

sodium hydroxide buffers for pH 9.4 to 12.1; to obtain pH 14.5 the calculated quantity of sodium hydroxide was added. The amidines were dissolved in 95% ethanol to make  $5 \times 10^{-4}$  molar solutions. For each experiment the amidine solution was diluted with an equal volume of the appropriate buffer in the electrolysis cell and was allowed to attain thermal equilibrium in a constant temperature bath held at  $25 \pm 0.2^\circ$ . The concentrations of amidine ( $2.5 \times 10^{-4}$  molar) and of buffer proved to be satisfactory. The use of less alcohol led to separation of solid amidine, and the use of more concentrated buffer solutions led to separation of buffering salts. The buffer action was adequate to yield consistent results which apparently were unaffected by either dissolved carbon dioxide or the negligible quantities of reduction products formed at the cathode.

The measurements were made with a Leeds and Northrup Electro-Chemograph operating at the 10 microampere range of the recorder. The "half-curve" potentials were obtained by manual operation of the polarizer at the end of each run. For each experiment the potential at the anode (quiet mercury pool) was measured against a saturated calomel electrode using a Leeds and Northrup portable potentiometer, and these voltages were used to change all "half-curve" potentials to half-wave potentials referred to the saturated calomel electrode at  $25^\circ$ , as shown in Table II.<sup>23</sup> The dropping mercury cathode operated at a pressure of 35 cm.; the drop time, for open circuit, was about 5.4 seconds. The calibration of the capillary gave  $m^2/st^{1/2} = 1.14 \text{ mg.}^2/\text{sec.}^{-1/2}$ . Characterization of the capillary according to Müller<sup>24</sup> gave a capillary constant  $K = 40.94 \text{ cm. sec./mg.}$ , and the radius of the capillary orifice  $\rho = 18.0 \mu$ .

To remove dissolved oxygen from the solution in the electrolysis cell nitrogen was bubbled through it; the nitrogen (from a commercial cylinder) was first passed through distilled water and then through a solution of the same composition as that in the cell. Blanks were run at each pH on the buffer-alcohol solution without amidine, and the readings were used as residual current corrections in obtaining the values of the diffusion currents listed in Table I.

For the cryoscopic determinations of molecular weights in naphthalene the procedure of v. Auwers<sup>25</sup> was used. The naphthalene was recrystallized twice from aqueous ethanol. The solute was compressed into pellets. Super-

cooling was held to  $0.02\text{--}0.03^\circ$ . For each solution at least two separate sets of measurements were made, the individual depressions of the freezing point varying not more than  $0.002^\circ$ . The approximate form of the freezing-point equation was employed in calculating the molecular weights.

**Catalytic Reduction.**—In each case 4.5 g. (0.0176 mole) of I, II or III was dissolved in 150 ml. of methanol (in which I is most, and III least, soluble), and the solution was transferred to the pressure bottle of an Adams and Vorhees machine.<sup>26</sup> About 4 g. of Raney nickel (wet with ethanol) was added, and hydrogenation was effected at an initial pressure of 33–35 lb. per sq. in., the pressures being recorded at five-minute intervals. The times required for complete reduction of the nitro groups of I, II and III were respectively fifteen, sixty and ninety minutes. Hydrogenation was limited to the nitro groups; earlier attempts to hydrogenate the C=N bond of N,N'-diphenylacetamidine were unsuccessful.<sup>27</sup>

### Summary

1. The tautomerism of amidines with mobile hydrogen is discussed in the light of recent developments, and with respect to the possibility that influences might be brought to bear to stabilize a single tautomer.

2. Polarographic examination of the three isomeric N-phenyl-N'-nitrophenyl acetamidines indicated the nitro group of the ortho isomer to be much more readily reduced (especially at pH 2.2 and at 7–9.4) than the nitro group of the *m*- or *p*-isomer. Catalytic hydrogenations of the three compounds confirmed this finding. Molecular weight determinations showed the para isomer to be more extensively associated than the ortho isomer. These differences may be explained as the result of internal hydrogen bonding (chelation), a phenomenon possible only in the ortho isomer, and which represents in some degree a stabilization of one tautomer.

(26) "Organic Syntheses," Coll. Vol. I, 1941, p. 66.

(27) The catalytic hydrogenations were run by H. Leon Bradlow.

PHILADELPHIA, PENNSYLVANIA

RECEIVED SEPTEMBER 30, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

## Infrared Absorption Spectra of Tetramethyl Compounds

By C. W. YOUNG,<sup>1</sup> J. S. KOEHLER AND D. S. MCKINNEY

The molecular vibrational spectra of the tetramethyl compounds of C, Si, Sn and Pb, and of the analogous tetramethylammonium ion, have been considered in a number of papers,<sup>2–12</sup> but as yet no

(1) Present address: Massachusetts Institute of Technology, Cambridge, Mass. This paper is from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Science in Chemistry, C. I. T., 1946. Presented in part at the April, 1946, meeting of the American Chemical Society in Atlantic City.

(2) K. W. F. Kohlrausch and D. Barnés, *Anales soc. españ. fis. quim.*, **30**, 733 (1932).

(3) K. W. F. Kohlrausch and F. Köppl, *Z. physik. Chem.*, **B26**, 209 (1934).

(4) D. H. Rank and E. R. Bordner, *J. Chem. physik.*, **3**, 248 (1935).

(5) D. H. Rank, *ibid.*, **1**, 572 (1933).

complete assignment of the fundamental frequencies has been given. This paper presents the infrared absorption spectra from 1 to  $15\mu$  of tetramethylsilicon and tetramethylgermanium obtained by means of a rock salt prism spectrometer. With the aid of a grating spectrometer, the na-

(6) N. G. Pai, *Proc. Roy. Soc. (London)*, **149**, 29 (1935).

(7) A. B. Duncan and J. W. Murray, *J. Chem. Phys.*, **2**, 146, 642 (1934).

(8) J. T. Edsall, *ibid.*, **5**, 225 (1937).

(9) C. F. Kettering and W. W. Sleator, *Physics*, **4**, 39 (1933).

(10) F. T. Wall and C. R. Eddy, *J. Chem. Phys.*, **6**, 107 (1938).

(11) S. Silver, *ibid.*, **7**, 1113 (1939); **8**, 919 (1940).

(12) T. F. Anderson, *ibid.*, **4**, 161 (1936).

TABLE I  
 NORMAL MODE CLASSIFICATION OF THE  $(\text{CH}_3)_4\text{X}$  MOLECULE

Description	Symmetry class of the point group $T_d$				
	$A_1$	$A_2$	E	$F_1$	$F_2$
$\text{CH}_3$ non-symmetrical stretching			$\nu_5^{\text{CH}}(e)$	$\nu_9^{\text{CH}}(f_1)$	$\nu_{13}^{\text{CH}}(f_2)$
$\text{CH}_3$ symmetrical stretching	$\nu_1^{\text{CH}}(a_1)$				$\nu_{14}^{\text{CH}}(f_2)$
$\text{CH}_3$ non-symmetrical deformation			$\nu_6^{\text{CH}}(e)$	$\nu_{10}^{\text{CH}}(f_1)$	$\nu_{15}^{\text{CH}}(f_2)$
$\text{CH}_3$ symmetrical deformation	$\nu_2^{\text{CH}}(a_1)$				$\nu_{16}^{\text{CH}}(f_2)$
$\text{CH}_3$ rocking			$\nu_7^{\text{CH}}(e)$	$\nu_{11}^{\text{CH}}(f_1)$	$\nu_{17}^{\text{CH}}(f_2)$
Skeletal non-degenerate	$\nu_3(a_1)$				
Skeletal doubly-degenerate			$\nu_8(e)$		
Skeletal triply-degenerate					$\nu_{18}(f_2)$
Skeletal triply-degenerate					$\nu_{19}(f_2)$
$\text{CH}_3$ torsion		$\nu_4(a_2)$		$\nu_{12}(f_1)$	
Activity	Raman pol.	inactive	Raman depol.	inactive	Raman depol., infrared

ture of the spectra of these latter two compounds and of tetramethylmethane in the  $3\mu$  region has been investigated under high resolution. Consideration of published Raman and infrared data, together with the new data given here, shows that a reasonably complete assignment can be given for the vibrational frequencies found in the spectra of the tetramethyl compounds mentioned.

### Experimental

The spectrometers have been described by others.<sup>13,14</sup> The spectra were taken in the usual cell-in, cell-out method, using a rock salt dummy. Readings were usually taken every slit width, sometimes two per slit width where it seemed advisable.

The sample of tetramethylmethane was obtained from J. G. Aston, and was used as received, except that it was passed over anhydrous calcium sulfate while introducing the gas into the cell. Professor Aston states that the material had a purity of 99.3 mole per cent. Details of its preparation are to be found in a paper by Aston and Messerly.<sup>15</sup>

The tetramethylsilicon used in this investigation was furnished by L. D. McGraw, and was prepared essentially by the method described by Aston, Kennedy and Messerly,<sup>16</sup> except that McGraw used methyl bromide instead of the iodide, b. p.  $26.54 \pm 0.05^\circ$  at 760 mm.

Tetramethylgermanium was prepared from germanium tetrachloride by means of the Grignard reaction, using methylmagnesium chloride in *n*-butyl ether solvent. The product was shaken with three portions of cold concentrated sulfuric acid and washed three times with distilled water. The material was then distilled from a small Claisen flask, b. p.  $42.8\text{--}43.6^\circ$  at 740 mm.

The germanium tetrachloride was prepared from germanium metal by a method similar to that of Dennis and Hance,<sup>17</sup> b. p.  $82.2^\circ$  at 740 mm.

Both the tetramethylsilicon and tetramethylgermanium were passed over anhydrous calcium sulfate while introducing the gases into the absorption cells.

### Results

The infrared spectra of tetramethylmethane, tetramethylsilicon and tetramethylgermanium are

(13) D. S. McKinney, C. E. Leberknight and J. C. Warner, *THIS JOURNAL*, **59**, 481 (1937).

(14) C. E. Leberknight and J. A. Ord, *Phys. Rev.*, **51**, 430 (1937).

(15) J. G. Aston and G. H. Messerly, *THIS JOURNAL*, **58**, 2354 (1936).

(16) J. G. Aston, R. M. Kennedy and G. H. Messerly, *THIS JOURNAL*, **63**, 2343 (1941).

(17) L. M. Dennis and F. E. Hance, *ibid.*, **44**, 304 (1922).

shown in the accompanying figures. In order to conserve space certain tables (IV–IX) are not included here.<sup>18</sup> Tables IV–IX contain a complete assignment, including overtones and combination frequencies, of all existing data on the tetramethyl compounds, Raman and infrared. Readers interested in obtaining detailed information on the spectra shown here are referred to these tables. In the case of tetramethylmethane the values were read off as accurately as possible from the spectrograms published by the Bureau of Standards.<sup>19</sup> Jones, Friedel and Hinds<sup>20</sup> have also published the infrared spectrum of tetramethylmethane. However, their spectrum does not show any bands not given by the former spectrogram. The infrared frequencies given in the tables for tetramethyltin and tetramethyllead were read from the spectrograms of Kettering and Sleator.<sup>9</sup>

### Discussion

The assignment of frequencies given in the tables is based on the assumption that the molecules have the symmetry of the point group  $T_d$ . Table I determines the numbering of the fundamental frequencies characteristic for the tetrahedral molecule of this symmetry. The convention used for designating and ordering the frequencies is similar to that adopted by Herzberg.<sup>21</sup>

Table II lists the assigned fundamental frequencies for the six compounds named, and indicates where we still lack data on the fundamental frequencies of the compounds. Frequencies in parentheses have not been observed but are derived from various considerations to be discussed later. As shown in Table I, the higher frequencies are associated with "inner vibrations" of the

(18) Copies of these tables, with notes, Document 2383, may be obtained from the American Documentation Institute (Science Service), 1719 G Street, N. W., Washington, D. C. Photoprints \$1.50; microfilm 50¢.

(19) Am. Pet. Inst. Res. Project 44. Natl. Bureau Standards Catalog of Infrared Spectrograms. Serial No. 104. Tetramethylmethane, contr. by the Univ. of Okla. Res. Inst.

(20) L. C. Jones, R. A. Friedel and G. P. Hinds, Jr., *Ind. Eng. Chem., Anal. Ed.*, **17**, 349 (1945).

(21) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945.

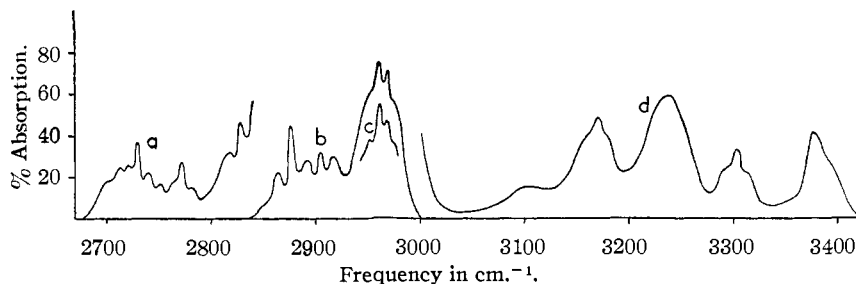


Fig. 1.—Infrared spectrum of tetramethylmethane (grating spectrometer): cell length used, 5.4 cm.; slit widths, 1-2 cm.<sup>-1</sup>; pressures: (a) 215 mm., (b) 7 mm., (c) 2.5 mm., (d) 550 mm.

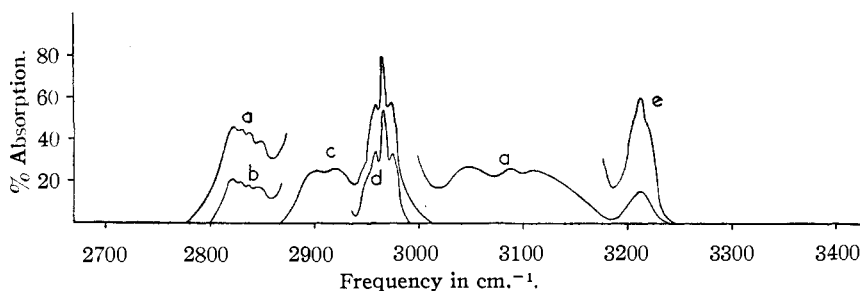


Fig. 2.—Infrared spectrum of tetramethylsilicon (grating spectrometer): cell length used, 5.4 cm.; slit widths, 1-2 cm.<sup>-1</sup>; pressures: (a) 128 mm., (b) 57 mm., (c) 8 mm., (d) 3 mm., (e) 617 mm.

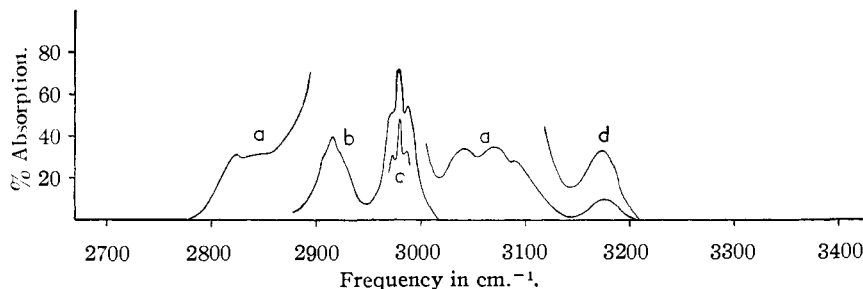


Fig. 3.—Infrared spectrum of tetramethylgermanium (grating spectrometer): cell length used, 5.4 cm.; slit widths, 1-2 cm.<sup>-1</sup>; pressures: (a) 187 mm., (b) 10 mm., (c) 5 mm., (d) 311 mm.

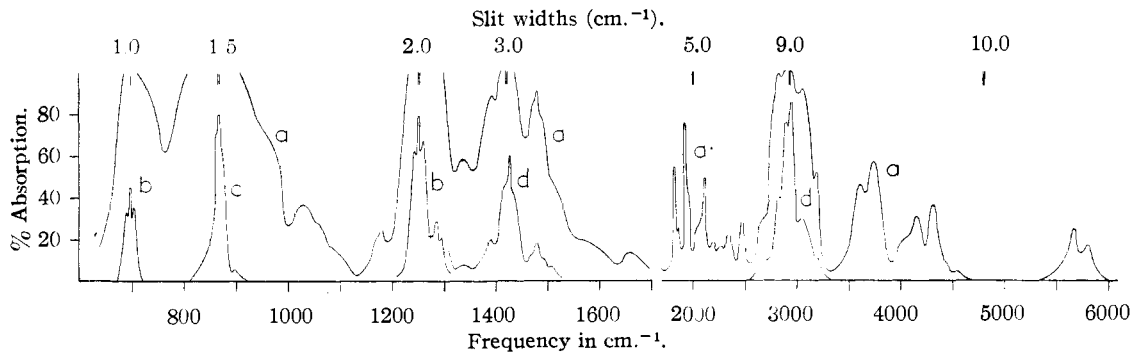


Fig. 4.—Infrared spectrum of tetramethylsilicon (prism spectrometer): cell length used 6.5 cm.; pressures: (a) 733 mm., (b) 9 mm., (c) 1 mm., (d) 76 mm.

methyl groups; the lower frequencies are ascribed to the skeletal vibrations imagined as occurring with the carbon-hydrogen bonds rigid.

A comparison of the fundamental frequencies of the methyl halides<sup>21</sup> with corresponding frequen-

cies arising from similar vibrations of the tetramethyl compounds is illuminating (Table III). The parallel is striking. The three lower frequencies are rather strongly dependent on changes in bond strength. The higher frequencies associated

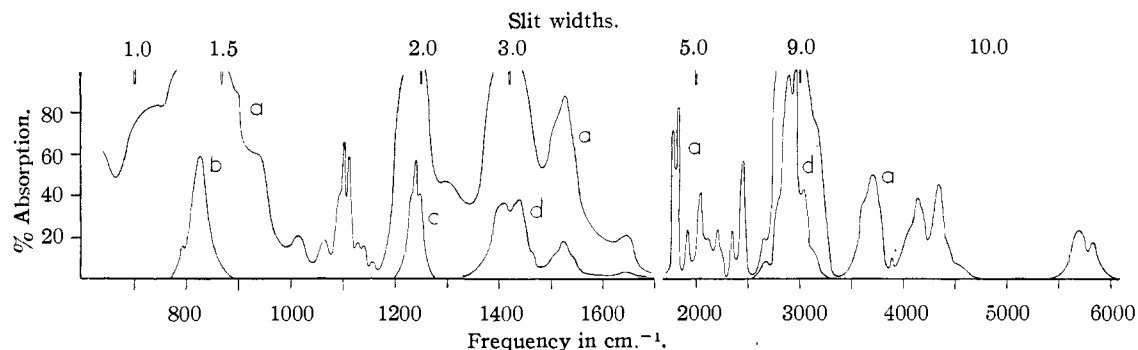


Fig. 5.—Infrared spectrum of tetramethylgermanium (prism spectrometer): cell lengths used, 15.8 cm. at 383 mm., 6.5 cm. at other pressures; pressures: (a) 383 mm., (b) 6 mm., (c) 17 mm., (d) 89 mm.

mainly with the carbon-hydrogen bond are much less affected. The  $\nu_2(a_1)$  mode for the methyl halides, and the corresponding  $\nu_2^{CH}(a_1)$  mode for

TABLE II  
THE FUNDAMENTAL FREQUENCIES (IN  $\text{cm.}^{-1}$ ) OF THE  
TETRAMETHYL COMPOUNDS

	(CH <sub>3</sub> ) <sub>4</sub> -N <sup>+</sup>	(CH <sub>3</sub> ) <sub>4</sub> C	(CH <sub>3</sub> ) <sub>4</sub> -Si	(CH <sub>3</sub> ) <sub>4</sub> -Ge	(CH <sub>3</sub> ) <sub>4</sub> -Sn	(CH <sub>3</sub> ) <sub>4</sub> Pb
$\nu_1$	2930	2911	2919	(2917)	2915	2918
$\nu_2$	1289	1252	1254	(1244)	1200	1170
$\nu_3$	752	733	598	(540)	506	460
$\nu_4$	?	?	?	?	?	?
$\nu_5$	3037	2955	2963	(2982)	2979	2999
$\nu_6$	1455	1455	1430	(1442)	(1465)	(1462)
$\nu_7$	1173	925	869	(830)	(776)	767
$\nu_8$	372	335	202	(110)	(100)	(100)
$\nu_9$	(3037)	(2955)	(2964)	(2982)	(2979)	(2999)
$\nu_{10}$	(1455)	(1455)	(1430)	(1442)	(1465)	(1462)
$\nu_{11}$	(1173)	(925)	(869)	(830)	(776)	(767)
$\nu_{12}$	?	?	?	?	?	?
$\nu_{13}$	3037	2962	2967	2982	2979	2999
$\nu_{14}$	2828	2876	2919	2917	2915	2918
$\nu_{15}$	1455	1455	1430	1442	1465	1462
$\nu_{16}$	1418	1370	1254	1244	1205	1169
$\nu_{17}$	1289	1280	869	830	776	767
$\nu_{18}$	955	925	696	(590)	526	473
$\nu_{19}$	455	414	239	(200)	152	130

TABLE III<sup>a</sup>  
COMPARISON OF FUNDAMENTAL FREQUENCIES (IN  $\text{cm.}^{-1}$ )  
OF METHYL HALIDES AND TETRAMETHYL COMPOUNDS

		CH <sub>3</sub> F	CH <sub>3</sub> Cl	CH <sub>3</sub> Br	CH <sub>3</sub> I
I	$\nu_3(a_1)$	1048	732	611	533
II	$\nu_8(e)$	1196	1015	952	880
III	$\nu_2(a_1)$	1475	1355	1305	1252
IV	$\nu_3(e)$	1471	1455	1445	1440
V	$\nu_1(a_1)$	2965	2966	2972	2970
VI	$\nu_4(e)$	2982	3042	3056	3060

	(CH <sub>3</sub> ) <sub>4</sub> -N <sup>+</sup>	(CH <sub>3</sub> ) <sub>4</sub> -C	(CH <sub>3</sub> ) <sub>4</sub> -Si	(CH <sub>3</sub> ) <sub>4</sub> -Ge	(CH <sub>3</sub> ) <sub>4</sub> -Sn	(CH <sub>3</sub> ) <sub>4</sub> -Pb
I	$\nu_3(a_1)$	752	733	598	(540)	506
II	$\nu_8^{CH}(e)$	1173	925	869	(830)	(776)
III	$\nu_2^{CH}(a_1)$	1289	1252	1254	(1244)	1200
IV	$\nu_3^{CH}(e)$	1455	1455	1430	(1442)	(1465)
V	$\nu_1^{CH}(a_1)$	2930	2911	2919	(2917)	2915
VI	$\nu_4^{CH}(e)$	3037	2955	2967	(2982)	2979

<sup>a</sup> The values for the methyl halides have been taken from Herzberg.<sup>21</sup> It is to be noted that the designations for the methyl halides are the same as those used by Herzberg and are not to be confused with the designations applied to the tetramethyl compounds. A given Roman numeral indicates frequencies to be compared in going from the methyl halides to the tetramethyl compounds.

the tetramethyl compounds are also mainly carbon-hydrogen bond frequencies, namely, the methyl symmetrical deformation. However, the lower  $\nu_3(a_1)$  for each of the two types of compounds has the same symmetry as the higher  $\nu_2(a_1)$ . As a result, the higher frequency is pushed upward as the concomitant increase in the lower frequency takes place. There is an increasing tendency toward resonance between the two modes of vibration as the  $\nu_3(a_1)$  frequency increases. This explains why the methyl symmetrical frequency changes as much as it does even though it is due essentially to a carbon-hydrogen vibration.

Aside from the strongly suggestive analogy between the methyl halide series and the tetramethyl series, there are a number of other factors which confirm the correctness of the assignment proposed. In general, the four lowest frequencies found for each compound are assigned to the skeletal vibrations, with exceptions to be noted. This is in the main concordant with the approximate calculations made by a number of authors,<sup>2,8,10,11</sup> using a pentatomic spherical top model as an approximation to the tetramethyl compounds. Polarization data are of help in picking out the  $A_1$  frequencies. The skeletal mode  $\nu_3(a_1)$  has this symmetry and should appear totally polarized in the Raman spectra. The 752  $\text{cm.}^{-1}$  band for tetramethylammonium ion, the 506  $\text{cm.}^{-1}$  band for tetramethyltin, and the 460  $\text{cm.}^{-1}$  band for tetramethyllead have been reported from strongly polarized Raman shifts. Polarization data are lacking for the other compounds. However, the 733  $\text{cm.}^{-1}$  band for tetramethylmethane and the 598  $\text{cm.}^{-1}$  band for tetramethylsilicon appear as sharp, strong Raman bands. This is significant, since the totally symmetric vibrations usually show the sharpest and strongest lines in the Raman effect.

There are uncertainties for the two lowest skeletal modes of tetramethyltin and tetramethyllead. Rather arbitrarily the lowest modes,  $\nu_8(e)$ , for tetramethylgermanium, tin, and lead have been taken to be about 100  $\text{cm.}^{-1}$ . Duncan and Murray<sup>7</sup> state that the 130  $\text{cm.}^{-1}$  shift found by them for tetramethyllead appears as a broad

Raman line. There is some indication that the band is actually double, and may be a superposition of two bands. According to the above assignment, the  $\nu_8(e)$  and  $\nu_{19}(f_2)$  frequencies would be overlapped for the lead compound if this is correct.

Pai<sup>6</sup> gives a moderately strong Raman shift of 262  $\text{cm.}^{-1}$  for tetramethyltin. If it is a fundamental, the reason for its appearance is unaccounted for by the scheme of assignment proposed here. Hence, it is ascribed to a combination of the two lower fundamentals. It is possible that the 152  $\text{cm.}^{-1}$  shift for this compound is a superposition of the two lowest skeletal frequencies. The 262  $\text{cm.}^{-1}$  shift may then be the first overtone of the  $\nu_{19}(f_2)$  frequency.

The skeletal modes of tetramethylgermanium have been guessed at from certain overtone and combination bands appearing in the infrared spectrum, as well as by interpolation between the corresponding fundamentals for tetramethylsilicon and tetramethyltin.

The highest of the four skeletal modes has been assigned to  $\nu_{18}(f_2)$ . Such an assignment appears to give best agreement with the approximate calculations made for the skeletal modes. In the case of tetramethylammonium and tetramethylmethane the large increase in bond strength between the central atom and the methyl group carbon considerably increases the  $\nu_{18}(f_2)$  frequency. As a result the lower carbon-hydrogen vibrations of symmetry  $F_2$  are greatly modified by interaction between the skeletal mode and the carbon-hydrogen modes. It is to be expected that the  $\nu_{18}^{\text{CH}}(f_2)$  and  $\nu_{17}^{\text{CH}}(f_2)$  frequencies will be pushed up considerably as a result. It is a noteworthy fact that the 1370  $\text{cm.}^{-1}$  band for tetramethylmethane appearing in the infrared spectrum has not been found in the Raman spectrum, although the selection rules allow it. The 1418  $\text{cm.}^{-1}$  Raman shift found by Edsall for tetramethylammonium is quite weak and has also been assigned to  $\nu_{16}^{\text{CH}}(f_2)$ .

The  $\nu_{16}^{\text{CH}}(f_2)$ ,  $\nu_{17}^{\text{CH}}(f_2)$  and  $\nu_{18}(f_2)$  frequencies for tetramethylmethane and tetramethylammonium are in reality combinations of skeletal and carbon-hydrogen vibrations. Hence, to say that one is a carbon-hydrogen frequency, another a skeletal frequency, is admittedly a somewhat arbitrary procedure for these compounds.

The assignments of the rest of the frequencies follow the analogies shown between the methyl halides and the tetramethyl compounds. That the same frequency is generally assigned to vibrations of the same nature in the methyl groups, whatever the symmetry class, is evidence that the type of degeneracy has little influence on these characteristic motions for the tetramethyl compounds, except as noted where there is an influence on the  $F_2$  frequencies due to interaction with the lower skeletal frequency.

The methyl rocking and deformation frequencies are considered to depend on the symmetry

class as shown for tetramethylmethane and tetramethylammonium. The  $\nu_{18}(f_2)$  skeletal vibration should not affect the methyl motions which have other than  $F_2$  symmetry. For example, in tetramethylmethane the  $\nu_7^{\text{CH}}(e)$  vibration is assigned to the 925  $\text{cm.}^{-1}$  Raman shift, although it is also assigned to the  $\nu_{18}(f_2)$  skeletal mode. Support for this assignment is found in the fact that Rank and Bordner<sup>4</sup> show this as a broad band. An analogous situation exists with regard to  $\nu_2^{\text{CH}}(a_1)$  and  $\nu_{17}^{\text{CH}}(f_2)$  which are assigned to the 1252  $\text{cm.}^{-1}$  shift. It is also possible that there are some Raman frequencies corresponding to these bands which have been missed because of low intensity in the Raman effect. For instance, the  $\nu_7^{\text{CH}}(e)$  frequency for tetramethylmethane perhaps should appear as a weak Raman shift of the order of 1100  $\text{cm.}^{-1}$ .

Two fairly strong bands are reported by Edsall<sup>8</sup> for tetramethylammonium corresponding to Raman shifts of 1173 and 1289  $\text{cm.}^{-1}$ . These have been assigned to different symmetry classes for the methyl rocking vibrations.

The vibrations inactive in either Raman or infrared are assumed to have frequencies corresponding to the active modes of the same nature.

Several features of the spectra around 3000  $\text{cm.}^{-1}$  for tetramethylmethane and tetramethylammonium ion are unclear. Edsall<sup>8</sup> gives three polarized bands for tetramethylammonium at 2930, 2967 and 2991  $\text{cm.}^{-1}$ , respectively. The 2930  $\text{cm.}^{-1}$  band has been chosen as  $\nu_1^{\text{CH}}(a_1)$ . The other bands lie a little too high to be sure that they are due to Fermi resonance of  $2\nu_{15}$  and  $2\nu_6$  with  $\nu_1^{\text{CH}}(a_1)$ . These overtones might appear polarized since they have totally symmetric components. A fairly small change in the measured values would allow these assignments. The inactive  $\nu_{10}^{\text{CH}}(f_1)$  frequency also would appear as an overtone in this region since the doubly excited vibration has active components.

The assignments for tetramethylmethane in the 2900–3000  $\text{cm.}^{-1}$  region are also highly tentative. Since Fermi resonance occurs between the highest carbon-hydrogen frequencies and the doubly excited transitions corresponding to the unsymmetrical deformation frequencies, no satisfactory exact explanation can be given for the number of frequencies appearing in this region. This is also true for tetramethylsilicon. A similar kind of Fermi resonance is known to exist for the methyl halides.

Inspection of the grating spectrograms shows the considerable overlapping of the bands in the  $3\mu$  region for tetramethylmethane and tetramethylsilicon.

Practically all the other bands found in existing Raman and infrared data may be explained reasonably as doubly excited overtone or combination bands in accordance with the assignment of fundamentals in Table II. There are a comparatively few of the weakest bands which require the

assumption of triply excited vibrations. All the overtone and combination assignments may be chosen to fit the selection rules.

Table II gives no assignment for the torsional vibrations due to internal rotation of the methyl groups. They are inactive for compounds having the symmetry  $T_d$ . Since all existing data can be reasonably explained as due to other vibrations, it seems highly dubious that it would be worthwhile at the present stage of investigation to attempt to derive the torsional frequencies from overtone or combination bands.

The calculations made by Silver<sup>11</sup> for the  $A_1$  and  $E$  frequencies are in the main concordant with the assignment proposed here as may be seen by reference to his paper. That the calculations of Silver are not in closer agreement with observed data is probably to be ascribed to the fact that a simple valence force potential is not very satisfactory for the tetramethyl compounds for the same reasons that such a potential field does not adequately describe the methyl halides.

The assignments suggested here must certainly be considered tentative in many respects, but they may have the merit of suggesting further investigations of the Raman and infrared spectra of this interesting series of compounds, particularly in attempts to find those fundamental frequencies

which in a number of cases are undoubtedly missing as yet.

**Acknowledgments.**—The authors wish to thank Professor J. G. Aston and Dr. L. D. McGraw for furnishing the samples of tetramethylmethane and tetramethylsilicon, respectively. The assistance of Dr. C. E. Leberknight in putting the grating spectrometer in working order is greatly appreciated. Thanks are also due to Dr. R. A. Friedel for discussion of several features of the tetramethylmethane spectrum.

### Summary

The infrared absorption spectra of tetramethylsilicon and tetramethylgermanium from 1 to  $15\mu$  obtained on a rock salt prism spectrometer, are presented.

With the aid of a grating spectrometer, the nature of the spectra of the above two compounds and of tetramethylmethane has been investigated in the  $3\mu$  region under high resolution.

An assignment of all known Raman and infrared frequencies of the tetramethyl compounds of C, Si, Ge, Sn and Pb, and of tetramethylammonium ion is proposed on the basis of a molecular model having the symmetry of the point group  $T_d$ .

CAMBRIDGE, MASS.

RECEIVED JANUARY 27, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

## Filters for the Isolation of the 3130 Å. Spectral Group of the Mercury Arc

BY ROY E. HUNT<sup>1</sup> AND WALLACE DAVIS, JR.<sup>1</sup>

A number of filters have been suggested<sup>1a-4</sup> for the isolation of the mercury arc triplet near 3130 Å. However, no systematic data have been reported correlating spectroscopic purity of this wavelength with filter concentration and resultant loss of intensity in the region of 1% total extraneous radiation.

The purpose of the present work was primarily to determine the impurities in the 3130 Å. triplet when nickel chloride, potassium chromate and potassium biphthalate solutions are used as filters. The source was intended for use in the photolysis of certain ketones, hence, only solutions expected to give high purity were tested. The investigation was extended to obtain semi-quantitative data on the relative effectiveness of several of the filter components suggested in the literature for removing specific impurities in the desired group.

In view of the nature of the filters available, extraneous radiation was divided into five cate-

gories: 1, ultraviolet radiation below 3000 Å.; 2, 3020 Å.; 3, 3342 Å.; 4, 3660 Å.; 5, all radiation above 3660 Å., including the visible and near infrared.

An additional region, the infrared of wave length longer than  $1.2\mu$  would be absorbed by 10 cm. of water in any of the liquid filter solutions.<sup>5</sup>

Bowen,<sup>1a</sup> testing solutions in 10-cm. spherical quartz flasks, which served also to condense the radiation, proposed the use of nickel chloride in hydrochloric acid, potassium chromate in sodium hydroxide, and potassium biphthalate. He found impurities amounting to 4-6% in the ultraviolet using a photoelectric cell to measure the various individual lines as dispersed through a quartz prism. He observed further that the biphthalate solution required continued renewal by means of a flow system.

The use of a solution containing cobaltous sulfate and nickel sulfate, mixed, was proposed by Bäckstrom<sup>2</sup> to eliminate the visible as well as most of the 3660 Å. line. He used biphthalate to remove the wave lengths below 3130 Å. and also

(1) National Research Council Pre-Doctoral Fellows.

(1a) E. J. Bowen, *J. Chem. Soc.*, 2236 (1932).

(2) H. J. L. Bäckstrom, *Naturwissenschaften*, **21**, 251 (1933).

(3) E. J. Bowen, *J. Chem. Soc.*, 76 (1935).

(4) R. Spence and W. Wild, *ibid.*, 352 (1937).

(5) J. Strong, "Procedures in Experimental Physics," Prentice-Hall, Inc., New York, N. Y., 1945, p. 370.