PRINCIPAL SPECTRAL PARAMETERS OF THE RAMAN-SCATTERING LINES OF TETRAMETHYLSILANE AND METHYLCHLOROSILANES

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PRINCIPAL SPECTRAL PARAMETERS OF THE RAMAN-SCATTERING LINES OF TETRAMETHYLSILANE AND METHYLCHLOROSILANES

(Presented by Academician I. V. Obreimov, May 31, 1968)

By the photoelectric method we have studied the Raman spectra of the compounds $(CH_3)_4Si$, $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, and CH_3SiCl_3. The fundamental frequencies, integral and peak intensities, half-widths, and degrees of depolarization of the lines were measured. In the scales $5b'^2 + 7g'^2$ and $5b'^2 + 13g'^2$, corrected relative scattering coefficients (standard intensities) were calculated. Values of the invariants of the tensors of polarizability derivatives were obtained. Taking into account the local-field correction, calculated on the basis of refractive-index dispersion data, the absolute cross sections of spontaneous Raman scattering of light were calculated for the methylchlorosilanes in the case of the exciting mercury line 4358 Å and the ruby-laser light 6943 Å. Measurements of the spectral characteristics were carried out in the liquid phase at a temperature of 25-30°. The 802 cm^{-1} line of cyclohexane was taken as the standard. The procedure of our investigation has been described previously (^{1}). The results are given in Tables 1-3.

The interpretation of the normal-vibration frequencies (Table 1) is based on calculations of the potential functions of molecules of this homologous series ($^{2-4}$)*. Difficulties are associated with the assignment of the 700 and 761 cm^{-1} lines in the spectrum of trimethylchlorosilane. Which of them belongs to the antisymmetric vibration ν_{as}(Si—C)? The possible ambiguity in assigning these lines is discussed in (^{5}). Data on integral intensities in the Raman spectra do not provide complete clarity in answering the question posed. Both lines are depolarized and weak in Raman scattering. Studies in infrared absorption show that, in the 600-765 cm^{-1} region in the gas phase, three bands appear: 637, 699, and 764 cm^{-1}. The absolute intensities of these bands are respectively 120, 70, and $170 \cdot 10^{-9}$ cm^2/molecule • sec. The 637 cm^{-1} band undoubtedly belongs to the symmetric stretching of the Si–C bond. Of the two remaining bands, in accordance with the selection rules, the vibration ν_{as}(Si—C) should be assigned to 764 cm^{-1}. It has a greater intensity than 637 cm^{-1}. The 699 cm^{-1} band is almost 2 times weaker and, apparently, is composite.

The principal fraction of the scattered light in the compounds studied (70-90%) is due to vibrations of the methyl groups, with 60-80% due to stretching vibrations of the C—H bonds. Replacement in tetramethylsilane of CH_3 groups by chlorine atoms strongly affects the parameters of the stretching vibrations of Si—C and even, in part, the properties of C—H. The lines ν_s(Si—C), with accumulation of chlorine atoms at silicon, increase in frequency from ~ 600 to 760 cm^{-1}. Their intensity S systematically decreases and, on going from $(CH_3)_4Si$ to CH_3SiCl_3, decreases by a factor of 7. The force coefficient K_Q(Si—C) increases from 4.62 to $5.29 \cdot 10^5$ cm^{-2}. The observed facts are explained by a great—

* In ($^{2-4}$) references are given to other works devoted to spectroscopic studies of the compounds $(CH_3)_nSiCl_{4-n}$.

Table 1

Main parameters of the Raman scattering lines of tetramethylsilane and methylchlorosilanes

Interpretation	Frequency $\Delta\nu$, cm^{-1}	Intensity at the maximum I_0	Integral intensity I_∞	Half-width δ, cm^{-1}	Degree of polarization ρ_{ICT}	Scattering coefficients $S \cdot 100$	Scattering coefficients $R \cdot 100$	Tensor invariants α': $b^2 \cdot 10^8$, cm$^2 \cdot$ g^{-1}	Tensor invariants α': $g^2 \cdot 10^8$, cm$^2 \cdot$ g^{-1}
$(CH_3)_4Si$									
δ (CSiC) E	201	85	1340	23,4	0,68	55	83	0,55	1,49
δ (CSiC) F_2	244	50	820	24,0	0,68	41	62	0,41	1,10
ν (Si—C) A_1	596	310	765	2,7	0,05	143	144	6,42	0,29
ν (Si—C) F_2	697	35	435	18,9	0,86	57	94	0	1,95

Interpretation	Frequency $\Delta\nu$, cm^{-1}	Intensity at the maximum I_0	Integral intensity I_∞	Half-width δ, cm^{-1}	Degree of polarization ρ_{ICT}	Scattering coefficients $S \cdot 100$	Scattering coefficients $R \cdot 100$	Tensor invariants α': $b^2 \cdot 10^8$, cm$^2 \cdot$ g^{-1}	Tensor invariants α': $g^2 \cdot 10^8$, cm$^2 \cdot$ g^{-1}
ρ (CH_3) E, F_2	863	10	185	28,5	0,78	30	48	0,12	0,94
δ_s (CH_3) F_2	1252	–	18	–	0,85	4	7	0	0,15
δ_s (CH_3) A_1	1265	–	22	–	0,10	8	9	0,36	0,03
δ_{as} (CH_3) E, F_2	1420	15	190	21,8	0,73	57	86	0,40	1,61
ν_s (C–H) A_1, F_2	2902	95	1410	23,2	0,07	1609	1648	70,81	4,51
ν_{as} (C–H) E, F_2	2958	80	1330	22,9	0,86	947	1564	0	32,20
$(CH_3)_3SiCl$									
δ (CSiCl) E	186	120	1310	17,9	0,86	42	69	0	1,40
δ (CSiC) A_1	232	–	–	–	–	–	–	–	–
δ (CSiC) E	243	70	860	19,2	0,86	36	60	0	1,23

Interpretation	Frequency $\Delta\nu$, cm^{-1}	Intensity at the maximum I_0	Integral intensity I_∞	Half-width δ, cm^{-1}	Degree of polarization ρ_{ICT}	Scattering coefficients $S \cdot 100$	Scattering coefficients $R \cdot 100$	Tensor invariants α': $b^2 \cdot 10^8$, cm^2· g^{-1}	Tensor invariants α': $g^2 \cdot 10^8$, cm^2· g^{-1}
ν (Si—Cl) A$_1$	466	75	700	15,9	0,04	94	94	4,31	0,15
ν (Si—C) A$_1$	636	150	490	4,4	0,08	88	91	3,86	0,28
ν (Si—C) E	761	15	130	14,3	0,86	17	28	0	0,58
ρ (CH$_3$) A$_1$, E	850	10	110	24,6	0,68	18	27	0,18	0,48
δ_s (CH$_3$) A$_1$, E	1260	10	40	11,8	0,60	10	14	0,14	0,23
δ_{as} (CH$_3$) A$_1$, E	1415	15	110	20,7	0,68	31	46	0,31	0,83
ν_s (C—H) A$_1$, E	2901	120	1030	13,1	0,03	1114	1106	51,30	1,30
ν_{as} (C—H) A$_1$, E	2969	70	1120	27,6	0,86	734	1211	0	24,90

$(CH_3)_2SiCl_2$

Interpretation	Frequency $\Delta\nu$, cm^{-1}	Intensity at the maximum I_0	Integral intensity I_∞	Half-width δ, cm^{-1}	Degree of polarization ρ_{ICT}	Scattering coefficients $S \cdot 100$	Scattering coefficients $R \cdot 100$	Tensor invariants α': $b^2 \cdot 10^8$, cm$^2 \cdot$ g^{-1}	Tensor invariants α': $g^2 \cdot 10^8$, cm$^2 \cdot$ g^{-1}
δ ($SiCl_2$) A_1	170	–	1220	–	0,77	36	57	–	–
τ ($SiCl_2$) A_2	178	–	1220	–	0,77	36	57	–	–
δ (CSiC) A_1	235	–	1020	–	0,77	41	65	–	–
γ ($SiCl_2$) B_1	243	–	1020	–	0,77	41	65	–	–
ρ ($SiCl_2$) B_2	298	–	–	–	–	–	–	–	–
ν (Si–Cl) A_1	464	250	1140	9,7	0,02	127	143	5,98	0,00
ν (Si–Cl) B_2	533	15	140	21,0	0,77	13	20	0,06	0,36
ν (Si–C) A_1	690	70	290	7,9	0,22	48	55	1,74	0,43
ρ (CH_3) A_2	803	20	120	13,3	0,77	16	26	0,08	0,50
δ_s (CH_3) A_1, B_1	1267	5	25	18,0	0,47	7	9	0,15	0,13

Interpretation	Frequency $\Delta\nu$, cm^{-1}	Intensity at the maximum I_0	Integral intensity I_∞	Half-width δ, cm^{-1}	Degree of polarization ρ_{ICT}	Scattering coefficients $S \cdot 100$	Scattering coefficients $R \cdot 100$	Tensor invariants α': $b^2 \cdot 10^8$, cm$^2 \cdot$ g^{-1}	Tensor invariants α': $g^2 \cdot 10^8$, cm$^2 \cdot$ g^{-1}
δ_{as} (CH$_3$) A$_1$,B$_1$, A$_2$, B$_2$	1400	10	110	7,0	0,71	29	44	0,23	0,80
ν_s (C–H) A$_1$, B$_1$	2908	120	900	17,5	0,03	936	928	29,00	1,10
ν_{as} (C–H) A$_1$, B$_1$, A$_2$, B$_2$	2978	75	820	23,6	0,77	526	831	2,63	16,21
CH_3SiCl_3									
δ (SiCl$_3$) E	163	170	1400	11,7	0,77	37	57	0,19	1,15
δ (SiCl$_3$) A$_1$	230	115	1430	17,6	0,73	55	82	0,39	1,65
ν (Si–Cl) A$_1$	450	320	1290	6,5	0,01	158	148	7,57	0,06
ν (Si–Cl) E	566	20	300	26,6	0,77	29	44	0,15	0,89
ν (Si–C) A$_1$	759	25	140	10,2	0,52	21	28	0,40	0,44

Interpretation	Frequency $\Delta\nu$, cm^{-1}	Intensity at the maximum I_0	Integral intensity I_∞	Half-width δ, cm^{-1}	Degree of polarization ρ_{ICT}	Scattering coefficients $S \cdot 100$	Scattering coefficients $R \cdot 100$	Tensor invariants α': $b^2 \cdot 10^8$, cm$^2 \cdot$ g^{-1}	Tensor invariants α': $g^2 \cdot 10^8$, cm$^2 \cdot$ g^{-1}
ρ (CH_3) E	801	5	50	17,6	0,77	7	11	0,04	0,22
δ_s (CH_3) A_1	1268	–	20	5,8	0,16	6	6	0,22	0,04
δ_{as} (CH_3) E	1406	10	120	17,0	0,73	30	45	0,20	0,89
ν_s (C–H) A_1	2910	100	550	8,8	0	567	528	27,23	0
ν_{as} (C–H) E	2982	40	500	20,3	0,84	315	465	0,32	10,39

···by the strong electron-attracting action of the chlorine atoms. In the presence of these atoms, the spectroscopic properties of the Si—C bond change; it becomes stronger. The ν_s(Si—C) line in tetramethylsilane is the narrowest. Its half-width is an order of magnitude smaller than that of the other lines. On going to methylchlorosilanes this line broadens. In methyltrichlorosilane its half-width is 4 times greater than in tetramethylsilane. In the direction considered, there also increases the degree—

Table 2

Dispersion of the refractive index of methylchlorosilanes

λ, Å	$(CH_3)_3SiCl$ at 20°	$(CH_3)_3SiCl$ at 30°	$(CH_3)_2SiCl_2$ at 20°	$(CH_3)_2SiCl_2$ at 30°	CH_3SiCl_3 at 20°	CH_3SiCl_3 at 30°
6563	1.38664	1.38075	1.40237	1.39662	1.40823	1.40244
5893	1.38895	1.38300	1.40474	1.39894	1.41060	1.40476
5468	1.39089	1.38493	1.40673	1.40092	1.41259	1.40672
4861	1.39460	1.38857	1.41051	1.40464	1.41640	1.41046
4358	1.39907	1.39296	1.41510	1.40913	1.42096	1.41096

λ, Å	$(CH_3)_3SiCl$ at 20°	$(CH_3)_3SiCl$ at 30°	$(CH_3)_2SiCl_2$ at 20°	$(CH_3)_2SiCl_2$ at 30°	CH_3SiCl_3 at 20°	CH_3SiCl_3 at 30°

Table 3

Absolute differential cross sections of Raman scattering of light per molecule, in units of solid angle, for the Stokes lines of methylchlorosilanes (in 10^{-30} cm^2)

Molecule	$\Delta\nu$, cm^{-1}	L	$(d\sigma/d\Omega)_\parallel$	$d\sigma/d\Omega$	$d\sigma_T/d\Omega$	$(d\sigma/d\Omega)_\parallel^{(r)}$
$(CH_3)_3SiCl$	466	2.970	13.72	14.00	14.56	2.01
$(CH_3)_3SiCl$	636	2.968	8.99	9.36	10.09	1.29
$(CH_3)_3SiCl$	761	2.966	1.67	2.92	5.42	0.24
$(CH_3)_3SiCl$	2901 *	2.943	16.31	16.56	17.04	1.75
$(CH_3)_3SiCl$	2969 *	2.942	5.98	10.47	19.44	0.64
$(CH_3)_2SiCl_2$	464	3.109	19.75	19.94	20.33	2.89
$(CH_3)_2SiCl_2$	533	3.108	1.02	1.66	2.94	0.15
$(CH_3)_2SiCl_2$	690	3.106	4.38	4.92	6.01	0.63
$(CH_3)_2SiCl_2$	803	3.106	0.85	1.38	2.44	0.12
$(CH_3)_2SiCl_2$	2908 *	3.080	9.71	9.92	10.35	1.04
$(CH_3)_2SiCl_2$	2978 *	3.079	4.88	7.92	14.01	0.52
CH_3SiCl_3	450	3.161	26.08	26.21	26.45	3.83
CH_3SiCl_3	566	3.159	4.59	7.44	13.13	0.67
CH_3SiCl_3	759	3.156	1.44	1.95	2.96	0.20
CH_3SiCl_3	2910	3.131	8.98	8.98	8.98	0.96
CH_3SiCl_3	2982	3.130	5.48	9.43	17.35	0.58

Notes. $(d\sigma/d\Omega)_\parallel$ is the cross section for the case of parallel directions of the polarization vectors of the incident and scattered radiation (wavelength 4358 Å) and scattered radiation; $d\sigma/d\Omega$ is the total cross section for $\parallel$ and $\perp$ polarizations of the incident and scattered radiation. $d\sigma_T/d\Omega$ is the full differential cross section for the case of exciting natural light at 4358 Å. $(d\sigma/d\Omega)_\parallel^{(r)}$ is the scattering cross section for exciting light of a ruby laser, 14,400 cm^{-1}.

* In calculating the cross sections for these lines, the degeneracy factor was not taken into account.

the degree of depolarization of the corresponding wave. The symmetry of the polarizability tensor departs increasingly from spherical.

The intensities of the symmetric and antisymmetric stretching vibrations $\nu(C—H)$ decrease as the number of methyl groups in the molecule decreases. At the same time, complete additivity is not observed when these quantities are added. As the number of chlorine atoms at silicon increases, the fraction of scattering attributable to each equivalent CH_3 group increases. In work (^{6}), using infrared absorption spectra as an example, it was shown that in the general case the dependence of intensities on the number of identical groups in a molecule is very difficult to determine. The influence of chlorine atoms is also manifested in measuring the vibrational frequencies $\nu(C—H)$. The frequency of the antisymmetric vibration $\nu_{as}(C—H)$ increases in the considered series of molecules by more than 20 cm^{-1}.

Characteristic of methylchlorosilanes are the stretching vibrations $\nu(\mathrm{Si—Cl})$. The symmetric lines lie in the region 450-470 cm^{-1}. They are intense and almost completely polarized. The antisymmetric lines are strongly depolarized and are $\sim$ 100 cm^{-1} higher in frequency. The course of the changes in the parameters of the $\nu(\mathrm{Si—Cl})$ lines is also connected with the mutual influence of the corresponding vibrations.

Table 1 gives the dispersion of the refractive index of methylchlorosilanes*. The refractive index is higher for the compound containing the larger number of chlorine atoms. Methylchlorosilanes are characterized by mean dispersion; the dispersion coefficient for them is the same and is equal to 50. With an increase in temperature by 10°, the refractive index decreases by approximately 0.006.

Table 2 presents the absolute differential cross sections of spontaneous Raman scattering of light. The effective-field correction L (^{7}) takes values from 2.9 to 3.2. In calculating the cross sections, a transition was made from the 802 cm^{-1} line of cyclohexane to the 459 cm^{-1} line of CCl_4. For the latter, the multiplier $5b'^2 + 7g'^2$ was taken to be $13 \cdot 10^{-8}$ cm^4/g (^{8}). In calculating $(d\sigma/d\Omega)_{\parallel}^{(r)}$, the dependence of the scattering coefficient S on the frequency of the exciting light was neglected.

If the polarization direction of the incident wave parallel to the scattered wave is considered, then the waves $\nu_s(\mathrm{Si—Cl})$ and $\nu_s(\mathrm{C—H})$ have the largest scattering cross sections. With an increase in the number of Si–Cl bonds, these parameters also increase substantially.

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Note: Figure translations are in progress. See original paper for figures.