Effect of solution on isotopic properties of complexes of SiF_4 and BF_3 in the process of separation of isotopes of Silicon and Boron by the method of chemical exchange rectification

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Ab initio calculations of isotope reduced partition function ratios (β-factors) and separation factors of isotopes of silicon and boron in the systems fluoride of the element — its complex with organic solvent have been carried out. These systems are used for separation of isotopes of boron and silicone by the method of chemical exchange rectification (chemical isotope exchange method with thermal phase reversal).

It has been shown that usual *ab initio* calculations of vibrational frequencies of the fluoride of boron or silicon and their complex with solvent cannot predict experimental values of isotope separation factor. For the correct description it is necessary to take into account the polarizing effect of solvent on the complex. To study this effect the Polarized Continuum Model (PCM) has been used. In all cases our theoretical results corresponded quite well with experimental results for the systems previously studied. This result opens up possibility of directed search for systems suitable for separation of isotopes by the method of chemical exchange rectification.

Introduction

Development of effective method for separation of isotopes of silicon is of great importance. The problem is that natural silicon, which consists mostly of isotope ^{28}Si (92.2297 at.%), also contains isotopes ^{29}Si (4.6832 at.%) and ^{30}Si (3.0872 at.%). Using of silicon with natural isotope composition as a material for microelectronics the presence of a mixture of isotopes in the crystal leads to a decrease of thermal conductivity, which increases the heat dissipation in processors and other chips.

Thus purification of silicon not only from chemical impurities but also of ^{29}Si and ^{30}Si is an important topical problem able to achieve a breakthrough in microelectronics.

Isotopes of boron are widely used in various fields of science and technology because of strong differences in their nuclear properties (the absorption thermal neutron cross-section for nuclides ^{10}B and ^{11}B differs by 80000 times). Main application of nuclide ^{10}B is nuclear power (control rods and coatings that protect against neutron radiation). Is used and the isotope ^{11}B (neutron diffraction studies, microelectronics etc.). Isotope effects of boron in nature are used as a method of research in geochemistry [1].

The most inexpensive and effective method of isotope separation is chemical isotope exchange, in particular — chemical exchange rectification (chemical isotope exchange method with thermal phase reversal). In the process of isotope separation by method of chemical exchange rectification exchanging chemical forms are gaseous volatile compound containing target isotope, and solution of labile complex of this substance in non-volatile[1] (as a rule, organic) solvent. Compared with systems using chemical reversal of the flow, chemical exchange rectification characterized by simplicity of implementation, absence of dump and several other advantages and compared with the usual rectification — high value of isotope separation factor.

The aim of this work was to develop the method for *ab initio* calculation of isotope separation factor in the system using chemical exchange rectification, that will allow for the prediction and the direct search for promising systems for isotope separation.

Adducts of silicon tetrafluoride and boron trifluoride and possibility of their use in the systems with chemical exchange rectification

Silicone tetrafluoride forms adducts with various substances containing the donor atom (N or O) [2]. Silicone atom in the molecule can increase its coordination number to 5 or 6 using two (of five) vacant *d*-orbitals.

Boron trifluoride forms complexes with various compounds containing donor

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[1]at the temperature of the process

atom of oxygen (Fig.1) or nitrogen [3]. Ethers [4], especially anisole [5] are used in practice for separation of isotopes of boron. Now search for complex-forming solvents more effective from practical and economical points of view is carried out. In particular, systems using complexes of BF_3 with trialkylphosphates and nitromethane are under study [6].

Adducts with oxygen-containing substances (donor atom O)

Complexes of silicon tetrafluoride with aliphatic alcohols

Silicone tetrafluoride is readily soluble in aliphatic alcohols. It was previously assumed that it forms complexes of type $SiF_4 \cdot 4ROH$ [7], connected by strong hydrogen bonds $H \cdots F$, with tetrahedral coordination of silicon atoms is not changed. But *ab initio* calculations of complexes of SiF_4 with alcohols consistently indicate that complexes with coordination number 6 in which two molecules of alcohol coordinated by silicon atom via oxygen atom (see Fig.2) are more stable than "hydrogen-bonded" complexes.

The evident advantage of alcohols is lability of SiF_4—alcohol complexes, which provides good kinetics of process of chemical exchange rectification. Therefore alcohols attracted the attention of researchers, and in series of papers [8–10] the results presented in Tab.1 were obtained. As can be seen from the Table, chemical exchange rectification in the system $SiF_4(gas) - SiF_4 \cdot 2ROH(liq.)$ provides high isotope separation factors. These values are approximately an order of magnitude exceed the separation factors to be achieved by other methods.

Table 1. Experimental values of $\ln \alpha_{28-30}$ in systems SiF_4 (gas) $- SiF_4 \cdot 2ROH$(liquid), measured by single equilibration method

Alcohol	T, K	$\ln \alpha$	Alcohol	T, K	$\ln \alpha$
CH_3OH	293	0.022 [8]	$C_5H_{11}OH$	277	0.040 [9]
C_2H_5OH	293	0.016 [8]		293	0.017±0.010 [10]
	297	0.020 [9]	$C_6H_{13}OH$	293	0.017 ±0.010 [10]
C_3H_7OH	297	0.020 [9]		293	0.039 [10]
C_4H_9OH	270	0.034 [9]	$C_8H_{17}OH$	293	0.019±0.020 [10]

	277	0.031 [9]	iso-C$_3$H$_7$OH	293	0.010 [8]
	293	0.017±0.004 [10]	iso-C$_3$H$_7$OH	297	0.007 [9]
	296	0.024 [9]	sec-C$_4$H$_9$OH	297	0.009 [9]
	297	0.024 [9]			
	302	0.021 [9]			

Today all works on using alcohols as a complex-forming solvents for chemical exchange rectification are experimental, search for systems with high separation factors is purely empirical. Reason for this is that the *ab initio* calculation of isotope separation factors in such systems gives the results are far from those obtained experimentally.

From our point of view, this is due to the fact that *ab initio* calculation of isotope separation factors in the system SiF$_4$ (gas) − complex SiF$_4$-alcohol (liq.) ignored the effect of solvation.

Adducts of silicone tetrafluoride with other oxygen-containing substances

Silicone tetrafluoride forms weak complexes with acetylacetone and tropolone, as well as somewhat more stable complexes of 1:2 type with oxymethylene, oxetane, tetrahydrofurane (THF), tetrahydropyran, dimethyl ether etc., stable in solutions at low temperatures [2].

The most stable among these substances, SiF$_4$·2(CH$_2$)$_3$O (ΔH^0 for the reaction SiF$_4$·2 ligand (solid) = SiF$_4$(gas) + 2 ligand (gas) is 56.9 kJ/mol) exists up to 13.6°C, others are stable only at the temperatures below 0°C.

In addition, silicone tetrafluoride forms very stable 1:2 complexes with pyridine-N-oxide, dimethylamine-N-oxide, trimethylphosphine oxide, tricyclohexylphosphine oxide, dimethylformamide and dimethyl sulfoxide. These compounds are white microcrystalline substances with melting point above 110°C, insoluble in non-polar organic solvents. These complexes are too stable and therefore unsuitable for separation of isotopes by the method of chemical exchange rectification.

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Adducts of SiF$_4$ and BF$_3$ with ammonia and amines (nitrogen as a donor atom)

Silicone tetrafluoride forms strong complexes with ammonia and amines, in which one SiF$_4$ molecule bonded with two (rarely one) donor atoms of nitrogen. Most of these complexes are solid substances soluble in organic solvents and stable at room temperature.

The use of these adducts can provide significant isotope separation factor in the system SiF$_4$(gas) $-$ complex of SiF$_4$ (liq.), but complexes with N-donor ligands are unsuitable for separation of isotopes of silicon by the method of chemical exchange rectification, because they are too stable compounds and therefore promise bad kinetics of isotope exchange.

Ab initio study of complexes of silicone tetrafluoride and boron trifluoride

All *ab initio* computations were performed using the PC GAMESS[2] [11,12] program. For basis set search we have performed preliminary calculations of equilibrium geometric parameters and vibrational frequencies for molecules SiF$_4$ and BF$_3$ using various bases (see Tab.2). As one can see from Tab.2, contrary to the expected, introduction of polarization and diffuse functions does not improve the agreement between the experimental and calculated results. Accordingly, we have used bases RHF/6-311 and MP2/6-311. β-factors and isotope separation factors have been calculated as usual (see [13]). Results of calculation of β-factors for a number of complexes of SiF$_4$ and BF$_3$ with organic solvents are presented in Tab. 3 while in Tab. 4 we have presented calculated isotope separation factors together with experimental data.

Table 2. Vibrational frequencies (cm^{-1}) and bond lengths (Å) in molecules SiF$_4$ and BF$_3$, calculated by *ab initio* methods using various bases. (In brackets we present the degeneracy of corresponding frequency)

[2]now Firefly

	SiF$_4$				
	Exp. [14]	RHF/6-311	MP2/6-311	RHF/6-311++G**	MP2/6-311++G**
$\nu_1(1)$	800	834	773	846	781
$\nu_2(2)$	264	269	251	281	262
$\nu_3(3)$	1014.4	1078	1012	1083	1013
$\nu_4(3)$	386.35	401	375	412	383
r(Si–F)	1.555	1.5458	1.5739	1.5429	1.5700
	BF$_3$				
	Exp. [14]	RHF/6-311	MP2/6-311	RHF/6-311++G**	MP2/6-311++G**
$\nu_1(1)$	888	942	877	950	888
$\nu_2(1)$	696.7	744	698	741	695
$\nu_3(2)$	1463.3	1550	1450	1557	1459
$\nu_4(2)$	480.7	502	470	510	476
r(B–F)	1.3110	1.2922	1.3137	1.2925	1.3123

Table 3. Effect of solvent and basis on $\ln \beta$ values
of complexes SiF$_4$ and BF$_3$ (T=300K)

Molecule	RHF/6-311	MP2/6-311	RHF/6-311++G**	MP2/6-311++G**
Substitution ^{28}Si/^{30}Si				
SiF$_4^\dagger$	0.0889	0.0805	0.0898	0.0810
SiF$_4 \cdot$ 2CH$_3$OH	0.0716	0.0659	0.0695	—
PCM	0.0648	0.0610	—	—
SiF$_4 \cdot$ 2C$_2$H$_5$OH	0.0713	0.0656	0.0692	—
PCM	0.0656	0.0609	—	—
SiF$_4 \cdot$ 2C$_3$H$_7$OH	0.0713	—	—	—
SiF$_4 \cdot$ 2i-C$_3$H$_7$OH	0.0699	—	—	—
SiF$_4 \cdot$ 2acetone	0.0692	0.0637	—	—
PCM	0.0677	0.0578	—	—
SiF$_4 \cdot$ 2THF	0.0699	0.0646	—	—

PCM	0.0657	—	—	—
Substitution ^{10}B/^{11}B				
BF$_3$	0.2417	0.2199	0.2429	0.2213
BF$_3 \cdot$ anisole	0.2304	0.1899	—	—
PCM	0.2012	0.1852		
BF$_3 \cdot$ acetone	0.2058	0.1895	—	—
PCM	0.2055	0.1840	—	—
BF$_3 \cdot$ CH$_3$NO$_2$	0.2350	0.2059	0.2369	0.2092
PCM	0.1968	0.1802	0.2005	0.1832
BF$_3 \cdot$ THF	0.2090	0.1930		
PCM	0.2042	0.1871		
BF$_3 \cdot$ NH$_3$	0.2127	0.1972	0.2127	0.1956
BF$_3 \cdot$ aniline	0.2101	0.1944	—	—
PCM	0.2096	0.1884	—	—

†Value of $\ln \beta$ for SiF$_4$, estimated from experimental frequencies is 0.082 at 300K

Table 4. Effect of solvent and basis on separation factors ($\ln \alpha$, T=300K) in the system SiF$_4$ (gas) — complex of SiF$_4$ (liq.) and BF$_3$ (gas) — complex of BF$_3$ (liq.)

Molecule	Exp.	RHF/6-311	MP2/6-311	RHF/6-311++G**	MP2/6-311++G**
Substitution ^{28}Si/^{30}Si					
SiF$_4 \cdot$ 2CH$_3$OH	0.022 [8]	0.017	0.015	0.020	—
PCM		0.024	0.020	—	—
SiF$_4 \cdot$ 2C$_2$H$_5$OH	0.016— 0.020 [8, 9]	0.018	0.015	0.021	—
PCM		0.023	0.020	—	—
SiF$_4 \cdot$ 2C$_3$H$_7$OH	0.020 [9]	0.018	—	—	—
SiF$_4 \cdot$ 2i-C$_3$H$_7$OH		0.019	—	—	—
SiF$_4 \cdot$ 2acetone		0.020	0.017	—	—
PCM		0.021	0.023	—	—

SiF$_4 \cdot$ 2THF		0.019	0.016	—	—
PCM		0.023	—	—	—
Substitution ^{10}B/^{11}B					
BF$_3 \cdot$ anisole	0.030 [6]	0.011	0.030	—	—
PCM		0.041	0.035	—	—
BF$_3 \cdot$ acetone		0.036	0.030	—	—
PCM		0.036	0.036	—	—
BF$_3 \cdot$ CH$_3$NO$_2$	0.044 [6]	0.007	0.014	0.006	0.012
PCM		0.045	0.040	0.042	0.038
BF$_3 \cdot$ THF	0.042 [4]	0.033	0.027		
PCM		0.038	0.033		
BF$_3 \cdot$ NH$_3$		0.029	0.023	0.030	0.026
BF$_3 \cdot$ aniline		0.032	0.026	—	—
PCM		0.032	0.032	—	—

Account for the effect of solvate

When calculating the vibrational frequencies and β-factors of molecules in solution, effect of electrostatic interaction with solvent on solute molecule is usually neglected. In most cases (solutions in non-polar solvents etc.) this approach is quite reasonable. However, when solvent is polar and molecule of solute includes polar bonds, influence of solvent on solute molecule may be important. To study this issue with respect to complexes of SiF$_4$ and BF$_3$ we have used continuum model of solvation.

Continuum models of solvation form a cavity containing the solute molecule, while the solvent outside the cavity is thought of as a continuous medium and is categorized by some physical data (the dielectric constant etc.). The electric field of the charged particles comprising the solute interact with this background medium, producing a polarization in it, which in turn feeds back upon the wavefunction of the solute.

Currently one of the best models of this type is Polarizable Continuum Model (PCM) [15–17].

This method places a solute in a cavity formed by a union of spheres centered on

each atom. Compared with other models, PCM model also includes a more exact treatment of the electrostatic interaction with the solvent, as the electrostatic potential of the solute generates an "apparent surface charge" on the surface of the cavity. The computational procedure divides this surface into small tesserae, on which the surface charge (and contributions to the gradient) are evaluated. Procedures are provided not only for the computation of the electrostatic interaction of the solute with the apparent surface charges, but also for the cavitation energy, and dispersion and repulsion contributions to the solvation free energy.

PCM model is implemented in the program PC GAMESS (second order Møller-Plesset perturbation theory (MP2) — starting with version 7.1). Recently, this model has been successfully applied for theoretical calculation of separation factor of iron isotopes in the system Fe^{2+} — Fe^{3+} [18].

In PCM model solvent characteristics are effective radius of solvent molecule (RSOLV) and dielectric constant (EPS). Calculation of some additional properties in case of non-polar solvents (were not calculated in this study) requires also data on square of the zero frequency refractive index, thermal expansion coefficient, molar volume, surface tension and its thermal coefficient, and the so called "cavity microscopic coefficient", usually taken to be zero.

Currently the data for following solvents studied in this work are initially stored in GAMESS program: CH_3OH, C_2H_5OH, CH_3NO_2, $C_6H_5NH_2$, acetone and tetrahydrofurane. For anisole we have used the following values: EPS=4.30, RSOLV=2.83Å.

Results of calculations using the PCM model are shown in Tab.3. As one can see from this table, the effect of solvent on value of $\ln \beta$ and isotope separation factors in systems with complexes of SiF_4 and BF_3 is decisive. So, for the isotope exchange of SiF_4 with methanol complex $SiF_4 \cdot 2CH_3OH$ without taking into account the effect of solvent at 300K *ab initio* calculation predicts separation factor $\ln \alpha_{28/30}$=0.017, while taking into account the effect of solvent predicts $\ln \alpha_{28/30}(PCM)$=0.024. Accordingly, for complex with ethanol $\ln \alpha_{28/30}$=0.018, $\ln \alpha_{28/30}(PCM)$=0.023.

For complexes of SiF_4 account for the effect of solvent with the use of the PCM model increases bond length Si—F. Simultaneously, bond lengths Si—O (or Si—N) decrease (see Tab.5). As for vibrational frequencies, they decrease, that leads to decrease of the $\ln \beta$ value. Similar effect is observed in the case of the complexes of

BF_3.

Table 5. Bond lengths Si—F, B—F, Si—O and B—O and vibrational frequencies (cm^{-1}). This table shows only the frequencies of ^{28}Si and ^{11}B isotopic forms which contribute more than 5% to overall value of $\ln\beta$ at 300K

	MP2/6-311	PCM MP2/6-311
$SiF_4 \cdot 2C_2H_5OH$	504(12%), 869(31%), 892(31%) r(Si—F)=1.659—1.663Å r(Si—O)=1.914Å	484(15%), 828(32%), 836(24%), 853(10%) r(Si—F)=1.668—1.669Å r(Si—O)=1.883Å
$BF_3 \cdot$ anisole	606(7%), 1238(7%), 1248(32%), 1301(21%), 1323(22%) r(B—F)=1.350—1.365Å r(B—O)=1.698Å	653(6%), 854(6%), 1179(7%), 1187(9%), 1198(20%), 1232(18%), 1259(23%) r(B—F)=1.361—1.372 r(B—O)=1.622

Disadvantage of alcohols for separation of isotopes of silicon is their possibility to react with silicon tetrafluoride giving compounds with siloxane bond following by formation of a complex. In this regard, the practice is to use alcohols with high molecular masses (C_4 —C_7). In [9] is reported that alcohols of normal structure provide a higher separation factor than the alcohols with a branched carbon chain. However, this result is confirmed neither by results of calculations presented in Tab.3 nor by measurements of separation factor in isotope exchange countercurrent column in the same work [9]. Isotope separation factor of silicon in the system SiF_4(gas) — $SiF_4 \cdot 2ROH$(liq.) is almost independent of R. This makes it possible to choose a complex-forming solvent based only on technological considerations.

It is also evident that the use of tetrahydrofurane and acetone as complex-forming solvent gives the same separation factor, as well as alcohols. It draws attention to the search for promising systems for isotope separation, not confining ourselves to only alcohols as complex-forming solvents.

Conclusion

As seen from the stated above, *ab initio* methods can be very useful for assessment of influence of different ligands within a given stoichiometry of the complex. They also make it possible to study the variability of $\ln\beta$ depending on the ligand. This makes it possible to find system having optimal isotope separation factor.

It is shown that *ab initio* calculation of isotope separation factors in systems including weak-bonded complexes, it is necessary to take into account the effect of solvent that determines the nature of the observed isotope effect.

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Captions in article A.V.Bochkarev "Influence of solution on isotopic properties of complexes of SiF_4 and BF_3 in the process of separation of isotopes of Silicon and Boron by the method of chemical exchange rectification"

Fig.1. Complexes of boron trifluoride with anisole and nitromethane

Fig.2. Complexes of silicone tetrafluoride with methanol and THF

Abstract of the paper "Influence of solution on isotopic properties of complexes of SiF_4 and BF_3 in the process of separation of isotopes of Silicon and Boron by the method of chemical exchange rectification"

Ab initio calculations of isotope reduced partition function ratios (β-factors) and separation factors of isotopes of silicon and boron in the systems fluoride of the element − its complex with organic solvent have been carried out. These systems are used for separation of isotopes of boron and silicone by the method of chemical exchange rectification (chemical isotope exchange method with thermal phase reversal).

It has been shown that usual *ab initio* calculations of vibrational frequencies of the fluoride of boron or silicon and their complex with solvent cannot predict experimental values of isotope separation factor. For the correct description it is necessary to take into account the polarizing effect of solvent on the complex. To study this effect the Polarized Continuum Model (PCM) has been used. In all cases our theoretical results corresponded quite well with experimental results for the systems previously studied. This result opens up possibilities of directed search for systems suitable for separation of isotopes by method of chemical exchange rectification.
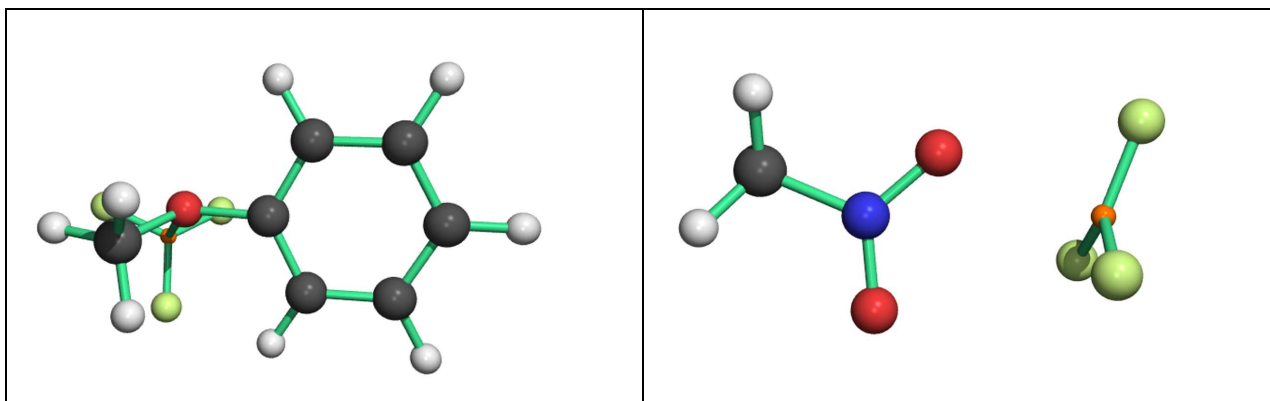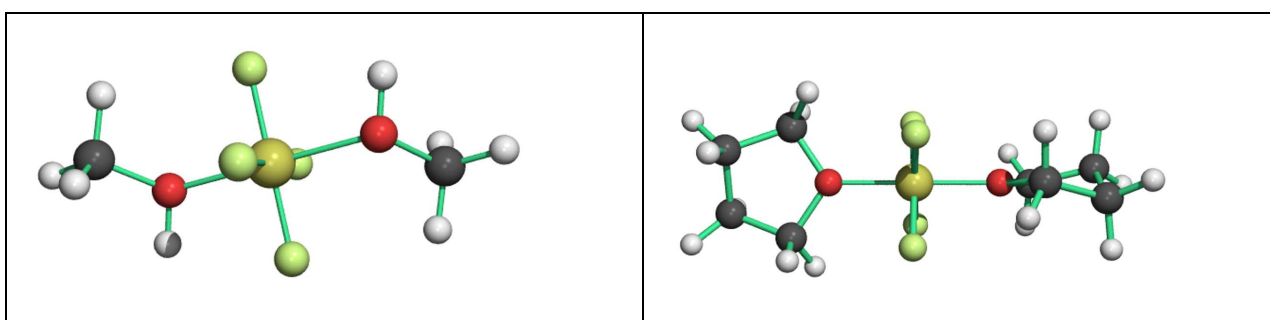
Figure 1. BF$_3$ complexes with anisole and nitromethane

Figure 2. Complexes of silicon tetrafluoride with methanol and THF