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The Infrared Spectra of the Phenyl Compounds of Group IVb, Vb, and VIIb Elements

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FOREWORD

This report was prepared by the Analytical Branch of the Physics Laboratory, Materials Central, Wright Air Development Division. The work was initiated under Project No. 7360, "The Chemistry and Physics of Materials," Task No. 73615, "Compositional, Atomic, and Molecular Analysis," with 1st Lt. Larry A. Harrah, Miss M. T. Ryan, and Dr. Christ Tamborski acting as project engineers.

The report covers work performed from January 1959 to July 1960.

The authors wish to thank Professor H. Gilman of the Chemistry Department, Iowa State University, for supplying some of the compounds used in this study.

ABSTRACT

The infrared spectra between 2 and 35 microns of a large number of phenyl compounds of group IVb, Vb, and VIIb elements are presented. The spectral features of interest in qualitative and quantitative analysis are discussed and empirical correlations between the spectra and properties of the central metal atom demonstrated. The spectra beyond 15 microns are shown to be particularly useful in the quantitative identification of this class of materials.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

Freeman F. Bentley

FREEMAN F. BENTLEY
Chief, Analytical Branch
Physics Laboratory
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INTRODUCTION

The infrared and Raman spectra of the parent molecule of this series, benzene, have been studied by a great number of investigators. Probably the most complete data on this molecule are those of Ingold and co-workers,(1, 2, 3)*, who have studied both the infrared and Raman spectra of benzene and its deuterium derivatives.

Herzberg (4) has summarized the assignments for the vibrations of this molecule and the arguments for the proposed planar structure (D_{6h} symmetry).

In a molecule of D_{6h} symmetry containing 12 atoms, 20 fundamental vibrations are possible, 10 nondegenerate and 10 doubly degenerate. Of these 20 fundamentals, 9 are inactive in both the infrared and Raman spectra. The frequencies of these inactive fundamentals have been calculated by Lord and Andrews (5), using force constants determined from observed frequencies.

More recently Ingold and co-workers (3) suggested slightly different assignments for these inactive fundamentals and with corrections by Mair and Hornig (6) and by Miller (7), these assignments are accepted today.

Figure 1 gives the form of these normal vibrations for a X_6Y_6 molecule together with the numbering system of Herzberg (4). Table 1 gives the frequencies of these vibrations in benzene based on the presently accepted assignments.

Using the approximation that the substituent groups behave as if they are monatomic, monosubstitution on the benzene ring reduces the symmetry to C_{2v}, splitting the 10 degenerate fundamentals, and gives a total of 30 fundamental vibrations for these molecules. Three of these are of species A_2 and hence forbidden in the infrared. The remaining 27 are infrared active. Randle and Whiffen (8) have discussed the assignment of the fundamentals of substituted benzenes based on this approximation. Of the 30 vibrations listed, only 6 appear to be sensitive to the nature of the substituent atom. However, several of the frequencies that are not substituent dependent are nevertheless useful in identifying monosubstitution on the benzene ring.

Although the compounds studied in this laboratory are not of C_{2v} symmetry, the departure of the ring system from C_{2v} symmetry is not great. Therefore the assignments of Randle and Whiffen (8) for the monosubstituted benzene ring system will be accepted in the following discussions.

The purpose of this report is not to propose assignments for the various fundamental vibrations of these molecules but to derive empirical relationships of use in the identification of new compounds. The spectra of the phenyl compounds of Group IVb and Vb elements are compared here with the spectra of the halobenzenes for that purpose.

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*Numbers in parentheses refer to References (p. 9).

Table 1

Vibrational Frequency Assignment of Benzene				
Vibrational Species	Frequency No.	Frequency (cm^{-1})	Description	Activity
A_{1g}	ν_1	3062	ν C-H	R
A_{1g}	ν_2	992	ν C-C	R
A_{2g}	ν_3	1340	δ C-H $\parallel$	F
A_{2u}	ν_4	673	δ C-H $\perp$	IR
B_{1u}	ν_5	3060	ν C-H	F
B_{1u}	ν_6	1010	δ C-C-C $\parallel$	F
B_{2g}	ν_7	995	δ C-H $\perp$	F
B_{2g}	ν_8	703	ν C-C-C $\perp$	F
B_{2u}	ν_9	1310	ν C-C	F
B_{2u}	ν_{10}	1152	δ C-H $\parallel$	F
E_{1g}	ν_{11}	850	δ C-H $\perp$	R
E_{1u}	ν_{12}	3080	ν C-H	IR
E_{1u}	ν_{13}	1485	ν C-C	IR
E_{1u}	ν_{14}	1037	δ C-H $\parallel$	IR
E_{2g}	ν_{15}	3047	ν C-H	R
E_{2g}	ν_{16}	1596	ν C-C	R
E_{2g}	ν_{17}	1178	δ C-H $\parallel$	R
E_{2g}	ν_{18}	606	δ C-C-C $\parallel$	R
E_{2u}	ν_{19}	975	δ C-H $\perp$	F
E_{2u}	ν_{20}	405	δ C-C-C $\perp$	F

ν Denotes a stretching vibration
δ Denotes a bending vibration ($\parallel$ in plane, $\perp$ out of plane)
R Raman active
IR Infrared active
F Forbidden or inactive

EXPERIMENTAL

The spectra in the rocksalt region (2 to 16 microns) were obtained using a Baird Associates Model "B" double beam recording spectrophotometer. The spectra were measured when possible as solutions in carbon disulfide and bromoform. In some cases where the solubility in these solvents was prohibitively small, the spectra were obtained as potassium bromide pellets or nujol mulls.

The spectra in the region from 15 to 35 microns were obtained using a modified Perkin-Elmer Model 21 double beam recording spectrophotometer with caesium bromide optics (9). They were obtained as caesium bromide pellets except for the halobenzenes which were measured as the pure liquids in fixed path cells.

DISCUSSION

The Rocksalt Region (2 to 16 microns)

The spectra in the rocksalt region of the phenyl compounds of elements heavier than silicon are quite similar and show increased similarity until in the heavier substituent atoms they appear almost identical.

The spectra are characterized by a general shift to longer wavelengths with increasing mass accompanied by increased sharpness. In each series the transition from the first to the second member gives the greatest spectral shifts as would be expected.

Although many of the bands in the rocksalt region appear to shift to longer wavelengths with mass increases, only three bands show major position changes, these are the two "X sensitive" vibrations noted by Randle and Whiffen (8) and the out-of-plane hydrogen "umbrella" deformation between 755 and 725 cm^{-1} .

Figures 2, 3, and 4 show some of the spectra of the simple compounds of group IVb, Vb, and VIIb elements.

The higher of these "X sensitive" vibrations, located between 1190 and 1050 cm^{-1} has been discussed by Kross and Fassel (10) who studied compounds of the type $\Phi_n M$ of Group IVb, Vb, and VIIb elements, where n is the valence of the group. They show a linear relationship within each group between frequency and the square of the electronegativity of the atom. The slopes are related to the primary valence of the group. The compounds measured in this laboratory include the type $\Phi_6 MM'$ where M and M' are group IVb elements as well as type $\Phi_z X_y M$ where M is a group IV, Vb, or VIIb element and X is H, OH, or Cl. This frequency obeys the relationship of Kross and Fassel (10) for all these compounds regardless of the additional groups attached to the M atom. This frequency, therefore, appears to be a function of the electronegativity of the element attached directly to the ring but not of the electronegativity of the substituent group. Figure 5 shows this behavior.

In the compounds of the type $\Phi_6 MM'$ studied in this laboratory a band appears in this region for both ΦM and $\Phi M'$ as would be expected. This, however, offers no distinction between mixtures containing both types of phenyl groups and compounds containing both structures.

The spectra of the $\Phi_6 MM'$ compounds are given in Figures 6 through 9.

The second "X sensitive" vibration ranges in frequency in the halobenzenes from 806 cm^{-1} in fluorobenzene to 654 cm^{-1} in iodobenzene. As pointed out by Randle and Whiffen (8) these frequencies are more easily determined from Raman spectra because of their strong polarization. This vibration is of little qualitative value in the infrared spectra of the IVb and Vb derivatives.

The out-of-plane (umbrella) hydrogen deformation (ν_4 Herzberg), occurring between 755 and 725 cm^{-1} in our compounds, has been studied by Margoshes and Fassel (11) who found that in the monosubstituted benzenes, the frequency decreased linearly with increasing reduced mass of the diatomic group M-carbon. With one exception, our compounds were in very good agreement with this observed behavior. This vibration in phenyldichloroiodide is located at the same frequency as in chlorobenzene rather than at the frequency of iodobenzene. This suggests that the group might possibly have the structure $\Phi - I^{-I^+}_{-Cl}$ rather than $\Phi - I^{+-Cl^-}_{-Cl}$ which is very unlikely since the band at 1065 cm^{-1} is in the expected position for the $\Phi - I^{+-Cl^-}_{-Cl}$ structure.

Two additional bands occur in this region which are of considerable value in the qualitative identification of structues involving the bonding of a benzene ring to a heavier atom. The first, a band in the range 1451-1428 cm^{-1} is assigned by Randle and Whiffen (8) as a planar ring deformation (ν_{13} Herzberg). This band is located near 1461 cm^{-1} for the lighter substituent elements such as fluorobenzene and moves to 1430 cm^{-1} in iodobenzene. In the group IVb and Vb compounds this vibration is located at 1428 cm^{-1} for all compounds of elements heavier than silicon. Young and co-workers (12) attributed this band and the band in the 1190-1050 cm^{-1} region as well, to phenyl silicon vibrations. As can be seen from our data these bands are more closely associated with the phenyl group perturbed by the heavy substituent atom rather than with a particular phenyl-M linkage. This observation was also commented on by Noltes and co-workers (13).

The second, the out-of-plane ring deformation in the 701-675 cm^{-1} region (ν_8 Herzberg) shows very interesting behavior. The frequency of this vibration varies only slightly for the materials studied but appears to have a constant position for all the halogens, another for the group Vb compounds, and a third for the group IVb compounds. These data are summarized in table 2.

Table 2

Frequency of Vibration 8 (Herzberg) for Group IVb, Vb, and VIIb Elements		
Benzene		703
Group IV	Substituted Benzenes (18)	697-701
Group V	(6)	688-693
Group VII	(4)	682-683
Group IV	With Halogens (4)	692-696
Group V	With Halogens (1) ϕ_3SbCl_2	682
	Poly Halogen (1) $-ICl_2$	675

As can be seen, the replacement of a phenyl group with a halogen in the $\Phi_n M$ compounds results in a lowering of the frequency of this vibration. This behavior suggests a dependence on the effective electronegativity of the substituent. It is, however, not a simple electronegativity dependence since each series groups well. The product of the electronegativity of the central atom and the (reduced mass)$^{1/2}$ of the group C-M is approximately constant for each series. Figure 10 shows a plot of the frequencies as a function of the reciprocal of this product with a curve drawn through the points.

The frequencies for phenyl compounds, in which the substituent was other than the simple IVb, Vb, or VIIb element, were placed on the curve, and an effective electronegativity was calculated from their position. Table 3 gives the results of these calculations. The product of electronegativity and (reduced mass)$^{1/2}$ is labeled π. Reduced mass is labeled μ. The calculated electronegativity ($\pi/\mu^{1/2}$) is compared with the electronegativity (X) of the central atom. The last column gives the difference (Δ).

In the cases Φ_3SnCl, Φ_2SnCl_2 and Φ_3CCl, halogens are replacing phenyl groups and as would be expected, the effective electronegativity is changed only slightly while for Φ_3SbCl_2 and ΦICl_2, two chlorines are added rather than replacing a phenyl group giving rise to a much greater change in effective electronegativity. Further confirmation is given by the negative deviations observed when hydrogen replaces phenyl as in Φ_2NH and Φ_3CH. The agreement here is only qualitative due to the small spectral shifts involved and the rather large uncertainties (2 cm^{-1}) in our measurements. Nevertheless, we postulate a dependence on the electronegativities of the group to which the benzene ring is attached as follows:

$$\bar{\nu} = \frac{K}{X_g(\mu_{c-m})^{\frac{1}{2}}}$$

where X_g is the group electronegativity, K is a constant, and μ is reduced mass.

Table 3

Calculated Electronegativities From Vibration 8 (Herzberg)							
		8	$\frac{1}{\pi}$	π	$\pi/\sqrt{\mu}$	$\overline{X}$	Δ
ϕ_3	Sb Cl_2	682	.096	10.40	3.14	1.89	+ 1.25
ϕ_2	Sn Cl_2	692	.147	6.80	2.06	1.66	+ .40
ϕ	I Cl_2	675	.060	16.70	5.04	2.65	+ 2.39
ϕ_3	Sn Cl	696	.168	5.95	1.80	1.66	+ .14
ϕ_3	Sn OH	696	.168	5.95	1.80	1.66	+ .14
ϕ_2	NH	693	.152	6.57	2.59	2.96	-.37
ϕ_3	CCl	697	.173	5.78	2.36	2.51	-.15
ϕ_3	CH	699	.183	5.46	2.22	2.51	-.29

For compounds of the general formula $\Phi_x - M^{-Ay}_{-Bz}$, X_g is given by an expression such as

$$\overline{X}_g = \overline{X}_m + k\left[(x-1)\,\overline{X}_\phi + Y\overline{X}_a + Z\overline{X}_b\right] \qquad (2)$$

where
- $\overline{X}_m$ = electroneg. of the central atom
- $\overline{X}_\phi$ = electroneg. of the phenyl group
- $\overline{X}_a$ = electroneg. of A
- $\overline{X}_b$ = electroneg. of B
- k = a constant (transmissivity) characteristic of each group in the periodic chart.

With an M dependency of this type, this vibration is particularly useful in connection with the vibration in the 9-micron region in determining the atom M in M-Φtype compounds. It can be used also when the atom M is known, to determine Z in compounds of the type $\Phi_y MX_z$ where the group X is halogen, hydrogen, or hydroxyl. This band is somewhat broad and it is not known whether splitting can be observed in compounds of the type $\Phi_3 M - M'\Phi_2$ where M and M' are group IVb and Vb elements respectively. If such splitting can be observed, this vibration could be very useful in distinguishing structures of this type.

The Caesium Bromide Region

In the region beyond 15 microns the spectra of these compounds become quite distinctive. For the simple compounds of the type $\Phi_x M$, where x is the valence of atom M, two bands of medium-to-strong intensity occur in the range 520 to 190 cm^{-1}. The first of these bands ranging from 507 - 433 cm^{-1} is an "X sensitive" vibration described by Randle and Whiffen (8) as a C-X out-of-plane deformation (ν_{19} Herzberg). This band tends to split into a band group in the more asymmetric trivalent compounds. In the halobenzenes it is a single peak and in the group IVb compounds it is split into a doublet whose splitting varies directly with the mass of the central atom. In all the compounds studied, this vibration shows a small mass dependency with a limit of about 433 cm^{-1} for infinite mass (See figure 11).

The spectra of the simple $\Phi_x M$ compounds are shown in Figure 12 through 14.

The position of this vibration, for a given atom M is relatively constant in the molecules studied.

A second vibration, ν_{18}, occurs between 520 cm^{-1} and 190 cm^{-1}. This gives rise to a band of medium-to-strong intensity and is visible in the spectra of the lighter compounds in Figures 12 through 14. The frequency of this vibration is quite mass dependent and is very characteristic of a particular M-Φ linkage. Although not shown here, we have studied the region from 300 to 190 cm^{-1} using a Perkin-Elmer Model 12C single beam instrument equipped with caesium iodide optics. With this instrument we have observed ν_{18} in the heavier elements of each series. With the exception of the compounds containing Φ-carbon linkages this frequency is linearly dependent on the reciprocal of the reduced mass of the Φ-M group taken to the one-half power. A plot of these frequencies is given in Figure 15. This absorption frequency is almost entirely governed by the atom attached

to the benzene ring and is quite useful in identifying the particular linkage. Compounds containing halogen as well as mixed Φ-M bonds also show this vibration for each of the Φ-M species present.

Figure 16 shows the spectra of the Φ_6M_2 compounds. With the exception of hexaphenyl disilane, the spectra are almost identical to the Φ_4M compounds. The additional band in hexaphenyldisilane, not present in tetraphenyl silane, cannot be attributed to a vibration of the benzene ring. Two vibrations are likely to occur in this region: (1) the silicon-silicon stretch, and (2) the axial deformation of the two silicon atoms, within the cage of practically stationary phenyl groups. The first of these is forbidden in the infrared and violation of the selection rules is not likely to give a band of the observed intensity. Based on reasonable assumptions as to the bending force constants for Φ-Si bonds we have estimated the frequency of the second vibration to be 312 cm^{-1}. The observed frequency of 352 cm^{-1} is in reasonable agreement with this value. On this basis the analogous vibration in the digermane should be in the vicinity of 217 cm^{-1} distannane 188 cm^{-1} and dilead at 154 cm^{-1}. A weak band is observed for hexaphenyl digermane at approximately 210 cm^{-1}.

The spectra of the mixed Φ_6MM' compounds are shown in Figures 17 and 18. In each case vibration ν_{19} is split into components attributable to both types of Φ-M linkages. ν_{18} also appears for both types of linkages. Several other weak or medium bands appear that are not present in the Φ_6M_2 type compounds. In particular a band of medium intensity constantly occurs in the region of ν_{18} for the heavier of the two Φ-M linkages. Although not shown here, the data found in the region beyond 35 microns confirm this occurrence even in the heavier tin and lead compounds studied. This band is tentatively assigned to the M-M' stretching vibration which will become infrared active in the asymmetric Φ_6MM' molecules.

Several weak bands of uncertain origin also occur in this region enabling the positive identification of these mixed compounds. Unlike the spectra in the rocksalt region, these spectra are quite distinctive and enable the worker to quickly identify the more complex molecules. It is easy to distinguish here between mixtures of compounds and pure compounds containing more than one type of Φ-M linkage. This is particularly useful in the analysis of reaction products encountered in the synthesis of these materials.

Figure 19 shows the spectra of some halogen substituted compounds. Bands in the 28 to 35 micron region in the chlorostannanes are probably associated with the tin chlorine stretching vibrations and are in the vicinity of a strong band of tin tetrachloride located at about 26 microns. The band just visible at the limit of the triphenyldichlorostibine spectrum probably is the antimony-chlorine stretch. This vibration in antimony trichloride occurs in the vicinity of 30 microns.

Figure 20 compares the spectra in the 2 to 15 micron region of tetraphenylstannane, triphenylchlorostannane, and diphenyldichlorostannane. As can be seen from these spectra, it is a difficult if not impossible task to distinguish these compounds in this region. Quantitative analysis of triphenylchlorostannane in the presence of tetraphenylstannane is virtually impossible, using this region. Figure 21 shows the spectra of these compounds in the 15 to 35 micron region. It is immediately obvious that not only is it qualitatively possible to identify these components but quantitative analysis is also possible.

CONCLUSION

The spectra of the compounds of group IVb, Vb, and VIIb elements in the 2 to 15 micron region, although quite characteristic of monosubstituted benzenes, are not sufficient for the qualitative identification of new synthetic materials in this class.

Additional substitution on the central atom of this type of compound, particularly with a halogen atom, changes the spectra only slightly.

The extension of the infrared spectra beyond 15 microns compliments the information found in the rocksalt region and enables the worker to more quickly identify new structures as well as providing a valuable means of quantitative analysis of reaction products containing this class of material.

The range of this study was limited to the region from 2 to 52 microns. The information gained, however, indicates the desirability of extending the range to 100 or 200 microns in order that the compounds of the heavier elements (Pb, Bi, Br, I) be fully characterized.

BIBLIOGRAPHY

1. Bailey, C. R., Hale, J. B., Ingold, C. K., and Thompson, J. W., J. Chem. Soc., 931 (1936)

2. Ingold, C. K., Angus, W. R., and Lecke, A. H., J. Chem. Soc., 925 (1936)

3. Ingold, C. K., et al, J. Chem. Soc., 222, 235, 239, 244, 245, 252, 255, 272, 288, 299, 316 (1946)

4. Herzberg, G., Infrared and Raman Spectra of Polyatomic Molecules, D. Van Nostrand Company, Inc., New York, (1945) pp. 118, 362-269

5. Lord, R. C., Jr. and Andrews, D. H., J. Phys. Chem., 41, 149 (1937)

6. Mair, R. D. and Hornig, D. F., J. Phys. Chem., 17, 1236, (1949)

7. Miller, F. A., J. Chem. Phys., 24, 996 (1956)

8. Randle, R. R. and Whiffen, D. H., "Molecular Spectroscopy," Institute of Petroleum, London, (1955) p. 111

9. Bentley, F. F., Wolfarth, E. F., Srp, N. E., and Powell, W. R., Spectrochimica Acta, 13, 1 (1958)

10. Kross, R. D., and Fassel, V. A., J. Am. Chem. Soc., 77, 5858 (1955)

11. Margoshes, M., and Fassel, V. A., Spectrochimica Acta, 7, 14 (1955)

12. Young, C. W., Servais, P. C., Currie, C. C., and Hunter, M. J., J. Am. Chem. Soc., 70, 3758 (1948)

13. Noltes, J. G., Henry, M. C., and Janssen, M. J., Chemistry and Industry, 298 (1959)

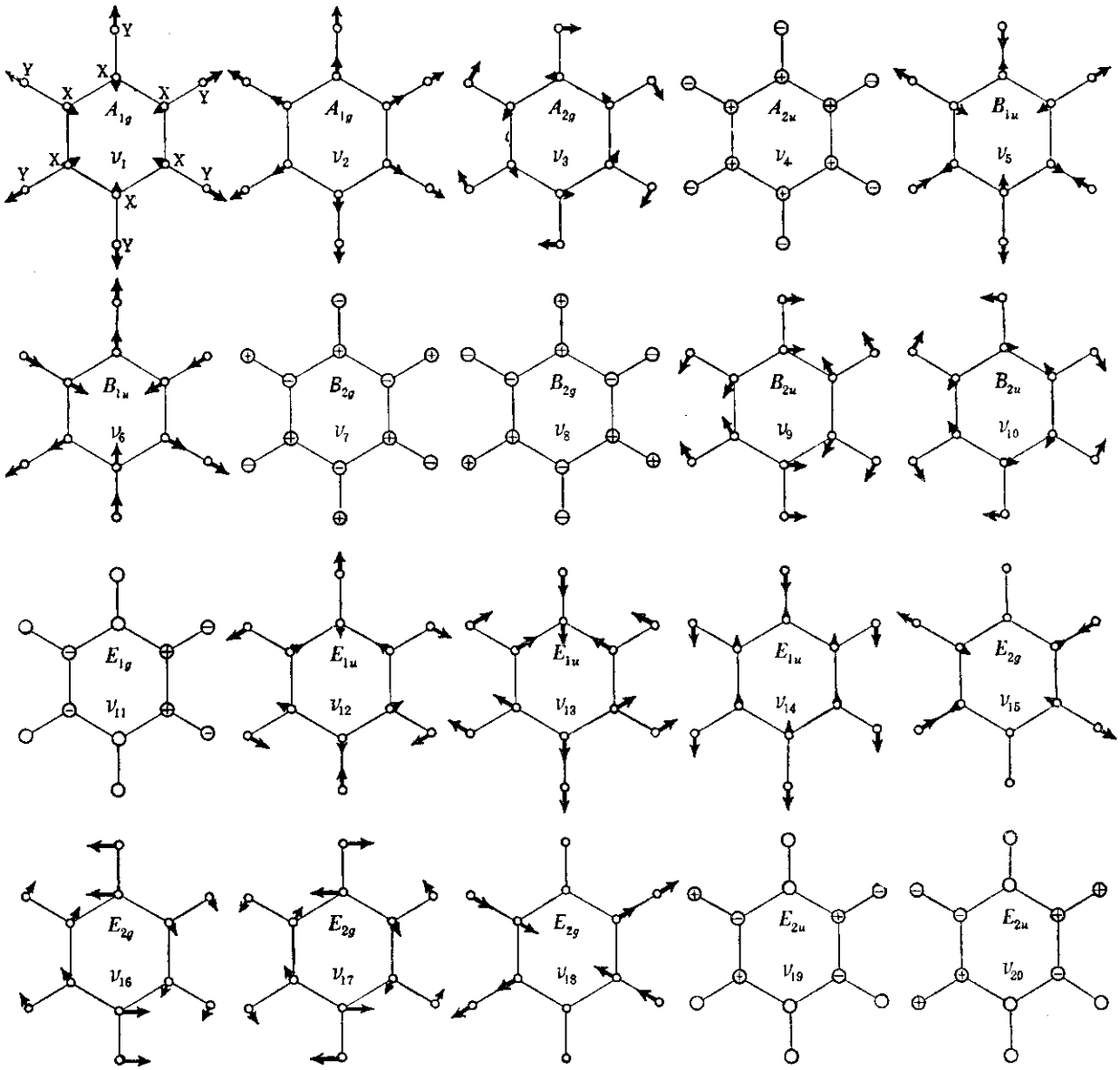

Figure 1. Normal Vibrations of X_6 Y_6 Molecule from Herzberg (4)

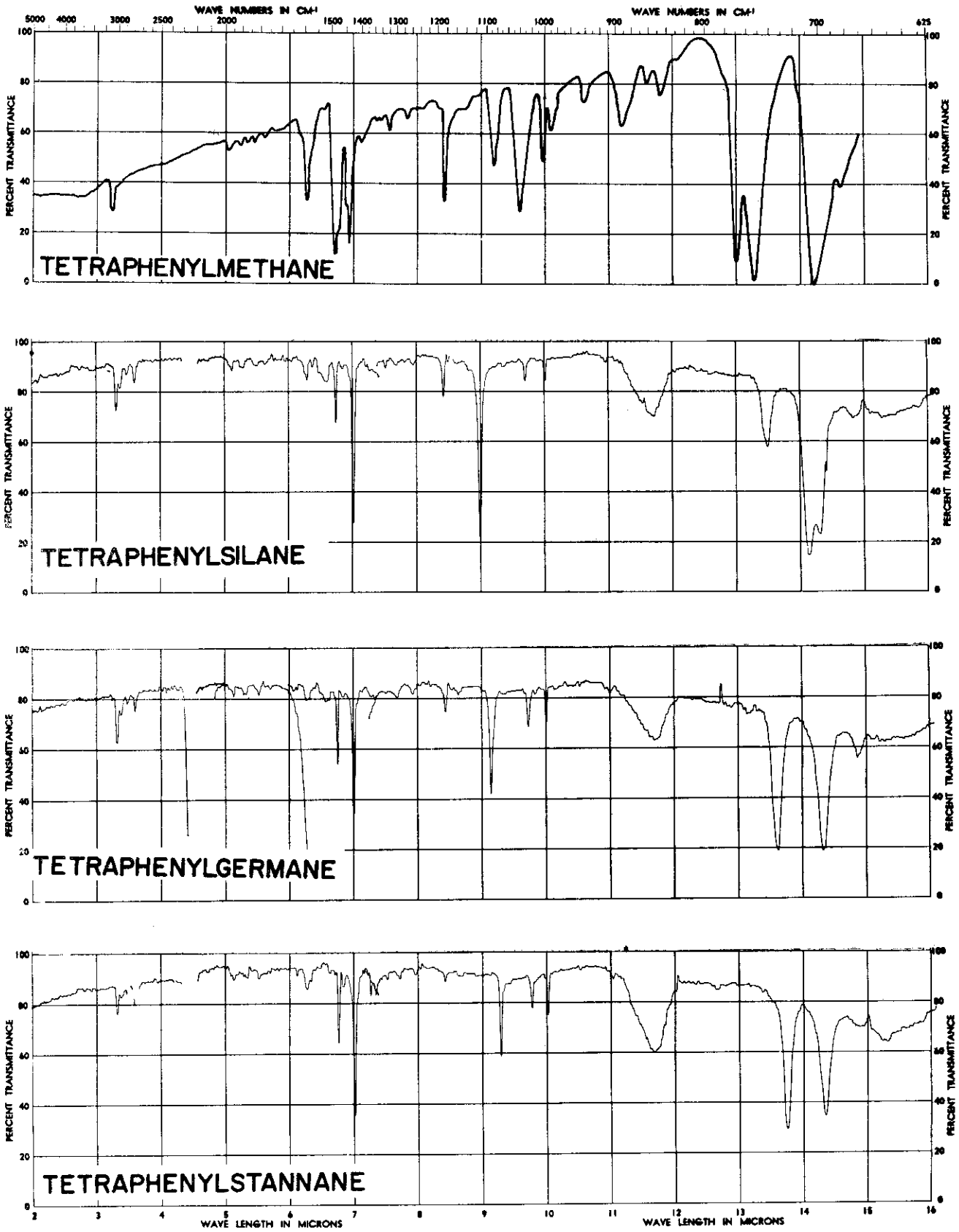

Figure 2. Spectra from 2 to 15 microns of Tetraphenylmethane, Tetraphenylsilane, Tetraphenylgermane, and Tetraphenylstannane

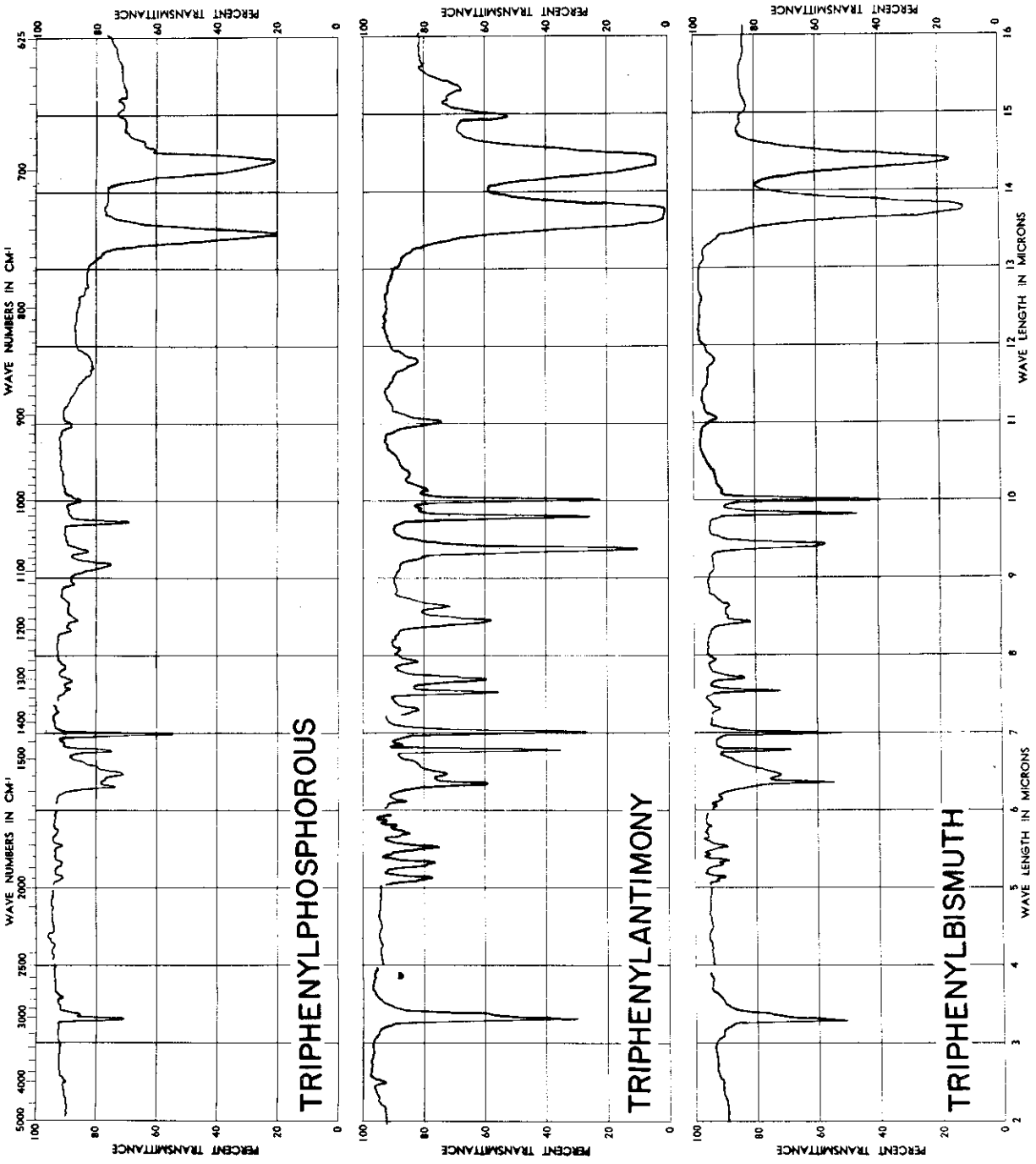

Figure 3. Spectra from 2 to 15 microns of Triphenylphosphorous, Triphenylantimony, and Triphenylbismuth

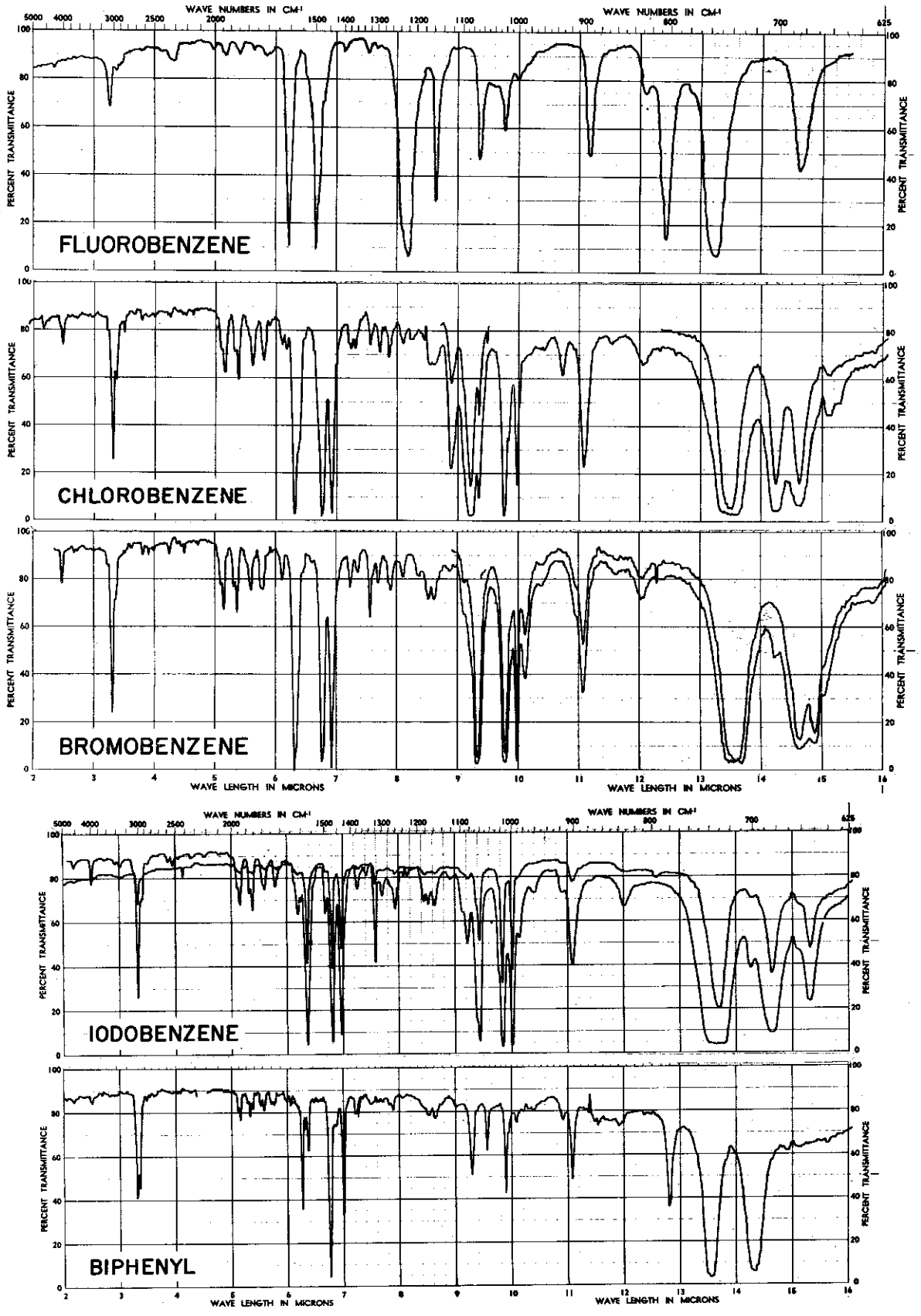

Figure 4. Spectra from 2 to 15 microns of Fluorobenzene, Chlorobenzene, Bromobenzene, Iodobenzene, and Biphenyl

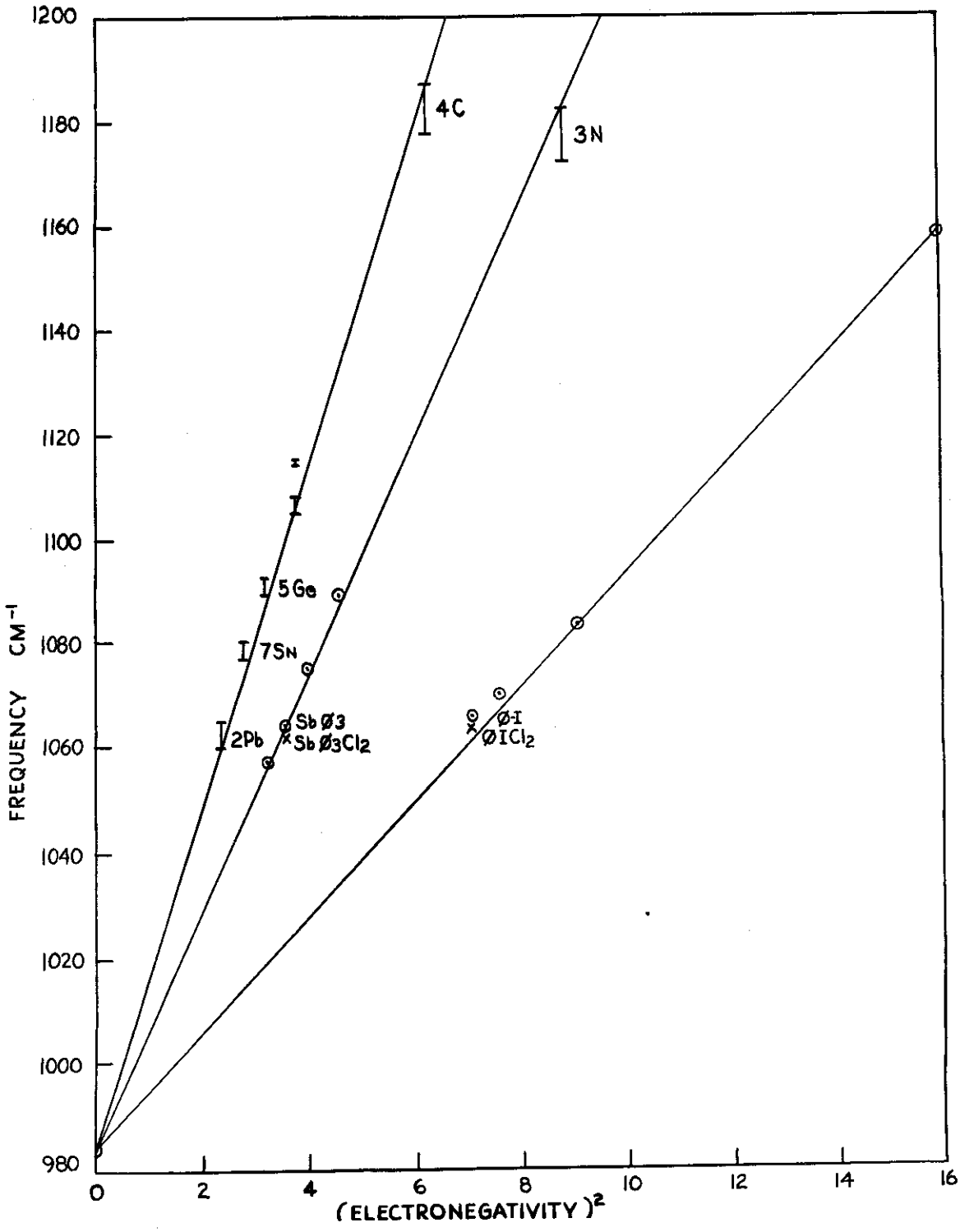

Figure 5. Plot of Frequency vs. Electronegativity^2 for 1190 to 1050 cm^{-1} Absorption Band

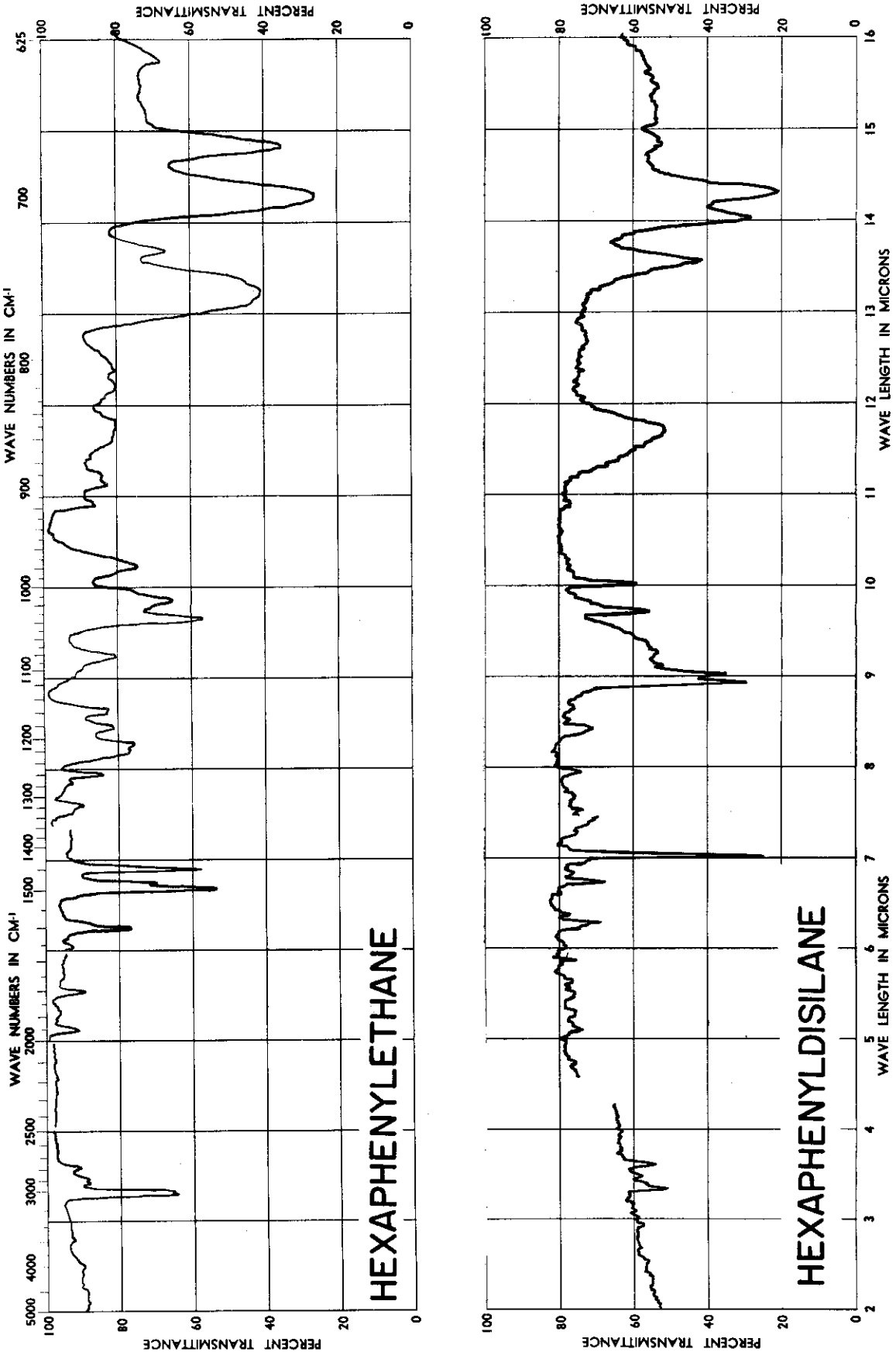

Figure 6. Spectra from 2 to 15 microns of Hexaphenylethane and Hexaphenyldisilane

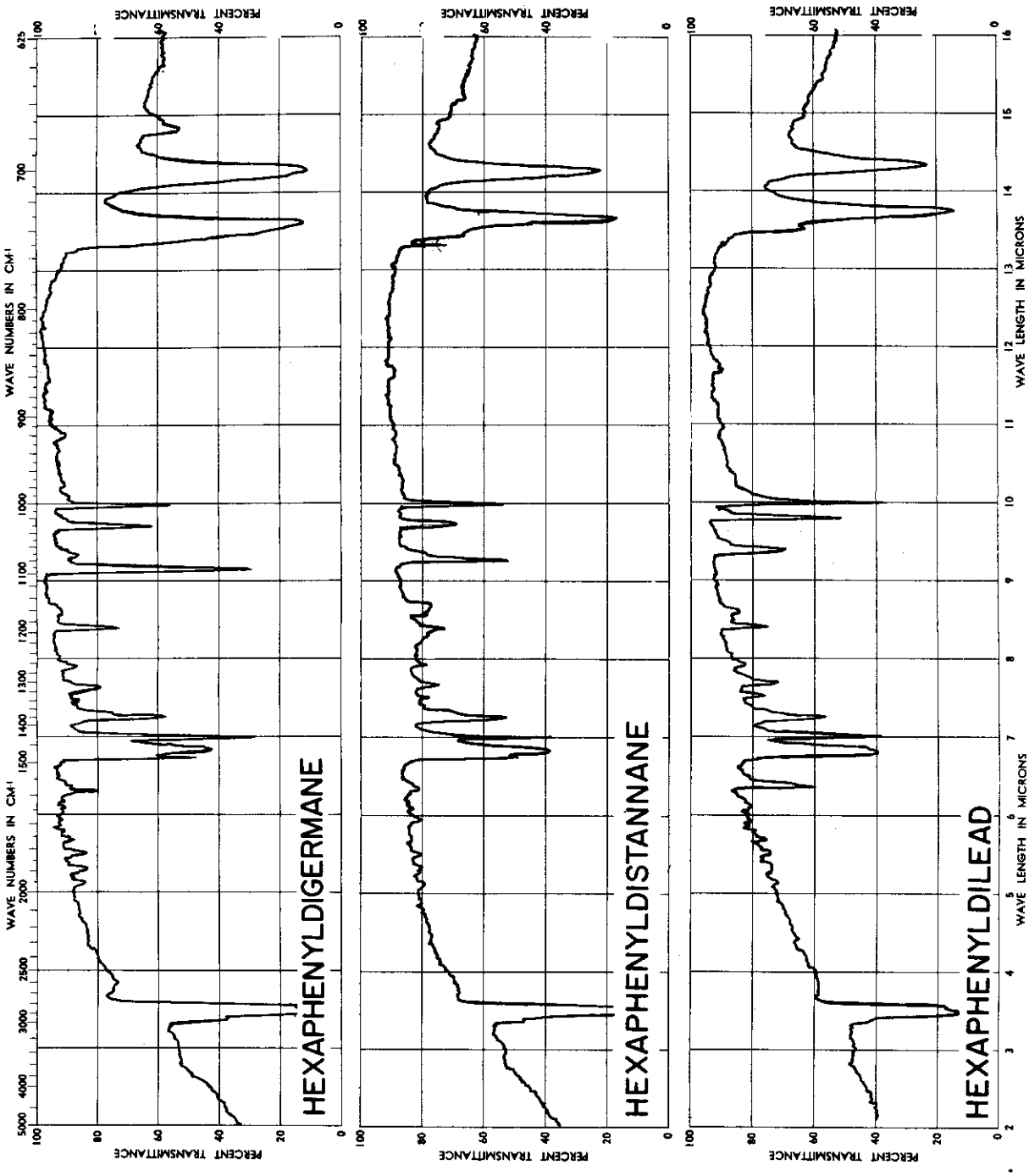

Figure 7. Spectra from 2 to 15 microns of Hexaphenyldigermane, Hexaphenyldistannane, and Hexaphenyldilead

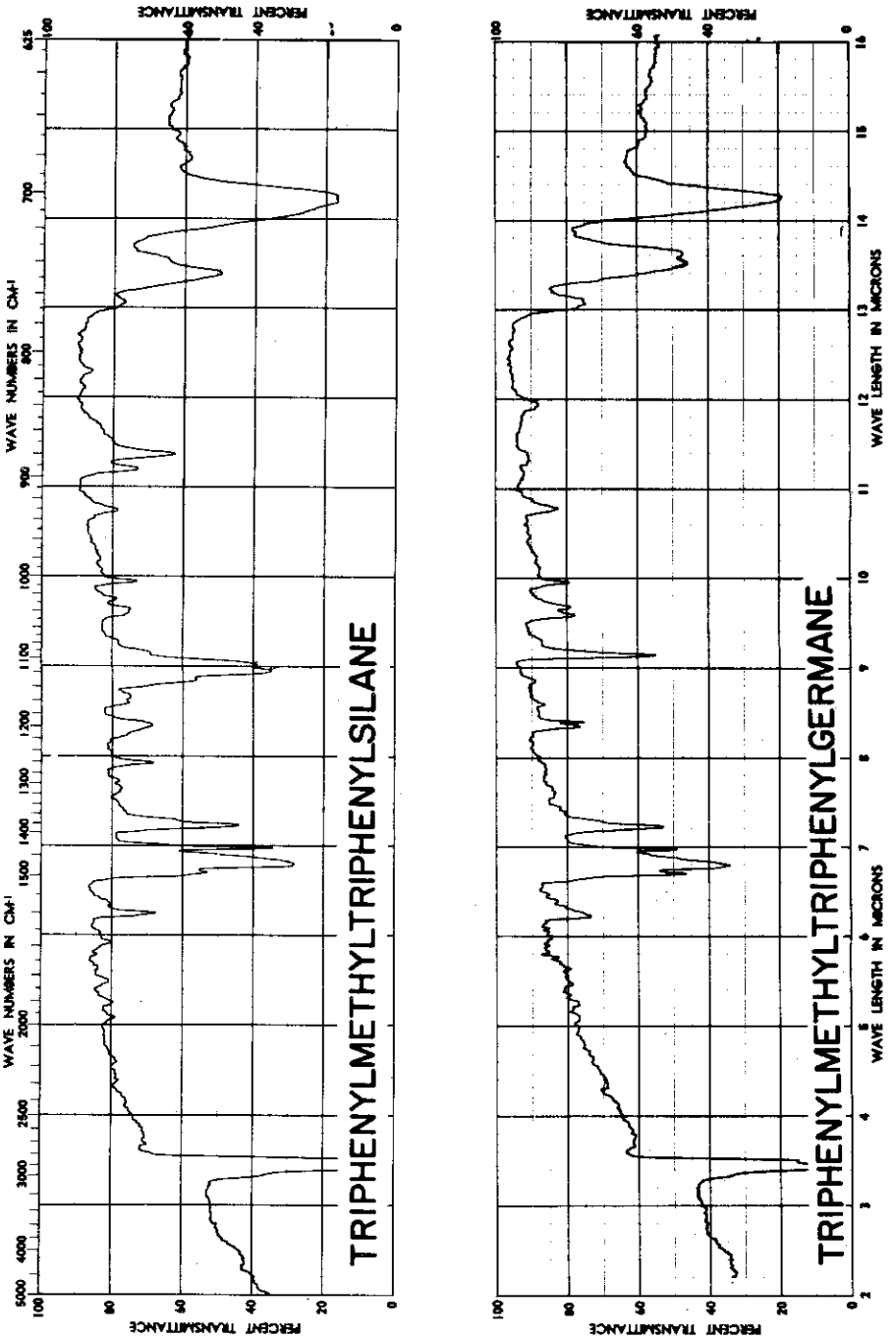

Figure 8. Spectra from 2 to 15 microns of Triphenylmethyltriphenylsilane and Triphenylmethyltriphenylgermane

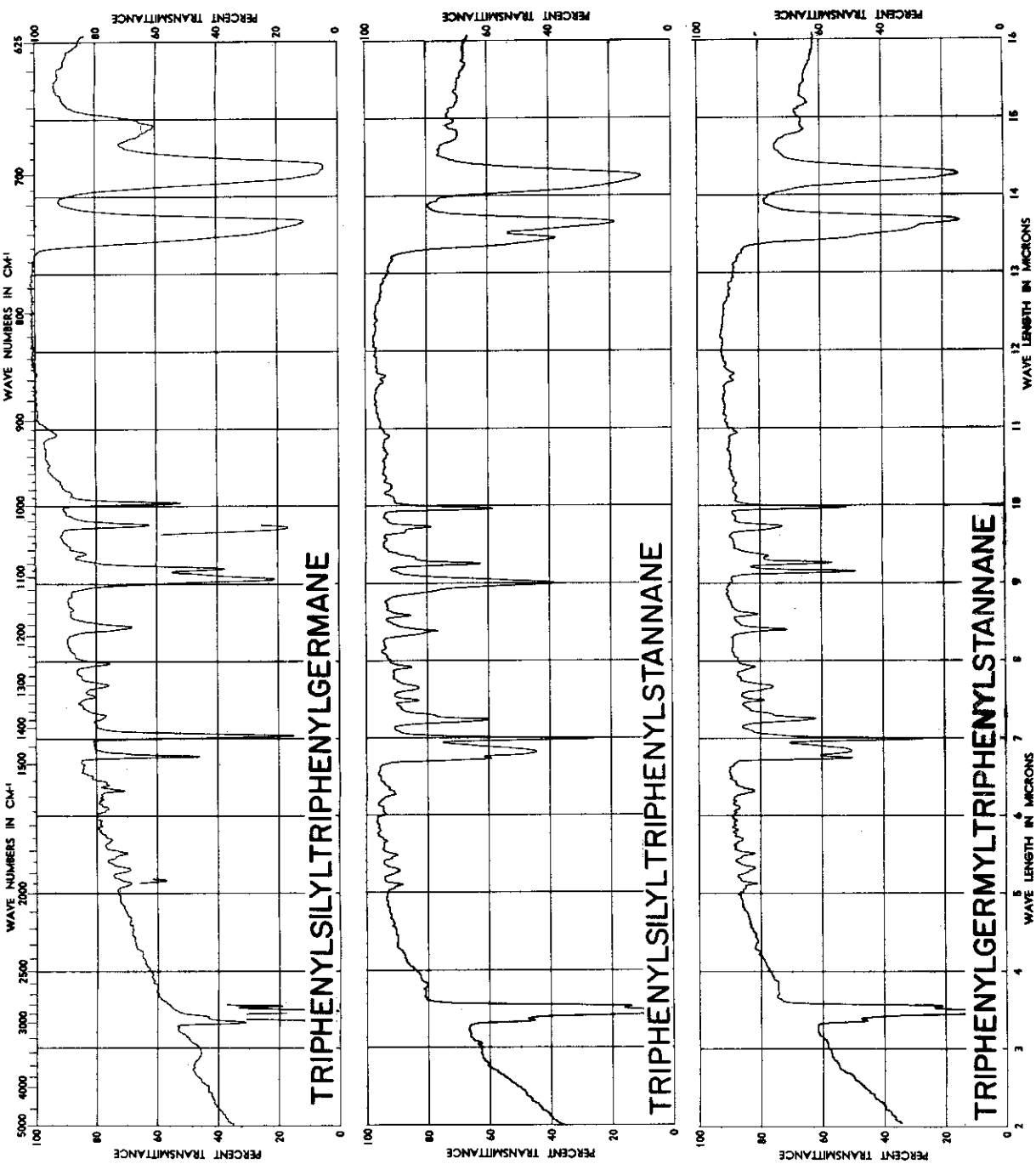

Figure 9. Spectra from 2 to 15 microns of Triphenylsilyltriphenylgermane, **Triphenylsilyltriphenylstannane** and Triphenylgermyltriphenylstannane

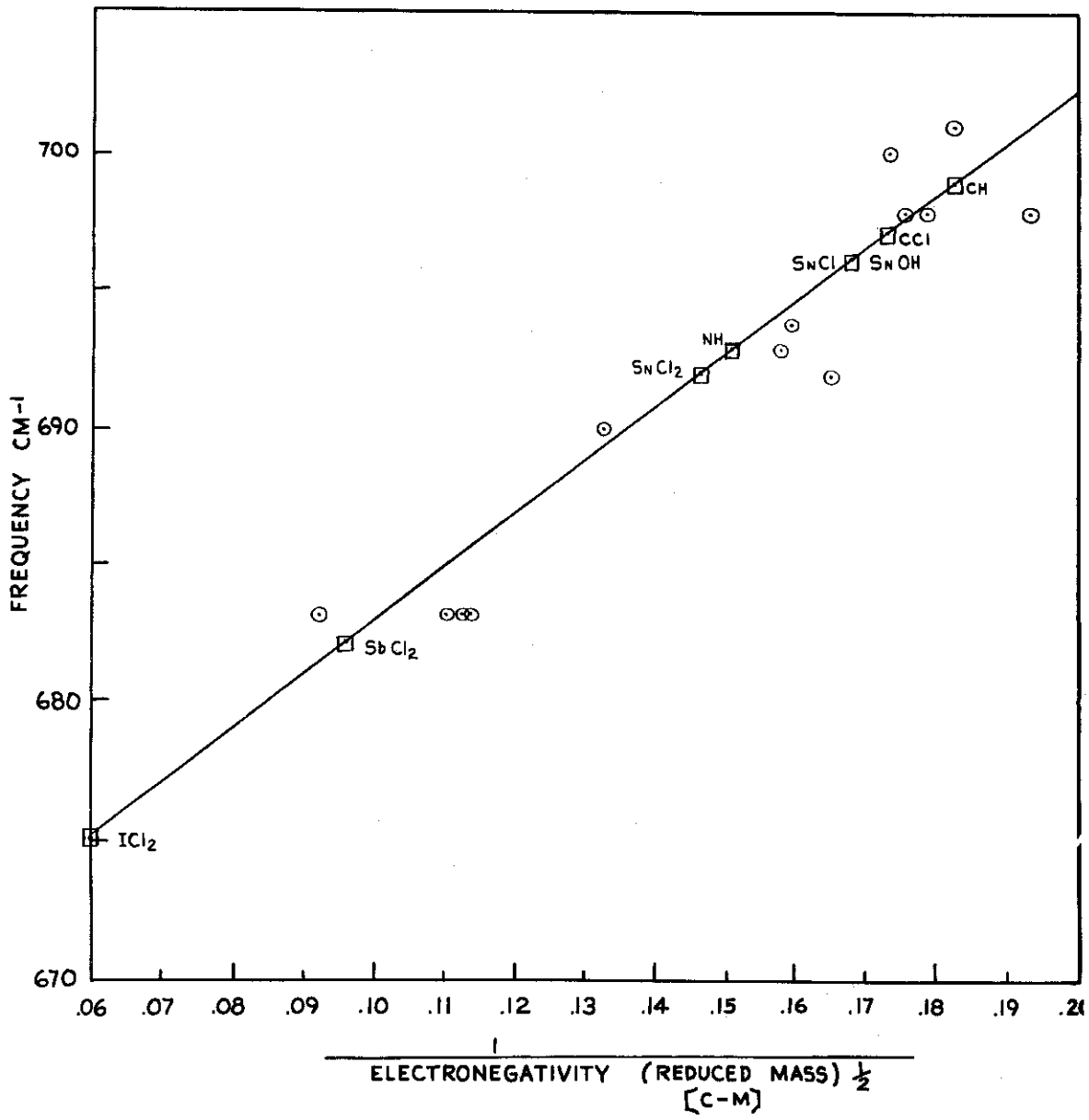

Figure 10. Plot of Frequency vs. Reciprocal of Product of Electronegativity and (Reduced Mass of C-M)$^{\frac{1}{2}}$ for ν_8 (Herzberg)

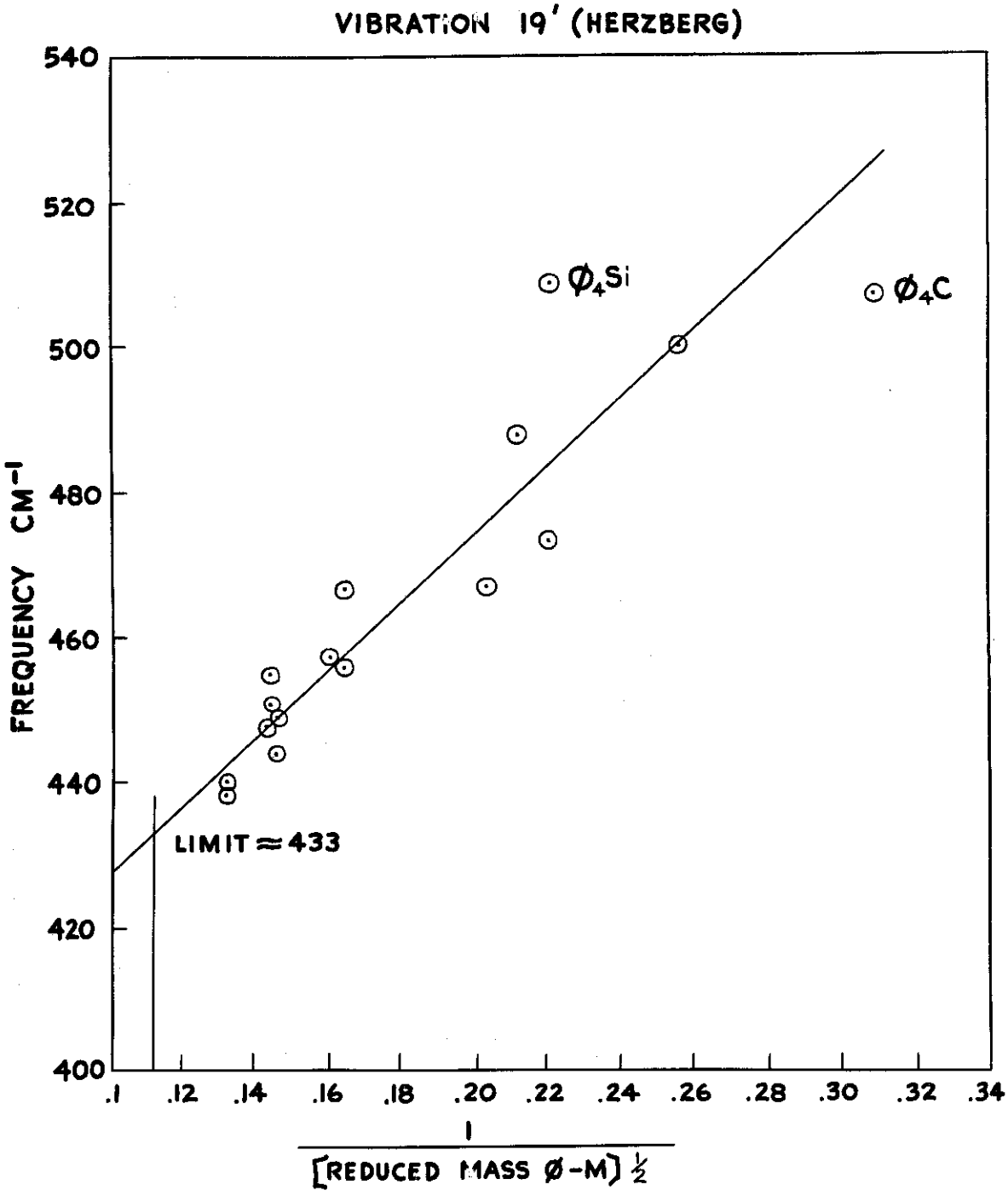

Figure 11. Plot of Frequency vs. Reciprocal of (Reduced Mass of Φ-M)$^{\frac{1}{2}}$ for ν_{19} (Herzberg)

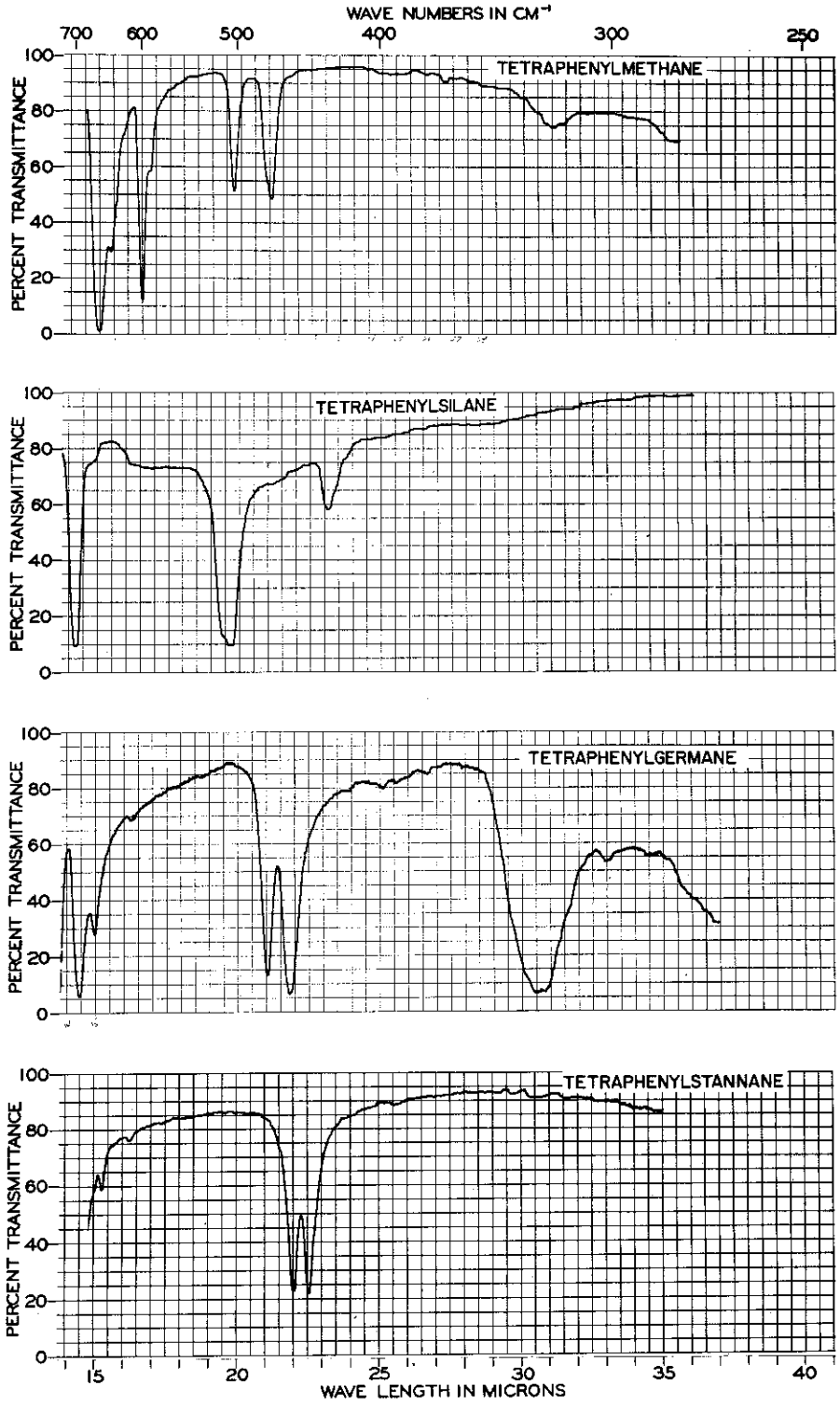

Figure 12. Spectra from 15 to 35 Microns of Tetraphenylmethane, Tetraphenylsilane, Tetraphenylgermane, and Tetraphenylstannane

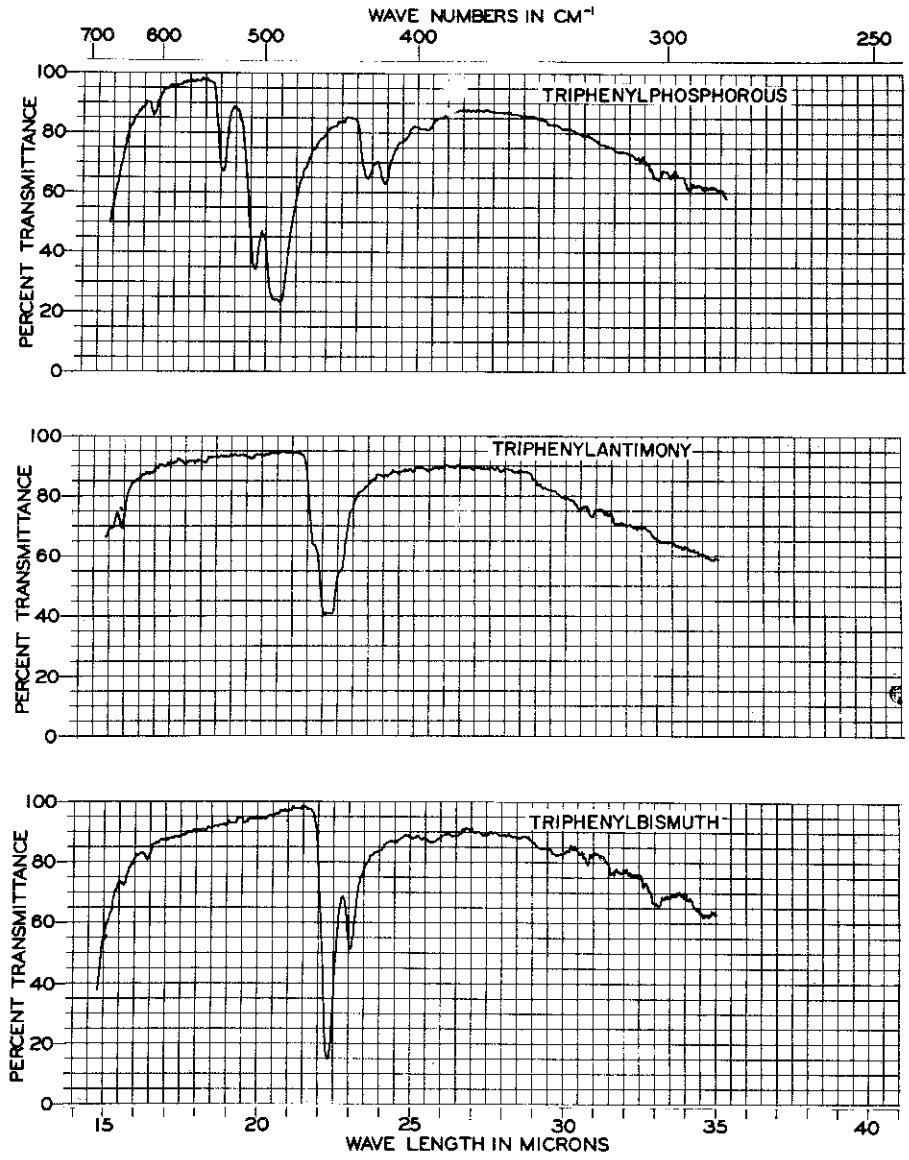

Figure 13. Spectra from 15 to 35 Microns of Triphenylphosphorous, Triphenylantimony, and Triphenylbismuth

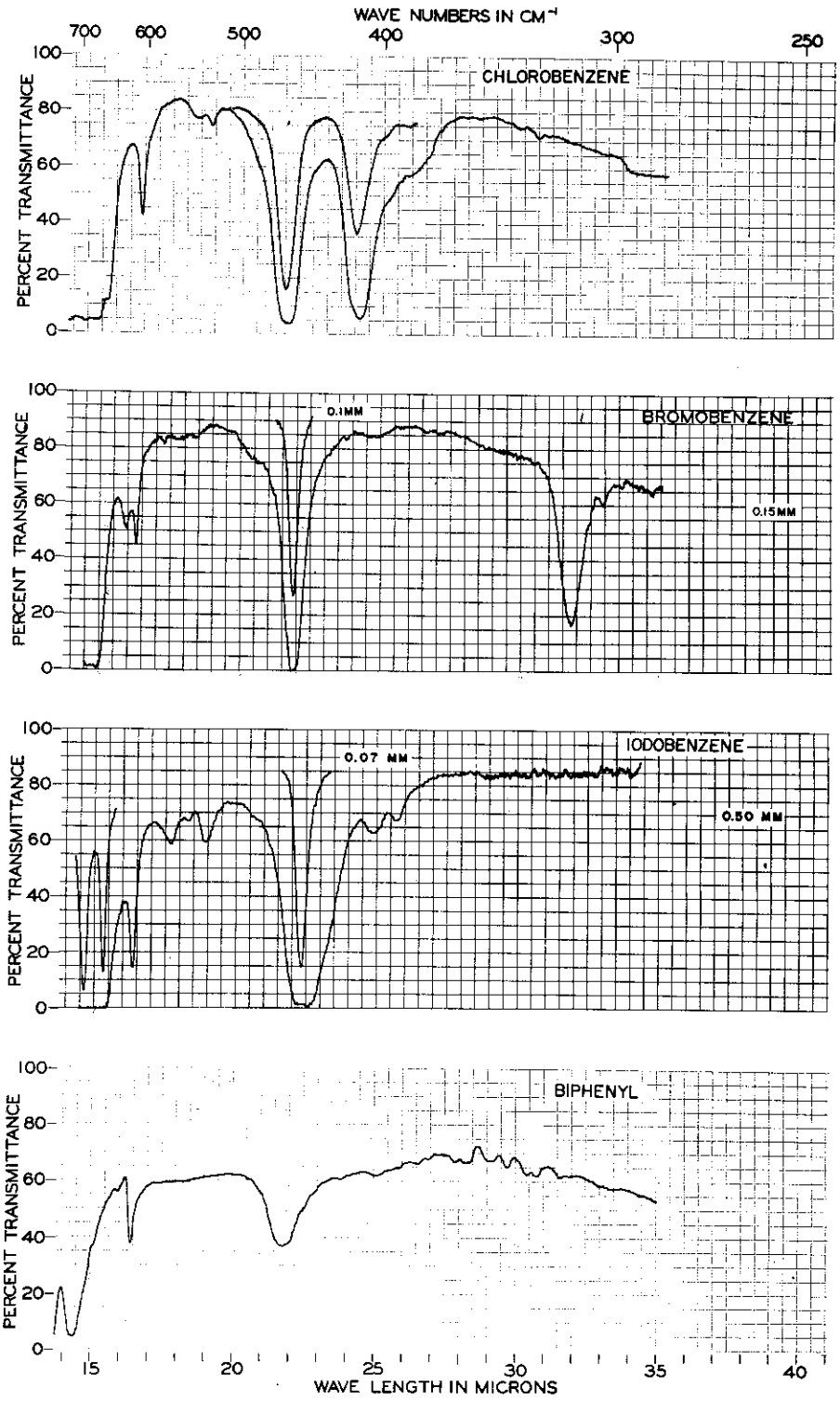

Figure 14. Spectra from 15 to 35 Microns of Chlorobenzene, Bromobenzene, Iodobenzene, and Biphenyl

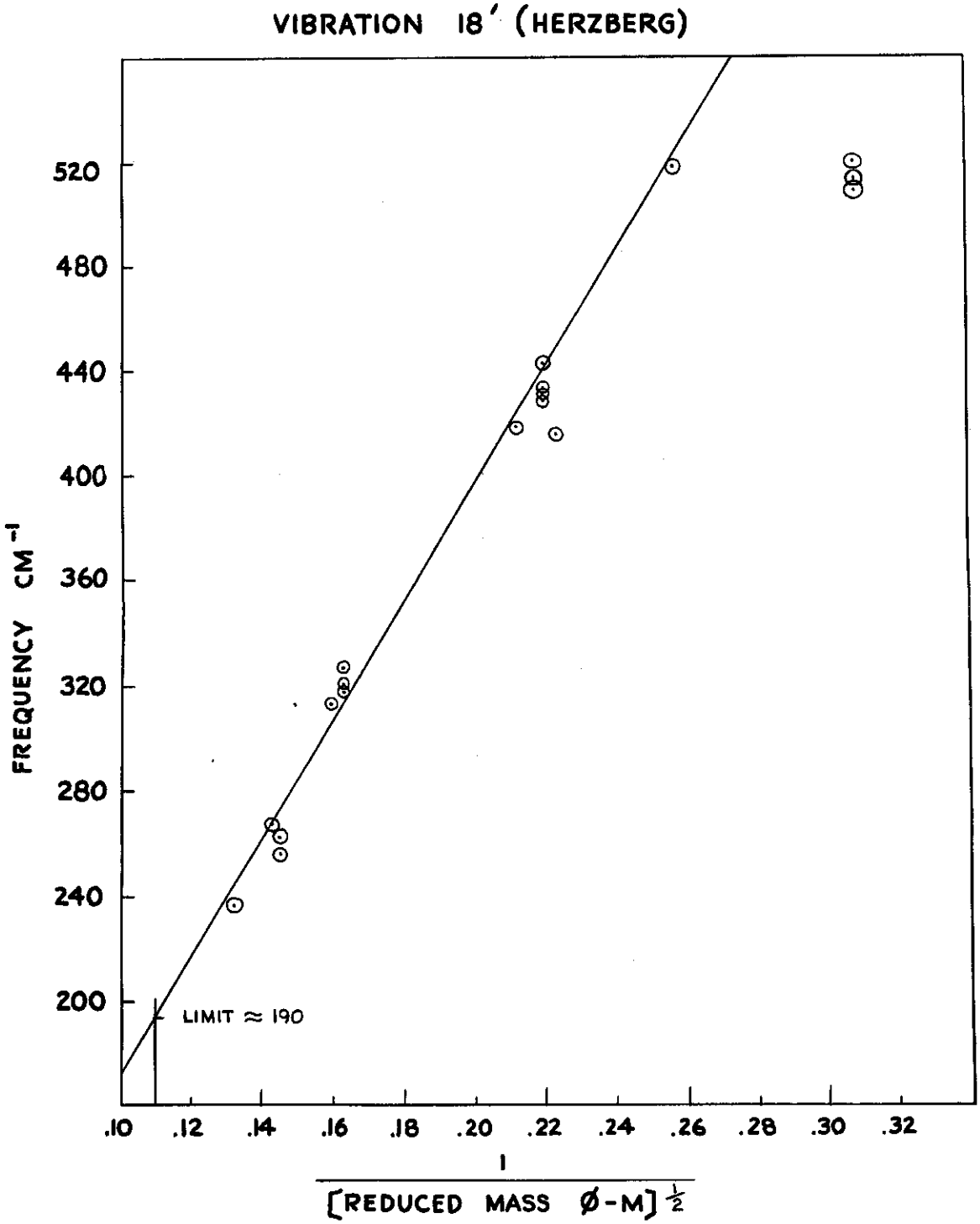

Figure 15. Plot of Frequency vs. Reciprocal of (Reduced Mass of Φ-M)$^{\frac{1}{2}}$ for ν_{18}' (Herzberg)

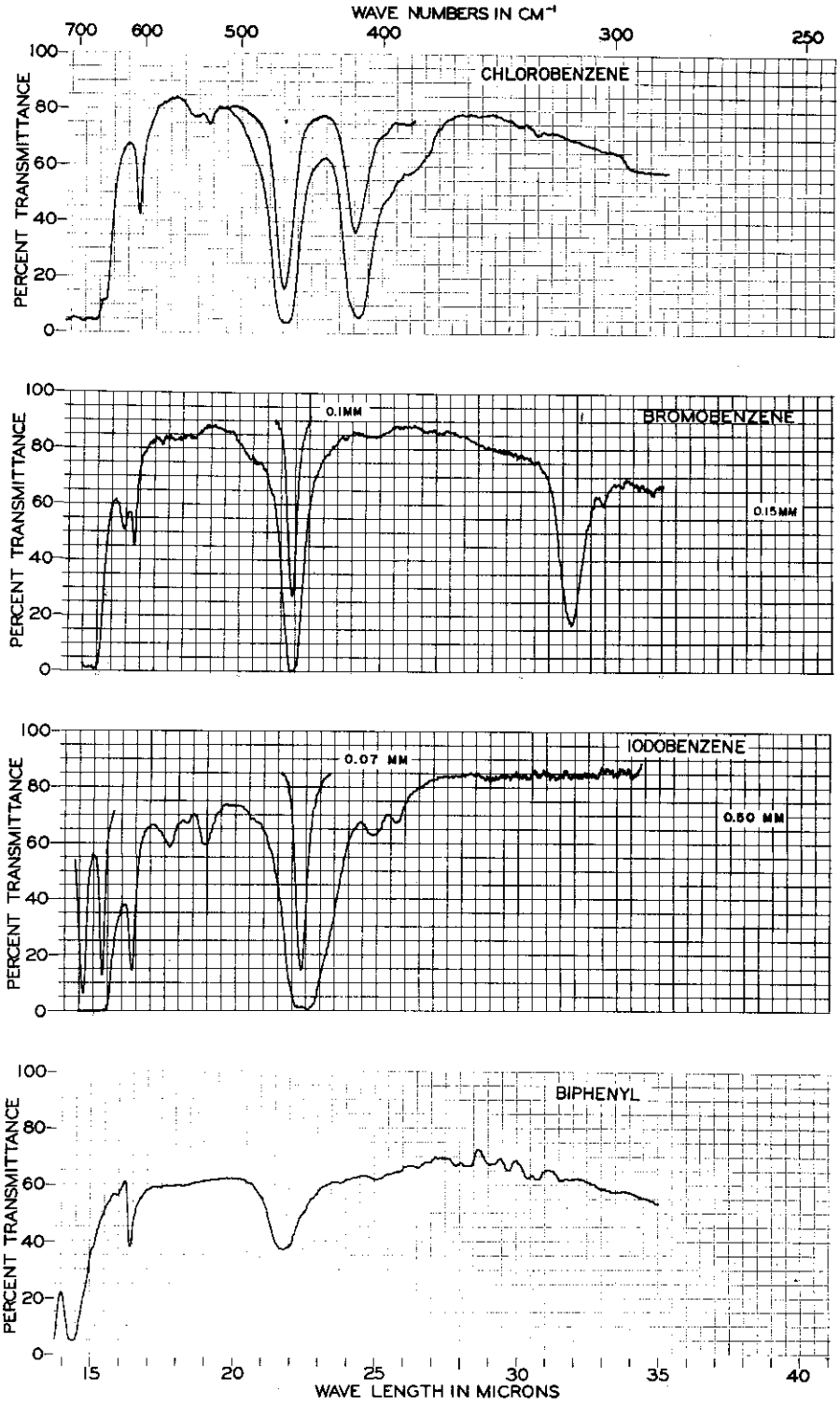

Figure 14. Spectra from 15 to 35 Microns of Chlorobenzene, Bromobenzene, Iodobenzene, and Biphenyl

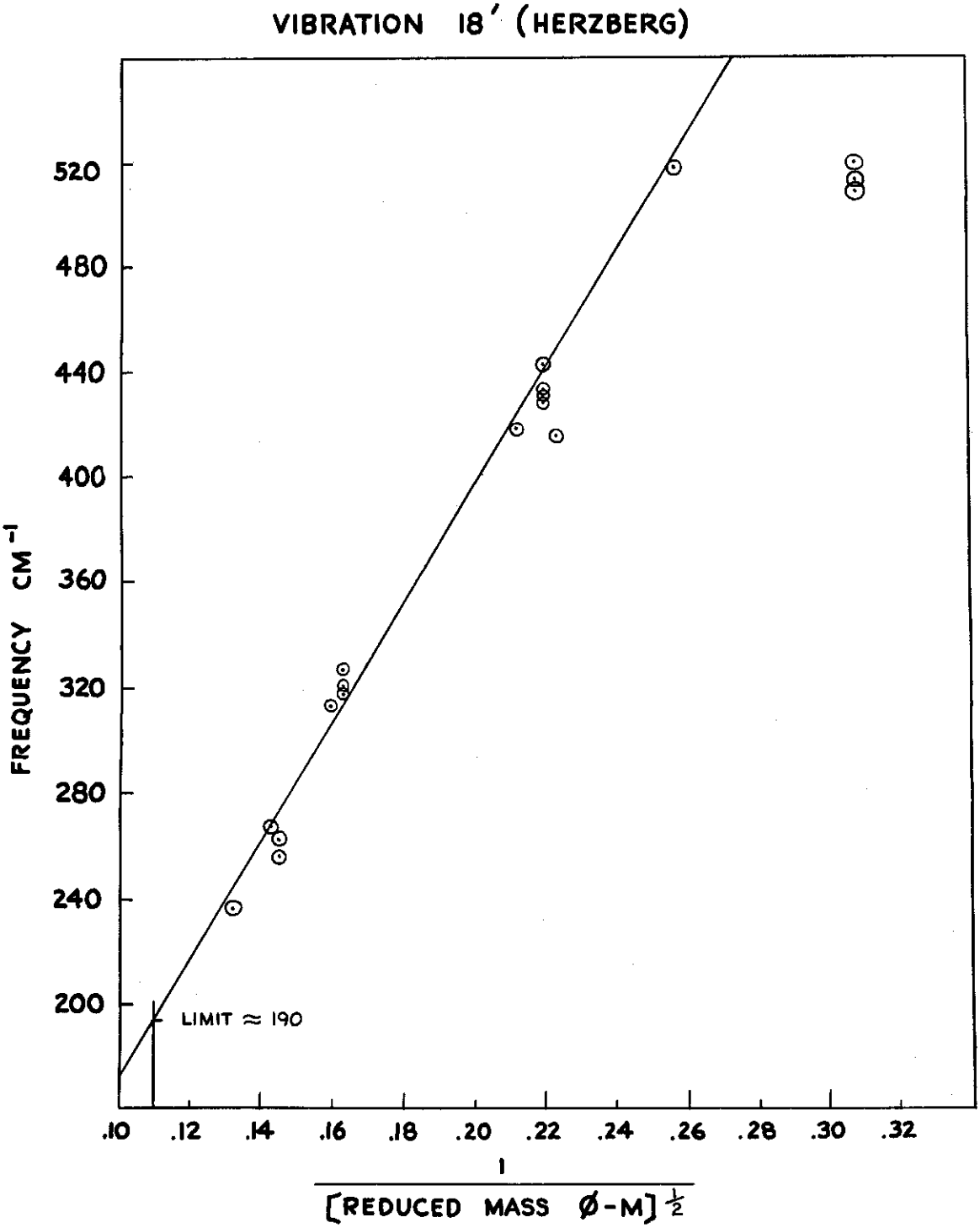

Figure 15. Plot of Frequency vs. Reciprocal of (Reduced Mass of Φ-M)$^{\frac{1}{2}}$ for ν_{18}' (Herzberg)

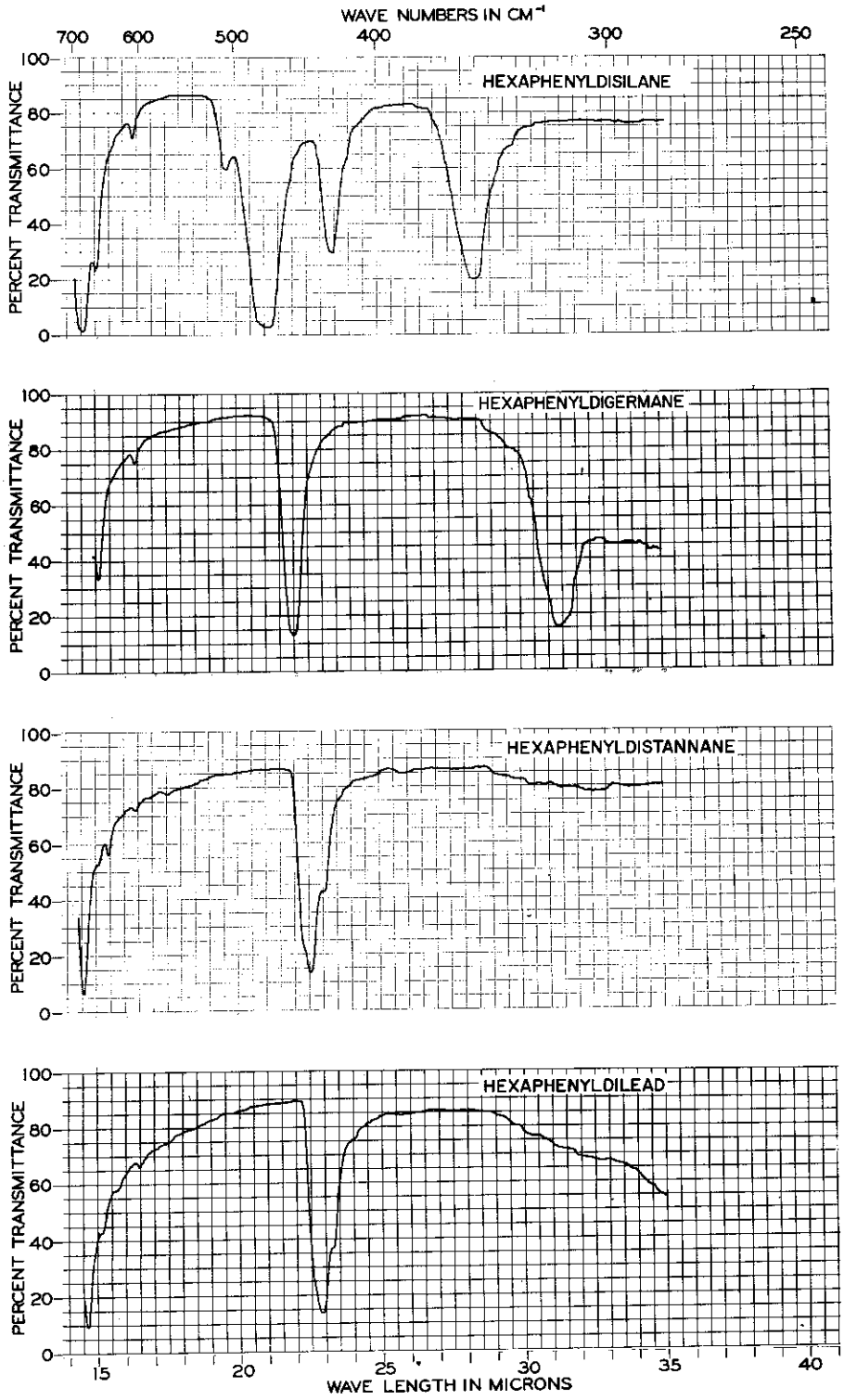

Figure 16. Spectra from 15 to 35 Microns of Hexaphenyldisilane, Hexaphenyldigermane, Hexaphenyldistannane, and Hexaphenyldilead

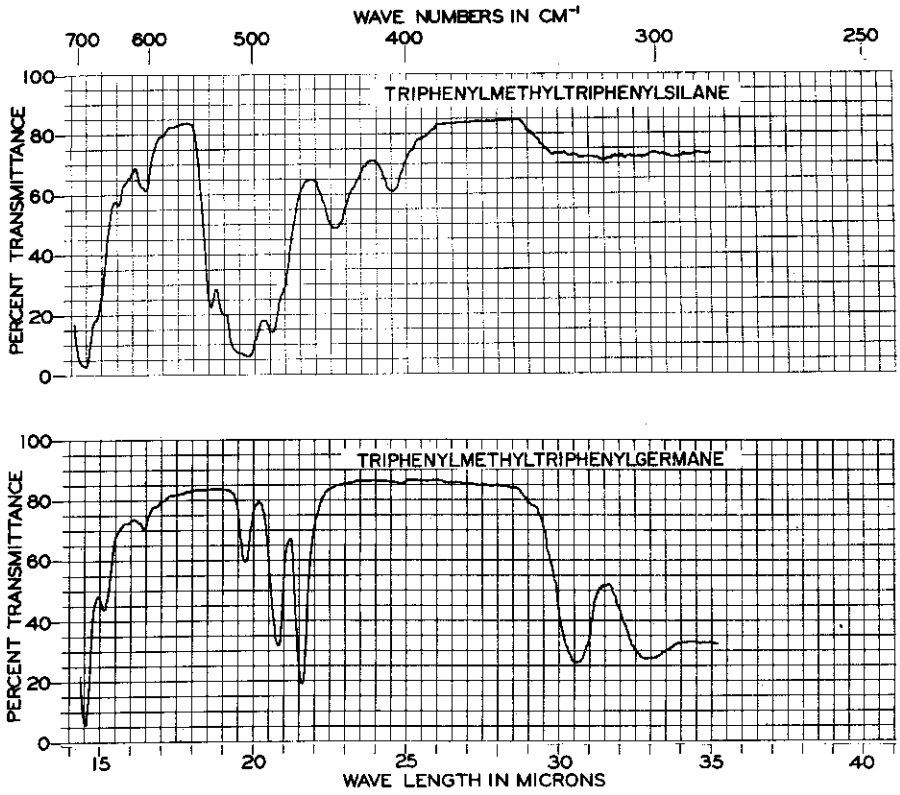

Figure 17. Spectra from 15 to 35 Microns of Triphenylmethyltriphenylsilane and Triphenylmethyltriphenylgermane

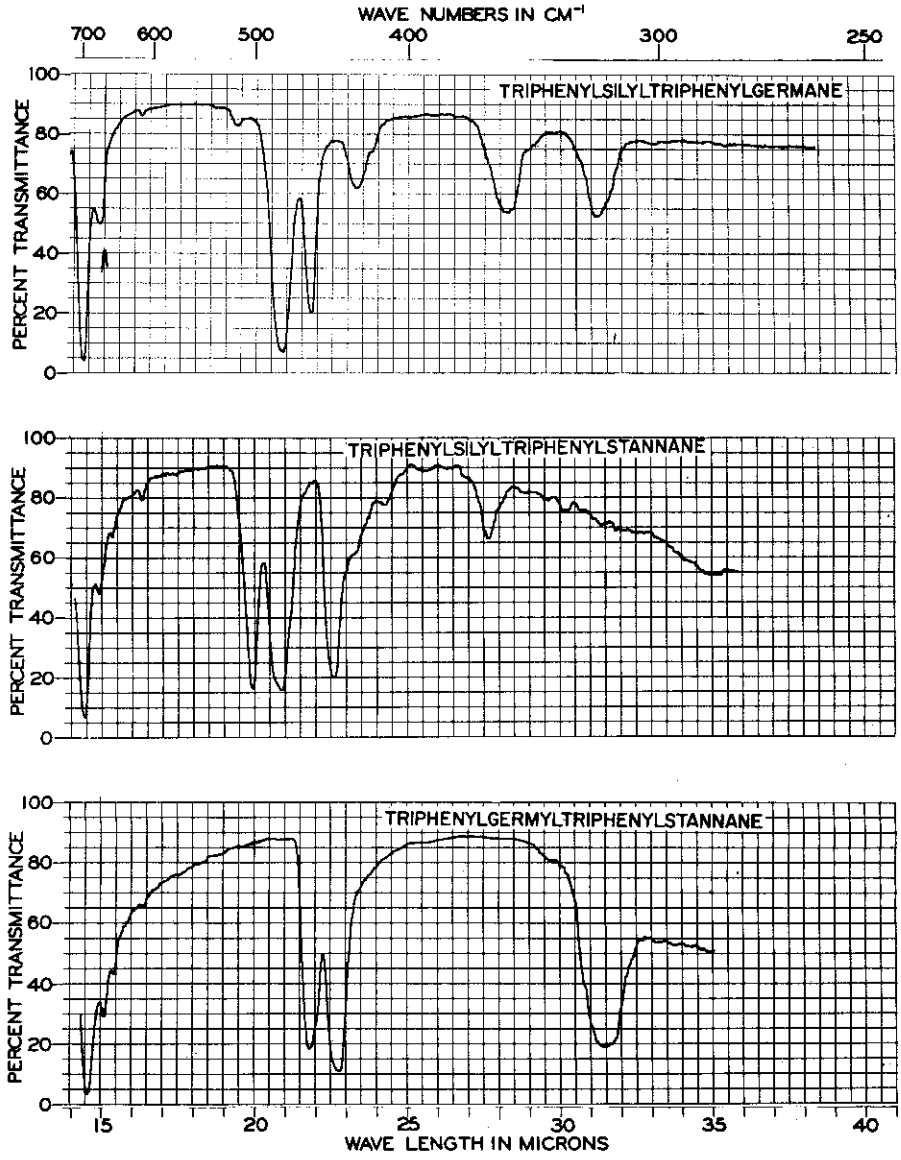

Figure 18. Spectra from 15 to 35 Microns of Triphenylmethyltriphenylgermane, Triphenylsilyltriphenylstannane and Triphenylgermyltriphenylstannane

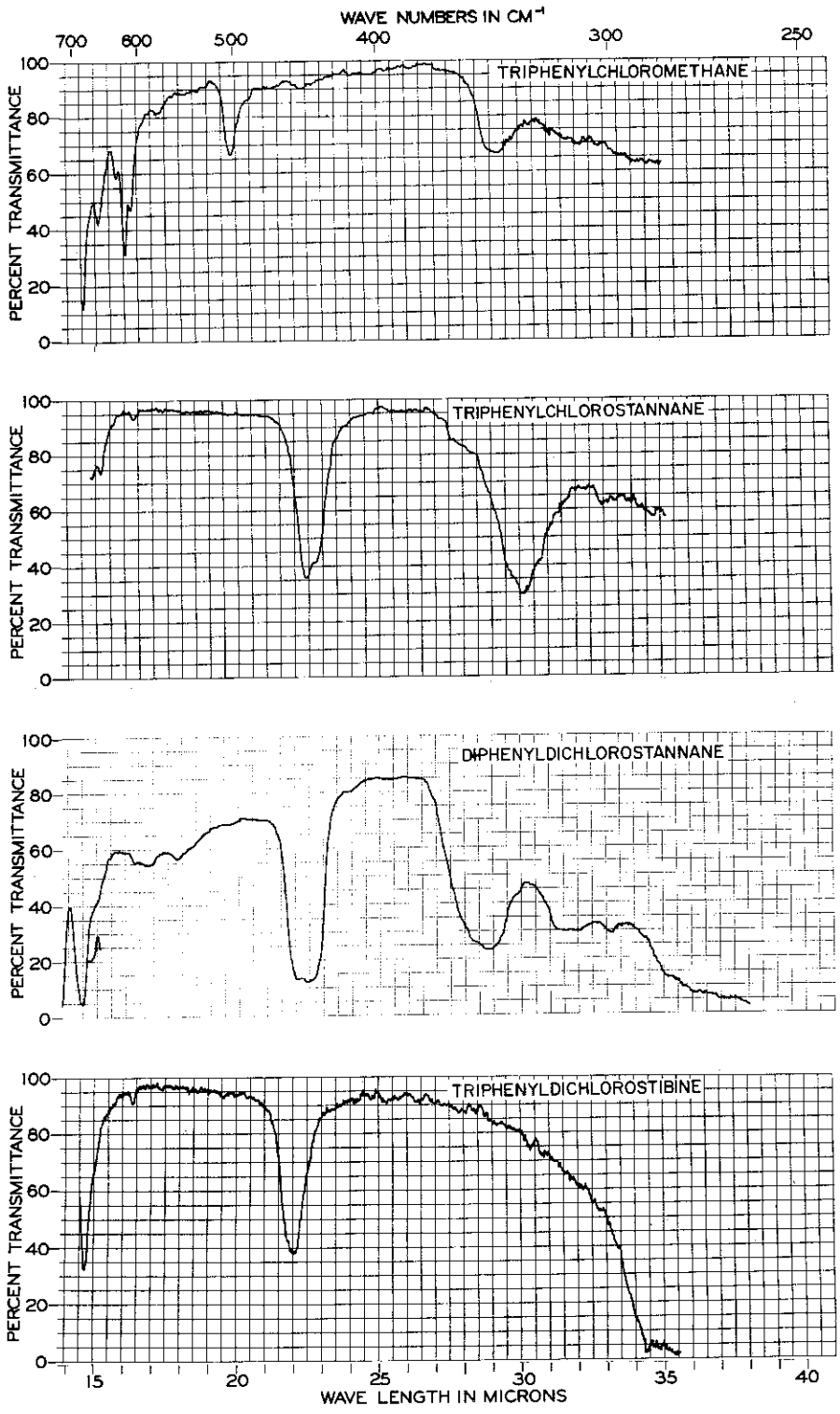

Figure 19. Spectra from 15 to 35 Microns of Triphenylchloromethane, Triphenylchlorostannane, Diphenyldichlorostannane, and Triphenyldichlorostibine

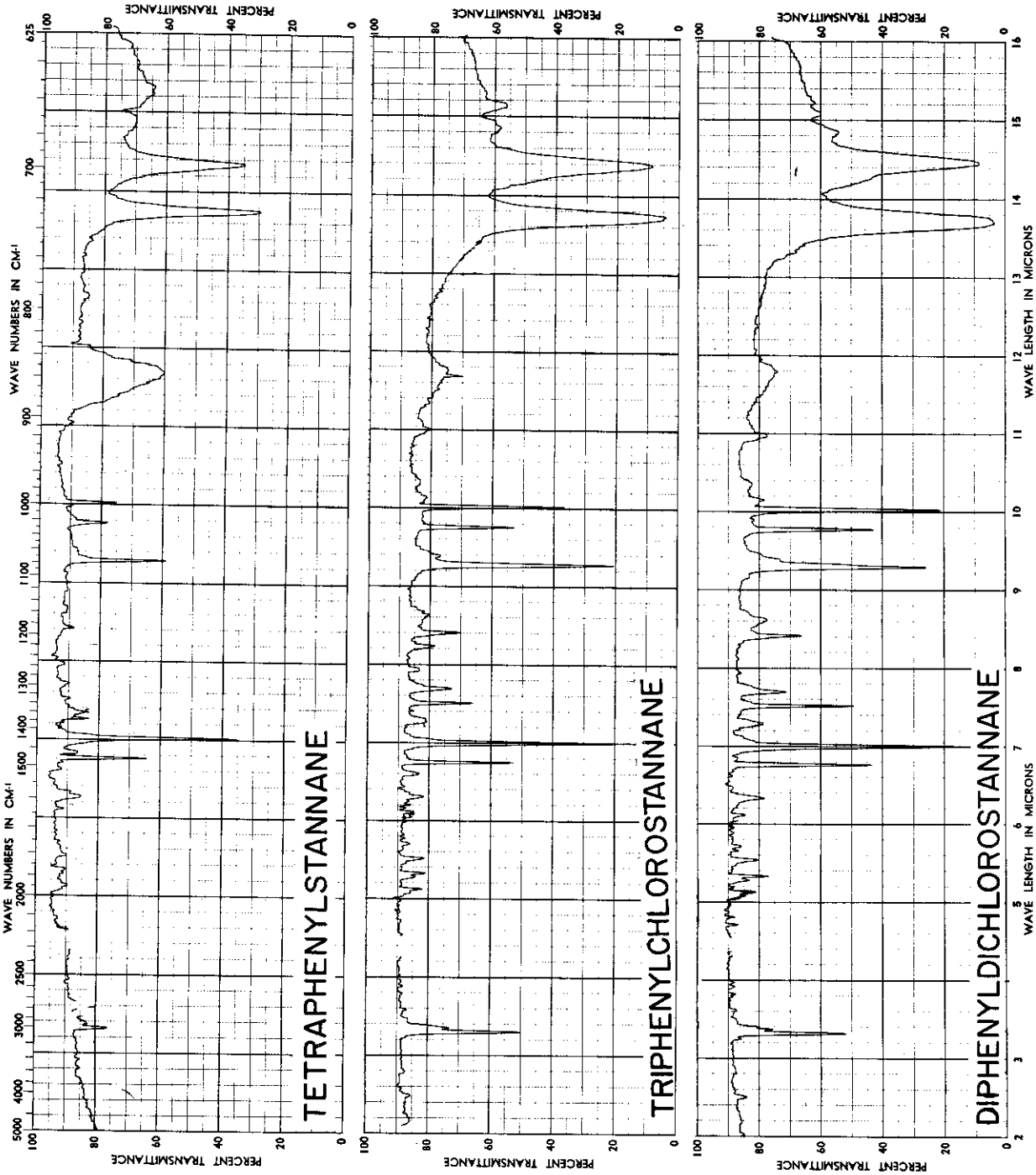

Figure 20. Spectra from 2 to 15 Microns of Tetraphenylstannane, Triphenylchlorostannane, and Diphenyldichlorostannane

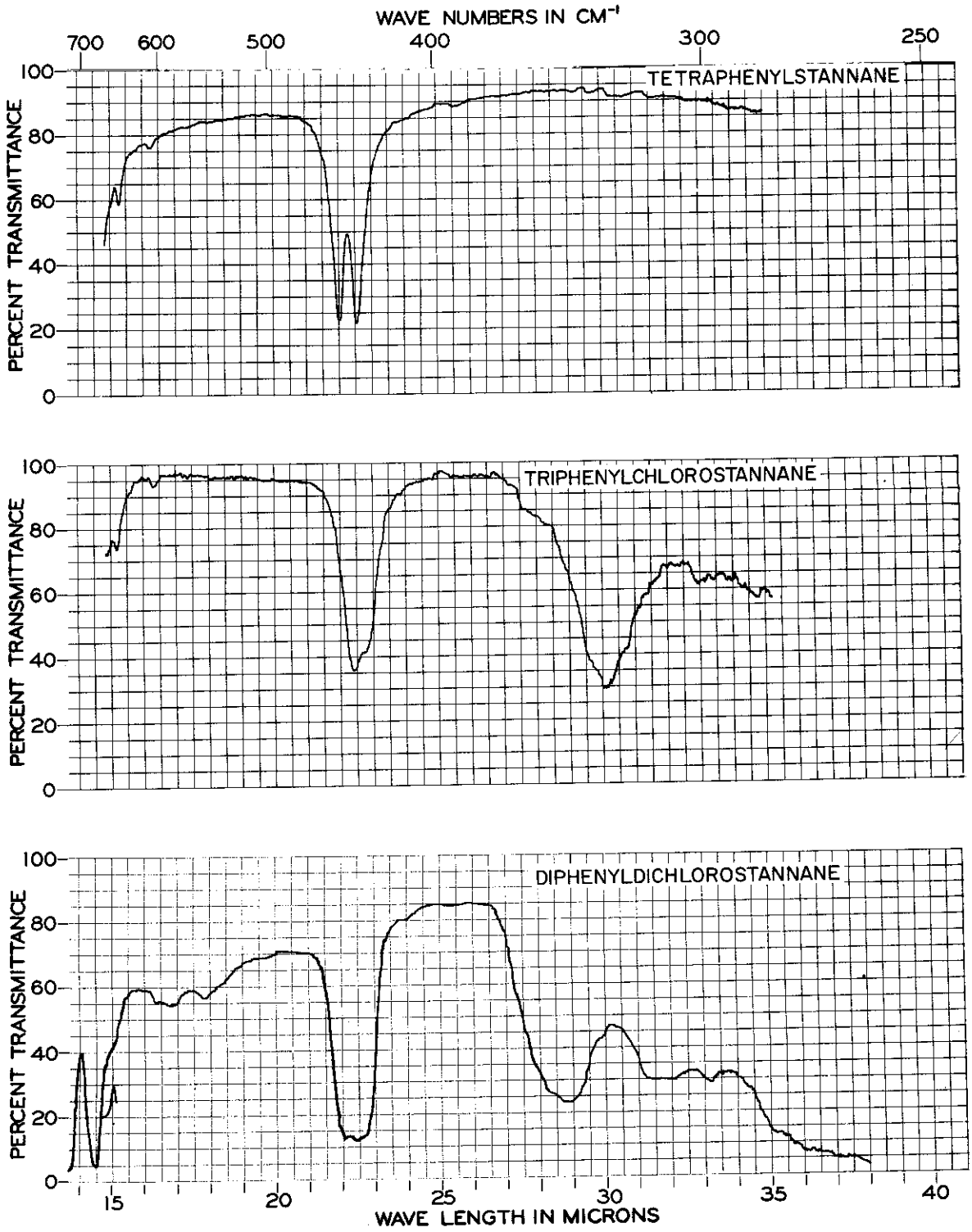

Figure 21. Spectra from 15 to 35 Microns of Tetraphenylstannane, Triphenylchlorostannane, and Diphenyldichlorostannane