# Infrared and Raman spectra and normal coordinate analysis of disilylchloride

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Abstract—Disilylchloride has been synthesized by chlorination of disilane with boron trichloride. FTIR spectra have been obtained of the vapour phase and Raman spectra of the liquid phase of this molecule. The spectra are fully assigned for the first time. A normal coordinate analysis is carried out and the refined force constants are compared to previous works on disilane, disilyliodide and silylchloride. The height of the potential energy barrier to internal rotation in disilylchloride is also evaluated.

## INTRODUCTION

ALTHOUGH several methods have been described to obtain  $Si_2H_5Cl$  [1–6], the spectroscopic literature on this molecule is very scarce. CRAIG *et al.* [1] reported the i.r. spectrum and proposed tentative assignments of bands found in the 700–2200 cm<sup>-1</sup> region, and DRAKE and GODDARD [5] identified this molecule by <sup>1</sup>H NMR spectroscopy and described the main features of its Raman spectra. On the other hand, DURIG *et al.* [7] have published a very complete work on the ro-vibrational spectra, structure and normal coordinates of Si<sub>2</sub>H<sub>5</sub>I, which has proved very useful for the present investigation.

We have synthesized  $Si_2H_5Cl$  and recorded its Raman and FTIR spectra, in an attempt to obtain a complete vibrational assignment of its fundamental vibrations. The second goal of this work was to perform a subsequent normal coordinate analysis, which provides information on the potential function of this molecule, as well as on the vibrational properties of the SiH<sub>3</sub> and Si<sub>2</sub>H<sub>5</sub> groups.

### EXPERIMENTAL

CRAIG et al. [1] obtained  $Si_2H_5Cl$  as a product of the reaction between  $Si_2H_5I$  and AgCl. ABEDINI et al. [2] found that the preparation of this compound is possible by the reaction of  $Si_2H_6$  with HCl if the products are carefully purified. The chlorination of disilane by reaction with silver chloride [3, 4] or boron trichloride [5, 6] are also alternative means of obtaining this molecule.

We chose this last option.  $Si_2H_6$  was made to react with BCl<sub>3</sub> (ratio 3:1) in a reaction vessel of 42 ml, which was then held at 0°C for 8 h [6]. The product was fractioned by trap-to-trap distillation through a trap at -63°C, another one at -96°C, and finally  $Si_2H_5Cl$  was collected in a last trap at -196°C.

Disilane had been prepared by reduction of hexachlorodisilane (Aldrich) with lithium aluminium hydride (Merck) in a solution of dibutyl ether [8, 9].

Infrared spectra were obtained in the  $500-3500 \text{ cm}^{-1}$  region on a Perkin-Elmer Fourier transform spectrometer model 1725X, equipped with a Globar source and DTGS detector. A 10 cm cell was used for gaseous samples at different pressures and room temperature. Two spectra are shown in Fig. 1 recorded at pressures of (a) 7 and (b) 67 torr. Spectrum (b) shows saturated absorptions at 900 and 2200 cm<sup>-1</sup>, but was useful to measure band positions for the weaker bands.

The Raman spectrum was recorded in the liquid phase at room temperature on a Jobin Yvon U-1000 spectrometer with double monochromator, using a Spectra Physics  $Ar^+$  165 laser as exciting source (Fig. 2).

A summary of all features observed in our spectra is given in Table 1, together with proposed assignments as discussed below.

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Fig. 1. FTIR spectra of gaseous  $Si_2H_5Cl$  at room temperature: (a) 7 torr; (b) 67 torr.



Fig. 2. Raman spectrum of liquid  $Si_2H_5Cl$  at room temperature.

Table 1. Observed bands in the IR and Raman spectra and assignments for Si<sub>2</sub>H<sub>5</sub>Cl

IR (gas)	Rel. intens.	Raman (liquid)	Rel. intens. and depol.	Proposed assignment
3077	vw			$\nu_3 + \nu_{14}$
2980	vw			$v_6 + v_{12}$
2798	vw			$v_2 + v_{15}$
2538				
2519	w			$\nu_3 + \nu_{17}$
2360				
2340	m			$2\nu_5 + \nu_{15}$
2180	vs	2185	s, p	$\nu_{12}$
2164	vs			$v_1, v_{13}$
2154	vs	2155	vs, p	$\nu_2$
2145	vs			$\nu_3$
1866	vw			$2\nu_{14}$
1622				
1602	m			$\nu_3 - \nu_{16}$
1584				
1289	vw			$v_6 + v_9$
1174	vw			$\nu_{14} + 2\nu_{18}$
949				
935	s	925		$\nu_{14}$
885	m	870	vw	$\nu_4$
853				
843	vs	834	vw	$\nu_5$
834				
806	w			$\nu_6$
767	vs	759	w	$\boldsymbol{\nu}_7$
716				
707	m	707	vw	
669	w			$\nu_{15}$
583	s			~
543	S	554	w	$\nu_{16}$
520	s	534	m, p	$\nu_8$
489	w	493	vw, p	Vy
		435	m, p	$\boldsymbol{\nu}_{10}$
		416	m, p	_
		396	s, p	$\nu_{17}$
		230	vw	-
		198	w	_
		154	w	$\nu_{11}$
		122	w	Via

v very, s strong, w weak, m medium, p polarized.

#### VIBRATIONAL ASSIGNMENT

Since no previous structural study on  $Si_2H_5Cl$  was known to us, we assumed a  $C_s$  symmetry for this molecule, with the two tops in a staggered conformation, by comparison with other related molecules, like  $Si_2H_5I$  [7], and in accordance with the known structure of ethyl halides [10, 11].

This  $C_s$  symmetry leads to the following classification of the 18 normal modes of this molecule: 11A' (symmetric with respect to the molecular plane of symmetry) and 7A" (antisymmetric). All modes are both IR and Raman active. The A' modes give rise to IR hybrid bands (with  $\mu_{aa}$  and  $\mu_{bb}$  in principle different from zero) and to Raman polarized bands. The A" modes give IR c-type bands (only  $\mu_{cc} \neq 0$ ) and Raman depolarized bands.

These characteristics, as well as group frequency considerations and comparison with related molecules, led us to propose the assignment that is described below. By reference to the local symmetry of the SiH<sub>3</sub> group, we will label certain A' modes as symmetric or antisymmetric, in the usual way employed in the literature. In order to avoid confusion

with the proper  $C_s$  symmetry of this molecule, the adequate  $C_s$  species is always explicitly indicated in parentheses, together with the standard description of the mode.

## $SiH_3$ modes

SiH<sub>3</sub> stretching modes. Three bands are expected for the three stretching modes of the SiH<sub>3</sub> group, two A' and one A":  $v_1(A')$ , antisymmetric,  $v_3(A')$ , symmetric and  $v_{13}(A'')$ , antisymmetric. The  $v_1(A')$  and  $v_{13}(A'')$  modes appear as a degenerate band and have been assigned to the very strong gas phase IR band observed at 2164 cm<sup>-1</sup>. The  $v_3(A')$  mode is assigned to the very strong IR band at 2145 cm<sup>-1</sup>. This assignment is in agreement with those proposed for similar compounds [7, 9].

SiH<sub>3</sub> bending modes. There are five bending modes of the SiH<sub>3</sub> group: three deformations (2A' + A'') and two rocking modes (A' + A''). The deformations have been assigned in the IR spectrum as the medium intensity band at 885 cm<sup>-1</sup> ( $\nu_4(A')$ , antisymmetric), the very strong one at 843 cm<sup>-1</sup> ( $\nu_5(A')$ , symmetric), and the medium band at 933.5 cm<sup>-1</sup> ( $\nu_{14}(A'')$ , antisymmetric), which correspond to the liquid phase Raman bands at 870, 834 and 925 cm<sup>-1</sup>, respectively, the latter one being depolarized.

The two rocking modes were assigned for Si<sub>2</sub>H<sub>5</sub>I [7] as the IR lines at 515 (A') and 549 (A'') cm<sup>-1</sup> (520 and 565 cm<sup>-1</sup> in the Raman spectrum of the solid). In a similar way, we have assigned these bands as follows:  $\nu_9(A')$ , symmetric, at 489 cm<sup>-1</sup> (weak) in the IR and 493 cm<sup>-1</sup> (polarized) in the Raman; and  $\nu_{16}(A'')$ , antisymmetric, at 543 cm<sup>-1</sup> (strong) in the IR and 554 cm<sup>-1</sup> (depolarized) in the Raman.

#### $SiH_2$ modes

SiH<sub>2</sub> stretching modes. Two stretching modes (A' + A'') are expected for the SiH<sub>2</sub> group:  $\nu_2(A')$ , symmetric, and  $\nu_{12}(A'')$ , antisymmetric. Similarly to Si<sub>2</sub>H<sub>5</sub>I [7], these modes are expected to fall at higher frequencies than the SiH<sub>3</sub> modes when the SiH<sub>2</sub> group is bounded to a halogen. The  $\nu_2(A')$  mode has been assigned in this work to the very strong band observed at 2154 cm<sup>-1</sup> in the IR spectrum of the gaseous substance, and to the very strong and polarized band observed at 2155 cm<sup>-1</sup> in the Raman spectrum of the liquid. The  $\nu_{12}(A'')$  antisymmetric stretching mode has been assigned to the very strong IR band at 2180 cm<sup>-1</sup>, that appears at 2185 cm<sup>-1</sup> in the Raman spectrum.

SiH<sub>2</sub> bending modes. These modes are classified as 2A' + 2A''. The two A' modes are the SiH<sub>2</sub> deformation  $\nu_6$  and the SiH<sub>2</sub> wagging  $\nu_7$ . The two A'' modes are the SiH<sub>2</sub> twisting  $\nu_{15}$  and the SiH<sub>2</sub> rocking  $\nu_{17}$ . We have assigned  $\nu_6(A')$  to the weak IR band at 806 cm<sup>-1</sup> and  $\nu_7(A')$  to the very strong IR band at 767 cm<sup>-1</sup>. The Raman band of the latter vibration is weak and appears at 759 cm<sup>-1</sup>. A similar assignment was proposed for Si<sub>2</sub>H<sub>5</sub>I [7], (CH<sub>3</sub>)<sub>2</sub>SiH<sub>2</sub> [12] and CH<sub>3</sub>SiH<sub>2</sub>Cl [13].

Finally,  $\nu_{15}(A'')$  has been assigned to the weak IR band at 669 cm<sup>-1</sup> and  $\nu_{17}(A'')$  to the Raman band at 396 cm<sup>-1</sup>.

## Skeletal modes

We consider now the four skeletal vibrational modes: the Si-Si and Si-Cl stretching modes, the Si-Si-Cl bending mode and the torsional mode. The first three of these modes are in-plane motions and therefore they belong to the A' symmetry species, whereas the torsion is of A'' symmetry.

The  $v_{10}(A')$  Si-Si stretching mode has been assigned to a polarized Raman line of medium intensity that is observed at 435 cm<sup>-1</sup>. This mode appears at 432 cm<sup>-1</sup> for Si<sub>2</sub>H<sub>6</sub> [14] and at 446 cm<sup>-1</sup> for Si<sub>2</sub>H<sub>5</sub>I [7].

We have assigned the  $\nu_8(A')$  Si–Cl stretching mode to the strong IR band at 520 cm<sup>-1</sup>, which corresponds to the polarized Raman band of medium intensity at 534 cm<sup>-1</sup>. This mode was assigned for SiH<sub>3</sub>Cl [15] to the IR band at 551 cm<sup>-1</sup> and for methylchlorosilane [13] to the 501 cm<sup>-1</sup> Raman band, whereas for methyldichlorosilane [13] the mean value for the two Si–Cl stretching modes was 534.5 cm<sup>-1</sup>.

#### Disilylchloride

The  $v_{11}(A')$  Si-Si-Cl bending mode has been assigned to the weak Raman line at 154 cm<sup>-1</sup>, higher in frequency than the corresponding Si-Si-I bending mode in Si<sub>2</sub>H<sub>5</sub>I [7], which appears at 105 cm<sup>-1</sup>.

Finally, the  $v_{18}(A'')$  torsional mode, antisymmetric with respect to the symmetry of the SiH<sub>3</sub> group, appears in the Raman spectrum of the liquid at 122 cm<sup>-1</sup> (depolarized). This mode was assigned by DURIG and HAWLEY [13] at 165 cm<sup>-1</sup> for methylchlorosilane and at 173 cm<sup>-1</sup> for methyldichlorosilane.

#### MOLECULAR MODEL

The molecular structural parameters used for  $Si_2H_5Cl$  are shown in Table 2. They were taken from different sources, mainly from the  $Si_2H_5I$  paper [7], where high precision microwave data were used to refine the parameters. Thus, the parameters for the Si–SiH<sub>3</sub> part of the molecule were taken directly from the similar part of  $Si_2H_5I$ , but also the Si–H bond length and the SiSiH ( $\varepsilon$ ), SiSiCl ( $\delta$ ) and HSiH ( $\theta$ ) angles for the Si–SiH<sub>2</sub>Cl group were assumed to be the same as those for  $Si_2H_5I$ . The Si–Cl bond distance was taken from an IR study of SiH<sub>3</sub>Cl [15].

A few words should be added with respect to the angles that complete the geometry of this molecule, namely HSiH ( $\alpha$ ) (in the SiH<sub>3</sub> moiety) and HSiCl ( $\gamma$ ), and whose value is needed both to permit an easy calculation of the Cartesian coordinates of all the atoms, and, which is more important, to write down the angular redundancy conditions that are found when a complete set of internal coordinates is used (see below).

For the SiH<sub>3</sub> group, where all three HSiH ( $\alpha$ ) angles are assumed to be equal, as well as all three SiSiH ( $\beta$ ) angles, the well known geometry condition

$$2(1 - \cos \alpha) = 3\sin^2\beta \tag{1}$$

applies. For the  $SiH_2Cl$  part we derived a similar, but more involved, geometry condition:

$$\sin^2 \delta(1 + \cos \theta) = 2(\cos^2 \gamma + \cos^2 \varepsilon - 2\cos \gamma \cos \varepsilon).$$
(2)

Equations (1) and (2) were therefore used to calculate the values of the  $\alpha$  and  $\gamma$  angles that appear in Table 2.

The molecule is depicted in Fig. 3, where the Cartesian axes that make the inertial tensor diagonal are also shown. The moments of inertia are  $I_a = 48.19$ ,  $I_b = 216.59$  and  $I_c = 253.04$  au Å<sup>2</sup>. The molecule is therefore a prolate quasi-symmetric top, with an asymmetry parameter of  $\kappa = -0.92$  ( $\kappa = 1$  for a prolate symmetric top).

## NORMAL COORDINATE ANALYSIS

A normal coordinate analysis was carried out with the aims of, first, testing the validity of our assignments; second, providing a force field for this molecule for the first time;

Table 2. Molecular structural parameters assumed for  $Si_2H_5Cl$ 

Bond lengths (Å)	Bond angles (°)
Si-H: $r = 1.491$ (in SiH <sub>3</sub> group) Si-Si: $R = 2.336$ Si-H: $d = 1.478$ (in SiH <sub>2</sub> Cl group) Si-Cl: $D = 2.049$	HSiH: $\alpha = 107.58$ (in SiH <sub>3</sub> group) SiSiH: $\beta = 111.3$ (in SiH <sub>3</sub> group) HSiH: $\theta = 110$ (in SiH <sub>2</sub> Cl group) SiSiH: $\varepsilon = 111.8$ (in SiH <sub>2</sub> Cl group) HSiCl: $\gamma = 108.18$ SiSiCl: $\delta = 106.7$

and, finally, comparing the refined force constants with those of similar or related molecules.

We worked within the usual Wilson FG matrix method. We used 20 internal coordinates  $q_i$  as described in Table 3. With these, 18 normalized symmetry coordinates  $S_m$  were chosen following the definitions of DURIG *et al.* for CH<sub>3</sub>CH<sub>2</sub>X molecules [16], as shown in Table 4. In order to adequately take into account the symmetry of the molecule, we defined two redundancy coordinates  $R_n$  corresponding to the derivatives of the geometry relations [(1) and (2)] that exist among the angles of either top. After derivation, we find for the SiH<sub>3</sub> group the usual relation:

$$2\sin \alpha(\Delta \alpha_1 + \Delta \alpha_2 + \Delta \alpha_3) - 3\sin 2\beta(\Delta \beta_1 + \Delta \beta_2 + \Delta \beta_3) \equiv 0.$$
(3)

For the SiH<sub>2</sub>Cl part, the redundancy condition turns out to be:

$$2(\cos\delta\cos\gamma - \cos\varepsilon)\sin\varepsilon(\Delta\varepsilon_1 + \Delta\varepsilon_2) + 2(\cos\varepsilon\cos\delta - \cos\gamma)\sin\gamma(\Delta\gamma_1 + \Delta\gamma_2) + 2[2\cos\varepsilon\cos\gamma - \cos\delta(1 + \cos\theta)]\sin\delta\Delta\delta + \sin^2\delta\sin\theta\Delta\theta \equiv 0.$$
(4)

The symmetry coordinates involving the corresponding angle bendings can therefore be chosen to be orthogonal to these redundancy conditions.

A force field refinement was performed using the program AJEF [17], which allows relations to be imposed upon the parameters to be refined. This is useful when approximate force field models, like the well known Urey-Bradley or Valence Force Field models, are to be employed.

We took initial values for the force constants referred to internal coordinates from the Si<sub>2</sub>H<sub>5</sub>I work [7] and from a SiH<sub>3</sub>Cl work [18]. With these, the F matrix in symmetry coordinates  $F_{sym}$  was nearly diagonal, and only diagonal elements were allowed to refine, with the following further constraints:  $F_{1,1} = F_{13,13}$  and  $F_{2,2} = F_{12,12} = 2.69$  mdyn Å<sup>-1</sup> (fixed to the value or Ref. [7]). Our refined set of symmetry force constants is shown in Table 5,



Fig. 3. The molecular model adopted for Si<sub>2</sub>H<sub>5</sub>Cl. Axes *abc* are the principal axes referred to the centre of mass.

Bond stretchings	Angle bendings
Si-H <sub>i</sub> bonds: $\Delta r_i$ (i = 1, 3) in SiH <sub>3</sub> group	H <sub>i</sub> SiH <sub>i</sub> angles: $\Delta \alpha_k (k = 1, 3)$ in SiH <sub>3</sub> group
Si–Si bond: $\Delta R$	SiSiH <sub>i</sub> angles: $\Delta \beta_i (i=1,3)$ in SiH <sub>2</sub> group
Si-H <sub>i</sub> bonds: $\Delta d_i$ (i = 1,2) in SiH <sub>2</sub> Cl group	HSiH angle: $\Delta \theta$ in SiH <sub>2</sub> Cl group
Si-Cl bond $\Delta D$	SiSiH angles $\Delta \varepsilon_i (i = 1, 2)$ in SiH <sub>2</sub> Cl group
	HSiCl angles $\Delta \gamma_i (i=1,2)$
Torsion	SiSiCl angle: $\Delta \delta$
H <sub>1</sub> SiSiCl angle between planes: $\Delta \tau$	

Table 3. Internal coordinates used in the normal coordinate analysis

Table 4. Symmetry coordinates  $S_i$  and redundancies  $R_i$  defined in this work

A" species
$S_{12} = 2^{-1/2} (\Delta d_1 - \Delta d_2)$ $S_{13} = 2^{-1/2} (\Delta r_2 - \Delta r_3)$ $S_{14} = 2^{-1/2} (\Delta \alpha_2 - \Delta \alpha_3)$ $S_{15} = 2^{-1} (\Delta \epsilon_2 - \Delta \epsilon_1 - \Delta \gamma_2 + \Delta \gamma_1)$ $S_{16} = 2^{-1/2} (\Delta \beta_2 - \Delta \beta_3)$ $S_{17} = 2^{-1} (\Delta \epsilon_2 - \Delta \epsilon_1 + \Delta \gamma_2 - \Delta \gamma_1)$ $S_{18} = \Delta t$

Factors m, n, p, q, s and t calculated to satisfy Eqns (3) and (4) using equilibrium values of angles as given in Table 2. Angular coordinates are scaled with a weighting factor of 1 Å.

Table 5. Force constants in symmetry coordinates refined in this work. Initial values are also given for comparison. Units are mdyn  ${\hat A}^{-i}$ 

	A' sp		A" species		
	Refined	Initial		Refined	Initial
$F_{1,1}$	2.6545	2.682	F <sub>12,12</sub>	2.69*	2.69
$F_{2,2}$	2.69*	2.69	$F_{13,13}$	2.6545†	2.682
$F_{3,3}$	2.6918	2.682	$F_{14,14}$	0.4352	0.397
$F_{4,4}$	0.3889	0.397	$F_{15, 15}$	0.3005	0.3235
F <sub>5.5</sub>	0.3884	0.4073	$F_{16, 16}$	0.4122	0.419
$F_{6,6}$	0.3656	0.295	$F_{17, 17}$	0.3869	0.4135
$F_{7,7}$	0.4938	0.4103	$F_{18, 18}$	0.0054	0.0033
F <sub>8.8</sub>	2.3599	2.980	$F_{15,17}$	0.0415*	0.0415
F <sub>9.9</sub>	0.3835	0.419			
$F_{10, 10}$	1.8254	1.919			
$F_{11,11}$	0.7492	0.563			
$F_{5,10}$	0.0308*	0.0308			
$F_{5,11}$	0.0862*	0.0862			
$F_{9,11}$	-0.178*	-0.178			

\* Value kept fixed in the fit.

† Fixed to  $F_{1,1} A'$  species value.

Table 6. Force constants in internal coordinates obtained in this work, and bibliography values for Si<sub>2</sub>H<sub>3</sub>I [7], Si<sub>2</sub>H<sub>6</sub> [14] and SiH<sub>3</sub>Cl [18]. Units are mdyn Å<sup>-1</sup> for the stretching coordinates, mdyn for stretch-bend interactions, and mdyn. Å for bending coordinates

		This work	Si <sub>2</sub> H <sub>5</sub> I [7]	Si <sub>2</sub> H <sub>6</sub> [15]	ClSiH <sub>3</sub> [17]
	$f_{\rm r}$	2.6670	2.682	2.690	
	f <sub>R</sub>	1.8254	1.919	1.838	
	fa	2.69*	2.69		
•	$f_{\rm D}$	2.3559			2.98
	$f_a(trans)$	0.3512	0.397	0.436	
	$f_a(gauche)$	0.3281			
	$f_{\beta}(trans)$	0.3307	0.419	0.396	
	$f_{\beta}(gauche)$	0.3163			
	$f_{\theta}$	0.3656	0.295†		
	$f_{\epsilon}$	0.3070	0.410†		
	$f_{\gamma}$	0.2836	0.327†		
	$f_{\delta}$	0.7492	0.563†		
	$f_{\tau}$	0.0054			
	$f_{\pi}$	0.0124			
	$f_{\mathbf{R}a}$	0.0129			
	$f_{\mathbf{R}\beta}$	-0.0121			
	$f_{aa}(trans)$	-0.084			
	$f_{a\sigma}(gauche)$	-0.061			
	$f_{\beta\beta}$	-0.067			
	$f_{\epsilon\epsilon}$	-0.078			
	$f_{\gamma\gamma}$	-0.019			
	$f_{\alpha\beta}$	-0.065			
	fud	0.036			
	$f_{\beta\delta}(trans)$	-0.179	-0.218		
	$f_{\beta\delta}(gauche)$	0.039			
	$f_{\epsilon\gamma}$	-0.102	0.045		

\* Value kept fixed in the fit of the present work.

<sup>†</sup> Value for SiH<sub>2</sub>I part.

Table 7. Assignment of fundamental modes and main values of potential energy distribution for  $Si_2H_5Cl$ 

ν	Obs.	Calc.	Assignment and PED
A' spe	cies		
$\nu_1$	2164	2164.0	1.00 SiH <sub>3</sub> antisym. str.
$\nu_2$	2154	2154.4	1.00 SiH <sub>2</sub> sym. str.
v3	2145	2145.0	1.00 SiH <sub>3</sub> sym. str.
$\nu_{\perp}$	885	884.9	0.92 SiH <sub>3</sub> antisym. def., 0.07 SiH <sub>3</sub> rock
$v_5$	843	843.1	0.88 SiH <sub>3</sub> sym. def., 0.08 SiH <sub>2</sub> scissors
V.6	806	805.9	0.84 SiH <sub>2</sub> wag, 0.13 SiH <sub>2</sub> scissors
$v_7$	767	767.6	$0.75 \text{ SiH}_2 \text{ scissors}, 0.12 \text{ SiH}_2 \text{ wag}, 0.05 \text{ SiH}_3 \text{ sym. def.}$
$\nu_8$	520	520.6	0.55 SiH <sub>3</sub> rock, 0.25 Si-Cl str., 0.13 Si-Si str.
Vy	489	488.7	0.65 Si-Cl str., 0.30 SiH <sub>3</sub> rock
$v_{w}$	435	435.0	0.78 Si-Si str., 0.08 SiH <sub>3</sub> rock
$v_{11}$	154	153.2	1.00 SiSiCl bend
A" spe	cies		
$\nu_{12}$	2180	2179.7	1.00 SiH <sub>2</sub> antisym. str.
$\nu_{13}$	2164	2164.1	1.00 SiH <sub>3</sub> antisym. str.
$\nu_{14}$	933.5	933.5	0.93 SiH <sub>3</sub> antisym. def., 0.07 SiH <sub>3</sub> rock
V 15	669	668.9	0.94 SiH <sub>2</sub> twist, 0.05 torsion
$\boldsymbol{\nu}_{16}$	543	543.0	$0.90 \text{ SiH}_3 \text{ rock}, 0.07 \text{ SiH}_3 \text{ antisym. def.}$
$\nu_{17}$	396	396.0	$0.97 \text{ SiH}_2 \text{ rock}$
$\nu_{18}$	122	122.0	0.95 torsion, 0.05 twist

#### Disilylchloride

The reduced moment of inertia  $I_r$  [20] can be calculated from the structural parameters of Table 2. The reduced moment of inertia constant

$$F = h/8\pi^2 c I_{\rm r} \tag{6}$$

then turns out to be  $3.188 \text{ cm}^{-1}$ . Using this value and the wavenumber of the torsional band from our Raman spectrum,  $\nu_r = 122 \text{ cm}^{-1}$ , we estimate a barrier height to internal rotation of  $V_3 = 519 \text{ cm}^{-1}$  (1.49 kcal mol<sup>-1</sup>). This value seems quite reasonable compared to that calculated for Si<sub>2</sub>H<sub>6</sub> [14],  $V_3 = 439 \text{ cm}^{-1}$  (1.26 kcal mol<sup>-1</sup>). The barrier is slightly higher for Si<sub>2</sub>H<sub>5</sub>Cl, in a similar way to what is found for monohalogenated substituted ethanes [20].

#### DISCUSSION

Since no force constant calculations had been previously performed for this molecule, we have to take the Si<sub>2</sub>H<sub>5</sub>I [7] and the Si<sub>2</sub>H<sub>6</sub> [14] works as references. All vibrations that are practically "pure" (coefficient of potential energy distribution higher than 0.90) are well accounted for by small adjustments of the corresponding diagonal force constants of Si<sub>2</sub>H<sub>5</sub>I in the symmetry coordinate basis. The exception is of course the SiSiCl bending mode, where the force constant  $F_{11,11}$  is much higher than that of the SiSiI bending mode. The Si–Cl stretch occurs at higher frequency that the Si–I stretch and is heavily mixed with the nearby SiH<sub>3</sub> rocking mode. In the first stages of the refinement process, we had attempted to represent the two SiH<sub>3</sub> rocking modes by one single force constant, keeping  $F_{16,16} = F_{9,9}$  in the fit, in a similar way to the condition upon the Si–H stretchings (i.e.  $F_{13,13} = F_{1,1}$ ). It was impossible, however, to maintain this restriction if reasonable values were wanted for the calculated wavenumbers, as a consequence of the above mentioned interaction, and the  $F_{9,9}$  constant turns out to be lower than expected.

The bending modes are more strongly blended in Si<sub>2</sub>H<sub>5</sub>Cl than in the reference iodine compound. Thus, larger changes are required to the corresponding force constants in order to reproduce the observed wavenumbers. A similar situation to that mentioned above for the SiH<sub>3</sub> rock was found for  $F_{14,14}$  and  $F_{4,4}$ , which had to be released independently, after attempts to maintain their values equal. This is a consequence of the mode mixing characteristic of this molecule.

With respect to the force constants in internal coordinate representation, we can see that practically all interaction constants are small, with the exception of that between the SiSiH ( $\beta$ ) and SiSiCl ( $\delta$ ) (*trans*) angles,  $f_{\beta\delta}$ . A similar result was found for Si<sub>2</sub>H<sub>3</sub>I. Another similarity is found with respect to the Si–Cl stretching force constant. The value obtained in the present work is considerably smaller than that calculated for silyl chloride [18]. DURIG *et al.* [7] observed a smaller value for the Si–I stretching constant in Si<sub>2</sub>H<sub>5</sub>I than that previously reported for SiH<sub>3</sub>I [19]. Our result seems to support the hypothesis proposed by DURIG *et al.* [7] of a weakening of the Si–X bond in the disilyl compound relative to the silyl compound.

With our model, slightly different values are obtained for the bending force constants of the  $\alpha$  and  $\beta$  angles in position gauche or trans with respect to the Cl atom. The average values of  $f_{\alpha}$  and  $f_{\beta}$  are smaller than the corresponding values for Si<sub>2</sub>H<sub>5</sub>I. This is probably also a consequence of the more extensive mode mixing found for Si<sub>2</sub>H<sub>5</sub>Cl among all bending modes of A' symmetry. The  $f_{\alpha}$  values are larger than the  $f_{\beta}$  values, in a similar way to what was found for Si<sub>2</sub>H<sub>6</sub> [14], and opposite to the results for Si<sub>2</sub>H<sub>5</sub>I, where apparently these force constants had been switched. For the SiH<sub>2</sub>Cl moiety, we also find that the force constant  $f_{\theta}$  (HSiH angle) is larger than  $f_{\varepsilon}$  (SiSiH angle), following the same pattern than the corresponding  $f_{\alpha}$  and  $f_{\beta}$ .

We can assume a threefold oscillation barrier for the internal rotation of the silyl group with respect to the heavier  $SiH_2Cl$  moiety, given by:

$$V = (1/2)V_3(1 - \cos 3\alpha). \tag{5}$$

compared to initial values. Corresponding values for the force constants referred to internal coordinates are shown in Table 6 together with previously reported values.

Table 7 summarizes the result of the normal coordinate analysis for  $Si_2H_5Cl$ . Observed values of the fundamental vibrations of this molecule are compared to calculated values obtained with our refined force field, and a description of each normal vibration is also given by means of the potential energy distribution of the corresponding normal coordinate.

Using the force constants of Table 5 we have also calculated the wavenumber of the fundamental vibrations of the isotopomers with  ${}^{37}Cl$ ,  ${}^{29}Si_2$  and  ${}^{28}Si^{29}Si$ . They are available upon request.

It is difficult to give an accurate estimation of the uncertainties of the results of this work. The principal source of uncertainty lies in the approximations involved in the structural parameters. The wavenumbers used for the force constant refinement were not corrected for anharmonicity, and the force field used is also a very simplified model. The relative uncertainties generated in the fitting process are quite small, especially since only diagonal force constants were allowed to refine, and can be ignored in the whole process. A conservative estimate would admit an uncertainty of  $\pm 0.02$  mdyn Å<sup>-1</sup> in the force constants referred to internal coordinates and  $\pm 20$  cm<sup>-1</sup> in the torsional barrier. The overall accuracy could be much improved if the proper geometry of this molecule were determined, and if overtone transitions of the torsional mode were observed, for example in a far-IR study.

#### CONCLUSION

A complete assignment of the IR and Raman spectrum of  $Si_2H_5Cl$  has been carried out for the first time. A normal coordinate analysis has been performed that supports the assignment and reveals the mixing of the symmetric bending vibrations of this molecule. Force constants in internal coordinate representation compare well with previous values for related molecules. An estimation of the barrier to the internal rotation of the silyl group is also performed.

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