PRINCIPAL PARAMETERS OF THE VIBRATIONAL RAMAN SPECTRA OF CYCLIC POLYDIMETHYLSILOXANES

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PRINCIPAL PARAMETERS OF THE VIBRATIONAL RAMAN SPECTRA OF CYCLIC POLYDIMETHYLSILOXANES

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This paper presents the results of measurements of frequencies, integral and peak intensities, degrees of depolarization, and half-widths of lines in the Raman spectra of liquid cyclic polydimethylsiloxanes $[(CH_3)_2SiO]_n$ ($n = 4$—7). Corrected relative scattering coefficients have been calculated in the scales $5b'^2 + 7g'^2(S)$ and $5b'^2 + 13g'^2(R)$, as well as the components of the tensor of the derivative of the polarizability.

It is very important to elucidate the regularities in the behavior of the parameters of the Si–O bond as a function of ring size, and also in comparison with linear polydimethylsiloxane chains. They should reflect features in the geometry of the molecule and in the distribution of the electron cloud within it, and indicate possible changes in these factors. Until now, in applying spectroscopic methods to the study of the physicochemical properties of $[(CH_3)_2SiO]_n$, only the frequencies of spectral lines and qualitative intensities have been considered ([1–6]).

In the present work the experimental studies were carried out on a DFS-12 instrument by the photoelectric method at a scanning rate of 0.05—0.07 cm^{-1}/sec. The samples were studied in the liquid phase at room temperature. The 802 cm^{-1} line of cyclohexane was chosen as the standard. For control, the spectra were also photographed with an ISP-51. The calculation of the true parameters was performed using the methods of Bazhulin and Sushchinskii ([7,8]).

The values of the spectral characteristics obtained for the fundamental vibrations are presented in Table 1. The interpretation of the frequencies was carried out taking into account earlier studies of the vibrational spectra ([4–6]). In the spectrum of each compound one can readily distinguish a line lying in the region 480—495 cm^{-1} and belonging to the totally symmetric stretching vibration ν_s(Si—O) of the Si–O–Si bridge. It is very intense and completely polarized. The frequency of this vibration, on going from the tetramer to more complex rings, increases within a range of 15 cm^{-1}. The scattering coefficient S increases in the molecule D_6 ($D = (CH_3)_2SiO$) by a factor of 1.5 in comparison with D_4, and in D_7 in comparison with D_5 by 10%. The half-width of the ν_s(Si—O) line varies from 19 to 16 cm^{-1}. In the molecules D_4, D_5, and D_6, S (or R) increases in proportion to the number of Si–O–Si units in the ring. In D_7 this parameter correspondingly increases if one takes its summed value for the lines 495 and 523 cm^{-1}.

Dielectric studies of cyclosiloxanes ([9,10]) showed that they, like linear chains, possess a dipole moment. The ring form at $n > 3$ is not planar, which is confirmed by X-ray structural and spectroscopic analysis ([11,12]). In both linear and cyclic molecules, considerable internal mobility is observed. In siloxane bridges this phenomenon is associated with internal rotations ("nonplanar" deformation vibrations) and the nonrigidity of the angle

Table 1

Principal parameters of the Raman lines of cyclic polysiloxanes

Interpretation	$[(CH_3)_2SiO]_4$: Frequency $\Delta\nu$, cm^{-1}	Intensity I_∞	Intensity maximum I_0	Half-width δ, cm^{-1}	Depolarization degree ρ	Scattering coefficient $S\cdot100$	Tensor derivatives α': $b^2\cdot10^8$, cm^4 g^{-1}	Tensor derivatives α': $g^2\cdot10^8$, cm^4 g^{-1}	Scattering coefficient $R\cdot100$	$[(CH_3)_2SiO]_5$: Frequency $\Delta\nu$, cm^{-1}	Intensity I_∞	Intensity maximum I_0	Half-width δ, cm^{-1}	Depolarization degree ρ	Scattering coefficient $S\cdot100$	Tensor derivatives α': $b^2\cdot10^8$, cm^4 g^{-1}	Tensor derivatives α': $g^2\cdot10^8$, cm^4 g^{-1}	Scattering coefficient $R\cdot100$
δ(SiOSi)	145	245	30	16,5	0,71	16	0,13	0,46	25	155	480	50	21	0,82	40	0,08	1,31	65
δ(OSiO)	170	165	16	16,5	(0,74)	(13)	(0,08)	(0,37)	20									
δ_s(CSiC)	199	1075	92	24,5	(0,74)	(95)	(0,62)	(2,81)	150	194	1065	72	33	0,83	111	0,17	3,67	180
δ(CSiO)	259	110	10	22	0,72	13	0,10	0,37	20	243	–	–	–	–	–	–	–	–
δ(CSiO)	341	40	6	18	0,39	8	0,20	0,12	10	293	25	3	21,5	0,39	5	0,12	0,07	6
δ(D)	376	–	–	–	–	–	–	–	–	349	20	2	29	0,11	6	0,26	0,03	7
	452	40	9	8	0,29	10	0,33	0,12	12	389	20	2	23,5	0,34	5	0,15	0,07	6
ν_s(Si–O)	479	640	55	19	0	215	10,30	0	208	488	640	61	18,0	0	277	13,32	0	269
	543	–	–	–	–	–	–	–	–	530	–	–	–	–	–	–	–	–
$\nu + \delta_\perp$	633	–	–	–	–	–	–	–	–	639	–	–	–	–	–	–	–	–
ν_s(Si–C)	660	40	10	6,5	0,68	11	0,11	0,31	17	669	55	10	10,5	0,76	20	0,11	0,60	31
$\rho(CH_3)$, ν_s(Si–C)	691	150	18	16,5	0,84	44	0,04	1,47	72	685	205	22	18,5	0,79	76	0,28	2,39	120
ν_s(Si–C)	715	240	45	10,0	0,11	114	4,78	0,50	120	714	270	55	9,0	0,13	155	6,30	0,80	166
ν_{as}(Si–C), $\rho(CH_3)$	792	85	17	12	(0,81)	(30)	(0,08)	(0,96)	48	794	105	16	15,0	0,80	47	0,15	1,51	75

Interpretation	$[(CH_3)_2SiO]_4$: Frequency $\Delta\nu$, cm^{-1}	Integral intensity I_∞	Intensity maximum I_0	Half-width δ, cm^{-1}	Depolarization degree ρ	Scattering coefficient $S \cdot 100$	Tensor derivatives α': $h^2 \cdot 10^8$, $cm^4 \cdot g^{-1}$	Tensor derivatives α': $g^2 \cdot 10^8$, $cm^4 \cdot g^{-1}$	Scattering coefficient $R \cdot 100$	$[(CH_3)_2SiO]_5$: Frequency $\Delta\nu$, cm^{-1}	Integral intensity I_∞	Intensity maximum I_0	Half-width δ, cm^{-1}	Depolarization degree ρ	Scattering coefficient $S \cdot 100$	Tensor derivatives α': $h^2 \cdot 10^8$, $cm^4 \cdot g^{-1}$	Tensor derivatives α': $g^2 \cdot 10^8$, $cm^4 \cdot g^{-1}$	Scattering coefficient $R \cdot 100$
$\rho(CH_3)$, ν_{as}(Si–C)	812	20	3	18,5	(0,81)	(7)	(0,02)	(0,22)	11									
$\rho(CH_3)$	867	35	6	15	(0,43)	(16)	(0,38)	(0,27)	20	874	75	6	25,5	0,43	43	1,04	0,74	57
	887	25	4	15	(0,43)	(12)	0,28	0,20	16									
ν_{as}(Si–O)	1053	–	–	–	–	–	–	–	–	~1067	–	–	–	–	–	–	–	–
$\delta_s(CH_3)$	1261	130	8	10,0	0,29	24	0,77	0,28	29	1260	35	8	10,5	0,51	30	0,58	0,61	41
$\delta_{as}(CH_3)$	1408	150	15	24,5	0,85	94	0,04	3,20	155	1411	137	15	23,0	0,81	110	0,28	3,57	170
ν_s(C–H)	2905	1300	128	18,5	0,02	3432	163	2,5	3348	2903	1260	132	19,0	0,02	4145	194	3,3	4080
ν_{as}(C–H)	2964	980	102	18,0	0,70	1664	16,14	46,22	2?28	2963	1000	105	19,0	0,78	2050	8,8	64,3	3260
δ(SiOSi)	178	610	50	23,5	0,80	63	0,20	2,01	103	147	(525)	–	–	(0,79)	(57)	(0,21)	(1,80)	(91)
δ(OSiO)										173	(570)	–	–	(0,79)	(73)	(0,27)	(2,29)	(116)
δ_s(CSiC)	190	880	55	32,5	0,86	105	0	3,61	173	227	–	–	–	–	–	–	–	–
δ(CSiC)	224	–	–	–	–	–	–	–	–	239	–	–	–	–	–	–	–	–
δ(CSiO)	261	–	–	–	–	–	–	–	–	340	–	–	–	–	–	–	–	–
	325	–	–	–	–	–	–	–	–	371	–	–	–	–	–	–	–	–
δ(D)	394	–	–	–	–	–	–	–	–	398	–	–	–	–	–	–	–	–
	493	615	64	17,0	0	321	15,42	0	310	495	500	53	16,0	0	322	14,50	0	292
ν_s(Si–O)										523	(90)	–	–	–	–	–	–	(53)
$\nu + \delta_\perp$	583	–	–	–	–	–	–	–	–	563	–	–	–	–	–	–	–	–
	633	–	–	–	–	–	–	–	–	620	–	–	–	–	–	–	–	–

Assignment																
ν_s(Si–C)	660	–	–	–	–	–	–	–	–	–	–	–	–	–	–	26
ν_s(Si–O), $\rho(CH_3)$	688	140	26	12.0	0.86	61	0	2.09	–	100	690	210	24	15.5	9.31	177
ν_s(Si–C)	712	330	50	9.0	0.12	159	6.57	0.76	–	170	713	220	40	9.5	0.66	191

Assignment																
ν_{as}(Si–C)	798	120	16	17.0	0.85	61	0.26	2.07	–	100	797	145	12	20.0	2.62	140
$\rho(CH_3)$	867	–	–	18.0	0.49	32	0.66	0.63	–	–	869	66	6	19.0	0.83	63
ν_{as}(Si–O)	~1043	–	–	–	–	–	–	–	–	–	~1050	–	–	–	–	–
$\delta_s(CH_3)$	1260	27	8	12.0	0.52	33	0.59	0.65	39	1262	34	6	12.0	0.53	54	
$\delta_{as}(CH_3)$	1411	125	7	22.5	0.86	417	49	2.05	245	1413	150	43	20.0	5.43	370	
ν_s(C–H)	2902	425	127	25.0	0.03	4890	227	5.1	4833	2906	4245	117	19.5	0.43	5645	
ν_{as}(C–H)	2962	1065	105	19.0	0.85	2514	1.66	85.0	4120	2966	1025	94	20.5	97.2	4664	

Notes. 1. Reproducibility of the results in the range 5-10%; in parentheses are indicated less precise values.
2. $\delta(D)$ –vibrations associated with deformation angles of the cyclic framework; $\nu+\delta_\perp$ –combinations of the vibration ν_s(Si–O–Si) and "out-of-plane"vibrations of the cycle.
3. In parentheses ([3], [4]) are additionally recorded lines lying in the region $\tilde{\nu} < 90$ cm^{-1}.
4. Discussion of the parameter P, carried out, for example, in ([13]).

Si – O – Si. The mentioned feature of the molecules under consideration is clearly manifested in the distribution of scattering intensities in the spectrum. The share of deformation vibrations of the framework $C_xSi_yO_z$ in cyclic compounds accounts for a significant total value, varying within the limits of 130-170 units. Linear polydimethylsiloxane chains are characterized by greater freedom of deformation. If in octamethylcyclotetrasiloxane D_4 each Si – O – Si unit corresponds to a value S of 40 units, then in hexamethyldisiloxane it is 100 units. ([13]) The frequency of the symmetric stretching vibration ν_s(Si – O – Si) in $[(CH_3)_3Si]_2O$ is higher by 39 cm^{-1}.

The antisymmetric stretching vibration ν_{as}(Si – O – Si) appears in the Raman spectrum as a very weak line lying in the region 1030-1070 cm^{-1}. In the infrared absorption spectrum it is registered in the interval 1060-1090 cm^{-1} and is very intense. The possible position of the vibrations ν(Si – O – Si) in compounds of various classes is discussed in the review ([14]).

The vibrations in the CH_3 groups are sufficiently isolated from one another. This is confirmed by the course of the intensities in the series of molecules considered. The symmetric line ν_s(C – H) gives a fraction of the scattered light two times greater than the antisymmetric ν_{as}(C – H). In both the first and the second cases the scattering coefficients increase linearly with an increase in the number of methyl groups in the molecule. The deviation from linearity is no more than 5%. Additivity of the characteristics is also manifested fairly well for the internal and external deformation vibrations $\delta(CH_3)$.

In accordance with the selection rules, the intense polarized line 710-715 cm^{-1} should be assigned to the totally symmetric stretching vibration $\nu_s(\mathrm{Si-C})$. This line is characteristic in frequency, intensity, degree of depolarization, and half-width in all the compounds considered. To $\nu_{as}(\mathrm{Si-C})$ belongs the depolarized line 792-799 cm^{-1}. For the corresponding vibration the scattering S also increases on going to more complex cyclosiloxanes, but no strict linear dependence is observed for the total intensity. The half-width of the antisymmetric line increases systematically as the ring becomes more complex, which may be explained by an increase in the mutual influence between this vibration and the ring vibrations.

The depolarized line 685-691 cm^{-1}

cannot be regarded as belonging only to ν_s(Si—C). This vibration is, to a large extent, an asymmetric torsional vibration of the methyl groups.

The low frequencies 147-452 cm^{-1} correspond to deformation vibrations of the skeleton. Their assignment to normal vibrations should be regarded as preliminary. In D_5 and D_6 the lines at 194 and 190 cm^{-1} are anomalously broad and, apparently, double.

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