

The Vibrational Spectra and Structures of Hexachlorodisilazane and Hexamethyldisilazane

E. A. ROBINSON* and Keinosuke HAMADA

Chemical Laboratory, Faculty of Education
Nagasaki University, Nagasaki

(Received October 21, 1971)

Abstract

The spectroscopic and structural investigations of hexachlorodisilazane and hexamethyldisilazane are reported. According to their spectra, the structure of those molecules seem to be D_{3d} . Generally, a rigid D_{3d} is indistinguishable from an internal rotating D'_{3h} according to vibrational spectra. However, in this case, the molecules appear to be D'_{3h} structure with free rotation of SiX_3 ($\text{X}=\text{Cl, Me}$) groups.

Introduction

The vibrational spectra and structures of hexachlorodisilazane and hexamethyldisilazane have already been reported,^{1,2)} but there is a difference in assignments of some bands and in determinations of molecular structure between the references and the present work.

The present authors have observed the vibrational spectra of above compounds, especially the excellent quality Raman spectra using a laser Raman spectrometer.

The structures of those molecules seem to be D_{3d} structure, on the basis of the selection rules of skeletal fundamentals, being different from the C_{2v} structure previously reported,^{1,2)} The analogous molecules, disiloxane and disiloxane- d_6 ³⁾ have been indicated by vibrational analysis that the point group symmetry of the molecules is D_{3d} , and hexamethyldisilane⁴⁾ has been seemed to be D'_{3h} by vibrational and electron diffraction analysis.

* Department of Chemistry, University of Toronto, Toronto, Canada

Experimental

Materials. Ammonia gas diluted with nitrogen gas was passed into ether containing silicon tetrachloride at -75°C , in order to synthesize hexachlorodisilazane^{5,6}. Hexamethyldisilazane was purchased. Those compounds were purified by distillation.

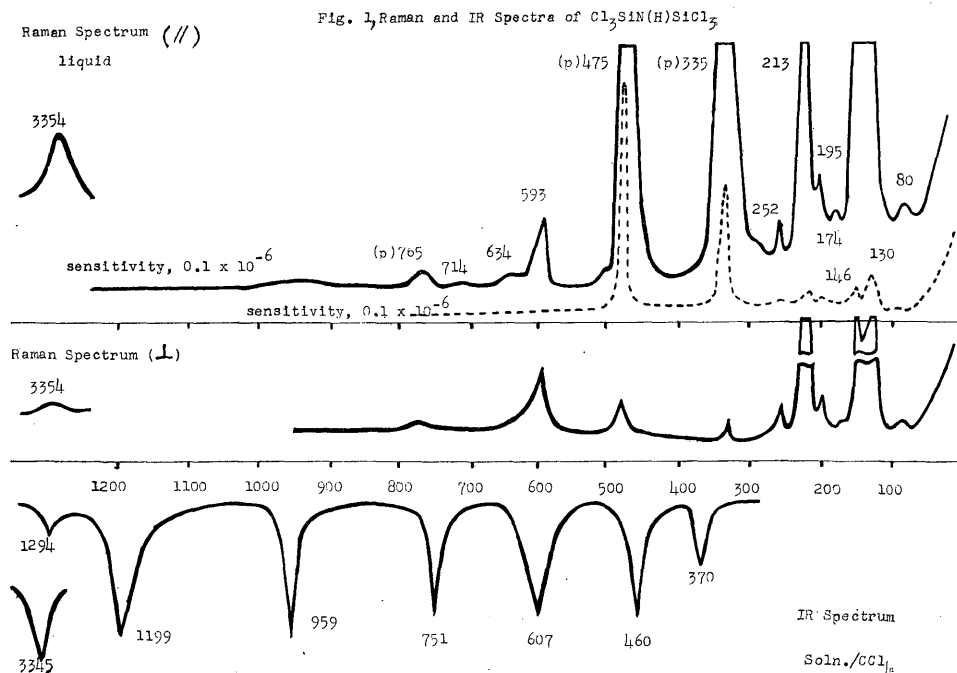
Measurements. Raman spectra were recorded on a Spex 1401 using an argon or a krypton ion laser. Infrared spectra were measured with a Perkin-Elmer 521 spectrometer which had KRS-5 optics. So infrared spectra could not be measured under about 300 cm^{-1} .

Results and Discussion

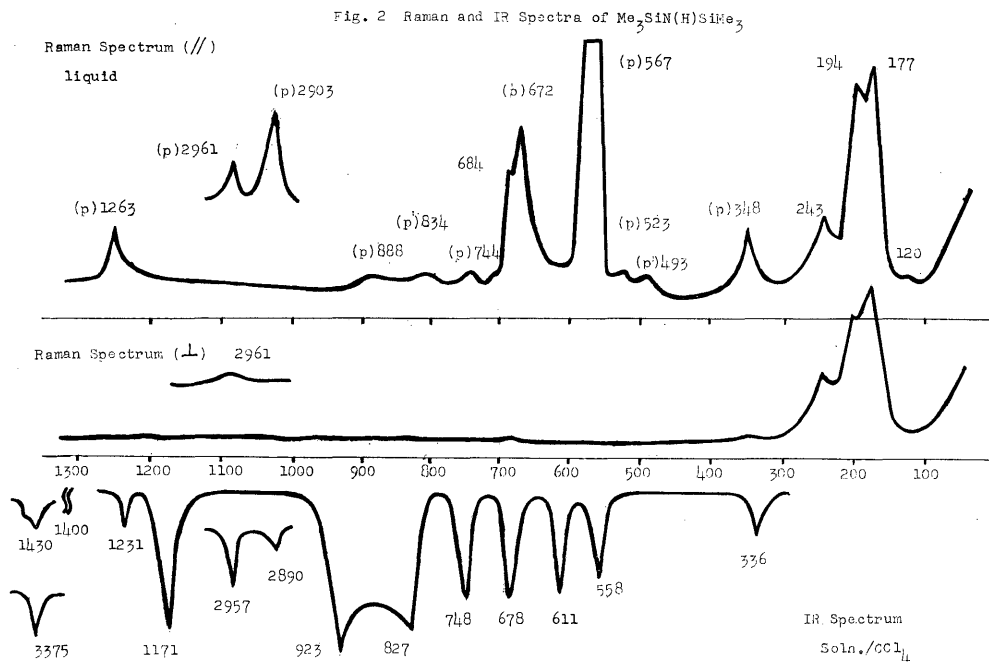
The Raman and infrared spectra of hexachlorodisilazane and hexamethyldisilazane are given in Figs. 1 and 2.

The spectra, if complete, are too simple to be interpreted on the basis of C_{2v} or C_s symmetry. And the lack of coincidences between infrared and Raman frequencies implies a symmetry centre in the molecule.

The provable structure with a symmetry centre is that of point group D_{3d} , D_{3h} and D'_{3h} . But the rigid D_{3d} and D_{3h} which are under certain fixed orientations of SiY_3 ($\text{Y} : \text{Cl, Me}$) groups have to be excluded, because disila-



In Raman spectrum of Fig.1, 765 cm^{-1} band is corrected to be depolarized band and 714 cm^{-1} band, to be polarized band.



zane derivatives have NH group which can not be regarded as a point when it is at standstill. So the only plausible structure of compounds seems to be D'_{3h} structure for free internal rotation of SiY_3 group.

However, the present experimental results indicate that D_{3d} is more preferable to D'_{3h} in those disilazane derivatives as shown in Table 1, because the three depolarized Raman band frequencies of species E_g have no coincidences with IR band frequencies in the point group D_{3d} , but the four depolarized Raman band frequencies of species E' have to be coincident with IR band frequencies in the point group D_{3h} and D'_{3h} .

The assignments of SiCl_3 stretching, deformation and rocking bands shown in Table 1 owe greatly to those of SiCl_3 of trichloromonofluorosilane^{7,8}). The assignments of Si-N-Si bending bands are still ambiguous, because their wave numbers might be too high to be expected.

The assignments of methyl group are shown in Table 2 by analogy with other molecules^{4,9}).

A rigid D_{3d} structure is compatible with a D'_{3h} structure in which the SiCl_3 groups undergo free internal rotation about a linear Si-N-Si axis.

Because it has generally been accepted that in the ethane-like molecules, the spectrum is expected to deviate from D_{3d} selection rules at some unspecified low value of the barrier to internal rotation¹⁰).

Table. 1 Symmetry Species, Selection Rules and Frequency Assignments of Skeletal Fundamentals of $\text{Cl}_3\text{SiN(H)SiCl}_3$ and $\text{Me}_3\text{SiN(H)SiMe}_3$

Species	Vibrn. No.	Approximate Form of Vibrn.	Selection Rule		$\text{Cl}_3\text{SiN(H)SiCl}_3$		$\text{Me}_3\text{SiN(H)SiMe}_3$	
			D_{3d}		Raman	IR	Raman	IR
			Raman	IR				
A_{1g}	1	Si-N-Si stretch.	$a(p)$	ia	(p)714w	—	(p)744w	—
	2	Si-Y stretch.	$a(p)$	ia	(p)475vs	—	(p)567vs	—
	3	Si-Y ₃ deform.	$a(p)$	ia	(p)335vs	—	(p)348m	—
A_{1u}	4	Torsion	ia	ia	—	—	—	—
A_{2u}	5	Si-N-Si stretch.	ia	a	—	1199vs	—	1171vs
	6	Si-Y stretch.	ia	a	—	460vs	—	558m
	7	Si-Y ₃ deform.	ia	a	—	370m	—	336w
E_g	8	Si-Y stretch.	$a(dp)$	ia	634w	—	684m	—
	9	Si-Y ₃ deform.	$a(dp)$	ia	213vs	()	243m	()
	10	Si-Y ₃ rock.	$a(dp)$	ia	130vs (146vs)	()	177vs (194s)	()
E_u	11	Si-N-Si bend.	ia	a	—	607vs	—	611s
	12	Si-Y stretch.	ia	a	—	751s	—	748s
	13	Si-Y ₃ deform.	ia	a	—	()	—	()
	14	Si-Y ₃ rock.	ia	a	—	()	—	()

a indicates Raman or IR active and ia , Raman or IR inactive.

() indicates IR active but the band lies below the observational limit. Y is Cl or Me.

Table. 2 Frequency Assignments of CH_3 of $\text{Me}_3\text{SiN(H)SiMe}_3$, $\text{Me}_3\text{SiSiMe}_3$, and Me_3SiCl

Approximate Form of Vibrn.	$\text{Me}_3\text{SiN(H)SiMe}_3$		$\text{Me}_3\text{SiSiMe}_3^{(4)}$	$\text{Me}_3\text{SiCl}^{(5)}$
	Raman	IR		
CH_3 asym. stretch.	(p)2961	2957	2955	2977
CH_3 sym. stretch.	(p)2903	2890	2893	2912
CH_3 asym. deform.		1430	1373	1454
" "		1400	1317	1415
CH_3 sym. deform.	(p)1263		1245	1260
CH_3 asym. rock.	(p) 832	827	883	857
CH_3 sym. rock.	(p) 672	678	833	767

Table. 3 Frequency assignments of NH of $\text{Cl}_3\text{SiN(H)SiCl}_3$
and $\text{Me}_3\text{SiN(H)SiMe}_3$

Form of Vibrn.	$\text{Cl}_3\text{SiN(H)SiCl}_3$		$\text{Me}_3\text{SiN(H)SiMe}_3$	
	Raman	IR	Raman	IR
NH stretch.	(p) 3354m	3345m	not measured	3375m
NH deform.		959vs		923vs

- 1) H. Kriegsmann, *Z. f. Electrochemie*, **61**, 1088 (1957)
- 2) H. Bürger, K. Burczyk, F. Höfler and W. Sawodny, *Spectrochimica Acta*, **25A**, 1891 (1969)
- 3) R. C. Lord, D. W. Robinson and W. C. Schumb, *J. Amer. Chem. Soc.*, **78**, 1327 (1955)
- 4) K. Shimizu and H. Murata, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chemical Section)* **77**, 343 (1956)
- 5) W. C. Schumb, *J. Amer. Chem. Soc.*, **75**, 6085 (1953)
- 6) H. Bürger, M. Schulze und U. Wannagat, *Inorg. Nucl. Chem. Letters*, **3**, 43 (1967)
- 7) K. Hamada, G. A. Ozin and E. A. Robinson, *Can. J. Chem.*, **49**, 477 (1971)
- 8) K. Hamada, G. A. Ozin and E. A. Robinson, *Bull. Chem. Soc. Japan*, **44**, 2555 (1971)
- 9) A. L. Smith, *J. Chem. Phys.*, **21**, 1997 (1953)
- 10) J. F. Griffiths, *Spectrochimica Acta*, **25A**, 965 (1968)