UCRL-11236

University of California

Ernest O. Lawrence Radiation Laboratory

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

SOME PROPERTIES OF NORMAL- AND ISO-TETRASILANE

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted for publication in
J. Inorganic Chem.

UCRL-11236

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

SOME PROPERTIES OF NORMAL- AND ISO-TETRASILANE

Sudarshan D. Gokhale and William L. Jolly

December 1963

Contribution from the Department of Chemistry, and
Inorganic Materials Research Division of the Lawrence
Radiation Laboratory, University of California
Berkeley, California

Some Properties of Normal- and *Iso*-Tetrasilane

By Sudarshan D. Gokhale[1] and William L. Jolly

The two isomers of tetrasilane were prepared in an ozonizer-type electric discharge and isolated by gas chromatography. The isomers were identified, consistently, by their nmr spectra, their infrared spectra and their relative volatilities.

---

(1) Permanent address: Chemistry Division, Atomic Energy Establishment, Trombay, Bombay.

Introduction

Stock *et al*[2] obtained normal tetrasilane from the products of the

(2) A. Stock, P. Stiebeler and F. Zeidler, Ber., 56, 1695 (1923).

reaction of magnesium silicide with hydrochloric acid, but they were unable to isolate the branched-chain isomer. Fehér *et al*[3] achieved a

(3) F. Fehér, H. Keller, G. Kuhlbörsch and H. Luhleich, Angew. Chem, 70, 402 (1958).

partial separation of the two isomers by fractional distillation and reported the boiling and freezing points, densities, and refractive indexes of the isomers. Borer and Phillips[4] and Fehér and Strack[5]

(4) K. Borer and C. S. G. Phillips, Proc. Chem. Soc., 189 (1959).

(5) F. Fehér and H. Strack, Naturwiss., 50, 570 (1963).

showed that the mixture of silanes obtained from the reaction of magnesium silicide with aqueous acid can be separated into many components, including *n*- and *iso*-tetrasilane, by gas chromatography.

We have prepared a mixture of higher silanes by an electric discharge method similar to that used to prepare the higher germanes[6]

(6) J. E. Drake and W. L. Jolly, J. Chem. Soc., 2807 (1962).

and trisilane[7]. The isomers of tetrasilane were separated by gas

(7) E. J. Spanier and A. G. MacDiarmid, Inorg. Chem., 1, 432 (1962).

chromatography and identified by their relative volatilities, by their infrared spectra, and, most unequivocally, by their nmr spectra.

Experimental

The tetrasilanes were prepared from pure silane by the ozonizer-type electric discharge method,[6,7] subjecting the products higher than trisilane to gas-liquid chromatographic separation. The details of the method will be published elsewhere. Generally the ratio of n-tetrasilane to iso-tetrasilane was 5:1.

The infrared spectra were obtained with Perkin-Elmer Infracord Spectrophotometers (NaCl Model 137B and KBr Model 137) using a 5-cm. NaCl cell and a 6-cm. KBr cell, respectively. The spectra are given in Figure 1. The infrared spectrum of normal tetrasilane shows bands at the following frequencies (cm^{-1}): 2155 (s), 1020 (s), 935 (m), 917 (w), 879 (s), 748 (w), 741 (w), 701 (sh; m), 694 (s), 662 (s), 535 (w), 470 (w). The spectrum of iso-tetrasilane shows bands at the frequencies (cm^{-1}): 2210 (w), 2155 (s), 1000 (w), 945 (sh; w), 935 (m), 915, 906, 898 (m), 871 (s), 866 (s), 698 (sh; m), 693 (s).

The vapor pressure of n-tetrasilane was found to be 10.0 ± 1.0 mm at 0° and 29.5 ± 1.0 mm at 25°. The vapor pressure of iso-tetrasilane could not be measured accurately because even our best sample

contained perhaps as much as 5% impurity. However, we can state that, at 0°, the vapor pressure of iso-tetrasilane is more than 5 mm higher than that of n-tetrasilane. In the chromatographic separation, the iso-isomer preceded the normal isomer, in keeping with the vapor pressure measurements.

The mass spectrum of n-tetrasilane showed a fragmentation pattern of the four different types of ions with the following relative order of intensities: $Si_3^+ > Si_2^+ > Si_4^+ > Si_1^+$; this order is the same as that found for n-tetragermane[8]. The mass spectrum of iso-tetrasilane was

(8) J. E. Drake and W. L. Jolly, Proc. Chem. Soc., 379, (1961).

not obtained.

The isomers were diluted with "conditioned" tetramethylsilane (TMS) for measurement of the nmr spectra. "Conditioned" TMS was prepared by treating the middle fraction of a fractional distillation of TMS with silane, followed by fractional condensation on the vacuum line using traps at -78°, -130°, and -196°. The TMS which collected in the -130° trap was used to dilute the tetrasilanes enough to fill the nmr tubes to the optimum height. It also served as an internal standard. The proton magnetic resonance spectra were obtained using the A-60 and 100 Mc Varian Associates nmr spectrometers[9].

(9) The cooperation and help given by Varian Associates in permitting us to use their 100 Mc spectrometer is gratefully acknowledged.

The spectra are presented in Figures 3 to 5. For completeness, spectra were obtained for disilane and trisilane also. Figure 2 shows the ^{29}Si satellite spectra for trisilane at 100 Mc and 60 Mc. The ppm values given are to lower field of the TMS.

Discussion

The more volatile isomer of tetragermane was assumed to be the branched-chain isomer, in analogy to the relative volatilities of the butane isomers. In our following discussions of the infrared spectra and nmr spectra, it will be seen that this assignment is born out.

Infrared Spectra.- In the infrared spectrum of iso-tetrasilane $[(SiH_3)_3SiH]$, one expects the presence of bands due to the SiH group and the absence of bands due to the SiH_2 group. The weak absorption at 2210 cm^{-1}, on the high frequency side of the main Si-H stretching frequency band, probably corresponds to a stretching frequency of the SiH group. It is apparent from our study of the nmr spectrum that the SiH proton is shielded more than the SiH_3 protons. We conclude that the SiH bond has a higher electron density, and that therefore it is stronger and has a higher stretching frequency than a corresponding bond in an SiH_3 group.

There is no significant absorption in the KBr region or in the 720 - 830 cm^{-1} region in the case of iso-tetrasilane at 10 mm pressure, whereas there is a strong absorption band at 662 cm^{-1} and a weak absorption band at 748 cm^{-1} in the case of n-tetrasilane. The infrared spectrum of trisilane shows similar, but much weaker, absorptions in

the 740 - 750 cm^{-1} and 570 - 590 cm^{-1} regions. It is therefore suggested that these bands are due to the SiH_2 group.

The strong absorption band near 870 cm^{-1} in both tetrasilanes, presumably due to the SiH_3 symmetrical deformation, is split in the case of iso-tetrasilane. The analogous type of resonance splitting of the methyl symmetrical deformation band, due to more than one methyl group on a carbon atom, is observed in the infrared spectra of alkanes.[10]

---

(10) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", John Wiley & Sons, Inc., New York, 1958, p. 24.

We suggest that the band with distinct PQR branches centered at 906 cm^{-1} in the iso-tetrasilane spectrum corresponds to an SiH bending mode. Infrared spectra of the silanes seem to be less complex than the corresponding spectra of the alkanes because the Si-Si vibration frequencies are much lower than the Si-H vibration and bending frequencies.[11]

---

(11) G. W. Bethke and M. K. Wilson, J. Chem. Phys., 26, 1113 (1957).

Nmr Spectra.- The nmr spectrum of trisilane at 60 Mc is complicated, just as it is at 40 Mc,[12] because the chemical shift and coupling

---

(12) J. J. Turner, "High Resolution NMR Spectroscopy", Thesis, Cambridge Univ., October, 1960.

---

constant between the SiH_3 and SiH_2 protons are of the same order of

magnitude. At 100 Mc, the spectrum is relatively simple, but by far the best spectra are found in the ^{29}Si satellites. The ^{29}Si satellite spectra of trisilane at both 100 and 60 Mc are shown in Fig. 2. As expected, the $^{29}SiH_3$ resonance is split into a triplet, and the $^{29}SiH_2$ resonance is split into a septet, of which only five lines are apparent in Fig. 2.

The nmr spectrum of n-tetrasilane at 60 Mc is shown on the left side of Figure 3, and that at 100 Mc is shown in Figure 4. It will be noticed that the main resonance is complicated in each case.[13] However,

---

(13) The general shape of the main resonance is similar to that of n-tetragermane[6] and is a mirror image of that of n-butane.[14]

(14) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., New York, 1959, p. 235.

---

the ^{29}Si satellite spectra (shown in Fig. 4 for 100 Mc) are simple. As expected, the $^{29}SiH_3$ resonance is split into a triplet. The $^{29}SiH_2$ resonance is split into a sextet, of which only four components are apparent in Fig. 4, by the five protons which are nearby. Apparently the $H_3Si-^{29}SiH_2-$ and $^{29}SiH_2-SiH_2$ coupling constants are of very similar magnitude. On the low-field side of the main resonance, the $^{29}SiH_3$ and $^{29}SiH_2$ resonances are well separated. On the high-field side, the resonances overlap but are still recognizable.

The nmr spectrum of iso-tetrasilane at both 60 Mc (Fig. 3) and 100 Mc (Fig. 5) is simple. The strong SiH_3 resonance is a doublet,

and the weak SiH resonance is split into ten components, of which two or three are lost in the noise and cannot be seen in Fig. 5. The $^{29}SiH_3$ sattelite bands are shown in Fig. 5.

The chemical shifts are given in Table I. We have included our data for disilane and trisilane for comparison purposes. It is clear from the data that, as we increase the number of silicon atoms bonded to a silicon atom adjacent to a silyl group, the shielding of the protons in the silyl group decreases. This effect is just the opposite of that predicted from simple electronegativity considerations, and parallels the variations in chemical shifts of the CH_3 group in ethyl halides[15] and of the SiH_3 group in disilanyl halides.[16]

---

(15) B. P. Dailey and J. N. Shoolery, J. Am. Chem. Soc., 77, 3977 (1955).

(16) M. Abedini, C. H. Van Dyke, and A. G. MacDiarmid, unpublished data.

¶ The increase in shielding on going from the SiH_3 group to the SiH group is explicable in terms of the reduced electronegativity of silicon compared with hydrogen.

The H-H and ^{29}Si-H coupling constants are given in Table II. They are of the same order of magnitude as those reported by Abedini et at.[16] Although the mechanism of the spin-spin interaction is not clearly understood, it is logical to expect that if this interaction is through the bonds it should decrease with an increase in the number of interposed bonds. The value of 3.5 to 4 cps for the coupling constant

of vicinal protons in the higher silanes and the value of 2.75 cps of geminal protons in silane reported by Ebsworth and Turner,[17] indicate

(17) E. A. V. Ebsworth and J. J. Turner, J. Chem. Phys., 36, 2631(1962).

that something other than mere "through-bond" interaction is involved. In the case of saturated hydrocarbons, vicinal proton coupling constants lie in the range of 5-8 cps, and the geminal proton coupling constant in methane is 12.4 cps.[18]

(18) Ref. 14, pp. 193, 236.

Acknowledgment.- This research was supported by the U. S. Atomic Energy Commission.

Table I. Chemical shifts in ppm (± 0.02) to low field of TMS

Compound	$-SiH_3$	$-SiH_2-$	$-\overset{\vert}{\underset{\vert}{Si}}H$
Si_2H_6	3.26		
Si_3H_8	3.36	3.18	
n-Si_4H_{10}	3.36	3.26	
iso-Si_4H_{10}	3.42		2.93

Table II. Coupling constants in cps

Compound	$\overline{H_3Si\text{-}SiH_n}$ ± 0.2	$^{29}\overline{Si\text{-}H_3}$ ± 1.0	$^{29}\overline{Si\text{-}H_2}$ ± 1.0
Si_2H_6	3.5	199	
Si_3H_8	4.0	199	194
n-Si_4H_{10}	3.7	199	197
iso-Si_4H_{10}	4.0		

FIGURE CAPTIONS

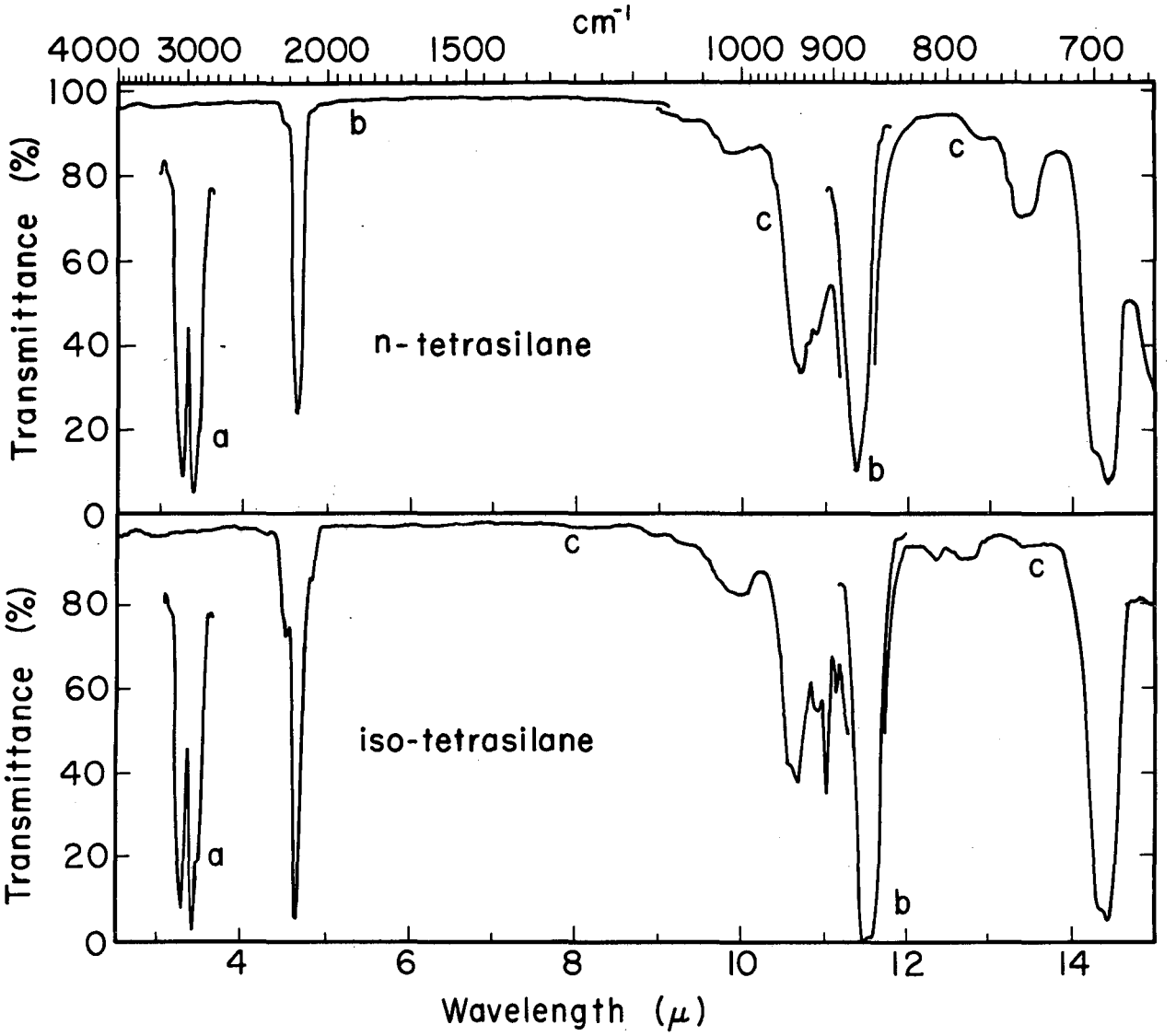
Fig. 1. Infrared spectra of normal- and iso-tetrasilane.
a: polystyrene calibration. b: 5 mm. pressure in 5-cm. cell. c: 10 mm. pressure in 5-cm. cell.

Fig. 2. Nmr spectra of trisilane at 100 and 60 Mc. Satellite resonances shown are to low field of main resonances.

Fig. 3. Nmr spectra of normal- and iso-tetrasilane. Main resonances at 60 Mc.

Fig. 4. Nmr spectrum of normal-tetrasilane. Main and satellite resonances at 100 Mc.

Fig. 5. Nmr spectrum of iso-tetrasilane. Main and satellite resonances at 100 Mc.



MUB-2290

Fig. 1

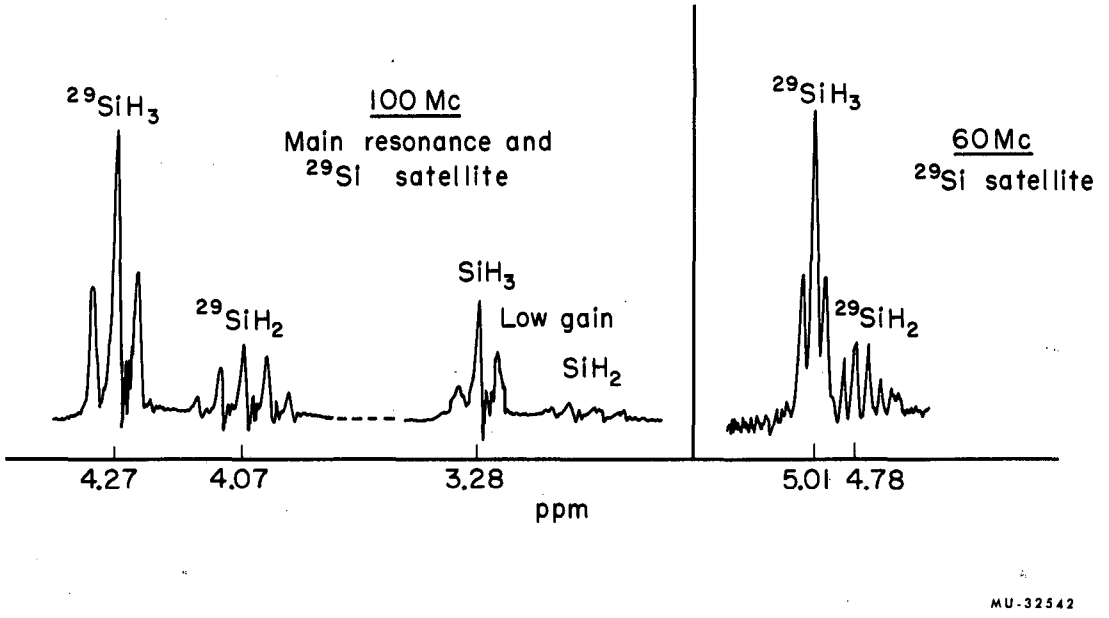

$^{29}SiH_3$
100 Mc
Main resonance and
^{29}Si satellite
$^{29}SiH_2$
SiH_3
Low gain
SiH_2
4.27
4.07
3.28
ppm
$^{29}SiH_3$
60 Mc
^{29}Si satellite
$^{29}SiH_2$
5.01
4.78
MU-32542

Fig. 2

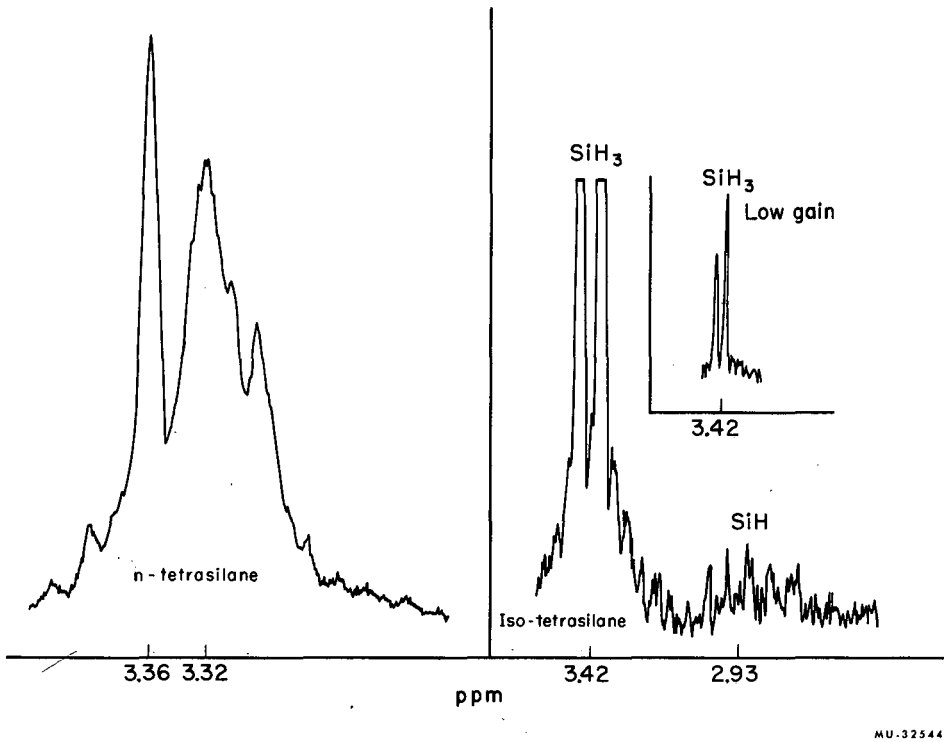

SiH3
SiH3
Low gain
3.42
SiH
n-tetrasilane
Iso-tetrasilane
3.36 3.32
3.42
2.93
ppm
MU-32544

Fig. 3

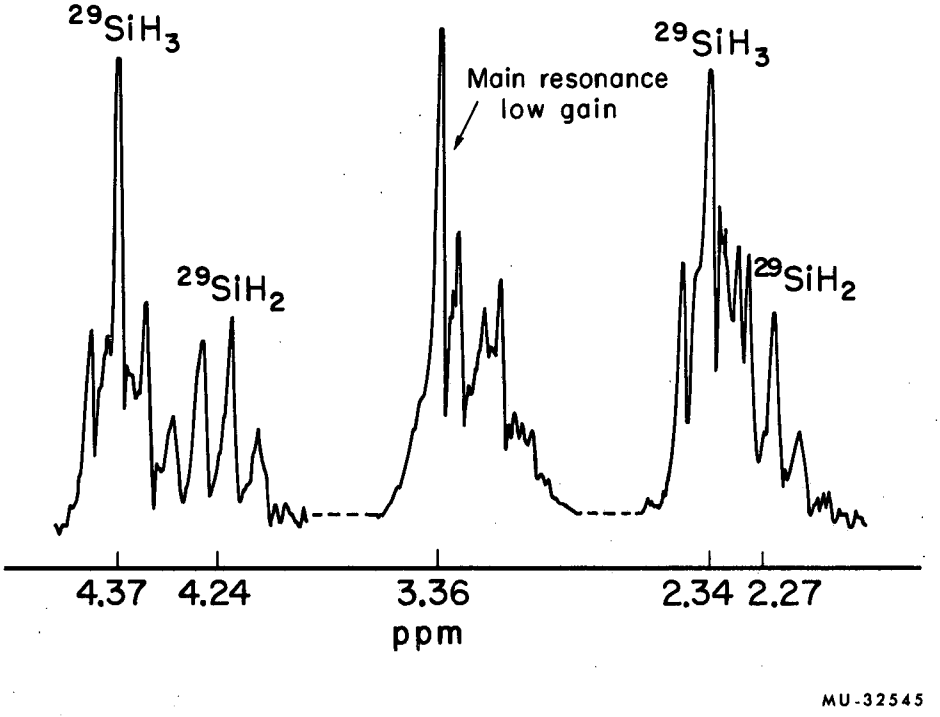

$^{29}SiH_3$
$^{29}SiH_2$
Main resonance
low gain
$^{29}SiH_3$
$^{29}SiH_2$
4.37
4.24
3.36
2.34
2.27
ppm
MU-32545

Fig. 4

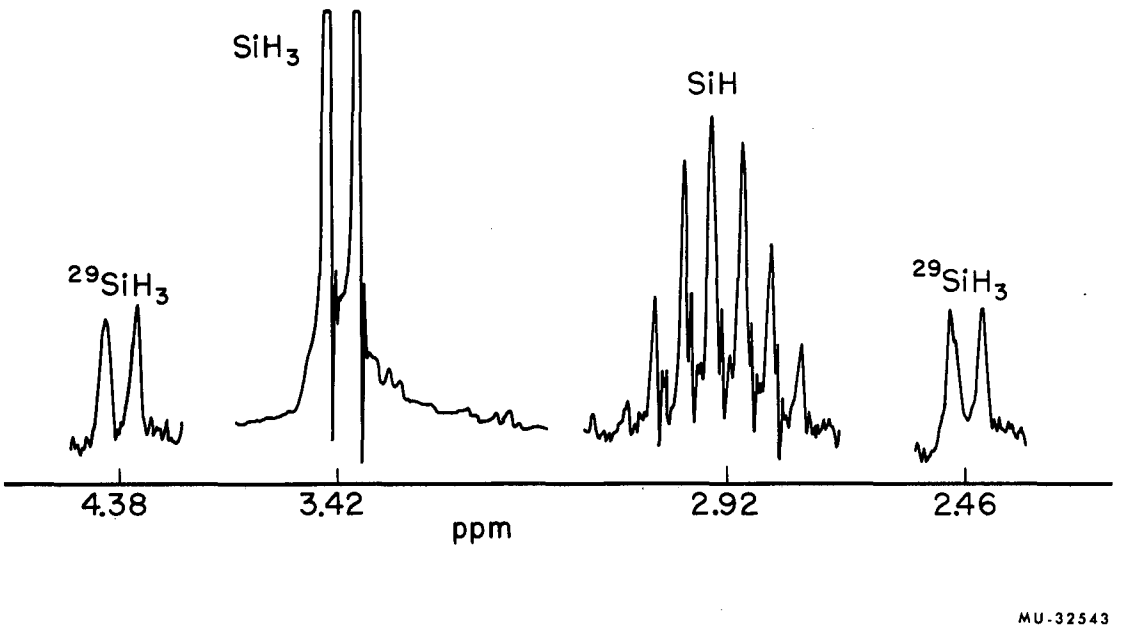


Fig. 5

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.