CONSTRUCTION OF VIBRATIONAL BASIS SPECTRA OF MULTICOMPONENT SYSTEMS

1. AEROSIL

I. V. Markichev, I. Natkanets, and E.F. Sheka

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Aerosil (pyrogenous dispersed silica) is considered as a three-component system consisting of a silica core, hydroxyl shell, and adsorbed water. Factoring was carried out for its amplitude-weighted vibrational state density (AWSD) spectra obtained using inelastic neutron scattering at 10 K into the spectra of the components comprising this system. The factoring method used is based on the postulate of lack of correlation of the basis spectra. The factoring was carried out by the construction of physically significant basis spectra satisfying the zero linear correlation coefficient criterion for a set of AWSD spectra of the starting and modified samples of Aerosil A380.

Dispersed amorphous silica is obtained by condensation and polymerization accompanied by decomposition (in most cases, hydrolysis) of silicon tetrahalides or their orthoorganic esters as well as salts of silicic acid. Polymerization leads to the formation of siloxane chains (SiOSi) and nonplanar rings of different sizes. These chains form an amorphous structure in space (core or skeleton) of dispersed silica. The same structural elements form its surface. Excess valence is found for some of the surface silicon atoms since their bonds are saturated only from the internal side. This excess is saturated in the presence of water molecules by hydroxyl groups, leading to a uniform coating of the surface of dispersed silica by a hydroxyl shell. Under atmospheric conditions and in the presence of water found during the manufacture of silica, hydroxylated silica adsorbs a considerable amount of water. This adsorbed water forms a hydrate shell. Optical and chemical studies indicate that both the hydrate and hydroxyl shells as well as the silica core retain their chemical individuality to a considerable extent in dispersed silica samples. Thus, industrial dispersed silica products may be seen as composites consisting of the three abovementioned components.

Studies of the structurally dynamic properties of the surface zone of dispersed silicas have been carried out for more than 50 years. Chemical methods have long been used in such studies, while spectrometric methods were introduced at the end of the 1960's, including IR and Raman vibrational spectroscopy and NMR spectroscopy. However, in light of experimental difficulties as well as difficulties in the interpretation of the results, the data obtained were largely qualitative. The major progress achieved in the past decade in computer chemistry permits us to attempt a quantitative interpretation of the results. However, the conversion of computer chemistry into a working tool for obtaining a quantitative model of the structurally dynamic properties has been complicated by the circumstance that the object of investigation is always a cluster fragment of the system studied. As a consequence, an experimental analog must be found for this computational fragment. Silica computational fragments have long been selected among three types of structural formations: siloxane core clusters, hydroxyl shell, and adsorption sites interacting with water molecules. The abovementioned three silica components are sets of these structural formations. Thus, the measurement of their vibrational spectra is a necessary condition for the development of computational modelling. In the present work, we attempted to obtain the vibrational spectra of the components of globular dispersed silica (Aerosil).

The inelastic scattering of thermal neutrons (ISN) is a very efficient method for the study of vibrational spectra. At first glance, this method would seem unsuitable for the study of the surface zone due to the great length of free flight of neutrons within matter (on the order of 10^{-2} m). However, if the specific surface of the substance is great and coated with

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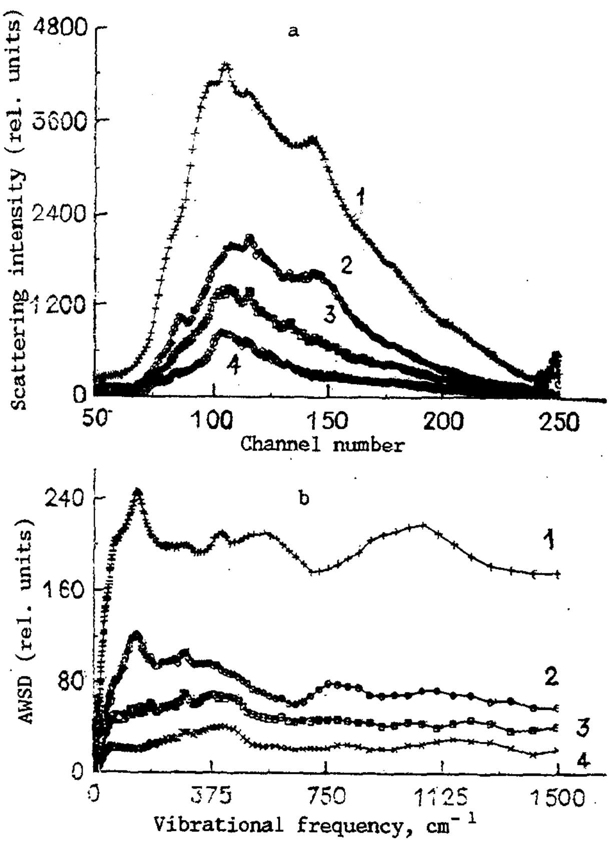

Fig. 1. Experimental vibrations spectra of the A380 family at 10°K: a) flight time spectra and b) AWSD spectra; 1) air-dried; 2) dried; 3) deuterated; 4) glass.

hydrogen-containing molecules, the situation is improved since the surface vibrations become available for observation along with bulk vibrations. In this case, the situation is favorable not only for the vibrations of hydrogen-containing adsorbates themselves but also for vibrations of the surface atoms of the non-hydrogen-containing base, entraining adsorbate hydrogen atoms as the result of the "implant effect."

From this viewpoint, the saturation of the surface zone of dispersed silica by hydrogen atoms and the large contribution of the atoms of this zone to the total number of atoms favors the use of ISN spectroscopy for the study of the vibrational spectra of this composite system. The method for the construction of basis vibrational spectrum of a multicomponent system to determine the vibrational spectra of Aerosil components was described in detail in our previous work [1]. This work will be indicated in references as 1, while references to the equations in it will be given with double numbering such as (1.2).

1. DESCRIPTION OF THE SAMPLES

The industrial pyrogenous dispersed silica product (Aerosil) [2] was obtained in the high-temperature hydrolysis of $SiCl_4$ in an oxygen—hydrogen flame in the following reaction

$$SiCl_4 + O_2 + H_2O \rightarrow SiO_2 + 4HCl.$$

The powder is an agglomerate of small spherical particles. The range of the relative particle size is ±40% [2]. The brand of Aerosil is given in accord with its specific surface. The specific surface of sample A380 was 380 m^2/g. The mean particle diameter usually evaluated using the following equation

$$D\,[\text{Å}] = 6\cdot 10^4/\rho\cdot S,$$

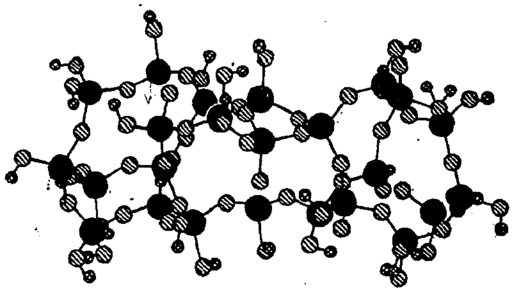

Fig. 2. Cluster of globular silica [9].

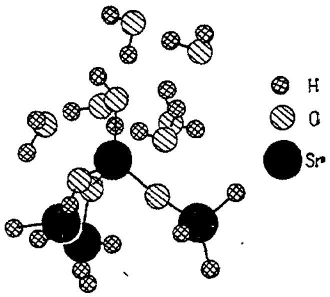

Fig. 3. Silanol site of water adsorption in Aerosi
OH—$Si(OSiH_3)_3$ with seven water molecules [9].

where D [Å] is the particle diameter angstroms, ρ is the sample density in g/cm^3, and S is the specific surface in m^2/g, should be 70 Å for the sample studied. However small-angle x-ray scattering (SAXS) measurements [3] gave a value of 150 Å. This starting industrial product will be designated *air-dried* A380. Three modifications were obtained from this sample.

The starting A380 sample was heated in the air for 6 h at 750°C give *dried* A380.

The starting sample of A380 was also subjected to isotope exchange of the hydrogen atoms in the hydroxyl and hydrate shells by deuterium according to the following scheme:

heating in the air 750°C, 4 h	cooling in heavy water vapor 24 h to room temperature
heating in the air 750°C, 4 h	cooling in heavy water vapor 24 h to room temperature
heating in the air 750°C, 4 h	cooling in heavy water vapor 24 h to room temperature

This procedure gave *deuterated* A380.

Starting A380 was sintered at 1200°C to give a monolithic glassy substance designated A380 *glass*. These four samples form the Aerosil A380 family.

The flight time ISN spectra were obtained on a KDCOG-1M inverse geometry spectrometer and treated by the standard procedure [4]. The background was subtracted by construction of a basis using the zero correlation coefficient criterion (ZCC criterion) [1]. The ISN spectra of the Aerosil A380 family taken at 10 K are given in Fig. 1a, while the corresponding doubly amplitude-weighted state density (AWSD) spectra obtained using the VIS program [4] in accord with Eq. (1.18) and normalized relative to 100 g sample and 1 h measurements are given in Fig. 1b. The spectral parameters and discussion of the temperature dependence are given in our previous work [5].

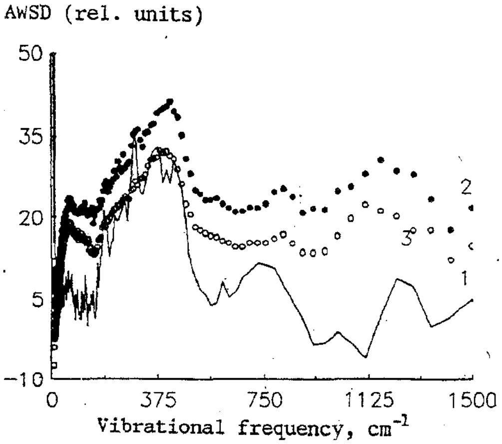

Fig. 4. AWSD spectra of the core of Aerosil A380 at 10 K: 1) partial spectrum $Sp_3^{(1)}$ (variant 1); 2) spectrum of A380 glass $Sp^{(4)}$; 3) spectrum of quartz glass, experiment [5].

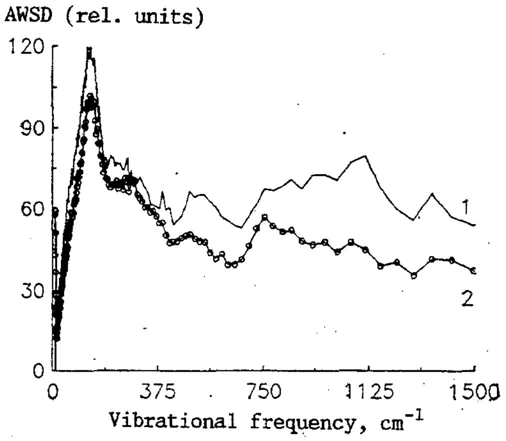

Fig. 5. AWSD spectra of hydroxyl shell of A380 at 10 K: 1) partial spectrum $Sp_2^{(2)}$ (variant 1); 2) difference of experimental spectra $DSp^{(24)} = Sp^{(2)} - Sp^{(4)}$.

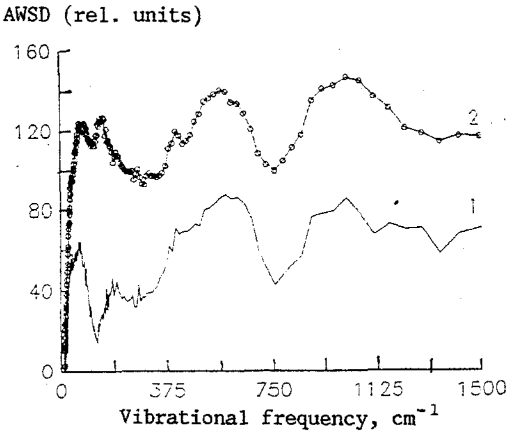

Fig. 6. AWSD spectra of adsorbed water of A380 at 10 K: 1) partial spectrum $Sp_1^{(1)}$ (variant 1); 2) difference of experimental spectra $DSp^{(12)} = Sp^{(1)} - Sp^{(2)}$.

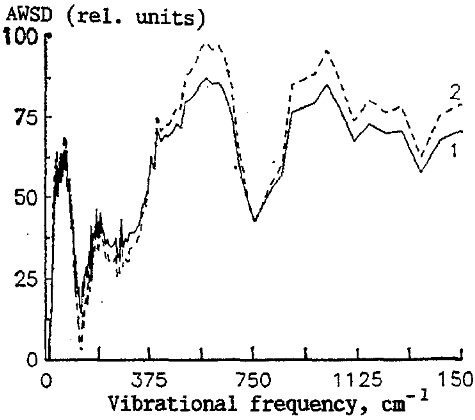

Fig. 7. Partial AWSD spectra of the adsorbed water on A380 at 10 K; 1) variant 1; 2) variant 2.

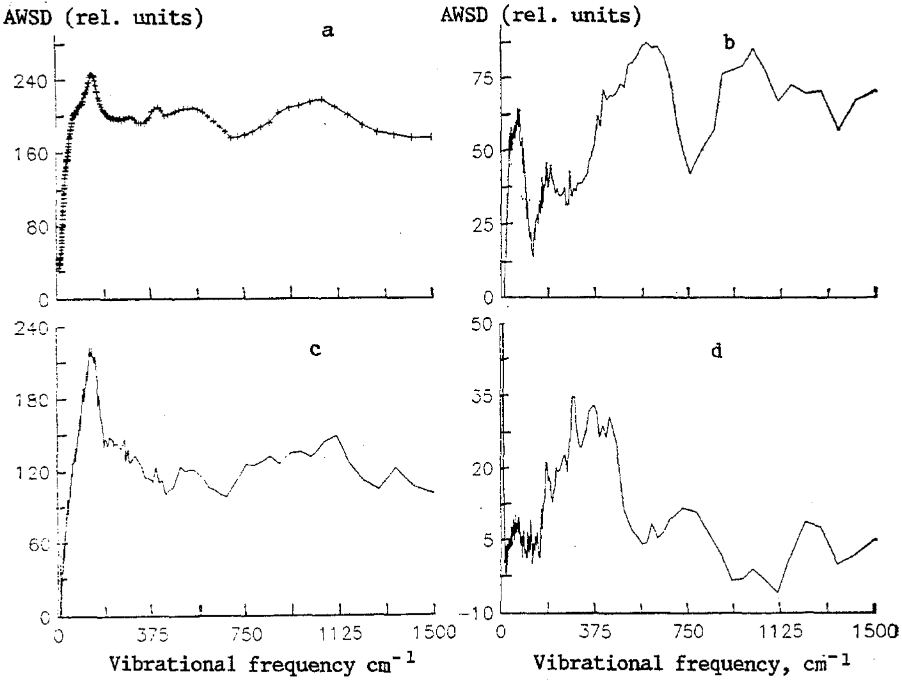

Fig. 8. AWSD spectra of *air-dried* Aerosil A380 and partial spectra of its components at 10 K: a) starting Aerosil; b) adsorbed water; c) hydroxyl shell; d) core.

2. CHARACTERISTICS OF THE BASIS SPECTRA OF AEROSIL COMPONENTS

As noted above, the industrial A380 product is a complex system consisting of three components: a silica core, hydrate shell, and hydroxyl shell [2]. Optical and chemical studies [2, 6-8] have indicated that these three components significantly retain their individuality, which suggests the existence of three basis or characteristic vibrational spectra of the Aerosil components and permits us to consider the total system of its normal coordinates consisting of three subsystems, which are independent to a first approximation. These spectra in the terminology adopted in our previous work [1] form a triplet of basis spectra $\{Sp_i(r)\}$, where the subscripts $i = 1, 2, 3$ correspond to the spectra of the hydrate shell, hydroxyl shell, and silica core, respectively.

The simplest physical sense is found for basis spectrum Sp_3, which corresponds to the bulk vibrations of the silica core. Figure 2 shows one of the models of the core corresponding to the globular structure of Aerosil [9]. In addition to the water and hydroxyl group vibrations in the hydrate and hydroxyl shells, vibrations are also found for atomic groups interacting with these systems. Thus, the vibrational spectrum of the hydrate layer, which mostly consists of the vibrations of adsorbed water, should also have vibrations for the water adsorption site. One of the possible models for this site obtained in quantum chemical calculations is shown in Fig. 3. The vibrations of the set of such fragments comprise basis spectrum Sp_1.

Only some of the surface hydroxyl groups in Aerosil participate in the adsorption of water [2], while the major fraction of these groups remains free. It is specifically these groups, which form the hydroxyl shell. In addition, the hydrogen atoms of these groups are involved through the "implant effect" [10] in the vibrations of the surface silicon atoms and of the silica core oxygen atoms. Thus, the basis spectrum of the hydroxyl shell Sp_2 also includes the spectrum of the surface vibrations of the core sensitized by the hydrogen of the hydroxyl groups.

The experimental AWSD spectra of the starting and modified Aerosil form a set $\{Sp^{(j)}(\omega)\}$, in which the values of $j = 1, 2, 3, 4$ correspond to the spectra of *air-dried* A380, *dried* A380, *deuterated* A380 and A380 Aerosil *glass*. In accord with Eq. (1.1), assuming a linear system, each experimental spectrum $Sp^{(j)}$ may be factored into the spectra of the components

$$Sp^{(j)} = \sum_{i=1}^{m} k_i^{(j)} \mathrm{Sp}_i, \tag{1}$$

where spectra Sp_i are the basis spectra described above.

The factoring of the vibrational spectra (Eq. (1)) after renormalization into the partial spectra of the *air-dried* A380 sample (see Eq. (1.12)) will appear as follows:

$$\begin{aligned} Sp^{(1)} &= \mathrm{Sp}_1^{(1)} + \mathrm{Sp}_2^{(1)} + \mathrm{Sp}_3^{(1)}, \\ Sp^{(2)} &= \alpha_1 \mathrm{Sp}_1^{(1)} + \alpha_2 \mathrm{Sp}_2^{(1)} + \alpha_3 \mathrm{Sp}_3^{(1)}, \\ Sp^{(3)} &= \beta_1 \mathrm{Sp}_1^{(1)} + \beta_2 \mathrm{Sp}_2^{(1)} + \beta_3 \mathrm{Sp}_3^{(1)}, \end{aligned} \tag{2}$$

where spectra $Sp_i^{(1)}$ are the partial spectra of the hydrate shell, hydroxyl shell, and silica core. Let us assume that these spectra satisfy the ZCC criterion in form (1.13).

We should note that the spectrum of the *deuterated* sample $Sp^{(3)}$ should also have terms $Sp_4 = Sp_{D_2O}$ and $Sp_5 = Sp_{OD}$, corresponding to the AWSD spectra from heavy water and deuterated hydroxyl groups. However, since the total fraction of atoms of the surface zone is small and since the neutron scattering cross-section on the deuterium atoms is much less than the corresponding cross-section on protium, the contribution of these terms may be neglected to a first approximation.

Apart from system (2), we still have spectrum $Sp^{(4)} \simeq Sp_3^{(1)}$. The basis for this is the uncertainty concerning the extent, to which the spectrum of the monolithic core coincides with the spectrum of the core of the particles. This question will be examined in greater detail below.

The relationships between the coefficients of system (2) must be determined in order to select the pathways for the construction of the basis in form (1.3). Parameters α_3 and β_3 are determined by the natural circumstance that the partial spectrum of the silica core is the same for all the samples, i.e.,

$$\mathrm{Sp}_3^{(1)} = \alpha_3 \mathrm{Sp}_3^{(1)} = \beta_3 \mathrm{Sp}_3^{(1)} \quad \text{or} \quad \alpha_3 = 1,\ \beta_3 = 1. \tag{3a}$$

The literature data [2] indicate that the adsorbed water and a portion of the hydroxyl groups are eliminated from the Aerosil surface upon drying at 750°C. Thus, the following relationships are established:

$$\alpha_1 = 0, \alpha_2 < 1. \tag{3b}$$

The weighting contributions of the partial spectra of water and the hydroxyl shell in the spectrum of the *deuterated* sample $Sp^{(3)}$ should be much less than unity since the intensity of scattering in this sample due to neutron scattering in the silica

TABLE 1. Set of Factoring Coefficients of Vibrational Spectra*

	Hydrate shell $Sp_1^{(1)}$	OH shell $Sp_2^{(1)}$	Core $Sp_3^{(1)}$
$Sp^{(1)}$ air-dried	$\underline{1}$	$\underline{1}$	$\underline{1}$
$Sp^{(2)}$ dried	**0**	*0,54*	**1**
$Sp^{(3)}$ deuterated	*0,21*	*0,21*	**1**

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*The underlined values were taken by definition; the values in heavy type are from physicochemical data.

core and residual hydrogen atoms is much less than the intensity of scattering in the *air-dried* sample, which follows from Fig. 1. Thus,

$$\beta_1 << 1, \beta_2 << 1. \tag{3c}$$

The relative content of atoms substituted as the result of deuterium exchange in the hydrate and hydroxyl shells is approximately identical. Thus,

$$\beta_1 = \beta_2 = \beta. \tag{3d}$$

Hence, we obtain a system of conditions placed on the coefficients of the system of equations (2), which has the following form:

$$\begin{gathered} \alpha_3 = 1, \quad 0 < \beta_1 < 1; \\ \beta_3 = 1, \quad 0 < \beta_2 < 1; \\ \alpha_1 = 0, \beta_1 = \beta_2 = \beta; \\ \alpha_2 < 1. \end{gathered} \tag{4}$$

In addition to Eqs. (4), the integral intensities of the experimental and basis spectra are parameters of the problem.

3. CONSTRUCTION OF THE BASIS: VARIANT 1

Following the procedure described in Section 1, let us construct the difference spectrum

$$DSp^{(13)} = Sp^{(1)} - Sp^{(3)}.$$

This spectrum is a linear combination of basis spectra Sp_1 and Sp_2 and, in accord with Eqs. (4), have the following form:

$$Dsp^{(13)} = (1 - \beta)Sp_1^{(1)} - (1 - \beta)Sp_2^{(1)}.$$

Let us construct the residual spectrum

$$RSp^{(113)} = Sp^{(1)} - \alpha^{(113)}DSp^{(13)}$$

the require that it correlate with the spectrum $DSp^{(13)}$, i.e., that the following condition hold

$$C(RSp^{(113)}, DSp^{(13)}) = 0.$$

Let us use Eq. (1.10) to find coefficient $\alpha_0^{(113)}$. As a result, we obtain the spectra

$$\alpha_0^{(113)} DSp^{(13)} = \mathrm{Sp}_1^{(1)} + \mathrm{Sp}_2^{(1)},$$
$$R_0 Sp^{(113)} = \mathrm{Sp}_3^{(1)}.$$

Partial spectrum $\mathrm{Sp}_3^{(1)}$ is given in Fig. 4 along with the experimental spectra of the Aerosil glass $Sp^{(4)}$ and quartz glass [5]. This figure indicates that the calculated spectrum of the core is similar in form and absolute intensity in the region of the major peak to the spectra of both amorphous monolithic glasses. The observed differences will be discussed below.

Let us now examine the difference spectrum

$$DSp = Sp^{(2)} - Sp_3^{(1)}.$$

According to Eq. (4), this spectrum is equal to $\alpha_2 \mathrm{Sp}_2^{(1)}$, i.e., is the partial spectrum of the hydroxyl shell in the spectrum of *dried* A380. This spectrum is shown in Fig. 5. For comparison, the difference spectrum $DSp^{(24)} = \mathrm{Sp}^{(2)} - \mathrm{Sp}^{(4)}$ is also given, which, assuming that spectrum $Sp^{(4)}$ describes the silica core of the Aerosil particles and spectrum $Sp^{(2)}$ describes dehydrated and partially dehydroxylated Aerosil, also is the partial spectrum of the hydroxyl shell in $Sp^{(2)}$. This figure shows that both spectra are virtually identical. The difference in the spectra above 450 cm^{-1} is related to differences in the subtracted core spectra (see Fig. 4).

Using the difference spectrum obtained above $\alpha_0^{(113)} DSp^{(13)} = \mathrm{Sp}_1^{(1)} = \mathrm{Sp}_2^{(1)}$ and the partial spectrum $\mathrm{Sp}_2^{(2)} = \alpha_2 \mathrm{Sp}_2^{(1)}$, let us construct the residual spectrum

$$RDSp = \mathrm{Sp}_1^{(1)} + \mathrm{Sp}_2^{(1)} - \alpha \mathrm{Sp}_2^{(2)}$$

and require satisfaction of the condition that this spectrum not correlate with spectrum $\mathrm{Sp}_2^{(2)}$ in the form: $C(RD\mathrm{Sp}, Sp^{(2)}) = 0$. Having determined α_0 in accord with Eq. (1.10), we obtain

$$\alpha_0 \mathrm{Sp}_2^{(2)} = \mathrm{Sp}_2^{(1)} \text{ and } R_0 DSp = Sp_1^{(1)}.$$

The partial spectrum of adsorbed water is given in Fig. 5. along with the difference spectrum $D\mathrm{Sp}^{(12)} = Sp^{(1)} - Sp^{(2)}$, which, according to our concept of the system studied, should consist of spectrum $\mathrm{Sp}_1^{(1)}$ and the spectrum of the hydroxyl group eliminated upon drying. This figure indeed shows great similarity between spectra $DSp^{(12)}$ and $\mathrm{Sp}_1^{(1)}$ although the contribution of spectrum $\mathrm{Sp}_2^{(1)}$ to spectrum $DSp^{(12)}$ is undoubtedly significant.

Thus, basis of system (2) is constructed and the set of factoring coefficients $k_i^{(j)}$ of the system of the experimental spectra relative to this basis is given in Table 1.

CONSTRUCTION OF THE BASIS: VARIANT 2

The construction of the basis spectra of the Aerosil components may be carried out by another method. Let us construct the spectrum

$$DSp^{(12)} = Sp^{(1)} - Sp^{(2)}.$$

According to Eqs. (2) and (4), this spectrum is a linear combination of two basis spectra:

$$DSp^{(12)} = \mathrm{Sp}_1^{(1)} + (1 - \alpha_2)\mathrm{Sp}_2^{(1)}.$$

In turn, the spectrum of *dried* A380 is a linear combination of basis spectra $Sp_2^{(1)}$ and $Sp_3^{(1)}$

$$Sp^{(2)} = \alpha_2 Sp_2^{(1)} + Sp_3^{(1)}. \tag{5}$$

Let us introduce an auxiliary "construction spectrum" Sp, which satisfies the following conditions:

a) spectra $DSp^{(12)} - Sp$ and $Sp^{(2)} + Sp$ should not correlate, i.e.,

$$C(DSp^{(12)} - Sp, Sp^{(2)} + Sp) = 0; \tag{6}$$

b) spectrum Sp is a linear combination of experimental spectra

$$Sp = aSp^{(1)} + bSp^{(2)} + cSp^{(3)}. \tag{7}$$

Let us search for a solution in the form $Sp = \gamma Sp_2^{(1)}$. This spectrum clearly satisfied condition (6) since

$$C(DSp^{(12)} - Sp, Sp^{(2)} + Sp) = C(Sp_1^{(1)}, Sp_2^{(1)}) + C(Sp_1^{(1)}, Sp_3^{(1)}) = 0 \tag{8}$$

Substituting Eq. (7) into Eq. (6) and removing the condition of lack of correlation, we obtain a quadratic equation for coefficients a, b, and c. Using Eq. (7) and system (2), we obtain the formula

$$a + b + c = 0, \tag{9}$$

which guarantees the lack of a contribution of spectrum $Sp_3^{(1)}$ to the spectrum sought Sp. The second equation relates the integral intensity I of spectra Sp according to Eq. (7) to the integral intensities of the experimental spectra in the form

$$I = a\varphi^{(1)} + b\varphi^{(2)} + c\varphi^{(3)}. \tag{10}$$

Equation (8) shows that the introduction of the construction spectrum permits us to determine the spectrum of the hydrate shell. Hence, its intensity is related to the integral intensity of the spectrum of this shell I_1, specifically

$$I = \varphi^{(1)} - \varphi^{(2)} - I_1. \tag{11}$$

Let us assume that the value of I_1 in Eq. (11) is equal to the integral intensity of the spectrum of the hydrate shell calculated in variant 1 (see Fig. 6). Then, the lefthand side of Eq. (10) becomes known and this equation may be used as a condition relating coefficients a, b, and c. Using Eqs. (9)-(11), we find the roots of the quadratic equation and calculate the spectrum of the hydrate component in accord with Eq. (8). The spectrum thereby calculated is shown in Fig. 7 along with the spectrum determined using variant 1. This figure shows that these spectra are almost identical. The differences between them may be considered the error in the factoring method and are rather small such that the partial spectrum $Sp_1^{(1)}$ is rather reliable.

Knowing spectrum $Sp_1^{(1)}$, we may construct the other basis spectra using the set of experimental spectra $Sp^{(j)}$. The spectra of the hydroxyl shell and silica core thereby calculated proved identical to the spectra determined above. Thus, we have obtained a physically significant basis for system (2) satisfying the actual physical conditions.

CONCLUSION

Figure 8 gives the starting AWSD spectrum of *air-dried* A380 and the set of the three basis spectra $\{Sp_i^{(1)}\}$ of its components. All the spectra are positive and their sum exactly reproduces spectrum $Sp^{(1)}$. The basis spectra obtained are important not only as "characteristic" spectra of the Aerosil components but also as experimental forms of those AWSD spectra, which may now be reliably calculated by computer [9].

In conclusion, we note the observed difference in spectra *1* and *2* in Fig. 4. The intensity of the calculated spectrum *1*, whose reliability was confirmed by the entire set of results obtained, in the entire spectral range is less than the intensity of spectrum *2* and the difference between them is similar in its major details to difference spectrum *2* in Fig. 6. Spectra *2* and *3* are undoubtedly very similar and also differ somewhat at 160-190 cm^{-1}, where the major low-frequency peaks of the spectra of the hydrate and hydroxyl shells are found. This permits us to relate the observed difference in spectra *1* and *2* with the residues of these shells captured in the bulk of A380 *glass* during its sintering. The existence of 0.3-0.5 wt. % water is sufficient for a quantitative explanation of the difference. The possibility of the existence of such amounts of water in the glass has been confirmed by a number of chemical tests [2].

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