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Technological polymorphism of disperse amorphous silicas: inelastic neutron scattering and computer modelling

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Abstract. The review gives a systematic account of the results of detailed studies of the vibrational spectra of a series of industrial amorphous highly disperse silicas (aerosil, silica gel, aerogel) with the aid of inelastic neutron scattering. The observed phenomenon of technological polymorphism and the results of the quantum-chemical modelling of the structures and vibrational spectra of the corresponding polymorphic modifications are discussed. The bibliography includes 113 references.

I. Introduction

Silicas are substances whose structures are based on silicon dioxide.[1] This class of compounds combines both natural substances (ranging from quartz and cristobalite to semiprecious stones) and artificial substances (ranging from quartz glass to aerogel). The family of amorphous highly disperse silicas, incorporating aerosils, aerosilogels, silica gels, porous glasses, silochromes, and aerogels, occupies a special place among them.[2,3]

It is difficult to overestimate the importance of highly disperse silicas for chemistry and chemical engineering. They are used in large amounts in the chemical industry as adsorbents, fillers, and loosening agents[4] and also in medicine as medicinal drugs, intensifiers of biological activity of substances and medicinal drugs, chemisorbents, preservatives for live vaccines, etc. The uniqueness of silicas is due to their high surface activity, the nature of which is being vigorously investigated.[5,6]

Numerous studies have been devoted to the surface activity of disperse silicas, most of them having been carried out by empirical chemical methods. It was not until the end of the 1960s that spectrometric methods — vibrational IR and Raman spectroscopy[7–13] and NMR spectroscopy[14] – began to be used for the investigation of silicas. However, both due to experimental complexities and the difficulties in the interpretation of the data, the results proved in many respects to be qualitative, which hindered the employment of optical vibrational spectroscopy for the investigation of the structures and compositions of these substances.

In contrast to the optical vibrational spectroscopy, considerable progress on these lines has been achieved in recent years in neutron vibrational spectroscopy[15,16] because of the possibility of the reliable isolation of the parts of the spectrum corresponding to definite structural fragments of the system, including also the surface. This last advance should be noted particularly, since it is well known that inelastic thermal neutron scattering (INS) constitutes in the general case a bulk-phase research technique owing to the considerable mean free path of neutrons in the medium (of the order of 10^{-2} m).[17] However, if the specific surface increases, as happens in the case of highly disperse substances, or if the surface of the specimen is coated by hydrogen-containing substances [the nuclei of the lightest hydrogen isotope (protium), referred to below simply as hydrogen, have an exceptionally high neutron scattering cross-section and the amplitude of their displacements during vibrations is also high], then the contribution of the scattering by the surface vibrations increases significantly. The situation is favourable not only for hydrogen-containing adsorbents but also for the vibrations of the support as a result of the 'riding effect'.[18,19] Disperse silicas satisfy both conditions examined above, so that the application to them of INS spectroscopy proved extremely successful. As a result of a special series of experiments,[20–29] it has been possible to determine both the vibrational spectra of the bulk (or core) of a series of representatives of these substances and the vibrational spectra of the surface regions. The data obtained for a set of different industrial silicas proved fundamentally significant. It was shown that different vibrational spectra of the cores and surface regions corresponding to the silicas investigated are so different that it became necessary to assign these substances to fundamentally different structural formations.[30–32] Thus a phenomenon, called technological polymorphism, has been observed spectroscopically.[30] It served as the basis of a new algorithmic approach to the computational modelling of the substances investigated.[30–32] The modelling, carried out at the level of modern quantum-chemical methods,[33–35] made it possible to construct models of

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the structures which explain the behaviour of the vibrational spectra of different types of silicas and to establish an unambiguous relation between this phenomenon and the differences between the chemical technologies employed for the preparation of the products. The validity of the proposed approach was demonstrated by the successful comparison of the calculated and experimental vibrational spectra measured with the aid of INS.

The aim of the present review is to give a systematic account of the results obtained and the methods for their treatment in order to discover and develop an approach to the study of a specific phenomenon — technological polymorphism. This phenomenon, first thoroughly investigated for disperse silicas, proved to be one of the distinctive features of nanomaterials of virtually any class[36] and its understanding is one of the decisive factors for the creation of the basic materials for the immediate future.

II. General characteristics of disperse silicas

1. Structural properties and IR absorption

Disperse amorphous silicas are obtained in the condensation and polymerisation accompanying the hydrolysis of silicon tetrahalides, their organic orthoesters, and silicic acid salts.[1] The polymerisation leads to the formation of siloxane (SiOSi) chains and nonplanar rings with different numbers of atoms. The spatial disposition of these chains and rings gives rise to the bulk structure (core) of the silica. The same chains and rings make up its surface. The valence bonds involving the surface silicon atoms are then saturated only on the inner side of the surface. On the outer side there is a 'valency excess', which is saturated by hydroxy-groups in the presence of water molecules. The active surface centres produced readily adsorb water, as a result of which a characteristic shell consisting of hydroxy-groups and adsorbed water arises around the siloxane core. This view of the structure of amorphous disperse silicas has been described in the well known monograph by Iler.[1] During the years which have elapsed since its publication, this view has not undergone significant changes despite the solution of many of the specific problems (see the latest monographs[4,5]). Fig. 1 illustrates a structural scheme for disperse silica, which was implicitly adopted for products of any origin as recently as three years ago. The siloxane chain represents the surface layer of the atoms of the base, the fragments of its inward branching simulating the development of bulk-phase structure. The unsaturated bonds of the surface silicon atoms are blocked by hydroxy-groups, but both the number of groups per silicon atom and their distribution on the surface have not been in general clearly determined. The outer layer of the fragment is occupied by the molecules of adsorbed water, the positions of which relative to the surface groups are illustrated to a large extent arbitrarily. In essence, the model clearly presents the interpretation of the atomic structure of the bulk phase and the surface of disperse silica which has arisen on the basis of the study of their IR absorption spectra.

Attempts to investigate the vibrational spectra of disperse silicas by optical spectroscopic methods (IR absorption and total internal distorted IR reflection, Raman scattering) have been undertaken repeatedly.[7-13] However, owing to the intense absorption by the siloxane matrix,[37] the studies have been concentrated mainly in the spectral range 3000–4000 cm^{-1}, which contains the stretching vibrational frequency of the hydroxy-groups and water. The results obtained yield a contradictory picture even when combined with deuterium–hydrogen exchange data[11,13] and remain to a large extent qualitative, which can be seen from the generalised picture presented in Table 1. It follows from the table that it is virtually impossible to establish the differences between, for example, aerosil, silica gel, and aerogel on the basis of data obtained in the range 3000–4000 cm^{-1}. As regards the most structure-sensitive regions in the ranges 0–400 cm^{-1} and 500–1000 cm^{-1}, the first is fully obscured in the IR spectra by the absorption due to the siloxane core, while the second has been little investigated (for the same reason).[37-39] The available information about this spectral range is derived mainly from the analysis of compound frequencies.

The main conclusions reached on the basis of the study of the IR absorption reduced to the following:

1. The similarity of the behaviour of different disperse silicas in a series of basic reactions[1-5] suggests the similarity of the structures of their surfaces and for this reason investigations are mainly carried out on different specimens of aerosil as the chemically purest silica.

2. As a result of the concentration of studies mainly in the spectral range 3000–4000 cm^{-1}, the principal objects of study are the hydroxyl coating and the adsorbed water.

3. The surface of aerosil is uniformly coated by silanol groups with a density of ~0.046 of a group on 1 $Å^2$, which corresponds to an average distance between them of 0.7 Å.[5] The existence of silanediol groups is not disputed, but according to the data of different workers their proportion varies from 4% to 40%.[5,14] Silanetriol groups have not been detected on the surface of aerosil under the usual conditions.[40]

4. The adsorbate–support system in the case of the water–silica system consists of two partners: the silanol group and the water molecule. The problem reduces to the type of interaction between the partners. Some workers support the view that the interaction between water and silica is of the coordinative type,[6] whilst others suggest that the water molecule is bound to a hydroxyl centre via a hydrogen bond. Among the recent studies devoted to this question, special mention must be made of the studies by Lygin and coworkers,[14,41,42] who attempted to account for the mechanism of the adsorption of water on the basis of the investigation of the dynamics of the deuterium–hydrogen exchange involving the hydroxy-groups by monitoring the intensities of the absorption bands due to the OH and OD

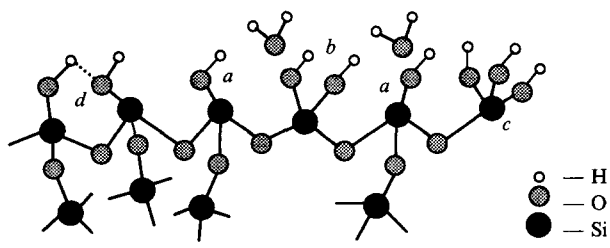


Figure 1. Schematic representation of the structure of amorphous silica: (*a*) silanol groups; (*b*) a silanediol group; (*c*) a silanetriol group; (*d*) hydrogen-bonded groups.

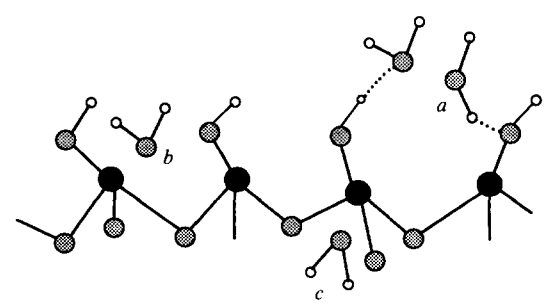


Figure 2. Schematic representation of the positions of the adsorbed water molecules on the surface of amorphous silica:[6] (*a*) hydrogen-bonded water; (*b*) water coordinated in the *cis*-position; (*c*) water coordinated in the *trans*-position.

Table 1. The absorption band frequencies for the vibrations of the free hydroxy-groups of silicas treated at high temperatures.[13]

Specimen	T/°C	Frequency/cm^{-1}		Interpretation
		OH	OD	
Porous glass	550	4540	–	Compound stretching vibrations of the free hydroxy-groups in SiOH and the SiO groups
	750	4500	–	Compound stretching and deformation vibrations of the free hydroxy-groups in SiOH
Aerogel	700	4520	3363	Compound stretching and out-of-plane deformation vibrations of the free hydroxy-groups in SiOH and SiOD
Porous glass	750	3850	2840	Compound deformation vibration of the free hydroxy-groups in SiOH and SiOD and compound stretching vibrations in SiO_4
	550	3749	2761	Stretching vibrations of the free hydroxy-groups in SiOH and SiOD
	600	3740	2760	–
Silica gel	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	–	Stretching vibrations of the hydroxy-groups in $Si(OH)_2$
Porous glass	400	2000	–	Combination and overtone vibrations of the silica core
		1870	–	
Aerogel	600	1635	–	–
Silica gel	400	950	–	Deformation vibrations in SiOH or the stretching vibrations of the OH group relative to Si
	400	870	–	Deformation vibrations in SiOH
Aerogel	700	770	603	Out-of-plane deformation vibrations in SiOH

groups (at 3749 and 2761 cm^{-1} respectively). Two conclusions were reached on the basis of these investigations: (1) water is adsorbed on hydroxy-groups and (2) on the surface of aerosil there are sections with significantly different rates of adsorption of water, i.e. there are hydroxy-groups with significantly different structures. Similar conclusions have been reached[43] from calculations by the method of molecular dynamics. The possible positions of the water adsorbed on silica are illustrated in Fig. 2.

Overall, studies of the IR absorption failed to provide answers to the following principal problems of the chemistry of disperse silicas:

to what extent are the structures of the cores of different industrial forms of amorphous disperse silicas identical;

how are their surfaces formed and what is the distribution of the hydroxy-groups on the latter;

what are the conditions for the existence of silanol, silanediol, and silanetriol groups on the surface;

what are the mechanisms of the adsorption of different substances, primarily water, on the surfaces of these products.

This situation made it necessary to seek new ways for discriminating between substances. Inelastic neutron scattering is an effective spectroscopic method. This made it possible to transfer the study of the vibrational spectrum to the range 0–1500 cm^{-1}, which contains the most structure-sensitive deformation and torsional vibrations of the hydroxy-groups, water, and the siloxane cores, and to raise the question of the measurement of the vibrational spectra of individual structural components of each silica specimen.

2. Application of inelastic neutron scattering spectroscopy to the study of vibrational spectra

INS spectroscopy is a comparatively new method for the study of surfaces. Initially studies with the aid of elastic (diffraction) and inelastic (vibrational spectroscopy) neutron scattering[17,44] were directed to the study of the bulk-phase characteristics, because, owing to the high penetrating capacity of the neutron, the contribution of the surface atoms to the scattering spectrum of the specimen was small. However, as stated in the Introduction,

the situation became more favourable for highly disperse specimens, which has been confirmed in relation to disperse silicas. In the study of the INS by these specimens, the principal advantages of neutron spectroscopy were fully manifested: sensitivity to the nuclei of hydrogen atoms and to the hydrogen–deuterium isotope substitution, the absence of selection rules in energy transfer, the involvement of a broad spectrum of vibrational states in the scattering process, etc.

One of the first productive studies of the vibrations of water adsorbed on a silica surface was carried out in 1981.[45] The preceding studies in the period 1964–1975[46–48] devoted to this problem were carried out at room temperature, which limited the possibility of studying low-frequency vibrational modes. Two specimens of silicas (silica gel) were investigated[45] at 15 K: Gasil 200 (calculated pore diameter 21 Å, specific surface 850 $m^2 g^{-1}$) and Spherisorb S20W (89 Å and 232 $m^2 g^{-1}$ respectively). The main result of this investigation was the demonstration that the spectrum of the vibrations of water within the silica gel pores differs from the vibrational spectrum of ordinary ice (Fig. 3) and that the spectral maximum, located at 80 meV (640 cm^{-1}) undergoes a bathochromic shift on passing from silica gel with a small pore diameter to one with a large pore diameter. Thus it is seen from Fig. 3 that, for the maximum moisture content in the specimen, the principal peak of the spectrum virtually coincides with the principal band in the spectrum of H_2O ice, the position of which is indicated by a vertical straight line. When the specimen is dried, the position of this peak in the silica gel spectrum shifts towards lower frequencies. A similar effect has been observed also on passing to a specimen with a smaller pore size. In the discussion of the causes of this shift, a model involving the adsorption of water on neighbouring surface hydroxy-groups was proposed, but this model was merely qualitative.

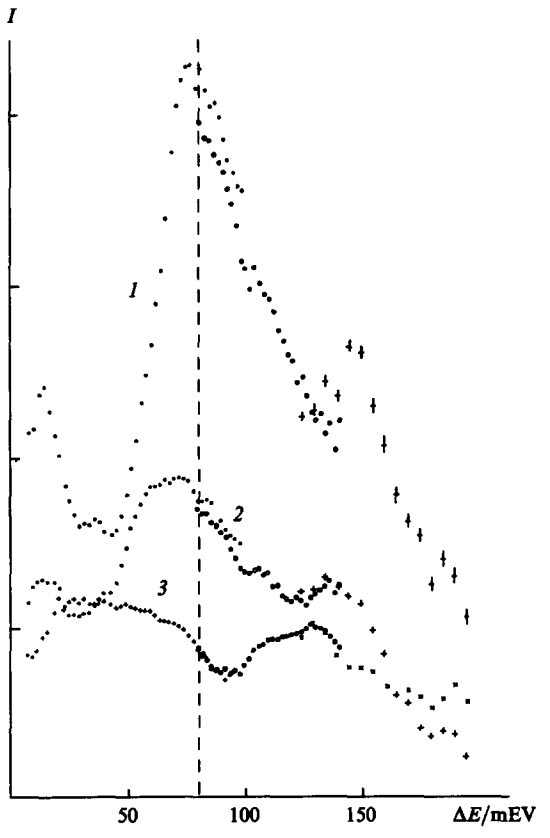


Figure 3. INS spectra of the silica gel Gasil 200 ($T = 15$ K) for different moisture contents in the specimen.[45] Moisture content (%): (*1*) 13; (*2*) 4; (*3*) specimen dried at 150 °C.

It was also established that the properties of water in the region of contact with the surface differ significantly from its properties in the bulk phase. Thus the density,[49] diffusion coefficient,[50] and viscosity of water[51,52] change in the vicinity of the silica surface. A diffraction study[52–55] showed that the water in the pores has the structure of ice in the cubic modification *Ic*; under these conditions, ordinary ice consists of hexagonal crystals *Ih*. This effect can be explained by the change in the structure of water near the silica surface, but the explanations remain qualitative particularly bearing in mind the remark made by Li et al.[56] that the structures of the surfaces of the silicas themselves are different. On the basis of model calculations and experiments at 15 K on a Vycor glass specimen (a boron-containing glass) with an average pore diameter of 30 Å and a specific surface of 180 $m^2 g^{-1}$, it was shown in the same study that there is no distinct interface in the form of layers of different density in the silica–water system. It was postulated that in fact the ice structure in the layers subject to a marked influence of the surface is similar to the structure of liquid water, where a large number of hydrogen bonds have been broken. Comparison of the vibrational spectra of water adsorbed on glasses with the spectra of ordinary ice,[57] which proved to be fairly similar (Fig. 4), led to the conclusion that the water in the Vycor glass pores is present in two forms: as the bulk-phase water and as the water adsorbed on the walls of the pores. This conclusion has been confirmed by the considerable similarity between the difference spectrum of the 'air-dry specimen – ice' and the spectrum of a 'dried specimen' (Fig. 5). On the basis of this similarity, the hypothesis that quasi-free water is present in the pores was put forward.[56] However, the paper presents only qualitative considerations concerning the contribution of the ice spectrum to the spectrum of the glass specimen with a 100% moisture content.

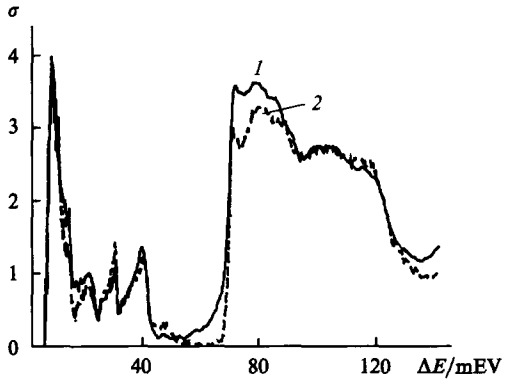


Figure 4. INS spectra of ice: (*1*) ice in the porous Vycor glass;[56] (*2*) hexagonal ice.[57]

Among the latest studies on the vibrational spectroscopy of surfaces using INS, mention should be made of investigations of silicas the surfaces of which were modified by various organic compounds,[58] the surface vibrations of hydrogen adsorbed on nickel[59] and molybdenum,[60] the vibrations of water and ammonia adsorbed on manganese and zirconium oxides,[61] and the vibrational spectra of quartz glass[62] and natural silica minerals such as zeolites[63] and opal.[64] A large series of studies has been devoted to the vibrational spectra of different modifications of ice.[65–76] A series of studies[77–81] devoted to fractal excitations in aerogel should be considered separately.

It is seen from the above survey that INS makes it possible to raise the question of the study of the surfaces of disperse silicas. However, the inadequate number of systematic experimental spectroscopic studies and failure to consider the problem of the differentiation of the surface components of the vibrations from the overall spectrum have led to failure to obtain virtually any important results at this point.

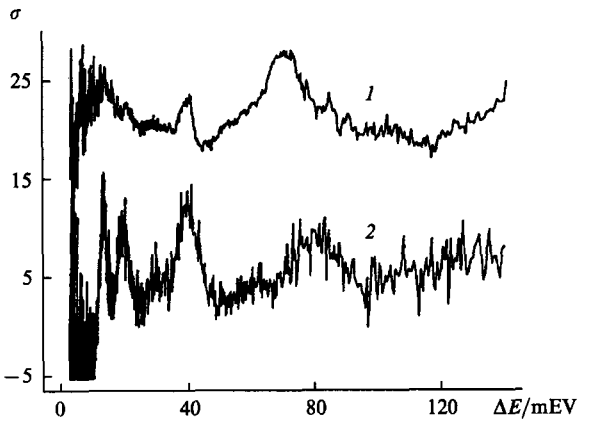


Figure 5. INS spectra of water adsorbed on the walls of the pores in the porous Vycor glass:[56] (*1*) residual moisture content in the dried specimen 10%; (*2*) 'specimen with 100% moisture content – hexagonal ice' difference spectrum.

The problem of discriminating between different silicas has been to a large extent solved in a series of investigations[20-29] undertaken with the aim of systematic study of the vibrational spectra of specimens of different disperse silicas prepared in a definite manner. They included a detailed consideration of the additive model of the composition of a disperse silica and a refinement of the concepts of the core and of the hydroxyl and water shells. A differential-correlation method for the determination of the spectra of the system from the experimentally measured spectra on the basis of the postulate that the spectra of independent systems are not correlated has been proposed and justified. The principal stages of this investigation, which led to a new type of formation of polymorphic modifications — technological polymorphism — are presented below. The results of computational modelling designed to understand this phenomenon at the atomic level will be presented in the succeeding Sections.

III. Techniques for the measurement and treatment of inelastic neutron scattering spectra

1. Primary treatment of the spectra

INS vibrational spectroscopy is based on the fact that, having entered the test specimen, a thermal energy neutron can transfer part of its energy in the excitation of a vibrational mode in the substance or can absorb this excitation, acquiring the corresponding energy and undergoing inelastic scattering thereby. The change in the energy of the neutron can be detected by various procedures.[17,44] The scattering of the next neutron takes place independently of the previous one with excitation – absorption of the same or a different vibrational mode, as a result of which it is possible to obtain the vibrational spectrum of the test specimen by measuring the neutron scattering intensity during the scanning of the energy transferred or acquired by the neutron.

In the experimental method for the determination of the energy lost by the neutron during time of flight, which is the principal procedure for the measurement of the INS in a high-flux IBR-2 reactor,[82] the INS spectrum can be described (see, for example, Bokhenkov et al.[83]) by the function

$$N(t_0) = \Delta t_0 \iiint \mathrm{d}E_0\,\mathrm{d}E\,\mathrm{d}t\,F(E_0,E,t_0,t)\sigma(E_0,E,\phi,T)\ , \qquad (1)$$

where $N(t_0)$ is the number of neutrons which have arrived in the analyser during the time interval Δt_0 at time t_0, $\sigma(E_0, E, \phi, T)$ describes the scattering law for the 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 instrument function, which includes the energy distribution of the incident and scattered neutrons and the time synchronisation condition. The neutron scattering cross-section σ is described by the following sum in the general case:

$$\sigma(\omega,t) = \sigma^{(1)}(\omega,T) + \sigma^{(\mathrm{mph})}(\omega,T) + \sigma^{(\mathrm{mpl})}(\omega,T)\ , \qquad (2)$$

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

The single-phonon incoherent scattering cross-section has the form

$$\sigma^{(1)}(\omega,\phi,T) = \sum_i \frac{\mathrm{d}^2\sigma_i^{\mathrm{inc}}}{\mathrm{d}\omega\,\mathrm{d}\Omega} \qquad (3)$$

$$= \frac{k}{k_0}\frac{\hbar|Q|^2}{2M\omega}\sum_i (b_i^{\mathrm{inc}})^2 \frac{\exp(-2W_i)}{1-\exp(-\hbar\omega/kT)} G_i(\omega)\,,$$

$$G_i(\omega) = \frac{1}{M_i}\sum_j \int \mathrm{d}q|A_j^i(q)|^2\delta[\omega-\omega_j(q)]\ . \qquad (4)$$

Here $G_i(\omega)$ is the density of the vibrational states of the substance weighted quadratically in terms of the amplitudes of the displacements of the ith nucleus,[83,84] k_0 and k are the wave vectors of the incident and scattered neutrons, Q is their difference, b_i^{inc} is the amplitude of the incoherent scattering by the ith nucleus (the cross-sections for scattering by the nuclei forming part of the composition of the silicas are presented in Table 2), M_i is the mass of the ith nucleus, W_i is the Debye–Waller factor, A_j^i is the amplitude of the displacement of the ith nucleus corresponding to the jth vibrational mode, and $\hbar\omega = E_0 - E$ is the transmitted energy. The quantity

$$G(\omega) = \sum_i (b_i^{\mathrm{inc}})^2 G_i^{\mathrm{inc}}(\omega)\,, \qquad (5)$$

is referred to as the doubly amplitude-weighted density of states (AWDS). This quantity can in fact be obtained from the experimental spectrum (1) by solving the converse problem subject to the condition that the scattering spectrum is determined by single-phonon processes. However, deconvolution problems are in general not soluble, so that in experimental practice involving INS a somewhat approximate function $\tilde{G}(\omega)$ serves as an analogue of the exact function $G(\omega)$. It is defined[82] as

$$\tilde{G}_T(\omega) = \frac{N_T[t(\omega)]}{\phi[t(\omega),E(\omega)]K(\omega,T)}\ . \qquad (6)$$

Table 2. Overall neutron scattering cross-sections.[17]

Atom/substance	Overall scattering cross-section σ°/barn[a]
H	81.5
D	7.6
O	4.24
Si	2.2
OH	85.74
OD	11.84
H_2O	167.24
D_2O	19.44
SiO_2	10.68

[a] σ° is determined by the sum of the cross-sections of the nuclear coherent and incoherent scattering by the nth type nucleus.

Here $\phi[t(\omega),E(\omega)]$ is the transformed apparatus function of the spectrometer, while the function $K(\omega, T)$ has the form

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

and can be readily calculated, provided that the angular configuration of the experiment is known.

The spectra $N(t)$ presented below were obtained on a KDSOG-1M time-of-flight spectrometer with inverse geometry in the IBR-2 high-flux reactor.[82] All the spectra were normalised with respect to the same number of scattering nuclei (per 100 g of the substance) and the same time of measurement. This makes it possible to carry out a quantitative comparative analysis of the spectra obtained. The low temperature served as a sufficient basis for the hypothesis that single-phonon scattering processes play a dominant role in the $N(t)$ spectra,[84] which made it possible to determine the required AWDS spectra in conformity with Eqn (6).

2. The set of disperse silicas

The series of studies discussed were carried out for three industrial highly disperse silica products: type A380 aerosil (specific surface 380 $m^2\ g^{-1}$), the silica gels SG100 and SG20 (average pore diameters 100 and 20 Å respectively), and the aerogel AG200 (density 200 kg m^{-3}). In conformity with the principal model according to which disperse silicas of any origin are three-component systems consisting of a silica core and hydroxyl and hydrate shells,[1] specimens differing in the partial contributions of these components were prepared. Each of the silicas investigated was represented by an isotypical set of specimens.

An air-dry specimen is the final product of the corresponding technological chain. It was stored in the open air at room temperature and the corresponding humidity. The spectrum of the air-dry specimen will be henceforth designated by $\mathcal{S}p^{(1)}$. The dried specimen was obtained by drying the air-dry specimen in air at a temperature specific to each specimen. The spectrum of the dried specimen will be designated by $\mathcal{S}p^{(2)}$.

A deuteriated specimen was obtained by a deuterium exchange procedure involving the successive drying of the specimen in a closed vessel with subsequent cooling in heavy water vapour; the drying–cooling cycle was repeated several times. The spectrum of the deuteriated specimen will be designated henceforth by $\mathcal{S}p^{(3)}$.

The set of spectra $\{\mathcal{S}p^{(j)}\}$ constitutes the basis for the determination of the spectra of the individual components of the silicas using the differential-correlation method for the resolution of the initial spectra.[85]

3. The construction of the basis for the spectrum of a complex system. Criterion of a zero linear correlation coefficient

Any method for the resolution of the spectrum of a complex system into the spectra of its components is based on an additive model, according to which the overall spectrum of the system $\mathcal{S}p^{(j)}$ can be represented by the sum of spectra:

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

Here $k_i^{(j)}$ are the weighting factors of the spectra, the product $k_i^{(j)}Sp_i$ represents the partial spectrum of the ith component in the overall compound spectrum $\mathcal{S}p^{(j)}$, and j are the numbers of the independent spectra of the test system referring to its modifications differing in the partial contributions of the components. The spectra Sp_i are referred to as the basis spectra.

Two limiting cases are known for which the resolution of the compound spectrum $\mathcal{S}p^{(j)}$ has been achieved. In the first, which may be called the case of the complete set of basis spectra, all the basis spectra Sp_i are known and the order n of the system of the initial Eqns (8) is unity. The solution of the problem involves the finding of the coefficients $k_i^{(j)}$. It is usually believed that the best solution is that which corresponds to the condition for a minimum in the discrepancy functional[86]

$$\chi^{(j)} = \sum_{r}^{N}\left[\mathcal{S}p^{(j)}(r) - \sum_{i=1}^{m} k_i^{(j)} Sp_i(r)\right]^2\ , \quad (9)$$

where the summation is carried out with respect to N points in the spectrum. The method based on this criterion is well known as the method of least squares. Both the experimentally measured spectra and model functions of the exponential, Gaussian, Lorentzian, etc. types can be used as the spectra Sp_i.[86] The parameters of the resolution to be determined are the weighting factors $k_i^{(j)}$ and the parameters of the model functions.

In the second case, or in the case of a complete set of weighting factors, all the coefficients $k_i^{(j)}$ are known, the order of the system of initial equations is $n = m$, and the basis spectra Sp_i are to be determined. Eqns (8) reduce to a system of linear algebraic equations. The main problem in its solution is that of determinedness.[87,88] The interpretation of the AWDS spectra of disperse silicas, the problem of the resolution of the overall spectrum into those of the core and the hydroxyl and water components arose naturally. From the mathematical standpoint, it involved the resolution of the compound spectrum when neither the basis spectra nor the corresponding weighting factors were fully known. A differential-correlation method was proposed for the solution of this problem.[85] It involves the construction of a physically significant basis Sp_i for the system, which is based on the equation

$$Sp_i = \sum_{j=1}^{n} æ_i^{(i)} \mathcal{S}p^{(j)}\ ,\ i = 1,\ 2,\ \ldots,\ m, \quad (10)$$

on the assumption that there is no linear correlation between the basis spectra Sp_i. This requirement was formulated as the criterion of a zero correlation coefficient of the basis spectra (the ZCC criterion), which is an analogue of the condition for the orthogonality of n-dimensional vectors. In other words, if the components of the complex system can be regarded as independent, then their basis spectra are also not correlated. Using the expression for the second moment of the standard deviations of two physical quantities,[86] it is possible to obtain a mathematical expression for this criterion in the form

$$\rho = \frac{\sum_{r}^{N}\left[Sp_i(r) - \overline{Sp_i}\right]\left[Sp_k(r) - \overline{Sp_k}\right]}{\left\{\sum_{r}^{N}\left[Sp_i(r) - \overline{Sp_i}\right]^2 \sum_{r}^{N}\left[Sp_k(r) - \overline{Sp_k}\right]^2\right\}^{1/2}}\ , \quad (11)$$

where

$$\overline{Sp_i} = \frac{1}{N}\sum_{r}^{N} Sp_i(r)\,, \quad (12)$$

represents the average spectral line, and N denotes the number of points in the spectrum. The condition involving the equality $\rho = 0$ implies that the numerator in Eqn (11) is zero, which is represented conventionally as follows:

$$C(Sp_i, Sp_k) = 0\ . \quad (13)$$

It is easy to show that Eqn (13) is valid not only for the pair of spectra Sp_i and Sp_k but also for their linear combinations of the type

$$C\left(Sp_i, \sum_{s\neq 1}^{m} k_s\, Sp_s\right) = 0\,,$$

or

$$C(Sp_i + Sp_l, \sum_{s\neq i,l}^{m} k_s\, Sp_s) = 0. \quad (14)$$

The practical employment of the ZCC criterion begins with finding the simplest linear combination (10) in order to express the left-hand component in Eqn (14). In the limit, it is a simple difference $D\mathcal{S}p^{(jj')} = \mathcal{S}p^{(j)} - \mathcal{S}p^{(j')}$. This difference spectrum should correctly reproduce either the form of the Sp_i spectrum or the sum of the spectra $Sp_i + Sp_l$, i.e. it should define them to within a constant multiplier. The right-hand component in Eqn (14) can be represented as the residual spectrum

$$R\mathcal{S}p^{(iij')} = \mathcal{S}p^{(j)} - a^{(iij')}D\mathcal{S}p^{(ij')},$$

where $a^{(iij')}$ is a parameter ensuring the absence of correlation between the spectra $R\mathcal{S}p^{(iij')}$ and $D\mathcal{S}p^{(ij')}$ in the form of Eqn (14).

By solving Eqns (14) for $a^{(iij')}$, we find the required value of this parameter:

$$a_0^{(iij')} = \frac{\sum_r^N D\tilde{\mathcal{S}}p^{(ij')}(r)\tilde{\mathcal{S}}p^{(j)}(r)}{\sum_r^N \left[D\tilde{\mathcal{S}}p^{(ij')}(r)\right]^2}, \qquad (15)$$

where

$$D\tilde{\mathcal{S}}p^{(ij')} = D\mathcal{S}p^{(ij')} - \overline{D\mathcal{S}p}^{(ij')},$$

while

$$\tilde{\mathcal{S}}p^{(j')} = \mathcal{S}p^{(j)} - \overline{\mathcal{S}p}^{(j')}.$$

The bar above the expression denotes the average spectral lines [Eqn (11)]. The spectrum $a_0^{(iij')}D\mathcal{S}p^{(ij')}$ represents either the basis spectrum Sp_i or the sum of the basis spectra $Sp_i + Sp_l$. On the other hand, the residual spectrum

$$R_0\mathcal{S}p^{(iij')} = \mathcal{S}p^{(j)} - a_0^{(iij')}D\mathcal{S}p^{(ij')}$$

describes the residual combination of basis spectra entering into $\mathcal{S}p^{(j)}$ after the subtraction of the spectrum $a_0^{(iij')}D\mathcal{S}p^{(ij')}$ from the latter. By repeating this procedure and scanning with respect to the indices j and j', it is possible to determine the entire set of basis spectra $\{Sp_i\}$. This method has been used successfully to obtain the basis spectra of aerosil, silica gel, and aerogel.[25-27]

IV. Vibrational spectra of disperse silicas

1. Aerosil

a. Specimens and initial spectra

An air-dry specimen of the aerosil A380 is a powder consisting of small spherical particles with a specific surface of 380 $m^2\ g^{-1}$. According to low angle X-ray measurements, the average particle size is 150 Å.[19] After the specimen had been heated in air for 6 h at 750 °C, dried A380 was obtained. In its turn, the dried specimen was subjected to isotopic substitution of hydrogen atoms in the hydroxyl and water shells by deuterium atoms in the following sequence: three heating steps in air (750 °C, 4 h) with subsequent cooling in heavy water vapour to room temperature. This resulted in the formation of a deuteriated A380 specimen.

The set of these three specimens comprised the aerosil A380 family. The time-of-flight INS spectra of the specimens of this family together with the AWDS spectra obtained in accordance with Eqn (6) are presented in Fig. 6. In addition to the spectra of the three specimens indicated above, the figure presents the $N(t)$ and AWDS spectra of the glass obtained by sintering the aerosil. In a certain sense, these are reference spectra representing the spectrum of the bulk-phase vibrations of close-packed silica (see below).

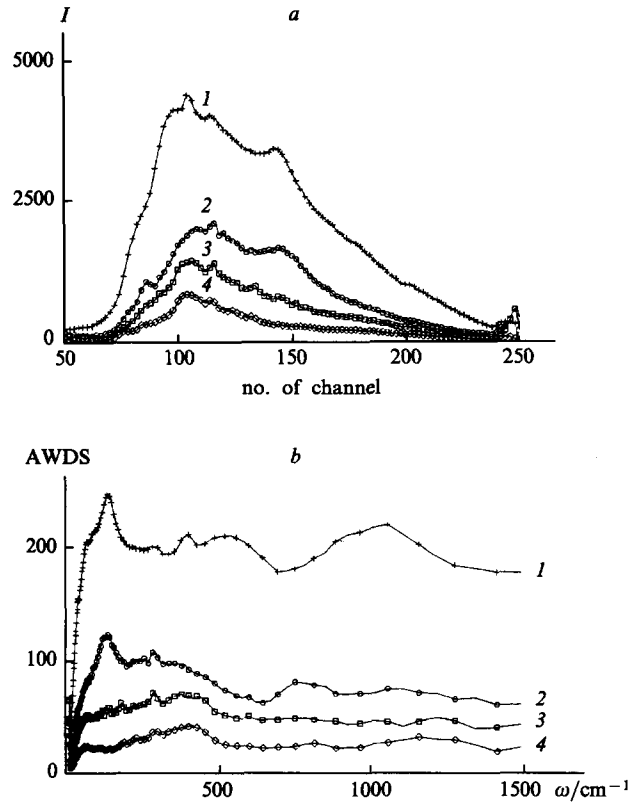


Figure 6. Experimental vibrational spectra of the A380 aerosil family ($T = 10$ K):[20] (a) time-of-flight INS spectra; (*b*) AWDS spectra; (*1*) air-dry specimen; (*2*) dried specimen; (*3*) deuteriated specimen; (*4*) aerosil glass.

b. Basis spectra of components of aerosil

Formulation of the problem of the resolution of the initial spectra. The spectra of the aerosil components constitutes a set of three basis spectra $\{Sp_i\}$, where the indices $i = 1, 2, 3$ correspond to the spectra of the water shell, the OH shell, and the silica core. Whereas the physical significance of the basis spectrum Sp_3 is fairly clear, a more detailed consideration is needed for the first two spectra. Apart from the vibrations of water and the hydroxy-groups, they include the vibrations of groups of atoms with which these differentiated systems interact. Thus one should include in the vibrational spectrum of the hydrate shell the vibrations of the silicon–oxygen centre (with the corresponding composition) linked to it. The number of such centres, interacting with water, is known[1,5] to be much smaller than the total number of hydroxy-groups on the surface even under the conditions of the complete saturation of the surface by adsorbed water. The remaining three groups form the hydroxyl shell. The vibrations of these groups constitute the basis of the vibrational spectrum of the hydroxyl shell. However, in addition to this, the vibrations of the surface silicon atoms and of the oxygen of the silica core make an appreciable contribution to the given vibrational spectrum. The above two types of vibrations affect the hydrogen atoms of the hydroxy-groups participating in the corresponding vibrational motions as a consequence of the familiar 'riding effect'.[18,19]

The experimental AWDS spectra of the initial and modified aerosils normalised with respect to 100 g of the mass of the specimen give rise to the set $\{\mathcal{S}p^{(j)}(\omega)\}$, in which the quantities $j = 1, 2, 3$ correspond to the spectra of the air-dry, dried, and deuteriated specimens. If the partial spectra of the air-dry specimen are designated as the basis spectra, then Eqns (8) assume the form (overleaf):

$$\mathcal{S}p^{(1)} = Sp_1^{(1)} + Sp_2^{(2)} + Sp_3^{(3)} ,$$
$$\mathcal{S}p^{(2)} = \alpha_1 Sp_1^{(1)} + \alpha_2 Sp_2^{(2)} + \alpha_3 Sp_3^{(3)} , \quad (16)$$
$$\mathcal{S}p^{(3)} = \beta_1 Sp_1^{(1)} + \beta_2 Sp_2^{(2)} + \beta_3 Sp_3^{(3)} .$$

Before proceeding to the construction of this basis, it is necessary to derive the relations between the coefficients of Eqn (16), the knowledge of which makes it possible to optimise the construction of the difference spectra. We shall consider this procedure in relation to aerosil. The parameters α_3 and β_3 are determined from the equality

$$Sp_3^{(1)} = \alpha_3 Sp_3^{(1)} = \beta_3 Sp_3^{(1)} ,$$

which follows from the identity of the spectra of the silica core in all the specimens. Thus

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

It is known from literature data [1] that, when aerosil is dried at 750 °C, the adsorbed water and some of the hydroxy-groups are fully removed from the surface and the following two relations are established thereby:

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

The weighted contributions of the partial spectra of water and the hydroxyl shell to the spectrum of the deuteriated specimen $\mathcal{S}p^{(3)}$ must be much less than unity because, as a consequence of the strong suppression of the scattering by hydrogen nuclei, the intensity of the scattering by this specimen is much lower than the intensity of the scattering by the air-dry specimen, which follows from Fig. 6. Thus

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

It is also known [1] that the percentage content of the atoms substituted as a result of deuterium exchange in the water and hydroxyl shells is fairly accurately the same, so that

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

Thus the following conditions are imposed on the coefficients of Eqn (16):

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

In conformity with Eqns (18), the system of basic Eqns (16) is transformed into

$$\mathcal{S}p^{(1)} = Sp_1^{(1)} + Sp_2^{(1)} + Sp_3^{(1)}$$
$$\mathcal{S}p^{(2)} = 0 + \alpha_2 Sp_2^{(1)} + Sp_3^{(1)} \quad (19)$$
$$\mathcal{S}p^{(3)} = \beta Sp_1^{(1)} + \beta Sp_2^{(1)} + Sp_3^{(1)} .$$

Construction of the basis. When the differential-correlation method for the resolution of the spectrum of multicomponent systems is used, there is a possibility of a set of different versions determined by the selection of the initial difference spectrum in Eqns (14). It has been shown that [25-27] the same final result is then achieved with an adequate accuracy. We shall consider as an example one such version. We construct the initial difference spectrum in the form

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

It is a linear combination of the basis spectra Sp_1 and Sp_2 and, in conformity with Eqns (19), it assumes the form

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

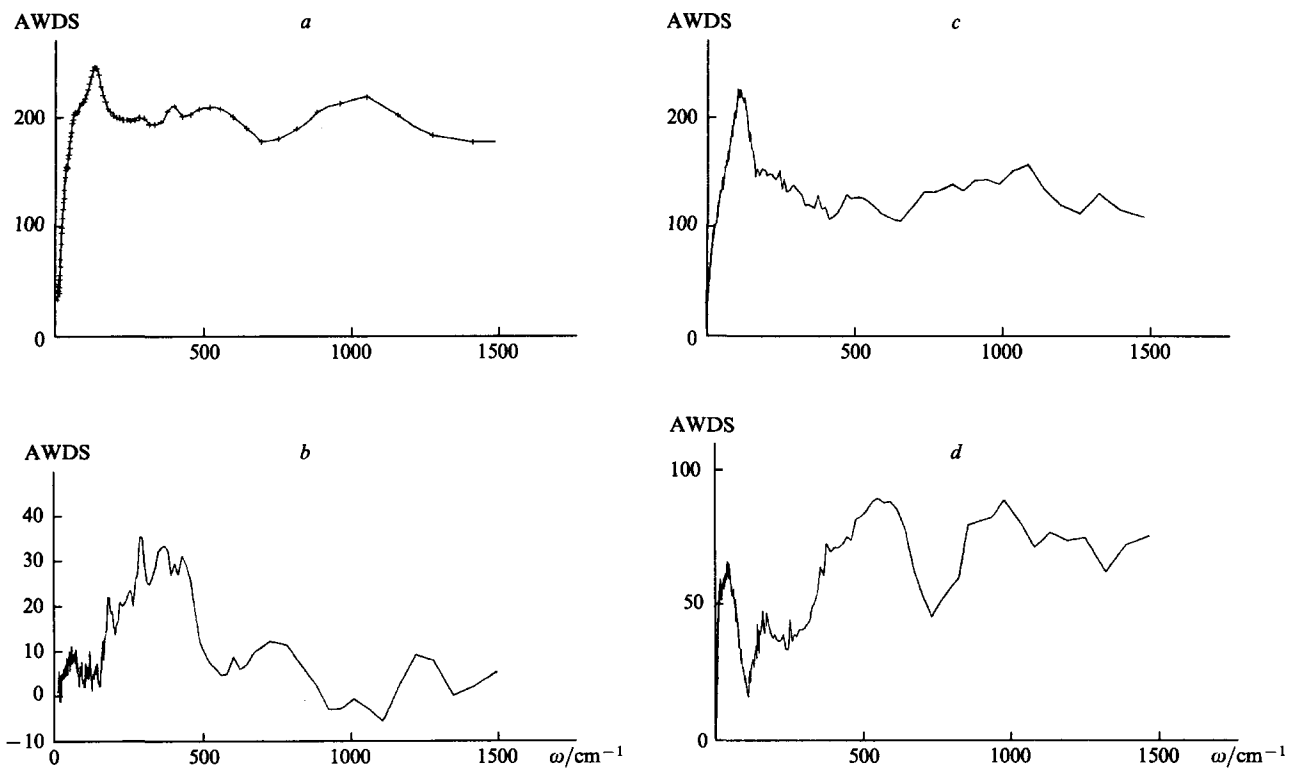


Figure 7. Overall AWDS spectrum of an air-dry specimen (*a*) and the basis spectra of the components of the aerosil A380: (*b*) core; (*c*) hydroxyl shell; (*d*) adsorbed water ($T = 10$ K).[25]

We construct the residual spectrum

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

and impose the requirement that it is not correlated with the spectrum $D\mathcal{S}p^{(13)}$,i.e. that condition (14) holds in the form

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

Ultimately we obtain the spectra

$$a_0^{(113)}D\mathcal{S}p^{(13)} = Sp_1^{(1)} + Sp_2^{(1)} , \quad (24)$$
$$R_0\mathcal{S}p^{(113)} = Sp_3^{(1)} .$$

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

We now consider the difference spectrum

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

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

$$RD\mathcal{S}p = a_0^{(113)}D\mathcal{S}p^{(13)} - a^{(21)}D\mathcal{S}p^{(21)}, \quad (26)$$

and impose the requirement that the ZCC conditions hold between this spectrum and the spectrum $D\mathcal{S}p^{(21)}$ in the form

$$C(RD\mathcal{S}p, D\mathcal{S}p^{(21)}) = 0 . \quad (27)$$

Having determined $a_0^{(21)}$ in conformity with Eqn (15), we obtain

$$a_0^{(21)}D\mathcal{S}p^{(21)} = Sp_2^{(1)}, \quad \text{and} \quad R_0D\mathcal{S}p = Sp_1^{(1)} . \quad (28)$$

Thus the basis of Eqns (19) has been constructed. Fig. 7 presents the AWDS spectra of an air-dry aerosil specimen together with the spectra of its three components.[25] It has been established[24] that the initial spectra of air-dry aerosils with different specific surfaces (and particle sizes) agree satisfactorily, so that the basis spectra constructed refer to the entire class of aerosils.

2. Silica gels

a. Specimens and initial spectra

The series of studies under discussion dealt with the vibrational spectra of two families of silica gels originating from industrial specimens of type KSM-G (lumpy, finely porous, granulated silica) manufactured by the Mendeleev Chemical Factory and characterised by different pore sizes, namely 20 and 100 Å (SG20 and SG100 respectively). The family of each silica gel included three specimens:[26] $j = 1$ — air-dry initial industrial specimen stored at room temperature and under the usual conditions of humidity; $j = 2$ — dry specimen obtained from the initial specimen by drying in air for 72 h at 135 °C; $j = 3$ — deuteriated specimen obtained from the initial specimen as a result of three drying cycles at 135 °C with subsequent maintenance for 24 h in heavy water vapour at room temperature.

An additional study was made of the spectrum of rapidly frozen water, which is necessary for the comparative analysis of the spectrum of the aqueous component.

The experimental INS spectra of specimens belonging to the SG20 and SG100 families and the corresponding AWDS spectra obtained in conformity with Eqn (6) have been described in detail.[20]

b. Basis spectra of components of silica gels

The procedure used to obtain the basis spectra of silica gels is similar to that described above for aerosil with the sole difference that, as a consequence of somewhat different relations between the coefficients of Eqn (16), the basic system of equations assumes the form[26]

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

Figs 8 and 9 present the spectra of air-dry specimens together with the basis spectra of their components. Two features of the spectra obtained are striking. First, the basis spectra of the test silica gel specimens are significantly different. This factor, i.e. the

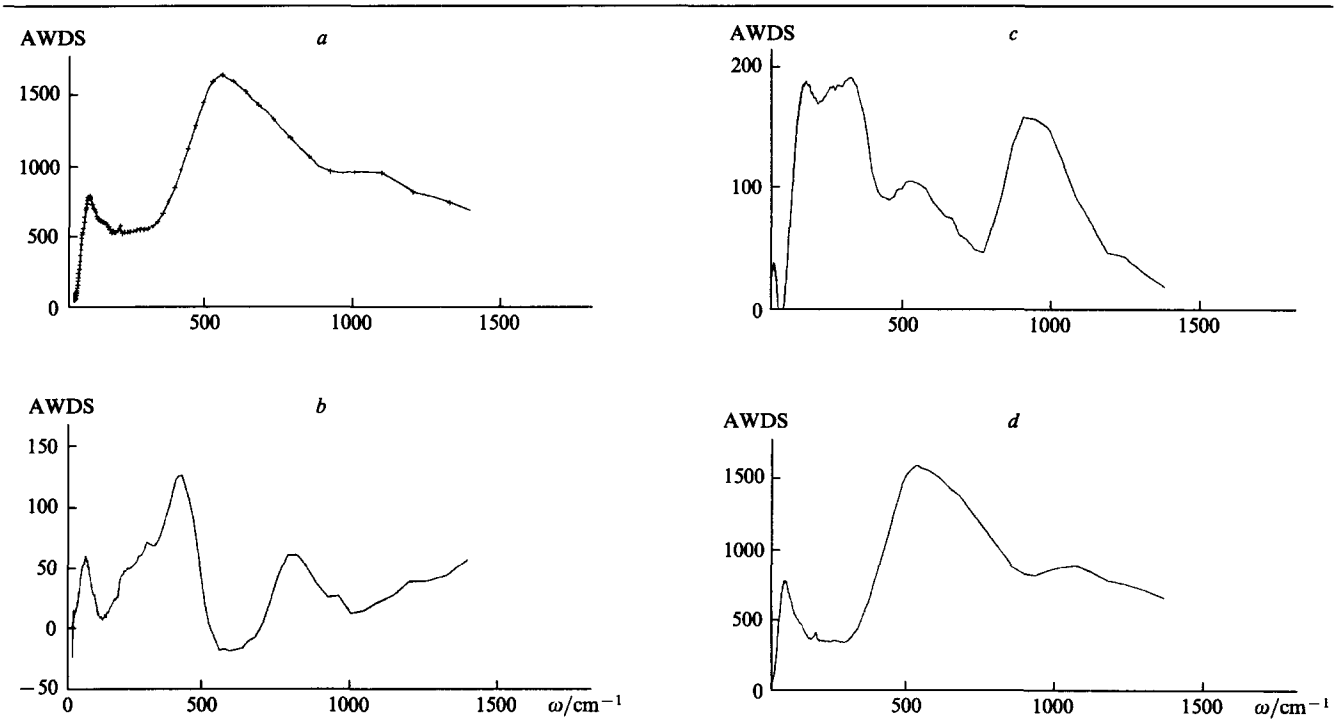


Figure 8. Overall AWDS spectrum of an air-dry specimen (*a*) and the basis spectra of the components of the silica gel SG20: (*b*) core; (*c*) hydroxyl shell; (*d*) aqueous component ($T = 10$ K).[26]

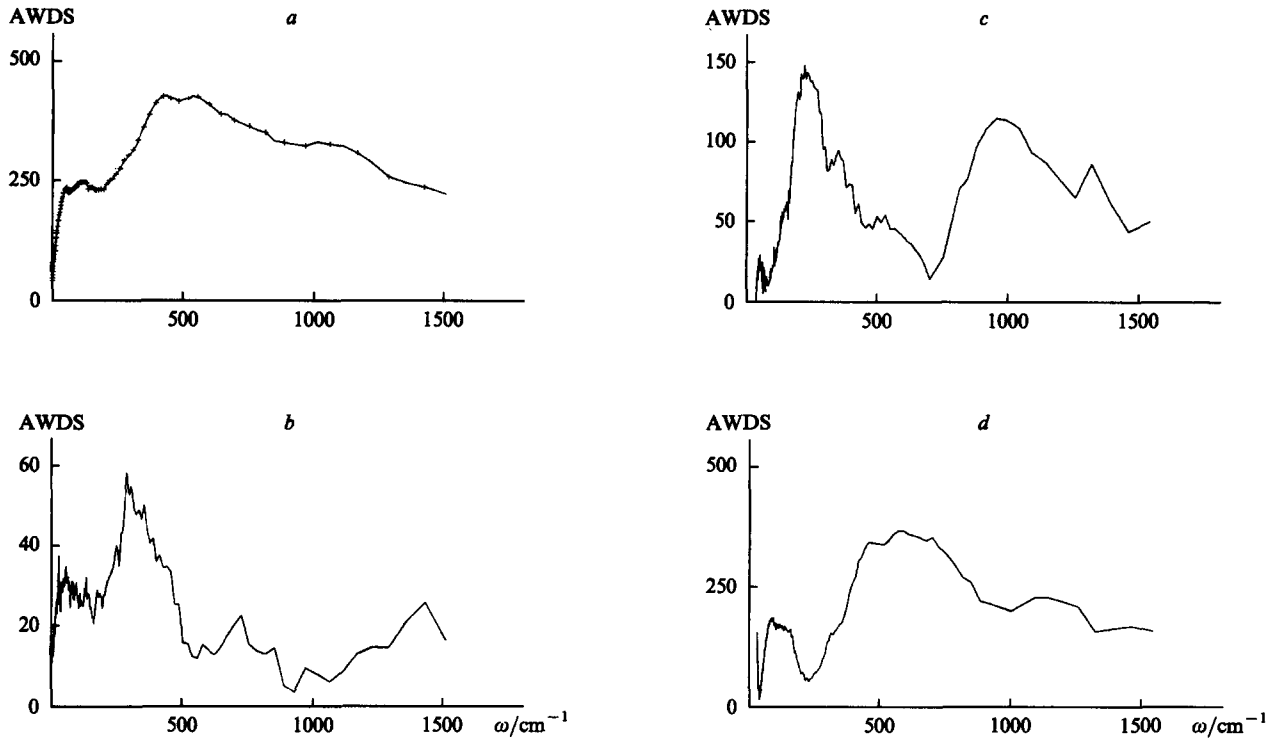


Figure 9. Overall AWDS spectrum of an air-dry specimen (*a*) and the basis spectra of the components of the silica gel SG100: (*b*) core; (*c*) hydroxyl shell; (*d*) aqueous component ($T = 10$ K).[26]

poor reproducibility of the absorption spectra of silica gels, has also been noted in the study of their IR absorption.[8,11,12] As will be shown below, this difference is not associated with the difference between the values of the numerical parameter describing the pore sizes and is determined by the exceptional lability of the structure of the silica gels, as a consequence of which it is virtually impossible in principle to achieve the reproducibility of the spectra on passing from one silica gel specimen to another.

The second feature concerns the basis spectra of the water shells. In contrast to aerosil with its globular structure, in the porous structures of silica gels water may be not only adsorbed but may be also retained in a quasi-free form. Therefore, in characterising the aqueous component of this substance, it is more correct to speak of the retained water. Fig. 10 presents the AWDS basis spectra of the aqueous components of the silica gels SG20 and SG100 together with the spectra of the rapidly frozen water. Despite the clear-cut difference between the spectra of the aqueous components of both specimens, the similarity of both spectra of the rapidly frozen water is striking. Such an evident similarity, which has been observed also by other investigators[45,56] (Figs 3 and 4), confirms the earlier conclusion[56] that the silica gel pores contain water of two types: water adsorbed on the inner surfaces of the pores and quasi-free water.

In conformity with this view, it has been postulated[26] that the basis spectra *1* and *2* in Fig. 10*a* consist of the spectra of the adsorbed and quasi-free water. The observed difference between the spectra of water in the silica gels SG20 and SG100 can then be explained qualitatively. The finely porous silica gel SG20 contains more water [about 16 mass% (it is known that the smaller the pore, the greater the amount of water retained in it as a consequence of the greater surface tension)][1] and its main bulk comprises quasi-free water. This is the reason why the AWDS spectrum of the water component of SG20 is in this case so similar to the spectrum of rapidly frozen water. Owing to the large pore size, silica gel SG100 retains less water (~5 mass%) and its AWDS spectrum therefore manifests the spectrum of the adsorbed water, which is almost completely masked in the first case. [A similar conclusion has been reached by Li et al.[56] (Figs 4 and 5).]

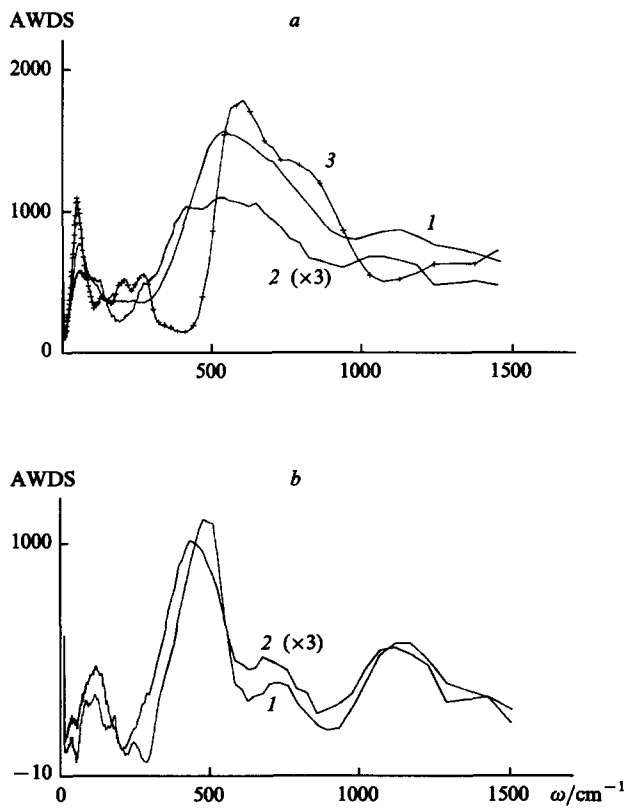


Figure 10. AWDS basis spectra of the aqueous components of silica gels ($T = 10$ K):[26] (*a*) overall spectra; (*b*) spectra of adsorbed water; (*1*) silica gel SG20; (*2*) silica gel SG100; (*3*) rapidly frozen water.

The spectra of water of both types have been obtained separately by means of qualitative analysis using the differential-correlation method for the resolution of the spectra of a complex system. It was postulated that the quasi-free and adsorbed water are separated in space. As in the case of aerosil, the adsorbed water is understood as complex structural formations incorporating water molecules interacting with the adsorption centres. It has also been postulated that the internal coordinate systems of the adsorbed and quasi-free water are independent, so that their vibrational spectra should not be correlated if one disregards the false correlation induced by the random coincidence of the frequencies of the vibrational modes.

The procedure used to resolve the initial basis spectra of the aqueous components were as follows.[26] In conformity with Eqns (16), it is possible to set up the following system of equations:

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

where superscript j denotes the number of the initial spectrum: $j = 1$ corresponds to the AWDS basis spectrum $Sp_1^{(1)}$ of the water shell of the silica gel SG20 (curve *1*, Fig. 10*a*), $j = 2$ corresponds to the AWDS basis spectrum $Sp_1^{(1)}$ of the silica gel SG100 (curve *2*, Fig. 10*a*), and $j = 3$ corresponds to the AWDS spectrum of 1 g of the rapidly frozen water (curve *3*, Fig. 10*a*).

The quantities Sp_1 and Sp_2 in Eqns (30) denote the basis spectra of the quasi-free and adsorbed water, which are assumed to be the same for both silica gels. On the basis of studies[55,56] in which it is claimed that the INS spectra of free ice and the ice within the pores are virtually maintained [remain the same?], it was postulated that the vibrational spectrum of free water $\mathcal{S}p^{(3)}$ determines the form of the basis spectrum Sp_1.

If one constructs two difference spectra

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

and imposes the requirement that the ZCC criterion holds in the form

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

then, by solving these equations it is possible to determine the coefficients $a_0^{(13)}$ and $a_0^{(23)}$ in accordance with Eqn (15) and to obtain the spectra $D_0\mathcal{S}p^{(13)} = Sp_2(1)$ and $D_0\mathcal{S}p^{(23)} = Sp_2(2)$. These spectra are presented in Fig. 10*b*. They proved to be virtually identical. The percentage contents of free (η_{fr}) and adsorbed (η_{ad}) water in the test silica gel specimens corresponding to the coefficients $a_0^{(13)}$ and $a_0^{(23)}$ are presented in the equations for the ZCC criterion [Eqns (32)].[26]

Specimen	η_{fr}	η_{ad}
Silica gel SG20	14.0	3.7
Silica gel SG100	1.8	1.3

However, the identity of the AWDS spectra of the adsorbed water in the two silica gels is surprising against the background of the large difference between their two other basis spectra. This finding is apparently based on the competition between two processes: the formation of a 'drop' of the quasi-free water and adsorption. Evidently, among the set of silicon–hydroxyl centres of three types, forming the hydroxyl shell of silica gel and ensuring the adsorption of water, only one centre may prove capable of competition (otherwise, the water would not have collected into drops). Naturally, this centre is the same in each silica gel, which is in fact the reason for the identity of the AWDS spectra of the water adsorbed on it. As will be shown below, this explanation received a well-founded confirmation in the quantum-chemical modelling of the model structures of silica gels.

3. Aerogel

a. Specimens and initial spectra

The test specimen of the aerogel AG200[27] consisted of a monolithic lump of a solid substance with a mass density of 200 kg m^{-3}. The specimen, stored in air, was initially air-dry; it was dried in air at 100 °C for seven days, which resulted in a dried specimen. The latter was in its turn subjected to the $H \rightarrow D$ isotope exchange. The specimen was maintained at 100 °C under atmospheric conditions for 12 h and was then placed in a desiccator, where it was kept for 12 h in heavy water vapour. The cycle was repeated with the specimen maintained for 6 h at each stage, which resulted in a deuteriated specimen. The time-of-flight INS spectra of the family of the above aerogel specimens and the corresponding AWDS spectra, obtained in conformity with Eqn (6), have been described in detail.[27]

b. Basis spectra of the components of the aerogel

In contrast to aerosil and silica gels, the chemistry of the surface of the aerogel has been studied to a much lesser extent. The initial inferences concerning the structure of the aerogel surface were made on the basis of the analysis of the chemical-technological process involving its preparation. According to the scheme employed in this process,[3] the principal component of the aerogel cores is a siloxane chain and the main contribution to the hydrogen-containing surface region comes from the hydroxy-groups, the number of which increases with increase in the length of the polymer chain.

In the isolated chains, each silicon atom of the siloxane core is linked to two hydroxy-groups. Consequently, the polymer structure formed consists of a chain of silanediol groups. On the other hand, if the chains are cross-linked in pairs, giving rise to a strip, then the silicon atoms of the strip each carry only one hydroxy-group. It has been suggested that this type of cross-linking process actually occurs in gel formation.[3]

The presence of silanol or silanediol groups on the surface of the silica core usually leads to the adsorption of water under atmospheric conditions. The existence of adsorbed water on the surface of the aerogel has been confirmed by the mass-spectrometric study of the products desorbed from its surface on heating to 100–150 °C.[3] This is also indicated by the analysis of the measured INS spectra.[27] Thus, when the specimen is dried under conditions corresponding to the preferential desorption of water, its vibrational spectrum undergoes a significant change in form and its integral intensity diminishes almost by a factor of two. Comparison of the AWDS spectra within the family of the AG200 specimens shows that the maintenance of the initial AG200 specimen in heavy water vapour reduces the intensity of the spectrum almost by a factor of three. This shows that the surface region of the air-dry aerogel contains an appreciable number of hydrogen atoms, because isotope exchange is concentrated mainly in this region. The marked smearing of the structure of the spectrum on raising the temperature may be regarded as another confirmation of the presence of water in the surface region of the aerogel.[27] Such smearing is similar to that observed in the spectra of air-dry aerosil and silica gel specimens,[22] which has been attributed to the facilitation of the diffusion of water on the surface with increase in temperature.

Thus the surface region of the air-dry aerogel contains hydroxy-groups and adsorbed water. By analogy with other disperse silicas, the aerogel becomes as a result of this a three-component system consisting of a silica core and hydroxyl and aqueous components.

The ratios of the coefficients in Eqn 16, describing three experimental spectra of aerogel specimens, proved similar to the ratios for silica gels, so that Eqns (29) serve as a basis also for the aerogel. By repeating the procedure described above for silica gel, it is possible to obtain a set of basis spectra of the aerogel, which

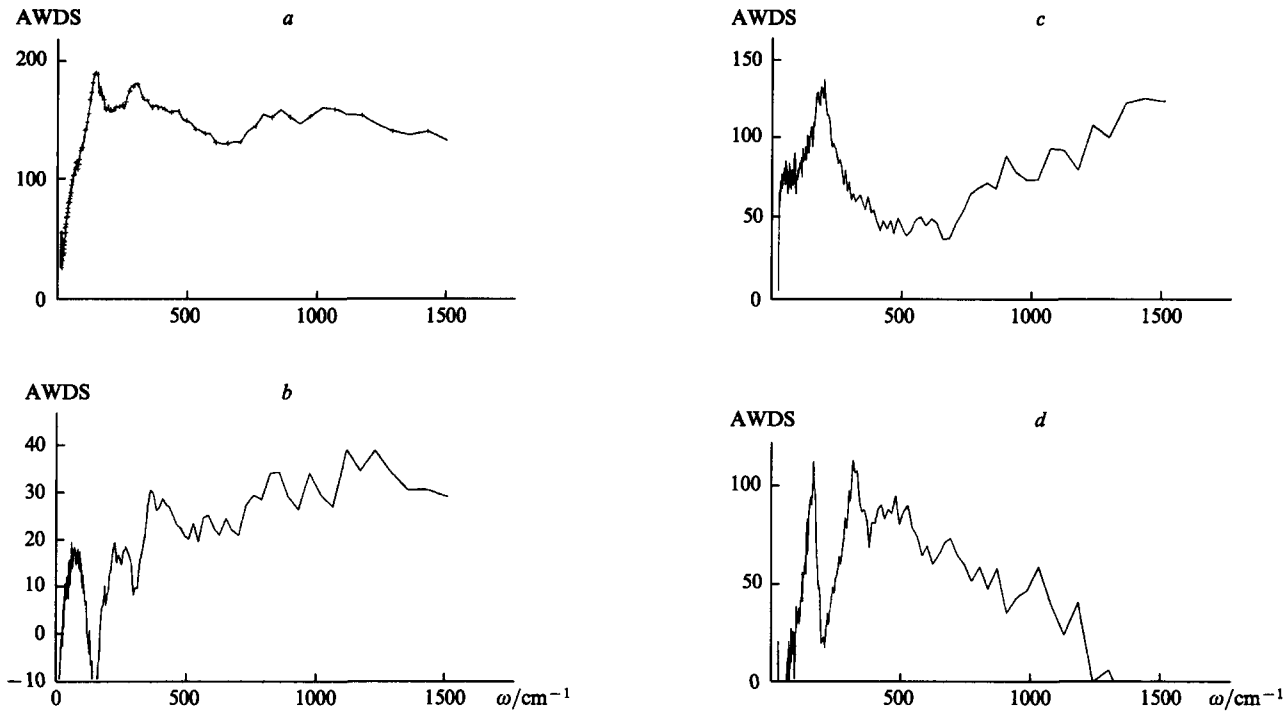


Figure 11. Overall AWDS spectrum of an air-dry specimen (*a*) and the basis spectra of the components of the aerogel AG200: (*b*) core; (*c*) hydroxyl shell; (*d*) adsorbed water ($T = 10$ K).[27]

are presented in Fig. 11 together with the spectra of the air-dry specimen. The clearly expressed 'quasi-molecular' structure of the spectra presented can be seen. As regards the vibrational spectrum of the core, its structure is more characteristic of polymers than a close-packed amorphous solid (see, for example, Gribov[89]). This agrees with the chain model of the aerogel core, which is a consequence of specific polymerisation and condensation processes in the preparation of disperse silica.[90] The narrow band form of the spectra of adsorbed water indicates, on the one hand, the absence of a collective interaction between the molecules, and, on the other, the same type of orientation of the adsorbed water molecules. The latter indicates in its turn a definite uniformity of the adsorption centres and that they are fairly widely scattered.

V. Comparative analysis of the vibrational spectra of disperse silicas and their components

1. Vibrational spectra of silica cores

The basis vibrational spectra of the cores of the test silicas are presented in Fig. 12. In addition, the figure shows (curve *2* in Fig. 12*a*) the vibrational spectrum of the glass obtained by sintering the aerosil A380. It is seen that the spectra of the cores of all the substances have a similar form and resemble the spectrum of the glass, which corresponds to the bulk-phase vibrations of close-packed silica (each consists of four bands located in the same spectral regions). At the same time, considerable differences are observed both between the spectra of disperse silicas and between the latter and the spectrum of the glass. This concerns the distribution of the intensities in each spectrum and of the absolute intensities of each of them. The vibrational spectrum of the aerosil core is closest to that of the spectrum of the glass, while the vibrational spectrum of the aerogel is most different. It is a remarkable fact that the spectra of the cores of the two silica gels investigated (SG100 and SG20) with different average core sizes (100 and 20 Å) differ significantly from one another.

Analysis of the differences observed in the form of the spectra can be conveniently begun with a brief description of the spectrum of the glass. Four bands in the regions 0–200 cm^{-1} (*I*), 200–500 cm^{-1} (*II*), 500–950 cm^{-1} (*III*), and 950–1300 cm^{-1} (*IV*) clearly stand out in this spectrum. According to the analysis of the vibrational spectrum of the free SiO_4^- ion[6] and the α-quartz crystal,[91] the deformation vibrations associated with the variation of the O–Si–O angle make the main contribution to region *II*. In regions *III* and *IV*, this role is assumed by the symmetrical and asymmetric stretching vibrations of the Si–O bond. Calculation of the vibrational spectra of a series of large model clusters has shown that this assignment can be extended also to amorphous structures. According to the calculation, region *I* of the vibrational spectrum of the core is made up of the vibrational modes of the translational motion of the atoms and the deformation vibrations associated with changes in the Si–O–Si angles. The assignment of the frequencies in regions *II*–*IV* agrees with that quoted above.

The aerosil glass and aerosil. As already stated, the spectra of this pair of substances (Fig. 12*a*) are closest to one another. A similar conclusion was reached on the basis of IR absorption spectra.[39] This finding undoubtedly indicates that the structure of the aerosil core is close-packed. The AWDS spectra of the glass show that the intensity of the bands in the ranges 0–220 cm^{-1} and 560–1500 cm^{-1} appreciably exceeds that of the aerosil spectrum. A detailed analysis of the difference spectrum suggested[25] that this difference is caused by the presence in the glass, in contrast to the 'absolutely dry' (by definition) aerosil core, of small amounts of adsorbed water. For a quantitative explanation of the observed difference, 0.3 mass%–0.5 mass% of water is sufficient. The possibility of the existence of such amounts of water in the glass has been confirmed by several pieces of chemical evidence.[6]

Silica gels. Regions *I*–*IV* again stand out clearly in the basis spectra of the silica gel cores (Figs 12*b* and 12*c*). However, a significant rearrangement of the spectra and an increase in their

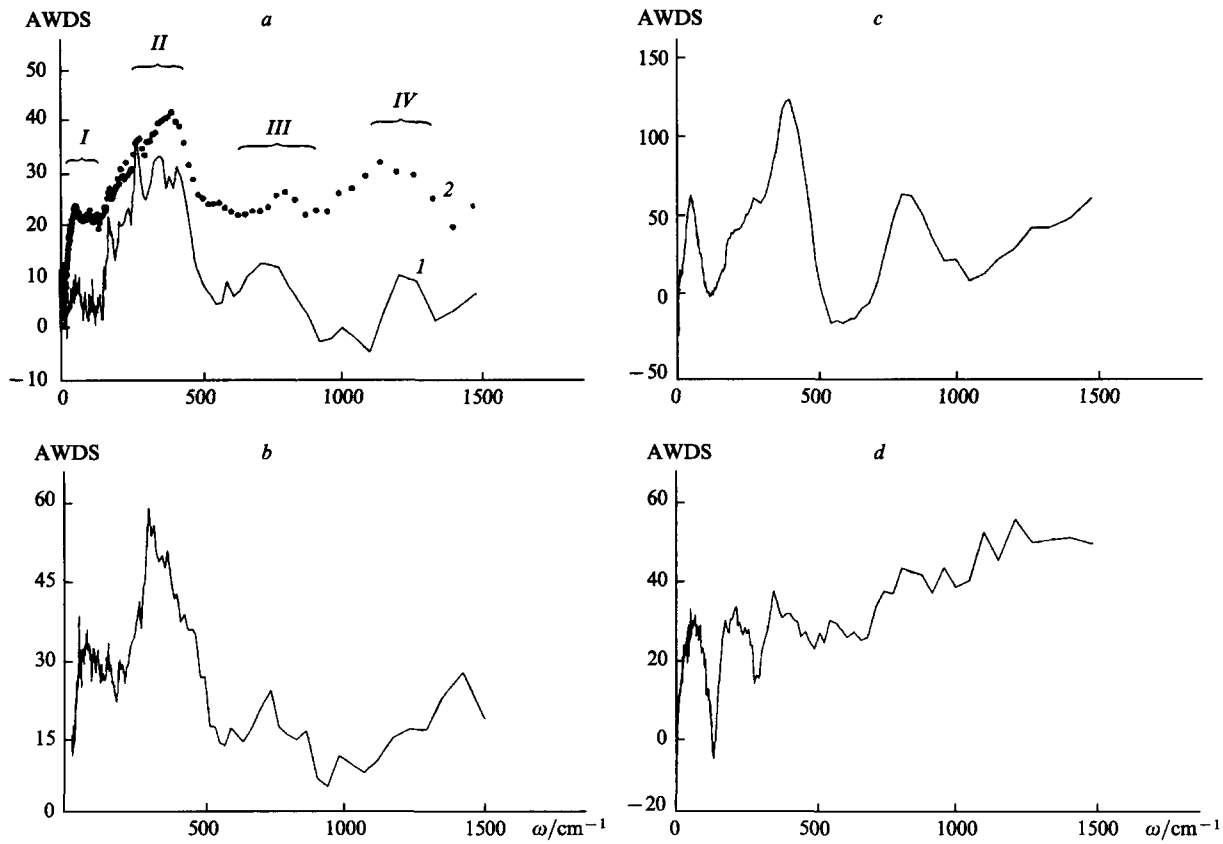


Figure 12. Basis vibrational spectra of the cores of disperse silicas ($T = 10$ K):[28] (*a*) aerosil A380 (curve *1*) and glass (curve *2*); (*b*) silica gel SG100; (*c*) silica gel SG20; (*d*) aerogel AG200.

intensity compared with the spectrum of aerosils are striking. The main characteristic feature of these spectra is, as stated above, the fact that they differ for different silica gels. This is manifested to the greatest extent in regions *I* and *II* corresponding to deformation vibrations. These changes can be understood if one postulates that a fairly broad distribution of the Si–O–Si and O–Si–O angles exists in the silica gels and that, on passing from one specimen to another, the distribution changes. The changes in the region of the deformation vibrations are accompanied by appreciable changes also in regions *III* and *IV* of the Si–O bond stretching vibrations. The combination of these findings permits the conclusion that the structures of the silica gels investigated differ from one another and that they all differ appreciably from the close-packed structure.

Aerogel. The principal characteristic feature of the basis vibration spectrum of the aerogel core (Fig. 12*d*) is its narrow band 'quasi-molecular' structure, as a result of which it resembles the vibrational spectra of polymers.[89] On the other hand, the narrow-band structure of the basis spectrum in regions *I* and *II* indicates narrow distributions of the deformation modes in the region where the angles in the silicon–oxygen tetrahedra vary, which indicates, in its turn, a quasi-regular structure of the test substance. Consequently, the aerogel core constitutes a new type of structure in addition to the aerosil and silica gel structures.

Comparative analysis of the basis vibrational spectra of the cores of the test silicas permitted the conclusion that there is a qualitative difference between the structures of these substances, which indicates the presence of several polymorphic modifications of disperse amorphous silica. The difference between the core structures entails also a difference between the structures of the surface regions of the test materials.

2. Vibrational spectra of the hydroxyl components

The basis vibrational spectra of the hydroxyl components of the set of disperse silicas under discussion are presented in Fig. 13. Despite the appreciable differences between the spectra, it is possible to distinguish in all of them two vibrational regions characteristic of and common to all of them: 0–380 cm^{-1} (*I*) and 700–1100 cm^{-1} (*II*). The differences between the spectra may be characterised in terms of the differences between the structures in these regions and also in terms of the intensity of the continuous spectrum of the support and the absolute intensity.

The torsional vibrations of the OH group relative to the Si–OH bond (region *I*) and the deformation vibrations of this bond (region *II*) make a significant contribution to the vibrational modes corresponding to the differentiated regions *I* and *II*. The third structural element of the basis spectra of the hydroxyl components is the vibrations of the set of atoms of the silica core affecting the hydroxy-groups (the 'riding effect').[18,19] This effect consists of the following features. The hydrogen atoms linked to the oxygen atoms of the hydroxy-group participate also in other vibrational modes, describing, for example, the deformation of the Si–O–Si and O–Si–O angles, the stretching and deformation vibrations of the Si–O bond, etc. Owing to the anomalously high sensitivity of neutron scattering to hydrogen atoms, there is a response to the set of core vibrations, so that the frequencies due to the corresponding support arise in the AWDS spectra of the hydroxyl components, the range of which coincides with the range of the bulk-phase vibrations of the base illustrated in Fig. 12.

The narrow-band structure of the vibrational spectra of the hydroxyl components of aerosil and aerogel in region *I* indicates a certain uniformity of the orientations of the OH groups relative to the silicon atoms to which they are bound. From this one may conclude that the hydroxy-groups on the surfaces of both

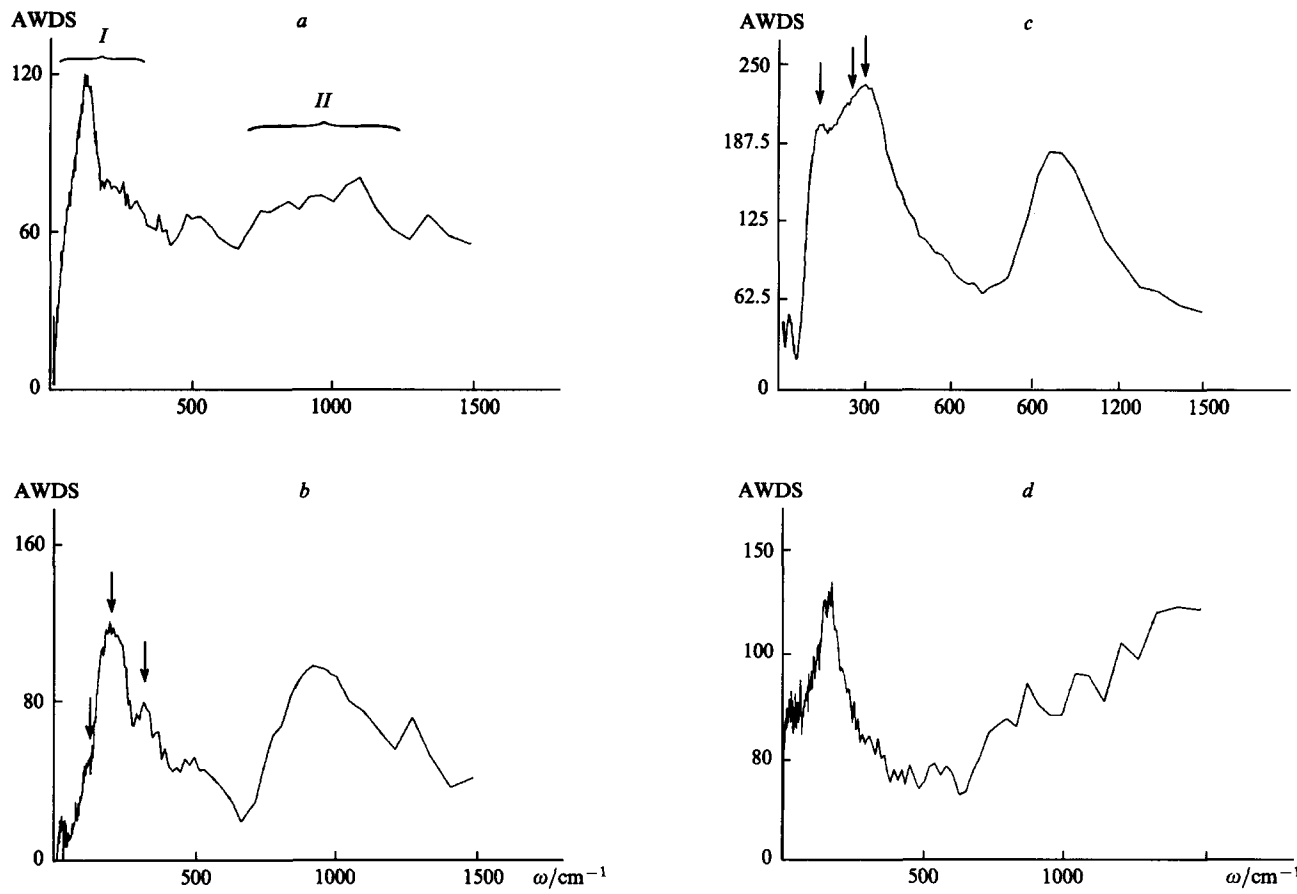


Figure 13. Basis vibrational spectra of the hydroxyl components of disperse silicas (T = 10 K):[28] (*a*) aerosil A380; (*b*) silica gel SG100; (*c*) silica gel SG20; (*d*) aerogel AG200.

substances are predominantly of the same type. This agrees with the results of studies on the structure of the hydroxyl coating on aerosil,[5] which established that 80%–85% of the surface hydroxy-groups are of the silanol type. The closeness in frequency of the first peaks in the aerosil and aerogel spectra and the similarity of their shapes suggests that silanol groups play the main 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 different silica gels have a complex structure in region *I* and an intense and distinct peak in region *II*. The spectra of different silica gels also differ significantly from one another. The line intensities in the spectrum of the hydroxyl vibrations in the silica gel SG20 are twice as high as in the spectrum of the silica gel SG100. The principal structural differences are concentrated in region *I*: a redistribution of the intensities between the three characteristic peaks at frequencies of 80, 230, and 380 cm^{-1}, designated by arrows in Figs 13*b*, and 13*c*, is observed. The position of the first peak coincides with the positions of the peaks in the vibrational spectra of aerosil and aerogel.

The observed characteristics of the vibrational spectra of the hydroxyl components of silica gels have been explained qualitatively on the basis of the analysis of the possible structure of the hydroxyl shell on silicas.[28] The hydroxyl components may be made up of silicon–hydroxyl groups of three types: silanol $(OH)_1$, silanediol $(OH)_2$, and silanetriol $(OH)_3$. They all exhibit deformation vibrations of the Si–OH bond with similar frequencies,[5] so that the vibrational spectrum of the hydroxyl component of any composition should contain a band in the region of 1000 cm^{-1}, which can in fact be observed in the spectra in Fig. 13. We may note that the band in the spectra of silica gels is much more distinct than in the spectra of aerosil and aerogel.

The vibrational spectrum of the hydroxyl component of aerosil is in essence the vibrational spectrum of silanol groups. The difference between this spectrum and the vibrational spectra of the hydroxyl components of silica gels can be interpreted as evidence that the silanol groups, even if they are present in the hydroxyl component of the silica gel (which is indicated by the presence in the silica gel spectra of a peak with a maximum at 80 cm^{-1}), they are not the main element. It has been concluded that silanediol and silanetriol groups should participate in the formation of the hydroxyl components of silica gels. The possible presence of these groups in the loose structure of silica gel had already been reported.[40]

Thus the hydroxyl component of silica gel is a set of different silicon–oxygen groups, the weighting factors of which depend on the structure of the silica core. The difference between the structures of the silica cores of both silica gels determine also the different structures of the hydroxyl components.

3. Vibrational spectra of the adsorbed water

Fig. 14 presents the basis vibrational spectra of the aqueous components of aerosil, aerogel, and silica gel.[26]

The results of quantum-chemical calculations on the interaction of water with an isolated silanol centre have shown[92,93] that the nature of the vibrational modes changes significantly when the number of water molecules attached to the centre is altered.[93] In the case of a single molecule, the vibrational spectra of the water molecule coordinated to the silicon atom and the molecule bound to the centre by a hydrogen bond are strikingly characteristic. When the number of attached molecules reaches six, the overall spectrum acquires features typical for both characteristic spectra indicated above. However, in conformity with the analysis of the vibrational modes, the adsorption

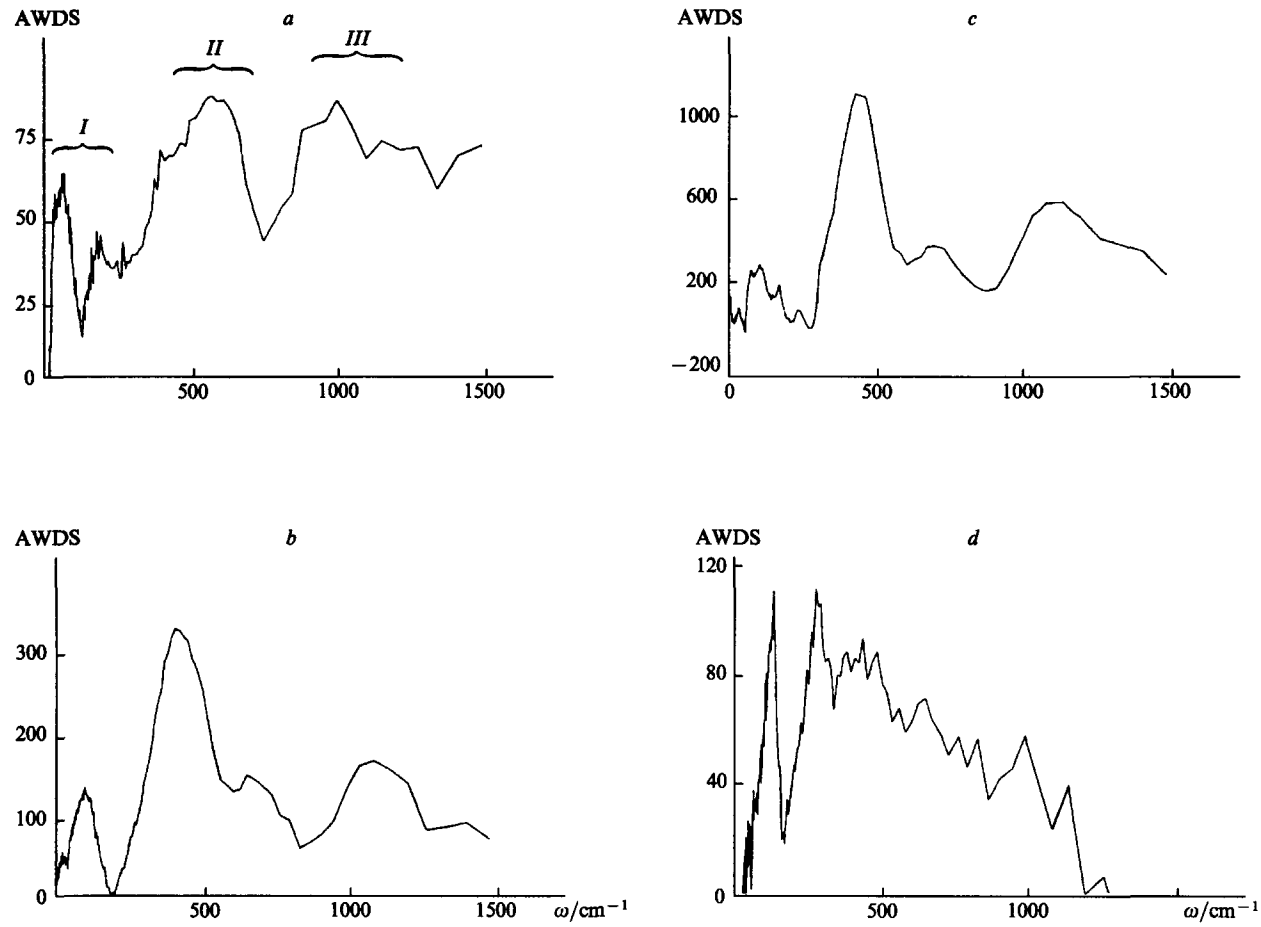


Figure 14. Basis vibrational spectra of water adsorbed on disperse silicas ($T = 10$ K):[28] (*a*) aerosil A380; (*b*) silica gel SG100; (*c*) silica gel SG20; (*d*) aerogel AG200.

complex vibrates under these conditions as a single whole in which the structurally differentiated coordinated and hydrogen-bonded molecules are not dynamically distinguishable. The details of this analysis can be found in the communication of Khavryuchenko and Sheka.[93] The characteristic nature of the vibrational spectra of single water molecules will be used below for a qualitative description of the characteristic features of the spectra illustrated in Fig. 14.

Three spectral ranges may be distinguished in these spectra. The low-frequency range 0–350 cm^{-1} (*I*) contains the stretching vibrational frequencies of the Si...OH_2 groups, the torsional vibrational frequencies of these groups, and the deformation vibrational frequencies of the hydrogen bonds of the interacting water molecules. The middle frequency range 350–850 cm^{-1} (*II*) is characterised by an intense structural peak and is mainly due to the deformation vibrations of the hydrogen bonds. This peak is the principal structural element in the spectrum of rapidly frozen water (Fig. 10*a*). The high-frequency region of the spectrum (850–1200 cm^{-1}) contains two peaks, which are associated with the deformation vibrations of the water molecule coordinated to the silicon atom and with the deformation vibrations of the Si–OH bond forming part of the adsorption centre.

The adsorbed water in the silicas investigated has been subjected to structural-dynamic analysis based on the above assignment of the vibrational modes.[28] The spectrum of the water adsorbed on aerosil shows that the adsorption of water on its surface is of a collective type, i.e. the water molecules form a 'quasi-drop' on the silanol centre during the adsorption process.[24,28,93] This hypothesis has been confirmed by calculations of the equilibrium configurations of the water molecules on large clusters, modelling the aerosil structure (see Section VII).

The spectrum of the water adsorbed on silica gel (Figs. 14*b* and 14*c*) differs significantly from the spectrum of water adsorbed on aerosil. This shows that the nature of the centres responsible for the adsorption of water on these silicas is different, which agrees with the conclusion reached in the previous section. Analysis of the spectrum of the water adsorbed on silica gel from the standpoint of the assignment of the frequency ranges *I*–*III*[28] led to the following conclusions. As in the case of aerosil, the adsorption of water on silica gel takes place collectively because the double peak in region *II* predominates in the vibrational spectrum. The form of this peak is similar to that of the analogous peak in the spectrum of rapidly frozen water (Fig. 10*a*), but the former is displaced towards lower frequencies and the ratio of the intensities of its components is different. This may be a consequence of the binding of the water 'drop' to the adsorption centre. Comparison of the spectra of water adsorbed on aerosil and silica gel shows that such binding of the drop is weaker in the case of silica gel than in the case of aerosil. The 900 cm^{-1} peak is absent from the spectrum of water adsorbed on silica gel, which indicates the virtually complete absence of coordinated water on the surface. The considerable width of the peak in region *I* indicates, as in the case of aerosil, the collective nature of the adsorption of water. The surprising coincidence of the spectra of adsorbed water for both silica gels noted above can be naturally explained by the above analysis and also the analysis of the structure of the hydroxyl shells of silica gels. Since these shells consist of a set of three silicon–hydroxyl groups, the water

molecule interacts with each independently, so that a competition of the groups in relation to the adsorption of water arises. The 'strongest' group, corresponding to the highest energy of the bonds between the water molecules and the centre, wins under these conditions. Since this group is one of the three indicated above, it should be the same both for the silica gel SG100 and the silica gel SG20. Thus the spectra of the adsorbed water should be identical for both silica gels and the difference between them reduces merely to the difference between the absolute intensities, which is associated with the fraction of the adsorption centres on the surfaces of silica gels differentiated in this way.

The AWDS spectrum of the water adsorbed on aerogel (Fig. 14*d*) differs markedly from the spectra presented above. In the first place, one should conclude that there is no distinct intense peak in region *II* of this spectrum, which indicates a significantly smaller number of hydrogen bonds between the water molecules on the aerogel surface. It has therefore been postulated[28] that the layer of adsorbed water is formed not by drops, as in the case of aerosil and silica gel, but predominantly by isolated molecules. This conclusion has also been confirmed by the distinctly structured nature of the vibrational spectrum of the low-frequency region *I*. The positions of the peak maxima in this region are nevertheless close to the positions of the peak maxima in the aerosil spectrum (Fig. 14*a*). This shows that the main water adsorption centre in aerogel is also a silanol group, which is in full agreement with the conclusions reached in the preceding section. The conclusion reached has been confirmed also by the presence of a maximum at 900 cm^{-1}. It is less pronounced than the maximum in the spectrum of water in aerosil but is observed quite reliably. According to Markichev et al.,[28] the change in the ratio of the intensities at the maxima in the spectra of water in aerosil and aerogel reflects the fundamentally different character of the adsorption in these substances: collective in the case of aerosil and individual in the case of aerogel. The latter conclusion is quite natural if we recall that water is adsorbed on the free outer surfaces of small aerosil particles. The steric hindrance to the formation of a drop is determined solely by the density of the silanol groups on the surface. It has been established experimentally that this density is such that it corresponds to an average distance between the silanol centres of ~7 Å.[6] This is sufficient for the formation of a quasi-drop, consisting of several water molecules, on an isolated silanol centre. In contrast to this, the active surface of aerogel is internal,[3] so that the role of steric hindrance to the formation of a quasi-drop is enhanced.

The above comparative analysis of the basis spectra of the components of the disperse silicas investigated made it possible to establish, despite its qualitative nature, that aerosils, silica gels, and aerogels should be regarded as fundamentally different structural formations. Here it is important to note that these differences extend to both bulk-phase, core structures and to the structures of the surface regions on these substances. Since the substances differ solely by the technology used in their preparation, the observed structural variability constitutes the phenomenon of technological polymorphism in an amorphous disperse silica.

VI. Technological polymorphism and classification of disperse amorphous silicas

The establishment of the existence of technological polymorphism in amorphous disperse silicas is important both intrinsically and as a basis for a new approach to the formulation of the problem of the computational modelling of these substances. In the development of this approach, it proved convenient to classify the observed modifications, formulating for each of them a set of distinctive features.[32] This was achieved by employing the principal crystal-chemical criteria proposed by Liebau.[94]

1. Fundamentals of the crystal chemistry of silicates

In his fundamental study, Liebau showed[94] that silicates are characterised by an extremely pronounced variability of their chemical and structural properties of a much greater extent than any other group of chemical compounds (with the exception of organic carbon compounds). At the same time, analysis of about 1000 compounds established that all the silicates can be divided into a small number of classes and subclasses in conformity with the classification based on the following fairly simple crystal-chemical principles:

1. Since the Si–O bond is the strongest in all the silicates investigated, the principal fragment determining the structure of the silicate is the polyhedron (SiO_n) and the type of structure is determined by the ways in which the polyhedra are linked to one another.

2. The coordination number of silicon (CN) in compounds having the general formula $M_xSi_yA_z$ and Si–A–M bonds tends to increase (CN > 4). This tendency is stronger the higher the electronegativity of the nearest neighbours — the A atoms. Oxygen has an intermediate electronegativity and may be incorporated in both the tetrahedra (SiO_4) and the octahedra (SiO_6), the tetrahedra being preferred.

3. The tetrahedra (SiO_4) are linked to one another usually via the vertices and not via their edges and faces.

4. One oxygen atom can participate in not more than two tetrahedra (SiO_4).

5. For each silicate anion, the difference between the number of junctions Δs between different tetrahedra (SiO_4) [where s is the number of junctions, i.e. the number of oxygen atoms in the tetrahedron (SiO_4) incorporated in other tetrahedra (SiO_4)] tends to decrease.

6. The bond lengths and bond angles tend to deviate from the average values $(Si-O)_{av} = 1.62$ Å, $(O-Si-O)_{av} = 107.47°$, and $(Si-O-Si)_{av} = 140°$ as little as possible. These six rules are not laws, exceptions to them being known,[94] but nevertheless their infringement is in most cases energetically unfavourable and therefore improbable.

A series of parameters have been introduced in order to describe the way in which the tetrahedra (SiO_4) are linked to one another in silicates. Without listing all the parameters, we shall consider the most important of these for further consideration, namely the dimensionality and multiplicity. The dimensionality of tetrahedral silicate structures D characterises the type of packing in the initial structural units and assumes the values $D = 0-3$. Thus isolated tetrahedra (SiO_4) as well as isolated cyclic and acyclic fragments have the dimensionality $D = 0$: $D = 1$ for isolated chains, $D = 2$ for isolated layers, and $D = 3$ for skeletal structures.[94] The multiplicity M characterises the formation of multiple tetrahedral structures with the same dimensionality as the initial structural units [isolated tetrahedra (SiO_4), isolated chains, isolated rings, and isolated layers].

The general nomenclature for silicates, presented in Table 3, has been introduced in conformity with the values of these parameters. Silicates with isolated tetrahedra (one, two, and three) belong to the class of oligosilicates. Silicates whose anions consist of rings comprising the tetrahedra (SiO_4) are referred to as cyclosilicates. Depending on whether they contain isolated, double, or triple rings, the prefixes mono-, di-, etc. are added to their names. Structures containing silicate chains are called polysilicates. They can be further subdivided into monopolysilicates with isolated chains, dipolysilicates with double chains or strips, etc. Phyllosilicates are made up of layers of tetrahedra (SiO_4); they can also be subdivided into mono- and diphyllosilicates. Silicates with a three-dimensional framework consisting of the tetrahedra (SiO_4) are called tectosilicates.

Further subdivision of silicates into subclasses is determined by the operation of the general parsimony principle, which presupposes that, for a specified composition, the system tends to have the minimum possible number of geometrically and chemically different groups.[94]

Table 3. The chemical nomenclature for silicates.[94]

Class	Dimensionality	Multiplicity (M)		
		1	2	3
Oligosilicates	0	Monosilicates	Disilicates	Trisilicates
Cyclosilicates	0	Monocyclosilicates	Dicyclosilicates	Tricyclosilicates
Polysilicates	1	Monopolysilicates	Dipolysilicates	Tripolysilicates
Phyllosilicates	2	Monophyllosilicates	Diphyllosilicates	Triphyllosilicates
Tectosilicates	3	Tectosilicates		

2. Classification of disperse silicas in conformity with the crystal chemistry of silicates

The principal crystal-chemical rules presented above contain nothing specific to crystal structures and it was therefore natural to suppose that they hold also in the case of amorphous structures.[32]

Crystalline silicates with mixed dimensionality and multiplicity are unknown in nature. This is apparently to be expected also for the amorphous state, so that amorphous structures can also be classified in accordance with Table 3. A specific feature of the test substances is the establishment of a classification mode for each of them, which is possible in the analysis of the technological procedure used in their preparation.[32]

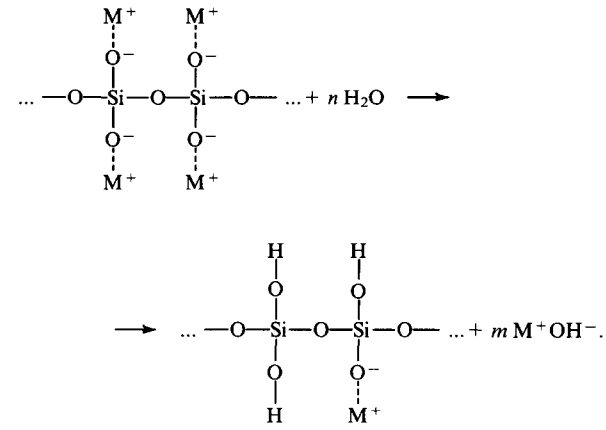
Disperse silicas are obtained under the conditions of the simultaneous occurrence and competition of two processes: the hydrolysis of the initial product, which leads to the formation of silicon–oxygen tetrahedra containing between one and four hydroxy-groups, and the subsequent polycondensation of these fragments.[1-3] Polycondensation results in the formation of the nucleus of the future structure of the final product: particles of aerosil, a silica gel sol, and 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 are carried out, and external conditions (temperature, pressure, etc.).

Aerosil. Silicon tetrachloride is used to obtain aerosil. It is hydrolysed in an oxygen–hydrogen flame at atmospheric pressure and a temperature of about 2000 K. The hydrolysis, which proceeds in accordance with the reaction

$$SiCl_4 + 4H_2O = 4HCl + Si(OH)_4 ,$$

results in the formation of orthosilicic acid, the product of the polycondensation of which is in fact aerosil. The solid nuclei formed in the plasma are carried away from this zone and enter a cold zone, forming larger agglomerates, which are virtually ideal spherical particles of amorphous silica. The process involving polycondensation, the formation of nuclei, and their agglomeration is in many respects similar to the formation of small metal particles.[95]

Silica gel. Silica gel is usually obtained from aqueous solutions of alkali metal silicates in the presence of an acid.[2] The silicates employed are known to contain even in the initial state chains of the tetrahedra (SiO_4), which serve as the nuclei of the future solid-state structure. The essential feature of the process may be represented by considering the following simplified scheme:



The metal silicate hydrolyses in aqueous solution, which leads to the formation of chains of the tetrahedra (SiO_4) of differing length in which each silicon atom is linked to two hydroxyls. Such chains are known to cyclise at high concentrations to form rings with different numbers of silicon atoms. The hydroxide anion is capable of rupturing the Si–O–Si linkage connecting neighbouring tetrahedra, so that a dynamic equilibrium is established after a time in solution between the ring formation and disruption processes. In order to shift the equilibrium towards polycondensation, an acid is added to the solution, whereupon the ring disruption process virtually ceases and rings are actively formed in the medium and merge with one another. The primary hydrolytic process does not usually go to completion, so that negative oxygen ions are retained in the rings, holding solvated metal ions in their vicinity. It has been established[2] that the presence of such solvated ions plays a decisive role in the stabilisation of the gel.

Aerogel. The technological industrial process for the preparation of this product is based on the acid- or alkali-catalysed hydrolysis of tetraethyl orthosilicate (TEOS):[90]

$$Si(OEt)_4 + nH_2O \longrightarrow (RO)_3SiOH + m\,EtOH ,$$

R = H, Et.

The 'initial silanol' obtained as a result of this reaction can have a complex composition depending on the nature of the group R. The hydrolysis is accompanied by the condensation of the 'silanols', completed by the formation of a silicate polymer:

$$(RO)_3SiOH + OH^- \longrightarrow (RO)_3SiO^- + H_2O ,$$

$$(RO)_3SiO^- + (RO)_3SiOH \longrightarrow (RO)_3SiOSi(RO)_3 + OH^- .$$

The growth of the polymer chain is controlled by the concentration of water and TEOS and by the pH of the solution. The acid-catalysed processes lead to the formation of short chains as a rule. If the catalyst is an alkali, longer chains are obtained. The combination and cross-linking of the chains results in the formation of the gel.

Analysis of the technological processes for the preparation of various disperse silicates has shown that the structural fragments making up the structure of the future product are different in all three cases.[32] Thus the 'principle of close packing' of the tetrahedra (SiO_4) in the bulk phase operates in the formation of the aerosil particles. According to Liebau's classification,[94] the dimensionality of the structure obtained is three and, by analogy with tectosilicates, aerosil was assigned to the class of amorphous tectosilicas.

The principal structural unit in silica gels comprises ring structures of arbitrary composition, the dimensionality of which is $D = 0$, as a result of which they were assigned to the class of amorphous cyclosilicas, analogous to cyclosilicates.

The principal structural element of the aerogel framework comprises chains. In this case, the dimensionality of its structure is unity and it was therefore classified as an amorphous polysilica analogous to polysilicates.

Thus amorphous tecto-, cyclo-, and poly-modifications are the technological polymorphic forms of disperse silicas. This idea served as the basis of an algorithm, which was used in the construction of model structures of amorphous silicas.

VII. Computational modelling of the initial structures of amorphous silicas

The concept underlying the computational modelling of polyatomic systems, which has made it possible to achieve the closest approach to the description of the properties of real nanomaterials, has been actively developed during the last few years.[15,31,36] This concept is based on a joint spectral experiment including computational and real experiments linked by feedback. The modelling process is regarded as a problem the successful solution of which is determined by the optimum selection of four of its main components, namely: (a) the quantum-chemical method for calculations relating to polyatomic clusters of nanometer size; (b) the procedure for calculations on the available powerful high-speed computers; (c) a structure-sensitive experimental method for testing the validity of the results obtained; (d) an adequate experimental object ensuring the establishment of a feedback between the calculations and the real experiment.

The need to operate with clusters of nanometer size leads to a conclusion in favour of one of the quantum-chemical semiempirical methods. Significant progress in this field has been achieved in recent years both by virtue of the stimulating studies of Dewar's school[96] and as a result of the development of new computational methods or new versions of those already existing. Zaets's program packs on computational chemistry, based on the MNDO, MNDO/H, AM1 (*sp* basis set) (CLUSTER-Z1 program pack),[97] and NDDO (*spd* basis set) (CLUSTER-Z2 program pack)[98] methods, should be included among the latter. These program packs have been executed in a form, which ensures a high accuracy of the computation for polyatomic systems combined with a comparatively small expenditure of computing time. When installed on the personal computers of the PC AT 486/Pentium and SUN SPARCstation class, they made it possible to perform calculations in a short time for a wide variety of polyatomic clusters of nanometer size, in particular systems such as silica, silicon nitride, nickel, aluminium, etc. (for a brief review of the results, see Sheka et al.[36]).

However, the calculated data obtained do not as yet solve the problem of modelling, since the question of the correspondence of these data to reality arises. The nanometer clusters used as the model have no molecular analogues, so that the principal characteristic of the molecular system — the energy and other integral characteristics — become merely descriptive quantities and cannot be subjected to an experimental test. Only vibrational spectra, which are largely determined by a short-range interaction, are the actual the property of the system for which the cluster approximation is sufficiently accurate. From the standpoint of the numerical experiment, the modelling of the surface does not differ from the modelling of the core structure. However, the need for a feedback in relation to the real experiment at the level of the investigation of the vibrational spectra requires that the investigator select an object which is as close as possible to the clusters being modelled. This is why in the course of the numerical modelling of the adsorption properties of the surfaces of nickel,[19,99,100] silica,[32-35] and silicon nitride[101] the vibrational spectra of the corresponding modifications of these substances having nanometer size were employed as the experimental parameter.

When the problem of the computational modelling of a large cluster is formulated, the qualitatively new problem of the selection of the procedure for the modelling of the initial structure arises. It is well known[102] that in most cases chemical interactions are of the short-range type, so that structural elements separated by distances exceeding the chemical bond length hardly affect one another. As a result of this, there arises the risk that the site and direction of the development of the structure 'will not be guessed correctly'. The situation is frequently aggravated by the fact that nonrigid structures, to which those of silica belong in particular, are characterised by a large set of close minima on the total electronic energy surface. One of the ways of solving this problem involves algorithmic modelling, the essential feature of which consists in the construction of the initial structure of the cluster with the aid of a definite algorithm based on 'evidence of the origin' of the corresponding product containing a set of distinctive features characteristic only of the latter.[103] This approach has been used in the modelling of the structures of disperse silicas.[32-35]

1. Computational modelling of aerosil

The computational modelling of the structure and adsorption properties of aerosil[33] consisted of the following stages:

1. the construction of the initial structures of polyatomic clusters of nanometer size;
2. computational modelling by means of semiempirical quantum-chemical methods of the structures constructed;
3. computational modelling of the adsorption properties of the clusters investigated in relation to water molecules;
4. calculation of the doubly amplitude-weighted density of the vibrational states of the cluster and of inelastic neutron scattering spectra with subsequent comparison of the calculated and experimental spectra.

a. Initial structural models

On proceeding to the construction of the initial clusters, it is useful to introduce the concept of small, medium, and large clusters having brought them into correspondence with the principal ideas concerning crystal-chemical fragments and the types of their packing in conformity with the assignment of the test structure to a particular structural class. The main structural fragment of silicates and silicas is the silicon – oxygen tetrahedron (SiO_4). This tetrahedron is in fact usually considered in the computational modelling of silica systems (see, for example, Refs 6, 92, 104, and 105). However, in the light of the multivariability of the structures of disperse silicas, such a model cluster is inadequate for the description of their properties. Therefore, in the computational modelling of this family of substances, special definitions were formulated and introduced: the concept of a small cluster as a structural model of a peripheral (surface) functional group was introduced; the concept of a cluster of medium size as a structure describing the packing of small clusters in accordance with the classification of the structure and reproducing correctly the short-range distribution of atoms; the concept of a large cluster as a structure in the ideal version designed to reflect the correct bulk-phase structure of the substance and the distribution of functional groups on its surface.

Since aerosil is an amorphous tectosilica, the clusters modelling the structure of its core must be of the skeletal close-packed type. The close-packed crystal structures of silica are known to contain rings of siloxane chains with a small number of members: four-membered in quartz[106] and six-membered in cristobalite[107] and tridymite.[108]

The structural models of individual small rings are presented in Fig. 15. They were obtained as a result of total optimisation by the AM1 method with the aid of the quantum-chemical programs of the CLUSTER-Z1 pack.[33] These and all subsequent calculations were performed on personal computers of the type PC AT 386/387-33 and 486-66. The clusters are presented in a projection 'from above'.

We may note that, although the silicon atoms are located in one plane only in the Si3c cluster, in the remaining clusters the

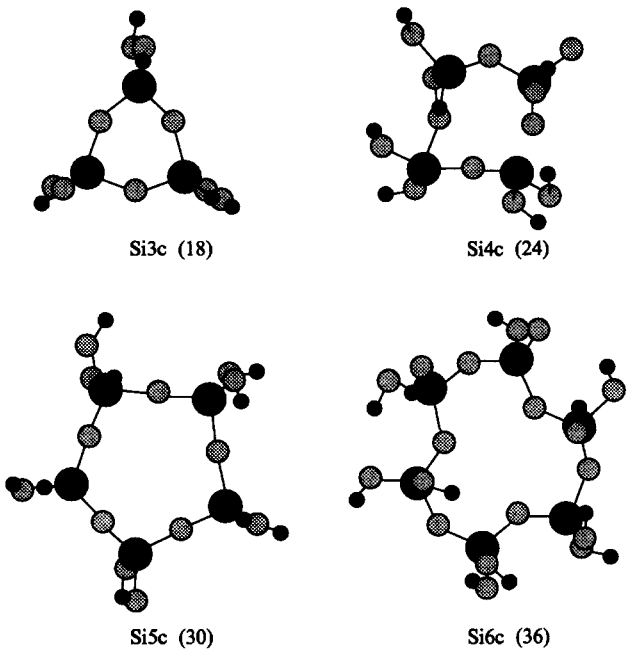


Figure 15. Small rings of silicon–oxygen tetrahedra Si*n*c (calculation by the AM1 method);[33] *n* is the number of silicon atoms in the ring (c) (here and in Fig. 16 the numbers of atoms in the cluster are indicated in brackets).

silicon rings are also close to planarity. In contrast to these, large rings with more than six carbon atoms have a distinctly nonplanar structure. The structure made up of large rings is inevitably looser. Thus polyhedra the faces of which consist of small rings served as a model of the bulk-phase structure of aerosil. In constructing model 'structures', preference was given to nonplanar six-membered rings ('hexagons') because the nuclei of the aerosil particles are formed at a high temperature where the β-cristobalite crystal structure is more stable.[33] The choice of the 'hexagon' motif made it possible to propose a fairly simple algorithm for the successive growth in the size of the model cluster, which can be represented by the formula

$$\mathrm{Si6c} + 4n\,\mathrm{Si} + 6m\,\mathrm{Si},$$

where $n = 1, 2, 3$ and $m = 1, 2, 3\ldots$ for $n > 3$. This algorithm corresponds to a development of the cluster structure such that the addition of the first four silicon atoms to the basic Si6c six-membered ring is accompanied by the formation of an adamantane-like skeleton containing three 'hexagons' (Fig. 16*a*). The addition of each succeeding group of four silicon atoms leads to the formation of three new 'edges', from which new 'faces' of the cluster being formed are produced, so that the Si10 cluster is converted into a Si14 cluster and the latter into a Si18 cluster, etc. Under these conditions, the cluster grows in width and its development in depth, starting with $n = 3$, requires the addition of six silicon atoms. The set of Si10, Si18, and Si24 clusters obtained as a result of the application of this algorithm is presented in Fig. 16.

b. Analysis of the model structures of aerosil

Whereas the first member of this series can be assigned to clusters of medium size, the last two clusters belong to the class of large ones. Analysis of their structure shows that the selected algorithm for the growth in the size of the cluster not only reproduces the bulk-phase structure of the substance but also makes it possible to discover the trend in the distribution of the functional groups on its surface. In the test system, these are silanol $(OH)_1$ and silanediol $(OH)_2$ groups. With increase in the size of the cluster, the silanediol groups, which are the only ones present in the isolated rings (Fig. 15), are gradually substituted by silanol groups

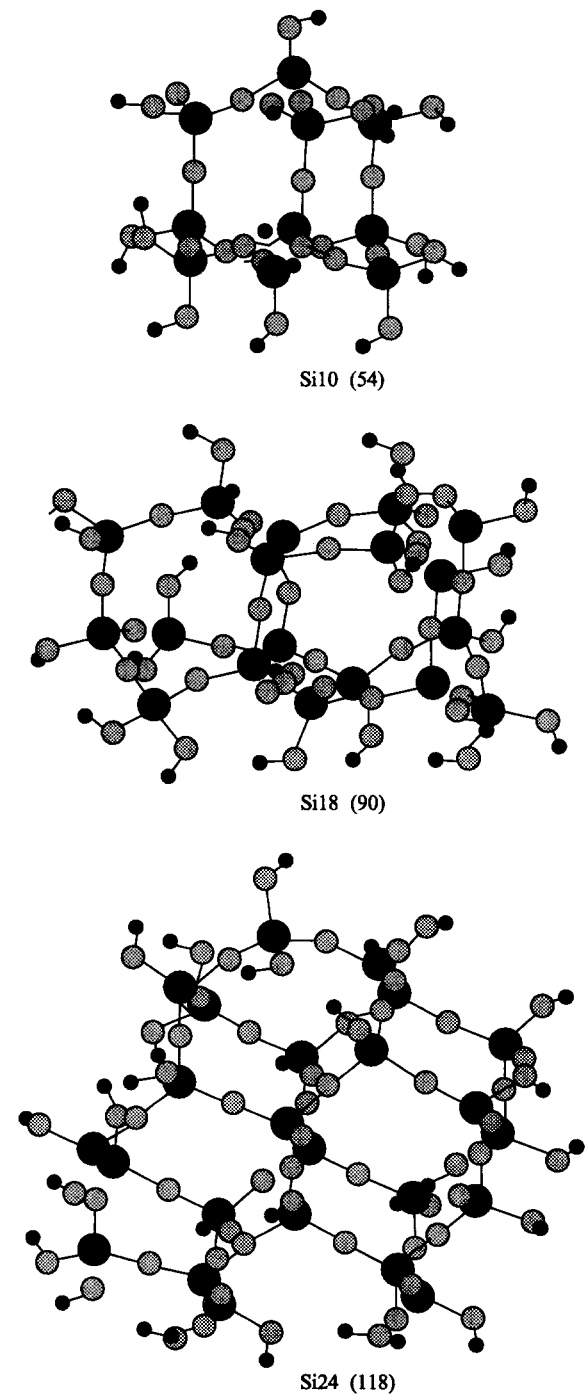


Figure 16. Clusters with a close-packed structure (calculation by the AM1) method.[33]

and are displaced to the periphery. Fig. 16 shows that cyclic close-packed structures contain no silanetriol groups. These groups arise only when a kind of branching of the structure takes place.[33]

Table 4 presents the numerical characteristics of the clusters demonstrating the dynamics of the variation in the numbers of silanol and silanediol groups in the clusters of the close-packed structure. The table shows that there are no $(OH)_1$ groups in the isolated cyclic clusters. These groups appear only in the compactly bound structure of the Si10 cluster. The ratio of the numbers of the $(OH)_1$ and $(OH)_2$ groups still indicates the predominance of the silanediol groups under these conditions. It is known from experimental results that the hydroxyl shell of the aerosil particles may contain not more than 20% of

Table 4. Quantitative characteristics of the model clusters of aerosil.[33]

Cluster	Number of atoms			Number of groups		Linear size/Å	
	Total	Si	O	$(OH)_1$	$(OH)_2$	min.	max.
Rings							
Si3c	18	3	3	–	3	3.57	6.62
Si4c	24	4	4	–	4	3.62	8.11
Si5c	30	5	5	–	5	3.65	9.00
Si6c	36	6	6	–	6	3.62	8.72
Si8c	48	8	8	–	8	5.60	11.34
Si10c	60	10	10	–	10	5.18	13.07
Si14c	84	14	14	–	14	5.18	15.71
Bulk-phase 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

silanediol groups.[5] Thus it is evident that neither the free rings themselves nor the compact structures made up of a small number of rings can serve as an acceptable model of the structure of an aerosil particle. With increase in the size of the cluster, the ratio of the hydroxy-groups changes in favour of silanols (see the Si14 cluster and so on) and tends to increase. This increase is slow, but estimates have shown that, when the selected algorithm for the increase in the size of the cluster is used, the ratio of the numbers of the $(OH)_1$ and $(OH)_2$ groups may reach 5 – 6 in favour of the former when the size of the cluster increases to dimensions comparable with 100 – 200 Å. It is then evident from the analysis of model structures that the silanediol groups exist mainly at the apices of the terminal edges, i.e. on the irregularities of the structure of a real particle. The tendency in the variation of the structure of the hydroxyl shell of the clusters thus discovered means that the specific content of the hydroxy-groups on the surface of aerosil should vary in opposition to the variation of its specific surface (radius), which has in fact been observed experimentally.[109]

The proposed algorithm for the growth of the cluster is undoubtedly not the only one possible — it merely corresponds to the most probable structures of the close-packed amorphous silica, reflecting fully the quaternary coordination of the silicon atoms in the dense structure formed by the 'hexagons'. The irregularity of the structure over the macroscopic distances characteristic of the amorphous state is apparently due to the fact that four-, five-, and six-membered rings adjoin one another among close-packed atoms. However, the considerations presented above concerning the tendency towards the distribution of the functional groups in a real particle remain valid for rings of all sizes.

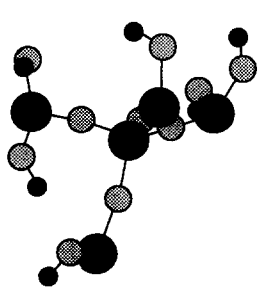


Figure 17. A fragment of the Si18 cluster (calculation by the AM1 method) demonstrating the alternating distribution of the surface Si atoms with the hydroxy-groups and tetrahedral Si atoms coordinated only to the siloxane oxygen atoms.[33]

Taking into account the foregoing, the Si18 cluster may be regarded as the real model of the surface of an aerosil particle. This applies not only to the distribution of the hydroxy-groups but also to the formation of the experimentally established[5] alternating structure comprising silicon atoms in which a silicon atom attached to a hydroxy-group adjoins another surface silicon atom involved in tetrahedral coordination with only four siloxane oxygen atoms (Fig. 17).

On the basis of the results obtained, the following models of the small, medium, and large clusters of the model structures of aerosil may be proposed.

The principal functional group on the surface of aerosil is an isolated silanol group. As a result of this, the simplest model of a small cluster may be a silicon – oxygen tetrahedron based on three silicon atoms and containing one OH group. The interaction of this cluster with water has been considered as the basic model.[15,92,100,110] The results agree satisfactorily with experimental vibrational spectra of water adsorbed on the surfaces of aerosil particles.

A similar small cluster with a silanediol group may serve as the simplest model of isolated silanediol groups on the surface of aerosil. These groups are located on structural irregularities and their contribution to the aqueous and hydroxyl components of aerosil is comparatively small. As shown above, silanetriol groups are foreign to the close-packed aerosil structure and as external formations are naturally unstable; their presence on the surfaces of aerosil particles is hardly possible.

The model Si10 cluster is an example of a cluster of medium size reproducing the packing of small clusters. The Si18 and Si24 model clusters are large clusters which not only model the bulk-phase packing in the core of an aerosil particle but also describe the distribution of the hydroxy-groups on its surface. Apparently a further increase in the size of the cluster is hardly useful because it is unlikely that qualitatively new information would be obtained in view of the small radius of action of the chemical interaction forces.

The structures presented have been used to calculate the vibrational spectra of the core and the hydroxyl component of aerosil and also the spectra of the water adsorbed on them.

c. Vibrational spectra of the core and the hydroxyl component

Fig. 18 presents the experimental AWDS basis spectrum of the aerosil core and two calculated spectra. The latter were obtained with the aid of the COSPECO program pack for computational vibrational spectroscopy.[111] The field strength data were obtained in a quantum-chemical calculation in terms of the AM1 approximation (with the CLUSTER-Z1 program pack). The first spectrum refers to the Si18 cluster (Fig. 18, curve *2*). It has already been stated above that this cluster is a realistic model of a

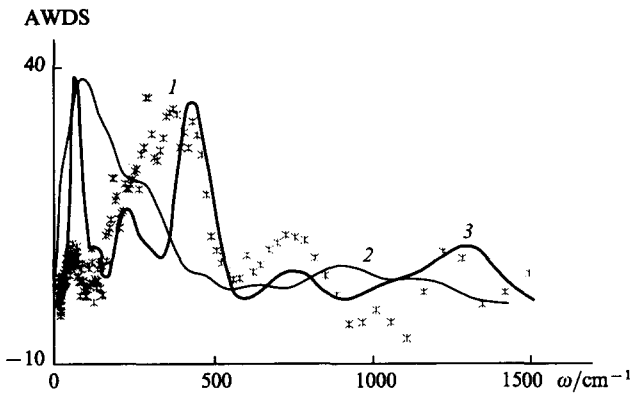


Figure 18. Vibrational spectrum of the aerosil core: (*1*) experimental curve ($T = 10$ K);[25] (*2*) calculation for the Si18 cluster; (*3*) calculation for the Si10ch siloxane chain under cyclic boundary conditions.[103]

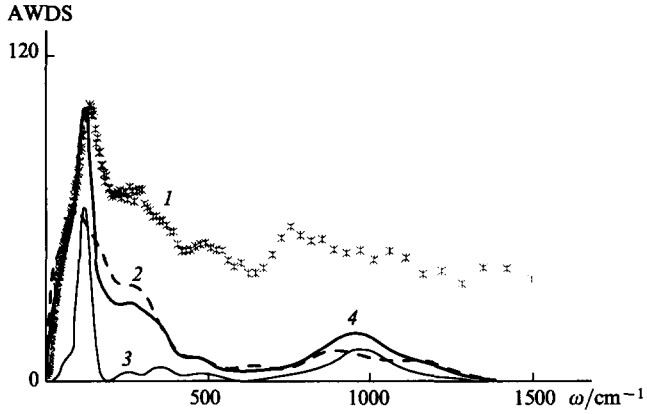


Figure 19. Vibrational spectrum of the hydroxyl coating on aerosil: (*1*) experimental curve ($T = 10$ K);[25] (*2*) calculation for the hydroxyl coating on the Si18 cluster; (*3*) calculation of the surface vibrations of the Si18 cluster; (*4*) the sum of curves *2* and *3*.[103]

large cluster. At the same time, the calculated spectrum differed so much from the experimental one that this appeared discouraging at first sight. Analysis of the causes of the observed discrepancy revealed a completely new problem. The point is that the vast majority of the silicon atoms of this cluster are found to be surface atoms after careful examination, so that their kinematic behaviour differs significantly from the behaviour of the inner atoms while the force constants are fully retained for each selected pair of atoms. In order to eliminate this effect within the framework of the clusters considered, it was necessary to increase their size almost by an order of magnitude, which rendered any computational study unrealistic. However, another approach to the solution of this problem is also possible. In considering the structures of the close-packed Si18 and Si24 clusters, one may note that they consist of a set of Si–O–Si chains inclined to the basis plane† of the clusters. Each three neighbouring chains in sections parallel to this plane form a typical close-packed hexagonal structure. Thus the chain may be regarded as a translationally equivalent structural unit with the aid of which the bulk-phase structure of aerosil may be constructed. Fig. 18 presents the results of the calculation of the vibrational spectrum corresponding to a chain containing ten silicon atoms for cyclic boundary conditions (curve *3*). The force constants in this chain were taken from the Si18 cluster. Evidently, the calculated and experimental spectra agree well. The band at 80 cm^{-1} is an exception. It is due to the out-of-phase translational motion of the silicon–oxygen tetrahedra. With increase in the length of the chain, it splits into an increasing number of components and its maximum diminishes, so that for several hundred silicon atoms it will undoubtedly assume a form consistent with experiment. The complete agreement between the positions of the maxima of all the bands in the calculated and experimental spectra is striking.

Fig. 19 presents the experimental and calculated AWDS spectra of the hydroxyl coating of aerosil. Curve *2* corresponds to the spectrum presented above for the Si18 cluster, which represents the vibrational spectrum of the surface atoms. Curve *3* represents the vibrational spectrum of the atoms bound to the ten $(OH)_1$ groups contained in the Si18 cluster. As stated in Section IV, the hydroxyl component of the AWDS spectrum of aerosil should consist of the vibrational spectra of the hydroxy-groups and the surface core atoms sensitised by these hydroxy-groups as a result of the 'riding effect'. The real AWDS spectrum represents a combination of these spectra with the correct ratio of the hydroxy-groups and surface silicon atoms. Curve *4* in Fig. 19 corresponds to the sum of the spectra *2* and *3* in proportions of 1:1. Evidently, this spectrum agrees very well with the experimental one.

d. Compositional structure and vibrational spectrum of adsorbed water

The reliability of the results of the modelling of the structure of an aerosil particle made it possible to consider in greater detail the problem of the adsorption of water.[93] As stated above, the Si10 cluster belongs to the class of medium-size clusters, which makes it possible to reproduce the real structural correspondence between an isolated functional group and the core of the substance. Fig. 20 presents the optimised structure of this cluster (for further details, see Khavryuchenko and Sheka[93]), interacting with six water molecules (MNDO/H approximation, CLUSTER-Z1 program pack).[97]

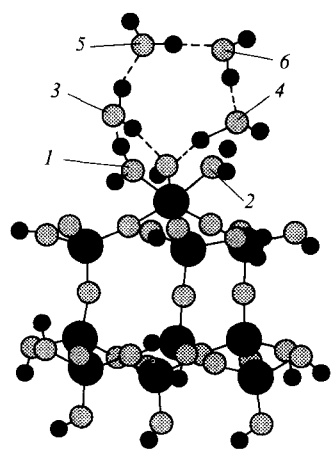


Figure 20. The Si10w6 (72) cluster with six water molecules (calculation by the MNDO/H method).[103]

Water molecules are adsorbed collectively on the aerosil surface, which confirms the conclusion reached as a result of a qualitative analysis of the experimental spectrum of the water adsorbed on aerosil (see Section V). The first two molecules are coordinated to the silicon atom of a silanol group, whereupon its coordination number becomes six. The remaining water molecules are hydrogen-bonded. Fig. 21 presents the

† The introduction of the term basis plane is in this case arbitrary. It implies the section which reveals the hexagon ornament of the structure.

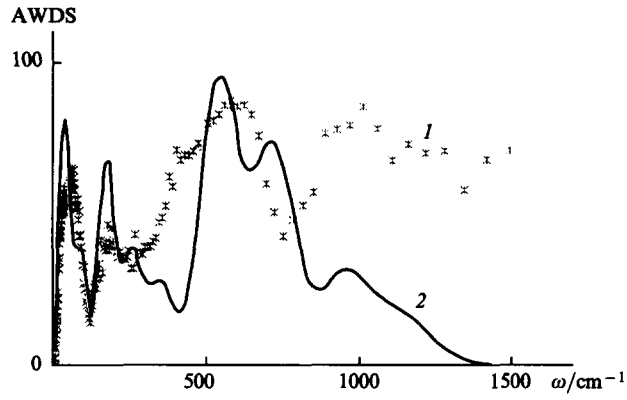


Figure 21. Vibrational spectrum of the water adsorbed on aerosil:[103] (*1*) experimental curve ($T = 10$ K);[25] (*2*) calculation for the Si10w6 cluster.[103]

experimental and calculated AWDS spectra. As in the preceding spectra, the calculated spectra were slightly corrected as regards frequency.

Evidently, the principal features of the calculated and measured spectra agree. The higher intensity of the experimental spectrum compared with the calculated one in the high-frequency region may be associated with the contribution of two and more multiphonon states in the experimental spectrum. The unduly low intensity in the low-frequency region is associated with the fact that the composition of the water adsorption complexes on the surface of aerosil is nonuniform:[93] apart from the centres containing six molecules, there are centres in which the number of molecules ranges from one to five. The problem of obtaining complete agreement between the calculated and experimental spectra thus includes the problem of the determination of the number of these centres.

The satisfactory agreement obtained between the calculated and experimental basis spectra of the aerosil components on the whole indicates the legitimacy of the models presented, describing the close-packed structure of amorphous silica.

2. Computational modelling of silica gels

Silica gel is known to be characterised by a considerable variability of its properties.[2] This applies both to the poor reproducibility of the product already in the stage involving its preparation and to the variation of its properties and their sensitivity to external conditions. One may claim that the principal property of silica gel is the 'flow' of its structure, so that each silica gel specimen does not represent the same and fixed structural state of amorphous silica but constitutes an 'instantaneous photograph' in a chain of structural transformations. In view of the foregoing, the problem of the modelling of the silica gel structure is by no means simple, since it is not known which particular 'instantaneous photograph' of the real structure is to be reproduced. Proceeding to the modelling of the structural clusters of silica gel, Khavryuchenko and Sheka [34] did not have as their aim the reproduction of a particular structural configuration. Their aim was to find answers to the following principal questions which are associated nowadays with the silica gel structure,[28] namely: how are the silica gel pores formed; on what factors does their size depend; why do the vibrational spectra of the core and hydroxyl shell of silica gel depend on the pore size; what does the experimentally observed adsorbed and quasi-free water in the pores represent; why does the vibrational spectrum of the adsorbed water not depend on the pore size.

The structure of silica gel (cyclosilica) is based on rings of silicon–oxygen tetrahedra of different size. It has been noted that the loose structure characteristic of silica gel is made up of rings of fairly large size. The structural models of several such large rings were first constructed and optimised within the framework of the MM2 program[112] and were then additionally optimised by the AM1 method with the aid of the CLUSTER-Z1 program pack.[97] It was found that, with increase in its size, the structure of the ring increasingly deviates from planarity. At the same time, an appreciable tendency towards the 'cellular subdivision' of the ring with formation of smaller rings is observed.

It is natural to suppose that the silica structure is produced as a result of rings of different size being joined together. It is noteworthy that the rings must be sufficiently large, since the condensation of rings with four, five, and six silicon atoms leads to the formation of close-packed structures of the type of aerosil or quartz glass.[33] There is no doubt that these small rings also participate in the formation of the silica gel structure, but they are most likely to play merely a binding role.

Large rings are as a rule highly distorted and nonplanar, so that on combination of, say, two such rings, they may 'fold up'. Bearing in mind that the gel is formed in the presence of solvating alkali metal ions, it is logical to suppose that the main role of the ion is to stabilise such a structure. Fig. 22 presents one of the possible structures formed by two rings containing seven and eight silicon atoms and having two common siloxane bonds. Evidently, these rings represent the 'folds of a half-open blister'. The presence of a solvated ion within this structure probably prevents its folding up and promotes the extension of the rings. On this basis, it has been postulated that silica gel consists of a solid framework having the structure of an open network similar to the pattern on a poorly inflated football with an irregular shape.[34] In contrast to the cells on the usual football or the regular fullerene structures of the C_{60} and C_{70} types, the cells in this framework do not consist of ideal hexagons and pentagons but are nonplanar rings of silicon–oxygen tetrahedra of different size. The retention of the form of the framework during synthesis is ensured by the solvated ions (one or several), after the removal of which pores of different size remain.

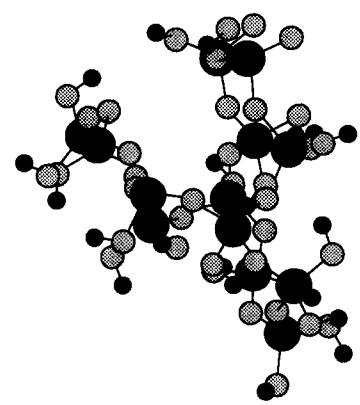


Figure 22. The Si13dc(75) cluster consisting of two rings (Si7c and Si8c) (initial model).[34]

It is important to note that the formation of the rings, contact between them, and the formation of the framework bounding the pore are undoubtedly statistical processes. They are naturally subject to the influence of external conditions. Thus certain rings may be opened in some cases. Their number is determined, in particular, by the concentration of acid. This probably explains the difficulty of reproducing the silica gel structures, mentioned above. The aggregation of such elementary frameworks in accordance with the close-packing principle, applied to spherical or quasi-spherical particles, leads in its turn to the formation of a globular mesostructure, which has in fact been observed experimentally.[2]

In conformity with the foregoing, the hierarchy of clusters describing the silica gel structure is as follows. The small structures modelling the peripheral functional groups (in the given case hydroxy-groups) are closed and open cyclic structures comprising eight and more silicon atoms as well as the sites of contact between two rings. The clusters of medium size, reproducing the packing of small clusters and the short-range distribution of atoms, are model macrocyclic structures, which may differ in the type of junctions incorporating one, two, and more silicon atoms. The large clusters, representing the distribution of atoms over long distances and the distribution of functional groups, may be considered to comprise a fragment of the surface of the framework consisting of 2–3 junctions.

The proposed model of the silica gel structure does not conflict with the known macroscopic properties of this substance. Furthermore, it makes it possible to explain qualitatively a number of microscopic properties which have not been accounted for hitherto, including vibrational spectra. It is seen from the models presented that the silica gel core consists of an open network comprising chains of siloxane bonds. The large width of the size distribution of the rings in this structure and its lability are evident, as a result of which there is a possibility of the variability of the distribution of the Si–O–Si and O–Si–O bond angles from specimen to specimen, with which the principal changes in the observed spectra of the core are associated (Fig. 8).[26]

The hydroxyl components of silica gels represent a set of three silicon-hydroxyl groups, namely the silanediol groups of the closed rings, the silanetriol groups at the ends of the opened rings, and the silanol groups at the points of contact between the rings. Thus their vibrational spectra are compound. They depend on the number of silicon-hydroxyl groups of different types. On the other hand, it is evident that the ratios of the numbers of these groups are statistically distributed over a fairly wide range of values and may be different even for different fractions of the products of the same technological cycle. It has been postulated[34] that the difference between the observed vibrational spectra of the hydroxyl components of the silica gels SG100 and SG20, presented in Fig. 9, is in fact associated with this factor.

As regards the vibrational spectrum of the adsorbed water (Fig. 13*b*), its constancy under conditions such that the adsorption centres are heterogeneous and compete with one another reflects the fact that the same centre wins this competition in each specimen. Since such a centre is one of the three possible silicon-hydroxyl groups, it is common to all the specimens. Calculations, which are being continued, will make it possible to discover which particular silicon-hydroxyl groups determine the adsorption of water in silica gel. In contrast to aerosil, in the structures of silica gels both identical and different silicon-hydroxyl groups adjoin one another, so that the simplest small clusters, representing isolated groups in aerosil, cannot be regarded as suitable structural models. This is why the rings themselves or fairly extended fragments of these rings as well as their junctions should be considered as small clusters in the case of silica gel.

3. Computational modelling of aerogel

The simplest model of the structure of aerogel (a polysilica) is a chain of silicon–oxygen tetrahedra.[32] Each silicon atom in this chain is linked to two oxygen atoms of the siloxane chain and to two hydroxy-groups. Thus the principal functional group of the hydroxyl component of aerogel, consisting of isolated chains, should be a silanediol group. However, comparative analysis of the basis vibrational spectra of the hydroxyl components of different disperse silicas (see Section V) established that the main element of the hydroxyl component of aerogel is a silanol group. It is natural to postulate that aerogel is not a monopolysilica made up of single chains but is a dipolysilica or a more complex one (see Liebau's classification[94]), the structural fragments of which are double or more complex strips. In view of the large number of capillary cavities in the macrospecimen, it is difficult to suppose that it consists of multichain strips, since its density should then be fairly high. It is most likely that the number of chains in the strips hardly exceeds 2–3. One of the possible structures of this kind is presented in Fig. 23. The structure is nonplanar. Attention should be drawn to the quasi-regular structure of the cells in the middle section of the chain. The principal size parameter of the model cluster is the length of the strip and therefore the boundary between a cluster of medium size and a large cluster is fairly arbitrary. The point of junction of several strips, one of the possible models of which is illustrated in Fig. 24, constitutes a special site within the structure.

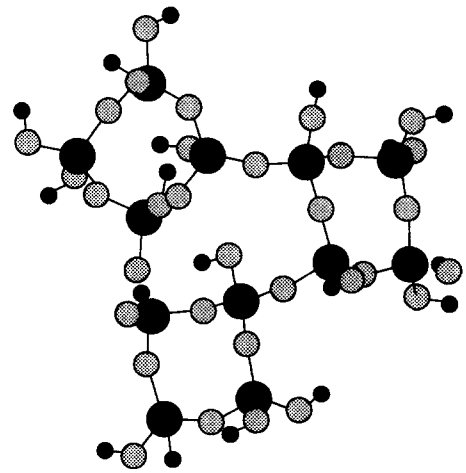


Figure 24. Cluster involving the junction of the Si12b(63) strips (initial model).[35]

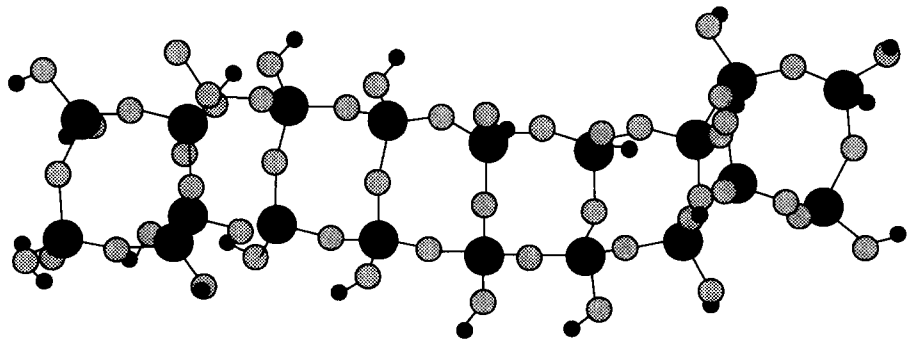


Figure 23. The Si20b(96) strip cluster (initial model).[35]

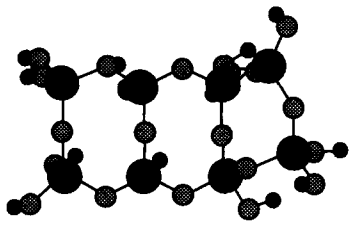


Figure 25. A small cluster of the structure of aerogel Si8b(42) (initial model).[35]

The main functional groups on the periphery of the strip are silanols. Nevertheless, it is evident from the analysis of the model of the aerogel structure that the cluster containing an isolated silanol group and constituting a satisfactory model of the silanol groups of aerosil cannot model the functional groups of aerogel. The reason for this is the fact that, in contrast to aerosil, the silanol groups in aerogel are arranged in a sequence where they adjoin one another at a distance of ~ 3.5 Å, so that several groups participate in the interaction of the chain-strip with water. Another cause is the significant different between the core chain structure of the siloxane bonds of aerogel and the close-packed aerosil structure. As a consequence of this, the small cluster, needed according to Khavryuchenko and Sheka[35] for the modelling of the functional groups and for the consideration of the interaction of aerogel with water, must have a fairly complex structure. One of the possible models of this cluster is illustrated in Fig. 25.

The model structures of aerogel presented here agree well with the existing ideas about its structure[3] specified in detail at the atomic level. At the same time, they make it possible to explain a distinctive feature of the vibrational spectra of its components — the narrowness of their bands. This form of the spectra is known to be characteristic of polymers,[89] which yet again confirms that the model presented for this silica is reasonable.

* * *

The physicochemical phenomenon examined above has been called technological polymorphism. This verbal construction does not imply simply following the fashion for new terms but has proved to have a rich inner significance. The polymorphism of amorphous silicas has been established reliably from the vibrational spectra which constitute 'fingerprints' of the structure of the substance. The existence of such polymorphism is well known for labile systems.[113] One could confine oneself to this reference and attempt to describe qualitatively the disperse amorphous silicas investigated in terms of the degree of their lability. However, the path based on the properties of the substance which are characteristic of it alone and which permit the introduction of a characteristic numerical parameter (or parameters), with the aid of which it is possible to achieve their classification, proved much more productive. Thus, in the case of amorphous substances with a molecular structure, success in the understanding of the polymorphic modes of the amorphous state was achieved by considering these modes as the corresponding prototypes of the mesophases in the liquid crystal state.[113] The classification of the amorphous phases made it possible to discuss immediately specific structural models of the substance. In the case of disperse silicas, such a classification guide proved to be the technology of the preparation of the products and the classification parameters were the dimensionality and multiplicity of the structures formed on packing the silicon–oxygen tetrahedra. The structural classification modes established made it possible not only to take a new look at various representatives of the substance considered, but also to propose a fairly unambiguous algorithm for the modelling of the corresponding structures.

Another indication of the fruitfulness of the terminology introduced here is the possibility of extending it to the entire class of nanomaterials to which the silicas presented above belong. A characteristic feature of these substances is the considerable contribution of surfaces and interfaces to their structure. This factor renders, in its turn, the nanomaterials exceptionally sensitive to the technology of their preparation and to the conditions under which they are kept. As is well known to technologists, because of this the chemical formula of the substance in reality describes a whole family of nanoproducts. The situation frequently arises where the investigator of the fundamental effects in such materials is extremely concerned by the 'dirt' on the surface of the specimen. However, this 'dirt' on the surface and on the interfaces of the nanomaterials obeys strictly the laws of chemical interaction and can be identified or predicted with the aid of a combined study of the same technological polymorphism. This approach has been applied successfully, for example, in the case of the family of silicon nitride powders of different origin.[101] Particular attention should be drawn to the fact that in this combined approach quantum-chemical modelling is converted into an active computational procedure and acquires the importance of an analysing instrument. This is particularly important in connection with the gradual onset of the era of nanotechnology, which brings our accustomed material world to the level of practical manipulation of atoms.

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