

Technological polymorphism of dispersed amorphous silicas: neutron inelastic scattering on vibrations and computer modeling

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The results of a detailed study of the vibrational spectra of a number of commercially produced amorphous, highly dispersed silicas (aerosil, silica gel, and aerogel) using inelastic neutron scattering are reviewed. The observed phenomenon of technological polymorphism and the results of the quantum-chemical modeling of the structure and vibrational spectra of the corresponding polymorphic modifications are discussed. © 1996 American Institute of Physics. [S1063-7796(96)00502-9]

1. INTRODUCTION

The class of chemical compounds known generally as “silicas” and including both natural materials from quartz and cristobalite to semiprecious stones and also man-made materials from quartz glass to aerogel has as its basis a very simple compound: silicon dioxide SiO_2 (Ref. 1). The family of amorphous highly dispersed silicas including aerosils, aerosil gels, silica gels, porous glasses, silochromes and aerogels forms a part of this class.^{2,3}

The importance of highly dispersed silicas for chemistry and chemical technology cannot be overestimated. They are used in large quantities in chemical manufacturing as adsorbents, fillers, and extenders.⁴ Silicas are also well known as medications, as agents which support the biological activity of substances and drugs, and as hemosorbents, conservants for living vaccines, and so on. Their numerous applications are a consequence of their unique surface activity, the nature of which has been studied intensively for a long time.^{5,6}

There have been many studies devoted to dispersed silicas. For a fairly long time they have been carried out primarily by empirical chemical methods, and the use of spectro-metric methods—IR and Raman vibrational spectroscopy^{7–13} and NMR spectroscopy (see the review in Ref. 14)—began only in the late 1960s. However, owing to both experimental complications and difficulties in interpreting the data, the results are to a large degree qualitative, so that it is difficult to use optical vibrational spectroscopy to study the structure and composition of these materials.

In contrast to optical studies, in recent years there has been great progress in neutron vibrational spectroscopy, owing to the possibility of reliably isolating the parts of the spectrum corresponding to certain structural fragments of the system, including the surface. The latter should be particularly noted, because it is well known that inelastic thermal-neutron scattering (INS) is generally a technique for studying the bulk, owing to the long neutron mean free path in matter (of order 10^{-2} m).¹⁷ However, if the specific area is increased, as occurs in the case of highly dispersed materials, and if the sample surface is covered with hydrogen-

containing material (protium nuclei possess an exceptionally high neutron-scattering cross section, and the amplitude of their vibrational displacements is large), the contribution of scattering on surface vibrations is significantly increased. This is a favorable situation not only for hydrogen-containing adsorbents, but also for vibrations of the substrate as a result of the “riding effect.”^{18,19} Dispersed silicas satisfy both of these conditions, so that the application of INS spectroscopy to them has proved extremely successful. By carrying out a series of specially designed experiments,^{20–29} it was possible to determine the vibrational spectra of the bulk, or core, of several such materials and the vibrations of the surface zones. The results obtained for a series of different commercially produced silicas were of fundamental significance. It was shown that for the silicas studied, the core and surface vibrational spectra are so different that these materials must be classified as fundamentally different structures.^{30–32} In this way the phenomenon called technological polymorphism was discovered through the spectrum.³⁰ It formed the basis of a new, algorithmic approach to the computer modeling of these materials.^{30–32} This modeling, performed using the most modern techniques of quantum chemistry,^{33–35} has made it possible to construct structural models which explain the behavior of the vibrational spectra of various types of silicas. It has also made it possible to determine a unique relation between this phenomenon and the differences between the chemical technologies used to obtain the products. The success of this approach has been checked by comparing the calculated and experimental vibrational spectra measured using INS.

The goal of the present review is to systematize the results and methods of analyzing them in order to explain and develop the approach for studying the specific phenomenon of technological polymorphism. This phenomenon was first studied carefully for dispersed silicas, and proved to be one of the distinguishing features of nanomaterials of practically any class.³⁶ Therefore, understanding it is crucial for creating basic materials in the very near future.

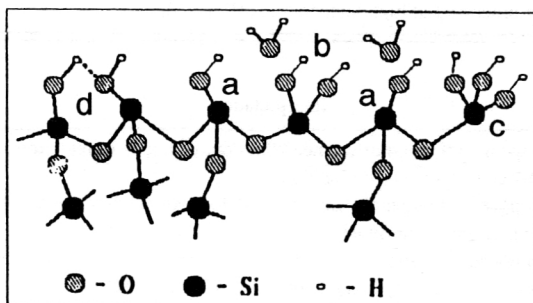


FIG. 1. Schematic representation of the structure of amorphous silica. (a) Silanol groups; (b) silandiol group; (c) silantriol group; (d) groups bound by a hydrogen bond.

2. GENERAL CHARACTERISTICS OF DISPERSED SILICAS

2.1. Structural properties and IR absorption

It is well known that amorphous dispersed silicas are obtained in the condensation and polymerization accompanied by hydrolysis of silicon tetrahalogenides, ortho-organic ethers of them, and silica salts.¹ Polymerization leads to the formation of siloxane (SiOSi) chains and nonplanar cycles with different numbers of members. When packed in space, these chains and cycles form the bulk structure (the core) of silica. The same chains and cycles form its surface. The valence bonds of the surface atoms of silicon are saturated only from the inner side of the surface. There is a "valency excess" on the outside surface, which is saturated in the presence of water molecules by the joining of hydroxyl groups of various configurations. The resulting active surface centers willingly adsorb water, so that around the stable siloxane core there appears a characteristic cloud consisting of hydroxyl groups and adsorbed water. This view of the structure of amorphous dispersed silicas is described in the well known monograph of Iler.¹ Although many particular problems have been solved (see the later monographs^{4,5}), this view has not undergone any significant changes since it was first developed. For example, in Fig. 1 we show the structure of dispersed silica which was taken to apply to a product of any origin without comment until three years ago. In this scheme the siloxane chain is a surface layer of base atoms. The fragments of its branching inside mimic the development of the bulk structure. The unsaturated bonds of the surface silicon atoms are closed by hydroxyl groups, where both the number of groups per silicon atom and their distribution over the surface are, in general, not clearly determined. The outside layer of this structural fragment is occupied by molecules of adsorbed water, the location of which relative to the surface groups is also to some degree arbitrary. This model essentially gives a clear representation of the understanding of the atomic structure of the bulk and the surface of dispersed silica which has been used as the basis for studying their IR absorption spectra.

There have been repeated attempts to study the vibrational spectra of dispersed silicas using optical spectroscopy (IR absorption and reflection, disrupted total internal reflection, Raman scattering; see Refs. 7–13). However, owing to the very strong absorption of the siloxane matrix,³⁷ the stud-

ies have mainly been concentrated in the range 3000–4000 cm^{-1} in which the frequencies of the valence vibrations of the hydroxyl groups and water are located. The results, even when deuterium–protium exchange is included, are contradictory (see Refs. 11 and 13) and remain semi-qualitative, as can be seen from the generalized picture given in Table I. This table shows that by using the data in the range 3000–4000 cm^{-1} it is practically impossible to distinguish between, for example, aerosil, silica gel, and aerogel. Regarding the most structure-sensitive ranges 0–400 cm^{-1} and 500–1000 cm^{-1} , the former is completely hidden in the IR spectra by the absorption of the siloxane bulk, and the latter has been little studied for the same reason (see Refs. 37–39). The existing information on this region has mainly been extracted from analysis of the compound frequencies.

The main conclusions obtained on the basis of IR absorption studies reduce to the following.

(1) The similarity of the behavior of different dispersed silicas in a series of basic reactions (see Refs. 1–5) suggests that their surface structures are similar, so that studies have mainly focused on different samples of aerosil, as it is the most chemically pure silica.

(2) Because the research is mainly concentrated in the range 3000–4000 cm^{-1} , the main objects of study are the hydroxyl covering and the adsorbed water.

(3) The aerosil surface is uniformly covered by silanol groups with density ~ 4.6 group/ nm^2 , which corresponds to an average distance between groups of 0.7 nm.⁵ The existence of silandiol groups is not disputed, but the fraction of them according to the data of various authors varies from 4 to 40% (Refs. 5 and 14). Silantriol groups are not seen on the surface of an aerosil under ordinary conditions.⁴⁰

(4) The adsorbate–substrate system in the case of water plus silica consists of two partners: a silanol group and a water molecule. The difference between the results of different authors reduces to the question of the type of interaction between the partners. Some authors favor a coordination nature of the water adsorption centers,⁶ while others think that the water molecule binds to a hydroxyl center via a hydrogen bond. Among the recent studies devoted to this question, that of Lygin and co-workers^{14,41,42} should be singled out. Those authors attempt to explain the water adsorption mechanism on the basis of study of the dynamics of deuterium–protium exchange in hydroxyl groups by monitoring the intensity of the absorption bands of the OH and OD groups (3749 and 2761 cm^{-1} , respectively). Two conclusions were drawn on the basis of these studies: (1) adsorption of water occurs on hydroxyl groups; (2) on the aerosil surface there exist sections with significantly different rates of water adsorption, i.e., there exist hydroxyl groups of quite varied structure. The authors of Ref. 43 arrived at similar conclusions on the basis of calculations using the method of molecular dynamics. The different possible locations of water adsorbed on silica are shown in Fig. 2.

In the end, studies of IR absorption have not answered the following basic questions of the chemistry of dispersed silicas:

- How similar are the core structures of various manu-

TABLE I. Frequencies of vibrational absorption bands of free hydroxyl groups of silicas processed at high temperatures (Ref. 13).

Sample	Frequency, cm^{-1}			Interpretation
	t°, C	OH	OD	
Porous glass	550	4540		Compound vibration of valence vibrations of free hydroxyl groups in SiOH and SiO valence vibrations
	750	4550		Compound vibration of valence and deformational vibrations of free hydroxyl groups in SiOH
Aerogel	700	4520	3363	Compound vibration of valence and extraplanar deformational vibrations of free hydroxyl groups in SiOH and SiOD
Porous glass	750	3850	2840	Compound vibration of deformational vibrations of free hydroxyl groups in SiOH and SiOD and valence vibrations in SiO_4
	550	3749	2761	Valence vibrations of free hydroxyl groups in SiOH and SiOD
Silica gel	600	3740	2760	
	400	3749	2761	
	940	3748		
	500	3740		
Aerosil	940	3750		
	500	3748		
Aerogel	700	3750	2740	
Aerosil	450	3743		
	400	3737	2755	
	400	3747	2760	
Silica gel	400	3500		Valence vibrations of hydroxyl groups in $\text{Si}(\text{OH})_2$
Porous glass	400	2000		Combination and harmonic vibrations of the silica core
		1870		
Aerogel	600	1635		
Silica gel	400	950		Deformational vibrations of SiOH or valence vibrations of the OH group about Si
	400	870		Deformational vibrations in SiOH
Aerogel	700	770	603	Extraplanar deformational vibrations in SiOH

factured forms of amorphous dispersed silicas?

- How is their surface formed, and what is the distribution of hydroxyl groups on the surface?
- Under what conditions do silanol, silandiol, and silantriol groups exist on the surface?
- What are the adsorption mechanisms of various materials, in particular, water, on the surface of these products?

Finding the answers to these questions made it necessary to seek new ways of distinguishing between different materials. Inelastic neutron scattering has proved to be an effective spectral tool. It has made it possible to extend spectral studies of the vibrational spectrum to the range $0-1500 \text{ cm}^{-1}$, which contains the most structure-sensitive deformational, torsional, and fan-like vibrations of hydroxyl

groups, water, and the siloxane core. It also has become possible to obtain the vibrational spectra of the individual structural components of each silica sample.

2.2. The use of inelastic neutron-scattering spectroscopy for studying vibrational spectra

Inelastic neutron-scattering (INS) spectroscopy is a relatively new technique of studying surfaces. The original studies using elastic (diffraction) and inelastic (oscillation spectroscopy) neutron scattering^{17,44} were oriented toward the study of bulk characteristics, because the contribution of surface atoms to the scattering spectrum of a sample was imperceptibly small, owing to the high penetrability of the neutron. However, as mentioned in the Introduction, the situation becomes more favorable for highly dispersed samples, as has been confirmed for the case of dispersed silicas. The study of the INS from these samples has fully revealed the main advantages of neutron spectroscopy: sensitivity to protium nuclei and to isotopic protium-deuterium replacement, the absence of selection rules in energy transfer, the involvement of a broad spectrum of vibrational states in the scattering process, and so on.

One of the first studies which obtained results on the vibrations of water adsorbed on a silica surface was performed in 1981.⁴⁵ The earlier studies of 1964–1975 (Refs. 46–48) devoted to the same problem were carried out at room temperature, which limited the possibilities of studying low-frequency vibrational modes. The authors of Ref. 45 studied two silica samples (silica gels) at a temperature of

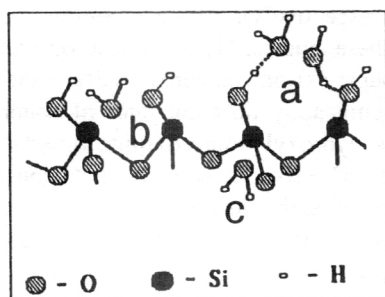


FIG. 2. Schematic representation of the location of adsorbed water molecules on the surface of amorphous silica (Ref. 6). (a) Water joined by a hydrogen bond; (b) water coordinated in a cis-location; (c) water coordinated in a trans-location.

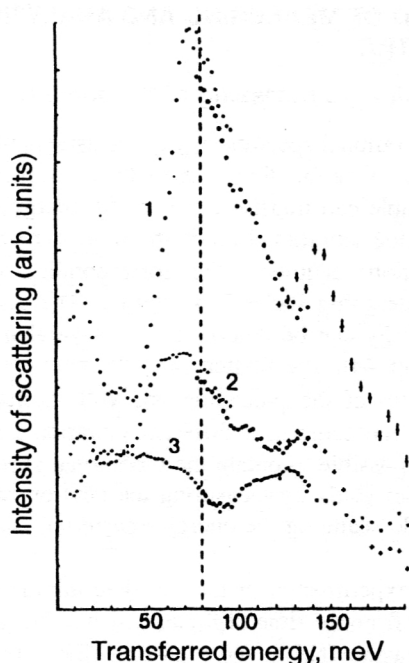


FIG. 3. INS spectra from the silica gel Gasil1200 at 15 K (Ref. 45) for various moisture contents: (1) 13%; (2) 4%; (3) sample dried at 150 °C.

15 K: Gasil1200 (calculated pore diameter 21 Å, specific area 850 m²/g), and Spherisorb S20W (89 Å and 232 m²/g). The main result of the study was to establish that the spectrum of vibrations of water in the pores of a silica gel differs from the vibrational spectrum of ordinary ice (see Figs. 3 and 4), and it was discovered that the shift of the spectral maximum located at 640 cm⁻¹ to the low-frequency region is increased in going from a silica gel with small pore diameter to one with smaller pore diameter. For

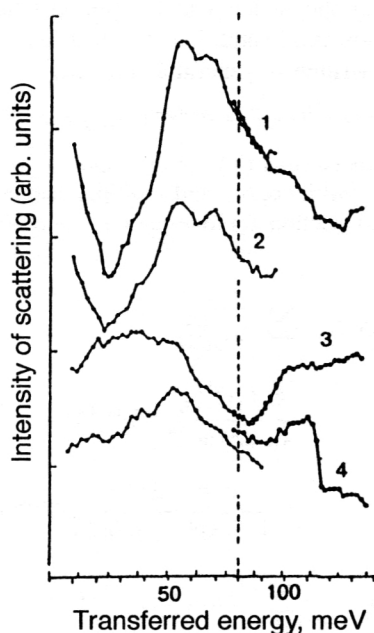


FIG. 4. INS spectra from the silica gel Spherisorb S20W at 15 K (Ref. 45) for various moisture contents: (1) 3%; (2) 2%; (3) 1%; (4) sample dried at 110 °C.

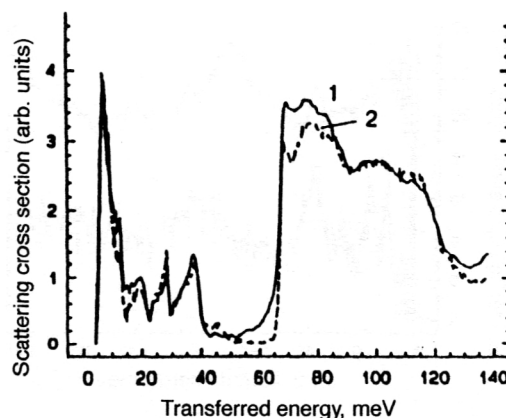


FIG. 5. INS spectra from ice. (1) Ice in porous Vycor glass (Ref. 56); (2) hexagonal ice (Ref. 57).

example, in Fig. 3 we see that for maximum moisture content of the sample the main peak of the spectrum practically coincides with the principal band in the spectrum of ice H₂O, the location of which is shown by the vertical dashed line. When the sample is dried, the location of this peak in the spectrum of a silica gel is shifted to the low-frequency region. A similar effect is observed in going to a sample with smaller pore size. A model of water adsorption on adjacent surface hydroxyl groups was proposed to explain this shift, but the model was very qualitative in nature.

It was also established that the properties of water in the region of contact with the surface differ significantly from the properties of water in the bulk. For example, near the surface of silica the density,⁴⁹ diffusion coefficient,⁵⁰ and viscosity^{51,52} are changed. Diffraction studies⁵²⁻⁵⁵ have shown that the water in the pores has the structure of cubic ice Ic; under such conditions, ordinary ice is a hexagonal crystal Ih. This effect is explained by a change of the structure of water near the silica surface, but the explanations remain qualitative, especially when the fact, noted in Ref. 56, that the structure of the silica surfaces themselves differ is taken into account. In the same study it was shown, on the basis of model calculations and an experiment performed at temperature 15 K using a sample of Vycor glass (containing boron) with average pore diameter 30 Å and specific area 180 m²/g, that in the silica-water system there is no clear surface boundary in the form of layers of varying density. It was also suggested that in fact the structure of ice in layers experiencing a strong surface effect is not completely crystalline, but is similar to the structure of liquid water, where a large number of hydrogen bonds are broken. After comparing the vibrational spectra of water adsorbed on glasses with the spectra of ordinary ice,⁵⁷ which turned out to be quite close (see Fig. 5), it was concluded that water is present in the pores of Vycor glass in two forms: in the form of bulk water and in the form of water adsorbed on the pore walls. This conclusion is confirmed by the great similarity between the air-dry sample-ice difference spectrum and the spectrum of the dried sample (See Fig. 6). Because of this similarity, the authors of Ref. 56 hypothesized that quasifree water is present in the pores. However, that study presents only qualitative considerations regarding the contribution of the spec-

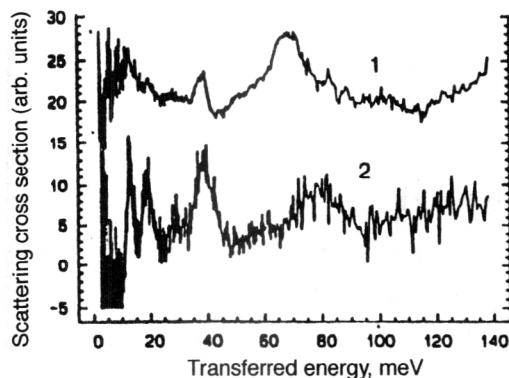


FIG. 6. INS spectra of water adsorbed on the walls of pores in porous Vycor glass (Ref. 56). (1) Dried sample with 10% moisture content remaining; (2) sample with 100% moisture content—hexagonal ice difference spectrum.

trum of ice to the spectrum of a glass sample with a moisture content of 100%.

Of the recent studies on surface vibrational spectroscopy using INS, we note the study of silicas whose surface is modified by various organic compounds,⁵⁸ the study of the surface vibrations of light hydrogen adsorbed on nickel⁵⁹ and molybdenum,⁶⁰ the study of the vibrations of water and ammonia adsorbed on oxides of manganese and zirconium,⁶¹ and the study of the vibrational spectra of quartz glass⁶² and natural silica minerals like zeolites⁶³ and opal.⁶⁴ A large number of studies have been devoted to the vibrational spectra of various modifications of ice.^{65–76} The series of studies^{77–81} devoted to fractal excitations in aerogel should also be noted.

We see from this list that INS makes it possible in principle to study the surface of dispersed silicas. However, owing to the shortcomings of systematic experimental spectroscopic studies and the absence of any method for separating the surface component of the vibrations from the complete spectrum, no results of practical importance have been obtained at this stage. The problem of distinguishing between various silicas has to a large degree been solved in the series of studies of Refs. 20–29, undertaken with the special goal of systematically studying the vibrational spectra of samples of various dispersed silicas prepared in a certain manner. In them the additive composition model of a dispersed silica has been studied in detail, and the concepts of the core and the hydroxyl and water shells have been refined. A difference–correlation method was proposed and justified for determining the spectra of the components of a complex system from the experimentally measured spectra on the basis of the postulate that the spectra of independent systems are uncorrelated. In Secs. 3–5 below we shall present the basic stages of this study which demonstrate the existence of a new type of formation of polymorphic modifications: technological polymorphism. Then in Secs. 6 and 7 we shall present the results of computational modeling for the purpose of understanding this phenomenon at the atomic level.

3. METHOD OF MEASURING AND ANALYZING THE INS SPECTRA

3.1. Preliminary processing of the spectra

The vibrational spectroscopy of inelastic neutron scattering is based on the fact that a thermal neutron incident on the studied sample can transfer a part of its energy to the excitation of some vibrational mode in the matter or can absorb this excitation, acquiring the corresponding energy and thereby undergoing inelastic scattering. The change of the neutron energy can be determined by several methods (see Refs. 17 and 44). The scattering of the next neutron occurs independently of the preceding one with excitation or absorption of the same or a different vibrational mode. As a result, it is possible to obtain the vibrational spectrum of the sample under study by measuring the neutron scattering intensity while scanning the energy transferred from or to the neutron.

In the experimental method of determining the neutron energy loss from the time of flight, which is the main method used to measure INS at the high-flux IBR-2 reactor at the Joint Institute for Nuclear Research at Dubna,⁸² the INS spectrum is the function (see, for example, Ref. 83)

$$N(t_0) = \Delta t_0 \iint \int dE_0 dE dt F(E_0, E, t_0, t) \sigma(E_0, E, \phi, T), \quad (1)$$

where

$$F(E_0, E, t_0, t) = A(E_0, E, t_0, t) \rho(E_0, t) n(E_0) \Phi(E). \quad (2)$$

Here $N(t_0)$ is the number of neutrons arriving at the analyzer during the time interval Δt_0 by the time t_0 , $\sigma(E_0, E, \phi, T)$ describes the scattering on nuclei (E_0 and E are the energies of the incident and scattered neutrons, ϕ is the scattering angle, and T is the temperature), and $F(E_0, E, t_0, t)$ is the instrumental function of the detector, including the energy distribution of the incident and scattered neutrons and the time-synchronization condition. The neutron scattering cross section σ is written in general as the sum

$$\sigma(\omega, T) = \sigma^{(1)}(\omega, T) + \sigma^{(\text{mph})}(\omega, T) + \sigma^{(\text{mpl})}(\omega, T), \quad (3)$$

where the superscripts (1), (mph), and (mpl) correspond to one-phonon, multiphonon, and multiple scattering.

The cross section for one-phonon incoherent scattering has the form

$$\begin{aligned} \sigma^{(1)}(\omega, \phi, T) &= \sum_i \frac{d^2 \sigma_i^{\text{incoh}}}{d\omega d\Omega} \\ &= \frac{k}{k_0} \frac{\hbar |\mathbf{Q}|^2}{2M\omega} \sum_i (b_i^{\text{incoh}})^2 \\ &\quad \times \frac{\exp(-2W_i)}{1 - \exp(-\hbar\omega/kT)} G_i^{\text{incoh}}(\omega), \\ G_i^{\text{incoh}}(\omega) &= \frac{1}{M_i} \sum_j \int d\mathbf{q} |\mathbf{A}_j^i(\mathbf{q})|^2 \delta(\omega - \omega_j(\mathbf{q})). \end{aligned} \quad (4)$$

Here $G_i^{\text{incoh}}(\omega)$ is the density of vibrational states of the material, weighted by the squared displacement amplitudes of the i th nucleus,^{83,84} k_0 and \mathbf{k} are the wave vectors of the

TABLE II. Total neutron scattering cross sections (Ref. 17).

Atom/material	Total scattering cross section* σ^0 , b
H	81.5
D	7.6
O	4.24
Si	2.2
OH	85.74
OD	11.84
H ₂ O	167.24
D ₂ O	19.44
SiO ₂	10.68

*The quantity σ^0 is defined as the sum of the cross sections of nuclear coherent and incoherent scattering on a nucleus of type n .

incident and scattered neutrons, \mathbf{Q} is their difference, b_i^{incoh} is the amplitude for incoherent scattering on the i th nucleus (the cross sections for scattering on the nuclei contained in silicas are given in Table II), M_i is the mass of the i th nucleus, W_i is the Debye–Waller factor, \mathbf{A}_j^i is the displacement amplitude of the i th nucleus corresponding to the j th vibrational mode, and $\hbar\omega = E_0 - E$ is the energy transfer. The quantity

$$G(\omega) = \sum_i (b_i^{\text{incoh}})^2 G_i^{\text{incoh}}(\omega) \quad (5)$$

is referred to as the doubly amplitude-weighted density of states (AWDS). It is this quantity which can be obtained from the experimental spectrum (1) by solving the inverse problem with the condition that the scattering spectrum is generated by one-phonon processes. However, as is well known, problems with the inverse convolution cannot be solved in general, and therefore in practice in an INS experiment the analog of the exact function $G(\omega)$ is a slightly coarser function $\tilde{G}(\omega)$ defined as⁸²

$$\tilde{G}_T(\omega) = \frac{N_T(t(\omega))}{\Phi(t(\omega), E(\omega)) \times K(\omega, T)}. \quad (6)$$

Here $\Phi(t(\omega), E(\omega))$ is the transformed instrumental function of the spectrometer, and the function $K(\omega, T)$ has the form

$$K(\omega, T) = \frac{k}{k_0} \frac{\hbar |\mathbf{Q}|^2}{2\omega} \frac{\exp(-2W_i)}{1 - \exp(-\hbar\omega/kT)}, \quad (7)$$

and is easily calculated if the angular configuration of the experiment is known.

The spectra $N(t)$ given below were obtained by using the time-of-flight spectrometer of the inverse geometry KDSOG-1M at the high-flux IBR-2 reactor at JINR.⁸² All the spectra were normalized to the same number of scattered nuclei (per 100 g of matter) and the same measurement time. This makes it possible to perform a quantitative relative analysis of these spectra. The low temperature was a sufficient basis for assuming that one-phonon scattering processes dominate in the spectra $N(t)$,⁸⁴ so that Eq. (6) could be used to determine the desired AWDS spectra.

3.2. The set of dispersed silicas

The series of studies reported here were performed for three commercially produced highly dispersed silicas: A380 aerosil (specific area 380 m²/g), SG100 and SG20 silica gels (average pore diameter 100 and 20 Å, respectively), and AG200 aerogel (density 200 kg/m³). According to the basic model, in which dispersed silicas of any origin form a three-component system consisting of the silica core and the hydroxyl and hydrate shells,¹ samples differing in the partial contributions of these components were prepared. Each of the silicas studied was represented by a set of samples of a single type.

An *air-dry sample* is the original sample obtained as the final product of the corresponding technological chain and stored in the open air at room temperature and the corresponding humidity. The spectrum of an air-dry sample will be called $Sp^{(1)}$.

A *dried sample* is the product obtained by drying an air-dry sample in air at a certain temperature for each silica. The spectrum of a dried sample will be called $Sp^{(2)}$.

A *deuterized sample* is the sample obtained as a result of the deuterium-exchange procedure, which consists of the systematic drying of the sample in a closed vessel followed by cooling in heavy water vapor; the drying–cooling cycle was repeated several times. The spectrum of a deuterized sample will be called $Sp^{(3)}$.

The set of spectra $\{Sp^{(j)}\}$ forms the basis for obtaining the spectra of the individual components of silicas using the difference–correlation method of decomposing the initial spectra.⁸⁵

3.3. Construction of the basis for the spectrum of a complex system. Criterion for zero linear correlation coefficient

Any method of decomposing the spectrum of a complex system into its component spectra is based on the additive model, according to which the complete spectrum of the system $Sp^{(j)}$ can be represented as a sum of spectra:

$$Sp^{(j)} = \sum_{i=1}^m k_i^{(j)} Sp_i. \quad (8)$$

Here the $k_i^{(j)}$ are the weight factors of the spectra, the product $k_i^{(j)} Sp_i$ is the *partial spectrum* of the i th component in the complete spectrum $Sp^{(j)}$, and j labels the independent spectra of the system in question, which pertain to modifications of the system differing in the partial contributions of the components. The spectra Sp_i themselves are called the *basis spectra*.

There are two well known limiting cases in which the solution for the decomposition of the composite spectrum $Sp^{(j)}$ has been obtained. In the first, the case of a *complete set of basis spectra*, all the basis spectra Sp_i are known and the order of the system of initial equations (8) is $n = 1$. The solution of the problem consists of finding the coefficients $k_i^{(j)}$. The best solution is usually judged to be the one which corresponds to the minimum of the discrepancy functional⁸⁶

$$\chi^{(j)} = \sum_r \left[S_p^{(j)}(r) - \sum_{i=1}^m k_i^{(j)} S_{p_i}(r) \right]^2, \quad (9)$$

where the summation runs over the \mathcal{N} points of the spectrum. The method based on this criterion is well known as the least-squares method. The spectra S_{p_i} can be either the experimentally measured spectra or model functions like exponentials, Gaussians, Lorentzians, and so on.⁸⁶ The defining parameters of the expansion are the weights $k_i^{(j)}$ and the parameters of the model functions.

In the second case, or the case of a *complete set of weights*, all the coefficients $k_i^{(j)}$ are known, the order of the system of initial equations is $n=m$, and the basis spectra S_{p_i} are to be found. The system (8) reduces to a system of linear algebraic equations, and the main problem in solving it is the problem of definiteness.^{87,88}

The problem of expanding the complete spectrum into the spectra of the core, the hydroxyl component, and the water component arises naturally in the process of analyzing the AWDS spectra of dispersed silicas. From the mathematical point of view it can be classified with the problems arising in the decomposition of a composite spectrum when neither the basis spectra nor the weights corresponding to them are completely known. It has been suggested that this problem be solved by the difference-correlation method,⁸⁵ which amounts to constructing a physically meaningful basis $\{S_{p_i}\}$ of the system according to a linear algebraic scheme

$$S_{p_i} = \sum_{j=1}^n \kappa_j^{(i)} S_p^{(j)}, \quad i = 1, 2, \dots, m, \quad (10)$$

assuming that there is no linear correlation between the basis spectra S_{p_i} . This requirement has been formulated as the *criterion for zero correlation coefficient* of the basis spectra (the ZCC criterion), which is the analog of the condition of orthogonality of n -dimensional vectors. In other words, *if the components of a complex system can be assumed to be independent, the basis spectra of these components are not correlated with each other*. Using the expression for the second moment of the standard deviations of two physical quantities,⁸⁶ it is easy to obtain the mathematical expression of this criterion:

$$r = \frac{\sum_r \mathcal{N} [S_{p_i}(r) - \overline{S_{p_i}}] [S_{p_k}(r) - \overline{S_{p_k}}]}{\sqrt{\sum_r \mathcal{N} [S_{p_i}(r) - \overline{S_{p_i}}]^2 \sum_r \mathcal{N} [S_{p_k}(r) - \overline{S_{p_k}}]^2}}, \quad (11)$$

where $\overline{S_{p_i}} = (1/\mathcal{N}) \sum_r S_{p_i}(r)$ is the average of the spectral lines and \mathcal{N} is the number of points in the spectrum. The condition that r be zero corresponds to zero numerator in (11), which is conveniently written as

$$C(S_{p_i}, S_{p_k}) = 0. \quad (12)$$

It is easy to show that Eq. (12) is valid not only for pairs of spectra S_{p_i} and S_{p_k} , but also for linear combinations of them of the form

$$C\left(S_{p_i}, \sum_{s \neq i}^m k_s S_{p_s}\right) = 0, \quad (13)$$

or

$$C\left(S_{p_i} + S_{p_l}, \sum_{s \neq i, l}^m k_s S_{p_s}\right) = 0. \quad (14)$$

The practical use of the ZCC criterion begins with finding the simplest linear combination (10) for the expression of the left-hand partner in (14) in the limit of a simple difference $\mathcal{D}S_p^{(jj')} = S_p^{(j)} - S_p^{(j')}$. This difference spectrum must correctly represent the form of either the spectrum S_{p_i} , or the sum of spectra $S_{p_i} + S_{p_l}$, i.e., it must determine them up to a constant. Then the right-hand partner in (14) can be represented as the residual spectrum $\mathcal{R}S_p^{(jj')} = S_p^{(j)} - a^{(jj')} \mathcal{D}S_p^{(jj')}$, where $a^{(jj')}$ is a parameter ensuring that there is no correlation between the spectra $\mathcal{R}S_p^{(jj')}$ and $\mathcal{D}S_p^{(jj')}$ in the form (14).

Solving Eq. (14) for $a^{(jj')}$, we obtain the value of this parameter:

$$a_0^{(jj')} = \frac{\sum_r \mathcal{N} \mathcal{D}\tilde{S}_p^{(jj')}(r) \times \tilde{S}_p^{(j)}(r)}{\sum_r \mathcal{N} (\mathcal{D}\tilde{S}_p^{(jj')}(r))^2}, \quad (15)$$

where

$$\mathcal{D}\tilde{S}_p^{(jj')} = \mathcal{D}S_p^{(jj')} - \overline{\mathcal{D}S_p^{(jj')}},$$

$$\tilde{S}_p^{(j)} = S_p^{(j)} - \overline{S_p^{(j)}}.$$

The overbar denotes the average lines of the spectra [see (11)]. The spectrum $a_0^{(jj')} \mathcal{D}S_p^{(jj')}$ is either the basis spectrum S_{p_i} or the sum of basis spectra $S_{p_i} + S_{p_l}$. Meanwhile, the residual spectrum $\mathcal{R}_0 S_p^{(jj')} = S_p^{(j)} - a_0^{(jj')} \mathcal{D}S_p^{(jj')}$ describes the residual combination of basis spectra entering into $S_p^{(j)}$ after the spectrum $a_0^{(jj')} \mathcal{D}S_p^{(jj')}$ is subtracted from it. Repeating this procedure and scanning over the indices j and j' , we can determine the entire set of basis spectra $\{S_{p_i}\}$. This method has been used successfully to obtain the basis spectra of aerosil, silica gel, and aerogel.²⁵⁻²⁷

4. VIBRATIONAL SPECTRA OF DISPERSED SILICAS

4.1. Aerosil

a) Samples and initial spectra

An air-dry sample of A380 aerosil is a powder consisting of small spherical particles with specific area 380 m²/g. According to small-angle x-ray scattering (SAXS) measurements, the average particle size is 150 Å.¹⁹ Heating of this sample in air for 6 hours at temperature 750 °C produces dried A380. In turn, the dried sample was subjected to isotopic replacement of protium atoms in the hydroxyl and water shells by deuterium atoms according to the following procedure:

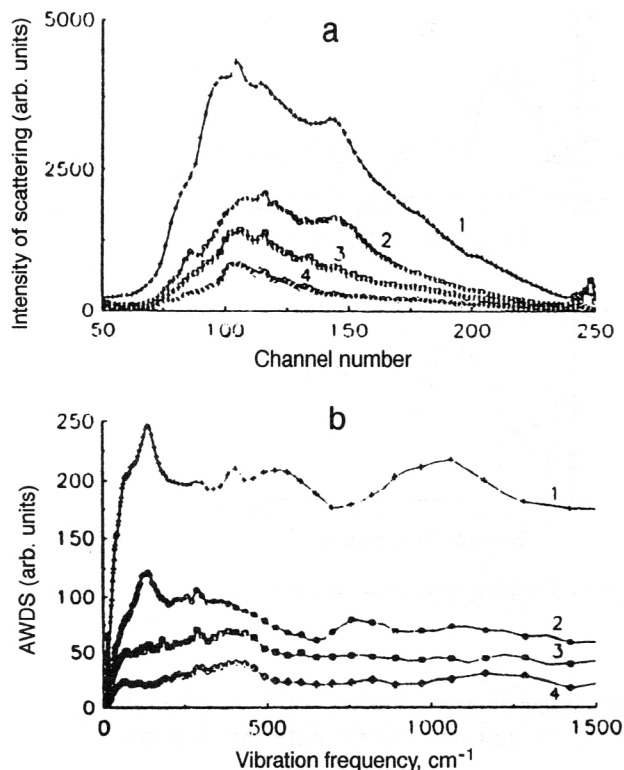


FIG. 7. Experimental vibrational spectra of the family of A380 aerosil at 10 K (Ref. 20). (1) Air-dry sample; (2) dried sample; (3) deuterized sample; (4) aerosil glass. (a) Time-of-flight INS spectra; (b) AWDS spectra.

heating in air 750 °C, 4 hours	→	cooling in heavy-water vapor to room temperature	→
heating in air 750 °C, 4 hours	→	cooling in heavy-water vapor to room-temperature	→
heating in air 750 °C, 4 hours	→	cooling in heavy-water vapor 24 h to room-temperature.	

A deuterized sample of A380 was obtained as a result. The set of these three samples formed the A380 aerosil family. The time-of-flight INS spectra of the samples of this family together with the AWDS spectra obtained according to (6) are shown in Fig. 7. In addition to the spectra of the three samples described above, this figure shows $N(t)$ and the AWDS spectrum of glass obtained by sintering of aerosil. These spectra are in some sense reference spectra, as they represent the spectrum of bulk vibrations of densely packed silica (see Sec. 5.1 below).

b) Basis spectra of the aerosil components

Formulation of the problem of decomposing the initial spectra. The spectra of the aerosil components form a triplet of basis spectra $\{Sp_i\}$, where the subscripts $i=1,2,3$ correspond to the spectra of the water shell, the OH shell, and the silica core, respectively. The physical meaning of the basis spectrum Sp_3 is fairly clear, but the first two spectra should be discussed in more detail. In addition to the vibrations of water and hydroxyl groups, they naturally include the vibrations of the groups of atoms with which these isolated systems interact. For example, the vibrational spectrum

of the hydrate shell must include vibrations associated with its silicon-oxygen center of the corresponding composition. The number of such centers interacting with water is, as is well known,^{1,5} much smaller than the total number of hydroxyl groups on the surface, even when the surface is completely saturated by adsorbed water. The remaining free groups form the hydroxyl covering. The vibrations of these groups form the basis of the vibrational spectrum of the hydroxyl covering. However, in addition to this there is a noticeable contribution to this vibrational spectrum from vibrations of surface silicon atoms and oxygen of the silica core activated by the hydrogen atoms of hydroxyl groups participating in the corresponding vibrational motion, owing to the well known "riding effect."^{18,19}

The experimental AWDS spectra of the initial and modified aerosils normalized to a mass of 100 g form the set $\{Sp^{(j)}(\omega)\}$, in which the values $j=1,2,3$ correspond to the spectra of air-dry A380, dried A380, and deuterized A380. If the partial spectra of the air-dry sample are treated as the basis spectra, the system (8) will become

$$\begin{aligned} Sp^{(1)} &= Sp_1^{(1)} + Sp_2^{(1)} + Sp_3^{(1)}, \\ Sp^{(2)} &= \alpha_1 Sp_1^{(1)} + \alpha_2 Sp_2^{(1)} + \alpha_3 Sp_3^{(1)}, \\ Sp^{(3)} &= \beta_1 Sp_1^{(1)} + \beta_2 Sp_2^{(1)} + \beta_3 Sp_3^{(1)}. \end{aligned} \quad (16)$$

Before turning to the construction of this basis, it is necessary to find the relations between the coefficients of the system (16), knowledge of which permits the optimized construction of the difference spectra in (14). Let us consider this procedure for the example of aerosil. The parameters α_3 and β_3 are determined by the natural condition that the partial spectrum of the silica core be the same for all samples, i.e.,

$$Sp_3^{(1)} = \alpha_3 Sp_3^{(1)} + \beta_3 Sp_3^{(1)}, \quad \text{or} \quad \alpha_3 = 1 \quad \text{and} \quad \beta_3 = 1. \quad (17a)$$

It is known from the data in the literature¹ that when aerosil is dried at 750 °C the adsorbed water and some of the hydroxyl groups are completely removed from its surface, so that the following two relations hold:

$$\alpha_1 = 0 \quad \text{and} \quad \alpha_2 < 1. \quad (17b)$$

The weighted contributions of the partial spectra of water and the hydroxyl covering to the spectrum of the deuterized sample $Sp^{(3)}$ must be much smaller than unity, because, as follows from Fig. 7, the intensity of the scattering on it is much lower than the intensity of the scattering on the air-dry sample, owing to the very strong suppression of scattering on water nuclei. Therefore,

$$\beta_1 \ll 1 \quad \text{and} \quad \beta_2 \ll 1. \quad (17c)$$

It is also known¹ that the percentage of atoms in the water and hydroxyl coverings replaced as a result of deuterium-exchange are very nearly identical, so that

$$\beta_1 = \beta_2 = \beta. \quad (17d)$$

Therefore, the following conditions are imposed on the coefficients of the system of equations (16):

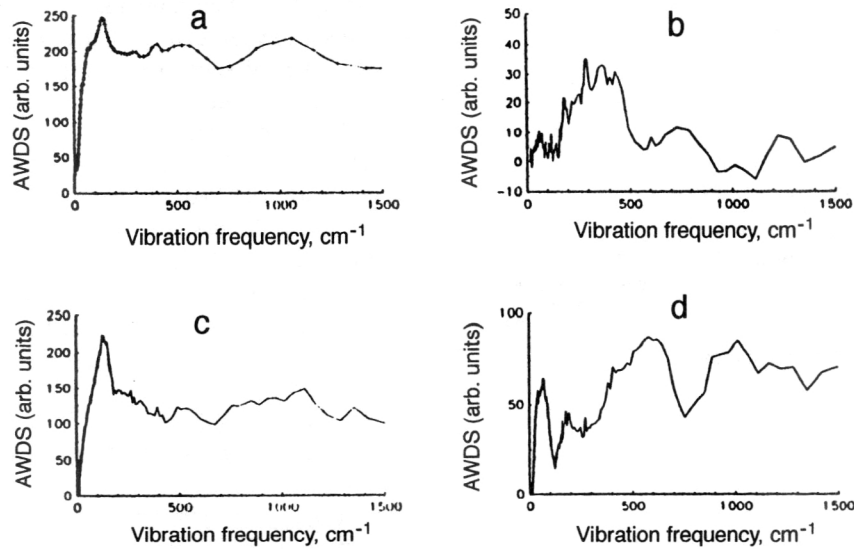


FIG. 8. AWDS basis spectra of the components of A380 aerosil at 10 K (Ref. 25). (a) Complete spectrum of the air-dry sample; (b) core, (c) hydroxyl covering, (d) adsorbed water.

$$\begin{aligned} \alpha_3 &= 1 & 0 < \beta_1 < 1 \\ \beta_3 &= 1 & 0 < \beta_2 < 1 \\ \alpha_1 &= 0 & \beta_1 = \beta_2 = \beta. \\ \alpha_2 &< 1 \end{aligned} \quad (18)$$

According to (18), the system of basic equations (16) is transformed to

$$\begin{aligned} Sp^{(1)} &= Sp_1^{(1)} + Sp_2^{(1)} + Sp_3^{(1)}, \\ Sp^{(2)} &= \alpha Sp_2^{(1)} + Sp_3^{(1)}, \\ Sp^{(3)} &= \beta Sp_1^{(1)} + \beta Sp_2^{(1)} + Sp_3^{(1)}. \end{aligned} \quad (19)$$

Construction of the basis. In using the difference-correlation method of decomposing the spectrum of a multi-component system, it is possible to have a set of variants determined by the choice of initial difference spectrum in (14). As was shown in Refs. 25–27, the same final result is obtained with good accuracy. Let us consider one such variant as an example. We construct the initial difference spectrum in the form

$$\mathcal{D}Sp^{(13)} = Sp^{(1)} - Sp^{(3)}. \quad (20)$$

It is a linear combination of the basis spectra Sp_1 and Sp_2 , and according to (19) has the form

$$\mathcal{D}Sp^{(13)} = (1 - \beta)[Sp_1^{(1)} - Sp_2^{(1)}]. \quad (21)$$

We construct the residual spectrum

$$\mathcal{R}Sp^{(113)} = Sp^{(1)} - a^{(113)}\mathcal{D}Sp^{(13)}, \quad (22)$$

and require that it not be correlated with the spectrum $\mathcal{D}Sp^{(13)}$, i.e., that the condition (14) be satisfied in the form

$$C(\mathcal{R}Sp^{(113)}, \mathcal{D}Sp^{(13)}) = 0. \quad (23)$$

In the end we obtain the spectra

$$\begin{aligned} a_0^{(113)}\mathcal{D}Sp^{(13)} &= Sp_1^{(1)} + Sp_2^{(1)}, \\ \mathcal{R}_0Sp^{(113)} &= Sp_3^{(1)}. \end{aligned} \quad (24)$$

The corresponding coefficient $a_0^{(113)}$ is given by (15).

Let us now consider the difference spectrum

$$\mathcal{D}Sp^{(21)} = Sp^{(2)} - Sp_3^{(1)}. \quad (25)$$

According to (19), it is $\alpha_2 Sp_2^{(1)}$, i.e., it is the partial spectrum of the hydroxyl covering in the spectrum of dried A380. Using the difference spectra $a_0^{(113)}\mathcal{D}Sp^{(13)}$ and $\mathcal{D}Sp^{(21)}$, we construct the residual spectrum

$$\mathcal{R}\mathcal{D}Sp = a_0^{(113)}\mathcal{D}Sp^{(13)} - a^{(21)}\mathcal{D}Sp^{(21)}, \quad (26)$$

and require that the ZCC conditions be satisfied between this spectrum and the spectrum $\mathcal{D}Sp^{(21)}$ in the form

$$C(\mathcal{R}\mathcal{D}Sp, \mathcal{D}Sp^{(21)}) = 0. \quad (27)$$

Determining $a_0^{(21)}$ in accordance with (15), we obtain

$$a_0^{(21)}\mathcal{D}Sp^{(21)} = Sp_2^{(1)} \quad \text{and} \quad \mathcal{R}_0\mathcal{D}Sp = Sp_1^{(1)}. \quad (28)$$

Thus, the basis of the system (19) has been constructed. In Fig. 8 we show the AWDS spectrum of the air-dry sample of aerosil together with the spectra of its three components.²⁵ As has been established experimentally,²⁴ the initial spectra of air-dry aerosils with different specific area (and particle size) are very nearly identical, so that the constructed basis spectra pertain to the entire class of aerosils.

4.2. Silica gels

a) Samples and initial spectra

In the series of studies that we are discussing, the vibrational spectra of two families of silica gels originating from initial manufactured samples of the brand KSM-G (lumpy, small-pore, granulated) were studied. These were produced by the Mendelev Chemical Factory and are characterized by different pore sizes, in particular, 20 and 100 Å (SG20 and SG100, respectively). The family of each silica gel included three samples.²⁶

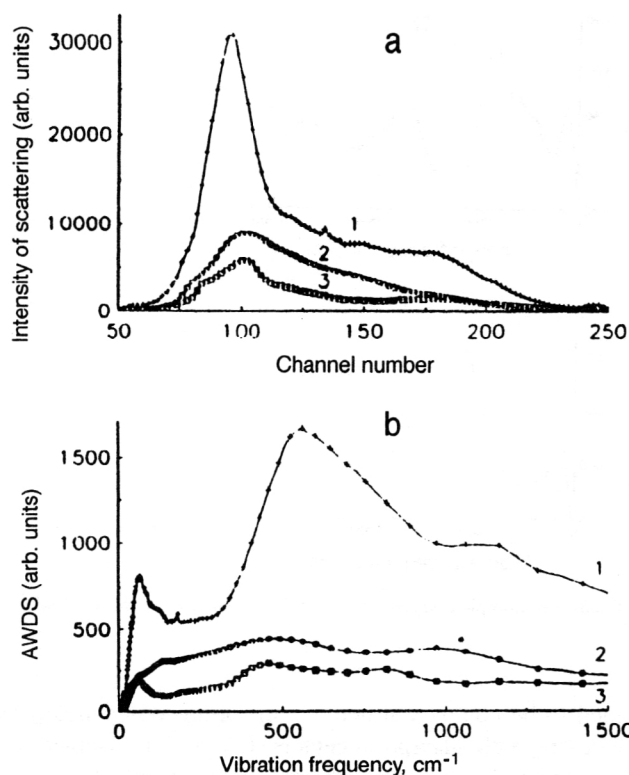


FIG. 9. Experimental vibrational spectra of silica gels of the SG20 family, 10 K (Ref. 20). (1) Air-dry sample; (2) dried sample; (3) deuterized sample. (a) Time-of-flight INS spectra; (b) AWDS spectra.

$j=1$, air-dry initial manufactured sample, stored at room temperature and ordinary humidity;

$j=2$, dried sample obtained from the initial sample by drying in air for 72 hours at temperature 135 °C;

$j=3$, deuterized sample, obtained from the initial sample by three cycles of drying at 135 °C followed by storage for several days in heavy-water vapor at room temperature.

The spectrum of quickly quenched water was also studied; it is needed for comparative analysis of the spectrum of the water component.

The INS spectra of samples of the SG20 family of silica gels and the corresponding AWDS spectra obtained by using (6) are given in Fig. 9. The analogous spectra of samples of the SG100 family of silica gels are given in Fig. 10.

b) Basis spectra of the components of silica gels

The procedure for obtaining the basis spectra of silica gels is analogous to that described above for aerosil; the only difference is that because of the somewhat different relations between the coefficients of the system (16), the fundamental system of equations has the form²⁶

$$\begin{aligned} Sp^{(1)} &= Sp_1^{(1)} + Sp_2^{(1)} + Sp_3^{(1)}, \\ Sp^{(2)} &= \alpha_1 Sp_1^{(1)} + Sp_2^{(1)} + Sp_3^{(1)}, \\ Sp^{(3)} &= \beta Sp_1^{(1)} + \beta Sp_2^{(1)} + Sp_3^{(1)}. \end{aligned} \quad (29)$$

In Figs. 11 and 12 we show the spectra of air-dry samples together with the basis spectra of their components. Two features of the spectra should be noted when comparing

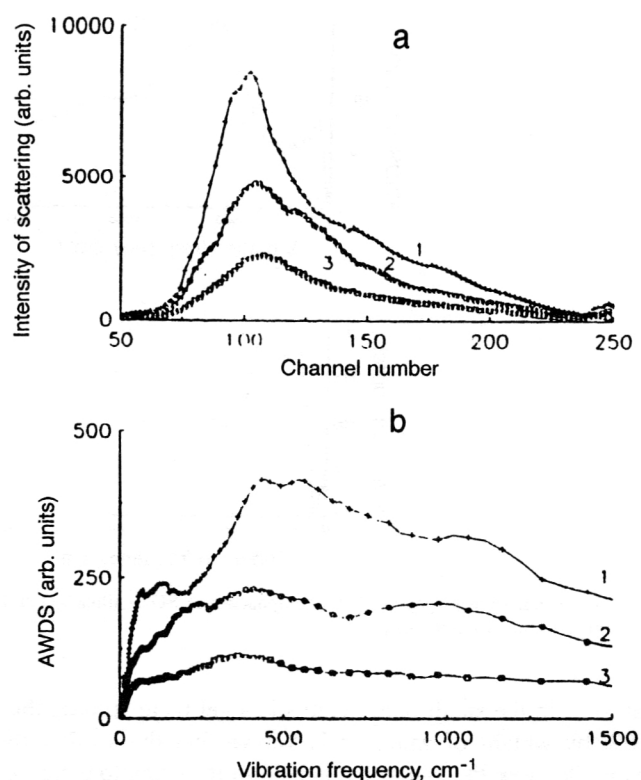


FIG. 10. The same as in Fig. 9, but for SG100 silica gel (Ref. 20).

the figures. First, the basis spectra of the studied samples of silica gel are quite different. This fact, noticed as poor reproducibility of the absorption spectra of silica gels, has also been seen in studies of their IR absorption.^{8,11,12} As will be shown in Sec. 7.2, this difference is not related to any difference in the numerical parameter describing the pore sizes, but is due to the exceptional lability of the structure of silica gel. Consequently, reproducibility of the spectra in going from one sample of silica gel to another is essentially impossible.

The second feature concerns the basis spectra of the water coverings. In contrast to aerosil with its globular structure, in the porous structures of silica gels water can not only be adsorbed, but can also be held in quasifree form. Therefore, in characterizing the water component of this material it will be more accurate to speak of the held water. In Fig. 13 we give the AWDS basis spectra of the water components of SG20 and SG100 silica gels together with the spectrum of quickly quenched water. In spite of the clearly noticeable difference of the spectra of the water components of the two samples, the two spectra are quite similar to the spectrum of quickly quenched water. A similarity this strong, which has also been noticed by other authors^{45,46} (see Sec. 2.2, Figs. 3–5), supports the above conclusion about the presence of two types of water in the pores of silica gel: water adsorbed on the inner surface of the pores and quasifree water.

In accordance with this point of view, it has been suggested²⁶ that the basis spectra 1 and 2 in Fig. 13a are composite and composed of the spectra of adsorbed and quasifree water. Then the observed difference of the spectra of water in SG20 and SG100 silica gels can be explained quali-

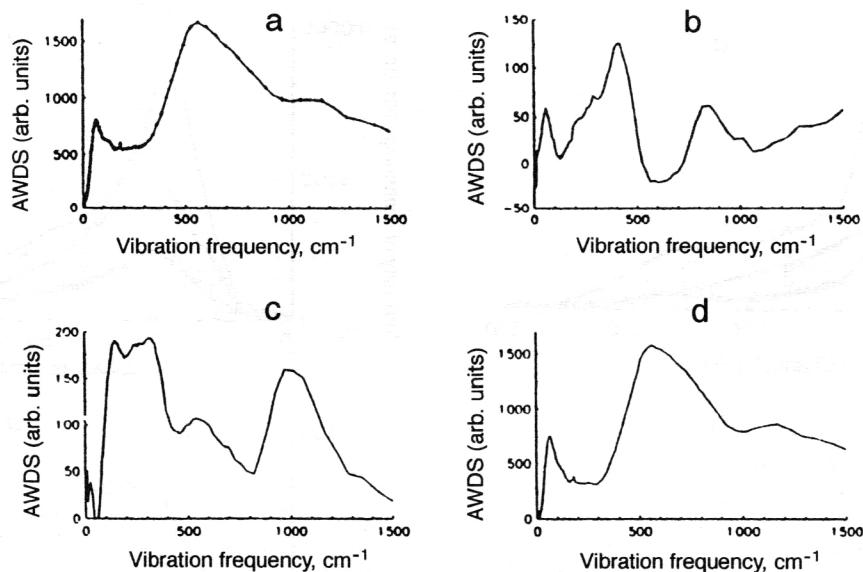


FIG. 11. AWDS basis spectra of the components of SG20 silica gel at 10 K (Ref. 26). (a) Complete spectrum of air-dry sample; (b) core, (c) hydroxyl covering, (d) water component.

tatively. In the small-pore SG20 silica gel there is more than 16% by weight of water (it is known that the smaller the pore, the more the water that is held in it, owing to enhancement of surface-tension forces¹), and most of it is quasifree water. This is why the AWDS spectrum of the water component of SG20 in this case is so similar to the spectrum of quickly quenched water. Owing to the large pore size, less water is held in SG100 silica gel (about 5% by weight), so that in its AWDS spectrum the spectrum of adsorbed water which was practically completely masked in the former case shows through.³ On the basis of this qualitative analysis, the difference-correlation method of decomposing the spectra of a complex system was used to obtain the individual spectra of the two types of water. Here it was assumed that the quasifree water and the adsorbed water are spatially separated. As in the case of aerosil, the adsorbed water is as-

sumed to be complex structures, including water molecules interacting with adsorption centers. It was also assumed that the systems of internal coordinates of the adsorbed and quasifree water are independent, so that their vibrational spectra should not be correlated if the false correlation due to random coincidence of the frequencies of vibrational modes is neglected.

The procedure for decomposing the initial basis spectra of the water components is the following.²⁶ According to (16), we can write down the system of equations

$$\begin{aligned} Sp^{(1)}(\omega) &= Sp_1(\omega) + Sp_2(\omega), \\ Sp^{(2)}(\omega) &= \alpha_1 Sp_1(\omega) + \alpha_2 Sp_2(\omega), \\ Sp^{(3)}(\omega) &= \beta Sp_1(\omega), \end{aligned} \quad (30)$$

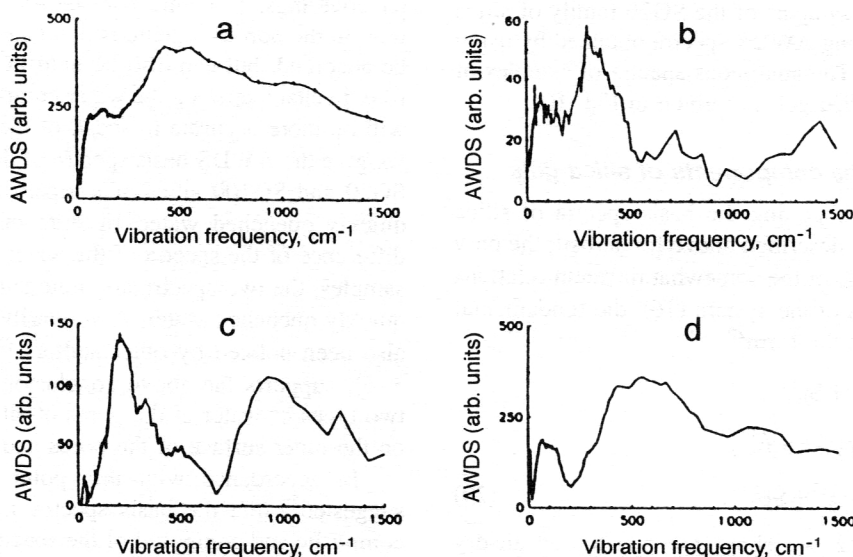


FIG. 12. The same as in Fig. 11, but for SG100 silica gel (Ref. 26).

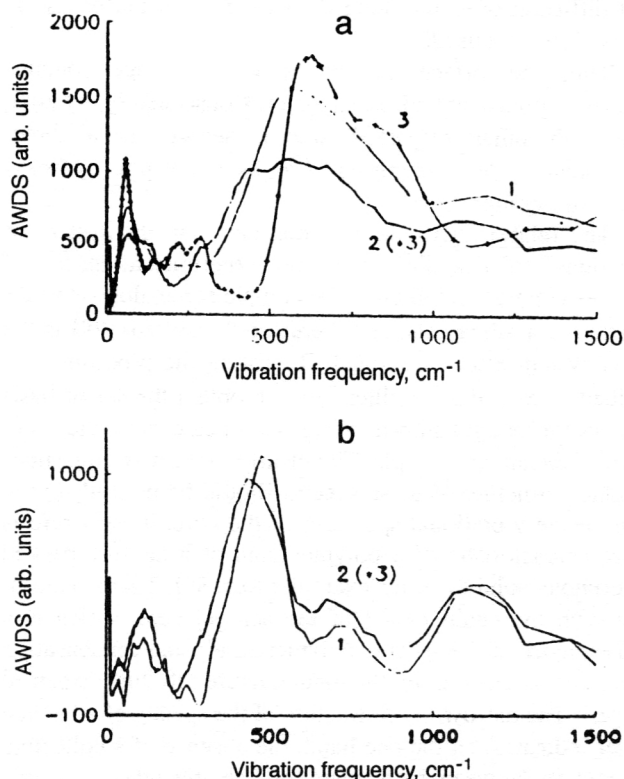


FIG. 13. AWDS basis spectra of the water components of silica gels, 10 K (Ref. 26). (1) SG20 silica gel; (2) SG100 silica gel; (3) quickly quenched water. (a) Water components; (b) adsorbed water.

where the index j labels the initial spectra in the following order:

$j=1$, the AWDS basis spectrum of the water covering $Sp_1^{(1)}$ of SG20 silica gel [curve 1 in Fig. 13a];

$j=2$, the AWDS basis spectrum of the water covering $Sp_1^{(1)}$ of SG100 silica gel [curve 2 in Fig. 13a];

$j=3$, the AWDS spectrum of 1 gram of quickly quenched water [curve 3 in Fig. 13a].

In (30), Sp_1 and Sp_2 are the basis spectra of the quasifree and adsorbed water, which are assumed to be identical in the two silica gels. On the basis of Refs. 55 and 56, which state that the INS spectra of free ice and ice in pores are practically preserved, it was assumed that the vibrational spectrum of free water $Sp^{(3)}$ determines the shape of the basis spectrum Sp_1 .

If we construct the two difference spectra

$$\begin{aligned} \mathcal{D}Sp^{(13)} &= Sp^{(1)} - a^{(13)}Sp^{(3)}, \\ \mathcal{D}Sp^{(23)} &= Sp^{(2)} - a^{(23)}Sp^{(3)}, \end{aligned} \quad (31)$$

and require that the ZCC criterion be satisfied in the form

$$\begin{aligned} C(\mathcal{D}Sp^{(13)}, Sp^{(3)}) &= 0, \\ C(\mathcal{D}Sp^{(23)}, Sp^{(3)}) &= 0, \end{aligned} \quad (32)$$

then by solving these equations we can determine the coefficients $a_0^{(13)}$ and $a_0^{(23)}$ in accordance with (15) and obtain the spectra $a_0^{(13)}Sp^{(3)} = Sp_2(1)$ and $a_0^{(23)}Sp^{(3)} = Sp_2(2)$. These spectra are shown in Fig. 13b. They turned out to be practically identical. In Table III we give the percentage content of

TABLE III. Percentage content of quasifree and adsorbed water in silica gels (Ref. 26).

Sample	η_f	η_{ad}
SG20 silica gel	14.0	3.7
SG100 silica gel	1.8	1.3

free (η_f) and adsorbed (η_{ad}) water in the studied samples of silica gel corresponding to the coefficients $a_0^{(13)}$ and $a_0^{(23)}$ in the equations of the ZCC criterion (32).

However, the fact that the AWDS spectra of the adsorbed water in the two silica gels are identical is surprising in view of the great difference between them in the two other basis spectra. At the root of this fact is apparently the competition between two processes: the formation of a “drop” of quasifree water and adsorption. Obviously, among the three types of silicon–hydroxyl centers (from silanol to silantriol) forming the hydroxyl covering of the silical gel and enabling water adsorption, only one center can turn out to be competitive (otherwise the water would not collect into drops). Naturally, this center is the same for each of the silica gels of the complete set, so that the AWDS spectra of the water adsorbed on them are identical. As will be shown in Sec. 7.2, this explanation is confirmed in the quantum-chemical modeling of the model structures of silica gels.

4.3. Aerogel

a) Samples and initial spectra

The studied sample of AG200 aerogel²⁷ was a monolithic piece of solid material with a mass density of 200 kg/m³. The sample kept in air is the initial air-dry sample. This sample was dried in air at temperature 100 °C for 7 days, as a result of which the dried sample was obtained. This sample was in turn subjected to isotopic H→D exchange. The sample was held for 12 hours at 100 °C under atmospheric conditions and then placed in an exsiccator, where it was kept for 12 hours in heavy-water vapor. The cycle was repeated with the duration of the two stages equal to 6 hours. The deuterized sample was obtained as a result. The time-of-flight INS spectra of this family of aerogel samples and the corresponding AWDS spectra obtained using (6) are shown in Fig. 14.

b) Basis spectra of the aerogel components

In contrast to aerosil and silica gels, the surface chemistry of aerogel has been little studied. The first ideas about the surface structure of aerogel were developed on the basis of analysis of the chemical–technological manufacturing process. According to the scheme for this process,³ the main component of the aerogel core is the siloxane chain, and the main contribution to the hydrogen-containing surface zone comes from hydroxyl groups, an increase in the number of which is accompanied by an increase in the length of the polymer chain. These groups compensate for the free valencies of the silicon atoms of the siloxane framework of the chain.

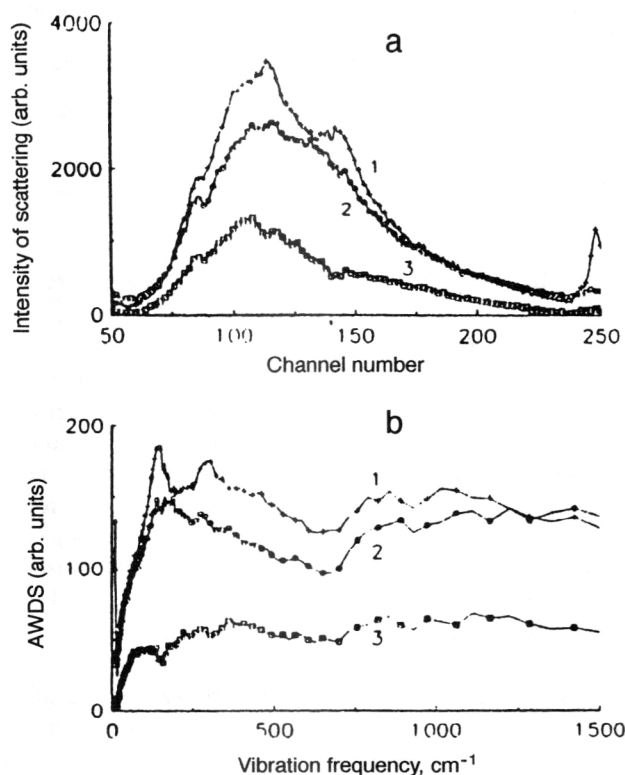


FIG. 14. Experimental vibrational spectra of the AG200 aerogel family, 10 K (Ref. 27). (1) Air-dry sample; (2) dried sample; (3) deuterized sample. (a) Time-of-flight INS spectra; (b) AWDs spectra.

In isolated chains, each silicon atom of the siloxane framework is bound to two hydroxyl groups. Therefore, the resulting polymer structure is a chain of silandiol groups. If chains are joined together in pairs to form a band, the silicon atoms of this band are then bound to only a single hydroxyl group; in other words, the external hydroxyl centers are silanols. It is thought that it is precisely this joining process which occurs in gel formation.³

Under atmospheric conditions, the presence of silanol or silandiol groups on the surface of the silica core usually leads to adsorption of water. The existence of adsorbed water on the surface of an aerogel is confirmed by mass-spectrometer studies of the products desorbed from its surface in heating to 100–150 °C.³ This is also suggested by the analysis of the vibrational spectra shown in Fig. 14. We see from this figure that when the sample is dried under conditions which favor the desorption of water, the shape of its vibrational spectrum changes considerably and its integrated intensity is decreased by nearly a factor of two. At the same time, comparison of the AWDs spectra within the family of AG200 samples shows that retention of the initial AG200 sample in heavy-water vapor lowers the spectral intensity by nearly a factor of two. This observation is a direct indication that the surface zone of air-dry aerogel contains a significant number of hydrogen atoms, because the isotope exchange is mainly concentrated in this zone. Another confirmation of the presence of water in the surface zone of the aerogel is the rather smeared structure of the spectrum as the temperature is raised,²⁷ similar to that observed for the spectra of air-dry samples of aerosil and silica gel;²² this is related to the fact

that diffusion of water along the surface is enhanced as the temperature is raised.

Thus, the surface zone of the air-dry aerogel contains hydroxyl groups and adsorbed water. Consequently, by analogy with other dispersed silicas, aerogel is a three-component system consisting of a silica core plus hydroxyl and water components.

The relation between the coefficients in the system of equations (16) describing the three experimental spectra of aerogel samples turned out to be completely analogous to the relations for silica gels, and therefore the system (29) is the basis system also for aerogel. Repeating the procedure described in Sec. 4.2 for silica gel, we obtain the set of basis spectra for aerogel shown in Fig. 15 together with the spectrum of the air-dry sample. The clearly expressed “quasimolecular” structure of these spectra should be noticed. In the case of the vibrational spectrum of the core, its structure is more characteristic of a polymer than of a densely packed amorphous solid (see, for example, Ref. 89). This is consistent with the chain model of the aerogel core, which is a consequence of the specific polymerization and condensation processes occurring in the manufacture of this dispersed silica.⁹⁰ The narrow-band structure of the spectra of adsorbed water indicates, on the one hand, the absence of a collective interaction between molecules and, on the other, a single type of orientation of their locations on the surface. In turn, the latter indicates that the adsorption centers are rather uniform and well spaced over the surface.

5. COMPARATIVE ANALYSIS OF THE VIBRATIONAL SPECTRA OF DISPERSED SILICAS AND THEIR COMPONENTS

5.1. Vibrational spectra of the silica cores

The basis spectra of the core vibrations for the silicas studied are shown in Fig. 16. In addition, in Fig. 16a (curve 2) we show the vibrational spectrum of glass obtained by sintering A380 aerosil. We see from this figure that the core spectra of all the materials certainly have the same shape and are similar to the glass spectrum, which is the spectrum of bulk vibrations of densely packed silica, in the sense that each of them consists of four bands located in the same spectral regions. In addition, we observe significant differences both between the spectra of various dispersed silicas and between them and the glass spectrum. This is true of the intensity distributions in each of the spectra, i.e., the spectral shapes, and the absolute intensities of each of them. The vibrational spectrum of the aerosil core is closest to the glass spectrum. The vibrational spectrum of aerogel is farthest from it. It should especially be noted that the core spectra of the two silica gels studied, SG100 and SG20 with different average pore size (100 and 20 Å), strongly differ from each other.

It is convenient to begin our analysis of the differences observed in the shapes of the spectra with a brief description of the glass spectrum. In this spectrum we clearly see four bands in the ranges 0–200 cm⁻¹ (1), 200–500 cm⁻¹ (2), 500–950 cm⁻¹ (3), and 950–1300 cm⁻¹ (4). According to the analysis of the vibrational spectrum of the free ion

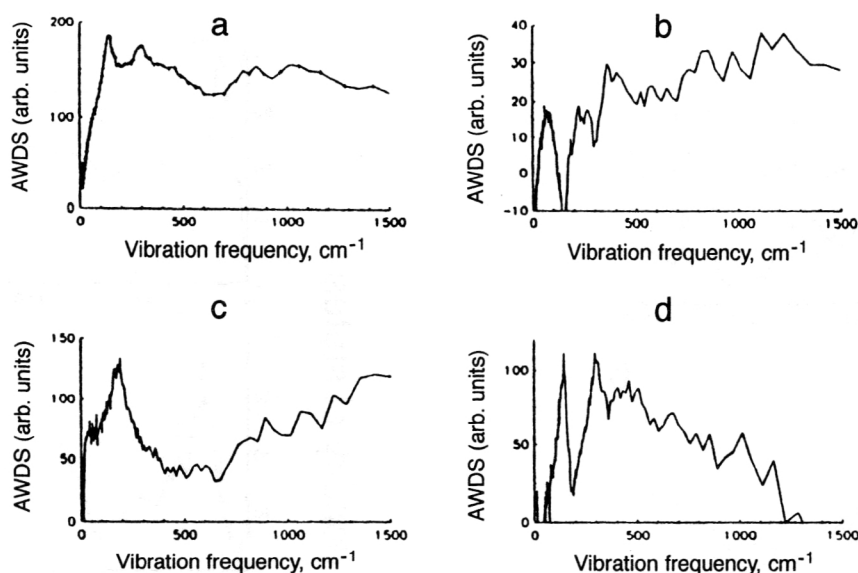


FIG. 15. AWDS basis spectra of the components of AG200 aerogel, 10 K (Ref. 27). (a) Complete spectrum of the air-dry sample; (b) core, (c) hydroxyl covering, (d) adsorbed water.

SiO_4^- (Ref. 6) and the α -quartz crystal,⁹¹ the main contribution in region 2 comes from deformational vibrations associated with variation of the O–Si–O angle. In regions 3 and 4 the dominant contribution comes from symmetric and asymmetric valence vibrations of the Si–O bond. Calculation of the vibrational spectrum of a number of large model clusters shows (see Sec. 7.1) that this explanation can also be extended to amorphous structures. According to the calculation, region 1 of the core vibrational spectrum is produced by the vibrational modes of translational motion of atoms and deformational vibrations associated with variation of the Si–O–Si angles. The assignment of the frequencies in regions 2–4 is consistent with that given above.

Aerosil glass and aerosil. As already mentioned, the spectra of this pair [see Fig. 16a] are very similar. A similarity has also been noted in the IR-absorption spectra.³⁹ This fact undoubtedly indicates that the structure of the aerosil core is densely packed. The intensity in the AWDS spectra of glass is significantly greater than that in the aerosil spectrum in the ranges 0–220 and 560–1500 cm^{-1} . After detailed analysis of the difference spectrum in this region, the authors of Ref. 25 suggested that this difference arises from the presence in glass of small amounts of adsorbed water, in contrast to the “absolutely dry” (by definition) aerosil core. An amount of water equal to 0.3–0.5 percent by weight is sufficient to explain quantitatively the observed difference.⁴⁾ The possibility that such amounts of water exist in glass is confirmed by a number of chemical indicators.⁶

Silica gels. Regions 1–4 are again clearly distinguishable in the basis spectra of the cores of silica gels [see Figs. 16b and 16c]. However, one should note the significant rearrangement of the spectra and the increase of their intensity over that of the aerosil spectrum. As mentioned above, the main feature of these spectra is that they differ for different silica gels. This difference is manifested most clearly in regions 1 and 2, corresponding to deformational vibrations as-

sociated with variation of the Si–O–Si and O–Si–O angles. These variations can be understood if it is assumed that a rather broad distribution of possible Si–O–Si and O–Si–O angles exists in silica gels and that the shape of this distribution changes in going from one sample to another. The changes in the region of deformational vibrations are accompanied by significant changes also in regions 3 and 4 of valence vibrations of the Si–O bonds. This set of facts suggests that the structures of the silica gels studied differ from each other and differ strongly from the densely packed structure.

Aerogel. The principal feature of the basis spectrum of core vibrations of aerogel [see Fig. 16d] is its narrow-band, “quasi-molecular” structure, which makes it resemble the vibrational spectrum of polymers.⁸⁹ The narrow-band structure of the basis spectrum in regions 1 and 2 suggests that the distributions of the deformational modes in the region of variation of the angles in the silicon–oxygen tetrahedra are narrow, which, in turn, suggests that the material has a quasi-regular structure. Therefore, the aerogel core is a new type of structure distinct from the aerosil and silical gel structures.

Comparative analysis of the basis spectra of core vibrations for the silicas studied thus leads to the definite conclusion that the structures of these materials differ qualitatively, thereby suggesting the existence of several polymorphic modifications of dispersed amorphous silica. The difference between the core structures also leads to a difference in the structure of the surface zones of the materials studied.

5.2. Vibrational spectra of the hydroxyl components

The basis spectra of the vibrations of the hydroxyl components of the studied set of dispersed silicas are shown in Fig. 17. In spite of the significant differences between the spectra, in all of them it is possible to distinguish the same two characteristic vibrational ranges: 0–380 cm^{-1} (1) and 700–1100 cm^{-1} (2). The differences between the spectra

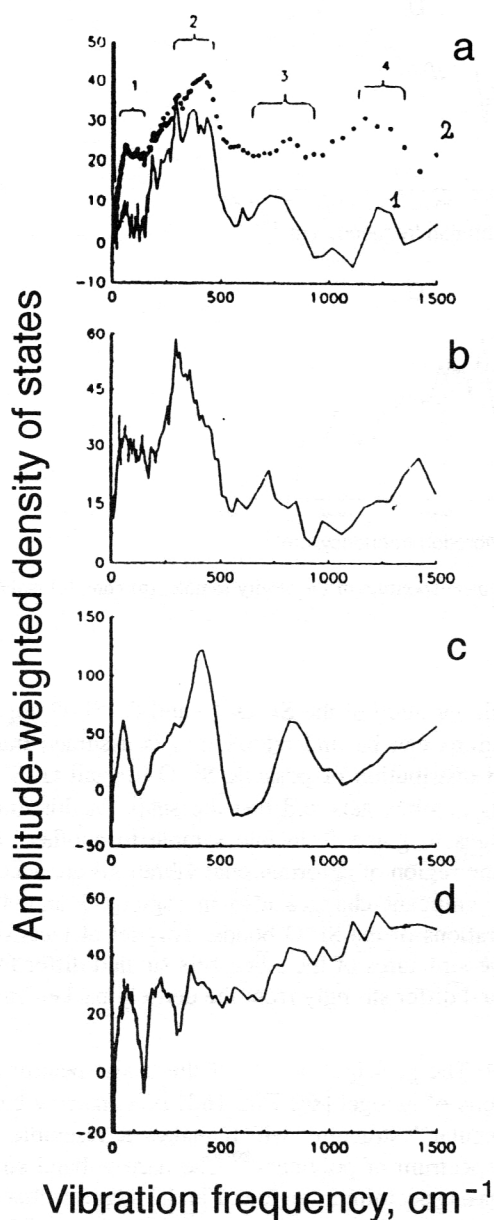


FIG. 16. Basis spectra of core vibrations in dispersed silicas, $T = 10$ K (Ref. 28). (a) A380 aerosil (1) and glass (2); (b) and (c) SG100 and SG20 silica gels, respectively; (d) AG200 aerogel.

can therefore be characterized by the difference between the structures in these regions, and also by the intensity of the continuous background spectrum and the absolute intensity.

According to the results of the calculation of the cluster vibrational spectrum given in Sec. 7.1 below, the dominant contribution to the vibrational modes corresponding to the distinguished regions 1 and 2 comes from torsional vibrations of the OH group relative to the Si–OH bond (region 1) and deformational vibrations of this bond (region 2). The third structural element of the basis spectra of the hydroxyl components corresponds to vibrations of the surface atoms of the silica core, which are activated by hydroxyl groups (rather, by the protium atoms of these groups). This activation ultimately originates in the “riding effect” mentioned

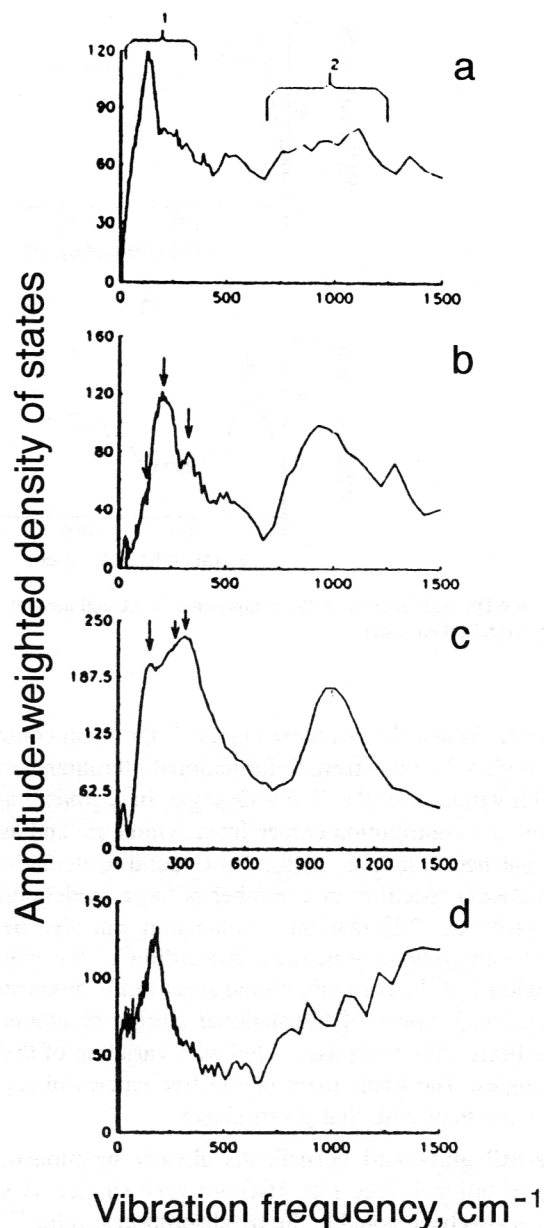


FIG. 17. Basis spectra of vibrations of the hydroxyl components of dispersed silicas, $T = 10$ K (Ref. 28). (a) A380 aerosil; (b) SG100 silica gel; (c) SG20 silica gel; (d) AG200 aerogel.

earlier,^{18,19} which amounts to the following. Protium atoms bound to oxygen atoms of hydroxyl groups also participate in other vibrational modes corresponding to, for example, the deformation of Si–O–Si and O–Si–O angles, valence and deformational vibrations of Si–O bonds, and so on. Owing to the anomalously high sensitivity of neutron scattering to protium atoms, surface vibrations of the core are activated. This leads to the appearance of a corresponding background, close in shape to the spectra shown in Fig. 16, in the AWDS spectra of the hydroxyl components of silicas. This effect will be studied quantitatively in Sec. 7.1 below.

The narrow-band structure of the vibrational spectra of the hydroxyl components of aerosil and aerogel in region 1 suggests a certain uniformity in the orientation of OH groups relative to the silicon atoms to which they are bound. From

this one can conclude that there is predominantly one type of hydroxyl group on the surface of both materials. This observation is consistent with the results of studies of the structure of the hydroxyl covering of aerosil,⁵ as a result of which it has been established that 80–85% of the surface hydroxyl groups are silanol groups. The closeness of the first peaks in the aerosil and aerogel spectra on the frequency scale and their similar shapes suggest that silanol groups also play the dominant role on the aerogel surface.

In contrast to the spectra of the hydroxyl components of aerosil and aerogel, the vibrational spectra of these components in silica gels possess a complicated structure in region 1 and an intense, well expressed peak in region 2. When comparing them, one should again note the difference between the vibrational spectra of the hydroxyl components of different samples. The spectrum of hydroxyl vibrations in SG20 silica gel is twice as intense as that in SG100 silica gel. The main structural differences are concentrated in region 1. They can be described as a redistribution of the intensity between the three characteristic peaks at frequencies 80, 230, and 380 cm^{-1} , observed in both spectra and indicated by the arrows in Fig. 17b. The location of the first peak coincides with the location of the peaks in the vibrational spectra of aerosil and aerogel.

A qualitative explanation of the observed features of the vibrational spectra of the hydroxyl components of silica gels has been given on the basis of analysis of the possible structure of the hydroxyl covering of silicas.²⁸ The hydroxyl components of these materials can be formed by silicon-hydroxyl groups of three types: silanol (OH)₁, silandiol (OH)₂, and silantriol (OH)₃. All these groups possess deformational vibrations of the Si–OH bond close in frequency.⁵ Therefore, the vibrational spectrum of the hydroxyl component of any compound must contain a band near 1000 cm^{-1} , which is in fact observed in the spectra in Fig. 17. It should be noted that this band is much more clearly expressed in the silica gel spectra than in the aerosil and aerogel spectra.

The vibrational spectrum of the hydroxyl component of aerosil is essentially the vibrational spectrum of the silanol groups. The difference between this spectrum and the vibrational spectrum of the hydroxyl components of silica gels can be taken as evidence that silanol groups, if they are actually present in the hydroxyl component of silica gel (as may be indicated by the presence of a peak at 80 cm^{-1} in the spectra of silica gels), are not the principal element. It must therefore be concluded that the formation of the hydroxyl components of silica gels must involve silandiol and silantriol groups. The possible presence of such groups in the friable structure of a silica gel has already been reported.⁴⁰

Thus, the hydroxyl component of a silica gel is formed by a set of various silicon–oxygen groups, the weight factors of which depend on the structure of the silica core. Consequently, the difference between the structures of the silica cores of the two silica gels, established in the preceding section, also determines the difference between the structures of the hydroxyl components. This difference can be described as a redistribution of the weight factors of the various types

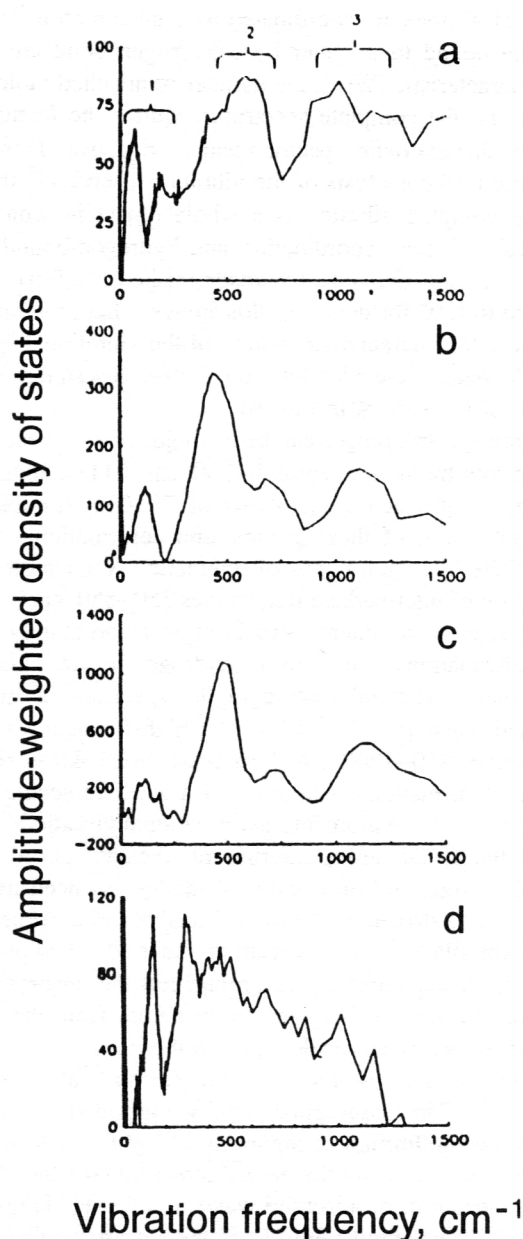


FIG. 18. Basis vibrational spectra of the water components of dispersed silicas, $T = 10$ K (Ref. 28). (a) A380 aerosil; (b) SG20 silica gel; (c) SG100 silica gel; (d) AG200 aerogel.

of silicon–oxygen groups in going from one silica gel to another.

5.3. The vibrational spectra of adsorbed water

In Fig. 18 we show the basis vibrational spectra of the water components of aerosil and aerogel: the spectra of the adsorbed water and the spectra of water adsorbed on silica gels that were extracted above (see Sec. 4.2) from the basis spectra of the water components of these gels.²⁶

The results of a recent quantum-chemical calculation of the interaction of water with an isolated silanol center⁹² show that the nature of the vibrational modes significantly changes when the number of water molecules attached to the center is changed. In the case of a single molecule, the vibrational

spectra of a molecule coordinated by a silicon atom⁹³ and a molecule bound to a center by a hydrogen bond are strikingly characteristic. When the number of attached molecules reaches six, the complete spectrum acquires the features of the two characteristic spectra mentioned above. However, according to the analysis of the vibrational modes,⁹² the adsorption complex vibrates as a whole object in which the structurally distinct coordination and hydrogen-bound molecules are not dynamically distinguished. Referring the reader to Ref. 92 for details of this analysis, here for simplicity we use the characteristic nature of the vibrational spectra of single water molecules for a qualitative description of the features of the spectra in Fig. 18.

Three spectral ranges can be distinguished in these spectra. The low-frequency region $0\text{--}350\text{ cm}^{-1}$ (1) contains the frequencies of valence vibrations of $\text{Si}\cdots\text{OH}_2$ groups, torsional vibrations of these groups, and deformational vibrations of the hydrogen bonds of interacting water molecules. The region of intermediate frequencies $350\text{--}850\text{ cm}^{-1}$ (2) is characterized by an intense structural peak and mainly arises from deformational vibrations of hydrogen bonds. This peak is the main structural feature in the spectrum of quickly quenched water [see Fig. 13a]. The high-frequency part of the spectrum $850\text{--}1200\text{ cm}^{-1}$ contains two peaks associated with the deformational vibrations of a water molecule coordinated by a silicon atom and deformational vibrations of the bond of the $\text{Si}\text{--}\text{OH}$ group entering into the adsorption center.

This assignment of vibrational modes has been used as the basis for a structural–dynamical analysis of adsorbed water in these silica.²⁸ The spectrum of water adsorbed on aerosil has been explained by assuming that the adsorption of water on the surface is collective in nature from the viewpoint of the water molecules, i.e., in the adsorption process the water molecules form a “quasidrop” at a silanol center.^{24,28,92} This assumption is fully confirmed by calculations of the equilibrium configurations of water molecules on large clusters modeling the aerosil structure (see Sec. 7.1).

The spectrum of adsorbed water in silica gel [Figs. 18b and 18c] differs significantly from the spectrum of water in aerosil. This indicates that the origin of the centers responsible for water adsorption in these silicas is different, which is in complete agreement with the conclusion obtained in the preceding section. Analysis of the spectrum of adsorbed water in silica gel from the viewpoint of assigning the frequency regions 1–3 (Ref. 28) leads to the following conclusions. As in the case of aerosil, adsorption of water in silica gel occurs collectively, since the double peak in region 2 dominates in the vibrational spectrum. The shape of this peak is similar to that of the analogous peak in the spectrum of quickly quenched water [see Fig. 13a], but the peak is shifted to the low-frequency region and the ratio of the intensities of its components is different. This may be a natural consequence of the binding of a water “drop” to an adsorption center. Comparing the spectra of water adsorbed on aerosil and silica gel, we see that this binding of the drop is weaker for silica gel than for aerosil. The spectrum of water adsorbed on silica gel has no peak at 900 cm^{-1} , which indicates the practical absence of water coordinationally bound to its surface. The broadness of the peak in region 1, as in the

case of aerosil, indicates that water adsorption is collective in nature. The surprising fact, noted earlier, that the spectra of adsorbed water are the same for the two silica gels acquires a natural explanation in view of the analysis described above and also the analysis of the structure of hydroxyl shells of silica gels. Since, as was shown in the preceding section, these shells consist of a set of three silicon–hydroxyl groups, namely, $(\text{OH})_1$, $(\text{OH})_2$, and $(\text{OH})_3$, the water molecule interacts with each of these groups independently, causing them to compete for water adsorption. Under these conditions the “strongest” wins; in this case this is the one with the largest binding energy between the water molecules and the center. Since this strongest grouping is one of the three listed above, it must be the same for both SG100 silica gel and SG20 silica gel. Therefore, the spectra of adsorbed water must be identical for the two silica gels, and the only difference between them is in their absolute intensities, which is related to the fraction of adsorption centers thus selected on the surface of the silica gels.

The AWDS spectrum of water adsorbed on aerogel [Fig. 18d] is strikingly different from the spectra given above. First, this spectrum does not contain a clearly expressed intense peak in region 2, which indicates that there are significantly fewer hydrogen bonds between the water molecules on the aerogel surface. It has therefore been suggested²⁸ that the layer of adsorbed water in this case is formed not by drops, as in the case of aerosil and silica gel, but predominantly by isolated molecules. This conclusion is also confirmed by the clearly expressed structure of the vibrational spectrum in the low-frequency region 1, the form of which is characteristic of localized individual states. The position of the maxima in this region is nevertheless close to the position of the maxima in the aerosil spectrum [see Fig. 18a]. This indicates that the main water adsorption center in aerogel is the silanol group, which is completely consistent with the conclusions of the preceding section. This conclusion is also supported by the presence of the maximum at 900 cm^{-1} in the spectrum. It is less clearly expressed than in the spectrum of water in aerosil, but is quite reliably observed. In the opinion of the authors of Ref. 28, the change of the ratio of intensities at the maxima in the water spectra for these two aerosilicas reflects the fundamentally different nature of adsorption in them: collective in the case of aerosil, and isolated in the case of aerogel. This conclusion appears quite natural when it is recalled that for aerosil adsorption occurs on the free outer surface of small particles. Steric hindrances to drop formation can arise only from the density of silanol groups on the surface. It has been established experimentally that this density corresponds to an average distance of 7 \AA between silanol centers.⁶ This distance is sufficient for the formation at an isolated silanol center of a quasidrop consisting of several water molecules. In contrast, the active surface of aerogel is the inner surface,³ so that steric hindrances play a more important role in quasidrop formation.

In spite of its qualitative nature, this comparative analysis of the basis spectra of the components of the dispersed silicas under study reliably shows that aerosils, silica gels, and aerogels should be viewed as fundamentally different

TABLE IV. Chemical nomenclature of silicates (Ref. 94).

Dimension <i>D</i>	Multiplicity <i>M</i>		
	1	2	3
0 Oligosilicates	Monosilicates	Disilicates	Trisilicates
0 Cyclosilicates	Monocyclosilicates	Dicyclosilicates	Tricyclosilicates
1 Polysilicates	Monopolysilicates	Dipolysilicates	Tripolysilicates
2 Phyllosilicates	Monophyllosilicates	Diphyllosilicates	Triphyllosilicates
3 Textosilicates	Textosilicates		

structures. It is important to note that they differ not only in their bulk structures, but also in the structures of their surface zones. Since these materials are distinguished only by their production technology, the observed structural variation is a manifestation of the phenomenon of technological polymorphism in dispersed amorphous silica.

6. TECHNOLOGICAL POLYMORPHISM AND THE CLASSIFICATION OF DISPERSED AMORPHOUS SILICAS

The existence of technological polymorphism in dispersed amorphous silicas is important in itself and as the foundation of a completely new approach to the problem of the computer modeling of these materials. The development of this approach requires classification of the modifications which have been found after determining the distinctive features of each modification and introducing certain numerical classification parameters.³² It was possible to carry out this program by using the basic crystallo-chemical criteria proposed by Liebau.⁹⁴

6.1. Foundations of the crystallo-chemistry of silicates

In the fundamental study of Liebau⁹⁴ it was shown that silicates are characterized, to a higher degree than any other group of chemical compounds (except for organic compounds), by extremely high variability of their chemical and structural properties. After analyzing about 1000 compounds, it was established that silicates can nevertheless be divided into a small number of classes and subclasses in accordance with a classification based on the following fairly simple crystallo-chemical principles.

(1) Since in all the silicates studied the most stable bond is the Si–O bond, the basic fragment determining the structure of a silicate is the polyhedron $[\text{SiO}_n]$, and the type of structure is determined by the ways in which these polyhedrons are bound to each other.

(2) The coordination number (CN) of silicon in silicon compounds with the general formula $\text{M}_x\text{Si}_y\text{A}_z$ and Si–A–M bonds tends to grow, $\text{CN} > 4$, the more strongly, the higher the electrical negativity of the nearest neighbors, the atoms A. Oxygen has an intermediate value of electrical negativity and can enter into both $[\text{SiO}_4]$ tetrahedra and $[\text{SiO}_6]$ octahedra. Tetrahedra are preferred. For example, of the 874 silicates studied, octahedral anions were found in only 16.

(3) $[\text{SiO}_4]$ tetrahedra are joined together most often at a vertex rather than at an edge or a face.

(4) One oxygen atom can belong to no more than two $[\text{SiO}_4]$ tetrahedra.

(5) For a given silicate anion, the difference Δs between the values of s of all the $[\text{SiO}_4]$ tetrahedra (where s is the number of links, i.e., the number of oxygen atoms in the $[\text{SiO}_4]$ tetrahedron joined to other $[\text{SiO}_4]$ tetrahedra) tends to decrease.

(6) The lengths of the bonds and the valence angles deviate as little as possible from the average values:

$$\langle d(\text{Si}-\text{O}) \rangle = 1.62 \text{ \AA}, \quad \langle (\text{O}-\text{Si}-\text{O}) \text{ angle} \rangle = 109.47^\circ,$$

$$\langle (\text{Si}-\text{O}-\text{Si}) \text{ angle} \rangle = 140^\circ.$$

These six rules are not laws of nature, and there are known exceptions,⁹⁴ but nevertheless the violation of these rules is in most cases energetically unfavorable and thus of low probability.

Several parameters have been introduced to describe how $[\text{SiO}_4]$ tetrahedra are joined together. Instead of listing them, we discuss a point which is important for what follows, namely, *dimensions* and *multiplicities*. The dimension D of silicate tetrahedral structures characterizes the type of packing in the original structural units and takes values $D=0,1,2,3$. For example, isolated $[\text{SiO}_4]$ tetrahedra and also isolated cycle and non-cycle fragments have dimension $D=0$. For isolated chains $D=1$, for isolated layers $D=2$, and for frameworks $D=3$ (Ref. 94). The multiplicity M characterizes the formation of multiple tetrahedral structures of the same dimension as the original structural units (isolated $[\text{SiO}_4]$ tetrahedra, isolated chains, isolated cycles, and isolated layers).

The basic nomenclature of silicates given in Table IV is introduced in accordance with the values of these parameters. Silicates with isolated tetrahedra (one, two, three) are referred to as *oligosilicates*. Silicates whose anions form a cycle consisting of $[\text{SiO}_4]$ tetrahedra are called *cyclosilicates*. Depending on whether they contain isolated cycles, double cycles, or a larger number of cycles, the prefix *mono-*, *di-*, etc., is added to the name. Structures containing silicate chains are called *polysilicates*. They can be further subdivided into *monopolysilicates* with isolated chains, *dipolysilicates* with double chains or bands, and so on. *Phyllosilicates*, formed by layers of $[\text{SiO}_4]$ tetrahedra, can similarly be fur-

TABLE V. Quantitative characteristics of model clusters of aerosil (Ref. 33).

Cluster	Number of atoms			Number of groups		Linear size, A	
	Total	Si	O	(OH) ₁	(OH) ₂	min.	max.
Rings							
Si3c	12	3	3	—	3	3.57	6.62
Si4c	16	4	4	—	4	3.62	8.11
Si5c	20	5	5	—	5	3.65	9.00
Si6c	24	6	6	—	6	3.62	8.72
Si8c	32	8	8	—	8	5.60	11.34
Si10c	40	10	10	—	10	5.18	13.07
Si14c	56	14	14	—	14	5.18	15.71
Bulk Structures							
Si10	54	10	12	4	6	8.57	11.16
Si14	72	14	18	8	6	9.00	14.30
Si18	90	18	24	10	7	10.52	15.41
Si24	118	24	36	15	7	10.52	16.02

ther subdivided into *mono-* and *diphyllsilicates*. Silicates with a three-dimensional framework of [SiO₄] tetrahedra are called *tectosilicates*.

Silicates can be divided into subclasses of the classification given above because the general *principle of economy* (parsimony) holds. According to it, a system of a given composition tends to have the minimum possible number of geometrically and chemically differing groups.⁹⁴

6.2. Classification of dispersed silicas according to the crystallo-chemistry of silicates

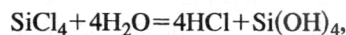
The basic rules of crystallo-chemistry given above do not involve anything specific to the crystalline structure, and thus it is natural to assume that they are also satisfied for amorphous structures.³²

No crystalline silicates with mixed dimensionality and multiplicity are known in nature. This should also apparently be true of the amorphous state. Consequently, amorphous structures can also be classified as in Table IV. The special feature of these materials is that the classification for each can be established by analyzing the technological production procedure.³²

Dispersed silicates are obtained in the simultaneous occurrence and competition of two processes: hydrolysis of the initial product leading to the formation of silicon-oxygen tetrahedra containing from one to four hydroxyl groups, followed by polycondensation of these fragments.¹⁻³ Polycondensation produces the nucleus of the future structure of the

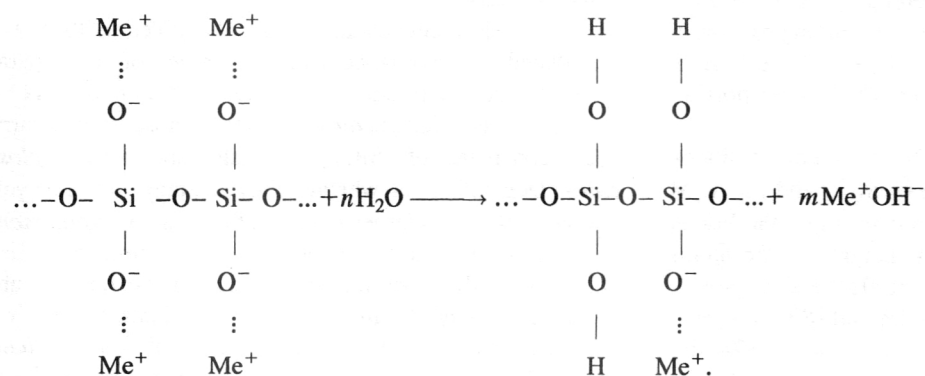
final product: a particle of aerosil, a silica gel salt, or an element of the capillary structure of aerogel. The technological procedures differ in the initial products subjected to hydrolysis, the medium in which these processes occur, and the external conditions (temperature, pressure, and so on).

Aerosil. Aerosil is obtained by subjecting four-chlorine silicon to hydrolysis. The hydrolysis is performed in an oxygen-hydrogen flame at atmospheric pressure and at a temperature of about 2000 K. The hydrolysis, occurring as the reaction



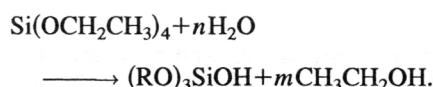
produces orthosilicate acid, the polycondensation of which produces aerosil. The solid nuclei formed near the flame are removed from this region and, upon arriving in a cold region, form larger agglomerates, which are practically ideal spherical particles of amorphous silica. The process of polycondensation and formation of nuclei and agglomerates is in many respects similar to the process by which small particles of metals are obtained.⁹⁵

Silica gel. Silica gel is usually obtained from aqueous solutions of silicates of alkali metals in the presence of acid.² It is known that the silicates in question contain chains of [SiO₄] tetrahedra already in the initial state, and these are undoubtedly the precursors of the future solid structure. The process can be represented schematically as

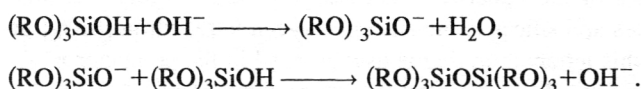


Hydrolysis of the metal silicate occurs in the aqueous solution, resulting in the formation of chains of $[\text{SiO}_4]$ tetrahedra of various lengths in which each silicon atom is bound to two hydroxyl anions. It is known that when the concentration is high these chains easily close, forming cycles with various numbers of silicon atoms. The hydroxyl anion can break the Si—O—Si bond connecting adjacent tetrahedra, so that over time a dynamical equilibrium of cycle formation and breaking processes is established in the solution. Acid is introduced into the solution to shift the equilibrium in favor of polycondensation. This causes the cycle-breaking process to practically stop, and the active process of cycle formation and fusion of cycles with each other occurs in the medium. The initial hydrolysis is usually not completed, so that negative oxygen ions remain in the cycles which keep solvated positive metal ions near the cycle. It has been found² that the presence of such solvated ions plays a decisive role in stabilizing the gel.

Aerogel. The main technological process for manufacturing this product is either acid- or alkali-catalyzed hydrolysis of tetraethylorthosilicate $[\text{Si}(\text{OCH}_2\text{CH}_3)_4]$ (TEOS)⁹⁰



The "initial silanol" obtained as a result of this reaction can be a complex compound, depending on the component R, which can be either a hydrogen atom H or an ethyl group C_2H_5 . Simultaneously with the hydrolysis process, condensation of the produced "silanols" occurs, which is completed by the production of silicate polymer according to the scheme



The growth of the polymer chain is controlled by the concentrations of water and TEOS and the pH of the solution. Processes with acid catalysis generally produce short chains. If the catalyst is alkaline, the chains are longer. The gel is produced when the chains combine.

Thus, analysis of the technological processes by which various dispersed silicas are obtained shows that the structural fragments forming the structure of the future product are completely different in the three cases. It is obvious that the principle of maximum packing of $[\text{SiO}_4]$ tetrahedra in space is operating in the formation of aerosil particles. According to the Liebau classification,⁹⁴ the dimension of the resulting structure is $D=3$, and by analogy with tectosilicates aerosil is classified as an *amorphous tectosilica*.³²

In the case of silica gels, their basic structures are cycles of rather arbitrary composition with dimension $D=0$, so that they are classified as *amorphous cyclosilicas*, analogous to cyclosilicates.³²

Chains are the main structural element of the aerogel framework. In this case the dimension of the structure is $D=1$, so that it is classified as an *amorphous polysilica*, analogous to polysilicates.³²

Thus, the technological polymorphic forms of dispersed silicas are the amorphous tecto-, cyclo-, and polymodifica-

tions. These ideas form the basis of the qualitative algorithm used to construct model structures of amorphous silicas.³²

7. COMPUTER MODELING OF THE INITIAL STRUCTURES OF AMORPHOUS SILICAS

During the last few years the concept of computer modeling of multiatomic systems has actively developed to the point where it is becoming possible to describe the properties of real nanomaterials.^{15,31,36} This concept is based on a combined spectral experiment incorporating feedback between a computer experiment and a real experiment. The modeling process is viewed as a synthetic problem, the successful solution of which is determined by the optimal choice of four of its basic components, namely: (a) *the quantum-chemical method of calculating* multiatomic clusters of size on the scale of nanometers; (b) *a method of realizing the calculations* using fast computers; (c) *a structure-sensitive experimental technique* for checking the correctness of the results; and (d) *a suitable experimental object*, so that feedback between the calculations and the actual experiment can be achieved.

The necessity of using clusters of size on the scale of nanometers naturally leads to the use of one of the available quantum-chemical semiempirical methods. Significant progress has been achieved in this area in recent years, owing both to the stimulating studies of Dewar and co-workers,⁹⁶ and to the development of new computational tools or new versions of existing ones. Among the latter are the copyrighted program packages in computational chemistry written by Zaets and based on the MNDO, MNDO/H, AM1 (sp-basis) (CLUSTER-Z1; Ref. 97), and NDDO (spd-basis) (CLUSTER-Z2; Ref. 98) methods. These packages are realized in a form which ensures high accuracy in the calculation of multiatomic systems for relatively small computer time. Installed on personal computers like the PC AT 486/Pentium and the SUN SPARC station, they have made it possible to perform in a short time calculations of a variety of multiatomic clusters of nanometer size for such systems as silica, silicon nitride, nickel nitride, aluminum nitride, and so on (see Ref. 36 for a brief review of the results).

However, the data obtained do not by themselves solve the problem of computer modeling, since the important question arises of how these data correspond to the physico-chemical reality. The nanometer clusters used as the model do not have molecular analogs; they are just a helpful "figment of the imagination." Therefore, the main characteristic of a molecular system—the binding energy—and other integral characteristics are only descriptive and cannot be experimentally tested. Only the vibrational spectra, which are predominantly described by the short-range interaction, are a property of the system for which the cluster approximation is fairly accurate. From the point of view of a numerical experiment, modeling of the surface is no different from modeling of the bulk structure. However, the requirements of feedback using a real experiment at the level of the vibrational spectra shift the focus of the problem to choosing an experimental object which is as close as possible to the modeled clusters. Therefore, to check the results obtained by the numerical modeling of the adsorption properties of the sur-

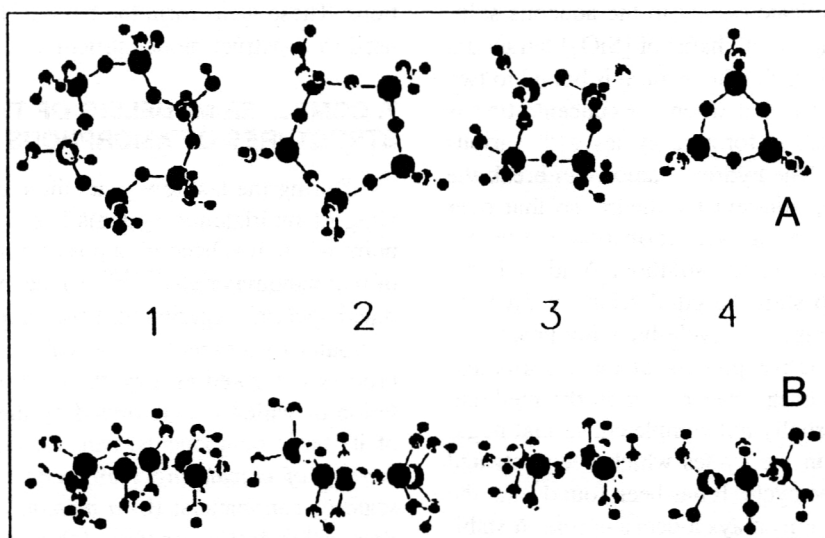


FIG. 19. Small cycles of silicon-oxygen tetrahedra *Sinc* (AM1) (Ref. 33). The number n is the number of silicon atoms in a cycle. (1) Si3c (18); (2) Si4c (24); (3) Si5c (30); (4) Si6c (36). The method of calculation and the number of atoms in a cluster are given in parentheses. A and B are two projections (see the text).

face of nickel,^{19,99,100} silica,³²⁻³⁵ and silicon nitride,¹⁰¹ the common experimental parameter was taken to be the vibrational spectra of the corresponding nanodimensional modifications of these materials.

In the computer modeling of a large cluster a qualitatively new problem arises: that of choosing the method of modeling the initial structure. It is well known¹⁰² that in most cases chemical interactions are short-range, so that structural elements separated by distances exceeding the lengths of chemical bonds have practically no effect on each other. The danger therefore arises of "not guessing" the location and direction of development of the structure. The situation is often complicated by the fact that nonrigid structures like, in particular, silica structures, are characterized by a set of closely spaced minima on the total-energy surface. Algorithmic modeling provides one way out of this situation. This amounts to constructing an initial structure of the cluster using a certain algorithm based on "evidence of the origin" of the corresponding product, containing a set of distinguishing features possessed by only this product.¹⁰³ This is the approach that has been used to model the structures of dispersed silicas.³²⁻³⁵ It is based on the algorithmized representation of the technological polymorphism of these materials.

7.1. Computer modeling of aerosil

The computer modeling of the structure and adsorption properties of aerosil³³ consisted of the following steps:

- (1) Construction of the initial structures of the multiatomic clusters of nanometer size.
- (2) Computer modeling of the cluster structure using semi-empirical quantum-chemical techniques.
- (3) Computer modeling of the adsorption properties of the clusters for water molecules.
- (4) Calculation of the doubly amplitude-weighted density of vibrational states of the clusters and the neutron

inelastic-scattering spectra followed by comparison of the calculated and experimentally measured spectra.

a) Initial structural models

When constructing the initial clusters, it is useful to introduce the concept of small, intermediate, and large clusters consistent with the basic ideas about crystallo-chemical fragments and the type of packing according to the structural class of the material. The basic structural fragment of silicates and silicas is the silicon-oxygen tetrahedron [SiO₄]. It is this tetrahedron that is usually used in the computer modeling of silica systems (see, for example, Refs. 6, 93, 104, and 105). However, owing to the large variation in the structures of dispersed silicas, this model cluster is completely insufficient for describing their properties. Therefore, special definitions were used in the computer modeling of this family of materials. The concept of *small cluster* was introduced as the structural model of the peripheral (below, surface) functional group; the concept of *intermediate cluster* describes the packing of small clusters according to the structural classification and correctly describes the distribution of atoms of *near order*; the concept of *large cluster* is ideally intended to reflect the correct bulk structure of the material and the distribution of functional groups on its surface. These ideas become meaningful only when applied to each object studied.

Since aerosil is an amorphous tectosilica, the clusters modeling the structure of its core must have a densely packed framework. It is known that densely packed crystalline structures of silica contain cycles of siloxane chains with a small number of members: four-member cycles in quartz¹⁰⁶ and six-member cycles in cristobalite¹⁰⁷ and tridymite.¹⁰⁸

The structural models of individual small cycles are shown in Fig. 19. They were obtained by full optimization by the AM1 method, using the quantum-chemical program package CLUSTER-Z1 (Ref. 33). This and all the subse-

quent calculations were performed on personal computers of the type PC AT 386/387-33 and 486-66. The clusters are represented in two projections such that the top view (A) corresponds to their maximum size and the side view (B) to their minimum size.

It should be noted that the silicon atoms lie strictly in a single plane only in the Si3 cluster, while in the others the silicon rings are close to planar. In contrast, large cycles involving more than 6 silicon atoms possess a clearly expressed nonplanar structure (see Fig. 27 and Sec. 7.2). It is therefore obvious that the "faceted" faces of a dense bulk structure are conveniently constructed by using only small "rigid" cycles, shown in Fig. 19. A structure composed of large cycles will necessarily be more friable. Therefore, the model of the bulk structure of aerosil will be polyhedra whose faces are formed by small cycles. In constructing the model structures preference was given to six-member cycle-hexagons, so that the nuclei of the aerosil particles are formed at high temperature, at which the crystalline structure of β -cristobalite is more stable.³³

The choice of hexagonal form suggests the following simple algorithm for the subsequent growth in size of the model cluster:

$$\text{Si}6c + 4n\text{Si} + 6m\text{Si}, \text{ where } n = 1, 2, 3$$

$$\text{and } m = 1, 2, 3, \dots \text{ for } n > 3.$$

This algorithm corresponds to the development of the cluster structure in which the addition of the first four silicon atoms to the basic hexagon Si6c is accompanied by the formation of three new hexagons, which are the faces of a closed four-faceted figure. The addition of each subsequent group of four silicon atoms leads to the formation of three new edges, along which two new faces are formed, so that the four-faceted cluster Si10 is transformed into the six-faceted cluster Si14, the six-faceted cluster Si14 is transformed into the eight-faceted one Si18, and so on. Here the width of the cluster grows. For it to grow in depth, beginning with $n=3$, the structure can grow by the addition of six silicon atoms. The set of clusters Si10, Si18, and Si24 obtained using this algorithm is shown in Fig. 20.

b) Analysis of the model structures of aerosil

Whereas the first term of this series can be classified as a cluster of intermediate size, the last two clusters now fall in the large category. Analysis of their structure shows that the cluster-growth algorithm that we have used not only generates the bulk structure of the material, but also reveals the trend in the distribution of functional groups on the surface. In the object in question these are the silanol (OH)₁ and silandiol (OH)₂ groups. As the cluster size increases, the silandiol groups, existing exclusively in isolated cycles (see Fig. 19), are gradually replaced by silanol groups and pushed out to the periphery. As can be seen from Fig. 20, there are no silantriol groups in closed, densely packed structures. These groups appear only in a unique branching of the structure, which is shown in Fig. 21 for the example of the opti-

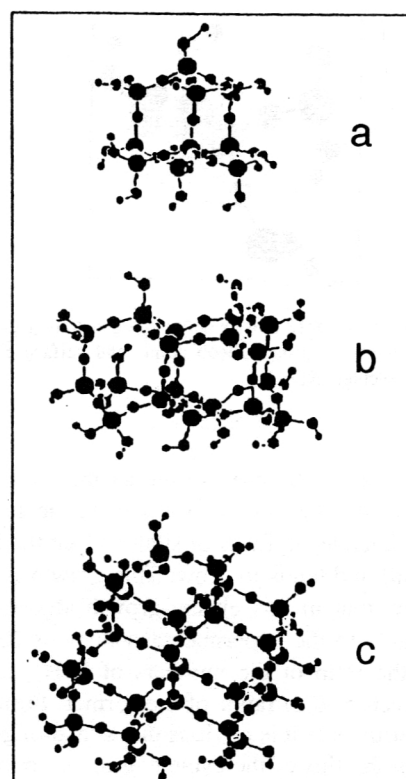


FIG. 20. Clusters of a densely packed structure (AM1) (Ref. 33). (a) Si10 (54); (b) Si18 (90); (c) Si24 (118).

mized structure of the Si11 cluster. The foundation of this cluster is the optimized structure of the Si10 cluster, shown in Fig. 20.

In Table V we give the numerical characteristics of the clusters showing the dynamics of the change of the ratio of the numbers of silanol and silandiol groups in the clusters of a densely packed structure. We see from this table that there are no (OH)₁ groups at all in isolated cyclic clusters. These groups appear only in the compactly bound structure of the Si10 cluster. Here the ratio of the numbers of (OH)₁ and (OH)₂ groups remains in favor of the silandiols. It is well known experimentally that the hydroxyl covering of an aerosil particle can contain no more than 20% silandiol groups.⁵ It is therefore completely obvious that neither free cycles themselves nor compact structures formed from a small

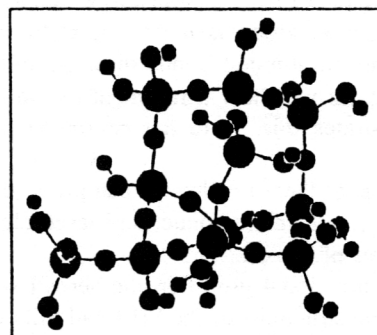


FIG. 21. The Si11 cluster (60) (AM1), modeling the silantriol group in a densely packed structure (Ref. 33).

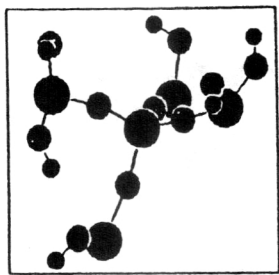


FIG. 22. Fragment of the Si18 cluster (AM1) demonstrating the alternating distribution of "empty" surface silicon atoms and surface silicon atoms bound to a silanol center (Ref. 33).

number of cycles can be used to model the structure of an aerosil particle. As the cluster size grows, the ratio of hydroxyl groups changes in favor of silanols (see the Si14 cluster and beyond) and tends to grow. This growth is slow, but estimates show that in this cluster-growth algorithm, when sizes comparable to the experimental values of 100–200 Å are reached, the ratio of the numbers of $(\text{OH})_1$ and $(\text{OH})_2$ groups can reach 5–6 in favor of the former. From analysis of the model structures it is obvious that silandiol groups will mainly exist at the tips of the cycle edges, i.e., on irregularities of the surface structure of a real particle. This trend in the variation of the structure of the hydroxyl covering of the clusters implies that the specific content of hydroxyl groups on the aerosil surface must change in the direction opposite to its specific area (radius), as has been found experimentally.¹⁰⁹

This cluster-growth algorithm is certainly not unique; it only corresponds to the most probable structures of a densely packed amorphous silica, fully reflecting the fourfold coordination of the silicon atoms in the dense structure formed by hexagons. Apparently, the irregularity of the structure at macroscopic distances unique to the amorphous state arises from the fact that in the dense packing of atoms, four-, five-, and six-member cycles adjoin each other. However, the above remarks about the trend in the distribution of functional groups in a real particle remain valid for cycles of all sizes.

In view of this, the Si18 cluster can be regarded as a fairly realistic model of the surface of an aerosil particle. This is true not only of the distribution of hydroxyl groups, but also of the formation of the experimentally established⁵ alternating structure of silicon atoms, in which a silicon atom carrying a hydroxyl group is located next to an "empty" atom having no unsaturated bonds directed away from the surface. In Fig. 22 we show a fragment of the Si18 cluster which demonstrates this. Here the central silicon atom is empty.

On the basis of these results, we can propose the following models of small, intermediate, and large clusters of the model structures of aerosil.

The basic functional group on the aerosil surface is, as follows from the structures of the Si18 and Si24 clusters, the isolated silanol group. Therefore, the simplest model of a small cluster might be a silicon–oxygen tetrahedron based on three silicon atoms and containing one OH group. The

interaction of this cluster with water has been used as the basic model in Refs. 15, 92, 93, 100, and 110. The results obtained are in satisfactory agreement with the experimental data on the vibrational spectra of water adsorbed on the surface of aerosil particles.

An analogous small cluster with silandiol grouping can serve as the simplest model of an isolated silandiol group on the aerosil surface. As mentioned above, these groups are located on irregularities of the structure, and their contribution to the water and hydroxyl components of aerosil is relatively small. Silantriol groups are, as shown above (see Fig. 21), completely alien to the densely packed aerosil structure and, being outsiders, are naturally extremely unstable. Accordingly, it is hardly possible for them to exist on the surface of aerosil particles.

The Si10 model cluster is an example of a cluster of intermediate size produced by the packing of small clusters. The Si18 and Si24 model clusters are large clusters modeling not only the bulk packing in the core of the aerosil particle, but also describing the distribution of hydroxyl groups on its surface. Further growth of the cluster is apparently not useful, because it is unlikely that any qualitatively new information would emerge, owing to the small range of the chemical-interaction forces. The structures described above have been used to calculate the vibrational spectra of the core and the hydroxyl component of aerosil, and also the spectra of water adsorbed on them.

c) Vibrational spectra of the core and the hydroxyl component

In Fig. 23 we show the experimental AWDS basis spectrum of the aerosil core together with two calculated spectra. The calculated spectra were obtained using the package of programs for computational vibrational spectroscopy COSPECO.¹¹¹ The data on the force field were obtained by the above-described quantum-chemical calculation in the AM1 approximation of the program package CLUSTER-Z1. The first of these spectra (see curve 2) pertains to the Si18 cluster. We have already noted above that this cluster is a realistic model of a large cluster. In addition, the spectrum calculated for it differs so greatly from the experimental one that at first we were discouraged. In analyzing the reasons for this discrepancy, we arrived at a completely new problem. The point is that the overwhelming majority of silicon atoms of this cluster turn out, upon careful inspection, to be surface atoms, so that the kinematical behavior of these atoms differs significantly from that of the bulk atoms for fixed values of the force constants for each chosen pair of atoms. This kinematical effect can be eliminated for the clusters in question by increasing the cluster size by nearly an order of magnitude, which makes any computational study completely unfeasible. However, another solution is possible. By studying the structure of the densely packed Si18 and Si24 clusters, one sees that they consist of a set of Si–O–Si chains arranged obliquely to the basal plane⁵ of the clusters. Every three adjacent chains in sections parallel to this plane form the typical hexagonal structure of dense packing. Therefore, the chain can be viewed as a translationally equivalent structural unit, which can be used to reconstruct the bulk structure

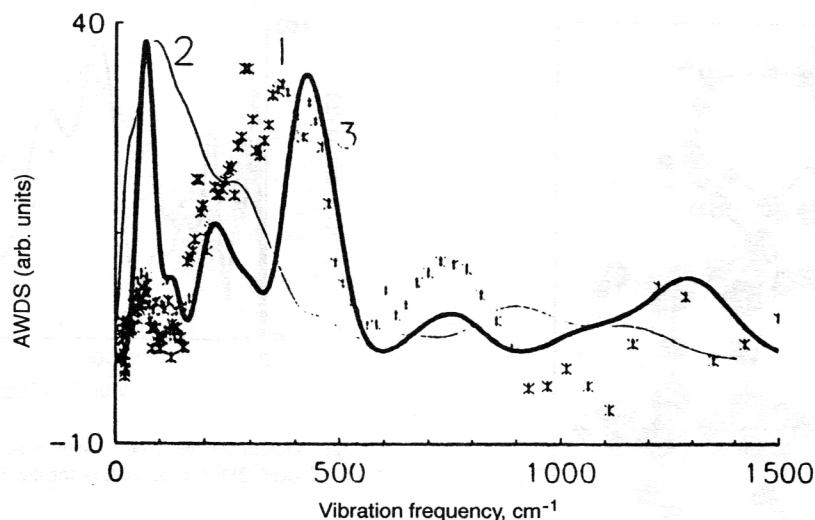


FIG. 23. Vibrational spectrum of the aerosil core. (1) Experiment, $T=10$ K (Ref. 25); (2) calculation for the Si18 cluster; (3) calculation for the siloxane chain Si10ch with cyclic boundary conditions (Ref. 103).

of the aerosil. The results of calculating the vibrational spectrum, shown by curve 3 in Fig. 23, correspond to a chain containing 10 silicon atoms for cyclic boundary conditions. The force constants in this chain were obtained by using the data from the calculation of the Si18 cluster. We see from this figure that the calculated and experimental spectra agree well with each other. The exception is the band at 80 cm^{-1} . This band arises from out-of-phase translational motion of the silicon-oxygen tetrahedra. As the chain length increases it splits into more and more components and its maximum decreases, so that when there are several dozen silicon atoms it certainly takes the form corresponding to experiment. The complete agreement between the locations of the maxima of all the bands in the calculated and experimental spectra should be noted. This agreement was obtained using the data from CLUSTER-Z1 without any correcting parameters.

In Fig. 24 we show the experimental and calculated

AWDS spectra for the hydroxyl covering of aerosil. Curve 2 corresponds to the spectrum given in Fig. 23 above for the Si18 cluster, which, as already stated, is the vibrational spectrum of the surface atoms. Curve 3 is the vibrational spectrum of atoms bound to the ten $(\text{OH})_1$ groups contained in the Si18 cluster. As noted in Sec. 4.1, the hydroxyl component of the AWDS spectrum of aerosil must consist of the vibrational spectrum of the hydroxyl groups and the vibrational spectrum of the surface atoms of the core activated by these hydroxyl groups as a result of the riding effect. The actual AWDS spectrum is the set of these spectra with the correct ratio of the numbers of hydroxyl groups and surface silicon atoms. Curve 4 in Fig. 24 corresponds to the total spectrum with the ratio 1:1. We see that this spectrum agrees very well with the experimental one.

This model of the densely packed structure of aerosil³³ can therefore be taken to be well justified because of the

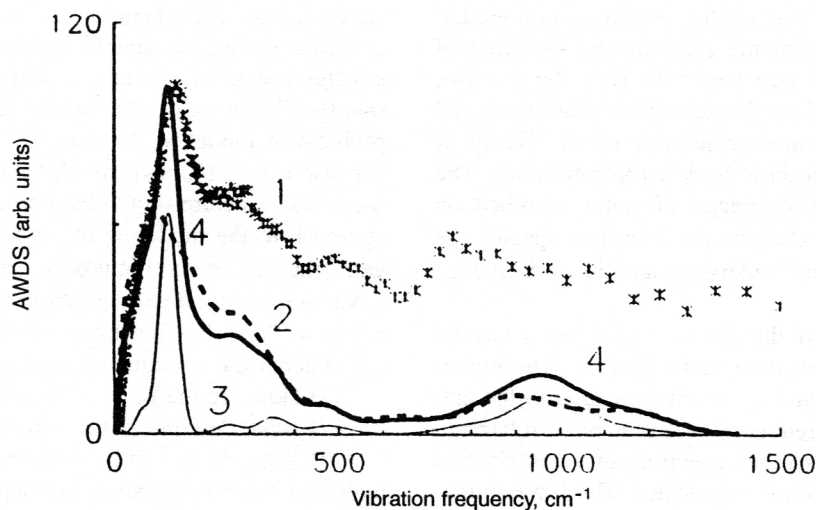


FIG. 24. Vibrational spectrum of the hydroxyl covering of aerosil. (1) Experiment, $T=10$ K (Ref. 25); (2)–(4) calculation: (2) hydroxyl covering of the Si18 cluster; (3) core-surface of the Si18 cluster; (4) sum of (2) and (3) (Ref. 103).

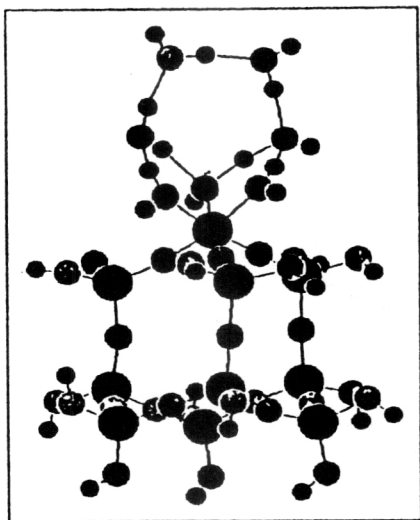


FIG. 25. The Si10w6 cluster (72) with six water molecules (MNDO/H) (Ref. 103).

agreement between the vibrational spectra of the core and the hydroxyl covering of the aerosil particle.

d) Compositional structure and vibrational spectrum of adsorbed water

The high reliability of the results of modeling the structure of an aerosil particle allowed us to study in more detail the problem of the adsorption of water on this particle.⁹³ As noted above, the Si10 cluster is of intermediate size, and reproduces the real structural correspondence of an isolated functional group and the bulk of the material. In Fig. 25 we show the fully optimized structure of this cluster interacting with six water molecules. This result was obtained in the MNDO/H approximation of the program package CLUSTER-Z1 (Ref. 97), since it was necessary to correctly take into account the water bonds formed. The details of the modeling of the interaction of water with the functional groups of the aerosil surface are given in Ref. 93.

Water molecules are adsorbed on the aerosil surface collectively, which confirms the conclusion obtained on the basis of qualitative analysis of the experimental spectrum of water adsorbed on aerosil (see Sec. 5.3). Here the first two molecules are coordinated by the silicon atom of the silanol group, saturating its coordination number to six. The other molecules are bound with these basic hydrogen bonds. The experimental and calculated spectra of water adsorbed on aerosil are shown in Fig. 26. Like the preceding spectra, the calculated spectra have not undergone additional frequency correction.

We see from this figure that the calculated and measured spectra are very similar in their main features. The higher intensity of the experimental spectrum compared to the calculated one in the high-frequency region may be related to the presence in the experimental spectrum of a contribution from two- and higher multiphonon states. The lower intensity in the low-frequency region is related to the fact that the content of adsorbed water complexes on the aerosil surface is heterogeneous.⁹³ In addition to centers containing six mol-

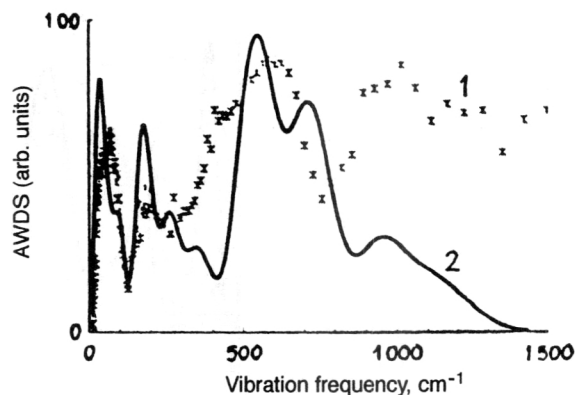


FIG. 26. Vibrational spectrum of water adsorbed on aerosil. (1) Experiment, $T = 10$ K (Ref. 25); (2) calculation for the Si10w6 cluster (Ref. 103).

ecules, there are centers with from one to five molecules. The question of the complete agreement between the calculated and experimental spectra therefore involves the problem of determining the number of these centers. The satisfactory agreement of the spectra shown in Fig. 26 indicates that of the possible diversity of adsorption complexes, the center with six water molecules gives practically the dominant contribution.

On the whole, the good agreement between the calculated and experimental basis spectra of the aerosil components undoubtedly indicates the correctness of the models of Fig. 20 describing the densely packed structure of amorphous silica.

7.2. Computer modeling of silica gels

As is well known from numerous data² and shown above, silica gel is one of the least understood materials. The reason for this is hidden in the well known variability of its properties. This pertains both to the poor reproducibility of the product even at the manufacturing stage, and to the variation of its properties and their extreme sensitivity to changes of the external conditions when it is used. It can therefore be stated that the main feature of silica gel is the "flow" of its structure, since each sample of silica gel is not a single fixed structural state of amorphous silica, but an "instantaneous snapshot" in a series of structural transformations. Thus, the problem of modeling the structure of silica gel is not easy, because it is not known which "instantaneous snapshot" of the actual structure should be reproduced. Therefore, in their approach to the modeling of the structural clusters of silica gel,³⁴ the authors did not take on the problem of reproducing a definite structural configuration. Their goal was to find answers to the following basic questions which can now be asked about the structure of silica gel.²⁸

- (1) How are the pores of silica gel formed?
- (2) What determines the pore size?
- (3) Why do the vibrational spectra of the core and the hydroxyl covering of silica gel depend on the pore size, as found experimentally?
- (4) What are the adsorbed and quasifree water found experimentally in the pores?

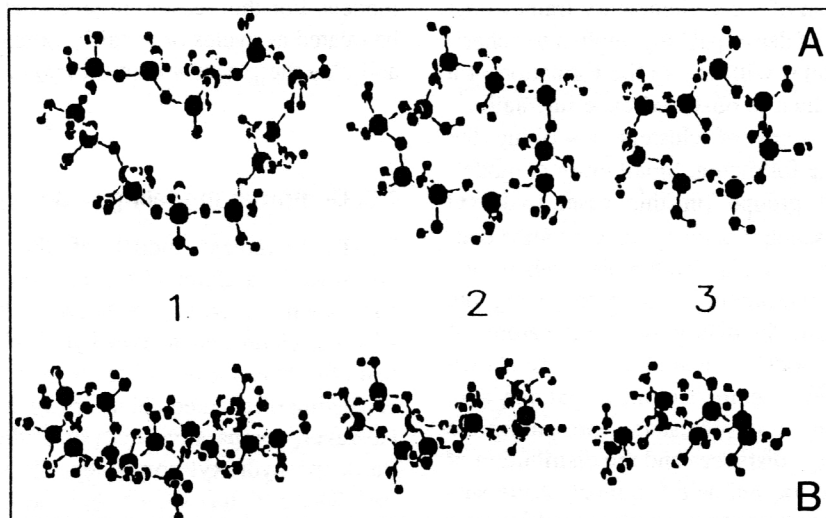


FIG. 27. Large cycles of silicon-oxygen tetrahedra *Sinc* (AM1) (Ref. 34). (1) Si8 (48); (2) Si10 (60); (3) Si14 (84). A and B are two projections (see the text).

(5) Why is the vibrational spectrum of the adsorbed water independent of the pore size?

As was stated in Sec. 6.2, the structure of silica gel-cyclosilica is based on cycles of chains of silicon-oxygen tetrahedra of various sizes. It was noted that the friable structure typical of silica gel can be formed only by cycles of fairly large size. In Fig. 27 we show structural models of several large cycles. These structures were initially constructed and optimized by using the MM2 program,¹¹² and then they were further optimized by the AM1 method, using the computational chemistry program package CLUSTER-Z1.⁹⁷ Each cycle is shown in two projections such that the top view (A) corresponds to the maximum size, and the side view (B) corresponds to the minimum size. We see from this figure that as the cycle size increases the structure becomes less and less planar. We simultaneously observe a marked tendency to "cell division" of the cycle with the formation of smaller cycles.

Since large cycles are not unstable either from the thermodynamical or from the microscopic point of view, it is natural to assume that the structure of silica gel is produced by the joining together of cycles of different sizes. It should be noted that the cycles must be sufficiently large, because condensation of cycles with four, five, or six silicon atoms leads to the formation of densely packed structures of the aerosil or quartz-glass type.³³ These small cycles also are undoubtedly involved in the formation of the structure of silica gel, but most likely they play only a binding role.

As can be seen from Fig. 27, large cycles are strongly warped, so that it is easy to foresee that when, say, two such cycles join, they can "collapse." However, if it is recalled that gel formation occurs in the presence of solvated ions of alkali metal, it becomes natural to assume that the main role of the ions is to stabilize this structure. In Fig. 28 we show one of the possible structures produced by two cycles containing 7 and 8 silicon atoms and having two common siloxane bonds. In the projection shown in the figure it is clearly seen that these cycles form the halves of a "half-open

shell." Obviously, the presence of a solvated ion inside this structure prevents its collapse and facilitates extension of the cycles. This leads to the natural further assumption that silica gel is a rigid framework with a structure like that of a net collapsing a poorly inflated football.³⁴ The cells of this framework, in contrast to a football or true buckyball structures like C_{60} and C_{70} , are not perfect hexagons and pentagons, but nonplanar chain-like cycles of silicon-oxygen tetrahedra of different sizes. The tension of the structure at the time of synthesis is ensured by the solvated ions (one or several), and after they are removed pores of various sizes are left.

It is important to note that the formation of cycles and their attachment to each other and formation of the framework surrounding a pore are undoubtedly statistical processes. Naturally, they are strongly affected by external conditions. For example, some cycles can be broken. The number of such cycles is determined, in particular, by the acid concentration. This apparently also explains the above-mentioned difficulty of reproducing the structures of silica

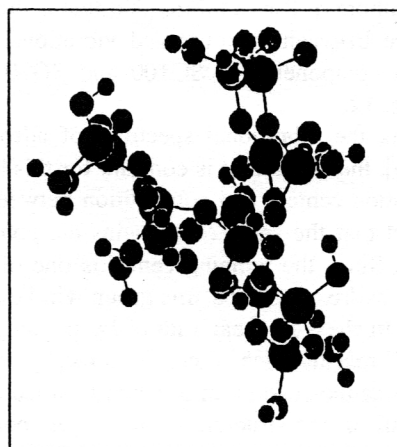


FIG. 28. Si13dc cluster (75) consisting of an Si7c cycle and an Si8c cycle (MM2) (Ref. 34).

gel. In turn, the aggregation of these elementary frameworks according to the principle of dense packing applied to spherical or quasispherical particles will lead to the formation of a globular mesostructure, which is observed experimentally.²

Accordingly, the hierarchy of clusters describing the structure of silica gel is the following. Small clusters modeling peripheral functional groups (in this case, hydroxyl groups) correspond to closed and open cyclic structures containing 8 or more silicon atoms and also the place where two cycles join. Clusters of intermediate size reproducing the packing of small clusters and the distribution of the atoms of near order correspond to model structures like those shown in Fig. 27. They can differ in composition, containing one, two, or more silicon atoms. Large clusters representing the distribution of atoms at large distances and the distribution of functional groups must be viewed as a fragment of the surface of a framework consisting of two or three links of the type shown in Fig. 27.

This concept of the model of the silica gel structure is consistent with the known macroscopic properties of this material. In addition, it permits the qualitative explanation of a series of microscopic properties which have so far been unexplained, including the vibrational spectra shown in Sec. 4.2. It is seen from these models that the core of silica gel is a net consisting of chains of siloxane bonds. The broadness of the size distribution of the cycles in this structure and its lability are obvious, and it follows, in particular, that the distribution of Si–O–Si deformational angles can certainly vary from sample to sample, which is related to fundamental changes in the observed core spectra²⁶ (see Fig. 11).

According to this model of the structure, the hydroxyl components of silica gels are formed by a set of three silicon–hydroxyl groups, namely, silandiol groups of closed cycles, silantriol groups at the ends of open cycles, and silanol groups at the places where cycles join. Therefore, the hydroxyl components of silica gel are heterogeneous, and their vibrational spectra are composite. Accordingly, the spectra will depend on the number of silicon–hydroxyl groups of the various types. At the same time, it is obvious that the ratio of the numbers of these groups is statistically distributed in a fairly wide range and can be different even for different fractions of products of the same technological cycle. The authors of Ref. 34 think that this is the reason for the difference between the observed vibrational spectra of the hydroxyl components of SG100 and SG20 silica gels shown in Fig. 12.

Regarding the vibrational spectrum of adsorbed water [see Fig. 13b], the fact that it is constant for this heterogeneity of adsorption centers and competition between them reflects the fact that the same center wins the competition in each sample. Since the winning center is one of three possible silicon–hydroxyl groups, this group will be common to all samples. In the very near future the ongoing computer modeling will reveal which silicon–hydroxyl group does actually determine the adsorption of water in silica gel. In contrast to aerosil, in the structure of silica gels both identical and different silicon–hydroxyl groups are located side by side, so that the simplest small clusters, which are isolated groups in aerosil, cannot be viewed as suitable structural

models. For this reason, in silica gel the small clusters must be treated as cycles or as fairly extended fragments of cycles, and also the places where they join.

7.3. Computer modeling of aerogel

The simplest model of the structure of aerogel–polysilica is a chain of silicon–oxygen tetrahedra.³² In this chain each silicon atom is bound to two oxygen atoms of the siloxane chain and to two hydroxyl groups. Therefore, the main functional group of the hydroxyl component of aerogel, consisting of isolated chains, must be the silandiol grouping. However, comparative analysis of the basis vibrational spectra of the hydroxyl components of various dispersed silicas (see Sec. 5.2) has shown that the main element of the hydroxyl component of aerogel is the silanol group. It is therefore natural to assume that aerogel is not a monopolysilica formed by single chains, but a di- or more complicated polysilica (see the classification in Ref. 94), the structural fragments of which are double or more complex bands. Owing to the large volume of capillary space in a macroscopic sample, it is difficult to assume that it consists of multichain bands, because then its density would have to be rather high. It is most likely that the number of chains in the bands is no greater than 2 or 3. One of the possible structures of this type is shown in Fig. 29. The structure is nonplanar. The quasi-regular structure of the cells in the central part should be noted. The basic size parameter of the model cluster is the band length, so that the boundary between a cluster of intermediate size and a large cluster is rather arbitrary. A special place on the structure is where several bands stick together. In Fig. 30 we show one possible model of this, described by a cluster of intermediate size.

The basic functional groups on the band periphery are silanols. Nevertheless, from analysis of the model of aerogel structure it is obvious that a cluster containing an isolated silanol group which is also a good model of the silanol groups of aerosil cannot model the functional groups of aerogel. The first reason for this is the fact that in contrast to aerosil, silanol groups in aerogel are located side by side with spacing of order 3.5 Å, so that several groups will participate in, for example, an interaction between a chain–band and water. The second reason is the significant difference between the core chain structure of the siloxane bonds of aerogel and the densely packed structure of aerosil. Because of this a small cluster, which in the opinion of the authors of Ref. 35 is needed for modeling functional groups and studying the interaction between aerogel and water, must have a rather complicated structure. One possible model of such a cluster is shown in Fig. 31.

The model structures of aerogel that we have shown are in good agreement with the existing ideas about its structure³ and supply details at the atomic level. In addition, they allow explanation of a distinctive feature of the vibrational spectra of its components: their narrow-band structure. It is well known that spectra of this type are typical of polymers,⁸⁹ which again confirms the suitability of the essentially polymeric model of this silica.

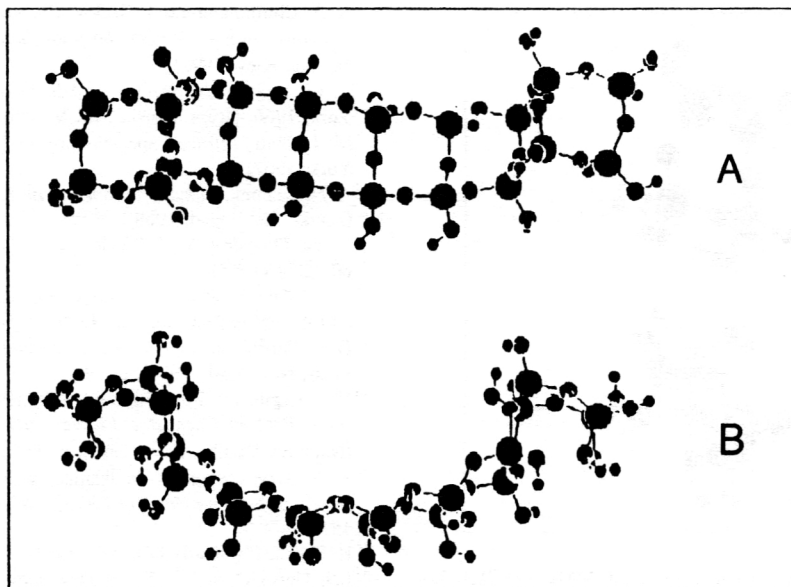


FIG. 29. The Si20b band cluster (MM2, 96) (Ref. 35). (A) Top view; (B) side view.

8. CONCLUSION

The fundamental physico-chemical phenomenon discussed above has been termed technological polymorphism. This is not simply a tribute to the fashion for new terms; it has turned out to be rich with meaning. The polymorphism of amorphous silicas has been reliably established from their vibrational spectra, which are the “fingerprints” of the structure of a material. The existence of such polymorphism is quite well known for labile systems. It would be possible to limit ourselves to such systems and try to qualitatively describe these dispersed amorphous silicas according to the degree of their lability. However, it has proved much more fruitful to follow the route based on the properties of the material which are peculiar only to it and which permit the introduction of a typical numerical parameter (or parameters) for classifying the materials in question. For example, in the case of amorphous materials with molecular structure, the understanding of the polymorphic modes of the amorphous

state has been advanced by viewing these modes as the corresponding prototypes of mesophases of the liquid-crystal state.¹¹³ The classification of amorphous phases has directly made it possible to judge the specific structural models of the material. In the case of dispersed silicas, a guide to classification is provided by the manufacturing technology, and the classification parameters are the dimension and multiplicity of the structures formed in the packing of silicon-oxygen tetrahedra $[\text{SiO}_4]$. The established classificational structural modes have not only permitted a new approach to the various types of material, but also have provided a fairly unique algorithm for modeling the corresponding structures.

Another indication of the fruitfulness of the new terminology is the possibility of generalizing it to the entire class of nanomaterials, which includes the silicas discussed above. The characteristic feature of these materials is the important contribution to their structure from surfaces or interfaces. This, in turn, makes nanomaterials exceptionally sensitive to

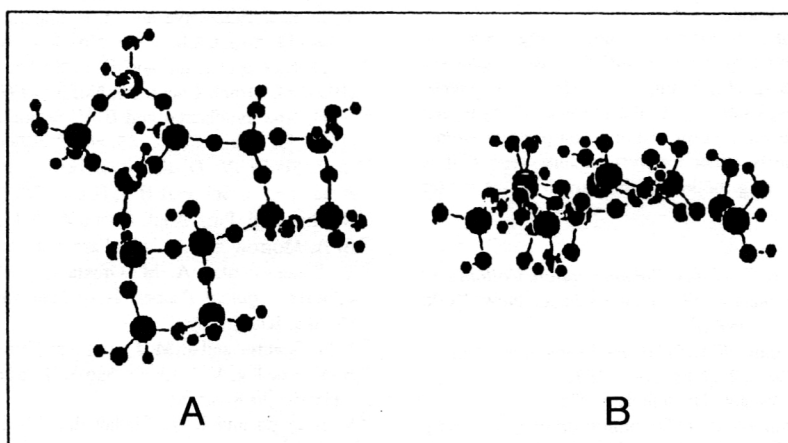


FIG. 30. Cluster corresponding to the sticking of Si12b bands (MM2, 63) (Ref. 35). (A) Top view; (B) side view.

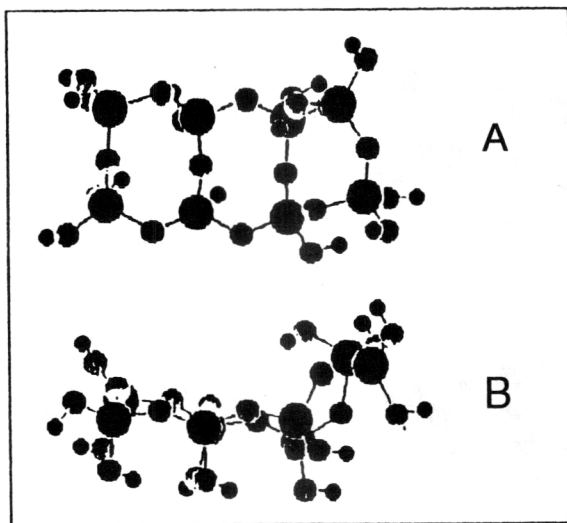


FIG. 31. A small cluster of the aerogel structure Si8b (MM2, 42) (Ref. 35). (A) Top view; (B) side view.

the technology by which they are prepared and the conditions under which they are stored. Therefore, as technicians well know, the chemical formula of the material actually describes a family of nanoproducts. On the other hand, one often encounters the situation where the investigator of fundamental quantum effects in nanomaterials is seriously troubled by "dirt" on the surface of the sample. However, this "dirt" on the surface and interfaces of nanomaterials rigorously obeys the chemical interaction laws and can be identified or predicted by a complex analysis of this technological polymorphism. This approach has been successfully implemented in, for example, the case of a family of silicon nitride powders of various origin.¹⁰¹ It should be specially noted that in this complex approach, quantum-chemical modeling is transformed into active computational atomic behavior and becomes a tool of analysis. This is especially important in connection with the upcoming era of nanotechnology, which will transform the ordinary world of objects to the level of practical atomic behavior.

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³The authors of Ref. 45 arrived at a similar conclusion; see Figs. 3 and 4.

⁴The fact that such a small amount of water is sufficient to explain the nearly 50% effect in the AWDS spectra in Fig. 16a is due to the exceptionally high sensitivity of the INS intensity to the presence of hydrogen atoms due to the large amplitude for neutron scattering on protium atoms.

⁵The use of the term basal plane is rather arbitrary in this context. It is understood to be the section showing the hexagonal pattern of the matter structure.

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