INTEGRAL INTENSITIES

PHYSICS

1967

SovietRxiv

Abstract

Full Text

UDC 535.338.42

PHYSICS

V. A. ARBUZOVA, I. F. KOVALEV, E. N. TIKHOMIROVA,
M. G. VORONKOV, L. A. ZHAGAT

INTEGRAL INTENSITIES
IN THE INFRARED ABSORPTION SPECTRA
OF METHYLETHOXYSILANES $(CH_3)_nSi(OC_2H_5)_{4-n}$ $(n = 0, 1, 2, 3)$

(Presented by Academician I. V. Obreimov, 14 IV 1966)

1. For tetraethoxysilane and methylethoxysilanes, data on infrared absorption spectra are available in the literature, but only the frequencies of the principal bands have been measured ([1–7]). In spectroscopic studies of tetraalkoxysilanes, much attention has been attracted by the central group SiO_4. A similarity has been noted in the structure of $Si(OR)_4$, which include this group, and silicates. The effects of the influence on the SiO_4 group of different radicals bonded to oxygen are of interest.

In order to clarify more thoroughly the features of the SiO_4 group and of the Si—O—C bridge, we have studied in detail the integral intensities, absorption coefficients at the maximum, and half-widths of the bands in infrared vibrational absorption spectra. A calculation of the force constants for the tetrahedral skeleton of the molecules was also carried out, and electro-optical parameters were estimated.

2. Dimethyldiethoxysilane was obtained by the reaction of tetraethoxysilane with polydimethylsiloxane in the presence of KOH ([8]). Trimethylethoxysilane and methyltriethoxysilane were synthesized simultaneously by an analogous route from the cohydrolysis product of methyltrichlorosilane and trimethylchlorosilane (1 : 3). All compounds $(CH_3)_nSi(OC_2H_5)_{4-n}$ were purified by distillation on an efficient column over metallic sodium.

The spectra were recorded with an IKS-14 instrument in solutions of CCl_4 and CS_2, and also as the pure liquid, in the range 400—3000 cm^{-1}. The scanning rate for the LiF, NaCl, and KBr prisms was, respectively, 12; 5 and 1—3.3 cm^{-1}/min. The band parameters were calculated using the methods described in ([9,10]). The complete instrumental function was determined as the sum of the spectral expression of the geometrical slit width and the diffraction resolution limit.

3. The assignment of frequencies to normal vibrations and the parameters of the principal bands are given in Table 1. In interpreting the spectra we used the data obtained by us on the frequencies, intensities, and degrees of depolarization of lines in the spectra of combination scattering,

as well as calculations carried out for the molecular skeleton. The totally symmetric stretching vibrations ν_s(Si—O) in all compounds correspond to very weak bands lying in the range 605—660 cm^{-1}. The frequency and intensity of the vibration ν_s(Si—O) systematically increase when methyl groups at silicon are replaced by ethoxyl groups. The antisymmetric vibrations ν_{as}(Si—O) in methylethoxysilanes correspond to bands in the infrared absorption spectra that are very intense and change little in frequency, 790—820 cm^{-1}. The intensity of the ν_{as}(Si—O) band, within the experimental error, increases linearly in going from trimethylethoxysilane to tetraethoxysilane. In this direction there is also observed, both in the infrared spectra and in the combinational scattering a considerable broadening of the bands ν_s(Si—O) and ν_{as}(Si—O) is observed. These effects are due to interaction of the polar Si—O—C_2H_5 bonds and to a change in molecular symmetry. The silicon–oxygen bond becomes stronger: the force constants K_q(Si—O), corresponding to stretching of this bond, successively take the values 6.00; 7.76; 8.87 and 9.14 (10^6 cm^{-2}).

Table 1

Parameters of the principal absorption bands in the infrared spectra*

$(CH_3)_nSi(OC_2H_5)_{4-n}$ $(n = 0, 1, 2, 3)$

Interpretation	Frequency ν_0, cm^{-1}	Absolute intensity $A \cdot 10^9$, cm^2/(molecule s)	Absorption coefficient at the maximum k_{max}, cm^{-1}	Half-width of the band γ, cm^{-1}
$Si(OC_2H_5)_4$				
δ(SiOC)	476	medium	–	–
ν_s(Si—O)	658	45	(70)	(40)
ν_{as}(Si—O)	793	1390	3750	23
$\rho(CH_3)$	811	265	1200	14
ν_{as}(C—C)	964	1460	3650	25
ν_s(C—O)	1083	1760	6600	16
ν_{as}(C—O)	1106	3960; total 5720	9660	22
$\rho(CH_3)$	1162	910	3840	13
$\delta_s(CH_3)$	1295	280	730	20
	1364	130	(600)	(9)
	1389	315	1750	8
$\delta_{as}(CH_3)$	1441	200	700	15
	1458	weak	–	–
	1481	90	400	16
ν_s(C—H)	2876	830	–	–

Interpretation	Frequency ν_0, cm^{-1}	Absolute intensity $A \cdot 10^9$, $cm^2/(molecule \cdot s)$	Absorption coefficient at the maximum k_{max}, cm^{-1}	Half-width of the band γ, cm^{-1}
	2890	830	–	–
	2930	830	–	–
ν_{as}(C—H)	2941	1430	–	–
	2976	1430	4300	19
$CH_3Si(OC_2H_5)_3$				
(SiOC)	447	medium	–	–
ν_s(Si—O)	644	30	70	22
$\rho(CH_2)$	731	100	380	19
$\rho(CH_3)$	779	630	3500	11
$\rho(CH_3)$	811	(100)	(3700)	–
ν_{as}(Si—O)	822	(1050); total 1600	–	–
$\rho(CH_3)$	831	(450)	–	–
ν_{as}(C—C)	960	1310	3550	24
ν_s(C—O)	1084	1800	6400	18
ν_{as}(C—O)	1107	2000; total 3800	5600	24
$\rho(CH_3)$	1127	2000; total 3800	–	–
$\rho(CH_3)$	1168	580	2400	14
$\delta_1(CH_3)$	1267	310	1900	9
	1296	160	570	17
	1366	40	400	8
	1389	–	1400	10
$\delta_s(CH_2)$	1417	220	–	–
δ_{as}(CH)	1445	160	500	25
	1463	160	–	–
	1483	50	300	16
ν_s(C—H)	2872	940	–	–
	2892	940	–	–
	2898	940	–	–
	2923	940	–	–
ν_{as}(C—H)	2942	1150	–	–
	2975	1150	3900	20

Interpretation	Frequency ν_0, cm^{-1}	Absolute intensity $A \cdot 10^9$, $cm^2/(molecule \cdot s)$	Absorption coefficient at the maximum k_{max}, cm^{-1}	Half-width of the band γ, cm^{-1}
$(CH_3)_2Si(OC_2H_5)_2$				
ν_s(Si—O)	623	19	60	20
ν_s(Si—C)	689	(50)	–	–
ν_{as}(Si—C)	730	140	580	17
ν_{as}(Si—O)	796	610	4000	12
$\rho(CH_3)$	844	1400	6400	16
ν_{as}(C—C)	945	1100	3800	22
ν_s(C—O)	1080	1115	4300	19
ν_{as}(C—O)	1110	1700	5400	23
$\rho(CH_3)$	1164	320	1900	12
$\delta_s(CH_3)$	1258	490	6500	5
	1294	weak	–	–
	1361	(30)	–	–
	1388	240; total 270	1700	8
$\delta_{as}(CH_3)$	1442	140	520	(19)
	1450	140	520	–
	1478	50	300	12
	1490	very weak	–	–
ν_s(C—H)	2872	730	(1500)	–
	2890	730	–	–
	2928	730	–	–
ν_{as}(C—H)	2940	730	–	–
	2975	920	3300	20
$(CH_3)_3SiOC_2H_5$				
ν_s(Si—O)	605	very weak	–	–
ν_s(Si—C)	622	(0.23)	(45)	(6)
	686	100	500	16
$\rho(CH_2)$	726	weak	–	–
$\rho(CH_3)$	745	(270)	–	–
ν_{as}(Si—C)	754	(160); total 430	–	–
$\rho(CH_3)$	840	900	4300	15
	853	390	2150	13
$\rho(CH_2)$	947	620	2500	20
ν_s(C—O)	1079	(620)	2600	17
$\rho(CH_3)$	1109	(710); total 1330	3600	18
$\rho(CH_3)$	1163	250	1000	20
$\delta_s(CH_3)$	1250	450	(6400)	(5)
	1264	450	–	–
	1289	100	500	18

Interpretation	Frequency ν_0, cm^{-1}	Absolute intensity $A \cdot 10^9$, $cm^2/(molecule \cdot s)$	Absorption coefficient at the maximum k_{max}, cm^{-1}	Half-width of the band γ, cm^{-1}
	1358	very weak	–	–
	1389	110	1100	(6)
	1405	very weak	–	–
δ_{as}(CH)	1440	130	(350)	–
	1450	130	–	–
	1479	130	–	–
ν_s(C—H)	2874	450	–	–
	2898	450	–	–
	2932	450	–	–
ν_{as}(C—H)	2946	970	–	–
	2960	970	–	–
	2972	970	2400	(35)

* **Notes:**
1. Designations: ν –stretching vibration, δ –deformation vibration, ρ –rocking vibration, s –symmetric band, as –antisymmetric, medium –band of medium intensity, weak –weak, very weak –very weak.
2. The reproducibility of the results in measurements in solutions of different concentrations was within an average accuracy of up to 5%. Less accurate values, obtained for overlapping bands, are indicated in parentheses.

The bands assigned to the symmetric and antisymmetric stretching vibrations ν(C—O) lie in the region 1080-1110 cm^{-1}, are close to one another in frequency, and retain their position in the spectrum in all the compounds considered. The half-width of these bands changes almost not at all.

In this connection, as a first approximation one may take the group C_2H_5 as a single "atom" and regard the bridge Si—O—C_2H_5 as a single whole.

It should be noted that the vibration ν(Si—O) is strongly split into symmetric and antisymmetric components in the systems RSiOSiR′ as compared with ROSiOR′. In the former, the interval in frequency positions reaches 500 cm^{-1} ([7,11]); in the latter it is approximately 200 cm^{-1}. Apparently, in the first case a considerable resonance interaction of the vibrations of the groups RSi—O and O—SiR′ occurs through the oxygen atom.

The stretching vibrations ν_s(C—C) and ν_{as}(C—C) are observed in the region 940–960 cm^{-1}. In the IR spectrum, a strong broad asymmetric band is recorded in this region, resulting from the superposition of these vibrations.

The vibrations ν(C—H) are quite characteristic in intensity. Each of the CH_3 and C_2H_5 groups accounts for a definite share in the total intensity of the

C—H frequencies, and this share is preserved in passing from one compound to another.

4. Using experimental data on the intensities of the antisymmetric vibrations Si—O and Si—C, we have attempted to calculate electro-optical parameters. The problem was solved in the first approximation of the bond-optical scheme ([12]) for the molecular skeleton. It was assumed that the electro-optical parameters are identical in all the compounds, that the derivatives of the dipole moment of the Si—O bond with respect to changes in the angles adjacent to it are equal, and that the corresponding derivatives for the Si—C bond may be neglected. As a result, the following values were obtained, accurate to the significant digit:

$$\partial\mu_1/\partial q_1 - \partial\mu_1/\partial q_1' = 3.88, \qquad \partial\mu_1/\partial\alpha - \partial\mu_1/\partial\alpha' = 2.04,$$

$$\partial\mu_2/\partial q_2 - \partial\mu_2/\partial q_2' = 0.90 \text{ (D/Å)},$$

$$\mu_1 = \mu(\text{Si—O}) = 2.14, \qquad \mu_2 = \mu(\text{Si—C}) = 1.13 \text{ (D)}.$$

The calculated values have only an approximate significance, since at present it does not appear possible to measure intensities in the low-frequency region of the spectrum and thereby obtain a more complete set of initial experimental data, or to take into account the correction associated with the change in the light field acting on the molecule in a condensed medium as compared with the gaseous state.

Saratov State
Pedagogical Institute

Institute of Organic Synthesis
Academy of Sciences of the Latvian SSR

Received
11 VII 1966

REFERENCES

[1] R. E. Richard, H. W. Thompson, J. Chem. Soc., 1949, 124.
[2] A. P. Kreshkov, Yu. Ya. Mikhailenko, G. F. Yakimovich, ZhFKh, 28, 537 (1954).
[3] M. Hayashi, J. Chem. Soc. Japan (Pure Chem. Sect.), 79, 436 (1958).
[4] A. N. Lazarev, M. G. Voronkov, Optics and Spectroscopy, 4, 180 (1958).
[5] H. Kriegsmann, K. Licht, Zs. Elektrochem., 62, 1163 (1958).
[6] A. N. Lazarev, Optics and Spectroscopy, 8, 511 (1960).
[7] A. Marchand, J. Valade et al., J. chim. phys. et phys.-chim. biol., 59, 1442 (1962).

[8] M. G. Voronkov, ZhOKh, 29, 907 (1959).
[9] A. V. Iogansen, Optics and Spectroscopy, 16, 813 (1964).
[10] V. N. Smirnov, Vestn. Mosk. Univ., ser. mekh., matem., astr., fiz., khim., 6, 10 (1960).
[11] N. A. Chumaevskii, Optics and Spectroscopy, 10, 69 (1961).
[12] L. A. Gribov, *Theory of Intensities in the Infrared Spectra of Polyatomic Molecules*, Publishing House of the Academy of Sciences of the USSR, 1963.

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