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Some factors affecting the Raman frequencies of the carbon-mercury bond

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SOME FACTORS AFFECTING THE RAMAN FREQUENCIES

OF THE CARBON-MERCURY BOND

by

Frank Stephen Martin

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Plant Chemistry

Approved:

Signature was redacted for privacy.

In charge of Major work

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Dean of Graduate College

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INTRODUCTION

That atoms could be bound together to form molecules has been recognized throughout the development of the science of chemistry. Late in the seventeenth century Boyle considered chemical combination to be the result of atomic association. Later Dalton evolved his atomic and molecular theories. Since these early beginnings the ideas of valence have grown until at the present time three general types of interaction between atoms are recognized: (1) electrostatic attraction between ions, (2) formation of covalent linkages between atoms, and (3) intermolecular action or van der Waal's forces.

The first complete formulation of the facts concerning valence was perhaps that of G.N. Lewis (28). His fundamental ideas were: (1) the various atoms in a compound have a tendency to take on or give up electrons in such a way as to become surrounded by a shell of eight electrons; (2) the tendency exists for certain electrons, to which the binding power is ascribed, to be geometrically localized between the two atoms bound together, and (3) the tendency exists for these bonding electrons to occur in pairs. The bonding electrons may be shared equally as in the hydrogen molecule or unequally as in the sodium chloride molecule. Between

these two extremes all degrees of sharing are possible.

The modern theories of chemical binding developed by quantum mechanical methods all lead back to the fundamental ideas of Lewis. These theories attempt to give at least a semi-quantitative mathematical description to the matter of chemical binding, and in so doing place emphasis on the Lewis theory in different ways. Depending on the method of approach, three theories of chemical binding may be distinguished. As outlined by Kronig (27) these are:

(1) The Heitler and London theory.

This theory starts from the states of the separate atoms entering into a compound and interprets the saturation of valences and the electron pair bond by the neutralization of the electron spins.

(2) The Pauling and Slater theory.

In this theory the states of individual electrons of the atoms are considered and, for the first time, a physical meaning is given to the directed nature of the valence bond.

(3) The Mulliken and Hund theory.

This theory is based upon the properties of the electrons in the molecule as a whole. It does not consider separately the atoms which make up the molecule.

These modern theories tend to strengthen the idea that

a chemical bond is due to the sharing of electrons. Then the character of the bond between two atoms should be dependent upon the nature of the sharing of the electrons forming the bond. Furthermore, since certain groups or radicals retain their identity in a large number of organic molecules, these radicals may be considered as units. The character of the bond formed between an organic radical and an atom should be a function of the ease with which the radical will share an electron. In other words, the nature of the bond should be a function of the electron sharing ability of the organic radical.

The electron sharing ability should furnish a basis for arranging all organic radicals in a series analagous to the electrochemical series of the elements. If such an arrangement of radicals exists, one should find a regular variation of the polar properties of compounds containing the radicals. For example, the ionization constant of a compound such as $R-C\overset{=O}{-}OH$ should vary as R is replaced by successive members of the series. A regular variation should also be noted in the dissociation constants of a series of primary amines, $R-NH_2$, as R is varied. That the electron sharing ability of the radical should affect these ionizations can be made more obvious by a consideration of a compound such as R-O-H. If R has a strong tendency to take on electrons it would tend to pull them away from the oxygen atom, thus leaving the oxy-

gen more positive. This more positive oxygen atom would in turn pull an electron from the hydrogen atom and allow the hydrogen to pass off as a positive ion. On the other hand if R has a greater tendency to give up an electron, the compound would tend to ionize to give R^+ and OH^-. Hixon and Johns (10) found that the functional relationship between the electron sharing ability of radicals and the ionization of primary amines could be expressed by an equation of the type:

$$\text{Log } K = ke^{ax+b} + C$$

where   K = dissociation constant,

x = electron sharing ability

k, a, b, and C = constants.

This equation served as a basis for arranging the radicals in a series according to their electron sharing ability as measured by its effect on ionization. The order found for the radicals is shown in table I.

Table I.   Radicals arranged in the order of increasing electron sharing ability.

Methyl	Phenyl
Ethyl	o-tolyl
Propyl	p-bromo
Tertiary Butyl	p-chloro
Allyl	alpha-naphthyl
Benzyl	p-nitrophenyl
p-anisyl	m-nitrophenyl
p-tolyl	o-chlorophenyl
m-tolyl	o-nitrophenyl
o-anisyl	cyanide

Later work has confirmed this order for the radicals, and seems to indicate that the idea of electron sharing ability is a fundamental concept. The evidence for this concept may be outlined as follows:

I. Indirect chemical evidence.

    A. Equilibrium constants in water.

        1. Ionization of organomercury nitrates (14).

        2. Ionization of alpha-substituted pyrrolidines (5, 34).

        3. Ionization of alpha-substituted pyrrolines (34).

        4. Ionization of N-substituted pyrrolidines (5).

    B. Equilibrium constants in methanol.

        1. Ionization of carboxylic acids (9).

        2. Ionization of primary amines (9).

        3. Ionization of substituted pyrrolidines (9).

    C. Equilibrium constants in ethanol.

        1. Ionization of carboxylic acids (9).

        2. Ionization of primary amines (9).

        3. For the reaction

$$2RHgI \rightleftharpoons R_2Hg + HgI_2 \quad (12).$$

        4. For the reaction

$$RHgCN + HCl \rightleftharpoons RHgCl + HCN \quad (2).$$

D. Equilibrium constants in benzene.

    1. For the reaction

$$Cl_3CH(OH)SR \rightleftharpoons Cl_3CHO + RSH \quad (13).$$
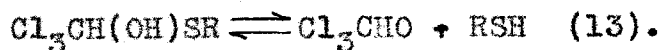
II. Indirect physical evidence.

    A. The atomic refractivity of mercury in a series

        of R-Hg-R compounds (4).

    B. Thermal stability (decomposition temperature).

        1. R-Hg-CN (3).

        2. R-Hg-NO$_3$ (11).

        3. R$_2$Hg (4).

In all cases listed as indirect chemical evidence the effect was measured by observing the change in some polar property of a compound containing the radical. The reactions used in all these studies were reversible. The methods for measuring electron sharing ability are indirect because the effect of the radical must be measured indirectly by its effect as transmitted through an intervening atom or group. For example, to produce a variation in the dissociation of RNH$_3$OH the radical must transmit its effect through the nitrogen atom.

A more direct method would be to consider some property of the bond by which the radical is attached to an atom or group. This should show in a more direct manner the exact nature of the effect which the radical has upon the R-X bond.

As suggested by Carr, (3) refractive index studies should prove a step in this direction. Fajans and Joos (8) and Smyth (33) have shown that refraction can be used as a measure of the constraint under which electrons act in molecules. Applying the ideas developed by these authors Carr (4) reasoned that in a series of compounds such as R-Hg-CN or R-Hg-R the atomic refraction of mercury should vary with the electron sharing ability of the radical. In the mercury atom alone the electrons act under the influence of a certain constraining force which may be calculated from the refractivity of the mercury atom. Then if the mercury is attached to a radical, the electrons of the mercury atom which form the bond between R and Hg will be influenced also by the constraining force exerted on them by the radical R. The constraining effect of the radical should cause the atomic refractivity of the mercury atom in the compound to be different from that observed for free mercury.

Table II shows the atomic refractivities of mercury and the thermal decomposition temperatures for a number of compounds as determined by Carr (4). For the cyanides the atomic refraction of the mercury was calculated by subtracting the molar refraction of R-CN from that of R-Hg-CN. Likewise the molar refraction of R-R was subtracted from that of R-Hg-R to obtain the atomic refraction of the mercury in the R-Hg-R compounds.

Table II. The atomic refractivity of mercury and decomposition temperature for some organomercurials.

Compound	Decomposition temperature (degrees)	Atomic refraction of Hg
CH_3HgCN	260-270	10.19
C_2H_5HgCN	245-265	11.53
$C_6H_5CH_2HgCN$	208-216	13.07
$o-ClC_6H_4CH_2HgCN$	210-215	13.07
C_6H_5HgCN	Above 250	10.58
$p-CH_3C_6H_4HgCN$	Above 250	9.35
$(C_3H_7)_2Hg$	190	12.25
$(C_6H_5CH_2)_2Hg$	170	13.81
$(C_6H_5)_2Hg$	300	11.42
Hg vapor (8)		13.94

This table shows that when the atomic refractivity of the combined mercury has a maximum value the resulting compound is very unstable. A maximum in the refraction corresponds to a minimum constraint for the electrons. That the mercury atom in dibenzylmercury and benzylmercury cyanide is loosely bound is shown by the ease with which it is removed by the application of heat. On heating, these compounds decompose according to the following equations:

$$R-Hg-R \xrightarrow{(heat)} R--R + Hg$$

$$R-Hg-CN \xrightarrow{(heat)} R--CN + Hg$$

If the order of the radicals shown in table I is retained, the curves obtained by plotting the electron sharing ability of the radicals against the thermal stability of the organomercury compounds shows a minimum. On the other hand, the curve of the atomic refraction of mercury in these compounds shows a maximum. This maximum occurs at the same point on the electron sharing ability axis as does the minimum in the thermal stability curve. If the radicals are arranged in the order of increasing atomic refractivity of the mercury, they assume approximately the same order found by Kharasch (17, 18, 19), from a study of the irreversible splitting of unsymmetrical organomercury compounds.

Undoubtedly there are several factors which determine the electron sharing ability of an organic radical. The two types of methods outlined previously may place emphasis on these factors in different ways. For example, assume that two factors important in determining the electron sharing ability of the radical are mass and symmetry. The radicals could be arranged simply in the order of increasing mass. On the other hand, the dielectric constant of a series of compounds of the type R-X could serve as a basis for classifying the radicals. Obviously this method would place much more emphasis on symmetry than on mass. Until the exact factors which determine the electron sharing ability of a radical are known and the effect of each determined, the

order of the radicals cannot be definitely fixed. A direct study of the carbon-mercury bond throughout a series of compounds should help to clarify these questions. To make such a study was the chief purpose of this investigation.

STATEMENT OF THE PROBLEM

The purpose of the present study may be outlined as follows:

1. To investigate the theoretical possibilities of using Raman spectra as a tool in the elucidation of electron sharing ability.

2. To assemble apparatus suitable for Raman spectra studies.

3. To obtain and study the Raman spectra of a series of compounds of the type R_2Hg.

THEORETICAL CONSIDERATIONS

When the molecule is considered as a dynamic system in the interpretation of Raman spectra, there are several simple postulates which are basic. As outlined by Andrews (1) they are:

1. The frequencies of the Raman shifts correspond to the characteristic fundamental mechanical frequencies in the molecule.

2. The masses of the vibrating mechanical system are the nuclei of the atoms arranged in space as indicated by X-ray studies of crystal structure and by deductions from stereo chemistry.

3. The forces under which these masses vibrate may, as a first approximation, be considered as acting along the lines associated with the chemical valence bonds. They can be characterized by two elastic constants, the stretching constand and the bending constant. The stretching constant gives the restoring force when the two atoms are pulled apart unit distance from their equilibrium positions in the molecule. The bending constant gives the restoring force when the angle is altered between the bonds joining a central atom to two other atoms.

4. The amplitude of vibration will be so small compared with the equilibrium distances between any two atoms that the variation of the force with distance will obey Hooke's law.

5. The elastic constants for any type of bond are independent of the structure of the molecule in which it occurs, if there are no neighboring dipoles present. (The exact description of the forces between the atoms varies considerably with the author and the type of molecule being considered.)

The fifth of these postulates has a direct bearing upon the present problem. As a preliminary test of this postulate, consider the Raman frequencies observed for methyl chloride, methyl bromide, and methyl iodide. These compounds show the following frequencies: 710, 594, and 522 due to the C--X bond. Substituting these values into the equation for a simple harmonic oscillator one can calculate the elastic constant k for the C--X bond.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \qquad (1)$$

$$\text{or} \quad k = 4\pi^2 \mu \nu^2$$

$$\text{where} \quad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

where k = force constant

μ = reduced mass

ν = frequency of vibration

m_1, m_2 = mass of vibrating particles.

This procedure yields three values for k in dynes per cm.:
3.12 x 10^{-5}, 2.61 x 10^{-5}, 2.15 x 10^{-5}, respectively.

The variation of k may be interpreted as meaning that the strength of the C--X bond increases as we pass from the iodide to bromide to chloride. The stability of these compounds increases in this same order. The degree of ionization of the halogen acids decreases in this order.

In carrying this procedure over to the more complex organic molecules which show numerous lines, one must assume that a particular observed frequency may be associated with one bond in the molecule. The validity of this assumption is evidenced by the fact that whenever a carbon-hydrogen bond occurs in a compound frequencies near 3000 cm.$^{-1}$ are observed. Likewise, if a carbon-carbon bond is present frequencies near 1000 are observed. Theoretical considerations also support this assumption. A study made by Lewis (29) on coupled vibrations showed that if groups of vibrating particles are coupled together, there should be two results. First, frequencies should be observed which are slight modifications of and grouped around the frequencies observed when the groups vibrate alone. Second, there should be frequencies present which are slight modifications of the frequencies observed if the individual groups are considered as rigid units to form a new system. The frequencies observed for a particular bond vary somewhat with the structure of the molecule. A

study of this variation should help to explain the nature of
the electron sharing ability of organic radicals.

A bond chosen for such a study should show a frequency
in a region of the spectrum free from lines due to other bonds.
The C≡N bond fulfills this condition remarkably well. All
compounds having the C≡N bond exhibit a frequency near 2100
cm.$^{-1}$ while if no such bond is present in the compound no
frequency is observed in this region. If the C≡N group is
considered as a system of two particles, it should have a
single frequency which may be called ν_o. Then if this group
is coupled to another group, R, ν_o should be shifted slightly
to a new position, ν_1. The modification of ν_o, i.e. $\nu_1 - \nu_o$,
is a direct measure of the coupling coefficient between R and
the CN group. The coupling coefficient is defined as the
ratio between the coupling within the group and the coupling
between the groups. Then if the binding within the C≡N and
R groups remains unchanged when the two are coupled together,
the shift in ν_o, $\nu_1 - \nu_o$, will measure the strength of the
coupling. If the strength of an R--CN bond is determined by
the electron sharing ability of the radical R, then $\nu_1 - \nu_o$
will be a function of electron sharing ability.

Table III shows the frequencies reported (6) for a
number of compounds of the type R--CN.

Table III. Frequencies reported for a series of cyanides.

Compound	ν_1	$\nu_1 - \nu_0$
CN (ion)	2080	0
HCN	2094	14
CH_3CN	2250	170
C_2H_5CN	2246	166
C_3H_7CN	2245	165
$(CH_3)_2CHCH_2CN$	2245	165
$(CH_3)_2CHCH_2CH_2CN$	2241	161
$C_6H_5CH_2CN$	2248	168
$o-CH_3C_6H_4CN$	2225	145
C_6H_5CN	2227	147
CN--CN	2334	254

Table III shows that there is a variation in the frequency due to the C≡N bond as the radical is changed. Although the total variation over the whole series is slight, this frequency tends toward a maximum in methyl or benzyl cyanides. If the R-C bond is so strong that the R-C group vibrates as a unit, then from equation (1) the C≡N frequency should vary inversely with the mass of R. However, the exact mass of the radical which is effective is uncertain. Therefore this effect cannot be evaluated directly.

The foregoing discussion shows that to obtain useful information from Raman spectra studies on a series of compounds the series should possess the following characteristics.

1. The individual compounds should show frequencies in a region free from other lines.

2. The frequency or frequencies studied should vary con-

siderably as R is varied.

Since refractive index (4) and thermal stability data (4) are available for a series of R-Hg-R compounds these were chosen for the present study. They should be well suited to such a study for several reasons. First, since R is attached directly to the mercury the effect on the R-Hg bond can be observed directly as R is varied. Second, since the mercury is very heavy the frequencies of the molecule associated with it should be low and fall in a region relatively free from other Raman lines.

As an approximation one may consider the symmetrical mercury compounds as composed of three particles, and represent them as shown in Figure I.

Figure I. Model of a symmetrical organo-mercury compound.

K_1 represents the restoring force in dynes when the mass m is displaced unit distance from its equilibrium position. In this sense, K_1 measures the strength of the carbon-mercury bond. K_α represents the restoring force when the angle between the two carbon-mercury valence bonds

is altered, hence it measures the resistance of the carbon-
mercury bond toward bending.

Insofar as they are available dipole moment measure-
ments and electron diffraction studies (32) indicate that
molecules of this type are linear. At least the two valence
bonds of the mercury form an angle of 180° with one another.
Any deviation from a linear structure in the radical itself
will not be very important in the present considerations.
Yates (39) used a linear model as shown in Figure I and cal-
culated the fundamental frequencies for the system. The
modes of vibration corresponding to these frequencies are
shown in Figure II.

Several interesting and useful relationships are shown
by these equations. As is apparent from equation (2) ν_1
is independent of the mass of the mercury. Therefore if k_1
can be determined by a separate means, equation (2) offers
a method for evaluating the effective mass of R. Equation
(6) offers a means for evaluating k_1 which does not ex-
plicitly involve the mass of the radical. Equation (5)
should prove of value in locating ν_3 provided, of course,
m can be evaluated and ν_1 located. Theoretical considera-
tions beyond the scope of this thesis show that ν_1 , the
symmetrical frequency, should be the most intense frequency
observed in the Raman spectra.

In order to test the validity of this method, it may

$$\mathcal{V}_1 \qquad \mathcal{V}_2 \qquad \mathcal{V}_3$$
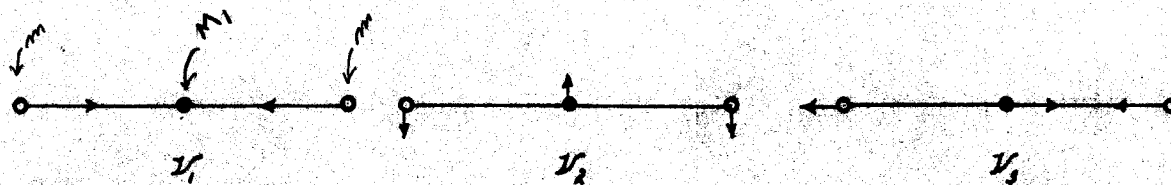
The equations for the fundamental frequencies are:

$$\mathcal{V}_1 = \frac{1}{2\pi}\sqrt{\frac{k_1}{m}} \qquad (2)$$

$$\mathcal{V}_2 = \frac{1}{2\pi}\sqrt{\frac{2k_\alpha}{M}} \qquad (3) \qquad M = \frac{m M_1}{2m + M_1}$$

$$\mathcal{V}_3 = \frac{1}{2\pi}\sqrt{\frac{k_1}{M}} \qquad (4)$$

Using these equations the following relations may be obtained.

$$\frac{\mathcal{V}_3}{\mathcal{V}_1} = \sqrt{\frac{2m + M_1}{M_1}} \qquad (5)$$

$$\mathcal{V}_3^2 - \mathcal{V}_1^2 = \frac{k_1}{2\pi^2 M_1} \qquad (6)$$

$$k_1 = 4\pi^2 m_1 \mathcal{V}_1^2 \qquad (7)$$

$$k_\alpha = \frac{m M_1 \mathcal{V}_2^2}{2\pi^2 (M_1 + 2m)} \qquad (8)$$

$$\text{or} \qquad k_\alpha = \frac{2\pi^2 m \mathcal{V}_1^2 \mathcal{V}_2^2}{\mathcal{V}_3^2} \qquad (9)$$

Figure II. The modes of vibration and equations for a linear triatomic molecule.

be applied to the diethyl- and dimethylmercury compounds.
Thompson and Linnett (35) have made a rather complete dy-
namical study of these molecules and have assigned the fre-
quencies observed by Pai (31) to the fundamental modes of
vibration of the molecular model. The modes of vibration
and observed frequencies are shown in Figure III. The
numbers in parenthesis are the intensities of the observed
Raman lines.

Table IV shows the observed and calculated frequencies
for diethyl- and dimethylmercury. The values for the force
constants for the carbon-mercury and carbon-carbon bonds
seem rather improbable. However, the general agreement
with the experimentally observed frequencies is rather good.
Still closer agreement between the experimentally observed
and calculated frequencies was obtained by these authors
when they selected the calculated frequencies from two sets
of data. One set of data was calculated assuming the
structure shown in Figure III. The other calculations were
based upon a structure in which one ethyl group of Figure
III was rotated 180° about the carbon-mercury bond. The
close agreement between the calculated and observed re-
sults is not surprising when one considers there were a
total of six constants which were adjusted to obtain seven
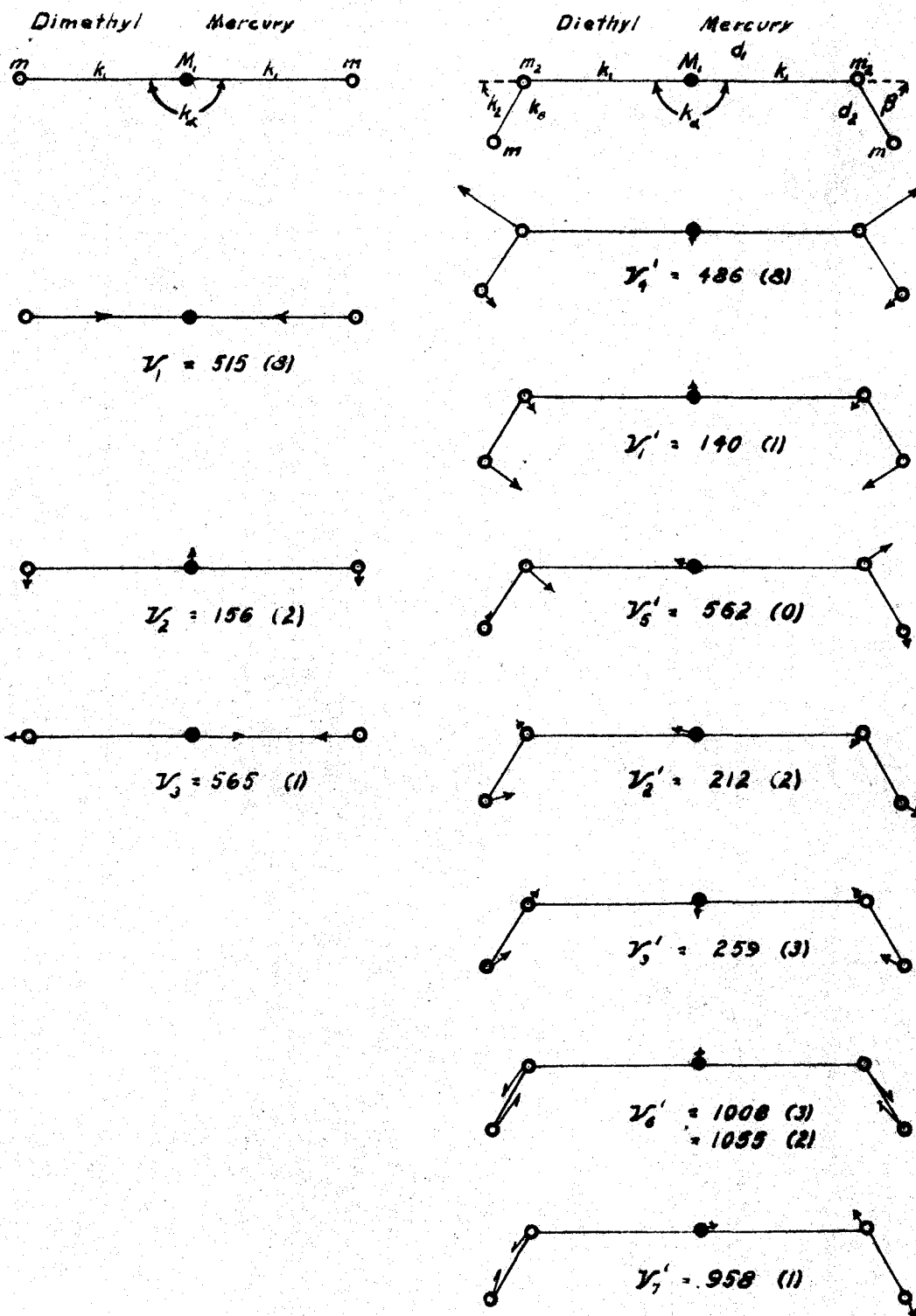frequencies.

Figure III. Modes of vibration for dimethyl and diethyl mercury.

Table IV. Observed and calculated frequencies for diethyl-
and dimethylmercury.

Diethylmercury		Dimethylmercury	
Observed	Calculated	Observed	Calculated
140 (1)	135 ν_1'	156 (2)	--
212 (2)	215 ν_2'	255 (0)	--
259 (3)	255 ν_3'	515 (8)	--
329 (0)	---	565 (1)	--
	495		
485 (8)	480 ν_5'	700 (3)	--
562 (0)	---		
633 (0)	---		
958 (1)	970 ν_7'		
1008 (3)	985 ν_6'		
1055 (2)	---		

The following constants were used in calculating the
above frequencies.

Constants for $(C_2H_5)_2Hg$

$k_1 = 1.7 \times 10^5$ dynes per cm.

$k_2 = 3.9 \times 10^5$ dynes per cm.

$k_\alpha = 1.7 \times 10^{-11}$ dyne cm. per radian

$k_\beta = 0.6 \times 10^{-11}$ dyne cm. per radian

$\beta = 65°$

$d_1 = 2.25 \times 10^{-8}$ cm.

$d_2 = 1.54 \times 10^{-8}$ cm.

$m = 15$

$m_2 = 14$

$M_1 = 201$

Constants for $(CH_3)_2Hg$

$k_1 = 2.33 \times 10^5$ dynes per cm.

or $k_1 = 2.44 \times 10^5$ dynes per cm.

$k_\alpha = 0.46 \times 10^{-11}$ dyne cm. per radian

or $k_\alpha = 0.48 \times 10^{-11}$ dyne cm. per radian

$m = 15$

$M = 201$

Table V shows the results obtained by applying equations (6), (7), (8) and (9) to the observed frequencies for diethyl- and dimethylmercury as given in Table IV.

Table V. Calculated constants for diethyl- and dimethyl-mercury.

Constant	k_1	k_1	k_1	k_α	k_α	ν_3/ν_1	$\frac{2m + M}{M}$	m
Equation	(6)	(7)	(4)	(9)	(8)			(5)
$(CH_3)_2Hg$	3.16	2.34	2.45	0.09	0.09	1.1	1.07	16.7
$(C_2H_5)_2Hg$	4.67	4.05	4.31	0.13	0.13	1.16	1.17	11.3
		1.95*	2.28*	0.06	0.07		1.07*	

*$m = CH_2$ used to calculate these values.

The frequencies used in these calculations were:

Dimethylmercury   Diethylmercury

$\nu_1 = 515$ $\nu_1 = 486$

$\nu_2 = 156$ $\nu_2 = 140$

$\nu_3 = 565$ $\nu_3 = 562$

Table V shows that fairly good agreement with the results of Thompson and Linnett (35) can be obtained by applying equation (7) and considering the CH_2 group as vibrating against the mercury atom. However, equation (6) seems to offer a more logical procedure. In applying this equation one assumes a three body system and calculates the restraining force acting on the group vibrating against the mercury. The constant, k_1, which is a measure of this force, is not a measure of the strength of the carbon-mercury bond unless R vibrates as a whole. That this is true may be seen
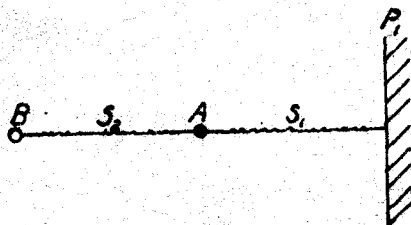
from a consideration of Figure IV.

Figure IV. Coupled vibrators with a fixed support.

In Figure IV two particles A and B are attached to a fixed point P by means of springs S_1 and S_2. If A vibrates while B remains in a fixed position the constraining force on A is the sum of the forces due to S_1 and S_2. On the other hand, if A and B vibrate as a unit, i.e. S_2 does not change its length, the constraining force on the group A B is that due to S_1 alone. The application of equation (6) should yield results more indicative of the actual binding between R and Hg than are the constants found in an arbitrary way by Thompson and Linnett.

The above considerations show that Raman spectra studies should be of value in the present problem. They should help to explain the nature of the R-Hg bond in two ways: first, by variations in the frequencies due to the carbon-mercury bond, and, second, by variations in the frequencies character- istic of R when it vibrates as a unit. The frequencies due

to vibrations within the radicals will, of course, have to be obtained from the Raman spectra of simpler compounds containing the radicals. Whether any exact relationship exists between the Raman frequencies and the electron constraint as measured by the atomic refraction is not known.

EXPERIMENTAL

The Spectrograph

The spectrograph used was constructed by the College Instrument shop. The optical parts were purchased from the Bausch and Lomb Optical company. The prism is mounted in a cast iron case at one side of which the collimator tube carrying a lens of 65 mm. diameter and 600 mm. focal length is fixed. In front of the lens is mounted a unilateral slit of 20 mm. height. The slit carries a V-shaped Hartman diaphragm for regulating its height. The width of the slit is adjustable by means of a micrometer screw. The drum of the screw is divided so that the width of the slit can be adjusted to a hundredth of a millimeter.

The camera lens system consists of two achromatic doublet lenses separated by a distance of 117.4 mm. The lens nearest the prism has a diameter of 65 mm. and the diameter of the second is 50 mm. This combination brings the spectrum into focus at approximately 70 mm. back of the second lens. The objective is mounted on a carrier provided with a screw adjustment so that its distance from the prism may be varied.

The plate holder is mounted directly back of the camera lens and may be rotated or moved horizontally away from the objective. The plate holder is adjustable vertically so that the several spectrograms may be taken on the same plate.

The instrument was originally designed to use a hollow prism filled with ethyl cinnamate. The side of the prism, which had a refractive angle of 65°, was 150 mm. long and 95 mm. high. Ethyl cinnamate should be particularly suited for this purpose because of its high dispersion and low average index of refraction. However, with this liquid in the prism a sharp focus could not be obtained. The Raman lines obtained with the liquid prism were so diffuse and irregular that they could not be measured. Further difficulty was encountered due to polymerization of the ethyl cinnamate. This effect was noticed only after washing and vacuum distilling a sample of the liquid which had become slightly colored on standing for a year and a half. The purification process probably removed some stabilizing agent added originally by the manufacturer of the ester.

A review of the constants for a large number of liquids indicated that methyl salicylate or ethyl anthranilate should serve as a satisfactory substitute for ethyl cinnamate. Since methyl salicylate was available, attempts were made to use it in the prism. The definition of lines was as unsatisfactory as when ethyl cinnamate was used. This result

suggested the possibility that the defect might lie either
in the lens system of the instrument or in the glass parts
of the prism itself. Examination of the prism faces with
a test plate showed that they were not sufficiently flat for
use. Furthermore, they were so thin that the weight of the
liquid caused them to bulge slightly. Since the prism it-
self was defective, no further search for a suitable substi-
tue for ethyl cinnamate was made.

The definition obtained was very satisfactory when the
liquid prism was replaced by a smaller 60° glass prism. The
dispersion was only about two-thirds as great and the in-
tensity much less with the glass prism. The exposure time
with this prism was rather long. Greater accuracy could
have been obtained with a satisfactory liquid prism. How-
ever, since considerable time and money would have been
necessary to secure a satisfactory liquid prism, the glass
prism was used throughout.

The entire spectrograph was placed in a constant tem-
perature bath to avoid any expansion or contraction of the
instrument during long exposures. The thermostat was ori-
ginally intended to prevent convection currents due to
temperature changes in the liquid prism.

Figure V shows typical spectrograms obtained with each
of these prisms.
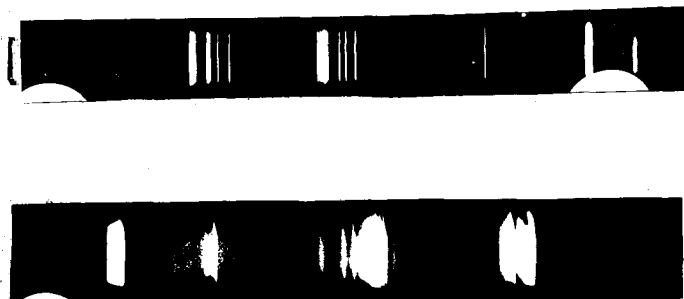
Figure V. Spectrograms taken with liquid and glass prisms.

These spectrograms are the Raman spectra of carbon tetrachloride and have been enlarged to approximately the same size. On the original plates the length of the spectrum between the two mercury arc lines 4358 Å and 4916 Å was 5 mm. with the liquid prism. The distance between these lines using the glass prism was 3 mm.

The Excitation Unit

The usual experimental arrangement as recommended by Wood (37) was not satisfactory for use with the spectrograph available. Due to the construction of the plate holder the tube holding the liquid under observation could not be viewed from the rear of the spectrograph. Therefore the tube could not be accurately aligned and a very large amount of stray light was reflected from the walls of the tube into the spectrograph. Another disadvantage of Wood's arrangement was that it required alignment of the tube each time it was

refilled. The arrangement shown schematically in Figure VI
was finally adopted as being the most satisfactory. This
apparatus is a modification of that used by Dadieu and
Kohlrausch and described by Kohlrausch (22).

The liquid or solution to be investigated was held in tube
T. This tube was made by sealing a flat piece of plate Pyrex
glass into a Pyrex tube (12 mm. outside diameter). A collar
at the top rested on the condenser C to support the tube.
The condenser C was also constructed from Pyrex tubing, the
inside diameter being just slightly larger than the outside
diameter of the Raman tube T. A solution was circulated
through the condenser C for two purposes: to keep the liquid
in T cold and to serve as a light filter.

The reflector R was constructed in the form of an el-
liptical cylinder from polished sheet aluminum. The top and
bottom were made elliptical so that if the arc were placed
at one focus, all light leaving it would be concentrated on
the tube T placed at the other focus. A slit in the top
allowed a glass filter F to be inserted between the arc and
the Raman tube. The reflector was mounted on a stand pro-
vided with a screw arrangement so that R could be raised or
lowered. The stand also carried a support for the total re-
flecting prism P_1. This support could be raised or lowered
without moving the reflector. A means was also provided for
moving P_1 horizontally. The stand could be tilted by means
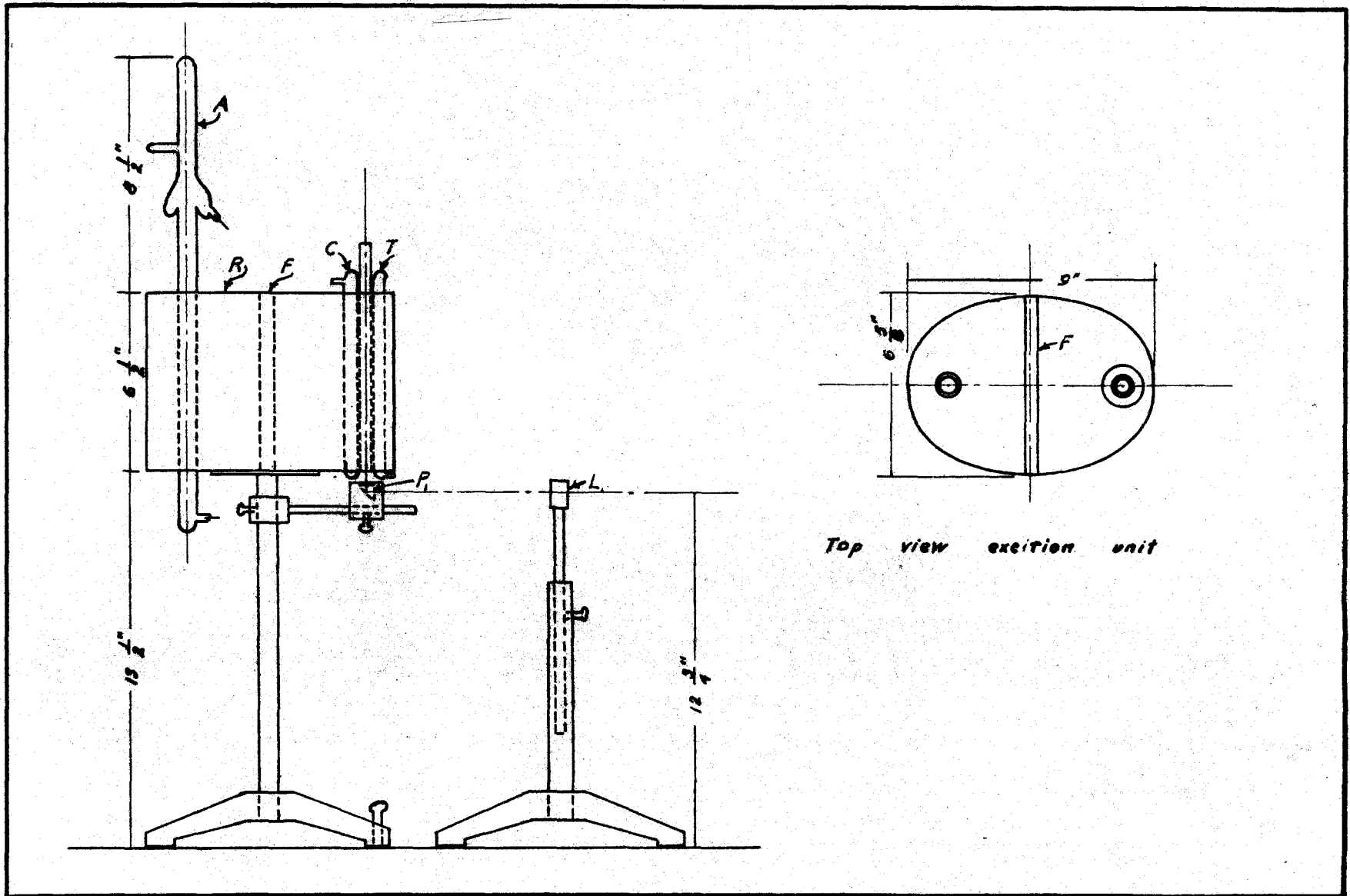
Top view excition unit

Figure VI.   Diagram   of   assembled   excitation   unit.

of leveling screws in the base. The lens L_1 was placed on a separate stand which was bolted to the table.

D.C. mercury arcs of several designs were made and tested but the design shown in Figure VI proved most satisfactory. This arc was constructed from Pyrex tubing (19 mm. outside diameter). The rather large diameter was chosen to insure complete illumination of the liquid in the Raman tube. When in use an external resistance was placed in series with the arc to limit the current to 5 - 5.5 amperes. A blast of air from an electric fan was directed against the arc to keep it cooled. The holes in the top and bottom of the reflector through which the arc passed had a diameter about twice that of the arc in order to insure good circulation of air.

Attempts were made to use a General Electric type H-2 110 volt A.C. mercury lamp. Although this type of lamp was very convenient to use it was unsatisfactory because of the high temperature at which it operated. At this temperature the continuous mercury spectrum between 4000 and 5000 Å was quite intense. Another disadvantage was that a small amount of argon was present in the lamp and gave rise to several lines in the region in which the Raman lines were found. When the lamp was cooled sufficiently to reduce the continuous light, the 4358 Å mercury line used to excite the Raman spectra was only about one-fifth as intense as this line
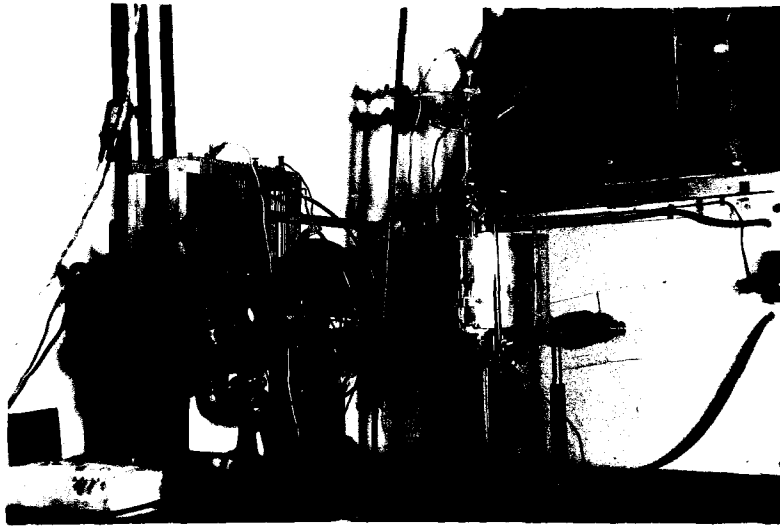
Figure VII.   The assembled excitation
unit.

from the D.C. arc. For these reasons the D.C. arc was preferable.

Figure VII is a photograph of the assembled excitation unit.

Light Filters for Obtaining a Monochromatic Source

Light filters are used in Raman spectra work for several purposes. These purposes and the materials commonly used are given in the following outline.

1. Filters to remove violet and ultra violet light.

    a. Corning Noviol-0 glass.

    b. Quinine sulfate solution.

2. Filters to remove continuous light from mercury arc between 4000 and 5000 $\overset{o}{A}$.

    a. Cobalt salts.

    b. Corning No. 585 glass filter.

    c. Concentrated didymium chloride solution (25).

    d. Iodine in carbon tetrachloride solution.

3. To isolate a single mercury arc line (21).

    a. For 5791 and 5770 $\overset{o}{A}$ lines.

        (1) Saturated potassium dichromate solution.

    b. For 5461 $\overset{o}{A}$ line.

        (1) Potassium dichromate plus neodymium nitrate solution.

 c. For 4358, 4348, and 4339 $\overset{o}{A}$ lines.

  (1) Cobalt glass plus quinine sulfate solution.

 d. For 4047 $\overset{o}{A}$ line.

  (1) Cobalt glass plus quinine sulfate solution.

 e. For 3663, 3655 and 3650 $\overset{o}{A}$ lines.

  (1) Methyl violet 4R plus nitroso dimethyl

  aniline.

The particular choice of filter depends, of course,
upon the purpose to be accomplished. Any filter designed to
isolate a single mercury line usually reduces the intensity
of the line isolated. This necessitates longer exposure but
considerably simplifies the interpretation of the spectro-
grams. Glass filters are very convenient to use but usually
greatly reduce the intensity of the line isolated. Solutions
are rather inconvenient but may be chosen to give selective
absorption in almost any region of the spectrum. This is
particularly true for organic dyes but these are objection-
able because they tend to change with use. Since the organo-
mercury compounds to be studied were decomposed by violet and
ultra violet light, the 4358 $\overset{o}{A}$ mercury line was used for ex-
citation.

 All light below 4358 $\overset{o}{A}$ was cut out by a plate of
Corning Noviol-A glass inserted at F, Figure VI. Another
Corning filter, ultra blue purple No. 585, was also inserted
at F to remove light of longer wave length. This combination

reduced the intensity of the 4358 Å mercury line by about 80 percent, so whenever possible the No. 585 filter was not used. In these cases a solution 0.05 M in $CuSO_4$ and 0.05 M in $CoSO_4$ was circulated through the condenser C. This solution helped to reduce the continuous mercury arc spectrum between 4000 and 5000 Å. The copper sulfate was added to remove the infra-red light which, in some cases, caused rapid decomposition of the mercury compounds.

In some earlier experiments the outside of the Raman tube was painted with colored lacquer made by adding 10 cc. of a saturated methyl alcohol solution of Rhodamine B and 10 cc. of a saturated methyl alcohol solution of aniline red to 50 cc. of clear lacquer. Several dyes were investigated for this purpose but none proved very satisfactory. The lacquer did not stick to the glass very well and had to be renewed occasionally. Furthermore, the intensity of the 4358 Å line was considerably reduced, so the use of these filters was discontinued.

Figure VIII shows the effect of various filters. These photographs are enlargements of spectrograms of the mercury arc. They were taken by inserting an aluminum rod with a conical tip into the condenser C (Figure VI) in place of the Raman tube. The conical tip served to reflect the light from the arc into the spectrograph. Since the only purpose of the experiment was to compare the filters, no attempt was
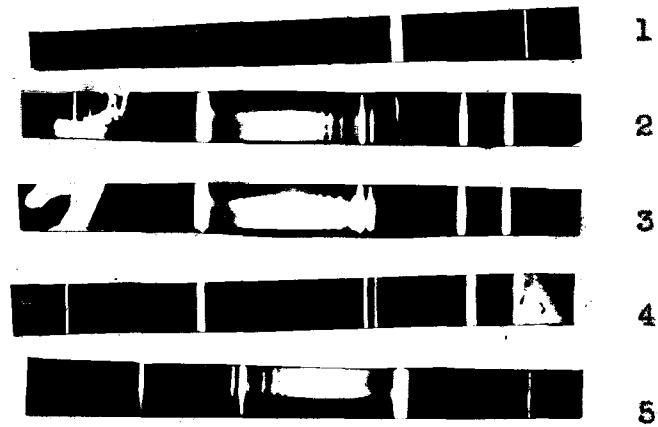
1. Noviol A + CuSO$_4$ + NH$_4$OH (excess)

2. Noviol A + CuSO$_4$ + CoSO$_4$

3. Noviol A

4. Noviol A + Corning No. 585

5. Noviol A + lacquered tube

Figure VIII. Comparison of filters.

made to secure uniform illumination of the slit. The light
sent into the spectrograph had passed through the filters
in the same manner as when the Raman spectrum of a solution
was being taken. The exposures shown in Figure VIII were
taken for 15 minutes with 4.75 amps. current through the arc.

When the lacquered tube was used, cooling of the liquid
in the Raman tube was accomplished by allowing tap water to
run through the condenser C (Figure VI). Some of the spectro-
grams were taken with solutions saturated at 40°. This
temperature was maintained by circulating the $CoSO_4$ - $CuSO_4$
filter liquid through a copper coil in a thermostat and then
through the condenser C. The water in the thermostat was
held at 48°. With the thermostat at that temperature the
filter solution could be circulated slowly through condenser
C and maintain the temperature inside the Raman tube at 42° -
43°. Control of this temperature was important when solutions
were used. If crystallization took place, the unmodified
mercury light was reflected into the spectrograph and ruined
the spectrogram.

Adjustment of the Spectrograph and Alignment
of the Auxiliary Apparatus

An iron arc was used as a light source and the spectro-
graph was adjusted in the usual manner. The collimator was
removed and focused on a distant object. Then, after setting the

prism on minimum deviation for green light, the plate holder
was fixed and a sharp image of the slit formed on a ground
glass plate in the plate holder by moving the objective lens.
The spectrum was so small that an eyepiece was used for vis-
ual observation during this adjustment. A series of spectro-
grams of the iron arc were taken with various settings of
the objective and plate holder. The best adjustment was se-
lected by an examination of these plates.

In order to obtain satisfactory spectrograms in Raman
spectra work all light coming directly from the light source
must be prevented from entering the spectrograph. Unless
this is accomplished, the continuous light from the arc
will mask the weak Raman lines. One source of this ex-
traneous light is that reflected from the walls of the Raman
tube. However, if the alignment is good, the condensing
lens L_1 and the slit dimensions can be chosen so that no
light from the walls of the tube enters the spectrograph (30).
The condensing lens used had a focal length of 10 cm. and
was placed 15 cm. from the slit. The slit length and width
were 5 mm. and 0.125 mm., respectively. The front of the Ra-
man tube was placed 18 cm. from the condensing lens.

For aligning the apparatus a small light was placed
at the plate holder so that the prism was completely illumi-
nated. This produced a square diverging beam of light from
the slit of the spectrograph. An outline of the beam was

drawn on a white card placed about two feet in front of the
slit. By drawing the diagonals of the square so obtained,
the center of the beam was located. The lens L_1 (Fig. VI)
was next brought into place and raised until the center of
the beam was in the same position as before. The stand
holding the lens was then bolted to the table to insure its
staying in place.

With the condenser C clamped at the focus of the ellip-
tical reflector, tube T was inserted and the total reflecting
prism P_1 adjusted. This adjustment was accomplished by al-
lowing parallel light to enter through the top of T and mov-
ing P_1 until T appeared to extend straight back from the front
face of the prism. P_1 was then firmly clamped in position.

The stand holding the tube and prism assembly was next
brought into place and the height of the reflector-prism
assembly adjusted. The position of the stand was regulated
so that the square beam of light from the slit fell in the
center of the front face of P_1. The stand was then tilted
by means of leveling screws in the base until the beam of
light from the slit as seen on a piece of ground glass was
exactly in the center of the top of T.

When the slit was almost covered by the Hartman dia-
phragm, the beam formed a small spot of light on the ground
glass. The tilting naturally disturbed the previous setting
of the height of P_1, and, therefore, the height was read-

justed. The alternate adjustment of the height and tilting
was repeated until both were correct. The alignment of the
reflector and prism was considered correct when the following
conditions existed.

1. A square of light from the prism was exactly in the
center of P_1.

2. A square of light from the prism was exactly in the
center of the bottom of tube T when viewed from the top.

3. A spot of light corresponding to the slit was ex-
actly in the center of the top of T.

The adjustment outlined placed the center of the Raman
tube on the optical axis of the lens system. The relative
positions of the condensing lens L_1, the spectrograph slit,
and Raman tube were calculated using the method outlined by
Nielsen (30). This method tends to send light into the
spectrograph from the maximum volume of liquid in the tube
while excluding that reflected from the walls of the tube.

The spectrograph was further protected from stray light
by placing a cardboard tube from the slit to the prism P_1.
The tube had a hole in the bottom so that it could be slipped
over the lens L_1. The open end at P_1 and the space between
P_1 and the reflector were carefully covered with black velvet.
Another piece of black velvet was used to cover the top of
the Raman tube and condenser. With these precautions no
light could be seen through the spectrograph when the Raman

tube was empty. When the tube was filled, the mercury arc lines were just visible. The lines seen were probably due to scattering by the liquid rather than reflection.

The mercury arc was supported on a separate stand and brought into adjustment at the focus of the reflector each time a new spectrogram was taken. A separate stand was used so that the weight of the arc and the impact of the mercury falling through the arc during operation would not disturb the adjustment of the Raman tube and prism. A removable panel in the back of the reflector allowed the arc to be removed for starting.

Light from an iron arc for a reference spectrum was scattered down through the condenser C and sent into the spectrograph by the prism P_1. This was accomplished by placing the arc on a shelf above and to one side of the reflector and clamping a piece of opalescent glass at an angle of 45° directly above C. This arrangement was used so that the reference spectrum could be obtained on each plate without disturbing any adjustments of the apparatus.

Plates Used

Eastman type II-O, III-O, II-J and III-J plates were used at various times. The J plates have a maximum sensitivity at 5100 Å, while the O plates are most sensitive between

4000 and 4600 Å. Since the lines due to the carbon-mercury bond fall below 4600 Å, the O plates were most satisfactory for showing these lines. The type II plates were much faster than the type III, but were so grainy that accurate measurement of the lines on them was difficult. Furthermore, scattered light from the arc and the slight fluorescence of some of the solutions produced considerable continuous background on these plates. This background had a tendency to mask weak Raman lines. It also made intensity estimates rather indefinite except for the strongest lines observed. In spite of the longer exposures necessary the type III-O plates were the most satisfactory.

The exposed plates were developed for seven and one-half minutes in Eastman D-19 developer at 18° C. The plates were then fixed in Eastman F-5 fixer for 10-15 minutes and washed in running water for at least one hour.

The Compounds Investigated

With the exception of dibenzylmercury and mercuric chloride, the compounds used were furnished by Dr. I.B. Johns. C.P. mercuric chloride was used. The dibenzylmercury was synthesized by the method of Jones and Werner (15).

The solid compounds were all recrystallized just before use from the solvent to be used when taking the Raman spectrum.

The liquid compounds were redistilled twice under reduced
pressure immediately before use.

Taking the Spectrograms

Before taking each spectrogram the alignment of the
apparatus was checked. The flow of liquid through the con-
denser was adjusted and its temperature regulated. The Ra-
man tube containing the solution or liquid was allowed to
stand in place for 30 minutes. This procedure allowed any
convection or eddy currents to die out and gave sufficient
time for the tube to come to constant temperature. All so-
lutions were prepared and filtered three times through
No. 50 Whatman filter paper immediately before use. The
filter paper, funnel, and Raman tube had been washed thor-
oughly with the solvent to eliminate any foreign materials
or loose particles of filter paper. The removal of suspended
solid particles was absolutely essential in order to reduce
the continuous background to a minimum.

The arc was started and allowed to run for 30 minutes
before starting to take a spectrogram. The exposure time
varied considerably depending on the concentration and nature
of the compound being investigated. The type of plate em-
ployed was also taken into consideration in determining the
exposure time. After each exposure the Raman tube was re-
moved, the length of the slit reduced, and an iron reference

spectrum taken across the middle of the Raman spectrum.
Several plates were taken for each compound and the best
ones selected for measurement.

Measurement of the Plates*

The Raman "shifts" were obtained by first calculating
the actual frequency and subtracting this from the frequency
of the exciting line. The actual frequencies were determined
from the position of the Raman line on the plate relative to
two standard iron lines. The actual frequencies could not be
obtained directly by linear interpolation because the dis-
persion was not quite linear. The deviation from a linear
relationship was determined by measuring the iron spectrum.
These deviations were plotted against frequencies obtained
by linear interpolation. The corrections to be applied to
the calculated frequencies of the Raman lines were read di-
rectly from this graph.

Table VI shows the data necessary for the construction
of the correction curve. The wave-lengths for the iron
lines measured are listed in column 1. Column 2 shows the
position on the plate measured in millimeters. The fre-
quencies (in vacuum) in the third column were obtained from
a table (16) which converted the wave-lenths (Angstroms) in
air into frequencies in cm.$^{-1}$ in vacuum. The calculated

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*The method described was suggested by Dr. F.H. Spedding.

Table VI. Data for the correction curve used in calculating
frequencies.

λ air	Position (mm.)	ν vac.	ν calc.	Correction
4271.8	110.132	23402.9	23402.9	
4382.4	.215	23345	23333	12
4307.9	.404	23207	23172	35
4315.1	.451	23168	23133	35
4325.8	.527	23111	23068	43
4383.3	.918	22806	23737	69
4404.8	111.058	22696	23618	78
4415.1	.128	22643	23559	84
4494.6	.623	22243	23139	104
4528.6	.827	22076	23966	110
4592.7	112.193	21768	21656	112
4603.0	.246	21719	21611	108
4667.5	.595	21419	21315	104
4678.9	.648	21367	21270	97
4691.4	.715	21310	21213	107
4707.3	.803	21238	21139	99
4736.8	.944	21106	21019	87
4789.6	113.193	20873	20808	65
4859.8	.523	20572	20528	44
4872.0	.579	20521	20481	40
4891.0	.664	20439	20409	30
4903.3	.713	20387	20367	20
4939.7	.865	20239.6	20238.6	0

frequencies of column 4 were obtained by linear interpolation between the iron lines: λ, 4271.8 and λ, 4939.7 Å. The interpolated frequencies were calculated on a Monroe calculator. Assuming linear dispersion, the wave numbers per millimeter were found according to the following formula.

$$\frac{\text{frequency (cm.}^{-1}\text{) of 4271.8 - frequency (cm.}^{-1}\text{) of 4939.7 Å}}{\text{position (mm.) of 4271.8 - position (mm.) of 4939.7 Å}} = \frac{\text{cm.}^{-1}}{\text{mm.}}$$

$$\frac{23402.9 - 20239.6}{113.865 - 110.132} = 847.6560 \text{ cm.}^{-1} \text{ per mm.}$$

The calculator was set to divide. Then 23402.9, the frequency of the 4271.8 Å line, was set on the lower left hand dial of the calculator, and 110.132, the position of this line, was set on the upper right hand dial. The dispersion, 847.6560, was set on the board in such a position that when the reading on the upper right hand dial was increased one mm., 847.656 cm.$^{-1}$ were subtracted from the reading on the lower left hand dial. The operation then consisted in moving the carriage to the proper position and depressing the plus or minus bar until the upper right hand dial read the position of the line whose frequency was being calculated. The lower left hand dial then gave the calculated frequency of the line. The difference between this calculated frequency and the actual frequency gave the correction which had to be applied to give the correct frequency. These corrections are listed

in column 5 of Table VI.

Measurements on several plates of the same type proved that, within the limits of accuracy obtained, the dispersion and corrections did not vary from one plate to another. Therefore, the average corrections determined from three plates were plotted against the calculated wave numbers. Such a graph is shown in Figure IX. The curve actually used was plotted to a much larger scale.

To determine the Raman frequencies the position of the lines on the plate were measured and the frequencies calculated by linear interpolation as for the iron lines. The 4271.8 iron line was always used as a starting point in setting the calculator. This line was easily located and rather sharp so that it could be measured accurately. After calculating the frequency of a Raman line the correction as read from Figure IX was applied to give the correct frequency of the line in wave numbers. The difference between this value and 22938, the frequency of the mercury 4358 $\overset{o}{A}$ line used for excitation, gave the Raman "shift" or frequency.

Type III-J plates were used in constructing the correction curve. Measurements on several type II-O plates showed that the corrections were not quite the same for these plates. Since the II-O plates were not sensitive above 4600 $\overset{o}{A}$, there were not enough iron lines in the region investigated to give a complete correction curve. Therefore, the
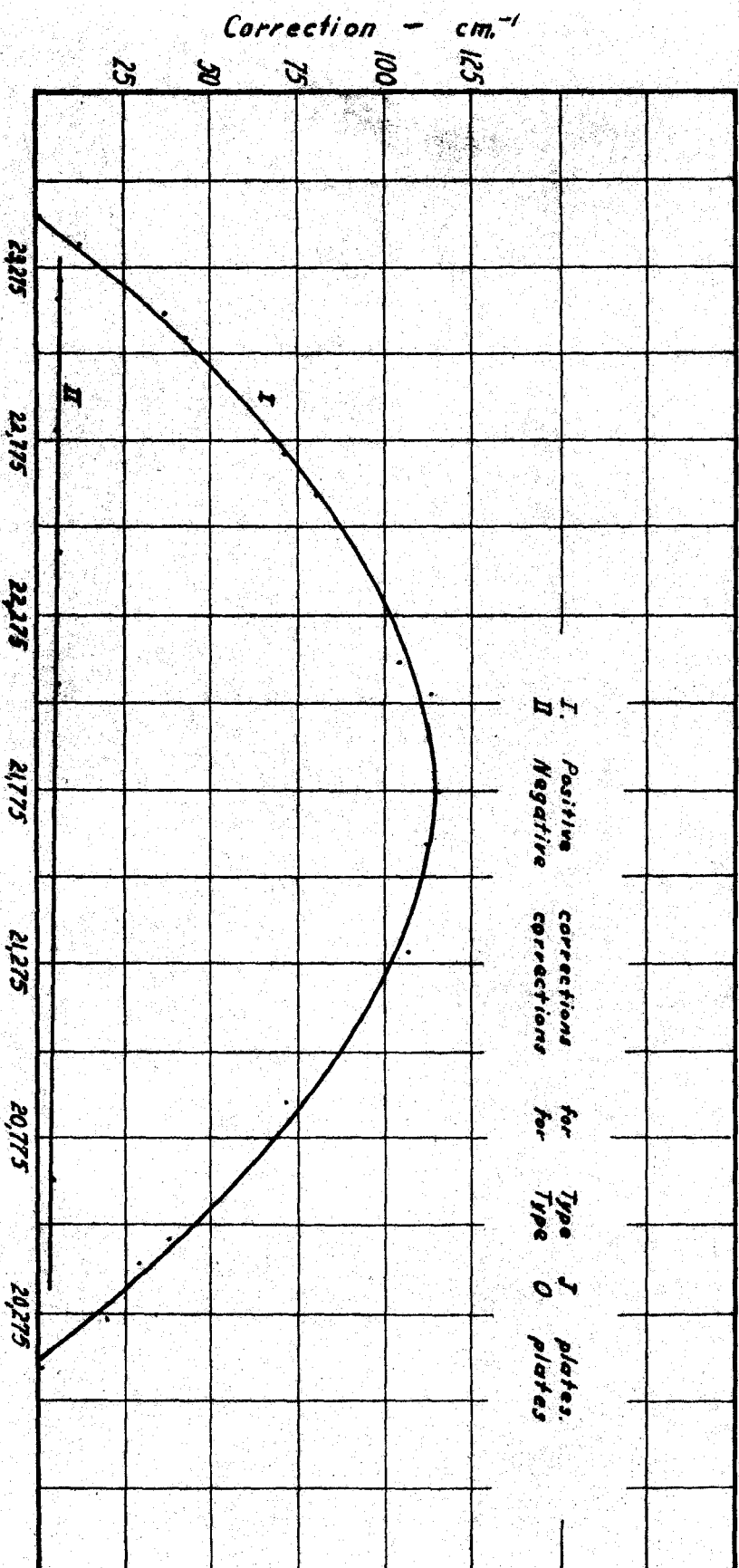
Figure II. Corrections for non-linear dispersion.

frequencies of all the iron lines present were calculated just as for the type III-J plates. The difference between these calculated values and the actual frequencies were plotted against the calculated values. This curve gave a second correction to be applied when a type II-O plate was used. This second correction curve is shown in Figure IX. The fact that the Raman frequencies found for the solvents check those reported in the literature shows that this method is adequate.

A consideration of the dispersion and accuracy of the measuring instrument indicated that the limit of accuracy to be expected was about three or four wave numbers. However, in cases where the lines were weak or where there was considerable general blackening of the plate, the accuracy was considerably less than this value. Since the lines due to the carbon-mercury bond are strong, the exact location of all weak lines was not attempted. No measurements were made in the region near 3000 cm.$^{-1}$ where the Raman lines due to the carbon-hydrogen bond are located.

The Spectrograms and Data

Diethylmercury

1. The pure compound.

Type of plate	III-J
Filter	Noviol A and lacquered tube
Exposure	Six hours
Enlargement of spectrogram	

Lines observed   140, 212, 264 (3),

487 (10), 662, band 1350-1370, band 940-1050,

1002 (3), 1178 (9), 1469 (2). The numbers in

parenthesis are estimated intensities. If no

estimates are indicated, the lines were either

very weak or the continuous background on the

plate made intensity estimates impossible.

The enlargement is seven times as long as the

actual spectrogram.

Pai (31) has reported the following lines in ad-

dition to those listed here: 562 (0), 958 (1),

1055 (2), 1370 (1), 1421 (2), 2857 (1), 2896 (3),

2992 (1). The last three of these are in a region

not investigated in the present work.

2. Solution in carbon tetrachloride.

Type of plate	III-J
Filter	Noviol A, lacquered tube
Concentration	0.3 mol fraction diethyl-mercury
Exposure	20 hours

Enlargement of
spectrogram

Lines observed   480 (9), 999 (1) 1177

(5), 1448. There was considerable general

blackening in the region above 1350 so that

the value 1448 is probably not very accurate.

3. Solution in acetone.

Type of plate   III-J

Filter   Noviol A, lacquered tube

Concentration   0.13 mol fraction di-
                                  ethylmercury

Exposure   20 hours

Enlargement of
spectrogram

Lines observed   136, 204, 265?, 320,

    483 (5), 1172 (1), 1469.

Di-n-propylmercury

    1. The pure compound.

Type of plate   III-J

Filter   Noviol A, lacquered tube

Exposure   Nine hours

Enlargement of
spectrogram

Lines observed   276 (3), 381 (3), 501

    (10), 585 (4), 791 (0), 863 (1), 1016 (2),

    1048 (2), 1158 (10), 1267 (00), 1326 (00),

    1446 (2).

2. Solution in carbon tetrachloride.

Type of plate	III-J
Filter	Noviol A, lacquered tube
Concentration	0.33 mol fraction di-n-propylmercury
Exposure	37 hours
Enlargement of spectrogram	

Lines observed   171, 384 (2), 501 (3),
590 (2), 1006, 1059, 1160. No lines above
$\Delta \nu = 1200$ could be measured on this plate be-
cause of general blackening. Decomposition
of the compound in solution was rather no-
ticeable.

Dibenzylmercury

1. Solution in carbon tetrachloride.

Type of plate	II-O
Filter	Noviol A, Corning 585, $CuSO_4$
Concentration	0.01 mol fraction di-benzylmercury
Temperature	40° C.
Exposure	20 hours
Enlargement of spectrogram	
Lines observed	560 (3), 638, 996 (2),

1085 (4), 1205.

2. Solution in acetone.

Type of plate	II-O
Filter	Noviol A, Corning No. 585, $CuSO_4$
Concentration	0.01 mol fraction
Temperature	40° C.
Exposure	20 hours
Enlargement of spectrogram	
Lines observed	175 (1), 260, 325, 560

(4), 638, 690, 810, 997 (1), 1080 (2), 1153,

1203 (1).

A great deal of difficulty was encountered due to the decomposition of the dibenzylmercury. In spite of all precautions the spectrograms were badly fogged and very difficult to measure. Intensity estimates other than weak or strong could not be made. In this case, as was generally true, the plates obtained for the acetone solution were so black between 4650 and 4916 Å that only very strong lines could be found in that region. The lower limit of this region corresponds to a Raman frequency of about 1450 cm.$^{-1}$. The light responsible for this darkening of the plate came from the mercury arc and was scattered into the spectrograph by the finely divided mercury which precipitated from the compound.

The reactive nature of dibenzylmercury was shown by an attempt to obtain its spectrum in carbon disulfide. After an exposure of only a few hours at room temperature the bottom of the Raman·tube was covered with a yellowish black sludge. The nature of this material was not investigated, but its yellow color indicated that it was not entirely mercury. Therefore, a reaction must have taken place between the carbon disulfide and the dibenzylmercury. Under similar conditions carbon disulfide alone showed no decomposition.

Diphenylmercury

1. Solution in carbon tetrachloride.

Type of plate	III-J
Filter	Noviol A, $CuSO_4$, $CoSO_4$
Concentration	Saturated at 40° C.
Temperature	40° C.
Exposure	Six hours
Enlargement of spectrogram	
Lines observed	·152 (2), 340, 382, 555

(4), 580, 619, 652 (3), 700, 997 (4), 1060, 1185, 1162, 1262, 1370.

The diphenylmercury was very stable in carbon tetrachloride. Donzelot and Chaix (7) have obtained the Raman spectrum of this compound in the molten state and report the

following lines: 158, 210, 650, 704, 998, 1024, 1574, 3049.

Kohlrausch (20) recently reported an investigation of diphenylmercury in chloroform. The lines reported were: 148 (5), 208 (5), 998 (4), 1570 (1).

The line found by these authors at $\Delta\nu$ 210 could not be confirmed because a carbon tetrachloride line falls at 217. The spectrograph would not resolve two lines so close together. Since the carbon tetrachloride lines were over-exposed, intensity estimates on the line at 217 would not show a close additional line due to the solvent.

Mercuric cyanide

Numerous attempts to obtain the spectrum of mercuric cyanide in carbon tetrachloride and acetone yielded only one line at 2200 cm.$^{-1}$. This line is due to the $C\equiv N$ bond and has been reported by several authors. Woodward (38) found 2195 cm.$^{-1}$ for the water solution. Krishnamurti (26) reported 2192 cm.$^{-1}$ for the crystalline mercuric cyanide. He also found a very weak line at 276 cm.$^{-1}$.

Enlargement of
spectrogram

Mercuric chloride

1. Solution in acetone.

Type of plate	II-O
Filter	Noviol A, Corning No. 585, CuSO$_4$
Concentration	Saturated at 40° C.
Temperature	40° C.
Exposure	7.5 hours
Enlargement of spectrogram	
Lines observed	321 (8)

This result is in agreement with that of Woodward (38) who found 320 cm.$^{-1}$ for a water solution of mercuric chloride.

The acetone solution was slightly yellow after the exposure but no mercury was precipitated.

Di-p-tolylmercury

Di-p-tolylmercury was so insoluble that no spectrum could be obtained. Numerous attempts gave only negative results. One plate showed a weak unresolved band between 1420 and 1571 cm.$^{-1}$. This spectrogram was taken of the saturated solution in carbon tetrachloride at 40° C. The compound showed no signs of decomposition. A very clear spectrogram was obtained on a type III-J plate after an 80 hour exposure, but no lines due to the di-p-tolylmercury could be found.

Enlargement of
spectrogram

Di-alpha-naphthylmercury

This compound was also too insoluble in any solvent to yield results.

Compilation of Data

Table VII contains the frequencies observed for the compounds investigated. No separation on the basis of the solvent used has been made because any variations due to the solvent were less than the experimental error in measuring the frequencies. This is in agreement with the work of West and Arthur (36). These investigators studied the effect of nonionizing solvents on the Raman frequencies of HCl, HBr, and SO_2. The maximum value for $\frac{\Delta \nu}{\nu}$ was 0.03, which was attained only with a solvent having a dielectric constant 14.

Figure X is a graphical representation of the data in Table VII. This diagram shows only lines below $\Delta \nu$ 1300 cm.$^{-1}$ The height of the lines represents approximately the relative intensities estimated visually. The lines shown for dimethylmercury are those reported by Pai (31).

Table VII. Frequencies of a series of organomercury compounds, R_2Hg.

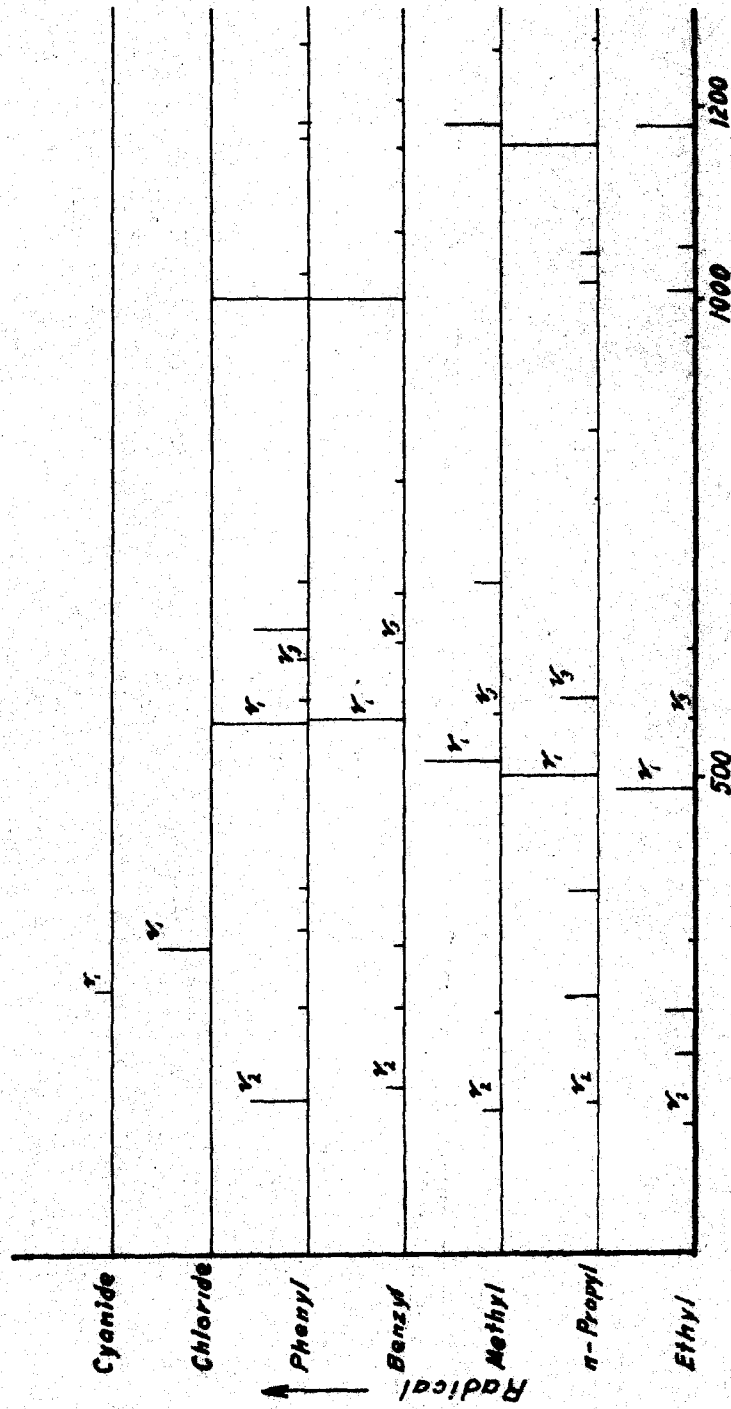| Propyl	Ethyl	Methyl	Benzyl	Phenyl	Chloride	Cyanide
171 (0)	140 (1)	152 (2)	175 (m)	152 (5)	321 (5)	276 (w)
276 (3)	212 (2)	255 (0)	260	340		
381 (3)	264 (3)	515 (8)	325	382		
501(10)	329 (0)	565 (1)	560 (5)	555 (s)		
585 (4)	486 (8)	700 (3)	638	580		
791 (0)	562 (0)	1182 (6)	690	619		
863 (1)	633 (0)	1258 (1)	810	652 (s)		
1016 (2)	958 (1)		996 (s)	700		
1084 (2)	1008 (3)		1070	997 (s)		
1158(10)	1055 (2)		1153	1060		
1267(00)	1178 (6)		1205	1185		
1326(00)	1370 (1)			1262		
1446 (2)	1421 (3)			1370		
	1455 (3)					

Figure I. Diagram of Raman spectra of R_2Hg compounds.

DISCUSSION AND CONCLUSIONS

Selection of Fundamental Frequencies

Thompson and Linnet (35) have shown rather conclusively that the fundamental frequencies of dimethylmercury are: ν_1 , 515; ν_2 , 156; and ν_3 , 565. The symmetrical frequency ν_1 is very strong and lies in a region of the spectrum free from other lines. As may be seen from Figure X WKP, a strong line near 500 cm.$^{-1}$ was observed for each compound. This frequency has been designated ν_1 .

Equation (5) indicates that the ratio of ν_3 to ν_1 should be fairly constant. Values for $\sqrt{\dfrac{2m+M}{M}}$ in Table VIII vary from 1.38 to 1.06. The frequencies marked ν_3 in Figure X are those which seem the most probable as indicated by the mass ratio. Diphenylmercury is the only case offering two possibilities for ν_3 . The value at 652 cm.$^{-1}$ was chosen since 580 cm.$^{-1}$ gave an unreasonable value for the force constant.

The lowest frequency observed in each case was designated as ν_2 . The frequencies in this region are undoubtedly associated with the mercury atom, since no frequencies are observed in this region in other compounds containing the radicals.

Radical	m*	ν_1	ν_2	ν_3	$k_s \times 10^{-5}$ (6)	$k_t \times 10^{-5}$ (7)	$k_i \times 10^{-5}$ (4)	$k_\delta \times 10^{-5}$ (9)	$k_\alpha \times 10^{-5}$ (8)	ν_3/ν_1	$\sqrt{\dfrac{2m+M}{M}}$
Propyl	a	501	171	585	5.4	6.3	6.1	0.27	0.28	1.17	1.20
	b					2.1	2.5	0.09	0.12		1.07
Ethyl	a	186	140	562	4.7	4.1	4.3	0.13	0.13	1.16	1.14
	b					2.0	2.3	0.06	0.07		1.07
Methyl	a	515	156	565	3.2	2.4	2.5	0.09	0.09	1.10	1.072
	b							0.01	0.09		1.07
Benzyl	a	560	175	638	5.5	16.7	11.4	0.63	0.42	1.14	1.38
	b					2.6	2.9	0.10	0.11		1.07
Phenyl	a	555	152	652	6.9	13.9	10.9	0.38	0.30	1.19	1.33
	b					2.2	2.7	0.06	0.07		1.06
Chloride	a	321				2.2					1.16
	b										
Cyanide	a	276				1.2					1.12
	b										

*a, m = radical; b, m = CH₂

Table VIII. Fundamental frequencies and force constants for R₂Hg compounds.

Calculation of Force Constants

Table VIII shows the values for the force constants cal-
culated using the equations on p. 23. The values obtained for
k_1 from equation (6) represent the restoring force acting on
the vibrating group. If the radical vibrates as a unit, k_1
represents the force constant for the carbon-mercury bond.
However, if only the CH_2 group attached directly to the mer-
cury atom vibrates, k_1 represents the force constant for the
carbon-mercury bond plus the fraction of the force constant
for the adjacent carbon-carbon bond which is effective in re-
straining the CH_2 group.

A consideration of the last two columns in Table VIII
gives an indication of the type of vibration being executed.
In the aliphatic compounds the radical seems to be vibrating
almost as a unit because when the mass of the radical is sub-
stituted into the right-hand side of equation (5) the result
is more nearly in agreement with the ratio of ν_3 to ν_1 than
when the mass of the CH_2 group is used. The values of the
force constants calculated from equations (4) and (7) are also
in better agreement with those from equation (6) when the mass
of the radical as a whole is used. The same reasoning shows
that in the benzyl and phenyl compounds the radical does not
vibrate as a unit. The vibration seems almost entirely lim-
ited to the CH_2 group in dibenzylmercury.

The rather high value for k_1 of diphenylmercury using equation (6) is about half-way between the values for k_1 using equation (7) when the mass is taken as the whole group and when the mass is taken as a carbon atom. This can be explained by the fact that two adjacent carbon-carbon bonds contribute to the restraining force represented by this constant. A study of the Raman spectra of di-iso-propylmercury should show whether or not this effect is peculiar to the benzene ring. The values of k_1 for mercuric chloride and mercuric cyanide are rather small as is usually the case when the bond is nearly of the ionic type.

The small values for the bending constants indicate that the aliphatic R_2Hg compounds are very flexible. k_α for diphenyl- and dibenzylmercury is about $0.4 - 0.5 \times 10^{-5}$, which is about the same as the value for k_α for the carbon-carbon bond. k_α for the carbon-carbon bond is usually about 0.54×10^{-5} (23). Therefore, diphenyl- and dibenzylmercury are more rigid molecules than the other compounds investigated.

<div align="center">

Comparison of Force Constants, Stability,

and Refraction Data

</div>

Figure XI shows k_1, k_α, and ν plotted against the electron sharing ability of the radicals. The k_1 curve which is plotted to a proportionally larger scale than the other curves indicates that the placing, on the abscissae, of the
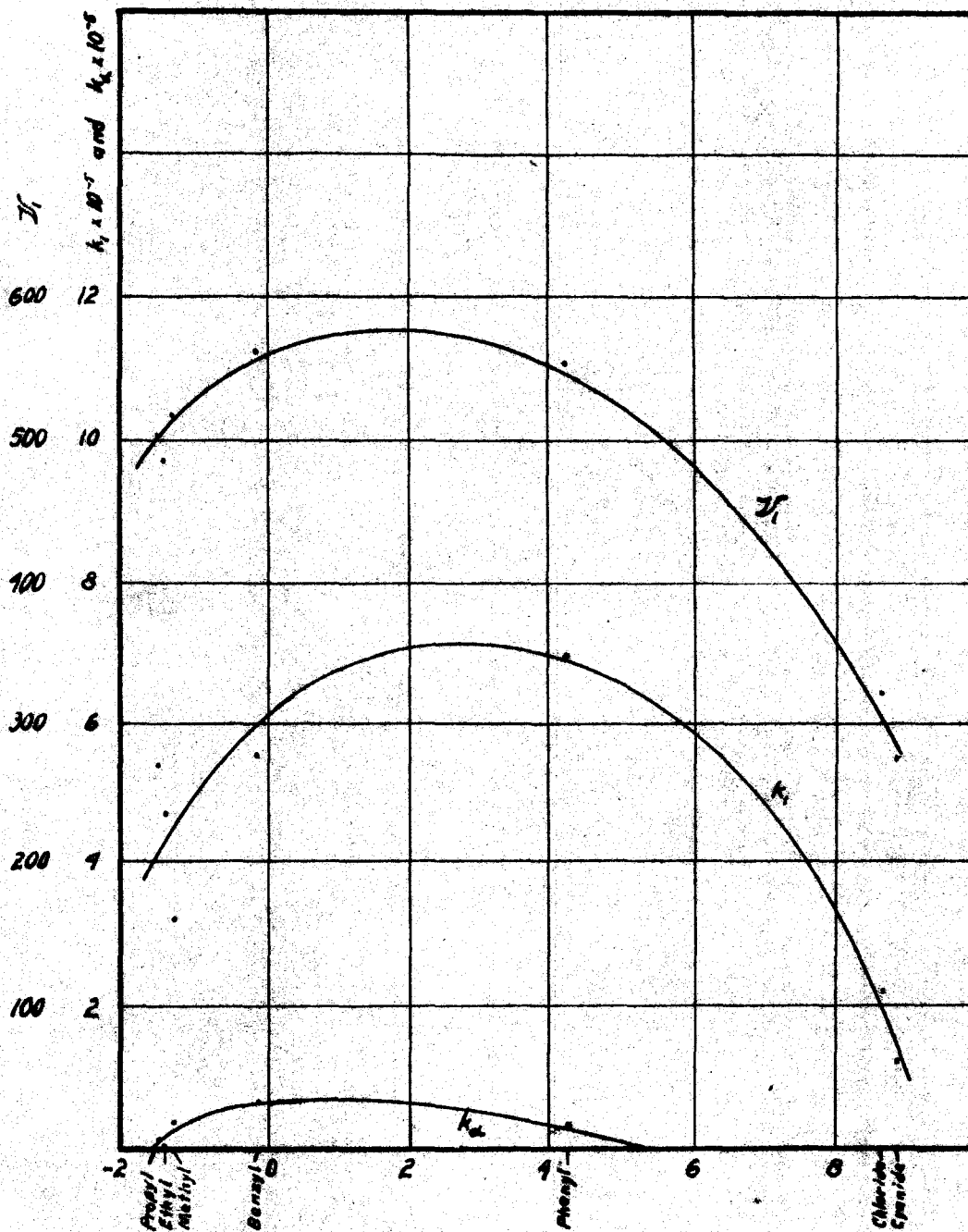
Figure II. Relation between k_1, k_a, and ν_1 and the electron sharing ability.

methyl, ethyl and propyl radicals may not be quite correct. These were originally placed by Johns and Hixon (10) from values of the dissociation constants of the amines, RNH_2. The dissociation constants of the aliphatic amines were so close together that the placing of these radicals on this basis may have been uncertain. The order indicated by the force constants is methyl, ethyl, propyl. However, the frequencies ν are in the order ethyl, propyl, methyl. The question arises then as to which constant should be used to place the radicals. However, as was explained on page 13, this question cannot be answered at the present time.

The curves of Figure XI are very similar in shape to those obtained by Carr (4) for the atomic refraction of mercury in R_2Hg and RHgCN compounds. These curves are shown in Figure XII. Figure XII also shows the variations in thermal stability of the organomercury compounds. The abscissae values for the minimum for each thermal stability curve coincides with that of the maximum for the corresponding refractivity curve. The curves of Figure XI all exhibit a maximum at this same point. A consideration of the refraction and thermal stability curves shows that when the mercury atom in the molecule has its electrons under about the same constraint as in mercury vapor, the compound is unstable toward heat. That the compound having the lowest decomposition temerature does not have the lowest force constant may be sur-
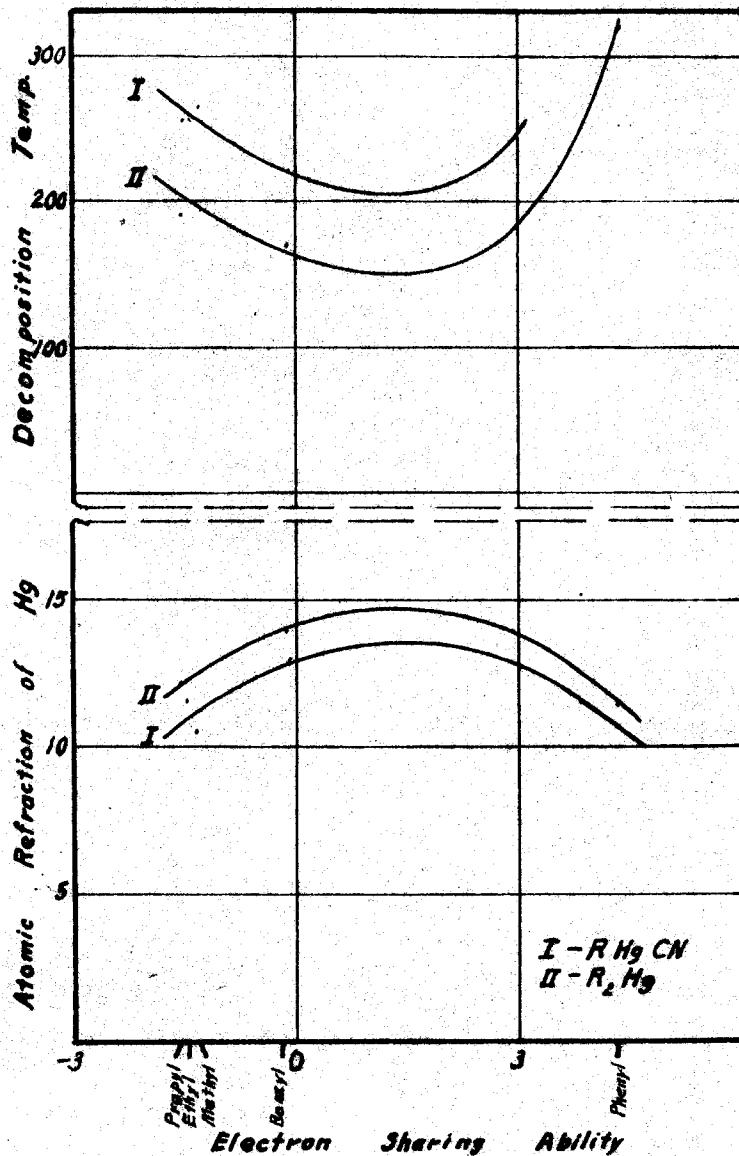
Figure XII. Relation between electron sharing ability and decomposition and refraction data.

prising. However, the constants calculated according to equation (6) contain a contribution due to the neighboring carbon-carbon bond. The exact magnitude of this effect cannot be calculated at the present time.

Another point to be considered is the nature or mechanism of the dissociation by heat. Two mechanisms may be considered. The molecule might dissociate from its ground electronic state by passing to a higher vibrational level. In this case there might be a direct relationship between the force constant and the decomposition temperature. On the other hand, the molecule might first absorb energy enough to pass into a higher electronic state before dissociation. In this case there should be no correlation between the decomposition temperature and the Raman frequencies or force constants. Raman spectra studies give information concerning only the ground electronic level. Ultra violet absorption studies should prove helpful in explaining the mechanism of the thermal dissociation of these compounds.

Figure XIII is a graph in which the refraction of the mercury in RHgCN compounds is plotted against the force constants calculated from R_2Hg compounds.

With the exception of dibenzylmercury the points fall on a smooth curve which appears to be a parabola. The equation for such a curve would be of the form $(y-a)^2 = bx + c$, where y is the force constant, x the atomic refraction of the

mercury, and a, b, and c are constants. The a of this e-
quation might be the contribution to k_1 of the adjacent car-
bon-carbon bond. The molecular refraction would then be a
linear function of the square of the force constant. The
molecular refraction is known to depend upon the polariza-
bility of the molecule (33). Whether any relationship exists
between the force constant and polarizability is not known.
Complete refraction and Raman spectra studies on a series of
compounds in which the force constants could be accurately
determined should help to clarify this point.

Figure XIII. Relation between force constants and
refraction in organo-mercury compounds.
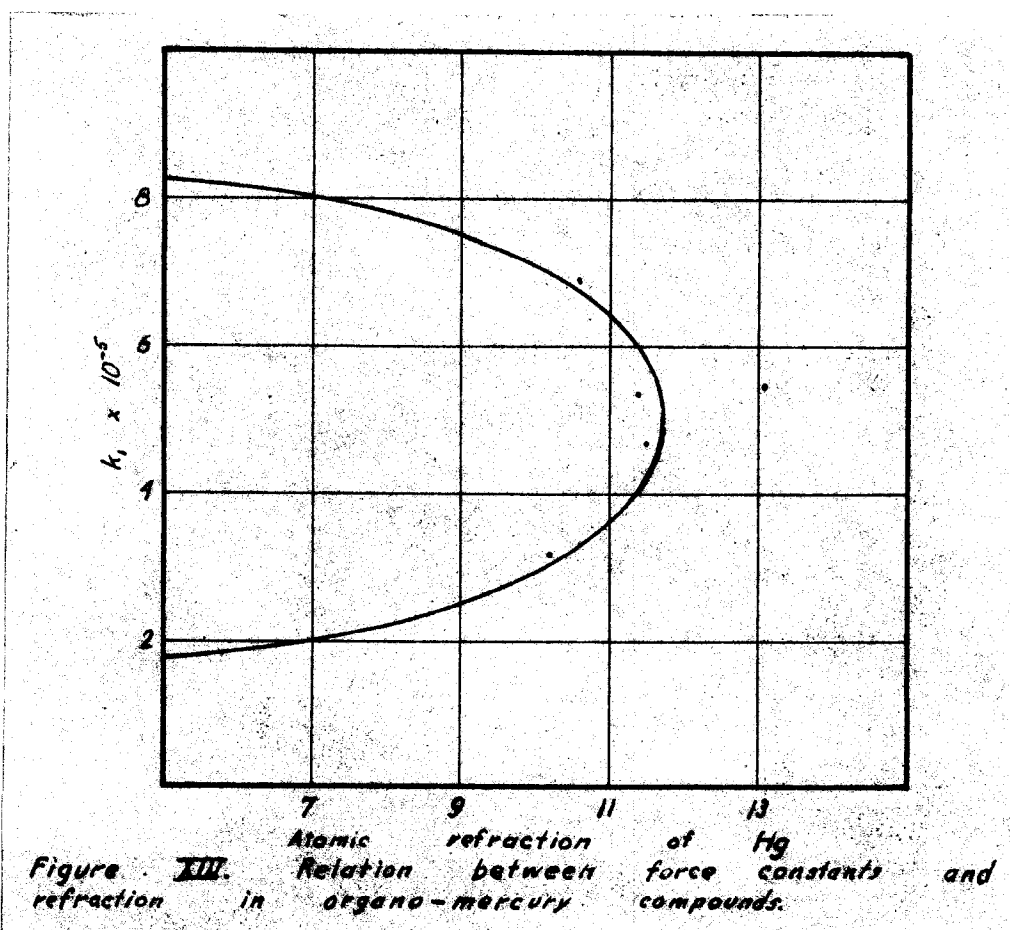
Variations in the Frequencies Due to
Vibrations within the Radicals

Information concerning the nature of the carbon-mercury bond can also be obtained from a consideration of the frequencies due to the radicals attached to the mercury atom. The strong line near 1180 cm.$^{-1}$ in aliphatic compounds is due to the carbon-hydrogen bond. In compounds containing no neavy element this frequency falls near 1450 cm.$^{-1}$. As the molecule becomes more complex or when heavy elements are added, this frequency tends to shift to a different value. Some compounds exhibit several lines in this region. The splitting and shifting of the components of this line or energy level should depend upon the strength of the coupling and the mass of the group added. In the saturated hydrocarbon series one line is noticed around 1450 cm.$^{-1}$ up to hexane. In the spectrum of hexane this line appears to be split into three lines: 1148, 1313, 1455, which have been reported (24). About the same splitting is observed for ethyl alcohol. Lines at 1273 and 1456 cm.$^{-1}$ have been reported for this compound (24). For ethyl iodide the lines reported are 1194 and 1430 (24).

The lower limit of the splitting at 1158 cm.$^{-1}$ for the aliphatic organomercury compounds indicates a rather loose binding between the carbon and mercury. Considering the large mass of the mercury atom this is not a large displacement.

Comparison with the shift for the iodides suggests that the carbon-mercury bond is weaker than the carbon-iodine bond. Since this frequency is almost constant in all the aliphatic organomercury compounds, the strength of the bond must not vary greatly.

SUMMARY

1. Theoretical considerations have been made which show that Raman spectra studies should be of aid in elucidating the nature of the electron sharing ability of organic radicals.

2. Apparatus and experimental procedure for observing Raman spectra have been described.

3. The Raman spectra of diethylmercury, di-n-propylmercury, dibenzylmercury, diphenylmercury, mercuric chloride and mercuric cyanide have been observed.

4. The fundamental frequencies of the R_2Hg compounds have been used to calculate force constants for the vibrating groups.

5. The frequencies due to the vibrations within the radicals have been compared with those observed for the radicals in other compounds.

6. The information obtained from the Raman spectra of the R_2Hg compounds has been compared with that obtained from thermal stability and refraction studies.

7. The following conclusions have been made:

    a. The radicals in the aliphatic compounds vibrate almost as units.

b. The radicals do not vibrate as units in the aromatic compounds.

c. The force constants place the radicals in the order methyl, ethyl, propyl, benzyl, phenyl, chloride, cyanide.

d. The aliphatic R_2Hg compounds are very flexible while the aromatic compounds are very rigid.

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