Stereochemistry of Silicon

BØRGE BAK, JØRGEN BRUHN and JOHN RASTRUP-ANDERSEN

Chemical Laboratory of the University of Copenhagen, Copenhagen, Denmark

New! measurements of microwave frequencies of SiD_3Cl and SiD_3F in conjunction with earlier measurements on SiH_3Cl and SiH_3F enable the authors to calculate the silicon-chlorine distance in ordinary and deuterated silyl chlorides. The results were 2.0479 ± 0.0007 Å and 2.0486 ± 0.0007 Å respectively. The silicon-fluorine distances in ordinary and deuterated silylfluorides were found to be 1.595 ± 0.010 Å in both cases.

Silicon-hydrogen and silicon-deuterium distances and the valence angles were estimated. The changes in these quantities caused by the substitution of one hydrogen atom in silane by chlorine or fluorine are small and about the same as in the pairs CH_4, CH_3Cl and CH_4, CH_3F.

Preparation and properties of SiD_3Cl and SiD_3F are described.

In the classical paper by Kipping [1] it was shown that compounds of the type SiXYZW, where X, Y, Z, and W are mono-valent radicals, can be separated into optical isomers. This excludes a *planar* arrangement of silicon and its four ligands. Later, X-ray determination of the crystal structure of SiI_4 by Hassel and Kringstad [2] revealed that the four iodine atoms were situated in the corners of a regular tetrahedron with silicon in the centre. A pyramidal arrangement with silicon at the top was thereby eliminated. A similar result for SiH_4 was found by Tindal, Straley and Nielsen [3] by the use of infrared technique. Since the bonds of tetrahedral SiX_4 molecules almost by necessity must be directed towards the corners of a *regular* tetrahedron the interesting problem of the direction and magnitude of possible deviations from regularity in cases like SiX_3Y, SiX_2Y_2 etc. remained to be solved. In a number of cases where electron-diffraction technique could be applied [4-6] deviations were found but the results were too inaccurate to give more than a rough idea of the angular and linear irregularities so demonstrated.

By the advent of microwave technique (1945—46) conditions for further progress again became favourable. 1948, Sharbaugh [7] published measurements on $Si^{28}H_3Cl^{35}$ and $Si^{28}H_3Cl^{37}$. 1949, Townes and collaborators [8] found the microwave absorption of $Si^{30}H_3Cl^{35}$. In 1950, Sharbaugh and collaborators [9] published their results for the three isotopic species Si [28,29,30] H_3F. All three

papers agreed in the statement that the silyl halides examined are symmetric tops. Such molecules have two different principal moments of inertia. The smaller moment (about the Si-halogen axis) we shall consistingly denote by I_A, the greater by I_B (adding, of course, extra symbols if we want to indicate the moment of a particular molecule). It is easy to derive that

$$(I_B - \tfrac{1}{2}I_A)m_{SiY_3X} = a^2 m_{Si}m_X + 3(a + d_Y \cos\varphi_Y)^2 m_Y m_X + 3d_Y^2\cos^2\varphi_Y m_{Si}m_Y \quad (1)$$

where Si is a silicon isotope, Y a hydrogen isotope and X a halogen atom. m_{SiY_3X} is the mass of SiY_3X, a is the Si-X distance, d_Y the Si-Y distance. φ_Y is the supplementary angle of the X-Si-Y angle. The relation between *observed* microwave absorption frequency, ν_{obs} (cm^{-1}), and I_B is

$$\nu_{obs} = \frac{h}{4\pi^2 c I_B} (J + 1) = 2B \; (J + 1) \quad (2)$$

where J is the rotational quantum number of the *lower* of the two states involved, c the velocity of light and B the rotational constant. Experience has shown that (2) reproduces microwave spectra to a high degree of accuracy for small J-values. The highest J to be used in the following is $J = 1$. Unfortunately, microwave spectra of symmetric tops tell nothing of I_A. If, therefore, microwave absorption for, say, $Si^{29}D_3Cl^{35}$ is observed, only the magnitude of I_B (in this case denoted by $I_B^{29,D,35}$) results. This information is insufficient for a calculation of the three geometrical parameters, a, d_Y, and φ_Y. If it is assumed, however, that isotopic molecules have identical dimensions, it is seen that observation of microwave absorption for at least *three* isotopic species of the same compound enables one to carry through a calculation of a, d_Y, and φ_Y. This was what was actually done by Townes et al.[8] in the case of *silyl chloride*. They found $a = 2.050 \pm 0.001$ Å; $d_H = 1.50$ Å; $\varphi_H = 72°\,2'$, but the magnitude of the two last-mentioned parameters must have been difficult to fix because of the quasi-degeneracy of the equations to solve. To avoid this complication Sharbaugh et al.[9] chose, in the case of *silyl fluoride*, to assume that $\varphi_H = 72°\,6'$. They calculated $a = 1.593 \pm 0.002$ Å and $d_H = 1.50 \pm 0.03$ Å. Now, in the paper by Nielsen[3] it was shown that $d_H = 1.456$ Å in SiH_4. (Here, $\varphi_H = 70°\,32'$). So far it looked, therefore, as if substitution of one hydrogen atom in SiH_4 by fluorine or chlorine would cause fairly large changes in the remaining Si-H bonds. Since this is definitely known *not* to be the case for the methyl halides it was decided to provide further experimental material in order to be able to calculate d_H and φ_H with somewhat higher accuracy.

EXPERIMENTAL PART

Preparation of SiD₃Cl and SiD₃F (B. B. and J. B.). 4 g Mg₂Si (from Mg and Si) was slowly added to a solution of DCl (from 60 g C₆H₅COCl and 2 g D₂O) in 22.8 g D₂O in a stream of dry hydrogen. SiD₄ and impurities (Si₂D₆ etc.) were condensed in a liquid-air trap. After evacuation at $-190°$ C the temperature of the trap was raised to $-125°$ C. The pressure rose to 380 mm Hg. In small portions the vapors were admitted to an adjacent, evacuated trap cooled in liquid air, until the vapor-pressure in the trap at 125° C had fallen to 35 mm Hg. The rest was discarded and the collected material transferred to a container, kept at $-118°$ C from which practically the whole sample could be distilled at 470 mm Hg. In this way 100 ml portions were repeatedly prepared (1 atm., 20° C), representing a 8 % yield of SiD₄ (based on Mg₂Si).

52 ml SiD$_4$ (1 atm., 20° C) were brought to reaction with 38 ml DCl (1 atm., 20° C) over AlCl$_3$ (resublimed) at 100° C in a 120 ml flask. Contact between the reaction mixture and the greased stopcock was prevented by means of a drop of mercury. After three hours the reaction mixture:

$$SiD_4 + DCl \rightleftharpoons SiD_3Cl + D_2$$
$$SiD_3Cl + DCl \rightleftharpoons SiD_2Cl_2 + D_2 \; etc.$$
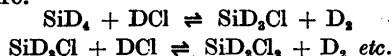
was cooled in liquid air. The deuterium formed (27 ml at 1 atm., 20° C) was pumped off and the remaining 63 ml gases were carefully fractionated. 20 ml SiD$_3$Cl (vapor-pressure 45 mm Hg at −72° C) were collected. Yield: 40 % based on SiD$_4$. The sample so obtained was practically free of SiD$_2$HCl since no line corresponding to the Si-H vibration could be seen in the infrared absorption spectrum. The microwave spectrum showed that it was also free of SiD$_2$Cl$_2$. SiD$_3$Cl (and SiH$_3$Cl) can be stored for months at −78° C in a glass container without undergoing any change. At room temperature and 0.5−1 atm. it is likewise stable for shorter periods (1−2 hours). In handling the compound it is important to note that even a trace of water converts it very rapidly into (SiD$_3$)$_2$O from which it is hard to separate.

SiH$_3$F has earlier been produced from SiH$_3$Cl and SbF$_3$ (catalyst: SbCl$_5$). In preliminary experiments it was shown that the use of SbCl$_5$ is superfluous. The following procedure was finally followed: 9.1 ml SiD$_3$Cl (1 atm., 20° C) was left for 12 hours in a 12 ml flask (greased stopcock protected by mercury) in contact with 250 mg resublimed SbF$_3$. Then the flask was cooled in liquid air and subsequently evacuated (0.2 ml D$_2$ was formed). The reaction mixture was fractionated at −118° C where a constant-boiling fraction (4.4 ml (1 atm., 20° C)) was obtained at 46 mm Hg. The infrared absorption spectrum showed no sign of the presence of hydrogen-containing compounds, but both microwave and infrared absorption curves showed that probably the sample was contaminated with SiD$_2$F$_2$. Since, however, the Stark patterns used in microwave spectroscopy are widely different for symmetric tops (SiD$_3$F) and asymmetric rotors (SiD$_2$F$_2$) the unambigous identification of a microwave line as originating from SiD$_3$F is not prevented.

MEASUREMENT OF MICROWAVE ABSORPTION OF SiD$_3$Cl AND SiD$_3$F.
(B. B. AND J. R−A.)

Since both silicon and chlorine consist of a mixture of stable isotopes of rather high concentration (Si[28]: 90 %; Si[29]: 6 %; Si[30]: 4 %; Cl[35]: 75 %; Cl[37]: 25 %) 'heavy' silyl chloride is a mixture of 6 isotopic species while 'heavy' silyl fluoride is composed of 3 species. Microwave absorption corresponding to four of the chlorides and all three fluorides was found (Table 1).

Table 1. Observed microwave absorption frequencies for isotopic silyl fluoride and chloride molecules.

Species	Transition	ν_{obs} MHz	$I_B \times 10^{40}$ gcm^2	B MHz
Si[28]D$_3$F	$J = 0 \to 1$	24507.0	68.461	12253.5
Si[29]D$_3$F	»	24352.2	68.897	12176.1
Si[30]D$_3$F	»	24204.5	69.316	12102.2
Si[28]D$_3$Cl[35]	$J = 1 \to 2$	23670.8	141.759	5917.7
Si[29]D$_3$Cl[35]	»	23402.6	143.383	5850.6
Si[30]D$_3$Cl[35]	»	23147.9	144.961	5787.0
Si[28]D$_3$Cl[37]	»	23091.4	145.316	5772.8
Si[28]H$_3$F	$J = 0 \to 1$	28655.8	58.549	14327.9
Si[29]H$_3$F	»	28393.4	59.090	14196.7
Si[30]H$_3$F	»	28145.2	59.611	14072.6
Si[28]H$_3$Cl[35]	$J = 1 \to 2$	26695.2	125.698	6673.8
Si[30]H$_3$Cl[35]	»	25943.2	129.342	6485.8
Si[28]H$_3$Cl[37]	»	26049.6	128.813	6512.4

The observations placed below the line in the middle of Table 1 were made by the previously cited authors [7-9]. Due to the spin of the chlorine nucleus the microwave absorption of all the chlorides exhibits a hyperfine structure. Since the quadrupole coupling is very nearly the same for light and heavy silyl chloride the correction terms for quadrupole coupling found by Sharbaugh [7] for SiH_3Cl^{35} and SiH_3Cl^{37} could be taken over without appreciable error. The value $h = 6.6237.10^{-27}$ ergsec was used for Planck's constant in calculating I_B.

MOLECULAR DIMENSIONS OF SILYL CHLORIDE AND FLUORIDE.

a. Silyl chloride

It is easy to derive from (1) that

$$a_H \frac{m_{Cl^{35}}}{m_H} - 3d_H \cos\varphi_H = K^{30-28,H,35} \tag{3}$$

$$a_H \frac{m_{Si^{28}H_3}}{m_H} + 3d_H \cos\varphi_H = K^{28,H,37-35} \tag{4}$$

where $K^{30-28,H,35} = \sqrt{\dfrac{(I_B^{30,H,35} - I_B^{28,H,35})\, m_{Si^{28}H_3Cl^{35}}\, m_{Si^{30}H_3Cl^{35}}}{m_H^2\, (m_{Si^{30}} - m_{Si^{28}})}}$

and $K^{28,H,37-35} = \sqrt{\dfrac{(I_B^{28,H,37} - I_B^{28,H,35})\, m_{Si^{28}H_3Cl^{37}}\, m_{Si^{28}H_3Cl^{35}}}{m_H^2\, (m_{Cl^{37}} - m_{Cl^{35}})}}$

In the calculations to follow the atomic masses used were:

Si^{28}: 27.9866; Si^{29}: 28.9866; Si^{30}: 29.9832: Cl^{35}: 34.9786;
Cl^{37}: 36.9775; F: 19.0049; H: 1.008123; D: 2.014708,

all in the physical atomic weight scale. The corresponding value of Avogadros number used is $6.0251 \cdot 10^{23}$.

By addition of (3) and (4) a formula giving a_H as a function of measured quantities is easily derived (5):

$$a_H = \frac{m_H}{m_{Si^{28}H_3Cl^{35}}}\, (K^{30-28,H,35} + K^{28,H,37-35}) \tag{5}$$

By insertion it is found that
$$a_H = 2.0479 \ \text{Å}$$

Microwave absorption frequencies of silyl chloride and fluoride molecules *not* containing the rare isotopes Si^{29} and Si^{30} are reliable to $\pm$ 0.2 MHz, while the rest may be assumed to be good to $\pm$ 0.3 MHz. This means an uncertainty in the calculated a_H value of 7 in the fourth decimal place so that

$$2.0472 \ \text{Å} < a_H < 2.0486 \ \text{Å}$$

If a similar calculation is carried through in order to find a_D, the Si-Cl distance in the 'heavy' species, we find that

$$a_D = 2.0486 \ \text{Å and that } 2.0479 \ \text{Å} < a_D < 2.0493 \ \text{Å}$$

The values of a_H and a_D refer to the molecules in their ground state where the only internal energy left is the zero-point energy. In their ground state isotopic molecules do not possess identical structures but only very nearly so. Since the zero-point energy may be thought of as kinetic and since of two isotopic molecules the lighter has the higher zero-point energy this means that as a rule bond lengths will decrease slightly with increasing molecular weight in a series of isotopic molecules. In the calculations above it was tacitly assumed that the very small differences in zero-point energy between molecules which only differ in silicon or chlorine isotopes, have no effect on the interatomic distances. However, molecules differing in *hydrogen* isotopes have rather different zero-point energies. Here, we may expect structural differences which, due to the small masses of hydrogen and deuterium, must be expected to be most pronounced in the magnitude of the parameters d_H, d_D, φ_H, and φ_D. Indeed, the values found for a_H and a_D verify this assumption. Generally it must be expected that $d_H > d_D$ and $\varphi_H \neq \varphi_D$. In the case of the methyl halides Miller, Aamodt, Dousmanis and Townes [10] got the results of Table 2.

Table 2. Position of hydrogen and deuterium atoms in light and heavy methyl halides.

	d_H, d_D	φ_H, φ_D		d_H, d_D	φ_H, φ_D		d_H, d_D	φ_H, φ_D
CH_3Cl	1.113	71° 36′	CH_3Br	1.113	72° 21′	CH_3J	1.113	72° 33′
CD_3Cl	1.104	71° 50′	CD_3Br	1.104	72° 34′	CD_3J	1.104	72° 46′
$d_H - d_D$	0.009			0.009			0.009	
$\varphi_D - \varphi_H$		14′			13′			13′
Deviations from CH_4	0.02	1° 4′		0.02	1° 49′		0.02	2° 1′
	0.01	1° 18′		0.01	2° 2′		0.01	2° 14′

For the silyl chlorides and fluorides deviations from regularity of the same order of magnitude were found by Bak, Rastrup-Andersen and Bruhn [12]. Since then, Monfils [11] has studied the fine-structure of the infrared bands of silyl chloride. He found $I_A^{28,H,35} = (9.89 \pm 0.15) \times 10^{-40}$ gcm^2. Strictly spoken this result probably is a 'hybrid' between the true $I_A^{28,H,35}$ (vibrational ground level) and I_A for a vibrationally excited level (such details cannot be seen from Monfils' note) but the error committed by setting $I_A^{28,H,35} = 9.89$ 10^{-40} gcm^2 cannot be great. (In the case of OCS it has been found that the moment of inertia of a molecule, vibrationally excited by one quantum, deviated less than 0.5 % from the moment in the ground state.)

By inserting the calculated value of a_H in (3) we find that

$$d_H \cos\varphi_H = 0.476 \pm 0.002 \text{ Å} \tag{6}$$

$$I_A^{28,H,35} = 3m_H d_H^2 \sin^2\varphi_H = (9.89 \pm 0.15) \times 10^{-40} \text{ gcm}^2 \text{ gives}$$
$$d_H \sin\varphi_H = 1.405 \pm 0.012 \text{ Å} \tag{7}$$

It follows that

$$\varphi_H = 71°\ 15' \pm 15' \text{ and } d_H = 1.483\ \text{Å} \pm 0.010\ \text{Å}$$

In SiH$_4$, $\varphi_H = 70°\ 32'$ » $d_H = 1.456\ \text{Å} \pm 0.010\ \text{Å}$

The deviation in φ_H and d_H, are, therefore, respectively 43' and 0.027 Å. These numbers correspond very well with what was found for methyl chloride (Table 2). The results suggest that d_D, the Si-D distance in the heavy silyl chloride, may be one or two hundredths of an Å smaller than d_H as found for methyl chloride. Consequently we look for solutions in the region where 1.49 Å $\geqq d_D \geqq$ 1.46 Å. The point of interest now is whether we shall find φ_D to be close to and a little greater than φ_H.

By inserting the value of a_D calculated above in the 'heavy' equation corresponding to (3) we find $d_D \cos\varphi_D = 0.469 \pm 0.002$. $d_D = 1.460$ Å, therefore, corresponds to $\varphi_D = 71°\ 11'$—$71°\ 21'$ while $d_D = 1.490$ Å corresponds to $\varphi_D = 71°\ 34'$—$71°\ 44'$. It is seen that φ_D and φ_H are about equal. Furthermore it is seen that if we fix d_H to 1.483 Å and if we suppose that $d_H - d_D = 0.009$ Å as in CH$_3$Cl we get $\varphi_D = 71°\ 27'$ (mean value) which happens to be 12' greater than φ_H. For CH$_3$Cl and CD$_3$Cl this difference was found to be 14' (Table 2).

b. Silyl fluoride

Not much could be added to the communication by Bak, Bruhn and Rastrup-Andersen [13]. Due to the lack of fluorine isotopes an equation like (5) cannot be derived giving the silicon-fluorine distance as a function of measured quantities. Since

$$a_H\ \frac{m_F}{m_H} - 3d_H\cos\varphi_H = K^{30-28,H,F} \tag{8}$$

and

$$a_D\ \frac{m_F}{m_D} - 3d_D\cos\varphi_D = K^{30-28,D,F} \tag{9}$$

we can derive $a = \dfrac{m_H m_D}{m_F(m_D - m_H)}\ \Big\{ K^{30-28,H,F} - K^{30-28,D,F} + 3(d_H\cos\varphi_H -$

$$-d_D\cos\varphi_D)\Big\} \tag{10}$$

where the difference between a_H and a_D has been neglected which was found to be correct for silyl chloride.

By omitting the last term of this equation we find

$$a = 1.595 \pm 0.002\ \text{Å}$$

If we assume that $|d_H - d_D| \leqq 0.01$ Å and $|\varphi_H - \varphi_D| \leqq 1°$ an upper limit to the error in a, caused by this uncertainty, is 0.008 Å. Therefore,

$$a = 1.595 \pm 0.010\ \text{Å}.$$

By inserting in (8) and (9) it is found that

$$d_H\cos\varphi_H = 0.476 \pm 0.040\ \text{Å}$$

and that $d_D\cos\varphi_D = 0.474 \pm 0.020\ \text{Å}$

i. e. these products are about equal to the corresponding quantities for the silyl chlorides although the uncertainty is larger due to lacking experimental data. As shown by Bak, Bruhn and Rastrup-Andersen [12] by their graphical method it can be shown that if it is assumed that also in this case $d_H—d_D \sim 0.01$ Å, φ_H and φ_D come very close to the tetrahedral value 70° 32′. But it is impossible to give $|\varphi_H—70° 32′|$ and $|\varphi_D—\varphi_H|$ with any satisfactory degree of accuracy.

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