in the latter case. They also reported that the ^{31}P - ^{1}H spin-

spin coupling in a series of derivatives appeared to vary uniformly, increasing as the chemical shift moved to lower fields. Each of these factors was explained by spin-spin coupling theory and hybridisation effects. If the σ- electron contact contribution to the spin-spin coupling constant is taken as proportional to the s-character in the phosphorus hybrid orbital of the phosphorus-carbon bond, this contribution will depend on the electronegativity of the substituent groups. As this electronegativity increases, the positive charge on phosphorus will be enhanced as will the s-character in the P-C bond. If this greater s-character increases the contact contribution to the coupling constant then the observed increase in J_{PH} as the proton signals shift to lower fields is readily explained. However, examination of the values given in Table 4.1A shows clearly that no correlation may be seen between chemical shift values and spin-spin coupling constants for the complexes considered in this study.

The chemical shifts for monosubstituted derivatives show a different order from shifts for the trans disubstituted complexes and this suggests that correlation of phosphorus charge and chemical shift is not possible for a series of very similar complexes. Thus, it is difficult to explain why $P(OMe)_3W(CO)_5$ has a greater chemical shift than corresponding chromium or molybdenum derivatives while $[P(OMe)_3]_2W(CO)_4$ shows the lowest shift for the trans disubstituted complexes. Further, the coupling constants while showing the same order for mono and trans disubstituted complexes have J_{PH} values increasing in order Cr $\ll$ Mo $\ll$ W and for the disubstituted derivatives only, coupling constant-chemical shift trends (J increasing, shift decreasing) are opposite to those reported by Hendrickson and coworkers. These results do not indicate whether the σ-electron contribution to J_{PH} is significant as they cannot be said to provide any measure of the positive charge on phosphorus. Consequently, the theory developed to rationalise coupling constants and chemical shifts in alkylphosphorus compounds is not useful in discussing organometallic complexes of the type considered here. As the parameters in Table 4.1A are those for the phosphorus (III) derivatives with the simplest proton arrangement, it is fairly clear that the proton magnetic spectra of more complex derivatives will be of limited use in bonding discussions. This limitation combined with second order splitting effects has restricted the study of proton N.M.R. spectra to observation of the parameters and discussion of virtual coupling effects. The phosphorus-31 N.M.R. work carried out by groups such as Ogilvie, Jenkins and Verkade[131] and Grim and coworkers[28] has failed to establish an unequivocal relation between ^{31}P N.M.R. parameters and metal-phosphorus bonding characteristics. This is also true for proton N.M.R. parameters.

Triethylphosphite derivatives

Parameters from the spectra of the triethylphosphite ligand and its complexes are given in Table 4.1B. As may be seen, the methyl protons give a 1:2:1 triplet as expected for coupling with the CH_2 protons while these latter protons show a quintet structure having relative intensity 1:4:6:4:1. This may be explained by assuming both ^1H - ^1H and ^{31}P - ^1H spin-spin coupling which produces two overlapping quartets. Baldeschwieler and Randall[139] carried out a series of double resonance experiments which gave CH_3 - CH_2 coupling in triethylphosphite equal to the P - CH_2 coupling. Thus the CH_2 quintet is sharp and has approximately equal spacing to that of the methyl triplet. The phosphorus atom does not couple to the β-carbon atom in the ethyl group (i.e. $J_{P-H_\beta} \sim 0$).

In both the mono- and trans disubstituted complexes, the methyl signal has a spin-spin coupling pattern similar to that of the free ligand (i.e. a 1:2:1). The chemical shift is slightly greater for the complexes, the monosubstituted derivatives having identical shifts (8.68 τ) equal to that of the molybdenum and tungsten disubstituted complexes while $[P(OEt)_3]_2Cr(CO)_4$ has $\tau_{CH_3} = 8.70$. Little information concerning bonding properties in the metal-ligand link may be derived from these parameters. The spin-spin coupling constants, while showing behaviour similar to that for trimethylphosphite complexes are equally unhelpful. The coupling constant decreases from ligand to complexes except for the disubstituted tungsten derivative which has the opposite effect. The CH_2 signal shows more complex behaviour due to the phosphorus spin coupling effects and virtual coupling is seen for the molybdenum and tungsten disubstituted derivatives. The monosubstituted complexes have CH_2 signals similar to that of the free ligand (i.e. a 1:4:6:4:1 quintet) and are shifted downfield with respect to the triethylphosphite. The chemical shifts decrease in order $Mo > Cr > W$ and $^{31}P - H$ coupling constants ($= J_{HH}$) have a similar relation $Mo > Cr = W$. The disubstituted complexes have consistently higher chemical shifts and double resonance techniques would be necessary to assign peak separations. The trans disubstituted chromium derivative has a CH_2 pattern which may best be described as an unresolved quintet. The five peaks are readily observed but they coalesce to give a wide unresolved pattern. The trans disubstituted molybdenum and tungsten derivatives have a CH_2 pattern comprising nine peaks, intensity ratio 1:2:4:6:6:6:4:2:1 which must be attributed to the effects of virtual coupling across the P-M-P bond.

Triisopropylphosphite derivatives

The proton magnetic resonance signals expected for triisopropylphosphite and its complexes are a doublet for the methyl protons and a septet possibly split by coupling to the phosphorus atom for the unique proton. The doublet is observed as a strong signal in the free ligand and in each of the complexes. No phosphorus-proton coupling is seen in any of the compounds. The CH signal is generally very weak and consequently it was difficult to determine the multiplicity and relative intensity of the peaks making up the signal.

The chemical shift is again larger for the complex signals than for the free ligand both in the CH_3 and CH cases and the mono and trans disubstituted complexes have very similar shifts. It is interesting to note that the very well defined coupling pattern for the methyl protons is not split by the phosphorus atom (i.e. $^4J_{PH} \sim 0$) while the coupling constant J_{CH-CH_3} varies as $W > Mo > Cr$ between 5.3 and 6.5 cps. In the triisopropylphosphite complexes, if the downfield shift is taken as related to the positive charge on phosphorus, some correlation with bonding ideas may be derived. The proton chemical shifts of the trans disubstituted chromium phosphite complexes are consistently greater than those for the analogous tungsten complexes. The $^{31}P - ^{1}H$ coupling constants when observed show $J_{PH}(Cr) < J_{PH}(W)$ but as these are less well developed theoretically than chemical shift ideas, no explanation for this order may be given at present. The charge on phosphorus depends on the σ-accepting and π-donating properties of the central metal atom. The most recently reported discussion on the role of π-bonding in the metal VI hexacarbonyls suggests the order $W > Cr > Mo$ for π-backbonding ability[38]. As the backbonding ability is less for chromium than tungsten it may be expected that the phosphorus is more positive in the chromium derivative giving the higher chemical shift. Brown and Rawlinson[103] have carried out self consistent field calculations on the metal VI hexacarbonyls which indicate σ-bonding ability increasing in order Mo, W$<$Cr which would, if the order is similar in the derivatives, suggest further enhancement of the phosphorus positive charge. The CH signal split by spin-spin interaction between the CH and $(CH_3)_2$ groups gave a very complex pattern which could not be analysed using the spectra obtained. Thus virtual coupling effects were not seen although by analogy with the trimethylphosphite and triethylphosphite derivatives, this effect is probably present.

Triisopropylphosphine and tri-n-butylphosphine derivatives

The spectra of these ligands and derivatives showed rather complex peak structures due to second order splitting and without a construction of the theoretical N.M.R. spectrum expected for the spin-spin splitting patterns (for example, as in a computer study by Swalen and Reilly[140]) it is not possible to gain significant information from the spectra.

Thus the metal VI carbonyl phosphite derivatives have first order N.M.R. spectra which may be interpreted by simple N.M.R. theory. Virtual coupling is observed when two phosphite groups are trans situated in a disubstituted complex of molybdenum or tungsten, this coupling extending through five bonds to the protons on the β-carbon only. Indeed, coupling of protons on the β-carbon to the phosphorus of the same ligand is not observed. The chromium atom does not transmit spin data; molybdenum and tungsten atoms do. Trans disubstituted chromium complexes therefore have spectra very similar to those of the monosubstituted derivatives. The chemical shifts for protons in complexes is greater than in the free ligands and the observed order of chemical shifts for the group VI metal derivatives may be related to the positive charge on phosphorus. Such correlation agrees with present ideas on electron transfer within the metal-phosphorus bond. No information was found from the spectra of phosphine derivatives as these are more complex second order types.

^{13}C N.M.R. RESULTS AND DISCUSSION

The chemistry of phosphorus compounds has recently been expanded to include a wide study of the carbon-13 N.M.R. of the compounds. Previous N.M.R. studies have been primarily concerned with the proton or phosphorus-31 nuclei as a probe to indicate changes in bonding around the phosphorus. This has been discussed in relation to the proton magnetic resonance data obtained in this work and phsophorus-31 studies reported in the literature for some of the complexes considered here. The study of ^{13}C nuclear magnetic resonance has only recently been extensively used in phosphorus chemistry and although the technique was used in a study of iron pentacarbonyl in 1958[141], its general use in metal carbonyl chemistry has been slow to develop. In the last two years, a number of papers have appeared dealing exclusively with the carbon-13 N.M.R. spectra of transition metal complexes[142-144] and a report of the spectra of PPh_3 and $PPh_3Mo(CO)_5$ has also appeared.[145]

While low abundance and low sensitivity of the ^{13}C nucleus have made resonance studies relatively infrequent, ^{13}C parameters are of interest in bonding studies of metal carbonyl derivatives. This may be seen by considering the various factors which cause N.M.R. data to have relevance to bonding studies. The phosphorus (III) ligands considered in this study have either a direct phosphorus-carbon bond or a phosphorus-oxygen-carbon bond. The carbon-13 resonance is a direct "probe" of the electronic structure around the phosphorus atom. The increased number of parameters involving coupling constants between ^{31}P - ^{13}C, ^{183}W -^{31}P - ^{13}C etc. may be used to expand our ideas about the tungsten-phosphorus bond.

Ramsey's theory of chemical shifts[146] postulates two contributions to the shielding experienced by a nucleus, the paramagnetic and diamagnetic shieldings. The size of these contributions is related to the mass of the nucleus involved, being approximately equal but of opposite signs in the case of proton spectra. The paramagnetic shielding becomes more important as the atomic number of the atom increases. Phosphorus, while having a relatively high atomic number, has the complication of possible d-orbital involvement to an unknown extent and this will have an indeterminate effect on the obtained shifts. The carbon-13 nucleus presents a good intermediate case and for this reason, work has been concentrated on developing a coherent theory designed to rationalise carbon-13 chemical shifts. Until recently, this work was confined to the study of spectra of organic compounds and even now the application and interpretation of ^{13}C resonance techniques is far from routine. The only spectra of complexes similar to those considered in this study was in the work by Gansow and Rimura on triphenylphosphine molybdenum pentacarbonyl.

Spectra for some of the monosubstituted and one of the trans disubstituted complexes along with those for the molybdenum and tungsten hexacarbonyls were obtained and the parameters from these are listed in Table 4.2. Spectra for the ligands $P(OMe)_3$, $P(OEt)_3$, $P(OPr^i)_3$ and PBu^n_3 are also reported. Spectra were recorded on a Bruker HFX-13 22.63 MHz spectrometer. Liquid complexes were run neat and solids as saturated methylene chloride solutions using T.M.S. internal reference. Chemical shifts were obtained on a 12.5 KHz sweep over approximately one hour and coupling constants were run at 1.25 KHz sweep in from 3 to 20 hour runs. All spectra were proton noise decoupled using a wide band decoupler operating at 90 MHz.

Chemical shifts of carbonyl carbon atoms

As may be seen from Table 4.2A, the carbonyl carbon-13 shifts show little variation on formation of a complex from the metal hexacarbonyl or between complexes containing different ligands. The signal shifts downfield on formation of monosubstituted complexes for example from 193.7 ppm. in tungsten hexacarbonyl to a maximum of 200.4 ppm. for the trans carbonyl carbon-13 shift in trinbutylphosphine tungsten pentacarbonyl. The single disubstituted complex studied shows a further shift downfield from 206.4 ppm. in $P(OMe)_3Mo(CO)_5$ to 210.3 ppm. in $[P(OMe)_3]_2Mo(CO)_4$. These results may be correlated with the expected degree of metal to carbon backbonding within a series of complexes of a single metal atom. Thus the chemical shifts for the cis carbonyl groups in complexes $LW(CO)_5$ increase in order of L $CO < P(OMe)_3 < P(OEt)_3 < PBu^n_3$ while the molybdenum complexes have cis carbonyl shift order $CO < P(OMe)_3 < P(OEt)_3 <$ disubstituted $P(OMe)_3$.

TABLE 4.2

A. CARBON-13 CHEMICAL SHIFT RESULTS

COMPLEX	δ (CO) cis	δ (CO) trans	δC^{α}	δC^{β}	δC^{γ}	δC^{δ}
$Mo(CO)_6$	204.1					
$P(OMe)_3Mo(CO)_5$	206.4	209.2	52.1			
$P(OEt)_3Mo(CO)_5$	206.8	208.7	62.1	16.7		
$P(OPr^i)_3Mo(CO)_5$	206.3	209.7	57.0	24.3		
$[P(OMe)_3]_2Mo(CO)_5$	210.3		51.7			
$W(CO)_6$	193.7					
$P(OMe)_3W(CO)_5$	196.5	199.5	52.8			
$P(OEt)_3W(CO)_5$	197.2	199.6	61.8	16.3		
$PBu^n_3W(CO)_5$	198.6	200.4	29.8	26.8	24.7	13.6
$P(OMe)_3$			49.7			
$P(OEt)_3$			57.0	17.2		
$P(OPr^i)_3$			67.2	25.6		
PBu^n_3			28.6	27.9	24.8	14.0

TABLE 4.2 (Contd.)

B. CARBON-13 COUPLING CONSTANT RESULTS

COMPLEX	$J(^{31}P\text{-}M\text{-}^{13}C)$ cis	$J(^{31}P\text{-}M\text{-}^{13}C)$ trans	$J(^{183}W\text{-}^{13}C)$ cis	$J(^{183}W\text{-}^{13}C)$ trans	$J(P\text{-}C^{\alpha})$	$J(P\text{-}C^{\beta})$	$J(P\text{-}C^{\gamma})$	$J(P\text{-}C^{\delta})$
$P(OMe)_3Mo(CO)_5$	7.3	18.3			4.3			
$P(OEt)_3Mo(CO)_5$	6.7	18.9			3.6	6.0		
$[P(OMe)_3]_2Mo(CO)_4$	13.4				0.6			
$P(OMe)_3W(CO)_5$	11.6	37.2	125.1	139.1	3.6			
$P(OEt)_3W(CO)_5$	10.9	36.6	125.1	138.5	4.3	6.1		
$PBu^n_3W(CO)_5$	7.3	18.9	124.4	142.1	25.0	12.2	0.6	0.6
$P(OMe)_3$					10.5			
$P(OEt)_3$					12.2	4.9		
PBu^n_3					13.4	14.6	10.9	0.6
$W(CO)_6$			125.0					

It is seen, therefore, that as the presently accepted ability for the group VI metal atom to backbond by π-overlap increases, the carbon-13 chemical shift in the carbonyl group decreases. The chemical shift of the cis carbonyl group is appreciably less than that of the trans carbonyl and in a preliminary report of work in this area[147] this difference was attributed to one of two possible sources. These were stereochemical effects and ligand electronic effects. Comparison of spectra of the monosubstituted complexes shows that ligand effects are an important factor.

Chemical shifts of other carbon atoms

The ^{13}C chemical shift of carbon atoms in the substituent groups of the phosphorus III ligands change only slightly on formation of the complexes when compared to the free ligand values. The sense of the change is not, however, consistent for all carbon atoms. Trimethylphosphite derivatives show a shift of 49.7 ppm. in the free ligand which increases to 52.1 ppm. in the monosubstituted molybdenum complex and to 52.8 ppm. in the analogous tungsten complex. The trans disubstituted molybdenum derivative has a ^{13}C chemical shift of intermediate value (51.7 ppm.). Thus, in these derivatives, complexing of the ligand causes shift of the carbon-13 resonance to lower fields, this shift being related to the central metal atom and the degree of substitution. Triethylphosphite derivatives have two carbon atoms in the substituent groups, each of which shows different chemical shift behaviour on complex formation. The chemical shift of the oxygen bonded carbon atom increases on complexing from a value of 57.0 ppm. in the free ligand to 62.1 ppm. in the monosubstituted molybdenum complex and to 61.8 in the monosubstituted tungsten derivative. It is noted, however, that this shift is greater in the molybdenum than in the tungsten complex. As the results for the monosubstituted chromium complex and the disubstituted triethylphosphite derivatives of chromium, molybdenum and tungsten are not yet available, it would be premature, on the evidence quoted above, to seek to rationalise the carbon-13 chemical shift behaviour for substituent carbons bonded to oxygen in these complexes in terms of possible molecular factors such as electronegativity or bond angle effects. This particularly true when the results for the only triisopropylphosphite derivative reported are taken into account. This shows for $P(OPr^i)_3Mo(CO)_5$ that the chemical shift of the ^{13}C bonded to the oxygen in the ligand moves to higher fields on complexing, the free ligand value being 67.2 ppm. compared to a value in the complex of 57.0 ppm.

It will be necessary to obtain the carbon-13 N.M.R. parameters for the other triisopropylphosphite derivatives of the group VI metal carbonyls before the significance of this result may become apparent. The chemical shifts of the carbonyl carbon atoms in $P(OPr^i)_3Mo(CO)_5$ are also seen to be somewhat anomalous when compared with the values in trimethylphosphite and triethylphosphite complexes. The cis CO carbon shows an increase in chemical shift from $P(OMe)_3$ to $P(OEt)_3$

derivatives in both molybdenum and tungsten monosubstituted derivatives, while the $P(OPr^{i})_3Mo(CO)_5$ has a ^{13}C shift for the cis carbonyl group which is lower than that for either of the other phosphite derivatives. It is clear, however, that any discussion of these chemical shift parameters must await more extensive studies.

The series of complexes $LM(CO)_5$ and trans $L_2M(CO)_4$ with $M = Cr$, Mo and W and $L = P(OMe)_3$, $P(OEt)_3$, $P(OPr^{i})_3$, $P(OPh)_3$, PPr^{i}_3, PBu^{n}_3, PPh_3 and $P(C_6H_{11})_3$ have been submitted for carbon-13 N.M.R. investigation although as in phosphorus-31 N.M.R. studies, the low solubility of the derivatives may prevent spectral investigation. Using results for these complexes along with those of, for example, durene which have been determined and reported[148] it will, perhaps, be possible to propose a theory of carbon-13 chemical shift effects. As the theoretical basis for understanding and predicting ^{31}P chemical shift remains fairly empirical and, indeed, qualitative after many years of study on fairly readily obtained spectra, it would be surprising if the analogous carbon-13 theory emerged without a similar amount of experimental study and theoretical development.

The chemical shift of the β-carbon in the phosphorus substituent is seen to move to higher fields on complexing a phosphite ligand which is opposite to the effect on the α-carbon shift. A recent study on carbon-13 and phosphorus-31 chemical shifts of some tertiary phosphines by Mann[149] concluded that observed chemical shifts in these compounds behaved in a similar way to such shifts in the substituent alkane groups. It was suggested that such changes were possibly dependent on bond angle changes. The carbon-13 chemical shifts for the n-butyl carbon atoms in PBu^n_3 have been obtained in this study and chemical shifts for the complexed ligand in $PBu^n_3W(CO)_5$ are reported. On complexing, the chemical shift of the α-carbon moves slightly to lower fields. The remaining three carbon atoms in the butyl structure have the opposite effect, moving to higher fields on complexing. Thus in both phosphine and phosphite derivatives, the α-carbon has resonance at lower fields in the complexes than in the free ligand while the more remote carbon atoms show the opposing effect. This unique effect on the α-carbon atoms may have some relation to the effect of the central metal atom on the electron distribution around the phosphorus atom and hence may contribute to bonding information concerning such metal phosphorus linkages.

Spin-spin coupling constants

Three types of spin-spin coupling effects have been studied and reported for the complexes considered. These are the coupling of ^{31}P to the ^{13}C atom of the carbonyl groups situated cis and trans to the phosphorus III ligand, coupling of ^{31}P with ^{13}C within the alkyl or alkoxy group of the ligand and, for tungsten complexes, the ^{183}W - ^{13}C coupling mechanism. One of the most useful aspects of carbon-13 resonance studies is that the number of N.M.R. parameters obtained for complexes such as those considered is significantly higher than was previously possible using only ^{31}P and ^{1}H magnetic resonance. In particular, the transmittance of spin data through various atoms in the systems is indicated by the spin-spin coupling constants. These experimental results should provide information which will help to rationalise bonding effects and some of the results have a qualitative relation to metal ligand bonding theory as it is presently accepted.

The values of $|J(^{31}P - M - ^{13}C)|$ for a single metal atom are related to the change in chemical shift on altering the ligand. As the chemical shift increases, the coupling constant decreases for both cis and trans carbonyl interactions. The $^{31}P - M - ^{13}C$ cis coupling is appreciably less than the $^{31}P - M - ^{13}C$ trans interaction. The other $^{31}P - ^{13}C$ coupling constants reported are those within the ligand. The trimethylphosphite derivatives each show J_{PC} values appreciably less than that in the free ligand and the triethylphosphite derivatives show a similar effect for the α- carbon while the β- carbon coupling has the free ligand coupling lower than that in the complexed ligand. It is interesting to note that for trans $[P(OMe)_3]_2Mo(CO)_4$, the phosphorus-carbon coupling is very low ($\leqslant 0.6$ cps) giving an order of $|J_{PC}|$ for molybdenum complexes of free ligand $>$ monosubstituted $>$ trans disubstituted.

The tungsten-carbon coupling constants are seen to have order $|J_{WC}|$cis$<|J_{WC}|$trans which may be correlated with the $^{31}P - M - ^{13}C$

couplings and the accepted π-backbonding arguments. The $|J_{WC}|$ trans values obtained range from 138.5 to 142.1 ppm. in the carbonyl phosphines and equals 125.0 ppm in $W(CO)_6$. $|J_{WC}|$ cis values are all within 0.6 ppm. of the hexacarbonyl value. Thus trans interaction constants are more sensitive to ligand change than are cis effects as expected from simple π-bonding theory. As coupling constant information for these types of complexes becomes more readily available, it may be possible to observe meaningful correlation among the three principle coupling mechanisms, $^{31}P - W - ^{13}C$, $^{31}P - W - ^{31}P$ and $^{183}W - ^{13}C$. Meanwhile, it is essential that results such as those reported here should be obtained and tabulated as an impetus to theoretical approaches which might clarify any trends and subsequently relate these to plausible bonding ideas.

MASS SPECTRA

Mass spectra of metal carbonyl complexes are now frequently reported in the literature as, for example, in recent studies of manganese and tungsten complexes.[165,166] In this study, the mass spectra of only a few of the metal VI carbonyl phosphine complexes are discussed in relation to previous similar results.

Generally, mass spectra provide two factors of primary importance concerning any molecule. The first is an indication of the molecular weight of a complex by means of the m/e value of the molecular ion. Frequently in a mass spectrum the highest m/e value may correspond to the molecular ion which gives the molecular weight of the molecule. Another application of mass spectral results is their use in indicating possible fragmentation patterns of the molecule. The position and intensity of the mass spectral peaks may be related to certain fragments of the molecule and, along with metastable peak positions these give an indication of the pattern of molecular breakdown under electron impact. Metastable ions are observed when an ion is impacted during flight and kinetic energy is removed by a neutral fragment. Thus for an ion mass m_1 which fragments to ion mass m_2, conclusive proof of this fragmentation pattern is only provided when a metastable ion mass m* is observed, this metastable ion being related to the masses m_1 and m_2 by the expression

$$m^* = m_2^2/m_1$$

It has not been possible in this study to give a complete fragmentation pattern for any of the complexes considered. Only a very small number of metastable peaks are observed mainly because the geometry of the spectrometer is not primarily designed for such measurements. This inevitably limits the information which may be derived from mass spectra although it is possible, by analogy, to discuss the spectral results in relation to possible fragmentation patterns. Thus the loss of carbonyl groups has been reported by King[167] for trisdimethylaminophosphine complexes of metal VI hexacarbonyls while other relevant studies have been carried out on $[P(OMe)_3]_2Cr(CO)_4$[168] and $[P(OMe)_3]_2W(CO)_4$[44]. The parent hexacarbonyls have also been studied and show successive loss of carbonyl groups.[169,170] These studies along with others concerned with the phosphorus III ligand mass spectra[171,172] may be used to interpret the spectra being considered here.

As the spectra of the complexes could not be obtained readily for practical reasons and some previous closely related results have been reported, only a few of the complexes prepared are investigated. The results, including possible fragment assignments are given in Table 4.3 and include those for $[P(OEt)_3]_2Cr(CO)_4$ and $[P(OMe)_3]_2W(CO)_4$ which have been re-examined and, for the latter spectrum, partly reassigned.

Results and discussion

$P(OEt)_3Cr(CO)_5$

The m/e values along with suggested ion fragments are given in Table 4.3A along with the relative intensities of the observed peaks. No metastable peaks have been observed in this spectrum and the fragment ions given in the table and discussed below are assigned by comparison of positions and relative intensities with previously recorded spectra of analogous metal carbonyl derivatives. Loss of carbonyl groups successively is observed, each of the ions $P(OEt)_3Cr(CO)_n^+$ with n = 0 - 5 being observed. The $P(OEt)_3Cr^+$ peak has the greatest intensity as has been observed for LM^+ and L_2M^+ fragments in previous studies on similar complexes. However, the $[P(OMe)_3]_2W^+$ fragment in the mass spectrum of $[P(OMe)_3]_2W(CO)_4$ is of very low intensity. The $P(OEt)_3Cr(CO)_5$ is also seen to lose an ethoxy group to form $P(OEt)_2Cr(CO)_5^+$ and from this fragment, successive loss of carbonyl is again observed. In this case, only the fragments $P(OEt)_2Cr(CO)_n^+$ with n = 1, 2, 4 and 5 are recorded and the $P(OEt)_2Cr^+$ ion is not observed.

Loss of an ethyl group from the $P(OEt)_3Cr^+$ is observed giving a fragment $O = P(OEt)_2Cr^+$ which is probably a phosphonate. Loss of acetaldehyde is seen from this fragment and also from the $P(OEt)_3Cr^+$ ion directly. This loss of acetaldehyde is analogous to the observed loss of formaldehyde from $P(OMe)_3Cr^+$ in fragmentation of $[P(OMe)_3]_2Cr(CO)_4$ for which a metastable peak has been observed[168].

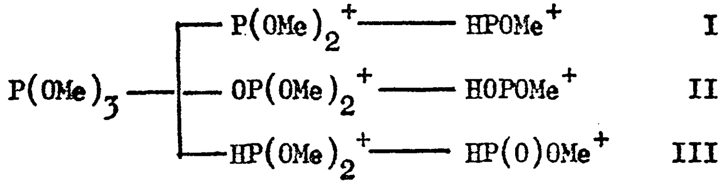
The ethyl group loss has been observed both in this work and previously[44] for the corresponding trans disubstituted derivative $[P(OEt)_3]_2Cr(CO)_4$ and is confirmed by a metastable peak observed in each case.

$\underline{[P(OEt)_3]_2Cr(CO)_4}$

The spectrum of this complex has been described in a previous study[44] and that obtained here is very similar in most respects. It has been found necessary, however, to reassign three of the fragments on the basis of their m/e value. The principal ion fragments of the spectrum are given in table 4.3B and in this spectrum, two metastable peaks are observed, one at m/e = 368.9 corresponding to loss of a CO fragment from $P(OEt)_3Cr(CO)_3P(OEt)_2{}^+$ and the other at m/e = 328.2 which corresponds to loss of an ethyl group from the $[P(OEt)_3]_2Cr^+$ fragment. Successive loss of carbonyl groups from the parent ion is not observed in this case while loss of an ethoxy group is seen as in the monosubstituted complex spectrum. The successive loss of carbonyl from the fragment $P(OEt)_3Cr(CO)_4P(OEt)_2{}^+$ is seen, each of the ions $P(OEt)_3Cr(CO)_nP(OEt)_2{}^+$ n = 0 - 4 being observed. This may be compared to the monosubstituted case where the $P(OEt)_2Cr(CO)_3{}^+$ fragment was not observed, nor was the $P(OEt)_2Cr^+$ fragment. The $[P(OEt)_3]_2Cr^+$ ion has the greatest relative intensity in this spectrum and loss of an ethyl group from this fragment is observed and a corresponding metastable peak is seen. Loss of acetaldehyde is proposed as the subsequent step in fragmentation of $[P(OEt)_3]_2Cr^+$ after ethyl loss and the resulting ion may lose a further ethyl group. Loss of acetaldehyde may also be seen from the $P(OEt)_3CrP(OEt)_2^+$ ion fragment although at the lower m/e values it is more difficult to assign the peaks without the evidence of metastable peak positions. Merely considering the m/e values does not allow unambiguous assignment of the ion structure and it is not possible to propose the fragmentation patterns to which each m/e peak may be related. Thus there is a fragment m/e value 236 which may be $P(OEt)_3CrOEt^+$ and may be derived from fragmentation of either $P(OEt)_3CrP(OEt)_2^+$ or $[P(OEt)_3]_2Cr^+$. The fragment m/e = 219 which was previously assigned as $P(OEt)_3Cr^+$ is most probably, from its m/e value $HCrP(OEt)_3^+$ which may be the result of acetaldehyde loss from $P(OEt)_3Cr(OEt)^+$. Fragments at m/e of 190 and 174 are possibly due to an ion resulting from loss of an ethyl group from $HCrP(OEt)_3^+$ and the ion $HCrP(OEt)_2^+$ respectively. Loss of acetaldehyde from the fragment 190 may be seen as similar fragmentation to that observed for the $[P(OEt)_3]_2Cr^+$ which also lost ethyl and acetaldehyde groups in succession.

$\underline{P(OMe)_3W(CO)_5}$

This monosubstituted derivative shows successive loss of carbonyl groups from the parent $P(OMe)_3W(CO)_5^+$ and also loss of a methoxy group from this ion followed by successive loss of carbonyl groups. In this molecule, each of the ion fragments $P(OMe)_3W(CO)_n^+$ and $P(OMe)_2W(CO)_n^+$ n = 0 - 5 are seen as compared to the $P(OEt)_3Cr(CO)_5$ molecule which showed only four of the possible fragments in the latter case. Both the $P(OMe)_3W^+$ and $P(OMe)_2W^+$ fragments are observed and their relative intensities are fairly high although the $P(OMe)_3W^+$ is not the strongest peak in the spectrum as was the analogous peak in the $P(OEt)_3Cr(CO)_5$ spectrum. While the fragments containing $P(OMe)_3$ in the tungsten derivative are significantly more intense than those containing $P(OMe)_2$, this is not true for analogous fragments of the chromium complex. Loss of a methyl group followed by loss of HCHO from the $P(OMe)_3W^+$ ion is seen and direct loss of HCHO from that fragment is also proposed. These observations may be correlated with the mass spectrum of the free ligand, $P(OMe)_3$ which has been assigned three fragmentation paths[168,173] as shown



$$P(OMe)_3 \left[\begin{array}{llll} — P(OMe)_2^+ & — & HPOMe^+ & \mathrm{I} \\ — OP(OMe)_2^+ & — & HOPOMe^+ & \mathrm{II} \\ — HP(OMe)_2^+ & — & HP(O)OMe^+ & \mathrm{III} \end{array} \right.$$

Thus loss of the methyl group corresponds to fragmentation pattern II and loss of HCHO from $P(OMe)_3W^+$ may be seen as analogous to pattern III. Loss of HCHO from $P(OMe)_2W^+$ is not, however, observed in this complex. Two metastable peaks are observed for carbonyl loss, one in each of the fragmentation patterns involving $P(OMe)_3W(CO)_n^+$ and $P(OMe)_2W(CO)_n^+$.

$[P(OMe)_3]_2W(CO)_4$

The spectrum of this complex has been discussed previously[44] and shows similar loss of carbonyl groups from both $[P(OMe)_3]_2W(CO)_4^+$ and $P(OMe)_3W(CO)_4P(OMe)_2^+$ ion fragments as has been seen for the other metal carbonyl phosphite complexes. Loss of a methyl group is observed from $[P(OMe)_3]_2W^+$ although the HCHO loss seen in $[P(OMe)_3]_2Cr(CO)_4$ fragmentation is not seen in the analogous tungsten complex. The ion fragments are given along with relative intensities in Table 4.3D.

$PPr^i_3Cr(CO)_5$

The ion fragments and relative intensities are given in Table 4.3E, these principally consisting of fragments arising from carbonyl loss from $PPr^i_3Cr(CO)_5^+$ and $PPr^i_2Cr(CO)_5^+$. Metastable peaks are observed for two of the carbonyl losses, each of which is from a $PPr^i_3Cr(CO)_n^+$ fragment. The $PPr^i_3\ Cr(CO)_n^+$ $n = 0 - 5$ fragments are seen along with fragments $PPr^i_2Cr(CO)_n^+$ $n = 0, 1, 2, 4$ and 5. Generally, the $PPr^i_3Cr(CO)_n^+$ fragments are more intense than the $PPr^i_2Cr(CO)_n^+$ ions with the $(CO)_1$ fragment being the most intense. In the $P(OMe)_3W(CO)_5$ fragmentation, the $(CO)_3$ and $(CO)_2$ containing fragments were more intense than that containing $(CO)_1$. A metastable peak corresponding to loss of a C_3H_6 group from $PPr^i_3Cr^+$ is also observed, the fragment formed being $HCrPPr^{i+}_2$ which is analogous to the $HCrP(OEt)_2^+$ fragment observed for $[P(OEt)_3]_2Cr(CO)_4$ fragmentation.

Formation of the fragment $H_2PPr^iCr^+$ and subsequent H_3 loss has been assigned by analogy with reported fragmentation patterns of triethylphosphine[172]. No metastable peaks are observed for these possible fragmentations.

$[P(OPr^i)_3]_2Cr(CO)_4$

This spectrum reported in Table 4.3F is fairly similar to that of the complex $[P(OEt)_3]_2Cr(CO)_4$. No metastable peaks are observed and therefore the fragments are assigned by analogy with this latter complex and the other complexes reported previously. Loss of isopropoxy group from the complex and successive loss of carbonyl groups from the resulting ion and from the complex itself is observed. Fragments $[P(OPr^i)_3]_2Cr(CO)_n^+$ n = 0, 1, 3, 4 and $P(OPr^i)_3Cr(CO)_nP(OPr^i)_2^+$ n = 0, 2, 3, 4 are seen compared to the triethylphosphite derivative in which only n = 0 or 4 $[P(OEt)_3]_2Cr(CO)_n^+$ fragments were observed along with fragments $P(OEt)_3Cr(CO)_nP(OEt)_2^+$ n = 0 - 4. Loss of an isopropyl group followed by loss of C_3H_6O is observed from $[P(OPr^i)_3]_2Cr^+$ analogous to the loss of ethyl group and C_2H_4O in $[P(OEt)_3]_2Cr(CO)_4$ fragmentation. The fragment $P(OPr^i)_3CrOPr^{i+}$ is observed as is the $P(OPr^i)_3Cr^+$ ion, the latter giving isopropyl and C_3H_6O loss.

Conclusion

The spectra considered here are representative of both mono and trans disubstituted metal carbonyl phosphorus III derivatives. The number of spectra reported has been limited only by practical difficulties of obtaining spectra. Clearly, however, if no metastable peaks are observed, the more complex m/e regions cannot be assigned readily to ion fragments as various atom combinations may correspond to any one m/e value and fragmentation patterns cannot be constructed to eliminate any of these possibilities. The analysis of the spectra by analogy with other results is only helpful if the fragmentation is fairly clear which is not true of these complexes apart from the loss of carbonyl groups and loss of one of the substituent groups on the trivalent phosphorus. This is seen for all the complexes studied.

Experimental

Spectra were recorded on an AEI MS-9 mass spectrometer having ionising electron voltage of 70 e.v. and heated inlet temperature of 220 - 240°C.

TABLE 4.3

Mass Spectra of Complexes. Tables.

TABLE 4.3

A. MASS SPECTRUM OF $P(OEt)_3Cr(CO)_5$

m/e values given are for the most abundant ion.

	m/e	ION	RELATIVE INTENSITY
A	358	$P(OEt)_3Cr(CO)_5^+$	8
B	330	$P(OEt)_3Cr(CO)_4^+$	1
C	313	$P(OEt)_2Cr(CO)_5^+$	2
D	302	$P(OEt)_3Cr(CO)_3^+$	1
E	285	$P(OEt)_2Cr(CO)_4^+$	2
F	274	$P(OEt)_3Cr(CO)_2^+$	2
G	246	$P(OEt)_3Cr(CO)^+$	38
H	229	$P(OEt)_3Cr(CO)_2^+$	1
I	218	$P(OEt)_3Cr^+$	100
J	201	$P(OEt)_2Cr(CO)^+$	2
K	189	I - Et	4
L	174	I - CH_3CHO	9
M	145	K - CH_3CHO	8

No metastable peaks observed.

TABLE 4.3 (Contd.)

B. MASS SPECTRUM OF $[P(OEt)_3]_2Cr(CO)_4$

	m/e	ION	RELATIVE INTENSITY
A	496	$[P(OEt)_3]_2Cr(CO)_4^+$	19
B	451	$P(OEt)_3Cr(CO)_4P(OEt)_2^+$	15
C	423	$P(OEt)_3Cr(CO)_3P(OEt)_2^+$	2
D	395	$P(OEt)_3Cr(CO)_2P(OEt)_2^+$	5
E	384	$[P(OEt)_3]_2Cr^+$	100
F	367	$P(OEt)_3Cr(CO)P(OEt)_2^+$	2
G	355	E - Et	5
H	339	$P(OEt)_3CrP(OEt)_2^+$	15
I	311	G - CH_3CHO	3
J	295	H - CH_3CHO	3
K	282	I - Et	5
L	263	$P(OEt)_3Cr(OEt)^+$	22
M	219	L - CH_3CHO	42
N	190	M - Et	10
O	174	$P(OEt)_2CrH^+$	12
P	146	N - CH_3CHO	14

Metastables 368.9 C → D −CO

328.2 E → G −Et

TABLE 4.3 (Contd.)

C. MASS SPECTRUM OF $P(OMe)_3W(CO)_5$

	m/e	ION	RELATIVE INTENSITY
A	448	$P(OMe)_3W(CO)_5^+$	77
B	420	$P(OMe)_3W(CO)_4^+$	31
C	417	$P(OMe)_2W(CO)_5^+$	19
D	392	$P(OMe)_3W(CO)_3^+$	85
E	389	$P(OMe)_2W(CO)_4^+$	19
F	364	$P(OMe)_3W(CO)_2^+$	95
G	361	$P(OMe)_2W(CO)_3^+$	10
H	336	$P(OMe)_3W(CO)^+$	40
I	333	$P(OMe)_2W(CO)_2^+$	14
J	308	$P(OMe)_3W^+$	80
K	305	$P(OMe)_2W(CO)^+$	9
L	293	J - Me	11
M	278	J - HCHO	19
N	277	$P(OMe)_2W^+$	46
O	273	L - HCHO	46
P	262	WPO_2Me^+	100
Q	247	$HWP(OMe)^+$	41

Metastables 340.3 D → F −CO
312.2 G → I −CO

TABLE 4.3 (Contd.)

D. MASS SPECTRUM OF $[P(OMe)_3]_2W(CO)_4$

	m/e	ION	RELATIVE INTENSITY
A	544	$[P(OMe)_3]_2W(CO)_4^+$	100
B	516	$[P(OMe)_3]_2W(CO)_3^+$	26
C	513	$P(OMe)_3W(CO)_4P(OMe)_2^+$	53
D	488	$[P(OMe)_3]_2W(CO)_2$	33
E	485	$P(OMe)_3W(CO)_3P(OMe)_2^+$	6
F	460	$[P(OMe)_3]_2W(CO)^+$	53
G	432	$[P(OMe)_3]_2W^+$	4
H	417	G – Me	95
I	339	$P(OMe)_3WOMe^+$	13
J	308	$P(OMe)_3W^+$	13
K	293	$PO(OMe)_2W^+$	20
L	278	$HWP(OMe)_2^+$	6
M	277	$P(OMe)_2W^+$	13
N	263	K – HCHO	13
O	262	WPO_2Me^+	20
P	247	$HWP(OMe)^+$	6
Q	246	$WP(OMe)^+$	6

TABLE 4.3 (Contd.)

E. MASS SPECTRUM OF $\mathrm{PPr}^{i}_{3}\mathrm{Cr(CO)}_{5}$

	m/e	ION	RELATIVE INTENSITY
A	352	$\mathrm{PPr}^{i}_{3}\mathrm{Cr(CO)}_{5}^{+}$	9
B	324	$\mathrm{PPr}^{i}_{3}\mathrm{Cr(CO)}_{4}^{+}$	2
C	309	$\mathrm{PPr}^{i}_{3}\mathrm{Cr(CO)}_{5}^{+}$	1
D	296	$\mathrm{PPr}^{i}_{3}\mathrm{Cr(CO)}_{3}^{+}$	1
E	281	$\mathrm{PPr}^{i}_{2}\mathrm{Cr(CO)}_{4}^{+}$	1
F	268	$\mathrm{PPr}^{i}_{3}\mathrm{Cr(CO)}_{2}^{+}$	2
G	240	$\mathrm{PPr}^{i}_{3}\mathrm{Cr(CO)}^{+}$	19
H	225	$\mathrm{PPr}^{i}_{2}\mathrm{Cr(CO)}_{2}^{+}$	1
I	212	$\mathrm{PPr}^{i}_{3}\mathrm{Cr}^{+}$	100
J	197	$\mathrm{PPr}^{i}_{2}\mathrm{Cr(CO)}^{+}$	2
K	170	$\mathrm{PPr}^{i}_{2}\mathrm{CrH}^{+}$	2
L	169	$\mathrm{PPr}^{i}_{2}\mathrm{Cr}^{+}$	1
M	128	$\mathrm{H_2PPr}^{i}\mathrm{Cr}^{+}$	1
N	125	$\mathrm{M - H_3}$	2

Metastable peaks			
	297.9	A → B	− CO
	187.4	G → I	− CO
	136.4	I → K	$-\mathrm{C_3H_6}$

TABLE 4.3 (Contd.)

F. MASS SPECTRUM OF $[P(OPr^i)_3]_2Cr(CO)_4$

	m/e	ION	RELATIVE INTENSITY
A	582	$[P(OPr^i)_3]_2Cr(CO)_4^+$	7
B	554	$[P(OPr^i)_3]_2Cr(CO)_3^+$	2
C	523	$P(OPr^i)_3Cr(CO)_4P(OPr^i)_2^+$	9
D	498	$[P(OPr^i)_3]_2Cr(CO)^+$	2
E	495	$P(OPr^i)_3Cr(CO)_3P(OPr^i)_2^+$	1
F	470	$[P(OPr^i)_3]_2Cr^+$	100
G	467	$P(OPr^i)_3Cr(CO)_2P(OPr^i)_2^+$	1
H	427	$F - Pr^i$	4
I	411	$P(OPr^i)_3CrP(OPr^i)_2^+$	6
J	369	$H - C_3H_6O$	32
K	368	$I - Pr^i$	5
L	353	$P(OPr^i)_3CrHP(OPr^i)^+$	1
M	325	$K - Pr^i$	10
N	321	$P(OPr^i)_3CrOPr^i\ ^+$	6
O	261	$P(OPr^i)_3Cr^+$	15
P	218	$O - Pr^i$	12
Q	160	$P - C_3H_6O$	10
R	117	$CrOPHO^+$	11

CHAPTER 5

INFRARED SPECTRA AND METAL PHOSPHORUS BONDING

INFRARED SPECTRA

The use of infrared spectra taken in the stretching carbonyl frequency region for monitoring reactions and distinguishing the configurations of derivatives formed in such reactions has been covered fairly extensively in the section dealing with preparative work while the general principles involved in using infrared spectra in conjunction with symmetry theory were outlined in the general introduction. The purpose of this section is to study the carbonyl stretching frequencies of the complexes in some detail. The rapid development in instrumentation and the continuing interest in relating such carbonyl frequencies and their parameters to changes in bonding characteristics have produced a series of increasingly accurate studies of carbonyl stretching frequency measurements. It has been observed in this study that to obtain a sample sufficiently pure to give acceptable infrared spectra in highly concentrated solutions requires extensive purification and in some cases may be virtually impossible. The occurrence of cis disubstituted derivative peaks in spectra of the trans disubstituted complexes has been briefly discussed in the treatment of the preparations of the latter derivatives. More recent developments concerning "anomalous" peaks which have been observed for complexes such as monosubstituted and disubstituted metal carbonyl derivatives containing phosphorus III ligands were reported by Bigorgne and coworkers[52]. They were the first workers to propose factors other than low local symmetry as an explanation for the appearance of peaks which are observed for a perturbed symmetry, although forbidden in the ideal symmetry itself.

The infrared spectra of the complexes obtained for very highly concentrated solutions are reocrded in Table 5.1. The frequencies are reported in cm^{-1} and are accurate to ± 0.2 cm^{-1}. Spectral peaks in the region 2200 - 1800 cm^{-1} have been recorded for cyclohexane solutions of approximately 10^{-2}M concentrations. This compares with concentrations of approximately 5×10^{-4}M to 10^{-3}M which give the E mode of such complexes a maximum absorption value (i.e. < 1% transmittance). Many previous reports of the carbonyl stretching frequencies in metal carbonyl complexes have been based on solutions of low concentration and recorded on instruments of low accuracy. However, some of the earliest work on the group VI metal carbonyl phosphine complexes reported the possibility of unpredicted peaks being present in the infrared spectra of these complexes. For example, Poilblanc and Bigorgne[72] and Cotton and Kraihanzel in early studies each assigned peaks in infrared spectra to forbidden modes of the accepted symmetry species. These were, in fact, the B_1 mode of monosubstituted $LM(CO)_5$ and the B_{1g} (and in some cases A_{1g}) modes of transdisubstituted $L_2M(CO)_4$ along with splitting of the E modes in each case. Since then, there have been many reported examples of such peaks observed for similar complexes.[66,67,134,135]

TABLE 5.1

Carbonyl Stretching Frequencies for Monosubstituted and trans Disubstituted Complexes

TABLE 5.1

A. MONOSUBSTITUTED COMPLEXES

COMPLEX	ASSIGNMENT											
	A_1^2			B_1			A_1^1			E		
	ν	T%	$\Delta\nu$	ν	T%	$\Delta\nu$	ν	T%	$\Delta\nu$	ν	T%	$\Delta\nu$
$P(OMe)_3Cr(CO)_5$	2073.4	18	3	1991.4	8	5	1964.2	49	6	1949.2	85	9
$P(OMe)_3Mo(CO)_5$	2079.7	6	2	1995.5	5	5	1967.6	24	5	1954.0	62	7
$P(OMe)_3W(CO)_5$	2079.5	10	2	1988.4	6	5	1961.7	36	6	1946.9	78	6
$P(OEt)_3Cr(CO)_5$	2071.0	11	2	1988.6	6	7	1960.7	35	7	1946.2	70	7
$P(OEt)_3Mo(CO)_5$	2078.5	13	3	1993.8	8	6	1964.4	44	7	1951.3	80	7
$P(OEt)_3W(CO)_5$	2078.0	6	3	1986.2	4	5	1958.4	25	4	1944.4	60	6
$P(OPr^i)_3Cr(CO)_5$	2069.6	7	2	1987.9	5	5	1958.3	22	4	1943.1	50	7
$P(OPr^i)_3Mo(CO)_5$	2077.2	15	3	1993.0	10	7	1961.2	48	6	1948.4	81	8
$P(OPr^i)_3W(CO)_5$	2076.4	12	2	1985.3	8	7	1955.8	40	5	1941.2	77	7
$PPr^i_3Cr(CO)_5$	2058.0	10	3	1971	vvw		1940	sh		1935.6	55	9
$PPr^i_3Mo(CO)_5$	2067.7	12	3	1977.5	vvw		1941.8			1941.8	73	7
$PPr^i_3W(CO)_5$	2066.7	12	3	1969.5	vvw		1938.4	sh		1933.2	74	10
$PBu^n_3Cr(CO)_5$	2059.2	10	2	1972.0	vvw		1943.3	26	5	1935.0	72	5
$PBu^n_3Mo(CO)_5$	2068.2	8	2	1978.5	vvw		1947.2	sh		1941.6	70	7
$PBu^n_3W(CO)_5$	2067.4	16	3	1970.5	vvw		1941.6	sh		1935.9	86	7

ν frequency (cm^{-1})

T% Transmittance

$\Delta\nu$ width at half height

TABLE 5.1 (Contd.)

B. TRANS DISUBSTITUTED COMPLEXES

COMPLEX	ASSIGNMENT							
	A_{1g}		B_{1g}			E_u		
	ν		ν	T%	$\Delta\nu$	ν	T%	$\Delta\nu$
$P(OMe)_3{}_2Cr(CO)_4$	2035.0	vvw	1964.5	3	6	1913.9	54	11
$P(OMe)_3{}_2Mo(CO)_4$	2044.5	vvw	1972.5	3	10	1921.4	50	12
$P(OMe)_3{}_2W(CO)_4$	2041.4	vvw	1965.5	2	10	1914.2	46	10
$P(OEt)_3{}_2Cr(CO)_4$	2030.5	vvw	1961.0	2	8	1908.0	40	12
$P(OEt)_3{}_2Mo(CO)_4$	2041.2	vvw	1969.4	3	10	1916.2	47	14
$P(OEt)_3{}_2W(CO)_4$	2038.5	vvw	1962.4	3	11	1909.0	42	18
$P(OPr^i)_3{}_2Cr(CO)_4$	2028.2	vvw	1959.6	7	10	1902.4	68	20
$P(OPr^i)_3{}_2Mo(CO)_4$	2039.2	vvw	1968.5	3	11	1911.3	38	16
$P(OPr^i)_3{}_2W(CO)_4$	2036.0	vvw	1960.9	3	12	1904.3	42	18
$(PPr^i_3)_2Cr(CO)_4$						1868.5	72	8
$(PPr^i_3)_2Mo(CO)_4$						1879.3	80	8
$(PPr^i_3)_2W(CO)_4$						1871.8	58	7
$(PBu^n_3)_2Cr(CO)_4$						1874.5	66	5
$(PBu^n_3)_2Mo(CO)_4$						1885.3	90	15
$(PBu^n_3)_2W(CO)_4$						1877.4	65	9

Monosubstituted complexes

The complexes $LM(CO)_5$ are each seen to have four peaks in the carbonyl stretching region of their infrared spectra. If L is considered to be a radially symmetric ligand, the overall symmetry of the molecule is C_{4v} and only three active infrared modes are required by symmetry studies for the carbonyl stretching motions. These three modes comprise two A_1 modes (which interact) and an E mode which in each of the monosubstituted complexes studied is seen to be symmetric and unsplit. The observed mode which is not active in pure C_{4v} symmetry environments is the B_1 mode. Its activity has been discussed recently by Bigorgne and coworkers[52]. Their approach to the problem of explaining such anomalous peaks was confined to the two cases $P(OMe)_3Mo(CO)_5$ and $PPh_3Mo(CO)_5$ (although many other examples of other configurations and derivatives were also considered). The infrared spectrum of the ligand trimethylphosphite was seen to have three bands which were assignable to P - O vibrations,[136] the two bands at lower frequency being taken as due to the E vibration in C_{3v} symmetry. This was considered as evidence that the three P - O bonds in trimethylphosphite are nonequivalent. While the structure of ligand molecules of type $P(OR)_3$ is not fully understood, this result for trimethylphosphite was used to propose a mechanism by which the B_1 mode in monosubstituted molecules $LM(CO)_5$ could be activated. This mechanism involved the action of an asymmetric electric field deriving from the carbonyl bonds on the P - O - C - H bonds of the phosphite ligand. This electric interaction is not uniform as the three P - O bonds in the phosphite are not equivalent in their orientation with respect to any carbonyl group.

Considering the B_1 mode as indicated in Figure 5.1, this can only be active if a molecular dipole moment exists in some orientation with respect to the C_4 axis. For this to be true, there must be some asymmetric perturbation acting on the carbonyl groups and this was attributed to internal asymmetry of the ligands involved, in trimethylphosphite as indicated above, the nonequivalence of the P - O bonds and in the triphenylphosphine complex, an asymmetric interaction involving the phenyl rings. In this treatment, the local symmetry of the carbonyl groups in the molecule is considered to be retained, this contention being supported by infrared intensity and Raman polarisation results for some of the complexes treated. However, some of the results are not strictly applicable to the complexes discussed here and Bigorgne does not provide evidence that the local symmetry of the $M(CO)_5$ and $M(CO)_4$ groups in mono and trans disubstituted complexes respectively is retained in their phosphite derivatives. Further, as the complex trans $Mo(CO)_4I_2$ exhibits the forbidden B_{1g}

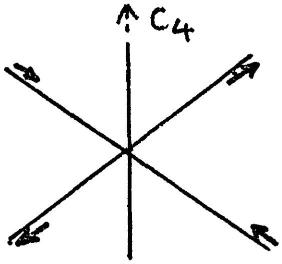


Figure 5.1

mode (assuming D_{4h} symmetry) in its spectrum and this must be explained by a lowering of the symmetry of the carbonyl groups, it seems probable that symmetry lowering is at least partially responsible for the appearance of similar peaks in the spectra of complexes containing phosphorus III ligands. However, this contention is entirely non empirical and it is now necessary to present experimental evidence which supports the involvement of local symmetry lowering as opposed to asymmetric interactions between the carbonyls and phosphite ligand.

In the treatment of Bigorgne and coworkers it is noted that the appearance of the B_1 mode in the $LM(CO)_5$ type complexes is seen in the case of "asymmetric" ligands only. These ligands included truly asymmetric structures such as PCl_2Ph and $PCl(OR)_2$ along with ligands such as $P(OMe)_3$ and PPh_3, the asymmetry of which derive from some internal structural inequivalence factor which allows non equivalent interactions to occur with the carbonyl groups in the molecule. Other ligands such as trialkylphosphines PR_3 which have symmetrically arranged P - C bonds could not produce the non equivalent interactions on carbonyl groups and the infrared spectra of monosubstituted complexes containing such ligands were reported as having no B_1 mode. In the present study, three trialkyl phosphite ligands and two trialkyl phosphine ligands were used and in each spectrum of a monosubstituted complex formed with chromium, molybdenum and tungsten, a peak corresponding to the B_1 mode was assigned. The B_1 mode assigned in the spectra of the phosphite complexes occurs between 1985 and 1996 cm^{-1} and varies with changing metal atom as does the E mode, i.e. Mo > Cr > W. This series is also observed for the B_1 mode of trialkylphosphine complexes while the frequency of the peak is between 1969 and 1979 cm^{-1}. If the Cotton Kraihanzel parameters k_1, k_2 and k_i are calculated using the $2A_1$ + E frequency values and the frequency of the B_1 peak is then calculated using the appropriate secular equations, the obtained value correlates with the observed peak to within 5 cm^{-1}. While such correlation does not prove the validity of the assignment of the B_1 peak the assignment is reasonable on the basis of frequency and intensity values and the correlation reinforces this assignment. Thus B_1 modes are observed and assigned in the infrared spectra of complexes $LM(CO)_5$ where L is a "symmetric" trialkylphosphine ligand and this is taken as evidence that the anomalous peaks occurring in metal carbonyl phosphine derivatives may at least partially derive from symmetry lowering rather than internal asymmetric interactions of the molecule.

It is interesting to consider the relative intensities of the B_1 modes both within the phosphite series and on changing from phosphite to phosphine as ligand. Generally, the intensity of the B_1 mode decreases in order Cr > Mo > W which might be expected on the basis of an increasing metal atom bulk causing the perturbation of symmetry to be less effective. A further observation concerning the phosphite derivatives is that the intensity of the B_1 mode increases relative to the E mode in the series $P(OMe)_3 < P(OEt)_3 < P(OPr^i)_3$. Perturbation of the $M(CO)_5$ entity by phosphite ligands increases in order $P(OMe)_3 < P(OEt)_3 < P(OPr^i)_3$ due, in part, to ligand steric effects.

If the intensities of the B_1 modes observed in the spectra of monosubstituted complexes with trialkylphosphine ligands are compared with those obtained for the trialkylphosphite complexes, it is seen that while the B_1 modes are readily observed in the latter case at low concentrations, a highly concentrated solution is required in the former case. Generally PR_3 derivatives have B_1 modes only one fifth as intense as those of $P(OR)_3$ derivatives. This difference in intensity is readily understood as deriving from the degree of asymmetry inherent in the ligand. Thus phosphite ligands which have non equivalent P - O bonds give a fairly strong perturbation from C_{4v} symmetry while phosphines, which do not show this non equivalence give only weak symmetry lowering effects and hence a low intensity B_1 mode.

Disubstituted complexes

Spectra obtained for the trans disubstituted complexes may be considered in a similar manner to those of monosubstituted complexes in that the number of carbonyl stretching frequencies observed is greater than that required by D_{4h} symmetry which would exist if the ligands were axially symmetric. The E_u mode which is infrared active in D_{4h} symmetry is seen along with two further peaks to higher energies for phosphite complexes only. The E_u peak observed for phosphite complexes is generally asymmetric with a large half width ($5 - 10$ cm^{-1}) suggesting incipient splitting of the two components of the E_u mode. The phosphine derivatives have symmetric E_u peaks although at high concentrations, a peak due to a small amount of the cis derivative causes asymmetry of the former peaks. Thus the observed effect of phosphite ligands on metal carbonyl derivative infrared spectra is present in both mono and trans disubstituted derivatives while phosphine ligand effects have been detected in monosubstituted complexes only. It is probable that the A_{1g} and B_{1g} peaks arising from trans $(PR_3)_2$ $M(CO)_4$ M = Cr, Mo, W are present but undetected due to their low intensity and masking by contaminant peaks.

The peaks in the energy regions at approximately 1965 cm^{-1} and 2040 cm^{-1} have been assigned to the B_{1g} and A_{1g} modes respectively. They each have reproducible intensity ratios (compared to E_u) although the A_{1g} mode is very weak and comparison is thus difficult. The overall symmetry of the molecule may be lowered by the phosphite ligand as in monosubstituted complexes. Cotton-Kraihanzel approximate secular equations for trans $L_2M(CO)_4$ (Fig. 1.1) require $A_{1g} > B_{1g} > E_u$ and reducing the symmetry would provide spectra of the form obtained

One further study of the infrared spectra concerned assignments in the energy region containing δMCO and νMC skeletal deformations.

TABLE 5.2

δ MCO and ν MC Absorption Frequencies for Monosubstituted and trans Disubstituted Complexes

TABLE 5.2

A. MONOSUBSTITUTED COMPLEXES

COMPLEX	δ MCO	ν MC
$P(OMe)_3Cr(CO)_5$	672, 654	
$P(OMe)_3Mo(CO)_5$	607, 580	400, 376
$P(OMe)_3W(CO)_5$	598, 571	400
$P(OEt)_3Cr(CO)_5$	670, 654	
$P(OEt)_3Mo(CO)_5$	604, 580	398, 374
$P(OEt)_3W(CO)_5$	598, 574	384
$P(OPr^i)_3Cr(CO)_5$	675, 658	
$P(OPr^i)_3Mo(CO)_5$	605, 581	404, 373
$P(OPr^i)_3W(CO)_5$	599, 575	384
$PPr^i_3Cr(CO)_5$	678, 661	
$PPr^i_3Mo(CO)_5$	612, 585	380
$PPr^i_3W(CO)_5$	605, 577	385
$PBu^n_3Cr(CO)_5$	676, 656	
$PBu^n_3Mo(CO)_5$	610, 583	401, 380
$PBu^n_3W(CO)_5$	601, 575	385

B. DISUBSTITUTED COMPLEXES

COMPLEX	δ MCO	ν MC
$[P(OMe)_3]_2Cr(CO)_4$	679, 641	
$[P(OMe)_3]_2Mo(CO)_4$	620, 571	400
$[P(OMe)_3]_2W(CO)_4$	615, 568	400
$[P(OEt)_3]_2Cr(CO)_4$	679, 645	
$[P(OEt)_3]_2Mo(CO)_4$	620, 574	395
$[P(OEt)_3]_2W(CO)_4$	614, 568	395
$[P(OPr^i)_3]_2W(CO)_4$	677, 644	
$[P(OPr^i)_3]_2Mo(CO)_4$	621, 575	400
$[P(OPr^i)_3]_2W(CO)_4$	616, 570	400
$(PPr^i_3)_2Cr(CO)_4$	680, 640	
$(PPr^i_3)_2Mo(CO)_4$	631, 577	
$(PPr^i_3)_2W(CO)_4$	627, 571	404
$(PBu^n_3)_2Cr(CO)_4$	681, 641	391
$(PBu^n_3)_2Mo(CO)_4$	630, 574	402
$(PBu^n_3)_2W(CO)_4$	625, 570	404

Previous studies[152,153] assigned the δMCO absorptions in phosphine substituted hexacarbonyls to 700 - 500 cm^{-1} and νMC absorptions in these complexes to 500 - 300 cm^{-1}. Applying the symmetry rules to the complexes (assuming the ligands to be radially symmetric) allows a calculation of the theoretical number of bands by group theory. This has been reported by Adams for a wide variety of complexes[154]. For monosubstituted complexes three νMC and four δMCO bands are expected while the transdisubstituted complexes should have one νMC and two δMCO bands. There are many problems encountered when attempting to obtain and assign spectra in this region. The free ligands have absorptions in the region, which may mask complex absorptions and coupling between vibrations of the same symmetry is possible which may cause the spectra to be complicated. Bands assigned as δMCO and νMC in the complexes are given in Table 5.2. the former assigned by their higher frequency and greater intensity. Such assignments have been made previously by Manning[155] and by Parker and Stiddard[156] using this criterion. The former study discussed complexes πCpFe(CO)$_2$I, assigning the M(CO)$_2$ bending and stretching modes. Parker and Stiddard reported infrared data for methyl π-cyclopentadienyl carbonyl complexes of manganese and iron as part of extensive work on spectra of metal complexes. This work includes rigorous assignment of metal carbonyl and other absorptions in lower energy regions which support the qualitative assignments given here. As the number of bands observed is generally less than the number given by group theory it is difficult to assign the peaks with any certainty. The δMCO absorptions occur at higher energies for chromium derivatives than for the molybdenum or tungsten derivatives. The νMC absorptions are observed in the region 500 - 350 cm^{-1} for some of the complexes and each of the peaks observed occurs at approximately the same energy value, about 400 cm^{-1}. It is surprising that the size of the metal has such a small effect on the frequency value and further, no relation can be seen between the metal carbon stretching frequency and bonding characteristics. This is consistent with the metal ligand bonding discussion below which suggests that metal ligand σ-π transfer alters in a complex way with substituent changes in these complexes.

METAL PHOSPHORUS BONDING

Early discussion of the nature of the metal phosphorus bond in metal VI carbonyl derivatives containing phosphorus III ligands centred on the possible interpretation of observed parameters in terms of σ- and π-bonding effects. Little work had been done on the molecular orbital theory of such complexes and thus the relative populations of the approximate molecular orbitals were unknown. This necessitated a purely empirical approach to possible bonding characteristics. Thus, for example, the carbonyl stretching frequency values and subsequently derived parameters were obtained and observed trends were rationalised on the basis of qualitative approaches to metal-carbonyl and metal phosphorus bonding. Initially, lowering of the carbonyl stretching frequencies on phosphine substitution in a metal VI hexacarbonyl was attributed to the poorer π-accepting ability of the phosphine with respect to the carbonyl. This argument was used to construct a table of ligands arranged in order of "π-accepting" (i.e. carbonyl frequency lowering) ability. Studies of the carbonyl stretching frequency values of two series of metal carbonyl phosphine complexes[22,69] allowed the following series of phosphine ligands to be constructed

$$CO > PCl_3 > P(OPh)_3 > PPh_3 > PMe_3 > PEt_3 > PBu^n_3 \quad P⬡_3$$

This series shows the order of ν(CO) in $LM(CO)_5$ complexes, $M(CO)_6$ having the highest frequency and $M(CO)_5P⬡_3$ the lowest (taking a weighted average of the peaks). These approaches to the bonding properties of phosphines in such complexes were pursued by many workers invoking a wider variety of spectral parameters in an effort to observe a reliable "probe" for bonding characteristics of the metal phosphorus link. These studies have been outlined briefly in the general introduction where an historical view of the activity in this field has been given with little comment on the validity or merit of the approaches adopted.

Previous attempts to correlate experimental results with theory were made to determine the amount of σ- and π-overlap involved in the M - P bond. Thus, force constant results were interpreted by Cotton[137] as evidence of π-bonding ability for phosphine ligands. Angelici[19], however, interpreted the stretching carbonyl frequencies of some phosphine monosubstituted derivatives of tungsten hexacarbonyl to show no such π-bonding. These approaches both involved the study of infrared stretching frequencies and derived parameters. Work of a similar nature carried out by Graham[34] has proposed a method of attributing quantitative relative values to σ- and π-bonding abilities. Graham's technique requires calculation of the Cotton-Kraihanzel force constants for monosubstituted carbonyl derivatives of type $LM(CO)_5$. The change in σ- and π-effects on changing ligands could be directly related to changes in the readily calculated force constants. The expressions are $\Delta k_1 = \Delta\sigma + 2\Delta\pi$ and $\Delta k_2 = \Delta\sigma + \Delta\pi$ where Δ indicates a change from some reference value and k_1, k_2 refer to the trans and cis carbonyls respectively. Solving these equations for $\Delta\sigma$, $\Delta\pi$ give a series of values which claimed to reflect the σ- and π-bonding abilities of the ligands L in $LM(CO)_5$. While such an approach is attractively simple, the extent of the approximations employed make the quantitative results obtained entirely unreliable.

In Table 5.3 the Cotton-Kraihanzel force constants and Graham parameters are listed for a series of monosubstituted phosphine complexes. As may be seen from the values of $\Delta\sigma$ and $\Delta\pi$ parameters the variation on ligand change is different for each of the metal atoms and is small. The most important criticism, from the point of view of analysing possible σ-π bonding effects, if that these parameters and others derived in a similar manner do not produce new information. They cannot be used as reliable indicators of bonding properties or for comparison with other spectroscopic data.

The principle study in this work concerned the electronic spectra of the metal VI carbonyl phosphine derivatives. A previous investigation of similar complexes[44] proposed a possible correlation between the position of the lowest energy charge transfer peak of monosubstituted derivatives $LM(CO)_5$ and the π-bonding ability of the phosphorus III ligand L. Taking account of recent developments in bonding theory relating to possible σ- and π-overlap effects in metal-ligand linkages and the results of the present study on the electronic spectra of an extended range of such phosphine complexes, any simple correlation of this type is no longer justified on the available evidence. Work by Hall and Fenske[150] on molecular orbital

TABLE 5.3

Cotton-Kraihanzel Force Constant Parameters and Graham $\Delta\sigma$, $\Delta\pi$ Parameters for Monosubstituted Complexes

TABLE 5.3

COMPLEX	k_1	k_2	k_i	$\Delta\sigma$	$\Delta\pi$
$C_6H_5Cr(CO)_5$	15.04	15.77	0.32	0	0
$P(OMe)_3Cr(CO)_5$	15.80	15.94	0.30	-0.42	0.59
$P(OEt)_3Cr(CO)_5$	15.75	15.90	0.30	-0.45	0.58
$P(OPr^i)_3Cr(CO)_5$	15.72	15.85	0.30	-0.52	0.60
$PPr^i_3Cr(CO)_5$	15.41	15.71	0.30	-0.49	0.31
$PBu^n_3Cr(CO)_5$	15.47	15.72	0.30	-0.53	0.48
$C_6H_5Mo(CO)_5$	15.10	15.84	0.32	0	0
$P(OMe)_3Mo(CO)_5$	15.86	16.03	0.30	-0.36	0.57
$P(OEt)_3Mo(CO)_5$	15.81	15.99	0.31	-0.41	0.56
$P(OPr^i)_3Mo(CO)_5$	15.76	15.95	0.31	-0.44	0.55
$PPr^i_3Mo(CO)_5$	15.43	15.84	0.31	-0.33	0.33
$PBu^n_3Mo(CO)_5$	15.53	15.84	0.31	-0.43	0.43
$C_6H_5W(CO)_5$	15.07	15.75	0.32	0	0
$P(OMe)_3W(CO)_5$	15.78	15.95	0.32	-0.31	0.51
$P(OEt)_3W(CO)_5$	15.73	15.91	0.32	-0.34	0.50
$P(OPr^i)_3W(CO)_5$	15.69	15.87	0.33	-0.38	0.50
$PPr^i_3W(CO)_5$	15.40	15.74	0.32	-0.35	0.34
$PBu^n_3W(CO)_5$	15.45	15.75	0.32	-0.38	0.38

calculations for $M(CO)_{6-x}L_x$ where M = Cr, Mn, Fe; L = Cl, Br, I; x = 1, 2 suggests that the carbonyl stretching force constants are affected by both the degree of π-backbonding to the 2π carbonyl orbital and the degree of σ-donation from the 5σ orbital in the bonded carbonyl group. This in turn indicates that electron distribution within metal-ligand bonds depends on the interaction of both mechanisms (σ- and π-overlap). Indeed, a series of semi-empirical molecular orbital treatments on various transition metal carbonyl derivatives carried out by Fenske and coworkers[37,150,151] has produced convincing evidence that the previously accepted qualitative approaches to metal-ligand bonding in carbonyl complexes are unjustified on the theoretical bases proposed.

The very early ideas presented by Orgel and others, proposing a synergic bonding effect which allowed formation of a strong bond by mutual σ-π bonding mechanisms are supported by the recent theoretical studies. Changing the electronic distribution around the metal atom by replacing one or more of the carbonyl groups by other ligands creates considerable alteration in the population of the σ- and π-carbonyl orbitals involved in the metal-carbonyl bond. Two principle factors may be derived from these and other studies of bonding characteristics in transition metal carbonyl derivatives. First, it must now be considered desirable to obtain approximate overlap populations for model carbonyl complexes before any meaningful theory of σ-π effect separation can be proposed. One of the most interesting aspects of Fenske's work is the improved ability to correlate parameters with changes in electron distributions and while such quantitative results derive from approximate molecular orbital methods, the approximations cannot be said to invalidate the results. The second feature of this more precise approach to bonding in metal carbonyl complexes is a warning against facile theories of π-bonding in such complexes. It is clear from the calculations that the effects of changing environment on electronic structure in metal carbonyls is of an extremely disruptive nature. It is, therefore, improbable that the electronic spectral parameters reported here may be related directly to any metal-ligand π-bonding effects.

It is, however, interesting to note that the lowest energy charge transfer peaks and Cotton-Kraihanzel force constants for a series of monosubstituted complexes are in a similar order. Monosubstituted phosphite complexes have higher energy charge transfer peaks and greater stretching force constants than similar phosphine complexes. However, if the individual phosphine and phosphite derivative parameters are considered, no consistent series is observed for the lowest charge transfer energy peak for the three group VI metal complexes. It may be said that infrared and electronic spectral parameters of these metal carbonyl derivatives are related. Complexes $LM(CO)_5$, arranged in series, according to ligand L, increase as $CO > P(OR)_3 > PR_3 > NR_3$ for force constant and charge transfer parameter results. A detailed understanding of these series with metal ligand bonding effects will, however, require further work on semiempirical molecular orbital diagrams and a clearer understanding of bonding in metal carbonyl complexes.

CONCLUSION

CONCLUSION

The study of metal carbonyl phosphine complexes of the type discussed above has been developing for some ten years and inevitably the emphasis has changed as instrumentation and theoretical concepts have developed and improved. The study of preparative work has tended, recently, to take second place to spectroscopic investigations although methods of improving preparative work are regaining importance. An example of this, relevant to complexes of the type discussed here, is Chatt's recent work on catalysed preparation of some di- and trisubstituted metal VI carbonyl phosphine derivatives[78]. The preparations reported in the present work are all straightforward, using direct replacement of the carbonyl groups by phosphorus III ligands. However, the care required in maintaining suitable conditions for reaction and for obtaining pure complexes causes the preparation time to be fairly long and it is possible that a more convenient preparative technique could eliminate some of the time consuming aspects of such simple preparations.

While the infrared spectra of the types of derivatives discussed are well documented and have been discussed and interpreted by many authors, the ultraviolet spectra which in principle may provide more direct information on the electronic environment around the metal atom of such complexes have not been studied extensively. The reasons for this have been discussed above and the study of ultraviolet spectra may, in the future, broaden in scope to include studies of spectra recorded at different temperatures. This technique has been seen to allow assignment of peaks having intermediate values of extinction coefficient, i.e. in the approximate region $\varepsilon \sim 500 - 5,000$ l cm^{-1} mole^{-1} and if more definite assignments may be obtained in this way, correlation of energy transitions with energy levels will be more readily achieved. As the molecular orbital theory for metal carbonyl derivatives is developing rapidly and the use of photoelectron spectroscopy is becoming more common. Significant information concerning energy levels and orbital functions may be obtained from these, interpretation of ultraviolet spectra should become more precise and hence more useful in discussing the electronic behaviour in complex molecules. The use of curve analysis by constructing a curve outline from a combination of (for example) Gaussian distribution curves has, however, been seen to be of limited use for resolving the extreme overlap observed in most of the spectra considered. The range of possible Gaussian interpretations of the curves is often greater than may be reasonably accepted and such analyses alone may not be accepted as reliable evidence of unresolved peak parameters. Use of the Gaussian analyses in conjunction with spectra of analogous derivatives may allow a reasonable interpretation of the overlap pattern. However, when spectra taken at different temperatures are considered, the effect of the temperature change on the band parameters may be less than the experimental error present in Gaussian analysis. In these cases great care must be taken when any interpretation is suggested on the basis of the Gaussian analyses and for very weak peaks (which are the principal types resolved by curve analysis only) the value of such analyses must remain very tentative.

Studies of infrared carbonyl stretching frequencies, ultraviolet spectral parameters and proton N.M.R. parameters seem to indicate that no consistent relation may be detected between these spectral parameters and the degree and type of bonding changes in the metal-ligand bonds in these complexes. This is in agreement with recent studies which suggest that the bonding in such complexes varies in a manner which is dependent on the ligand involved but which may not readily be related to individual bonding changes in any one metal-ligand bond.

Several studies have been reported on the effect of changing the environment around a metal atom on the orbital populations in carbonyl groups bonded to that metal. These suggest that ligand changes in substituted metal carbonyls cause the metal-ligand σ- and π-bonding systems to be altered in such a way that σ-overlap changes compensate π-overlap and vice versa. The most important factor to emerge from these most recent studies is that any spectroscopic results either represent a small change arising from opposing quantitative changes in σ- and π-orbital populations or indicate transitions between energy states (or approximate one electron energy levels) which may not be defined even qualitatively. The parameters for the infrared and ultraviolet spectra obtained in this study may be related to the former and latter cases respectively and while the observed spectra are directly determined by the electronic and vibrational wave functions of the molecules, the parameters may not be related in any simple way to changes in individual bonding properties. The situation will certainly improve as more photoelectron spectral results become available. Photoelectron spectra record electron removal from a molecule providing energy measurements which may be approximated to the one electron energy levels in the molecule. Using this technique combined with electronic absorption spectra which record transitions between energy states and molecular orbital theory which allows construction of approximate molecular wave functions, the ultraviolet spectroscopic parameters may be expected to correlate with energy transitions derived from the molecular orbitals and photoelectron spectra.

It can be said, however, at present that the status of ultraviolet spectroscopy as it is used in metal carbonyl derivative studies is very similar to that of infrared spectroscopy as it was in the middle 1960's. The use of ultraviolet spectroscopy has been less popular than that of infrared spectroscopy because useful information is more easily derived in the latter case and instrumentation and recording is correspondingly simpler for the infrared spectra.

APPENDIX

APPENDIX

Trifluorophosphine derivatives of manganese and rhenium decacarbonyl

Introduction

Monosubstituted and disubstituted trifluorophosphine derivatives of manganese decacarbonyl (axially substituted) have been reported in the literature by Kasenally[157] and more recently by Sheline and coworkers[158]. As these complexes and the analogous rhenium derivatives provide convenient sources of spectroscopic data, they may be used in force constant analysis of the parent carbonyl molecules $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. It was suggested that infrared and raman results of diaxial derivatives could provide sufficient experimentally observed frequencies for a full carbonyl force constant analysis. Some of the parameters obtained from this analysis would then be employed in an analogous study of the decacarbonyls. $M_2(CO)_8L_2$ has five carbonyl stretching modes (3 Raman and 2 infrared). There are also five carbonyl-carbonyl force constants associated with this molecule and hence it is possible to use the observed frequencies for full carbonyl force constant analysis. The $M_2(CO)_{10}$ molecule has seven carbonyl stretching modes (4 Raman and 3 infrared) and nine carbonyle force constants. It therefore requires additional data for carbonyl force constant analysis. This work is a natural extension to a partial analysis reported by Haas and Sheline[159] using infrared results for $(PF_3)_2Mn_2(CO)_8$ and general interest in the dimanganese decacarbonyl system and its infrared carbonyl stretching frequencies. These studies have included infrared spectra of carbon-13 carbonyl enriched samples[160], a Raman study of $Mn_2(C\ )_{10}$[161] and a force constant approach[162] which treated axial and equatorial carbonyls as two separate groups (carbonyl factored approach). Each of these studies increased the precision with which the stretching carbonyl frequencies could be obtained and advanced the possibility of solving a complete carbonyl force constant analysis of the molecule. Indeed, Bor in his paper reporting stretching frequencies for carbon-13 enriched molecules[160] recalculated the nine possible carbonyl force constants from the infrared active and inactive modes thus obtained. However, the possibility of obtaining sufficient data from Raman and infrared spectra of dimanganese decacarbonyl and its trifluorophosphine derivatives would allow an independent means of calculating force constants without determining the position of infrared forbidden carbonyl stretching modes. It would also be possible to extend this work to the dirhenium decacarbonyl by use of spectroscopic results from its PF_3 derivatives. It was therefore decided that the reaction between $M_2(CO)_{10}$ M = Mn, Re and PF_3 should be attempted in order to obtain samples of $M_2(CO)_9PF_3$ and $M_2(CO)_8(PF_3)_2$ (axially substituted) suitable for infrared and raman studies.

Experimental

Sheline and coworkers in their report of the reaction between $Mn_2(CO)_{10}$ and PF_3 employed two principal techniques of reaction.

These were, reaction in a metal bomb with high temperature and pressure conditions and ultraviolet irradiation of a mixture of the reactants at approximately 100°C for three hours. The products from each of these reactions were found to be mixtures of derivatives having different degrees of substitution. A previous preparation using sealed glass carius tubes heated in a carius oven was reported by Kasenally to give the diaxial derivative only. This method was used as reported for both $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ reactions with PF_3.

Dimanganese decacarbonyl derivatives

Dimanganese decacarbonyl (0.5g) was placed in a carius tube (12" x 1") on a vacuum line and trifluorophosphine (approximately 2ml.) was condensed into the tube at -196°C. The carius tube was then sealed on the line and placed in a carius oven, heated at 120°C for 48 hours. After reaction, the tube was removed from the oven and placed in a dewar of liquid nitrogen. It was opened carefully by "hot spotting" and any excess trifluorophosphine was allowed to boil off at room temperature in a fume hood. A yellow solid was formed in variable yield along with a black residue which coated the carius tube and may be oxidation products. The solid melts at 65°C.

Analysis.	Found	Complex	C 21.22	H 0.0	F 20.5	P 10.85
	Calc.	$(PF_3)_2Mn_2(CO)_8$	C 18.82	H 0.0	F 22.36	P 12.15
	Calc.	$(PF_3)Mn_2(CO)_9$	C 24.00	H 0.0	F 12.62	P 6.90

As may be seen from the analysis figures, the product obtained is clearly not $(PF_3)_2Mn_2(CO)_8$ or $(PF_3)Mn_2(CO)_9$. The infrared spectrum in the stretching carbonyl region shows a great many peaks with a very strong absorption at about 2010 cm^{-1}, two medium absorption peaks at 2034 cm^{-1} and 2026 cm^{-1} and many other weak peaks. All infrared spectra were run in cyclohexane using a Perkin Elmer 257 spectrophotometer calibrated using a polystyrene peak at 1603 cm^{-1}. As Kasenally[157] has assigned peaks at 2037 cm^{-1} and 2014 cm^{-1} to the diaxially substituted derivative while Sheline[156] reports peaks at 2029 cm^{-1} and 2012 cm^{-1} as the strongest bands in this complex, it seems clear that the complex obtained in the above preparation is a mixture of the monosubstituted and disubstituted derivatives. It was expected that reaction of this product with PF_3 would cause further substitution of carbonyl and hence an increase in the proportion of the disubstituted derivative in the mixture.

The product obtained as described above (0.2g) was placed in a carius tube on the vacuum line and trifluorophosphine (approx. 1ml) condensed into the tube. This was then sealed as before and heated for 48 hours at 120°C in the oven. The product, obtained as above, was a yellow solid which melts at 80°C and has infrared stretching carbonyl frequencies at 2014 cm^{-1} and 2026 cm^{-1}, the position of the latter peak being observed as a shoulder on the very intense peak. It is clear from the infrared spectra that this complex differs from that obtained previously and the analysis figures confirm that the complex is the disubstituted derivative.

Analysis C 19.13 H 0.0 F 22.01 P 11.87

The monosubstituted derivative was obtained from the first reaction product by two sublimations at 25°C/0.01 mm. This derivative has two principal infrared carbonyl absorptions at 2013 cm^{-1} and 2034 cm^{-1} and has melting point 86°C.

Dirhenium dodecacarbonyl derivatives

The method as described above was used in an attempt to prepare the analogous derivatives of $Re_2(CO)_{10}$. nder similar conditions, no reaction was observed at 120°C over a period of four days. At 250°C over 48 hours a grey-white solid which was soluble in pentane and could be sublimed at vacuum (50°C/0.1 mm) was obtained. The sublimed material was a white solid melting at 44°C. This solid was found to be very unstable in air even when kept at low temperature. The infrared spectrum in the carbonyl stretching region shows peaks at 2030 cm^{-1} and 2062 cm^{-1} but as there is considerable $Re_2(CO)_{10}$ left, the spectra are not sufficiently clear to allow any assignments.

Raman spectra could not be obtained on a cyclohexane solution of the manganese derivatives as rapid decomposition was observed in the laser beam. The rhenium derivative obtained was impure and unstable and no Raman studies could be attempted on it. As the Raman data was essential to further development of the force constant analysis work, this had to be abandoned.

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