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Silicon Nanocrystals Stabilized by Organic Radicals: Spectral and Theoretical Study

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Abstract—Samples of silicon nanocrystals with surfaces modified by various organic ligands are synthesized. Their IR spectra are studied and interpreted. The quantum-chemical calculations of the vibrational spectra of model compounds are performed. A chemical bond between the ligands and nanosilicon particles is concluded on the basis of a comparison of the experimental and calculated data.

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INTRODUCTION

Nanocrystalline silicon (nc-Si) attracts attention of researchers due to possible photovoltaic, optoelectronic, and medical–biological applications [1] caused by the photoluminescence of nc-Si in the visible spectral range. Similar photoluminescence is related to the violation of the selection rule for the wave number because of the so-called quantum constraint [1, 2].

The formation of an organic shell by the cross-linking of an organic ligand to the nc-Si surface becomes an important synthetic task for the efficient practical application of nc-Si and for the preparation of related novel materials with useful properties. In the simplest case, the role of organic ligands is reduced to preventing nanoparticle coagulation.

Thus, an important task appears: to determine whether the cross-linking of the organic ligand to the nc-Si surface occurred or not [3]. IR spectroscopy can rapidly and exactly show the presence or absence of a Si–C bond, and the assignment of vibration frequencies in the IR spectra of silicon nanoclusters with an organic shell in combination with quantum-mechanical calculations gives an adequate solution of the spectral problem.

It is accepted that the cross-linkage of the organic ligand to the silicon nanoparticle surface can be proved by three main bands in the IR spectrum, namely, by the band at 740–780 cm^{-1} (depending on the ligand, its position can change) attributed to stretching vibrations of the Si–C bond and by the bands at 1250–1270 and ~1450 cm^{-1} assigned to vibrations of the $Si–CH_3$ and $Si–CH_2$ groups [4–7].

The purpose of this work is to study the possibility of forming a Si–C chemical bond in nc-Si, whose surface is modified by a series of alkyl and aryl ligands, using the study of the IR absorption spectra of the synthesized samples and the results of the density functional theory quantum-chemical calculations demonstrating a high efficiency for similar compounds in combination with relatively low computational expenses.

EXPERIMENTAL

Bromopentafluorobenzene C_4F_9Br (SIAS&M-Invest, 99.98%), C_4H_9I (reagent grade), C_6H_5I (reagent grade), 1,2-dimethoxyethane (SigmaAldrich, ~99%), potassium (SigmaAldrich, 99.5%), tetrabromosilane and tetrachlorosilane (SigmaAldrich, 99.99%), mercury (AlfaAesar, 99.9%), and granulated lithium (AlfaAesar, 99%) were used for the synthesis of silicon nanoparticles.

Samples of $(C_6F_5)_m–Si_n$ (**1**), $(C_4F_9)_m–Si_n$ (**2**), $(C_4H_9)_m–Si_n$ (**3**), and $(C_6H_5)_m–Si_n$ (**4**) were synthesized using earlier developed procedures [3, 8–13]. A detailed procedure for the preparation of sample **2** is presented as an example.

Synthesis of nc-Si with perfluorobutyl ligands was carried out by several stages.

(1) The initial dispersion of nc-Si was synthesized in a Schlenk flask with a magnetic stirrer. The flask was purged with argon, and dried 1,2-dimethoxyethane (50 mL) and metallic potassium (2.93 g, 75 mmol) were added. The flask with the mixture was heated to 85°C in a glycerol bath. Then a solution of $SiBr_4$ (5.91 g, 17 mmol) in dimethoxyethane (10 mL) was added in an argon flow. As in [10], a yellow polydispersed solution was obtained in 4 h. According to the published data, this solution was formed by silicon

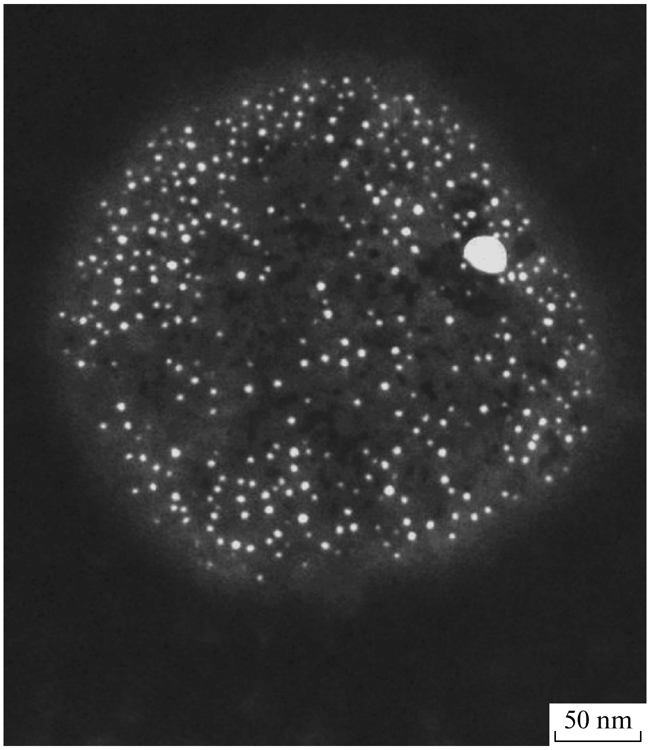

Fig. 1. Survey TEM image of silicon nanoparticles stabilized by perfluorobutyl radicals. The light spot at the right upper corner is caused by a shadow from a gold particle of the grid of the sample holder.

nanoparticles covered with bromine ions. The content of residual Br ions was determined by the titration of the obtained dispersion (1 mL) with a 0.04 M solution of KOH. The concentration of Br ions on the nanosilicon surface was 0.08 mol/L.

(2) The alkylating agent (perfluorobutyllithium) was obtained (in an amount providing its 20% excess over the bromide ligands on nc-Si) by the reaction of perfluorobutyl iodide with lithium amalgam at a 10% excess of the latter over C_4F_9I.

Lithium amalgam was prepared in a Schlenk flask with an air condenser and a calcium chloride tube. The flask was purged with argon, mercury (6.65 g, 33 mmol) and lithium (0.025 g, 3.6 mmol) were added, and the flask with the mixture was heated in an oil bath to 200°C. Mercury and lithium were stirred in an argon flow for several seconds to the homogeneous state, and the amalgam was cooled to room temperature.

Perfluorobutyllithium was synthesized in the same Schlenk flask in which lithium amalgam was prepared. The flask was placed in a bath with a cooling mixture (ice with NaCl) at –17°C, dimethoxyethane (5 mL) and perfluorobutyl iodide (0.28 mL, 1.65 mmol) were added, and the mixture was magnetically stirred for 50 min.

(3) Perfluorobutyl ligands were grafted to the nc-Si surface in a Schlenk flask at –17°C upon the addition of the dispersion (17 mL) of nc-Si modified with bromine obtained at the first stage. The reaction was carried out with stirring for 1 h. An intensely dark yellow dispersion formed by nc-Si particles with the shell of the perfluorobutyl ligands was obtained and treated for 1 min with dry hydrogen chloride to remove a perfluorobutyllithium excess. The synthesized sample was studied by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR TEM) (Fig. 1, 2).

The nc-Si particles with the perfluorophenyl, butyl, and phenyl ligands (samples **1**, **3**, and **4**, respectively) were synthesized similarly.

The electron microscopic studies of nc-Si were carried out using a TITAN 80–300 high-resolution transmission electron microscope (FEI, United States) with a corrector of spherical probe aberration. The samples were studied in the light- and dark-field modes at an accelerating voltage of 300 kV. The chemical compositions of the samples were determined by energy dispersive X-ray analysis (EDXA). The experimental data were processed and interpreted using the DigitalMicrograph (Gatan) and TIA (FEI) program packages. For the TEM studies, the samples were prepared using the method of suspension deposition on

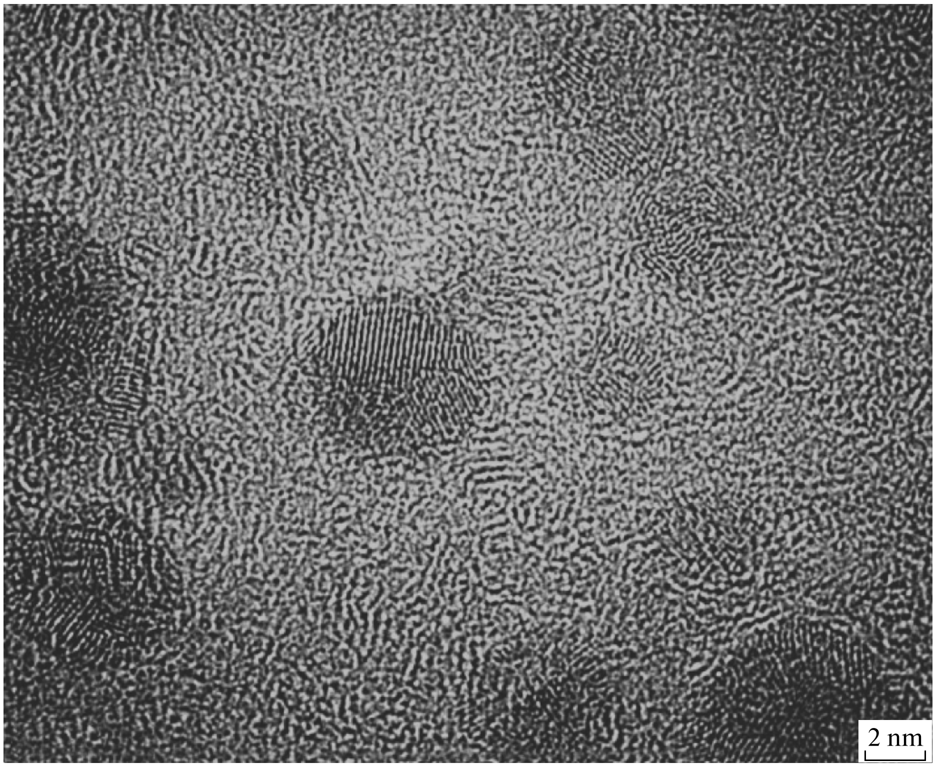

Fig. 2. HR TEM image of silicon nanoparticles stabilized by perfluorobutyl radicals.

standard gold electron microscopic grids with a thin carbon film.

The HR TEM studies of the samples were carried out on a JEOL JEM 2100F/Cs instrument (JEOL Co., Ltd.) with an autoemission source (FEG) equipped with a corrector of spherical aberrations (CEOS GmbH, Germany), a Tridiem energy filter, and an analyzer of electron energy loss spectra (Gatan, Inc., United States). The TEM images were detected at an accelerating voltage of 200 kV and an exposure time of 90 s in the light-field mode of transmission microscopy.

The procedure of sample preparation for analysis included the dispersing of a weighed sample in a 0.2% aqueous solution of sodium dodecyl phosphate in the Sapfir ultrasound bath (150 W, 22 kHz) for 20 min at room temperature, after which the obtained suspension (100 μL) was deposited on the copper grid precovered with polyvinylformaldehyde resin.

The IR spectra of the isolated from the dispersion and dried powders of the samples were recorded on a Tensor 27 FT-IR spectrometer (Bruker) in the attenuated total internal reflectance mode with a resolution of 1 cm^{-1} averaging a signal over 32 scans. The spectra of the precursors were obtained from a capillary layer of the substances.

Calculation methods. The experimental IR absorption spectra of the obtained samples were interpreted on the basis of the results of the quantum-mechanical spectra of the model compounds using the Gaussian 09 program package [14]. The initial data were prepared and the obtained results were visualized using the Chemcraft program [15]. The optimized structures and harmonic force fields were calculated by the density functional theory using the B3LYP [16], wB97XD [17, 18], and M062X [19] functionals and a series of basis sets (6-31G*, 6-31+G**, 6-311++G**, and aug-cc-pVDZ [20]). The quantum-chemical force field was converted to the full system of internal coordinates. The direct vibrational problem with the calculation of the potential energy distribution over vibrations [21] was solved using the SPEKTR program package [22–24].

The level of the quantum-mechanical calculation was chosen by a comparison of the calculated IR spectra of modifying molecules with the experimental spectra. This procedure, in particular, for a C_6F_5Br molecule, established that the application of the wB97XD functional with the 6-31+G** basis set was a sufficient level for the calculation (Fig. 3).

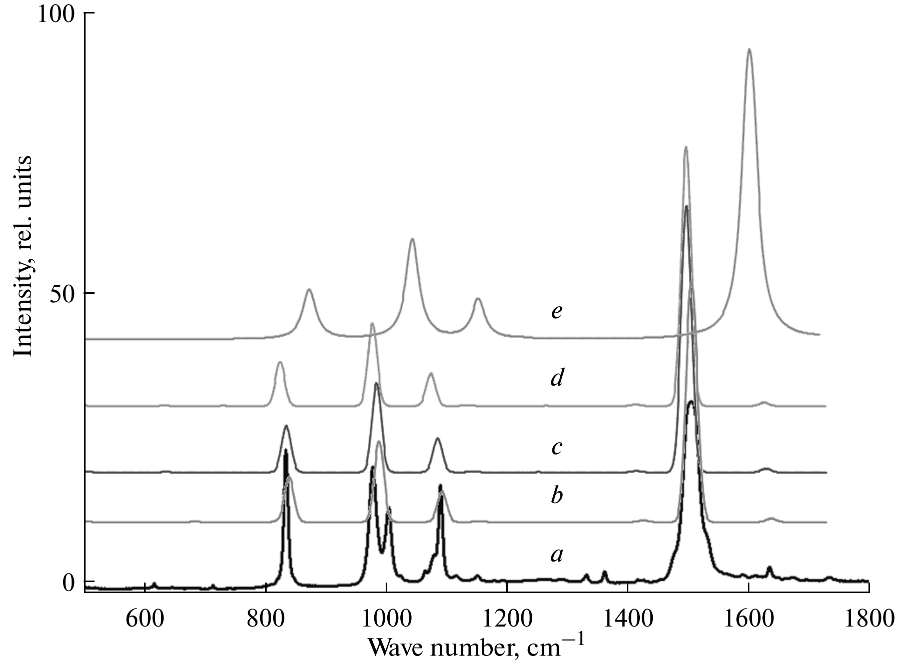

Fig. 3. IR spectra of the C_6F_5Br molecule: (*a*) experimental and calculated at the (*b*) wB97XD 6-31+G**, (*c*) wB97XD 6-311++G**, (*d*) wB97XDaug-cc-pVDZ, and (*e*) HF 6-311++G** levels.

RESULTS AND DISCUSSION

IR spectroscopy in combination with quantum-chemical calculations was used as the main method for the characterization of the synthesized products. The purpose of the spectral studies was to prove the chemical binding of the organic radicals with the nanosilicon surface by searching for the vibration band of the Si–C bond in the spectra and, possibly, by an analysis of changes in the positions and intensities of bands of the modifier molecules due to the reaction.

At the first stage, we calculated the vibrational spectra of the model compounds. The compounds in which the organic ligand is bound to the silicon atom terminated by three silyl groups, i.e., molecules $C_6F_5Si(SiH_3)_3$ (**I**), $C_6F_5Si(SiH_3)_3$ (**I**), $C_4F_9Si(SiH_3)_3$ (**II**), $C_4H_9Si(SiH_3)_3$ (**III**), and $C_6H_5Si(SiH_3)_3$ (**IV**), were chosen as model compounds [25]. The full (dependent) systems of internal coordinates introduced for these molecules included the coordinates of bond extension, changes in bond angles, and shifts of bonds from the plane and the torsional coordinates.

The following results of the calculations of the model compounds are given in Tables 1–4: the characteristic ranges of vibrations of the functional groups, band intensities, and their conventional assignment.

It follows from the calculation results that the bands corresponding to the ν(Si–C) stretching vibrations lie at 650–850 cm^{-1} and have a low intensity (from 1.85 to 38.17 km/mol) compared, for example, to the intensity of the near lying band corresponding to the $\delta(SiH_3)$ bending vibrations, being ~450 km/mol.

The spectra of the synthesized samples are more complicated that those of the model compounds and modifiers of the surface. The broad bands of the ν(Si–O) stretching vibrations (~1100 cm^{-1}) and those of adsorbed water molecules and hydroxyl groups (at ~3300 and 1640 cm^{-1}), whose intensity changes strongly from sample to sample, predominate in the spectra. Several weak bands appear against their background, including those in the studied range (Fig. 4).

The experimental IR spectra of the synthesized samples were compared with the spectra of the modifiers and the calculated spectra of the model compounds (Figs. 5–8). The weak bands that can be attributed to the Si–C stretching vibrations are indicated by arrows.

The experimental spectra are compared with the calculation results in Table 5.

The bands of intrinsic vibrations of the ligands are also observed in the spectra, but their shifts and intensity redistribution (according to the calculation results for the precursors and model molecules) impede reliable interpretation.

Thus, we synthesized the nc-Si samples with the surface modified by several organic ligands. Their IR spectra were studied and interpreted. The quantum-

Table 1. Calculated at the wB97XD/6-31+G** level band frequencies and intensities in the IR spectra, the normal vibration shapes, and the conventional assignment of the bands of the model molecule $C_6F_5Si(SiH_3)_3$

ν, cm^{-1}	I, km/mol	PED*, %	Assignment
2067–2107	52.21–96.29	100 (Si–H)	ν(Si–H)
1634–1618	7.55–45.81	100 (C–C)	ν(C–C)
1363–1502	24.14–394.68	50 (C–F), 50 (C–C)	ν(C–C)
1252–1268	0.47–24.84	80 (C–F), 20 (C–C–C)	ν(C–F)
1110	7.37	100 (C–F)	ν(C–F)
1064	201.81	70 (C–F), 18 (C–C–C), 12 (Si–C)	ν(C–F)
952	189.43	100 (C–F)	ν(C–F)
902–921	3.87–70.30	100 (H–Si–H)	$\delta_s(SiH_3)$
827–867	133.02–389.43	55 (H–Si–H), 45 (Si–Si–H)	$\delta(SiH_3)$
809	21.42	90 (Si–C), 10 (C–F)	ν(Si–C)
730	4.31	100 (C–C–F)	δ(C–F)

* PED is the potential energy distribution (the same as in Tables 2–5).

Table 2. Calculated at the wB97XD/6-31+G** level band frequencies and intensities in the IR spectra, the normal vibration shapes, and the conventional assignment of the bands of the model molecule $C_4F_9Si(SiH_3)_3$

ν, cm^{-1}	I, km/mol	PED, %	Assignment
2146–2178	16.57–151.58	100 (Si–H)	$\nu_s(Si{-}H_3)$
1305–1362	10.63–106.12	90 (C–C), 10 (C–F)	ν(C–C)
1253–1266	157.34–374.36	65 (C–F), 10 (F–C–F), 25 (C–C)	ν(C–F)
1216–1229	154.15–100.05	80 (C–F), 20 (C–C)	ν(C–F)
1181	49.62	90 (C–F)	ν(C–F)
1144	190.25	100 (C–F)	ν(C–F)
1124	41.76	50 (C–F), 40 (F–C–F), 10 (C–Si)	ν(C–F)
1111	57.70	100 (C–F)	ν(C–F)
1017	58.22	70 (C–F), 20 (C–C), 10 (C–Si)	ν(C–F)
912–932	9.48–62.54	100 (H–Si–H)	$\delta_s(SiH_3)$
833–875	60.42–475.26	90 (H–Si–H), 10 (Si–Si–H)	$\delta_{as}(SiH_3)$
782	38.17	65 (C–Si), 15 (C–C), 20 (C–F)	ν(Si–C)
716	74.93	60 (C–F), 20 (C–C–F), 20 (C–Si)	δ(CF)

Table 3. Calculated at the wB97XD/6-31+G** level band frequencies and intensities in the IR spectra, the normal vibration shapes, and the conventional assignment of the bands of the model molecule $C_4H_9Si(SiH_3)_3$

ν, cm^{-1}	*I*, km/mol	PED, %	Assignment
2895–2982	0.01–58.99	100 (C–H)	$\nu_s(CH_3)$ and $\nu_{as}(CH_2)$
2121–2143	4.26–320.28	100 (Si–H)	$\nu_s(SiH_3)$
1364–1454	0.55–8.88	50 (H–C–H), 50 (C–C–H)	δ(CH) and $\delta_s(CH_2)$
1256–1337	0.60–2.64	100 (C–C–H)	δ_s(C–H)
1169–1182	0.44–2.58	50 (C–C–H), 50 (Si–C–H)	$\delta(CH_3)$
1058	9.03	45 (C–C–H), 35 (C–C), 20 (C–C–C)	ν(C–C)
1015	1.37	100 (C–C)	ν(C–C)
1003	1.63	50 (Si–C–H), 50 (C–C–H)	$\delta(CH_3)$
971	5.18	100 (C–C)	ν(C–C)
880–921	0.95–120.66	100 (H–Si–H)	$\delta(SiH_3)$
858–860	5.37–11.69	69 (C–C), 21 (C–C–H), 10 (C–C–C)	ν(C–C)
836–839	391.17–439.90	50 (Si–Si–H), 50 (H–Si–H)	$\delta(SiH_3)$
680	10.74	78 (C–Si), 12 (C–C–C), 10 (Si–C–C)	ν(Si–C)

Table 4. Calculated at the wB97XD/6-31+G** level band frequencies and intensities in the IR spectra, the normal vibration shapes, and the conventional assignment of the bands of the model molecule $C_6H_5Si(SiH_3)_3$

ν, cm^{-1}	*I*, km/mol	PED, %	Assignment
3046–3080	2.13–30.44	100 (C–H)	ν(C–H)
2124–2144	2.51–264.36	100 (Si–H)	ν(Si–H)
1405–1570	0.10–11.03	50 (C–C), 50 (C–C–H)	δ(C–H)
1261–1308	2.00–3.28	50 (C–C), 50 (C–C–H)	δ(C–H)
1140–1169	0.09–1.33	100 (C–C–H)	δ(C–H)
1068	16.53	50 (C–C), 25 (C–Si), 25(C–C–C)	ν(C–C)
1006–1057	0.60–2.11	50 (C–C), 50 (C–C–H)	δ(C–H)
971	1.77	50 (C–C–C), 50 (C–C)	δ(C–C–C)
910–921	0.16–77.34	100 (H–Si–H)	$\delta(SiH_3)$
839–879	169.21–462.78	50 (H–Si–H), 50 (Si–Si–H)	$\delta(SiH_3)$
673	1.85	54 (C–Si), 20 (C–C–C), 16 (C–C–H)	ν(Si–C)

Table 5. Comparison of the experimental and calculated frequencies and intensities of the Si–C stretching vibrations

Sample	Calculation			Experiment	
	ν, cm^{-1}	*I*, km/mol	PED, %	ν, cm^{-1}	assignment
1	809	21.41	70 (Si–C), 25 (C–F), 5 (C–C)	811	ν(Si–C)
2	782	38.17	65 (C–Si), 15 (C–C), 20 (C–F)	785	ν(Si–C)
3	680	10.72	66 (C–Si), 20 (C–C–C), 14 (Si–C–C)	685	ν(Si–C)
4	673	1.85	54 (C–Si), 20 (C–C–C), 16 (C–C–H), 10 (C–C)	674	ν(Si–C)

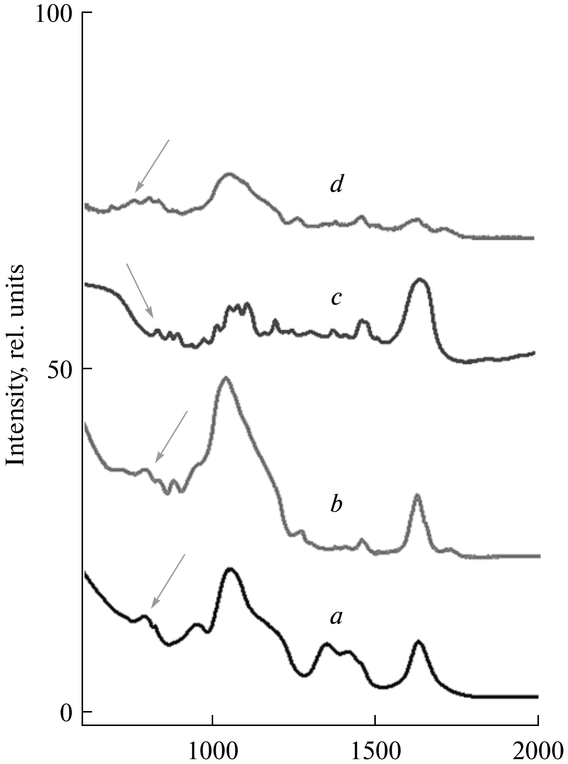

Fig. 4. IR spectra of nc-Si samples: (*a*) **2**, (*b*) **3**, (*c*) **1**, and (*d*) **4**.

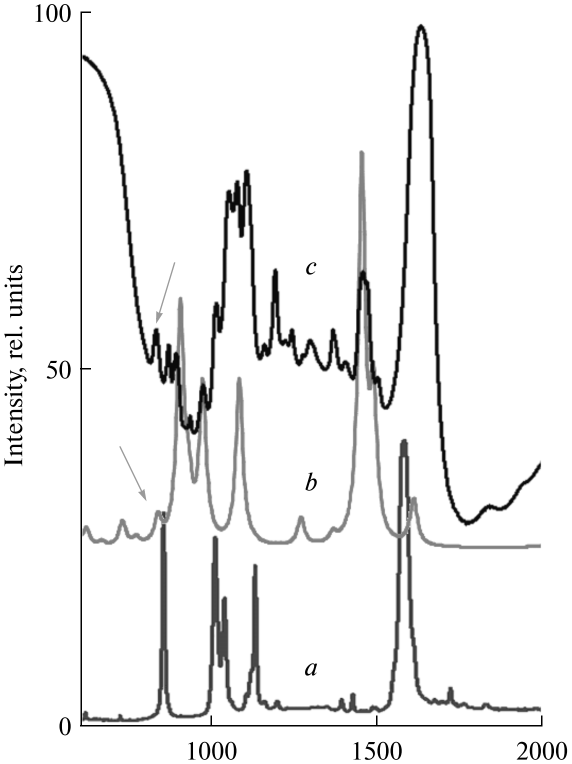

Fig. 5. Experimental IR spectra of the (*a*) precursor C_6F_5Br and (*c*) sample of the expected composition (C_6F_5)–Si, and (*b*) the calculated spectrum of the model molecule $C_6F_5Si(SiH_3)_3$.

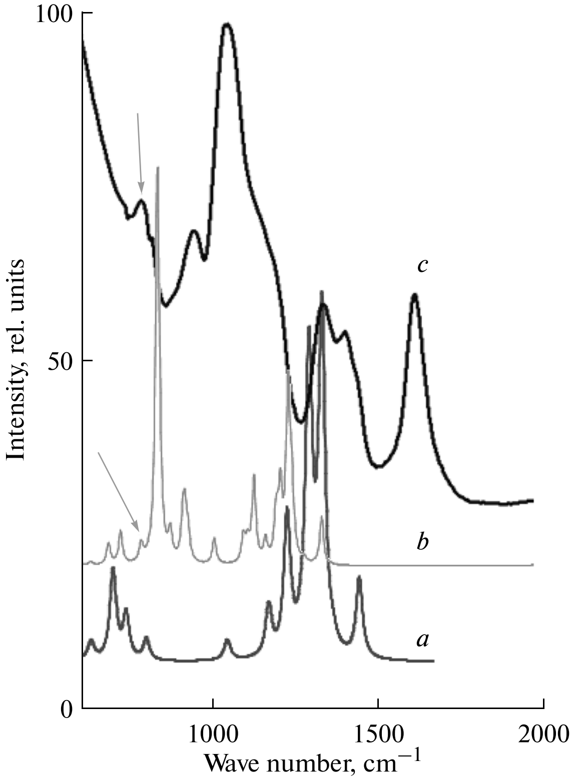

Fig. 6. Experimental IR spectra of the (*a*) precursor C_4F_9Br and (*c*) sample of the expected composition $(C_4F_9)-(Si)_n$ and (*b*) the calculated spectrum of the model molecule $C_4F_9Si(SiH_3)_3$.

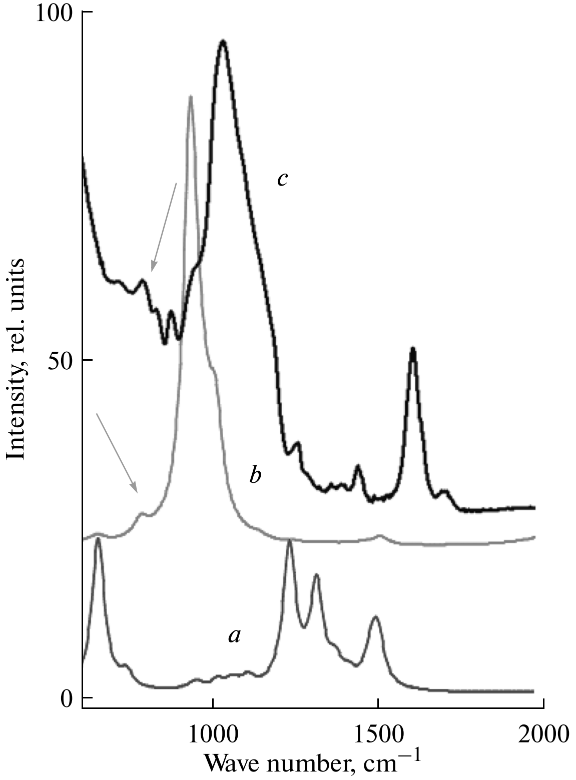

Fig. 7. Experimental IR spectra of the (*a*) precursor C_4H_9I and (*c*) sample of the expected composition $(C_4H_9)-(Si)_n$ and (*b*) the calculated spectrum of the model molecule $C_4H_9Si(SiH_3)_3$.

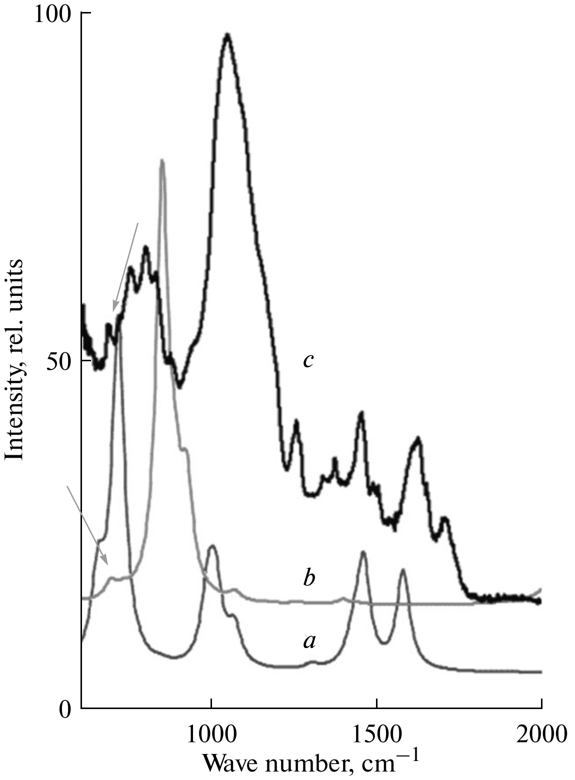

Fig. 8. Experimental IR spectra of the (*a*) precursor C_6H_5I and (*c*) sample of the expected composition $(C_6H_5)-(Si)_n$ and (*b*) the calculated spectrum of the model molecule $C_6H_5Si(SiH_3)_3$.

mechanical spectra of the model compounds were performed. The conclusion about the chemical bond between the radicals and nanosilicon particles was made on the basis of the comparison of the experimental and calculated data.

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