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The Infra-Red and Raman Spectra of Dimethyl Mercury and Dimethyl Zinc*

H. S. GUTOWSKY**

Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts

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The infra-red spectra of dimethyl mercury and dimethyl zinc and the Raman spectrum of dimethyl mercury have been observed. A frequency assignment has been proposed for dimethyl mercury, and that of dimethyl zinc has been modified. The results support a linear C—M—C structure, in agreement with quantum-mechanical predictions, and also D_{3h} symmetry with essentially free rotation of the methyl groups. A normal coordinate analysis has been made of the fundamental frequencies and valence-type force constants deduced therefrom. The values of the force constants pertaining only to the methyl groups agree very well with values obtained in other molecules; others indicate the relatively easy deformability of the C—M—C figure axis. Differences between the dimethyl mercury and dimethyl zinc force constants indicate greater ionic character in the C—Zn bond. Values of 2.45 and 2.39×10^6 dynes/cm are obtained for the C—Hg and C—Zn stretching force constants. The relation of these values to current suggestions concerning the dependence of bond strengths on atomic parameters is briefly discussed.

INTRODUCTION

DIMETHYL zinc¹ and several of the Group IV tetramethyl derivatives² appear to be the only metal alkyls whose infra-red and Raman spectra have been investigated in detail and reasonably complete frequency assignments proposed. However, many of the various M—C force constants have not been calculated from these assignments, and in general there is a lack of quantitative physical data for the metallo-organic compounds. Difficulty of preparation and handling are probably the main deterrents to their study, but these may be overcome by the exercise of reasonable care.

Further data on the metal alkyls are of interest for several reasons. The co-relation of bond force constants with atomic parameters requires a wide range of data, and reliable results for various M—C bonds are useful in this connection.³ Quantum theory predicts certain bond hybridization in various cases, and structural determination from spectral data affords a check on the

theory in favorable instances. Also, the nature and distance dependence of the repulsive forces restricting rotation of groups of atoms about a chemical bond is a problem of fundamental importance. Available data on ethane and dimethyl acetylene might profitably be extended to intermediate linear compounds $\text{CH}_3\text{—M—CH}_3$. Accordingly, a detailed investigation of the infra-red and Raman spectra of dimethyl mercury and dimethyl zinc was undertaken.

Several investigations of the spectra of these compounds have been reported. Fehér, Kolb, and Leverenz⁴ give the results of two independent studies of the Raman spectra, including polarization measurements. They also discuss critically the earlier Raman data published by Pai⁵ and Venkateswaran.⁶ The infra-red spectrum of dimethyl zinc has been observed by Thompson, Linnett, and Wagstaffe,¹ who proposed a frequency assignment using the then available Raman data. They considered their results as most consistent with a linear C—Zn—C structure.

EXPERIMENTAL

1. Dimethyl Mercury

a. Preparation of sample. The dimethyl mercury used in these experiments was prepared by

* Based on a thesis submitted in partial fulfillment of the requirements for the Ph.D. degree at Harvard University. The research reported herein was facilitated by support extended Harvard University by the Navy Department, Office of Naval Research, under ONR Contract N5ori76.

** Present address: Department of Chemistry, University of Illinois, Urbana, Illinois.

¹ H. W. Thompson, J. W. Linnett, and F. J. Wagstaffe, *Trans. Faraday Soc.* **36**, 797 (1940).

² C. W. Young, J. S. Koehler, and D. S. McKinney, *J. Am. Chem. Soc.* **69**, 1410 (1947).

³ W. Gordy, *J. Chem. Phys.* **14**, 305 (1946).

⁴ F. Fehér, W. Kolb, and L. Leverenz, *Zeits. f. Naturforsch.* **2a**, 454 (1947).

⁵ N. G. Pai, *Proc. Roy. Soc. (London)* **A149**, 29 (1935).

⁶ S. Venkateswaran, *Ind. J. Phys.* **5**, 145 (1930).

the reaction between CH_3MgBr and HgCl_2 in ether solution.⁷ It was purified by redistillation over freshly precipitated Ag_2O . The product used had a boiling point range of 92.3 to 92.5°C at 772 mm.

b. Infra-red spectrum. Measurements were made on the gas in a 30-cm cell with KBr windows using the automatic prism spectrometer described by Gershinowitz and Wilson,⁸ subsequently modified.⁹ All spectral data were obtained at room temperature. Pressures of 4.7, 2.6, and 0.5 cm of the gas were used. Since the vapor pressure of dimethyl mercury is only 6.5 cm at room temperature, the absorption of the liquid was also measured, primarily to determine whether any bands were missing in the gas at the low pressures used. The liquid was run in a 0.13-mm NaCl cell on a Baird Associates infrared spectrophotometer.¹⁰ The absorption curves for gas and liquid are given in Figs. 1 and 2, respectively, and the band frequencies are summarized in Table I. The band at 1125 cm^{-1} in the liquid spectrum, 1135 cm^{-1} in the gas, appeared only in samples which had been exposed

to light for long periods of time and is attributed to an impurity formed by photo-chemical decomposition, perhaps $\text{CH}_3\text{—Hg—Hg—CH}_3$.¹¹ The calibration of the Harvard spectrometer was checked during the period of operation, and the data from it are probably accurate to $\pm 2 \text{ cm}^{-1}$ at wave-lengths below 2000 cm^{-1} and $\pm 5 \text{ cm}^{-1}$ above. For the Baird instrument, the calibration is well within the manufacturer's maximum tolerances of ± 0.02 micron, or $\pm 1.0 \text{ cm}^{-1}$ at 625 cm^{-1} and $\pm 15 \text{ cm}^{-1}$ at 3000 cm^{-1} .

c. The Raman spectrum. Since Pai's observations⁵ of the Raman spectrum do not include polarization data, and the author was unaware of Fehér's⁴ work at the time, it seemed advisable to re-examine the Raman spectrum and make polarization determinations. The spectrograph used¹² will be described in detail elsewhere at a later date. The dispersion is approximately 48.3A/mm in the region of the Hg 4358.3A line which was used as the exciting line in these experiments; shorter wave-lengths were eliminated with a Wratten 2A filter.

Polarization data were obtained by the use of

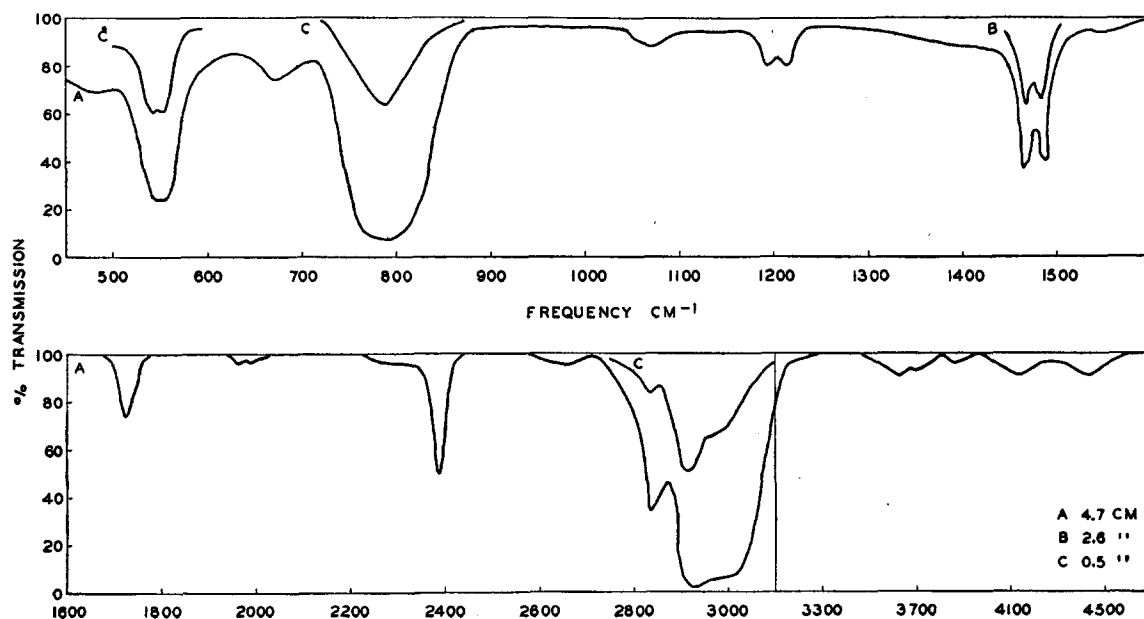


FIG. 1. Infra-red absorption spectrum of $\text{Hg}(\text{CH}_3)_2$ gas.

⁷ H. Gilman and R. E. Brown, *J. Am. Chem. Soc.* **52**, 3314 (1930).

⁸ H. Gershinowitz and E. B. Wilson, Jr., *J. Chem. Phys.* **6**, 197 (1938).

⁹ W. L. Hyde, 1948 Ph.D. thesis, Harvard University.

¹⁰ W. S. Baird, H. M. O'Bryan, G. Ogden, and D. Lee, *J. Opt. Soc. Am.* **37**, 754 (1947).

¹¹ F. O. Rice and B. L. Evering, *J. Am. Chem. Soc.* **56**, 2105 (1934).

¹² W. E. Brown, 1948 Ph.D. thesis, Harvard University.

TABLE I. The infra-red spectrum of $\text{Hg}(\text{CH}_3)_2$, gas and liquid.*

Gas ν cm^{-1}		Liquid ν cm^{-1}	
550	(8)		
675	(1)		
788	(9)	778	(10)
1070	(2a)	1050	(2)
		1125	(1) impurity
1205	(2a)	1190	(5)
1475	(6a)	1445	(8a)
1735	(3)	1720	(4)
1980	(0a)	1950	(1a)
2390	(5)		
2660	(0)		
2835	(6)	2885	(10) unresolved
2970	(10a) partially resolved		
3660	(1a)	3630	(2a)
3855	(0)	3840	(0)
4150	(1)	4140	(2)
4435	(1)	4400	(3)

* a, bimodal band; the cm^{-1} value is for the band center. The numbers after the band frequency are relative apparent intensities.

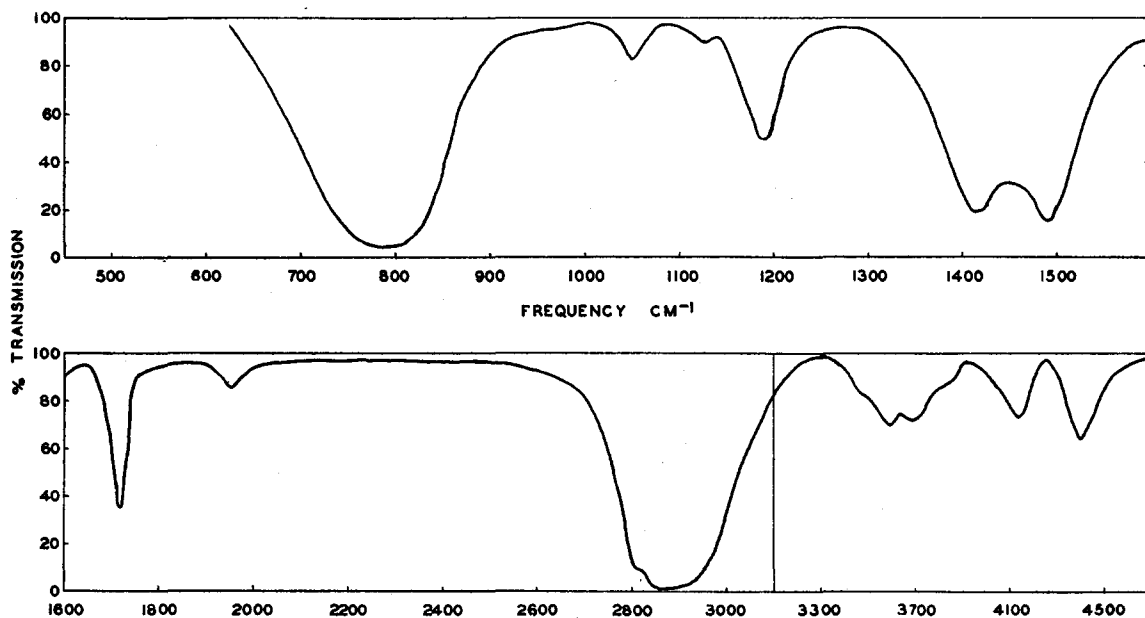
Polaroid, separate exposures being made with the plane of polarization parallel to and perpendicular to the axis of the Raman tube as suggested by Edsall and Wilson.¹³ Semiquantitative estimates of the degree of polarization were made by comparing microphotometer tracings of the \parallel and \perp exposures analogous to the method

described by Crawford and Horwitz.¹⁴ The various results are included in Table II.

2. Dimethyl Zinc

a. Preparation of sample. Two samples of $\text{Zn}(\text{CH}_3)_2$ were used. The first of these was prepared by heating $\text{Hg}(\text{CH}_3)_2$ with an excess of granular zinc in a sealed Pyrex tube at about 185°C for five days. The other sample was furnished through the kindness of Professor E. G. Rochow. It had been prepared by the reaction between zinc and methyl iodide.

b. Infra-red spectrum. The observed infra-red spectrum of the gas is given in Fig. 3, and the data are summarized in Table III, along with the results of Thompson, Linnett, and Wagstaffe.¹ The parts of the spectrum marked B were observed with the Harvard instrument at a gas pressure of 5 cm of mercury in a 30-cm cell with KBr windows. The region from 450 to 650 cm^{-1} was run with a KRS-5 prism in conjunction with a LiF mirror to reduce the amount of stray radiation. The region from 2700 to 3100 cm^{-1} was run with the CaF_2 prism on the Harvard instrument to obtain some resolution of the C-H stretching frequencies. The balance of the

FIG. 2. Infra-red absorption spectrum of $\text{Hg}(\text{CH}_3)_2$ liquid.

¹³ J. T. Edsall and E. B. Wilson, Jr., *J. Chem. Phys.* **6**, 124 (1938).

¹⁴ B. L. Crawford, Jr. and W. Horwitz, *J. Chem. Phys.* **15**, 268 (1947).

spectrum represents data from the Baird instrument on the gas at a pressure of 16 cm in a 5-cm NaCl cell.

The sample prepared from $\text{Hg}(\text{CH}_3)_2$ showed a very weak band at 1135 cm^{-1} which, however, was not present in the other sample, while the latter gave three additional bands readily attributable to CH_3I . The data herein presented are those from the " $\text{Hg}(\text{CH}_3)_2$ " sample, minus the 1135-cm^{-1} band, which presumably is from the same impurity mentioned in connection with the infra-red spectrum of dimethyl mercury. The 1450-cm^{-1} band is very weak, and the bands reported by TLW¹ at 1541, 1887, and 2105 cm^{-1} were not observed at all, perhaps because of a smaller effective absorbing path.

FREQUENCY ASSIGNMENTS

1. Introduction

There are two possible structures for the C-M-C skeleton, linear or bent, the latter having C_{2v} symmetry. For a linear model the methyl groups may be staggered, D_{3d} ; eclipsed, D_{3h} ; or there may be free rotation D_{3h}' . The modes of vibration and the selection rules for

TABLE II. The Raman spectrum of dimethyl mercury (*l*).*

Summary per FKL** $\Delta\nu\text{ cm}^{-1}$	This research $\Delta\nu\text{ cm}^{-1}$
156 (1)	grating ghost obscures
514 (20b, 0.23)	515 (8, 0.5)
700 (3b, 0.81)	700 (3, dp)
	786 (0)
1030 (0, 0.48)	
1181 (12, 0.37)	1184 (6, 0.4)
1258 (00) ?	1246 (0) ?
1392 (0, 0.65)	1402 (1)
1443 (0, 0.90)	
1706 (00, 0.77)	
2341 (0)	
2869 (1/2) } (0.21)	2869 (2d, dp)
2909 (6b) }	2910 (4, 0.1)
2965 (1b, 0.26 ?)	2969 (3b, dp)

* d, diffuse; b, broad; dp, depolarized; the numbers after $\Delta\nu$ are intensity and polarization, respectively.

** See reference 4.

these symmetries are available elsewhere;^{1,15} D_{3h} and D_{3h}' are governed by the same rules.¹⁶

It is apparent that the symmetry is probably not C_{2v} . Such a bent model allows 21 fundamentals, all of which are active in both infra-red and Raman, while Tables V and VI, which summarize the data and assignments, list only seven coincidences between the Raman and infra-red spectra among over fifty frequencies. This

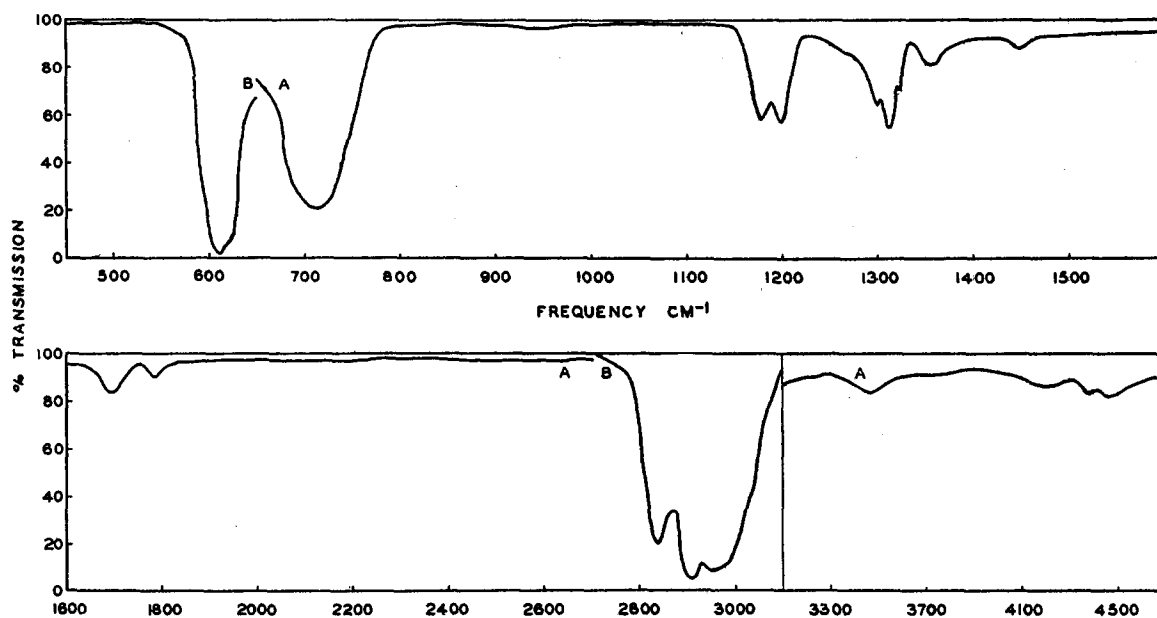


FIG. 3. Infra-red absorption spectrum of $\text{Zn}(\text{CH}_3)_2$ gas.

¹⁵ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).

¹⁶ J. B. Howard, J. Chem. Phys. 5, 442 (1937).

TABLE III. The infra-red spectrum of dimethyl zinc (g).*

TLW** ν cm ⁻¹	This research ν cm ⁻¹
617 (vs)	614 (10)
704 (vs)	710 (10)
1180 (s)	1190 (5a)
1305 (m)	1315 (5f)
1350 (w)	1358 (2)
1445 (vw)	1450 (0)
1541 (w)	
1692 (m)	1700 (2)
1789 (mw)	1785 (1)
1887 (vw)	
2105 (vw)	
	2840 (8c)
2924 (vs)	2935 (10a)
3450 (s)	3445 (2)
4167 (w)	4200 (1)
4386 (m)	4400 (2a)
5781 (w)	—

* a, bimodal; f, has 2 shoulders; c, shoulder; the numbers and other letters after the band frequency indicate relative apparent intensities.

** See reference 1.

conclusion is supported elsewhere,^{1,4,15} and therefore a linear model is assumed in all subsequent discussion.

Of the three linear configurations, the eclipsed D_{3h} form is eliminated by the generally accepted nature of the physical interactions restricting rotation. The D_{3d} symmetry differs from the D_{3h} , the selection rules and vibrational modes for which are given in Table IX, in not allowing the E' fundamentals to be Raman active. The coincidences between Raman and infra-red spectra ascribed to ν_8 and ν_{10} for dimethyl mercury and ν_8 , ν_9 , and ν_{10} for dimethyl zinc as well as the appearance of the very low Raman frequencies at about 150 cm⁻¹, which seem assignable only as ν_{11} , favor the D_{3h} model. The rules governing the species of combination bands for this symmetry (also D_{3h}) are given in Table IV.

2. Frequency Assignment for Dimethyl Mercury

Considering first the fundamental frequencies, the polarized Raman lines at 2910, 1182, and 515 cm⁻¹ can be only the A_1' vibrations. The

TABLE IV. Combination table for D_{3h} symmetry.

A_1'	A_1''	A_2'	A_2''	E'	E''
A_1''	A_1'	A_2''	A_2'	E''	E'
A_2'		A_1'	A_1''	E'	E''
A_2''			A_1'	E''	E'
E'				$A_1''+A_2'+E'$	$A_1''+A_2''+E''$
E''					$A_1'+A_2'+E'$

high intensity and sharpness of these bands are in keeping with this assignment. The designation of the frequencies as ν_1 , ν_2 , and ν_3 , respectively, is unambiguous, since the values for ν_1 and ν_2 are typical of the methyl group and ν_3 is in the range expected for the skeletal stretching.

The coincidence in Raman and infra-red frequencies at 2966 cm⁻¹ is readily assigned as the E' C—H stretching ν_8 , excluding Fehér's doubtful finding that the line is polarized. Although the 1475 cm⁻¹ vibration appears only in the infra-red, the E' CH₃ deformation generally is found very close to this value, and the band is accordingly designated as ν_9 . From intensity considerations, both the 788 and 550-cm⁻¹ infra-red bands are probably fundamentals. The 550-cm⁻¹ band is too low to be a methyl vibration, and since the 786-cm⁻¹ Raman line coincides with the 788-cm⁻¹ infra-red band, the coincidence is assigned as the CH₃ rocking ν_{10} . The only frequency assignable as the C—Hg—C bending ν_{11} is the 156-cm⁻¹ line observed in the Raman. Although Pai⁶ observed a Raman line at 255 cm⁻¹, this has been shown to be spurious,⁴ and hence the 155-cm⁻¹ line is the only frequency available in the expected bending range.

The remaining Raman frequencies must be assigned as the E'' fundamentals, as combinations, or as overtones. The 2869-cm⁻¹ line is probably the C—H stretching ν_{12} . The assignment of the 700-cm⁻¹ line as the CH₃ rocking ν_{14} is in accord with its observed depolarization, and the value agrees with the corresponding vibration of E' symmetry. This leaves only the CH₃ deformation, ν_{13} , unassigned and the lines at 1030, 1252, 1397, and 1443 cm⁻¹ from which to choose. The 1030-cm⁻¹ line is low for ν_{13} and has a polarization of 0.48 which confirms the assignment of it as the overtone $2\nu_3$ (1030 cm⁻¹). The 1252-cm⁻¹ line is of doubtful reality and furthermore could be attributed readily to $\nu_7+\nu_{14}$ (1250 cm⁻¹). The choice between 1397 and 1443 cm⁻¹ is a more difficult one. Both can be assigned as combinations: 1397 cm⁻¹ as $2\nu_{14}$ (1400 cm⁻¹) and 1443 cm⁻¹ as $\nu_7+\nu_{10}$ (1437 cm⁻¹). Because ν_{13} is depolarized, the polarization data do recommend to some extent the 1443-cm⁻¹ line. Moreover, in general E' and E'' CH₃ deformation frequencies are not widely separated. Accordingly ν_{13} is assigned as the 1443-cm⁻¹ Raman line.

TABLE V. Observed frequencies, assignments, and calculated frequencies for combination bands of dimethyl mercury.

Infra-red (g) ν cm ⁻¹	Raman (l) $\Delta\nu$ cm ⁻¹	Assignment	Species for combinations	Calc. Freq. ν cm ⁻¹
	156 (1)	ν_{11}		
	515 (20, 0.30)	ν_3		
550 (8)		ν_7		
675 (1)		$\nu_3 + \nu_{11}$	E'	671
	700 (5b, 0.81)	ν_{14}		
788 (9)	786 (0) ?	ν_{10}		
	1030 (0, 0.48)	$2\nu_3$	A_1'	1030
1070 (2a)		$\nu_3 + \nu_7$	A_2''	1065
	1182 (12, 0.38)	ν_2		
1205 (2a)		ν_6		
	1252 (00) ?	$\nu_7 + \nu_{14}$	E'	1250
	1397 (0, 0.65)	$2\nu_{14}$	$A_1' + A_2' + E'$	1400
	1443 (0, 0.90)	ν_{13}		
1475 (6a)		ν_9		
	1706 (00, 0.77)	$\nu_2 + \nu_8$	A_1'	1697
1735 (3)		$\nu_2 + \nu_7$	A_2''	1732
	2341 (0)	$\nu_{10} + \nu_{11} + \nu_{13}$	$A_1'' + A_2'' + 3E''$	2340
1980 (0a)		$\nu_2 + \nu_{10}$	E'	1969
2390 (5)		$\nu_2 + \nu_6$	A_2''	2387
2660 (0)		$\nu_2 + \nu_9$	E'	2657
	2869 (2d, dp)	ν_{12}		
(2880) (6)		ν_5		
	2910 (6, 0.1)	ν_1		
2970 (10a)	2965 (3b, dp?)	ν_8		
3660 (1a)		$\nu_{10} + \nu_{12}; \nu_8 + \nu_{14}$	$A_1'' + A_2'' + E''$	3656; 3666
3855 (0)		$\nu_1 + \nu_{10} + \nu_{11}$	$A_1' + A_2' + E'$	3853
4150 (1)		$\nu_2 + \nu_8$	E'	4148
4435 (1)		$\nu_8 + \nu_9$	$A_1' + A_2' + E'$	4441

The A_2'' fundamentals are to be drawn from the remaining infra-red bands. The value of the C—H stretching, ν_5 , is complicated by the overlapping of it with ν_8 , and possibly with $2\nu_{13}$. The band maximum at 2835 cm⁻¹ is hardly ν_5 , since the latter is a || type band which should show definite P , Q , and R branches. The \perp band, ν_8 , is a band formed by the unresolved Q branches of the sub-bands against the weaker background of scattered P and R lines; this results from I_A/I_B being small. It appears possible that the shoulder at 2835 cm⁻¹ is the P branch of ν_5 , with the Q and R branches overlapping ν_8 . Such an interpretation gives an estimated value of 2880 cm⁻¹ for ν_5 . The CH₃ deformation, ν_6 , might be either the 1070 or 1205-cm⁻¹ band, which are the only unassigned bands in the appropriate range. The 1070-cm⁻¹ band is interpretable as the combination $\nu_3 + \nu_7$ (1065 cm⁻¹), whereas no such interpretation presents itself for the 1205-cm⁻¹ band; assignment of it as $\nu_3 + \nu_{14}$ (1215 cm⁻¹) violates the selection rules. This, as well as the higher intensity of the 1205-cm⁻¹ band, suggests its assignment as ν_6 . The chief objection to this assignment is that the 1205-cm⁻¹ band does not

exhibit a Q branch which is predicted for a || type band in symmetric top molecules.¹⁷ However, I_A/I_B is small in dimethyl mercury, and the Q branch should be correspondingly less intense though perhaps not completely missing. Moreover, the separation of the maxima of the P and R branch band envelopes is 14 cm⁻¹, which agrees well with the value of 13.5 cm⁻¹ computed for ν_6 at room temperature from I_B , so ν_6 is assigned as 1205 cm⁻¹. The strong band at 550 cm⁻¹ must be the C—Hg—C stretching, ν_7 , which value agrees well with the assigned value for the corresponding symmetrical stretching, ν_3 . All other observed bands have been readily assigned as combinations or overtones, obeying the selection rules, for which the calculated frequencies agree well with the experimental values as listed in Table V.

3. Frequency Assignment for Dimethyl Zinc

Initial normal coordinate calculations, as well as a qualitative comparison of the dimethyl mercury spectra with the frequency assignment proposed earlier for dimethyl zinc,¹ suggested

¹⁷ See G. Herzberg, reference 15, p. 414 *et seq.* for a detailed description of the band envelopes expected.

TABLE VI. Observed frequencies, assignments, and calculated frequencies for combination bands of dimethyl zinc.

Infra-red (ν) ν cm ⁻¹	Raman (ν) $\Delta\nu$ cm ⁻¹	Assignment	Species for combinations	Calc. freq. ν cm ⁻¹
	144 (1)	ν_{11}		
	488 (1) ?	$\nu_{14} - \nu_{11}$	$A_1'' + A_2'' + E''$	476
615 (10)	504 (20b, 0.18)	ν_3		
		ν_7		
707 (10)	620 (3b, 0.80)	ν_{14}		
		ν_{10}		
	898 (00) ?	$\nu_{13} - (\nu_{14} - \nu_{11})$	$A_1' + A_2' + 3E'$	899
	1013 (00)	$2\nu_3$	A_1'	1008
	1135 (0)	$\nu_3 + \nu_{14}$	E''	1124
	1158 (15, 0.32)	ν_2		
1185 (5a)		ν_6		
	1189 (0)	$\nu_3 + \nu_{10}$	E'	1211
	1244 (0)	$\nu_7 + \nu_{14}; 2\nu_{14}$	$E'; A_1' + A_2' + E'$	1235; 1240
1310 (5f)	1313 (00) ?	$\nu_2 + \nu_{11}$	E'	1304
1354 (2)		$\nu_3 + \nu_{10} + \nu_{11}$	$A_1' + A_2' + E'$	1355
	1388 (0)	ν_{13}		
1448 (0)	1440 (00)	ν_9		
1541 (0) ?		$\nu_{11} + \nu_{13}$	$A_1'' + A_2'' + E''$	1532
	1648 (00) ?	$\nu_2 + \nu_3$	A_1'	1662
1696 (2)		$\nu_3 + \nu_6$	A_2''	1689
1787 (1)		$\nu_2 + \nu_7$	A_2''	1773
1887 (00) ?		$\nu_2 + \nu_{10}$	E'	1865
2105 (00) ?		$\nu_{13} + \nu_{10}$	$A_1'' + A_2'' + E''$	2095
(2870) (8)	2833 (1/2b)	ν_{12}		
		ν_5		
	2898 (4, 0.05)	ν_1		
2935 (10a)	2948 (1b, 0.61)	ν_8		
3448 (2)		$\nu_3 + \nu_8$	E'	3444
4185 (1)		$2\nu_{14} + \nu_8; \nu_7 + \nu_8 + \nu_{14}$	$A_1' + A_2' + E';$ $A_1' + A_2' + 3E'$	4175; 4180
			$A_1' + A_2' + E'$	
4393 (2a)		$\nu_8 + \nu_9$	A_2''	4384
5781 (1)		$\nu_1 + \nu_5$		5772

that the latter required revision. The infra-red spectrum of dimethyl zinc was reinvestigated primarily to determine if any band was present in the observable region below 600 cm⁻¹, which is the limit of the earlier work.¹ Table VI summarizes the various available data and gives the assignments arrived at herein.

The general criteria for the frequency assignment are the same as for dimethyl mercury, and only the specific arguments will be considered here. Regarding the fundamentals, the absence of any infra-red band in the 430 to 615-cm⁻¹ region requires that the 615-cm⁻¹ infra-red band be assigned as ν_7 , the A_2'' C—Zn stretching, in order to obtain a C—Zn force constant consistent with that from ν_3 , the assignment of which can hardly be questioned. The coincidence with the 620-cm⁻¹ Raman frequency is ascribed as an accidental degeneracy, and the assignment of the latter to the E'' CH₃ rocking ν_{14} is indicated. The 707-cm⁻¹ infra-red band originally assigned to ν_7 is transferred to the E' CH₃ rocking ν_{10} . The A_1' Raman assignments of TLW¹ are con-

firmed by the later polarization measurements.⁴ These assignments and also ν_6 and ν_{11} are unchanged. It appears preferable to change the assignment for the E' CH₃ deformation ν_9 . This vibration, involving the H—C—H angular distortion, usually appears in the 1450–1475-cm⁻¹ region and can be assigned to the coincidence between Raman and infra-red spectra at 1447 cm⁻¹. ν_{13} should be in the region 12–1400 cm⁻¹, and of the four Raman lines reported therein, the 1388-cm⁻¹ value appears most likely. As in dimethyl mercury, the assignment of the A_2'' C—H stretching frequency is complicated by the overlapping of the infra-red bands. Employing identical arguments in this case, ν_5 is assigned the value 2870 cm⁻¹. The resolution of the C—H stretches in Fehér's Raman data and his polarization measures permit the assignment of ν_1 , ν_8 , and ν_{12} as 2898, 2940, and 2833 cm⁻¹, though the value for ν_{12} seems low. As a matter of fact, the 2833-cm⁻¹ line is interpretable as $\nu_9 + \nu_{13}$ (2832-cm⁻¹) but is assigned as ν_{12} for the lack of anything better.

TABLE VII. *G* matrix for CH₃-M-CH₃.*

A_1' and A_2''	$\mu_H + \mu_C$	$-\frac{4}{3}\rho\mu_C$	$-\frac{\sqrt{3}}{3}\mu_C$
		$2\rho^2\mu_H + \frac{16}{3}\rho^2\mu_C$	$\frac{4\sqrt{3}}{3}\rho\mu_C$
			$\mu_C + 2a\mu_M$
E' and E''	$\mu_H + \frac{4}{3}\mu_C$	$-\frac{2\sqrt{2}}{3}\rho\mu_C$	$-\frac{2\sqrt{6}}{3}a\mu_C$
	$\frac{5}{2}\rho^2\mu_H + \frac{8}{3}\rho^2\mu_C$	$-\frac{\rho^2}{4}\mu_H + \rho\left(\epsilon + \frac{\rho}{3}\right)\mu_C$	$\frac{2\sqrt{3}}{3}\epsilon\rho a\mu_C$
		$\rho^2\mu_H + \frac{3}{2}\left(\epsilon + \frac{\rho}{3}\right)^2\mu + 3\epsilon^2 a\mu_{CM}$	$\sqrt{3}\epsilon\left(\epsilon + \frac{\rho}{3}\right)a\mu_C + 2\sqrt{3}\epsilon^2 a\mu_M$
			$2\epsilon^2 a(\mu_C + 2\mu_M)$

* $\rho = (1/C-H) = (1/d)$; $\epsilon = (1/C-M) = (1/D)$; $a = \begin{cases} 1 & \text{for } A_1'', E'' \\ 0 & \text{for } A_1', E' \end{cases}$.

The remaining bands have all been assigned as combinations or overtones which obey the selection rules and for which the computed frequencies agree fairly well with the observed values. The calculated frequencies for several of the doubtful combination bands is not very good, suggesting that some of them might not be real.

NORMAL COORDINATE ANALYSIS

The methods developed by Wilson¹⁸ have been used throughout this section. The internal coordinates α , β , γ , r , and η are defined as small displacements in the H-C-H, H-C-M, C-M-C bond angles and C-H, C-M bond distances. Symmetry coordinates, normalized, orthogonal, linear combinations of these internal coordinates, transforming according to the appropriate irreducible representations of the group D_{3h} , were obtained by a simple extension of the method used by Meister and Cleveland.¹⁹ The redundancies resulting in the A_1' and A_2'' factors were removed by setting one symmetry coordinate in each factor identically equal to zero, expressing the condition that the sum of the angle changes in each methyl group is zero. The general factored *G* matrix, obtained for D_{3h} symmetry, is given in Table VII, and the diagonal terms of the corresponding valence force *F* matrix in Table VIII. In the *F* matrix subscript 2 refers to methyl-methyl interactions, and the primes indicate those interactions in-

volving staggered atoms. As a check, the *F* and *G* matrices were determined independently using Lippman's method.²⁰

In computing the numerical values of the *G* matrix, tetrahedral bond angles were assumed for the methyl groups. 1.10Å was adopted as the C-H bond distance, d ,²¹ and 2.20Å was used for the C-Hg distance, D .²² No direct measurement of the C-Zn bond distance appears to be available, and an estimated value of 2.05Å was introduced. This was obtained by taking the sum of the covalent radius of zinc in the metal crystal and the covalent radius of carbon²³ and estimating a correction for the higher covalent radius of zinc in the metal crystals by analogy to mercury. The 1942 values of the International Committee on Atomic Weights were used. The conversion factor 5.8905×10^{-2} used in transforming cm^{-1} to λ corresponds to Birge's 1941 table of fundamental constants.

The computed and observed fundamental frequencies are listed in Table IX; the numerical *F* matrix elements used in the calculations, as well as the force constants identified therewith, are given in Table VIII. Considering the probable effects of anharmonicity and the differences between the vibrational frequencies in the liquid

²⁰ Caro W. Lippman, Jr., unpublished. See reference 26 for a synopsis of the method.

²¹ J. W. Simmons, W. Gordy, and A. G. Smith, Phys. Rev. **74**, 243 (1948).

²² L. O. Brockway and H. O. Jenkins, J. Am. Chem. Soc. **58**, 2036 (1936).

²³ L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), second edition.

¹⁸ E. B. Wilson, Jr., J. Chem. Phys. **7**, 1047 (1939); *ibid.* **9**, 76 (1941).

¹⁹ A. G. Meister and F. F. Cleveland, Am. J. Phys. **14**, 13 (1946).

TABLE VIII. F matrix and force constants.*

General diagonal terms			Hg(CH ₃) ₂	Numerical values	Zn(CH ₃) ₂
A_1'	F_{11}	$f_r + 2f_{rr} + f_{rr_2} + 2f_{rr_2}'$	4.79×10^5		4.79×10^5
	F_{22}	$(d^2/2) \{ (f_\alpha + f_\beta) + 2(f_{\alpha\alpha} + f_{\beta\beta}) + c \}$	0.390×10^{-11}		0.375×10^{-11}
	F_{33}	$f_\eta + f_{\eta\eta}$	2.45×10^5		2.39×10^5
A_2''	F_{55}	$f_r + 2f_{rr} - f_{rr_2} - 2f_{rr_2}'$	4.79×10^5		4.79×10^5
	F_{66}	$(d^2/2) \{ (f_\alpha + f_\beta) + 2(f_{\alpha\alpha} + f_{\beta\beta}) - c + d \}$	0.406×10^{-11}		0.390×10^{-11}
	F_{77}	$f_\eta - f_{\eta\eta}$	2.45×10^5		2.39×10^5
E'	F_{88}	$f_r - f_{rr} + f_{rr_2} - f_{rr_2}'$	4.55×10^5		4.55×10^5
	F_{99}	$d^2(f_\alpha - f_{\alpha\alpha} + f_{\alpha\alpha_2} - f_{\alpha\alpha_2}')$	0.573×10^{-11}		0.550×10^{-11}
	F_{10-10}	$d^2(f_\beta - f_{\beta\beta} + f_{\beta\beta_2} - f_{\beta\beta_2}')$	0.417×10^{-11}		0.331×10^{-11}
E''	F_{11-11}	$D^2 f_\gamma$	0.457×10^{-11}		0.276×10^{-11}
	F_{12-12}	$f_r - f_{rr} - f_{rr_2} + f_{rr_2}'$	4.55×10^5		4.55×10^5
	F_{13-13}	$d^2(f_\alpha - f_{\alpha\alpha} - f_{\alpha\alpha_2} + f_{\alpha\alpha_2}')$	0.549×10^{-11}		0.508×10^{-11}
	F_{14-14}	$d^2(f_\beta - f_{\beta\beta} - f_{\beta\beta_2} + f_{\beta\beta_2}')$	0.333×10^{-11}		0.258×10^{-11}
Force constants					
f_r dynes/cm			4.63×10^5		4.63×10^5
f_{rr}			0.08		0.08
f_η			2.45		2.39
$d^2 f_\alpha$ dyne cm/radian			0.530×10^{-11}		0.530×10^{-11}
$d^2 f_\beta$			0.359		0.274
$D^2 f_\gamma$			0.457		0.276
$d^2 f_{\alpha\alpha}$			-0.031		0.001
$d^2 f_{\beta\beta}$			-0.016		-0.021
$d^2(f_{\alpha\alpha_2} + f_{\beta\beta_2})$			0.031		0.033
$d^2(f_{\alpha\alpha_2} - f_{\alpha\alpha_2}')$			0.012		0.021
$d^2(f_{\beta\beta_2} - f_{\beta\beta_2}')$			0.042		0.037

* $C = (f_{\alpha\alpha_2} + f_{\beta\beta_2}) + 2(f_{\alpha\alpha_2}' + f_{\beta\beta_2}')$; $d = -2(2f_{\alpha\beta} + f_{\alpha\beta}' - 2f_{\alpha\beta_2} - f_{\alpha\beta_2}')$.

Raman spectrum and the gaseous infra-red spectrum, the number of significant figures given for several of the force constants is too large. They are given as being the actual values used. In the determination of the force constants, the higher frequencies were successively split out of a given factor. These constants were then substituted in the expanded secular equation and the frequencies computed. Successive approximations were made to the force constant, till the computed frequencies agreed with the observed values.

There are insufficient data to evaluate many of the interaction constants explicitly. In view of this it seemed preferable to disregard all off-diagonal elements in the F matrix. The off-diagonal element $f_{\alpha\eta} - f_{\beta\eta}$ appears in the A_1' and A_2'' factors and is usually considered to be of physical significance. Its evaluation depends on first assigning values to the diagonal elements, for which in this case there appear no *a priori* means. The introduction of typical values found in other cases for $f_{\alpha\eta} - f_{\beta\eta}$,²⁴ has little effect on f_η and increases F_{22} and F_{66} by only about 2 percent. Analogous reasons led to the neglect

of the $f_{\alpha\beta}$ terms in F_{66} . The A_1' C—H F_{11} value of 4.79×10^5 dynes/cm is from ethane,²⁵ and the value of 0.530×10^{-11} dyne cm/radian for $d^2 f_\alpha$ is from the results of Decius for the methyl halides.²⁶ The C—H frequencies are fitted moderately well by using the diagonal element f_{rr} . The remaining systematic deviations indicate the fit could be improved somewhat by introducing small f_{rr_2} and f_{rr_2}' terms of dubious physical significance. Similarly, $f_{\eta\eta}$ is neglected because of its small magnitude, although values could be assigned by fitting ν_3 and ν_4 exactly. Subject to the effects of omitting $f_{\alpha\eta} - f_{\beta\eta}$, $f_{\alpha\beta}$, and the off-diagonal elements, several of the methyl vibration interaction terms were evaluated. The end-end interactions are determinable only as the combinations given in Table VIII.

DISCUSSION

On the basis of a simple bond orbital analysis²⁸ the C—Hg—C skeleton of dimethyl mercury would be expected to be linear because of hybridization of the 6s mercury orbital with the 6p orbitals to give the two bond orbitals of maximum strength $1/\sqrt{2}(S+P_x)$, $1/\sqrt{2}(S-P_x)$

²⁴ B. L. Crawford, Jr. and S. R. Brinkley, Jr., J. Chem. Phys. 9, 69 (1941).

²⁵ F. Stitt, J. Chem. Phys. 7, 297 (1939).

²⁶ J. C. Decius, J. Chem. Phys. 16, 214 (1948).

TABLE IX. Observed and computed fundamental frequencies.

D_{3h}'			Dimethyl mercury			Dimethyl zinc		
			Obs.	Comp.	% Dev.	Obs.	Comp.	% Dev.
A_1'	C-H stretching	ν_1	2910 cm^{-1}	2882 cm^{-1}	-0.96	2898 cm^{-1}	2883 cm^{-1}	-0.65
RP	CH_3 bending	ν_2	1182	1181	*	1158	1158	*
	C-M-C stretching	ν_3	515	512	-0.58	504	505	*
A_1''	torsion	ν_4	—	—	—	—	—	—
A_2''	C-H stretching	ν_5	2880	2883	+0.10	2870	2884	+0.49
IR,	CH_3 deformation	ν_6	1205	1205	*	1185	1185	*
	C-M-C stretching	ν_7	550	549	*	615	610	-0.81
E'	C-H stretching	ν_8	2966	2921	-1.52	2940	2920	-0.68
R	CH_3 deformation	ν_9	1475	1475	*	1444	1444	*
IR, \perp	CH_3 rocking	ν_{10}	787	787	*	707	707	*
	C-M-C bending	ν_{11}	156	156	*	144	144	*
E''	C-H stretching	ν_{12}	2869	2921	+1.85	2833?	2921	+3.23
R	CH_3 deformation	ν_{13}	1443	1443	*	1388	1388	*
	CH_3 rocking	ν_{14}	700	700	*	620	620	*

* Used in computing force constants.

which are linear along the x axis. The same reasoning applies to zinc where the hybridization is between the $4s$ and $4p$ orbitals. Brockway and Jenkins²² were not able to draw any conclusions regarding the linearity of dimethyl mercury from their electron diffraction investigations because of the high background of atomic scattering. The generally accepted linear configurations for the mercury, cadmium, and zinc halides²⁷ is indirect support for the linearity of the dimethyl compounds. However, the strongest evidence bearing on the linearity of these molecules comes from the lack of any appreciable number of coincidences between the infra-red and Raman spectra. A bent model requires that all fundamentals be active in both infra-red and Raman spectra, yet, among over fifty observed frequencies, there are only seven coincidences. TLW¹ conclude in their frequency assignment for dimethyl zinc that it is linear, and the additional data obtained since then confirm their conclusion. Moreover, the results of the normal coordinate analysis provide further corroboration of the linear structure.

The low values assigned the skeletal bending are perhaps a bit surprising. Indeed, Kohlrausch²⁸ assumes the Raman lines in the vicinity of 150 cm^{-1} do not belong to the vibrational spectrum. However, the bending frequencies must lie below 400 cm^{-1} , and no other values are

available for the assignment. A D_{3d} configuration would give the molecules a center of symmetry and make the bending inactive in the Raman, but the other observed coincidences preclude this possibility. The lines may be interpreted as combination bands: $\nu_2 - 2\nu_3$ for both dimethyl mercury and zinc, and also as $\nu_{14} - \nu_7$ for dimethyl mercury. The normal coordinate analysis suggests that the low frequencies do correspond to the bending, for the values of D^2f_γ are of the same magnitude as d^2f_β . Verification of the assignments could be made by observing the region in the infra-red with the aid of residual rays; the suggested combination for dimethyl zinc is only Raman active.

The extent of the rotational freedom of the methyl groups is an intriguing problem. The coincidences between the Raman and infra-red spectra in E' and the proposed interpretation of the low Raman frequency as the skeletal bending require D_{3h}' or D_{3h} symmetry. The latter is ruled out by the generally accepted views regarding the nature of the interactions restricting rotation,²⁹ leaving essentially free rotation as the most likely interpretation. The questionable appearance of ν_9 and ν_{10} in the Raman spectra may result from either the inherently low intensity of E' Raman lines or from only partial relaxation of the selection rules because of small, but still finite, hindrance to free rotation. The fine structure of the \perp infra-red bands is another possible means of investigating the

²⁷ See G. Herzberg, reference 15, p. 287 for references to the pertinent literature.

²⁸ K. W. F. Kohlrausch, *Ramanspectren* (Becker and Erler, Leipzig, 1943), p. 182.

²⁹ E. N. Lassettre and L. B. Dean, Jr., *J. Chem. Phys.* **16**, 151 (1948).

rotational restrictions.³⁰ Heat capacity data might also profitably be obtained.

The results of the normal coordinate analysis appear to be satisfactory, bearing in mind the reservations made in the frequency assignments. Nineteen force constants, two of which are from other molecules, are used in computing twenty-six frequencies, with a root-mean-square deviation of 1 percent for the ten frequencies not directly used in determining the force constants. A comparison of the force constants d^2f_β and D^2f_γ suggests that dimethyl zinc is a more readily deformable molecule than dimethyl mercury, a result perhaps of greater ionic character in the C—Zn bonds. $d^2f_{\alpha\alpha}$ is also appreciably smaller for dimethyl zinc perhaps for the same reason. The magnitudes of the interaction terms are of the same order as values reported for similar interactions elsewhere, except f_{rr} , which in methane derivatives appears to have a lower value of about 0.03×10^5 dynes/cm.²⁶

In more complicated molecules it often becomes expeditious to consider groups as units in deriving force constants or assigning frequencies, and a comparison of the more exact values for f_γ and f_η , obtained from the normal coordinate analysis, with the results from such an approximation affords a check on the accuracy of the approximation methods. Using the general formulae for a linear XY_2 molecule¹⁵ and $M_\gamma = 15$, values for f_γ and f_η were computed from the corresponding assigned frequencies. The results in units of 10^5 dynes/cm are tabulated below along with the normal coordinate values for comparison. The agreement is surprisingly good, with the XY_2 values consistently low.

		Hg(CH ₃) ₂		Zn(CH ₃) ₂	
		XY_2	n.c.	XY_2	n.c.
F_η	ν_3	2.35	—	2.26	2.39
F_η	ν_7	2.32	2.45	2.29	—
f_γ	ν_{11}	0.094	0.095	0.063	0.066

³⁰ J. B. Howard, J. Chem. Phys. 5, 451 (1937).

The correlation of force constants with atomic parameters is of considerable interest. Recently, Gordy³ has suggested a semi-empirical expression that appears to have fairly wide applicability. The stretching force constant k , in 10^5 dynes/cm is given as $k = aN(X_A X_B / d^2)^{\frac{1}{2}} + b$, where a and b are empirical constants having the values 1.67 and 0.30 for stable molecules in their normal covalent state. N is the bond order, X_A and X_B are the electronegativities of the bonded atoms, and d the bond distance in angstroms. Using Gordy's values for X (Hg 1.0, Zn 1.2, C 2.55) and 2.20 and 2.05A for the C—Hg and C—Zn bond distances, and $N=1$, his equation gives 1.33 and 1.62 for the C—Hg and C—Zn force constants, contrasting with the directly obtained values 2.45 and 2.39. A partial explanation is available in that the electronegativities Gordy uses for Hg and Zn may be incorrect. Substituting the observed force constants in Gordy's equation, electronegativities of 2.66 and 2.22 are computed for Hg and Zn, respectively. These values agree better with those from thermal data, 1.9 and 1.5 for Hg and Zn,³¹ than with those proposed by Gordy, but appear definitely to be too high, suggesting the possible importance of other factors in the poor fit between the experimental and predicted force constants.

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³¹ M. Haissinsky, J. phys. radium 7, 7 (1946).