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Raman, IR, NMR, and NQR of Chlorofluorosilanes

Keinosuke HAMADA*, G. A. OZIN, and E. A. ROBINSON
Department of Chemistry, University of Toronto, Toronto, Canada

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Excellent-quality Raman spectra of chlorofluorosilanes have been observed using a laser Raman spectrometer. These Raman spectra will be reported here and compared with the IR spectra of those compounds. In additon, the fluorine NMR and the chlorine NQR of chlorofluorosilanes have been measured. The fluorine chemical shifts of chlorofluorosilanes increase with an increase in the number of fluorine atoms in each compound. The chlorine quadrupole resonance has been observed only for trichloromonofluorosilane, and the resonance frequency is 19.753 MHz at −196°C.

Experimental

Materials. The chlorofluorosilanes were prepared using the method of Booth and Swinehart,[1] in which a Swarts-type reaction was used. Silicon tetrachloride was partially fluorinated using antimony trifluoride and incorporating antimony pentachloride as a catalyst, and the chlorofluorosilanes were separated using trap-to-trap distillation techniques. The separated fractions were found to be sufficiently pure for Raman and IR spectroscopic measurements.

Measurements. Raman spectra were recorded on a Spex 1401 using an argon or a krypton-ion laser. The infrared measurements were done with a Perkin-Elmer 521 spectrometer whose optic material was silver chloride. The NMR spectra of fluorine for the compounds were obtained with a Varian Associate HR-60 high-resolution spectrometer operating at 56.4 MHz. The NQR measurements of chlorine for the compounds were done with a super-regenerative-type spectrometer.

Results and Discussion

Raman and IR. Table 1 shows the Raman and IR spectra for chlorofluorosilanes in the gas phase. The vibrational data for tetrafluorosilane and tetrachlorosilane have previously been reported,[2–4] and the figures for tetrachlorosilanes are cited from Ref. 4. The vibrational data for chlorofluorosilanes are tabulated in Table 1 with reference to the correlation diagram, the polarization data, the band contours of some infrared spectra, and the vibrational spectra of other SiX_mY_{4-m}-type molecules.

NMR. The fluorine chemical shifts of chlorofluorosilanes relative to an inner standard, trichloromonofluoromethane, are shown in Table 2. The fluorine chemical shifts, δ ppm, increase with an increase in the number of fluorine atoms. This trend in the chemical shifts for $SiCl_mF_{4-m}$ is same as that in the BCl_mF_{3-m}, $POCl_mF_{3-m}$, PCl_mF_{5-m}, and CCl_mF_{4-m} series

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[*] Present address: Faculty of Education, Nagasaki University, Bunkyo-cho, Nagasaki

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Table 1. Raman and IR spectra of $SiCl_mF_{4-m}$ in gas state

T_d SiF_4 Raman	IR
1025 wbr	1025 s
(p) 798 s	*ia*
389 mwbr	*a*
260 wbr	*ia*

C_{3v} SiF_3Cl Raman	IR
1004 vw	1010 s
(p) 878 w	876 s
(p) 593 s	590 m
(p) 351 mw	*a*
255 vw	*a*
222 w	*a*

C_{2v} SiF_2Cl_2 Raman	IR
987 vw	990 s
(p) 915 w	912 s
638 w	656 s
(p) 520 s	513 w
(p) 324 mw	*a*
303 w	*a*
279 w	*a*
210 w	*ia*
(p) 174 mw	*a*

T_d $SiCl_4$ Raman	IR
608	
(p) 422	
220	
148	

C_{3v} $SiFCl_3$ Raman	IR
(p) 947 vw	942 s
638 wbr	634 s
(p) 464 s	*a*
(p) 240 m	*a*
283 mw	*a*
166 m	*a*

Raman spectra are obtained at 600 mmHg and 25°C, and IR at 30 mmHg and 25°C.
ia means IR inactive and *a*, IR active, but the IR spectrum did not appear because of AgCl optic material.

Table 2. Chemical shifts of $SiCl_mF_{4-m}$ to CCl_3F

Compound	Chemical shift Hz	Chemical shift δ ppm
SiF_4	−9188	163
$SiClF_3$	−7640	135
$SiCl_2F_2$	−6320	112
$SiCl_3F$	−5316	94

and is opposite to that in the PCl_mF_{3-m} and $P(NMe_2)_mF_{3-m}$ series[5,6] in direction. The chemical shifts in the $Si(Et)_mF_{4-m}$ and $Si(Me)_mF_{4-m}$ series have the minimum value of a chemical shift at 2 or 3 fluorine atoms in each series.

NQR. The only chlorine quadrupole resonance frequency observed for trichloromonofluorosilane at −196°C is a resonance of 19.753 MHz between the running frequencies of 18.8 and 22.0 MHz. Silicon tetrachloride has four resonance lines whose average value is 20.391 MH.[7] It is not sure whether trichloromonofluorosilane has only one resonance line like trichlorosilane,[8] or whether the lines other than the one line have just not yet appeared. The chlorine quadrupole resonance for dichlorodifluorosilane has not yet been found. This might be because the present authors have not been able to get a NQR spectroscopically-pure substance. They have also not been able to obtain NQR spectroscopically-pure trifluoromonochlorosilane.

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