2316 Russian Chemical Bulletin, International Edition, Vol. 50, No. 12, pp. 2316—2324, December, 2001

Binary molecular complexes of silicon tetrafluoride with water, methanol, and dimethyl ether. Quantum-chemical study

S. K. Ignatov,[a]* P. G. Sennikov,[b] A. G. Razuvaev,[a] and L. A. Chuprov[a]

[a]N. I. Lobachevsky University of Nizhnii Novgorod,
23 prosp. Gagarina, 603600 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 65 8592. E-mail: ignatov@ichem.unn.runnet.ru
[b]Institute 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@ihps.nnov.ru

The molecular structures, the energies of complex formation, and the vibrational spectra of the binary molecular complexes of SiF_4 with water, methanol, and dimethyl ether were calculated by the *ab initio* MP2 method with the basis sets up to 6-311++G(2d,2p). In the complexes, which have been detected previously by IR spectroscopy in low-temperature (12—15 K) inert matrices, the five-coordinate Si atom is in a distorted trigonal-bipyramidal environment, which is formed through the donor-acceptor interaction of the O atom with the Si atom and is additionally stabilized by the H...F hydrogen bonds.

Key words: silicon tetrafluoride, binary complexes, matrix isolation, *ab initio* quantum-chemical calculations.

Complexes of silicon halides with various ligands have been under investigation over many years.[1—4] Most of studies were devoted to stable compounds, which were isolated in the individual form and bore, primarily, nitrogen-containing ligands,[5—7] whereas complexes with oxygen-containing ligands have been less studied. In the early studies,[8—10] the solid 1 : 4 and 1 : 2 adducts of SiF_4 with MeOH and ethers were isolated. These adducts were prepared by the reactions of SiF_4 with methanol and ethers at room or lower temperatures. The molecular structures, the nature of the chemical bonds, and the vibrational spectra of these compounds are still open questions.[11] The formation of weak gas-phase complexes with oxygen-containing donors, including water and low-molecular-weight organic molecules, are much less studied.[12] However, this information is gaining in importance because of a wide use of highly pure SiF_4 in new fields of technology. When analyzing the efficiency of different procedures for the purification of SiF_4, one should take into account the possibility of chemical reactions of the main compound with H_2O impurities[13] as well as of solvolysis and exchange reactions with organic compounds. Generally, these reactions proceed at low temperatures whereby binary complexes, which are unstable under ambient conditions, are put in the forefront.

The binary complexes of SiF_4 with water, methanol, and dimethyl ether were first experimentally discovered[12] by IR spectroscopy in low-temperature (12—15 K) argon and nitrogen matrices. These complexes were described as compounds of compositions $SiF_4 \cdot H_2O$, $SiF_4 \cdot MeOH$, and $SiF_4 \cdot Me_2O$ in which the chemical bond is formed through the partial electron density transfer from the molecule of the oxygen-containing compound to the SiF_4 molecule.[12] The *ab initio* MP2/6-311++G(d,p) calculations[14] of the fragments of the potential energy surface (PES) for the $SiF_4—H_2O$ system revealed the only stable complex of composition $SiF_4 \cdot H_2O$, which contains the five-coordinate Si atom and the donor-acceptor Si...O bond formed through the partial electron density transfer from the O atom of the H_2O molecule to the sp-orbitals of the Si atom. The calculated frequency shifts in the IR spectra that occur upon the formation of this complex agree well with the experimental values obtained in a low-temperature matrix. Under the conditions of an inert matrix, the formation of the octahedral $SiF_4 \cdot 2H_2O$ complexes is energetically unfavorable and no local minima on the potential energy surface correspond to hydrogen-bonded structures. Nevertheless, the molecular structure, the energy, and the spectral characteristics of the complexes of SiF_4 with low-molecular-weight oxygen-containing organic ligands remained unknown. In addition, there is no direct evidence that the complexes of SiF_4 with organic ligands found previously[12] are binary donor-acceptor compounds structurally related to $SiF_4 \cdot H_2O$.

In the present study, we undertook a theoretical investigation of the molecular structures, the energies of complex formation, and the vibrational spectra of the complexes of SiF_4 with H_2O, MeOH, and Me_2O for the purpose of making the assignments in the experimental IR spectra measured in a low-temperature solid matrix. Although the complexes of SiF_4 with water have been studied previously, we carried out calculations for this

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2211—2218, December, 2001.

system using a more complete basis set with the aim of refining the results and performing the correct comparison of the calculated values with those obtained for the SiF_4—MeOH and SiF_4—Me_2O systems. In addition, we carried out conformational analysis of the $SiF_4 \cdot H_2$ complex to estimate the effect of the internal rotation of the H_2O molecule on the structure of the complex, its energy, and vibrational frequencies.

Calculation procedure

All calculations were carried out by the *ab initio* SCF method with inclusion of the electron correlation according to the second-order Möller—Plesset perturbation theory (MP2) with the 6-311G++G(d,p), 6-311++G(2d,p), and 6-311++G(2d,2p) basis sets. In addition to the full geometry optimization, we calculated the vibrational frequencies and absolute intensities for all stationary points. All calculations were performed using the PC GAMESS program.[15,16] Thermodynamic calculations were carried out with the use of the PC GAMESS program and the original MOLTRAN program, which takes into account the contributions of internal rotations of unhindered groups to thermodynamic functions. The correction for the basis set superposition error was made using the standard counterpoise method.[17] The fragments of intermolecular PES for the SiF_4—H_2O and SiF_4—MeOH systems were examined using the original ADANIMEHS program, which has specially been developed for rapid scanning of PES. In the studies of the internal rotation profiles, the energies at PES points were calculated with the use of the GAUSSIAN-94 program[18] according to the MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods employing spherical (5d) polarization basis functions. Although the exponents of the polarization functions of the Si atom involved in the GAUSSIAN-94 program differ slightly from those employed in the GAMESS program, these differences (as well as the differences between the Cartesian and spherical functions) have no noticeable effect on the geometry of the structures under study and their relative energies.

Results and Discussion

The molecular structure of the $SiF_4 \cdot H_2O$ complex was optimized at the MP2/6-311++G(d,p),

Table 1. Bond lengths and bond angles in the starting compounds and the complexes optimized by the MP2 method with the use of different basis sets[a]

Geometric parameter	Value I	Value II	Value III
	SiF_4		
Bond/Å			
Si—F	1.587	1.569	1.569
	H_2O		
Bond/Å			
O—H	0.960	0.963	0.958
Angle/deg			
H—O—H	103.4	104.6	104.3
	MeOH		
Bond/Å			
O—H	0.960	0.964	0.958
C—O	1.422	1.425	1.426
Angle/deg			
C—O—H	107.2	108.0	108.1
	Me_2O		
Bond/Å			
C—O	1.411	1.415	1.415
Angle/deg			
C—O—C	110.6	110.9	110.7
	$SiF_4 \cdot H_2O$[b]		
Bond/Å			
Si...O	2.791/2.786	2.838/2.837	2.868/2.863
O—H	0.961/0.961	0.964/0.964	0.959/0.959
Si—F(1)	1.597/1.598	1.578/1.578	1.577/1.578
Si—F(2)	1.585/1.590	1.567/1.571	1.567/1.571
Si—F(3), F(4)	1.590/1.587	1.572/1.569	1.572/1.569
H...F[c]	2.866/3.036	2.844/3.059	2.835/3.067
Angle/deg			
H—O—H	104.3/104.3	105.1/105.1	104.9/104.8
Si—O—H	118.4/139.1	114.9/135.6	113.0/131.7
	$SiF_4 \cdot$ MeOH		
Bond/Å			
Si...O	2.540	2.674	2.663
O—H	0.962	0.965	0.960
Si—F(1)	1.603	1.581	1.581
Si—F(2)	1.595	1.574	1.575
Si—F(3), F(4)	1.590, 1.593	1.572, 1.570	1.571, 1.570
C—O	1.431	1.432	1.432
H...F	2.691	2.800	2.783
Angle/deg			
C—O—H	108.4	108.6	108.6
Si—O—H	132.4	129.1	128.0
	$SiF_4 \cdot Me_2O$		
Bond/Å			
Si....O	2.579	2.671	2.656
C—O	1.422	1.423	1.423
Si—F(1)	1.602	1.581	1.582
Si—F(2)	1.595	1.575	1.575
Si—F(3), F(4)	1.591	1.571	1.571
Angle/deg			
C—O—C	110.4	110.8	110.5
Si—O—C	132.1	128.8	127.3

[a] The calculations were carried out at the MP2/6-311++G(d,p) (I), MP2/6-311++G(2d,p) (II), and MP2/6-311++G(2d,2p) (III) levels. The atomic numbering scheme corresponds to that presented in Fig. 1.

[b] Data for the eclipsed and staggered conformations are given in the numerator and denominator, respectively.

[c] The distance between the H atom of the OH group and the nearest F atom.

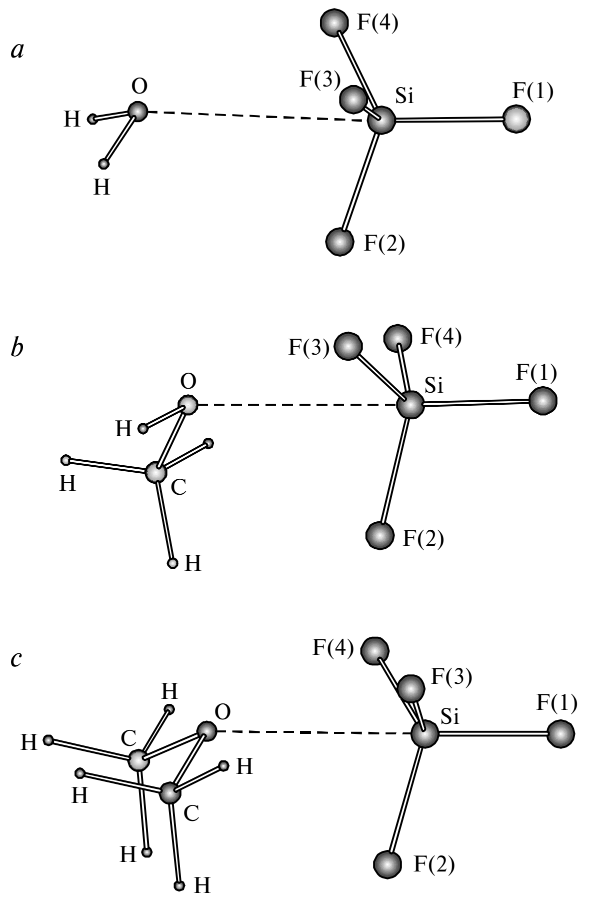

Fig. 1. Optimized structures of the $SiF_4 \cdot H_2O$ (*a*), $SiF_4 \cdot MeOH$ (*b*), and $SiF_4 \cdot Me_2O$ complexes (*c*).

MP2/6-311++G(2d,p), and MP2/6-311G++(2d,2p) levels. The optimized geometric parameters are given in Table 1. Although intuition suggests that the hydrogen-bonded Si—F...H—OH structure can be formed, we found only one stable structure, *viz.*, a distorted trigonal-bipyramidal structure with the Si...O bond and the H atoms deviating from the Si—O bond of the molecule toward the F atoms (Fig. 1, *a*). Optimization with the use of various starting configurations led either to the rearrangement giving rise to an oxygen-coordinated complex or to decomposition into the initial monomers. The conformation of the complex containing the water molecule in the axial position is unstable and occurs as the transition state between two distorted structures.

In the bipyramidal structure of the $SiF_4 \cdot H_2O$ complex, the intramolecular rotation of the water molecule about the Si—O bond gives rise to two conformations, *viz.*, the staggered conformation (the H atoms of the H_2O molecule are located between the F atoms of silicon tetrafluoride) and the eclipsed conformation (the H atoms are opposite to the F atoms). Both conformations are characterized by the symmetry group C_s and their IR spectra show no noticeable differences. Although estimations of the relative stabilities at different levels of the theory and the correction for the basis set superposition error lead to somewhat contradictory results (Table 2), the calculations at the higher level (MP2/6-311++G(2d,2p)), both with and without correction for the superposition error, demonstrated that the eclipsed conformation is energetically more favorable. The difference between the energies of two conformations is only 0.2 kJ mol^{-1}. The consideration of internal rotation is of importance for estimating the thermodynamic parameters. Hence, it was of interest to evaluate the potential of internal rotation and to elucidate whether a less favorable conformation corresponds to a local minimum or to the top of the potential barrier. For this purpose, we carried out direct scanning of the profile of the potential energy surface for the internal rotation of the H_2O molecule about the Si—O bond with full geometry optimization of the monomers according to the *ab initio* method (MP2/6-311++G(d,p)) and the density functional theory (B3LYP/6-311++G(d,p)). The calculated potential curves of rotation of the H_2O mol-

Table 2. Total energies of the complexes (E) and the energies of complex formation, which were calculated without regard for (ΔE) and corrected for the basis set superposition error ($\Delta E + BSSE$) and for the zero-point energy ($\Delta E + BSSE + ZPE$) at the MP2/6-311++G(d,p), MP2/6-311++G(2d,p) (in parentheses), and MP2/6-311++G(2d,2p) (in square brackets) levels

Complex	$-E$ /au	$-\Delta E$	$-(\Delta E + BSSE)$	$-(\Delta E + BSSE + ZPE)$
		kJ mol^{-1}		
$SiF_4 \cdot H_2O$*	764.294884	23.5/22.8	11.3/11.4	5.4/5.5
	(764.437396)	(19.9/19.5)	(11.5/11.4)	(6.3/6.2)
	[764.442863]	[17.5/17.2]	[11.5/11.3]	[6.5/6.3]
$SiF_4 \cdot MeOH$	803.468616	28.6	13.0	8.2
	(803.619453)	(24.4)	(14.5)	(10.0)
	[803.626120]	[23.9]	[14.4]	[9.7]
$SiF_4 \cdot Me_2O$	842.650040	32.6	14.4	10.6
	(842.809176)	(28.5)	(16.6)	(12.8)
	[842.817467]	[29.0]	[16.8]	[12.5]

* Data for the eclipsed and staggered conformations are given in the numerator and denominator, respectively.

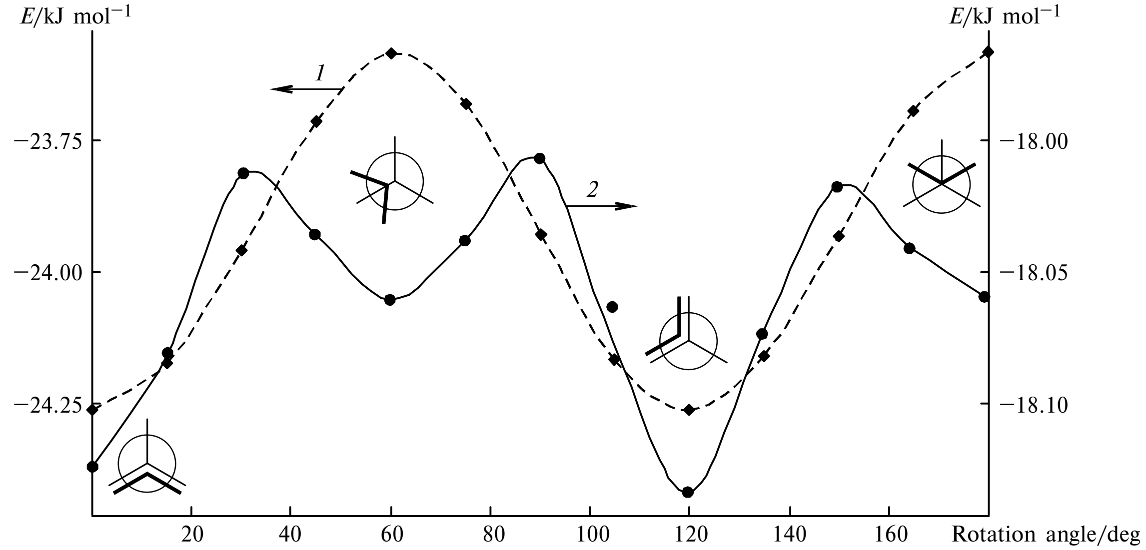

Fig. 2. Potential energy curves for rotation of the water molecule about the Si—O bond in the $SiF_4 \cdot H_2O$ complex calculated by the MP2/6-311++G(d,p) (*1*) and B3LYP/6-311++G(d,p) (*2*) methods; *E* is the relative energy.

ecule are shown in Fig. 2. It can be seen that the *ab initio* method and the density functional theory gave different results. The calculations by the MP2 method revealed that the eclipsed conformation corresponds to a local minimum, whereas the staggered conformation corresponds to the top of the potential barrier with the height of 0.8 kJ mol^{-1}. The calculations according to the density functional theory demonstrated that both the eclipsed and staggered conformations correspond to local minima, the difference between the energies of these conformations being only 0.05 kJ mol^{-1} and the height of the barrier to rotation being 0.09 kJ mol^{-1}.

All the estimated values of the rotation barriers are much smaller than the basis set superposition error and the correction for the zero-point energy. In addition, the difference between the energies of two conformations (several tenths or hundredths of kJ · mol^{-1}) is, apparently, comparable with the accuracy of the Boys—Bernardi's counterpoise method used for eliminating the basis set superposition error.[17]

Hence, the geometry optimization and scanning of PES employing different quantum-chemical methods with the basis sets up to 6-311++G(2d,2p) provide evidence that the eclipsed conformation of the $SiF_4 \cdot H_2O$ complex is energetically most favorable. No unambiguous conclusions can be made about the staggered conformation, and its stability is still an open question. It can be said with assurance that the difference between the energies of these conformations and the height of the barrier separating these conformations are no larger than the energies of thermal vibrations under ambient conditions and, hence, virtually free rotation of the H_2O molecule occurs in the gas-phase $SiF_4 \cdot H_2O$ complex. It can also be concluded that the conformational differences have virtually no effect on the moderate- and high-frequency vibrational modes in the IR spectra (the frequencies higher than >300 cm^{-1}), which is of importance in the discussion of the nature of splitting of the IR bands under matrix isolation conditions.

Hence, the trigonal-bipyramidal structure of the $SiF_4 \cdot H_2O$ complex agrees with the data obtained previously at the MP2/6-311++G(d,p) level,[14] with the results of quantum-chemical studies of the analogous $SiF_4 \cdot NH_3$ [5,7] and $BF_3 \cdot NH_3$ systems,[19] and with the donor-acceptor nature of this complex, which was assumed based on the examination of the IR spectrum of the $SiF_4 \cdot H_2O$ complex in a low-temperature inert matrix.[12] The complexes of SiF_4 with MeOH and Me_2O have presumably analogous structures. Actually, the optimized structures of these complexes (see Fig. 1, *b*, *c*) are similar to that of the $SiF_4 \cdot H_2O$ complex and can be described as a distorted trigonal bipyramid. The optimized geometric parameters of these complexes are given in Table 1. As in the case of the $SiF_4 \cdot H_2O$ complex, the $H_3C—OH$ and $H_3C—O—CH_3$ molecules in the latter complexes deviate from the axis of the C—O bond, the angle of deviation being virtually equal in all cases. It can be assumed that this deviation occurs due to the fact that the out-of-plane donor-acceptor bond involving the O atom is more favorable and not due to hydrogen bonding. As in the case of the complex with the H_2O molecule, virtually free rotation of the MeOH and Me_2O molecules about the Si—O bond takes place. The results of calculations demonstrated that the interatomic Si...O distance decreases in the series of H_2O, MeOH, and Me_2O as the basicity of the oxygen-containing donor increases with the simultaneous substantial elongation of the terminal Si—F(1) bond and the other Si—F bonds. The most pronounced elongation and weakening of the Si—F(1) bond is observed in the $SiF_4 \cdot Me_2O$ complex.

The energies of complex formation, including those corrected for the basis set superposition error (*BSSE*) and the zero-point energy, calculated at different levels of the theory are given in Table 2. From these data it follows that the energies of complex formation taking into account the correction $\Delta E + BSSE$ are close to each other. In the case of the two best levels of the theory, these energies differ by at most 0.5 $\text{kJ} \cdot \text{mol}^{-1}$, which indicates that the convergence is achieved at the high levels of the theory thus producing the reliable results. Hence, the most reliable estimates obtained for the energies of complex formation for the $SiF_4 \cdot H_2O$, $SiF_4 \cdot MeOH$, and $SiF_4 \cdot Me_2O$ complexes without considering the zero-point energy are −11.3, −14.4, and −16.8 $\text{kJ} \cdot \text{mol}^{-1}$, respectively. The calculations performed with inclusion of the zero-point energy led to weakening of the bond by 4—5 $\text{kJ} \cdot \text{mol}^{-1}$; the energies of complex formation thus obtained are −6.5, −9.7, and −12.5 $\text{kJ} \cdot \text{mol}^{-1}$, respectively.

In the calculated spectrum of the $SiF_4 \cdot H_2O$ complex (Table 3), the OH stretching frequencies are 1660, 3851, and 3991 cm^{-1}. Two of these frequencies (1660 and 3991 cm^{-1}) correspond to the bands observed in the experimental spectrum at about 1600 (splitting into 1598 and 1600 cm^{-1}) and 3722 cm^{-1}. The band of the complex at 3851 cm^{-1} was not observed in the experimental spectrum due to its low intensity. The corresponding calculated shifts of the bending and stretching frequencies of the water molecule (+5 and −16 cm^{-1}) in the complex agree well with the experimental values (+5 (or 7, see Table 3) and −8 cm^{-1}, respectively). In the region of 998—1100 cm^{-1}, the complex gives two bands at 1015 and 1024 cm^{-1} (in the vicinity of the band of the starting SiF_4 molecule at 1014 cm^{-1}) and a new intense band at 975 cm^{-1} to which the shift of −39 cm^{-1} corresponds. The experimental spectrum of the $SiF_4 \cdot H_2O$ complex shows two new bands at 984 and 991 cm^{-1}. Previously,[14] these bands have been attributed to the fact that the intense vibration band of the complex (975 cm^{-1}) is split in the matrix. The calculated frequency shift (−39 cm^{-1}) agrees well with the experimental values (−39 and −32 cm^{-1}). Apparently, two other bands of the Si—F antisymmetric stretching vibration (1015 and 1024 cm^{-1}) fall in the region of strong absorption of residual SiF_4 due to which they were not observed in the experimental spectrum. The assignment of the bending vibration band of SiF_4 at 400 cm^{-1} (to which the shift of 12 cm^{-1} corresponds) is in doubt. The calculated spectrum has three bands at 382, 392, and 397 cm^{-1} (the shifts are −8, +2, and +7 cm^{-1}, respectively) with approximately equal intensities. Apparently, the calculation underestimated the frequency (382 cm^{-1}) and the real shift of this vibration is smaller than 8 cm^{-1}. In such a situation, the spectrum has only one of the frequencies (397 cm^{-1}), whereas two other frequencies are masked by absorption of residual SiF_4. This explanation is supported by the fact that the calculated shifts of these bands are very sensitive to the level of calculations. The calculated shifts obtained at the MP2/6-311++G(d,p) level are −3, +3, and +14 cm^{-1}, which are in good agreement with the experimental value (+12 cm^{-1}).

Hence, the quantum-chemical calculations of the vibrational frequencies confirmed the suggestion, which was has been made previosuly based on the analysis of the experimental IR spectrum in a low-temperature matrix, that the complex of SiF_4 with H_2O that formed under these conditions is the donor-acceptor binary $SiF_4 \cdot H_2O$ compound.[12] The molecule of this compound has a distorted trigonal-bipyramidal structure.[14]

It can be assumed that the complexes of SiF_4 with MeOH and Me_2O formed under analogous conditions

Table 3. Calculated (MP2/6-311++G(2d,2p)) vibrational frequencies of the starting SiF_4 and H_2O monomers (ν_m/cm^{-1}) and their complex (ν_c/cm^{-1}), the intensities in the IR spectra (I/km mol^{-1}), and the frequency shifts ($\Delta\nu/\text{cm}^{-1}$) compared with the experimental values obtained in an argon matrix at 12 K

Experiment[a]			Calculation				Assignement
ν_m[20]	ν_c[12]	$\Delta\nu$	ν_m	ν_c	I_c	$\Delta\nu$	
264[b]			267[b]	274	32	7	δ^s(Si—O—H)
264[b]			267[b]	300	2	33	δ^{as}(Si—O—H)
388[b]			390[b]	382	70	−8	$\delta^s(SiF_3)$
388[b]			390[b]	392	59	2	$\delta^s(SiF_3)$ + δ^s(Si—O—H)
388[b]	400	12	390[b]	397	55	7	$\delta^s(SiF_3)$ + δ^{as}(Si—O—H)
801[b]			784[b]	778	1	−7	$\nu^s(SiF_4)$
1023[b]	984, 991[c]	−39, −32[c]	1014[b]	975	278	−39	ν^{as}(Si—F(1)) + $\delta^s(SiF_3)$
1023[b]	Nontransparent region of residual SiF_4		1014[b]	1015	238	1	$\nu^{as}(SiF_4)$
1023[b]			1014[b]	1024	239	10	$\nu^{as}(SiF_4)$
1593 s	1598, 1600[c]	5, 7	1655	1660	80	5	δ(H—O—H)
3657 m			3864	3851	19	−14	ν^s(O—H)
3730 m	3722	−8	3991	3975	87	−16	ν^{as}(O—H)

[a] Notations: s and m are strong and medium IR bands, respectively.

[b] Vibrations of the SiF_4 molecule.

[c] Splitting in the matrix.[14]

Table 4. Calculated (MP2/6-311++G(2d,2p)) vibrational frequencies of the starting SiF_4 and MeOH monomers (ν_m/cm^{-1}) and their complex (ν_c/cm^{-1}), the intensities of the IR bands (I/km mol^{-1}), and the frequency shifts ($\Delta\nu$/cm^{-1}) compared with the experimental values obtained in an argon matrix at 12 K

Experiment[a]			Calculation				Assignement
ν_m[20]	ν_c[12]	$\Delta\nu$	ν_m	ν_c	I	$\Delta\nu$	
264[b]			267[b]	274	4	7	$\delta^s(SiF_4) + \omega(OH)$
264[b]			267[b]	282	6	15	$\delta^s(SiF_4) + \omega(OH)$
295(?)	(844)[c]	(549)[c]	269	417	99	148	$\omega(OH)$ with respect to the C—O bond
388[b]			390[b]	375	102	−15	$\delta^{as}(SiF_4) - \omega(OH)$
388[b]			390[b]	384	36	−6	$\delta^{as}(SiF_4) + \omega(OH)$
388[b]	406	18	390[b]	394	49	4	$\delta^{as}(SiF_4)$
801[b]	(844)[c]	(43)[c]	784[b]	774	1	−10	$\nu^s(SiF_4)$
1023[b]	972, 952[d]	−51, −71[d]	1014[b]	955	315	−59	$\nu^{as}(SiF_4) - \nu(Si—O)$
1023[b]	Nontransparent region of residual SiF_4		1014[b]	1007	201	−7	$\nu^{as}(SiF_4)$
1023[b]			1014[b]	1019	179	5	$\nu^{as}(SiF_4)$
1033 v.s			1053	1053	136	0	ν(C—O) − δ(C—O—H)
1060 w			1094	1091	27	−3	ρ(Me) − δ(C—O—H)
1165 ia			1186	1191	1	5	ρ(Me)
1345 s			1387	1379	24	−8	ρMe + δ(C—O—H)
1455 m			1506	1506	2	0	δ^s(Me)
1477 m			1529	1535	5	5	δ^{as}(Me)
1477 m			1542	1541	6	−1	δ^{as}(Me)
2844 s			3068	3085	40	17	ν^s(Me)
2960 s			3142	3168	28	26	ν^{as}(Me)
3000 m			3185	3221	11	36	ν^{as}(Me)
3681 m			3914	3857	53	−57	ν(O—H)

[a] Notations: v.s, s, m, and w are very strong, strong, medium, and weak IR bands, respectively; ia are bands inactive in the IR spectrum.

[b] Vibrations of the SiF_4 molecule.

[c] Alternative assignments of the band at 844 cm^{-1} (see the text).

[d] Splitting in the matrix.[14]

are also binary compounds (see Fig. 1) and their vibrational characteristics would be expected to correspond to the experimental spectra observed in an argon matrix. Table 4 gives the results of calculations of the vibrational frequencies and the intensities of the bands in the IR spectrum of the binary complex of SiF_4 with MeOH compared with the experimental frequencies of the starting compounds and the complex formed under the conditions of low-temperature matrix isolation.

The spectrum of $SiF_4 \cdot MeOH$, like that of the $SiF_4 \cdot H_2O$ complex, is characterized by the frequency shift and splitting of the antisymmetric stretching vibration of SiF_4 in the matrix giving rise to high-intensity bands at 972 and 952 cm^{-1} (the shifts are −51 and −71 cm^{-1}, respectively). In the calculated spectrum of the bipyramidal binary complex $SiF_4 \cdot MeOH$ (see Fig. 2, *b*), this vibration has the frequency of 955 cm^{-1}, which corresponds to the shift of −59 cm^{-1}. As in the case of $SiF_4 \cdot H_2O$, two other normal modes (1007 and 1019 cm^{-1}) have small shifts and are, apparently, masked by high-intensity bands of free SiF_4. The antisymmetric bending vibration of SiF_4 (388 cm^{-1}) observed upon the complex formation is characterized by the positive shift of 18 cm^{-1}, which is in agreement with the calculated positive value (+4 cm^{-1}).

Unlike the spectrum of the $SiF_4 \cdot H_2O$ complex, some characteristic features of the IR spectrum of the SiF_4—MeOH system in a low-temperature matrix have no evident explanation based on the model of the bimolecular complex. Thus, the shifts of the OH and Me stretching vibration bands remain to be explained. It can be seen from the data in Table 4 that at least two of these bands (the calculated frequencies for the complex are 3085 and 3857 cm^{-1}) are characterized by high intensities and the shifts (+17 and −57 cm^{-1}, respectively) sufficient for these bands to be manifested in the IR spectrum. According to the results published previously,[12] the examination of the IR spectrum in the region of stretching vibrations of the OH and Me groups revealed no shifts of the bands in this region. This situation is attributable to the fact that the region of 2800—3000 cm^{-1} has a large number of split and broadened high-intensity IR bands of nonbonded methanol due to which new medium-intensity bands are difficult to notice at low concentrations of the complex. Taking into account that the calculated shift and intensity of the OH stretching vibration band of the MeOH molecule are −57 cm^{-1} and 53 km mol^{-1}, respectively, the absence of the shift of this band in the experimental spectrum remains unclear.

The appearance of the IR band in the region of 700—900 cm^{-1} is also an open question. Under the conditions of a low-temperature argon matrix at 14 K, the addition of methanol to the reaction mixture gives rise to an IR band at 844 cm^{-1}. Since the latter band is pronounced and highly intense, it cannot be assigned to an impurity or the physical interaction of the monomer with the substrate.[12] The intensity of this band increased as the concentration of methanol in the reaction mixture was increased. Apparently, this band should be assigned to the complex involving the MeOH molecule. It can be seen from Table 4 that there is only one vibration in the region of 700—900 cm^{-1} to which the band at 844 cm^{-1} can be assigned, *viz.*, the symmetric stretching vibration of SiF_4 inactive in the IR region (the experimental and calculated frequencies are 801 cm^{-1} and 784 cm^{-1}, respectively). However, this assignment implies a large positive shift of the Si—F stretching vibration (+43 cm^{-1}), which is highly improbable in the case of a weak complex. The results of calculations demonstrated that the formation of the complex, as expected, leads to a small negative shift (−10 cm^{-1}). In addition, the intensity of this band in the spectrum of the complex is very low due to a weak distortion of the symmetry of SiF_4 upon complex formation, which is inconsistent with the experimental data. Hence, the band at 844 cm^{-1} cannot be assigned to the symmetric stretching vibration of SiF_4.

The assignment of this band to the antisymmetric stretching vibration of SiF_4 (1023 cm^{-1}), which is shifted to the long-wavelength region (the shift is −179 cm^{-1}), is also unlikely in the case of a rather low energy of formation of the binary complex. The preliminary estimates[14] demonstrated that this shift is characteristic of octahedral ternary complexes in which the configuration of SiF_4 is substantially distorted due to a higher energy of complex formation. However, this provides no explanation for the nature of the bands at 972 (952) and 406 cm^{-1}. In addition, several IR bands would be expected to appear in the region of 700—900 cm^{-1}, which lacks support from any experimental evidence.

In our opinion, the band at 844 cm^{-1} is most probably associated with the H...F hydrogen bonding between the OH group of methanol and the F atom of silicon tetrafluoride with very strong anharmonicity of the atom-atom potential. In the free monomers, this vibration is absent due to hindered rotation of the OH group about the C—O bond whose IR frequency was estimated[20] (different data) at 200—300 cm^{-1}. After complex formation, the rotation of the OH group becomes impossible and the H atom is oriented so that the H...F distance is no larger than 2.7—2.8 Å. The formation of the H...F bond is responsible for the appearance of a new vibration band with a rather high intensity whose calculated frequency is 417 cm^{-1} (the shift is +148 cm^{-1}). Although this frequency is far removed from 844 cm^{-1} (formally, the shift corresponds to +549 cm^{-1}), it should be remembered that the theory gives the inaccurate description of vibrations possessing strong anharmonicity. This point of view is also indirectly supported by the facts that only one IR band (406 cm^{-1}) of the antisymmetric bending vibration of SiF_4 is observed in the vicinity of 400 cm^{-1} and none of the bands in this spectral region corresponds to the calculated intense vibration of the hydrogen bond at 417 cm^{-1}. The formation of the H...F bond would be expected to lead to strong anharmonicity of the atom-atom potential of the O—H bond and even to the occurrence of a double minimum giving rise to the ionic $F...H^+...O^-$ structure as a result of which the vibrational frequency increases substantially. This is a plausible explanation for the absence of the shift of the OH stretching frequency. Although the above-considered arguments are insufficient for the unambiguous assignment of the band at 844 cm^{-1} and this problem calls for further investigation, the assignment of this band to the stretching vibration of the H...F bonds seems to be favored over other alternatives.

The data for the $SiF_4 \cdot Me_2O$ complex given in Table 5 show that this system, like two systems considered above, gives characteristic bands at 969 and 962 cm^{-1}. These bands were assigned[12,14] to the Si—F stretching vibration, which is split due to the matrix effect. The calculations demonstrated that the formation of the bipyramidal binary complex causes splitting of the triply degenerate antisymmetric stretching vibration of SiF_4 (1014 cm^{-1}) into three intense bands at 1020, 1007, and 959 cm^{-1} (the corresponding shifts are +6, −6, and −55 cm^{-1}). The first two bands (the shifts are +6 and −6 cm^{-1}) fall in the region of high-intensity vibrations of SiF_4 and are not observed in the experimental spectrum. The shift of the third band (−55 cm^{-1}) agrees well with the shifts of the experimental bands at 969 and 962 cm^{-1} (−54 and −61 cm^{-1}, respectively). In this spectral region, bands belonging to vibrations of the Me_2O molecule are experimentally observed at 917, 1078, and 1180 cm^{-1}. The negative shifts of the first two bands (−11 and −24 cm^{-1}, respectively) agree well with the calculated values of −15 and −9 cm^{-1}, respectively. The small positive shift of the last-mentioned band (+1 cm^{-1}) is inconsistent with the calculated value (−8 cm^{-1}). First, this can be explained by the strong dependence of the shift on the level of calculations (calculations with different basis sets gave shifts from +2 (MP2/6-311++G(d,p)) to −9 cm^{-1} (MP2/6-311++G(2d,p)). Another probable reason is that the value determined for the gaseous phase was considered as the experimental vibrational frequency of the Me_2O molecule, whereas the calculations were carried out in a low-temperature matrix as a result of which the frequency can be shifted by several reciprocal centimeters. This may be responsible for the opposite sign of the shift with respect to the calculated value.

In the C—H stretching vibration region, the band at 3006 cm^{-1} was experimentally observed. Its shift (+10 cm^{-1}) agrees well with the calculated value (+15 cm^{-1}). However, as in the case of MeOH, the

Table 5. Calculated (MP2/6-311++G(2d,2p)) vibrational frequencies of the starting SiF_4 and Me_2O monomers (ν_m/cm^{-1}) and their complex (ν_c/cm^{-1}), the intensities of the IR bands (*I*/km mol^{-1}), and the frequency shifts ($\Delta\nu$/cm^{-1}) compared with the experimental values obtained in an argon matrix at 12 K

Experiment[a]			Calculation				Assignement
ν_m[20]	ν_c[12]	$\Delta\nu$	ν_m	ν_c	*I*	$\Delta\nu$	
203 ia			196	199	0	3	$\delta^{s}(SiF_4) + \delta^{as}(Si—O—C)$
242 w			250	261	10	11	$\delta^{s}(SiF_4) + \omega^{s}(Me)$
264[b]			267[b]	281	0	14	$\delta^{s}(SiF_4) + \delta^{as}(Si—O—C)$
264[b]			267[b]	290	19	23	$\delta^{s}(SiF_4) + \omega^{s}(Me)$
388[b]			390[b]	377	86	−13	$\delta^{as}(SiF_4)$
388[b]			390[b]	393	47	3	$\delta^{as}(SiF_4)$
388[b]			390[b]	394	39	4	$\delta^{as}(SiF_4)$
418 m			418	431	2	13	$\delta(C—O—C)$
801[b]			784[b]	773	0	−11	$\nu^{s}(SiF_4)$
928 s	917	−11	948	932	179	−15	$\nu^{as}(SiF_4) + \nu^{s}(C—O)$
1023[b]	969, 962[c]	−54, −61[c]	1014[b]	959	179	−55	$\nu^{s}(C—O) + \nu^{as}(SiF_4)$
1023[b]	Nontransparent region of residual SiF_4		1014[b]	1007	207	−6	$\nu^{as}(SiF_4)$
1023[b]			1014[b]	1020	191	6	$\nu^{as}(SiF_4)$
1102 v.s	1078	−24	1130	1120	63	−9	$\rho(Me') + \rho(Me'') + \nu^{as}(C—O)$
1150 ia			1175	1176	0	1	$\rho(Me') + \rho(Me'')$
1179 v.s	1180	1	1206	1198	69	−8	$\rho(Me') + \rho(Me'') + \nu^{as}(C—O)$
1227 ia			1208	1212	6	4	$\rho(Me') - \rho(Me'')$
1244 w			1281	1285	5	5	$\rho(Me') - \rho(Me'') + \delta(C—O—C)$
1452 m			1482	1480	1	−2	$\delta^{s}(Me)$
1452 m			1510	1509	0	−1	$\delta^{s}(Me)$
1464 m			1510	1516	1	6	$\delta^{as}(Me)$
1464 ia			1521	1525	9	4	$\delta^{as}(Me)$
1464 m			1526	1529	17	2	$\delta^{as}(Me)$
1464 m			1542	1540	5	−2	$\delta^{as}(Me)$
2817 s			3014	3033	35	19	$\nu^{s}(Me)$
2817 s			3021	3038	51	17	$\nu^{s}(Me)$
2925 s			3077	3106	72	29	$\nu^{as}(Me)$
2952 ia			3084	3112	0	28	$\nu^{as}(Me)$
2996 s			3185	3201	10	16	$\nu^{as}(Me)$
2996 s	3006	10	3202	3217	10	15	$\nu^{as}(Me)$

[a] For the notations, see Table 4.

[b] Vibrations of the SiF_4 molecule.

[c] Splitting in the matrix.[14]

experimental spectrum of the SiF_4—Me_2O system in a low-temperature matrix has no new bands in the region of vibrations of the Me group (the calculated frequencies are 2817 and 2925 cm^{-1}) whose calculated intensities and shifts (+19 and +29 cm^{-1}, respectively) are quite sufficient for these bands to be manifested in the IR spectrum.

It should be noted that new vibrations in the region of 800—900 cm^{-1} are absent both in the experimental and calculated IR spectra of the SiF_4—Me_2O system. This fact is indirect evidence that the band at 844 cm^{-1} in the IR spectrum of the SiF_4—MeOH system is associated with vibrations of the OH group.

To summarize, the comparison of the low-temperature IR spectra with the results of quantum-chemical calculations allows the conclusion that the formation of donor-acceptor complexes is the major tendency in the SiF_4—oxygen-containing donor systems, which is manifested under the conditions of a low-temperature inert matrix. The formation of hydrogen-bonded structures involving the SiF_4 and H_2O molecules is unfavorable and PES contained no local minima corresponding to structures formed only through hydrogen bonding. Consequently, broadening of the OH stretching vibration bands observed in gas-phase mixtures of SiF_4 with a water vapor[21] occurs, apparently, due to interactions of hydroxy-containing hydrolysis products with H_2O (and, probably, with HF) rather than due to formation of hydrogen-bonded complexes of SiF_4. The complexes of SiF_4 with water, methanol, and dimethyl ether generated in low-temperature inert matrices at helium temperature have distorted trigonal-bipyramidal structures.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 00-03-32094).

References

1. N. M. Alpatova and Yu. M. Kessler, *Zh. Strukt. Khim.,* 1964, **5**, 332 [*J. Struct. Chem.* (*USSR*), 1964, **5** (Engl. Transl.)].
2. I. R. Beattie, *Rev. Chem. Soc.*, 1964, **17**, 382.
3. A. A. Ennan and B. M. Kats, *Usp. Khim.*, 1974, **43**, 1186 [*Russ. Chem. Rev.*, 1974, **43** (Engl. Transl.)].
4. V. O. Gel´mbol´dt and A. A. Ennan, *Koord. Khim.,* 1983, **9**, 579 [*Sov. J. Coord. Chem.,* 1983, **9** (Engl. Transl.)].
5. J. Hu, L. J. Schaad, and B. A. Hess, *J. Am. Chem. Soc.*, 1991, **113**, 1463.
6. B. S. Ault, *Inorg. Chem.*, 1981, **20**, 2817.
7. C. J. Marsden, *Inorg. Chem.*, 1983, **22**, 3177.
8. J. P. Guertin and M. Onyszchuk, *Can. J. Chem.*, 1963, **41**, 1477.
9. J. P. Guertin and M. Onyszchuk, *Can. J. Chem.*, 1968, **46**, 987.
10. L. A. Gavrilova, V. O. Gel´mbol´dt, A. A. Ennan, P. N. Yurkevich, and L. V. Ostapchuk, *Koord. Khim.,* 1986, **4**, 489 [*Sov. J. Coord. Chem.,* 1986, **4** (Engl. Transl.)].
11. L. V. Ostapchuk, L. A. Gavrilova, and A. A. Ennan, *Zh. Neorg. Khim.,* 1982, **27**, 344 [*J. Inorg. Chem. USSR*, 1982, **27**, No. 2 (Engl. Transl.)].
12. B. S. Ault, *J. Am. Chem. Soc.*, 1983, **105**, 5742.
13. G. G. Devyatykh and P. G. Sennikov, *Usp. Khim.*, 1995, **64**, 817 [*Russ. Chem. Rev.*, 1995, **64**, No. 9 (Engl. Transl.)].
14. S. K. Ignatov, P. G. Sennikov, B. S. Ault, A. A. Bagatur´yants, A. A. Simdyanov, A. G. Razuvaev, E. Yu. Klimov, and O. Gropen, *J. Phys. Chem.*, *A*, 1999, **103**, 8328.
15. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
16. PC GAMESS home page: http://classic.chem.msu.su/gran/gamess/index.html.
17. S. B. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553.
18. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *GAUSSIAN-94, REVISION D.1*, Gaussian, Inc., Pittsburgh (PA), 1995.
19. D. G. Evans, G. A. Yeo, and T. A. Ford, *Faraday Discuss. Chem. Soc.*, 1988, **86**, 55.
20. T. Shimanouchi, *Tables of Molecular Vibrational Frequencies*, Consolidated Volume 1, National Bureau of Standards, New York, 1972, 1.
21. P. G. Sennikov, M. A. Ikrin, S. K. Ignatov, A. A. Bagatur´yants, and E. Yu. Klimov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 92 [*Russ. Chem. Bull.*, 1999, **48**, 93 (Engl. Transl.)].

Received January 19, 2001;
in revised form May 23, 2001