MÖSSBAUER AND SYNTHETIC STUDIES OF BENZOCYCLOOCTATETRAENES

IRON CARBONYL COMPLEXES

A Thesis submitted for the Degree of MASTER OF SCIENCE

by

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I certify that all the work presented in this thesis is my own except where clear reference is made to the work of others.
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Studies of iron carbonyl complexes of benzocyclooctatetraene have shown the presence of a small but definite asymmetry in linewidths and intensities in the dinuclear complex BCOTFe₂(CO)₆ which is attributed to the presence of two slightly non-equivalent iron sites. The precision necessary to obtain these results was affected by many experimental factors and to counteract this it was necessary to repeat many observations. Frozen solution spectra obtained with small (∼10 mg) quantities of material gave results consistent with those obtained from the spectra of solids. An analysis of the errors in the Mössbauer parameters is given and experimental techniques designed to minimise these errors, especially for frozen solution samples, are described. Synthetic studies directed towards rendering the iron sites in the dinuclear complex BCOTFe₂(CO)₆ more non-equivalent were not particularly successful because of low yields and the difficulty in separating the desired compounds from complex mixtures.
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1. Introduction

1.1 Scope of the Investigation

Metal carbonyls form a diversified range of complexes with olefinic ligands. Mononuclear and polynuclear complexes with cyclic polyolefins, particularly cyclooctatetraene and its derivatives, are especially interesting because of their fluxional behaviour in solution (dynamic behaviour in the solid state for two cyclooctatetraene complexes has also been observed). The elucidation of the structures of such complexes rests mainly on X-ray diffraction and nuclear magnetic resonance data. Mössbauer spectroscopy has also been used, especially where X-ray studies have not been made, to confirm or deny a particular structure. The critical application of such results to homopolynuclear complexes will be discussed. In such cases the reliability of the deductions made from Mössbauer spectroscopy is often questionable due to lack of resolution in the spectra.

This investigation was directed towards obtaining accurate and precise Mössbauer spectral parameters for iron carbonyl complexes of benzocyclooctatetraene. These compounds had been first synthesised in this Department and had been found to be non-fluxional, in contrast to their cyclooctatetraene analogues. It was thought that Mössbauer spectroscopy would be of particular help in the investigation of their structures. Attempts were made to resolve the absorptions due to two different iron atom sites in one of these complexes, both by chemical means and by a refinement in the techniques used for obtaining Mössbauer spectra.
It was soon apparent that one was working at the limits of resolution of the equipment (and possibly also of the spectroscopic method) and severe technical difficulties had to be overcome before reliable results could be obtained from the spectra. The synthetic studies were hindered by low yields and the inability to isolate pure complexes in some cases. Moreover soon after this work was begun a more careful nmr study was published which demonstrated the fluxional nature of benzocyclooctatetraene complexes.

Nevertheless, certain useful results were obtained, particularly in the resolution studies. The application of the experimental methods employed together with the knowledge of the capabilities of the instrumentation and the spectroscopic method may be of significant advantage in future studies.

1.2 Fluxional Molecules

In the last fifteen years or so an interesting class of iron carbonyl-olefinic complexes has been discovered. These are the so-called dynamic or fluxional molecules of which cyclooctatetraene iron tricarbonyl (I) was the first example known.\textsuperscript{1,2}

\begin{equation}
\text{Fe(CO)}_3
\end{equation}

(1) Structure in solid state

Since its discovery many other fluxional complexes have been synthesised, mostly containing iron or ruthenium.\textsuperscript{3-7}
In equation 1-1 the movement of the iron tricarbonyl group around the ring constitutes the dynamic behaviour. As a result of this movement all eight protons of the ring become "equivalent", i.e. they exhibit the same chemical shift. This occurs only if the rate of equilibration of all the possible forms is sufficiently rapid on the nmr time scale. At room temperature this is normally the case for all known dynamic molecules, including (I), but if the temperature is lowered far enough it is possible to freeze out the instantaneous structure (Ia). This instantaneous structure gives separate resonances for the protons which are associated with the coordinated double bonds and for those protons which are associated with the uncoordinated double bonds (τ values in mixed Freon solvents: H-1,8 5.22; H-2,7 5.45; H-3,6 3.55; H-4,5 3.81). 8

All cyclic polyolefins in which there are three or more conjugated double bonds may form fluxional complexes with iron carbonyls. Moreover, the fluxional behaviour is not necessarily restricted to solution, although it is more readily observed there, but may occur also in the solid state. 9

Besides complexes of type (I) in which there is only one metal atom bound to the ring, many other fluxional complexes are known where there are two metal atoms bound to the ring. An isomer of COTFe₂(CO)₆, (II), was one of the first examples known. 4,10 Not all such polynuclear complexes are fluxional however; for example another isomer of COTFe₂(CO)₆, (III), 1,2 exhibits separate resonances for the ring protons at room temperature. 11 The reason why (III) is non-fluxional will be discussed later.
1.21 Mechanism of the Fluxional Process

The mechanism of the fluxional behaviour of COTRu(CO)_3 in solution has been deduced by careful analysis of nmr spectra taken over a wide temperature range. The ruthenium complexes are used in such studies because of their slower rates of interconversion and hence the higher temperatures of their fully resolved (limiting) spectra as compared to the iron complexes. It is probable that the same mechanism applies to all fluxional cyclic polyolefin complexes.

In this mechanism the M(CO)_3 (M = metal) moiety moves around the ring in a sequence of 1,2 shifts, with the double bond system of the ring adjusting accordingly (equation 1-2).

The observation that the β and γ resonances collapsed most readily with increasing temperature was only consistent with a process of 1,2 shifts. This was confirmed by comparing
computer simulated spectra with the experimental ones.

1.22 Rate of Interconversion

The rate of interconversion of the instantaneous structures for some molecules has been measured using the results of mechanistic studies and computer simulation. Both the energy of activation $E_a$ and the temperature $T_L$ of the limiting spectrum have been used as measures of the ease of conversion. Table 1-I presents such data for several complexes.

<table>
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<tr>
<th>Compound</th>
<th>$T_L$ (K)</th>
<th>$E_a$ (kcal/mole)</th>
<th>Reference</th>
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<tr>
<td>BCOTFe(CO)$_3$ ($a$)</td>
<td>278</td>
<td>18.6</td>
<td>13</td>
</tr>
<tr>
<td>NCOTFe(CO)$_3$ ($b$)</td>
<td>363</td>
<td>31.0</td>
<td>13</td>
</tr>
<tr>
<td>COTFe(CO)$_3$</td>
<td>&lt;118</td>
<td>7.2</td>
<td>14</td>
</tr>
<tr>
<td>COTRu(CO)$_3$</td>
<td>133</td>
<td>9.4</td>
<td>12</td>
</tr>
<tr>
<td>BCOTFe$_2$(CO)$_6$</td>
<td>165</td>
<td>8.1</td>
<td>13</td>
</tr>
</tbody>
</table>

Notes: (a) BCOT = benzocyclooctatetraene

(b) NCOT = 2,3 naphthocyclooctatetraene

1.3 Non-Fluxional Complexes

As noted previously the complex COTFe$_2$(CO)$_6$, (III), is non-fluxional. The structure shown is actually that found in the solid state.$^{15}$ From the appearance of the room temperature nmr spectrum$^{11}$ it was inferred that the complex retained the same structure in solution. Assuming this, then the absence of fluxional behaviour can be attributed to the unfavourable geometry of the double bonds relative to the iron atoms,
precluding the formation of the instantaneous structure (IIIa) which is necessary for the occurrence of dynamic equilibrium.

Some other complexes, for example (IV) and (V), show no marked change in their nmr spectra over a wide temperature range and hence are non-fluxional. Actually the structure of (V) has not been fully determined, there being two possibilities (Va) and (Vb).

These are in fact the two possible tautomers of a non-existent dynamic equilibrium but the presence of an unsymmetrical substituent on the cyclooctatetraene ring would render them distinct even if there was dynamic interconversion. The non-fluxional behaviour of (IV) and (V) has been explained on the basis that the substituents withdraw electron density from the ring double bonds to which they are directly conjugated making these double bonds unavailable for
coordination to the metal.

1.4 Application of Mössbauer Spectroscopy to the Study of Polynuclear and Fluxional Molecules

Differentiation between molecules such as (II) and (III) and the elucidation of their structures is by no means an easy task and misinterpretation of spectroscopic results has resulted in incorrect structures being proposed in some cases. The potential application of $^{57}$Fe Mössbauer spectroscopy is twofold:

(i) If solutions of complexes are cooled at a sufficient rate instantaneous structures may be obtained whose nmr spectra may be difficult to interpret but whose Mössbauer spectra might give more information. This could be very helpful in those cases where complexes have small solubilities at low temperatures.

(ii) For polynuclear complexes (fluxional or non-fluxional) different metal atom sites in the molecule may be distinguished, even while the molecule is undergoing dynamic interconversion.

As an example of the application of the first technique consider the hypothetical unsymmetric complexes (VIa) and (VIb).

![Diagram of complexes VIa and VIb]
The nmr spectra of such species would be similar. If $X$ is a bulky group, in which case the stereochemistry about the iron atom in (VIb) would be different to that in (VIa), then the quadrupole splittings would be different for each of the isomers. If $X$ is a strongly electron donating or withdrawing group then the isomer shifts would be different due to the greater effect that $X$ would have on the electron density of the iron atom in (VIb).

If a mixture of (VIa) and (VIb) is obtained on cooling then one might expect to see significant line broadening (when compared to the symmetrical complex $X=H$). Conversely if no line broadening is observed it would indicate that only one isomer is present.

The second technique relies on much the same principles but could be applied to solids as well as to frozen solutions. Different sites will produce both different quadrupole splittings and isomer shifts. The problem with both techniques is that the differences between isomer shifts and quadrupole splittings for different iron sites may be very small and unresolved in the Mössbauer spectrum. Varying the solvent (first technique) or the temperature (both techniques) may help.

Herber$^{17,18}$ and Grubbs$^8$ have made studies of cyclooctatetraene complexes using the first technique but did not apply it specifically to asymmetric complexes such as (VIa) and (VIb).

Studies attempting to resolve absorptions due to different iron atoms have been applied to a variety of polynuclear complexes, besides cyclooctatetraene derivatives.
Success has been varied and absorber preparation methods are important. Further reference to such work is made in Section 4 - "Mössbauer Results".

1.5 Benzocyclooctatetraene Complexes

Benzocyclooctatetraene forms two complexes with diiron nonacarbonyl or triiron dodecacarbonyl: a yellow monoiron complex (VII) and the reddish-orange diiron complex (VIII). For the formation of the diiron complex the iron-iron bond must be already present in the metal carbonyl (thus benzocyclooctatetraene fails to react with iron penta carbonyl); it cannot be formed by reaction of the monoiron complex with metal carbonyl.

The structure (VII) was assigned to the monoiron complex on the basis of spectroscopic data while the structure (VIII) of the diiron complex was inferred by analogy with the corresponding iron and ruthenium complexes of cyclooctatetraene. The presence of a benzene ring in (VIII) effectively removes one double bond from potential coordination to an iron atom and so a structure for a benzocyclooctatetraene complex

* Small amounts of an unstable yellow complex were also isolated but it was not identified. See Section 5.5.
analogous to (III) is not possible.

The nmr results of Stucki and Whitlock,\textsuperscript{13} which shows (VIII) (and (VII)) to be fluxional, precludes structures of types (VIIIb) and (VIIIc), analogous to ones proposed for related complexes, for the diiron complex. Either of these structures would give a temperature independent nmr spectrum.

\[
\text{Fe(Fe(CO)\textsubscript{3})\textsubscript{2}C_{8}H_{12}Fe(Fe(CO)\textsubscript{3})\textsubscript{2}}
\]

Thus the structure (VIII) is by elimination the only likely one for benzocyclooctatetraene diiron hexacarbonyl.

The presence of two non-equivalent iron atoms A and B should produce a Mössbauer spectrum of one of the following forms

(a) Two pairs of quadrupole doublets

(b) A three line spectrum

(c) An apparent quadrupole doublet with one or both lines broadened with respect to those of (VII).

One of the first two situations would arise if either the isomer shifts or the quadrupole splittings of A and B were sufficiently different. If the isomer shifts and the quadrupole splittings were very similar case (c) would be observed.

Possible ways of differentiating between these two iron atoms were envisaged if the Mössbauer spectrum of (VIII) should prove inconclusive:

(a) Substitution of a CO group at one of the iron sites
by another ligand such as P\(\phi\), or As\(\phi\). This would hopefully alter either the isomer shift or the quadrupole splitting of the iron atom at this site, compared to the other iron atom, for this to be apparent in the spectrum.

(b) Replacement of one of the iron atoms by a different metal, thereby allowing the Mössbauer spectrum of a monoiron complex to be obtained. Comparison of this spectrum with that of the parent diiron complex should make apparent any line broadening due to the presence of a slightly non-equivalent iron atom.

(c) Substitution of an electron releasing group X in the benzocyclooctatetraene ring at positions 1 and 6:

\[
\begin{align*}
\text{(OC)}_3\text{Fe} & \quad \text{Fe(CO)}_3 \\
\text{X} & \quad \text{I} \\
\text{I} & \quad \text{X}
\end{align*}
\]

The substituent bound to the instantaneous double bond would not be likely to alter the electron density on the iron atom bound to this double bond since the electron donation from the filled C=C orbital into the metal \(\sigma\) acceptor orbital should be counterbalanced by electron release from the metal \(d\pi\) orbital into the \(\pi^*\) antibonding orbitals of the two carbon atoms. Hence the contribution to the isomer shift of this iron atom by the C=C\(\rightarrow\)Fe bonding should not change if substitution occurs.

However the substituent bound to the carbon atom which is bonded to Fe should increase the electron density on this
carbon atom and by delocalisation this should increase the electron density on the iron atom. Depending on whether this increased density goes into 3d orbitals (resulting in increased shielding of the 4s electrons) or into 4s orbitals the isomer shift should either increase or decrease respectively.

For none of these approaches is it possible to predict the extent to which the spectrum might be changed, and hence whether any differences would be observable. For this reason every effort was made to obtain narrow absorption lines in order to maximize resolution.

In this work the synthetic studies required in the first two methods are reported. Preparative difficulties prevented the application to the Mössbauer spectra.

2.2 General Preparative Methods

These fall mainly into three classes:
(a) Thermal reactions of metal carbonyl-polyolefin mixtures.
(b) Photochemical reactions.
(c) Ligand exchange.

2.2.1 Thermal Reactions of Metal Carbonyls with Polyolefins.

The most common method for the preparation of metal carbonyl-polyolefin complexes is to reflux a mixture of the metal carbonyl and polyolefin in an appropriate solvent at the desired boiling point. The reaction is carried out under an inert atmosphere in a closed vessel. The products are frequently air-sensitive.

For the preparation of iron complexes all these iron carbonyls have been used although the more reactive methacrylonitrile and decenecarbonyl usually give the best yields. The choice of the solvent is important, principally because of its boiling point which determines the definite reaction temperature. In solvent...
2. Synthetic and Structural Considerations

2.1 Synopsis

Some synthetic methods for the preparation of metal carbonyl complexes of cyclic polyolefins will be discussed together with their limitations and their application to the present work. The nature of metal-ring and metal-metal bonding will be considered in several examples. For polynuclear complexes a wide variety of structural types seems possible and where the metals concerned have Mössbauer-active nucleides (e.g. Fe and Ru), Mössbauer spectroscopy may be a useful tool in the elucidation of structure.

2.2 General Preparative Methods

These fall mainly into three classes:

(a) Thermal reactions of metal carbonyl-polyolefin mixtures.

(b) Photochemical reactions.

(c) Ligand exchange.

2.21 Thermal Reactions of Metal Carbonyls with Polyolefins

The most common method for the preparation of metal carbonyl-polyolefin complexes is to reflux a mixture of the metal carbonyl and polyolefin in an appropriate solvent of desired boiling point. The reaction is carried out under an inert atmosphere as the complexes are frequently air-sensitive. For the preparation of iron complexes all three iron carbonyls have been used although the more reactive nonacarbonyl and dodecacarbonyl usually give the best yields. The nature of the solvent is important principally because of its boiling point which determines the effective reaction temperature. In solvents
of high boiling point the thermodynamically-more stable complex
is preferentially formed while at low temperatures a less stable
complex may predominate due to its faster rate of formation.
Thus 1,3,5,7 tetramethylcyclooctatetraene (TMCOT) (IX), reacts
with Fe₂(CO)₉ in refluxing n-oxtane (B.P. 125°) to give com-
plexes (X-XIIa) with (XIIa) as the main product. Reaction with
Fe₃(CO)₁₂ instead of Fe₂(CO)₉, in the same solvent, gives mainly
(XIII) with only very small amounts of (XI) and (XIIa). In
contrast when n-hexane (B.P. 63°) is used as solvent in the
reaction with Fe₂(CO)₉, only (XIV) is isolated in low yield.
This compound is readily converted into (XIIa) on heating.⁷

Scheme I - Complexes from TMCOT
(For the sake of clarity the methyl group has been omitted from these structures and is instead shown as a solid line).

A similar dependence on the solvent used is found in the reactions of ruthenium carbonyl, Ru$_3$(CO)$_{12}$, with cyclooctatetraene (COT) (Scheme 2). $^6,12$

Scheme 2 - Ruthenium Cyclooctatetraene Complexes

\[
\text{heptane} \xrightarrow{+ \text{Ru}_3(\text{CO})_{12}} \text{octane} \xrightarrow{+ \text{COT}} \text{XV} + \text{XVI} + \text{XVII} \xrightarrow{\text{XVIII}}
\]

Compounds (XV-XVII) are analogues of the corresponding iron compounds (I, II, XIIb) respectively.

The complex formed in octane is a fluxional molecule containing a cluster of ruthenium atoms bound to the cyclooctatetraene rings.
Two enantiomorphs of (XVIII) have been isolated.\textsuperscript{20}

In certain cases reaction of Ru\textsubscript{3}(CO)\textsubscript{12} with solvent occurs, as when the carbonyl is refluxed in aromatic hydrocarbons (arenes) such as toluene, xylene and mesitylene. The cluster compounds Ru\textsubscript{6}C(CO)\textsubscript{17} and Ru\textsubscript{6}C(CO)\textsubscript{14} (arene) are formed, albeit in low yield.\textsuperscript{21} Similar reactions with iron carbonyls are virtually unknown although Fe\textsubscript{5}(CO)\textsubscript{15}C has been isolated from the reaction of Fe\textsubscript{3}(CO)\textsubscript{12} and methylphenyl acetylene.\textsuperscript{22}

In all these compounds an isolated carbon atom is located inside a cage of metal atoms.\textsuperscript{22-24}

2.22 Photochemical Syntheses

Photolysis of metal carbonyl olefin mixtures has also been used as a method for the synthesis of complexes but from a thorough investigation of the literature it does not seem to have had much application as thermal reactions. Few reactions were found which were shown to proceed under photolytic conditions but not under thermal conditions. The photochemical reactions of COT itself and some of its complexes have however received some study. Thus COTFe(CO)\textsubscript{3} (I) is photolysed in deoxygenated hexane to give COTFe\textsubscript{2}(CO)\textsubscript{5} (XII\textsubscript{b}) as the only complex isolated; the latter is also formed by the photolysis of COT[Fe(CO)\textsubscript{3}]\textsubscript{2} (III) (Scheme 3).\textsuperscript{25}

**Scheme 3 - Photolysis of Cyclooctatetraene Complexes**

\[
\text{COTFe(CO)}_3 \xrightarrow{hv} \text{COTFe}_2\text{Fe(CO)}_3 + \text{COT} + \text{CO}
\]
Photolysis of (I) or Fe(CO)$_5$ in the presence of excess COT gives iron tricarbonyl complexes (XIX-XX) of cyclooctatetraene dimers;$^{26,27}$ one of these complexes can also be formed by the thermal reaction of the appropriate COT dimer, bullvalene (XXII) with Fe$_2$(CO)$_9$. $^{26}$ Both complexes when photolysed with iron pentacarbonyl yield an unusual triiron complex (XXI) (Scheme 4).$^{27}$

**Scheme 4 - Photolytic Transformations of Complexes of COT Dimers**

\[
\text{COTFe(CO)$_3$ + COT} \quad \xrightarrow{\text{hv}} \quad (\text{OC)}_3\text{Fe}_{\text{cyclooctatetraene}} + \text{Fe(CO)$_3$} \\
\text{Fe(CO)$_5$} \quad \xrightarrow{\text{hv}} \quad \text{Fe}_2(\text{CO)}_9 \\
\]
The structure of the triiron complex was determined by X-ray diffraction; a previous incorrect structure deduced from nmr data showed that two of the iron atoms were in equivalent sites. The possible application of Mössbauer spectroscopy in such a case is obvious although in the light of results with other complexes it may not be as helpful as desired in proving the existence of non-equivalent iron sites.

The complexes (XIX) and (XX) differ in their nmr behaviour with temperature. While (XX) has a temperature independent nmr spectrum, that of (XIX) is temperature dependent and hence the molecule is fluxional. However the mechanism of the fluxional behaviour of (XIX) is obviously different to the mechanism given in section 1.21 (the Fe(CO)\textsubscript{3} moiety is bonded to a ring containing only two double bonds) and probably precedes by a series of degenerate Cope rearrangements as occurs in the parent molecule, bullvalene (XXII).

Further examples of photolytic reactions are given in later parts of this section.

2.23 Other Methods

A fairly recent method, ligand exchange, seems to hold promise for future synthetic work. In this process the desired polyolefin ligand displaces another which is already present in a pre-formed complex (equation 2-1).

\[
\text{R}_1\text{M(CO)}_3 + \text{R}_2 \rightarrow \text{R}_2\text{M(CO)}_3 + \text{R}_1
\]

The displacement of cycloocta-1,5-diene from its ruthenium tricarbonyl complex by cycloheptatriene is one example as is the displacement of cycloheptatriene itself from the complex C\textsubscript{7}H\textsubscript{8}Fe(CO)\textsubscript{2} by COT.\textsuperscript{1}
Side reactions can occur with this method. For example in the reaction of benzylideneacetone with cycloocta-1,5-diene ruthenium tricarbonyl displacement of carbon monoxide occurs with the concomitant formation of a hydride bridge between two ruthenium atoms.\(^3\)

Benzylideneacetone iron tricarbonyl, BDAFe(CO)\(_3\), (XXIII), is a recent reagent for the synthesis of complexes by ligand exchange. It holds special potential for the preparation of complexes of unstable valence tautomers. Thus whereas the equilibrium 2-2 favours the bicyclic compound (XXIV), reaction of the equilibrium mixture with BDAFe(CO)\(_3\) gives solely the complex (XXVI) derived from the tricyclic compound (XXV).

\[
\begin{align*}
\text{C}_6\text{H}_5 - \text{CH} & \equiv \text{CH} \text{CH}_3 \\
\text{(OC)}_3\text{Fe} & \equiv \text{O} \\
(\text{XXIII})
\end{align*}
\]

\[
\begin{align*}
\text{(XXIV)} & \quad \text{Keq} = 0.025 \ (45^\circ) \\
\quad \text{2-2} & \quad \text{BDAFe(CO)}_3 \\
(\text{XXV})
\end{align*}
\]

The pure tautomer (XXV) can be obtained by the reaction of (XXVI) with cerium nitrate at low temperature.

In contrast the reaction of the equilibrium mixture with Fe\(_2\)(CO)\(_9\) (thermally) or Fe(CO)\(_5\) (photochemically) gave only a very small yield of (XXVI) as well as other complexes.\(^3\)
The stabilisation conferred on highly reactive organic molecules by complexation with metal carbonyls has been used in attempts to generate such molecules; for example norbornadienone\textsuperscript{34} and pentalene,\textsuperscript{35} which are at present unknown in the free state. It is a potentially valuable method where few others are available.

2.3 Rearrangements and Isomerisations

Many of the organic molecules from which complexes are synthesised are prone to rearrangement thermally or photo-lytically either as the free organic ligand or when complexed to metal carbonyl groups. As mentioned previously complexation may stabilise one particular molecule in a rearrangement or isomerisation pathway.

The formation of conjugated polyolefins from their non-conjugated isomers is one of the earliest known examples. In some cases the free isomer is isolated and in others the metal carbonyl polyolefin complex is obtained.

Thus Armet and Pettit\textsuperscript{36} found that heating cycloocta-1,5-diene with catalytic amounts of Fe(CO)\textsubscript{5} gave free cycloocta-1,3-diene whereas with 1,4 cyclohexadiene the iron tricarbonyl complex of the 1,3 isomer was isolated.

The results of such thermal reactions can be contrasted with observations of Gustorf and Koerner\textsuperscript{37} who found that photolysis of 1,3 or 1,5 cyclooctadiene with Fe(CO)\textsubscript{5} gave the iron tricarbonyl complex of the starting isomer but that the 1,3 complex was less stable than that from cycloocta-1,5-diene (in contrast with the free polyolefins). This instability was thought to be due to the conformational strain resulting from the forcing of the conjugated double bonds into one plane by
coordination.

In reactions of ruthenium carbonyl with certain polyolefins hydride abstraction is known to occur. For example in the reaction with cycloheptatriene the main product isolated is a fluxional molecule (XXVII) in which a hydride ion has been transferred from one cycloheptatriene ring to another (equation 2-3).\(^{31}\)

\[
\begin{align*}
\text{heptane} & \quad \text{Ru}_3(\text{CO})_{12} \\
& \quad \text{Ru}_3(\text{CO})_6(\text{C}_7\text{H}_7)(\text{C}_7\text{H}_9) \quad 62\% \quad 2-3 \\
(\text{XXVII})
\end{align*}
\]

In some cases the complexation reaction itself causes structural change. Thiophene on reaction with iron pentacarbonyl or triiron dodecacarbonyl gives the complex (XXVIII) by elimination of sulphur.\(^{38}\)

\[
\begin{align*}
\text{S} & \quad + \quad \text{Fe}(\text{CO})_5 \\
& \quad \text{or} \quad \text{Fe}_3(\text{CO})_{12} \\
& \quad \Delta \\
& \quad \text{Fe}(\text{CO})_3 \\
\end{align*}
\]

The same product has also been obtained from acetylene and iron carbonyls.\(^{39,40}\)

Sometimes rearrangement is quite severe and products totally unrelated to the original polyolefin are formed. Reaction of Ru\(_3\)(CO)\(_{12}\) with various cyclooctatetraenes yields besides the normal cyclooctatetraene complexes (such as (XV)-
(XVII))$^{6,12}$ a complex Ru$_3$(CO)$_8$(C$_8$H$_6$) (XXIX)$^{41}$ derived from the unstable pentalene molecule. Unlike a similar iron complex, (XXIX) is fluxional.

\[
\begin{align*}
\text{(XXIX)} & \\
& \text{[Diagram]} \\
\end{align*}
\]

2.4 Application to the Benzocyclooctatetraene Series

As mentioned in section 1.4 the benzocyclooctatetraene diiron complex (VIII) cannot be formed from the monoiron complex and excess iron carbonyl. Thus reaction of (VII) with Fe$_3$(CO)$_{12}$ in refluxing benzene gave the parent hydrocarbon BCOT and no complexes. In an attempt to form a complex with a heteronuclear metal-metal bond a rather novel approach which does not seem to have been used before was adopted. Reaction of either Fe(CO)$_5$ or Fe$_3$(CO)$_{12}$ with Ru$_3$(CO)$_{12}$ yielded the mixed metal carbonyls Fe$_2$Ru(CO)$_{12}$, FeRu$_2$(CO)$_{12}$ and H$_2$FeRu$_3$(CO)$_{13}$, all easily separable by thin layer chromatography.

Thermal reaction of a mixture of these heteronuclear carbonyls with BCOT gave mononuclear complexes (VII) and (XXXII) and a band containing BCOTFeRu(CO)$_6$ (XXX), BCOTRu$_2$(CO)$_6$ (XXXI) and BCOTFe$_2$(CO)$_6$ (VIII) all identified by their mass spectra (Scheme 5). By repeated thin layer chromatography separation of (XXX) and (XXXI) from (VIII) could be achieved but separation of (XXX) and (XXXI) from each other was not obtained. Hence the detection of whether one or both of the
isomers (XXXa or XXXb) is present is likely to be even more
difficult. The only method capable of achieving the separation
required seems to be high pressure liquid chromatography.
However as only microgram quantities can be conveniently
processed by this means (with the facilities available) this
method has not been attempted since Mössbauer spectra in the
cells used required a minimum of about 10 milligrams of compound.

Scheme 5 - Reaction of BCOT with a Mixture of Heteronuclear
Carbonyls (consisting mainly of Fe₂Ru(CO)₁₂)

In all the synthetic sequences with the benzocyclo-
octatetraene system it was assumed that the ring system was
stable under the thermal conditions employed and that no
peculiar rearrangements occurred. This was thought to be a
reasonable assumption because of the stability conferred by
the presence of the benzene ring and the fact that the less
stable cyclooctatetraene remains essentially intact under
the same conditions (but see the formation of the pentalene complex Ru$_3$(CO)$_8$(C$_8$H$_6$) (XXIX), from COT). On this basis the above structures were assigned to the complexes (XXX-XXXII). Because of the failure to obtain the diiron complex (VIII) from (VII) and Fe$_3$(CO)$_{12}$ it was thought unlikely that a heteronuclear complex could be prepared by the same means, using Ru$_3$(CO)$_{12}$ instead of Fe$_3$(CO)$_{12}$. However the observation of (a) Abel and Moorhouse that Ru$_3$(CO)$_{12}$ reacts thermally with COTFe(CO)$_3$ to give (XXXIII), and (b) COTFe(CO)$_3$ and Fe(CO)$_5$ react photolytically, (scheme 6), prompted further investigation.

**Scheme 6 - Reactions of COTFe(CO)$_3$ with Ruthenium & Iron Carbonyls**

COTFe(CO)$_3$ + Ru$_3$(CO)$_{12}$ $\xrightarrow{\text{xylene}}$ COTRuFe(CO)$_5$ (XXXIII)

COTFe(CO)$_3$ + Fe(CO)$_5$ $\xrightarrow{\text{hv}}$ COT[Fe(CO)$_3$]$_2$ (III)

In a preliminary experiment a mixture of COTFe(CO)$_3$ and Ru$_3$(CO)$_{12}$ in benzene was photolysed under nitrogen. Only a trace amount of material other than reactants was obtained on work-up but in view of the low solubility of Ru$_3$(CO)$_{12}$ in benzene this was not unexpected. The thermal reaction of BCOTFe(CO)$_3$ with Ru$_3$(CO)$_{12}$ in benzene was more successful. From the reaction mixture thin layer chromatography yielded several bands the slowest of which obviously consisted of several components. Mass spectral analysis showed that the diruthenium complex (XXXI) and the mixed iron-ruthenium complex (XXXa or XXXb) were the main constituents of this band. Because of the lack of success in the separation of
these components previously this line of attack was not pursued.

The other main line of synthetic work was directed towards the synthesis of a substituted diiron complex of the form (XXXIVa) or (XXXIVb).

![Diagram](image)

Stucki and Whitlock\textsuperscript{13} claimed to have prepared BCOTFe\textsubscript{2}(CO)\textsubscript{5}(P\textsubscript{φ3}) ((XXXIVa), L = P\textsubscript{φ3}) from BCOTFe\textsubscript{2}(CO)\textsubscript{6} and triphenylphosphine in cyclohexane at 100°.\textsuperscript{*} The position of substitution on the iron atom B was deduced from the P-H coupling observed for H-5 and H-6 but not for H-3 and H-8.

In the author's work reaction of BCOTFe\textsubscript{2}(CO)\textsubscript{6} with P\textsubscript{φ3} in refluxing benzene gave BCOT and a compound tentatively identified from its mass spectrum as Fe(CO)\textsubscript{4}P\textsubscript{φ3}. Similarly reaction of BCOTFe(CO)\textsubscript{3} with excess P\textsubscript{φ3} gave BCOT and Fe(CO)\textsubscript{3}(P\textsubscript{φ3})\textsubscript{2}. This displacement of the parent polyolefin from its complex by P\textsubscript{φ3} is not unknown. Thus Manuel and Stone\textsuperscript{1} obtained Fe(CO)\textsubscript{3}(P\textsubscript{φ3})\textsubscript{2} from the reaction between COTFe(CO)\textsubscript{3} and P\textsubscript{φ3}, while Gustorff and Hogan\textsuperscript{37} in reaction of P\textsubscript{φ3} with cycloocta-1,5-diene iron tricarbonyl and cycloocta-1,5-diene bis (iron tetracarbonyl), obtained Fe(CO)\textsubscript{3}(P\textsubscript{φ3})\textsubscript{2} and Fe(CO)\textsubscript{4}P\textsubscript{φ3} respectively.

\textsuperscript{*} whether cyclohexane was used or as seems more likely, methylcyclohexane, is not clear.
In comparison, reaction of \( \text{COTFe(CO)}_3 \) with either triphenylstibine or triphenylarsine displaces a CO group but not the polyolefin\(^1\) (equation 2-4).

\[
\text{COTFe(CO)}_3 + M\Phi_3 \rightarrow \text{COTFe(CO)}_2 M\Phi_3
\]

Thus it seems quite possible that \( \text{BCOTFe}_2(\text{CO})_6 \) and \( M\Phi_3 \) would give \( \text{BCOTFe}_2(\text{CO})_5 M\Phi_3 \) (\( M = \text{Sb, As} \)).

2.5 Structural Types and Structure Determination

The metal carbonyl complexes of cyclic polyolefins can be conveniently grouped into three classes:

(a) complexes containing only one metal atom

(b) complexes containing more than one metal atom but with no metal-metal bonds present

(c) complexes containing more than one metal atom and having metal-metal bonds.

Complexes of class (a) present comparatively little difficulty in the determination of their structures, the main problem centres around the structure of the complexed polyolefin - whether it has rearranged or not in the process of forming the complex. The cases of complexes from equilibrium tautomers (section 2.23) and the isomerisation of certain polyolefins (section 2.3) are two examples. The use of nuclear magnetic resonance and ultraviolet spectroscopy is fairly definitive in such work. Mössbauer spectroscopy is useful for complexes of Mössbauer-active nucleides in determining whether a 1,3, 1,4 or 1,5 diene is bound to a metal atom as these different ways of bonding all alter the stereochemistry about the metal atom and hence affect the
quadrupole splittings noticeably.

Mononuclear complexes of iron containing one to four carbon monoxide groups\(^1,45,46\) bound to the metal atom are known although tricarbonyl or tetracarbonyl species are more common. The latter are often unstable and decompose to the tricarbonyl compounds. Mass spectrum analysis provides an excellent means of determining the number of carbon monoxide groups present as successive loss of all CO's is usually observed.\(^47\)

The determination of the structure of complexes in classes (b) and (c) is much more involved. The more convenient spectroscopic methods (nmr, I.R., U.V. and Mössbauer) are often not adequate for an unambiguous structural assignment. Bridging carbon monoxide groups may be detected by infra-red spectroscopy (\(\nu_{\mathrm{CO}}\) (bridging)\(~1850-1700\) cm\(^{-1}\), \(\nu_{\mathrm{CO}}\) (terminal) \(~2125-1900\) cm\(^{-1}\))\(^48\) but the stretching frequencies of the differently bound carbon monoxide ligands does vary considerably and the two sometimes overlap.

Undoubtedly the definitive method in this area is X-ray diffraction analysis. This is virtually the only reliable means of detecting a metal-metal bond, short internuclear distances indicating the presence of such a bond\(^*\) and large distances indicating its absence (intermediate values are more difficult to interpret). For instance, the photolysis of the cyclobutadiene complex (XXXV) affords the diiron complex (XXXVI) which has an extremely short iron-iron bond distance of 2.177 Angstroms (Table 2-I). From this it has

\(^*\) Providing the complex is diamagnetic; this is true of all the complexes in this work.
been concluded that a triple bond exists between the two iron atoms. Examples of compounds with very different iron-iron distances are given in table 2-I.

\[
\text{Fe(Fe)}_3 \text{hV} \xrightarrow{\text{hexane}} \text{Fe Fe}
\]

Table 2-I

<table>
<thead>
<tr>
<th>Complex</th>
<th>Fe-Fe Distance Å</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(XXXVI)</td>
<td>2.177</td>
<td>Fe-Fe triple bond</td>
<td>49</td>
</tr>
<tr>
<td>(Bu+C≡CBu+)_2Fe_2(CO)_4</td>
<td>2.215</td>
<td>Fe-Fe double bond</td>
<td>50</td>
</tr>
<tr>
<td>Fe_2(CO)_9</td>
<td>2.523</td>
<td>Fe-Fe single bond</td>
<td>51</td>
</tr>
<tr>
<td>cycloheptatriene diiron</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hexacarbonyl (XXXVIII)</td>
<td>2.866</td>
<td>Fe-Fe single bond</td>
<td>52</td>
</tr>
<tr>
<td>COT[Fe(CO)_3]_2 (III)</td>
<td>5.15*</td>
<td>no Fe-Fe bond</td>
<td>15</td>
</tr>
</tbody>
</table>

* Calculated from data in reference.

Besides giving information indicating the presence of metal-metal bonds X-ray diffraction enables conclusions to be reached about the nature of metal-ring bonding. The distances of the iron atoms from the ring in COTFe_2(CO)_5 (XIIb) enabled Fleischer et al. to conclude that two three-centre bonds each
involving both iron atoms and a ring carbon atom were present and that each iron atom was bonded to three of the remaining six ring carbon atoms in a π-allylic fashion. Similar deductions were made for the ruthenium pentalene complex (XXIX). 41

However there does seem to be some correlation between $^{57}$Fe Mössbauer quadrupole splittings and the presence or absence of metal-metal bonding (presumably because of the effect of the latter on the stereochemistry of the iron atom). Thus the diiron complex (III) shows a quadrupole splitting similar to that of 1,3 diene iron tricarbonyl complexes such as (I), whereas the quadrupole splitting of (VIII) is markedly lower. This will be further discussed in section 4.

Table 2-II presents a summary of structures proposed and found for a variety of complexes.

**Additional Structures Mentioned in Table 2-II**

![Diagram](image_url)
Table 2-II
Summary of Various Structures Found in Cyclic Polyolefin Complexes of Iron and Ruthenium

<table>
<thead>
<tr>
<th>Complex</th>
<th>Structure</th>
<th>Structural Data&lt;sup&gt;(a)&lt;/sup&gt;</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>COTFe(CO)&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;(b)&lt;/sup&gt;</td>
<td>I</td>
<td>X-ray diffraction; f.</td>
<td>53</td>
</tr>
<tr>
<td>COTRu(CO)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>I, Ru analogue</td>
<td>X-ray diffraction; f.</td>
<td>54</td>
</tr>
<tr>
<td>BiCOTFe(CO)&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;(c)&lt;/sup&gt;</td>
<td>XIII</td>
<td>nmr; n.f.</td>
<td>7</td>
</tr>
<tr>
<td>COT[Fe(CO)&lt;sub&gt;3&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>III</td>
<td>X-ray diffraction; n.f.</td>
<td>15</td>
</tr>
<tr>
<td>COT[Ru(CO)&lt;sub&gt;3&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>III, Ru analogue</td>
<td>nmr; n.f.</td>
<td>6</td>
</tr>
<tr>
<td>COTFe&lt;sub&gt;2&lt;/sub&gt;(CO)&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;(b)&lt;/sup&gt;</td>
<td>II</td>
<td>nmr; f.</td>
<td>4,10</td>
</tr>
<tr>
<td>COTRu&lt;sub&gt;2&lt;/sub&gt;(CO)&lt;sub&gt;6&lt;/sub&gt;</td>
<td>II, Ru analogue</td>
<td>X-ray diffraction; f.</td>
<td>10</td>
</tr>
<tr>
<td>cis-COT[Fe(CO)&lt;sub&gt;3&lt;/sub&gt;]&lt;sub&gt;2&lt;/sub&gt;</td>
<td>XXXVII</td>
<td>nmr &amp; Mössbauer</td>
<td>4</td>
</tr>
<tr>
<td>CHTFe&lt;sub&gt;2&lt;/sub&gt;(CO)&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;(d)&lt;/sup&gt;</td>
<td>XXXVIII</td>
<td>X-ray diffraction; n.f.</td>
<td>52</td>
</tr>
<tr>
<td>COTEPOXFe&lt;sub&gt;2&lt;/sub&gt;(CO)&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;(e)&lt;/sup&gt;</td>
<td>XXXIX</td>
<td>nmr; n.f.</td>
<td>55</td>
</tr>
<tr>
<td>COTFe&lt;sub&gt;2&lt;/sub&gt;(CO)&lt;sub&gt;5&lt;/sub&gt;</td>
<td>XIIb</td>
<td>X-ray diffraction; f.</td>
<td>5</td>
</tr>
<tr>
<td>TMCOTFe&lt;sub&gt;2&lt;/sub&gt;(CO)&lt;sub&gt;5&lt;/sub&gt;</td>
<td>XIIa</td>
<td>X-ray diffraction; f.</td>
<td>56</td>
</tr>
<tr>
<td>COTRu&lt;sub&gt;2&lt;/sub&gt;(CO)&lt;sub&gt;5&lt;/sub&gt;</td>
<td>XIIb, Ru analogue</td>
<td>nmr; f.</td>
<td>12</td>
</tr>
<tr>
<td>COTRu&lt;sub&gt;3&lt;/sub&gt;(CO)&lt;sub&gt;4&lt;/sub&gt;</td>
<td>XVIII</td>
<td>X-ray diffraction; f.</td>
<td>20</td>
</tr>
</tbody>
</table>

Notes: (a) f. = fluxional; n.f. = non-fluxional.

(b) Analogous complexes are known for 1,3,5 cyclooctatriene<sup>3,57,58</sup> and 1,3,5 cyclooctatrienone.<sup>3</sup>

(c) BICOT = 1,3,5,7 tetramethylbicyclo[4.2.0]octa-2,4,7-triene; 1,3,5 cyclooctatriene analogue known.

(d) CHT = cycloheptatriene; COT analogue unknown.

(e) COTEPOX = cyclooctatetraene epoxide.
3. Theory

3.1 General Theory of the Mössbauer Effect

In view of the large number of literature sources available giving excellent accounts of the Mössbauer effect it would be inappropriate and superfluous to recapitulate the basic theory. Instead only those aspects which are relevant to the present work will be discussed here.

A Mössbauer absorption spectrum is characterised by the following parameters:

(a) Resonance effect magnitude
(b) Linewidth
(c) Quadrupole splitting
(d) Isomer shift
(e) Magnetic hyperfine splitting
(f) Temperature dependence of factors (a) - (e)

These will all be discussed in the following sections with principal reference to (a), (b) and (c).

3.2 Resonance Effect Magnitude

The fractional resonance effect $\varepsilon(v)$ at velocity $v$ is defined by

$$\varepsilon(v) = \frac{N(\infty) - N(v)}{N(\infty)}$$

where $N(\infty) =$ counts/channel off resonance (i.e. on baseline)

$N(v) =$ counts/channel at velocity $v$ near resonance.

(Note that the presence of a constant isomer shift $u$ between the source and absorber does not cause any loss of generality, as $v$ only then needs to be changed to $v + u$.)
In this definition it is assumed that the count rates off resonance and near resonance are only due to recoil and recoilless Mössbauer radiation. If this condition does not hold then a correction for counted background must be applied:

$$\varepsilon(v) = \frac{N(\infty) - N(v)}{N(\infty) - N(b)}$$  \hspace{1cm} 3-2

where $N(b) =$ background count rate, which is independent of velocity.

In the presence of background the maximum true resonance effect magnitude (which will henceforth be termed simply the true resonance effect) is given by:

$$\varepsilon(0) = \frac{N(\infty) - N(0)}{N(\infty) - N(b)}$$  \hspace{1cm} 3-3a

where $N(0) =$ count rate at resonance.

When no background correction is applied an apparent resonance effect $\varepsilon'(0)$ is obtained:

$$\varepsilon'(0) = \frac{N(\infty) - N(0)}{N(\infty)}$$  \hspace{1cm} 3-3b

This is the experimentally-measured quantity that is always referred to in this work. Obviously $\varepsilon(0) \geq \varepsilon'(0)$.

The corresponding expression for $\varepsilon'(v)$ can also be written as:

$$\varepsilon'(v) = \beta f \left[ 1 - \int_{0}^{\infty} e^{-\sigma(E)n} W_{e}(E) dE \right]$$  \hspace{1cm} 3-4

where

$$\sigma(E) = \frac{\Gamma^2}{4} \cdot \frac{\sigma_{e} f'}{(E - E_{0})^2 + \frac{\Gamma^2}{4}}$$  \hspace{1cm} 3-5

is the effective resonance absorption cross section,
and

\[ W_E(E) = \frac{\Gamma}{2\pi} \frac{1}{(E + E_0v/c - E_0)^2 + \Gamma^2/4} \]  

is the normalised energy distribution of a source assumed to be non-absorbing for resonance radiation.

\[ \beta = \frac{N(14.4)}{N(\infty)} = \frac{N(\infty) - N(b)}{N(\infty)} \]

is the fraction of Mössbauer radiation in the total radiation that lies within the window of the single-channel analyser.

Equation 3-4 can only be solved in the general case by numerical integration, but for \( \nu = 0 \) Mössbauer and Wiedemann\(^6^4\) showed that:

\[ \varepsilon'(0) = \beta f \left[ 1 - e^{-t_A/2} I_0(t_A/2) \right] \]

where \( t_A = n\sigma_f' \) is the absorber thickness,

\[ I_0(x) = J_0(ix) \]

is the zero-order Bessel function of imaginary argument.

The importance of equation 3-8 is that it allows \( \varepsilon'(0) \) to be computed as a function of the absorber thickness \( t_A \); this capability, together with a knowledge of the dependence of linewidth on \( t_A \) is quite useful and will be referred to again in Section 3.91. Equation 3-8 is directly applicable to the case of the spectrum of an absorber at two different temperatures, the spectra being taken under otherwise identical conditions (constant \( \beta \)):

Equations 3-3 and 3-7 give

\[ \varepsilon(0) = \frac{1}{\beta} \varepsilon'(0) \]
Hence for constant $\beta$:

$$\frac{\epsilon'(0)_{T_1}}{\epsilon(0)_{T_2}} = \frac{\epsilon'(0)_{T_1}}{\epsilon'(0)_{T_2}} = \frac{1 - e^{-t_{A_1}/2}}{I_0(t_{A_1}/2)}$$

For sufficiently small $t_A (<<1)$

$$I_0(t_{A/2}) \approx 1$$

$$e^{-t_A/2} \approx 1 - t_A/2$$

Hence

$$\frac{\epsilon'(0)_{T_1}}{\epsilon'(0)_{T_2}} = \frac{t_{A_1}}{t_{A_2}} = \frac{c\epsilon f'_{1}}{c\epsilon f'_{2}} = \frac{f'_{1}}{f'_{2}}$$

where $c = n_0 \sigma_0$.

The extent to which the approximations in equations 3-9 and 3-10 are valid will be considered in Section 3.91.

Equation 3-11 shows that to compare the recoil-free fractions at two different temperatures for a thin absorber only the ratio of the $\epsilon'(0)$ values need be known.

3.21 The Background Contribution $N(b)$

Although absolute values of the recoil-free fraction $f'$ were not being sought a knowledge of the contributing causes of background counting was necessary to enable maximum $\epsilon'(0)$ values to be obtained. This in turn enabled greater accuracy in the calculation of the peak parameters, especially for frozen solutions.

The energy distribution of the source radiation and the nature and thickness of the absorbing material determine the intensity of the radiation transmitted through the absorber. That part of this transmitted radiation that is not due to the Mössbauer transition and that falls within
the window of the single-channel analyser constitutes the background count rate.

This is due to:

(a) High energy radiation losing part of its energy within the detector and thereby falling within the window;
(b) X-rays due to the source falling within the window;
(c) High energy gamma radiation and X-rays being degraded by the absorber so that on reaching the detector they fall within the window.

Obviously, control of the single-channel analyser window setting and the ability of the detector to resolve adjacent peaks are of prime importance in minimising \( N(b) \). However, because these are variable factors, background contributions to the total count rate varied between experiments. The experimental geometry and the degree of collimation also were critical and since the low temperature and room temperature geometries were not identical direct comparison of \( \epsilon'(0) \) values at different temperatures was not strictly valid.

Various methods for measuring the background count rate have been described by Housley \(^65\) and others. \(^66,67\)

3.22 Asymmetry in Peak Intensities

Absorption peak intensities in a quadrupole-split spectrum may be different for the following reasons:

(a) Because peak intensities are a function of the angle \( \theta \) between the crystal axis and the source-detector axis, partial orientation of crystallites within a powdered sample can have the effect of preferentially increasing the intensity of one peak relative to that of the other.
For a single crystal of an iron compound the ratio of the peak intensities is

\[ P_1 = \frac{I(3/2+1/2)}{I(1/2+1/2)} = \frac{I_\pi}{I_\sigma} = \frac{3(1 + \cos^2 \theta)}{5 - 3\cos^2 \theta} \quad 3-12 \]

For a completely random powdered sample the expression in \( P_1 \) must be averaged over all possible values of \( \theta \):

\[ P_2 = \frac{\int_0^\pi (1 + \cos^2 \theta) \sin \theta d\theta}{\int_0^\pi (5/3 - \cos^2 \theta) \sin \theta d\theta} = 1 \quad 3-13 \]

Now if there is incomplete random orientation then the averaging process cannot be fully applied and the ratio of peak intensities is no longer unity.

(b) Anisotropy of the recoil-free fraction of the absorber. \(^{68}\)

Equation 3-13 was obtained on the assumption that the \( f' \) factor is angular-independent. In certain cases this is not true and we have

\[ f' = f'(\theta) \quad 3-14 \]

Application of this to equation 3-13 gives

\[ P_3 = \frac{\int_0^\pi f'(\theta)(1 + \cos^2 \theta) \sin \theta d\theta}{\int_0^\pi f'(\theta)(5/3 - \cos^2 \theta) \sin \theta d\theta} \quad 3-15 \]

and in the general case \( P_3 \neq 1 \).

Differentiation between cases (a) and (b) can be made by rotating the sample with respect to the source-detector axis. This will change \( P_1 \) (since the net angle in equation
3-12 will now be different) but not $P_3$ (functional dependence of $f'$ is invariant with angle). Thus if no change is observed in the $P$ value upon rotating the sample then the peak asymmetry is due only to the $f'$ anisotropy. If a change in the relative intensities is observed then certainly there is preferential orientation but there could also be a simultaneous $f'$ anisotropy in the sample. In this case further experimentation would be needed.

3.3 Linewidth

Experimentally one aims to obtain a linewidth which is the sum of the source and absorber linewidths, $\Gamma_s$ and $\Gamma_a$:

$$\Gamma_{\text{exp}} = \Gamma_s + \Gamma_a$$  \hspace{1cm} 3-16

Since $\Gamma_s$ is constant for a given source, direct comparisons of $\Gamma_a$ values can therefore be made. The lower limit $\Gamma_{\text{nat}}$ for both $\Gamma_s$ and $\Gamma_a$ is determined from the lifetime of the 14.4 Kev level of $^{57}$Fe:

$$\Gamma_{\text{nat}} = \frac{\hbar}{2\pi \tau} = \frac{\hbar}{2\pi} \frac{1}{t_{1/2} \log_e 2}$$  \hspace{1cm} 3-17

where $\tau$ is the average lifetime of the excited state.

However, there are many factors which cause the observed linewidth to be greater than that given by equation 3-16. These can be classified as "real" (properties of the material) and "experimental" (broadening caused by the equipment). As the identification and separation of all of these factors constituted a considerable part of this work a detailed discussion is given in Sections 3.8 and 3.9.
3.4 Quadrupole Splitting

Quadrupole splitting of spectral lines arises from the interaction of the nuclear quadrupole moment, $Q$, with an electric field gradient (e.f.g.) at the nucleus. For iron the ground state has $Q = 0$ and so only the 14.4 KeV energy level is split. Transitions from the single ground state level to each of the split excited state levels gives the two absorptions observed.

The electric field gradient is the gradient of the electric field $E$ at the nucleus and so is a tensor quantity with nine components. However, by suitable choice of axes the e.f.g. can be diagonalised and expressed in terms of three components along the $x,y,z$ axes

\[
\begin{align*}
V_{xx} &= \frac{\partial^2 V}{\partial x^2} \\
V_{yy} &= \frac{\partial^2 V}{\partial y^2} \\
V_{zz} &= \frac{\partial^2 V}{\partial z^2} = eq
\end{align*}
\]

These are related by $V_{xx} + V_{yy} + V_{zz} = 0$ 3-19a

The axes are further chosen so that

\[
|V_{zz}| \gg |V_{yy}| \gg |V_{xx}| \quad \text{(but not all equal)} \quad 3-19b
\]

The e.f.g. is commonly expressed in terms of $V_{zz}$ and an asymmetry parameter $\eta$ where

\[
\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad 3-20
\]

From equations 3-19 and 3-20, $0 \leq \eta \leq 1$.

The shifts in energy of the split levels for $^{57}$Fe are given by:-
\[
I_z = \frac{3}{2} \Delta E_1 = \frac{+\eta^2 qQ}{4} (1 + \frac{\eta^2}{3})^{\frac{1}{2}}
\]
\[
I_z = \frac{1}{2} \Delta E_2 = \frac{-\eta^2 qQ}{4} (1 + \frac{\eta^2}{3})^{\frac{1}{2}}
\]

where \(Q\) is the excited-state nuclear quadrupole moment. Since \(Q\) is positive the relative ordering of the \(I_z = \frac{3}{2}\) and \(I_z = \frac{1}{2}\) levels is determined by the sign of \(\eta\). The diagram below shows the energy levels for the cases \(\eta > 0\).

3.1 ENERGY LEVELS FOR \(^{57}\text{Fe}\) NUCLEUS IN AN ASYMMETRIC ELECTRIC FIELD WITH \(\eta > 0\)

The actual value of the quadrupole splittings \(\Delta\) is given by the separation of these levels:

\[
\Delta = \left| \frac{\eta^2 qQ}{4} (1 + \frac{\eta^2}{3})^{\frac{1}{2}} \right|
\]

Simple analysis of powdered (polycrystalline) spectra does not enable the value of \(\eta\) or \(\eta\) to be determined (the sign of \(\eta\) is of course undetermined by the expression for \(\Delta\)).

Since \(0 < \eta^2 < 1\), values of \(\Delta\) which differ by more than
16% cannot be solely attributed to changes in the asymmetry parameter.

The electric field gradients determining the size of $\Delta$ depend on the oxidation state of the central metal atom, the nature and distribution of the ligands about it, solvent interactions (in some cases the solvent acting as a ligand) or lattice contributions. Only the second contribution is likely to be of any significance for the compounds studied in this work although the effects of the solvent and the lattice were not ruled out entirely (compare results for solids, frozen cyclohexane and frozen n-butylbenzene solutions). A detailed discussion of those factors which cause a non-cubic electric field at the nucleus and hence give rise to an e.f.g. is beyond the scope of this work and can be found in several literature sources.\textsuperscript{59,69}

3.5 Isomer Shift $\delta$

The isomer shift is directly proportional to the difference between the electron densities at the nuclei of the absorber and the source. It is given by:

$$\delta = E_a - E_s = \frac{2}{5}\pi e^2 Z \left\{ r_e^2 - r_g^2 \right\} \left( |\psi(0)|^2_a - |\psi(0)|^2_s \right)$$

where $r_e$ and $r_g$ are the nuclear radii of the excited and ground states; $|\psi(0)|^2_a$ and $|\psi(0)|^2_s$ are the electron densities at the nucleus in the absorber and source respectively.

The electron densities are determined by relativistic effects and screening of electrons as well as orbital occupancy; s-electron density is generally the most important in their calculation.
The isomer shift is particularly useful for ionic compounds of iron where the electron density is sensitive to the oxidation state of the iron. For covalent compounds where molecular orbital interactions determine the electron densities, \( \delta \) is of much less significance due to its small variation and there is far greater difficulty in direct interpretation of its magnitude in terms of bonding.

Equation 3-23 expresses \( \delta \) relative to zero velocity (the latter occurs when source and absorber are in identical environments and hence \( \delta = 0 \)); it is more convenient to express \( \delta \) relative to a reference absorber, usually iron metal. Hence, if

\[
\begin{align*}
\delta_1 &= E_{Fe} - E_s \quad \text{for iron metal} \\
\delta_2 &= E_a - E_s \quad \text{for arbitrary absorber}
\end{align*}
\]

then the quoted isomer shift is

\[
\delta = \delta_2 - \delta_1 = E_a - E_{Fe}
\]

This has been the procedure followed in this work with iron metal as reference.

3.6 Magnetic Hyperfine Interaction

Interaction of the magnetic moment \( \mu \) of a nucleus with a magnetic field \( H \) changes the energy of a state by a value \( W \) given by

\[
W = - (\mu \cdot H) = - (\mu / I) mH
\]

where \( I \) is the nuclear spin and \( m \) is the magnetic quantum number which can acquire \( 2I + 1 \) values: \( I, I-1, \ldots, 0, \ldots, -I \).
The effect of the interaction is to completely remove the degeneracy of the energy levels for a given energy state. Thus in diagram 3-1 the ground state is now split \((m = +\frac{1}{2} \text{ and } m = -\frac{1}{2})\) and each of the excited state levels is split \((m = +\frac{3}{2}, m = +\frac{1}{2}, m = -\frac{1}{2}, m = -\frac{3}{2})\), to give a total of six sub-levels and eight possible transitions. However only six of these transitions are allowed by the selection rules for changes in \(m\).

Both quadrupole and magnetic hyperfine interactions can occur simultaneously; this is the most difficult situation to analyse in iron spectra. Fortunately, none of the compounds studied in this work exhibited magnetic behaviour making the analysis of the spectra much easier although losing potentially-useful information. For this reason it is not necessary to undertake a more detailed explanation of the magnetic hyperfine interaction.

3.7 Temperature Dependence of Parameters

All the parameters discussed are temperature dependent but in this work the dependence of the resonance effect magnitude and the linewidth on temperature were the most significant. The isomer shift undergoes a small second-order Doppler shift which is not important. The small changes in \(\Delta\) with temperature probably reflect variations in lattice contributions to the e.f.g.

Resonance effects increase markedly with decreasing temperature due to an increase in the recoil-free fraction. Apart from a proportional increase due to \(f'\), the increase in \(\epsilon(0)\) is also due to the greater effective thickness, \(t_A = n_o f'\), at lower temperatures.
The temperature dependence of $f'$ is a result of its strong relationship to nuclear vibration:

$$f' = \exp\left[-\langle x_y^2 \rangle / \chi^2 \right]$$

where $\langle x_y^2 \rangle$ is the mean square of the projection of the vibrational amplitude of the absorbing nucleus on the direction of motion of the gamma quantum,

and

$$\chi = \frac{hc}{2\pi E_y} = \frac{\lambda}{2\pi}$$

where $\lambda$ is the wavelength of the gamma quantum.

Various functional relationships of $f'$ with temperature have been determined for different crystal models.\(^{59}\)

The changes in linewidth which occurred with temperature were due to the absorber properties as the temperature of the source was kept constant. The properties of the absorber which cause the linewidth to be temperature dependent are amongst those that are discussed in the following sections.

### 3.8 Line Broadening

Linewidths as given by equation 3-16 are almost never observed, even under ideal experimental conditions. For a single absorption spectrum of a non-paramagnetic material the increased linewidth observed can be attributed almost solely to thickness effects. In paramagnetic materials relaxation phenomena occur which broaden lines. Diffusional line broadening becomes important for absorbers at high temperatures or for very viscous solutions (e.g. glycerol). Lack of resolution in a spectrum can also result in apparent line broadening. Before any investigation of any of these can be undertaken however, experimental contributions must either
be eliminated or allowed for. This is not always easy when the narrowest possible lines are desired.

The experimental causes of line broadening will be briefly discussed first, their elimination and estimation are considered more fully in the experimental work in Section 5.12.

3.81 Spectrometer Performance-Effect on Linewidth

The performance of a spectrometer can be measured not only by its velocity linearity and stability but also by the narrowness of the lines that can be obtained with a reference material.

The two performance criteria are intimately related, for the broadening of lines by a spectrometer arises mainly from a non-linear velocity/address correspondence with the multichannel analyser and from drift of the spectrometer with time. The first factor is heavily dependent on the quality of the transducer and the load it carries. All sources employed in this work were quite light and well below the weight-carrying capacity of the transducer (30 gm). Measurements of linewidths and peak positions of a standard iron foil sample were sufficient to enable an assessment of line broadening caused by the spectrometer. As it eventuated this contribution was small though reproducible and its absolute value was different at different velocity values.

3.82 Collimation

For an uncollimated point source the energy of a gamma quantum entering the detector window is distributed over the range \[ [v \cos \theta, v] \] where \( v \) = velocity of emitted gamma quantum along the source-detector axis and \( 2\theta \) = angle subtended at
the source by the detector window (diagram 3.2).

3.2 COLLIMATION OF POINT SOURCE

From diagram 3.2

\[ \cos \theta = \frac{L_D}{\sqrt{L_D^2 + (D/2)^2}} \]  

3-27

If a collimator of diameter \( C \) is placed at a distance \( L_C \) from the source then increased collimation is only obtained if \( \phi < \theta \), i.e. if

\[ C < \frac{D L_C}{L_D} \]  

3-28

The velocity range is now \([v \cos \phi, v]\) where

\[ \cos \theta < \cos \phi = \frac{L_C}{\sqrt{L_C^2 + (C/2)^2}} \]  

3-29

For practical purposes however the diameter \( S \) of the source must be taken into account: (diagram 3.3)
3.3 COLLIMATION OF FINITE DIAMETER SOURCE

\[
\theta = \text{maximum angle of accepted radiation}
\]

\[
\cos \theta = \frac{L_D}{\sqrt{L_D^2 + \left(\frac{D+S}{2}\right)^2}}
\]

A collimator only reduces \( \theta \) in this case if it is placed at a suitable distance \( L_C \) from the source. Thus three situations are possible:

(a) \( L_C < y = \frac{L_DS}{L+S} \)  

Increased collimation is obtained only if

\[
C < u = S - (D + S) \frac{L_C}{L_D}
\]

(b) \( L_C > y = \frac{L_DS}{D+S} \)  

Increased collimation is obtained only if

\[
C < t = (D + S) \frac{L_C}{L_D} - S
\]
(c) \( L_C = y = \frac{L_D S}{D+S} \)

No collimation possible.

In order to estimate the amount of broadening involved consider the application of equation 3-30 where there is no collimator; \( L_D = 20 \) cm, \( D = 3.4 \) cm, \( S = 0.8 \) cm were used; \( \cos \theta = 0.9945 \). Hence the velocity smearing is less than 1% in the most unfavourable case.

In practice it was found that changing collimators had little effect on linewidth although the resonance effect was increased by decreasing the collimator diameter.

Further discussion on collimation, with numerical values, is given in the experimental section.

3.83 Sample Uniformity and the Use of Correct Fitting Function

In every situation studied the assumption of uniform sample thickness was made. In such cases the Lorentzian fitting function used is adequate provided the sample is not too thick. The effect of non-uniformity on linewidths is difficult to assess. The accuracy of the linewidths obtained would certainly be less than for a uniform sample and the fitting of the experimental spectrum would be comparatively poorer (giving larger chi-square values) but whether the absolute values of the linewidths would be greater is impossible to predict.

In practice it was found that different solid absorbers of the same material gave approximately the same linewidth under otherwise identical conditions, hence the method used to prepare the solid absorbers gave a uniform sample. The variation in linewidths was greater for frozen solution
samples and showed no trend with the solute concentration.

3.84 Vibration

Unknown relative motion of the source and absorber can result in line broadening. This proved to be the most serious and difficult factor to eliminate amongst all the experimental causes of broadening. Moreover since the vibration appeared to be variable no allowance could be made for it with any conviction. The steps taken to eliminate vibration within the equipment are discussed in the experimental section.

3.9 Physical Properties of the Absorber Which Cause Line Broadening

Many factors can cause line broadening in the spectra of iron compounds. Several of these may occur simultaneously, making analysis of the broadening difficult. Fortunately most of these possible causes could be eliminated from consideration in this work either from prior knowledge or from observations of the spectra. Thus magnetic broadening due to relaxation effects\(^{70,71}\) or unresolved hyperfine fields\(^{72}\) was not likely to be present because the compounds studied were diamagnetic. This belief was confirmed by the absence of any hyperfine structure in the spectra even at low temperatures. Diffusional effects,\(^{73}\) which can result in either equal broadening of quadrupole-split lines (isotropic diffusion) or asymmetric broadening (anisotropic diffusion)\(^{74}\) were not of any significance at the relatively low temperatures of the experiments. A distribution of isomer shifts as observed in some iron alloys (e.g. stainless steel)\(^{67}\) or a distribution of electric field gradients as suggested for ferrous chloride glasses\(^{75}\) were thought unlikely in this study. A distribution in isomer
shifts only occurs when there is variation in the type and number of neighbours of the Mössbauer atom and is only appropriate to the situation where the Mössbauer atom is embedded in a matrix of other atoms, such as in an alloy.

A distribution of electric field gradients only occurs when the lattice contribution to the e.f.g. is significant. There was no a priori reason to suspect this for the compounds in this work and confirmation of the absence or insignificance of this factor was provided by the results obtained from the solid and frozen solution spectra.

The two factors which are relevant to this study are thickness effects and resolution.

3.91 Thickness Effects

A finite thickness $t_A$ of an absorber produces a broadening $h(t_A)\Gamma_{\text{nat}}$ so that for a single well resolved absorption the experimental linewidth is:

$$\Gamma_{\text{exp}} = \Gamma_s + \Gamma_a + h(t_A)\Gamma_{\text{nat}}$$

$h(t_A)$ is called the broadening function.

The evaluation of this function has received a great deal of attention and many good approximations to it have been proposed for absorbers which are not too thick. The general case of unequal source and absorber linewidths in an incompletely-resolved multiple-line spectrum is unfortunately the most difficult in which to give a good approximation for $h(t_A)$. The equations below are first applied to single absorptions and are then extended to well-resolved multiple absorptions.
For the case $\Gamma_s = \Gamma_a = \Gamma$ Bykov and Pham Zuy Hien showed that:

$$\Gamma_{\text{exp}} = \frac{K(t_A)}{1 - e^{-t_A/2} I_0(t_A/2)} \cdot \Gamma$$ 3-36

where $K(t_A) = t_A e^{-t_A/2} [I_0(t_A/2) + I_1(t_A/2)]$

and $I_1(x) =$ first order Bessel function of imaginary argument.

When $\Gamma = \Gamma_{\text{nat}}$ equation 3-36 can be brought to the form of equation 3-35 by setting:

$$h(t_A) = \frac{K(t_A)}{1 - e^{-t_A/2} I_0(t_A/2)} - 2$$ 3-37

$h(t_A)$ has in the limiting case $t_A \to 0$ the desired property $h(t_A) \to 0$. For $t_A \to \infty h(t_A) \to 2 \sqrt{t_A / \pi} - 2$.

Using numerical methods Visscher expressed the experimental linewidths as

$$\Gamma_{\text{exp}} = 2\Gamma h(t_A)$$ 3-38

where

$$h(t_A) = 1 + 0.135t_A \quad 0 \leq t_A \leq 5$$ 3-39a

$$h(t_A) = (1 + 0.145t_A - 0.0025t_A^2) \quad 4 \leq t_A \leq 10$$ 3-39b

Both the results of Bykov and Visscher agree with numerical results expressed graphically by Margulies and Ehrmann. The results of the latter are shown below, where $h(t_A)$ and $\epsilon(0)/\ell$ are shown as functions of the thickness $t_A$ of the absorber. Source thickness is assumed negligible.
For well-resolved multiple-peak spectra the above results can still be applied but the absorber thickness parameter has to be modified. Thus for an n-peak spectrum where the relative peak intensities are \( w_i \) (i = 1, ..., n) the effective thickness for the ith absorption is \( W_i t_A \). In the case of a quadrupole-split doublet, n = 2, and \( W_1 = 1/2 = W_2 \). Both the broadening and the resonance effect are less than for a single absorption (diagrams 3.4 and 3.5).

From diagram 3.5 the assumption that

\[
1 - e^{-t_A/2} I_0(t_A/2) = t_A/2 \quad \text{(equations 3.9 and 3.10)}
\]

made in Section 3.2 is seen to be a good approximation for \( t_A < 0.5 \).

When \( \Gamma_s \neq \Gamma_a \) the determination of \( h(t_A) \) is less rigorous and the approximations made in its derivation may not always be
valid. O'Connor gives

\[ h(t_A) = 0.27t_A \]  

so that

\[ \Gamma_{\text{exp}} = \Gamma_s + \Gamma_a + 0.27t_A\Gamma_{\text{nat}} \]

When absorptions are incompletely resolved the nature of the dependence of \( \Gamma_{\text{exp}} \) on \( t_A \) becomes more complicated.

### 3.92 Incompletely Resolved Absorptions

The presence of two different iron sites in a molecule can cause line broadening as a result of either the different isomer shifts or different quadrupole splittings due to each site. The resolution necessary to separate each peak is obscured by thickness effects as large thicknesses broaden each absorption causing the peaks to overlap considerably.

It was partially for this reason that frozen solution samples were studied, as the thickness of the sample could be altered by varying the concentration of the solute.

Bykov and Pham Zuy Hien showed that depending on the size of \( \Delta \) three different line shapes could occur for quadrupole split spectra:

(a) For small values of \( \Delta \) an apparent value absorption peak occurs with a minimum at \( v = \Delta/2 \).

(b) For an intermediate value of \( \Delta \) the absorption has a plateau shape.

(c) For larger values of \( \Delta \) the spectrum shows two minima with a separation \( \Delta_{\text{obs}} \). Even for an infinitely thin absorber the ratio \( \Delta_{\text{obs}}/\Delta \) only approaches unity for \( \Delta > 3\Gamma \).

Because the expressions given by Bykov were somewhat unwieldy, the program MOSFUN was written to calculate peak
shapes as a function of Δ for spectra consisting of two Lorentzian absorptions. This enabled the linewidth of an overlapped absorption of type (a) to be found relative to the linewidths of the individual peaks which were assumed to be equal.

Several methods for the reduction of linewidths and hence the improvement of resolution have recently become available. They are spectra convolution, the use of resonance filters and coincidence counting. The last method has the disadvantage of very long counting times although it is very efficient. Either of the first two methods could prove of great assistance in future work in resolving absorptions.
4. Results of Mössbauer Spectra

4.1 General

The spectra of both BCOTFe(CO)$_3$ and BCOTFe$_2$(CO)$_6$ were always apparent quadrupole doublets. No indication of resolution of the spectrum of the diiron complex into more than two peaks was ever observed, even for very thin samples. Consequently the examination of the linewidths of each peak in the apparent quadrupole-split spectrum of BCOTFe$_2$(CO)$_6$ was the only means by which the presence of non-equivalent iron sites in this compound could be shown. Both the relative linewidths of the peaks in the BCOTFe$_2$(CO)$_6$ spectrum and the broadening of each peak compared to the absorptions of BCOTFe(CO)$_3$ were considered relevant but for various reasons which will soon become apparent the first criterion proved the more reliable. The linewidths of BCOTFe(CO)$_3$ were used as a standard to which the linewidths due to true individual absorptions in BCOTFe$_2$(CO)$_6$ should approximate.

Mössbauer spectra of both complexes were recorded on solids and frozen solutions. Cyclohexane and n-butylbenzene were used as solvents, n-butylbenzene was specially chosen because of its high temperature dependence of the viscosity. This property has been found to ensure random orientation of the solute molecules in the frozen solution and hence in the absence of $f'$ factor anisotropy would produce equal absorption intensities in a true quadrupole doublet. Those frozen solution spectra denoted by asterisks in the tables were obtained on the spectrometer used by the A.N.U. Research School of Physical Sciences Solid State Group by courtesy of Dr. Don Price.
Calibration and low-temperature vibration checks of this and the author's spectrometer were with 12.5 µm thick natural iron foil. The use of the second spectrometer gave an independent check of the accuracy of the results.

As the resonance effects of the frozen solutions were usually less than 2% large numbers of counts (of the order of $1.5 \times 10^6$ baseline counts/channel) were accumulated for these spectra to ensure good statistical accuracy. The frozen solution spectra obtained by Dr. Don Price had much larger baseline counts than this (normally greater than $4.0 \times 10^6$ counts/channel) but over only 256 channels of memory. All spectra of the solid complexes had more than $10^5$ baseline counts/channel.

The extensive study of both compounds under a variety of conditions demonstrated the variations in spectral parameters obtained from separate experiments. For routine work the results obtained in any one experiment would have given sufficiently accurate parameters but the precision and accuracy required in this study, especially for linewidths, necessitated many repetitions, sometimes with slight variations in the experimental conditions. The totality of these results is given in Tables 4-I and 4-II.

4.2 Reliability of Fits

The fitting program used the modified chi-square statistic

$$
X_c^2 = \frac{X^2 \cdot ISCALE}{511 - N_p}
$$

where $N_p$ = number of variable parameters, as an indication of
Table 4-I: Spectral Parameters for BCOTFe(CO)$_3$

<table>
<thead>
<tr>
<th>$n_A$, T(K)</th>
<th>Exptl. Conditions$^\text{(a)}$</th>
<th>$\delta$</th>
<th>$\Delta$</th>
<th>$\Gamma_+$</th>
<th>$\Gamma_-$</th>
<th>$\varepsilon'_+ (%)$</th>
<th>$\varepsilon'_- (%)$</th>
<th>$\chi_C^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Solids</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70 77</td>
<td>H.N$_b$, L.T., cell 1</td>
<td>0.101</td>
<td>1.273</td>
<td>-</td>
<td>-</td>
<td>5.4</td>
<td>6.4</td>
<td>3.99</td>
</tr>
<tr>
<td>70 77</td>
<td>H.N$_b$, L.T., cell 1</td>
<td>0.098</td>
<td>1.260</td>
<td>-</td>
<td>-</td>
<td>4.6</td>
<td>5.6</td>
<td>2.78</td>
</tr>
<tr>
<td>70 77</td>
<td>H.N$_b$, L.T., cell 1</td>
<td>0.103</td>
<td>1.254</td>
<td>-</td>
<td>-</td>
<td>7.6</td>
<td>9.1</td>
<td>3.21</td>
</tr>
<tr>
<td>70 77</td>
<td>H.N$_b$, L.T., cell 1</td>
<td>0.094</td>
<td>1.276</td>
<td>-</td>
<td>-</td>
<td>8.4</td>
<td>10.0</td>
<td>3.51</td>
</tr>
<tr>
<td>74 77</td>
<td>L.N$_b$, L.T., cell 3</td>
<td>0.075</td>
<td>1.373</td>
<td>0.325</td>
<td>0.367</td>
<td>17.8</td>
<td>21.0</td>
<td>3.79</td>
</tr>
<tr>
<td>74 77</td>
<td>L.N$_b$, L.T., cell 3</td>
<td>0.085</td>
<td>1.275</td>
<td>0.280</td>
<td>0.303</td>
<td>18.1</td>
<td>21.4</td>
<td>1.33</td>
</tr>
<tr>
<td>74 77</td>
<td>L.N$_b$, L.T., cell 3</td>
<td>0.093</td>
<td>1.257</td>
<td>0.301</td>
<td>0.317</td>
<td>13.2</td>
<td>16.4</td>
<td>1.79</td>
</tr>
<tr>
<td>74 293</td>
<td>L.N$_b$, R.T.</td>
<td>-0.004</td>
<td>1.248</td>
<td>0.210</td>
<td>0.229</td>
<td>5.8</td>
<td>6.3</td>
<td>1.03</td>
</tr>
<tr>
<td>74 293</td>
<td>L.N$_b$, L.T., cell 3</td>
<td>0.004</td>
<td>1.256</td>
<td>0.237</td>
<td>0.243</td>
<td>4.0</td>
<td>5.6</td>
<td>1.27</td>
</tr>
<tr>
<td>74 293</td>
<td>L.N$_b$, L.T., cell 3$^\text{(b)}$</td>
<td>0.001</td>
<td>1.266</td>
<td>0.242</td>
<td>0.242</td>
<td>5.6</td>
<td>8.0</td>
<td>1.09</td>
</tr>
<tr>
<td>(b) Frozen solutions (i) cyclohexane matrix</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.9 77</td>
<td>*, rapidly cooled</td>
<td>0.055</td>
<td>1.252</td>
<td>0.271</td>
<td>0.256</td>
<td>1.03</td>
<td>1.00</td>
<td>0.88</td>
</tr>
<tr>
<td>1.9 77</td>
<td>*, slowly cooled</td>
<td>0.065</td>
<td>1.219</td>
<td>0.257</td>
<td>0.233</td>
<td>0.6</td>
<td>0.6</td>
<td>0.98</td>
</tr>
<tr>
<td>1.98 77</td>
<td>L.N$_b$, L.T., cell 2</td>
<td>0.082</td>
<td>1.275</td>
<td>0.248</td>
<td>0.248</td>
<td>1.3</td>
<td>1.2</td>
<td>1.03</td>
</tr>
<tr>
<td>3.32 77</td>
<td>L.N$_b$, L.T., cell 2</td>
<td>0.093</td>
<td>1.218</td>
<td>-</td>
<td>-</td>
<td>0.8</td>
<td>0.8</td>
<td>1.21</td>
</tr>
<tr>
<td>3.32 77</td>
<td>L.N$_b$, L.T., cell 2</td>
<td>0.092</td>
<td>1.236</td>
<td>-</td>
<td>-</td>
<td>0.7</td>
<td>0.7</td>
<td>1.11</td>
</tr>
<tr>
<td>3.44 77</td>
<td>L.N$_b$, L.T., cell 2</td>
<td>0.088</td>
<td>1.231</td>
<td>0.253</td>
<td>0.266</td>
<td>1.6</td>
<td>1.6</td>
<td>1.07</td>
</tr>
<tr>
<td>(ii) n-butylbenzene matrix</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.88 77</td>
<td>*</td>
<td>0.054</td>
<td>1.254</td>
<td>0.234</td>
<td>0.221</td>
<td>0.7</td>
<td>0.7</td>
<td>1.02</td>
</tr>
<tr>
<td>( n_A ), T(K)</td>
<td>Exptl. Conditions (a)</td>
<td>( \delta )</td>
<td>( \Delta )</td>
<td>( \Gamma_+ )</td>
<td>( \Gamma_- )</td>
<td>( \varepsilon'_+ (%) )</td>
<td>( \varepsilon'_- (%) )</td>
<td>( X_C^2 )</td>
</tr>
<tr>
<td>----------------</td>
<td>------------------------</td>
<td>--------</td>
<td>--------</td>
<td>-----------</td>
<td>-----------</td>
<td>----------------</td>
<td>----------------</td>
<td>--------</td>
</tr>
<tr>
<td>(a) Solids</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70  77</td>
<td>H.Nb, L.T., cell 1</td>
<td>0.106</td>
<td>0.978</td>
<td>-</td>
<td>-</td>
<td>5.6</td>
<td>6.1</td>
<td>2.70</td>
</tr>
<tr>
<td>70  77</td>
<td>H.Nb, L.T., cell 1</td>
<td>0.093</td>
<td>0.971</td>
<td>-</td>
<td>-</td>
<td>4.6</td>
<td>5.0</td>
<td>2.02</td>
</tr>
<tr>
<td>70  77</td>
<td>H.Nb, L.T., cell 1</td>
<td>0.097</td>
<td>0.970</td>
<td>-</td>
<td>-</td>
<td>4.6</td>
<td>5.0</td>
<td>2.06</td>
</tr>
<tr>
<td>74  77</td>
<td>L.Nb, L.T., cell 3</td>
<td>0.095</td>
<td>0.989</td>
<td>0.310</td>
<td>0.354</td>
<td>19.8</td>
<td>19.3</td>
<td>2.86</td>
</tr>
<tr>
<td>74  77</td>
<td>L.Nb, L.T., cell 3</td>
<td>0.097</td>
<td>0.988</td>
<td>0.315</td>
<td>0.358</td>
<td>19.2</td>
<td>18.7</td>
<td>4.33</td>
</tr>
<tr>
<td>74  77</td>
<td>L.Nb, L.T., cell 3</td>
<td>0.102</td>
<td>0.981</td>
<td>0.298</td>
<td>0.344</td>
<td>18.9</td>
<td>18.2</td>
<td>2.26</td>
</tr>
<tr>
<td>74  77</td>
<td>L.Nb, L.T., cell 3</td>
<td>0.108</td>
<td>0.979</td>
<td>0.318</td>
<td>0.361</td>
<td>17.7</td>
<td>17.6</td>
<td>2.14</td>
</tr>
<tr>
<td>74  140</td>
<td>L.Nb, L.T., cell 3</td>
<td>0.090</td>
<td>0.971</td>
<td>0.289</td>
<td>0.337</td>
<td>15.5</td>
<td>14.5</td>
<td>1.91</td>
</tr>
<tr>
<td>117 293</td>
<td>H.Nb, R.T.</td>
<td>0.023</td>
<td>0.925</td>
<td>0.194</td>
<td>0.242</td>
<td>1.3</td>
<td>1.1</td>
<td>1.21</td>
</tr>
<tr>
<td>70  293</td>
<td>H.Nb, R.T.</td>
<td>0.016</td>
<td>0.942</td>
<td>0.196</td>
<td>0.233</td>
<td>1.1</td>
<td>1.0</td>
<td>1.21</td>
</tr>
<tr>
<td>70  293</td>
<td>H.Nb, R.T.</td>
<td>0.014</td>
<td>0.942</td>
<td>0.208</td>
<td>0.260</td>
<td>1.0</td>
<td>1.0</td>
<td>1.31</td>
</tr>
<tr>
<td>74  293</td>
<td>L.Nb, R.T.</td>
<td>0.009</td>
<td>0.958</td>
<td>0.218</td>
<td>0.288</td>
<td>10.2</td>
<td>7.8</td>
<td>1.07</td>
</tr>
<tr>
<td>74  293</td>
<td>L.Nb, R.T.</td>
<td>0.009</td>
<td>0.957</td>
<td>0.222</td>
<td>0.284</td>
<td>10.1</td>
<td>7.8</td>
<td>1.11</td>
</tr>
<tr>
<td>(b) Frozen solutions (i) cyclohexane matrix</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.85 77</td>
<td>*</td>
<td>0.071</td>
<td>0.907</td>
<td>0.246</td>
<td>0.286</td>
<td>0.67</td>
<td>0.62</td>
<td>0.99</td>
</tr>
<tr>
<td>1.55 77</td>
<td>*</td>
<td>0.068</td>
<td>0.881</td>
<td>0.252</td>
<td>0.276</td>
<td>1.26</td>
<td>1.15</td>
<td>1.03</td>
</tr>
<tr>
<td>2.14 77</td>
<td>L.Nb, L.T., cell 2</td>
<td>0.101</td>
<td>0.902</td>
<td>0.292</td>
<td>0.284</td>
<td>1.5</td>
<td>1.5</td>
<td>1.11</td>
</tr>
<tr>
<td>3.43 77</td>
<td>L.Nb, L.T., cell 2</td>
<td>0.105</td>
<td>0.881</td>
<td>0.249</td>
<td>0.249</td>
<td>2.9</td>
<td>3.0</td>
<td>1.23</td>
</tr>
<tr>
<td>(ii) n-butylbenzene matrix</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.49 4.2</td>
<td>*</td>
<td>0.084</td>
<td>0.918</td>
<td>0.248</td>
<td>0.283</td>
<td>2.58</td>
<td>2.36</td>
<td>1.84</td>
</tr>
<tr>
<td>1.71 77</td>
<td>*</td>
<td>0.065</td>
<td>0.902</td>
<td>0.238</td>
<td>0.284</td>
<td>1.31</td>
<td>1.07</td>
<td>1.03</td>
</tr>
<tr>
<td>2.49 77</td>
<td>*</td>
<td>0.080</td>
<td>0.896</td>
<td>0.223</td>
<td>0.274</td>
<td>1.72</td>
<td>1.55</td>
<td>1.19</td>
</tr>
</tbody>
</table>
Notes on Tables 4-I and 4-II.

(a) Experimental conditions as follows:

H \text{Nb} -- High background count rate due to wide collimator used or poor detector resolution.

L \text{Nb} -- Low background count rate achieved with narrow collimator and detector with satisfactory resolution.

L.T., cell... -- Low temperature mounting of sample in cryostat using designated cell.

Cell 1 -- Polythene discs clamped inside brass holder.

Cell 2 -- Solid copper cell with soldered beryllium windows.

Cell 3 -- Solid copper cell with clamped beryllium windows.

R.T. -- Room temperature mounting of cell in lead/copper holder.

For further details refer to the experimental section.

Spectra denoted by asterisks were run by Dr Don Price using the rectangular polythene cell.

All except one of these samples were first cooled by direct immersion in liquid nitrogen and then mounted in the cryostat.

(b) Extra collimation between the absorber and detector was used.
the goodness of fit (\( \chi^2_c = 1 \) for a perfect fit; refer to Section 5.4).

It was evident from experience that good \( \chi^2_c \) values could be obtained from unreliable data (for instance where vibration had broadened the absorptions) and that poor values often occurred with apparently good quality data. The latter situation mainly applied to low-temperature results for the solid complexes and then more so for BCOTFe\(_2\)(CO)\(_6\) than for BCOTFe(CO)\(_3\). All frozen solution spectra showed good \( \chi^2_c \) values but only two spectra of the solid complexes (in each case BCOTFe(CO)\(_3\)) were reasonably well fitted. The following possibilities were considered as the causes of the poor fittings:

(a) The thickness of the absorber was too great with the result that the Lorentzian fitting model was not an adequate approximation to the data.

(b) The spectra of the diiron complex were not well fitted to a single pair of Lorentzians because of the presence of overlapping absorptions.

(c) Instrumental deficiencies (vibration, instability in electronics etc.)

(d) Poor geometry, radiation scattering.

(e) Non-uniformity of the sample.

(f) Fluctuations in the temperature of the sample.

(g) The minimisation procedure used in the program was not adequate for large resonance effects.

The large thicknesses of the solid samples were at first thought to be one of the likely causes since the spectra of the thinner frozen solutions were well fitted. However this may
simply be due to the poorer quality of data for these samples. The fact that good and bad fits were obtained on the same sample of BCOTFe(CO)$_3$, rendered this possibility even less likely. This last piece of information coupled with observations on iron calibration spectra where good and bad fits were obtained eliminated factors (e) and (g). Some instrumental deficiencies cannot be ruled out although if present they would have to have been variable between experiments. Sample fluctuations were usually only ±1K and therefore were unimportant.

The use of a tandem transducer so that two spectra could be recorded simultaneously would be of benefit in determining the significance of deficiencies in the electronics. The effect of scattering of the gamma radiation by the stainless steel tail of the cryostat was investigated by running spectra of samples of BCOTFe(CO)$_3$ in the cryostat at room temperature. The $\chi^2_c$ value was slightly larger than for spectra obtained with the sample mounted in the usual fashion but the fit was considerably improved by further collimating the transmitted radiation between the absorber and the detector. However since even the first of these results was considerably better than any obtained at low temperature it was concluded that scattering of radiation by the cryostat was not the sole cause of poor fits.

The only factor left to consider was (b) and this was examined by using different methods to fit some of the spectra of the diiron complex. These methods and their results will be discussed in the next section.
4.21 Effect of Quality of Fit on Calculated Parameters

Since poor fits had to be tolerated it was necessary to know the effect that a bad fit had on the spectral parameters. This is best illustrated by the results for several spectra of BCOTFe(CO)₃ and BCOTFe₂(CO)₆ at different temperatures:

Table 4-III

Dependence of Peak Parameters on Quality of Fit.

Data for Solid BCOTFe(CO)₃ (n_A = .074 g/cm²)

(Peak positions are in channels; linewidths are in mm/sec)

(a) 77K Reasonable Fit $\chi_c^2 = 1.329$

<table>
<thead>
<tr>
<th>Peak Position</th>
<th>$\Gamma_{exp}$</th>
<th>$\varepsilon'(0)^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>232.66</td>
<td>.280</td>
<td>.181</td>
</tr>
<tr>
<td>279.40</td>
<td>.303</td>
<td>.214</td>
</tr>
</tbody>
</table>

(b) 293K Good Fit $\chi_c^2 = 1.091$

<table>
<thead>
<tr>
<th>Peak Position</th>
<th>$\Gamma_{exp}$</th>
<th>$\varepsilon'(0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>235.53</td>
<td>.242</td>
<td>.056</td>
</tr>
<tr>
<td>281.87</td>
<td>.242</td>
<td>.080</td>
</tr>
</tbody>
</table>

Poor Fit $\chi_c^2 = 1.786$

<table>
<thead>
<tr>
<th>Peak Position</th>
<th>$\Gamma_{exp}$</th>
<th>$\varepsilon'(0)^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>232.69</td>
<td>.301</td>
<td>.132</td>
</tr>
<tr>
<td>278.77</td>
<td>.317</td>
<td>.164</td>
</tr>
</tbody>
</table>

Reasonable Fit $\chi_c^2 = 1.27$

<table>
<thead>
<tr>
<th>Peak Position</th>
<th>$\Gamma_{exp}$</th>
<th>$\varepsilon'(0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>235.61</td>
<td>.237</td>
<td>.040</td>
</tr>
<tr>
<td>281.56</td>
<td>.243</td>
<td>.056</td>
</tr>
</tbody>
</table>

Data for solid BCOTFe₂(CO)₆ (n_A = .074 g/cm²) at 77K fitted to two peaks:

$\chi_c^2 = 2.86$

<table>
<thead>
<tr>
<th>Peak Position</th>
<th>$\Gamma_{exp}$</th>
<th>$\varepsilon'(0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>237.55</td>
<td>.310</td>
<td>.198</td>
</tr>
<tr>
<td>273.81</td>
<td>.354</td>
<td>.193</td>
</tr>
</tbody>
</table>

$\chi_c^2 = 4.33$

<table>
<thead>
<tr>
<th>Peak Position</th>
<th>$\Gamma_{exp}$</th>
<th>$\varepsilon'(0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>237.48</td>
<td>.315</td>
<td>.192</td>
</tr>
<tr>
<td>273.72</td>
<td>.358</td>
<td>.187</td>
</tr>
</tbody>
</table>

*Because the window settings of the single-channel analyser were different for these spectra, the resonance effects are not strictly comparable.*
For all spectra the first peak is the positive velocity component.

From these results it can be seen that peak positions are virtually independent of the quality of the fit but linewidths may depend significantly on it. This was one of the reasons why it was necessary to accumulate many spectra.

Results obtained with iron calibration spectra (discussed in the experimental section) were essentially in agreement with the above, but the linewidths were much less dependent on the quality of the fit.

Diagrams 4-1 and 4-2 show plots of good and poor fits to spectra of solid BCOTFe(CO)₃ at 77K.

4.22 Fitting of the Spectra of BCOTFe₂(CO)₆

The spectra for the diiron complex were normally fitted as an apparent single quadrupole doublet. Attempts to fit four peaks or in one case three peaks were marginally successful but the fit was in these cases very sensitive to the initial values of the parameters. (A three peak spectrum could result from the fortuitous exact overlap of two of the four possible absorptions.) Often a good chi-square value could be obtained with a nonsensical set of parameter values. In view of the difficulty of the fitting program being able to produce sensible parameter values for closely-spaced peaks, the accuracy of the parameters obtained by fitting three or four peaks may be questionable. However if the linewidths turn out to be essentially the same and the areas are in the correct ratio (2:1:1 for a three peak fit and 1:1:1:1 for a four peak fit) the reliability of the results is enhanced. Results of fitting the same experimental spectrum
4.1 SPECTRUM OF SOLID BCOTFe(CO)$_3$ AT 77K
(Plotted in order of increasing velocity)
'Reasonable' Fit $\chi^2_c = 1.329$
4.2 SPECTRUM OF SOLID BCOT Fe(CO)$_3$ AT 77K

(Plotted in order of increasing velocity)

'Poor' Fit $X_c^2 = 1.786$
to two, three and four peaks are given in table 4-IV. The two peak fit to this spectrum is shown in Diagram 4-3.

Table 4-IV

Peak Parameters Obtained by Fitting a Spectrum of Solid BCOTFe$_2$(CO)$_6$ ($n_A = 0.074$ g/cm$^2$) at 77K to 2, 3 and 4 Peaks.

(a) 2 peak fit, all parameters variable $\chi_c^2 = 4.325$

<table>
<thead>
<tr>
<th>Peak Position</th>
<th>$\Gamma_{\exp}$</th>
<th>$\epsilon'(0)$</th>
<th>Fractional area</th>
</tr>
</thead>
<tbody>
<tr>
<td>237.48</td>
<td>.315</td>
<td>.192</td>
<td>.474</td>
</tr>
<tr>
<td>273.72</td>
<td>.358</td>
<td>.187</td>
<td>.526</td>
</tr>
</tbody>
</table>

(b) 3 peak fit, all parameters variable $\chi_c^2 = 2.076$

<table>
<thead>
<tr>
<th>Peak Position</th>
<th>$\Gamma_{\exp}$</th>
<th>$\epsilon'(0)$</th>
<th>Fractional area</th>
</tr>
</thead>
<tbody>
<tr>
<td>237.53</td>
<td>.323</td>
<td>.192</td>
<td>.497</td>
</tr>
<tr>
<td>270.91</td>
<td>.269</td>
<td>.110</td>
<td>.238</td>
</tr>
<tr>
<td>276.48</td>
<td>.288</td>
<td>.115</td>
<td>.265</td>
</tr>
</tbody>
</table>

(c) 4 peak fit, all parameters variable $\chi_c^2 = 1.426$

<table>
<thead>
<tr>
<th>Peak Position</th>
<th>$\Gamma_{\exp}$</th>
<th>$\epsilon'(0)$</th>
<th>Fractional area</th>
</tr>
</thead>
<tbody>
<tr>
<td>235.13</td>
<td>.277</td>
<td>.093</td>
<td>.210</td>
</tr>
<tr>
<td>239.27</td>
<td>.277</td>
<td>.121</td>
<td>.273</td>
</tr>
<tr>
<td>271.01</td>
<td>.283</td>
<td>.113</td>
<td>.259</td>
</tr>
<tr>
<td>276.51</td>
<td>.288</td>
<td>.110</td>
<td>.259</td>
</tr>
</tbody>
</table>

(Note: Peak positions are in channels and linewidths are in mm/sec)
4.3 SPECTRUM OF SOLID BCOTFe$_2$(CO)$_6$ AT 77K FITTED TO TWO PEAKS
(Plotted in order of increasing velocity) $\chi^2 = 4.325$
The results of the program MOSFUN indicated quantitatively the small change in overall peak width that could be expected for a composite peak formed by the overlap of two Lorentzian absorptions. These results are shown in Table 4-V and Diagram 4-4.

Table 4-V

<table>
<thead>
<tr>
<th>True Separation Δ (ch)</th>
<th>Width (ch)</th>
<th>Resonance Effect at Minima</th>
<th>Observed Separation Δ sep (ch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>17.5</td>
<td>.09</td>
<td>single peak</td>
</tr>
<tr>
<td>6</td>
<td>18.5</td>
<td>.087</td>
<td>&quot;</td>
</tr>
<tr>
<td>7</td>
<td>19.5</td>
<td>.083</td>
<td>&quot;</td>
</tr>
<tr>
<td>8</td>
<td>21.0</td>
<td>.078</td>
<td>&quot;</td>
</tr>
<tr>
<td>9</td>
<td>22.0</td>
<td>.074</td>
<td>&quot;</td>
</tr>
<tr>
<td>10</td>
<td>two peaks*, 24.0</td>
<td>.070</td>
<td>6</td>
</tr>
<tr>
<td>11</td>
<td>&quot;</td>
<td>25.0</td>
<td>.068</td>
</tr>
<tr>
<td>12</td>
<td>&quot;</td>
<td>26.0</td>
<td>.065</td>
</tr>
<tr>
<td>13</td>
<td>&quot;</td>
<td>28.0</td>
<td>.063</td>
</tr>
<tr>
<td>14</td>
<td>&quot;</td>
<td>28.5</td>
<td>.062</td>
</tr>
<tr>
<td>15</td>
<td>&quot;</td>
<td>29.5</td>
<td>.061</td>
</tr>
</tbody>
</table>

*For absorption profiles where two peaks are visually apparent the "width" is still taken as the total width across the composite peak.

Because of the difficulty in getting sensible fits to a four peak spectrum it was decided that fitting to an apparent
4.4 CALCULATED LORENTZIAN PROFILES FOR A TWO PEAK SPECTRUM

Counts per Channel

\[
\Delta = 5 \\
\Gamma = 17.5
\]

\[
\Delta = 9 \\
\Gamma = 22.0
\]

\[
\Delta = 15 \\
\Gamma = 29.5
\]
quadrupole doublet would be a better approach. The linewidths of each apparent single peak were compared to each other and to the linewidths for BCOTFe(CO)₃.

4.3 Calculation of Sample Thickness

The (dimensionless) sample thickness $t_A$ was calculated as follows:

$$t_A = n \sigma_0 f'$$

$\sigma_0$ is taken as $2.57 \times 10^{-18}$ cm$^2$

$t_A$ will be determined in units of the recoil-free fraction $f'$ of the absorber.

Calculation of $n$ (atoms $^{57}$Fe/cm$^2$)

$$n = \frac{n_A \times p \times 56.12 \times 0.0219 \times 6.023 \times 10^{23}}{W \times 57}$$

where $n_A$ = mass of compound/unit area (in g/cm$^2$)

$p$ = number of atoms of Fe in one molecule of compound

$W$ = molecular weight of compound.

Thus

$$n = 1.298673 \times 10^{22} \times \frac{n_A \times p}{W}$$

(4-1)

Hence

$$t_A = 3.33759 \times 10^4 \times \frac{n_A \times p}{W} \times f'$$

Since the spectra have more than one peak the value of $t_A$ for the $i$th peak is:

$$t_{A_i} = W_i t_A$$

where $W_i$ = relative intensity of the $i$th peak.

For BCOTFe(CO)₃ $p = 1$, $W = 293.85$. Hence:

$$t_{A_i} = 1.1358 \times 10^2 \cdot n_A \cdot f' \cdot W_i$$

The frozen solution with the greatest surface density had

$$n_A = 3.44 \times 10^{-3} \text{ g/cm}^2, \ W_1 = W_2 = \frac{1}{2}$$
Hence the thickness for each absorption in this spectrum was:

\[ t_{A_i} = 1.1358 \times 10^2 \times 3.44 \times 10^{-3} \times 0.5 f' \]

\[ = 0.195f' \ (<0.195). \]

For the solid spectra the absorption thicknesses were different for each peak due to unequal peak intensities; however an "average" thickness can be obtained by setting \( W_1 = W_2 = 0.5 \).

\[ n_A = 74 \times 10^{-3} \text{ g/cm}^2 \text{ was normally used.} \]

Thus \( t_{A_i} = 1.1358 \times 10^2 \times 74 \times 10^{-3} \times 0.5 f' \)

\[ = 4.20f' \ (<4.20) \]

Similarly BCOTFe\(_2\)(CO)\(_6\) with \( p = 2 \), \( W = 433.7 \) had:

\[ t_{A_i} = 1.5391 \times 10^2 n_A \cdot f' \cdot W_1 \]

The frozen solution with the greatest surface density had

\[ n_A = 3.43 \times 10^{-3} \text{ g/cm}^2, \ W_1 = W_2 = \frac{1}{2} \]

(assuming two peak fit). Hence the thickness for each absorption was

\[ t_{A_i} = 1.5391 \times 10^2 \times 3.43 \times 10^{-3} \times 0.5 f' \]

\[ = 0.264f' \ (<0.264) \]

The solid spectra of BCOTFe\(_2\)(CO)\(_6\) showed less asymmetry than those of BCOTFe(CO)\(_3\) and \( W_1 = W_2 = \frac{1}{2} \).

Hence for \( n_A = 74 \times 10^{-3} \text{ g/cm}^2 \) as was normally used,

\[ t_{A_i} = 5.69f' \ (<5.69) \]
The quantity $n_A$ for the frozen solution spectra was determined by the concentration $c_A$ (g/cm$^3$) of the solute and the thickness $t$ (cm) of the cell:

$$n_A = c_A \cdot t$$

4.4 Analysis of Spectra

The large amount of data accumulated posed several questions:

(a) Which were the more reliable sets of data in terms of absolute accuracy?

(b) What were the causes of the discrepancies in parameters obtained from different spectra of the same compound?

(c) What were the most likely values of the parameters and what was a realistic estimate of the errors in these parameters?

Since this work was also very much an evaluation of the performance of the spectrometer the answers to these questions would prove of benefit in future usage of the equipment.

In order to answer the above it is necessary to describe the varying conditions under which the spectra were obtained. Early results on solids at low temperature were obtained with a rather wide collimator. As mentioned in Section 3.82 this had the effect of decreasing the resonance effect magnitude relative to that obtained with a narrower collimator. In these early experiments the vibrational problems within the cryostat at low temperature had not been recognised and thus the linewidths obtained were quite large.
(typically \(\approx 0.45 \text{ mm/sec}\)) and not comparable to later results. Consequently these linewidths are not tabulated. Other parameters were affected only very slightly (checked with iron foil standard) and therefore were comparable to results obtained in later runs.

Eventually, when vibrational problems had been overcome, a reasonable degree of standardisation of experimental geometry was possible. A narrow collimator was always used for later experiments. The conditions of low-temperature experiments varied only due to the different settings of the window of the single-channel analyser that were necessary. Unfortunately but unavoidably, low-temperature and room-temperature spectra were not obtained under exactly the same conditions because of the presence of the cryostat in the low-temperature experiments. The effect this had on the fitting has already been mentioned in Section 4.2. The linewidths of those samples mounted in the cryostat but run at room-temperature were greater than those of samples mounted in the usual fashion (Table 4-I). The broadening of 0.02-0.03 mm/sec was attributed to random vibrations transmitted by the pumping line although the spectra of iron foil obtained under the same conditions showed no line broadening.

After considering the various data sets the values in Table 4-VI were arrived at as representing the most accurate values of the parameters. The errors in the parameters in each case were obtained by one of two means: either as the standard deviation of several determinations or, where only one data set was available, from the computed standard deviations of that fit.
Table 4-VI: Best values of Parameters for BCOTFe(CO)_3 (A) and BCOTFe_2(CO)_6 (B).

<table>
<thead>
<tr>
<th>Compound</th>
<th>T(K)</th>
<th>( \delta ) (b)</th>
<th>( \Delta )</th>
<th>( \Gamma_+ ) (c)</th>
<th>( \Gamma_- ) (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, solid</td>
<td>293</td>
<td>.000 ± .004 (3)</td>
<td>1.257 ± .009 (3)</td>
<td>.210 ± .006 (1)</td>
<td>.229 ± .005 (1)</td>
</tr>
<tr>
<td>B, solid</td>
<td>293</td>
<td>.014 ± .009 (5)</td>
<td>.945 ± .02 (5)</td>
<td>.208 ± .014 (5)</td>
<td>.261 ± .028 (5)</td>
</tr>
<tr>
<td>B, solid</td>
<td>140</td>
<td>.090 ± .002 (1)</td>
<td>.971 ± .003 (1)</td>
<td>.289 ± .004 (1)</td>
<td>.337 ± .004 (1)</td>
</tr>
<tr>
<td>A, solid</td>
<td>77</td>
<td>.089 ± .004 (2)</td>
<td>1.266 ± .009 (2)</td>
<td>.280 ± .003 (1)</td>
<td>.303 ± .003 (1)</td>
</tr>
<tr>
<td>B, solid</td>
<td>77</td>
<td>.100 ± .008 (7)</td>
<td>.979 ± .01 (7)</td>
<td>.298 ± .003 (1)</td>
<td>.344 ± .004 (1)</td>
</tr>
<tr>
<td>A, cyclohexane matrix</td>
<td>77</td>
<td>.089 ± .007 (4)</td>
<td>1.239 ± .036 (6)</td>
<td>.257 ± .014 (4)</td>
<td>.251 ± .018 (4)</td>
</tr>
<tr>
<td>B, cyclohexane matrix</td>
<td>77</td>
<td>.103 ± .002 (2)</td>
<td>.893 ± .014 (4)</td>
<td>.249 ± .003 (2)</td>
<td>.281 ± .005 (2)</td>
</tr>
<tr>
<td>A, n-butylbenzene matrix</td>
<td>77</td>
<td>.054 ± .005 (1)</td>
<td>1.254 ± .010 (1)</td>
<td>.234 ± .016 (1)</td>
<td>.221 ± .015 (1)</td>
</tr>
<tr>
<td>B, n-butylbenzene matrix</td>
<td>77</td>
<td>.072 ± .008 (2)</td>
<td>.899 ± .003 (2)</td>
<td>.231 ± .008 (2)</td>
<td>.279 ± .005 (2)</td>
</tr>
<tr>
<td>B, n-butylbenzene matrix</td>
<td>4.2</td>
<td>.084 ± .002 (1)</td>
<td>.918 ± .005 (1)</td>
<td>.248 ± .007 (1)</td>
<td>.283 ± .008 (1)</td>
</tr>
</tbody>
</table>

Notes:  
(a) Errors were calculated in either of two ways; as the standard deviation of a set of \( n \) values of the parameter, the value of \( n \) being given in brackets after the parameter; where only one data set was used the error is the computed error given by the fitting program.  
(b) All isomer shifts, except those for n-butylbenzene matrices, were calculated from the author's values. The discrepancy between these and the n-butylbenzene values is considered in Section 4.51.  
(c) Where only one value of the linewidths was used to give the final result, the narrowest such linewidth was chosen. The low-temperature linewidths include a considerable thickness broadening.
4.5 Spectral Parameters

In order to arrive at the consensus of most accurate values given in Table 4-VI it was necessary to determine the comparability of the different data sets. Thus $\epsilon'(0)$ values were not strictly comparable for all spectra due to the variations in collimators, detector resolution and single-channel analyser window setting. Linewidths were generally comparable although their absolute values were still greater than that expected from the natural linewidth, taking thickness into account. The determination of peak positions was the most reliable of all the fitted parameters. The effect on these of vibration and sample thickness (for the thicknesses used) was virtually negligible. Thus the commonly-quoted Mössbauer spectral parameters, the isomer shift and the quadrupole splitting, were the least affected of all parameters by variations in conditions.

4.5.1 Isomer Shifts

The isomer shifts of both complexes whether in the solid state or frozen matrix were within a small range of ±0.11 mm/sec. These are typical values for diamagnetic covalent complexes of iron. Most isomer shifts recorded in the literature for iron carbonyl complexes are within the range ±0.10 mm/sec relative to iron metal. In view of this small variation in isomer shifts it was inevitable that the isomer shifts due to each iron site in the diiron complex should be so similar.

Furthermore such small values of the isomer shift have large relative errors although the absolute error is quite small. The only important feature of the isomer shift
values was the discrepancy between results on different spectrometers but with each set being self-consistent. The absolute differences between the two sets was approximately 0.03 mm/sec which, while being a large relative error, was at first considered understandable in view of the calibration inaccuracies of each spectrometer and the inaccuracies in determining peak positions, especially for frozen solutions. The errors in the peak positions computed by the fitting program MOSFIT6 are usually less than the standard deviations within the sets of data in tables 4-I and 4-II. Calibration inaccuracies are mainly due to shifts in the zero velocity channel of the spectrometer with time.

The following example of BCOTFe(CO)$_3$ in cyclohexane ($n_A = 3.44$ mg/cm$^2$) illustrates the errors given by the fitting program:

**BCOTFe(CO)$_3$ spectrum (all values in channels)**

Peak 1 (positive velocity component) at $233.53 \pm 0.14$
Peak 2 (negative velocity component) at $279.14 \pm 0.14$
Centroid at $256.34 \pm 0.14$
Quadrupole splitting $45.61 \pm 0.28$

**Fe calibration spectrum**

Centroid at $259.60 \pm 0.08$
Velocity calibration $0.02699 \pm 0.00012$ mm/sec/ch

Isomer shift of BCOTFe(CO)$_3$ = $-3.26 \pm 0.22$ channels

$= +0.088 \pm 0.006$ mm/sec as the velocity calibration uncertainty is negligible in comparison to the uncertainty in the difference of the centroids.
Quadrupole splitting = 1.231 ± 0.013 mm/sec where the velocity calibration uncertainty is now significant (0.005 mm/sec).

Because of the changes in the zero velocity position of the spectrometer with time a better method for determining the error in the centroid of the iron spectrum was to average the values obtained from two calibration spectra taken before and after the spectrum of the complex BCOTFe(CO)₃:

Iron metal spectrum 1, centroid at 259.32
Iron metal spectrum 2, centroid at 259.60

The average centroid position of the iron spectrum is now at channel 259.46 ± 0.14 while the calibration is virtually unaltered. The isomer shift of BCOTFe(CO)₃ (using the same spectrum as above) is now -3.12 ± 0.28 channels = +0.084 ± 0.008 mm/sec. The shift in the position of zero velocity does not affect the quadrupole splitting.

The calibration procedure for the Research School of Physical Sciences spectra was almost identical to the second method except that only three iron calibrations in all were obtained. Using the two calibrations which were relevant to most of the spectra gave an error in the centroid of the iron spectrum of 0.010 mm/sec. For a single spectrum of BCOTFe(CO)₃ in cyclohexane (n_A = 1.9 mg/cm²) the corresponding error in its centroid was 0.007 mm/sec, giving a total error in the isomer shift of 0.017 mm/sec.

Thus the difference of 0.03 mm/sec between the sets of isomer shift values obtained on the two different spectrometers lies just outside the experimental error limits. The only explanation that the author can offer for this is that the true parameter errors are greater than those given by the
fitting program, particularly for small resonance effects as in the frozen solutions. The difference was not very perturbing as the isomer shifts were not significant in this work.

4.52 Quadrupole Splittings

For BCOTFe(CO)₃ no marked change in the quadrupole splitting with temperature, thickness or form was evident. The value found was that typical of 1,3 diene bound to an Fe(CO)₃ moiety (Table 4-VII). The agreement of the frozen solution values and those for the solid showed that any thickness effects on the quadrupole splitting of the solid were insignificant. Because the nature of the matrix had no effect on the magnitude of the quadrupole splitting it was concluded that the electric field gradients within this molecule are determined solely by intramolecular properties, the most important of which is the stereochemistry of the ligands about the iron atom (for example 1,5 diene iron tricarbonyl complexes show quadrupole splittings of 1.5-2.2 mm/sec). Similar results have been obtained for related molecules (Table 4-VII).

The diiron complex showed a slightly greater temperature dependence of the quadrupole splitting in the solid. Since absorber thickness did not cause overestimation of the quadrupole splitting of BCOTFe(CO)₃ it is improbable that this is the case for BCOTFe₂(CO)₆. Assuming this to be so then the solid state quadrupole splitting at 77K of 0.984 mm/sec is about 0.09 mm/sec higher than that for the frozen solutions. Since the latter was independent of the solvent used the change in quadrupole splitting between solid and
frozen solution is due only to the destruction of the crystal lattice and not to any participation of the solvent in bonding (this is very unlikely for cyclohexane anyway). The reason why the crystal lattice affects the e.f.g. in the diiron complex and not the monoiron complex is presumably due to the difference in the crystal structures.

The quadrupole splitting of BCOTFe₂(CO)₆ is similar to that of several other diiron complexes in the literature which are either known or presumed to have an analogous structure (Table 4-VII).

4.53 Resonance Effects

Resonance effects ε'(0) for both complexes under optimum conditions ranged from 1-2% in the frozen solutions to about 20% for the solids at liquid nitrogen temperature. Because the absolute value of the resonance effect was markedly affected by experimental conditions (e.g. sample alignment, collimation, detector resolution, and vibration) the values given are not very significant except when the conditions under which spectra were run were identical.

A comparison of ε'(0) values for the two complexes at the same temperature under identical conditions (β constant) gave an indication of the relative f' values:

For frozen solutions where t_A < 0.5 equation 3-11 is applicable.

\[
\frac{\varepsilon_1'(0)}{\varepsilon_2'(0)} \approx \frac{t_{A1}}{t_{A2}} = \frac{\frac{1}{2}n_1\sigma_0f_1'}{\frac{1}{2}n_2\sigma_0f_2'}
\]

Hence

\[
\frac{f_1'}{f_2'} = \frac{\varepsilon_1'(0)}{\varepsilon_2'(0)} \cdot \frac{n_2}{n_1}
\]
From equation 4-1

\[ \frac{n_2}{n_1} = \frac{n_{A_2} P_2}{n_{A_1} P_1} \cdot \frac{W_1}{W_2} \]

Therefore

\[ \frac{f_1'}{f_2'} = \frac{\epsilon_1'(0)}{\epsilon_2'(0)} \cdot \frac{n_{A_2} P_2}{n_{A_1} P_1} \cdot \frac{W_1}{W_2} \]

For BCOTFe₂(CO)₆, \( n_{A_1} = 2.14 \times 10^{-3} \text{ g/cm}^2 \) gave \( \epsilon_1'(0) = 0.015 \)

and BCOTFe(CO)₃, \( n_{A_2} = 3.44 \times 10^{-3} \text{ g/cm}^2 \) gave \( \epsilon_2'(0) = 0.016 \)

Hence

\[ \frac{f_1'}{f_2'} = \frac{0.015 \times 3.44 \times 10^{-3} \times 1.433.7}{0.016 \times 2.14 \times 10^{-3} \times 2.293.85} = 1.1 \]

Hence it was felt justifiable to assume that the recoil-free fractions of the two complexes were equal.

Note: The fact that there are possible four absorptions for BCOTFe₂(CO)₆ is immaterial as the absorptions in each pair of separated lines are almost at identical positions, hence the \( \epsilon'(0) \) values are additive. Thus if \( \epsilon_1'(0) = \epsilon_2'(0) = \frac{1}{4} t_A \) for two overlapping peaks in a four peak spectrum, then the observed intensity due to the composite peak

\[ = \epsilon_1'(0) + \epsilon_2'(0) = \frac{1}{2} t_A \]

4.54 Asymmetry in Peak Intensities

Of greater interest than the absolute values of the resonance effect was the relative intensity of the absorptions in each spectrum. Both complexes in the solid state showed considerable asymmetry in the peak intensities. For the monoiron compound the positive velocity peak was the less intense whereas the opposite was true for the diiron complex. The peak intensities for frozen solution spectra were nearly
equal in most cases suggesting that the asymmetry observed in the solids was due to partial crystal orientation rather than $f'$ factor anisotropy. In an attempt to confirm this a spectrum of BCOTFe$_2$(CO)$_6$ was obtained where the sample cell was rotated through 33 degrees with respect to its vertical axis. Although a change in the relative peak intensities compared to a normal spectrum was observed this was still within the error limits of the calculations:

**Effect of Rotation on Absorption Intensities**

<table>
<thead>
<tr>
<th>BCOTFe$_2$(CO)$_6$ solid 77K</th>
<th>$\varepsilon_+$ (a)</th>
<th>$\varepsilon_-$ (b)</th>
<th>$\varepsilon_+ / \varepsilon_-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample in normal position</td>
<td>19.8</td>
<td>19.3</td>
<td>1.026 ± 0.013</td>
</tr>
<tr>
<td>sample rotation through 33 degrees</td>
<td>17.7</td>
<td>17.6</td>
<td>1.006 ± 0.014</td>
</tr>
</tbody>
</table>

Notes: (a) uncorrected percentage resonance effect for positive velocity component.
(b) uncorrected percentage resonance effect for negative velocity component.

The asymmetry of the diiron complex could also be partially due to superimposition of two peaks at the positive velocity position but the effect would be quite small as the two negative velocity peaks were also quite close together.

4.55 Linewidths

The linewidth parameters given for the frozen solution spectra showed no definite variation with the thickness (equivalently, concentration) of the sample. Hence it was not possible to construct a graph of $\Gamma_{\exp}$ vs. $t_A$ and to
extrapolate to zero thickness to get the true value of $\Gamma_s + \Gamma_a$. The fragility of solid disks of less than 70 mg/cm$^2$ and the limited amount of the complexes available prohibited studies of the variation of linewidth with thickness for the solids. The lack of a definite variation of $\Gamma_{\text{exp}}$ with $t_A$ may be due to some or all of the following factors:

(a) The "quality" of the frozen solution spectra, as measured by the signal to noise ratio, was not sufficient to give the accuracy needed to emphasise small differences in linewidths between spectra.

(b) Distortion of the cell windows to varying extents making the calculation of $n_A$ from the concentration $c_A$ inaccurate.

(c) Different cooling rates producing samples of varying non-uniformity due to the growth of solvent-rich and solute-rich crystallites. To determine what effect this would have on the Mössbauer parameters the spectra of a sample of BCOTFe(CO)$_3$ in cyclohexane in the rectangular polythene cell were obtained for both rapid cooling (immersion in liquid nitrogen) and slow cooling (above vapour of liquid nitrogen and then immersion). These values, given in Table 4-I, do show differences but the significance of these is small in view of the deviations between all the results obtained for BCOTFe(CO)$_3$ in cyclohexane. Ruby et al. found that the Mössbauer parameters were independent of the cooling rate below a threshold of 10 degrees Kelvin/second. Vértes and Parak, in studies of paramagnetic Fe$^{3+}$ species, assumed that cooling by direct immersion in liquid helium was sufficiently rapid to preserve the chemical structure that
the frozen solutions had in the liquid state. Although the cooling rate of the author's polythene cell was not measured, its low mass (1 g) and small thickness probably enabled rapid cooling of the order of the above threshold figure to be achieved when it was cooled by immersion.

Because of the similarity of the parameters for the rapidly cooled and slow cooled samples and the lack of any definite trend of \( \Gamma_{exp} \) with \( t_A \) it was assumed that all linewidth values for the frozen solutions of BCOTFe(CO)\(_3\) were equally good estimates of limiting \((t_A = 0)\) behaviour. Thus their values were averaged to obtain the parameters in Table 4-VI.

The values for the linewidths of BCOTFe\(_2\)(CO)\(_6\) in frozen solutions fell into two classes:

(a) Fast-cooled samples in cyclohexane and in n-butylbenzene with \( \Gamma_+ < \Gamma_- \).

(b) Slow-cooled samples in cyclohexane with \( \Gamma_+ = \Gamma_- \).

The first set of values was obtained on the Research School of Physical Sciences spectrometer and the second set (2 values) with the author's apparatus.

The results obtained from solid samples at different temperatures were consistent with the first set of frozen solution results and so the linewidths for the two slow-cooled samples of BCOTFe\(_2\)(CO)\(_6\) in cyclohexane appear anomalous. Only two explanations are possible: either the rate of cooling affects the linewidths of BCOTFe\(_2\)(CO)\(_6\) or else the two results obtained in cyclohexane by the author are spurious. The first factor seems unlikely as other parameters were not affected and the results of BCOTFe(CO)\(_3\),
subjected to different cooling rates were in reasonable agreement. Confirmation of this factor being the cause could be made by running a slow-cooled sample on the Research School of Physical Sciences spectrometer. The second explanation seems paradoxical in that one set of values had small linewidths and the other large linewidths. Vibration in the equipment could explain the latter but it is difficult to see how small linewidths could arise. Further studies of frozen solutions in the author's apparatus would clarify the anomaly. Because of the apparent inconsistency of this second pair of results they were not used in calculating the average linewidths given in Table 4-VI.

4.6 Comparison With Literature Results

A comparison of isomer shifts and quadrupole splittings with those of similar compounds has already been made (sections 4.51 and 4.52). Linewidth values are given far less frequently in the literature than $\delta$ and $\Delta$. No doubt this is largely due to the fact that little useful chemical information was thought to be available from this parameter. Moreover it is likely that absolute values of the linewidth are far less accurate and precise than absolute values of either the isomer shift or the quadrupole splitting, especially in early work.

The results of Herber on studies of COTFe(CO)$_3$ (I) and COT[Fe(CO)$_3$]$_2$ (III) gave almost equal linewidths (0.01 mm/sec difference) for the absorptions in each spectrum and showed, from the quadrupole splitting data, the similarity in the bonding of the iron tricarbonyl group to the ring in each case. Emerson in studies of 1,3,5-cyclooctatriene diiron hexacarbonyl and cyclooctatetraene diiron hexacarbonyl (II)
falsely concluded that since the spectra only consisted of single quadrupole doublets the two iron sites were equivalent in each compound. No values of the linewidths were given. Pettit and Collins\(^4\) reported linewidths for a series of complexes of the type \(\text{RFe(CO)}_4\), where \(\text{R} = \text{olefin}\), and the values they obtained at 78K were fairly large (mostly >0.40 mm/sec). The sample thicknesses they used were not very great \((n_A \approx 80 \text{ mg/cm}^2)\) so the large linewidths are not solely a result of thickness broadening. Whether the values are accurate or broadened as a result of instrumental deficiencies is not clear.

Three studies which attempted to show the existence of non-equivalent iron sites within a molecule are relevant here. The first by Carty et al.\(^8\) was on the dimer \([\text{CpFe}_2(\text{CO})_3]_2\text{DPPA}\) whose structure (XL) was shown by X-ray diffraction to contain two different iron sites. Despite this Carty was unable to achieve resolution of individual peaks due to each site and instead obtained only an apparent quadrupole doublet, the linewidths of each absorption differing by at most 0.03 mm/sec (Table 4-VII). The second investigation by Herber et al.\(^8\) was more extensive. Again the basic structure (XXVIII) they were working with had been determined by X-ray diffraction. Frozen solution techniques were employed to minimise thickness broadening and to achieve random crystal orientation. In some but not all cases they were able to achieve resolution of a spectrum with very asymmetrical peak areas into three absorptions. They concluded that two quadrupole doublets were present in the spectra but that the negative components in each doublet fortuitously overlapped.
The third study by Schmid et al.\textsuperscript{90} on the complex (XLI) from N-trimethylsilyl-benzophenonimin was the only one in which visual resolution of separate quadrupole doublets was apparent. This resolution was possible due to the different quadrupole splittings for each site as the isomer shifts were only slightly different (0.11 mm/sec).

The results of this work are quantitatively very similar to those of Carty and probably represent the most extreme case of being able to definitely establish the non-equivalence of two iron atoms within a molecule.

4.7 Conclusions

The necessity for accumulating numerous spectra under different conditions is obvious in view of the accuracy and precision required in the parameter values and the lack of
such accuracy and precision in any one determination. Numerous technical problems can contribute to this and analysis of the reliability of the final values required careful appraisal of possible causes of error. Despite all this the following facts emerged from the study:

(a) BCOTFe$_2$(CO)$_6$ shows an asymmetry in linewidths which is most reasonably attributable to an unresolved pair of lines in one peak of the apparent quadrupole doublet. The absorption with the narrower linewidth also contains two peaks but their positions virtually coincide.

(b) The quadrupole splitting of BCOTFe$_2$(CO)$_6$ is significantly dependent on the environment of the molecule - whether it is in a crystalline lattice or a frozen glass. Hence electric field gradients at the iron nuclei in this compound are partially determined by the lattice.

(c) The asymmetry in absorption intensities for both compounds in the solid state was considerably reduced when frozen solutions were used. The asymmetry in intensities for solid BCOTFe(CO)$_3$ is probably solely due to partial crystal orientation as the frozen solutions showed equal resonance effects. The same is largely but not completely true for BCOTFe$_2$(CO)$_6$ as the frozen solutions of this compound still showed a small but definite asymmetry in the absorption intensities with $\varepsilon'_+(0) > \varepsilon'_-(0)$. This is consistent with the conclusion in (a) and is due to the virtual coincidence of two peaks in the positive velocity component of the apparent quadrupole doublet.

(d) Isomer shift and quadrupole splitting values for both compounds were very similar to those of related compounds
in the literature.

(e) Spectra which would normally be considered acceptable were obtained on samples containing less than ten milligrams of compound.

(f) Apart from one pair of anomalous results, no significant difference in the Mössbauer parameters was found for slow-cooled or rapidly-cooled samples of either compound. Thus the fluxional behaviour of the molecules is not mirrored by any change in the Mössbauer spectrum.

Unresolved problems such as differences in isomer shifts between laboratories and poor fitting did not affect the validity of the above conclusions.
<table>
<thead>
<tr>
<th>Compound*</th>
<th>δ(Fe)</th>
<th>Δ</th>
<th>Γ_{exp}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>COTFe(CO)$_3$ (I)</td>
<td>0.078</td>
<td>1.23</td>
<td>0.32</td>
<td>17</td>
</tr>
<tr>
<td>EPA</td>
<td>0.053</td>
<td>1.24</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>n-octane</td>
<td>0.083</td>
<td>1.16</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>COT[Fe(CO)$_3$]$_2$ (III)</td>
<td>0.113</td>
<td>1.23</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>C$_8$H$_6$(COOMe)$_2$Fe(CO)$_3$</td>
<td>0.073</td>
<td>1.27</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>C$_8$H$_6$CH$_2$OOOCFe(CO)$_3$</td>
<td>0.073</td>
<td>1.25</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>norbornadiene Fe(CO)$_3$</td>
<td>0.033</td>
<td>2.15</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>cycloocta-1,5-dieneFe(CO)$_3$</td>
<td>-0.027</td>
<td>1.83</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>cyclobutadieneFe(CO)$_3$</td>
<td>0.023</td>
<td>1.54</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>EPA</td>
<td>0.003</td>
<td>1.55</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>acenaphthalene Fe(CO)$_4$</td>
<td>-0.014</td>
<td>1.78</td>
<td>0.40, 0.36</td>
<td>46</td>
</tr>
<tr>
<td>[π-ally1Fe(CO)$<em>4$]$</em>{BF_4}$</td>
<td>0.056</td>
<td>0.93</td>
<td>0.38, 0.51</td>
<td>46</td>
</tr>
<tr>
<td>tropone Fe(CO)$_3$</td>
<td>0.058</td>
<td>1.49</td>
<td>-</td>
<td>91</td>
</tr>
<tr>
<td>1,3,5-cyclooctatrieneFe$_2$(CO)$_6$</td>
<td>0.068</td>
<td>0.88</td>
<td>-</td>
<td>91</td>
</tr>
<tr>
<td>cyclooctatrienoneFe(CO)$_3$</td>
<td>0.068</td>
<td>1.41</td>
<td>-</td>
<td>91</td>
</tr>
<tr>
<td>cyclooctatrienoneFe$_2$(CO)$_6$</td>
<td>0.098</td>
<td>0.84</td>
<td>-</td>
<td>91</td>
</tr>
<tr>
<td>thianaphthene Fe$_2$(CO)$_6$</td>
<td>0.008</td>
<td>1.11</td>
<td>-</td>
<td>91</td>
</tr>
<tr>
<td>[(π-C$_8$H$_5$)$_2$Fe$_2$(CO)$_3$]$_2$DPBA</td>
<td>0.273</td>
<td>1.94</td>
<td>0.28, 0.31</td>
<td>89</td>
</tr>
<tr>
<td>(295K)</td>
<td>0.193</td>
<td>1.95</td>
<td>0.24, 0.26</td>
<td>89</td>
</tr>
<tr>
<td>tricarbonylferroleFe(CO)$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>derivatives:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R=CH$_3$ (85.5K)</td>
<td>-0.010</td>
<td>1.157</td>
<td>0.592, 0.560</td>
<td>84</td>
</tr>
<tr>
<td>R=C$_2$H$_5$ (87K)</td>
<td>-0.006</td>
<td>1.163</td>
<td>0.587, 0.623</td>
<td>84</td>
</tr>
<tr>
<td>R=C$_2$H$_5$ n-butylbenzene (83.5K)</td>
<td>A 0.020</td>
<td>1.257</td>
<td>0.263, 0.296</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>B -0.055</td>
<td>1.019</td>
<td>0.237, 0.296</td>
<td>84</td>
</tr>
<tr>
<td>C$<em>{13}$H$</em>{16}$NSiMe$_3$Fe$_2$(CO)$_6$</td>
<td>A 0.026</td>
<td>1.460</td>
<td>0.319, 0.319</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>B -0.085</td>
<td>0.808</td>
<td>0.329, 0.329</td>
<td>90</td>
</tr>
</tbody>
</table>

* In solid state unless otherwise shown.

5. Experimental

5.1 Mössbauer Spectrometer

A block diagram of the complete system is given in Diagram 5.1. The system can be divided into two parts: spectrometer and cryostat with its ancillary equipment. The spectrometer consisted of the following components:

(a) Multi-channel analyser: Hewlett-Packard model 5401B.

(b) Mössbauer Unit consisting of Waveform Generator, Velocity Attenuator and Servo Amplifier and Transducer: all manufactured by 20th Century Electronics Ltd.

(c) Pre-amplifier, amplifier and single-channel analyser: all made by Canberra Instruments.

(d) Detector: xenon-filled proportional counter made by 20th Century Electronics Ltd and high voltage power supply (Canberra Instruments 3002 and later a Fluke 415B which is stable to ±0.2 volts at 2000 volts).

(e) Source supplied by the Radiochemical Centre, Amersham, England.

Plate 1 shows the console containing the units in (a) - (d) (except for detector and pre-amplifier).

The analyser has a total storage capacity of 1024 channels divided into four memory sub-groups each of 256 channels. The first channel in each memory sub-group stores the number of sweeps of the analyser memory that are made. For almost all spectra only the first memory half was used, as a compromise between counting times (necessarily longer for a given count rate the larger the memory) and resolution
5.1 MÖSSBAUER SPECTROMETER SYSTEM

The pumping assembly was operated in the multi-channel mode in which the slow rate of the memory was controlled by the waveform generator. The latter, besides supplying the sweep trigger and advance address pulse to the analyzer, delivered the selected advance address sequentially step by step. The waveform generator, giving an effective sawtooth output of the appropriate shape for use with the analyzer, had been preformed from a suitable waveform signal, which was generated by the waveform generator. The Multi-channel Analyser was used for measuring the shift of the lineshape of the spectrum. The Analyser was also used for measuring the non-linearity of the MÖSSBAUER experiment. The advance address was used to locate the position on the multi-channel analyser where the spectrum was to be recorded. The output devices were used for spectrum accumulation.
(increases with memory size). Thus channel zero in this case stored the number of sweeps of the memory and channels 1-511 were used for spectrum accumulation.

For the recording of Mössbauer spectra the analyser was operated in the multi-channel scaling mode where the sweep rate of its memory was controlled by the waveform generator. The latter, besides supplying the sawtooth drive waveform to the velocity attenuator, delivered start and advance address pulses to the analyser to begin a memory sweep and to sequentially step through the memory. The spectrum accumulation period occurs on the linear ramp of the sawtooth and was about 2/3 of the total period of 61 milliseconds (Figure 5.2). For a 512-channel memory this meant a dwell-time per channel of approximately 80 microseconds, including dead-time. For the 5401B analyser the latter was 2.2 microseconds between channels giving an effective dwell-time per channel of nearly 78 microseconds. The various waveforms supplied by the waveform generator were derived from a crystal oscillator, stated by the manufacturer as giving good stability.

The velocity attenuator enables selection of the desired velocity range by changing the slope of the linear ramp of the sawtooth supplied by the waveform generator. To achieve greater resolution the attenuator had been previously modified so that its effective velocity range for any one setting of the panel-mounted dial was decreased. For most of the spectra in this work a setting of 4.0 was used which was just slightly greater than that necessary to span the velocity range of the iron spectrum. Visual examination of the CRO trace of the waveform from the velocity attenuator indicated increasing non-linearity of the linear ramp as the velocity setting was
5.2 SAWTOOTH VELOCITY WAVEFORM

The waveform provides the engine for the velocity calibration. The voltage supplied to the wire coil is rather smooth.

5.3 WAVEFORM SUPPLIED TO DRIVE COIL

The conditions at which the calibration signal is to be set vary from place to place. The voltage supplied to the wire coil is rather smooth.
lowered.

The servo-amplifier provides the feedback for the control of the vibrator motion by comparing the signal from the velocity coil of the vibrator with the reference waveform from the velocity attenuator. The difference after amplification is used to modify the waveform applied to the drive coil of the vibrator. In order to produce a sawtooth drive the waveform supplied to the drive coil is a rather complex parabolic one (Diagram 5.3).

Since positive velocity occurs on the first half of the descent ramp of the sawtooth waveform the Mössbauer spectra that were obtained have velocity values decreasing from left to right. Later versions of the spectrum curve fitting program allowed for this and plotted the spectra with the velocity increasing from left to right in the usual way; however the actual peak positions given by the program were still based on the original decreasing velocity scale.

The Pye-Ling V47 vibration generator (Plate 2) carried the $^{57}$Co source which could be enclosed within a lead collimator which fitted onto the vibrator unit. Since the maximum stroke of the vibrator was only 0.25 cm the effect on collimation due to movement of the source was negligible. The source consisted of a nominal 10 microcurie content of $^{57}$Co diffused in palladium foil 6 µm thick. The source linewidth $\Gamma_s$ was specified to be 0.107 mm/sec.

The radiation spectrum of the source was observed using the pulse-height analysis mode of the analyser. In this mode an analogue-to-digital converter was used to sort incoming pulses according to their height.
5.4 PULSE-HEIGHT SPECTRA OF COLLIMATED SOURCE

--- Old detector
-- New detector

A width = 8.18 Kev (56.9% resolution)
B width = 3.05 Kev (21.2% resolution)

A width = 8.18 Kev (56.9% resolution)
B width = 3.05 Kev (21.2% resolution)
The pulses produced by the detector are amplified by the model 806 pre-amplifier which also integrated the pulses from the detector for presentation to the main amplifier (model 816). The latter was operated at a reasonably high gain (several hundred) in order to achieve satisfactory resolution in the pulse height spectrum of the source.

The model 830A single-channel analyser was used to select only that portion of the pulse height spectrum that contained the Mössbauer peak. To do this the analyser was set to the pulse height analysis mode and with visual monitoring the upper and lower level discriminators of the SCA were adjusted to allow only the selected radiation through. In the "normal" mode of the SCA this meant that only those incoming signals with amplitudes between the upper and lower level discriminator settings were allowed through into the multi-channel analyser.

The xenon proportional counters (several were used in the course of this work) had resolutions within the range 15-20% at 5.9 Kev. Typical operating voltages were around 2000-2100 volts. It was found the resolution of these counters, especially on the high energy side of the Mössbauer peak, deteriorated with time. This may have been due to the leakage air into the counter. The nett result of this deterioration was an inability to resolve the 21 Kev palladium X-ray from the Mössbauer peak which caused an increase in the background count rate. Pulse-height spectra of the same source, obtained with new and old detectors, are shown in Diagram 5.4.

5.11 Collimation

Two collimators were used in the course of this work:
a narrow collimator of 1 cm exit diameter and a wide collimator of exit diameter 1.8 cm.

For the wide collimator \( L_c = 2.2 \) cm and \( L_d = 14.0 \) cm were used. Using the notation of Section 3.82

\[
y = \frac{L_d S}{D + S} = \frac{14.0 \times 0.8}{14.2} = 2.67 \text{ cm.}
\]

Hence \( L_c < y \).

For this case \( u = 0.8 - \frac{4.2 \times 2.2}{14.0} = 0.14 \) cm < \( C = 1.8 \) cm and therefore there is no improvement in collimation.

For the narrow collimator \( L_c = 5.4 \) cm and \( L_d = 21.7 \) cm were used.

\[
y = \frac{L_d S}{D + S} = \frac{21.7 \times 0.8}{4.2} = 4.13 \text{ cm}
\]

Hence \( L_c > y \).

For this case \( t = \frac{4.2 \times 5.4}{21.7} - 0.8 = 0.25 \) cm < \( C = 1.0 \) cm and again there is no improvement in collimation.

As has been mentioned before, although the use of a narrower collimator did not improve linewidths, resonance effects were increased. This was due to the decrease in background radiation reaching the unshielded detector.

5.12 Calibration and Performance of The Spectrometer

Velocity calibration of the analyser address was made using a standard absorber of 12.5 \( \mu \)m thick natural iron foil which was supplied with the source. Simultaneously with each calibration the performance of the spectrometer, assessed in terms of linewidth broadening and drift in the velocity-channel synchronisation, was checked. Drift is caused by a deterioration in the characteristics of the electronic components of
the Mössbauer unit. In the short term (during an experiment) it causes line broadening and in the long term a change in the position of zero velocity occurs. The line broadening caused by drift is further augmented by that resulting from non-linearity in the linear ramp of the drive waveform. In order to monitor these effects it was sufficient to constantly calibrate the spectrometer with the standard absorber. As the spectral parameters, particularly the linewidth, were dependent on the experimental geometry it was necessary to adopt a fixed configuration which gave minimum linewidths for the standard absorber. This entailed using the narrower collimator (1 cm), a source-detector distance of 21.3 cm and mounting the absorber between lead and copper plates. The results of a typical calibration spectrum shown in Figure 5.5 are given in Table 5-I.

### Table 5-I

**Results** \(^{(a)}\) of a Typical Calibration Spectrum of the Standard Absorber

<table>
<thead>
<tr>
<th>PEAK</th>
<th>(c'(0))</th>
<th>Position (ch.)</th>
<th>Linewidth</th>
<th>Vel. calibration(^{(b)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.6</td>
<td>59.971</td>
<td>0.270</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10.6</td>
<td>144.530</td>
<td>0.246</td>
<td>(0.02681)</td>
</tr>
<tr>
<td>3</td>
<td>6.3</td>
<td>227.875</td>
<td>0.246</td>
<td>(0.02648)</td>
</tr>
<tr>
<td>4</td>
<td>6.4</td>
<td>291.143</td>
<td>0.243</td>
<td>(0.02668)</td>
</tr>
<tr>
<td>5</td>
<td>10.8</td>
<td>374.891</td>
<td>0.256</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>14.6</td>
<td>461.084</td>
<td>0.284</td>
<td></td>
</tr>
</tbody>
</table>

Average velocity calibration = 0.02666±0.00018 mm/sec/channel

**Notes:**

(a) Uncorrected resonance effects are given as percentages, linewidths in mm/sec and velocity calibrations in mm/sec/channel.

(b) Line positions of the iron peaks, in mm/sec, are taken from data of C. Violet and D. Pipkorn.\(^92\)
5.5 IRON CALIBRATION SPECTRUM
(Plotted in order of increasing velocity)
\[ \chi^2_c = 1.34 \]
Peaks one and six were never used for calibration purposes as their positions varied considerably from one spectrum to another largely because of variable non-linearity at the extremities of the drive waveform. Fortunately the absorptions of the complexes always fell within the range spanned by iron peaks three and four where the linearity of the waveform was very good.

Even with a standard geometry the positions and widths of the inner four peaks of the iron spectrum were subject to a small but definite variation between calibrations run at different points in time. Over a three month period the variation in the linewidths was 0.011 mm/sec for peak three and 0.018 mm/sec for peak four. During the same period the position of zero velocity varied by 0.025 mm/sec, partially attributable to the precision to which the velocity attenuator could be reset.

A second sample of iron foil 12.5 µm thick gave identical calibration results (linewidths, peak positions, etc.) to the original sample used. Calibration of the spectrometer used by the Research School of Physical Sciences Solid State Group was done using similar iron foil (i.e. same thickness and from same supplier) for which linewidths of 0.245-0.255 mm/sec were obtained for the inner two peaks, in excellent agreement with the author's results.

The suppliers of the source used 32 µm thick iron foil for their specification test, obtaining linewidths for the inner two peaks of 0.234 mm/sec, the thickness broadening being 0.03 mm/sec. Using a broadening function $h(t_A) = 0.27t_A$ one can calculate that the 12.5 µm thick foil should produce
a broadening of 0.012 mm/sec giving a total experimental linewidth of 0.216 mm/sec. This suggests that the spectrometers used by the author and Dr Don Price were both producing a broadening of \( \approx 0.03 \) mm/sec. If this was true for all spectra then the minimum observable linewidth would be 0.224 mm/sec \( (= 2\Gamma_{\text{nat}} + 0.03) \). However some spectra of both iron metal and of the two complexes were obtained on the author's spectrometer which had linewidths less than this value, suggesting that very little spectrometer broadening was present. A complete solution to this paradox was not reached.

5.2 Cryostat

The cryostat used for low temperature studies was an Oxford Instruments MD4A modular dewar. This cryostat is provided with liquid helium and liquid nitrogen cooled radiation shields surrounding the low temperature pot to which the sample cell is attached. A stainless steel outer tail is 'O' ring sealed to the main body for vacuum tightness. Entrance ports for electrical connections are provided near the tail. Coolant could be admitted to the low temperature pot from the helium can by means of a needle valve. In all of this work both the inner (helium) and the outer (nitrogen) cans were filled with liquid nitrogen which enabled 77K to be maintained at the sample block for about 39 hours without refilling. All radiation windows on the shields and tail were made of 0.1 mm thick aluminized "Mylar".

The cryostat was mounted on a frame connected to an aluminium plate equipped with wheels so that it could be freely manoeuvred into position on a supporting gantry (Plate 3).
For each run the outer tail of the cryostat was securely clamped to the same base to which the source transducer was bolted. A spectrum of iron foil taped to the outside of the vacuum casing gave narrow linewidths. Stainless steel flexible bellows were used on the vacuum pump connections to minimize any effects of vibration from the pumping line (Plate 4A). An extensive series of tests was undertaken when it was found that even with these precautions absorptions were considerably broadened. In certain test runs the cryostat was detached from the aluminium plate and allowed to stand freely, clamped in position at the base. In other test runs the cryostat was also disconnected from the pumping line and spectra were recorded with the cryostat thus completely isolated. In these cases however run times had necessarily to be kept short because without external pumping the vacuum in the cryostat gradually deteriorated causing the sample block temperature to increase. For a few cases spectra of iron foil and potassium ferrocyanide were recorded simultaneously. The iron foil was taped either to the nitrogen or helium radiation shields and the potassium ferrocyanide was mounted in the sample holder attached to the low temperature pot.

By these various means the location of vibration in the cryostat was identified. The majority of the vibration only occurred when the reservoir to which the sample was attached was cool and contained liquid nitrogen. The extent of the vibrational line broadening was about the same whether the sample was attached to the low temperature pot or whether it was attached to the helium radiation shield. It was much less when the sample was attached to the nitrogen radiation shield.
Furthermore very little vibration arrived from either the building or the pumping line.

Satisfactory spectra were eventually achieved by fixing stainless steel struts between the helium and nitrogen cans and keeping these cans continually topped up using an automatic filling device. This arrangement would prove unsatisfactory for spectra run at 4.2K due to the large heat leak into the helium can but it is possible that the line broadening does not occur when liquid helium is used, in which case the struts would not be needed.

5.21 Temperature Measurement

A gold+0.03 atomic % Fe/chromel thermocouple and a carbon resistor were used to measure sample block temperature. For the all-metal cells this was assumed to be the same as the actual sample temperature. The output of the carbon resistor went to an Oxford Instruments carbon thermometer which drove a 10 millivolt Heathkit recorder for a continuous record of temperature during a run. A second gold+0.03 atomic % Fe/chromel thermocouple attached to the low temperature pot of the cryostat was used in conjunction with an AEI thermocouple controller and a heater wound around the pot for running the single spectrum obtained at 140K. The temperature measuring equipment is shown in Plate 4B.

Both thermocouples had their reference junctions anchored onto the helium can base and thus these junctions were normally at 77K. Each thermocouple was calibrated by direct immersion of its test junction into liquid nitrogen, liquid oxygen and ice, the reference junction being kept at
ambient temperature (293K). These results are summarized in Table 5-II.

Table 5-II

Calibration of Thermocouples

Reference junctions at 293K.

<table>
<thead>
<tr>
<th>Test junction</th>
<th>Pot T/C</th>
<th>Sample T/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>e.m.f. E</td>
<td>dE/dT(b)</td>
</tr>
<tr>
<td>K</td>
<td>mV</td>
<td>µV/K</td>
</tr>
<tr>
<td>76.6(a)</td>
<td>4.044</td>
<td>16.5</td>
</tr>
<tr>
<td>89.4(a)</td>
<td>3.833</td>
<td></td>
</tr>
<tr>
<td>273.2</td>
<td>0.5952</td>
<td></td>
</tr>
</tbody>
</table>

Notes: (a) The boiling points of liquid nitrogen and liquid oxygen were corrected to the prevailing atmospheric pressure (70.8 cm).
(b) dE/dT values are averages for the range 76.6-89.4K.

5.3 Absorber Preparation

a) Solids. All solid absorbers were prepared by placing the weighed amount of powdered material in a stainless steel die and pressing at a pressure of nine tons per square inch for not less than twenty minutes. This procedure was not always successful at a first attempt in that the pressed disc would sometimes disintegrate upon removal from the die. An absorber prepared in this manner had a cross-sectional area of two square centimetres. For room temperature spectra the absorber was mounted on a "Sellotape" or "Mylar" film sandwiched between lead and copper plates (the latter to minimise transmission of lead X-rays), the whole assembly was then
placed in position between the source and detector on the Mössbauer bench.

b) Liquids. For frozen solution samples a weighed amount of compound was dissolved in a weighed amount of the appropriate solvent and the resulting solution was then quickly injected into the particular liquid cell that was used. The volume of solvent used was calculated from its density at 20°C and hence the concentration of solute was determined.

Sample mounting for low temperature work is described in the following section.

5.31 Design of Cells for Low Temperature Work

The "cold-finger" design of the cryostat necessitated a cell design with good thermal conductivity and vacuum tightness. For maximum gamma transmission the only window materials that could be used were beryllium, aluminium or a plastic such as polythene. Obviously beryllium or aluminium were the materials of choice for maximum thermal conductivity across the sample region at low temperatures (for example at 20K the thermal conductivity of polytetrafluoroethylene is approximately one-hundredth that of even low purity aluminium\(^9\)).

In early work a liquid cell was constructed from two polythene discs with a gold '0' ring between them, the assembly being clamped together in a brass holder. A similar cell, of slightly larger internal diameter and without the gold '0' ring, was constructed for solid samples (Figure 5.6). The brass holder was then placed within a copper block securely attached to the low temperature pot of the cryostat. Spring loadings held the brass sample holder tight against the copper block.
5.6 POLYTHENE/BRASS CELL USED FOR LIQUID AND SOLID SAMPLES

Polythene discs -++-- Brass plate

Scale: Full size
An entrance port in the brass holder was provided for a thermocouple probe and a carbon resistor was attached to the outside of the copper block. Difficulties with this system (for example the appearance of a "bubble" inside the cell because of distortion of the polythene windows when the brass plates were screwed together) and the inherent poor thermal conductivity of polythene compared to metals prompted the development of other cells for liquids.

Four types of cells were made, of similar basic design but differing in the method of sealing the cell windows to the cell body. All cell bodies were machined out of solid copper with provision for thermocouple and carbon resistor probes. In two cases the cell bodies were gold-plated to eliminate chemical attack by the injected solutions but this was later dispensed with as being unnecessary. The cell windows consisted of 1.0 inch diameter beryllium discs of 0.01 inch thickness. This combination of copper body plus beryllium windows was chosen as offering the greatest transmission of gamma radiation commensurate with maximum thermal conductivity across the sample region and was therefore thought to be most suitable for eventual liquid helium work with the cryostat available.

In the first type of cell "Fenwal" low temperature adhesive was used to cement the beryllium windows onto flanges 1.5 mm apart. The injection ports were sealed with rubber 'O' rings. After several successful cycles to 77K the adhesive joint began to crack and leak. In the second type of cell the beryllium windows were vacuum brazed at 800°C to the copper body using copper/silver eutectic. Unfortunately although the braze appeared satisfactory under the microscope the cell
leaked badly.

For the third type of cell (Plate 5A) the beryllium windows were first copper plated\textsuperscript{94} around the periphery and then soldered onto the cell body, using ordinary solder m.p. 190°C for the first window and Wood's metal m.p. 70°C for the second window. The latter window took several attempts to obtain a satisfactory seal. The injection ports were sealed with indium as the rubber 'O' rings used in the first design did not seal well when low melting point solvents (for example n-butyl benzene m.p. -82°C) were used. Presumably in such cases the 'O' ring froze before the solvent.

Because of the chemical treatment required in the electroplating process the beryllium windows were somewhat etched but this cell proved to be completely leak-tight. Total mass of the cell was 99 gm and cool down time from ambient to 77K was approximately seven minutes under optimum conditions. The cell volume was 0.55 cc and the path length for radiation was 2 mm.

The fourth type of cell (Plates 5A and 5B) employed an indium seal between a brass sealing ring and the beryllium window which sat directly on the cell body. Again the injection ports were sealed with indium. This cell was completely leak tight and offered the advantage of being demountable for cleaning but because of the extra sealing components it was considerably heavier than the third type of cell, weighing 227 gm. As a result of this extra mass and the relatively poor thermal contacts within the cell the cool down period from ambient to 77K was nearly four hours. The cell volume was 0.55 cc and the path length for radiation was 2 mm.
In addition to the polythene cell mentioned earlier another type of cell for solids was designed which had better thermal contacts. This cell, which was machined out of solid copper, carried two copper plates with holes for the radiation path. The absorber was mounted between two discs of 0.01 inch thick high purity beryllium and this assembly was then securely clamped to the cell body with one of the copper plates. Iron foil samples were mounted between the two copper plates clamped to the cell body without the beryllium discs.

The cryostat used by the Research School of Physical Sciences Solid State Group did not require a vacuum around the cell and a commercially available polythene cell with rather poor sealing was used. This cell had a volume of approximately 0.6 cc and a path length of 1 mm.

5.4 Fitting of Spectra

Fitting of spectra was carried out using a least squares minimisation program developed from one written by A. Milgrom of the University of Melbourne.

The function minimised is 

$$E = \sum_{i=1}^{n} (y_i - f_i)^2$$

where $y_i$ = experimentally observed counts/channel at ith channel

$f_i$ = computed function value counts/channel at ith channel.

$f$ is the Lorentzian function

$$f(x) = \theta_1 - \sum_{i=1}^{N} \frac{\theta_{2i}}{\left(2/\theta_{3i}\right)^2(x - \theta_{4i})^2 + 1}$$

$$= f_x(\theta_1, \theta_2, \ldots, \theta_p)$$

where $N = \text{number of peaks giving } p \text{ peak parameters where }$

$p = 3N + 1$

$\theta_{2i} = \text{dip of peak } i$
\[ \theta_{3i} \text{ = width at half-height of peak } i \]
\[ \theta_{4i} \text{ = position of peak } i \]
\[ \theta_1 \text{ = baseline counts/channel} \]

The Gauss-Newton method of minimisation is used.

In matrix notation
\[
Y = \begin{pmatrix}
y_1 \\
\vdots \\
y_n
\end{pmatrix}, \quad F = \begin{pmatrix}
f_1 \\
\vdots \\
f_n
\end{pmatrix}, \quad \theta = \begin{pmatrix}
\theta_1 \\
\vdots \\
\theta_p
\end{pmatrix}
\]

\[ E = (Y - F)'(Y - F) \]

Now
\[ \frac{\partial E}{\partial \theta} = -2\frac{\partial F'}{\partial \theta} \cdot (Y - F) \]
\[ = -2J'(Y - F) \]

where
\[ J = \begin{pmatrix}
\frac{\partial f_1}{\partial \theta_1} & \cdots & \frac{\partial f_1}{\partial \theta_p} \\
\vdots & \ddots & \vdots \\
\frac{\partial f_n}{\partial \theta_1} & \cdots & \frac{\partial f_n}{\partial \theta_p}
\end{pmatrix} \]
is the Jacobian of \( F \).

Now \( F = F^* + J^*.(\theta - \theta^*) \) by Taylor series expansion about \( \theta^* \) in \( p \) dimensional space, neglecting all terms of order higher than the first. \( J^* \) is used to denote \( J \) evaluated at \( \theta^*[\equiv J(\theta^*)] \).

Thus
\[ \frac{\partial E}{\partial \theta} = -2J'[Y-F^*+J^*.(\theta - \theta^*)] \]
\[ = 0 \text{ for minimum} \]

Therefore
\[ J'(Y-F^*) = J^*(\theta - \theta^*) \]

Hence
\[ \theta - \theta^* = (J'J^*)^{-1}J'(Y-F^*) \]

Finally \( J' \equiv J'(\theta) \) is approximated by \( J'^* \equiv J'(\theta^*) \).
Therefore \( \theta - \theta^* = (J' J^*)^{-1} J' (Y - F^*) \)

and thus

\[
\begin{align*}
\theta(1) &= \theta^* + (J' J^*)^{-1} J' (Y - F^*) \\
\theta(2) &= \theta(1) + (J'(1) J(1))^{-1} J(1) (Y - F(1)) \\
&\text{etc.}
\end{align*}
\]

defines the sequence of estimates of the parameters \( \theta \).

For reasonable choice of the initial estimate \( \theta^* \) the sequence above converges towards a correct minimum.\(^{95}\)

Several other methods of least squares fitting are available and some of these have been discussed by Duke and Gibbs.\(^{95}\) In most of the methods described by these authors the function minimised is

\[
G = \sum_{i=1}^{n} \frac{(y_i - f_i)^2}{y_i} = (Y - F)' N (Y - F)
\]

where

\[
N = \begin{pmatrix}
\frac{1}{y_1} & 0 \\
0 & \frac{1}{y_2} \\
0 & \cdots & \frac{1}{y_n}
\end{pmatrix}
\]

setting \( \frac{\partial G}{\partial \theta} = 0 \)

gives \( \theta - \theta^* = (J' N J^*)^{-1} J' N (Y - F^*) \)

The rational for using \( G \) rather than \( E \) is to weight the errors according to the statistical accuracy of the observation. The differences, if any, between the parameters \( \theta \) obtained by using \( G \) instead of \( E \) should only be apparent when there are large variations amongst the \( y_i \); i.e. for large resonance effects. Otherwise minimising \( G \) is equivalent to minimising \( E \).
It was necessary to scale the $y_i$, $f_i$, and $\theta_{2i}$ values in order that the calculations could be performed within the allowable range of the computer (Univac 1108). This was done by setting

$$y'_i = \frac{y_i}{ISCALE} \quad i = 1, 2, \ldots, n$$

$$\theta'_{2i} = \frac{\theta_{2i}}{ISCALE} \quad i = 1, 2, \ldots, N$$

with $ISCALE$ normally 1000.

This meant that terms in the program output involving $y_i$, $f_i$ or $\theta_{2i}$ had to be corrected to obtain their true values. The following terms were affected:

<table>
<thead>
<tr>
<th>Term</th>
<th>Correction Factor (Multiply by program output value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chi-square</td>
<td>ISCALE</td>
</tr>
<tr>
<td>Sum of Squares</td>
<td>ISCALE^2</td>
</tr>
<tr>
<td>Peak Dips $\theta_{2i}$</td>
<td>ISCALE</td>
</tr>
<tr>
<td>Baseline $\theta_1$</td>
<td>ISCALE</td>
</tr>
<tr>
<td>Exptl. &amp; Computed counts/channel</td>
<td>ISCALE</td>
</tr>
<tr>
<td>Variance $\theta_1$</td>
<td>ISCALE^2</td>
</tr>
<tr>
<td>Variance $\theta_{2i}$ i = 1, 2, ..., N</td>
<td>ISCALE^2</td>
</tr>
<tr>
<td>Terms of matrix P inverse:</td>
<td></td>
</tr>
<tr>
<td>$P_{ij}$ where neither i nor j is of</td>
<td>ISCALE^-2</td>
</tr>
<tr>
<td>the form $3m+2$ (m=positive integer)</td>
<td></td>
</tr>
<tr>
<td>$P_{ij}$ where one of i or j has this form</td>
<td>ISCALE^-1</td>
</tr>
<tr>
<td>$P_{ij}$ where both i and j have this form</td>
<td>1</td>
</tr>
</tbody>
</table>

The incorporation of these corrections into the program would be an easy task. In what follows it will be assumed that these corrections have been made.
The program outputs, besides estimates of the parameters \( \theta \), the following statistical information:

(a) The values of \( G \) and \( E \) from the final iteration.

(b) The matrix \( (J'J)^{-1} \) where \( J \) is calculated from the values of the parameters at the final iteration. \( (J'J)^{-1} \) is related to the covariance matrix \( V \) by

\[
V = \sigma^2 (J'J)^{-1}
\]

\[
= \frac{(Y - F)'(Y - F)}{n - p} \cdot (J'J)^{-1}
\]

\[
= \frac{E_{\text{final}}}{n - p} \cdot (J'J)^{-1}
\]

(c) The variances of the parameters \( \theta \) given by the diagonal elements of \( V \), \( \text{Var}(\theta_k) = v_{kk} \quad k = 1, 2, \ldots, p \)

\( G \) is \( \chi^2_{n-p} \) distributed and so

\[
\text{Prob}(G \geq G_{\text{final}})
\]

can be determined as an indication of the goodness of fit. \(^\dagger\)

The expected value of \( G \) is \( n-p \), hence \( \chi^2_c \equiv \frac{G}{n-p} = 1 \) and

\[
\text{Prob}(\chi^2_c \geq G_{\text{final}} / (n-p)) = 0.5 \text{ for a perfect fit.}
\]

\(^\dagger\) \( G \) is not the sole goodness of fit criterion available but is the most commonly used because of its convenient statistical relationship to probability. Ruby\(^{96} \) has proposed the criterion

\[
M = \frac{\sum_{i=1}^{N} \left( \frac{(y_i - f_i)^2}{y_i} - 1 \right)}{\sum_{i=1}^{N} \left( \frac{(y_0 - y_i)^2}{y_i} - 1 \right)}
\]

\((y_0 = \text{baseline counts/channel})\)

which is normalised so that its magnitude is not affected by the quality of the data (unlike \( G \)).
5.5 Preparation of Compounds

All melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. The infra-red spectrum of Fe(CO)$_3$(P$_3$)$_2$ was obtained on a Unicam SP200G spectrophotometer and nuclear magnetic resonance spectra were measured either on a Perkin-Elmer R-10 (60 MHz) or JEOL MH-100 (100 MHz) spectrometer in the stated solvent at room temperature. Mass spectra were obtained on a Varian CH7 mass spectrometer operating at 70eV. High mass numbers were checked against polyfluorokerosene reference. For preparative thin-layer chromatography 1 m x 20 cm x 0.1 cm plates of Merck silica gel HF$_{254+566}$ were used unless otherwise stated. All reaction and chromatography solvents were distilled before use. Petroleum ether was the fraction b.p. 40-70°C. All reactions involving metal carbonyls were carried out under nitrogen. The metal carbonyl-polyolefin complexes were stored in a freezer at 0°C or under nitrogen at room temperature. In the case of solutions of the polynuclear complexes extensive decomposition occurred with either storage method after short periods of time.

Benzocyclooctatetraene

This was prepared by the addition of benzyne to benzene using the method of Friedman and Lindow. The crude material produced by decomposition of the silver complex was treated with decolourising charcoal and recrystallised from aqueous methanol. This gave pale yellow crystals of satisfactory purity, m.p. 46-48°C (lit. 49.5-50°C). The nmr spectrum (60 MHz, d-6 DMSO) agreed with that reported previously. The mass spectrum had peaks at m/e 154 (molecular ion, 79%), 153 (base peak, 100%), 152 (43%), 128 (17%), 115 (6%), 76 (19%).
Triiron Dodecacarbonyl

This was prepared by oxidation of a solution of NaHFe(CO)₄ using the method given by King. The washed product was stored under nitrogen. Occasionally, after such storage, the triiron dodecacarbonyl was pyrophoric.

Benzocyclooctatetraene Iron Tricarbonyl and Benzocyclooctatetraene Diiron Hexacarbonyl

The method used was essentially that of Elix and Sargent: triiron dodecacarbonyl and benzocyclooctatetraene (7:4 molar ratio) were refluxed in benzene under nitrogen for forty-eight hours. The filtered reaction solution was concentrated and chromatographed on a silica gel plate with petroleum ether. Recovery of the diiron compound and the monoiron compound from the slowest and second slowest bands respectively gave products of sufficient purity for Mössbauer spectra. A third compound was isolated from a yellow band which moved slightly faster than BCOTFe(CO)₃. The mass spectrum of this compound had peaks at m/e 296 (molecular ion, 1%), 268 (16%), 240 (44%), 212 (86%), 184 (base peak, 100%), 153 (15%), 128 (39%). The presence of some BCOTFe(CO)₃ impurity may have given the peak at 153 in which case the compound would not appear to be derived from BCOT. The compound decomposed readily in solution, in contrast to BCOTFe(CO)₃. The mass spectrum of BCOTFe(CO)₃ showed peaks at m/e 294 (molecular ion, 1%), 266 (20%), 238 (23%), 210 (base peak, 100%), 184 (7%), 152 (27%), 132 (94%), 128 (20%). The mass spectrum of BCOTFe₂(CO)₆ showed peaks at m/e 434 (molecular ion, 2%), 406 (18%), 378 (23%), 350 (11%), 322 (45%), 294 (54%), 266 (78%), 238 (16%), 210 (base peak, 100%).
184 (13%), 153 (40%), 152 (39%), 132 (75%). Recrystallisation of both compounds was effected from petroleum ether to give benzocyclooctatetraene iron tricarbonyl as yellow-orange crystals m.p. 76.5-80°C (lit. 77-79°C) and benzocyclooctatetraene diiron hexacarbonyl as red-orange crystals m.p. 104-106°C dec. (lit. 109-111°C dec.). Recrystallisation of the latter compound entailed considerable loss.

Reaction of BCOTFe(CO)$_3$ with Triphenyl Phosphine

A solution of 80 mg of BCOTFe(CO)$_3$ and 212 mg of triphenyl phosphine in 20 ml of benzene was refluxed under nitrogen for 65 hours. The solution was filtered and the filtrate, after concentration, was chromatographed on a plate of silica gel with 75% petroleum ether/25% benzene. Besides starting materials a slow-moving band containing yellow compounds developed. Further chromatography of this band in 50% petroleum ether/50% benzene indicated one major component but separation could not be achieved. The mixture was recrystallised from petroleum ether/benzene to give yellow crystals m.p. 255°C dec. The mass spectrum was identical to that of Fe(CO)$_3$(P$_3$)$_2$.

Reaction of Benzocyclooctatetraene Diiron Hexacarbonyl with Triphenyl Phosphine

50 mg of the diiron complex and 36 mg of triphenyl phosphine were dissolved in 20 ml of benzene and the solution was refluxed under nitrogen for 28 hours. The reddish-brown solution was filtered and the black insoluble material on the filter was washed with 15 ml of warm benzene. The filtrate and washings were combined and concentrated to about 3 ml and chromatographed on a silica gel plate with 75% petroleum ether/25% benzene. Five bands were visible under ultra-violet
light and the three fastest were collected. The two other slow-moving bands were found to contain insufficient material for satisfactory analysis. The collected bands were analysed as follows (in increasing order of Rf values):

Band one decomposed rapidly on standing in benzene solution and so its mass spectrum could not be obtained. From its Rf value it appeared to be unreacted BCOTFe₂(CO)₆.

The mass spectrum of band two had a molecular ion at m/e 430 (4%) and showed successive loss of four carbon monoxide groups at m/e 402 (4%), 374 (8%), 346 (8%) and 318 (8%). The base peak was at m/e 277. The isotopic distribution in the molecular ion and in fragments formed by loss of CO indicated the presence of one iron atom in the molecule. The mass spectrum is consistent with the formula Fe(CO)₄P₃.

Confirmation of this assignment was provided by the observation of a small amount of the same fragmentation pattern in the mass spectrum of Fe(CO)₃(P₃)₂, in which complex the monotriphenyl phosphine iron tetracarbonyl compound is a likely impurity.

Band three had a mass spectrum identical to that of benzocyclooctatetraene. Melting point and comparison of Rf values confirmed this assignment.

**Reaction of Benzocyclooctatetraene Iron Tricarbonyl with Triiron Dodecacarbonyl**

80 mg of the monoiron complex and 153 mg of Fe₃(CO)₁₂ were dissolved in 12 ml of benzene and refluxed under nitrogen for 48 hours. The cooled solution was filtered and the black residue was washed with 10 ml of hot benzene. The yellow filtrate and washings were combined and evaporated to give
on cooling a dirty yellow solid m.p. 36-40°C. The mass spectrum of this solid was identical to that of benzocyclooctatetraene and the Rf value in petroleum ether was also the same as that of benzocyclooctatetraene.

**Preparation of Fe(CO)$_3$(P$_3$)$_2$**

1.05 g (4.0 millimoles) of triphenylphosphine and 1.01 g (2.0 millimoles) of Fe$_3$(CO)$_{12}$ were dissolved in 50 ml of dry tetrahydrofuran and the solution was refluxed on a steam bath for 7 hours. The solution was filtered and the precipitate was washed with 15 ml of cold tetrahydrofuran. The filtrate and washings were combined and evaporated to give a greenish-white residue. This was mixed with 60 ml of methanol to give, after filtration, a dirty-yellow precipitate and a green solution containing unreacted Fe$_3$(CO)$_{12}$. The precipitate was recrystallised from benzene to give yellow crystals of Fe(CO)$_3$(P$_3$)$_2$ m.p. 255-260°C dec. (lit. 272°C dec.).

I.R. (CHCl$_3$) ν C=O 1886 cm$^{-1}$ (lit. 1887 cm$^{-1}$).

Mass Spectrum: m/e 664 (molecular ion, 0.4%), 608 (-2CO, 0.8%), 580 (-3CO, 2.5%), 318 (-3CO-P$_3$, 3%), 262 (base peak, 100%), 183 (72%). No molecular ion at m/e 636 for the loss of one CO group was observed.

**Cyclooctatetraene Iron Tricarbonyl**

This was prepared by the method given in Inorganic Syntheses. The crude material was recrystallised from ethanol and sublimed at 50°C/0.1 mm to give pure material m.p. 93-95°C (lit. 94°C).
Photolysis of COTFe(CO)$_3$ with Ru$_3$(CO)$_{12}$ in Benzene

0.367 g (1.5 millimoles) of COTFe(CO)$_3$ (I) and 0.640 g (1.0 millimole) of Ru$_3$(CO)$_{12}$ were mixed with 150 ml of benzene in a pyrex vessel (some Ru$_3$(CO)$_{12}$ remained undissolved) and photolysed with an English Hanovia lamp for 11 hours. The solution was filtered and the filtrate concentrated and chromatographed on a silica gel plate with petroleum ether. Three bands developed; the fastest contained Ru$_3$(CO)$_{12}$ and the slowest COTFe(CO)$_3$. A trace amount of yellow material was present in the third band which was intermediate between the first two. Analysis was not attempted because of the small quantity of material available.

Reaction with Ru$_3$(CO)$_{12}$ with Fe(CO)$_5$ - Preparation of Fe$_2$Ru(CO)$_{12}$

In a preliminary experiment it was found that the main products of this reaction (FeRu$_2$(CO)$_{12}$; Fe$_2$Ru(CO)$_{12}$; Ru$_3$(CO)$_{12}$; H$_2$FeRu$_3$(CO)$_{13}$) could be satisfactorily separated using thin layer chromatography but because of the low solubilities and large amount (0.5 - 1.0 g) of compound desired it was decided to develop a method not using chromatography.

0.756 g Ru$_3$(CO)$_{12}$ and 10 ml Fe(CO)$_5$ (filtered) were mixed with 70 ml cyclohexane for several minutes (some Ru$_3$(CO)$_{12}$ remained undissolved) and then the solution was refluxed under nitrogen. After approximately twenty five minutes the red solution darkened. After seventeen and one half hours another 30 ml cyclohexane was added and the refluxing was continued for another twenty seven and one half hours. The cooled solution was filtered to give a black precipitate and a reddish-purple filtrate. The precipitate was washed with cold cyclohexane until the washings were almost colourless and these washings were added to the filtrate. The filtrate was evaporated to near dryness on a rotary evaporator to give
0.535 g of a black solid. Thin-layer chromatography and microscopic examination showed that this black solid consisted mainly of purple \( \text{Fe}_2\text{Ru(CO)}_{12} \) with a small amount of red \( \text{FeRu}_2(\text{CO})_{12} \). The mother liquor remaining contained \( \text{Ru}_3(\text{CO})_{12} \), \( \text{FeRu}_2(\text{CO})_{12} \), \( \text{Fe}_2\text{Ru(CO)}_{12} \) and \( \text{H}_2\text{FeRu}_3(\text{CO})_{13} \). Partial evaporation of the mother liquor yielded another 0.12 g of black solid consisting mainly of \( \text{Fe}_2\text{Ru(CO)}_{12} \) with some \( \text{FeRu}_2(\text{CO})_{12} \).

The total yield of crude \( \text{Fe}_2\text{Ru(CO)}_{12} \) was thus 0.655 g. The two impurities present, \( \text{FeRu}_2(\text{CO})_{12} \) and some cyclohexane-insoluble material, were not anticipated to lead to extra by-products in the next reaction and so further purification was not attempted.

The mass spectrum was essentially in agreement with that reported elsewhere. 102

**Reaction of BCOT with \( \text{Fe}_2\text{Ru(CO)}_{12} \)**

0.126 g (0.8 millimoles) BCOT was dissolved in 50 ml of cyclohexane and 0.500 g (0.9 millimoles) of \( \text{Fe}_2\text{Ru(CO)}_{12} \) was added. The solution was refluxed with stirring under nitrogen for 48 hours. The solution was filtered and the black residue was washed with 50 ml of warm cyclohexane. The combined filtrate plus washings were evaporated to a small volume and chromatographed on a silica gel plate with petroleum ether. Five bands were collected and are referred to in decreasing order of \( R_f \) values. The first band (pale yellow) was identified from its mass spectrum as \( \text{BCOTRu(CO)}_3 \). The second band (pale yellow) contained both \( \text{BCOTRu(CO)}_3 \) and an iron compound with molecular ion at \( m/e \) 296. This appeared to be identical to the unidentified compound from the reaction of BCOT with \( \text{Fe}_3(\text{CO})_{12} \). The third band (lemon-yellow) was identified as
BCOTFe(CO)₃. The fourth band (orange-yellow) contained the three polynuclear complexes BCOTFe₂(CO)₆, BCOTFeRu(CO)₆ and BCOTRu₂(CO)₆. The fifth band contained only BCOTRu₂(CO)₆. The near overlap of some bands caused the same compound to appear in more than one band. As band four contained the desired complex BCOTFeRu(CO)₆, further attempts were made to separate this. Band four was redissolved in cyclohexane and chromatographed with petroleum ether on a silica gel plate. The plate was allowed to develop twice (i.e. two passes of the solvent were made) but only trace amounts of the two fast bands (probably identical to bands two and three of the first separation) were apparent besides the main band which did not separate into individual components. The material from this composite band was dissolved in a small volume of cyclohexane and chromatographed on 20 cm × 20 cm × 0.025 cm plates of Merck silica gel F₂₅₄ with cyclohexane. Separation into three bands was achieved in one pass but two passes were made to improve the separation. The range of Rf values after the first pass was 0.14 to 0.21. The constituents of these bands were: the fastest band almost pure BCOTRu₂(CO)₆ m.p. 105-108°C dec.; second band BCOTRu₂(CO)₆ and BCOTFeRu(CO)₆; third band BCOTFeRu(CO)₆ and BCOTFe₂(CO)₆. The second band was present in the greatest quantity and only very small amounts of bands one and three were obtained. The nmr spectrum (100 MHz, CDCl₃) of band two showed absorptions at 3.1% (4H), due to the aromatic protons, a doublet centred at 5.55 (4H) and a doublet centred at 6.65 (2H) due to the complexed olefinic protons. Mass spectra: As with the iron complexes BCOTFe(CO)₃ and BCOTFe₂(CO)₆ successive loss of CO groups was observed followed
by fragmentation of the organic ligand. The intensities of the molecular ions were usually very weak. The fragmentation pattern, molecular ion and isotopic distribution in the molecular ion and its fragments were all used in identifying the various compounds. Isotopic distributions were obtained from the literature or calculated using program MASSPROG. These calculated distributions are shown in Figures 5.7 and 5.8. The distinct appearance of distributions containing Ru₂, RuFe and Fe₂ was particularly valuable for identifying the components in mixed bands.

BCOTRu(CO)₃ m/e 342 (molecular ion, 2%), 314 (-CO, 34%), 286 (-2CO, 22%), 258 (-3CO, 70%), 256 (65%), 128 (base peak, 100%). The predicted molecular ion for the complex (containing the most abundant ruthenium isotope ¹⁰²Ru) is at m/e 340 which indicates that the author's original assignment of the identity of this compound is incorrect, although the presence of an Ru(CO)₃ moiety is definitely established. Unfortunately the amount of compound available was so small that purification and further examination was not possible. Clearly the mass spectrum of authentic BCOTRu(CO)₃ is needed.

BCOTRu₂(CO)₆ m/e 526 and 525 (molecular ions for different isotopic combinations of Ru₂, both 9%), 498 (-CO, 55%), 470 (-2CO, 12%), 442 (-3CO, 68%), 414 (-4CO, 90%), 386 (-5CO, 41%), 358 (-6CO, 82%), 356 (base peak, 100%).

BCOTFeRu(CO)₆ m/e 480 (molecular ion, 4%), 452 (-CO, 30%), 424 (-2CO, 43%), 396 (-3CO, 29%), 368 (-4CO, base peak, 100%), 340 (-5CO, 62%), 312 (-6CO, 99%).
5.7 ISOTOPIC DISTRIBUTIONS FOR Fe₁, Fe₂ & RuFe

Fe₁

Relative Intensity

54  56  58  Mass No.

Fe₂

Relative Intensity

110 112 114 116  Mass No.

RuFe

Relative Intensity

152 154 156 158 160  Mass No.
5.8 ISOTOPIC DISTRIBUTIONS FOR Ru₁ & Ru₂

Ru₁

Ru₂
Reaction of BCOTFe(CO) 3 with Ru 3 (CO) 12

0.161 g (0.25 millimoles) of Ru 3 (CO) 12 and 0.222 g (0.75 millimoles) of BCOTFe(CO) 3 were mixed with 50 ml of benzene (some Ru 3 (CO) 12 remained undissolved) and the solution was refluxed under nitrogen for 58 hours. The resulting solution was filtered from a small amount of black precipitate which was washed with 15 ml of cold benzene. The combined filtrate and washings were evaporated to a small volume and chromatographed on a silica gel plate with petroleum ether. Five bands developed, the three slowest being collected. The first (slowest) band appeared to be a mixture of several orange, yellow and purple compounds. No further attempt was made to separate this mixture. The nmr and mass spectra of the mixture were very similar to that of the polynuclear compounds obtained from the reaction of BCOT with Fe 2 Ru(CO) 12. The second band (yellow) was identified as BCOTFe(CO) 3 from its mass spectrum. The third (yellow) band had a mass spectrum similar to that of the unidentified product from the reaction of BCOT with Fe 3 (CO) 12. Further analysis was not attempted because of the small amount of material available.
REFERENCES


76. J. Heberle, Nucl.Instr.& Methods, 58, 90 (1968).


98. J. Elix, private communication.


Appendix I

Notes on curve fitting program MOSFIT and its subroutines.

The program accepts data in the following manner:
Card one: number of data sets to be fitted.

The following cards occur for each set of data to be fitted.
Card two: comments on the spectrum etc.
Card three: values of various constants as follows:
   ICODE indicates start of data
   NOVER: number of overflows
   NPEAK: number of peaks
   CRIT: convergence criterion (usually $1.0 \times 10^{-4}$)
   ITER: maximum number of iterations allowed
   I_PLOT: plotting option 1 = no plot, 2 = plot of $YY(I)$
   (experimental counts/channel) and $G(I)$ (computed count/channel), 3 = plot of $YY(I)$ only.
   X AXIS: length of x axis for plotting
   Y AXIS: length of y axis for plotting
   SCALE: scaling factor for data (usually 1000)

Card four and after as required: initial estimates of baseline and dip, width, position for each peak in that order.

Paper Tape Data Input.

The tape inputs values of channel number for each tenth channel starting at channel 0 and counts/channel for each channel (channel 0 contains the number of sweeps of the memory of the analyser). The beginning of the tape contains a start of message (SOM) punch which the paper tape reader interprets.
as a question mark (?). The program reads this and immediately discards it.

Calculations - Main Program.

The program successively computes the matrices $J^*$, $J^*J^*$, $J^*'(Y - F^*)$, $(J^*J^*)^{-1}$ (see subroutines) and finally $(J^*J^*)^{-1}J^*'(Y - F^*)$.

Termination of the iterative procedure occurs when the maximum number of iterations allowed is used up or when

$$\text{TES} = \frac{\theta_1(n) - \theta_1(n-1)}{\theta_1(n)} < \text{CRIT}$$

$$\theta_1(n) = \text{value of } i\text{th parameter after } n \text{ iterations.}$$

$$\text{IPEAK} = 3\times N\text{PEAK} + 1$$

Calculations - Subroutines.

The real symmetric matrix $J^*J^*$ is to be inverted. The terms of $J^*J^*$ are input to these subroutines as the array $S(K)$.

MFACT finds the upper triangular matrix $R$ such that

$$(J^*J^*) = R'R$$

If $p_{ij}$ are the elements of $J^*J^*$ then the elements $r_{ij}$ of $R$ are given by

$$r_{1k} = \frac{p_{1k}}{r_{11}} \quad k = 1, 2, \ldots, n$$

$$r_{jk} = \frac{1}{r_{jj}} \left( p_{jk} - \sum_{i=1}^{j-1} r_{ij}r_{ik} \right) \quad j = 2, 3, \ldots, n$$

$$k = j, j+1, \ldots, n$$

UTRINV finds the inverse of $R$. If $r_{ik}$ are the elements of $R$ then the elements $r_{ik}$ of $R^{-1}$ are given by
\[
\bar{r}_{ik} = -\frac{1}{\bar{r}_{ii}} \left( \sum_{m=i+1}^{k} \bar{r}_{im} \bar{r}_{mk} \right) \quad i < k
\]

\[
\bar{r}_{ik} = \frac{1}{\bar{r}_{ii}} \quad i = k
\]

\[
\bar{r}_{ik} = 0 \quad i > k
\]

INSMAT computes the elements of \( J^* J^* : \- \)

\( (J^* J^*)^{-1} = (R'R)^{-1} = (R^{-1})(R')^{-1} = (R^{-1})(R^{-1})' \)

The elements \( \bar{p}_{ij} \) of \( (J^* J^*)^{-1} \) are given by

\[
\bar{p}_{ij} = \sum_{m=j}^{n} \bar{r}_{im} \bar{r}_{jm} \quad i = 1, 2, \ldots, n \quad j = i, i+1, \ldots, n
\]

Poor quality data, bad initial estimates or more often wrong scaling factor \( ISCALE \) usually cause the program to crash during calculations in the \( MFACT \) subroutine.
C MOESSBAUER CURVE FITTING
C FORMAT AND DIMENSION STATEMENTS

5 FORMAT (313, E8.1, 6X, I4, 21X, I2, 10X, 2F6.2, 1X, I5)
10 FORMAT (8(I2, F8.2))
15 FORMAT (I4, 10(1X, I6))
20 FORMAT (1H, 40H CHECK COMPATIBILITY OF DATA WITH PROGRAM)
25 FORMAT (I6)
30 FORMAT (1H, I6, 8X, F7.2, 6X, E15.6, 15X, E9.2)
35 FORMAT (1H1, 9H ITERATION, 4X, 11H CHI-SQUARED, 4X, 14H SUM OF SQUARES, 4X,
120HDIFFERENCE RATIO SUM)
40 FORMAT (1H, 18H INITIAL PARAMETERS)
45 FORMAT (1H0, 5H FINIS)
50 FORMAT (1I0, 31H CALCULATED VALUES OF PARAMETERS)
55 FORMAT (1H0, 28H CORRECTED INITIAL PARAMETERS)
60 FORMAT (1H, 12X, 9HBASELINE, F10.2, A2)
65 FORMAT (12A6)
70 FORMAT (1H1, 18H GENERAL COMMENTS, 12A6)
75 FORMAT (1H0, 50H PROGRAM IS FITTING LORENTZIANS TO 512 CHANNEL DATA)
80 FORMAT (1H, 10X, 3(F8.2, A2))
85 FORMAT (1H, 14X, 26HDIP WIDTH POSITION)
90 FORMAT (1H, 12X, 9H BASELINE, 4X, 13H PERCENT ERROR)
95 FORMAT (1H, 44H FIT HAS USED UP MAXIMUM NUMBER OF ITERATIONS)
100 FORMAT (1H, 5H CRIT=, E8.1, 14X, 5H ITER=, I4, 14X, 7H SCALE=, I6)
105 FORMAT (1H, 12X, 9HBASELINE, 4X, 13H PERCENT ERROR)
110 FORMAT (1H, 8X, F12.2, 6X, F7.2)
115 FORMAT (1H, 6H PEAK, 8X, 3H DIP, 5X, 13H PERCENT ERROR, 4X, 5H WIDTH, 2X, 13H PERCENT ERROR)
125 FORMAT (1H1, 5H INDEX, 4X, 11H EXPER. Y(I), 5X, 10H COMP. Y(I), 9X))
130 FORMAT (1H, 3(I3, 4X, F12.4, 2X, F12.4, 9X))
135 FORMAT (1H0, 4H PEAK, 2X, 11H PERCENT DIP, 7X, 4H AREA, 6X, 15H FRACTIONAL ARE

13EA)
140 FORMAT (1H, I3, 5X, F6.1, 3X, E15.6, 6X, F6.2)
145 FORMAT (1H, 12X, 9HBASELINE, 7X, 8H VARIANCE)
C START OF PROGRAM, DATA INPUT ROUTINE
READ (1,25) NUMBER
DO 470 NBR=1,NUMBER
READ (1,65) EXPLN
WRITE (3,70) EXPLN
READ (1,5) ICODE,NOVER,NPEAK,CRIT,ITER,IPLOT,XAXIS,YAXIS,ISCALE
KL=511
DO 200 I=1,KL
X(I)=FLOAT(I)
WRITE (3,100) CRIT,ITER,ISCALE
IPEAK=3*NPEAK+1
READ (1,10) (IFIXD(K),A(K),K=1,IPEAK)
DO 220 IP=1,IPEAK
CONST(IP)=BLANK
IF(IFIXD(IP).EQ.1)CONST(IP)=ASTRX
WRITE (3,40)
WRITE (3,60) A(l),CONST(l)
WRITE (3,85)
DO 225 IP=2,IPEAK,3
IP2=IP+2
WRITE (3,80) (A(L),CONST(L),L=IP,IP2)
WRITE (3,90)
READ (1,185)
DO 230 JI=0,510,10
JI9=JI+9
230 READ (1,15) JN,(IY(JM),JM=JI,J19)
235 IF (ICODE.EQ.111) GO TO 240
WRITE (3,20)
GO TO 475
240 IOVER=IOVER*1000000
245 A(1)=A(1)+FLOAT(IOVER/ISCALE)
250 WRITE (3,55)
WRITE (3,60) A(1),CONST(1)
WRITE (3,85)
DO 255 IP=2,IPEAK,3
255 WRITE (3,80) (A(L),CONST(L),L=IP,IP2)
DO 265 I=1,KL
260 DO 265 I=1,KL
265 Y(I)=IY(I)/FLOAT(ISCALE)+FLOAT(IOVER/ISCALE)
C EVALUATION OF PARTIAL DERIVATIVES
270 ITER=ITER+1
275 FN(I)=A(I)
DO 295 K2=2,IPEAK,3
K3=K2+1
K4=K2+2
280 Z=(2.0/A(K3))**2
W1=X(I)-A(K4)
G1=W1**2
U1=Z*G1+1.0
V1=U1**2
DO 285 K=K2,K4
IF(ABS(DFDA(K,I)).LE.1.E-18)DFDA(K,I)=0.
IF (DFDA(K,I).EQ.0.) GO TO 285
IF (ABS(DFDA(K,I)).GE.1.E-14) GO TO 285
IF (DFDA(K,I).GT.0.)DFDA(K,I)=1.0E-14
IF (DFDA(K,I).LT.0.)DFDA(K,I)=-1.0E-14
CONTINUE
FN(I)=FN(I)-(A(K2)/Ul)
CONTINUE
DO 305 I=1,KL
300 S(K)=0.0
305 DEltay(I)=Y(I)-FN(I)
K=0
DO 315 IP=1,IPEAK
DO 315 J=IP,IPEAK
IF (IFIXD(IP) .EQ.1) GO TO 315
IF (IFIXD(J).EQ .1) GO TO 315
K=K+1
DO 310 I=1,KL
310 S(K)=S(K)+DFDA(IP,I)*DFDA(J,I)
315 CONTINUE
C COMPUTATION OF ELEMENTS OF MATRIX Z
DO 325 IP=1,IPEAK
320 SUM=SUM+DELTAY(I)*DFDA(IP,I)
ZMAT(IP)=SUM
325 CONTINUE
IPAR=IPEAK
DO 330 IP=1,IPEAK
330 IPAR=IPAR-IFIXD(IP)
C INVERSION OF MATRIX P
CALL INSMAT (S,IPAR)
K=0
DO 345 IP=1,IPEAK
DO 345 J=1P,1PEAK
IF (IFIXD(IP).EQ.0.AND.IFIXD(J).EQ.0) GO TO 340
P(IP,J)=0.
P(J,IP)=P(IP,J)
GO TO 345
K=K+1
P(IP,J)=S(K)
P(J,IP)=P(IP,J)
CONTINUE
DO 355 IP=1,IPEAK
D(IP)=0.
IF (IFIXD(IP).EQ.1) GO TO 355
DO 350 K=1,IPEAK
D(IP)=D(IP)+P(IP,K)*ZMAT(K)
CONTINUE
DO 360 K=1,IPEAK
A(K)=A(K)+D(K)
C EVALUATION OF FITTED FUNCTION AND CHI-SQUARED TEST
TES=0
DO 370 K=1,IPEAK
TES=TES+ABS(D(K)/A(K))
CHI=0.
SQRS=0
DO 385 I=1,KL
FN(I)=A(I)
DO 380 K2=2,IPEAK,3
K3=K2+1
K4=K2+2
FN(I)=FN(I)-(A(K2)/(((2.0/A(K3))**2)*(X(I)-A(K4))**2+1.0))
SQRS=SQRS+(Y(I)-FN(I))**2
CHI=CHI+(Y(I)-FN(I))**2/FN(I)
MM=M-1
IF (M.GT.1) GO TO 390
WRITE (3,35)
WRITE (3,30) MM,CHI,SQRS,TES
IF (M.EQ.1) GO TO 400
IF (TES.LE.CRIT) GO TO 405
400 CONTINUE
C END OF ITERATION
WRITE (3,95)
WRITE (3,170)
WRITE (3,180)
DO 410 IP=1,IPEAK
P(J,IP)=P(IP,J)
WRITE (3,175) (P(IP,J),J=1,IPEAK)
WRITE (3,70) EXPLN
WRITE (3,50)
DO 415 K=1,IPEAK
ABC=511.0-FLOAT(IPEAK)
VAR(K)=P(K,K)*SQRS/ABC
WRITE (3,145)
WRITE (3,150) A(1),VAR(1)
WRITE (3,155)
DO 420 K=1,NPEAK
IM=3*K-1
IN=3*K+1
WRITE (3,160) K,(VAR(J),J=IM,IN)
WRITE (3,105)
WRITE (3,110) A(1),PERC(1)
WRITE (3,115)
DO 430 IP=1,NPEAK
K2=3*IP-1
K3=K2+1
K4=K2+2
WRITE (3,120) (IP,A(K2),PERC(K2),A(K3),PERC(K3),A(K4),PERC(K4))
AREA(25)=0.
DO 435 K=1,NPEAK
K2=3*K-1
K3=K2+1
AREA(K)=(A(K2)/A(1))*50.0*A(K3)*(2.129+1.0126)
AREA(25)=AREA(25)+AREA(K)
FR(K)=A(K2)*100.0/A(1)
DO 440 K=1,NPEAK
440 FRA(K)=AREA(K)*100.0/AREA(25)
WRITE (3,135)
WRITE (3,140) (K,FRA(K),AREA(K),FRA(K),K=1,NPEAK)
445 WRITE (3,165) IY(0)
DO 450 I=1,KL
K=KL+1-I
YY(I)=Y(K)
450 G(I)=FN(K)
455 WRITE (3,125)
DO 460 I=1,KL,3
I2=I+2
460 WRITE (3,130) (J,YY(J),G(J),J=I,I2)
C PLOTTING OPTIONS
IF (IPLOT.EQ.1) GO TO 470
DO 465 I=1,KL
YY(I)=YY(I)*100.0/A(1)
465 G(I)=G(I)*100.0/A(1)
CALL PLOTC (8,1,13.0,0)
C PLOT EXPERIMENTAL POINTS
CALL PLOT (0.5,0.5,-3)
CALL SCALE (X,XAXIS,KL,1)
CALL SCALE (YY,YAXIS,KL,1)
CALL AXIS (0.0,0.0,14HCHANNEL NUMBER,-14,XAXIS,0.0,X(KL+1),X(KL+2)
1)
CALL AXIS (0.0,0.0,20HPERCENT TRANSMISSION,20,YAXIS,90.00,YY(KL+1)
1,YY(KL+2))
CALL LINE (X,YY,KL,1,-1,13)
IF (IPLOT.EQ.3) GO TO 470
C PLOT COMPUTED FUNCTION
G(KL+1)=YY(KL+1)
G(KL+2)=YY(KL+2)
CALL LINE (X,G,KL,1,0,13)
CALL PLOT (0.0,0.0,999)
470 CONTINUE
475 WRITE (3,45)
CALL EXIT
END
SUBROUTINE INSMAT(S,IPAR)
C SUBROUTINE FOR MATRIX INVERSION
DIMENSION S(512)
IFUN(L,N)= (L-1)*IPAR-(L-1)*L/2+N
CALL MFACT(S,IPAR)
CALL UTRINV(S,IPAR)
DO 72 I= 1,IPAR
  DO 72 J= 1,IPAR
  IJ= IFUN(I,J)
  X= 0
  DO 71 M= J,IPAR
    IM= IFUN(I,M)
    JM= IFUN(J,M)
    71 X= X+S(IM)*S(JM)
  72 S(IJ)= X
RETURN
END
SUBROUTINE MFACT(S,IPAR)
C SUBROUTINE FOR FACTORIZATION OF POSITIVE DEFINITE SYMMETRIC MATRIX
DIMENSION S(512)
IFUN(L,N) = (L-1)*IPAR-(L-1)*L/2+N
S(1) = SQRT(S(1))
IF (IPAR.EQ.1) RETURN
X = 1./S(1)
DO 81 J = 2,IPAR

S(J) = S(J)*X
DO 84 K = 2,IPAR
KK = IFUN(K,K)
KM = K-1
DO 82 I = 1,KM
IK = IFUN(I,K)

S(KK) = S(KK)-S(IK)**2
IF (S(KK).LE.16) GO TO 85
S(KK) = S(KK)/10000
S(KK) = 100*SQRT(S(KK))
GO TO 86

S(KK) = SQRT(S(KK))
IF (K.EQ.IPAR) RETURN

KN = K+1
DO 84 L = KN,IPAR
KL = IFUN(K,L)
KO = K-1
DO 83 I = 1,KO
IK = IFUN(I,K)
IL = IFUN(I,L)

S(KL) = S(KL)-S(IK)*S(IL)
S(KL) = S(KL)/S(KK)
RETURN
END
SUBROUTINE UTRINV(S,IPAR)
C SUBROUTINE FOR INVERSION OF UPPER TRIANGULAR MATRIX
DIMENSION S(512)
IFUN(L,N) = (L-1)*IPAR-(L-1)*L/2+N
DO 94 J= 1,IPAR
KO= IFUN(J,J)
94 S(KO) = 1./S(KO)
IF (IPAR.EQ.1) RETURN
IIPAR = IPAR-1
DO 93 LM= 1, IIPAR
K= IPAR+1-LM
KN= K-1
DO 93 MM= 1,KN
J= K-MM
JK= IFUN(J,K)
X= 0
JO= J+1
DO 92 M= JO,K
JM= IFUN(J,M)
MK= IFUN(M,K)
92 X= X+S(JM)*S(MK)
JJ= IFUN(J,J)
93 S(JK)= -S(JJ)*X
RETURN
END
Appendix II

Notes on the Lorentzian function calculation program MOSFUN.

MOSFUN calculates the composite Lorentzian function for two peaks

\[ f(x) = B - \left( \frac{a_{21}}{\left( \frac{2}{a_{31}} \right)^2 (x - a_{41})^2 + 1} + \frac{a_{22}}{\left( \frac{2}{a_{32}} \right)^2 (x - a_{42})^2 + 1} \right) \]

where baseline B, linewidths \( a_{31} \) and \( a_{32} \) and position of peak 1, \( a_{41} \), are fixed data input. Sets of the integral values of \( f(x) \) are calculated as the position of peak 2, \( a_{42} \), is allowed to increment.
C COMPUTATION OF COMPOSITE LORENTZIAN FUNCTION FOR TWO PEAKS
C PEAK PARAMETERS ARE GIVEN AS DATA EXCEPT FOR POSITION OF PEAK 2
C POSITION OF PEAK 2 IS THE INDEX J

11 FORMAT (6F10.2)
21 FORMAT (514)
31 FORMAT (1H1, 30HINTEGER VALUES OF F(I) FOR J= , I4)
41 FORMAT (1H )
51 FORMAT (1H , 14, 10(1X,I6))
61 FORMAT (1H1, 8X, 15HPEAK PARAMETERS)
71 FORMAT (1H0, 10X, 12HBACKGROUN= , F10.2)
81 FORMAT (1H , 10X, 26HDIP WIDTH POSITION)
91 FORMAT (1H , SX, F10.2, 4X, FS.2, SX, F6.2)
101 FORMAT (1H0, 8X, 14HINPUT J VALUES)
111 FORMAT (1H , 8X, 8HISTART= ,14, 5X, 6HIEND= ,14, 5X, 6HINCR= ,14)

DIMENSION F(520),X(520),W(520),IVALUE(520),A(6)

C START OF PROGRAM
READ (1,11) (A(K), K= 1,6)
READ (1,21) !START, IEND, INCR
WRITE (3,61)
WRITE (3,71) A(1)
WRITE (3,81)
DO 200 I= 2,5,3
12= I+2
200 WRITE (3,91) (A(K), K= I,12)
WRITE (3,101)
WRITE (3,111) ISTART, IEND, INCR

C CALCULATION OF F(I)
IIEND=(IEND-ISTART)/INCR+1
DO 302 M= 1,IIEND
J= ISTART+(M-1)*INCR
DO 300 I= 1,511
X(I)= FLOAT(I)
W(M)= FLOAT(J)
Z1= (2.0/A(3))**2
Z2= (2.0/A(6))**2
Gl = (X(I) - A(4))^2
G2 = (X(I) - W(M))^2
Ul = Z1*Gl + 1.0
U2 = Z2*G2 + 1.0
F(I) = A(1) - (A(2)/Ul + A(5)/U2)

300 IVALUE(I) = IFIX(F(I))
IVALUE(0) = 0
WRITE (3, 31) J
WRITE (3, 41)
DO 302 I = 0, 510, 10
I9 = I + 9
302 WRITE (3, 51) I, (IVALUE(K), K = I, I9)
CALL EXIT
END
Notes on the mass spectra isotope peak intensity calculation program MASSPROG.

The program calculates relative peak intensities for the molecular combinations Ru$_2$ and RuFe, assuming the remainder of the molecule is monoisotopic. Data input are the relative abundances for ruthenium and iron isotopes. Output are the relative peak intensities for all the possible mass number combinations $I$ of Ru$_2$ or RuFe, the lowest mass number combination being assigned a value of $I$ equal to zero.
GCM651*MASSPROG.MAIN
1    C PROGRAM FOR CALCULATION OF MASS SPECTRUM PEAK INTENSITIES FOR RU2, RUFE
2    5                  FORMAT (12)
3    10                 FORMAT (9F6.2)
4    15                 FORMAT (5F6.2)
5    20                 FORMAT (1H,9(I2,1X,F6.2,1X,I2,1X))
6    25                 FORMAT (1H,5(I2,1X,F8.2,1X,I2,1X))
7    30                 FORMAT (1H,9(I1X,1HK,2X,5HRU(K),1X,2HLM,1X))
8    35                 FORMAT (1H,5(I1X,1HK,2X,7HRUFE(K),1X,2HMM,1X))
9    40                 FORMAT (1H,5X,F8.2,4X,12)
10   45                 FORMAT (1H0,10X,3HSUM,5X,1HI)
11    DIMENSION ARU(9), AFE(5), LM(81), RU(81), MM(45), RUFE(45)
12    READ (1,5) ISPEC
13       IF (ISPEC.EQ.2) GO TO 70
14    READ (1,10) (ARU(I), I=0,8)
15    WRITE (3,30)
16       DO 55 I=0,8
17       DO 50 J=0,8
18       L=9*(I+1)-8+J
19       LM(L)=I+J
20       50             RU(L)=ARU(I)*ARU(J)
21       L1=9*(I+1)-8
22       L2=9*(I+1)
23       55             WRITE (3,20) (K, RU(K), LM(K), K=L1, L2)
24    WRITE (3,45)
25       DO 65 I=0,16
26       SUM=0.0
27       DO 60 J=1,81
28       IF (I.EQ.LM(J)) SUM=SUM+RU(J)
29       60           CONTINUE
30       65             WRITE (3,40) SUM, I
31       IF (ISPEC.EQ.1) GO TO 95
32    70             READ (1,15) (AFE(I), I=0,4)
33    WRITE (3,35)
34       DO 80 I=0,8
35       DO 75 J=0,4
36       L=5*(I+1)-4+J
W.1(L) = I + J
RUFE(L) = ARU(I) * AFE(J)
L1 = 5 * (I+1) - 4
L2 = 5 * (I+1)
WRITE (3, 25) (K, RUFE(K), MM(K), K=L1, L2)
WRITE (3, 45)
DO 90 I = 0, 12
SUM = 0.0
DO 85 J = 1, 45
IF (I .EQ. MM(J)) SUM = SUM + RUFE(J)
CONTINUE
WRITE (3, 40) SUM, I
CALL EXIT
END