IR spectroscopic and *ab initio* quantum-chemical study of the products of hydrolysis of silicon tetrafluoride at low water concentrations

P. G. Sennikov,[a] M. A. Ikrin,[a] S. K. Ignatov,[b] A. A. Bagatur'yants,[c] and E. Yu. Klimov[a]*

[a]Institute of the Chemistry of High-Purity Substances, Russian Academy of Sciences,
49 ul. Tropinina, 603600 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 66 8666. E-mail: sen@hp.nnov.su
[b]N. I. Lobachevsky Nizhnii Novgorod State University,
23 prosp. Gagarina, 603600 Nizhnii Novgorod, Russian Federation.
E-mail: ignatov@qchem.nnov.su
[c]Center of Photochemistry, Russian Academy of Sciences,
7a ul. Novatorov, 117421 Moscow, Russian Federation.
E-mail: sasha@mx.icp.rssi.ru

According to the results of IR spectroscopic study and quantum-chemical calculations, hydroxo derivatives $SiF_{4-x}(OH)_x$ are formed in the course of hydrolysis of silicon tetrafluoride in the presence of small amount of water along with hexafluorodisiloxane.

Key words: silicon tetrafluoride, products of hydrolysis; IR spectroscopy, quantum-chemical calculations.

Silicon tetrafluoride is widely used for producing epitaxial layers of amorphous silicon and as a fluorinating agent in manufacturing SiO_2 fiber light pipes.[1] For these purposes SiF_4 with extremely low concentrations of oxygen- and/or hydrogen-containing impurities,[2] especially water and products of the hydrolysis of the main substance, is required. The most informative methods for the determination of impurities in SiF_4 are IR spectroscopy and mass-spectrometry.[3,4] It should be noted that the composition of the impurities in SiF_4 depends strongly on the method of preparation of the latter and the procedure for subsequent purification. Our preliminary study of IR spectra of gaseous SiF_4 synthesized by thermal decomposition of sodium hexafluorosilicate and containing water impurity showed the presence of an intense absorption band in the region near 3764 cm^{-1} and a weaker band at 3860 cm^{-1}. The aim of this work was to study the nature of the band at 3764 cm^{-1} in the IR spectrum of silicon tetrafluoride experimentally and theoretically using *ab initio* quantum-chemical calculations.

Experimental

Silicon tetrafluoride was obtained by thermal decomposition of sodium hexafluorosilicate and purified from volatile impurities by cryofiltration followed by rectification on a column with sampling the medium fraction.

IR spectra of gaseous SiF_4 in the region 800—4500 cm^{-1} were recorded on Specord M80 and IFS-120HR instruments with a resolution of 4 cm^{-1} and 0.1 cm^{-1}, respectively. A multipass cell with a length of the optical path (l) of 100 cm and a cell with l = 20 cm with ZnSe windows were used. Spectra of solutions in liquid CCl_4 were obtained in a cell with an optical path length of 10 cm (ZnSe windows) equipped with an inlet system that allowed introducing gaseous SiF_4 and H_2O. Carbon tetrachloride was purified by rectification until a residual moisture content of $5 \cdot 10^{-5}$ mol.% was achieved.

Calculation procedure. Quantum-chemical calculations of the equilibrium molecular structure and vibrational spectra of possible products of hydrolysis of SiF_4 were carried out by the *ab initio* SCF method with inclusion of correlation energy according to the density functional theory (DFT) using the B3LYP mixed exchange-correlation functional in the 6-311G(d,p) basis set (five-component basis set functions). The geometry optimization and calculations of vibrational frequencies were carried out using the GAUSSIAN 94 program.[5]*

Results and Discussion

In addition to bands at 3764 and 3860 cm^{-1}, those at 838 and 912 cm^{-1} are observed in the IR spectrum of gaseous freshly synthesized SiF_4 recorded with a low resolution (4 cm^{-1}). The latter bands were assigned[4] to stretching vibrations of the molecule of hexafluorodisiloxane, which is the main product of hydrolysis of SiF_4 occurring according to the following commonly accepted[3,4,6] scheme.

$$2\ SiF_4 + H_2O \rightleftharpoons Si_2F_6O + 2\ HF \qquad (1)$$

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In addition to the absorption band at 3764 cm^{-1}, two narrow lines near 3800 and 4100 cm^{-1} corresponding to H_2O and HF molecules, respectively, are clearly seen in the spectrum of a purified SiF_4 specimen recorded with a resolution of 0.1 cm^{-1} in a cell with a length of the optical path of 20 cm (Fig. 1, *a*). The addition of 2 mol.% of H_2O in the cell leads to an increase in both the intensities of the lines corresponding to H_2O and HF and those of structureless bands at 3764 and 3860 cm^{-1} (Fig. 1, *b*). The pattern of SiF_4 spectrum in the region 2700—3000 cm^{-1} remains unchanged after addition of D_2O, *viz*., the bands at 2710 and 2850 cm^{-1} appear (Fig. 2) and the ratio of their intensities approximately corresponds to that shown in Fig. 1, *b*. Thus, the bands in the region 3700—3900 cm^{-1} observed in the spectrum of gaseous SiF_4 are sensitive to water addition and can correspond either to hydroxyl-containing products of the hydrolysis of silicon tetrafluoride or to a SiF_4 complex with water. Previously,[7] the possibility of the formation of the latter in a SiF_4—H_2O mixture (8 : 1) in a low-temperature argon matrix has been reported. The author of Ref. 7 also observed spectral lines corresponding to HF and hexafluorodisiloxane, which are the main products of hydrolysis of SiF_4.

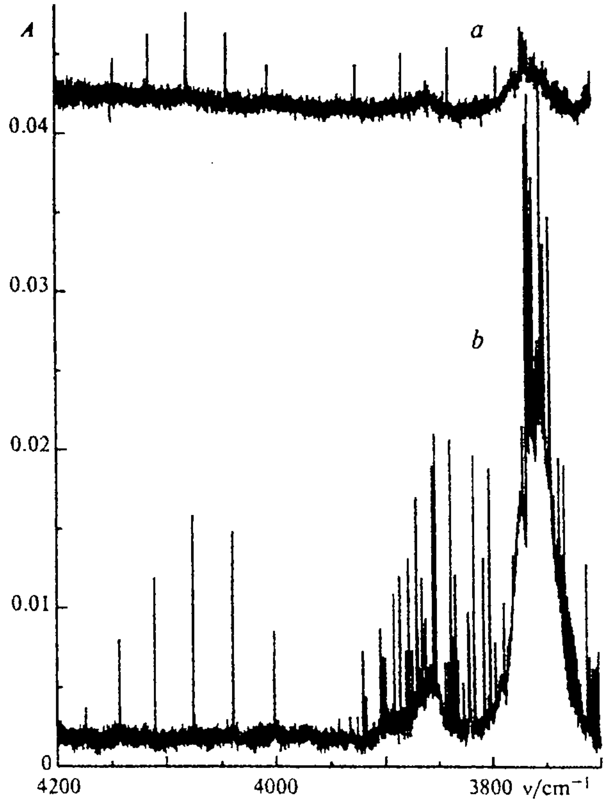

Fig. 1. IR spectra of gaseous SiF_4 in the region 3500—4200 cm^{-1}: *a*, specimen purified by rectification; *b*, the same specimen with water impurity (l = 20 cm, with a resolution of 0.1 cm^{-1}, T = 298 °C; $A = -\log(I_0/I)$).

The equilibrium molecular structures and vibrational spectra of plausible hydroxyl-containing products of the hydrolysis of SiF_4 (SiF_3OH and $SiF_2(OH)_2$ molecules) and those of the intermediate $SiF_4 \cdot H_2O$ complex were obtained from *ab initio* quantum-chemical calculations.

It is known that the harmonic vibrational frequencies thus determined are, as a rule, appreciably overestimated as compared with those observed experimentally. To compare the calculated and experimental data, the calculated vibrational frequencies should be corrected using a standard scale factor[8] obtained from calculations of reference compounds essentially differing from the substances under consideration. For this reason we rejected the idea of using the recommended value of the scale factor. The vibrational frequencies were corrected using the linear calibration function

$$\nu_{corr} = a\nu_{calc} + b, \qquad (2)$$

where ν_{calc} is the vibrational frequency obtained from *ab initio* calculations; ν_{corr} is the corrected vibrational frequency; *a* and *b* are the calibration coefficients found by the least squares method from comparing the experimental (ν_{exp}) and calculated frequencies (ν_{calc}) in the IR spectra of SiF_4 and H_2O:

$$\nu_{exp}(SiF_4,\ H_2O) = a\nu_{calc}(SiF_4,\ H_2O) + b. \qquad (3)$$

Experimental[9] and calculated vibrational frequencies of SiF_4 and H_2O used to fit *a* and *b* values are listed in Table 1. The coefficients *a* and *b* determined from Eq. (2) are 0.9497 and 44.59 cm^{-1}, respectively. The value of coefficient *a* is close to the recommended value of standard scale factor (0.9613) for a similar level of approximation (B3LYP/6-31G(d)). The correlation coefficient between the experimental and calculated frequencies for given *a* and *b* is 0.99994 and the mean absolute deviation of predicted values from experimentally observed frequencies of SiF_4 and H_2O is 12.3 cm^{-1}. This suggests that the found correction coefficients make

Table 1. The experimental (ν_{exp}), calculated (ν_{calc}), and corrected (ν_{corr}) using Eq. (1) vibrational frequencies and the experimental ($A_{exp} \cdot 10^{-8}$)[a] and calculated ($A_{calc} \cdot 10^{-8}$) integrated absorption coefficients of fundamental bands in the IR spectra of SiF_4 and H_2O

Compound	ν_{exp}[3,4]	ν_{calc}	ν_{corr}	A_{exp}[3,4]	A_{calc}	Assignment[b]
	cm^{-1}			10^8 cm^2 mol^{-1} s^{-1}		
SiF_4	264	254	286	—	—	δ, E
	388	372	398	1	26	δ, T_2
	801	773	779	—	—	ν_s, A_1
	1031	1018	1011	10	117	ν_{as}, T_2
H_2O	1595	1639	1601	22	29	δ, A_1
	3657	3810	3663	5	2	ν_s, A_1
	3756	3907	3755	25	12	ν_{as}, B_2

[a] For SiF_4, the relative intensities of the bands[10] are given.
[b] The following notations were used: δ, deformation; ν_s, symmetric stretching; and ν_{as}, antisymmetric stretching vibrations.

it possible to evaluate the vibrational frequencies of similar molecules on the basis of quantum-chemical calculations with an accuracy of ~12 cm^{-1}.

Using the described procedure, it is possible to assign the characteristic absorption bands observed in the spectrum of gaseous SiF_4 in the presence of water vapors as admixture. The calculated and corrected vibrational frequencies of possible products formed in the initial stage of hydrolysis (hydroxo derivatives SiF_3OH and $SiF_2(OH)_2$ and the suggested reaction intermediate, complex $SiF_4 \cdot H_2O$) are listed in Table 2. A special quantum-chemical study is dedicated to investigation of the structure, stability, and pathways of possible further transformations of intermediate SiF_4 complexes with water. Its results will be published elsewhere. Several stable structures corresponding to the above intermediate were found. In this work, we consider only the most stable structure, *viz.*, the donor-acceptor complex with the Si—O coordination bond, whose vibrational frequencies are listed in Table 2. The calculated equilibrium molecular structures of SiF_3OH, $SiF_2(OH)_2$ and that of the most stable complex $SiF_4 \cdot H_2O$ are shown in Fig. 3.

Table 2. Calculated values of vibrational frequencies (ν/cm^{-1}) and integrated absorption coefficients ($A/10^8$ cm^2 mol^{-1} s^{-1}) of the bands in the IR spectra of several possible products of the interaction between SiF_4 and H_2O

Compound	ν	$A \cdot 10^{-8}$	Assignment
SiF_3OH	386	24	$\delta(SiF_3)$
	398	27	$\delta(SiF_3)$
	405	26	$\delta(SiF_3)$
	740	74	$\delta(Si—O—H)$
	782	23	$\nu(Si—O) +$ $+ \nu(Si—F)$
	971	115	$\nu(SiF_3)$
	996	122	$\nu(SiF_3)$
	1030	102	$\nu(SiF_3)$
	3765	68	$\nu(O—H)$
$SiF_2(OH)_2$	409	23	$w(SiF_2)$
	762	17	$\delta(Si—O—H)$
	782	135	$\delta(Si—O—H)$
	786	33	$\delta(Si—O—H)$
	979	94	$\nu_s(Si—F)$
	980	135	$\nu_{as}(Si—F) +$ $+ \nu_{as}(Si—O—H)$
	1007	95	$\nu_{as}(Si—F)$
	3756	77	$\nu_{as}(O—H)$
	3759	37	$\nu_s(O—H)$
$SiF_4 \cdot H_2O$	420	64	$w(H_2O)$
	494	15	$\tau(H_2O)$
	759	0	$\nu(SiF_4)$
	943	140	$\nu(Si—F)$
	996	121	$\nu(Si—F)$
	1012	121	$\nu(Si—F)$
	1593	36	$\delta(H—O—H)$
	3663	12	$\nu(O—H)$
	3758	34	$\nu(O—H)$

Note. The following notations were used: δ, deformation; ν, stretching; ν_s, symmetric stretching; ν_{as}, antisymmetric stretching; w, wagging; and τ, torsional vibrations.

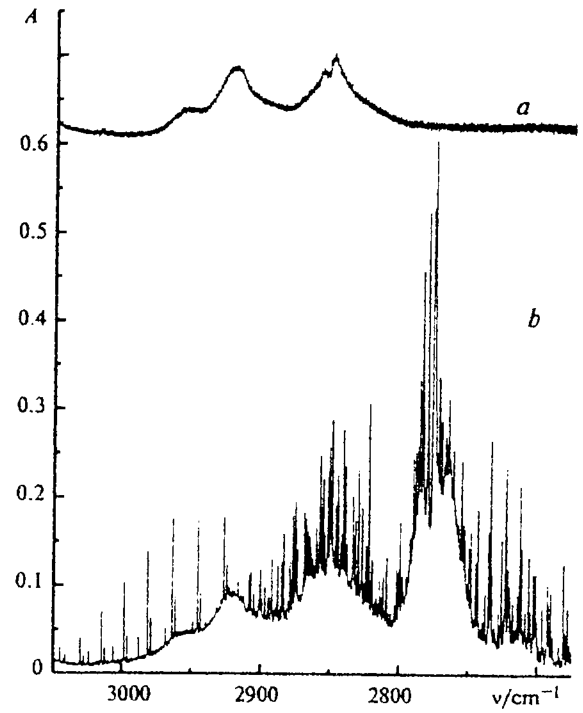

Fig. 2. IR spectra of gaseous SiF_4 in the region 3050—2650 cm^{-1}: *a*, without D_2O impurity; and *b*, with a D_2O impurity (l = 20 cm, with a resolution of 0.1 cm^{-1}).

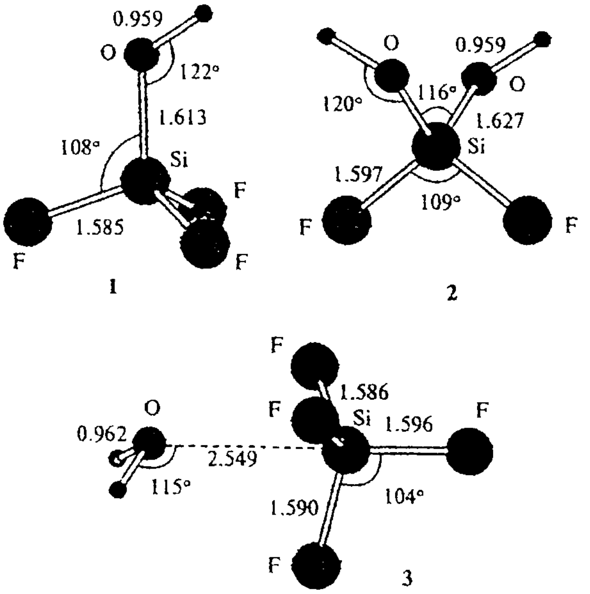

Fig. 3. Molecular structures of possible products of SiF_4 hydrolysis calculated by the *ab initio* B3LYP/6-311G(d,p) method: SiF_3OH (**1**), $SiF_2(OH)_2$ (**2**), and complex $SiF_4 \cdot H_2O$ (**3**). Bond lengths (Å) and bond angles are shown.

All calculated structures contain one or two O—H bonds whose vibrational frequencies lie in the interval 3756—3765 cm^{-1} (see Table 2) and fall within the region of a broad structureless band with the center at 3764 cm^{-1} observed in the IR spectrum of gaseous SiF_4. The structureless shape of this band and increase in its intensity with time and with increasing temperature is explained by the presence of at least three compounds, of which two are products of hydrolysis. The possible presence of several intermediate complexes of SiF_4 with water also favors the broadening of the band near 3764 cm^{-1} and the increase in its intensity.

To prove experimentally the assumption that the bands in the region 3700—3900 cm^{-1} correspond to hydroxyl-containing products of hydrolysis of SiF_4, the spectra of a solution of H_2O and SiF_4 in CCl_4 (Fig. 4, *a*) were studied. Addition of small amounts of gaseous SiF_4 to the solution has virtually no effect on the spectral pattern; however, the dissolution of an excess SiF_4 (relative to water) results in a change in the shape of the ν_1 and ν_3 bands (Fig. 4, *b*, *c*). A new band appears near 3685 cm^{-1} and reaches its maximum after about 24 h, whereas the intensities of the ν_1 and ν_3 bands decrease sharply. Most likely, this band should be assigned to OH-containing products of the SiF_4 hydrolysis formed according to Eq. (4)

$$2\,SiF_4 + x\,H_2O \rightleftharpoons SiF_{4-x}(OH)_x + x\,HF \qquad (4)$$

or, in the simplest case,

$$SiF_4 + H_2O \rightleftharpoons SiF_3OH + HF. \qquad (5)$$

Analogous changes in the region near 3685 cm^{-1} are observed in the IR spectrum of the solution of a mixture of SiF_4 and methanol in CCl_4 (Fig. 5, *a*, *b*). In this case a new band near 3685 cm^{-1} is also recorded, while the intensity of the band at 3645 cm^{-1} corresponding to the vibration of the methanol O—H bond remains rather high even 24 h after the moment of mixing both substances. It is likely that a reaction analogous to that described by Eq. (4) occurs in CCl_4:

$$SiF_4 + MeOH \rightleftharpoons SiF_3OH + MeF, \qquad (6)$$

and that the degree of alcoholysis is considerably lower than that of hydrolysis.

Thus, the results of our IR spectroscopic and quantum-chemical study make it possible to refine the known scheme of hydrolysis of SiF_4 (Eq. (1)) in the presence of small amounts of water. As follows from the IR spectra in the low-temperature matrix and from quantum-chemi-

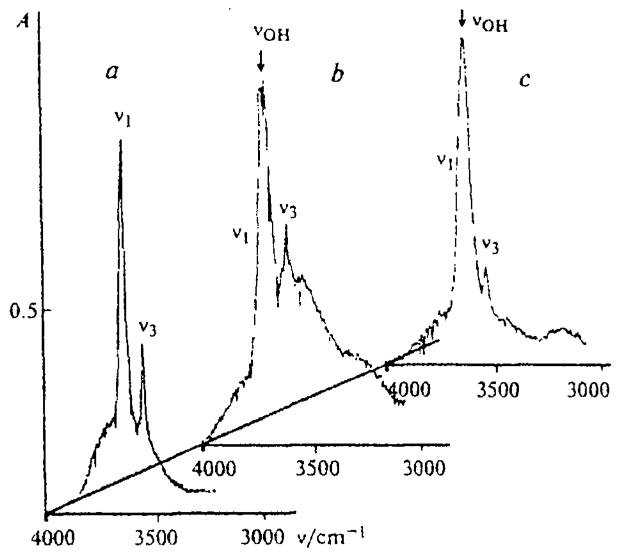

Fig. 4. IR spectra of the solution of a mixture of SiF_4 and water in CCl_4: *a*, immediately after mixing ($\nu_1(H_2O)$ is 3710 cm^{-1} and $\nu_3(H_2O)$ is 3616 cm^{-1}); *b*, after 1 h from the beginning of the reaction (ν(OH) is 3685 cm^{-1}); and *c*, after 24 h from the beginning of the reaction (l = 5 cm, with a resolution of 4 cm^{-1}).

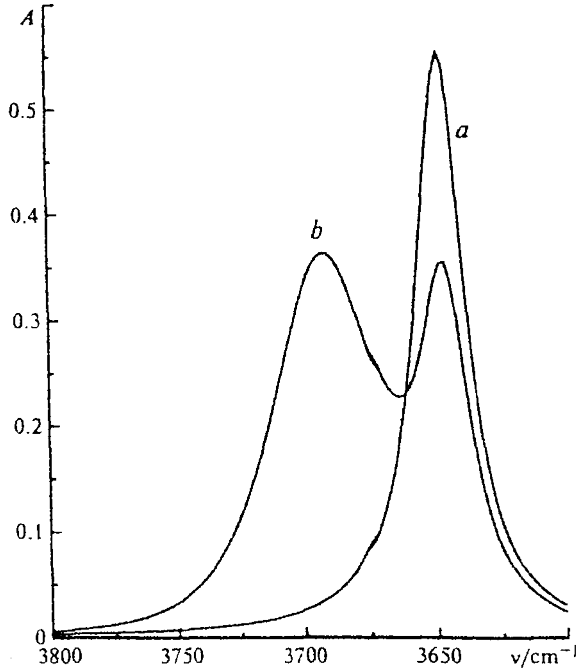

Fig. 5. IR spectra of the solution of a mixture of SiF_4 and methanol in CCl_4 in the region 3500—3800 cm^{-1}: *a*, immediately after mixing (ν(OH) is 3645 cm^{-1}) ; and *b*, after 24 h from the beginning of the reaction (l = 5 cm, with a resolution of 4 cm^{-1}, T = 290 °C). The spectra were smoothed by approximating the band contours by the Voight function.

cal calculations, in the initial stage the donor-acceptor complex $SiF_4 \cdot H_2O$ is formed. This leads to a decrease in the activation barrier to the reactions of the formation of hydroxyl-containing SiF_4 derivatives (in particular, trifluorosilanol):

$$SiF_4 + H_2O \rightleftharpoons SiF_4 \cdot H_2O \rightleftharpoons SiF_3OH + HF. \quad (7)$$

The band at 3685 cm^{-1} in the IR spectrum of SiF_4 in CCl_4 and the band at 3764 cm^{-1} in the IR spectrum of gaseous SiF_4 corresponds to a SiF_3OH molecule or, in the general case, to a $SiF_{4-x}(OH)_x$ molecule. In both cases these bands lie between those of symmetric and antisymmetric vibrations of water molecules.

Intense bands at 838 and 912 cm^{-1} corresponding to vibrations of the hexafluorodisiloxane molecule indicate that a further hydrolysis occurs following the scheme

$$SiF_3OH + SiF_4 \rightleftharpoons Si_2F_6O + HF. \quad (8)$$

Judging by the obtained IR spectra of gaseous SiF_4 in the presence of water vapors, both the initial compounds SiF_4 and H_2O and the hydrolysis products SiF_3OH, $SiF_2(OH)_2$, Si_2F_6O, and HF and, possibly, the intermediate complex $SiF_4 \cdot H_2O$ are in equilibrium.

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