A STUDY OF THE VIBRATIONAL SPECTRA OF

SOME MONOSUBSTITUTED BENZENE DERIVATIVES

OF GROUP VIA OF THE PERIODIC TABLE

BY

FAWZI S. RASHEED

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ABSTRACT

The vibrational frequencies for $(C_6H_5)_2Se$, $(C_6H_5)_2Te$, $(C_6H_5)_2Se_2$, $(C_6H_5)_2Te_2$, $(C_6H_5-S)_2Hg$, and $(C_6H_5-Se)_2Hg$ are completely assigned and are consistent with the vibrational assignments for $(C_6H_5)_2O$, $(C_6H_5)_2S$, and $(C_6H_5)_2S_2$ previously reported. Further, whereas $(C_6H_5)_2O$ and to a lesser extent $(C_6H_5)_2S$ show vibrational spectra consistent with non-equivalence of the two phenyl rings attached to the central atom, the spectra of the other molecules show little evidence for such non-equivalency of the two phenyl rings.

The infrared spectra of $(C_6H_5-X)_2Hg$, where X = S or Se, and the spectra of structurally related molecules indicate that the mercury atom has no significant effects on the vibrations of the phenyl ring other than slight displacements of some frequencies as a result of interactions of central skeletal vibrations with ring vibrations.

The vibrational assignments for $(C_6H_5)_2Te$ confirms the linearity of the Gordy Rule plot of the t-vibration for Group VIA Elements.

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FAWZI S. RASHEED

FOR

DEPARTMENT OF CHEMICAL ENGINEERING AND CHEMISTRY

NEW JERSEY INSTITUTE OF TECHNOLOGY

BY

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PREFACE

Infrared and Raman spectroscopy have been proven to be of tremendous value and one of the most extensively used techniques in studying molecular structure.

The fact that infrared spectroscopy has been in use for a variety of purposes in almost all industrial and research laboratories has made it of large interest to chemists. My thanks and gratitude to Dr. Howard Kimmel for his advice that has enabled me to put my interest in use by assigning the vibrational modes for some monosubstitued benzene compounds.

I have benefitted from this study and hope the reader will also find it of interest.

Fawzi S. Rasheed

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INTRODUCTION

Molecular vibrations have been extensively studied using Raman and I.R. spectroscopy. Interpretation and correlation of absorption bands are best understood in terms of molecular symmetry, where possible.

A valence force model consisting of point masses connected by elastic weak forces are used to describe the vibrational structure of the band system and to obtain calculated frequencies for the absorption bands. The calculated frequencies, using this model, agree fairly well with the experimental values and the model is used as a means of justifying the vibrational assignments.

Group theory is also used in classifying the molecular symmetry elements into groups and classes in order to simplify the interpretation problem at hand and to derive the symmetry restrictions of the selection rules for normal vibrations in the infrared and Raman phenomena.

In the force field model each point mass has three degrees of freedom corresponding to displacements in the direction of the three cartesian coordinate axes. Molecules consisting of n atoms have 3n degrees of freedom and any distortion of such a molecule can be given by them. Thus, it is apparent that the number of atoms and the molecular symmetry are responsible for the complexity or simplicity of the molecular spectrum.

Because of its highly symmetrical structure the vibrational spectra of benzene and its monosubstituted derivatives have been extensively

investigated. VARSANYI (19) has published a compilation of data and
he has given extensive discussions of vibrational assignments of the
spectra of benzene derivatives.

Complete vibrational assignments of the monohalogenobenzenes have
been carried out by WHIFFEN (20). Extensive vibrational studies of
benzene and other monosubstituted benzene derivatives have been carried
out by many workers because a large proportion of the vibrational bands
of monosubstituted benzene derivative is due to the normal modes of the
aromatic ring.

STEELE and LIPPINCOTT (17) have shown that the spectra of systems
containing weakly interacting benzene rings can be treated in terms of
monosubstituted benzene spectra. WHIFFEN (20) found that of the thirty
fundamental modes of vibrations of the monohalogenobenzenes there were
only six vibrations with an amplitude that depends on the mass or nature
of substituent x and termed them "x-sensitive" vibrations.

In this laboratory infrared and Raman spectra are obtained for
diphenyl diselenide, $(C_6H_5)_2Se_2$, diphenyl ditelluride, $(C_6H_5)_2Te_2$, diphenyl
disulphide mercury, $(C_6H_5-S)_2Hg$, and diphenyl diselenide mercury,
$(C_6H_5-Se)_2Hg$. For diphenyl selenide, $(C_6H_5)_2Se$, only the I.R. was obtained.
The infrared frequencies for diphenyl telluride, $(C_6H_5)_2Te$, are taken from
those tabulated by FRETZ and KELLER (2). In this study, frequency assign-
ments were then made for $(C_6H_5)_2Se$, $(C_6H_5)_2Te$, $(C_6H_5)_2Se_2$, $(C_6H_5)_2Te_2$,
$(C_6H_5-S)_2Hg$, and $(C_6H_5-Se)_2Hg$, by comparing the frequency data for these
molecules with frequency assignments reported for the monohalogenobenzenes (20),

diphenyl ether (6), and diphenyl sulphide and diphenyl disulphide (5).

MCWHINNIE et al (10, 11, 12) have studied the low frequency I.R. and

Raman spectra of diaryl ditellurides, diaryltellurium dihalides, and

phenyl tellurium trihalides. In their studies detailed assignments

of the spectra below 400 cm^{-1} are reported and diaryl ditelluride

structures are discussed.

KIMMEL (7) has studied the application of Gordy's Rule to the

t-vibration of monosubstituted phenyl derivatives of the general formula

$(C_6H_5)_nX$ where X represents any of the elements of Group IVA through

VIIA of the periodic table. The t-vibration assignments in the present

work has been made parallel to KIMMEL's findings.

Studies concerning the effect of the substituent groups on some

of the vibrations of the aromatic ring will be carried out similar to

that which obtained by MARGOSHES and FASSEL (9) for the out-of-plane

(C-H) bending vibrations in the region 625-900 cm^{-1}. Correlation studies

and assignments for the I.R. spectra (650 to 200 cm^{-1}) of monosubstituted

benzene derivatives by BROWN and his associates (1) will be also discussed.

GREEN (4) reported a detailed analysis of I.R. and Raman spectra for a

wide variety of alkyl and aryl compounds of mercury. MINK and VEGH (13)

reported experimental and calculated frequency values of phenyl-mercury

compounds.

In the present study correlation as well as assignment will be

sought for compounds of the general formula $C_6H_5-X-C_6H_5$, $C_6H_5-X-X-C_6H_5$,

and $C_6H_5-X-Hg-X-C_6H_5$ where X represents any element of Group VIA of the

periodic table. The fundamentals of the molecular vibrations have been classified according to the designations assigned by WHIFFEN (20).

EXPERIMENTAL

Diphenyl selenide and diphenyl diselenide were obtained from Eastman Kodak Co. Diphenyl ditelluride, diphenyl disulphide mercury, and diphenyl diselenide mercury were made available by courtesy of Professor C. R. Dillard, Brooklyn College of the City University of New York.

The infrared spectra were obtained from an I.R. Perkin-Elmer Model 467 double beam spectrophotometer in the range 4000-250 cm^{-1}. A Jarrel-Ash Model 400 Raman spectrometer, using a Spectra-Physics Argon Ion Laser with 2 watt maximum excitation power range was used for studying the Raman Effect.

Diphenyl selenide was received in a sealed ampule, and was opened in an inert atmosphere. It could not be purified because of excessive decomposition. Diphenyl selenide was studied as a capillary film using a cesium iodide cell. The infrared spectrum of the other molecules were obtained as KI disk. Standard liquid and solid sampling methods were used for obtaining the Raman spectra.

RESULTS

The infrared spectra were obtained for $(C_6H_5)_2Se$, $(C_6H_5)_2Se_2$, $(C_6H_5)_2Te_2$, $(C_6H_5-S)_2Hg$ and $(C_6H_5-Se)_2Hg$ as shown in Tables I through V. The infrared spectra of $(C_6H_5)_2Te$ shown in Table VI was tabulated by FRITZ and KELLER (2). But the frequency assignments were made in the present study. Raman spectra were also obtained for $(C_6H_5)_2Se_2$, $(C_6H_5)_2Te_2$, $(C_6H_5-S)_2Hg$ and $(C_6H_5-Se)_2Hg$.

A complete assignment of the ring mode frequencies was made for the first time for $(C_6H_5)_2Se$, $(C_6H_5)_2Te$, $(C_6H_5)_2Se_2$, $(C_6H_5)_2Te_2$, $(C_6H_5-S)_2Hg$ and $(C_6H_5-Se)_2Hg$. The assigned modes of related molecules were placed in Tables VI, VII and VIII for comparison purposes. In these tables some bands are affected by the substituent atom to a variable extent which reaches its maximum in the x-sensitive vibrations. These x-sensitive vibrations show a regular increase or decrease in frequencies as a result of the regular change in mass or electronegativity of the substituent atom.

The designations used are those of WHIFFEN (20), $\beta(C-H)$ and $\gamma(C-H)$ denote bending motions planar and non-planar with respect to the benzene ring, respectively. The C-H stretching vibrations were tentatively assigned according to the evidence given in the discussion and in an analogous fashion as those assigned by WHIFFEN (20) for halobenzenes. For diphenyl selenide spectra BROWN et al (1) assigned the band at 610 cm^{-1} to the s-vibration, the band at 321 cm^{-1} to the t-vibration, the band at 479-454 cm^{-1} to the y-vibration and the band at 244 cm^{-1} to the u-vibration.

The q-vibration has been assigned by KROSS and FASSEL (8) for diphenyl selenide at 1064 cm^{-1}. MCWHINNIE (12) in his study of some diaryl ditellurides described some of the low frequency modes as skeletal vibrations analogous to those assigned by SINK and HARVEY (16) for dimethyl ditelluride. He assigned the strongest Raman band, below 200 cm^{-1}, to the Te-Te stretching mode in diphenylditelluride. As shown in Table III this band appears at 171 cm^{-1} compared to 167 cm^{-1} obtained by the above author.

For diphenyl ditelluride MCWHINNIE (12) assigned the band at 398-350 cm^{-1} to the w-vibration, the band at 274 cm^{-1} to the u-vibration, the band at 255-204 cm^{-1} to the t-vibration and the band at 188-146 cm^{-1} to the x-vibration. In the present work 395 cm^{-1}, 231 cm^{-1}, 256 cm^{-1} and 204 cm^{-1} were assigned to the w-, u-, t-, and x-vibrations respectively.

For diphenyltelluride MCWHINNIE (10) assigned the medium infrared band at 386 cm^{-1} to the w-vibration, the strong infrared bands at 271, 261, 256 cm^{-1} to the t-vibration and the medium infrared bands at 184, 167 cm^{-1} to the x-vibration. As shown in Table VI for diphenyltelluride these assignments were used as reported by MCWHINNIE (10). KATON (6) made a complete assignment for diphenyl ether, as shown in Table VI, taking in consideration a structure possessing at most one plane of symmetry. This structure belongs to point group C_s with 39 vibrations of the A' symmetry class and 24 vibrations of the A" symmetry class. As shown in Table VI the ring mode vibrations are insensitive to the substituent and given the same frequency value for the two non-equivalent rings.

TABLE I

VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR DIPHENYL SELENIDE

I.R. Frequencies (cm^{-1})	Interpretation
3150 (w)	
3080 (m)	a_1, ν(C-H) b_1, ν(C-H)
3067 (s)	a_1, ν(C-H)
3040 (m,sh)	
3022 (m)	a_1, ν(C-H)
3003 (m)	b_1, ν(C-H)
2912 (w)	
2872 (v.w)	
2840 (v.w)	
2647 (v.w)	
2597 (v.w)	
2568 (v.w)	
2537 (v.w)	
2315 (v.w)	
2240 (v.w)	
2140 (v.w)	
1950 (w)	
1880 (w)	
1800 Iw)	
1770 (v.w)	
1750 (v.w)	

TABLE I (CONTINUED)

I.R. Frequencies (cm^{-1})	Interpretation
1735 (w)	
1650 (w)	
1615 (w)	
1582 (v.s)	a_1, ν(C–C)
1579 (v.s)	b_1, ν(C–C)
1562 (m,sh)	
1480 (v.w)	a_1, ν(C–C)
1440 (v.w)	b_1, ν(C–C)
1383 (w)	
1352 (v.w)	
1328 (w)	
1302 (m)	b_1, ν(C–C)
1265 (w)	b_1, β(C–H)
1237 (w)	
1180 (w)	a_1, β(C–H)
1158 (m)	b_1, β(C–H)
1098 (w)	
1080 (m)	b_1, β(C–H)
1070 (s)	a_1, x-sensitive
1025 (v.w)	a_1, β(C–H)
1001 (s)	a_1, ring
987 (w)	b_2, γ(C–H)

TABLE I (CONTINUED)

I.R. Frequencies (cm^{-1})	Interpretation
963 (w)	a_2, γ(C-H)
912 (w)	
900 (w)	b_2, γ(C-H)
866 (w)	
838 (w)	a_2, γ(C-H)
798 (w)	
774 (w)	
746 (v.w)	
734 (v.s)	b_2, γ(C-H)
690 (v.s)	
670 (m,sh)	
668 (s)	a_1, x-sensitive
615 (w)	b_1, α(C-C-C)
540 (v.w)	
520 (v.w)	
480 (s)	
458 (s)	b_2, x-sensitive
398 (v.w)	a_2, ϕ(C-C)
314 (w)	a_1, x-sensitive
300 (w)	

TABLE II

VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR DIPHENYL DISELENIDE

Frequencies		
I.R. (cm^{-1})	Raman (cm^{-1})	Interpretation
3076 (w)		b_1, ν(C-H)
3061 (w)	3060	a_1, ν(C-H)
3036 (w)		a_1, ν(C-H)
3018 (w)		
3000 (w)		b_1, ν(C-H)
2992 (w)		
1973 (v.w)		
1951 (w)		
1886 (v.w)		
1869 (w)		
1807 (v.w)		
1797 (v.w)		
1771 (v.w)		
1736 (v.w)		
1720 (v.w)		
1635 (v.w)		
1582 (m)		
1576 (m)		a_1, ν(C-C)
1564 (m)		b_1, ν(C-C)
1542 (w)		
1474 (s)		a_1, ν(C-C)
1437 (s)		b_1, ν(C-C)

TABLE II (CONTINUED)

Frequencies		
I.R. (cm^{-1})	Raman (cm^{-1})	Interpretation
1420 (w)		
1380 (w)		
1360 (w)		
1324 (w)	1310	b_1, ν(C-C)
1296 (w)		
1265 (w)	1270	b_1, β(C-H)
1230 (w)		
1200 (w)	1210	
1177 (w)		a_1, β(C-H)
1154 (w)		b_1, β(C-H)
1095 (w)		
1070 (m)		a_1, x-sensitive
1062 (m)		
1058 (m)		b_1, β(C-H)
1021 (s)		a_1, β(C-H)
1010 (w)		
999 (m)		a_1, Ring
982 (w)		b_2, γ(C-H)
965 (w)		a_2, γ(C-H)
915 (w)		
903 (w)		
899 (w)		b_2, γ(C-H)

TABLE II (CONTINUED)

Frequencies		Interpretation
I.R. (cm^{-1})	Raman (cm^{-1})	
865 (v.w)		
841 (w)		a_2, γ(C-H)
800 (v.w)		
735 (v.s)		b_2, γ(C-H)
689 (s)		b_2, ϕ(C-C)
664 (m)		a_1, x-sensitive
615 (w)		
610 (w)		b_1, α(C-C-C)
460 (m)		
		b_2, x-sensitive
454 (m)		
399 (w)		a_2, ϕ(C-C)
302 (w)		
	310	a_1, x-sensitive
	272	b_1, x-sensitive
	210	b_2, x-sensitive

TABLE III

VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR DIPHENYL DITELLURIDE

Frequencies		Interpretation
I.R. (cm^{-1})	Raman (cm^{-1})	
3160 (v.W)		a_1, ν(C-H)
3060 (m)		a_1, ν(C-H)
3008 (m)		b_1, ν(C-H)
2940 (v.w)		
2900 (v.w)		
2840 (v.w-w)		
2727 (m)		
2668 (m)		
2622 (w)		
2580 (w)		
2470 (w)		
2430 (w)		
2392 (w-m)		
2353 (w)		
2325 (w)		
1965 (v.w-w)		
1945 (v.w-w)		
1920 (v.w)		
1895 (v.w)		
1873 (v.w)		
1805 (v.w)		
1755 (v.w)		

TABLE III (CONTINUED)

Frequencies		
I.R. (cm^{-1})	Raman (cm^{-1})	Interpretation
1600 (w)		
1573 (m)		a_1, $\nu(C-C)$
1569 (m)	1568	b_1, $\nu(C-C)$
1557 (w)		
1526 (w)		
1507 (w)		
1494 (w)		
1471 (m)		a_1, $\nu(C-C)$
1464 (w)		
1455 (w)		
1436 (w)		
1432 (m)		b_1, $\nu(C-C)$
1422 (m)		
1418 (m)		
1403 (w)		
1392 (v.w)		
1371 (v.w)		
1350 (v.w)		
1332 (v.w)		
1321 (w)		b_1, $\nu(C-C)$
1292 (w)		
1255 (w)		b_1, $\beta(C-C)$

TABLE III (CONTINUED)

Frequencies		
I.R. (cm^{-1})	Raman (cm^{-1})	Interpretation
1230 (w)		
1207 (m)		
1168 (m)		a_1 , β(C-H)
1154 (m)		b_1 , β(C-H)
1110 (m)		
1090 (m)		
1073 (m)		a_1 , x-sensitive
1060 (m)	1060	b_1 , β(C-H)
1015 (m)	1016	a_1 , β(C-H)
996 (m)	998	a_1 , Ring
	986	b_2 , γ(C-H)
965 (m)		a_2 , γ(C-H)
920 (w)		
887 (m)		b_2 , γ(C-H)
847 (w)		
840 (w)		a_2 , γ(C-H)
797 (w)		
768 (w)		
724 (v.s)		b_2 , γ(C-H)
704 (m)		
685 (m)		b_2 , ϕ(C-C)
665 (w)		
		a_1 , x-sensitive
648 (m)	656	

TABLE III (CONTINUED)

Frequencies		Interpretation
I.R. (cm^{-1})	Raman (cm^{-1})	
620 (w)		
612 (w)	616	b_1, α(C-C-C)
609 (w)		
597 (w)		
490 (v.w)	480	
452 (m)		b_2, x-sensitive
395 (v.w)		a_2, ϕ(C-C)
365 (w)		
360 (w)		
352 (w)		
	256	a_1, x-sensitive
	231	b_1, x-sensitive
	204	b_2, x-sensitive
	171	
	93	
	62	
	51	
	31	

TABLE IV

VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR DIPHENYL-DISULPHIDE MERCURY

Frequencies		
I.R. (cm^{-1})	Raman (cm^{-1})	Interpretation
	3091	a_1 , $\nu(C-H)$
3055 (w)		a_1 , $\nu(C-H)$
3040 (w)		a_1 , $\nu(C-H)$
3015 (w)		
2993 (w)		b_1 , $\nu(C-H)$
2923 (v.w)		
2846 (v.w)		
1942 (v.w)		
1870 (v.w)		
1793 (v.w)		
1750 (v.w)		
1576 (w)	1576	a_1 , $\nu(C-C)$
1568 (w)		b_1 , $\nu(C-C)$
1494 (w)		
1471 (m)		a_1 , $\nu(C-C)$
1462 (m)		
1432 (m)		b_1 , $\nu(C-C)$
1380 (w)		
1326 (w)		b_1 , $\nu(C-C)$
1314 (v.w)		
1298 (w)		
1268 (v.w)		

TABLE IV (CONTINUED)

Frequencies		
I.R. (cm^{-1})	Raman (cm^{-1})	Interpretation
1248 (w)		b_1, β(C-H)
1209 (v.w)		
1179 (v.w)		
1170 (v.w)		
1160 (w)		[a_1, β(C-H)], [b_1, β(C-H)]
1131 (w)		
	1091	
1080 (m)		a_1, x-sensitive
1064 (m)		b_1, β(C-H)
1019 (m)	1025	a_1, β(C-H)
999 (w)	1005	a_1, Ring
965 (v.w)		a_2, γ(C-H)
940 (v.w)		
900 (w)		b_2, γ(C-H)
852 (v.w)		a_2, γ(C-H)
840 (v.w)		
780 (m)		
770 (m)		
743 (m)		
731 (v.s)		b_2, γ(C-H)
694 (m)	700	a_1, x-sensitive
682 (s)		b_2, ϕ(C-C)

TABLE IV (CONTINUED)

Frequencies		
I.R. (cm^{-1})	Raman (cm^{-1})	Interpretation
657 (w)		
644 (v.w)		
610 (w)		b_1, α(C-C-C)
522 (w)		
517 (v.w)		
510 (v.w)		
480 (m)	479	b_2, x-sensitive
473 (w)		
467 (v.w)		
418 (w)		
414 (w)		
407 (w)		a_1, x-sensitive
400 (w)		
380 (v.w)		a_2, ϕ(C-C)
360 (w)		
353 (w)	355	
349 (w)		
330 (v.w)		
322 (v.w)		
318 (v.w)		
310 (v.w)		
298 (v.w)		

TABLE IV (CONTINUED)

Frequencies		
I.R. (cm^{-1})	Raman (cm^{-1})	Interpretation
285 (v.w)		
273 (v.w)		
	258	
	188	b_2, x-sensitive
	142	
	118	
	107	
	90	
	84	
	38	

TABLE V

VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR DIPHENYL-DISELENIDE MERCURY

Frequencies		Interpretation
I.R. (cm^{-1})	Raman (cm^{-1})	
3065 (w)		a_1, ν(C-H)
3047 (w)	3052	a_1, ν(C-H)
3028 (v.w, sh)		
3008 (v.w)		b_1, ν(C-H)
2980 (v.w)		
2920 (v.w)		
2849 (v.w)		
1945 (v.w)		
1870 (v.w)		
1746 (v.w)		
1573 (m)	1574	a_1, ν(C-C)
1569 (w)		b_1, ν(C-C)
1496 (v.w)		
1470 (m)		a_1, ν(C-C)
1464 (w)		
1433 (s)		b_1, ν(C-C)
1373 (m)		
1326 (w)		b_1, ν(C-C)
1296 (m)		
1259 (w)		
1248 (w)		b_1, β(C-H)

TABLE V (CONTINUED)

Frequencies		Interpretation
I.R. (cm^{-1})	Raman (cm^{-1})	
1210 (v.w)		
1178 (w)		a_1, β(C-H)
	1162	b_1, β(C-H)
1110 (w)		
1099 (w)		
1079 (w)		
1070 (m)	1074	a_1, x-sensitive
1061 (m)		b_1, β(C-H)
	1038	
1017 (s)	1018	a_1, β(C-H)
998 (m)	1002	a_1, Ring
952 (v.w)		a_2, γ(C-H)
940 (v.w)		
900 (w)		b_2, γ(C-H)
844 (v.w)		a_2, γ(C-H)
800 (v.w)	802	
783 (w)		
771 (w)		
764 (w)		
726 (v.s)	732	b_2, γ(C-H)
684 (s)		b_2, ϕ(C-C)
664 (w)	672	a_1, x-sensitive
650 (v.w)		

TABLE V (CONTINUED)

Frequencies		
I.R. (cm^{-1})	Raman (cm^{-1})	Interpretation
610 (v.w)		b_1, $\alpha(C-C-C)$
523 (v.w)		
506	490	
465 (m)		b_2, x-sensitive
458 (w)		
455 (v.w)		
375 (v.w)	389	a_2, $\phi(C-C)$
334 (v.w)	359	
327 (v.w)		
315 (v.w)		a_1, x-sensitive
302 (v.w)		
299 (v.w)	298	
289 (v.w)		
280 (v.w)		
277 (v.w)	271	
	225	
	206	b_1, x-sensitive
	195	
	183	
	164	b_2, x-sensitive
	133	
	102	
	90	
	25	

DISCUSSION

In principle, assignments are made possible from a knowledge of the molecular structure and a study of the molecular force fields in order to determine the normal coordinates. In practice, this is possible only for simple molecules with a high degree of symmetry. In the present study assignments will depend primarily on correlations between the molecules under study and other molecules of similar structures which have been assigned previously. Additional information such as molecular structure, and the mass and electronegativity of the substituent atom will be considered.

The spectra of the $(C_6H_5-x)_2Hg$ molecules compare fairly well with the spectra of C_6H_5I and $(C_6H_5)_2X_2$. The mercury atom apparently has no significant effect on the vibrations of the benzene ring other than slight displacements of some frequencies as a result of the interactions of central skeleton bending vibrations with these vibrations. This is due to the reduced effect of mercury acting across the S-Hg or Se-Hg linkage. GREEN (3) found a straight forward correlation between the iodobenzene spectrum and the diphenylmercury and phenylmercuric sulphide spectra in the region between 3650 cm^{-1} and 375 cm^{-1}. In this region mode d for iodobenzene is obscured by the vibrational mode q, while the two modes are resolved in phenylmercuric sulphide, as is the case in the present study for $(C_6H_5-S)_2Hg$ and $(C_6H_5-Se)_2Hg$. He also suggested that the band at 1098 be assigned to mode d but he assigned it to the combination ban (v+w). MINK and VEGH (13) reported

experimental and calculated frequencies of phenylmercury derivatives. They performed a normal coordinate analysis for the in-plane vibrations of C_6H_5-Hg-x and obtained results that agree with the experimental data. The authors established frequency ranges for the 30 fundamental vibrations of the benzene ring using the reported data for about 15 phenyl derivatives of mercury. The given frequency ranges compare fairly well with some of the modes obtained in the present work. In all cases the structure of the phenyl mercury is given C_{2v} symmetry.

It appears that most of the x-sensitive vibrations should show a general trend of decreasing frequency with increasing mass of substituent atom. It is seen in Table VI that the t-vibration, which is considered primarily C-X stretching, shows a very large decrease in frequency as we go from $(C_6H_5)_2O$ to $(C_6H_5)_2S$, to $(C_6H_5)_2Se$, and to $(C_6H_5)_2Te$. The same trend in the t-vibration is shown in Table VIII for compounds of the general formula $(C_6H_5)_2X_2$ where X is S, Se, or Te. The q-vibration has been shown to be sensitive to the electronegativity of the substituent atom in halobenzenes and depends on conjugation (8). Thus, it is high in $(C_6H_5)_2O$ and decreases as we go toward $(C_6H_5)_2Te$. The r- and the x-vibrations also show a consistent decrease as a result of changing electronegativity and mass of substituent atom. Beside the six x-sensitive vibrations there is also some ring modes which show a slight sensitivity to the mass of substituent and the trend is observed for k-, m-, n-, and i-vibrations as shown in Table VI.

In Table VIII, a comparison of the spectra of $(C_6H_5-S)_2Hg$ and $(C_6H_5-Se)_2Hg$ shows that the frequencies of the vibrational modes are close except for the x-sensitive vibrations which decrease as the mass

and electronegativity of the substituent atom changes. For molecules

of the form $(C_6H_5)_2X_2$ where X is S, Se, or Te the changes in the x-

sensitive vibrations show the same pattern as previously discussed.

In addition to that K-, m-, a-, b-, e-, w-, and f-fibrations show a

slight decrease in frequency with increasing mass of the substituent

atom. A comparison of the $(C_6H_5)_2X$, $(C_6H_5)_2X_2$ and $(C_6H_5-X)_2Hg$ type

structure shows irregular changes because of the fact that the structural

changes involve more than one factor which influence the vibrational

frequencies in a complex manner. However, the spectra of $(C_6H_5-X)_2Hg$

and $(C_6H_5)_2X_2$ agree fairly well with each other since the heavy mercury

atom is too far from the benzene ring to affect the ring modes.

Table VII shows the effects of two nonequivalent rings where

splitting of the nearly degenerate skeletal bending vibrations increase

with the decreasing size and the increasing conjugation effect of the

substituent atom. One of the degenerate pair of vibrations of $(C_6H_5)_2X$

are in close correlation with the corresponding mode of vibration of

$C_6H_5-X-CH_3$. Thus, this vibration indicates an interaction between the

X and the phenyl ring which is the case in the $C_6H_5-X-CH_3$ spectra. The

other degenerate vibrations are in close correlation with the frequencies

obtained for toluene as will be discussed in structural considerations.

TABLE VI

FUNDAMENTAL VIBRATIONAL FREQUENCIES OF $(C_6H_5)_2X$ (X=O,S,Se, or Te)

Symmetry Species			Assignments	$(C_6H_5)_2O^{[6]}$		$(C_6H_5)_2S^{[5]}$		$(C_6H_5)_2Se$		$(C_6H_5)_2Te^{[2]}$	
A'	(a_1)	z_1	ν(C-H)	3089	3089			3150			
		z_2	ν(C-H)	3075	3075	3070		3067		3064	
		z_3	ν(C-H)	3068	3040	3058	3032	3040	3022		
		k	ν(C-C)	1600	1593	1584		1582		1574	
		m	ν(C-C)	1487	1487	1474		1480		1475	
		a	β(C-H)	1174	1164	1180		1180			
		b	β(C-H)	1023	1023	1026		1025		1017	
		p	ring	1003	1003	1002		1001		998	
		g	x-sensitive	1236	1198	1095	1083	1070		1063	
		r	x-sensitive	800	751[5]	696	701	668		662	645
		t	x-senstive	498	563	445	412	314		271, (261,256)[10]	
	(b_1)	z_4	ν(C-H)	3089	3089			3080			
		z_5	ν(C-H)	3015	3027	3000	3018	3003			
		l	ν(C-C)	1591	1585	1584		1579			
		n	ν(C-C)	1455	1455	1444		1440		1434	
		o	ν(C-C)	1335	1330	1329		1302		1324	
		e	β(C-H)	1284	1294	1274		1265		1297	
		c	β(C-H)	1153	1153	1159	1153	1158		1154	
		d	β(C-H)	1072	1072	1070		1070			
		s	(C-C-C)	602	616	617		615		611	
		u	x-sensitive	245	312	213	279				
A"	(a_2)	h	γ(C-H)	961	961	968		963			
		g	γ(C-H)	824	866	840		838			
		w	ϕ(C-C)	396	478	401		398		386[10]	
	(b_2)	j	γ(C-H)	979	979	985		987			
		i	γ(C-H)	894	904	917	900	912	900		
		f	γ(C-H)	749	749	749	738	746	734	726	
		v	ϕ(C-C)	690	698[5]	688		690		688	
		y	x-sensitive	481	478[5]	519	466	480	458	461	445
		x	x-sensitive	228	215	182	182			184	167[10]

TABLE VII

FUNDAMENTAL VIBRATIONAL FREQUENCIES OF $(C_6H_5)X(CH_3)$, $(C_6H_5)_2X$, $(C_6H_5)_2X_2$

Symmetry Species		Assignment	$(C_6H_5)_2O$ [6]		$(C_6H_5)O(CH_3)$ [4]	$(C_6H_5)S(CH_3)$ [4,5]	$(C_6H_5)_2S$ [5]		$(C_6H_5)_2S_2$ [5]
A'	(a_1)	z_1 $\nu(C-H)$	3089	3089	3079	3065			3150
		z_2 $\nu(C-H)$	3075	3075	3068	3055	3070		3075
		z_3 $\nu(C-H)$	3068	3040	3037	3005	3058	3032	3062
		k $\nu(C-C)$	1600	1593	1603	1585	1584		1578
		m $\nu(C-C)$	1487	1487	1497	1479	1474		1477
		a $\beta(C-H)$	1174	1164	1182	1185	1180		1179
		b $\beta(C-H)$	1023	1023	1019	1026	1026		1024
		p ring	1003	1003	995	999	1002		999
		q x-sensitive	1236	1198	1248	1100	1095	1083	1076
		r x-sensitive	800	751[5]	783	691	696	701	692
		t x-sensitive	498	563	444	416	445	412	412
	(b_1)	z $\nu(C-H)$	3089	3089	3098	3065			3150
		z $\nu(C-H)$	3015	3027	3007	3005	3000	3018	3008
		l $\nu(C-C)$	1591	1585	1593	1585	1584		1578
		n $\nu(C-C)$	1455	1455	1443	1441	1444		1439
		o $\nu(C-C)$	1335	1330	1338	1333	1329		1327
		e $\beta(C-H)$	1284	1294	1296	1300	1274		1276
		c $\beta(C-H)$	1153	1153	1153	1157	1159	1153	1157
		d $\beta(C-H)$	1072	1072	1076	1074	1070		1069
		s $\alpha(C-C-C)$	602	616	613	618	617		615
		u x-sensitive	245	312	258	212	213	279	247
A"	(a_2)	h $\gamma(C-H)$	961	961	957	957	968		967
		g $\gamma(C-H)$	824	866	819	834	840		843
		w $\phi(C-C)$	396	478		415	401		404

Vibrational Frequencies cm^{-1}

29

TABLE VII (CONTINUED)

Symmetry Species		Assignment		$(C_6H_5)_2O$[6]		$(C_6H_5)O(CH_3)$[4]	$(C_6H_5)S(CH_3)$[4,5]	$(C_6H_5)_2S$[5]		$(C_6H_5)_2S_2$[5]	
A"	(b₂)	j	γ(C-H)	979	979	975	967	985		983	
		i	γ(C-H)	894	904	882	895	917	900	898	
		f	γ(C-H)	749	749	754	739	749	738	741	736
		v	φ(C-C)	690	698	692	691	688		687	
		y	x-sensitive	481	478[5]	511	475	519	466	473	
		x	x-sensitive	228	215	209	181	182	182	223	

TABLE VIII

FUNDAMENTAL VIBRATIONAL FREQUENCIES OF $(C_6H_5)_2X_2$ and $(C_6H_5-X)_2Hg$ (X$\neq$S, Se, Te)

Symmetry Species			Assignment	Vibrational Frequencies cm^{-1}				
				$(C_6H_5)_2S_2$[5]	$(C_6H_5)_2Se_2$	$(C_6H_5)_2Te_2$	$(C_6H_5-S)_2Hg$	$(C_6H_5-Se)_2Hg$
A'	(a_1)	z_1	ν(C-H)	3150		3160	3091	
		z_2	ν(C-H)	3075	3061	3060	3055	3065
		z_3	ν(C-H)	3062	3036		3040	3047
		k	ν(C-C)	1578	1576	1573	1576	1573
		m	ν(C-C)	1477	1474	1471	1471	1470
		a	β(C-H)	1179	1177	1168	1178	1178
		b	β(C-H)	1024	1021	1016	1019 1025	1018
		p	ring	999	999	998 996	999 1005	998 1002
		q	x-sensitive	1076	1070	1073	1080	1070
		r	x-sensitive	692	664	665 648	694	663 672
		t	x-sensitive	412	310	256	407 414	315
	(b_1)	z_4	ν(C-H)	3150	3076		3091	
		z_5	ν(C-H)	3008	3000	3008	2995 3015	3008
		l	ν(C-H)	1578	1564	1568	1568	1569
		n	ν(C-C)	1439	1437	1432	1432	1433
		o	ν(C-C)	1327	1324 1310	1321	1326	1326
		e	β(C-H)	1276	1265 1270	1255	1248	1248
		c	β(C-H)	1157	1154	1154	1160	1162
		d	β(C-H)	1069	1062 1058	1060	1064	1061
		s	α(C-C-C)	615	610	612 616	610	610
		u	x-sensitive	247	272	231		206
A"	(a_2)	h	γ(C-H)	967	965	965	965	952
		g	γ(C-H)	843	841	847 840	852 840	842
		w	ϕ(C-C)	404	399	395	380 400	389 375

TABLE VIII (CONTINUED)

Symmetry Species				Assignment	$(C_6H_5)_2S_2$	$(C_6H_5)_2Se_2$	$(C_6H_5)_2Te_2$	$(C_6H_5-S)_2Hg$	$(C_6H_5-Se)_2Hg$
A"	(b_2)	j	$\gamma(C-H)$		983	982	986		
		i	$\gamma(C-H)$		898	903 899	887	900	900
		f	$\gamma(C-H)$		741 736	735	724	731	726
		v	$\phi(C-C)$		687	689	685	682	684
		y	x-sensitive		473	460 454	452	480	436
		x	x-sensitive		223	210	204	188	164

Structural Considerations

(i) $C_6H_5-X-C_6H_5$

Molecules of the general formual $C_6H_5-X-C_6H_5$ have various possible configurations that vary according to the nature of the substituent X. KATON (6) discussed three possible structures for diphenyl ether and showed that the structure possessing at most a plane of symmetry (point Group C_s) is consistent with the spectra obtained. In this structure the angle between the normals to rings I and II are $90°$ (x-ray data on similar molecules suggest it is unlikely to be $90°$). He ruled out the possibility of the other two structures (C_{2v}) on the basis of Raman polarization data. KATON obtained two sets of vibrational frequencies which were consistent with the presence of two electrically nonequivalent benzene rings. The orientation of ring I allows the π-electron cloud to overlap the lone pairs in the oxygen atom and give vibrations similar to those obtained for methyl phenyl ether (Table VII). The other set of vibrations corresponding to ring II are similar to those obtained for toluene because the ring is not suitably oriented for conjugation. A large number of benzene-like vibrations are insensitive to the substituent and therefore vibrations involving the two rings coincide, i.e., accidental degeneracy.

GREEN (5) suggested a similar structure for diphenylsulphide but he excluded the possibility of $90°$ and $0°$ for the angle between the normals to rings I and II by taking into consideration the corresponding angle in di-p-tolyl sulphide of $52°$ and in di-p-bromophenyl sulphide of $72°$.

Accordingly, the differences between the two sets of vibrational frequencies of diphenyl sulphide are expected to be smaller than that found for diphenyl ether. The angles between the normals to rings I and II in di-p-tolyltelluride, selenide, and sulphide are found to be 62°, 55°, and 56° respectively (b).

SHIRO (14,15) have used C_{2v} symmetry for dimethyl sulphide and dimethyl selenide in his study of the molecular vibrations and force fields. The dissimilarity between the two phenyl groups in diphenyl sulphide is smaller than that found for diphenyl ether because of the lower electronegativity and the larger size of sulphur atoms. Thus, we would expect little or no differences between the two phenyl rings in the case of diphenyl selenide and diphenyl telluride because of the increasing size and decreasing electronegativity in going from sulphur to selenium and tellurium.

(ii) $C_6H_5-X-X-C_6H_5$

SINK and HARVEY (16) reported that the structure of molecules of the type R_2X_2 (where R is H, cH_3, C_6H_5, etc. and X is a Group VI atom) has been the subject of several investigations and in each case a skewed structure with C symmetry was found. The dihedral angles betwen the two R-X-X planes (80° to 120°) which diminish as the size of the central (X) atom increases. The dihedral angle of CH_3SSCH_3 molecule is about 85°.and that for dimethyl diselenide ($CH_3SeSeCH_3$) molecule is about 82°. From their vibrational studies of $CH_3TeTeCH_3$ they concluded

that of the four most probable structures: trans (C_{2h}), Cis (C_{2v}) and skewed (C_2 or C_1) it is found that all twenty-four infrared and Raman allowed normal vibrations should be classified according to C_2 symmetry.

MCWHINNIE (12) in his study of the low frequency vibrational spectra of diaryl ditelluride found that the most probable configuration is one of approximately C_2 symmetry between the limiting planar cases of C_{2h} and C_{2v} symmetry shown below.

C_{2h} C_{2v}
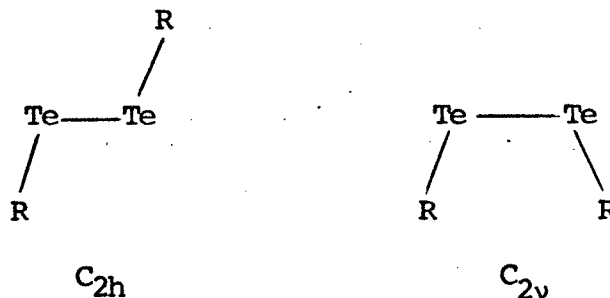
For diphenyl disulphide GREEN (5) suggested a free rotation around C_6H_5-S link which renders the two phenyl groups equivalent. Unlike the diphenyl sulphide, coupling is negligible as a result of the separation of the two phenyl groups over the S-S link. Thus, the spectrum resemble that of C_6H_5-S group, except for some vibrations which interact with the skeletal vibrations of R-S-S-R.

(iii) C_6H_5-X-Hg-X-C_6H_5
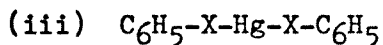
GREEN (4) suggested the C_{2v} symmetry for diphenyl mercury and dibenzyl mercury. Thus, as a first approximation, we might consider the diphenyl disulphide mercury and diphenyl disenlenium mercury as having the C_{2v} symmetry of monosubstituted benzene. Again, as in the case of C_6H_5-X-X-C_6H_5, no differences between the two phenyl groups would be expected.

C-H Stretching Vibrations: $\nu(C-H)$

The five modes of the C-H stretching vibrations were tentatively assigned as shown in Tables VI and VIII. As suggested by WHIFFEN (20) the summation frequencies k+m, k+n, l+m, and l+n fall in the same frequency range of the C-H stretching vibrations and Fermi interactions are likely to occur.

According to the selection rules all five bands are allowed in the infrared and Raman spectra. VARSANYI (19) has summarized the results of many research workers and suggested that the dependence of the frequency and intensity of the C-H stretching bands upon the electronegativity of the substituent are due to the reduction of the negative charge on the carbon atoms of the benzene ring. Because of the inductive effect of the substituent atom the polarity of the C-H bond decreases and reduces the intensity of the infrared bands of the C-H stretching vibrations. The C-H stretching vibration region of monosubstituted benzene derivatives can be divided into two types, calling type α that in which three group of bands can be separated from each other Z_4, Z_1, and Z_5 in order of decreasing frequency and type β that which cannot be resolved (19). The band corresponding to Z_5 is found to be the most intense infrared band while that corresponding to Z_1 is the only observable band in the Raman spectrum. It has also been found that upon the increase of the frequency the intensity of the band decreases. The degeneracy observed by WHIFFEN (20) for bands corresponding to Z_1 and Z_4 has been used in the present assignment whenever applicable.

C-C stretching vibrations: ν(C-C)

The five modes of the C-C stretching vibrations of many monosubstituted benzene derivatives are summarized by VARSANYI (19). He found that the k-vibration is generally between 1575 cm^{-1} (iodobenzene) and 1614 cm^{-1} (benzotrifluoride). The frequency of the k-vibration is highly insensitive to the substitution but shows higher intensities for compounds carrying electron-withdrawing substituents. The frequency of the 1-vibration of symmetry b$_1$ is found as a strong infrared band at about 1585 cm^{-1} for electron-withdrawing substituents otherwise it is found to be between 1562 cm^{-1} (iodobenzene) and 1597 cm^{-1} (fluorobenzene). The vibrational pair of symmetry a$_1$ and b$_1$ designated as m and n respectively by WHIFFEN (20) are rather insensitive to substitution. The m-vibration has a higher frequency of 1570-1510 cm^{-1} while the n-vibration has a 1440-1470 cm^{-1}. When the derivatives have an electron-acceptor substituent the m-vibration band becomes weak or almost absent from the spectrum. For heavy substituent, the band shifts to a lower frequency 1477-1483-cm^{-1}. The n-vibration on the other hand appears between 1448 and 1455 cm^{-1} for electron-acceptor substituents as is the case in diphenyl ether and diphenyl sulphide.

As a result of the normal co-ordinate calculations on monosubstituted benzenes, the vibration of row "o" was incorrectly looked for above 1600 cm^{-1} (19). For monohalogenobenzene derivatives WHIFFEN (20) followed Mair and Hornig (20) in establishing the frequency of this band at 1320-1326 cm^{-1}. VARSANYI (19) has established the frequency range 1300-1350 cm^{-1} for this band for monosubstituted benzene derivatives. As shown in Tables VI and VIII the vibration is assigned to the weak band at about 1325 cm^{-1}

In-plane C-H Deformation: $\beta(C-H)$

The five modes of C-H in-plane deformations are designated by WHIFFEN (20) as a, b, c, d, and e, where the a and b vibrations belong to symmetry species a_1 and its frequencies are almost unchanged from those of benzene at 1178 cm^{-1} and 1033 cm^{-1}.

It is found that the bands corresponding to the a and b vibrations are the most intense in the infrared, while in the Raman effect the vibration b is the most prominent.

The c, d and e vibrations belong to symmetry species b_1 and appear at 1150-1160 cm^{-1}, 1065-1082 cm^{-1}, and 1253-1331 cm^{-1} respectively.

WHIFFEN (20) has stated that in monosubstitution the increase in the mass of the substituent lowers the frequency of the totally symmetric b-vibration and enhances the intensity. On this basis WHIFFEN (20) concluded that the b-vibration has some C-X stretching character. The same kind of coupling would be predicted for the d-vibration since the heavy substituents enhance the intensity of this band. Thus WHIFFEN (20) explained how the d vibrational frequencies are obscured by the q-vibration in bromo- and iodo-benzene. He also predicted that the a-vibration would be depressed from its normal value of 1175 cm^{-1} by the adjacent q-vibration at 1220 cm^{-1} and by the a_1 combination band (v+y) at 1183 cm^{-1}. Such effects are observed for the b and d vibrations in the molecules reported in this study.

Ring Frequencies:

The assignment of vibrational mode p of symmetry species a_1 is best described by WHIFFEN (20) for monohalogenobenzenes as the extremely strong, polarized Raman line between 998-1010 cm^{-1} that arises from the trigonal ring breathings in which the substituent scarcely moves. Actually the frequency interval is much narrower than that obtained by WHIFFEN. For the series of compounds under investigation, it is found to be of the range 998-1005 cm^{-1}.

KOVNER's calculations, reported by VARSANYI (19), of the normal frequency of toluene has given 998 cm^{-1} while the experimental Raman frequency is 1004 cm^{-1}. The vibration is insensitive to the nature of the substituent since only three of the ring atoms are "breathing" and the other atoms remain practically at rest. According to the data reported by many research workers for the mono- and disubstituted benzenes, the vibration is found to be the strongest line in the Raman spectrum for all cases.

C-H out-of-plane vibrations: $\gamma(C-H)$

Of the five modes of the C-H out-of-plane vibrations the umbrella vibration (row f) is the dominating feature of the infrared spectra of the monosubstituted benzene derivatives. As indicated by WHIFFEN (20) the lowest of the three b_2 vibrations, the f-vibration, gives a very strong infrared band between 730 cm^{-1} and 755 cm^{-1} in the spectra of monohalogenobenzenes. He gave the frequency range 728-797 cm^{-1} as that of the f-vibration in the spectra of toluene, phenol, benzonitrile, chlorobenzene, and nitrobenzene (19). GREEN (5) has found the f-vibration to split in the spectra of diphenyl sulphide, whereas the $\alpha(C-C-C)$ mode "s" is not. MARGOSHES and FASSEL (9) in their study of the vibrational region 625-900 cm^{-1} of compounds of the type $(C_6H_5)_nM$ established that the vibrational frequency 725-775 cm^{-1} can be brought into linear correlation with the reduced mass of the substituent, i.e., the frequency shows a significant decrease with increasing the mass of the substituent. Thus, some decrease in the f-vibration frequency will be observed with increasing mass of substituent. They explained this relation in terms of the change of the force-constant and the band-length between the ring-carbon atom and the substituent as a result of changing the mass of the substituent. The medium infrared band of row i accounts for the second b_2 mode and is established by WHIFFEN (20) at 896-904 cm^{-1} in monohalogenobenzene spectra. Also it is found between 882 and 938 cm^{-1} in phenol, toluene, benzonitrile, chlorobenzene, and nitrobenzene spectra.

He also assigned the medium-intensity Raman band of row g at 824-847 cm^{-1} to the lower vibration of the two a_2 frequencies. This vibration did not change from those obtained for benzene.

WHIFFEN (20) justified his assignments for the remaining a_2 mode of row h and b_2 mode of row j at 965 cm^{-1} and 985 cm^{-1} respectively by using the evidence of the summation bands. It is found for the group of compounds under study that these two bands are fairly consistent with those obtained by WHIFFEN for monohalogenobenzenes. For the vibrational mode of row h, WHIFFEN (20) established the range 952-975 cm^{-1} and for j he has given the range 973-985 cm^{-1}.

Out-of-plane ring deformation: $\phi(C-C)$

Among the two strong infrared bands studied by MARGOSHES and
FASSEL (9) the v-vibration between 680 and 720 cm^{-1} is found to be
very consistent and highly insensitive to the nature of x. The
calculated value of KOVNER (19) for this vibration (696 cm^{-1}) is
found to be in good agreement with the experimental value of 690 cm^{-1}.
The range 682-694 cm^{-1} in the infrared spectra of 24 monosubstituted
benzene derivatives has also been established for this vibration by
JOSIEN and LEBAS (19).

From the foregoing the strong infrared band at 685-690 cm^{-1} for
the compounds under investigation is conclusively assigned to the
v-vibration of symmetry b_2. The frequencies obtained are also in good
agreement with those reported by WHIFFEN (20) for monohalogenobenzenes,
by GREEN (5) for diphenyl sulphide and diphenyldisulphide, and by
KATON (6) for diphenyl ether.

The out-of-plane ring deformation of row w is either forbidden
or very weak in both the infrared spectrum and the Raman spectrum.
BENTLEY and WOLFARTH (19) noted a very weak but almost constant frequency
band between 400 and 410 cm^{-1} and assigned it as mode 16a (w). According
to WHIFFEN (20) this frequency corresponds to the E_{2u} benzene frequency
at 405 cm^{-1} and the values obtained for the summation bands $2w$, $v+w$, and
$w+g$ using a value near 400 cm^{-1} are strong evidence for the assignment.
Thus, as shown in Tables VI and VIII, the weak to very weak band between
380 and 404 cm^{-1} is assigned to the w-vibration of symmetry a_2.

In-plane ring deformation ($\propto[C-C-C]$):

The frequency of the s vibration of symmetry class b_1 is rather stable since the amplitude of the substituted carbon atom is zero in the corresponding vibration (6b) of benzene (19).

JAKOBSON and BREWER (19) established the frequency range 606-624 cm^{-1}, CLEVELAND (19) assigned this vibration in the Raman spectra of alkylphenylethers at about 618 cm^{-1}, and ALEKASANIAN et al (19) found that not only the frequency but also the intensity of this band behave as independent data of the substituent's conjugative effect. Thus, it is found that the infrared band (610-615 cm^{-1}) of the s vibration is of weak to medium intensity in the Raman spectra.

x-sensitive vibrations: (x-sens.)

There are six vibrational modes in which the substituent X moves with appreciable amplitude and their frequencies are sensitive to the nature of X. Three of the x-sensitive vibrations are essentially C-X stretching modes of symmetry class a_1 and denoted by WHIFFEN (20) as q-, r-, and t-vibrations. The coupling between the C-X stretching and the ring mode occurs to a greater extent when the central atom is light and/or contains a lone-pair of electrons which interact with the π-electrons of the phenyl ring. Such a case has been encountered in diphenyl ether and to a lesser extent in diphenylsulphide. One of the remaining three x-sensitive vibrations is the C-X in-plane bending vibration of symmetry class b_1 and denoted as the u-vibration. The other two vibrations are C-X out-of-plane bending of symmetry class b_2 and denoted as y- and x-vibrations. The u-, y-, and x-vibrations couple to a greater extent with the C-H ring modes than the q-, r- and t-vibrations as will be shown in the following discussion.

c-x stretching vibrations:

Normal vibration 1 of benzene is found to couple with all sorts of C-X stretching vibrations. As shown by VARSANYI (19) in the case of heavy substituents or when the bond is weak the vibration is mostly a ring-mode which is illustrated by its more or less insensitive nature towards substitution. Thus the C-h (h=heavy) stretching vibration couples with normal mode 1 and has been given the letter r. The band is found between 1060 and 1100 cm^{-1} (19) and gives a strong band in the infrared region. In the case of heavy substituents the q-vibration contributes

to the intensity of the Raman line of the r-vibration (19). In

benzotrifluoride the first atom of the CF_3 group is "light" even

though the frequency of normal mode 1 is exceptionally low, 627 cm^{-1}.

According to VARSANYI (19) the C-C bond is so weak that the CF_3

group behaves like a heavy substituent and couples with the radial

skeletal vibration 6a.

For light substituents which either have a monoatomic structure

or contain asymmetric branching chains the frequency range is 730-830 cm^{-1}

For symmetrically branched substituents the range is 620-710 cm^{-1},

since the normal mode 1 couples to a greater extent with the scissoring

vibration of the side chain. Thus in halogenobenzenes the frequency

of fluorobenzene is assigned to the r-vibration where the fluorine atom

and the linking carbon vibrate in-phase, while the frequency above

1000 cm^{-1} in other halogenobenzenes is assigned to the q-vibration

where the halogen and the linking carbon vibrate in opposite phase.

GREEN (4) in his study of the C_6H_5-O-CH_3 and C_6H_5-S-CH_3 spectra

(Table VII) used the C_s symmetry group to assign the $11a_1+6b_2$ of mode a'

and $10b_1+3a_2$ of mode a". As shown also by GREEN (5) the ring mode r

involving C_6H_5-S stretching is recognized as the intense Raman line at

689 cm^{-1} and coincident with the v-vibration affording the characteristic

intense infrared absorption at 690 cm^{-1}.

In his study of diphenyl ether KATON (6) reversed the assignments

of the t- and y-vibrations for anisole and explained their low frequencies

in terms of interaction with bending fundamental at 554 cm^{-1}. He also

accounted for the second r-vibration at 751 cm^{-1} and explained its

coincidence with the f-vibration affording the strong frequency at 749 cm^{-1}.

The letter q is given by WHIFFEN (20) to the frequency of the C-1 (l=light) stretching vibration that falls closest to normal vibration 13 of benzene. The frequency interval 1100-1280 cm^{-1} in monosubstituted benzenes is given for the q-vibration by VARSANYI (19). He narrowed down the range by assuming a strong coupling between the C-1 stretching vibration and normal vibration 1, since the frequency does not drop below 1050 cm^{-1} irrespective of the atomic number of the substituent. The frequency of the q-vibration is determined rather by the extent of conjugation than by the mass of the substituent. Thus, the intensity of the band and the frequency increases as a result of the conjugation effect. This band is strong both in the infrared and the Raman spectra.

According to VARSANYI (19) the c-x stretching vibration in mono-substituted derivatives couples to normal vibration 1 or to normal mode 6a depending on whether the substituent is light or heavy. Accordingly, stretching vibration C-1 (l=light) is assigned to the normal mode 13 as shown during the discussion of the q-vibration. The C-h (h=heavy) stretching mode is assigned to vibration 7a as will be shown for the t-vibration.

KROSS and FASSEL (8) have studied the infrared spectra of the q-vibration in the range 1045-1185 cm^{-1} for monosubstituted benzene derivatives of the general formula $(C_6H_5)_nM$, where n is the valence of the substituent atom M (M represents any of the elements of

Group IVA, VA, VIA, and VIIA). Their plot of the frequency versus
the square of electronegativity of the substituent atom demonstrate
the linear relation found within each group. Their use of the
frequency data in obtaining the electronegativity of the substituent
atoms was criticized by VARSANYI (19) who claimed that the 1159 cm^{-1}
band assigned to the q-vibration of fluorobenzene is actually due to
the in-plane C-H deformation. For Group VIA KROSS and FASSEL (8)
attributed the deviation of the frequency for $(C_6H_5)_2Se$ from the
straight line to erroneous electronegativity data. By using the
frequency assignments obtained in the present work for the q-vibrations
of $(C_6H_5)_2Se$ and $(C_6H_5)_2Te$ the straight line passes through all points
of the plot. Thus, there is no ground for suspecting the electronegativity
data obtained by KROSS and FASSEL (8).

The vibration denoted by the letter t and some of the vibrations
denoted by the letter r correspond to vibration 6a. The frequency of
this vibration is very sensitive to mass change and bonding strength
of the substituent. The band appears between 250 cm^{-1} and 330 cm^{-1}
for heavy substituents and is assigned to normal mode 7a which corresponds
to the C-X stretching vibration. In the case of light substituents the
normal mode 6a has its maximum frequency value in phenol at 536 cm^{-1}.

BROWN et al (1) stated that the t- and y- vibrations occur at
about 500 cm^{-1} for light substituents. In this case they assigned the
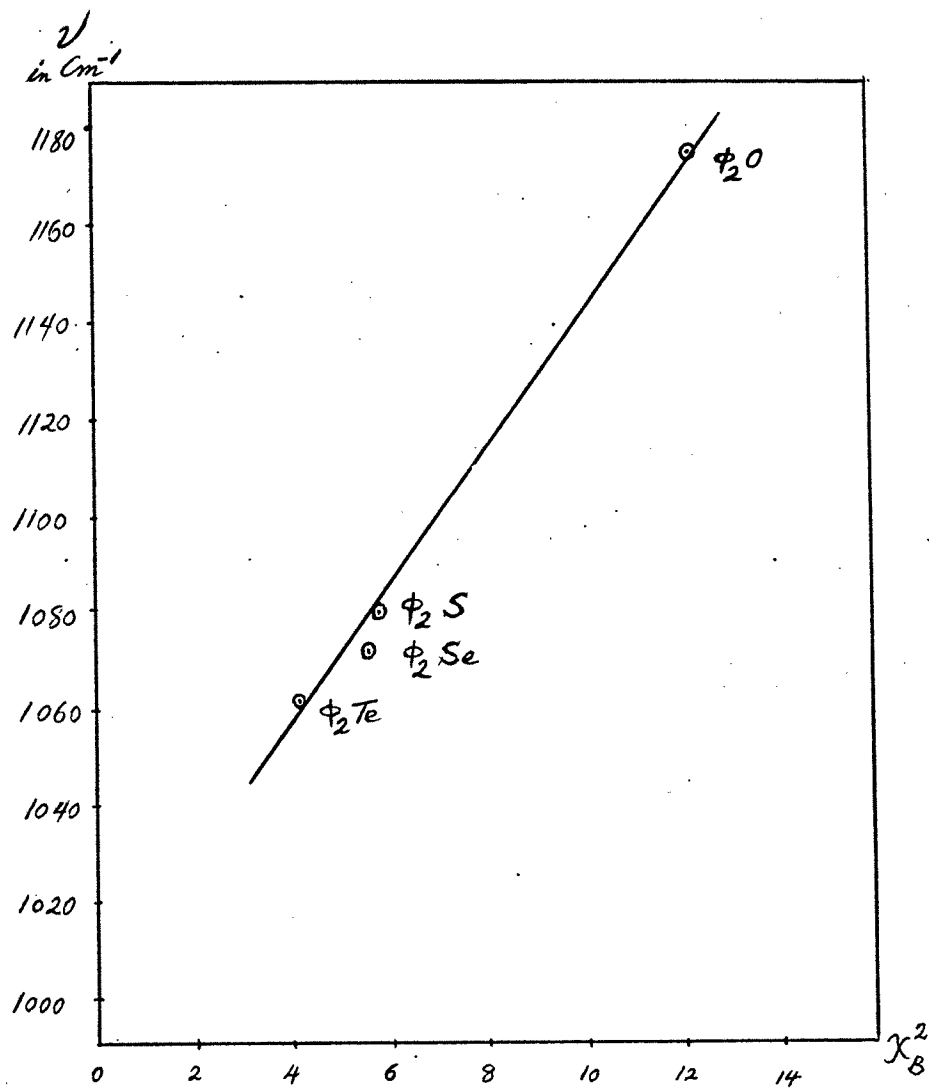higher intensity band to the y-vibration.

FIGURE 1. Plot of Frequency vs. (Electronegativity)^2 for q-Vibration (8).

As summarized by VARSANYI (19) the frequency of vibration 6a in monosubstituted benzenes is between 300 cm^{-1} and 530 cm^{-1} for light substituents. The infrared band and the Raman band of this mode are of medium intensity. KIMMEL (7) in his study of the t-vibration of molecules of the general formula $(C_6H_5)_nX$, where n is the valence of the substituent atom X of Group IVA through VIIA, has established a relation between the regular decrease in frequency going down a group and the C-X bond length. He applied Gordy's Rule in order to study the molecular parameters. According to Gordy's Rule the t-vibration of monosubstituted benzenes was considered a pure C$_6$H$_5$-X stretching vibration and the phenyl group can be treated as a point mass. Then the harmonic oscillator approximation was applied to the pseudodiatomic system and the equation

$$A\nu^2\mu = aN \frac{(X_A X_B)^{3/4}}{R^2} + b$$

was obtained, where X_A and X_B are the electronegativity of the phenyl group and the substituent atom respectively. The A, a, and b are constants. N is the bond order, μ is the reduced mass of (C_6H_5)-X pseudodiatomic system, ν is the frequency of the t-vibration, and R is the bond length in Angstrom. A plot of $\nu^2\mu$ versus $\frac{(X_B)^{3/4}}{R^2}$ is shown by KIMMEL (7) to give a straight line for those bands with the same value of n. The author was able to apply the Gordy's Rule to the t-vibration by using constants a and b that vary from Group to Group and which are different from those used by Gordy. The deviation of the first-row elements from the linear plot were explained by KIMMEL (7) as a result of the light mass of the central atom and the
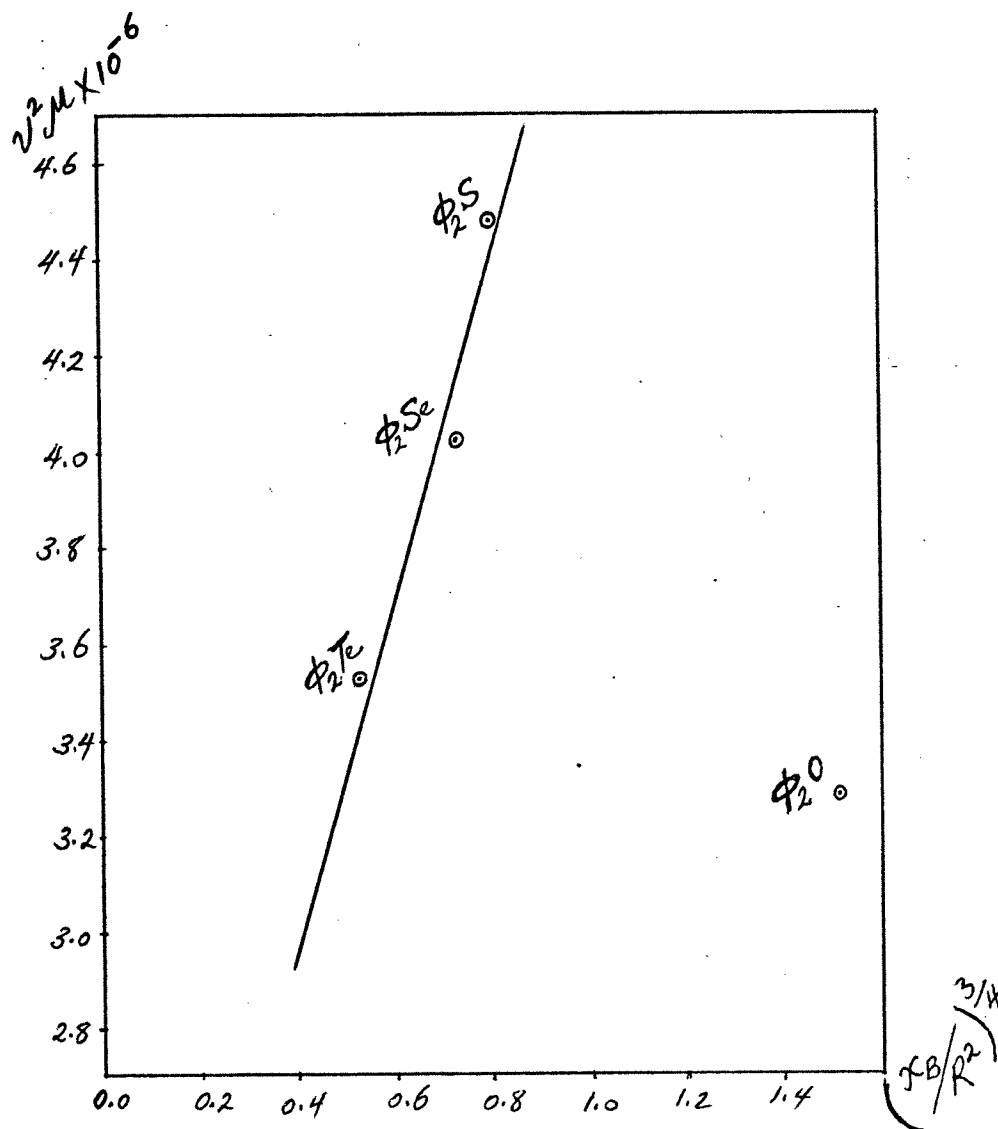
FIGURE 2. Plot of Gordy's Rule for the t-Vibration (7).

vibrational coupling between the lone-pair of electrons of the substituent and the π-electron cloud of the phenyl ring.

In the present work the t-vibration is assigned for $(C_6H_5)_2Te$ using the tabulated infrared spectrum of FRETZ and KELLER (2). Thus, by plotting $\nu^2\mu$ versus $\dfrac{(X_B)^{3/4}}{R^2}$ it was possible to obtain a straight line, as shown in Figure 2, in agreement with KIMMEL's prediction which is verified in the present work by obtaining the $(C_6H_5)_2Te$ frequency. The bond lengths were obtained from tables of SUTTON (18). The electronegativities were those of ALLRED and ROCHOW (21).

C-X in plane deformation:

The C-X in plane bending vibration of symmetry b_1 of row u gives a weak band in the Raman spectra. WHIFFEN (20) assigned the u vibrational mode to frequencies between 200 and 410 cm^{-1} for monohalogenobenzenes. The inverse relation between the mass of the substituent and the frequency led to assigning the frequency at 206 cm^{-1} for $(C_6H_5-Se)_2Hg$ to the u-vibration. The high frequency obtained for $(C_6H_5-S)_2Hg$, $(C_6H_5)_2S_2$, and $(C_6H_5)_2S$ is due to the conjugational interaction of the sulphur with the benzene ring as discussed by VARSANYI (19) for fluorobenzenes. In $(C_6H_5)_2S_2$ the frequency is displaced from that obtained for $(C_6H_5)_2S$ because of the interaction between the u-vibration with $(C_6H_5)-S-S$ bending mode.

C-X out-of-plane vibration (b_2)

The frequency intervals of the out-of-plane skeletal vibrations and C-X modes overlap. Polyatomic substituents are classified as "light" if there is free rotation around the C_{ar}-X bond, and considered "heavy" if rotation is prevented by conjugation as in C_{ar}-O or as a result of α-branching. The out-of-plane C-X vibrations, when X is "light" (e.g., CH_3, C_2H_5, C_3H_7, ...etc.), couple with normal mode 16b around 400 cm^{-1} (normal mode 17b meets this condition) and they couple with normal mode 10b when x is "heavy" since the principle of conservation of angular momentum demands a compensating rotation of the whole ring. These two vibrational modes are denoted by y and x respectively according to WHIFFEN (20). GARG (19) in his correlation calculation reached the conclusion that in monosubstituted benzenes the frequency of the x-vibration is always lower than 300 cm^{-1}. The calculated frequency of 212 cm^{-1} was obtained by KOVNER (19) for the X-vibration of toluene as compared to the experimental value of 217 cm^{-1}. This vibration gives a strong band in the Raman spectrum and is found between 140 and 250 cm^{-1}. In $(C_6H_5)_2S_2$ the frequency is displaced from that obtained for $(C_6H_5)_2S$ because of the interaction between the x-vibration and the C H -S-S bending mode. The frequency range 418-560 cm^{-1} has been established for vibration 16b (y) of monosubstituted benzenes by JAKOBSEN and BENTLYE (19). They found that the position of the band within this interval depends on the inductive effect of the substituent group of atom, i.e., for electron withdrawing groups or atoms the band

is found below 450 cm^{-1} and for electron donating groups or atoms (e.g.,

O and S) the frequency is close to 500 cm^{-1}. The strong to medium infrared

band between 445 and 480 cm^{-1} has been assigned to vibration y as shown

in Tables VI and VIII.

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