the order of the shift of the O–H and N–H frequencies is Cl > N > O > F. As is shown in Table V, this is in good accord with the order of the van der Waals radii of these atoms.

The above result is not to be expected from a point charge type of model, and suggests that if Y is large and polarizable the important effect at large distances is an overlap of the outer electrons of Y with the proton.

Both the very low frequencies found in strong hydrogen bonds and the recent neutron diffraction data (Fig. 8 and Table VI) indicate that in strong hydrogen bonds the X–H distance increases exponentially as the X–H...Y distance decreases. This seems to be in serious disagreement with semi-theoretical treatments of hydrogen bonding, such as that of Coulson and Danielsson.[14] In several recent treatments[15] it is either assumed or found that the amount of covalent character in the long H...Y bond is negligible, and it seems possible that these treatments fail to account for the rapid increase of the X–H distance in strong hydrogen bonds because they grossly underestimate the covalent character in the H...Y bond as Y approaches the hydrogen. In any case, the bad disagreement with hydrogen positions in strong hydrogen bonds does not justify faith in recent theoretical treatments.

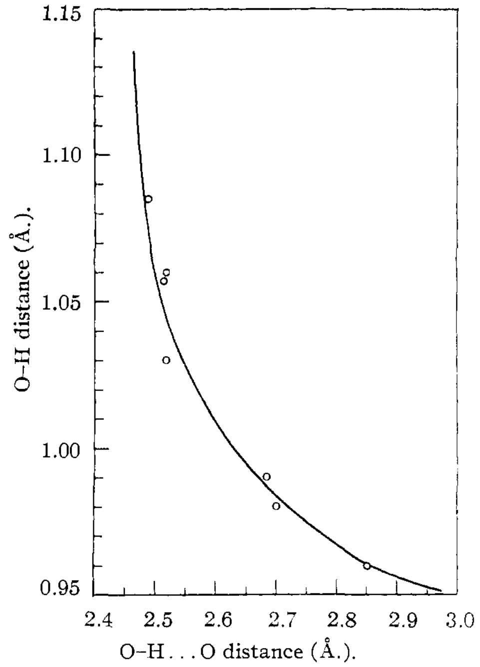

Fig. 8.—O–H...O distance *versus* O–H distance.

TABLE VI

THE RELATION BETWEEN O–H...O DISTANCE AND O–H DISTANCE

| Compound | O–H...O distance (Å.) | O–H Distance (Å.) | Method[f] |
|---|---|---|---|
| $(COOH)_2 \cdot 2H_2O$ | 2.85[a] | 0.96[a] | N.D. |
| $CaSO_4 \cdot 2H_2O$ | 2.70[b] | 0.98[c] | P.M.R. |
| $\alpha$-$HIO_3$ | 2.686 ± 0.009[a] | 0.990 ± 0.017[a] | N.D. |
| $KD_2AsO_4$ | 2.52[a] | 1.03[a] | N.D. |
| $KH_2AsO_4$ | 2.52[a] | 1.06[a] | N.D. |
| $(COOH)_2 \cdot 2H_2O$ | 2.518 ± 0.008[a] | 1.057 ± 0.016[a] | N.D. |
| $KH_2PO_4$ | 2.487 ± 0.005[d] | 1.085 ± 0.013[e] | N.D. |

[a] B. S. Garrett, Oak Ridge National Laboratory Report, No. 1745. [b] W. A. Wooster, *Z. Krist.*, 94, 375 (1936). [c] G. E. Pake, *J. Chem. Phys.*, 16, 327 (1948). [d] G. E. Bacon and R. S. Pease, *Proc. Roy. Soc.* (*London*), **A220**, 397 (1953). [e] S. W. Peterson, H. A. Levy and S. H. Simmonsen, *J. Chem. Phys.*, 21, 2084 (1953). [f] N. D., neutron diffraction; P.M.R., proton magnetic resonance.

Figure 8 suggests that for hydrogen bonds of ~2.45 Å. the hydrogen will be centered, tending to confirm that the hydrogen bond in nickel dimethylglyoxime, where O–H–O = 2.44 Å., is symmetric.

**Acknowledgment.**—The authors are indebted to Mr. Richard Hedges and Mr. Robert Kross for aid in obtaining spectra and to the Ames Laboratory of the Atomic Energy Commission for use of equipment. The Corn Industries Research Foundation has kindly provided a fellowship for one of us (K. N.).

(14) C. A. Coulson and U. Danielsson, *Arkiv Fysik*, **8**, 239, 245 (1955).

(15) For example, N. D. Coggeshall, *J. Chem. Phys.*, **18**, 978 (1950).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

# The Raman and Infrared Spectra of Tin Tetramethyl[1]

BY WALTER F. EDGELL AND CURTIS H. WARD[2]

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The Raman and infrared spectra of $Sn(CH_3)_4$ have been studied and compared with the results of earlier investigations. The fundamental frequencies of vibration are determined and the large number of combination and overtone bands in both spectra are explained in terms of them. The coupling between the skeletal vibrations and those modes characteristic of the methyl groups is discussed and the results compared to those for the other tetramethyl compounds of Group IVA elements.

## Introduction

The Raman and infrared spectra of several organotin compounds have been studied recently in this Laboratory. Such a study is of theoretical interest in connection with the nature of "group frequencies" and in particular with regard to the extent of coupling between the skeletal modes and those of the methyl groups. This paper deals with the study of tin tetramethyl. Although several previous workers have studied this compound,[3-8] considerable disagreement still appears to exist as

(1) Based upon a portion of the Ph.D. thesis of C. H. Ward, Purdue University, September, 1953.

(2) Purdue Research Foundation Fellow, 1950–1952; Allied Chemical and Dye Fellow, 1952–1953.

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

(4) G. Pai, *Proc. Roy. Soc.* (*London*), **149A**, 29 (1935).

(5) C. W. Young, J. S. Koehler and D. S. McKinney, THIS JOURNAL, **69**, 1410 (1947).

(6) H. Siebert, *Z. anorg. Chem.*, **263**, 82 (1950).

(7) H. Siebert, *ibid.*, **268**, 177 (1952).

(8) E. R. Lippincott and M. C. Tobin, THIS JOURNAL, **75**, 4141 (1953).

to the actual observed spectrum and to its interpretation. The recent paper of Lippincott and Tobin,[8] which appeared as the present paper was in preparation, reports the most complete study to date. However, our results are not in accordance with those reported above in several important aspects.

## Experimental

**Preparation.**—The tin tetramethyl was prepared by the method of Waring and Horton[9] and by an improved method employing *n*-butyl ether.[10] The first method requires the separation from large amounts of diethyl ether, the last portions of which are difficult to remove. Some previous spectroscopic work has been done on samples so contaminated. The second method reduces these difficulties. Both samples were purified by fractionation through a Todd column (40–50 plates) and the fraction distilling at 76.6° (748 mm.) (reported 76.8°, 76°) was used in the spectroscopic work. The progress of the purification was followed by infrared spectroscopy. Both samples gave identical results.

**Raman Spectrum.**—The Raman spectrum was recorded photoelectrically and photographically using an Applied Research Laboratories Raman spectrometer. This three prism instrument has a Schmidt type camera of focal aperature f/3.5 and a dispersion of 15 Å./mm. at 4358 Å. For photoelectric recording an exit slit periscope arrangement traverses the focal plane and directs the radiation to an external 1P21 photomultiplier tube. Low pressure, water-cooled mercury arcs served as the source. They were enclosed in a cylindrical, "light furnace" type of reflector system, which was coated with a silicone resin impigmented with $TiO_2$. No filters were used except in those special runs to distinguish lines excited by 4046 and 4077 from those excited by 4358 Å. A Wratten 2B filter was used for this purpose. The Raman spectrum was observed at 40 ± 5°. Exposure times varied from 15 seconds to 18 hours and slit widths from 50 to 500 $\mu$ for the photographic work. Frequencies were measured by graphical comparison to an Argon reference spectrum printed on the same film. Polarization measurements were made by the method described by Rank and Kagarise.[11] The spectrum of liquid $Sn(CH_3)_4$ is shown in Fig. 1 and in Table I.

TABLE I

THE RAMAN SPECTRUM OF $Sn(CH_3)_4$

| Frequency, cm.⁻¹ (obsd.) | Relative intensity | Polarization factor | Interpretation |
|---|---|---|---|
| 4130 | v.w. | .. | 2915 + 1205 = 4120 |
| 4108 | v.w. | .. | 2915 + 1194 = 4109 |
| 3235 | v.w. | .. | 2915 + 2(157) = 3229 |
| 2987 | 3.5 | 0.72 | $\nu_5(E)$, $\nu_{13}(F_2)$ |
| 2915 | 7.9 | 0.02 | $\nu_1(A_1)$, $\nu_{14}(F_2)$ |
| 2840 | v.w. | .. | 2987 − 157 = 2830 |
| 2368 | w. | .. | 2(1194) = 2388 |
| 2086 | v.v.w. | .. | 1445 + 508 + 157 = 2110 |
| 1974 | v.w. | .. | 1205 + 768 = 1973 |
| 1880 | v.w. | .. | 1205 + 508 + 157 = 1870 |
| 1719 | v.w. | .. | 1205 + 508 = 1713 |
| 1548 | v.w. | .. | 2(768) = 1536 |
| 1205 | 4.5 | 0.10 | $\nu_2(A_1)$ |
| 1194 | 3.8 | 0.65 | $\nu_{16}(F_2)$ |
| 1072 | v.w. | .. | 2(530) = 1060 |
| 996 | v.w. | .. | 2(508) = 1016 |
| 832 | v.w. | .. | 508 + 2(157) = 822 |
| 768 | m. | .. | $\nu_7(E)$, $\nu_{17}(F_2)$ |
| 664 | v.w. | .. | 508 + 157 = 665 |
| 530 | 3.9 | 0.83 | $\nu_{18}(F_2)$ |
| 508 | 10.0 | 0.04 | $\nu_3(A_1)$ |
| 370 | v.w. | .. | 530 − 157 = 373 |
| 298 | v.w. | .. | 2(157) = 314 |
| 157 | 6.1 | 0.80 | $\nu_8(E)$, $\nu_{19}(F_2)$ |

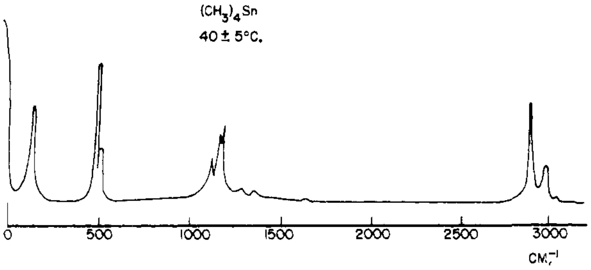

Fig. 1.—The Raman spectrum of $Sn(CH_3)_4$.

**Infrared Spectrum.**—The infrared spectra were obtained with a double beam infrared spectrometer (Perkin–Elmer Model 21). The spectral region from 2 to 25 $\mu$ was studied using $CaF_2$, NaCl and KBr optics. Sealed liquid cells[12,13] of thickness from 0.025 to 0.196 mm. were used for the study of the liquid. The extremely strong band at 13 $\mu$ was also studied using a capillary liquid cell[12,13] and in dilute $CS_2$ solution. The spectrum of gaseous $Sn(CH_3)_4$ was obtained with 10 cm. cells at pressures from 5 to 90 mm. The infrared spectrum of the gas is shown in Fig. 2 and of the liquid in Fig. 3. The frequencies of all the bands are given in Tables II and III.

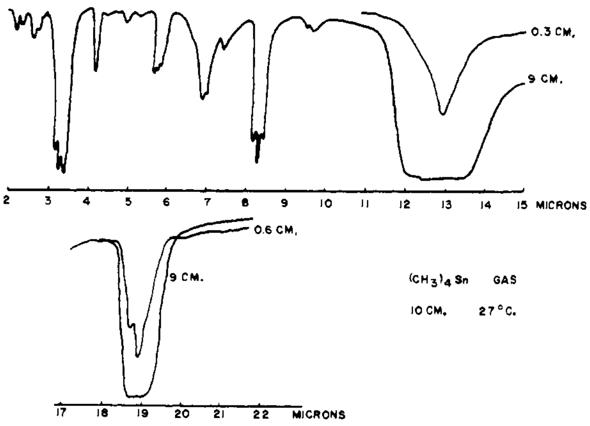

Fig. 2.—The infrared spectrum of $Sn(CH_3)_4$ (gas).

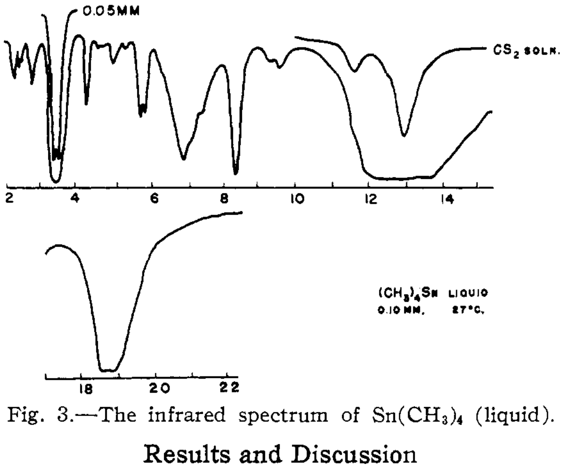

Fig. 3.—The infrared spectrum of $Sn(CH_3)_4$ (liquid).

## Results and Discussion

Previous Raman spectrum studies have been reported by Pai,[4] by Siebert,[6,7] and by Lippincott

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[9] C. E. Waring and W. S. Horton, THIS JOURNAL, **67**, 540 (1945).

[10] Walter F. Edgell and C. H. Ward, *ibid.*, **76**, 1169 (1954).

[11] D. H. Rank and R. E. Kagarise, *J. Opt. Soc. Am.*, **40**, 89 (1950).

[12] V. Z. Williams, *Rev. Sci. Instr.*, **19**, 135 (1948).

[13] R. C. Lord, R. S. McDonald and Foil A. Miller, *J. Opt. Soc. Am.*, **42**, 149 (1952).

TABLE II

THE INFRARED SPECTRUM OF $Sn(CH_3)_4$ (GAS)

| Frequency, cm.$^{-1}$ (obsd.) | Description | Relative intensity | Interpretation |
|---|---|---|---|
| 4439 | sh., br. | w. | 2991 + 1447 = 4438 |
| 4378 | s. | w. | 2919 + 1447 = 4366 |
| 4189 | s. | v.w. | 2991 + 1200 = 4191 |
| 4112 | s. | v.w. | 2919 + 1200 = 4119 |
| 3685 | s. | w. | 2919 + 771 = 3690 |
| 3595 | sh., br. | v.w. | 2(1205) + 1200 = 3610 |
| 3457 | sh., br. | v.w. | 2919 + 529 = 3448 |
| 3118 | sh., br. | v.v.w. | 2991 + 157 = 3148 |
| 3047 | s. | s. | ........ |
| 2991 | s. | s. | $\nu_{13}(F_2)$ |
| 2919 | s. | s. | $\nu_{14}(F_2)$ |
| 2812 | sh., br. | v.v.w. | 1447 + 1205 + 157 = 2809 |
| 2384 | s. | m. | 2(1200) = 2400 |
| 2232 | br. | v.w. | 1447 + 771 = 2218 |
| 2119 | v.br. | v.w. | 1205 + 771 + 157 = 2133 |
| 1975 | br. | v.w. | 1447 + 529 = 1976 or 1205 + 771 = 1976 |
| 1858 | br. | v.w. | 1200 + 508 + 157 = 1865 |
| 1740 | | | 1205 + 529 = 1734 or |
| 1730 | | | 1200 + 529 = 1739 |
| 1722 | s. | m. | |
| 1717 | | | 1200 + 508 = 1708 |
| 1708 | | | |
| 1698 | | | |
| 1447 | br. | m. | $\nu_{15}(F_2)$ |
| 1354 | br. | w. | 1200 + 157 = 1357 |
| 1207 | | | |
| 1200 | PQR | s. | $\nu_{16}(F_2)$ |
| 1192 | | | |
| 1056 | br. | v.w. | 2(529) = 1058 |
| 1034 | br. | w. | 529 + 508 = 1037 |
| 800 | sh. | v.v.w. | Impurity |
| 771 | v.v.br. | v.v.s. | $\nu_{17}(F_2)$ |
| 536 | | | |
| 529 | PQR | v.s. | $\nu_{18}(F_2)$ |
| 523 | | | |

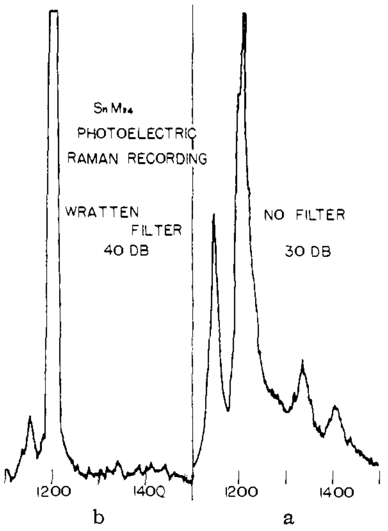

Fig. 4.—Raman spectrum of $SnMe_4$ between 1100–1500 cm.$^{-1}$: a, without Wratten filter; b, with Wratten filter.

TABLE III

THE INFRARED SPECTRUM OF $Sn(CH_3)_4$ (LIQUID)

| Frequency, cm.$^{-1}$ (obsd.) | Description | Relative intensity | Interpretation |
|---|---|---|---|
| 4422 | sh., br. | w. | 2982 + 1445 = 4427 |
| 4378 | s. | w. | 2914 + 1445 = 4359 |
| 4168 | s. | w. | 2982 + 1190 = 4172 |
| 4103 | s. | w. | 2914 + 1190 = 4104 |
| 3676 | s. | m. | 2914 + 764 = 3678 |
| 3605 | sh., br. | w. | 2(1205) + 1190 = 3600 |
| 3544 | sh., br. | v.w. | 2982 + 524 = 3506 |
| 3445 | sh., br. | v.w. | 2914 + 524 = 3438 |
| 2982 | s. | s. | $\nu_{13}(F_2)$ |
| 2914 | s. | s. | $\nu_{14}(F_2)$ |
| 2363 | s. | m. | 2(1190) = 2380 |
| 2216 | br. | v.w. | 1445 + 764 = 2209 |
| 2131 | br. | v.w. | 1205 + 764 + 157 = 2126 or 1445 + 524 + 157 = 2126 |
| 1962 | br. | w. | 1445 + 524 = 1969 or 1205 + 764 = 1969 |
| 1861 | br. | v.w. | 1190 + 508 + 157 = 1855 |
| 1717 | s. | m. | 1190 + 524 = 1714 |
| 1697 | s. | m. | 1190 + 508 = 1698 |
| 1445 | v.br. | s. | $\nu_{15}(F_2)$ |
| 1412 | sh., br. | m. | ........ |
| 1348 | sh., br. | m. | 1190 + 157 = 1347 |
| 1190 | s. | s. | $\nu_{16}(F_2)$ |
| 1050 | sh., br. | v.w. | 2(524) = 1048 |
| 1029 | br. | w. | 508 + 524 = 1032 |
| 764 | v.v.br. | v.v.s. | $\nu_{17}(F_2)$ |
| 524 | br. | v.s. | $\nu_{18}(F_2)$ |

and Tobin.[8] Our results are most nearly in agreement with those of Siebert. We resolve the line at 1200 cm.$^{-1}$ into a doublet at 1194 and 1205 cm.$^{-1}$ in agreement with the findings of Lippincott and Tobin. Apparently, however, we did not achieve as high a resolution as these workers since we did not obtain partial resolution of the line at 157 cm.$^{-1}$. We do not observe the lines reported only by Pai at 262, 952 and 1262 cm.$^{-1}$; they are certainly due to impurities. The same may be true for the line found by Siebert at 1434 and by Lippincott and Tobin at 1451 cm.$^{-1}$ and the line reported at 1046 by Pai and at 1053 by Lippincott and Tobin. We do not observe either of them.

Raman lines have been reported recently[8] at 1346 and 1400 cm.$^{-1}$, and the latter of these was assigned to a fundamental frequency of vibration. Figure 4a shows the detailed photoelectric recording of this region of the spectrum. The lines in question (which we find at 1335 and 1406 cm.$^{-1}$) are seen to the right of the 1200 doublet. However, these positions also correspond to the strong Raman lines 2915 and 2987 cm.$^{-1}$ if excited by the mercury line 4077 Å. instead of by the 4358 Å. line. If this latter interpretation were correct, these same lines also should appear, with greater intensity, excited by the stronger mercury line 4046 Å. The 2915 cm.$^{-1}$ line does indeed appear displaced 1144 cm.$^{-1}$ from the 4358 Å. mercury line; the presence of the 2987 cm.$^{-1}$ line (at about 1220 cm.$^{-1}$) is not obvious. And perhaps this fact led to the choice of 4358 Å. as the exciting mercury line and hence to a belief in the reality of displacements at 1346 and 1400 cm.$^{-1}$. A Wratten 2B gelatin filter strongly absorbs light in the 4100 Å. region while passing 4358 Å. with a slight diminution in intensity. Figure 4b shows the photoelectric recording of the same region of the spectrum taken with the Raman tube wrapped with several layers of this filter. The gain has been increased more than threefold to substantially overcompensate for the lessened 4358 Å. intensity reaching the sample. In this trace the Raman lines excited by 4358 Å. should appear stronger than in Fig. 4a. The "1144" line has been greatly reduced in intensity while the "1346" and "1400" lines have disappeared into the systemic noise. Moreover, while the apparent intensity of the 1200 cm.$^{-1}$ doublet has increased, it is much more narrow than shown in Fig. 4a. Thus a relatively strong line adjacent to and slightly overlapping 1205 cm.$^{-1}$ was removed by the filter. It can be concluded that the lines "1144" and *ca.* "1220 cm.$^{-1}$" are the Raman displacements 2715 and 2987 cm.$^{-1}$ excited by the mercury line 4046 Å. and the lines at "1346" and "1400," these same displacements excited by the mercury line 4077 Å.

Infrared spectra of tin tetramethyl have been previously reported by Kettering and Sleator[3] and by Lippincott and Tobin.[8] This work differs rather substantially from the above at wave lengths shorter than 5 μ. Presumably this results from the higher pressure, greater resolution and purer samples used in this study. At wave lengths longer than 5 μ our results are in reasonably good agreement with the earlier work except for the absence of an occasional impurity band. The very strong infrared band found at 771 cm.$^{-1}$ in the gas phase and at 764 cm.$^{-1}$ in the liquid phase has been reported[8] as a multiplet band in both phases. We have observed the peaks at 760 and 774 cm.$^{-1}$, reported[8] as strong for the gas phase, only with samples containing traces of ethyl ether and never when using the highly purified material. No shoulders were observed in this study for this band in the liquid state. The infrared band previously found[8] at 1118 cm.$^{-1}$ is also due to ethyl ether. About 1% ether is sufficient to give rise to this band.

## Assignment of Frequencies

The $Sn(CH_3)_4$ molecule, like the other tetramethyl compounds of Group IV elements, appears to have the symmetry of the tetrahedral point group $T_d$. The number of fundamental vibrations and the selection rules are listed in Table IV.

TABLE IV

SELECTION RULES FOR FUNDAMENTAL VIBRATIONS OF $Sn(CH_3)_4$

| Fundamental type | No. of fundamentals | Raman activity | Infrared activity |
|---|---|---|---|
| $A_1$ | 3 | Pol. | .... |
| $A_2$ | 1 | .... | .... |
| E | 4 | Depol. | .... |
| $F_1$ | 4 | .... | .... |
| $F_2$ | 7 | Depol. | Active |

In describing the vibrations it will be convenient to use the idea of *specific* (*and hypothetical*) characteristic motions.[14] Each such definite set of atomic displacements is chosen to be a possible fundamental vibration and hence each is orthogonal to all the others. It is useful to deal with the frequency which is characteristic of this definite motion. The actual vibrations are combinations of these simplified motions and the observed vibrational frequencies may be regarded as combinations of the corresponding characteristic frequencies. Because the tin atom is much heavier than the other atoms of this molecule these characteristic motions can be chosen to be good approximations to the actual vibrations in this case.

Consider first of all an "isolated" $CH_3$ group. Its modes may be described as the symmetrical stretching and deformation vibrations and the doubly degenerate, asymmetrical stretching and deformation vibrations. These motions in the "combined" molecule take place against a stationary tin atom. Orthogonality now requires that the methyl group be rigid in the remaining modes of motion. These may be described as skeletal stretching and deformation motions plus the torsional and rocking motions of the methyl group. The set of these simplified motions which form a possible group of fundamental modes for $Sn(CH_3)_4$ are found in Table V. When a methyl group vibrates, it deforms the Sn–C bond, and the extent to which the Sn atom moves depends upon the mass of the Sn atom and the stiffness of the bond. Since the mechanical strength of this bond is not great and the Sn mass is large, the displacement of the Sn atom is small. Thus there is little mass coupling between the $CH_3$ groups and little coupling between the skeletal and methyl vibrations and the descriptions of Table V are good approximations to the actual motions. Consider the vibrations $\nu_1$ and $\nu_{14}$. They consist of symmetrical stretching motions of the $CH_3$ groups and differ by the phase relationships between the motions of the several groups. It is a consequence of the above that these two frequencies should be nearly the same and might not be resolvable experimentally. The same may be expected for all motions of the methyl groups which differ only in this phase relationship. The confirmation of this expectation is the primary feature of the experimental spectra.

TABLE V

DESCRIPTION OF FUNDAMENTAL VIBRATIONS OF $Sn(CH_3)_4$

| Description | $A_1$ | $A_2$ | E | $F_1$ | $F_2$ |
|---|---|---|---|---|---|
| $CH_3$ asymmetrical stretch | | | $\nu_5$ | $\nu_9$ | $\nu_{13}$ |
| $CH_3$ symmetrical stretch | $\nu_1$ | | | | $\nu_{14}$ |
| $CH_3$ asymmetrical deformation | | | $\nu_6$ | $\nu_{10}$ | $\nu_{15}$ |
| $CH_3$ symmetrical deformation | $\nu_2$ | | | | $\nu_{16}$ |
| $CH_3$ rocking | | | $\nu_7$ | $\nu_{11}$ | $\nu_{17}$ |
| Skeletal stretching | $\nu_3$ | | | | $\nu_{18}$ |
| Skeletal deformation | | | $\nu_8$ | | $\nu_{19}$ |
| $CH_3$ torsion | | $\nu_4$ | | $\nu_{12}$ | |

The fundamental frequencies of $Sn(CH_3)_4$ are readily assigned in terms of these ideas and the observed polarization data of the Raman spectrum. The strong, polarized Raman line at 2915 cm.$^{-1}$ is assigned to the symmetrical $CH_3$ stretching

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[14] Walter F. Edgell, to be published.

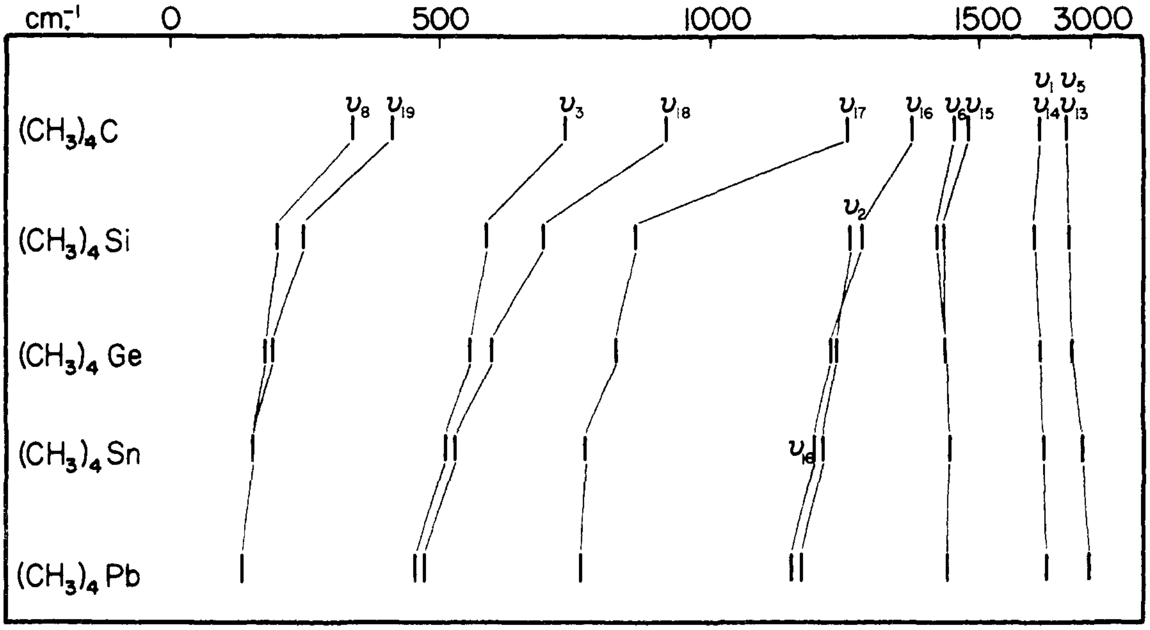

Fig. 5.—Fundamental frequencies of $M(CH_3)_4$ molecules.

fundamentals $\nu_1$ and $\nu_{14}$. The latter fundamental is observed in the infrared at 2914 cm.$^{-1}$ for the liquid and 2919 for the gas. The strong, depolarized Raman line at 2987 cm.$^{-1}$ is readily assigned to the asymmetrical $CH_3$ stretching modes $\nu_5$ and $\nu_{13}$. An infrared band corresponding to $\nu_{13}$ was observed at 2982 cm.$^{-1}$ in the liquid state and at 2991 cm.$^{-1}$ in the gaseous state. The strong infrared band at 1445 cm.$^{-1}$ in the liquid and 1447 in the gas arises from the asymmetrical deformation vibration $\nu_{15}$. The corresponding Raman line arising from either $\nu_6$ or $\nu_{15}$ was not found. Similar vibrations are either missing or give weak Raman lines in the various methyl tin halides.[15] The strong, polarized Raman line at 1205 cm.$^{-1}$ arises from the $A_1$ symmetrical $CH_3$ deformation vibration $\nu_2$. Another strong but depolarized Raman line is found at 1194 cm.$^{-1}$ and must be assigned to the $F_2$ symmetrical $CH_3$ deformation vibration $\nu_{16}$. The resolution of these two lines was achieved by both photographic and photoelectric techniques. The $\nu_{16}$ fundamental appears in the infrared spectrum of the liquid as a strong band at 1190 cm.$^{-1}$ and for the gas and a strong band at 1200 cm.$^{-1}$ with PQR branches. Here two non-skeletal fundamentals have been resolved which differ only in the phase relationship of the methyl group motions. The coupling is greatest here because the C atoms move by far the largest amount along the $CH_3$ axis, and hence the Sn–C bond, in the symmetrical deformation vibration.

The symmetrical skeletal stretching vibration $\nu_3$ gives rise to the polarized Raman line at 508 cm.$^{-1}$ while the $F_2$ vibration $\nu_{18}$ gives rise to the Raman line at 530 cm.$^{-1}$ and the infrared bands at 524 and 529 cm.$^{-1}$ for the liquid and gaseous states, respectively. A very strong infrared band is found at 771 for the gas and 764 cm.$^{-1}$ for the liquid which arises from the methyl rocking vibration $\nu_{17}$. The corresponding Raman line was found at 768 cm.$^{-1}$. There remain three fundamentals to be assigned, $\nu_8$, $\nu_{19}$ and $\nu_7$. Only one strong, diffuse Raman line at 157 cm.$^{-1}$ is left. Since $\nu_8$ and $\nu_{19}$ are expected in this region and, further, should have almost the same frequency, the Raman line is assumed to arise from this unresolved pair of fundamentals. The methyl rocking frequency $\nu_7$ is only active in the Raman effect. No line is found which cannot be otherwise explained as arising from a combination vibration. In view of the fact that vibrations which differ only by the phase of the motion of the different methyl groups have the same or nearly the same frequency in this molecule, $\nu_7$ is presumed to be the same as $\nu_{17}$. No attempt has been made to assign the inactive torsional frequencies.

The fundamental frequencies are collected in Table VI. Numerical values have been assigned to the inactive frequencies on the basis of the principles discussed above. Overtones and combinations of these fundamentals account for all the weaker lines in the Raman and infrared spectrum as indicated in Tables I–III.

TABLE VI

THE FUNDAMENTAL FREQUENCIES OF $Sn(CH_3)_4$

| Fundamental | ω (cm.$^{-1}$) | Fundamental | ω (cm.$^{-1}$) |
|---|---|---|---|
| $\nu_1$ ($A_1$) | 2915 | $\nu_{11}$ ($F_1$) | (768) |
| $\nu_2$ ($A_1$) | 1205 | $\nu_{12}$ ($F_1$) | i.a. |
| $\nu_3$ ($A_1$) | 508 | $\nu_{13}$ ($F_2$) | 2987 |
| $\nu_4$ ($A_2$) | i.a. | $\nu_{14}$ ($F_2$) | 2915 |
| $\nu_5$ (E) | 2987 | $\nu_{15}$ ($F_2$) | (1445) |
| $\nu_6$ (E) | (1445) | $\nu_{16}$ ($F_2$) | 1194 |
| $\nu_7$ (E) | 768 | $\nu_{17}$ ($F_2$) | 768 |
| $\nu_8$ (E) | 157 | $\nu_{18}$ ($F_2$) | 530 |
| $\nu_9$ ($F_1$) | (2987) | $\nu_{19}$ ($F_2$) | 157 |
| $\nu_{10}$ ($F_1$) | (1445) | | |

A graphical comparison of the fundamentals for tetramethyl molecules is given in Fig. 5. The

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(15) Walter F. Edgell and Curt H. Ward, to be published.

data of Rank, Saksena and Shull,[16] of Siebert, and of Lippincott and Tobin were used for all molecules but $Sn(CH_3)_4$. The previous tentative assignment of a band at 1250 cm.$^{-1}$ to $\nu_{17}$ in $Si(CH_3)_4$ is inconsistent with the trends shown here. A strong, infrared band has been observed[16] at 863 cm.$^{-1}$ for this molecule and we believe it is better assigned to $\nu_{17}$ as indicated in Fig. 5. The other methyl rocking frequency $\nu_7$ is very weak in all the molecules of this series and has not been assigned with certainty in any of them.

It should be noted that the nature of the atomic motions in $\nu_{17}$ and $\nu_{18}$ change when the central atom becomes light. In $C(CH_3)_4$ skeletal stretching and methyl rocking motions take place in both $\nu_{17}$ and $\nu_{18}$. However, the present evidence suggests that $\nu_{18}$ is more methyl rocking than skeletal stretching and *vice versa* for $\nu_{17}$.

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[16] D. H. Rank, B. D. Saksena and E. R. Shull, *Disc. Faraday Soc.*, **9**, 187 (1950).

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# The Molecular Structure of Trisilylamine $(SiH_3)_3N$[1,2]

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The structure of trisilylamine has been studied by electron diffraction in the gas phase. Assuming the molecule to have trigonal symmetry, the $Si_3N$ skeleton is found to be coplanar. The parameter values and limits of error are Si–N = 1.738 ± 0.020 Å., Si...Si = 3.005 ± 0.020 Å., Si–H = 1.54 ± 0.05 Å., ∠Si–N–Si = 119.6° to within 1.0°, $2a_{Si\ldots Si} = \overline{l^2}_{Si\ldots Si} - \overline{l^2}_{Si-N} = 0.0030 \pm 0.0014$ Å.[2] It appears likely that the coplanar bonding around the nitrogen atom occurs with only about 50% delocalization of the odd electron pair.

Professor A. B. Burg has called to our attention the interesting substance trisilylamine, which is a very weak electron donor in comparison with its analog trimethylamine, and in place of the ordinary Lewis acid–base type reaction with electron acceptors frequently undergoes disproportionation and exchange.[3] An attractive possible explanation of this different behavior is that relatively stable, unfilled d orbitals on the silicon atoms are conjugated with the unshared pair of electrons on the nitrogen atom, making the electrons less available for coördination with acceptor reagents. This conjugation would also, presumably, give rise to an increased nitrogen bond angle and an abnormally short Si–N bond distance, two points which could be readily checked by an electron diffraction investigation of the structure.

**Experimental.**—A sample of essentially pure trisilylamine was kindly supplied by Mr. Earnest A. Kuljian. The photographs were made and interpreted in the ways described in past reports from this Laboratory[4]; the electron wave length and the camera distance were about 0.06 Å. and 11 cm., respectively.

**Results.**—The radial distribution curve (Fig. 1) shows two strong peaks at 1.735 and 3.00 Å. These peaks are due to the bonded Si–N and non-bonded Si ... Si interactions, and correspond to an average bond angle of 120°, *i.e.*, to a coplanar $Si_3N$ skeleton.

Theoretical intensity curves were calculated for trigonally symmetrical models over the shape parameter ranges $1.694 \leqslant$ Si ... Si/Si–N $\leqslant 1.734$ (corresponding to ∠Si–N–Si = 115.6 to 120.2°[5]) and $1.102 \leqslant$ Si–N/Si–H $\leqslant 1.218$. In addition, the vibrational amplitude factor $\exp(-a_{ij}q^2)$ for the Si ... Si interactions was studied over the range $0 \leqslant a_{Si\ldots Si} \leqslant 0.0003$. In all models the coefficient $a_{Si-H}$ was given the value 0.00022, which is a reasonable value in view of general experience in these Laboratories. The effective value 1.25 was used for $Z_H$. In most models terms were included for only the Si ... Si and the bonded interactions; the effect of the N–H interaction was tested and found to be negligible. Of the curves shown (Fig. 1) A and H are unacceptable, D, E and F are acceptable but close to the limits of uncertainty, and B, C and G are in good agreement with the observed intensity. The usual detailed qualitative and quantitative (Table I is an example) procedures lead to parameter values corresponding closely to Model C except for $a_{Si\ldots Si}$. These values and their limits of error are Si–N = 1.738 ± 0.020 Å., Si ... Si = 3.005 to 0.020 Å., Si–H = 1.54 ± 0.05 Å., ∠Si–N–Si = 119.6° to within 1.0°, $2a_{Si\ldots Si} = \overline{l^2}_{Si\ldots Si} - \overline{l^2}_{Si-N}$ 0.0030 ± 0.0014 Å.[2]

**Discussion.**—The structure of trisilylamine provides a particularly satisfying explanation of its chemical behavior as a weak electron donor. The essentially coplanar $Si_3N$ group and the short Si–N bond length[6] indicate that the odd electron pair is involved to a considerable extent in $\pi$-bonding instead of being localized in a nitrogen orbital as in ammonia or the aliphatic amines.

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[2] Presented at the XII International Congress of Pure and Applied Chemistry, September, 1951, New York City, and at the International Congress of Crystallography, Stockholm, July, 1951.

[3] See A. B. Burg, First, Second, and Third Annual Technical Reports, "Investigation of Water Reactive Compounds" N6onr-238-TO-I (1947, 1948, 1949).

[4] See, for example, K. Hedberg and A. J. Stosick, THIS JOURNAL, **74**, 954 (1952).

[5] Trigonally symmetrical models with ∠Si–N–Si > 120° are of course not real; the curves are useful for interpolation, however.

[6] Two pairs of estimates for the SiN single- and double-bond lengths may be mentioned: (a) 1.80 Å. (1.17 + 0.74 − 0.09 |3.0 − 1.8|, V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941)) and 1.62 Å. (1.07 + 0.62 − 0.06 |3.0 − 1.8|, W. Gordy, *J. Chem. Phys.*, **15**, 81 (1947)), and (b) 1.87 and 1.67 Å. (L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, N. Y., 1940, p. 164).