

The theoretical research of the medium effect on the vibrational spectrum and the energy of intramolecular coordination $=O \rightarrow Si$ in (benzoyloxymethyl)trifluorosilane molecule

Swetlana G. Shevchenko *, Yulii L. Frolov, Aleksei V. Abramov, Mikhail G. Voronkov

A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences 1, Favorsky Street, Irkutsk, 664033, Russian Federation

Received 19 January 2005; revised 9 March 2005; accepted 10 March 2005
Available online 10 May 2005

Abstract

The characteristics of (benzoyloxymethyl)trifluorosilane $C_6H_5C(=O)OCH_2SiF_3$ containing a five-membered heterocycle closed by intramolecular coordination $=O \rightarrow Si$ bond (**Ia**) and its most stable acyclic isomer (**Ib**) have been calculated by HF, MP2(Full) non-empirical methods, and DFT(B3LYP) using 6-311G(d) and 6-311 + G(2d,p) basis sets. The (C_8H_{18} , C_6H_6 , $(C_4H_9)_2O$, $CHCl_3$, $(CH_2)_4O$, CH_2Cl_2 , CH_3CN) medium effect on the energy and structural characteristics, dipole moments, and vibrational spectra of **Ia** and **Ib** isomers was calculated by the DFT(B3LYP)/6-311 + G(2d,p) method in the Onsager SCRF model approximation. The DFT(B3LYP)/6-311 + G(2d,p) calculation reasonably reproduces the medium effect on coordination energy, geometry, dipole moments, and band frequencies in the vibrational spectrum of **Ia**.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Quantum chemical calculations; (Benzoyloxymethyl)trifluorosilane; Pentacoordinate silicon atom; Medium effect; Coordination energy; Dipole moment; Geometry; Vibration spectrum

1. Introduction

In the modern chemistry of pentacoordinate silicon organic derivatives special attention is given to (aroyloxymethyl)trifluorosilanes $XArC(=O)OCH_2SiF_3$ (AFS), named dragonoids [1]. The initial member of this series is represented by (benzoyloxymethyl)trifluorosilane $C_6H_5C(=O)OCH_2SiF_3$ (BFS). For more than 20 years, the nature of valence expansion of the central silicon atom caused by the $=O \rightarrow Si$ intramolecular coordination $=O \rightarrow Si$ bond formation was studied by different physical–chemical and theoretical methods [1–4]. The AFS molecular structure has been studied by X-ray diffraction method [5,6]. The high sensitivity of AFS vibrational

spectra to the medium effect allowed the development of the spectral procedures in the research of such interaction type [2,3]. However, the AFS vibration spectra were not exhaustively studied and interpreted until now.

Previously the present authors conducted HF/6-31G(d), MP2(FC)/6-31G(d) non-empirical and AM1 semi-empirical studies of isolated AFS molecules, including BFS isomers **Ia** and **Ib** [4]. The $=O \rightarrow Si$ energy coordination, dipole moments and structural parameters have been calculated. In harmonic approximation using standard valence-force field a direct vibrational problem has been solved for model (formylloxymethyl)trifluorosilane $H-C(=O)OCH_2SiF_3$ [7] and the 1-hydrosilatrane $HSi(OCH_2CH_2)_3N$ [8] molecules containing coordination bonds $=O \rightarrow Si$ and $N \rightarrow Si$, respectively. The vibrational spectrum, geometry and electronic structure of diverse isolated conformers of

* Corresponding author. Tel.: +7 3952 425519; fax: +7 3952 419396.
E-mail address: sw_shev@irioc.irk.ru (S.G. Shevchenko).

(acetoxymethyl)trifluorosilane $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{SiF}_3$ were examined using the HF/6-31G(d) method [9]. The BFS molecule geometry was calculated by non-empirical methods HF and MP2 with 6-31G(d), 6-311G(d), 6- and 311 + G(d,p) basis sets [4,10]. An attempt has been made at estimating the medium effect (DMPPhA) on the BFS geometry by HF/6-31G(d) with the help of the Onsager reaction field and Tomasi's polarized continuum (PCM) models [10]. Quantum-chemical examinations of the medium effect on the AFS and BFS vibration spectra as the vibration spectrum calculation of BFS have never been undertaken before.

The goal of the present work is comprehensive quantum-chemical investigation of medium effect on peculiar variations of the coordinate $=\text{O} \rightarrow \text{Si}$ bond, vibrational spectrum, total energy, dipole moment, and electronic structure of BFS.

2. Calculation procedure, results and discussion

The quantum-chemical calculations were performed by non-empirical MP2(Full), HF, and DFT(B3LYP) methods with 6-311 + G(2d,p) basis set (in some cases for the DFT(B3LYP) method with 6-311G(d) basis set) using standard program complex GAUSSIAN-03W [11]. The vibrational spectra, total energies, zero-point energies, dipole moments, and structural characteristics of two stable BFS isomers of C_s symmetry were calculated. One of them contains the intramolecular coordinate $=\text{O} \rightarrow \text{Si}$ bond closing the pentacoordinate heterocycle (**1a**). The other most stable isomer does not possess the coordinate $=\text{O} \rightarrow \text{Si}$ bond and has an acyclic structure with *trans-trans* orientation of $\text{C}(=\text{O})\text{--O--CH}_2\text{--SiF}_3$ chain (**1b**). The **1b** isomer exists exclusively in a gas phase at the temperature above 420 K [12]. The optimized geometries of these two stable structures are presented in Fig. 1. Coordination energy was estimated as the difference between total energies of **1a** and **1b** isomers. In the calculation no BSSE correction was taken into account, since for extended basis sets it cannot affect much the results [13].

The modeling of the effect of the medium polarity (C_8H_{18} , C_6H_6 , $(\text{C}_4\text{H}_9)_2\text{O}$, CHCl_3 , $(\text{CH}_2)_4\text{O}$, CH_2Cl_2 , CH_3CN) on the energy and structural characteristics, dipole moments, and vibrational spectra of isomers **1a** and **1b** was carried out by DFT(B3LYP)/6-311 + G(2d,p) in the Onsager self-consistent reaction field (SCRFF+Dipole) model approximation. Taking into account the optimized geometry, the radiiuses of spherical cavity were determined as: 545.0 pm for **1a** and 580.0 pm for **1b**.

At the present time, the nature of intramolecular coordinate $=\text{O} \rightarrow \text{Si}$ bond in AFS molecules [14] is theoretically described within Masher's hypervalence scheme [15] that was developed for pentacoordinate sil-

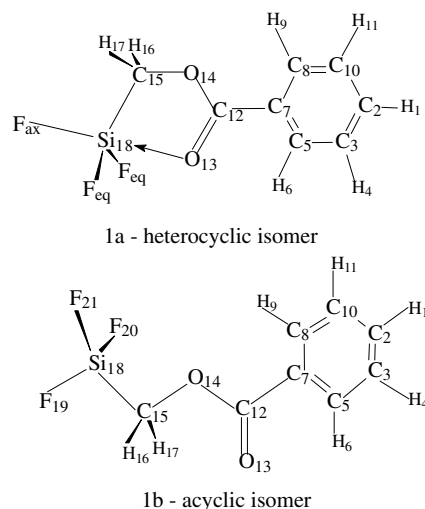


Fig. 1. Electronic structure of stable BSR according to DFT(B3LYP)/6-311 + G(2d,p) calculations: **1a**, heterocyclic isomer containing a $=\text{O} \rightarrow \text{Si}$ coordinate bond; **1b**, acyclic isomer containing a tetracoordinate silicon atom.

icon compounds [16,17]. Experimental examination of medium effect on the energy and spectral characteristics of BFS it was determined that their variation follows the model of three-center, 4-electron ($3c\text{--}4e$) binding for the $\text{C}=\text{O} \rightarrow \text{Si--F}_{\text{ax}}$ fragment, and depends exclusively on the medium polarity. Herewith, the observed strengthening of intramolecular coordinate interaction, increase of the BFS dipole moment, and variation of fundamental frequencies in IR spectrum are mostly described by the function of medium polarity $(\epsilon - 1)/(2\epsilon + 1)$ with a small contribution from the dispersion member $(n^2 - 1)/(2n^2 + 1)$ [2]. This all determined the choice of solvation Onsager SCRFF model.

The IR absorption spectra of the BFS in the 400–4000 cm^{-1} region were measured by IFS-25 Fourier spectrometer in tablets with KBr and in CCl_4 and CH_3CN solutions ($d = 0.003$ cm, $c = 0.01$ mol/l). The Raman spectrum of solid sample in the 200–2000 cm^{-1} region was recorded on Cary-81 Raman spectrometer with excited line at 4880 Å for a 1-Wt Ar laser.

2.1. The coordination energy

Table 1 shows calculated total energy of **1a** and **1b** structures of BFS, E_{tot} , total energy with zero-point energy corrections, E_{ZPE} (a.u.), coordination energy, E_{coord} (kJ/mol) in different mediums, and available literature data.

A distinguished feature of **1a** isomer structure is the presence of intramolecular coordinate bond $=\text{O} \rightarrow \text{Si}$. The quantum-chemical evaluation of energy of this type of interaction (25.3 kJ/mol), that was calculated by MP2(FC) non-empirical method with 6-31G(d) standard basis set [4], is considered in the literature as most concerted with the experimental value $E_{\text{coord}} = -28.5$

Table 1

Calculated values of total energy (E_{tot} , a.u.), total energy with zero-point energy correction (E_{ZPE} , a.u.), and coordination energy (E_{coord} , kJ/mol) for the **1a** and **1b** isomers of BFS in different mediums and available literature data.

Structure	Method [Reference]	ϵ	E_{tot}	E_{coord}	E_{ZPE}	E_{coord}
1a	DFT(B3LYP)/6-311G(d)	1.00	-1048.971951	-17.6	-1048.828494	-15.5
1b			-1048.965245		-1048.822590	
1a	DFT(B3LYP)/6-311 + G(2d,p)	1.00	-1049.035357	-12.3	-1048.892412	-10.4
1b			-1049.030685		-1048.888459	
1a		2.28	-1049.037064	-16.2		
1b			-1049.030881			
1a		4.90	-1049.038260	-19.1		
1b			-1049.030991			
1a		7.58	-1049.038726	-20.2		
1b			-1049.031034			
1a		35.90	-1049.039562	-22.2	-1048.896530	-19.9
1b			-1049.031093		-1048.888935	
1a	MP2(FC)/6-31G(d) [4]	1.00	-1046.171891	-25.3		
1b			-1046.162276			
1a	MP2(Full)/6-31G(d) + ZPE [10]					-22.8
1b						
1a	MP2(Full)/6-311 + G(2d,p)		-1047.227194	-16.7		
1b			-1047.220836			
1a	HF/6-31(d) [4]		-1044.220581	-14.1		
1b			-1044.215226			
1a	HF/6-311 + G(2d,p)		-1044.476688	-1.6		
1b			-1044.476064			

kJ/mol [12]. The later attempt to improve the convergence of the calculated and experimental values of the E_{coord} within MP2(Full)/6-31G(d) + ZPE method by including the ZPE correction had the opposite effect, $E_{\text{coord}} = -22.8$ kJ/mol [6]. The result of $E_{\text{coord}} = -14.1$ kJ/mol (HF/6-31G(d)), obtained earlier by one of the authors, thought to be underestimated owing to the neglect of electron correlation energy in the HF method [4]. Our DFT(B3LYP)/6-311G(d) calculation considering the electron correlation resulted in unexpectedly low value for coordination energy in contrast with the MP2(FC) method: -17.6 kJ/mol, without, and -15.5 kJ/mol, with zero-point energy corrections.

Recently [18] some results supporting the necessity to use in theoretical structural studies of molecules, containing third-row atoms, the basis sets including at least 2d functions. Starting from these data we have carried out HF, MP2(Full) and DFT(B3LYP) calculations of E_{coord} value employing balanced 6-311 + G(2d,p) basis set. The expansion of the functional basis of HF/6-311 + G(2d,p) calculation resulted in a physically unreasonable value of coordination energy, -1.6 kJ/mol. Schaefer and coworkers [19] have observed an analogous result in their HF/d95** calculations of energy parameters of the dissociation reaction of intermolecular complexes of tetrahalosilanes with ammonia $X_4\text{Si} \cdot \text{NH}_3$ ($X = \text{H}, \text{F}, \text{Cl}, \text{Br}$). Consideration of the effect of electron correlation in the MP2(Full) and DFT(B3LYP) methods with the expanded 6-311 + G(2d,p) basis set has led to further decrease of coordination energy (-16.7 kJ/mol

(MP2(Full) and -16.7 kJ/mol DFT(B3LYP)). In the DFT(B3LYP) + ZPE/6-311 + G(2d,p) calculation the allowance for zero point energy supplementary diminished the E_{coord} value to -10.4 kJ/mol. In MP2(Full) + ZPE/6-311 + G(2d,p) method, taking into account the zero-point energy can supplementary reduce the coordination interactions energy by ≈ 2 kJ/mol. Thus, the executed theoretical analysis suggests that the coordination energy value for the BFS molecule in the gas phase is in the range: -10 to -15 kJ/mol (-3 kcal/mol). This is considerably below earlier published experimental gas phase value of -28.5 kJ/mol (-6.8 kcal/mol) [12]. A repeated analysis of our experiment has shown our value to be overestimated owing to the observed hydrolysis of BFS. The refined experimental E_{coord} value is -3.6 kcal/mol.

The effect of medium in going from the gas phase to acetonitrile is not sensibly reflected on total energy change of isomer **1b**, but leads to a significant stabilization of isomer **1a**. This is expressed as an increase in coordination energy by a factor of 1.8 and 1.9 without and with allowance for zero-point energy, respectively (Table 1). The effect of medium polarity in the range $\epsilon = 1-36$ on the variation of E_{coord} value is graphically presented in Fig. 2A by a linear correlation between coordination energy and $(\epsilon - 1)/(2\epsilon + 1)$ function of dielectric constant of medium. The data of calculation are in good agreement with the experimentally observed BFS results providing strong evidence for the deciding influence of the medium polarity on variation of $=\text{O} \rightarrow \text{Si}$ coordinate interaction in BFS [2]. Thus, the

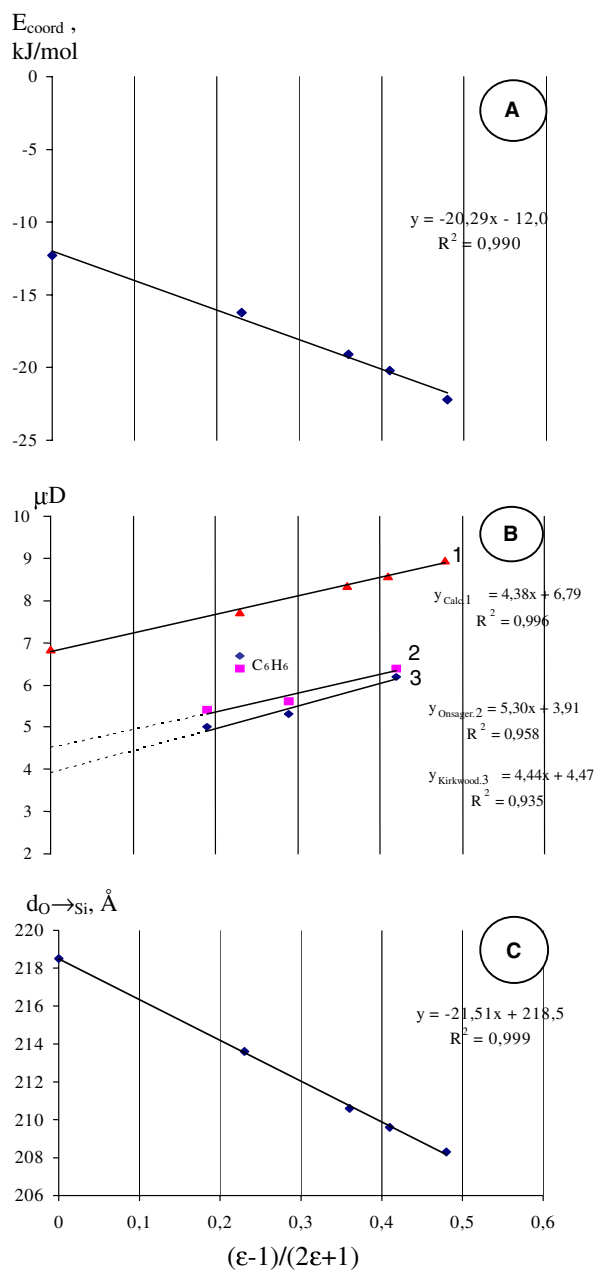


Fig. 2. The dependence of calculated characteristics of isomer **1a** in the BFS molecule on the medium polarity function $(\epsilon - 1)/(2\epsilon + 1)$: (A) coordination energy E_{coord} , kJ/mol; (B) dipole moments μ ; (D) 1 – $\mu_{\text{Calc.1}}$ by DFT(B3LYP)/6-311 + G(2d,p) calculation, 2 – experimental $\mu_{\text{Onsager.2}}$ (by Onsager method [20]), 3 – experimental $\mu_{\text{Kirkwood.3}}$ (by Kirkwood method [20]). (C) – The lengths of $d(\text{O} \rightarrow \text{Si})$ coordinate bond, Å.

use of the solvation Onsager model calculated by DFT(B3LYP)/6-311 + G(2d,p) leads to reliable variations of the $\text{=O} \rightarrow \text{Si}$ coordination energy with increasing the ϵ values of medium.

2.2. Dipole moments

The dipole moments of cyclic **1a** and acyclic **1b** structures of the BFS molecule were calculated for both iso-

lated molecules and those in various solvents. The results are presented in Table 2 alongside with the available literature data. As it can be seen from Table 2, the difference of the employed non-empirical methods and basis sets does not essentially affect the calculated value μ in the gas phase. The dispersion in $\Delta\mu$ values is: 0.63 D for **1a** structure and 0.36 D for **1b** structure. The agreement of calculated gas-phase dipole moments with the experiment did not seem possible earlier due to two reasons: (1) the absence of experimental dipole moments in a gas phase and (2) the impossibility of comparison with the experimental μ values in different solvents due to the expressed sensitivity of BFS dipole moment to the medium effect. The earlier experiments has proved the definite effect of polar characteristics of non-specific mediums on **1a** dipole moment change and the existence of μ linear dependence on the dielectric constant function of the solvent $f(\epsilon) = (\epsilon - 1)/(2\epsilon + 1)$ [20]. Based on that, we were able to forecast the dipole moment value for **1a** in the gas phase. Fig. 2B shows the dependencies of experimental dipole moments that were calculated by Onsager and Kirkwood methods [20] on the ϵ value of non-specific solvents C_8H_{18} , $(\text{CH}_2)_4\text{O}$, and CH_2Cl_2 . The values of dipole moments of isomer **1a** obtained by extrapolating to gas phase were defined by the range 3.9–4.5 D (Fig. 2B, lines 1 and 2). These values are not reproduced by any of mentioned calculations, including the result 5.72 D of semi-empirical AM1 method [4]. The consideration of the 2d functions in basis set gives only a small reduction of **1a** dipole moment $\Delta\mu$ within the framework of different methods: 0.17 D for B3LYP/(6-311G(d) \rightarrow 6-311 + G(2d,p)) and 0.45 D for HF/(6-31G(d) \rightarrow 6-311 + G(2d,p)). The discrepancy between the μ value, calculated by B3LYP/6-311 + G(2d,p), and supposed experimental value in the gas phase consists around 50% and sustains for the whole series of universal solvents. At the same time, the DFT(B3LYP)/6-311 + G(2d,p) method within the solvation Onsager model reproduces adequately to the experiment the character of **1a** dipole moment change for non-specific solvents. This is well illustrated by similarity of slopes in **1a** theoretical and experimental dependences of μ on the solvent polarity function $f(\epsilon)$ (Fig. 2B). Here-with, in the same interval of ϵ changes, the amplitude of increase of cyclic **1a** isomer dipole moment is much higher than that of acyclic isomer **1b** (2.11 D > 0.46 D).

For solvents that require consideration of specific interactions, such as C_6H_6 , for example, Onsager model fails to reproduce the character of **1a** dipole moment μ change (Fig. 2B). As shown in Fig. 2B, the μ value of **1a** in benzene is sufficiently deviates from the experimental lines 2 and 3 that probably caused by specific character of interaction between solvent and the BFS molecule [20]. In terms of the Onsager SCRF model, with regard to only non-specific interactions, **1a** dipole moment in

Table 2

The calculated and experimental values of dipole moments μ (D) and coordinate bond lengths $d(\text{O} \rightarrow \text{Si})$ (pm) of the **1a** and **1b** isomers in different mediums.

Medium	ϵ	$(\epsilon - 1)/(2\epsilon + 1)$	$d(\text{O} \rightarrow \text{Si})$	μ_{calc}			μ_{exp} [20]	
				1a	1b	Method [Reference]	Onsager	Kirkwood
Gas phase	1.00	0	218.5	6.83	2.47	DFT(B3LYP)/6-311 + G(2d,p)		
			216.8	7.12	2.60	MP2(total)/6-311 + G(2d,p)		
			222.7	6.49	2.24	HF/6-311 + G(2d,p)		
			214.3	6.94		MP2(FC)/6-31G(d) [4]		
C ₈ H ₁₈	1.95	0.19	214.3	7.57		DFT(B3LYP)/6-311 + G(2d,p)	5.00	5.40
C ₆ H ₆	2.28	0.23	213.6	7.72		DFT(B3LYP)/6-311 + G(2d,p)	6.40	6.70
(C ₄ H ₉) ₂ O	3.05	0.29	210.9	8.07		DFT(B3LYP)/6-311 + G(2d,p)	5.30	5.60
CHCl ₃	4.90	0.36	210.6	8.34		DFT(B3LYP)/6-311 + G(2d,p)		
C ₄ H ₈ O	7.58	0.41	209.6	8.58		DFT(B3LYP)/6-311 + G(2d,p)		
CH ₂ Cl ₂	9.14	0.42	209.2	8.66		DFT(B3LYP)/6-311 + G(2d,p)	6.20	6.40
CH ₃ CN	35.9	0.48	208.3	8.94	2.93	DFT(B3LYP)/6-311 + G(2d,p)		

C₆H₆ solution fits well into the theoretical dependence of $\mu \sim f(\epsilon)$.

Thus, the solvation Onsager SCRF model within DFT(B3LYP)/6-311 + G(2d,p) method reproduces fairly well the effect of medium polarity on dipole moment change of BFS **1a** isomer in non-specific solvents.

2.3. BFS Geometry

The realistic evaluation of calculated BFS structural parameters is complicated by the absence of experimental geometry in the gas phase and by the sensitivity of pentacoordinated silicon compound geometry to the medium effect. Therefore, the quality of calculation of structural parameters was analyzed by the comparison of their variation in the series: gas \rightarrow solvent \rightarrow crystal. In Table 3 there are the bond lengths surrounding the silicon atom in **1a** and **1b** molecules in a gas phase (DFT(B3LYP), MP2(Full), HF with basis set 6-311 + G(2d,p)) and in acetonitrile solution (DFT(B3LYP)/

6-311 + G(2d,p)), and also X-ray data for the crystal **1a** [6].

The equilibrium lengths of C–C bonds in benzene ring calculated using DFT(B3LYP) and MP2(Full) methods coincide in the limits of 0.1 pm for the structures containing tetra-**1b** and pentacoordinate **1a** silicon atom. The calculated lengths of these bonds that are not sensitive toward the medium effect, correspond to the available X-ray structural data [6] and are not reported in this work.

For theoretical chemistry, the pentacoordinate silicon atom is of special interest because it can be regarded as an electron-deficient center in the nucleophilic substitution reactions. The consideration of gas phase geometric parameters of the heterocyclic fragment of structure **1a** indicates that the all three calculation methods in expanded 6-311 + G(2d,p) basis set are agreed upon the total action of silicon AO rehybridization and coordination in going from the tetra-(acyclic isomer **1b**) to the pentacoordinate state (cyclic isomer **1a**), Δd , pm:

Table 3

Bond lengths calculated by different methods with 6-311 + G (2d,p) basis set and X-ray values for BFS isomers **1a** and **1b** in a gas phase and acetonitrile solution, (pm)

Bond	1a				Exp. [6] Cryst.	1b			
	HF	MP2(Full)	DFT(B3LYP)			HF	MP2(Full)	DFT(B3LYP)	
	$\epsilon = 1$	$\epsilon = 1$	$\epsilon = 1$	$\epsilon = 35.9$		$\epsilon = 1$	$\epsilon = 1$	$\epsilon = 1$	$\epsilon = 35.9$
C ₁₂ –C ₇	147.7	147.0	147.3	146.5	146.0	148.7	148.2	148.5	148.3
O ₁₃ =C ₁₂	120.1	123.1	122.9	123.8	124.3	118.3	121.0	120.6	120.6
O ₁₄ –C ₁₂	130.2	132.8	132.8	132.6	131.1	133.0	136.3	136.3	136.6
O ₁₄ –C ₁₅	142.8	144.9	145.2	145.1	146.8	141.8	144.0	143.9	143.8
Si ₁₈ –C ₁₅	187.7	188.0	188.6	188.8	185.5	185.4	184.9	185.7	185.7
Si ₁₈ –F _{ax19}	158.7	161.5	162.0	163.4	161.0	155.7	158.2	158.7	158.8
Si ₁₈ –F _{eq20}	156.1	158.9	159.4	160.0	157.7	155.5	158.0	158.5	158.5
					158.0				
Si ₁₈ \rightarrow O ₁₃	222.7	216.8	218.5	208.3	200.6				

Bond	HF	DFT(B3LYP)	MP2(Full)
C ₁₂ –C ₇	–1.0	–1.2	–1.2
O ₁₃ =C ₁₂	1.8	1.7	2.1
O ₁₄ –C ₁₂	–2.8	–3.5	–3.5
O ₁₄ –C ₁₅	1.0	1.3	0.9
Si–C ₁₅	2.3	2.9	3.1
Si–F _{ax}	3.0	3.3	3.3
Si–F _{eq}	0.6	0.9	0.9

Disregarding electron correlation energy in the HF/6-311 + G(2d,p) method leads to lower variations of the lengths of bonds by about 10–30%. The change of the silicon atom valence state is accompanied by primary lengthening of Si–F_{ax} and C₁₂=O₁₃ axial bonds and less significant lengthening of the Si–F_{eq} equatorial bonds that corresponds to the 3c–4e bonding model for a C=O → Si–F_{ax} fragment [17]. The transition from the tetra-**1b** to pentacoordinate structure **1a** is accompanied by the changes of valence angles solely in silicon atom surrounding and that are equal to: ∠F_{ax}SiC₁₅ 109.0° → 96.0°, ∠F_{ax}SiF_{eq} 107.9° → 100.2°, ∠F_{eq}SiC₁₅ 112.2° → 119.5°, and ∠O₁₃C₁₂C₇ 125.2° → 123.7° (by DFT(B3LYP)/6-311 + G(2d,p) calculation). The obtained structural parameters characterize the symmetry of pentacoordinate silicon atom surrounding in **1a** structure as a distorted trigonal bipyramid.

In the changing of the dielectric properties of medium (from gas phase to acetonitrile solution) the lengths of the O₁₄–C₁₂, O₁₄–C₁₅, and Si–C₁₅ bonds change insignificantly by 0.1–0.2 pm (Table 3). For these and for benzene ring bonds the comparison between calculated gas phase values and X-ray structural parameters of crystal **1a** is justified. The axial and equatorial bonds of C=O → Si(F_{eq})₂–F_{ax} fragment are more prone to influence of the medium polarity. They are lengthening in the series Δ*d*, pm: 1.4 (Si–F_{ax}) > 1.1 (O=C₁₂) > 0.6 (Si–F_{eq}). It is reasonable to suppose that these bonds extend while an **1a** molecule is passing from a solution to crystalline state. However, such tendency of bond length change has been observed only for O=C₁₂ axial bond (Table 3). The Si–F_{eq} equatorial and Si–F_{ax} axial bond lengths that are one of the most important structural characteristics of trigonal-bipyramidal surrounding of silicon vary in the series: *d*_{gas} < Δ*d*_{solv.} > Δ*d*_{cryst.}. Similar data were obtained earlier by HF/6-31G(d) calculation of the effect of medium (gas – DMSO) on BFS molecule geometry for the Onsager and Tomasi's PCM models [10]. The retention of an analogous tendency of variation of coordination bond length observed in our DFT(B3LYP)/6-311 + G(2d,p) calculation taking into account the effect of electron correlation and using the larger basis set involving 2d diffuse functions made us to resort to the analysis of X-ray structural data. Indeed, in the crystalline structure **1a** the anomalously short

lengths of Si–F_{ax} axial and Si–F_{eq} equatorial bonds could be caused by the effect of the crystal lattice [6].

An intramolecular coordinate X → Si, X = N, O, S bond is the most debated and important structural parameter of molecules containing pentacoordinate silicon atom. Such an interest can be explained by the high sensitivity of the X → Si bond to the influence of intra- and intermolecular electron effects and the possibility of obtaining indirect information about the energy of intramolecular coordination. Below, there are literature data and the results of gaseous coordination bond length *d*(O → Si), pm:

Basis set	HF	DFT (B3LYP)	MP2 (FC)	MP2 (Full)
6-31G(d)	214.0 [4]		214.0 [4]	212.5 [10]
6-311G(d)	208.9 [10]	215.7	213.6 [10]	215.8 [10]
6-311 + G(d)	208.8 [10]			
6-311 + G(d,p)	209.0 [10]			
6-311 + G(2d,p)	222.7	218.5		216.8

While analyzing the basis size influence on the HF and MP2(FC) calculated *d*(O → Si) bond length evaluation by the HF and MP2(FC) methods, it was determined that the transition from limited basis set 6-31G(d) to 6-311G(d) leads to some shortening of coordinate bond length *d*(O → Si) and does not depend on the following usage of diffuse functions on heavy atoms and additional polarized functions in HF/6-311 + G(d,p) method [4,10]. Our HF calculation with 6-311 + G(2d,p) basis set supplemented by 2d functions on heavy atoms, has shown a significantly 13.7 pm increase of the *d*(O → Si) bond length. An analogous extension of the basis set in MP2(Full) leads to monotonous increase in *d*(O → Si). Herewith, for qualitative enough 6-311 + G(2d,p) basis set, the O → Si coordination bond length is 5.8 pm shorter than the one gotten by HF method, but it agrees with the results of DFT(B3LYP) calculations. Thus, the most correlated evaluations of coordination bond length *d*(O → Si), as well as other bonds of **1a** cyclic and **1b** acyclic structures, were obtained by DFT(B3LYP) and MP2(Full) methods with the use of 6-311 + G(2d, p) basis set.

The perturbing of medium effect in the range of dielectric constant change ε = 1–36 leads to shortening of the coordinate O → Si bond by 10.2 pm (Tables 2, 3). At the same time, B3LYP calculation indicates the tendency of axial Si–F_{ax} bond elongation that together adequately reflects the theoretical postulates of three-center 4-electron bond model for =O → Si–F_{ax} axial fragment.

The linear dependence (Fig. 2C) between the calculated coordination bond length *d*(O → Si) and the

function $(\varepsilon - 1)/(2\varepsilon + 1)$ of medium polarity was revealed. The increase of medium polarity causes shortening of the O → Si coordinate bond length and strengthens intramolecular coordinate bonding that is described by equation:

$$d(\text{O} \rightarrow \text{Si}) = 1.0483E_{\text{coord}} + 230.99 \quad R^2 = 0.99.$$

For pentacoordinate organosilicon compounds, the obtained dependence the first time established the interrelation between complex-formation energy E_{coord} and O → Si coordinate bond length, that in highest degree characterizes the structural reorganization of the BFS molecule with a change of medium polarity.

2.4. Vibrational spectra

Using DFT(B3LYP)/6-311 + G(2d,p) calculation in harmonical approximation we have analyzed the **1a** (Table 4) and **1b** (Table 5) molecule vibration spectra both in an isolated state and in an acetonitrile solution. The isomers **1a** and **1b** possessed C_s symmetry, and for each of them there are 57 normal vibrations $38A_1 + 19A_2$, active in IR and Raman-spectra. Tables 4 and 5 contain approximate forms of normal vibrations of **1a** and **1b**, and available experimental frequencies. Frequency assignment has been done on the basis of an analysis of vibration localization, frequency behavior, and vibration intensities in different mediums (in gas phase, in CCl_4 and CH_3CN solutions, and in solid state), and comparison experimental IR and Raman spectra in solid state. Taking into account the fact that the calculation by the DFT(B3LYP) method leads to systematic overestimation of frequencies, the comparison of calculated and experimental frequencies made allowances of the scale factor (SF). For the **1a** vibrational spectrum in the 1700–400 cm^{-1} region (in acetonitrile solution) the SF has the value of 0.96 that corresponds to the following equation:

$$\nu_{\text{exp.}} = 0.96\nu_{\text{calc.}} + 62.6, \quad R^2 = 0.996.$$

For certain spectral regions the scale factors are often much higher and reported separately.

The theoretical study of the **1a** and **1b** vibrational spectra of the stable BFS isomers of the BFS molecule was designed to solve three main problems:

- the discovery of the coordination sensitive vibrations,
- the determination of sensitivity of calculated vibrations on the medium effect,
- the identification of vibrations with the maximum contribution of O → Si bond deformation.

2.5. 2900–3100 cm^{-1} region

In this region of the **1a** vibrational spectrum are seven bands of C–H stretching vibration that is in good agree-

ment with the calculation (Table 2). Five of these ν_{57-53} normal vibrations of A_1 symmetry belong to characteristic stretching vibrations of a benzene ring. Their frequencies and intensities have low sensitive to intramolecular coordination and to medium effect. Two lower-frequency normal vibrations 52 and 51 are related to characteristic asymmetrical A_2 and symmetrical A_1 stretching vibrations of the methylene group, $\nu_{\text{as}}\text{CH}_2$ and $\nu_{\text{s}}\text{CH}_2$, respectively. According to calculations, in the =O → Si bond formation their frequencies increase approximately by 30 cm^{-1} for gas phase, but do not depend much on the increase of medium polarity. Previously this has not been revealed during experimental and theoretical investigations of the BFS vibrational spectrum [3,7].

2.6. 1200–1700 cm^{-1} region

This spectral region contains the vibrational bands of carbonyl group and ester fragment, which are important for the analysis of coordination sensitivity and medium effect. The $\nu\text{C}=\text{O}$ calculated values in the gas phase for **1a** and **1b** isomers are 1692 and 1767 cm^{-1} , respectively (experimental 1750 cm^{-1} [21]). The scale factors for them are 1.00 and 0.99. The calculated vibrations $\nu_{50}\text{C}=\text{O}$ of A_1 symmetry in the spectra of both structures are not strictly form-characteristic. The $\nu_{50}\text{C}=\text{O}$ of **1b** isomer containing a tetracoordinate silicon atom the contribution of the $\angle\text{C}_8\text{C}_7\text{C}_{12}$ angle deformation was observed. For isomer **1a** containing pentacoordinate silicon atom this vibration inclusions the $\angle\text{C}_{12}\text{O}_{14}\text{C}_{15}$ angle deformation and the CH_2 group vibration. This is caused by formation in isomer **1a** of heterocycle closed by an intramolecular =O → Si coordinate bond. The calculation proves the strong decrease (by 75 cm^{-1}) in $\nu_{50}\text{C}=\text{O}$ when intramolecular coordination is realized in gas phase. This is in agreement with the experimentally observed lowering in frequency by 56 cm^{-1} . Modeling of the dipole–dipole interaction of **1a** isomer with the medium (acetonitrile) adequately reproduces the experimentally observed decrease in frequency $\nu\text{C}=\text{O}$: calculation – 32 cm^{-1} , experiment – 56 cm^{-1} , and agrees with the decrease in =O → Si bond length during increase in medium polarity. The given spectral criterion was used earlier to study an impact of different factors on the strength of =O → Si intramolecular coordination bond [2,3].

Previously, based on the experimental data for BFS molecule and normal coordinate analysis of $\text{H}-\text{C}(\text{O})\text{OCH}_2\text{SiF}_3$ model compound in this spectral region, one more conformational sensitive vibration at 1350 cm^{-1} (gas) that was assigned to asymmetrical vibration of C(O)–O–C esteric group was identified [2,7]. Its frequency increases up to 1366 cm^{-1} during transition to solid state. An increase in frequency of this stretching vibration during the coordinate heterocycle closing in

Table 4

The calculated DFT(B3LYP)/6-311 + G(2d,p) and experimental characteristics of vibration spectra of BFS **1a** isomer containing a pentacoordinate silicon atom (frequency ν , cm^{-1} , intensity I , KM/mol)

No.	Sym	Calculation				Assignment	Experiment, ν				
		$\epsilon = 1$		$\epsilon = 35.9$			IR				Raman
		ν	I	ν	I		$\epsilon = 1$ 460 K	$\epsilon = 2.28$	$\epsilon = 35.9$ KBr	Tab.	Solid
57	A_1	3208	2	3210	1	νCH		3120 w ^a			
56	A_1	3205	2	3205	3	νCH		3095 w		3091 w	
55	A_1	3191	9	3194	4	νCH		3075 m		3064 w	
54	A_1	3183	7	3187	4	νCH		3068 m		3049 w	
53	A_1	3170	1	3177	~0	νCH		3040 w			
								3016 w		3006 w	
52	A_2	3111	2	3114	3	$\nu_{\text{as}}\text{CH}_2$		2940 m		2961 w	
51	A_1	3069	10	3069	15	$\nu_{\text{s}}\text{CH}_2$		2855 w			
50	A_1	1692	342	1660	414	$\nu\text{C}=\text{O}$, $\delta\angle\text{C}_{12}\text{O}_{14}\text{C}_{15}$, $\rho_{\omega}\text{CH}_2$	1694 s	1655 vs	1638 s	1630 vs	1633 m
49	A_1	1641	32	1638	100	νCC , $\nu\text{C}_7\text{C}_{12}$, γCC , δCH	1640 m	1620 w	1620 w	1626 vs	1627 s
48	A_1	1618	27	1613	109	νCC , $\nu\text{C}=\text{O}$, γCC , δCH				1617 m	1618 m
							1600 s	1603 m	1602 w	1601 m	1602 vs
47	A_1	1530	4	1530	8	δCH , γCC , $\nu\text{C}_7\text{C}_{12}$		1583 m		1578 m	1579 m
46	A_1	1488	34	1488	55	δCH , γCC , νCC		1496 w	1444 s	1498 m	1499 w
45	A_1	1471	34	1471	55	$\delta_{\text{s}}\text{CH}_2$		1455 m	1421 s	1454 s	1456 w
								1416 m		1422 s	1442 w
								1349 s	1362 vs	1364 s	1378 s
44	A_1	1375	374	1377	563	$\nu_{\text{as}}\text{C}_7\text{C}_{12}\text{O}_{14}$, $\delta_{\text{s}}\text{CH}_2$, $\rho_{\omega}\text{CH}_2$, δCH					
43	A_1	1356	15	1359	25	δCH					
42	A_1	1336	23	1337	39	νCC , γCC , δCH , $\delta\angle\text{C}_7\text{C}_{12}\text{O}_{14}$, $\rho_{\omega}\text{CH}_2$		1320 w		1325 w	1329 w
								1310 w		1318 w	
41	A_1	1282	101	1276	113	$\nu_{\text{s}}\text{C}_7\text{C}_{12}\text{O}_{14}$, $\rho_{\omega}\text{CH}_2$		1258 s	1261 w	1275 w	1286 m
40	A_2	1239	11	1236	11	$\rho_{\text{t}}\text{CH}_2$		1240 w	1234 w	1257 s	1255 w
39	A_1	1203	30	1205	47	δCH		1200 vw	1200 w	1219 w	1216 w
										1209 w	
38	A_1	1188	1	1193	2	δCH		1177 w	1183 w	1168 w	1188 w
											1179 w
											1165 m
37	A_1	1148	86	1150	111	$\nu_{\text{as}}\text{C}_{12}\text{O}_{14}\text{C}_{15}$, $\nu\text{C}_7\text{C}_{12}$, δCH , γCC		1130 s	1139 m	1142 s	1140 m
											1130 m
36	A_1	1105	21	1107	29	δCH , νCC		1095 w		1104 w	
35	A_1	1048	15	1047	17	γCC , νCC , δCH		1070 w		1075 w	
34	A_1	1022	~0	1021	~0	γCC , CC		1025 w			
33	A_2	1013	~0	1021	1	ρCH , ρCC			1039 s	1028 m	1027 m
32	A_2	996	~0	998	~0	ρCH , ρCC				1002 w	999 vs
31	A_1	987	18	986	30	$\nu\text{O}_{14}\text{C}_{15}$, $\delta\angle\text{C}_{15}\text{SiO}_{13}$, $\delta\angle\text{C}_7\text{C}_{12}\text{O}_{14}$, γCC	990 s	963 vs	973 s	980 w	986 w
30	A_2	963	22	967	1	ρCH				969 m	964 w
29	A_2	962	180	946	230	$\nu_{\text{as}}\text{F}_{\text{eq}20}\text{SiF}_{\text{eq}21}$, $\rho_{\text{r}}\text{CH}_2$, ρCH , $\rho\angle\text{C}_{15}\text{SiO}_{13}$			945 m	948 m	
										938 vs	931 w
28	A_1	903	1	905	1	$\delta\angle\text{O}_{13}\text{C}_{12}\text{O}_{14}$, $\delta\angle\text{C}_{12}\text{O}_{14}\text{C}_{15}$, $\delta\angle\text{O}_{14}\text{C}_{15}\text{Si}$, $\rho_{\omega}\text{CH}_2$, γCC					902 m
27	A_1	866	106	862	~0	$\nu_{\text{s}}\text{F}_{\text{eq}20}\text{SiF}_{\text{eq}21}$, νSiC_{15} , $\nu\text{C}_{15}\text{O}_{14}$, $\delta\angle\text{O}_{13}\text{C}_{12}\text{O}_{14}$	890 s		864 m	863 s	
26	A_2	863	~0	855	171	ρCH					
25	A_2	824	2	828	3	ρCH , $\rho\angle\text{O}_{13}\text{C}_{12}\text{O}_{14}$					811 m
24	A_1	808	385	771	525	$\nu\text{Si}-\text{F}_{\text{ax}}$, $\delta\angle\text{O}_{14}\text{C}_{15}\text{Si}$	836 s		785 s	783 s	795 m
23	A_2	739	~0	736	3	$\rho_{\text{r}}\text{CH}_2$, $\rho\angle\text{O}_{14}\text{C}_{15}\text{Si}$					
22	A_2	730	72	734	78	ρCH , $\rho\angle\text{C}_7\text{C}_{12}\text{O}_{14}$					774 w
21	A_1	709	20	709	45	δCH , γCC , $\nu\text{C}_7\text{C}_{12}$, $\delta\angle\text{C}_{12}\text{O}_{14}\text{C}_{15}$, $\delta\angle\text{O}_{14}\text{C}_{15}\text{Si}$		715 s		719 s	
20	A_2	697	21	696	27	ρCC , ρCH		694 w		695 w	698 m
19	A_1	661	19	666	36	$\nu\text{O} \rightarrow \text{Si}$, νSiC_{15} , $\delta\angle\text{C}_{12}\text{O}_{14}\text{C}_{15}$, $\delta\angle\text{C}_{12}\text{O}_{13}\text{Si}$		681 m		684 m	679 w
18	A_1	633	~0	633	1	γCC , δCH				615 w	617 m
17	A_1	539	4	544	4	$\delta_{\omega}\text{SiF}_3$, $\delta\angle\text{C}_{12}\text{O}_{14}\text{C}_{15}$		542 w		548 w	548 w
16	A_1	477	50	487	69	$\nu\text{O} \rightarrow \text{Si}$, $\delta\angle\text{C}_{12}\text{O}_{14}\text{C}_{15}$, $\delta\angle\text{C}_5\text{C}_7\text{C}_{12}$, $\delta_{\omega}\text{SiF}_3$		484 m	495 w	495 s	
15	A_2	457	1	457	1	ρCC				443 w	
14	A_2	413	~0	413	~0	ρCC				418 w	417 m
13	A_1	394	22	398	24	$\nu\text{O} \rightarrow \text{Si}$, $\nu\text{C}_7\text{C}_{12}$, $\delta_{\omega}\text{SiF}_3$, $\delta\angle\text{C}_5\text{C}_7\text{C}_{12}$, γCC					403 w
12	A_2	342	10	349	11	$\rho_{\text{t}}\text{CH}_2$, $\delta_{\text{as}}\text{SiF}_3$					371 w
11	A_1	322	83	332	173	$\nu\text{O} \rightarrow \text{Si}$, $\rho_{\omega}\text{SiF}_{\text{eq}20}\text{F}_{\text{eq}21}$, $\delta\angle\text{C}_{12}\text{O}_{14}\text{C}_{15}$					360 w
10	A_1	315	34	317	28	$\nu\text{O} \rightarrow \text{Si}$, $\delta\angle\text{C}_5\text{C}_7\text{C}_{12}$, $\delta_{\omega}\text{SiF}_3$					326 w

(continued on next page)

Table 4 (continued)

No.	Sym	Calculation				Assignment	Experiment, ν				
		$\epsilon = 1$		$\epsilon = 35.9$			IR				Raman
		ν	I	ν	I		$\epsilon = 1$	$\epsilon = 2.28$	$\epsilon = 35.9$	Tab	Solid
					460 K	KBr					
9	A_2	284	3	302	4	$\rho_t C_7 C_{12} O_{13} Si$, $\rho_t CH_2$, ρCC					235 s
8	A_2	218	1	221	1	$\rho_t C_{12} O_{14} C_{15} Si$, $\rho_t CH_2$, $\rho \angle C_5 C_7 C_{12}$					217 w
7	A_1	177	26	186	53	$\nu O \rightarrow Si$, $\delta \angle O_{14} C_{15} Si$, $\rho_t SiF_3$					193 m
6	A_1	171	8	175	1	$\rho_t C_7 C_{12} O_{14} C_{15} Si$					
5	A_2	138	2	141	3	$\rho_t C_{12} O_{14} C_{15} Si$, $\rho_t CH_2$, ρ_t b.r.					
4	A_2	105	~ 0	108	~ 0	ρ_t h.c., ρ_t b.r.					107 w
3	A_1	79	9	90	8	$\nu O \rightarrow Si$, $\delta \angle O_{14} C_{15} Si$					91 w
2	A_2	47	~ 0	50	~ 0	ρ_t b.r., $\rho_t C_7 C_{12} O_{13} Si$, $\rho_t SiF_3$					
1	A_2	35	1	41	1	ρ_t b.r., ρ_t h.c., $\rho_t SiF_3$					

Types of vibrations: ν , stretching vibration of bonds; δ , internal deformation vibrations, δ_s , scissor vibration (for AX_2 groups); δ_w , umbrella vibration (for AX_3 group); external deformation vibration, ρ_r , pendular vibration (for AX_2); ρ_e , twice degenerate pendular vibration (for AX_3 group); ρ_w , fan vibration; ρ_t , torsion-deformation vibration (twist); ρ_τ , torsion vibration; benzene ring (b.r.) vibrations, γCC , planar skeleton vibration; δCH , planar deformation vibration of CH bonds with a change of $\angle CCH$ valence angles; ρCC , non-planar deformation of CC bonds; ρCH , non-planar deformation of CH bonds; ρ_t h.c., torsion vibration in five-member heterocycle.

^a Characteristics of relative intensities in spectra: vs, very strong; s, strong; m, moderate; w, weak; vw, very weak.

1a molecule and an increase in frequency during medium polarity growth were also used as the spectral criteria of an existence and strength of intramolecular $=O \rightarrow Si$ coordinate bond [2,3]. According to our calculation, the form of normal vibration 44 (Table 4) in **1a** isomer spectrum does not correspond to the standard interpretation and does belong to asymmetric vibration ν_{as} of $C_7-C_{12}-O_{14}$ group with supplementary contribution from $\delta_s CH_2$, $\rho_w CH_2$ methylene group vibrations, and angled deformations $\angle CCH$ of benzene ring. The $\nu_s C_7-C_{12}-O_{14}$ symmetrical vibration of A_1 symmetry (with additional contribution from $\rho_w CH_2$ vibrations of coordinate heterocycle methylene group) corresponds to the normal vibration 41 with 1282 cm^{-1} frequency. The scale factor for these vibrations is equal to 0.98. In **1b** acyclic isomer spectrum, the $\nu_{as} C_7-C_{12}-O_{14}$ vibration corresponds to one of most intensive normal vibration 41 with 1262 cm^{-1} frequency (Table 5). The DFT calculation reproduces a sharp increase of this vibration frequency by 114 cm^{-1} in the formation of intramolecular $=O \rightarrow Si$ coordinate bond in a gas phase. According to the theoretical estimate of the medium effect, the transition from a gas phase to acetonitrile is accompanied by a frequency increase of coordination-sensitive vibration ν_{44} in spectrum **1a** only by 2 cm^{-1} , vs. experimentally observed of 15 cm^{-1} .

2.7. 800–1200 cm^{-1} Region

This region of the spectrum contains bands of important stretching vibrations of the SiF_3 group, whose atoms directly participate in the formation of the 3-center, 4-electron axial bond in **1a** isomer. Two bands of valence vibrations $\nu_{as} Si-F$ and $\nu_s Si-F$ exist in tetra-valence silicon compounds containing SiF_3 group with local C_{3v} symmetry ($RSiF_3$) [3]. In the IR spectrum of a model

compound (tribenzyloxypropyl)trifluorosilane, $C_6H_5-C(=O)O(CH_2)_3SiF_3$, with a tetracoordinate silicon atom, the bands at 950 and 876 cm^{-1} (the CCl_4 medium) have been assigned to the corresponding vibrations [21]. These bands are not sensitive to variations in the medium polarity.

In the IR spectrum of an **1a** cyclic isomer in a gas phase at $T = 400\text{ K}$ there are three intensive bands at 990 , 890 and 830 cm^{-1} that were assigned to $\nu_{as} Si-F_{eq}$, $\nu_s Si-F_{eq}$, and $\nu Si-F_{ax}$ vibrations for trigonal-bipyramidal silicon atom configuration were detected [2,3]. The presence in the isomer **1a** spectrum of an intense band at 836 cm^{-1} (gas phase) corresponding to the $Si-F_{ax}$ bond stretching vibration provides a strong evidence for the existence of trigonal-bipyramidal surrounding of the silicon atom [1–3]. According to the calculation, the corresponding normal vibration 24 (scale factor 1.03) is mainly localized on $Si-F_{ax}$ bond and is related only to deformational vibration $\delta \angle O_{14} C_{15} Si$.

The calculated stretching vibration frequencies of equatorial bonds $\nu_{as} Si-F_{eq}/\nu_s Si-F_{eq}$ are equal to $965/957\text{ cm}^{-1}$ and $962/866\text{ cm}^{-1}$ for isolated isomers **1b** and **1a** (Tables 4, 5). The scale factors for these vibrations are equal $0.98/0.92$ and $1.03/1.03$, respectively. Of these, only the $\nu_s Si-F_{eq}$ vibration is sensitive to conformation variation. Its frequency decreases by 91 cm^{-1} in the formation of intramolecular $=O \rightarrow Si$ coordinate bond in a gas phase (Table 4).

As experimentally established, the $\nu Si-F_{ax}$ and $\nu Si-F_{eq}$ values decrease in the row $\Delta \nu Si-F_{ax} > \Delta \nu_{as} Si-F_{eq}$ when the medium polarity increases from a gas phase to acetonitrile. The B3LYP calculation reasonably reproduces the experimentally observed decrease of frequencies, $\Delta \nu Si-F_{ax} = 37\text{ cm}^{-1}$ (by experiment 51 cm^{-1}) and $\Delta \nu_{as} Si-F_{eq} = 16\text{ cm}^{-1}$ (by experiment 45 cm^{-1}), during above transition from a gas phase to acetonitrile.

Table 5

The calculated DFT(B3LYP)/6-311 + G(2d,p) characteristics of vibration spectrum of **1a** isomer containing a tetracoordinate silicon atom (frequency ν , cm^{-1} , intensity I , KM/mol)

No.	Sym.	$\epsilon = 1$		$\epsilon = 35.9$		Assignment
		ν	I	ν	I	
57	A_1	3210	2	3209	3	νCH
56	A_1	3202	4	3202	5	νCH
55	A_1	3188	12	3188	13	νCH
54	A_1	3179	9	3180	9	νCH
53	A_1	3167	1	3168	0.2	νCH
52	A_2	3080	3	3077	3	$\nu_{\text{as}}\text{CH}_2$
51	A_1	3042	17	3039	24	$\nu_{\text{s}}\text{CH}_2$
50	A_1	1767	274	1764	337	$\nu\text{C}=\text{O}$, $\delta\angle\text{C}_8\text{C}_7\text{O}_{12}$
49	A_1	1641	18	1640	26	νCC , $\nu\text{C}_7\text{C}_{12}$, γCC , δCH
48	A_1	1621	5	1621	6	νCC , γCC , δCH
47	A_1	1529	1	1529	1	δCH , γCC , $\nu\text{C}_7\text{C}_{12}$
46	A_1	1486	15	1486	18	δCH , γCC , νCC
45	A_1	1470	11	1470	13	$\delta_{\text{s}}\text{CH}_2$
44	A_1	1354	5	1355	5	δCH
43	A_1	1337	64	1337	48	δCH , $\delta\rho_{\omega}\text{CH}_2$, νCC , γCC , $\delta\angle\text{C}_{12}\text{O}_{14}\text{C}_{15}$
42	A_1	1333	53	1333	84	$\rho_{\omega}\text{CH}_2$, δCH
41	A_1	1262	315	1259	385	$\nu_{\text{as}}\text{C}_7\text{C}_{12}\text{O}_{14}$, $\rho_{\omega}\text{CH}_2$, δCH
40	A_2	1235	12	1235	13	$\rho_{\text{t}}\text{CH}_2$
39	A_1	1200	43	1200	59	δCH
38	A_1	1187	1	1188	1	δCH
37	A_1	1124	158	1121	186	$\nu_{\text{s}}\text{C}_7\text{C}_{12}\text{O}_{14}$, δCH , γCC , $\rho_{\omega}\text{CH}_2$
36	A_1	1100	74	1098	124	$\nu_{\text{as}}\text{C}_{12}\text{O}_{14}\text{C}_{15}$, δCH , νCC ,
35	A_1	1049	18	1049	22	γCC , νCC , δCH
34	A_1	1022	34	1022	4	γCC , νCC
33	A_2	1011	33	1013	~ 0	ρCH , ρCC
32	A_1	996	41	997	51	$\nu_{\text{s}}\text{C}_{12}\text{O}_{14}\text{C}_{15}$, γCC
31	A_2	995	~ 0	995	~ 0	ρCH , ρCC
30	A_2	965	184	963	166	$\nu_{\text{as}}\text{F}_{20}\text{SiF}_{21}$, $\rho_{\text{t}}\text{CH}_2$, ρCH , ρCC
29	A_2	960	15	960	55	ρCH
28	A_1	957	161	952	204	$\nu_{\text{s}}\text{F}_{20}\text{SiF}_{21}$, $\delta\angle\text{C}_{12}\text{O}_{14}\text{C}_{15}$
27	A_1	886	111	884	140	νSiC_{15} , $\delta_{\omega}\text{SiF}_3$, $\rho_{\text{t}}\text{CH}_2$, $\delta\angle\text{C}_{12}\text{O}_{14}\text{C}_{15}$, $\delta\angle\text{O}_{13}\text{C}_{12}\text{O}_{14}$
26	A_2	863	~ 0	863	~ 0	ρCH
25	A_1	856	185	853	262	$\nu\text{C}_{12}\text{O}_{14}$, $\delta\angle\text{O}_{13}\text{C}_{12}\text{O}_{14}$, $\delta_{\omega}\text{SiF}_3$, γCC
24	A_2	823	1	823	1	ρCH , ρCC , $\rho\angle\text{C}_7\text{C}_{12}\text{O}_{14}$, $\rho_{\text{t}}\text{CH}_2$
23	A_2	780	2	779	3	$\rho_{\text{t}}\text{CH}_2$, $\rho\angle\text{O}_{14}\text{C}_{15}\text{Si}$
22	A_2	721	84	720	94	ρCH , $\rho\angle\text{C}_7\text{C}_{12}\text{O}_{14}$
21	A_1	719	2	719	1	δCH , γCC , $\nu\text{C}_7\text{C}_{12}$, $\delta\angle\text{C}_{12}\text{O}_{14}\text{C}_{15}$
20	A_2	701	12	701	15	ρCC , ρCH
19	A_1	667	7	667	10	νSiC_{15} , γCC , $\delta\angle\text{O}_{13}\text{C}_{12}\text{O}_{14}$
18	A_1	634	1	634	1	γCC , δCH , $\delta\angle\text{C}_7\text{C}_{12}\text{O}_{13}$
17	A_1	497	2	497	2	$\delta\angle\text{C}_5\text{C}_7\text{C}_{12}$, $\delta\angle\text{C}_7\text{C}_{12}\text{O}_{14}$, $\delta\angle\text{O}_{14}\text{C}_{15}\text{Si}$
16	A_2	453	1	452	~ 0	ρCC
15	A_2	415	0	415	~ 0	ρCC
14	A_1	413	123	410	159	$\delta\angle\text{C}_{12}\text{O}_{14}\text{C}_{15}$, $\delta_{\omega}\text{SiF}_3$, $\delta\angle\text{O}_{13}\text{C}_{12}\text{O}_{14}$
13	A_1	380	21	381	30	$\nu\text{C}_7\text{C}_{12}$, $\delta_{\omega}\text{SiF}_3$, $\delta\angle\text{C}_5\text{C}_7\text{C}_{12}$, γCC
12	A_1	324	11	324	13	$\rho_{\text{t}}\text{SiF}_3$, $\delta\angle\text{C}_5\text{C}_7\text{C}_{12}$, $\delta\angle\text{C}_{12}\text{O}_{14}\text{C}_{15}$
11	A_2	312	16	312	18	$\rho_{\text{t}}\text{CH}_2$, $\rho_{\text{t}}\text{SiF}_3$
10	A_1	267	7	267	9	$\delta\angle\text{C}_5\text{C}_7\text{C}_{12}$, $\delta\angle\text{C}_{12}\text{O}_{14}\text{C}_{15}$, $\delta_{\omega}\text{SiF}_3$
9	A_2	224	2	223	2	$\rho\angle\text{O}_{14}\text{C}_{15}\text{Si}$, $\rho_{\text{t}}\text{CH}_2$
8	A_1	204	1	204	13	$\rho\angle\text{C}_{12}\text{O}_{14}\text{C}_{15}$, $\delta_{\omega}\text{SiF}_3$
7	A_2	195	1	195	1	ρ_{t} b.r., $\rho_{\text{t}}\text{C}_7\text{C}_{12}\text{O}_{14}\text{C}_{15}$, $\rho_{\text{t}}\text{SiF}_3$, $\rho_{\text{t}}\text{CH}_2$
6	A_1	145	2	145	2	$\rho_{\text{t}}\text{C}_7\text{C}_{12}\text{O}_{14}\text{C}_{15}\text{Si}$, ρ_{t} b.r., $\rho_{\text{t}}\text{SiF}_3$
5	A_2	114	1	114	2	$\rho_{\text{t}}\text{C}_{12}\text{O}_{14}\text{C}_{15}\text{Si}$, $\rho_{\text{t}}\text{CH}_2$, ρ_{t} b.r.
4	A_2	60	3	60	3	ρ_{t} b.r., $\rho_{\text{t}}\text{C}_7\text{C}_{12}\text{O}_{14}\text{C}_{15}$
3	A_1	53	1	54	2	$\delta\angle\text{O}_{14}\text{C}_{15}\text{Si}$
2	A_2	33	~ 0	33	~ 0	ρ_{t} b.r., $\rho_{\text{t}}\text{C}_{12}\text{O}_{14}\text{C}_{15}\text{Si}$, $\rho_{\text{t}}\text{SiF}_3$
1	A_2	22	1	21	1	ρ_{t} b.r., $\rho_{\text{t}}\text{SiF}_3$

In the spectrum of isomer **1a** the traditional asymmetric vibration $\nu_{\text{as}}\text{C}_{12}(\text{=O}_{13})\text{--O}_{14}\text{--C}_{15}$ of the ester fragment corresponds to normal vibration 37 of A_1 symmetry at frequency 1148 cm^{-1} . It is not characteristic in form and contains contributions from vibrations $\nu_{\text{C}_7\text{C}_{12}}$, δCH , and γCC . The asymmetric vibration $\nu_{\text{as}}\text{C}_{12}(\text{=O}_{13})\text{--O}_{14}\text{--C}_{15}$ in the **1b** acyclic isomer spectrum is included in vibration 36 of A_1 symmetry at frequency 1100 cm^{-1} . Its conformational sensitivity (transition from the Si tetra- to pentacoordinate compound) in **1a** isomer spectrum is less clearly expressed than that of asymmetric vibration 44 of the $\text{C}_7\text{--C}_{12}\text{--O}_{14}$ group. In the formation of intramolecular $\text{O} \rightarrow \text{Si}$ coordinate bond in the **1a** molecule in gas phase, the calculation predicts an increase in frequency of this vibration by 48 cm^{-1} in comparison with 114 cm^{-1} for $\nu_{\text{as}}\text{C}_7\text{C}_{12}\text{O}_{14}$. The calculated evaluation of the medium influence during the transition from gas phase to acetonitrile predicts only a small increase in vibration frequency ν_{36} by about 2 cm^{-1} .

2.8. 200–800 cm^{-1} region

The calculation of (formyloxymethyl)trifluorosilyl isomer vibrational spectrum with intramolecular $\text{=O} \rightarrow \text{Si}$ coordination in the valence-force field approximation indicates the contribution from deformation of this bond into three low-frequency vibrations at 360, 330, and 218 cm^{-1} [7]. The distinct feature of calculated DFT(B3LYP)/6-311 + G(2d,p) spectra of an **1a** cyclic isomer is the contribution of deformation of $\text{=O} \rightarrow \text{Si}$ coordinate bond in the wider region of the spectrum $700\text{--}70\text{ cm}^{-1}$ (Table 4) (in normal vibrations 19, 16, 13, 11, 10, 7, and 3 with calculated frequencies, respectively, 661 (SF = 1.03), 477 (SF = 1.01), 394, 322, 315, 177, and 79 cm^{-1}). The most significant contribution of $\text{=O} \rightarrow \text{Si}$ bond deformation was observed in vibrations with calculated frequencies 477, 322, 315, and 177 cm^{-1} . This fact is confirmed by their intensity increase 10–50 times in comparison with the corresponding vibrations of a **1b** acyclic isomer not containing $\text{=O} \rightarrow \text{Si}$ bond (Tables 4, 5). According to calculation, during the transition from a gas phase to the acetonitrile solution, the largest changes of frequencies in the **1a** isomer vibration spectrum were detected for vibrations 477, 322, 315, and 177 cm^{-1} . For the normal vibrations 19, 16, 13, 11, 10, 7, and 3, the calculation shows an increase in frequencies by 4–11 cm^{-1} with growing the medium polarity in the range of $\varepsilon = 1\text{--}36$. For normal vibration at 477 cm^{-1} , the calculation is supported by the experimental data of band frequency increase in going from solution in CCl_4 to CH_3CN ($484 \rightarrow 495\text{ cm}^{-1}$). All the above vibrations have of complicated form and mainly include the planar deformations of angles $\angle\text{C}_{12}\text{O}_{14}\text{C}_{15}$ and $\angle\text{C}_{12}\text{O}_{13}\text{Si}$ of heterocycle, and angle $\angle\text{C}_5\text{C}_7\text{C}_{12}$.

2.9. Region $< 200\text{ cm}^{-1}$

Calculation of normal vibrations in this region of **1a** and **1b** spectra reproduces 7 frequencies of complicated form vibrations. The normal vibrations 7, 6, and 3 are of the interest for the analysis of coordination.

The form of vibration 7 and its symmetry in the spectra of **1a** and **1b** isomers in a gas phase change during the transition from acyclic isomer to coordinate cyclic isomer. In the theoretical spectrum of the **1b** acyclic isomer, a low-intensity normal vibration 7 of A_2 symmetry at 195 cm^{-1} corresponds to the major contribution of torsional deformations of the benzene ring, $\text{C}_7\text{C}_{12}\text{O}_{14}\text{C}_{15}$ chain, SiF_3 and CH_2 groups. The scale factor for this vibration is equal to 1.09. In the spectrum of an **1a** cyclic isomer, the normal vibration 7 of A_1 symmetry, its frequency by 171 cm^{-1} is sufficiently lower, whereas its intensity is one order of magnitude higher. The vibration is major localized on the coordinate bond $\text{=O} \rightarrow \text{Si}$ and mixed only with deformation of the angle $\angle\text{O}_{14}\text{C}_{15}\text{Si}$ and torsional vibrations of SiF_3 group. In the spectrum of acyclic isomer **1b** normal vibration 6 of A_1 symmetry at 145 cm^{-1} corresponds to torsional deformations of the benzene ring and open chain $\text{C}(\text{=O})\text{OCH}_2\text{SiF}_3$. In coordinate structure **1a** spectrum the frequency of this vibration is higher 26 cm^{-1} (171 cm^{-1}). The normal vibration 3 with A_1 symmetry at 53 cm^{-1} in the spectrum of **1b** isomer represents the deformation of angle $\angle\text{O}_{14}\text{C}_{15}\text{Si}$. In the spectrum of an **1a** cyclic isomer, the form of this normal vibration corresponds to deformations of $\text{=O} \rightarrow \text{Si}$ bond and angle $\angle\text{O}_{14}\text{C}_{15}\text{Si}$ and the frequency 79 cm^{-1} is much higher. The scale factor of the vibration is 1.14. The vibrations 7 and 3 are most sensitive to change of medium polarity. In acetonitrile solution, their frequencies are increase on 9 and 11 cm^{-1} , respectively. Practically, normal vibrations 7 and 3 may be regarded as vibrations localized on intramolecular $\text{=O} \rightarrow \text{Si}$ coordinate bond.

The normal vibrations 5, 4, 2, and 1 of A_2 symmetry at 138, 105, 47 and 35 cm^{-1} , respectively, in gas phase spectrum of **1a** isomer correspond to the torsional deformations of a benzene ring mixed with different torsional deformations of coordinate heterocycle. The scale factor for normal vibration 4 is 1.02. In the presence of the $\text{=O} \rightarrow \text{Si}$ coordinate bond (in going from **1b** to **1a** isomer), frequencies of modes 5, 4, 2 and 1 increase on 24, 45, 14 and 13 cm^{-1} , respectively. Most probably, the formation of the coordinate heterocycle and charge redistribution in the carboxyl group change the force field of the molecule and reflect the effect of increasing of conjugation energy between π -systems of the carboxyl group and benzene ring. The increase of medium polarity during the transition to acetonitrile provides the further increase in frequencies by 3–6 cm^{-1} .

Thus, it has been established that the DFT(B3LYP)/6-311 + G(2d,p) calculation in the Onsager SCRF

approximation describes effect of unspecific mediums on the change of coordination energy, dipole moment and band frequencies in the vibrational spectrum of BFS molecule is adequate to the experimental data and the theoretical model of three-center, 4-electron (3c–4e) binding for the C=O \rightarrow Si–F_{ax} fragment.

References

- [1] M.G. Voronkov, *Izv. Akad. Nauk SSSR* 12 (1991) 2664 (Russ. Chem. Bull., Int. Ed. 12 (1991) Engl. Transl.).
- [2] G.A. Gavrilova, N.N. Chipanina, Yu.L. Frolov, L.I. Gubanova, V.M. D'yakov, M.G. Voronkov, *Izv. Akad. Nauk SSSR* 10 (1984) 2251 (Russ. Chem. Bull., Int. Ed. 10 (1984) Engl. Transl.).
- [3] Yu.L. Frolov, M.G. Voronkov, *J. Mol. Struct.* 217 (1990) 265.
- [4] Yu.L. Frolov, A.V. Abramov, N.N. Chipanina, T.N. Aksamentova, M.G. Voronkov, *Zh. Struct. Khim.* 40 (1999) 1051 (*J. Struct. Chem.* 40 (1999) Engl. Transl.).
- [5] E.A. Zelbst, V.E. Shklover, Yu.T. Struchkov, Yu.L. Frolov, A.A. Kashaev, L.I. Gubanova, V.M. D'yakov, M.G. Voronkov, *Zh. Struct. Khim.* 22 (1981) 82 (*J. Struct. Chem.* 22 (1981) Engl. Transl.).
- [6] A.A. Kashaev, E.A. Zelbst, M.P. Demidov, I.V. Rozhdestvenskaya, *Kristallografiya* 30 (1985) 1186.
- [7] G.A. Gavrilova, N.N. Chipanina, Yu.L. Frolov, L.I. Gubanova, M.G. Voronkov, *J. Organometal. Chem.* 418 (1991) 291.
- [8] I.S. Ignat'ev, A.N. Lazarev, S.G. Shevchenko, V.P. Baryshok, Yu.L. Frolov, *Izv. Akad. Nauk SSSR* 7 (1986) 1518 (Russ. Chem. Bull., Int. Ed. 7 (1986) Engl. Transl.).
- [9] I.M. Lazarev, G.V. Ratovsky, E.I. Brodskaya, N.F. Lazareva, *Zh. Obshch. khim.* 73 (2003) 1127 (*Russ. J. Gen. Chem.* 73 (2003) Engl. Transl.).
- [10] E.F. Belogolova, V.F. Sidorkin, *Russ. Chem. Bull., Int. Ed.* 52 (2003) 1472.
- [11] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *GAUSSIAN 03*, Revision B. 03, Gaussian, Inc., Pittsburgh PA, 2003.
- [12] M.G. Voronkov, V.Yu. Vitkovskii, L.V. Klyba, N.N. Chipanina, L.I. Gubanova, M.S. Sorokin, Yu.L. Frolov., in: 7th International Symposium on Organosilicon Chemistry, Kyoto, 1984, PT 43, p. 245.
- [13] F.B. Van Duijneveldt, J.G.C.M. van Duijneveldt-van de Rijdt, J.H. van Lenthe, *Chem. Rev.* 94 (1994) 1873.
- [14] M.G. Voronkov (Ed.), *Advances in Organosilicon Chemistry*, Chem Series, Mir, Moscow, 1985, p. 54.
- [15] J.I. Musher, *Angew. Chem.* 81 (1969) 68.
- [16] V.F. Sidorkin, V.A. Pestunovich, M.G. Voronkov, *Russ. Chem. Rev.* 49 (1980) 414.
- [17] Yu.L. Frolov, S.G. Shevchenko, M.G. Voronkov, *J. Organomet. Chem.* 292 (1985) 159.
- [18] Yu.L. Frolov, A.B. Vashenko, *Zh. Org. Khim.* 19 (2003) 1484 (*Russ. J. Org. Chem.* 19 (2003) Engl. Transl.).
- [19] A.Yu. Timoshkin, T.N. Sevast'yanova, E.I. Davydova, A.V. Suvorov, H.F. Schaefer, *Zh. Obshch. Khim.* 72 (2002) 1674 (*Russ. J. Gen. Chem.* 72 (2002) Engl. Transl.).
- [20] G.A. Gavrilova, T.N. Aksamentova, Yu.L. Frolov, N.N. Chipanina, V.B. Modonov, L.I. Gubanova, N.V. Chernov, B. Shirchin, M.G. Voronkov, *Metalloorgan. Khim.* 3 (1990) 1266.
- [21] G.A. Gavrilova, IR spectroscopic study of the interaction of the solvent with pentacoordinate organosilicon compounds. Dissertation for a degree of Candidate of Sciences (Ph.D. Equivalent), Irkutsk, 1984, pp. 48–65.