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THE INFRARED SPECTRA AND VIBRATIONAL ASSIGNMENTS FOR SOME ORGANO-METALLIC COMPOUNDS

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FOREWORD

This report was prepared by the Analytical Branch, Physics Laboratory. The work was initiated under Project No. 7360, "Materials Analysis and Evaluation Techniques," Task No. 736005, "Compositional, Atomic and Molecular Analyses". It was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Fred W. Behnke and Dr. C. Tamborski acting as project engineers.

This report covers the work conducted from October 1961 to December 1961.

ABSTRACT

The infrared spectra from $850 - 250 \text{ cm}^{-1}$ and the vibrational assignments of nine organometallic compounds are reported. The compounds investigated were members of the series $(\phi)_3\text{M-A}$ where $\text{M} = \text{Si, Ge, Sn}$ and $\text{A} = \text{H, Cl, Br}$.

From the infrared spectra which were obtained it was found that the region from $800 - 250 \text{ cm}^{-1}$ contains analytical bands for most of the nine compounds which were investigated.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



FREEMAN F. BENTLEY
Chief, Analytical Branch
Physics Laboratory
Directorate of Materials & Processes

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INTRODUCTION

Within the last few years great attention has been directed towards the field of inorganic polymers. In this Space Age more and more drastic requirements are being asked of materials, and the search for qualifying materials is a difficult, never ending task.

In the polymer field great emphasis is being placed upon the synthesis of polymers which will be able to withstand high temperatures. Inorganic polymers appear to be a possible solution. Preliminary results warrant an accelerated program on the synthesis and evaluation of physical properties of inorganic polymers.

One class of inorganic polymers is that containing the M-O-M linkage, e.g. Ge-O-Ge and Sn-O-Sn. Precursors of these polymers are $(\phi)_3M-A$ compounds where M = Si, Ge, Sn and A = H, Cl, Br. This report will present the infrared spectra and a discussion of the pertinent vibrational assignments of these compounds.

EXPERIMENTAL

The infrared spectra were obtained on a Perkin-Elmer Model 102 Infrared Spectrophotometer. This is a grating instrument which covers the infrared region from 4000 - 250 cm^{-1} and records linear wavenumber versus linear transmittance or absorbance. The spectra in this report were recorded at a spectral slit width of 3 cm^{-1} , coordinates of linear wavenumber versus linear transmittance and over the infrared region from 850 - 250 cm^{-1} . The instrument was purged with dry nitrogen to remove most of the atmospheric water vapor which gives rise to strong infrared modes around 500 - 250 cm^{-1} .

All of the nine organometallic compounds which were prepared had a melting point range of 1°C. The infrared spectra of these solid compounds were obtained from potassium bromide pellets at a concentration of 1 percent (3 mg of sample to 297 mg of KBr).

RESULTS

The infrared spectra from 850 - 250 cm^{-1} for the series $(\phi)_3M-A$, where M = Si, Ge, Sn and A = H, Cl, Br, are reproduced in figures 3 through 11. The decrease in percent transmittance from 250 cm^{-1} out is due to the presence of strong water vapor bands and the absorption of infrared energy near the cut-off frequency of the CsI prism. (This prism is used only as an order-sorter.)

All of the pertinent infrared bands with their vibrational assignment are summarized in table 1. In order to present a visual presentation of the shift in various vibrational modes throughout the series of nine compounds the bar graph of figure 1 was constructed. The Greek symbols at the top of the figure refer to the type of vibration occurring at that frequency. δ refers to a deformational mode and γ refers to a stretching mode. The "X" mode refers to an aromatic vibrational mode whose wavenumber position and intensity is greatly dependent on the nature of the substituted atom.

Figure 2 is a plot of $(k/\mu)^{\frac{1}{2}}$ versus wavenumber position of the Metal-Halide modes for the chloro and bromo members of the $(\phi)_3M-A$ series. k is the force constant which in this case is the difference in electronegativity between atoms M and A, μ is the reduced mass of atoms M and A and is equal to:

$$\frac{\text{Mass Atom (M)} \cdot \text{Mass Atom (A)}}{\text{Mass Atom (M)} + \text{Mass Atom (A)}}$$

The point for $(\phi)_3SnBr$ was not recorded on the infrared spectrum of that compound but was attained by extrapolation from $(\phi)_3SiBr$ and $(\phi)_3GeBr$.

DISCUSSION

For discussion purposes the nine organometallic compounds are divided into three groups, namely the hydrides, chlorides and bromides.

Group I $(\phi)_3SiH$, $(\phi)_3GeH$ and $(\phi)_3SnH$

The infrared spectra from $850 - 250 \text{ cm}^{-1}$ of these compounds are shown in figures 3, 4 and 5. All three compounds exhibit two strong vibrational modes around 730 and 695 cm^{-1} which are assigned to the C-H out-of-plane deformation of the aromatic ring and are characteristic of mono-substitution. The strongest vibration mode in each spectrum corresponds to the metal-hydrogen deformation and occurs at 805 cm^{-1} for $(\phi)_3SiH$ and at 565 cm^{-1} for $(\phi)_3SnH$. In the case of $(\phi)_3GeH$ the Ge-H deformation overlaps the C-H out-of-plane deformation of the aromatic ring and this is one of the few cases in which there is no absorption band which is useful for analytical purposes. The medium intensity vibrational mode corresponds to the so-called "X" sensitive vibration which is an aromatic ring stretching mode whose intensity and wavenumber position is greatly influenced by the nature of the substituted atom. For the three hydrides this mode decreases from $485 \text{ cm}^{-1} - 455 \text{ cm}^{-1}$ for the corresponding Si - Ge - Sn compound.

Group II $(\phi)_3SiCl$, $(\phi)_3GeCl$ and $(\phi)_3SnCl$

The infrared spectra from $800 - 250 \text{ cm}^{-1}$ for these compounds are shown in figures 6, 7 and 8. Again all the compounds exhibit the characteristic C-H out-of-plane deformations around 730 cm^{-1} and 695 cm^{-1} . Due to spatial geometry there are three C-H out of plane deformational modes for $(\phi)_3SiCl$ which is also true for the compound $(\phi)_3CCl$. The metal-chlorine stretching modes decrease with increasing mass of the metal atom from $540 \text{ cm}^{-1} - 375 \text{ cm}^{-1} - 327 \text{ cm}^{-1}$ and all three vibrational bands are useful for analytical purposes. The wavenumber shift of the metal-chlorine stretching mode is directly proportional to the force constant (in this case the difference in electronegativity

between the metal atom and the chlorine atom) of the metal-chlorine band and the reduced mass of the metal and chlorine atoms. This relationship is shown by the solid line in figure 2. The "X" sensitive modes for the chlorine compounds are at almost the same wavenumber positions as in their corresponding hydride compounds.

Group III $(\phi)_3\text{SiBr}$, $(\phi)_3\text{GeBr}$ and $(\phi)_3\text{SnBr}$

The infrared spectra from $800 - 250 \text{ cm}^{-1}$ for these compounds are shown in figures 9, 10 and 11. Here again the characteristic C-H out-of-plane deformation occurs around 730 cm^{-1} and 695 cm^{-1} . Unfortunately in this series only one metal-bromine stretching mode is shown in the infrared spectra of the three compounds. The Ge-Br stretching mode occurs at 309 cm^{-1} , the Si-Br stretching mode is overlapped by the "X" sensitive mode for $(\phi)_3\text{-Si}$ (490 cm^{-1}) and the Sn-Br stretching mode occurs outside of the wavenumber range of the infrared spectrophotometer which was used in this study. The wavenumber positions of the metal-bromine stretching mode for $(\phi)_3\text{SiBr}$ (taken as 490 cm^{-1}) and $(\phi)_3\text{GeBr}$ were plotted against the ratio of force constant and reduced mass. An extrapolation was made to the corresponding value of force constant to reduced mass ratio for $(\phi)_3\text{SnBr}$. The wavenumber result was 225 cm^{-1} as the position of the Sn-Br stretching mode for $(\phi)_3\text{SnBr}$. This relationship is shown by the dashed line of figure 2. Again the positions of the "X" sensitive modes have remained quite constant.

Following is a brief summary of the vibrational bands of the nine organometallic compounds studied which are useful for analytical purposes.

<u>BAND (cm^{-1})</u>	<u>CHARACTERIZES</u>
485 - 490	$\phi - \text{Si}$
455 - 460	$\phi - \text{Ge}$
445 - 446	$\phi - \text{Sn}$
805	Si - H
565	Sn - H
540	Si - Cl
375	Ge - Cl
327	Sn - Cl
309	Ge - Br

Table 1 and figure 1 summarize all of the vibrational modes which were discussed in this report.

REFERENCES

- 1 Randle, R.R. and Whiffen, D.H., Molecular Spectroscopy, Institute of Petroleum, London (1955) p. 11.

TABLE I
 INFRARED VIBRATIONAL MODES OF THE SERIES $(\phi)_3 M-A$
 (850 - 200 cm^{-1})

COMPOUND	METAL-H DEFORMATION	ϕ , C-H OUT-OF-PLANE DEFORMATION		" X " SENSITIVE MODE(ϕ -M)	METAL- HALOGEN STRETCHING
$(\phi)_3 \text{SiH}$	805	733	696	485	
$(\phi)_3 \text{SiCl}$		737	711	695	500
$(\phi)_3 \text{SiBr}$		735	710	692	490
$(\phi)_3 \text{GeH}$	720	734	707	695	455
$(\phi)_3 \text{GeCl}$		735		694	456
$(\phi)_3 \text{GeBr}$		737		693	460
$(\phi)_3 \text{SnH}$	565	727		693	446
$(\phi)_3 \text{SnCl}$		727		693	446
$(\phi)_3 \text{SnBr}$		727		693	445

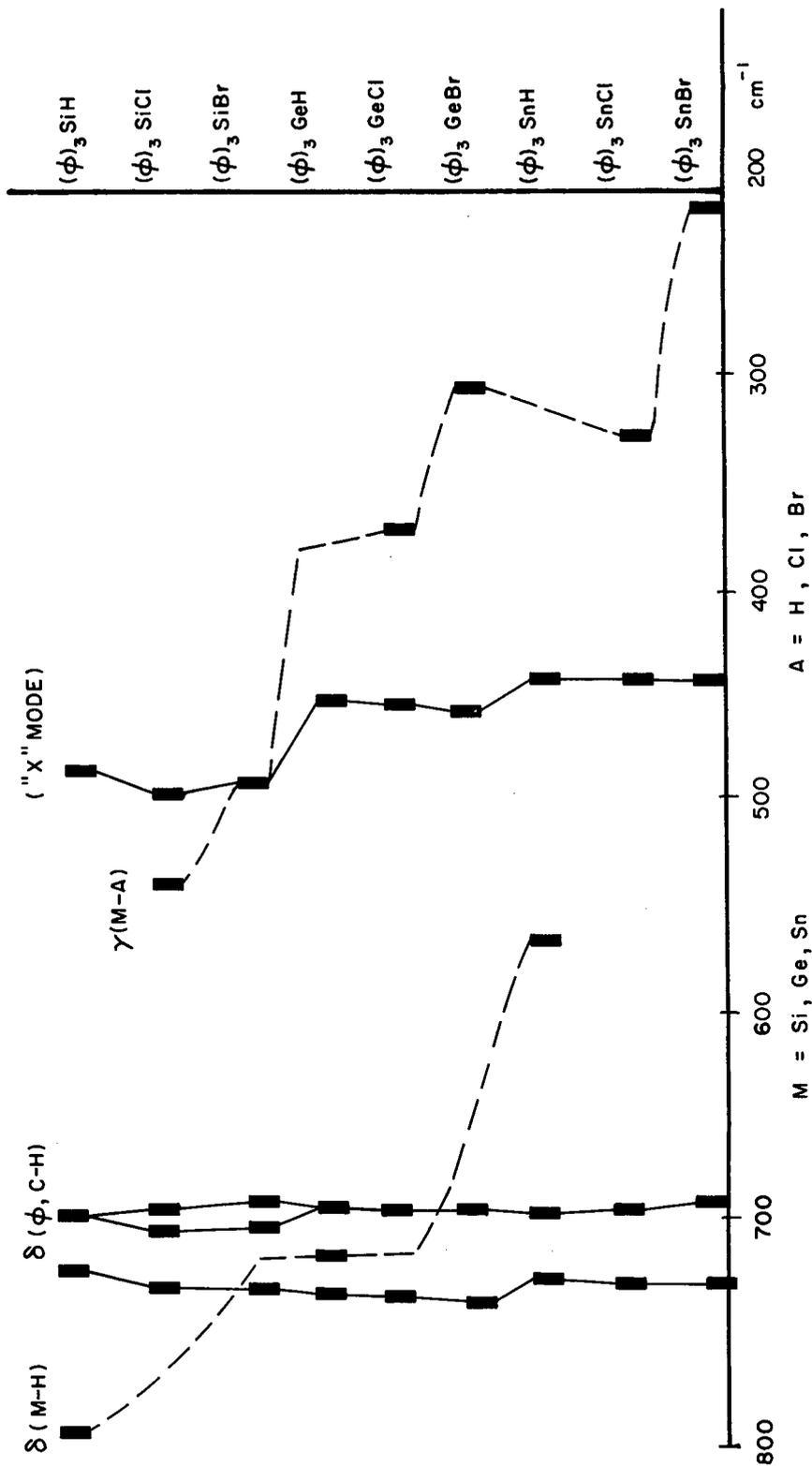


Figure 1. Bar Graph Plot of Infrared Vibrational Modes from 800 to 250 cm⁻¹ for the Series $(\phi)_3M-A$

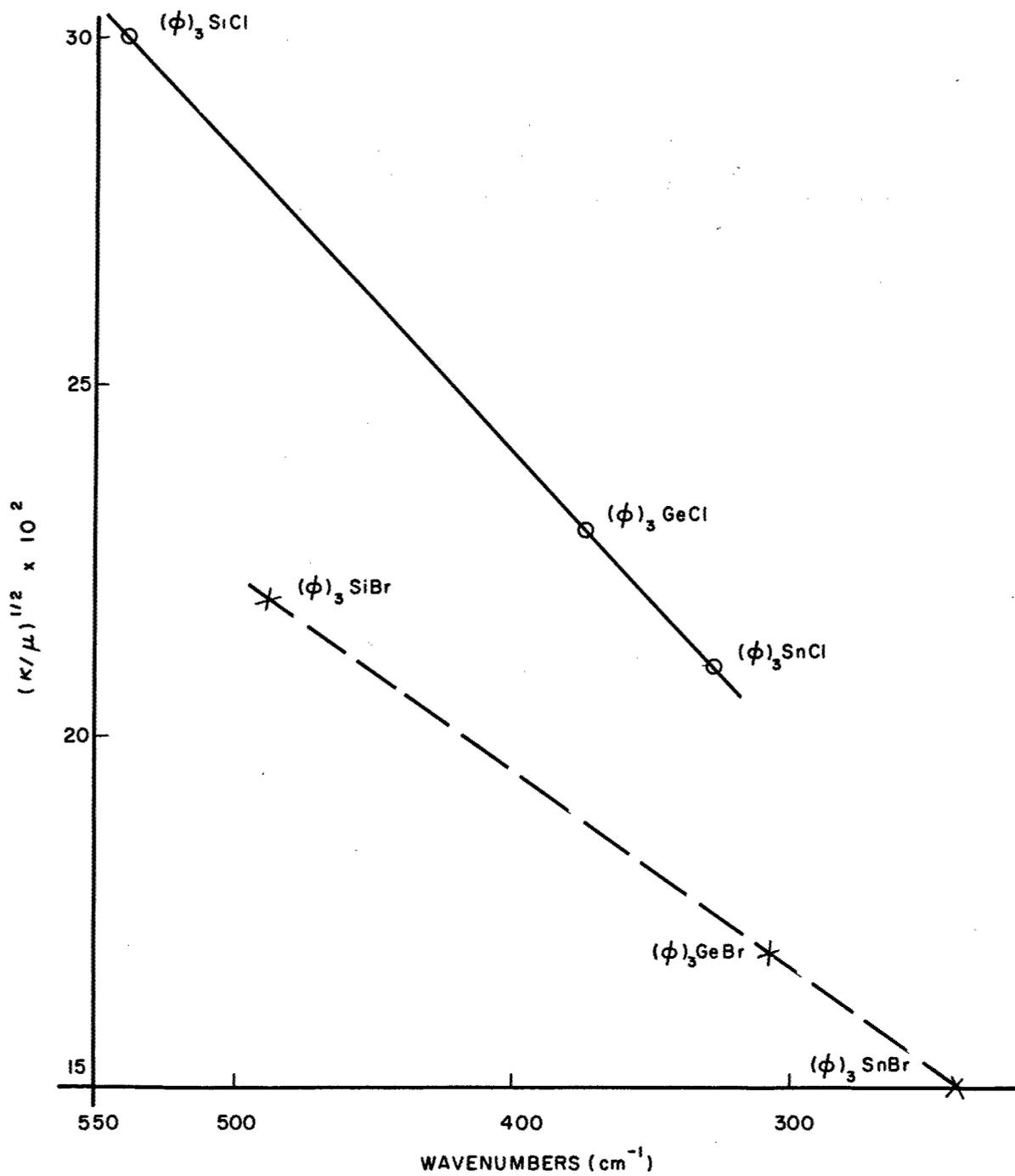


Figure 2. Plot of $(\kappa/\mu)^{1/2}$ vs Wavenumber Position of Metal-Halogen Stretching Mode for the Series $(\phi)_3\text{M-Br}$

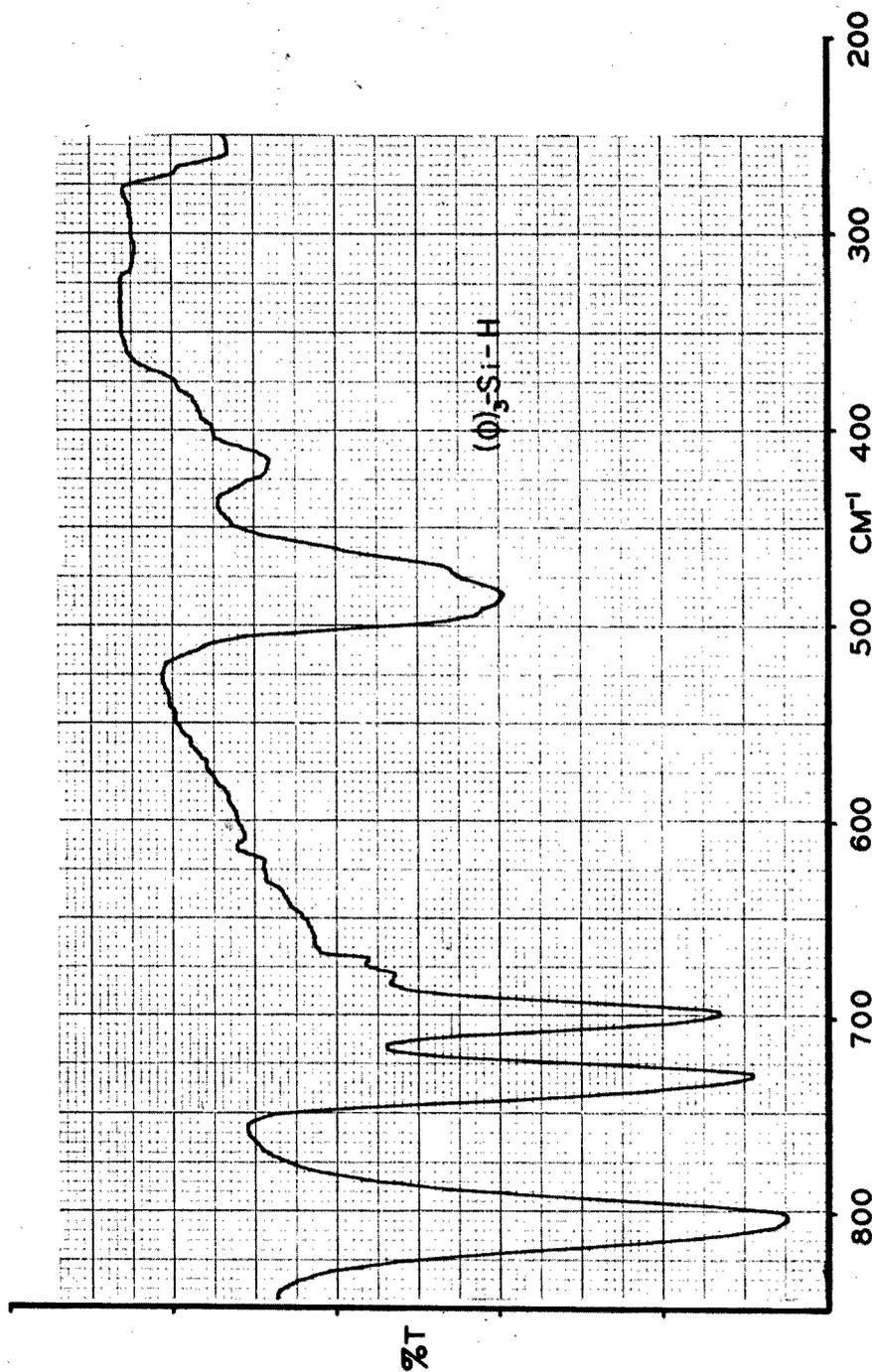


Figure 3. Infrared Spectrum of $(\phi)_3\text{SiH}$ (850 - 250 cm^{-1})

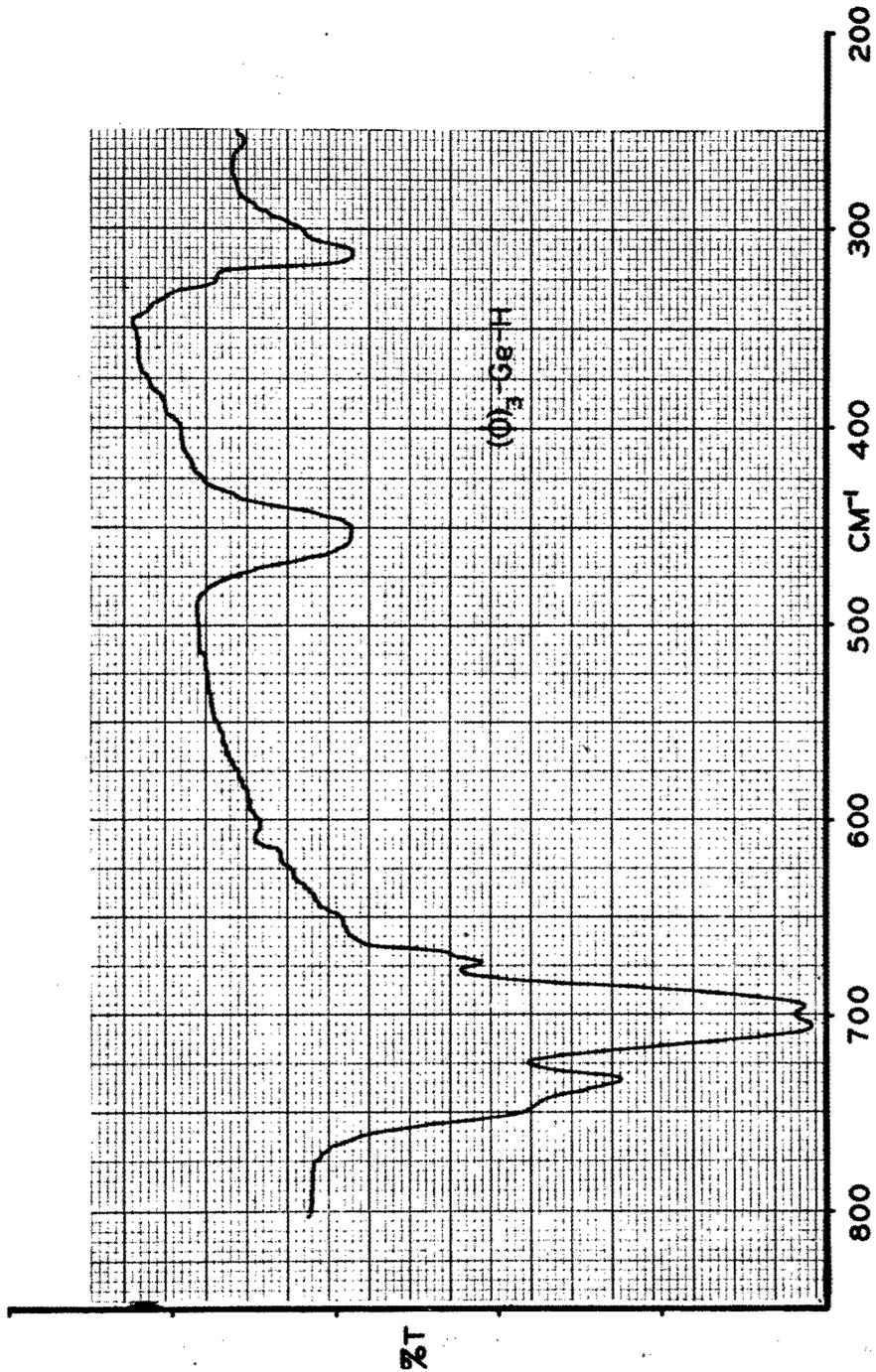


Figure 4. Infrared Spectrum of $(\phi)_3\text{GeH}$ (800 - 250 cm^{-1})

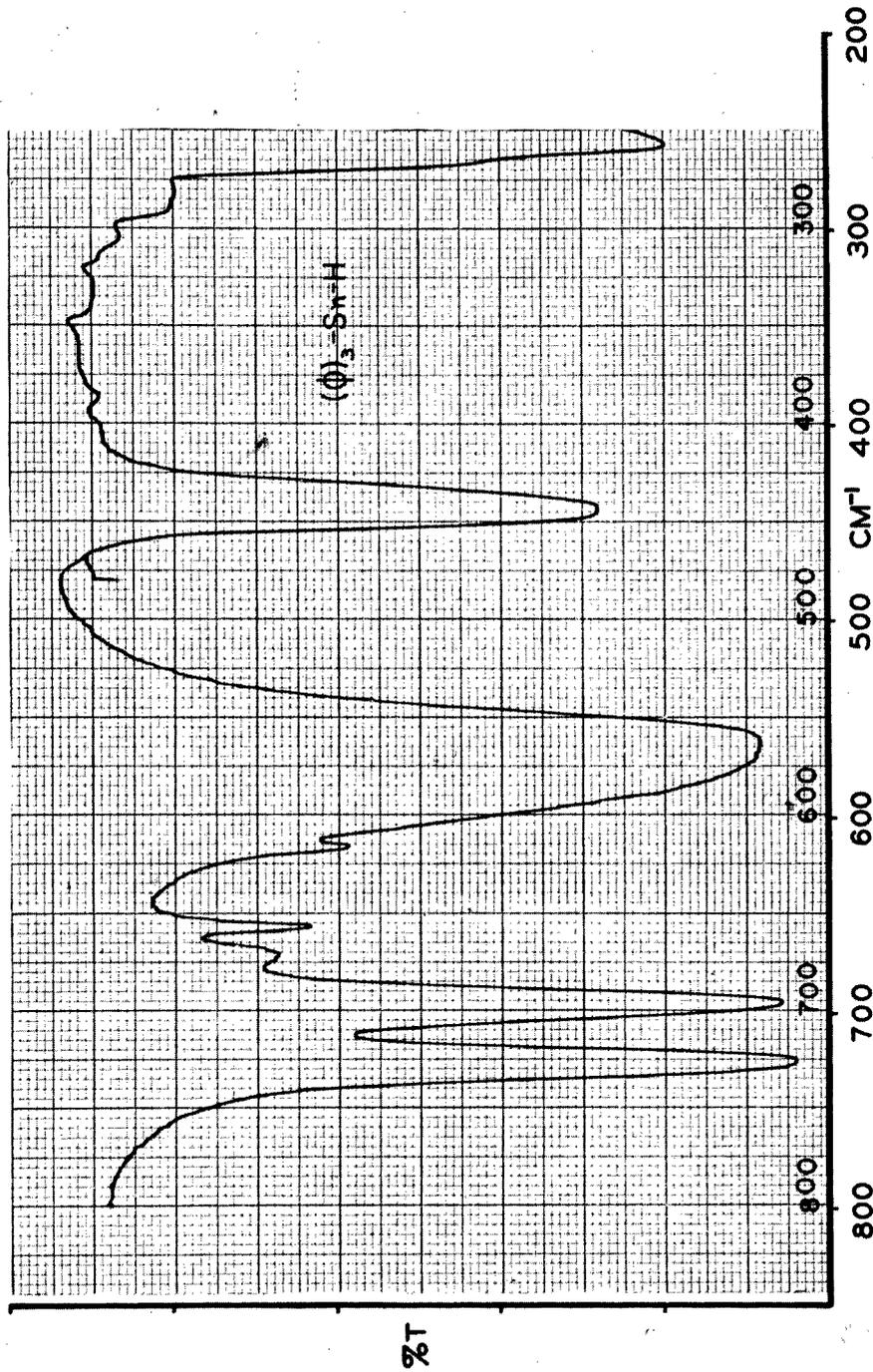
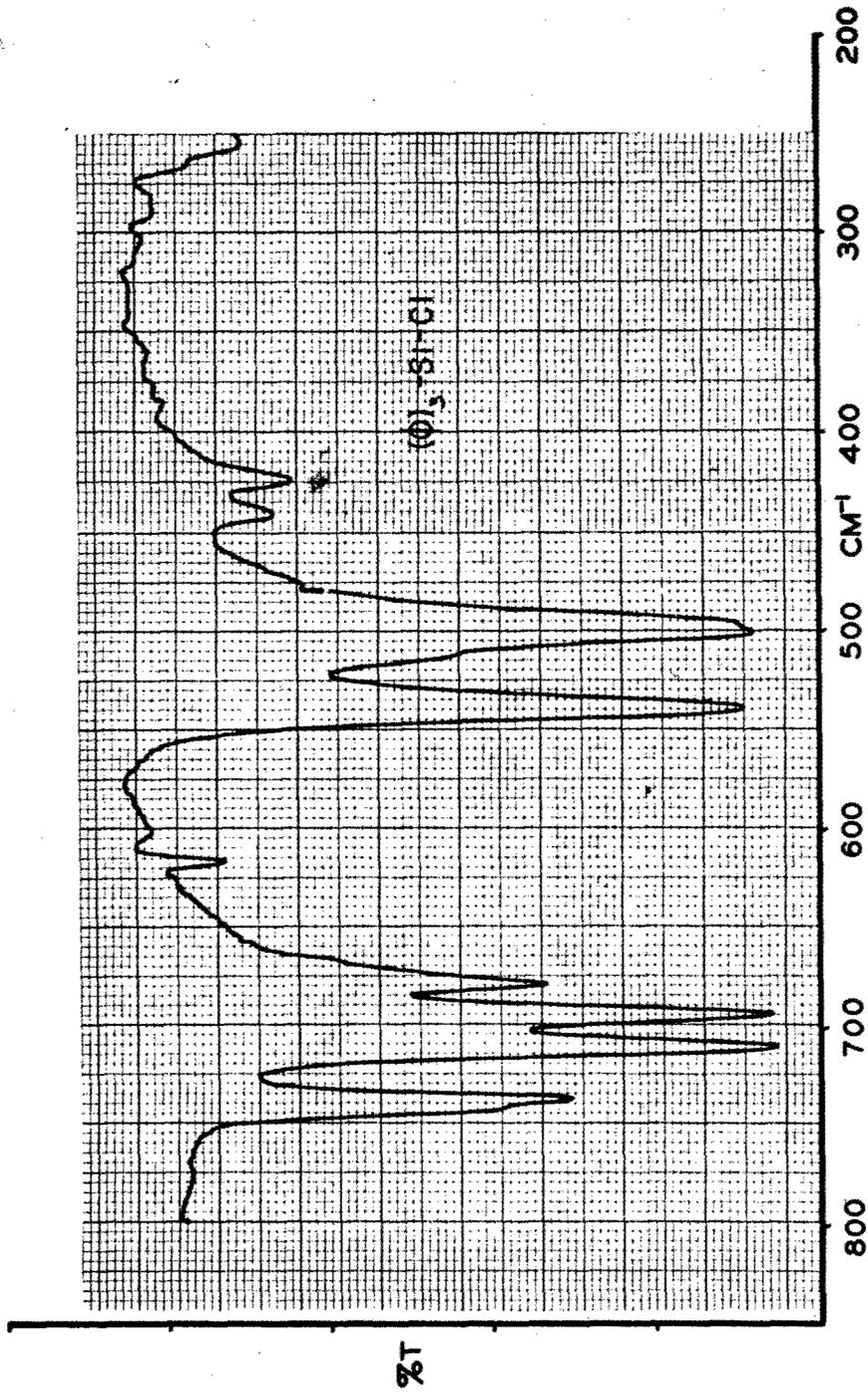


Figure 5. Infrared Spectrum of $(\phi)_3\text{SnH}$ (800 - 250 cm^{-1})

Figure 6. Infrared Spectrum of $(\phi)_5\text{SiCl}$ (800 - 250 cm^{-1})

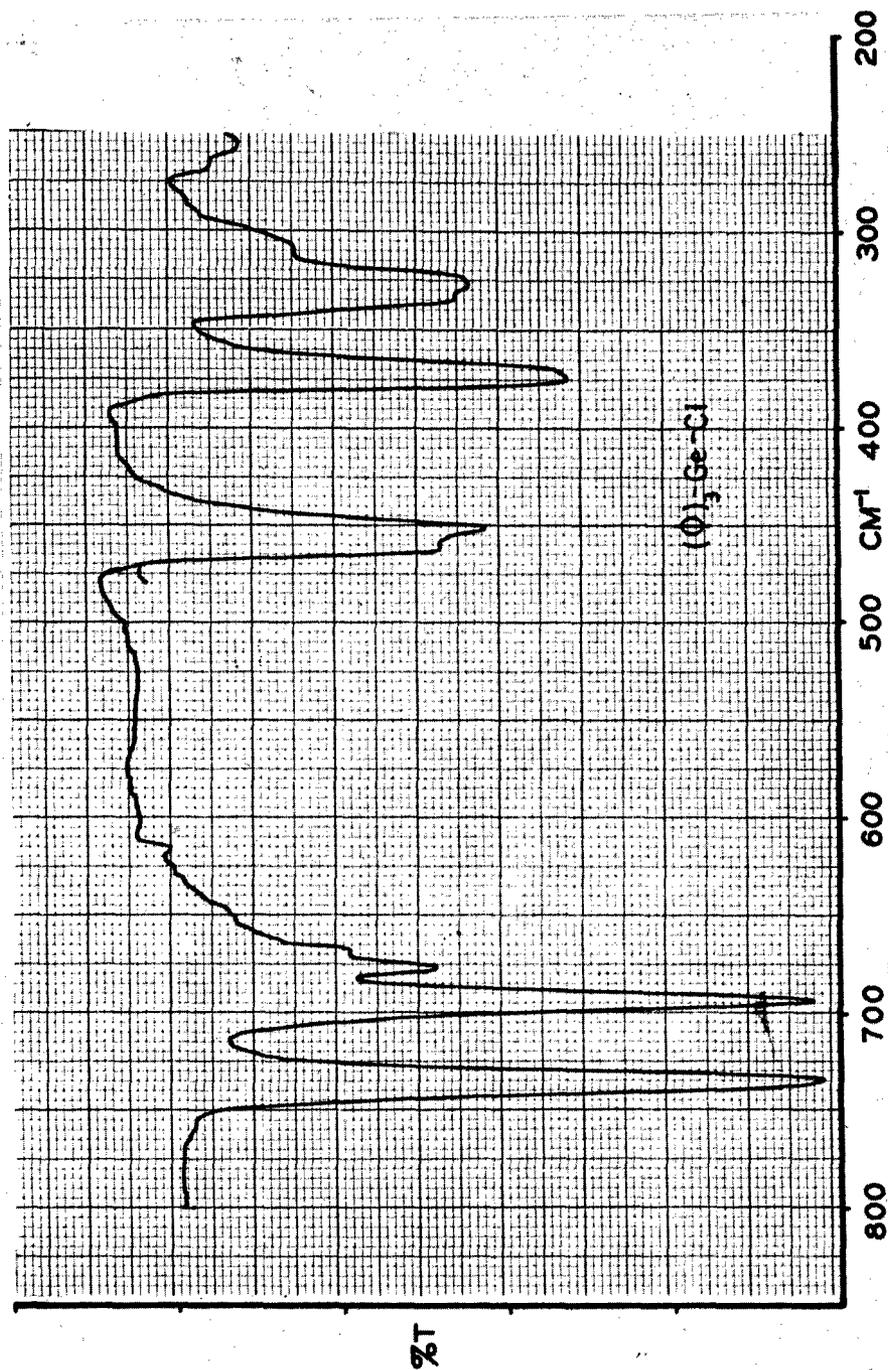


Figure 7. Infrared Spectrum of $(\phi)_3\text{GeCl}$ (800 - 250 cm^{-1})

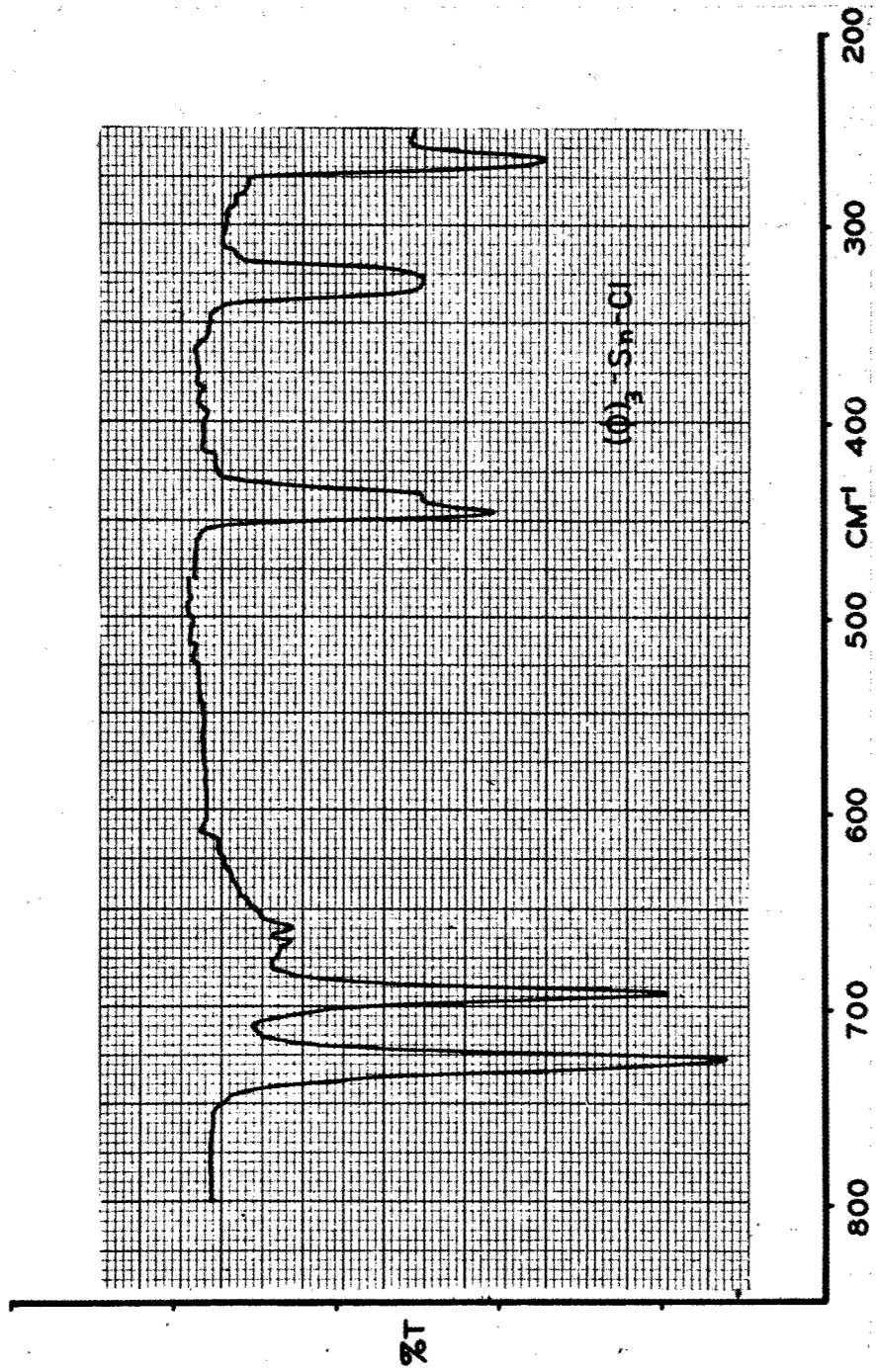


Figure 8. Infrared Spectrum of $(\phi)_3\text{SnCl}$ (800 - 250 cm^{-1})

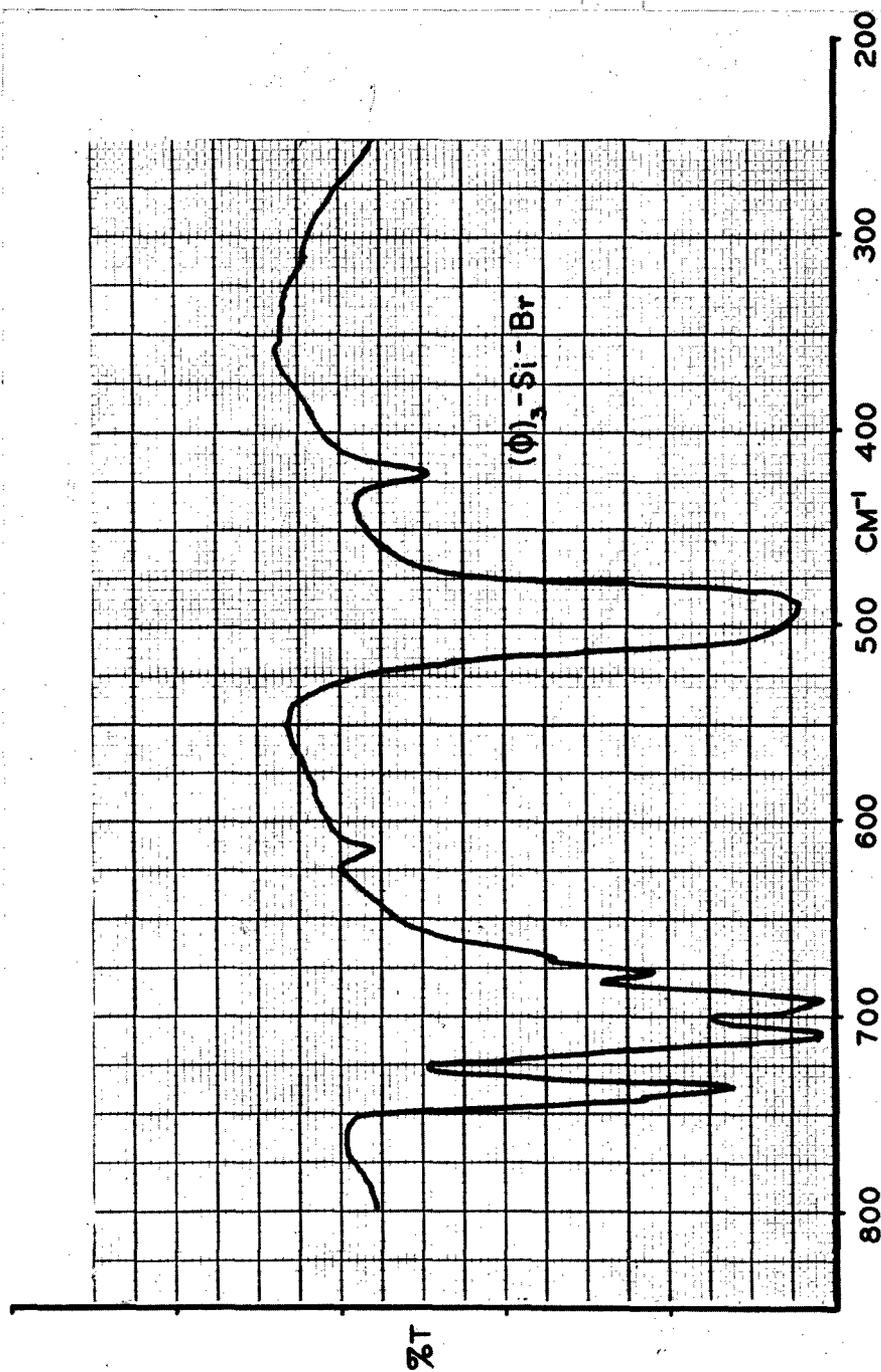


Figure 9. Infrared Spectrum of $(\phi)_3\text{SiBr}$ (800 - 250 cm^{-1})

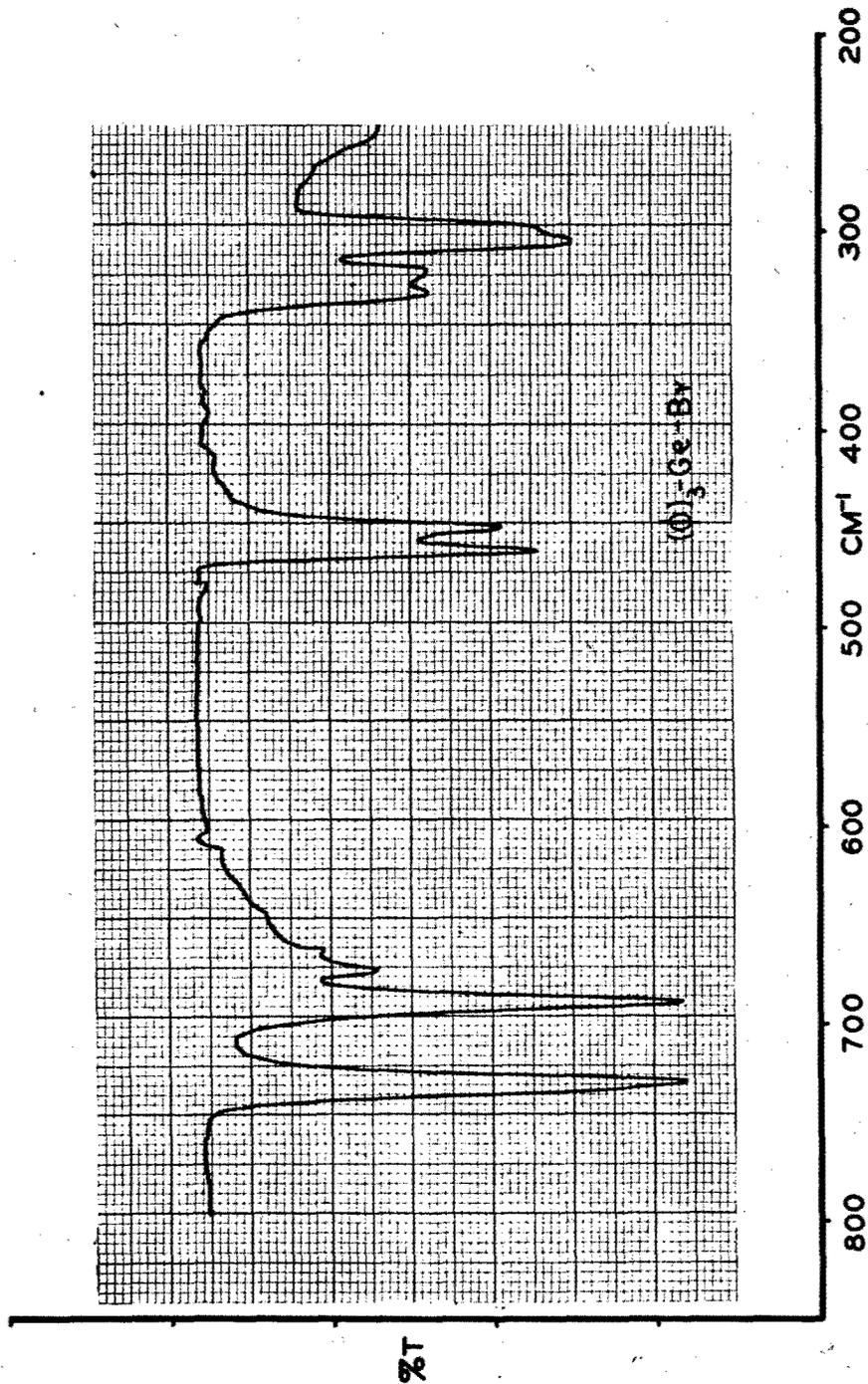


Figure 10. Infrared Spectrum of $(\phi)_3\text{GeBr}$ (800 - 250 cm^{-1})

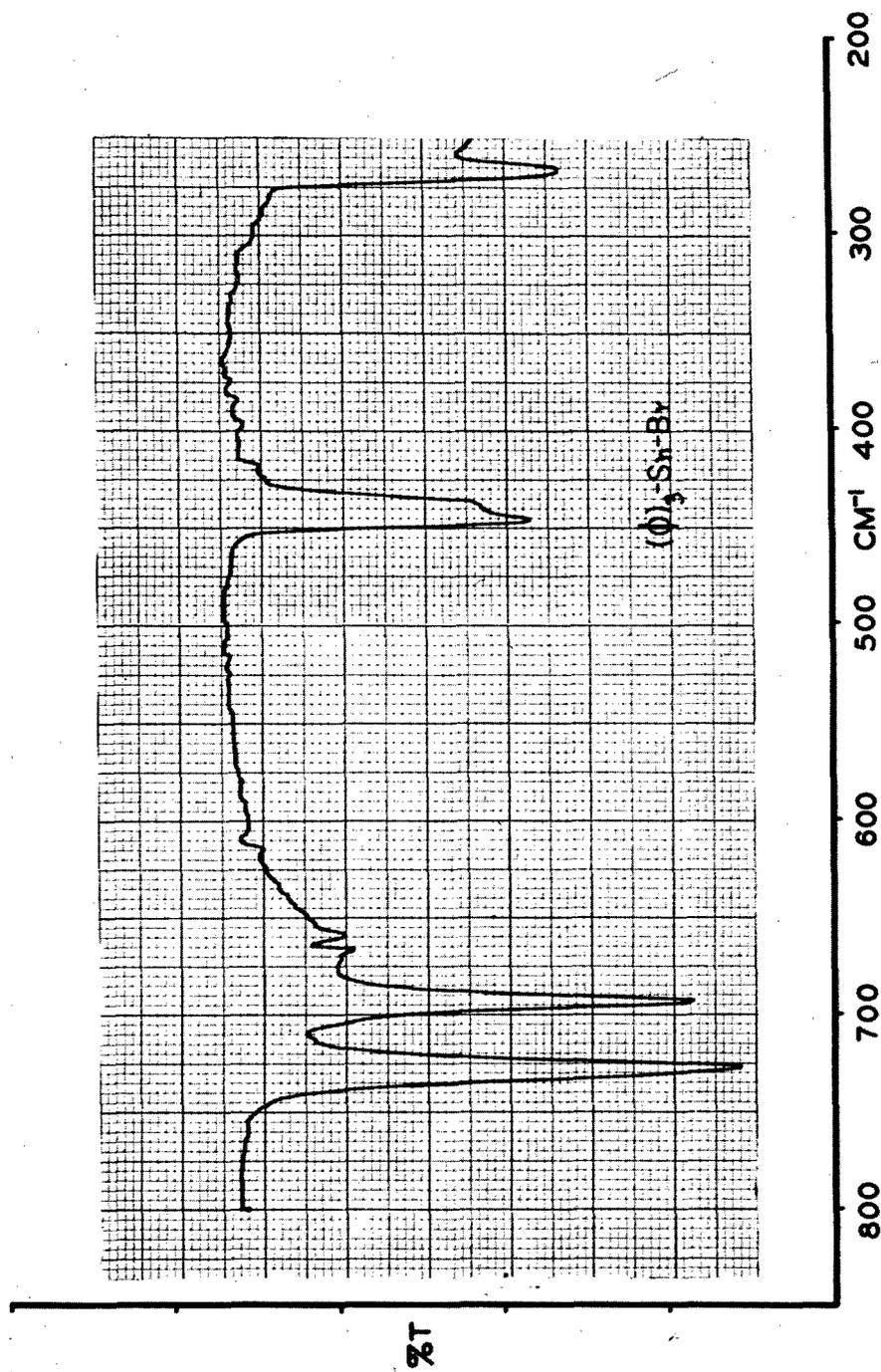


Figure 11. Infrared Spectrum of $(\phi)_3\text{SnBr}$ (800 - 250 cm^{-1})

Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. Rpt. No. ASD-TDR-62-224. THE INFRARED SPECTRA AND VIBRATIONAL ASSIGNMENTS FOR SOME ORGANOMETALLIC COMPOUNDS. Final report, March 1962, 15p incl. illus., tables.
Unclassified report

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(over)

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1. Infrared spectroscopy
2. Metalorganic compounds
- I. AFSC Project 7360 Task 736005
- II. Fred W. Behnke
- C. Tamborski
- III. Aval. fr. OHS:
- IV. In ASTIA collection

Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. Rpt. No. ASD-TDR-62-224. THE INFRARED SPECTRA AND VIBRATIONAL ASSIGNMENTS FOR SOME ORGANOMETALLIC COMPOUNDS. Final report, March 1962, 15p incl. illus., tables.
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