

UNCLASSIFIED

AD NUMBER
AD825158
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; Oct 1967. Other requests shall be referred to Air Force Materials Laboratory, Attn: MAYA, Wright-Patterson AFB, OH 45433.
AUTHORITY
AFSC/USAF ltr, 1 Jun 1972

THIS PAGE IS UNCLASSIFIED

AFML-TR-67-238
AD0825158

OFFICIAL FILE COPY

AN INFRARED AND RAMAN STUDY OF 1,1'-DISUBSTITUTED FERROCENE COMPOUNDS

J. N. WILLIS, JR., M. T. RYAN,
F. L. HEDBERG, and H. ROSENBERG

TECHNICAL REPORT AFML-TR-67-238

OCTOBER 1967

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Air Force Materials Laboratory (MAYA), Wright-Patterson Air Force Base, Ohio 45433.

AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO



BEST AVAILABLE COPY

20040302139

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

AN INFRARED AND RAMAN STUDY OF 1,1'-DISUBSTITUTED FERROCENE COMPOUNDS

*J. N. WILLIS, JR., M. T. RYAN,
F. L. HEDBERG, and H. ROSENBERG*

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Air Force Materials Laboratory (MAYA), Wright-Patterson Air Force Base, Ohio 45433.

FOREWORD

This report was prepared by the Analytical Branch, Materials Physics Division, Air Force Materials Laboratory. The work was initiated under Project No. 7367, "Experimental Techniques for Materials Research," Task No. 736702, "Physical-Chemical Methods for Materials Analysis," and administered by the Air Force Materials Laboratory, Directorate of Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, Lt. J. N. Willis, Jr., Project Engineer in conjunction with the Nonmetallics Division, Polymer Branch, (Dr. H. Rosenberg and Dr. F. L. Hedberg).

This report covers work performed from June 1966 to July 1967. The manuscript was released by the authors in July 1967 for publication.

This technical report has been reviewed and is approved.



FREEMAN F. BENTLEY
Chief, Analytical Branch
Materials Physics Division
Air Force Materials Laboratory

ABSTRACT

The infrared ($4000-55\text{ cm}^{-1}$) and Raman ($3200-75\text{ cm}^{-1}$) spectra of 1,1'-dibromo-, 1,1'-diiodo-, and 1,1'-dichloroferrocene are reported. An attempt is made to give a complete vibrational assignment for all fundamental vibrations of these molecules. The results of these assignments are compared to those of 1,1'-dimethylferrocene (Reference 2) and of monosubstituted benzenes (References 3, 10). The assigned frequencies were tested by utilizing the inequality rule of Whiffen and Steele.

This abstract has been approved for public release; its distribution is unlimited.

TABLE OF CONTENTS

SECTION	PAGE
I INTRODUCTION	1
II INFRARED SPECTRA	1
III RAMAN SPECTRA	2
IV EXPERIMENTAL	3
V INTERPRETATION	4
1. Class a_1	4
2. Class b_1	6
3. Class b_2	7
4. Class a_2	7
VI RING-METAL VIBRATIONS	8
VII RESULTS	9
REFERENCES	11

LIST OF ILLUSTRATIONS

FIGURE	PAGE
1. Infrared Spectrum of Liquid Film of 1,1'-Dichloroferrocene	19
2. Infrared Spectrum of Liquid Film of 1,1'-Dibromoferrocene	19
3. Infrared Spectrum of Liquid Film of 1,1'-Diiodoferrocene	19
4. Far Infrared Spectrum of 1,1'-Dibromoferrocene	20
5. Far Infrared Spectrum of 1,1'-Diiodoferrocene	21
6. Raman Spectra of Single Crystal 1,1'-Dichloroferrocene	22
7. Ring-Metal Tilting Vibration	23
8. Ring-Metal Stretching Vibration	23

TABLE

I Observed Vibrational Spectra of 1,1'-Dichloroferrocene	12
II Observed Vibrational Spectra of 1,1'-Dibromoferrocene	14
III Observed Vibrational Spectra of 1,1'-Diiodoferrocene	16
IV Assigned Frequencies Utilizing the Steele and Whiffen Inequality Rule	18

SECTION I

INTRODUCTION

The aromatic nature of metal cyclopentadienyl compounds has been a subject of discussion in the literature over the past several years. Lippincott and Nelson (Reference 1) have assigned the vibrational spectra of ferrocene and ruthenocene and compared the aromatic nature of ferrocene with benzene and tropylium ion. Bailey and Lippincott (Reference 2) have assigned the vibrational spectrum of 1,1'-dimethylferrocene and have compared the changes between the ferrocene-dimethylferrocene spectra with the benzene-toluene spectral changes.

The recent development of laser excitation has made accessible the previously difficult-to-obtain Raman spectra of colored ferrocene compounds. Also, the 1,1'-dichloro-, dibromo-, and diiodoferrocenes have recently been synthesized as part of a research program in this laboratory to develop ferrocene polymers. We have recorded the infrared and Raman spectra of these compounds and report here the vibrational assignment of the observed frequencies. A comparison of these assignments with the work of Whiffen (Reference 3) on the vibrational spectra of halobenzenes as well as the Bailey and Lippincott assignment of 1,1'-dimethylferrocene has provided some additional information on the aromatic nature of the cyclopentadienyl ring in ferrocene.

SECTION II

INFRARED SPECTRA

The infrared spectra were obtained over the range $55\text{--}4000\text{ cm}^{-1}$. The $55\text{--}350\text{ cm}^{-1}$ region was investigated using the Perkin-Elmer model 301 grating spectrophotometer. The $250\text{--}4000\text{ cm}^{-1}$ region was investigated using Perkin-Elmer model 521 and model 225 grating spectrophotometers. Atmospheric water vapor was removed from the various instruments by flushing with dry nitrogen. In the higher wavenumber region, the instruments were calibrated in the usual manner (Reference 4). The lower region was calibrated using atmospheric water vapor (Reference 5).

Liquid cells with CsI plates and various spacers were used to obtain the spectra of the three compounds in approximately 10% solutions of carbon disulfide and carbon tetrachloride. Infrared spectra were also recorded on liquid films of the three compounds using CsI plates. The spectra of the liquid films were almost identical to those observed for the solutions. Certain exceptions to this will be discussed later. To obtain liquid films of the 1,1'-dichloro- and dibromoferrocenes, it was necessary to use a small coil of nichrome wire heated by means of a Variac to just above the melting points of the compounds. The spectra of solid 1,1'-dichloroferrocene was obtained by heating the compound as discussed above and slowly lowering the temperature until the compound crystallized.

The spectra of all the compounds as saturated and dilute solutions in cyclohexane were recorded from 350 to 55 cm^{-1} . Liquid cells with polyethylene windows and a path length of about 1.0 mm were used in this region. The far infrared spectra of solid 1,1'-dibromoferrocene was obtained using 20 mg of sample in a matrix of 200 mg of low density polyethylene.

The frequency measurements reported for the region 4000-250 cm^{-1} were made from the expanded scale spectra of the liquid films and solutions. Figures 1 to 3 show typical infrared spectra of liquid films of the three samples from 4000-200 cm^{-1} . Figures 4 to 5 show the infrared spectra from 350 to 55 cm^{-1} of 1,1'-dibromo- and diiodoferrocene. Due to the limited amount of 1,1'-dichloroferrocene available, the far infrared spectrum was very poor. For this reason, it is not included. The measured frequencies are listed in Tables Ia, Ib, and Ic. These frequencies are believed to be accurate to $\pm 2 \text{ cm}^{-1}$ for the sharp bands and $\pm 4 \text{ cm}^{-1}$ for the weak bands.

SECTION III

RAMAN SPECTRA

The Raman spectra of the 1,1'-dichloro-, 1,1'-dibromo-, and 1,1'-diiodoferrocenes were investigated using a Perkin-Elmer model LR-1 spectrometer equipped with a Spectra Physics Model 125 helium-neon laser. All spectra were observed using 6328⁰A excitation with an estimated intensity of 50 mw. The spectra for 1,1'-dibromo- and 1,1'-diiodoferrocene were obtained in saturated solutions of benzene or carbon tetrachloride using a 0.2 ml multipass quartz cell. The spectra obtained from 1,1'-dichloroferrocene were taken using a small single crystal. Quite drastic changes were noted in certain bands in the spectrum when the crystal was rotated (Figure 6). All quoted frequencies were obtained with the Raman energy passing along the "A" axis. This sample was less pure than used for the infrared spectra. Since the Raman data for 1,1'-dibromo- and 1,1'-diiodoferrocene were obtained from solutions and the 1,1'-dichloroferrocene frequencies were taken from a single crystal, some shifts in frequency position are expected. The frequencies are expected to be accurate to $\pm 2 \text{ cm}^{-1}$ for the strong bands and $\pm 4 \text{ cm}^{-1}$ for the weak or broad bands.

SECTION IV

EXPERIMENTAL

1,1'-dichloroferrocene was prepared by a modification of the method of Nefedov and Nefedova (Reference 6) from 1,1'-bis(chloromercuri)ferrocene and cupric chloride with aqueous tetrahydrofuran as solvent in 18% yield. Purification by preparative vapor phase chromatography (V.P.C) afforded crystals with melting point 80° to 81°C of 99+% purity by V.P.C. analysis.

1,1'-dibromoferrocene was prepared by the method of Nesmeyanov et al (Reference 7) from ferrocenyl-1,1'-diboronic acid and cupric bromide. Purification by crystallization from hexane afforded material of melting point 54° to 56°C which was found to be 99% pure by V.P.C. analysis.

1,1'-diiodoferrocene was prepared by a modification of the method of Fish and Rosenblum (Reference 8) from 1,1'-bis(chloromercuri)ferrocene and 1,3-diiodo-5, 5-dimethylhydantoin with tetrahydrofuran as solvent in 50% yield. Purification by preparative V.P.C. afforded liquid 1,1'-diiodoferrocene of 99% purity by V.P.C. analysis. 1,1'-diiodoferrocene was found to degrade in the presence of copper or iron at elevated temperature (>170°C). This made it necessary to use an all glass-Teflon V.P.C. column. The column which was 3/8-in. O.D. and 1.5 ft in length, was packed with 10% Apiezon L on firebrick. Samples were injected directly onto the column which was held at 160°C. The purity of the 1,1'-diiodoferrocene was found to be 99% by V.P.C analysis.

When the purity of the 1,1'-disubstituted ferrocenes was very high (99.9%), there was a complete absence of the 1105 cm^{-1} band. The presence of this band in several of the compounds thought to be very pure led us to further check on the sample. Mass spectral data revealed that the impurity was a 1,2- or a 1,3-dihalogenated ferrocene. Thus far, we have been unable to remove this impurity from the samples in use.

SECTION V

INTERPRETATION

It is a good assumption that there is no interaction between rings of the disubstituted compound. Thus it becomes possible to interpret the ring modes of these compounds in terms of only one substituted ring. An isolated monosubstituted cyclopentadienyl ring where the substituent is considered a point group has C_{2v} symmetry. This would allow twenty-four fundamental modes ($8a_1 + 7b_1 + 3a_2 + 3b_2$) and three C-X modes ($a_1 + b_1 + b_2$). The assignment of these fundamentals is aided if one compares them to similar modes found in A the cyclopentadienyl rings of ferrocene and B the monosubstituted benzenes.

The compounds of primary interest in this study were 1,1'-dichloro-, 1,1'-dibromo-, and 1,1'-diiodoferrocene. All reference to 1,1'-disubstituted ferrocene compounds shall simply be referred to as "disubstituted". However, the spectra of two other 1,1'-disubstituted ferrocenes were also found to be helpful in this study. The compounds were 1,1'-dimethylferrocene and 1,1'-ferrocenedialdehyde. The dimethyl compound has been studied by Bailey and Lippincott (Reference 2) and the Raman frequencies quoted here are taken from that work. The approximate description of the fundamental vibrations is to be discussed by class.

CLASS a_1

Two a_1 and two b_1 C-H stretching modes are expected. The highest C-H stretching mode in ferrocene was found at 3099 cm^{-1} . This should give rise to an a_1 C-H stretching mode in the disubstituted compounds. The band found at 3110, 3105, and 3100 cm^{-1} is assigned to this mode. The degenerate C-H stretching modes observed in ferrocene at 3085 cm^{-1} should give rise to one a_1 and two b_1 C-H stretching modes. These are assigned to the bands at 3090, 3085, and 3080 cm^{-1} in the disubstituted haloferrocenes. There should be two a_1 and two b_1 C-C stretches in the substituted ferrocenes. These four modes arise from the ferrocene C-C stretching modes assigned to the band at 1560 cm^{-1} and the bands at $1408\text{-}1411\text{ cm}^{-1}$ (Reference 1). The two a_1 modes in the substituted compounds would be expected to appear as strong bands in the Raman spectrum. The Raman spectrum of dibromoferrocene shows four bands between $1350\text{ and }1410\text{ cm}^{-1}$, the two higher frequency bands being of greater intensity than the lower frequency bands. The Raman spectrum of diiodoferrocene shows two bands of medium intensity at 1404 and 1371 cm^{-1} . The Raman spectrum of dichloroferrocene also has two bands in this region at 1416 and 1384 cm^{-1} . No consistent infrared bands between $1450\text{ and }1600\text{ cm}^{-1}$ are observed for the dihalo compounds studied. However, a series of strong bands are found at lower frequencies between $1320\text{ and }1420\text{ cm}^{-1}$. These observations led to the consideration of reassigning the C-C stretching modes in ferrocene.

In support of this, several facts are presented:

1. The only reason used in assigning the $E_{2u} - E_{2g}$ C-C stretching modes in ferrocene to the weak band at 1560 cm^{-1} was the analogy to the similar mode in benzene. This band was not found in the spectra of ruthenocene or nickelocene (Reference 2).

2. There are weak bands in the Raman spectra of ferrocene and ruthenocene at 1356 cm^{-1} and 1360 cm^{-1} which could be assigned to these modes (Reference 1). This band was described as a combination band of $\omega_4 + \omega_{25}$ by Lippincott and Nelson. This combination predicts a band at 1353 cm^{-1} in ferrocene and at 1386 cm^{-1} in ruthenocene. The disagreement between calculated and observed values for this assignment in ruthenocene is clearly so large as to be suspect.

3. There is a similar band found in the Raman spectrum of cyclopentadienyl-Manganese tricarbonyl at 1365 cm^{-1} (Reference 9). However, no band is found in the Raman spectrum of this compound around 1560 cm^{-1} .

4. As stated above, a series of bands is found in the spectra of the dihalo compounds between 1410 and 1326 cm^{-1} (Table I). The Raman and infrared spectra indicate the presence of four fundamentals in this region.

This evidence has persuaded us to reassign the $E_{2g} - E_{2u}$ modes in ferrocene to 1356 cm^{-1} which is below the $E_{1g} - E_{1u}$ modes at 1408 and 1411 cm^{-1} . It follows that the highest a_1 mode in the dihalo series is assigned to the band at 1417 , 1410 , and 1402 cm^{-1} . The other a_1 mode is assigned to the band at 1385 , 1380 , and 1378 cm^{-1} , respectively. The two b_1 modes are assigned to the series 1360 , 1355 , and 1345 cm^{-1} and 1349 , 1342 , and 1326 cm^{-1} . To further this argument, a close study of analogous benzene modes was made. In the chloro-, bromo-, and iodobenzene series, four C-C stretching modes are observed. The two highest modes are observed around 1600 cm^{-1} as a strong band with an associated shoulder. In the case of benzaldehyde, the adjacent carbonyl group splits the two high frequency modes into bands of medium intensity. In 1,1'-ferrocenedialdehyde, the same splitting and enhancement of intensity is observed but not in the case of two lower modes (1370 and 1332 cm^{-1}).

The next a_1 mode closely resembles the vibration Whiffen calls "q" in monosubstituted benzene (Reference 3). In toluene (Reference 10) and in the halobenzenes (Reference 3), the bands Whiffen describes as "q" and "r" are found to interact to a considerable extent. These bands are a_1 modes and are X-sensitive. They arise from (A) the ring breathing and (B) C-X stretching modes. Since both of these modes involve considerable C-X stretching, they can no longer be adequately described as (A) or (B). They are better described as X-sensitive a_1 modes. The same phenomenon is found in substituted ferrocenes. The highest mass-sensitive band in the substituted ferrocenes is found at 1170 , 1152 , and 1142 cm^{-1} for

the halogen series and at 1229 cm^{-1} in dimethylferrocene (Reference 2). The next X-sensitive band of sufficient intensity in the infrared and Raman to be assigned to an a_1 fundamental is found at 884, 872, and 865 cm^{-1} in the halogen series. Lippincott and Bailey assigned this mode to the band at 1021 cm^{-1} in dimethylferrocene. The 1020 cm^{-1} band was found to be non-X-sensitive in the halogen series. The more likely choice for this assignment in dimethylferrocene is the band at 919 cm^{-1} .

The two a_1 C-H in-plane deformations which arise from the ferrocene modes at 1178 and 1002 cm^{-1} are expected close to these frequencies. The highest a_1 C-H deformation is assigned to the bands at 1178, 1178, and 1175 cm^{-1} in the halogen series due to their strength in the infrared and Raman spectra. The other a_1 mode is assigned to the strong band observed at 1020 cm^{-1} in the compounds studied. This leaves but one a_1 vibration. This mode arises from an E_{2g} ring distortion predicted to be at 880 cm^{-1} in ferrocene. There are three choices for this mode: a series of weak bands at 850 cm^{-1} , a series of strong bands around 820 cm^{-1} , or a series of strong-to-medium bands around 805 cm^{-1} . The band found around 820 cm^{-1} is best assigned to a b_2 C-H deformation due to its strength in the infrared. The Raman spectrum of diiodoferrocene and dichloroferrocene have bands at 847 and 833 cm^{-1} , respectively, but no bands around 800 cm^{-1} . The a_1 ring distortion is assigned to the bands around 850 cm^{-1} for the dihalo series. This agrees with the assignment in the case of dimethylferrocene. The 805 cm^{-1} series are best assigned to an a_2 C-H deformation. This band is found to be rather strong in the compounds studied. This vibration in dimethylferrocene was assigned to a band at 833 cm^{-1} which is also rather strong. It is unusual to find an a_2 fundamental so strong in the infrared spectrum. However, the appearance of this band is essentially unchanged from that in ferrocene where it appears as a shoulder on the strong 811 cm^{-1} band. The Steele and Whiffen inequality rule (Reference 11) was a great aid in this assignment (see Results for an explanation of this rule).

CLASS b_1

Four b_1 modes have already been discussed. Of the remaining four modes, the highest arises from the A_{2g} C-H deformation in ferrocene which is predicted to be at 1200 cm^{-1} . A weak band is observed at about 1205 cm^{-1} in all compounds studied which is assigned to the expected C-H deformation. The b_1 C-H deformation mode arising from the 1178 cm^{-1} mode in ferrocene is assigned to the bands found at 1153 cm^{-1} in the halogen series. The next mode arises from the 1010 cm^{-1} band in ferrocene. This mode is only directly observed in the spectrum of dibromoferrocene at 878 cm^{-1} . The corresponding band in dichloroferrocene is probably hidden by the strong band at 884 cm^{-1} . A band is observed at 883 cm^{-1} in the spectrum of the liquid film of diiodoferrocene which is probably the same vibration shifted somewhat due to the change in phase. This leaves one b_1 fundamental, an X-sensitive

mode which approximates a C-X in-plane bending. This arises from a C-H deformation found in ferrocene at 1010 cm^{-1} . The corresponding benzene frequencies are found at 297, 254, and 200 cm^{-1} (Reference 3). The band in the substituted ferrocenes is found at 251, 237, and 202 cm^{-1} .

CLASS b_2

The highest mode in this class arises from a C-H deformation at 1050 cm^{-1} in ferrocene. This mode is assigned to the strong bands between 1014 and 1010 cm^{-1} in this series. The ring deformation mode in ferrocene predicted to be at 500 cm^{-1} should give rise to a b_2 X-sensitive mode. In the substituted halobenzenes, this mode is assigned to bands at 457, 460, and 450 cm^{-1} . Lippincott and Bailey assign this mode at 632 cm^{-1} in dimethyl ferrocene. There are weak bands at 430, 421, and 402 cm^{-1} in the dihaloferrocene series which could be assigned to this mode. However, these are weak infrared bands and appear to be rather low in frequency for this assignment. This mode may be obscured by the intense bands associated with the ring-metal modes discussed below. The lowest b_2 mode is an X-sensitive mode approximately described as an out-of-plane C-X deformation. The corresponding bands for the chloro-, bromo-, and iodobenzene are found at 196, 181, and 166 cm^{-1} . This mode is assigned to the band at 225 in dichloro-, 206 in dibromo-, and 180 cm^{-1} in diiodoferrocene. The bands in dichloro- and dibromo- derivatives were only observed in the spectrum of the solid.

CLASS a_2

Although these bands are forbidden in the infrared spectrum, they are quite often observed in the spectrum of the liquid and solid. The mode occurring at the highest frequency is a C-H deformation arising from the 1050 cm^{-1} band in ferrocene. Weak bands found around 1050 cm^{-1} are assigned to this mode. The second a_2 vibration arises from the 834 cm^{-1} ring distortion in ferrocene and has already been discussed. The last a_2 mode is a ring deformation arising from the band in ferrocene estimated to be at 500 cm^{-1} . The mode is assigned to weak bands at 605, 599, and 592 cm^{-1} . This seems to indicate that the original estimate of 500 cm^{-1} for ferrocene is too low in this case.

SECTION VI

RING-METAL VIBRATIONS

The assignment of the ring-metal modes is aided by comparison with ferrocene. The "sandwich" compounds should have five infrared and Raman active modes; a symmetric and antisymmetric stretch, a symmetric and antisymmetric tilt and a bend. In this series of molecules, the possibility of more than one isomer exists. If the molecule existed in the trans form, the symmetry would be C_{2h} . This would preclude coincidences between infrared and Raman frequencies due to the ring-metal modes. The other isomers, two gauche forms and a cis form are of lower symmetry and selection rules allow coincidences for the ring-metal mode. Since coincidences are observed, one can assume that the molecules do not exist solely in the trans form. This evidence does not allow one to conclude that any one of the isomers is the predominant form.

The tilting modes are degenerate in ferrocene and the reduction in symmetry in the substituted compounds should split these modes. The symmetric ring tilt is found at 388 cm^{-1} in ferrocene. This mode is assigned to the bands at 390, 327-323, and $283\text{--}272\text{ cm}^{-1}$. The expected splitting is observed only in the dibromo- and diiodoferrocene. By analogy to ferrocene, the R-M antisymmetric tilt is assigned to 513, 498, and 490 cm^{-1} . The expected splitting was not observed in this mode.

The R-M antisymmetric stretch is found at 491, 488, and 483 cm^{-1} . In diiodoferrocene run as a film of the pure liquid the antisymmetric tilt and stretch appear as a broad band at 490 cm^{-1} . In CS_2 solution, splitting of these modes is observed. The symmetric ring-metal stretch is found at 303 cm^{-1} in ferrocene. The corresponding bands in the substituted compounds are expected to be very strong in the Raman spectra. Dichloro-, dibromo-, and diiodoferrocene have very strong bands in the Raman spectra at 344, 343, and 326 cm^{-1} which are assigned to this mode. The "low" frequency in the case of dichloroferrocene may be due to the different states from which the frequencies were obtained.

The last mode to be assigned is the ring-metal-ring bending. This mode was observed in our laboratory at 170 cm^{-1} in ferrocene (in cyclohexane solution). A band is found at 171 cm^{-1} in all of the dihalo compounds and is assigned to this mode.

SECTION VII

RESULTS

During this investigation, several bands in the infrared spectra were found to be phase sensitive. This was particularly obvious in the case of the ring-metal vibrations. The antisymmetric ring tilting vibration of dichloroferrocene was found at 513 cm^{-1} in solution, 502 cm^{-1} in the melt, and split into two bands at 500 and 510 cm^{-1} in the solid. This band is observed at 504 cm^{-1} in dibromoferrocene and at 490 cm^{-1} in diiodoferrocene in CS_2 solution. The symmetric ring-metal tilting and antisymmetric ring-metal stretching were also found to follow this pattern of shifting with changes in phase. The symmetric ring-metal stretching was not observed in dichloroferrocene, but in dibromoferrocene it also appears to shift with changes in phase.

A comparison of the solution spectra of the dihaloferrocenes indicates that all of the ring-metal vibrations shift to lower frequency from dichloro- to dibromo- to diiodoferrocene with the exception of the ring-metal-ring bending which was found at 171 cm^{-1} in all the compounds studied. The symmetric and antisymmetric ring tilting vibrations show a linear dependence on the square root of the reduced mass of $\text{Fe-C}_5\text{H}_4\text{-X}$, where X is the halogen (Figure 7). The antisymmetric and symmetric ring-metal stretching vibrations vary linearly as the electronegativity of the halogen (Figure 8).

As a result of this investigation and other studies, previous conclusions concerning the force constants of ferrocene seem to be questionable. A recent electron diffraction study of ferrocene (Reference 12) indicated that the C-H bonds in ferrocene are bent 5° out of the plane of the carbon ring towards the metal atom. The C-C bond length of $1.431\text{ \AA}$ calculated from the electron diffraction study is somewhat longer than the C-C bond length in benzene ($1.39\text{ \AA}$). A study of the cyclopentadienide anion by Sado et al (Reference 13) reports lower frequencies in the C_5H_5 ring for two of the C-C stretching modes than assigned in the C_5H_5 ring in ferrocene by Lippincott and Nelson (Reference 1). The anion has D_{5h} symmetry and the A_1' , E_1' , and E_2' C-C stretches were assigned at 983 , 1455 , and 1447 cm^{-1} , respectively. The comparable frequencies from the work of Lippincott and Nelson are 1105 , 1411 , and 1560 cm^{-1} , respectively. Yet normal coordinate analyses based on these widely different assignments for a C_5H_5 ring both yield force constants which indicate an aromatic C-C linkage. Our results on the dihaloferrocenes indicate agreement with the 1105 and 1411 cm^{-1} assignments but show a much lower frequency for the third C-C stretching mode. These facts indicate that a reexamination of the force constants for bonds in ferrocene is needed.

Since it is virtually impossible to get good vapor spectra of these compounds and at present no Raman polarization data are available, other means of checking the assignments

are needed. One method which has proven useful in other similar studies has been the use of the inequality rule of Steele and Whiffen (Reference 11). This rule states that any frequency, ν_j , of the lighter molecule has to be higher in frequency than the ν_{j+1} frequency of the heavier molecule. This, combined with the normal rule that for similar vibrations the ν_j frequency of the heavier molecule cannot be higher than the ν_j frequency of the lighter molecule, means that frequency ranges can be given for each vibration. The use of the inequality rule is shown in Table IV.

REFERENCES

1. E. R. Lippincott and D. R. Nelson, *Spectrochim. Acta*, 10, 307 (1958).
2. R. T. Bailey and E. R. Lippincott, *Spectrochim. Acta*, 21, 389 (1965).
3. D. H. Whiffen, *J. Chem. Soc.*, 1350 (1956).
4. IUPAC Table of Wavelength for the Calibration of Infrared Spectrometers, Butterworth, Inc., Washington, D. C. (1961).
5. H. M. Randall, D. M. Dennison, N. Ginsburg, and L. R. Weber, *Phys. Rev.*, 52, 160 (1937).
6. V. A. Nefedov and M. N. Nefedova, *Zhur. Obshchei Khim.*, 36, 122 (1966).
7. A. N. Nesmeyanov, V. A. Sayanova, and V. N. Droyd, *Dokl. Akad. Nauk SSSR*, 126, 1004 (1959).
8. R. W. Fish and M. Rosenblum, *J. Org. Chem.*, 30, 1253 (1965).
9. I. J. Hyams, R. T. Bailey, and E. R. Lippincott, *Spectrochim. Acta*, 23A, 273 (1967).
10. N. Fuson, C. Carrigan-Lagrange, and M. L. Josien, *Spectrochim. Acta*, 16, 106 (1960).
11. D. Steele and D. H. Whiffen, *Trans. Faraday Soc.*, 55, 369 (1959).
12. R. K. Bohn and A. Haaland, *J. Organometal. Chem.*, 5, 470 (1966).
13. A. Sado, R. West, H. P. Fritz, and L. Schafer, *Spectrochim. Acta*, 22, 509 (1966).

TABLE I

OBSERVED VIBRATIONAL SPECTRA OF 1,1'-DICHLOROFERROCENE ++

Infrared	Raman	Assigned
3110 w		$a_1 \nu \text{ C-H}$
3090 w		$a_1 \nu \text{ C-H} + b_1 \text{ CH}$
2210 w		?
1755 w		$884 + 884 = 1768 \text{ cm}^{-1}$
1725 w		$884 + 851 = 1725 \text{ cm}^{-1}$
1675 vw*		$851 + 819 = 1670 \text{ cm}^{-1}$
1650 vw*		$820 \times 2 = 1640 \text{ cm}^{-1}$
1560 vvw*		$1385 + 171 = 1556 \text{ cm}^{-1}$
1473 vw*		$884 + 605 = 1489 \text{ cm}^{-1}$
1417 vs	1416 w	$a_1 \nu \text{ C-C}$
1385 w-m	1384	$a_1 \nu \text{ C-C}$
1360 m		$b_1 \nu \text{ C-C}$
1349 sh		$b_1 \nu \text{ C-C}$
1258 w		$1014 + 251 = 1265 \text{ cm}^{-1}$
1205 w		$b_1 \delta \text{ C-H}$
1178 m		$a_1 \delta \text{ C-H}$
1170 s	1172 s	$a_1 \text{ X-sensitive}$
1153 w		$b_1 \delta \text{ C-H}$
1106 m	1111 vw	impurity
1050 w	1070 w	$a_2 \delta \text{ C-H}$
1022 s	1032 m	$a_1 \delta \text{ C-H}$
1014 m		$b_2 \delta \text{ C-H}$
1000 w-sh		impurity
900 sh		?
884 s	884 w	$a_1 \text{ X-sensitive and}$ $b_1 \text{ ring distortion}$

TABLE I (CONTD)

Infrared	Raman	Assigned
851 w	833 w	a_1 ring distortion
819 s		b_2 δ C-H
805 s		a_2 δ C-H
605 w	594 w	a_2 δ ring
513 s	507 vw	antisymmetric R-M tilting
491 s		antisymmetric R-M stretching
430 w*	422 w	b_2 δ ring ?
390 w	494 w-m	symmetric R-M tilting
	344 vs	symmetric R-M stretching
251 w**	252 s	b_1 X-sensitive
225 w**	- - - -	b_2 X-sensitive
171 w**	- - - -	R-M-R bending
† Frequencies are in reciprocal centimeters		
+ v(very), s(strong), m(medium), w(weak), br(broad), sh(shoulder)		
* obtained from liquid film		
** obtained from solid		

TABLE II

OBSERVED VIBRATIONAL SPECTRA OF 1,1'-DIBROMOFERROCENE † †

Infrared	Raman	Assignment
3105 m	3110 w	a_1 v C-H
3085 w		$a_1 + b_1$ C-H
1759 m		$872 + 878 = 1750$
1727 m		$872 + 850 = 1722$
1700 w		$872 + 820 = 1692$
1670 w		$850 + 820 = 1670$
1645 w		$820 \times 2 = 1640$
1630 w*		$820 + 809 = 1629$
1545 vw*		$1380 + 171 = 1551$
1473 w*		$878 + 599 = 1477$
1410 vs	1410 m	a_1 v C-C
1380 m	1381 w-m	a_1 v C-C
1355 m-s	1363 w**	b_1 v C-C
1350 w-sh		$1178 + 171 = 1349$
1342 w	1352 w**	b_1 v C-C
1202 w	1203 m	b_1 δ C-H
1178 m	1179 sh	a_1 δ C-H
1152 vs	1154 vs	a_1 X-sensitive + b_1 C-H
1106 w	1106 vw	impurity
1050 m	1059 m	a_2 δ C-H
1020 s	1021 s	a_1 δ C-H
1010 m-s		b_2 δ C-H
930 w		$599 + 339 = 938$
878 sh		b_1 ring distortion
872 vs	876 s	a_1 X-sensitive

TABLE II (CONTD)

Infrared	Raman	Assignment
850 w		a_1 ring distortion
820 s		b_2 δ C-H
809 m		a_2 δ C-H
612 vw		$419 + 206 = 625$
599 w	591 w	a_2 δ ring
498 vs		antisym. R-M tilting
488 vs-br	491 vw	antisym. R-M stretching
	456 w	$237 \times 2 = 464$
419 m-br	410 br	b_2 δ ring ?
339 w**	343 m	sym. R-M stretching
327 m } 323 m } split	305 w	sym. R-M tilting
262 vw		
237 w	225 w	b_1 X-sensitive
206 w**		b_2 X-sensitive
171 w		R-M-R bending
† Frequencies are in reciprocal centimeters		
+ v(very), s(strong), m(medium), w(weak), br(broad), sh(shoulder)		
* obtained from liquid film		
** obtained from solid		

TABLE III

OBSERVED VIBRATIONAL SPECTRA OF 1,1'-DIIDOFERROCENE ++

Infrared	Raman	Assignment
3100 m	3110 w	$a_1 \nu \text{ C-H}$
3080 w		$a_1 \nu \text{ C-H} + b_1 \nu \text{ C-H}$
1760 m		$865 + 883 = 1648$
1730 m		$883 + 848 = 1731$
1712 w		$865 + = 1713$
1670 m*		$820 + 848 = 1668$
1635 m*		$820 \times 2 = 1640$
1537 vw*		$1378 + 171 = 1549$
1422 vw		$1020 + 398 = 1418$
1402 s	1404 m	$a_1 \nu \text{ C-C}$
1378 s	1371 m	$a_1 \nu \text{ C-C}$
1345 s		$b_1 \nu \text{ C-C}$
1326 sh		$b_1 \nu \text{ C-C}$
1290 vw		$1020 + 275 = 1295$
1200 w		$b_1 \delta \text{ C-H}$
1175 w-m	1178 w	$a_1 \delta \text{ C-H}$
1150 sh		$b_1 \delta \text{ C-H}$
1142 s	1168 m	$a_1 \text{ X-sensitive}$
1050 m	1060 w	$a_2 \delta \text{ C-H}$
1020 vs	1017 m	$a_1 \delta \text{ C-H}$
1010 s		$b_2 \delta \text{ C-H}$
925 w		$592 + 326 = 918$
910 sh		?
883 sh*		$b_1 \text{ ring distortion}$
865 vs	864 s	$a_1 \text{ X-sensitive}$

TABLE III (CONTD)

Infrared	Raman	Assignment
848 m	847 w	a_1 δ ring
820 s		b_2 δ C-H
805 m		a_2 δ C-H
760 w*		$483 + 275 = 758$
592 w*	587 w	a_2 δ ring
490 vs	487 s	antisym. R-M tilting
483 vs-br		antisym. R-M stretching
398 m*	401 w-m	b_2 δ ring ?
323 w	326 s	sym. R-M stretching
283 m } split 272 m }	273 m	sym. R-M tilting
213 m	198 w	b_1 X-sensitive
202 m		?
180 m		b_2 X-sensitive
171 m		R-M-R bending
	78 w	$273 - 198 = 75$
† Frequencies are in reciprocal centimeters		
+ v(very), s(strong), m(medium), w(weak), br(broad), sh(shoulder)		
* obtained from liquid film		

TABLE IV
 ASSIGNED FREQUENCIES UTILIZING
 THE STEELE AND WHIFFEN INEQUALITY RULE

Ferrocene	1,1'-Dichloroferrocene	1,1'-Dibromoferrocene	1,1'-Diiodoferrocene
		<u>Class a₁</u>	
3099	3110	3105	3100
3085	3090	3085	3080
3085	1417	1410	1402
1408-1411	1385	1380	1378
1356	1178	1178	1175
1178	1170	1152	1142
1105	1022	1020	1020
1010	884	872	865
880	851	850	848
		<u>Class b₁</u>	
3085	3090	3085	3080
3085	3090	3085	3080
1408-1411	1360	1355	1345
1356	1349	1342	1326
(1200)	1205	1202	1200
1178	1153	1152	1150
1010	884	878	883
880	251	237	213
		<u>Class b₂</u>	
1050	1014	1010	1010
834	819	820	820
811	430	410	401
(500)	225	206	180
		<u>Class a₂</u>	
1050	1050	1050	1050
834	805	809	805
(500)	605	599	592

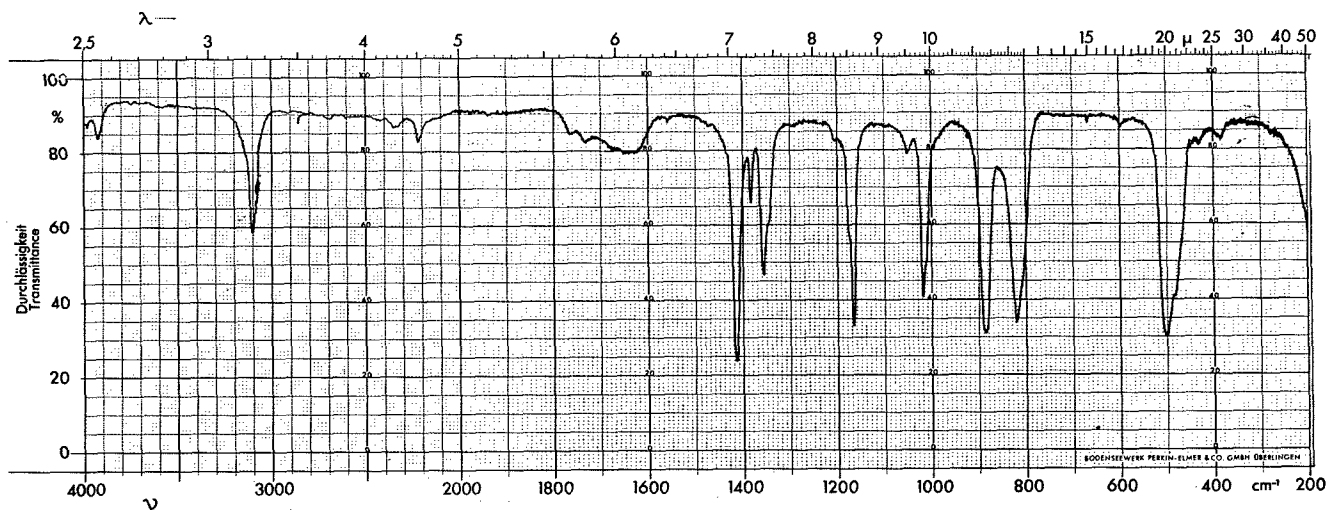


Figure 1. Infrared Spectrum of Liquid Film of 1,1'-Dichloroferrocene

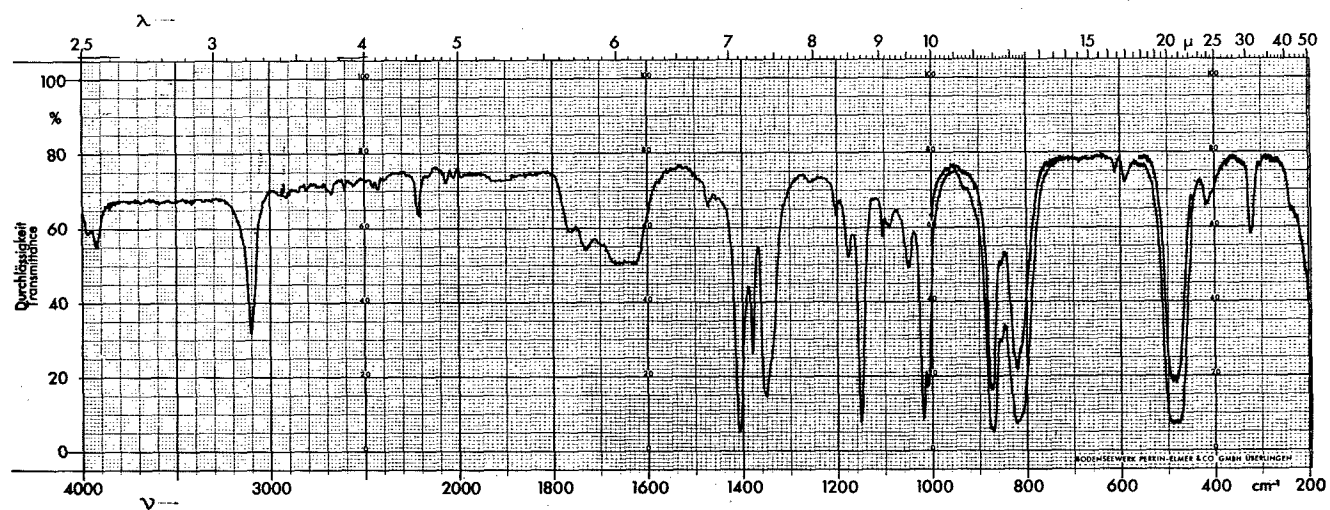


Figure 2. Infrared Spectrum of Liquid Film of 1,1'-Dibromoferrocene

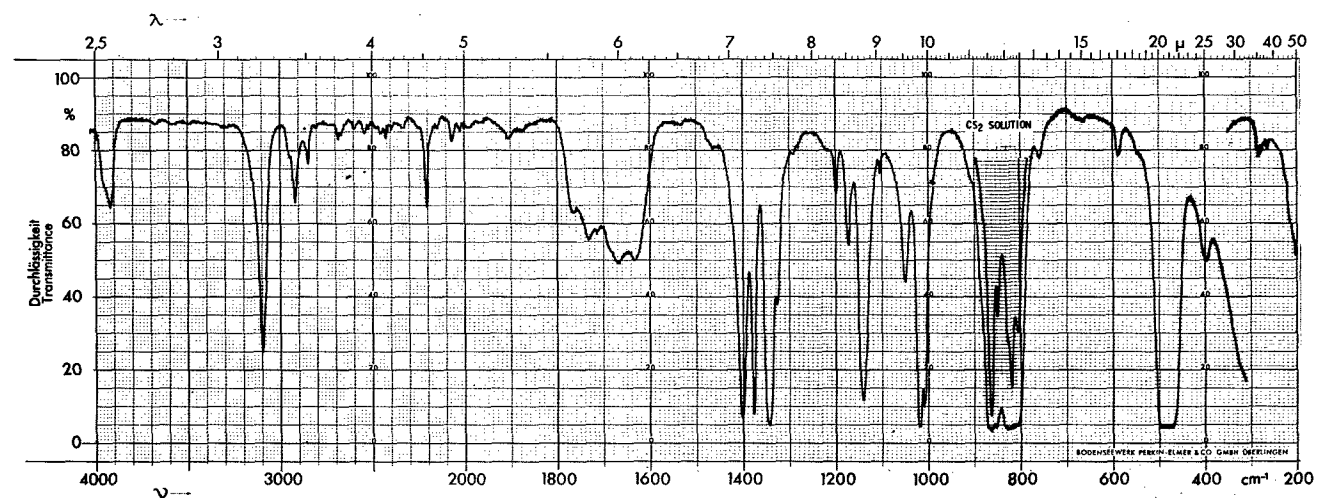


Figure 3. Infrared Spectrum of Liquid Film of 1,1'-Diiodoferrocene

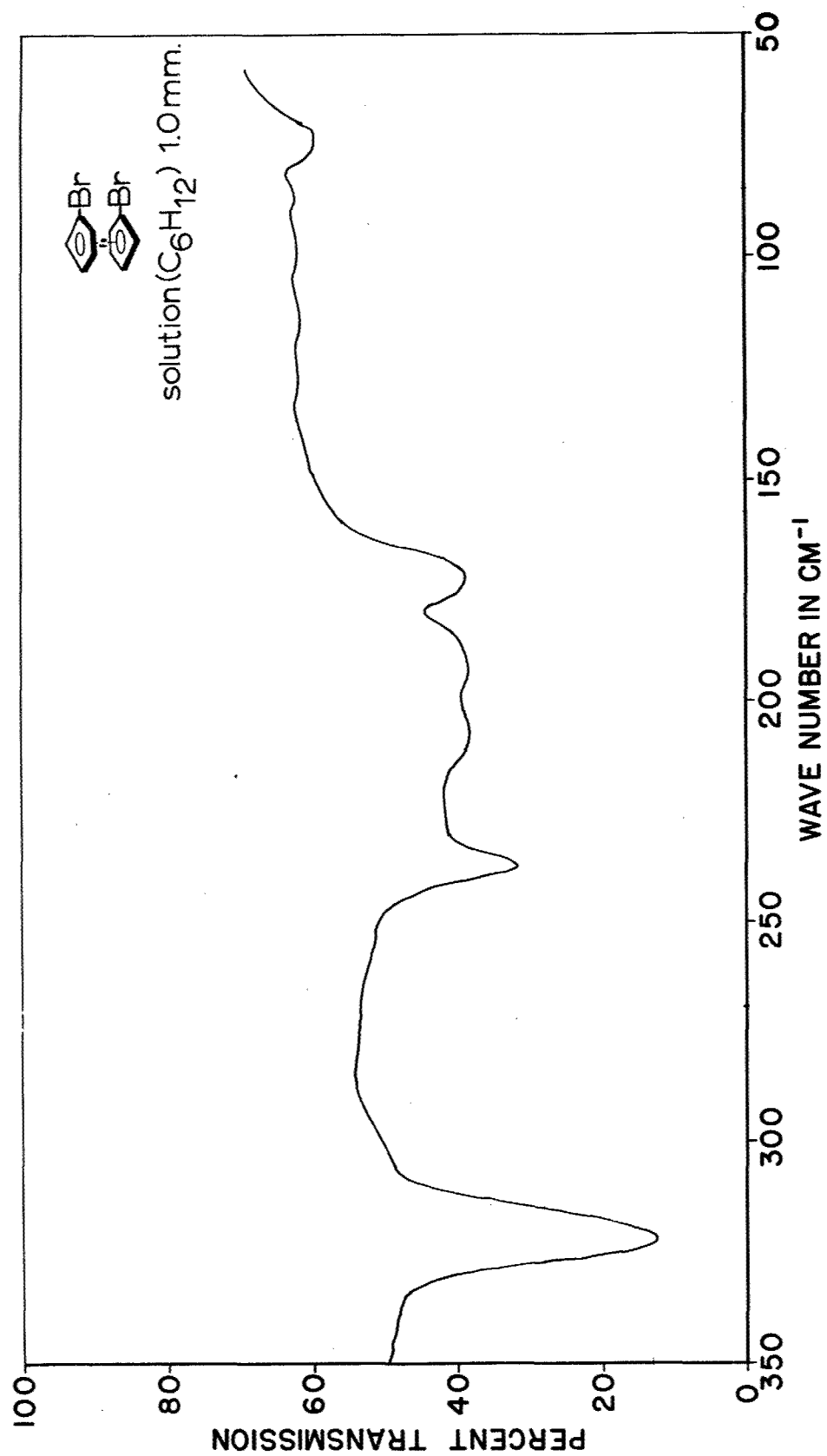


Figure 4. Far Infrared Spectrum of 1,1'-Dibromoferrocene

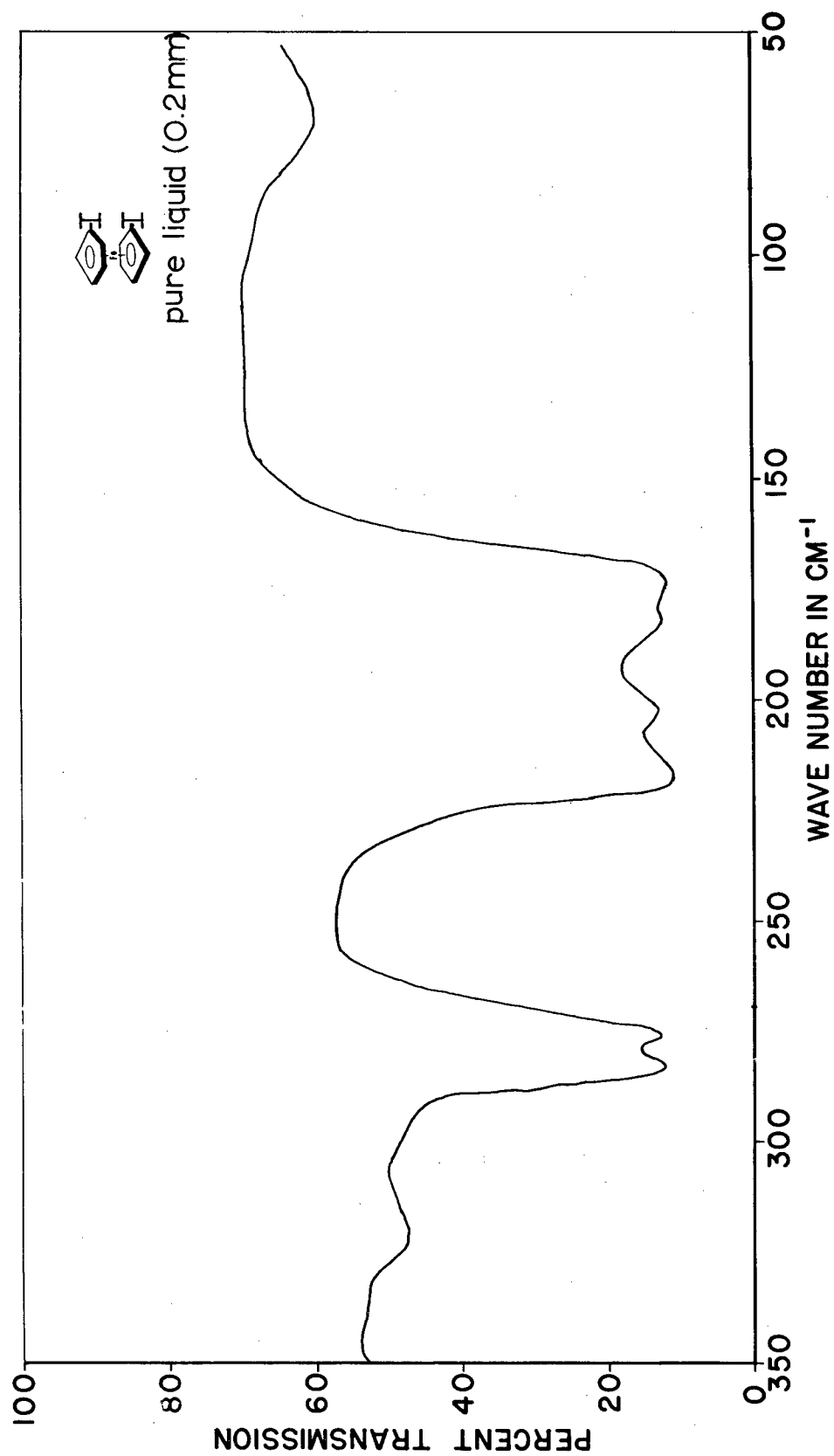


Figure 5. Far Infrared Spectrum of 1, 1'-Diiodoferrocene

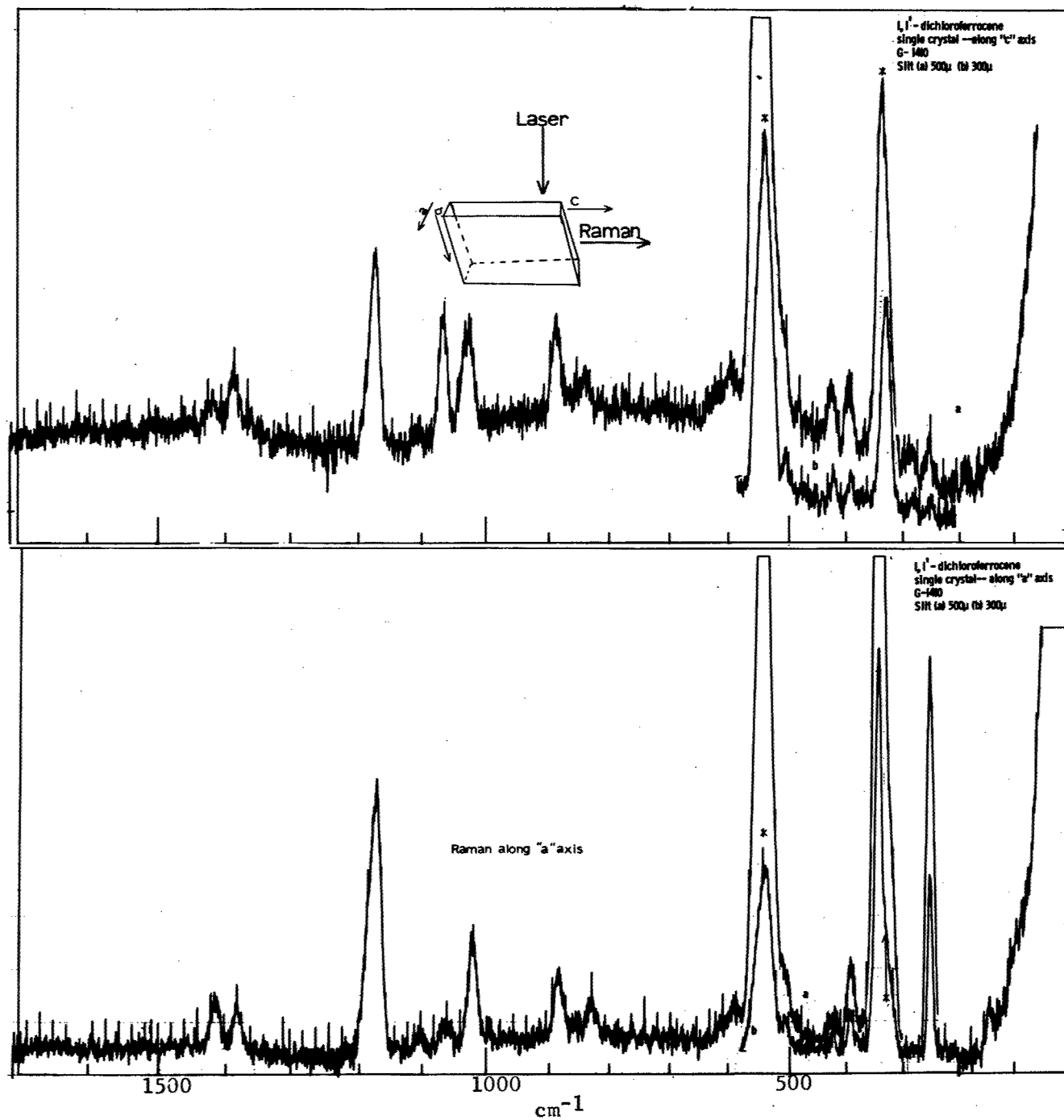


Figure 6. Raman Spectra of Single Crystal 1,1'-Dichloroferrocene

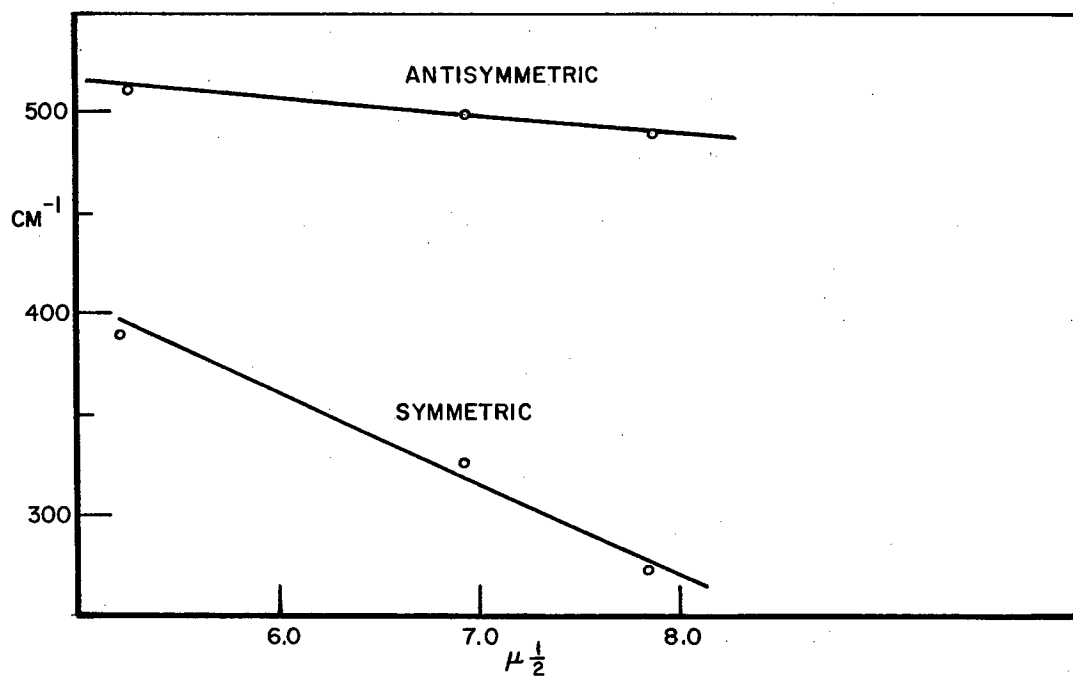


Figure 7. Ring-Metal Tilting Vibration

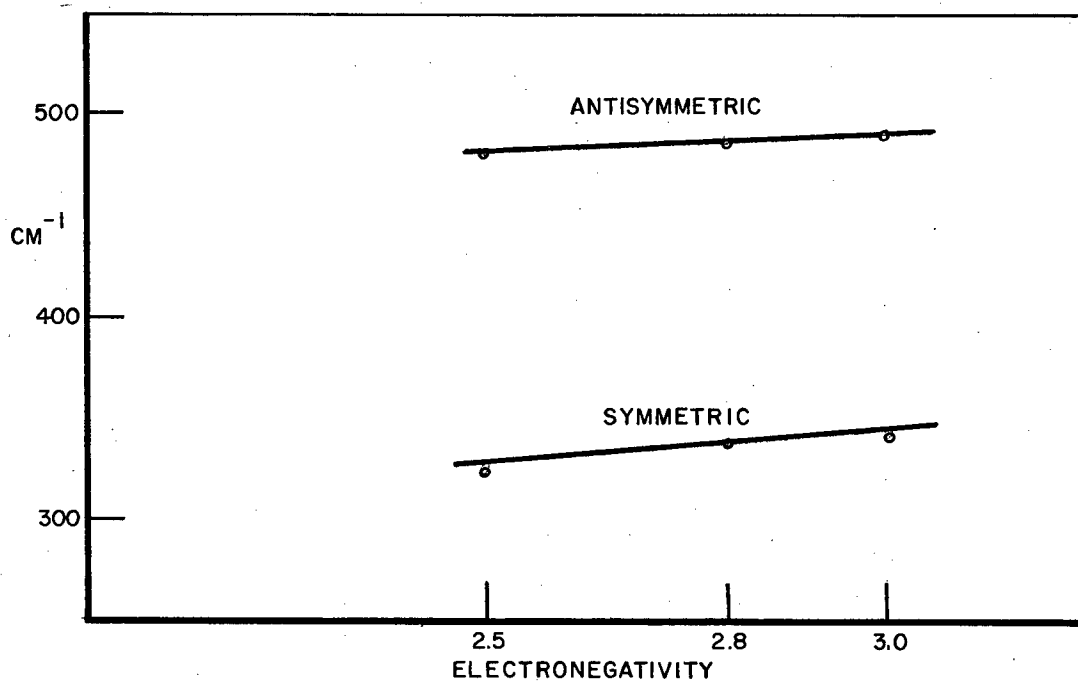


Figure 8. Ring-Metal Stretching Vibration

UNCLASSIFIED
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Infrared						
Raman						
Ferrocene						
Vibrational Assignment						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.