

Identification of the Products of Partial Hydrolysis of Silicon Tetrafluoride by Matrix Isolation IR Spectroscopy

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Abstract—Matrix isolation Fourier transform IR spectroscopy has been used for studying the products and mechanism of the silicon tetrafluoride reaction with water at various component ratios and reaction durations. Assignment of new bands in the spectrum confirms the earlier assumptions of first the formation of a molecular complex with water and later of trifluorosilanol, which finally condenses to give hexafluorodisiloxane.

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In order to meet the rapidly increasing demand of modern industry for amorphous and polycrystalline silicon, new sources and methods of preparation of this material are intensively sought after. Silicon tetrafluoride SiF₄ is a promising precursor to silicon as both massive samples and thin layers [1, 2]. This accounts for the growing interest of researchers in developing new methods of analysis of SiF₄ and studying its properties [3, 4].

The interaction with water (hydrolysis) is among the most important chemical reactions of silicon tetrafluoride. The major product of hydrolysis, stable in the gas phase, is hexafluorodisilixane Si₂F₆O [5, 7, 8]. Previously, IR spectroscopy [6] and mass spectrometry [7] showed that an intermediate product of hydrolysis is trifluorosilanol SiF₃OH, which is thermodynamically less favorable and is present in the reaction mixture in small amounts as a kinetic product because of the high activation energy of further transformations [9]. The thermodynamics of formation of these compounds in the gas phase was studied both theoretically by quantum-chemical methods and experimentally by high-resolution IR spectroscopy [9, 10]. The experimental equilibrium constants were consistent with the calculated values. The change in the concentrations of both products was monitored by observing the change in the intensities of broad featureless bands: the rather strong band at 838 cm⁻¹ due to symmetric Si–F stretching vibrations in the Si₂F₆O 2O molecule (the Si–O vibrations in this molecule give rise to the band at about 1200 cm⁻¹) and the weak band at 3762 cm⁻¹ due to the OH bond vibrations in the SiF₃OH molecule. However, monitoring the change in these bands in time does not answer the question of whether trifluorosilanol is the only and/or dominating OH-contain-

ing intermediate and gives no way to reliably interpret the kinetic dependences of the early hydrolysis stages. To solve this problem, one should study the fine structure of the absorption bands at 1000 and 3760 cm⁻¹ and elucidate how their separate components depend on the reaction conditions and duration. This task is however complicated by the fact that, in the region of 1000 cm⁻¹, strong antisymmetric vibrations of the Si₂F₆O and SiF₃OH molecules are overlapped with the extremely strong band ν^3 (1031.4 cm⁻¹) of SiF₄ per se [10]. The fine structure of the absorption bands of Si₂F₆O and SiF₃OH molecules at 1000 and 3760 cm⁻¹ cannot be studied even by high-resolution gas-phase IR spectroscopy. Previously [11], we studied the spectra of SiF₄ in a solution in liquid argon and krypton at 90 and 160–170 K, respectively. We showed that, in argon, the band ν_3 at 1008.0 cm⁻¹ is split into three components corresponding to silicon-28, -29, and -30 isotopes. The same spectrum also showed an impurity absorption band at 1015 cm⁻¹, which was presumably assigned to hexafluorodisiloxane. Unfortunately, this experimental method (which is an equilibrium one) cannot be used for studying mixtures of silicon tetrafluoride with water because of the extremely poor solubility of the latter in liquid noble gases. An alternative method for improving the resolution of absorption bands structureless at room temperature and detecting reaction products and unstable intermediates is matrix isolation IR spectroscopy with various gases as low-temperature matrices. The spectrum of SiF₄–water mixtures in an argon matrix at 14 K and a resolution of 1 cm⁻¹ was studied in [12]. The work focused on identification of weak complexes formed by the fluoride molecule with molecules of oxygen- and nitrogen-containing Lewis bases, including water as the weakest

base (electron density donor). It was found that the Si–F stretches in such a complex give rise to the band at 984 cm^{-1} and the silicon tetrafluoride band at 1025 cm^{-1} is split into a large number of narrow lines, no assignment for them having been reported. New bands also appear in the region of water bending vibrations ν_2 (1590 cm^{-1}) and antisymmetric stretching vibrations ν_3 (3700 cm^{-1}). Recently [13], the matrix spectrum of SiF_4 in argon, xenon, and nitrogen at 11 K in the region of the ν_3 band was studied by state-of-the-art FT IR spectroscopy with a resolution of 0.1 cm^{-1} . The spectrum in the argon matrix showed 24 lines due to the $^{28}\text{SiF}_4$, $^{29}\text{SiF}_4$, and $^{30}\text{SiF}_4$. The band at 1029.4 cm^{-1} was assigned to the $(^{28}\text{SiF}_4)_2$ dimer. Other regions of the silicon tetrafluoride spectrum were not considered in [13].

In the present work, we study spectral features of the bands in the low-temperature matrix spectra in argon of SiF_4 –water mixtures in the regions of the ν_3 modes of the fluoride and ν_2 and ν_1 and ν_3 modes of water, as well as in the regions of hexafluorodisiloxane absorption (800 – 860 and 1160 – 1200 cm^{-1}), in order to elucidate how their intensities and positions respond to the component ratio in a mixture and reaction duration and refine our insight into the mechanism of partial hydrolysis of silicon tetrafluoride.

EXPERIMENTAL

The IR spectra in an argon matrix were recorded on a setup comprising a Bruker IFS66v FTIR spectrophotometer and a Leybold ROK 10-300 closed cycle cryostat. With the use of a routine manometric technique, mixtures of SiF_4 and H_2O with various component ratios were prepared directly in the gas line and then mixed with argon in ratios of $1/50$ – $1/1000$. Matrices were deposited onto an aluminum substrate cooled to 12 K. Spectra were recorded in the range 4250 – 500 cm^{-1} with the use of a cooled MCT detector; the resolution was 0.2 cm^{-1} , and up to 400 scans were acquired. Silicon tetrafluoride (Air Liquide), containing less than 10 ppm of carbon monoxide, carbon dioxide, and C_1 – C_3 hydrocarbons, was used.

RESULTS AND DISCUSSION

The spectrum of commercially available silicon tetrafluoride usually shows a weak band of the hexafluorodisiloxane impurity (840 cm^{-1}) with a content of 10^{-2} – $1\text{ mol } \%$. Previously [4], we showed that, under equilibrium conditions in the gas phase, silicon tetrafluoride can also contain on the order of $10^{-3}\text{ mol } \%$ of water. These facts should be taken into account in interpretation of the matrix IR spectrum of initial SiF_4 . The bands arising from free water (as monomers and dimers) in the ν_2 and ν_1 and ν_3 regions were identified using specially recorded spectra of water, as well as invoking numerous data on the spectra of H_2O iso-

lated in the argon matrix (see, e.g., [14–17] and references therein).

Figure 1 shows portions of the spectrum of initial SiF_4 in the argon matrix with a dilution of $1 : 1000$ in the region of the ν_3 mode of silicon tetrafluoride and adjacent regions of hexafluorodisiloxane absorption, as well as in the regions of the water ν_2 and ν_1 and ν_3 modes. As is seen, these regions are well resolved. In the range 1010 – 1030 cm^{-1} containing the isotope components and the lines of the $(^{28}\text{SiF}_4)_2$ dimer at 1029.4 cm^{-1} , the positions and relative intensities of the observed lines are consistent with the data in [12, 13]. In the range 950 – 1000 cm^{-1} , there is a rather strong doublet with maxima at 985.1 (major) and 984.4 cm^{-1} assigned in [12] to Si–F vibrations in the complex with water traces. In the region of the water ν_2 mode, the doublet with maxima at 1592.2 and 1591.7 cm^{-1} , due to water molecules fixed in the Ar matrix (non-rotating molecules), sharply builds up. Very weak bands emerging at 3641.7 and 3723 cm^{-1} were assigned in [12] to water vibrations in the complex since no SiF_4 interaction products were observed.

The matrix spectra of silicon tetrafluoride with water additions are shown in Figs. 2–4. Figure 2 compares separate portions of the spectra of the following systems: (1) initial SiF_4 in argon with a dilution of $1 : 1000$ ($\text{Ar}/\text{SiF}_4 = 1000$), (2) the mixture containing excess fluoride with respect to water ($\text{Ar}/(\text{SiF}_4\ 23.8\text{ mbar} + \text{H}_2\text{O}\ 1.3\text{ mbar}) = 1000$, sample 1), and (3) the mixture containing equimolar amounts of fluoride and water ($\text{Ar}/(\text{SiF}_4\ 9.5\text{ mbar} + \text{H}_2\text{O}\ 9.1\text{ mbar}) = 1000$, sample 2). The intensity of the band at 985.1 cm^{-1} depends on the water content in a mixture. Significant changes are observed in the range 1020 – 1010 cm^{-1} : in both cases, a new band at 1018.8 cm^{-1} appears, its intensity being maximal at equimolar amounts of the components in a mixture. In the range 1020 – 1040 cm^{-1} , the intensity of the SiF_4 dimer band at 1029.4 cm^{-1} depends on the water concentration. In going from sample 1 to sample 2, this intensity decreases, while the band at 1027.8 cm^{-1} builds up. The range 1560 – 1660 cm^{-1} contains the lines and bending vibration bands of different water forms. With an increase in the water content, there is an increase in the intensities of the bands lacking in the spectrum of initial silicon tetrafluoride and in the spectrum of water at 1591.8 and 1589.4 cm^{-1} arising from so-called “hindered” water molecules in the matrix that form a complex with silicon tetrafluoride [14], as well as in the intensity of the band at 1593.1 cm^{-1} assigned to vibrations of the water molecules (acting as a proton acceptor) in the dimer [14]. The intensity of the band at 1610.5 cm^{-1} due to water molecules acting as proton donors is concurrently increased. In the region of the ν_3 antisymmetric water stretches (3500 – 3700 cm^{-1}), new bands are observed at 3641.9 and 3638.2 cm^{-1} . In the region of the ν_1 mode (symmetric stretching vibrations) of water, major changes are observed in the range 3750 – 3705 cm^{-1} : weak bands appear at 3723.1

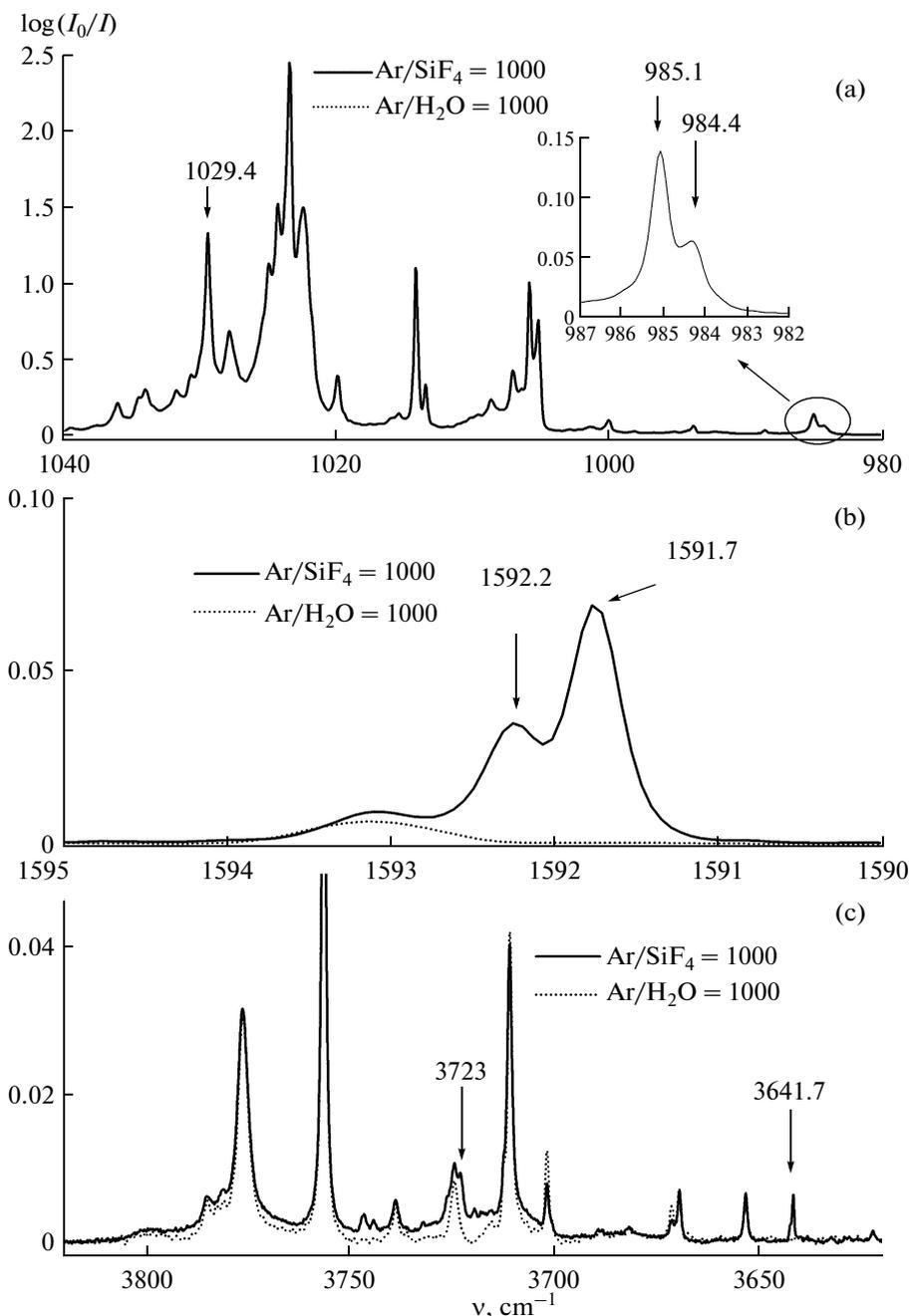


Fig. 1. Vibrational spectra of (a) $\text{Ar}/\text{SiF}_4 = 1000$ in the region of the ν_3 mode of silicon tetrafluoride, (b) $\text{Ar}/\text{SiF}_4 = 1000$ and $\text{Ar}/\text{H}_2\text{O} = 1000$ in the region of the ν_2 mode of water, (c) $\text{Ar}/\text{SiF}_4 = 1000$ and $\text{Ar}/\text{H}_2\text{O} = 1000$ in the region of the ν_1 and ν_3 modes of water (hereinafter, see Experimental for spectrum recording details).

and 3721.0 cm^{-1} . The simultaneously appearing band at 3708.2 cm^{-1} arises from the water dimer [14].

To obtain more detailed information of the above spectral features, we studied the spectra of silicon tetrafluoride–water mixtures at a lower dilution with argon (as a rule, 1 : 500).

Figure 3a shows the spectrum of $\text{SiF}_4/\text{Ar} = 500$ together with the spectra of $\text{Ar}/(\text{SiF}_4\ 51.8\text{ mbar} + \text{H}_2\text{O}\ 22.0\text{ mbar, sample 3})$ 1 and 16 h after mixing. In the

range $820\text{--}880\text{ cm}^{-1}$, the intensities of the bands at 862.6 , 850.9 , 846.8 , and 836.4 cm^{-1} increased in the course of reaction, the last band having a characteristic doublet contour like that observed for the weak band at 836.4 cm^{-1} in the spectrum of pure silicon tetrafluoride. The band at 985 cm^{-1} built up, while the low-frequency shoulder at 984.5 cm^{-1} became almost unobservable. In the range $1010\text{--}1020\text{ cm}^{-1}$, the new band at 1018.8 cm^{-1} appeared, and the band at

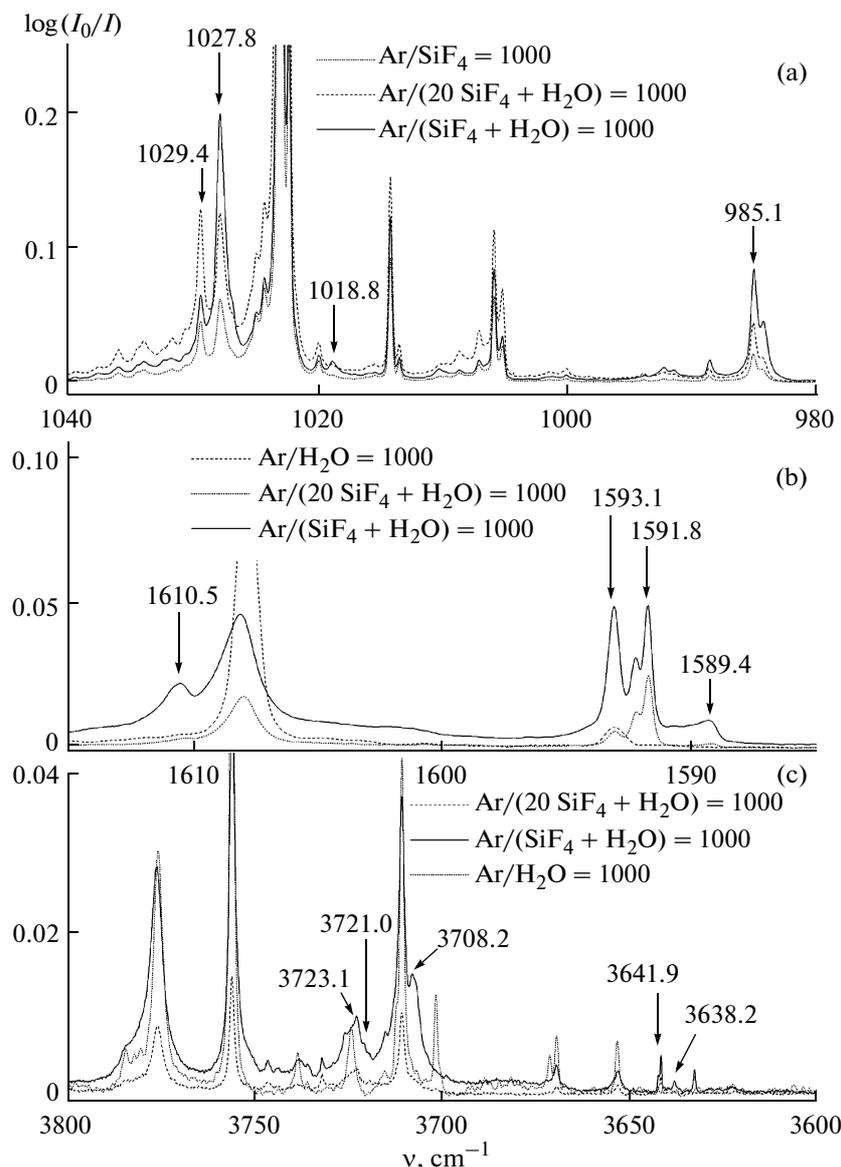


Fig. 2. Vibrational spectra of the systems Ar/SiF₄ = 1000, Ar/(SiF₄ + H₂O) = 1000, and Ar/(20SiF₄ + H₂O) = 1000 in the region of (a) ν_3 of silicon tetrafluoride, (ν_2 of water, and ν_1 and ν_3 of water (hereinafter, see text for the concrete component ratios).

1019.4 cm^{-1} was observed as the inflection between 1019.9 and 1018.8 cm^{-1} . The relative intensity of the band at 1029.4 increased. The intensity of the broad band with separate peaks in the range 1160–1280 cm^{-1} increased only slightly: even after a 16-h reaction period, it differed insignificantly from the band in the spectrum of initial silicon tetrafluoride. In the region of water bending vibrations (1560–1660 cm^{-1}) for the same mixture as in Fig. 3, the band with four maxima at 1600 cm^{-1} (Fig. 4a) became stronger (Fig. 4a). In the region of symmetric water stretches 3500–3700 cm^{-1} (Fig. 4b) the intensity of the bands at 3642, 3638.2, and 3628 cm^{-1} increased; in the region of antisymmetric vibrations 3700–3820 cm^{-1} , the intensity of the

band with maxima between 3723.2 and 3715.7 cm^{-1} became noticeably stronger.

The table summarizes the new lines and bands related to the silicon tetrafluoride–water interaction. It follows from these data that the structure of the bands at 1030 and 3760 cm^{-1} , as well as at 830, 1240, and 1600 cm^{-1} , in the spectra of silicon tetrafluoride and its mixtures with water, their relative intensities, and intensities of separate lines within each band depend in a rather complicated manner on the prehistory of a sample, the component ratio, and reaction duration. Nevertheless, these bands were assigned (table) on the basis of the previous quantum-chemical calculations of the thermodynamics and kinetics of

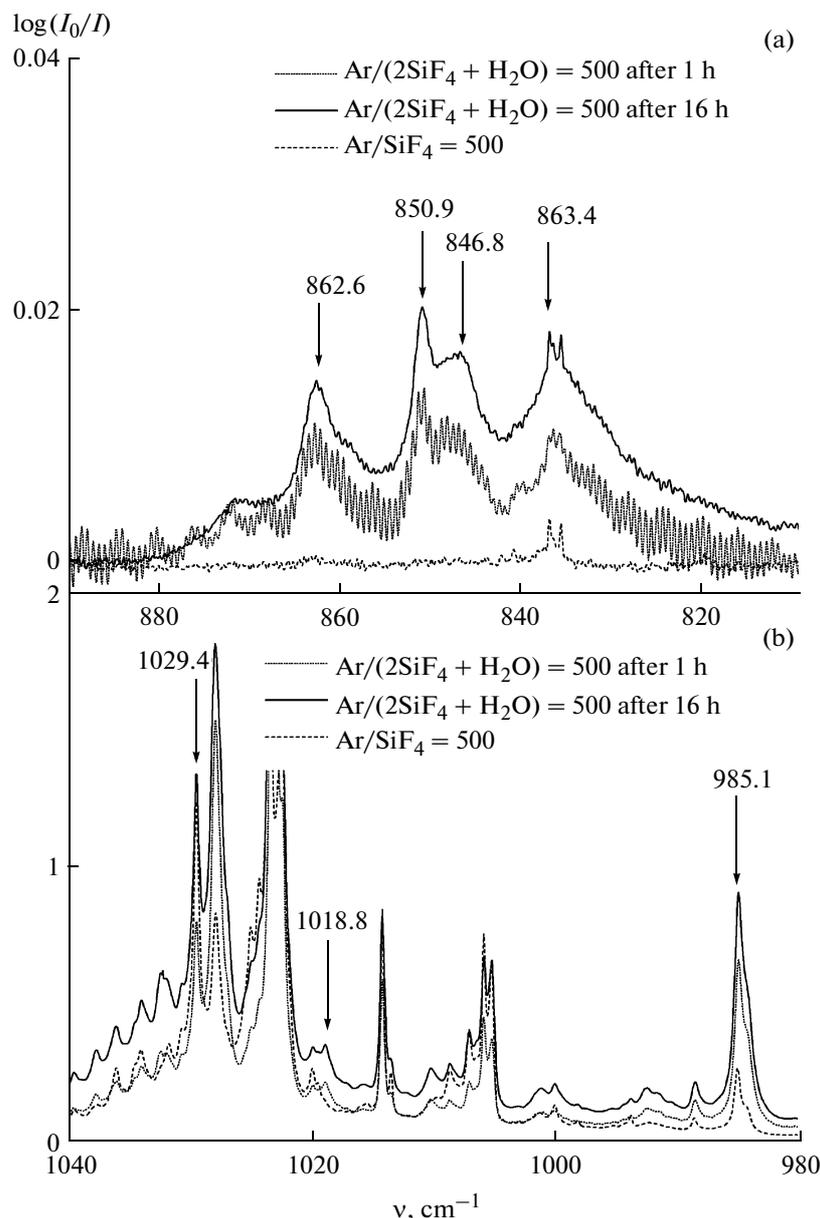


Fig. 3. Vibrational spectra of the Ar/(SiF₄ + H₂O) = 500 system 1 and 16 h after the mixing of the components (a) in the range 890–810 cm⁻¹ and (b) in the region of ν_3 of silicon tetrafluoride.

the silicon tetrafluoride reaction with water and the IR spectra of major products [6, 9, 10] and the results of studying their experimental spectra in the gas phase [4, 5, 7, 8] and in a low-temperature matrix [12, 13]. Once the components have been mixed, it takes much shorter time for them to interact than the time of recording the IR spectrum. Among the reaction products, the molecular complex of the donor–acceptor type F₄Si...OH₂ is noteworthy. The Si–F vibration in this complex gives rise to strong (985.1–984.4 cm⁻¹) and weaker doublets (992.5–991.6 cm⁻¹) due to vibrations of the same type. They split due to the matrix effect. A characteristic feature of chemical interaction

in this system is the appearance of new bands at 1019.4 and 1018.8 cm⁻¹ assigned to the natural vibrations of SiF₄ in this region [13]. The former band is detected either when the matrix concentration is increased at a constant component ratio or when a mixture is kept for a rather long time before deposition. According to the experimental [4, 7, 8] and computational [10] data, Si–F vibrations with an admixture of Si–O vibrations of Si₂F₆O and SiF₃OH molecules can be observed in this range. According to [9], formation of hexafluorodisiloxane is thermodynamically somewhat more favorable, whereas the energy barrier is lower for trifluorosilanol. Therefore, we can suggest that the

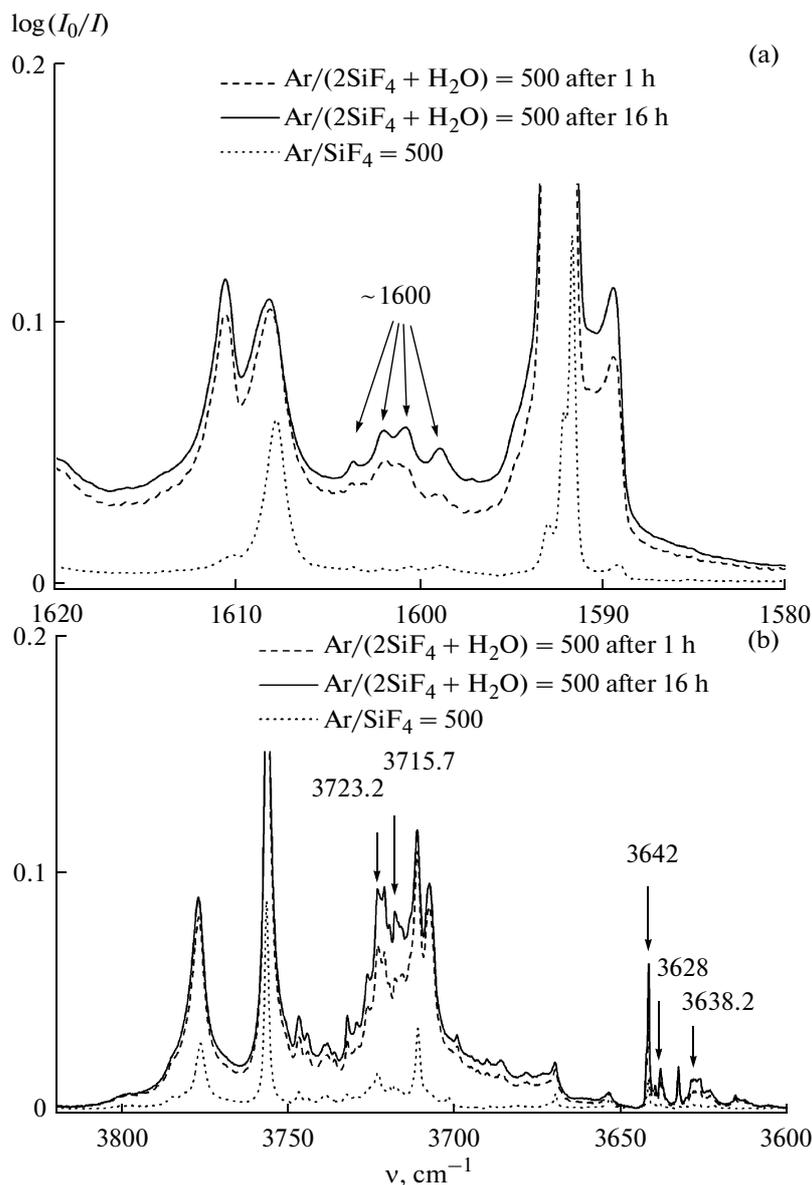


Fig. 4. Vibrational spectra of the $\text{Ar}/(\text{SiF}_4 + \text{H}_2\text{O}) = 500$ system 1 and 16 h after the mixing of the components in the region of (a) ν_2 of water and (b) ν_1 and ν_3 of water.

band at 1018.8 cm^{-1} is due to $\text{SiF}_3\text{OH}_3\text{OH}$ molecules; in addition, the spectrum also shows the band with peaks at 862.6 , 850.9 , 846.8 , and 836.4 cm^{-1} , which is absent (except a very weak peak at 836.4 cm^{-1}) in the spectrum of initial silicon tetrafluoride. Calculations predict that this range should contain the band of Si–O–H bending vibrations of the SiF_3OH molecule and the band of the difference between symmetric vibrations of two SiF_3 moieties of the $\text{Si}_2\text{F}_6\text{O}$ molecule, the intensity of the latter being approximately twice as low as the intensity of the former. It is worth noting that the strong (according to calculations) antisymmetric F–Si–F vibration band is near 980 cm^{-1} and can be overlapped with the band of the complex at 985 cm^{-1} (this can be responsible for the disappearance of the low-

frequency shoulder at this band in the spectrum of initial silicon tetrafluoride on adding water to it).

The Si–O–Si antisymmetric vibration band for the $\text{Si}_2\text{F}_6\text{O}$ molecule in the gas phase is observed at 1190 – 1260 cm^{-1} [8]. According to calculations, this band is the strongest one in the spectra of both molecules; however, because of a very large half-width and complex shape, its experimentally observed intensity is low. Nevertheless, we can state that the highest intensity of this band is achieved when the bands at 1019.4 and 836.4 cm^{-1} are simultaneously present in the spectrum. Calculations predict that the band at 1019.4 cm^{-1} should be 1.5 – 2 times as weak as the band at 1018.8 cm^{-1} of trifluorosilanol and should be observed in the spectrum of initial SiF_4 only with an increase in

Positions of the bands due to the products of the SiF₄ reaction with water in the IR spectrum in the argon matrix at 14 K and their assignment

ν_{\max} , cm ⁻¹	Assignment ([10] except * and **)	Intensity, km/mol [10]		
836.1	$\nu_s(\text{F}_3\text{Si}) - \nu_s(\text{SiF}_3)$ of the Si ₂ F ₆ O molecule	96		
848.1	$\nu_s(\text{F}_3\text{Si}) + \nu(\text{Si-O}) + \delta(\text{H-O-Si})$ of the SiF ₃ OH molecule	186		
851.38				
862.5	$\nu_{as}(\text{F-Si-F})$ in the complex with H ₂ O + $\nu_{as}(\text{F-Si-F})$ of the SiF ₃ OH molecule (?)	265		
984.4				
985.1				
1018.8				
1019.4				
1019.4			$\nu_{as}(\text{F}_3\text{Si}) + \nu_{as}(\text{F}_3\text{Si}) + \nu_s(\text{Si-O-Si})$ of the Si ₂ F ₆ O molecule	34
1212.6			$\nu_{as}(\text{Si-O-Si})$ of the Si ₂ F ₆ O molecule	692
1224.0				
1232.4				
1244.8				
1255.5				
1268.2				
1276.6				
1601.5	$\delta(\text{H-O-H})$ in the complex with SiF ₄	80		
3554.6 *	$\nu(\text{H-F})$ in the HF complex with H ₂ O [19–21]	—		
3628.0	$\nu_s(\text{H-O-H})$ in the HF complex with SiF ₄	23		
3638.2				
3642.2	$\nu_{as}(\text{O-H})$ of the SiF ₃ OH molecule	128		
3717.5				
3721.2				
3723.4				
3726.4				
3732.6				
3887.2 **	$\nu(\text{H-F})$ in the HF complex with SiF ₄ [18–20]	—		
3967.1				

the matrix concentration (on going from the dilution 1000 to 500).

Characteristic changes in the spectral ranges 1600 and 3500–3800 cm⁻¹ observed on adding water to silicon tetrafluoride should be caused only by the formation of the complex and trifluorosilanol. These changes are clearly seen in Figs. 2 and 4 related to various matrix concentrations and reaction times. As is seen, with an increase in the reaction duration, the intensity of the band at 1602 cm⁻¹ increases, whereas an increase in the matrix concentration leads to the shift of this band to 1599 cm⁻¹. This is likely associated with a change in the structure of the SiF₄–water complex since the above band was assigned to the bending vibrations of the water molecule in this complex [12]. In the region of the ν_3 antisymmetric mode of water molecules, new bands are observed at 3642.2, 3638.2, and 3628.0 cm⁻¹, which can be detected (especially the first one) even in the spectrum of initial silicon tetrafluoride. In the region of the ν_1 antisymmetric mode of water, an increase in the water content in a mixture or an increase in the reaction time leads to the appear-

ance and buildup of the band with peaks at 3762.6, 3726.4, 3723.4, and 3721.2 cm⁻¹. Its component at 3722 cm⁻¹ was assigned in [12] to antisymmetric stretches of the water molecule in the complex. With an increase in the matrix concentration, the spectrum is dominated by the band at 3717 cm⁻¹, which was previously almost unobservable due to the low absorptance, and the considerably weaker band at 3732.6 cm⁻¹. In our opinion, this band arises from O–H bond vibrations in the SiF₃OH molecule or in more complicated fluorosilanols. This band is centered at 3760 cm⁻¹ in the spectrum of the gas phase [4] and at 3685 cm⁻¹ in a carbon tetrachloride solution [6].

Our results allow us to give the following interpretation of the water-induced impurity absorption in the spectra of SiF₄ in the gas phase at a pressure of several hundreds of torrs and in the matrix at a rather high dilution. The water admixture contained in silicon tetrafluoride partially reacts with the host compound, and under equilibrium conditions, hexafluorodisiloxane predominates in the system (the bands at 836.4 and 1019.4 cm⁻¹ and the broad band with several peaks

in the range 1200–1260 cm^{-1} in the matrix; the band at 840 cm^{-1} and the broad band at 1200–1300 cm^{-1} in the gas phase). The presence of the trifluorosilanol admixture in the equilibrium system is betrayed in some cases by the inflection at 1018.4 cm^{-1} in the low-frequency wing of the band at 1020 cm^{-1} and the weak absorption at 3717 cm^{-1} in the matrix and by the very weak band at 3762 cm^{-1} in the gas phase, which is, as a rule, unobservable at low water contents. Under matrix isolation conditions, some water molecules remain bound to silicon tetrafluoride in the complex, which is indicated by the bands at 985 and 1602 cm^{-1} and the typical redistribution of the water band intensities in this region, as well as by the absorption at 3642.2, 3638.2, and 3628.0 cm^{-1} in the region of the ν_3 antisymmetric mode of water molecules and at 3732.6, 3726.4, 3732.4, and 3721.2 cm^{-1} in the region of the ν_1 symmetric mode of water molecules.

One of the products of the silicon tetrafluoride hydrolysis is hydrogen fluoride, which gives rise to rather weak narrow absorption bands at 3920–3970 cm^{-1} in the matrix spectrum. Self-association or complexation with other molecules leads to broadening of these bands and to their shift toward lower frequencies down to 3500 cm^{-1} [18]. For all water-containing systems, we observed extremely weak bands at 3967, 3877, and 3554.6 cm^{-1} , which are presumably due to the absorption of HF in different environments. The first two bands can arise from hydrogen fluoride bound to SiF_4 in a weak complex since they are close to the bands observed for similar complexes with WF_6 and MoF_6 [19]. The band at 3554.6 cm^{-1} coincides with the strongest band observed in the spectrum of the HF complex with water in the argon matrix [20]. It should be taken into account that hydrogen fluoride is rather prone to adsorption on the equipment walls. In the experiments on studying the SiF_4 hydrolysis in the gas phase at a pressure of several hundreds of millibars, the absorption bands of the nascent hydrogen fluoride are rather strong.

Thus, the FTIR absorption spectra of silicon tetrafluoride with water additions in the argon matrix at 14 K were studied at different component ratios and reaction times before the moment of matrix formation. New lines and bands were detected in the ranges 820–1200, 1600, and 3700–3900 cm^{-1} that arise from the products of partial hydrolysis of SiF_4 . Invoking the results of earlier experiments in the gas phase and quantum-chemical calculations of the intensities of SiF_3OH , $\text{Si}_2\text{F}_6\text{O}$, and $\text{F}_4\text{Si}\dots\text{OH}_2$ modes, we showed that, over a period of time much shorter than the spectrum recording time, silicon tetrafluoride reacts with water to form the 1 : 1 donor–acceptor complex and trifluorosilanol, which later partially converts into hexafluorodisiloxane SiF_3OH . The latter two products

are also stable in the gas phase and can be detected as impurities in silicon tetrafluoride.

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SPELL: 1. polycrystalline