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## MOLECULAR SPECTROSCOPY

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# Integral Intensities of Absorption Bands of Silicon Tetrafluoride in the Gas Phase and Cryogenic Solutions: Experiment and Calculation

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**Abstract**—The spectral characteristics of the SiF<sub>4</sub> molecule in the range 3100–700 cm<sup>-1</sup>, including the absorption range of the band  $\nu_3$ , are studied in the gas phase at  $P = 0.4\text{--}7$  bar and in solutions in liquefied Ar and Kr. In the cryogenic solutions, the relative intensities of the vibrational bands, including the bands of the isotopically substituted molecules, are determined. The absorption coefficients of the combination bands  $2\nu_3$ ,  $\nu_3 + \nu_1$ ,  $\nu_3 + \nu_4$ , and  $3\nu_4$  are measured in the solution in Kr. In the gas phase of the one-component system at an elevated pressure of SiF<sub>4</sub>, the integrated absorption coefficient of the absorption band  $\nu_3$  of the <sup>28</sup>SiF<sub>4</sub> molecule was measured to be  $A(\nu_3) = 700 \pm 30$  km/mol. Within the limits of experimental error, this absorption coefficient is consistent with estimates obtained from independent measurements and virtually coincides with the coefficient  $A(\nu_3) = 691$  km/mol calculated in this study by the quantum-chemical method MP2(full) with the basis set *cc-pVQZ*. © 2005 Pleiades Publishing, Inc.

## INTRODUCTION

Information about the spectral characteristics of the absorption bands of silicon tetrafluoride SiF<sub>4</sub> is of fundamental importance for the solution of many applied and scientific problems. Indeed, silicon tetrafluoride is widely used in microelectronics, fiber optics, and laser techniques. Recently, it was proposed to use isotopically enriched SiF<sub>4</sub> for obtaining monoisotopic silicon [1, 2]. Along with other fluorine-containing compounds, silicon tetrafluoride is a widespread air pollutant [3]. It is obvious that, in analysis of the composition of impurities in SiF<sub>4</sub> and measurement of its content in the atmosphere [4] and the waste gas of industrial plants [5], as well as upon study of some important reactions with the participation of SiF<sub>4</sub> [6], one should use reliable data on the integral intensities (absolute and relative) of the absorption bands of this molecule.

Data on the intensity of the strongest band  $\nu_3$  are also necessary for the interpretation of the results of spectroscopic studies of molecular complexes with the participation of SiF<sub>4</sub> [7] and van der Waals dimers (SiF<sub>4</sub>)<sub>2</sub> [8–10]. In the latter case, the spectral manifestations of dimerization are mainly determined by resonance dipole–dipole interactions and are proportional to the square of the derivative of the dipole moment  $P'_3$ . It is obvious that the mere possibility of unambiguous differentiation of the bands of dimers from the total

spectrum is determined by the accuracy of the quantity  $P'_3$  used in calculations.

However, experimental data about the electro-optical parameters of the SiF<sub>4</sub> molecule are incomplete. We are aware of seemingly only one early publication [11] devoted to the experimental determination of the absolute integral intensities of the main absorption bands of SiF<sub>4</sub> in the gas phase ( $A(\nu_3) = A_3 = 590$  km/mol and  $A(\nu_4) = 115$  km/mol). An obvious methodical drawback of this study is the use in the absorption measurements of strongly diluted mixtures of SiF<sub>4</sub> with a buffer gas, which is necessary for broadening of the rotational lines of the gas under study. A high chemical activity of SiF<sub>4</sub> could lead to its uncontrollable loss from the gas mixture and, as a consequence, to a decrease in the integral intensity of the absorption bands. The validity of this suggestion was supported by the data of [12], in which the absolute intensities of some absorption lines of pure SiF<sub>4</sub> were estimated with the help of ultrahigh resolution laser spectroscopy and it was found, in particular, that  $A_3 = 710 \pm 140$  km/mol.

In this study, we measured the absolute intensities of the IR absorption bands of SiF<sub>4</sub> in the one-component gas phase at an elevated pressure. The smearing of the fine structure of the bands necessary for the reliable measurement of the absorption (upon recording of spectra with a low resolution) is attained in these con-

ditions through self-broadening of the gas under study. In experiments with such a chemically active gas as SiF<sub>4</sub>, this approach has a number of merits. First, the measurements in the one-component system allow one to minimize the loss of chemically active SiF<sub>4</sub> due to its interaction with impurities adsorbed on the cell walls and, which is important, make it possible to monitor the stability of the sample by checking the linearity of the dependence of the integral intensity on the density. It is obvious that such an approach requires the use of cells with thin optical layers, especially in the case of intense absorption bands. Second, the relatively large derivative of the dipole moment of the SiF<sub>4</sub> molecule,  $P'_3 \approx 0.4$  D [10], leads to a strong resonance broadening of the band  $\nu_3$  [13] and other bands corresponding to the transitions to vibrational states combined with  $\nu_3$ . In connection with this, the smoothing of the contours of the *P*, *Q*, and *R* branches of the vibrational-rotational bands and, therefore, a decrease in the intensity of their maxima (primarily, the maximum intensity of the *Q* component) occurs at a relatively low pressure, which makes it possible to somewhat increase the optical path length.

We also studied the absorption spectra of solutions of SiF<sub>4</sub> in liquefied rare gases Ar and Kr. The use of this technique allows measurements of the relative intensity of the vibrational absorption bands of different orders to be made with a good accuracy (2–5%). The measurement accuracy of the absolute intensity of the absorption bands in cryogenic solutions is markedly lower [14], and, in our case, it is also reduced due to the loss of the chemically active substance. Nevertheless, we measured the absolute integral intensities of some combination bands of SiF<sub>4</sub> in a solution in Kr. The measurement results in cryogenic solutions make it possible to find the correction coefficients necessary for the calculation of the integrated absorption coefficients of the <sup>28</sup>SiF<sub>4</sub> molecule from the measurement data in the gas phase.

Additionally, we performed *ab initio* quantum-chemical calculations of the absorption coefficients  $A_3$  and  $A_4$  of the SiF<sub>4</sub> molecule by the method of self-consistent field (SCF) taking into account electron correlations and quadratic configurational interactions.

## EXPERIMENTAL

### *Measurement of the Integral Intensity in the Gas Phase*

Since the rotational constant of SiF<sub>4</sub> is small ( $B_0 = 0.13676$  cm<sup>-1</sup> [15]) and because of the occurrence of tetrahedral splittings, the density of the lines in the vibrational-rotational spectrum of silicon tetrafluoride is rather high and, at atmospheric pressure, the fine structure of this spectrum is smeared. The absolute intensities of the absorption bands were measured in the gas phase at elevated pressures of SiF<sub>4</sub> ( $P = 0.4$ –

7 bar), at which the fine rotational structure of the absorption bands is completely smeared. In the range 4000–800 cm<sup>-1</sup>, the spectra were measured in special high-pressure cells with BaF<sub>2</sub> windows sealed with Teflon. The thickness of the windows was equal to 0.8 cm, and their light diameter was 1 cm. For the most intense band  $\nu_3$ , the thickness of the absorption layer amounted to  $L = 93.5$  and 28.6 μm. The thickness of the absorption layer of the cells either evacuated or filled with He ( $P = 1$ –7 bar) was measured with an accuracy of 1–2% using the conventional interferometric technique [16]. In the case of the combination band  $\nu_1 + \nu_3$ , we used cells with a thicker path length ( $L = 0.085$  and 0.99 cm), whose maximal layer thickness was measured with a micrometer. The cells and the gas-admission system were made of Kh18N9T stainless steel. Before filling, the cells were evacuated to a pressure of  $\sim 10^{-2}$  Torr. In the range 0.4–7 bar, the pressure was measured with an acid-resistant compound pressure and vacuum gauge and with a vacuum gauge, the accuracy class of which was 0.4%. The density of the sample  $\rho$  at a given temperature and pressure was determined using the data about the virial coefficients from [17]. The integral intensity  $B_k$  of the band  $\nu_k$  was found from the experimental spectrum; then, the corresponding integrated absorption coefficient was calculated from the formula

$$A(\nu_k) = 2.01 \times 10^8 B_k / L\rho. \quad (1)$$

The gas phase spectra were measured with a resolution of 1 cm<sup>-1</sup> on an IFS-28 Bruker Fourier-transform spectrometer.

### *Measurement of the Absolute and Relative Intensities of the Absorption Bands of SiF<sub>4</sub> in Cryogenic Solutions*

The vibrational spectra of the solutions of SiF<sub>4</sub> in liquefied rare gases (Ar and Kr) were obtained using the standard techniques previously described in [14]. The absorption spectra were measured in a low-temperature cell made of stainless steel, which was supplied with ZnSe windows, sealed by indium gaskets, and had a length of 10 cm. The measurements in liquid Ar were performed at 90 K, and those in liquid Kr were made at temperatures of 160–170 K. The spectra were recorded with a resolution of 0.3 cm<sup>-1</sup> on an IFS-113 Bruker Fourier-transform spectrometer.

The absorption spectrum of SiF<sub>4</sub> in a solution in Ar consists of narrow,  $\Delta\nu_{1/2} = 1$ –4 cm<sup>-1</sup>, bands, each of which corresponds to a purely vibrational transition. This makes it possible to measure the integral absorption with a rather high accuracy (2–5%) and determine the relative intensities of the vibrational bands. The absolute intensities of some combination bands were measured in a solution in liquid Kr, in which the solubility of SiF<sub>4</sub> is markedly higher. To obtain a solution of a specified concentration, a gas mixture with the corre-

sponding ratio between the components ( $\text{SiF}_4$  and Kr) was prepared, which then was condensed into the cell. The concentration of  $\text{SiF}_4$  in the solutions in krypton was appreciably lower than the solubility limit, and this concentration was varied from 0.01 to 2 mol %. For each absorption band, from five to seven measurements of its integral intensity were performed.

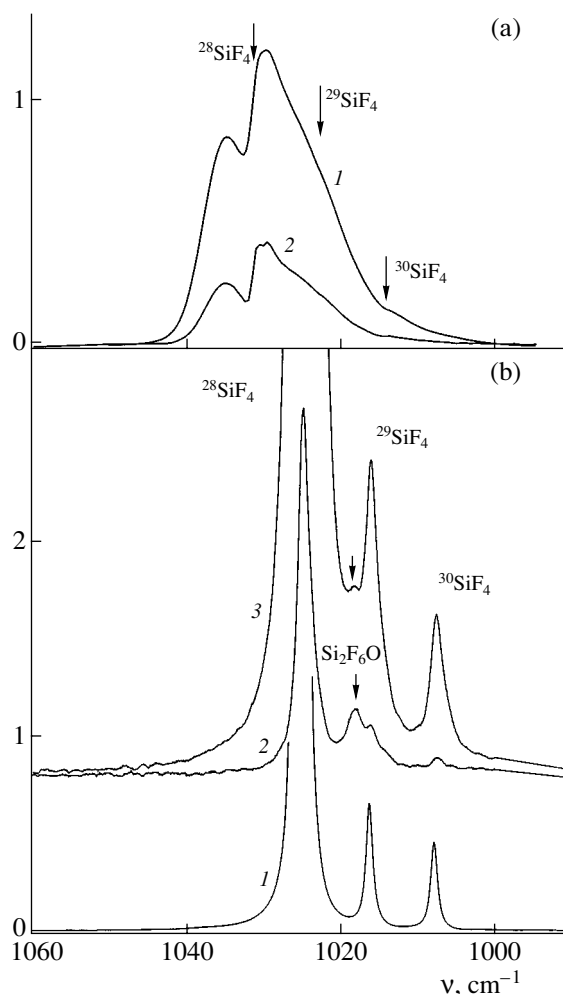
The samples of silicon tetrafluoride were prepared at the Russian Scientific Center Prikladnaya Khimiya and at the Institute of High-Purity Substances of the Russian Academy of Sciences and were used without any additional purification.

#### Methods of Quantum-Chemical Calculations

Quantum-chemical calculations were carried out by the ab initio SCF method, taking into account electron correlation by the Möller–Plesset perturbation theory (MP2) and quadratic configuration interaction with single and double excitations (QCISD) using the basis sets 6-311G(3df, 3pd) and *cc-pVQZ*. It has been shown previously that the variation of smaller basis sets does lead to divergent calculation results for the system under consideration. The MP2 calculations were performed both in the frozen-core approximation and explicitly taking into account the basic orbitals (MP2(full)). Complete optimization of the molecular geometry with subsequent calculation of the vibrational frequencies and absolute intensities was performed. The geometry of the molecule was optimized using the standard criteria for search termination. The vibrational frequencies were calculated in the harmonic approximation with the analytical calculation of the force constants in Cartesian coordinates. The absolute IR intensities of the fundamental vibrations were calculated in the dipole approximation with the use of the analytical derivatives of the dipole moment with respect to the normal coordinates. Calculations were performed with the Gaussian 98 program [19].

## RESULTS AND DISCUSSION

The frequencies and half-widths of the vibrational bands of  $\text{SiF}_4$  measured in the solution in Ar at 90 K are presented in Table 1. The shifts of the vibrational bands in the spectrum of the Kr solution of  $\text{SiF}_4$  with respect to the positions of these bands in the spectrum in the Ar solution fit into the additivity scheme and amount to (0.5–3)  $\text{cm}^{-1}$  [14]. Figures 1 and 2 show the absorption spectra of  $\text{SiF}_4$  in the solutions in Ar and Kr in the ranges of the fundamental transition  $\nu_3$  and of the combination transition  $\nu_1 + \nu_3$ ; the absorption spectra in the gas phase are also shown in these figures. It is seen from both figures that, in the range of the  $\nu_3$  and  $\nu_1 + \nu_3$  transitions, the bands of the isotopically substituted molecules  $^{28}\text{SiF}_4$ ,  $^{29}\text{SiF}_4$ , and  $^{30}\text{SiF}_4$  are observed; a similar pattern is also observed in the range of the transition  $2\nu_3$ . The relative intensities of the bands correspond to



**Fig. 1.** Absorption spectrum in the range of the  $\nu_3$  vibration of the  $\text{SiF}_4$  molecule. (a) The gas phase at 293 K: (1)  $P = 5$  bar and  $L = 28.6$   $\mu\text{m}$ , (2)  $P = 0.5$  bar and  $L = 93.5$   $\mu\text{m}$ ; (b) solutions of  $\text{SiF}_4$  in liquefied gases at  $L = 10$  cm: (1) solution in Ar at 90 K and concentration  $C = 1.3 \times 10^{-4}$  mol % and (2, 3) solution in Kr at  $T = 160$  K and (2)  $2.8 \times 10^{-4}$  mol % and (3)  $C \sim 0.1 \times 10^{-4}$  mol %. The arrows indicate the positions of the vibrational frequencies of the isotopically substituted  $\text{SiF}_4$  molecules and impurity  $\text{Si}_2\text{F}_6\text{O}$  molecules.

the natural abundance proportion of the silicon isotopes: 92.28% for  $^{28}\text{Si}$ , 4.67% for  $^{29}\text{Si}$ , and 3.05% for  $^{30}\text{Si}$ .

The characteristics of the  $\nu_3$  and  $\nu_4$  bands of isotopically substituted molecules are summarized in Table 2. Using the force field from [20], we calculated the frequencies and coefficients  $S_k$  of the vibration patterns of the normal modes taking into account the difference in the absorption coefficients of all the three isotopically substituted molecules. The isotope shifts  $\Delta\nu_3 = \nu_3(^{28}\text{SiF}_4) - \nu_3(\text{SiF}_4)$  measured for the solution in Ar are equal to 9  $\text{cm}^{-1}$  for  $^{29}\text{SiF}_4$  and to 17.5  $\text{cm}^{-1}$  for  $^{30}\text{SiF}_4$ . These shifts agree in value with the shifts calculated in

**Table 1.** Frequencies ( $\nu_k$ ) in the gas phase ( $\nu_{\text{gas}}$ ) and in an Ar solution ( $\nu_{\text{Ar}}$ ), half-widths ( $\Delta\nu_{1/2}$ ) in the Ar solution, relative intensities ( $\xi = A(\nu_k)/A(\nu_1 + \nu_3)$ ) of the vibrational bands of  $\text{SiF}_4$ , and estimates of integrated absorption coefficients  $A(\nu_k)$ 

Vibration	$\nu_{\text{gas}}^a$ , $\text{cm}^{-1}$	$\nu_{\text{Ar}}$ , $\text{cm}^{-1}$	$\Delta\nu_{1/2}$ , $\text{cm}^{-1}$	$\xi$	$A(\nu_k)$ , $\text{km/mol}$
$\nu_2^b$	264.2				
$\nu_4$	388.4				133
$2\nu_4$	776.3	771.5	2.2	0.095	0.25
$\nu_1^b$	800.6				
$\nu_3(^{30}\text{Si})$	1014.0	1008.0	1.0	8.3	
$\nu_3(^{29}\text{Si})$	1022.4	1016.3	1.1	12.6	
$\nu_3(^{28}\text{Si})$	1031.4	1025.2	1.0	265 <sup>d</sup>	690
$3\nu_4$	1164.2	1156.1	3.3	0.14	0.37
$\nu_1 + \nu_4$	1189.7	1185.0	2.5	1.06	2.76
$\nu_2 + \nu_3$	1294.05	1288.6	3.4	0.77	2.02
$\nu_3 + \nu_4$	1418.75	1409.3	3.5	0.02	0.052
$\nu_3 + 2\nu_4$	1804.5	1793.1	3.6	0.062	0.161
$\nu_1 + \nu_3(^{30}\text{Si})$		1802.8	1.4	0.029	
$\nu_1 + \nu_3(^{29}\text{Si})$		1811.1	1.5	0.049	
$\nu_1 + \nu_3(^{28}\text{Si})$	1828.2	1820.0	1.5	(1)	2.62
$2\nu_1 + \nu_4$		1983.2	2.5	0.0060	0.016
$2\nu_3(^{30}\text{Si})$		2011.8	4.5	0.02	
$2\nu_3(^{29}\text{Si})$		2028.7	5	0.05	
$2\nu_3(^{28}\text{Si})$	2059.1	2045.8	4.6	0.75	1.96
$\nu_3 + 3\nu_4$	2186	2175.5		0.0046	0.012
$\nu_1 + \nu_3 + 2\nu_4$	2602.55	2593		0.0006	0.0016
$2\nu_1 + \nu_3$	2623.8	2613.5	2.0	0.0026	0.0068
$\nu_1 + 2\nu_3$	2843	2838 <sup>c</sup>	5.0 <sup>c</sup>	0.0053 <sup>c</sup>	0.014
$3\nu_3^1$	3068.7	3050 <sup>c</sup>	2.2 <sup>c</sup>	0.0065 <sup>c</sup>	0.0017
$3\nu_3^{11}$	3090.6	3072 <sup>c</sup>		0.0003 <sup>c</sup>	0.0008

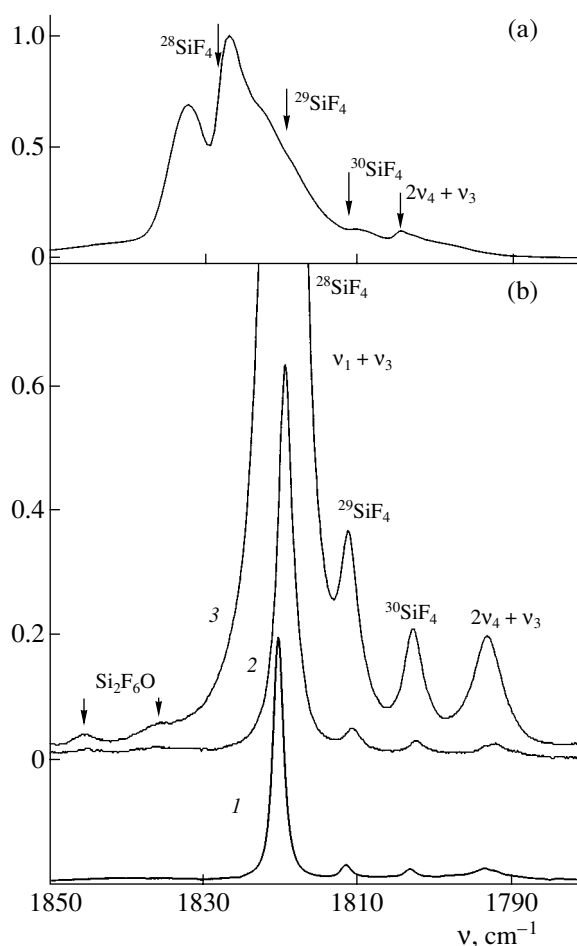
Notes: <sup>a</sup> Data from [20]; <sup>b</sup> obtained in [20] from the Raman spectrum; <sup>c</sup> obtained in [21] in the solution of  $\text{SiF}_4$  in liquid Ar at 90 K and  $L = 120$  cm; <sup>d</sup> obtained with the use of  $\xi$  and  $\eta$  for the  $\nu_3$  band of the  $^{30}\text{SiF}_4$  molecule in liquid Ar and at the natural abundance of the isotope 3.05%.

the harmonic approximation. The derivatives of the dipole moment are calculated under the assumption that the absolute intensities of the  $\nu_3$  and  $\nu_4$  bands are equal to  $A_3 = 691$  km/mol and  $A_4 = 143$  km/mol (the results of the calculations are given in Table 3). The changes in the absorption coefficients  $A_3$  and  $A_4$  of the  $^{29}\text{SiF}_4$  and  $^{30}\text{SiF}_4$  molecules characterize the relative intensities  $A(\text{SiF}_4)/A(^{28}\text{SiF}_4)$  presented in Table 2. The effective absorption coefficient of the band  $\nu_3$ , which is the sum of the corresponding  $\nu_3$  bands of the  $^{28}\text{SiF}_4$ ,  $^{29}\text{SiF}_4$ , and  $^{30}\text{SiF}_4$  molecules at the natural abundance proportion of the isotopes, is equal to  $0.997 A_3(^{28}\text{SiF}_4)$ .

The relative intensities  $\xi = A(\nu_k)/A(\nu_1 + \nu_3)$  presented in Table 1 are obtained by averaging of the mea-

surements in solutions in liquefied Ar at 90 K and in Kr at 160–170 K. The measurement errors of the relative intensities of the bands of the same order are within 2–5%. The rms deviations for all the bands do not exceed 10%. The relative intensity of the fundamental absorption band  $\nu_3$  of the  $^{28}\text{SiF}_4$  molecule was estimated using the relative intensity of the  $\nu_3$  band of the  $^{30}\text{SiF}_4$  molecule and the data from Table 2 on the changes in the absorption coefficients of the isotopes and their natural abundance contents. For clarity, the last column of this table presents the absolute intensities of the fundamental and combination bands of the  $^{28}\text{SiF}_4$  molecule calculated with the use of the relative intensities and the value  $A(\nu_3) = 690$  km/mol.

We were able to measure the absolute absorption coefficients of the  $\text{SiF}_4$  molecule in the solution in liquid Kr only for three bands of the second order and one band of the third order (see summary Table 4). For absorption bands with an intensity less than  $0.02 \text{ km/mol}$ , more reliable data were obtained from the absorption spectrum of the solution in liquid Ar in the layer  $L = 120 \text{ cm}$  [21]. Unfortunately, the measurement errors of the integral intensities of the bands in the range  $1200\text{--}1300 \text{ cm}^{-1}$  are appreciable owing to the overlap of these bands with intense absorption bands of the  $\text{Si}_2\text{F}_6\text{O}$  molecule. Hexafluorodisiloxane is the main impurity in the samples of  $\text{SiF}_4$ , and its concentration in the solution depends both on the conditions of obtaining  $\text{SiF}_4$  and on the conditions of experiments. The content of this impurity in the solutions and the gas phase estimated on the basis of data on the intensities of the analytical bands of  $\text{Si}_2\text{F}_6\text{O}$  from [22] was in the range  $0.02\text{--}2\%$ . Traces of the most intense band of  $\text{Si}_2\text{F}_6\text{O}$  located at  $1028 \text{ cm}^{-1}$  were observed in the range of the absorption band  $\nu_3$  of the  $\text{SiF}_4$  molecule in the solution in liquid Kr at large concentrations of  $\text{SiF}_4$  (see curve 3 in Fig. 1b). Upon dilution of the sample with krypton, the relative concentration of  $\text{Si}_2\text{F}_6\text{O}$  increases (Fig. 1b, curve 2). Table 4 presents the absorption coefficients  $A(\nu_k)$  corrected for the Lorentz field,  $A(\nu_k) = A_{\text{sol}}(\nu_k)/L(n)$ , where  $A_{\text{sol}}(\nu_k)$  is the integrated absorption coefficient of the band  $\nu_k$  measured in the solution in Kr and  $L(n) = (n^2 + 2)/9n = 1.16$  at  $T = 150 \text{ K}$ . It is seen from this table that, within the measurement accuracy, the absorption coefficients  $A(2\nu_3)$  and  $A(\nu_3 + \nu_1)$  coincide with the absorption coefficients measured in the gas phase. Figures 1 and 2 show that, in the gas phase, in the pressure range under study, complex smeared bands are observed in the range of the absorption bands  $\nu_3$  and  $\nu_3 + \nu_1$ , so that the contour of the  $\nu_3$  band contains the corresponding bands of all the three isotopically substituted  $\text{SiF}_4$  molecules and the contour of the  $\nu_3 + \nu_1$  band, apart from the bands of the isotopically substituted molecules, also contains the band  $2\nu_4 + \nu_3$ . The integral intensity ( $B_k$ ) of the  $\nu_3$  band was measured in the spectral range  $1050\text{--}995 \text{ cm}^{-1}$  and the integral intensity of the  $\nu_3 + \nu_1$  band was determined in the range  $1900\text{--}1735 \text{ cm}^{-1}$ . In order to obtain the integrated absorption coefficients of the absorption bands  $A_k$  of the  $^{28}\text{SiF}_4$  molecule from expression (1), one should take into account that, experimentally, one measures the integral intensity  $B_{\text{exp}}$  of the bands of the natural mixture of isotopically substituted molecules; therefore, for the  $\nu_3$  band of the  $^{28}\text{SiF}_4$  molecule,  $A(\nu_3) = 1.003A_{\text{exp}}(\nu_3)$ . For the  $\nu_1 + \nu_3$  band, one should take into account an additional correction owing to the overlap with the band  $\nu_3 + 2\nu_4$  (Fig. 2), which can be calculated using the data from Table 1 on the relative intensities of the bands of  $\text{SiF}_4$ . Accordingly, the integrated absorp-



**Fig. 2.** Absorption spectrum in the range of the  $\nu_1 + \nu_3$  vibration of the  $\text{SiF}_4$  molecule. (a) The gas phase at  $293 \text{ K}$ ,  $P = 4 \text{ bar}$ , and  $L = 0.99 \text{ cm}$ ; (b) solutions of  $\text{SiF}_4$  in liquefied gases at  $L = 10 \text{ cm}$ : (1) solution in Ar at  $T = 90 \text{ K}$  and concentration  $C = 1.5 \times 10^{-4} \text{ mol } \%$  and (2, 3) solution in Kr at  $T = 160 \text{ K}$  and (2)  $C = 5 \times 10^{-6} \text{ mol } \%$  and (3)  $C \sim 0.5 \times 10^{-4} \text{ mol } \%$ . The arrows indicate the positions of the vibrational frequencies of the isotopically substituted  $\text{SiF}_4$  molecules and vibrational transition  $2\nu_4 + \nu_3$ .

tion coefficient of the  $\nu_1 + \nu_3$  absorption band of the  $^{28}\text{SiF}_4$  molecule is equal to  $A(\nu_1 + \nu_3) = 0.946A_{\text{exp}}(\nu_1 + \nu_3)$ .

It is seen from Fig. 3 that, in the density range under study, the dependence of the integral intensity  $B(\nu_3)$  on the density is described with good accuracy by a straight line passing through the origin of the coordinate system,  $B(\nu_3) = -(0.01 \pm 0.03) + (10.58 \pm 0.02)\rho$ . The absorption coefficient  $A(\nu_3)$  can be found from the slope of this line. Similar dependences are also observed for the absorption bands  $2\nu_3$  and  $\nu_1 + \nu_3$ . The integrated absorption coefficients of the bands  $\nu_3$ ,  $2\nu_3$ , and  $\nu_1 + \nu_3$  measured in the gas phase are given in Table 4. The measurement accuracy of the integrated absorption coefficients  $A_k$  in the gas phase consists of the measurement accuracy of the integral intensity  $B_k$  ( $\sim 2\%$ ), the

**Table 2.** Frequencies ( $\nu_k$ ), isotope shifts ( $\Delta\nu_k$ ), vibration-pattern coefficients ( $S_k$ ), derivatives of the dipole moment ( $P'_k$ ), and relative intensities ( $\eta = A(\text{SiF}_4)/A(^{28}\text{SiF}_4)$ ) of the absorption bands of the isotopically substituted  $\text{SiF}_4$  molecules

Parameter	$^{28}\text{SiF}_4$ (92.28%)		$^{29}\text{SiF}_4$ (4.67%)		$^{30}\text{SiF}_4$ (3.05%)	
	$\nu_3$	$\nu_4$	$\nu_3$	$\nu_4$	$\nu_3$	$\nu_4$
$\nu$ , $\text{cm}^{-1}$	1043.9	389.7	1034.6	388.2	1025.9	386.8
$\Delta\nu_{\text{calc}}^*$ , $\text{cm}^{-1}$	0	0	9.3	1.5	18.0	2.9
$\Delta\nu_{\text{gas}}^*$ , $\text{cm}^{-1}$	0	0	9.3	1.5	17.4	2.9
$\Delta\nu_L^*$ , $\text{cm}^{-1}$	0		9.0		17.5	
$S_3$	0.0568	0.0053	0.0566	0.0051	0.0564	0.0049
$S_4$	-0.0586	0.1280	-0.0573	0.1279	-0.0560	0.1279
$P'_k$ , D	-0.421	0.273	-0.417	0.274	-0.413	0.275
$\eta$	1.000	1.000	0.971	0.996	0.945	0.995

\* The isotope shifts: calculated ( $\Delta\nu_{\text{calc}}$ ) and measured in the gas phase ( $\Delta\nu_{\text{gas}}$ ) and in the solution in liquid Ar ( $\Delta\nu_L$ ).

**Table 3.** Calculated total energies ( $E_{\text{tot}}$ ), Si–F bond lengths ( $R$ ), harmonic vibrational frequencies ( $\nu_k$ ), and intensities of the vibrational bands ( $A_k$ ) of the  $\text{SiF}_4$  molecule

Method	$E_{\text{tot}}$ , au	$R$ , Å	$\nu_1(A_1)$ , $\text{cm}^{-1}$	$\nu_2(E)$ , $\text{cm}^{-1}$	$\nu_3(F_2)$ , $\text{cm}^{-1}$	$\nu_4(F_2)$ , $\text{cm}^{-1}$	$A_3$ , km/mol	$A_4$ , km/mol	$A_3/A_4$
<i>Basis set 6-311G(3df)</i>									
MP2	-688.244387	1.5671	788.7	261.8	1028.9	389.1	636.9	134.2	4.74
MP2(full)	-688.501422	1.5635	793.4	263.6	1036.0	390.9	635.0	133.5	4.76
MP4(full)*	-688.544336	1.5647							
QCISD	-688.245992	1.5618	799.8	264.4	1040.7	392.9	651.9	139.5	4.67
<i>Basis set cc-pVQZ</i>									
MP2	-688.411336	1.5660	795.1	260.3	1032.8	383.6	692.0	142.2	4.87
MP2(full)	-688.583375	1.5592	802.8	262.5	1041.9	386.9	690.6	142.9	4.83
MP4(full)*	-688.626411	1.5596							

\* The calculation of the frequencies and intensities at this level is impossible due to program restrictions.

**Table 4.** Integrated absorption coefficients of the absorption bands of the  $^{28}\text{SiF}_4$  molecule measured in the gas phase, solution in liquid Kr, and calculated by the MP2 method with the *cc-pVQZ* basis set (the rms deviations are given in the parentheses)

Method	$\nu_3$	$\nu_4$	$2\nu_3$	$\nu_1 + \nu_3$	$\nu_3 + \nu_4$	$3\nu_4$
Gas [this study]	700(30)		2.0(1)	2.5(1)		
Gas [11]	595(60)	115(10)				
Gas [12]	710(140)					
Solution in Kr [this study]			2.1(3)	2.4(3)	0.040(6)	0.32(6)
Crystal [26]	690(20)	133(5)				
Calculation [this study]	690.6	142.9				

layer thickness (1–2.5%), the pressure (0.6–1%), the temperature (0.2%), and the density (1.5%). Accordingly, the total measurement accuracy of this parameter amounts to 5–7%. For the  $\nu_1 + \nu_3$  band, there arises an additional error of ~2% due to the population of the level  $\nu_1$  at room temperature [23].

It is seen from Table 4 that the integrated absorption coefficient  $A(\nu_3)$  measured in this study proved to be appreciably greater than that determined in [11]. Correspondingly, the derivative of the dipole moment  $P'_3$  of the  $^{28}\text{SiF}_4$  molecule was also increased. The value of this parameter can be calculated from the expression

$$P'_k = 0.895 \sqrt{A_k/g_k} \nu_k, \quad (2)$$

where, for  $\text{SiF}_4$ ,  $g_k = 3$ . It follows from this that, the derivative of the dipole moment of the triply degenerate vibration  $\nu_3$  of the  $^{28}\text{SiF}_4$  molecule amounts to  $P'_3 = 0.43 \pm 0.01$  D.

The derivative of the dipole moment can be estimated from independent measurements. Previously [24, 25], it was shown that, in a cubic molecular crystal, the longitudinal optical branch (LO), related to the splitting of a triply degenerate vibration of a molecule, lies at higher frequencies than the transverse optical (TO) branch and the value of the splitting is determined by the expression

$$\omega_{\text{LO}}^2 - \omega_{\text{TO}}^2 = \left( \frac{n^2 + 2}{3n} \right)^2 \frac{N}{\pi} \left( \frac{\partial \mu}{\partial Q} \right)^2. \quad (3)$$

Such a splitting was observed in the spectra of both Raman scattering and IR absorption of crystalline  $\text{SiF}_4$  [26, 27]. In expression (3),  $\omega$  is the frequency (in  $\text{s}^{-1}$ ),  $N$  is the number of the molecules in  $1 \text{ cm}^3$ ,  $\partial \mu / \partial Q$  is the derivative of the dipole moment with respect to the mass-weighted normal coordinate, and  $n$  is the refractive index. If, in expression (3), one introduces the frequency  $\nu = \omega/c$  (in  $\text{cm}^{-1}$ ); the dimensionless normal coordinate  $q = Q \sqrt{\gamma/M}$ , where  $\gamma = 4\pi^2 \nu M c / h$  and  $M$  is the reduced mass of the normal vibration; and assumes that  $\nu = (\nu_{\text{LO}} + \nu_{\text{TO}})/2$  and  $\Delta \nu_{\text{LO-TO}} = \nu_{\text{LO}} - \nu_{\text{TO}}$ , then expression (3) changes to the formula

$$\begin{aligned} \Delta \nu_{\text{LO-TO}} &= \left( \frac{n^2 + 2}{3n} \right)^2 \frac{2\pi N}{hc} \left( \frac{\partial \mu}{\partial q} \right)^2 \\ &= \left( \frac{n^2 + 2}{3n} \right)^2 3.14 \times 10^{-20} N (P'_3)^2. \end{aligned} \quad (4)$$

Expression (4) makes it possible to determine the derivatives of the dipole moment provided that the density of the crystal is known [24]. In [26], it was found that, in the Raman spectrum of crystalline  $\text{SiF}_4$  at 77 K, the splitting for the  $\nu_3$  band is equal to  $\Delta \nu_{\text{LO-TO}} = 68.4 \text{ cm}^{-1}$  and the splitting for the  $\nu_4$  band is  $\Delta \nu_{\text{LO-TO}} = 34.55 \text{ cm}^{-1}$ .

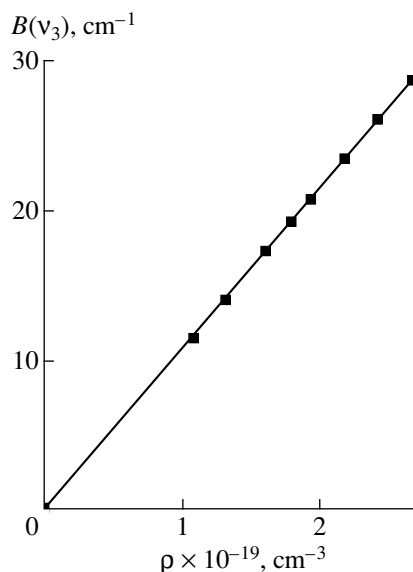


Fig. 3. Integral intensity of the absorption band  $\nu_3$  of the  $\text{SiF}_4$  molecule in relation to the gas density at  $T = 293$  K and  $L = 93.5 \mu\text{m}$ .

At 77 K,  $((n^2 + 2)/3n)^2 = 0.91$  and the number of molecules per unit volume  $N = 1.36 \times 10^{22} \text{ cm}^{-3}$ . Accordingly, the derivatives of the dipole moment with respect to the dimensionless normal coordinates are calculated to be  $P'_3 = 0.42 \pm 0.02$  D and  $P'_4 = 0.30 \pm 0.01$  D; i.e., they virtually do not differ from those determined in the gas phase. The estimates of the corresponding integrated absorption coefficients of crystalline  $\text{SiF}_4$  are given in Table 4.

It follows from the analysis of the calculation results presented in Table 3 that the value of the integrated absorption coefficient  $A_3 = 690.6 \text{ km/mol}$  calculated by the method MP2(full) with the *cc-pVQZ* basis set seems to be the most adequate. This basis set is rather wide, and it provides one of the best values of the bond length. Unfortunately, we were unable to perform calculations in this basis taking into account higher levels of correlation (QCISD). As can be seen from Table 3, taking into account the QCISD within the framework of the basis set 6-311G(3df) markedly affects the intensity, increasing its value by 15–16 km/mol. A rough extrapolation from the integrated absorption coefficients calculated by the method MP2(full)/*cc-pVQZ* to those determined by the method QCISD/*cc-pVQZ* yields the integrated coefficient  $A_3 \sim 709 \text{ km/mol}$ , which, within the measurement accuracy, virtually does not differ from the calculated and experimentally determined coefficients (Table 4). Table 3 shows the values of the total energy  $E_{\text{tot}}$  and the bond length  $R$  calculated by the method MP4, which give an idea of how well the higher calculation levels reproduce the geometry. Unfortunately, by virtue of the program restrictions, we

were unable to calculate the frequencies and intensities at this level.

Summing up, we should point out that, within the measurement accuracy, the integrated absorption coefficient of the  $\nu_3$  band of the  $\text{SiF}_4$  molecule measured in the gas phase in the one-component system coincides with that calculated by the method MP2/cc-pVQZ (Table 4). This coefficient  $A(\nu_3) \approx 700$  km/mol agrees with the estimates obtained in [12, 26] from independent measurements but proved to be considerably greater than the value  $A(\nu_3) = 595$  km/mol [11] traditionally used for  $^{28}\text{SiF}_4$ . The calculated absorption coefficient  $A(\nu_4) = 143$  km/mol also proved to be noticeably greater than that obtained in [11]. The integrated absorption coefficients of some combination absorption bands measured in the solution in liquefied Kr and in the gas phase coincide.

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