2-((1,1-$^2H_2$)ethyl)-3-oxohexanoate as a yellow oil (quantitative yield). The ester was hydrolyzed and decarboxylated [as in the synthesis of heptan-4-one (I), above] to give (2,2,6,6-$^2H_4$)heptan-4-one in 60% yield ($^2H_4$ > 99%).

(1,1,1,7,7,7-$^2H_6$)Heptan-4-one (IX). This synthesis uses the same procedures as that of VII above, except that in both steps (2,2,2-$^2H_3$)-iodoethane is used. The product (65 mg) was obtained as a colorless liquid ($^2H_6$ > 98%).

(2,6-$^{13}C_2$)Heptan-4-one (II). Preparation as for VII except that (1-^{13}C)iodoethane (^{13}C = 91%) was used. Yield 53 mg.

(2-^{13}C)Heptan-4-one (III) and (1-^{13}C)Heptan-4-one (IV). Preparation as for VIII except that (1-^{13}C)iodoethane (^{13}C = 91%) and (2-^{13}C)-iodoethane (^{13}C = 91%) were used for III and IV, respectively. Yields 60 and 65 mg, respectively.

The Formation of the α-$^2H_1$ and α-$^2H_2$ Enolate Ions of Heptan-4-one. The ions [$MeCH_2\bar{C}HCOCD_2CH_2Me$ plus $MeCH_2\bar{C}DCOCHDCH_2Me$] and [$MeCH_2\bar{C}HCOCHDCHMe$ plus $MeCH_2\bar{C}DCOCH_2CH_2Me$] were produced by the reaction between DO^- and the partially labeled compounds produced by shaking heptan-4-one with a fourfold excess (by volume) of NaOD for 15 min at 20 °C. The DO^-/NICI Spectrum showed the following incorporations for enolate ions: $^2H_0$ = 5%, $^2H_1$ = 45%, $^2H_2$ = 35%, and $^2H_3$ = 15%.

Acknowledgment. The synthetic part of this project was carried out with the aid of a grant from the Australian Research Grants Scheme. M.B.S. thanks the A.R.G.S. for the award of a postdoctoral fellowship. J.L.H. thanks the Natural Sciences and Engineering Research Council of Canada for continuing financial support. J.H.B. thanks the N.S.E.R.C. of Canada for an International Scientific Exchange Award during the tenure of which this work was completed.

(p–d) π Bonding in Fluorosilanes? Gas-Phase Structures of $(CH_3)_{4-n}SiF_n$ with n = 1–3 and of t-Bu_2SiF_2

Beate Rempfer,[†] Heinz Oberhammer,*[†] and Norbert Auner[‡]

Contribution from Institut für Physikalische und Theoretische Chemie, Universität Tübingen, 7400 Tübingen, West Germany, and Anorganisch Chemisches Institut, Wilhelms Universität—Münster, 4400 Münster, West Germany.

Received November 25, 1985

Abstract: The gas-phase structures (r_g values) of the methylfluorosilanes $(CH_3)_{4-n}SiF_n$ with n = 1–3 and of di-*tert*-butyldifluorosilane, t-Bu_2SiF_2, have been determined by electron diffraction. In the case of CH_3SiF_3 the microwave rotational constant was included in the structure analysis. In the methylfluorosilane series a steady decrease of Si–F and Si–C bond lengths is observed with increasing fluorination: Si–F = 1.600 (2), 1.586 (2), and 1.570 (2) Å and Si–C = 1.848 (2), 1.836 (2), and 1.828 (4) Å for $(CH_3)_3SiF$, $(CH_3)_2SiF_2$, and CH_3SiF_3, respectively. These trends are rationalized by increasing polar contributions and contraction of the silicon valence shell. Ab initio calculations for SiF_4 indicate that (p–d) π bonding is negligible. Substitution of the methyl groups in $(CH_3)_2SiF_2$ by *tert*-butyl groups leads to lengthening of Si–F and Si–C bonds and strong variations in the silicon bond angles: Si–F = 1.586 (2), 1.606 (4) Å; Si–C = 1.836 (2), 1.869 (3) Å; CSiC = 116.7 (6)°, 125.5 (11)°; and FSiF = 104.6 (4)°, 97.7 (8)° in $(CH_3)_2SiF_2$ and t-Bu_2SiF_2, respectively.

The bonding properties in silicon compounds have attracted considerable interest for many years, because some properties of these compounds differ strongly from those of analogous carbon or germanium derivatives. Among these properties are structural features such as experimental Si–X bond lengths (see Table I), which are always shorter than the sum of the respective covalent radii. If polar effects due to electronegativity differences are taken into account, as suggested by Schomaker–Stevenson,[6] the prediction for the Si–C bond is very close to the experimental value, but Si–X bonds with more electronegative atoms X are still predicted to be too long. The difference increases monotonically with increasing electronegativity of X and amounts to 0.16 Å for the Si–F bond in SiF_4. It has been suggested that (p–d) π bonding would account for this difference, and this concept has been widely accepted.[7] It has helped to rationalize structural features of many silicon compounds (e.g., $(SiH_3)_3N$[2] and $(SiH_3)_2O$[3]). According to this concept the unoccupied Si 3d orbitals are contracted in the presence of electronegative ligands, and electron transfer from the lone pairs of N, O, or F into these empty orbitals results in effective (p–d) π back bonding. On the other hand, a crude consideration of bond energies (Table I) makes it unlikely that (p–d) π bonding is responsible for the high bond energy of Si–F bonds (135 kcal/mol). As suggested by Pauling[6] the σ bond energy for an A–B bond can be estimated from the geometric mean of the bonds A–A and B–B. The differences Δ between these estimated values and the actual bond energies are due to polar or π bonding contributions. In the case of the Si–C bond, the small difference of 10 kcal/mol can very well be due to a small

Table I. Si–X Bonds Lengths (in Å) and Bond Energies for X = C and F (in kcal/mol)

	exptl	cov. radii	S.S.[a]
Si–C in $Si(CH_3)_4$	1.875 (2)[b]	1.94	1.88
Si–N in $(SiH_3)_3N$	1.734 (3)[c]	1.87	1.81
Si–O in $(SiH_3)_2O$	1.634 (2)[d]	1.83	1.77
Si–F in SiF_4	1.553 (2)[e]	1.81	1.71

	Si–C in Me_4Si	Si–F in SiF_4
E_b (exptl)[f]	70	135
σ[g]	60	40
Δ[h]	10	95
polar contr.	10	100

[a] Schomaker–Stevenson values. [b] Reference 1. [c] Reference 2. [d] Reference 3. [e] Reference 4. [f] Reference 5. [g] Geometric mean of Si–Si and X–X (X = C or F) σ bond energies. [h] $\Delta = E(\text{exptl}) - \sigma$.

[†] Universität Tübingen.

[‡] Wilhelms Universität—Münster.

(1) Beagley, B.; Monaghan, J. J.; Havitt, T. G. *J. Mol. Struct.* **1971**, *8*, 401.

(2) Beagley, B.; Conrad, A. R. *J. Chem. Soc., Trans. Faraday Soc.* **1970**, *66*, 2740.

(3) Almeningen, A.; Bastiansen, O.; Ewing, V.; Hedberg, K.; Traetteberg, M. *Acta Chem. Scand.* **1963**, *17*, 2455.

(4) Hagen, K; Hedberg, K. *J. Chem. Phys.* **1973**, *59*, 1549.

(5) Ebsworth, E. A. V. *Volatile Silicon Compounds*; Pergamon: Oxford, 1963.

(6) Pauling, L. *The Nature of Chemical Bond*; Cornell University: Ithaca, NY, 1960.

0002-7863/86/1508-3893$01.50/0

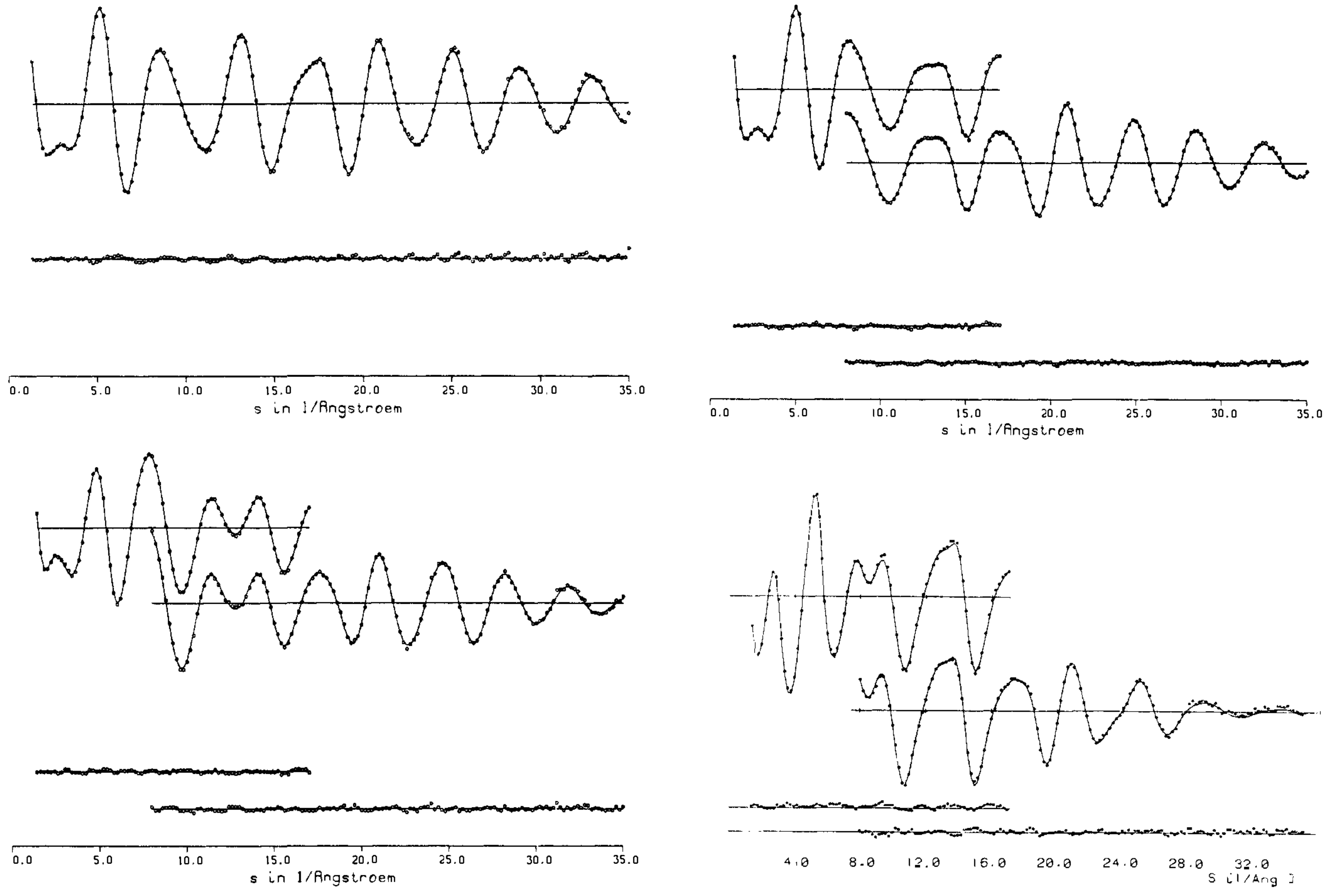

Figure 1. Experimental (···) and calculated (—) modified molecular intensities sM (s). (a) CH_3SiF_3, (b) $(CH_3)_2SiF_2$, (c) $(CH_3)_3SiF$, (d) *t*-Bu_2SiF_2.

polar contribution. For the Si–F bond (p–d) π contributions will certainly be less than 40 kcal/mol (σ bond energy) and can never make up for the large difference of 95 kcal/mol. Polar effects, however, can make large contributions to the bond energy. A quite realistic assumption of charge distribution in SiF_4 ($Si^{+1.6}$–$F^{-0.4}$) would contribute about 100 kcal/mol, i.e., close to the lacking 95 kcal/mol. The Schomaker–Stevenson concept for predicting bond lengths from covalent radii and atomic electronegativities does not consider the effects from other substituents and is strictly valid only for diatomic molecules. In larger molecules the polarity of a particular bond depends not only on the electronegativity difference between the two atoms involved but also on the electronegativity of other substituents. Thus, it is more likely that the failure of the Schomaker–Stevenson rule to predict correct Si–X bond lengths for electronegative X atoms is due to underestimation of polar effects and not only due to neglect of (p–d) π bonding.

The effects of various substituents (F or CH_3) on the Si–F and Si–C bond lengths can be studied systematically in the series $(CH_3)_{4-n}SiF_n$ with n = 0–4. Trends in these bond lengths can provide information on the bonding properties of these compounds and possibly give information about the importance of polar effects and/or Si 3d participation.

For the two tetrahedral compounds $(CH_3)_4Si$[1] and SiF_4,[4] accurate structure determinations by gas electron diffraction are known in the literature. CH_3SiF_3 has previously been studied by gas electron diffraction[8] and microwave spectroscopy,[9] but the uncertainties for the Si–C bond length are rather large in both cases (Si–C = 1.841 (15) Å from electron diffraction and Si–C = 1.812 (14) Å from microwave spectroscopy). From the B_0 rotational constant of the parent isotopic species of $(CH_3)_3SiF$,[10] an Si–F bond length of 1.55 Å is estimated assuming all other geometric parameters (Si–C = 1.87 Å). No structural study for $(CH_3)_2SiF_2$ is known in the literature.

Since information on bonding properties requires highly accurate geometric structures, we report electron diffraction studies of the mixed methylfluorosilanes, n = 1–3, and of di-*tert*-butyldifluorosilane in this paper.

Experiment Section

$(CH_3)_2SiF_2$ and $(CH_3)_3SiF$ were purchased from PCR Research Chemicals, Inc., Gainesville, FL. These samples were used without further purification.

CH_3SiF_3 has been prepared by fluorination of CH_3SiCl_3 with ZnF_2 in a sealed tube (100 °C/24 h). The pure compound (bp −30 °C/mp −73 °C) was isolated in 90% yield by trap-to-trap condensation at 10^{-3} torr.

t-Bu_2SiF_2 has been synthesized from *t*-Bu_2SiCl_2 using ZnF_2 in sulfolane as the fluorinating reagent (90 °C/4 days). The pure product was obtained by distillation under reduced pressure in ca. 90% yield. The identity of the moisture-sensitive compound was proved by spectroscopic measurements.[11] The starting compound *t*-Bu_2SiCl_2 was prepared by a slightly modified literature procedure.[12]

The electron diffraction intensities were recorded with the Balzers gas diffractograph KD-G2[13] at two camera distances (50 and 25 cm) and accelerating voltage of approximately 60 kV. The electron wavelength was determined from ZnO diffraction patterns. This calibration was checked by CO_2 diffraction patterns in the case of CH_3SiF_3. ZnO and CO_2 values for the wavelengths agreed within their standard deviations. ($\Delta\lambda/\lambda$ is smaller than 3×10^{-4} in all cases.) The samples were kept at −80 °C (CH_3SiF_3), −50 °C ($(CH_3)_2SiF_2$), −40 °C ($(CH_3)_3SiF$), and 20 °C (*t*-Bu_2SiF_2), and inlet system and nozzle were at room temperature

---

[7] Cruickshank, D. W. J. *J. Chem. Soc.* **1961**, 5486. Bürger, H. *Top. Curr. Chem.* **1967**, *9*, 1.

[8] Schwendeman, R. H. Ph.D. Thesis, University of Michigan, 1956; *Diss. Abstr.* **1958**, *18*, 1645.

[9] Durig, J. R.; Li, Y. S.; Tong, C. C. *J. Mol. Struct.* **1972**, *14*, 255.

[10] Gunton, R. C.; Ollom, J. F.; Rexroad, H. N. *J. Chem. Phys.* **1954**, *22*, 1942.

[11] Auner, N., unpublished results.

[12] Tyler, L. T.; Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1948**, *70*, 2876.

[13] Oberhammer, H. *Molecular Structures by Diffraction Methods*; The Chemical Society: London, 1976; Vol. 4, p 24.

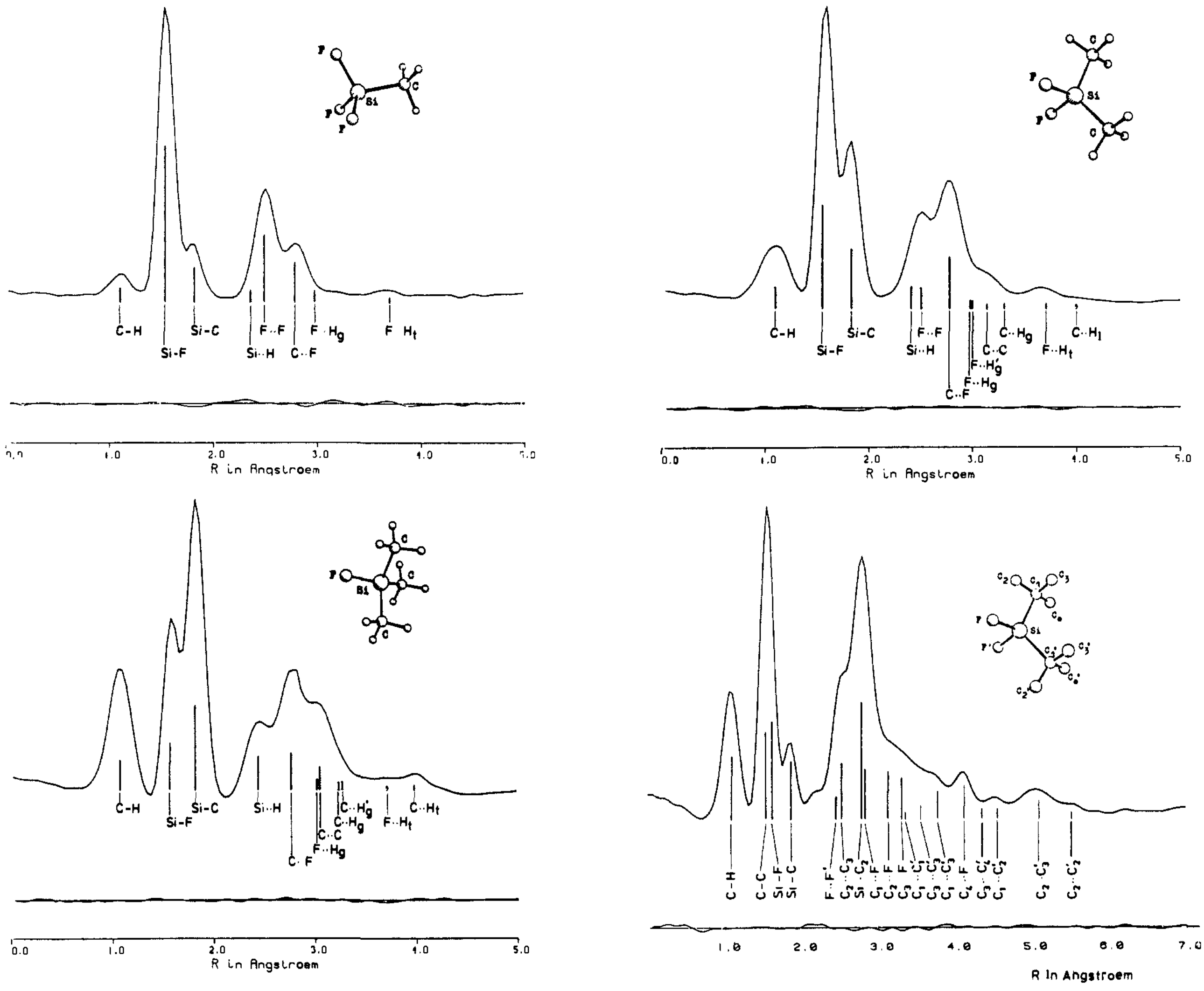

Figure 2. Experimental radial distribution functions and difference curves. (a) CH_3SiF_3, (b) $(CH_3)_2SiF_2$, (c) $(CH_3)_3SiF$, (d) t-Bu_2SiF_2.

in all cases. The camera pressure never exceeded 2.5×10^{-5} torr during the experiments. Exposure times were 8–12 and 17–30 s for the long and short camera distances, respectively. Two plates were selected for each compound and camera distance and were analyzed by the usual procedures.[14] Extraneous scattering, which was recorded without gas, was subtracted from the 25-cm data. The averaged molecular intensities for the s ranges 1.4–17 and 8–35 $Å^{-1}$ are presented in intervals of $\Delta s = 0.2$ $Å^{-1}$ in Figure 1.

Structure Analysis

All three bond distances in the methylfluorosilanes, C–H, Si–F, and Si–C, are well resolved in the radial distribution functions (Figure 2a–2c) which allows accurate determination of these bond lengths from electron diffraction data. In the case of t-Bu_2SiF_2 the C–C and Si–F bonds overlap in the strong peak at about 1.53 Å (Figure 2d). Preliminary geometric parameters derived from the radial distribution functions were refined in least-squares analyses based on the modified molecular intensities. A diagonal weight matrix was applied to the intensities with full weight for the s ranges 4–15 and 10–30 $Å^{-1}$, respectively. The scattering amplitudes and phases of J. Haase[15] were used. C_{3v} symmetry for the CH_3 groups with the C_3 axis along the Si–C or C–C bonds, respectively (no tilt angle), was assumed for all compounds. The final results for the geometric parameters of the methylfluorosilanes are summarized in Table II. For the sake of consistency the $r_\alpha{}^0$ bond distances for CH_3SiF_3 and the r_a distances for all other compounds were converted into r_g values. ($r_g = r_\alpha{}^0 + K_T + {}^3/_2 a(l_T{}^2 - l_0{}^2)$; K_T = perpendicular amplitudes at T (K), $a = 2$ $Å^{-1}$, and $r_g = r_a + l_T{}^2/r_a$.) The vibrational amplitudes are listed in Table III.

Table II. Geometric Parameters for $(CH_3)_{4-n}SiF_n$, $n = 0$–4, with 3σ Uncertainties

	$(CH_3)_4Si^{a,b}$	$(CH_3)_3SiF^a$	$(CH_3)_2SiF_2{}^a$	$CH_3SiF_3{}^c$	$SiF_4{}^{a,d}$
Si–C	1.875 (2)	1.848 (2)	1.836 (2)	1.828 (4)	
Si–F		1.600 (2)	1.586 (2)	1.570 (2)	1.553 (2)
C–H	1.115 (7)	1.110 (3)	1.132 (6)	1.139 (5)	
CSiC	109.5	111.5 (2)	116.7 (6)		
FSiF			104.6 (4)	106.8 (5)	109.5
HCH	109.8 (8)	108.2 (4)	111.2 (10)	108.6 (10)	
$R_{50}{}^e$		0.032	0.037	0.031	
$R_{25}{}^e$		0.062	0.040	0.058	

[a] r_g distances and r_a angles. [b] Reference 1. [c] r_g distances and r_α angles. [d] Reference 4. [e] $R = [\sum w_i\Delta_i{}^2/\sum w_i s_i{}^2 M_i(\text{exptl})^2]^{1/2}$; $\Delta_i = s_iM_i(\text{exptl}) - s_iM_i(\text{calcd})$; w_i = weight.

Methyltrifluorosilane. In a first step the five geometric parameters required to define the geometry and eight vibrational amplitudes were fitted to the molecular intensities. In the final analysis the rotational constant for the parent isotopic species (B_0 = 3.715 64 GHz)[9] was included in the refinement. The harmonic vibrational corrections $\Delta r = r_g - r_\alpha{}^0$ [16] (Table III) and $\Delta B = B_0 - B_z$[17] were calculated from the valence force field of Clark et al.[18] The torsional force constant (0.027 mdyn Å) was derived

---

(14) Oberhammer, H.; Willner, H.; Gombler, W. *J. Mol. Struct.* **1981**, *70*, 273.

(15) Haase, J. *Z. Naturforsch., A* **1970**, *25*, 936.

(16) Oberhammer, H. *J. Chem. Phys.* **1978**, *69*, 468.

(17) Kuchitsu, K.; Fukuyama, T.; Morino, Y. *J. Mol. Struct.* **1968**, *1*, 463.

(18) Clark, A. J. F.; Drake, J. E. *Spectrochim. Acta, Part A* **1981**, *37*, 391.

Table III. Vibrational Amplitudes for $(CH_3)_{4-n}SiF_n$, $n = 1-3$, and Harmonic Vibrational Corrections for CH_3SiF_3[a]

	CH_3SiF_3			$(CH_3)_2SiF_2$	$(CH_3)_3SiF$
	l(ed)[b]	l(sp)[c]	Δr[d]	l(ed)[b]	l(ed)[b]
C–H	0.069 (16)	0.078	0.0140	0.120 (12)	0.083 (6)
Si–F	0.043 (2)	0.042	0.0027	0.047 (2)	0.048 (3)
Si–C	0.048 (5)	0.050	0.0035	0.057 (3)	0.056 (2)
Si···H	0.124 (50)	0.120	0.0078	0.150 (15)	0.119 (5)
F···F	0.073 (4)	0.073	0.0020	0.067 (4)	
C···F	0.083 (7)	0.087	0.0017	0.093 (3)	0.085 (3)
C···C				0.095 (15)	0.098 (6)
F···H_g	0.49 (22)	0.210	0.0201	0.31 (5)[e]	0.28 (2)[f]
F···H_g'				0.31 (5)[e]	
C···H_g				0.31 (5)[e]	0.28 (2)[f]
C···H_g'					0.28 (2)[f]
F···H_t	0.29 (24)	0.116	0.0178	0.13 (2)[g]	0.10 (2)[h]
C···H_t				0.13 (2)[g]	0.10 (2)[h]

[a] Without values for H···H distances. Error limits are 3σ values. [b] From electron diffraction experiment. [c] From spectroscopic data. [d] $\Delta r = r_g - r_\alpha^0$. [e–h] Amplitudes with the same subscript were set equal.

Table IV. Results of Electron Diffraction Analysis for t-Bu_2SiF_2[a] for (a) Geometric Parameters (r_g Distances in Å, r_a Angles in deg), (b) Vibrational Amplitudes (Å) (without Nonbonded Distances involving Hydrogens), and (c) Agreement Factors[e]

		a	
Si–F	1.606 (4)	FSiF[b]	97.7 (8)
Si–C	1.869 (3)	CSiC	125.5 (11)
C–C	1.529 (4)	CCC	110.7 (4)
C–H	1.102 (4)	HCH	107.4 (8)
		CSiF	107.5 (4)
		tilt[c]	0.5 (5)
		b	
C–H	0.076 (4)	C_2···F C_3···F	0.16 (2)
C–C Si–F	0.047 (5)	C_3···C_3'	0.11 (4)
Si–C	0.059 (4)	C_1···C_3'	0.18 (4)
F···F′ C_2···C_3 C_1···F C_1···C_1'	0.067 (5)	C_4···F	0.10 (1)
		C_3···C_4'	0.17 (6)
		C_1···C_2'	0.12[d]
		C_2···C_3'	0.16 (3)
Si···C_2	0.133 (11)	C_2···C_2'	0.14[d]
		c	
R_{50}	0.042	R_{25}	0.071

[a] Error limits are 3σ values. [b] Dependent parameter. [c] Angle between C_3 axes of *tert*-butyl groups and Si–C bond directions. [d] Not refined. [e] For definition, see Table II.

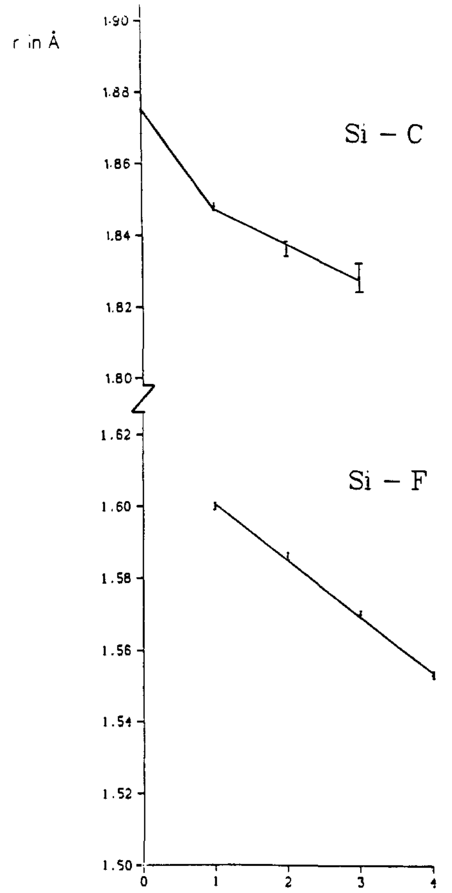

Figure 3. Variation of Si–F and Si–C bond lengths in the series $(CH_3)_{4-n}SiF_n$, $n = 0–4$.

from the microwave value for the torsional frequency (114 cm^{-1} [9]). Contributions of the torsional vibration to perpendicular amplitudes for torsion-independent distances were neglected.[16] The relative weight between molecular intensities and the rotational constant was adjusted until the experimental B_z value (3.7132 (4) GHz) was reproduced within its uncertainty. This uncertainty was estimated to be 15% of the harmonic correction ΔB.

Dimethyldifluorosilane. Assuming C_{2v} overall symmetry, six geometric parameters and nine vibrational amplitudes were refined simultaneously in the least-squares analysis. Assumptions for vibrational amplitudes are evident from Table III. Only one correlation coefficient had a value larger than |0.6|: FSiF/l(Si···H) = −0.80.

Trimethylfluorosilane. When C_{3v} symmetry was assumed and the constraints for the vibrational amplitudes (see Table III) were used, five geometric parameters and eight vibrational amplitudes were refined. No correlation coefficient had a value larger than |0.6|.

Di-*tert*-butyldifluorosilane. The radial distribution function is shown in Figure 2d. C_{3v} symmetry was assumed for the *tert*-butyl groups, with the methyl groups in staggered positions. Several least-squares analyses demonstrate that the twist angle τ for the *tert*-butyl groups about the Si–C bonds (C_2 overall symmetry) is zero or very small. $\tau = 0$ corresponds to C_{2v} symmetry, with the C–C bonds staggering the Si–F bonds. The fit between experimental and calculated intensities is unchanged for $\tau < 5°$ and becomes worse for $\tau > 5°$. In the final least-squares analysis, $\tau = 0$ was assumed and 9 geometric parameters including a tilt angle between the C_3 axes of the *tert*-butyl groups and the Si–C bond directions, together with 11 vibrational amplitudes were refined simultaneously. Assumptions for the vibrational amplitudes are evident from Table IV. The following correlation coefficients had values larger than |0.6|: CC/CCC = 0.70, CSiC/tilt = −0.76, CC/l(CC) = 0.88, SiF/l(CC) = −0.77, and CCC/l(CC) = 0.62. The final results are summarized in Table IV.

Discussion

The most striking results of this study is the monotonous and similar shortening of the Si–F and Si–C bond lengths with increasing fluorination in $(CH_3)_{4-n}SiF_n$ (see Figure 3). The only exception from this very regular behavior is the Si–C bond length in Me_4Si.

Two major effects can rationalize this very similar behavior of both bonds: (1) polar contributions and (2) contraction of the silicon valence shell. Minor effects on the bond lengths may also be due to slightly different hybridization, as indicated by the bond angle variations in Table II. The importance of attractive polar contributions and their increase with increasing fluorination is obvious. These contributions will certainly be smaller for Si–C bonds (the methyl carbon atom is assumed to carry a negative net charge) than for the Si–F bonds. Since the force constant for Si–C bonds (~3 mdyn $Å^{-1}$)[5] is considerably smaller than that for Si–F bonds (~6 mdyn $Å^{-1}$),[5] the effect on the bond shortening will be similar. The importance of valence shell contraction for silicon has been demonstrated by ^{29}Si NMR shifts in methylfluorosilanes.[19] A consistent interpretation of these data results

---

(19) Roelandt, F. F.; Van de Vondel, D. F.; Van den Berghe, E. V. *J. Organomet. Chem.* **1975**, *94*, 377.

in a simultaneous increase of the positive silicon net charge (from +0.5 in Me_4Si to +1.6 in SiF_4) and the Slater exponent for the valence orbitals 3s and 3p (from 1.44 in Me_4Si to 1.57 in SiF_4). This increase of the Slater exponent implies a decrease of the mean radius $\langle r \rangle$ of the valence orbitals from 0.73 Å in Me_4Si to 0.69 Å in SiF_4. This contraction of the silicon valence shell leads to a simultaneous shortening of both Si–C and Si–F bonds.

Since (p–d) π bonding would cause shortening of the Si–F bonds only, it cannot explain the very similar behavior of Si–F and Si–C bonds. There is no evidence for major d-orbital involvement. This conclusion is supported by the interpretation of UPS[20] and XPS[21] spectra of fluorosilanes. The interpretation of ab initio calculations for fluorosilanes is ambiguous. Experimental quantities, such as bond lengths or dipole moments, are reproduced better if d functions are included in the Si basis set. It is not obvious, however, whether such functions just compensate for an inadequate s,p basis set or whether they imply actual participation of Si 3d orbitals. Breeze et al.[22] interpret these functions as polarization functions, while Roelandt et al.[23] conclude from the population of d functions in the series SiH_4, SiH_3F, and SiH_2F_2 (0.151, 0.235, and 0.318 au) that Si 3d orbital involvement in bonding increases with increasing fluorination. On the other hand, such an increasing population of d functions with increasing fluorination has also been reported for the fluoromethane series.[24] Ab initio calculations for SiF_4[25] result in slightly better agreement with the experimental bond length (1.553 (2) Å) if Si d functions are included in the basis set (1.56 Å) than without such d functions (1.59 Å). A Mulliken population analysis, however, demonstrates, that these d functions compensate to a large extent for the inadequate s and p basis set, while (p–d) π contributions to the overlap population are very small (0.05 au).

In di-*tert*-butyldifluorosilane both Si–F and Si–C bonds are longer than in the dimethyl compound (1.606 (4) vs. 1.586 (2) Å and 1.869 (3) vs. 1.836 (2) Å). Due to the electron-releasing property of the *tert*-butyl groups, the positive net charge of silicon will be reduced, thus reducing polar effects and contraction of the silicon valence shell. These two effects can rationalize qualitatitively the lengthening of both bonds. Of course, other effects such as hybridization—the CSiC angle increases from 116.7 (6)° to 125.5 (11)° and the FSiF angle decreases from 104.6 (4)° to 97.7 (8)°—may also be responsible for different bonding properties in the methyl and *tert*-butyl compounds. The very small distortions of the *tert*-butyl groups (tilt and twist angles) indicate that steric effects are of minor importance. The shortest H···H contact between the two *tert*-butyl groups is greater than 2 Å.

Acknowledgment. Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. $MeSiF_3$, 373-74-0; Me_2SiF_2, 353-66-2; Me_3SiF, 420-56-4; $t\text{-}Bu_2SiF_2$, 558-63-4; $t\text{-}Bu_2SiCl_2$, 18395-90-9; ZnF_2, 7783-49-5; SiF_4, 7783-61-1.

---

[20] Cradock, S.; Ebsworth, E. A. V.; Whiteford, R. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2401.

[21] Perry, W. B.; Jolly, W. L. *Inorg. Chem.* **1974**, *13*, 1211.

[22] Breeze, A.; Collins, G. A. D.; Cruickshank, D. W. J. *J. Chem. Soc., Chem. Commun.* **1971**, 445.

[23] Roelandt, F. F.; Van de Vondel, D. F.; Van der Kelen, G. P. *J. Mol. Struct.* **1978**, *50*, 147.

[24] Dixon, D. Presented at the 7th Winter Fluorine Conference, Orlando, FL, 1985.

[25] Pfafferott, G.; Oberhammer, H.; Boggs, J. E., unpublished results.

Particle Bombardment (FAB) Mass Spectra of Methanol at Subambient Temperatures

R. N. Katz, T. Chaudhary, and F. H. Field*

Contribution from The Rockefeller University, New York, New York 10021.
Received November 25, 1985

Abstract: The spectra produced by methanol when bombarded with a mixed beam of argon ions and atoms with a nominal energy of 8 keV have been obtained at temperatures between 179 and 100 K. The spectrum of liquid methanol at 179 K consists primarily of clusters of methanol around the proton, $H(CH_3OH)_n^+$, where the maximum value of n observed is 18. The spectrum of solid methanol at 169 K is very similar to that of liquid methanol. Mixed methanol–water clusters produced as a result of water impurity are also observed. The spectrum of solid methanol at 100 K is quite different, for the $H(CH_3OH)_n^+$ ions lose their prominance, and the high mass spectrum (above m/z 60) is without character, consisting of ions at more or less every mass. The change in the spectrum is reversible. At an intermediate temperature (137 K) the spectrum is a mixture of the features observed at 169 and 100 K. This change in the character of the spectrum can be represented by plotting $\sum_n H(CH_3OH)_n^+/TIC$ (TIC = total ion current) as a function of T, and such a plot shows a sharp decrease between approximately 150 and 130 K. Evidence is presented that the phenomenon is not caused by surface melting produced by the particle bombardment or by surface charging.

Temperature effects in EI, CI, and FI/FD mass spectrometry have been the subject of investigation for approximately the past 15 years,[1-3] and work continues to the present.[4-10] In general the amount of fragmentation occurring for a given compound increases as the temperature increases, which is the result of the larger thermal energy content of the molecule ion at higher temperatures. However, virtually no studies have been made of the

---

[1] For electron ionization: Spiteller-Friedman, M.; Spiteller, G. *Justus Liebigs Ann. Chem.* **1968**, *712*, 179.

[2] For chemical ionization: Field, F. H. *J. Am. Chem. Soc.* **1969**, *91*, 2827.

[3] For field ionization: Knoppel, H.; Beckey, H. D. *Z. Naturforsch., A: Astrophys., Phys. Phys. Chem.* **1966**, *21A*, 1930. See also: Beckey, H. D. *Principles of Field Ionization and Field Desorption Mass Spectrometry*; Pergamon: Oxford, 1977; pp 223–230.

[4] Eadon, G.; Valente, H. *J. Am. Chem. Soc.* **1984**, *106*, 3521 (electron ionization).

[5] Bowen, R. D.; Maccoll, A. *Org. Mass Spectrom.* **1983**, *18*, 576 (electron ionization).

[6] Schildcrout, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 3852 (electron ionization).

[7] Griffiths, I. W.; Mukhter, E. S.; Harris, F. M.; Beynon, J. H. *Int. J. Mass Spectrom Ion Phys.* **1982**, *43*, 283 (photoionization).

[8] Shiraishi, H.; Otsuki, A.; Fuwa, K. *Bull. Chem. Soc. Jpn.* **1982**, 55, 1340 (field desorption).

[9] Sadovskaya, V. L.; Andronova, T. M.; Merimson, V. G.; Rosynov, B. V. *Org. Mass Spectrom.* **1980**, *15*, 473 (field desorption).

[10] Brand, W.; Beckey, H. D.; Fassbender, B.; Heindrichs, A.; Levsen, K. *Int. J. Mass Spectrom. Ion* Phys. **1980**, *35*, 11 (field desorption).

0002-7863/86/1508-3897$01.50/0