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INTEGRAL INTENSITIES
IN INFRARED VIBRATIONAL ABSORPTION SPECTRA
OF CYCLIC POLYDIMETHYLSILOXANES

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This paper presents the results of an experimental study of the principal parameters of vibrational absorption bands in the infrared spectra of cyclic polydimethylsiloxanes $[(CH_3)_2SiO]_n$ ($n = 4—7$), for which previously only the positions of the bands and their qualitative intensities had been measured ($^{1-6}$). In the region 400—3000 cm^{-1}, using an IKS-14 spectrophotometer, the frequencies, integral intensities, absorption coefficients at the maximum, and half-widths were measured. For the frequency interval 400—670 cm^{-1}, samples of the pure liquid were studied; for 700—860 cm^{-1} and 860—3000 cm^{-1}, solutions of different concentrations in CS_2 and CCl_4, respectively, were used. The spectrograms were processed mainly according to Johansen (^{7}). The obtained values of the spectral characteristics and the interpretation of the vibrational spectra are given in Table 1.

The infrared absorption spectrum of $[(CH_3)_2SiO]_n$ molecules has clearly expressed features. Owing to the character of the symmetry, the stretching vibrations of the Si–O–Si bridges in these molecules are split into a number of bands. The symmetric stretching bridge vibrations of the ring lie in the region 480—550 cm^{-1} and are rather weak. For one of these vibrations in each compound (480—495 cm^{-1}), a very strong polarized line is observed in the Raman spectrum. The opposite picture is characteristic of the antisymmetric vibrations ν_{as}(Si—O—Si), which appear in the region 1060—1100 cm^{-1}.

The distribution of intensities in the absorption spectra of the compounds under consideration shows that, with very high probability, levels corresponding to ring vibrations are excited in them. The antisymmetric vibrations ν_{as}(Si—O) account for 50—60% of the total absorption, excluding the unstudied region 150—450 cm^{-1}. In the liquid phase, for each compound, two vibrations ν_{as}(Si—O—Si) are recorded. In the spectra of D_6 and D_7 [$D = (CH_3)_2SiO$], the bands corresponding to these vibrations can be separated (although only with a rather large approximation). In D_5 they overlap more closely. In the spectrum of D_4, the vibrations are recorded as a single band. The anomalously large value of the half-width of ν_{as}(Si—O—Si), in calculations for D_4 and D_5 in the representation of a single band, indicates the superposition of two bands in this region. The most intense band ν_{as}(Si—O—Si) may reasonably be assigned to a degenerate type of vibrations. In the spectra of D_6 and D_7 it is 3-4 times more intense than the observed second band. The position of the intense band changes within 30 cm^{-1} as the ring increases. In compounds with an even number of Si–O–Si bridges it lies in the region 1075—1080 cm^{-1}.

Comparison of the total intensities for the ν_{as}(Si—O—Si) bands shows a systematic and fairly linear increase of this sum with increasing number of Si–O–Si bridges in the ring. The deviation from linearity lies within 10%. In hexamethyldisiloxane, the antisymmet-

Table 1

Principal parameters of the vibrational infrared absorption bands

Interpretation	Frequency ν, cm^{-1}, $[(CH_3)_2SiO]_4$	Integral intensity $A \cdot 10^9$, cm^2/molecule·sec, $[(CH_3)_2SiO]_4$	Absorption coefficient at maximum K_{max}, cm^{-1}, $[(CH_3)_2SiO]_4$	Half-width γ, cm^{-1}, $[(CH_3)_2SiO]_4$	Frequency ν, cm^{-1}, $[(CH_3)_2SiO]_6$	Integral intensity $A \cdot 10^9$, cm^2/molecule·sec, $[(CH_3)_2SiO]_6$	Absorption coefficient at maximum K_{max}, cm^{-1}, $[(CH_3)_2SiO]_6$	Half-width γ, cm^{-1}, $[(CH_3)_2SiO]_6$
ν_s(Si–O)	478551	–250	–500	–20.0	495516	90260	90200	24.736.0
$\nu + \delta_\perp$	629	v. wk.	–	–	587634	200v. wk.	180–	35.0–
ν_s(Si–C)	658	60	270	7.9	657667682	(280)med.	med.—sh.	——
$\rho(CH_3)$, ν_s(Si–C)ν_{as}(Si–C), $\rho(CH_3)$	694795—	460v. wk.	1500—	12.1—	699781	1030v. wk.	2350sh.	12.8—
$\rho(CH_3)$, ν_{as}(Si–C)	807	6400; total 5960	15 800	9.7	806818	8090; total 6990(770)	19 400(2000) sh.	10.7(11)
$\rho(CH_3)$	856877	total (380)	—	—	856871	total (620)	–sh.	—
ν_{as}(Si–O)	1076	16 000; total 15 060	19 900	44	10781098	22 660; total 21 940(5300)	17 200(4700)	3531
$\delta_s(CH_3)$	1264	2170	25 500	2.8	1263	3420	23 700	4.9

Interpretation	Frequency ν, cm^{-1}, $[(CH_3)_2SiO]_4$	Integral intensity $A \cdot 10^9$, cm^2/molecule·sec, $[(CH_3)_2SiO]_4$	Absorption coefficient at maximum K_{max}, cm^{-1}, $[(CH_3)_2SiO]_4$	Half-width γ, cm^{-1}, $[(CH_3)_2SiO]_4$	Frequency ν, cm^{-1}, $[(CH_3)_2SiO]_6$	Integral intensity $A \cdot 10^9$, cm^2/molecule·sec, $[(CH_3)_2SiO]_6$	Absorption coefficient at maximum K_{max}, cm^{-1}, $[(CH_3)_2SiO]_6$	Half-width γ, cm^{-1}, $[(CH_3)_2SiO]_6$
$\delta_{as}(CH_3)$	140514121448	– (240); total 390–	– (380)–	——	140614131448	– (440); total 800–	– (490)–	——
ν_s(C—H)	2909	190	300	24	2909	330	340	23
ν_{as}(C—H)	2966	1100	2500	18.4	2967	1560	2450	19.2

Table 1 (continued)

Interpretation	Frequency ν, cm^{-1}	Integral intensity $A \cdot 10^9$, cm^2/(molec. sec.)	Absorption coefficient at maximum K_{max}, cm^{-1}	Half-width γ, cm^{-1}	Frequency ν, cm^{-1}	Integral intensity $A \cdot 10^9$, cm^2/(molec. sec.)	Absorption coefficient at maximum K_{max}, cm^{-1}	Half-width γ, cm^{-1}
	$[(CH_3)_2SiO]_5$	$[(CH_3)_2SiO]_7$						
ν_s(Si—O)	482	40	60	24.9	490	–	–	–
ν_s(Si—O)	529	110	150	25.0	518	(300)	(150)	(44)
$\nu + \delta_\perp$	615	60	90	21.4	569	85	90	22.0
$\nu + \delta_\perp$					626	160	110	26.7
ν_s(Si—C)	671	(40)	–	–	672	weak	–	–
ν_s(Si—C)					678	weak	–	–
$\rho(CH_3)$, ν_s(Si—C)	698	680	1970	10.7	700	1240	2180	12.6
ν_{as}(Si—C), $\rho(CH_3)$	790	very weak	sh.	–	802	8950 7980	17 640	11.2
ν_{as}(Si—C), $\rho(CH_3)$	801	(8070) 6800	–	13.0	820	(1120) 7980	(2150)	(11)
ν_{as}(Si—C), $\rho(CH_3)$	815	weak	sh.	–				

Interpretation	Frequency ν, cm^{-1}	Integral intensity $A \cdot 10^9$, cm^2/(molek. sec.)	Absorption coefficient at maximum $K_{\max}$, cm^{-1}	Half-width γ, cm^{-1}	Frequency ν, cm^{-1}	Integral intensity $A \cdot 10^9$, cm^2/(molek. sec.)	Absorption coefficient at maximum $K_{\max}$, cm^{-1}	Half-width γ, cm^{-1}
$\rho(CH_3)$	856	(550)	–	–	859	(1120)	–	–
$\rho(CH_3)$	870	(550)	sh.	–	876	very weak	sh.	–
ν_{as}(Si—O)	1070	20 500	–	–	1057	(21 850) 24 200	(17 000)	(32)
ν_{as}(Si—O)	1087	28 200 20 500	16 000	62	1085	8200 24 200	5800	36
$\delta_s(CH_3)$	1262	2550	25 900	3.5	1263	4520	(20 000)	5.4
$\delta_{as}(CH_3)$	1405	750	–	–	1405	1160	–	–
$\delta_{as}(CH_3)$	1412	(380) 750	(440)	–	1413	(510) 1160	(490)	–
$\delta_{as}(CH_3)$	1448	750	–	–	1445	1160	–	–
ν_s(C—H)	2909	220	320	25	2910	320	300	24
ν_{as}(C—H)	2966	1450	2670	18.4	2966	1860	2250	19.3

Notes. 1. The summed intensities were determined independently and without taking into account the correction for wings. The parameters for the ν_{as}(Si—O) vibrations in D_4 and D_5 were calculated by representing them as a single band. 2. The reproducibility of the results in calculations of the parameters A and γ was generally within 5-10%. The coefficient $K_{\max}$ is usually calculated with a larger error. Less accurate values of the parameters, obtained for strongly overlapping bands, are given in parentheses. 3. Notation: ν –stretching vibration, δ –deformation, ρ –rocking, $\delta_{\perp}$ – "nonplanar" vibration of the ring, s –symmetric band, as –antisymmetric, av. –average intensity, weak –weak, very weak –very weak, sh. –shoulder.

band ν_{as}(Si—O—Si) is observed in the region of 1050 cm^{-1}. Its intensity ($1800 \cdot 10^{-9}$ cm^2/molecule $\cdot$ s) is several times smaller than the average value falling on each Si—O—Si unit in the cycles. A considerable value of the intensity is also characteristic of one of the antisymmetric stretching vibrations of the Si—C bond, with a frequency of 800-810 cm^{-1}. Although in this region there is superposition of closely spaced bands, and in separating them the introduction of a significant error is not excluded, here too the additivity factor is manifested. Of course, one cannot proceed from the assumption of an obligatory linear dependence of the intensity of the band under consideration on the number of identical bonds or groups corresponding to it in the molecule. In the general case this is a complex function (^{8}).

For methyl groups, the intensity of the antisymmetric stretching vibration ν_{as}(C—H) increases linearly with increasing ring size. The bands of the methyl groups are characteristic in intensity and polarization. These groups have rather closed electron shells.

Table 2

Physical constants of compounds $[(CH_3)_2SiO]_n$

n	B.p., °C (pressure, mm)	M.p., °C	d_4^{20}	n_D^{20}
4	175.8 (760)	17.6	0.9561	1.3968
5	101 (20)	−43.5	0.9597	1.3982
6	128 (20)	−3.0	0.9672	1.4015
7	151 (20)	−31.5	0.9728	1.4040

Thus, analysis of the integral intensities shows that the change in dipole moments in cyclic polydimethylsiloxanes occurs primarily in normal vibrations belonging to antisymmetric stretching vibrations of the Si—O—Si bridges and the Si—C bonds. The probabilities of transitions in symmetric deformation and antisymmetric stretching vibrations in methyl groups are also significant. In the molecules considered, the additive character of the integral intensities of infrared vibrational absorption bands is clearly manifested.

It is of interest to estimate the magnitude of the cross sections of spontaneous combination scattering for the polarized lines ν_s(Si—O). As an example, let us carry out calculations for the molecules $[(CH_3)_2SiO]_n$ ($n = 5, 6$), in whose spectra the frequencies 488 and 493 cm^{-1}, respectively, are identified with symmetric stretching vibrations of the Si—O bond. The scattering coefficients S of these vibrations (on the cyclohexane scale) are equal to 2.77 and 3.21. Proceeding from the local-field correction (^{3}), on the basis of formulas (1), (2) (^{9}), the complete absolute cross sections of combination scattering per molecule per unit solid angle $d\sigma/d\Omega$ for the Stokes wave 4358 Å are obtained as follows: in $[(CH_3)_2SiO]_5$, $41 \cdot 10^{-30}$ cm^2; in $[(CH_3)_2SiO]_6$, $47 \cdot 10^{-30}$ cm^2. In the case considered they will be the same for linearly polarized and for natural incident light. In the calculations of $d\sigma/d\Omega$, conversion was made to the standard line 459 cm^{-1} of CCl_4, for which the value $5b'^2 + 7g'^2$ was taken as $13 \cdot 10^{-8}$ cm^{4}g^{-1} (^{10}).

The investigated cyclic polydimethylsiloxanes were synthesized and purified by the previously described method (^{11,12}) (see Table 2).

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