Monatshefte für Chemie 111, 581—590 (1980)

Monatshefte für Chemie

The Vibrational Spectra of Linear and Branched Perchlorosilanes Si_nCl_{2n+2} and Their Simulation Using a Local Symmetry Force Field

K. Hassler, Edwin Hengge*, and W. Raml

Institute of Inorganic Chemistry, Technical University Graz,
A-8010 Graz, Austria

(Received 19 December 1979. Accepted 9 January 1980)

Infrared and *Raman* vibrational spectra of n-Si_4Cl_{10}, n-Si_5Cl_{12}, *neo*-Si_5Cl_{12} and $[(SiCl_3)_3Si]_2$ have been measured and assigned. A local symmetry force field has been developed to simulate vibrational spectra of all (noncyclic) perchlorosilanes Si_nCl_{2n+2} known today ($n = 2, 3, 4, 5, 8$). The observed spectra are reproduced satisfactorily $\left(\frac{1}{m}\sum\left|\frac{\Delta\nu}{\nu}\right| = 4\%,\ m = \text{total number of observed fundamentals}\right)$.

(Keywords: IR Spectra; Perchlorosilanes; Raman spectra)

Die Vibrationsspektren linearer und verzweigter Perchlorsilane Si_nCl_{2n+2} *und deren Simulierung mittels eines lokalen Symmetrie-Kraftfeldes*

Infrarot- und *Raman*-Spektren von n-Si_4Cl_{10}, n-Si_5Cl_{12}, *neo*-Si_5Cl_{12} und $[(SiCl_3)_3Si]_2$ wurden aufgenommen und zugeordnet. Ein lokales Symmetrie-Kraftfeld zur Simulation der Spektren aller bisher bekannten (nicht cyclischen) Perchlorsilane Si_nCl_{2n+2} ($n = 2, 3, 4, 5, 8$) wird angegeben. Die beobachteten Spektren werden zufriedenstellend reproduziert $\left(\frac{1}{m}\sum\left|\frac{\Delta\nu}{\nu}\right| = 4\%,\ m = \text{Gesamtzahl beobachteter Grundschwingungen}\right)$.

Introduction

Besides a wide variety of synthetic routes yielding mixtures of chlorosilanes Si_nCl_{2n+2} with different n's and structural isomers (e.g. the reaction of metal silicides with halogens[1,2] or the method of *Thiel* and *Schwarz*[3]) only a limited number of reactions leading to products with definite chain length and structure are known. The first three members of the series ($SiCl_4$, Si_2Cl_6 and Si_3Cl_8) are usually prepared by the silicide-

0026-9247/80/0111/0581/$ 02.00

Table 1. *Infrared- and Raman-Spectra (cm^{-1})*

n-Si$_4$Cl$_{10}$		
IR (l)	*Ra* (l)	assignment
	610 w, tp	ν_sSiSi$_2$ (a$_g$) ν_{as}SiCl$_3$ (b$_g$)
590 vs, b		ν_{as}SiCl$_3$ (a$_u$, b$_u$) ν_{as}SiCl$_2$ (a$_u$) ν_{as}SiSi$_2$ (b$_u$)
	593 w, tp	νSiSi^i (a$_g$)^a ν_{as}SiCl$_3$ (b$_g$)
485 m		ν_sSiCl$_2$ (b$_u$)
	583 w, p	ν_{as}SiCl$_3$ (a$_g$)
	441 w, p	ν_sSiCl$_2$ (a$_g$)
372 vs		ν_sSiCl$_3$ (b$_u$)
315 m	310 vs, p	„ν_sSiCl$_3$“ (a$_g$)
	220 w	δ_{as}SiCl$_3$ (b$_g$) δ_sSiCl$_3$ (a$_g$)
275 w		
242 vs 232 vs		δ_{as}SiCl$_3$ (a$_u$) δ_sSiCl$_3$ (b$_u$)
207 vs		δ_sSiCl$_2$ (b$_u$)
	196 m	δ_{as}SiCl$_3$ (a$_g$)
180 vs	186 m	δ_{as}SiCl$_3$ (b$_u$)
	155 w	ρSiCl$_2$ (b$_g$
	127 s, p	ρSiCl$_3$ (b$_g$) δ_s, τSiCl$_2$ (a$_g$, b$_g$)
	105 vs, p	γSiCl$_2$ (a$_g$) ρSiCl$_3$ (a$_g$)
150 sh		ρSiCl$_3$ (a$_u$) τSiCl$_2$ (a$_u$)
90 m, b		γSiCl$_2$ (a$_u$) ρSiCl$_2$ (b$_u$)

n-Si$_5$Cl$_{12}$		
IR (l)	*Ra* (l)	assignment
640 w, b		ν_{as}SiSi$_2{}^i$ (b$_2$)^a ν_{as}SiCl$_2$ (b$_1$)
590 vs, b	600 w 580 w	ν_sSiSi$_2{}^1$ (a$_1$)^a ν_{as}SiCl$_2$ (a$_2$) ν_{as}SiSi$_2{}^1$ (b$_2$)^a ν_sSiSi$_2{}^0$ (a$_1$)^a ν_{as}SiCl$_3$ (a$_1$, a$_2$) ν_{as}SiCl$_3$ (b$_1$) ν_{as}SiCl$_2$ (b$_1$) ν_{as}SiCl$_3$ (b$_2$)
	539 vvw	
488 vs	485 vvw	ν_sSiCl$_2$ (a$_1$) ν_sSiCl$_2$ (b$_2$)
455 vs	458 vvw	
	432 vvw	
407 s	404 w, p	ν_sSiCl$_2$ (a$_1$)
348 s		ν_sSiCl$_3$ (b$_2$)
304 m	303 vs, p	„ν_sSiCl$_3$“ (a$_1$)
275 w		
230 vs		τSiCl$_2$ (b$_2$)
220 vs	220 sh, p	δ_sSiCl$_3$ (a$_1$)
	197 w	δ_{as}SiCl$_3$ (a$_1$, b$_1$) δ_sSiCl$_3$ (b$_2$)
185 vs	180 w	δ_sSiCl$_2$ (a$_1$) δ_{as}SiCl$_3$ (b$_2$)
175 sh		τSiCl$_2$ (b$_1$)
156 w		
138 w		τSiCl$_2$ (b$_1$)
	127 s	δ_sSiCl$_2$ (a$_1$, b$_2$) τSiCl$_2$ (a$_2$)
107 sh	101 vs	ρSiCl$_3$ (a$_1$) τ, γSiCl$_2$ (a$_2$, b$_2$) ρSiCl$_3$ (b$_1$, b$_2$)
88 s		γSiCl$_2$ (a$_1$)
74 s		ρSiCl$_2$ (b$_1$)
54 w	54 m	ρSiCl$_2$ (b$_1$)

[a] i = inner SiSi-bond, o = outer SiSi-bond.

method and are easily separated and purified by destillation, but with increasing chain length severe difficulties concerning purification and identification arise. Besides the „classical“ methods for the determination of molecular structures such as elemental analysis, ebulliometric determination of molecular weights or volumetric determination *of n-*Si_4Cl_{10}*, n- and neo-*Si_5Cl_{12} *and* Si_8Cl_{18}

	neo-Si_5Cl_{12}			Si_8Cl_{18}	
IR (s)	*Ra* (s)[b]	assignment	IR (s)	*Ra* (s)	assignment
615 sh	613 w	$\nu_{as}SiSi_4$ (f_2)		600 m	$\nu_{as}SiCl_3$ (a_{1g})
597 vs	593 w	$\nu_{as}SiCl_3$ (e)		571 m	$\nu^1_{as}, \nu^2_{as}SiCl_3$ (e_g)
	559 w, p	ν_sSiSi_4 (a_1)		547 w	ν_sSiSi_3 (a_{1g})
553 m		$\nu_{as}SiCl_3$ (f_2)			$\nu_{as}SiSi_3$ (e_g)
397 m	402 vw	ν_sSiCl_3 (f_2)	585 vs, b		$\nu_{as}SiCl_3$ (a_{2u})
	315 vs, p	,,ν_sSiCl_3“ (a_1)			$\nu^1_{as}, \nu^2_{as}SiCl_3$ (e_u)
346 w			535 vs		ν_sSiSi_3 (a_{2u})
302 vw					$\nu_{as}SiSi_3$ (e_u)
240 s		δ_sSiCl_3 (f_2)	450 w, b	455 m	$\nu SiSi^i$ (a_{1g})[a]
195 s	201 vw	$\delta_{as}SiCl_3$ (f_2)		391 w	ν_sSiCl_3 (e_g)
	185 m	$\delta_{as}SiCl_3$ (e)	396 vs		ν_sSiCl_3 (e_u)
	130 m, sh	$\rho SiCl_3$ (e)		355 vw	
	118 vs, p	δ_sSiCl_3 (a_1)		296 vs	,,ν_sSiCl_3“ (a_{1g})
123 w		$\rho SiCl_3$ (f_2)		287 w	
78 vw	76 m	$\delta SiSi_4$ (e)	383 s		
	56 m	$\rho SiSi_4$ (f_2)	345 w		ν_sSiCl_3 (a_{2u})
				251 w	
				235 w	δ_sSiCl_3 (e_g)
			243 sh		δ_sSiCl_3 (a_{2u})
			237 vs		$\delta^1_{as}SiCl_3$ (e_u)
			200 sh		δ_sSiCl_3 (e_u)
				197 s	$\delta_{as}SiCl_3$ (a_{1g})
				189 s	
				181 s	$\delta^1_{as}, \delta^2_{as}SiCl_3$ (e_g)
			186 vs		$\delta_{as}SiCl_3$ (a_{2u})
			155 sh		ρ^1SiCl_3 (e_u)
				122 s	ρ^1SiCl_3 (e_g)
				108 s	δ_sSiCl_3 (a_{1g}, e_g), ρ^2SiCl_3 (e_g)
			107 w		$\rho SiCl_3$ (a_{2u}, e_u)
			78 m		$\delta_{as}SiSi_3$ (e_u)

[b] Polarization measurements on benzolic solution.

of the hydrogen evolved during alkaline hydrolysis, infrared and *Raman* spectroscopy combined with computer-assisted interpretation of the spectra as well as ^{29}Si nuclear magnetic resonance became more and more important during the last decade. Recently. new synthetic approaches allowed an expansion of our knowledge into the region of the Si_8-oligomers[4–6] and the collection of important physical data of these molecules (such as ^{29}Si chemical shifts[6]) that will be useful for future research in this area.

Experimental

n-Si_4Cl_{10}, *n*-, *neo*-Si_5Cl_{12} and $[(SiCl_3)_3Si]_2$ were prepared according to the procedures given in the literature[4–6]. IR-spectra of solid samples were recorded as nujol mulls, liquid chlorosilanes were thinned with nujol. The paraffine was deoxygenated and dried by vacuum destillation, all manipulations were performed in dry nitrogen atmosphere. The spectral regions above and below 300 cm^{-1} were examined with a Perkin Elmer 325 spectrometer and a Beckman 725 *Fourier* spectrophotometer, respectively. *Raman* spectra were taken with a SPEX Ramalog (50 mW He/Ne gas laser, 6,328 Å), polarization ratios are estimated. All frequencies are believed to be accurate to $\pm 2\,cm^{-1}$ with the exception of FIR measurements ($\pm 5\,cm^{-1}$).

Spectra

IR and *Raman* spectra of *n*-Si_4Cl_{10}, *n*-, *neo*-Si_5Cl_{12} and $[(SiCl_3)_3Si]_2$ are given in Table 1. The spectra are assigned assuming (for every individual molecule) the highest symmetry possible. Description of the modes follows the calculated potential energy distributions (PED).

n-Si_4Cl_{10} and $[(SiCl_3)_3Si)_2$ belong to point groups C_{2h} and D_{3d}, if symmetrical arrangement of the $SiCl_3$-groups around the central SiSi-bond is assumed, therefore requiring the rule of mutual exclusion. To a good approximation, the observed spectra display the features expected if it is taken into account that a number of coinciding lines must be assigned to different species (see section normal coordinate analysis). In the case of *n*-Si_4Cl_{10}, several IR bands are believed to originate from decomposition products (458 m, 440 m, 400 w). They are not included in Table 1. The "violation" of the rule of mutual exclusion at "ν_sSiCl_3" (a_g) (*Ra*: 310 vs, p. IR: 315 m) may be explained in different ways:

(i) combination band [127 (a_g) + 207 (b_u)], in *Fermi* resonance with ν_sSiCl_3 (b_u) (372 cm^{-1});

(ii) band resulting from decomposition products;

(iii) the actual symmetry of the molecule is not C_{2h}.

We prefer the first explanation since "ν_sSiCl_3" (corresponding to a "pulsation" of the whole molecule) usually exhibits the highest possible symmetry (in view of selection rules). However, the presence of a gauche conformer may not be excluded.

Similar considerations are valid for $[(SiCl_3)_3Si]_2$. With the exception of the FIR region, the spectra of *neo*-Si_5Cl_{12} are already known[7]. The spectra of *n*-Si_5Cl_{12} are best described in terms of C_{2v} symmetry.

For disilanes of the type Si_2X_6, the fundamentals having predominantly ν(SiSi) character (according to PED) are found in the region between 403 cm^{-1} (Si$_2$*Me*$_6$)[8] and 624 cm^{-1} (Si$_2$Cl$_6$)[9]. Vibrational coupling between νSiSi, ν_sSiX_3 and δ_sSiX_3[10] as well as the influence of the substituents on the SiSi-force constants are responsible for this wide range. *f*(SiSi) increases in the series $CH_3 < H < I \sim C_6H_6 < OCH_3 \sim Br < Cl < F$[9–12]. Caused by electronegativity, *f*(SiX) of disilanes decreases by 5–10% as compared with SiX_4.

Vibrational coupling in Si$_2X_6$-molecules is maximal in Si$_2$Cl$_6$[9] because of the little differences between the atomic masses of silicon and chlorine and the similar value of *f*(SiSi) and *f*(SiCl). Calculations on Si$_3$Cl$_8$[13] (C_{2v} symmetry) show that ν_sSiSi$_2$ of species a_1 mixes extensively with ν_sSiCl$_3$ and ν_sSiCl$_2$. ν_{as}SiSi$_2$ of species b_2 on the contrary is not coupled with ν_sSiCl$_3$ since the SiSi distance is not altered during ν_sSiCl$_3$ (ν_sSiCl$_3$ of species b_2 being an out of phase vibration).

Similar effects are expected if the chain length is increased. Coupling between ν_sSiSi$_n$ and ν_sSiCl$_n$ of the totally symmetric species results in a "breathing mode" of the whole molecule, giving rise to a strong *Raman* line whose frequency decreases with increasing chain length. Because of its high intensity, this mode may be used for easy identification of chlorosilanes (as, for instance, during a reaction). Table 2 gives the frequencies of "ν_sSiCl$_3$" for Si$_n$Cl$_{2n+2}$ molecules:

Table 2. "ν_sSiCl$_3$" *of chlorosilanes* Si$_n$Cl$_{2n+2}$ *(cm^{-1})*

Si$_2$Cl$_6$	Si$_3$Cl$_8$	*i*-Si$_4$Cl$_{10}$	*n*-Si$_4$Cl$_{10}$	*neo*-Si$_5$Cl$_{12}$	*n*-Si$_5$Cl$_{12}$	Si$_8$Cl$_{18}$
351	331	322	310	315	302	296

Normal Coordinate Analysis (NCA)

Wilson's FG-method was followed throughout the calculations. Geometrical parameters used were: r(SiSi) = 232 pm, r(SiCl) = 202 pm, all angles 109° 28′. Torsional angles were chosen in a way the most symmetrical conformer results. This simplification seems obvious if the number of predicted fundamentals (relating to different rotameres) is compared with the observed spectra.

Symmetry coordinates were constructed using the local symmetries of —SiCl$_3$ and —SiCl$_2$ groups. The following combinations of internal coordinates result (Table 3).

SiSi and SiCl force constants depend on the electronegativities of the remaining substituents on the silicon atom. If a chlorine atom is replaced by a SiCl$_3$ group, *f*(SiCl) decreases by 5–10% (SiCl$_4$ → Si$_2$Cl$_6$), *f*(SiSi) behaves similarly. We parameterized these effects using the following assumptions:

(i) variation of f(SiSi) and f(SiCl) with chain length is caused by electronegativity;

(ii) the electronegativity of a $SiCl_3$ group nearly equals that of a CH_3 group, this assumption being justified by a comparison of νSiH of

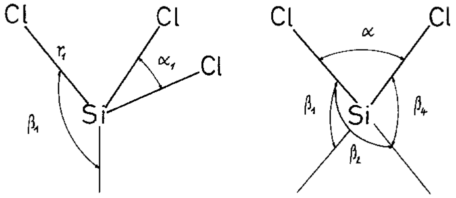

Fig. 1

Table 3. *Local symmetry coordinates of* $SiCl_3$, $SiCl_2$ *and* SiCl-*groups in chlorosilanes* Si_nCl_{2n+2}

	$—SiCl_3$	$—SiCl_2$	$—SiCl$
$\nu_s SiCl_n$	$r_1 + r_2 + r_3$	$r_1 + r_2$	r
$\delta_s SiCl_n$	$\alpha_1 + \alpha_2 + \alpha_3 — \beta_1 — \beta_2 — \beta_3$	$4\alpha — \beta_1 — \beta_2 — \beta_3 — \beta_4$	
$\nu^1_{as} SiCl_n$	$2r_1 — r_2 — r_3$	$r_1 — r_2$	
$\delta^1_{as} SiCl_n$	$2\alpha_1 — \alpha_2 — \alpha_3$		
$\rho^1 SiCl_n$	$2\beta_1 — \beta_2 — \beta_3$	$\beta_1 + \beta_2 — \beta_3 — \beta_4$	$2\beta_1 — \beta_2 — \beta_3$
$\nu^2_{as} SiCl_n$	$r_2 — r_3$		
$\delta^2_{as} SiCl_n$	$\alpha_2 — \alpha_3$		
$\rho^2 SiCl_n$	$\beta_2 — \beta_3$		
$\gamma SiCl_2$		$\beta_1 — \beta_2 + \beta_3 — \beta_4$	
$\tau SiCl_2$		$\beta_1 — \beta_2 — \beta_3 + \beta_4$	

$HSi(SiCl_3)_3$ (2,141 cm^{-1})[15] and $HSiMe_3$ (2,131 cm^{-1})[16] and the linear relationship between f(SiH) of $HSiX_3$ molecules and f(SiSi) of the corresponding disilanes X_3SiSiX_3;

(iii) replacement of several chlorine atoms results in a linear, cumulative effect.

f(SiSi) of Si_2Cl_6 and Si_2Me_6 are reported to be $2.4 \cdot 10^2$N/m (Ref.[9]) and $1.65 \cdot 10^2$N/m (Ref.[8]), respectively. Therefore, f(SiSi) decreases upon substitution of one chlorine atom by CH_3 (or equivalently, $SiCl_3$) by $(2.4 — 1.65)/6 = 0.125 \cdot 10^2$N/m. If one chlorine atom in a β-position is replaced by $SiCl_3$, an increment of $0.075 \cdot 10^2$N/m is subtracted [this value being estimated since no data are available, see (ii)]. Therefore, replacement of Cl by $—SiCl_2SiCl_3$ is thought to reduce f(SiSi) by

$0.2 \cdot 10^2$N/m, —$SiCl(SiCl_3)_2$ by $0.275 \cdot 10^2$, $Si(SiCl_3)_3$ by $0.35 \cdot 10^2$N/m. —$(SiCl_2)_2SiCl_3$ is set equal to $SiCl(SiCl_3)_3$, —$(SiCl_2)_3SiCl_3$ to $Si(SiCl_3)_3$, structural isomerism thus being neglected. In a similar way, SiCl force constants are parameterized: starting with $SiCl_4$ ($3.1 \cdot 10^2$N/m), the following increments are subtracted (if one chlorine atom is replaced):

—$SiCl_3$: 0.15, —$SiCl_2SiCl_3$: 0.25, $SiCl_2SiCl_3$: 0.35
—$(SiCl_2)_3SiCl_3$ = $Si(SiCl_3)_3$: 0.4; all values in 10^2N/m.

Deformation force constants are the same for all chlorosilanes [F (δ $SiCl_n$) weighted by r (SiCl), F (δ $SiSi_n$) by r (SiSi)]:

	$\delta_s SiCl_3$	$\delta_{as} SiCl_3$	ρ $SiCl_3$	$\delta_s SiCl_2$	γ $SiCl_2$	τ $SiCl_2$	ρ $SiCl_2$	δ $SiSi_n$
F ($\cdot 10^2$N/m)	0.18	0.178	0.14	0.18	0.17	0.17	0.12	0.08

The interaction force constants between two adjacent SiSi and SiCl bonds are fixed to $0.1 \cdot 10^2$N/m and $0.05 \cdot 10^2$N/m, respectively.

The following non-zero off diagonal force constants (10^2 N/m) were retained constant:

F (ν $SiSi_n/\nu_s SiCl_3$): 0,04
F (ν $SiSi_n/\delta_s SiCl_3$): —0,04
F ($\nu_s SiCl_3/\delta_s SiCl_3$): 0,11
F ($\nu_{as}^{1,2} SiCl_3/\delta_{as}^{1,2} SiCl_3$): —0,11
F ($\nu_{as}^{1,2} SiCl_3/\rho^{1,2} SiCl_3$): 0,13
F ($\delta_{as}^{1,2} SiCl_3/\rho^{1,2} SiCl_3$): —0,016
F (ν $SiSi_n/\nu_s SiCl_2$): 0,04
F (ν $SiSi_n/\delta_s SiCl_2$): —0,04
F ($\nu_s SiCl_2/\delta_s SiCl_2$): 0,11
F ($\nu_{as} SiCl_2/\rho$ $SiCl_2$): 0,05
F (ν $SiSi_n/\nu$ SiCl): 0,04

Generally, F_{ij}'s corresponding to $G_{ij} = o$ were kept zero. Table 4 gives the frequencies calculated with our model force field as well as the experimental values.

Discussion

The results of the normal coordinate analysis allow the following conclusions:

(i) NCA is able to distinguish between structural isomers (e.g. n-, i-Si_4Cl_{10}), but not between rotational isomers.

(ii) Increasing chain length does not lead to a serious complication of the spectra, because of the "group-frequency" character of several modes (e.g. ν_{as}, $\delta_{as} SiCl_3$, see Table 4). The number of observable transitions thus is reduced. Selection rules usually correspond to the conformer with the highest symmetry, giving no information on the actual conformation of the molecule.

Table 4. *Experimental and calculated fundamentals (cm^{-1}) of chlorosilanes* Si_nCl_{2n-2}

Si_2Cl_6 (D_{3d})		Si_3Cl_8 (C_{2v})		*n*-Si_4Cl_{10} (C_{2h})		*i*-Si_4Cl_{10} (C_{3v})		*n*-Si_5Cl_{12} (C_{2v})		*neo*-Si_5Cl_{12} (T_d)		Si_8Cl_{18} (D_{3d})		description	assignment				
$\nu_{exp.}$[9]	$\nu_{calc.}$	$\nu_{exp.}$[13]	$\nu_{calc.}$	$\nu_{exp.}$	$\nu_{calc.}$	$\nu_{exp.}$[17]	$\nu_{calc.}$	$\nu_{exp.}$	$\nu_{calc.}$	$\nu_{exp.}$	$\nu_{calc.}$	$\nu_{exp.}$	$\nu_{calc.}$		T_d	D_{3d}	C_{2h}	C_{3v}	C_{2v}
603	600	580	580	610	599	594	576	580	569	597	570	585	570	$\nu_{as}SiCl_3$	e	e_u	b_g	a_1	a_1
590	600	625	630	590	570	590	574	580	572	553	569	600	572		f_2	e_g		e	a_2
		625	628	590	600	590	579	590	570			571	567			e_g	a_u	e	b_1
		594	585	583	574			580	569			600	576			a_{1g}	a_g		b_2
												585	570			e_u			
												585	573			a_{2u}			
		610	610	590	580			640	622					$\nu_{as}SiCl_2$			a_u		b_1
				590	576			600	591								b_u		a_2
								590	580										b_1
		625	619			590	599	600	622	615	586	571	558	$\nu_{as}SiSi_n$	f_2	e_g		e	b_2
				590	592			640	633			585	547			e_u	b_u		b_2
624	630	605	617	593	614	594	617	580	588	559	509	455	470	ν_sSiSi_n	a_1	a_{1g}	a_g	a_1	a_1
				610	623			600	609			571	550			a_{1g}	a_g		a_1
												535	517			a_{2u}			
		404	410	372	367	398	398	348	340	397	396	391	393	ν_sSiCl_3	f_2	e_g	b_u	e	b_2
460	457											345	346			a_{2u}			
												396	377			e_u			
351	351	331	330	310	318	314	320	303	307	315	312	297	301	„ν_sSiCl_3“	a_1	a_{1g}	a_g	a_1	a_1
		480	479	441	443			485	474					ν_sSiCl_2			a_g		a_1
				485	481			404	398								b_u		a_1
								488	489										b_2
						506	496							$\nu SiCl$				a_1	

211	209	187	183	242	254	175	163	197	195	185	193	188	197	$\delta_{as}SiCl_3$	e	e_g	a_u	a_1	a_1
		182	182	196	187	185	183	197	200	195	182	188	197		f_2	e_g	a_g	e	b_1
179	179		173	180	179	198	191	197	199			186	189			e_u	b_u	e	a_2
								180	182			237	221			e_u			b_2
												189	187			a_{1g}			
												186	175			a_{2u}			
238	241	232	221	232	231	214	207	220	228	240	244	243	252	δ_sSiCl_3	f_2	a_{2u}	b_u	a_1	a_1
127	120	232	242	220	233	225	240	197	204	118	109	108	109		a_1	a_{1g}	a_g	e	b_2
				220	253							200	218			e_u	b_g		
				242	254							235	238			e_g	a_u		
		135	123	127	122			127	129					δ_sSiCl_2			a_g		a_1
				207	203			180	179								b_u		a_1
								127	121										b_2
132	128	149	157	127	140	112	111	101	95	130	133	122	125	$\rho SiCl_3$	e	e_g	b_g	a_1	b_1
74	84	116	111	105	106	120	113	101	111	123	110	108	102		f_2	e_g	a_g	e	a_1
			130	150	140	120	110		155			107	113			e_u	a_u	e	a_2
			101		119			101	107			155	134			e_u	b_u		b_2
													100			a_{1g}			
												107	109			a_{2u}			
		69	72	90	98			175	182					$\rho SiCl_2$			b_u		b_1
				155	165				77								b_g		a_2
								74	69										b_1
		116	115	105	109			220	233					$\gamma SiCl_2$			a_g		b_2
				90	92			101	105								a_u		b_2
								88	84										a_1
			96	127	119			127	118					$\tau SiCl_2$			b_g		a_2
								101	105										a_2
								138	135										b_1
		55	39		50	80	87	54	47	76	96		57	$\delta SiSiSi$	e	e_g	a_g	e	a_1
					29		48	54	46	56	43		31		f_2	a_{1g}	b_u	a_1	b_2
									21			108	113			e_g			a_1
													50			a_{2u}			
												107	102			e_u			
													24			e_u			

(iii) According to calculated PED's, strong mixing occurs between $SiCl_n$-deformation modes, the PED usually spreading out over several coordinates (e.g. $\rho\,SiCl_3$, $\rho,\tau,\gamma,\delta\,SiCl_2$). Vibrational coupling between $\nu_s SiSi_n$ and $\nu_s SiCl_n$ has already been mentioned.

(iv) Refinement of the given force field with iterative methods is hindered by vibrational coupling, large variations of bond stretch force constants leading to only slight variations of calculated frequencies. In the $SiCl_n$-deformation region, small off diagonal force constants may cause an interchange of modes (according to PED).

(v) The given force field is transferable to chlorosilanes with other substituents *M* by combining it with a local *M* force field using appropriately chosen off diagonal force constants. Electronegativity of *M* has to be taken into account. Applications to HSi_2Cl_5 and $Me_3SiSiCl_3$ resulted in good agreement between experimental and calculated frequencies.

Readers interested in details of the calculations are invited to write for additional data.

The authors thank the *Fonds zur Förderung der wissenschaftlichen Forschung*, Vienna, for financial support.

References

[1] *G. Martin*, J. Chem. Soc. **105**, 2835 (1914).
[2] *E. Hengge*, Halogen Chemistry (*V. Gutmann*, ed.), Vol. 2, and references cited therein. New York: Academic Press. 1967.
[3] *R. Schwarz* and *R. Thiel*, Z. anorg. allg. Chem. **235**, 247 (1938).
[4] *W. Raml* and *E. Hengge*, Z. Naturforsch. **34 b**, 1457 (1979).
[5] *W. Raml* and *E. Hengge*, Mh. Chem. **110**, 1257 (1979).
[6] *H. Marsmann*, *W. Raml*, and *E. Hengge*, Z. Naturforsch. **34 b**, in print.
[7] *R. Jannach*, Thesis, Technical University Graz, 1975.
[8] *F. Höfler*, Mh. Chem. **107**, 893 (1976).
[9] *F. Höfler*, *W. Sawodny*, and *E. Hengge*, Spectrochim. Acta **26 A**, 819 (1970).
[10] *F. Höfler*, *S. Waldhör*, and *E. Hengge*, Spectrochim. Acta **28 A**, 29 (1972).
[11] *E. Hengge*, Mh. Chem. **102**, 734 (1971).
[12] *F. Höfler* and *E. Hengge*, Mh. Chem. **103**, 1513 (1972).
[13] *F. Höfler*, Mh. Chem. **104**, 694 (1973).
[14] *E. B. Wilson*, *J. C. Decius*, and *P. C. Cross*, Molecular Vibrations—The Theory of Infrared and Raman Vibrational Spectra. New York: McGraw-Hill. 1955.
[15] *F. Höfler*, *R. Jannach*, and *W. Raml*, Z. anorg. allg. Chem. **428**, 75 (1977).
[16] *W. Förster* and *H. Kriegsmann*, Z. anorg. allg. Chem. **327**, 305 (1964).
[17] *F. Höfler* and *R. Jannach*, Inorg. Nucl. Chem. Letters **11**, 743 (1975).