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Quantum-Chemical Approaches to Identification of Nanostructures Synthesized by Molecular Layering Technique

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Abstract—Identification of nanostructures synthesized on silica surface by molecular layering technique was discussed with the example of vanadium oxide systems. Variation of technological factors in synthesis of the nanostructures was analyzed from the standpoint of controlling their chemical composition and local structure, as well as in the context of relationships with the stability and functional characteristics. It was shown that, based on chemical analysis and vibrational spectroscopy data, the element-containing nanostructures can be identified only ambiguously, while a promising alternative can be found in quantum-chemical modeling. The optimal modeling modes and methods were elucidated with the use of the cluster approach. The Gaussian03 calculations showed that the Si–O–V stretching vibration frequency varies with the number of the metal–silica surface bonds. The predictions for nanosystems with different local structures quantitatively agree with the experimental spectral characteristics and are suitable for identification of the objects examined.

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INTRODUCTION

Development of nanomaterials intended for diversified functional applications ranks among the key science and technology directions of the late XX–early XXI century. Since the 1990s, the nanotechnology and nanomaterials research centers have significantly grown in number. In a research institution, there hardly exists a team whose activities are not focused on nanotechnologies. In this situation, modern scientists believe that the term “nanotechnology” (currently used in a wide variety of projects and developments, ranging from fairly realistic to most unrealistic ones) is at risk of evolving into a sense-rich and vague concept [1].

Clearly, a realistic approach to nanotechnologies implies learning not only how to apply but also how to strictly, at the atomic-molecular level, control the processes involved in preparation of target objects measuring up to 100 nm at least in one of the three dimensions. When applied to some types of processes, the prefix nano- is legitimate only if they yield products (nanoproducts) having qualitatively different properties.

Extensive use of the new terminology in research activities creates an illusion of a radically new direction being developed. However, this is not quite the case; more precisely, the situation is totally different: Future miniaturization technologies were the subject of the talk “There is Plenty of Room at the Bottom” given by R. Feynman as early as 1960. At the same time, in one of his interviews Feynman emphasized his speaking about essentially known things [1].

After several years of “market noise the foam has settled,” and now it is evident that, in reality, nanotechnologies originated from scientific concepts and techniques proposed in the second half of the XX century [1].

An example of realistic approach to nanotechnology and nanomaterials research can be found in activities by Corresponding Member of the Russian Academy of Sciences V.B. Aleskovskii’s Scientific School. In 1952, based on the solid state chemistry concepts and achievements (studies by Mendeleev, Langmuir, Berthollet, Proust, Merrifeld, Shilov, and Shchukarev), Aleskovskii (at that time Professor of the Lensovet Leningrad Technological Institute) advanced

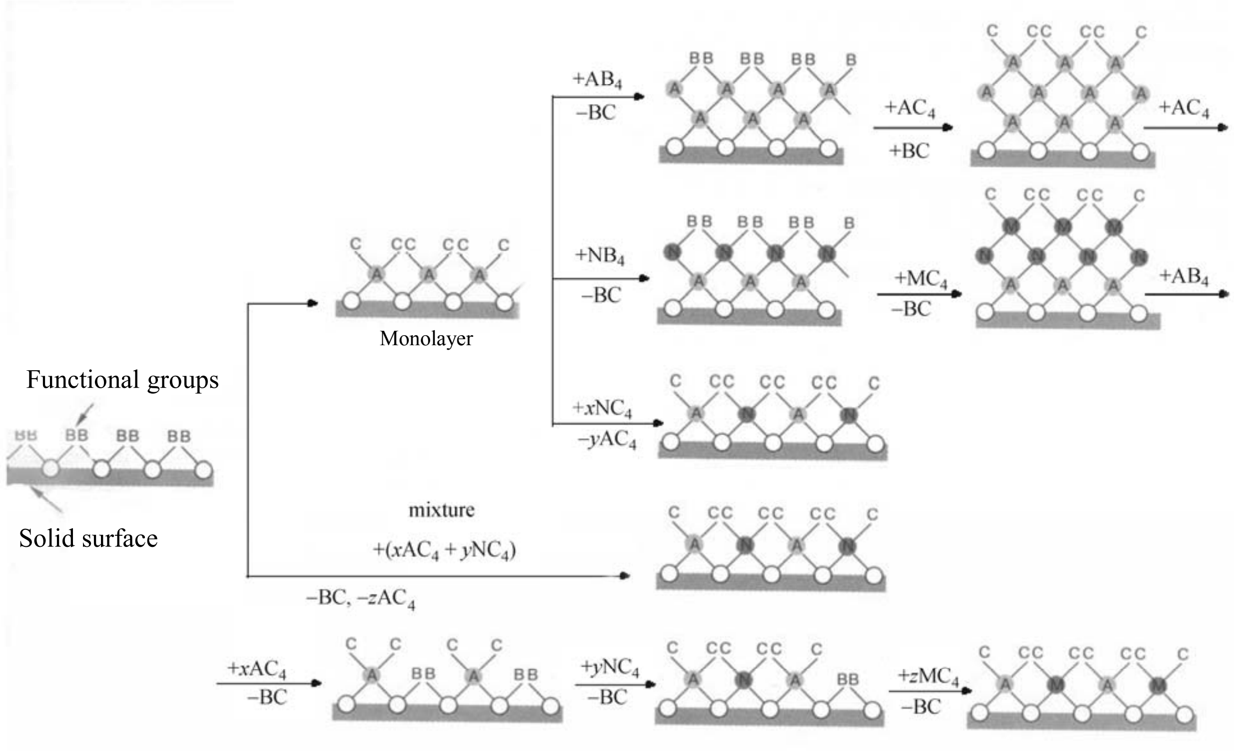

Fig. 1. Schematic of synthesis of surface nanostructures on silica matrix by molecular layering technique.

a “skeleton hypothesis” [2–4]. It states that all solids (crystalline or amorphous, organic or inorganic) can be regarded as consisting of a skeleton (e.g., that comprised of atoms linked by covalent bonds, or of other structural units) surrounded by groups functionalizing the broken surface bonds. According to this concept, physicochemical transformations of solids can proceed both via skeleton alteration (dissolution, leaching, etc.) and reactions of the surface functional groups with the chemicals fed from outside. This makes possible chemical assembly of a surface with desired composition and structure.

This approach was applied in development of a set of new synthesis techniques known as chemical assembling methods. By the middle 1960s–early 1970s, a team led by Aleskovskii advanced a physicochemical concept of synthesis of systems with desired chemical composition and structure by a variety of atomic-molecular chemical assembling techniques. For example, as early as 1965–1969 the molecular layering method was proposed, by which the first inorganic monomolecular and polymolecular layers were synthesized on the surface of solid-phase matrices (silicon single crystals, quartz, silica) [5–8]. In the years that followed, low-dimensional states attracted the interest of scientific community, which attached much significance to chemical assembling strategy issues.

The molecular layering method passed through several stages in its evolution, from the “skeleton hypothesis” advanced by Aleskovskii in 1952 and new synthesis principles proposed in 1963–1967 by Aleskovskii jointly with Prof. S. I. Kol’tsov, Lensovet Leningrad Technological Institute, via preparation of the first nanostructures in 1965–1969 and further extension of the basic and applied research activities in this sphere, to their commercial application. The new technology was employed in preparation of modified sorbents and indicators of gases (H_2O, NH_3, H_2S, SO_2, etc.) which find application in aviation instrument making. Also, the synthesized nanoalloyed ceramics based on corundum with titania surface nanoadditions is used in manufacture of insulators for X-ray tubes. At the same time, a number of problems still remain to be solved. This concerns identifying low-dimensional systems (from individual functional groups to nanolayers with desired thickness); choosing and optimizing their preparation mode; and forecasting the properties of target products. The accomplishment of these tasks relies increasingly on the use of modeling techniques, e.g., those utilizing quantum-chemical and thermodynamic approaches to description of nanotechnology processes and structures [9–14].

Here, we consider selected aspects of identification of surface low-dimensional systems synthesized by molecular layering technique and discuss the relevant quantum-chemical modeling results.

Basic Principles of Molecular Layering Method

Nowadays there exists a huge body of experimental data on synthesis of mono- and polylayers on the surface of chemically, structurally, and geometrically different solid matrices [3, 6–10].

One version of such synthesis procedures, the molecular layering technique, implies monolayer-by-monolayer building up on the solid matrix surface of structural units yielded by reactions between the functional surface groups of the matrix and the reagent fed thereto under conditions maximally distant from chemical equilibrium. (Foreign researchers assigned to this method a not fully adequate term of atomic layer epitaxy (ALE) or atomic layer deposition (ALD) [15–17].) Molecular layering allows synthesizing nanostructures with different compositions and structures (monolayers, in particular, multicomponent, Fig. 1c) on the matrix surface, as well as atomic assembling of the surface nano-, micro-, and macrostructures by successive multiple alternation between reactions, as prescribed by a special program (Figs. 1a, 1b). The method enables formation of nanolayers on the solid substrate surface accurately to within one monomolecular layer. The nanolayer thickness is governed by the number of molecular layering cycles comprised of a set of specific reactions, rather than by the substrate–reagent contact time. This implies a certain degree of self-organization in formation of the first and subsequent monomolecular layers by the molecular layering technique.

Among the molecular layering processes, the reactions of volatile halides with OH groups on the oxide matrix surface have received fairly extensive research efforts. By way of example, let us consider formation of a monolayer of element-oxochloride groups on the silica surface:

$$(\equiv\text{Si–OH}) + \text{XCl}_m \rightarrow (\equiv\text{Si–O–})_n\text{XCl}_{m-n} + n\text{HCl}, \quad (1)$$

X: Si ($m = 4$); Ti ($m = 4$); P ($m = 3$), PO ($m = 3$);
VO ($m = 3$); CrO_2 ($m = 2$) etc.

The element-oxide structures are obtained by chloride ion substitution in which water vapor serves as reagent:

$$(\equiv\text{Si–O–})_n\text{XCl}_{m-n} + (m-n)\text{H}_2\text{O} \rightarrow (\equiv\text{Si–O–})_n\text{X(OH)}_{m-n} + (m-n)\text{HCl}. \quad (2)$$

In synthesis of sulfide, nitride, and carbon surface nanostructures the element-oxochloride systems are treated with hydrogen sulfide, ammonia, and methane, respectively.

In preparation of multicomponent monolayers, as well as of nanostructures with alternating mono(nano) layers, the choice and feeding order of reagents are governed by properties of the new functional groups on the solid-phase matrix surface, synthesized in the preceding molecular layering cycle [18, 19]. The choice of a specific regime for the process should be dictated by the nature and properties of the initial substrate, the reagents used, and the newly formed surface functional groups.

In particular, the synthesis conditions affect the number of Si–O–X bonds (silica matrix) in an individual element-containing group. This number characterizes the stoichiometric composition and, to a certain extent, the structure of the resulting products; it is typically termed the functionality [3, 5–8] or denticity [20, 21]. Evidently, with increasing functionality the number of chlorine atoms bound to X atoms and, thereby, the number of OH groups formed from vapor phase hydrolysis, tend to decrease. This should gradually decrease the number of reactive centers in the subsequent layer deposition cycles and modify the structure growth mechanism, till molecular layering ceases.

During synthesis, the matrix surface can undergo a variety of local transformations different from those represented by schemes (1) and (2). For example, chloride treatment of silica can induce not only the main reactions (Fig. 2, routes 1 and 2) but also direct surface chlorination with substitution of hydroxo groups [22–24] (routes 3–5) or at strained siloxane bridges yielded by dehydroxylation [25, 26] (route 11). Also, water vapor treatment can lead not only to hydrolytic substitution of chlorine atoms by hydroxo groups in element-oxochloride moieties but also to Si–O–X bond cleavage [22, 23, 27, 28] under the action of water molecules (routes 8, 9) or hydrogen chloride evolved (route 7).

Thus, treatment of the substrate with reagents can induce a set of complex structural and chemical transformations. In the practical sense, this brings to the forefront the identification of the composition and structure of nanostructures prepared by molecular layering technique. Here, we discuss this task with the example of vanadium-oxide nanosystems synthesized on the silica surface. This choice was dictated, on the one hand, by the fact that these materials, in particular, those prepared by the molecular layering (ALE, ALD) technique, are fairly extensively studied [6–8, 29–31], and on the other, by the interest they attract as potential heterogeneous catalysts and modified sorbents [32–35].

Experimental Methods of Identification of Vanadium-Containing Nanostructures on the SiO_2 Surface

Silica surface treatment with $VOCl_3$ vapor can lead to formation of three types of moieties with different functionalities [6–8, 36]:

$$\equiv Si–OH + VOCl_3 \rightarrow \equiv Si–O–VOCl_2 + HCl, \quad (3)$$

$$2 \equiv Si–OH + VOCl_3 \rightarrow (\equiv Si–O–)_2VOCl + 2HCl, \quad (4)$$

$$3 \equiv Si–OH + VOCl_3 \rightarrow (\equiv Si–O–)_3VO + 3HCl. \quad (5)$$

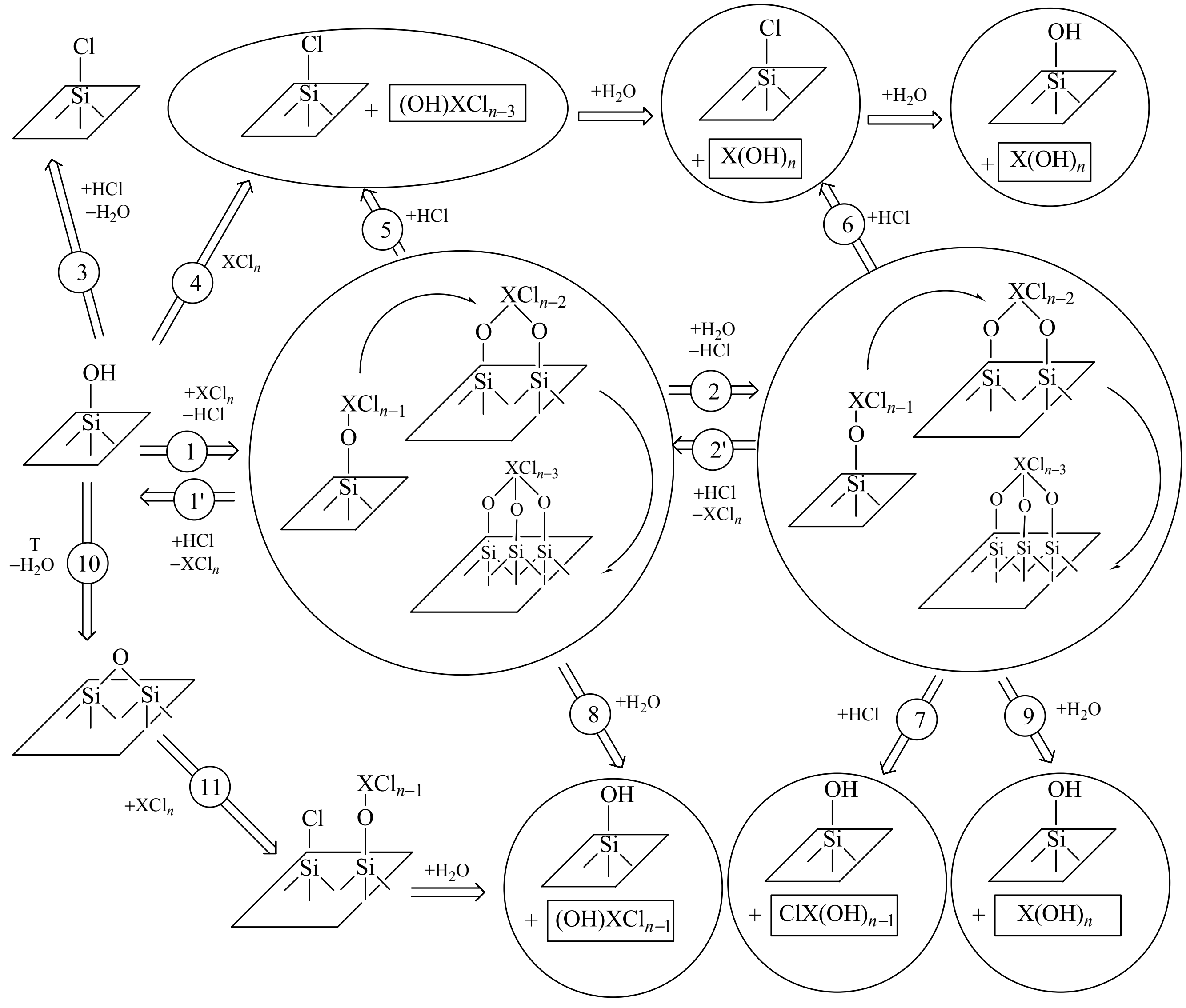

Fig. 2. Possible routes of local structural and chemical transformations induced by silica treatment with chloride and water vapors. Symbol T designates high-temperature treatment.

Which route will be followed by the reaction in each specific case is determined both by genesis of the initial silica and its treatment (above all, heat treatment) conditions.

Heat pretreatment is necessary for removing physically bound water molecules to preclude $VOCl_3$ hydrolysis. At the same time, silica calcination is known to induce dehydroxylation [37, 38]. Based on numerous relevant data (see, e.g., [6–8]), the pretreatment temperature was optimized at 180–200°C. This temperature range provides for the largest number of removed water molecules and the maximally preserved hydroxy cover of the silica surface. Variation of the annealing temperature causes changes in the concentration and positional relationships among the hydroxy groups on the silica surface. Thus, the functionality of the structures formed by molecular layering technique can be controlled within certain limits. For this reason, much attention in development of molecular layering technology is given to studies of the stoichiometric composition of the products as influenced by the synthesis temperature.

In one of the most widespread techniques, the composition of the products obtained with $VOCl_3$ reagent is characterized by the ratio of the specific amount of hydrogen chloride evolved in vapor phase hydrolysis to the vanadium content in solid products ([Cl]/[V]), as determined by chemical analysis methods. However, the reliability of this method is not very high. Notably, the available functionality data reported by various researchers for the products of synthesis of vanadium-containing structures by molecular layering (ALE/ALD) techniques are inconsistent. For example, chlorine was not detected in the surface layer of the products synthesized at 180°C [31], which suggests predominant formation of tridentate ≡VO moieties. At the same time, the ratio of the reaction products for the annealed ShSKG silica gel treated with $VOCl_3$ vapor at 180°C was estimated at $[Cl]/[V] \approx 0.5$, which fact was attributed to coexistence of bi- and tridentate structures [39]. In other studies [14, 36] the products obtained under close conditions were characterized by the $[Cl]/[V] \approx 1$ ratio corresponding to addition of bifunctional agents. Also, it was shown that, depending on the synthesis temperature, it is possible to obtain vanadium-oxochloride groups with other compositions. It was found [36] that, along with the precalcination temperature, certain impact on the composition of the synthesized structures is exerted by the conditions in other stages of molecular layering, in particular, chemisorption, desorption, and vapor-phase hydrolysis temperatures.

Surface chlorination (Fig. 2, routes 3–5, 11) causes an increase in the measured effective [Cl]/[V] ratio, i.e., leads to underestimation of the true denticity of the covalently bound groups. At the same time, we cannot rule out the possibility of inexhaustive substitution of chlorine atoms by hydroxo groups from the surface nanostructures in reactions with H_2O vapor. The same is true of a possible loss of hydrogen chloride by absorption from the gas phase during vapor-phase hydrolysis, which is responsible for overestimated average functionalities. Hence, the stoichiometric composition of the vapor phase hydrolysis products cannot be unambiguously derived from the [Cl]/[V] ratio, especially in the case of hydrolytic degradation (Fig. 2, routes 8, 9).

Thus, the data on the stoichiometric composition of the surface structures, derived from the [Cl]/[V] ratio, should be treated with care. At the same time, extensive application in identification of vanadium-containing grafted structures is found by spectral methods.

Vanadium oxide compounds are active in virtually all types of spectroscopy, including IR, Raman, NMR, XANES/EXAFS, etc. [32–35]. As known, spectral methods provide reliable structural information, suitable for assessing the reliability of quantum-chemical results for molecular systems. Below, we discuss the results of spectroscopic examinations of vanadium-containing surface-grafted structures.

Roozeboom et al. [40] were the first to apply Raman spectroscopy in studies of vanadium-oxide systems prepared by impregnation technique. Since then, this method has been conventionally used for this purpose. The Raman spectra of isolated vanadium-containing centers exhibit an intense peak at 1030–1040 cm^{-1}, associated with the stretching vibrations of vanadyl group. Close frequencies of the signal from the V=O vibrations in the $VOCl_3$ molecule [41], coupled with relevant ^{51}V NMR data [42], were interpreted as due to manifestation of stretching vibrations of the vanadyl group in the distorted tetrahedral surrounding of the vanadium atom. On this basis, Das et al. [42] hypothesized formation, in the absence of water vapor, of isolated tridentate (three-legged) vanadium-oxide structures.

Some researchers [32–35, 43] believe that contacts of such products even with moisture traces at room or decreased temperatures lead to Si–O–V bond cleavage and formation of polycondensed vanadium-oxide chains, or two-dimensional layers or even nuclei of bulk V_2O_5 phase. The shift of the 1030 cm^{-1} band to 995 cm^{-1} was interpreted as being due to profound destructive processes. An increase in vanadium concentration in impregnation products produced the same effect [32, 41].

As regards IR spectra, the early relevant publications were mostly focused on the absorption bands corresponding to the stretching vibrations of the O–H group. For example, upon treatment of silica with vanadium oxochloride, the band at 3750 cm^{-1}, associated with isolated silanols, decreased in intensity [44, 36]. The same concerns impregnated samples [34, 43], on which basis the covalent bonding of vanadium during impregnation was derived. The IR spectra of hydrated products prepared both by impregnation [43] and molecular layering [36] techniques also contained a weak signal at 3660 cm^{-1}, which was assigned to (V)–O–H vibrations.

Absorption at 905–930 cm^{-1} was observed *in situ* in IR diffuse transmission spectra of the $VOCl_3$ vapor treatment products of KCC-4 silica gel [36]. Also, vapor-phase hydrolysis caused partial restoration of the signal from silanols at 3750 cm^{-1} and the appearance of the (V)O–H bands at 3660 cm^{-1}. However, vapor-phase hydrolysis left virtually unaffected the intensity of the absorption band at 920 cm^{-1}, tentatively assigned to the Si–O–V vibrations. This fact was interpreted as testifying to water vapor resistance of low-dimensional vanadium oxide structures [36].

The IR and Raman spectra of vanadium oxide systems synthesized on silica surface by the impregnation method also contain absorption bands at 900–960 cm^{-1} [34, 45]. Relevant IR spectroscopic data for mixed xerogels of vanadium and silicon oxides also suggest a wide scatter of data on band positions within this range [46–47].

In this respect, much significance is attached to manifestations of the Si–O–V vibrations of the surface vanadium oxide centers in Raman spectra. Interestingly, the bands at 900–960 cm^{-1} received different interpretations in different periods. In 1993–2003, they tended to be unambiguously associated with the V–O–V bonds in polycondensed vanadium oxide moieties [32, 35, 43]; in 2005, two alternative assignments were suggested [33]; and in 2007 these bands were positively attributed to Si–O–V vibrations [34]. Of utmost importance for this evolution of these views were quantum-chemical calculations of vibrational states for vanadium oxide moiety on the SiO_2 surface [48–50], which attested to possible manifestation of Si–O–V vibrations at 900–1000 cm^{-1}.

Nevertheless, the above-mentioned scatter of spectral data still casts doubts in the Si–O–V assignment made for bands within the indicated range. Lee and Wachs [34] undertook *in situ* Raman and IR spectroscopic examinations specifically for identification of Si–O–V vibrations. The subjects of their studies were the impregnation products of Cabosil silica with vanadyl isopropoxide $VO(O^iPr)_3$ in nonaqueous media. Along with peak at 1043 cm^{-1}, the Raman spectra contained two weak bands at 970 and 905 cm^{-1} [34]. Based on shifts induced by hydrogen-deuterium exchange, the signal at 970 cm^{-1} was assigned to Si–OH vibrations, and that at 905 cm^{-1}, to Si–O–V stretching vibrations. At the same time, in the IR spectra the Si–O–V vibrations were manifested as a fairly narrow band at 925 cm^{-1} [34].

Wide scatter of the published spectral data can also be associated with different spectral manifestations of the vibrations for centers with different numbers of Si–O–V bonds. This hypothesis is also consistent with the above-mentioned differences in band positions, characteristic for vanadium oxide structures fixed on silica surface both by impregnation and molecular layering (ALE/ALD) techniques. Moreover, *in situ* IR spectra recorded during synthesis of vanadium oxide systems by molecular layering technique demonstrated a weak though distinct change in absorption band positions within the indicated range for the same sample. Even more profound changes are caused by temperature variation in various stages of synthesis [36]. Thus, it can be presumed with good reason that the local structure of element-containing nanostructures on the silica surface can be identified from changes in the spectral characteristics, observed in the 900–1000 cm^{-1} region.

However, such identification is impossible without spectra of systems with the known and identical functionalities of vanadium oxide centers. Unfortunately, this was not the case in most of the relevant works. In the case of impregnation and sol-gel synthesis techniques, the composition and structure of the local centers in the products cannot be determined because of the absence of chemical analysis data. Earlier studies utilizing the molecular layering (ALE/

ALD) and chemical grafting techniques revealed on the surface the coexisting centers having different denticities. In this context, of special interest is a series of studies [51–53] in which the Aerosil surface was subjected to $VOCl_3$ vapor treatment in a vacuum at room temperature. Those studies combined chemical analysis, ^{51}V NMR, and *in situ* EXAFS/XANES and IR spectroscopic examinations and on this basis unambiguously established formation on the Aerosil surface of monofunctional ≡Si–O–$VOCl_2$ vanadium oxochloride nanostructures exclusively. The difference spectra revealed an absorption band at 959 cm^{-1} which was reliably assigned to Si–O–V vibrations [51], as confirmed by ^{16}O–^{18}O isotope exchange experiments [52]. However, this seems to be the only presently known object for which Si–O–V vibrations were unambiguously identified.

Thus, despite a large number of relevant publications, vanadium-containing groups on SiO_2 surface cannot be identified by experimental methods exclusively. Since recently, quantum-chemical modeling methods have been actively applied for these purposes.

Quantum-Chemical Modeling as Identification Tool for Vanadium-Containing Centers on the Silica Surface

Quantum-chemical modeling belongs to the most information-rich techniques employed for identification of vanadium oxide moieties on Al_2O_3 [49–50, 54] and SiO_2 [48, 50, 54] surface. Of much significance in such modeling is the choice of the theory level, i.e., the calculational method and basis set of atomic orbitals. In the case of neat silica surface, a sufficient level can be found in B3LYP/6-31G* model [55, 56], while for vanadium-containing structures the situation is not so unambiguous. At the present time, all the relevant models are those based on modifications of the density functional theory method: B3LYP [48, 49], BP86 [50, 57], and PBE [57]. The atomic orbital basis varies from 3-21G [58, 59] to 6-31G* [58, 60, 61] and TZVP [48–50]. Hence, wide scatter of the modeled data may be associated with the choice of both the calculational method and the substrate surface model.

Thus, quantum-chemical modeling of the systems of interest should, above all, asses in unbiased manner the adequacy of the calculated predictions. This task can be accomplished as applied to molecular compounds of close nature solely (Table 1). The structural characteristics of the molecules comprising vanadium atoms, calculated even at the B3LYP/6-31G** level with Gaussian®03W program [62], reasonably agree with the experimental data. Significant departure is observed for the vanadyl V=O stretching vibrations only. For them, the calculated frequencies are overestimated by 50–150 cm^{-1} in all models of vanadium oxide and vanadium oxochloride moieties comprising the vanadyl group [48–50]. Most researchers seek to overcome this inconsistency by scaling all the calculated frequencies using a common multiplier [48–50]. However, a severe danger in inherent in such approach: The use of a multiplier affords reasonable agreement of the $\nu_{V=O}$ vibrational frequencies, but the frequencies of other vibrations prove to be too low. Overestimation of the calculated frequencies can be due to a systematic error in electronic structure calculations, in particular, due to basis set and theory level limitations or significant anharmonic effects.

Both a change to a larger, TZVP, basis set for atomic orbitals and introduction of anharmonic corrections through perturbation theory using fourth-order force field parameters in Gaussian03W program do not qualitatively change the situation with $\nu_{V=O}$ vibrational frequency calculations. This suggests that the density functional theory level is insufficient for p-bond description. Taking into account the electron correlation in the framework of the Møller-Plesset and coupled clusters CCSD corrections also does not afford acceptable accuracy.

At the same time, there is a need to consider anharnomic corrections for quantitatively describing the V–O and especially O–H stretching vibrations distinguished by strong anharmonism. Hence, harmonic frequency scaling seems to be ill-founded as applied to the electronic structure of the systems of interest [48–50], since the systematic errors in calculations for different vibration groups differ strongly: The V–Cl vibrations are adequately reproduced at the harmonic frequency level; the V–O vibrations require introduction of 15–20 cm^{-1} anharmonic corrections; the O–H vibrational frequency can be estimated with account of strong anharmonism (100–200-cm^{-1} corrections) only; and V=O vibrations are characterized by weak anharmonism, so that single-determinant approximation is unsuitable for quantitatively predicting their frequencies.

Modeling as applied to compounds on silica surface also entails some problems. Because of high degree of covalency in silica, the silanol groups on its

Table 1. Calculated vibrational characteristics of compounds comprising vanadium with pseudotetrahedral coordination [14]

Compound	Vibrational mode	Fundamental transition energy, cm^{-1}					References
		B3LYP/6-31G**		B3LYP/TZVP		experiment	
		harmonicity	anharmonicity	harmonicity	anharmonicity		
$VOCl_3$	ν (V=O) (a_1)	1162	1153	1115	1107	1048	[67]
	ν_{as}(V–Cl) (e)	508	502	499	494	508	
	ν_s(V–Cl) (a_1)	411	409	406	403	411	
	δ (V–Cl) (e)	259	257	257	255	246	
	δ(V–Cl) (a_1)	169	168	166	165	160	
	δ(V–Cl) (e)	129	129	127	126	124	
$(CH_3O)VOCl_2$	ν(C–O)	1104	1071	1090	1063	1069	[68]
	ν(V=O)	1146	1134	1104	1085	1030	
	ν(V–O)	694	685	671	662	674	
	$\nu(VCl_2)$	452 503	448 499	445 495	440 489	446 502	
$VO(OH)Cl_2$	ν[V–O(H)]	822	809	797	785	798	[69]
	ν[(V)O–H]	3828	3640	3816	3639	3650	[43]
$VO(O^iPr)Cl_2$	ν(V–O–C)	1000	970	989	–	952	[70]
	δ(V–O–C)	686	675	673	–	673	
	ν(O–C)	1127	1090	1127	–	1099	

surface most often are described with the use of cluster models. The latter typically saturate the surface Si–O bonds on silica with hydrogen atoms, like, e.g., those in H_3SiOH, $H_2Si(OH)_2$, and other compounds (Fig. 3a) [50, 57, 63]. However, the hydrogen "pseudoatoms" give a distorted picture of the electronic surrounding of the silicon atom in SiO_2. An alternative can be found in free valence saturation with OH groups (Fig. 3b) [55, 56, 64].

In any case, the size of the cluster model of the silanol groups can influence the prediction. The best way to assess this influence is to compare models of different sizes with a reliably identified real structure. In particular, a series of studies [51–53] unambiguously identified the $\equiv$Si–O–$VOCl_2$ monodentate groups and interpreted their spectra in the region of Si–O–V vibrations. Those results were compared with the modeled data based on clusters containing 1, 4, and 10 silicon atoms (see Figs. 3a–3d). This comparative analysis took into account one of the known artefacts in calculations of the vibrational states of molecular systems in terms of such models. Specifically, there exists strong coupling of the bending modes in Si–H groups involving hydrogen "pseudoatoms" with Si–O–V modes. This effect is typically eliminated by artificially increasing the mass of the "pseudoatoms," e.g., to that of deuterium [50] or to 1000 [48] and even 10^6 amu [65]. At the same time, it seems more reasonable to totally eliminate vibrational motion of the pseudoatoms by setting their mass to infinity. The validity of this technique was confirmed by Morrow and Hardin [21] who found that the SiO_2 network vibrations exert a comparatively weak influence on the characteristics of groups containing a heavy atom, covalently grafted to the silica surface.

As seen from Table 2, despite all presumptions and simplifications in modeling, the cluster size and the choice of "pseudoatoms" are of little importance, and the B3LYP/6-31G** theory predictions quantitatively agree with the experimental data. Like in the case of molecular objects (see Table 1), the only exception concerns the V=O bond characteristics.

Table 2. Experimental [51] and calculated parameters of –$VOCl_2$ groups on silica surface. Calculation by the B3LYP/6-31G** method

Parameter	Cluster model				Experiment
	H_3SiO–	$(HO)_3SiO$–	$(H_3SiO)_3SiO$–	$H_{15}O_{12}Si_{10}O$–	
Vibrational transition energy, harmonicity/anharmonicity, cm^{-1}					
ν(Si–^{16}O–V)	976/961	965/951	956	951	959
ν(Si–^{18}O–V)	930	921	914	910	929
ν(V=O)	1151/1141	1157/1152	1152	1159	1043 1019
Structural parameters					
r(V–O), Å	1.725	1.732	1.725	1.725	1.78
r(V–Cl), Å	2.168	2.167 2.170	2.169	2.168	2.16
r(V=O), Å	1.554	1.552	1.555	1.556	1.57
r(Si–V), Å	3.25	3.203	3.224	3.212	3.13
∠Si–O–V, deg	144	140	142	141	136
^{51}V NMR isotropic chemical shift, ppm					
Δ(^{51}V)	–306	–304	–314	–312	–295

Importantly, high-quality quantum-chemical calculations can be performed already with a minimal H_3Si–OH cluster*:* The vibrational and structural characteristics of such model differ insignificantly from those in larger models. The significance of this finding becomes evident when one changes to modeling of polyfunctional structures, in which case the deciding role is played by the positional relationships among the silanol molecules reacting with the same $VOCl_3$ molecule.

One of the simplest approaches to polyfunctional structure calculation considers several free silanols [14, 49, 64, 65]. It is presumed that, on SiO_2 surface, there are isolated reactive centers in high concentrations, that can be separated from one another by any distance and participate in Si–O–V bond formation in nanostructures of any denticity. This approach can be termed the "free silanol" model. Evidently, in terms of this model formation of polydentate groups is not

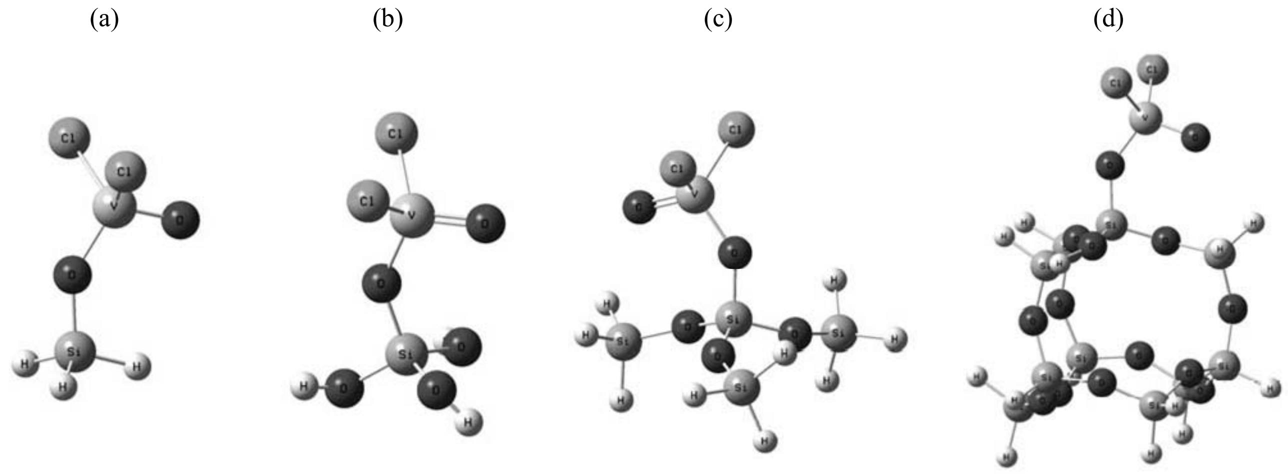

Fig. 3. Cluster models of –$VOCl_2$ groups on the silica surface.

Table 3. Vibrational transition energies of vanadium-containing nanostructures, obtained by “free” silanol model calculations in the harmonic and anharmonic approximations

Vibrational mode		Model				
		$H_3SiOVOCl_2$	$(H_3SiO)_2VOCl$	$H_3SiOVO(OH)_2$	$(H_3SiO)_2VO(OH)$	$(H_3SiO)_3VO$
Vibrational transition energy, harmonicity/anharmonicity, cm^{-1}						
ν[(V)O–H]	ν_s			3852/3685	3848/3661	
	ν_{as}			3848/3682		
ν(V=O)		1151/1141	1139/1130	1143/1132	1134/1125	1126/1115
ν(Si–O–V)	ν_s	976/961	996/978	980/962	999/983	1015/997
	ν_{as}		950/935		947/932	942/926
ν[V–O(H)]	ν_s			769/761	791/780	
	ν_{as}			814/807		
δ(Si–O–V)	δ_s	627/617	619/612	618/608	607/598	603/595
	δ_{as}		645/635		655/645	653/642
δ(V–O–H)	δ_s			665/637	685/622	
	δ_{as}			689/652		
ν(V–Cl)	ν_s	447/443	467/462			
	ν_{as}	500/495				

associated with any steric strains in the surface layer of the substrate. This model predicted possible splitting into symmetric and asymmetric components for the $\nu_{(Si–O–V)}$ vibrations of vanadium oxide moieties with hydrogen-saturated bonds in the (≡Si–O–)$_3$V=O tripoid structure [48–50]. However, neglecting the anharmonism and resorting to the $\nu_{(V=O)}$ bond scaling with a common multiplier led to a ~100-cm^{-1} difference between the predicted and experimental frequencies.

Model calculations for OH groups attached to the broken bonds also entail systematic errors. Khaliullin and Bell [65] modeled vanadium oxide groups with bi- and tridentate coordination using direct fixation of the silicon atom positions existing in β-crystobalite. In a similar way, vanadium oxide nanostructures of all the three denticity types were modeled with the use of $(HO)_3Si$–O– clusters [64]. That led to structural distortions, which necessitated fixing the positions of the hydrogen “pseudoatoms.” This afforded good agreement of the $\nu_{Si–O–V}$ vibrational frequency in the $[(HO)_3Si–O–]_3VOCl_2$ model with the experimental data [51]. However, the same parameters obtained in terms of the models of polydentate vanadium oxide moieties displayed unsatisfactory agreement with the experimental data on the spectral bands at 900–920 cm^{-1}. The Si–O–V normal modes, yielded by modeling for mono- and bidentate vanadium oxide structures on SiO_2 surface, also were strongly underestimated compared to the experiment. It should be noted that, in [61, 64], the vibrational characteristics were predicted with the use of a uniform scaling multiplier of 0.96, which could also be responsible for disagreement between the calculated and experimental data.

Thus, the above-discussed works share drawbacks in terms of lacking unity in choosing the theory level and cluster model and taking an essentially empirical approach of vibrational energy scaling. In this context, analysis of anharmonic effects seems to be of principal importance.

We carried out “free silanol” model calculations with H_3Si–O– clusters, whose results (Fig. 4, Table 3) also predict splitting of the Si–O–V stretching vibrations in polydentate structures into low-frequency asymmetric and high-frequency symmetric components. With anharmonic effects included, the calculated results proved to be close to the experimental data without the use of scaling multipliers. For

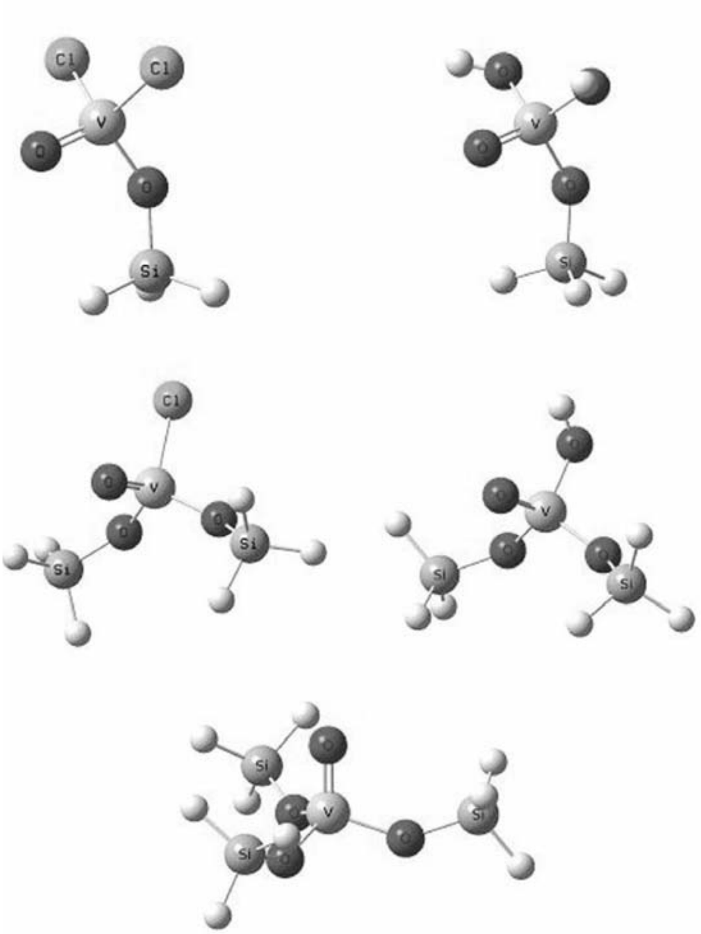

Fig. 4. "Free silanol"-based cluster models of vanadium-containing moieties with different functionalities.

example, the band positions at 932 and 926 cm^{-1} for vanadium-containing hydrated polydentate structures are very close to the band frequencies within 940–910 cm^{-1} as reported in numerous publications on the vibrational spectra of vanadium-containing products [32–35]. Model calculations suggest that the bands at 930–940 cm^{-1} should be assigned to bifunctional, and those at 910–920 cm^{-1}, to trifunctional vanadium-containing groups. The quantitative agreement between the calculated results and experimental IR spectral data for multifunctional ≡Si–O–VOCl$_2$ moieties was mentioned earlier. Hence, the ≡Si–O–VO(O$_2$) "umbrella" structure can be excluded from consideration [49, 64, 66].

The matrix element values for the fundamental transitions, calculated within the double harmonic approximation (Fig. 5), characterize the Si–O–V vibrations as the most intense both in Raman and IR spectra. However, by contrast to the band intensities derived by Gijzeman et al. [49] from hybrid calculations at various theory levels, direct calculation of the matrix elements in terms of the density functional theory shows that the IR spectra contain exclusively asymmetric, and Raman spectra, symmetric modes. This may be specifically responsible for a very low intensity of bands at 900–920 cm^{-1} in the Raman spectra of vanadium oxide moieties on the silica surface [32–35].

The calculations in harmonic approximation gave the OH vibrational frequency for the vanadium-containing centers, manifested upon water vapor exposure, that strongly exceed the experimental values. It is only with anharmonic corrections that one can obtain close-to-experimental values (Table 3). The predicted energy of fundamental transitions at 3661–3685 cm^{-1} is very close to the experimental value of 3660 cm^{-1} [43, 36]. This also confirms the adequacy of our calculations.

It should be noted that, for chlorine-containing structures, the model does not predict vibrations within

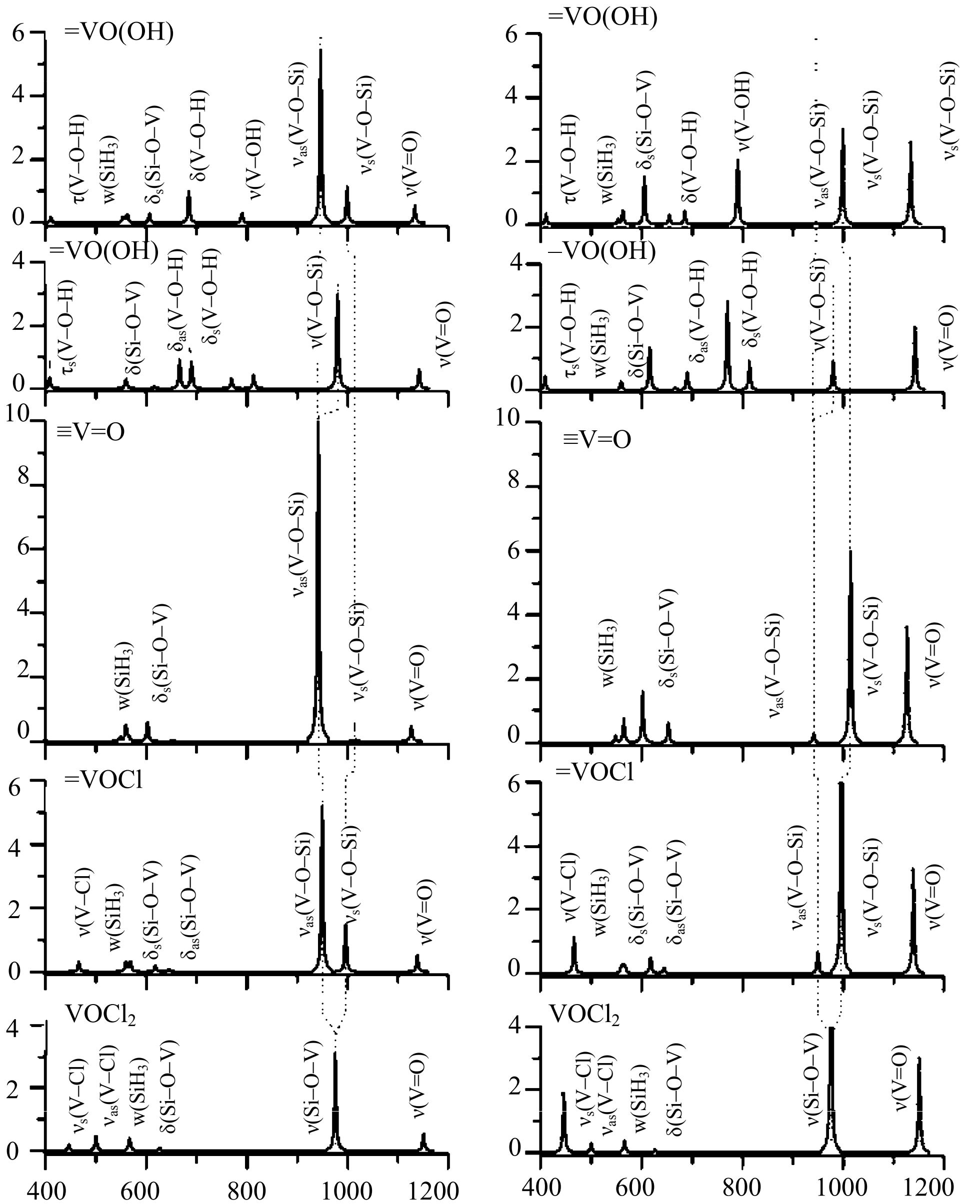

Fig. 5. (Left) IR and (right) Raman spectra of vanadium-containing structures with different functionalities on the silica surface, calculated in the harmonic approximation. The ordinate has the units of squared matrix element of transition. The spectral bands are represented by Lorenzian profiles with bandwidths of 2 cm^{-1}.

700–800 cm^{-1}, while hydroxylated centers should give bands corresponding to the V–OH stretching vibrations, whose intensity is sufficiently high for them to be recorded in IR, and especially in Raman, spectra (Fig. 5) within 760–807 cm^{-1}.

The quantum-chemical calculations predict δ(Si–O–V) bending vibrations with the energy corresponding to 600–644 cm^{-1}, intermediate between the V–Cl and V–OH vibrational frequencies. However, the probability calculations for these transitions predict negligible IR and Raman activities for such vibrations (see Fig. 5). A totally different situation is observed for δ(V–O–H) bending vibrations: We found that, in the IR spectra, they are superseded in intensity by Si–O–V vibrations only and are almost identical in intensity with ν(V–OH) vibrations in the Raman spectra. The energy of the corresponding vibrational transitions, 600–650 cm^{-1}, can be associated with weak experimental signals at 610–650 cm^{-1}.

Thus, the “free silanol” model quantum-chemical calculations allow predicting, with fairly high precision, virtually all the features of the experimental spectra, associated with the local groups unbound directly to the silica surface, e.g., ν(V–OH), ν(O–H), ν(V–Cl), etc. A reason to minor deviation of the calculated from experimental ν(Si–O–V) frequencies for polydentate structures can be found in neglecting possible steric strains by the “free silanol” model itself.

Specifically in analysis of steric strains it is evidently reasonable to expect further progress in quantitative prediction of the spectral characteristics of element-containing nanostructures prepared by molecular layering method.

CONCLUSIONS

The quantum-chemical analysis, whose results we presented above, does not exhaust its task with respect to local transformations of vanadium-containing nanostructures during synthesis on the silica surface by molecular layering technique and possible ways of identification of the resulting products. In particular, we did not discuss processes involving strained siloxane bridges formed from dehydroxylation and having enhanced reactivities [25, 26]. Also, we did not touch upon the chemical transformations in several molecular layering cycles. Lateral interactions among the neighbor element-containing structures, e.g., condensation of the OH groups linked to the modifying agent atoms [14, 36], are also beyond the scope of this study. The same is true of the redox processes and incorporation of the modifying agent into the subsurface layer of the substrate, which disturbs the siloxane network, etc.

Nevertheless, the discussed results provide an idea of the chemical processes involved in the molecular layering procedure in terms of complex chemical transformations whose outcomes in every stage of synthesis are determined by temperature factors, as well as by the nature and genesis of the solid-phase matrix used. The nanosized nature of the systems of interest generates major difficulties in identification of the composition and structure of the synthesis products, so much the more in their control by varying the technological factors.

In this context, much promise for further development of molecular layering nanotechnology is offered by combining synthesis experiments with complex physicochemical analysis and quantum-chemical modeling work. In our opinion, specifically this approach would allow implementation of complete potential of the molecular layering technology in directed synthesis of nanostructures and nanomaterials with desired properties.

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