

# An effect of “scattering by absorption” observed in near-infrared properties of nanoporous silica

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The obtained spectroscopic data for absorption and scattering characteristics of nanoporous silica in the wavelength range from 0.25 to 7  $\mu\text{m}$  are analyzed on the basis of the Mie theory. It is shown that aggregates of primary nanoparticles are responsible for relatively high scattering in the short-wave range from 0.25 to 1.4  $\mu\text{m}$ . But the presence of the aggregates and micron-size cracks in the samples cannot explain unusual behavior of scattering in the long-wave part of the spectral range. The attention of the authors is focused on understanding of strong scattering peaks observed at exactly the same wavelengths as the infrared absorption peaks of bulk silica: at  $\lambda=2.9$ , 5.3, and 6.1  $\mu\text{m}$ . The known physical effect of “scattering by absorption” is considered as a source of these scattering peaks. It means that absorption centers are assumed to be not uniformly distributed in the nanoporous matrix but collected in some micron-size regions. The estimates based on this hypothesis are supported by the fact that near-infrared absorption peaks are produced by silanol groups which may be nonuniformly distributed in the hydroxylated nanoporous silica.

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## I. INTRODUCTION

Various porous materials are widely used as thermal insulations in many engineering problems.<sup>1</sup> The majority of these materials are made of substances characterized by low thermal conductivity. Thus, the resulting thermal conductivity of the insulation decreases. But the low-conductivity substances are usually semitransparent in the visible and near-infrared spectral ranges. The latter makes especially important the correct account for thermal radiation mode of heat transfer in the porous material with a specific attention to spectral radiative characteristics in the near-infrared.<sup>2</sup>

One can formulate the following typical features of scattering and absorption characteristics of semitransparent porous materials:

1. The absorption coefficient is practically independent of the material morphology and can be calculated as

$$\alpha_\lambda = \alpha_\lambda^0(1 - p), \quad (1)$$

where  $\alpha_\lambda^0$  is the absorption coefficient of the bulk material of the same chemical composition and  $p$  is the porosity of the material under investigation.

2. The characteristics of scattering are insensitive to a weak absorption typical for semitransparent materials. The scattering coefficient  $\sigma_\lambda$  and asymmetry factor of scattering  $\bar{\mu}_\lambda$  can be usually predicted by analysis of the material morphology. It is especially important to take into account a contribution of the grains or particle aggregates, pores, and cracks of size comparable with the radiation wavelength.

The above general statements are confirmed by an experience of the authors in experimental study and theoretical modeling of various dispersed materials such as foams, porous ceramics, etc.<sup>2-7</sup> It should be noted that a relative mutual independence of absorption and scattering is not a specific property of some semitransparent porous materials but it is a general behavior of disperse systems containing the so-called optically soft particles which satisfy the conditions of the Rayleigh–Gans theory<sup>8,9</sup> (the term “optically soft” will be clarified below).

In a continuous work of engineers on developing of advanced thermal insulations, the composite materials based on nanoporous matrixes are considered as potentially very interesting “superinsulating” materials for application in aerospace and other important technologies.<sup>10</sup> The low conductivity of these materials is explained by (1) very small area of contact between single particles because of highly fragmented solid matter and high porosity (about 85%–90%) and (2) low contribution of a gas in pores because of very small size of the pores (less than the free path of gas molecules) equivalent to vacuum conditions. As a result, thermal radiation may give an important contribution to heat transfer through this highly porous material. It goes without saying that understanding of spectral radiative properties of advanced materials based on nanoporous matrixes is of great importance.

The recently reported results of experimental identification of the wide-range spectral properties of nanoporous silica showed an unusual behavior of the transport scattering coefficient  $\sigma_\lambda^{\text{tr}} = \sigma_\lambda(1 - \bar{\mu}_\lambda)$  both in the visible and near-infrared spectral ranges.<sup>11</sup> The use of the transport approximation for the scattering phase function and the above men-

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TABLE I. Properties of powders and samples under investigation.

Powder name	Wacker HDK-T30	Cabot Cab-O-Sil EH5	Degussa Aerosil COK84
Chemical composition (% in weight)	$\geq 99.8\%$ SiO <sub>2</sub>	$\geq 99.8\%$ SiO <sub>2</sub>	84% SiO <sub>2</sub> and 16% Al <sub>2</sub> O <sub>3</sub>
Diameter of particles	9 nm	7 nm	13.5 nm
Characteristic aggregate length	120 nm	200–300 nm	...
Sample thickness	2 mm	2 mm	2 mm
Sample porosity	0.87	0.86	0.86

tioned transport scattering coefficient is based on experience in study of similar radiative transfer problems.<sup>9,12</sup> Relatively strong scattering in the visible is explained by formation of aggregates of primary nanoparticles of silica. This statement has been confirmed by a detailed analysis reported by Lallich *et al.*<sup>11</sup> But strange behavior of the scattering coefficient in the near infrared range, where the local maxima of scattering appear to be at the wavelength of absorption peaks, is still awaiting the physical explanation.

It is an objective of this paper to suggest a physical model of resonance behavior of scattering of nanoporous silica. This model should give an explanation of the correlation between the “resonances” of scattering and the spectral peaks of the material absorption.

## II. EXPERIMENTAL DATA FOR NANOPOROUS SILICA

The traditional experimental procedure based on spectral measurements of both directional-hemispherical reflectance and transmittance has been employed. Two different spectrometers covering an overall spectral band of (250 nm; 20  $\mu\text{m}$ ) were used: a Varian Cary grating spectrometer on the (250 nm; 2.5  $\mu\text{m}$ ) spectral band and a Bruker IFS66V Fourier transform infrared spectrometer on the wavelength range (1.6  $\mu\text{m}$ ; 20  $\mu\text{m}$ ). For these measurements, the two spectrometers are equipped with integrating spheres made of polytetrafluoroethylene for the Varian Cary and of gold for the Bruker that collect hemispherically the radiation traveling through or reflected by the samples.

The samples of studied materials were produced by packing of silica nanoparticles under the pressure of about 60 bar. Different silica powders from three manufacturers were used to produce the samples (see Table I and paper in Ref. 11 for more details). The samples obtained are 25 mm diameter cylinders having different thicknesses ranging from 2.0 to 10.5 mm. Then, all the samples are weighted and as the volume and the composition (we consider pure silica) of each sample are known, we can deduce the porosity of the samples. The silica nanoparticles are hydrophilic: their surface chemistry results from on the presence of silanol groups Si–OH. The concentration of silanol at the surface of silica particles determines its moisture adsorption capacity. If the ambient gas contains water vapor, it takes only few minutes to adsorb water in the powder. It is a complicated task to dry the samples and to maintain small water content during the experiments. Therefore, all the results were obtained for hydrated samples at atmospheric conditions.

It is known that the hydroxyl in silanol groups is one of the major impurities in silica glass, increasing its optical

losses in the near and middle infrared.<sup>13–16</sup> In addition, the vibrational absorption bands of hydroxyl are observed at the fundamental absorption band at  $\lambda=2.72$   $\mu\text{m}$  and at some shorter wavelengths: 2.22, 1.39, and 0.9  $\mu\text{m}$ .<sup>14</sup> Water can exist in silica not only as hydroxyl in the form of silanol groups but also as molecular water which diffuses in the material and partially reacts with the silica molecules generating various chemical bonds. It is interesting that water species can be detected by near-infrared spectroscopy: hydroxyl in silica glasses has absorption bands at  $\lambda=2.72$  and 2.22  $\mu\text{m}$ , while molecular water has absorption bands at  $\lambda=2.94$  and 1.85  $\mu\text{m}$ .<sup>13,15</sup>

Even the interaction of water with bulk silica (the so-called surface hydroxylation) is a specific complex problem that has been studied in some details for many years.<sup>16,17</sup> As for microporous and nanoporous silica matrices, there is no similar data in the literature. One can only expect that the hydroxylation and water diffusion in highly porous samples may lead to much more strong effects of the material optical properties than in the case of samples of bulk silica.

It is important to note that there are no isolated primary nanoparticles in the samples. It appears that single particles are collected in relatively stable aggregates. The aggregate structure of the material illustrated in Fig. 1. This specific

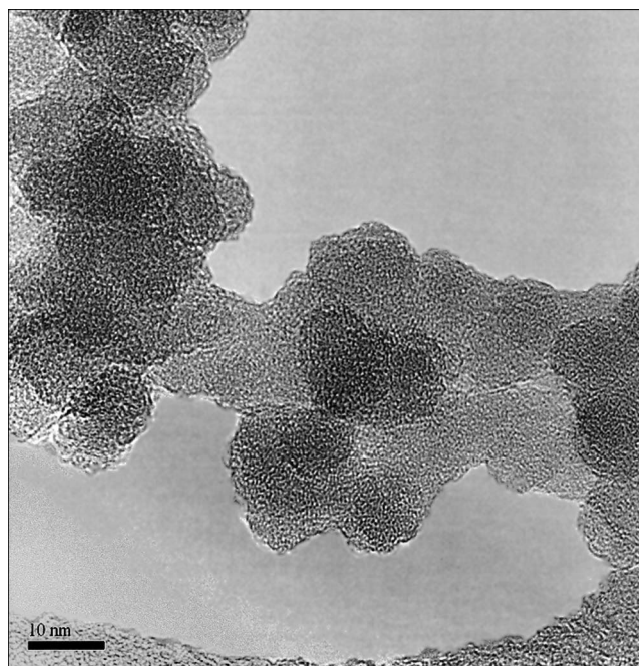


FIG. 1. Transmission electron microscopy micrograph of the Wacker HDK-T30 powder.

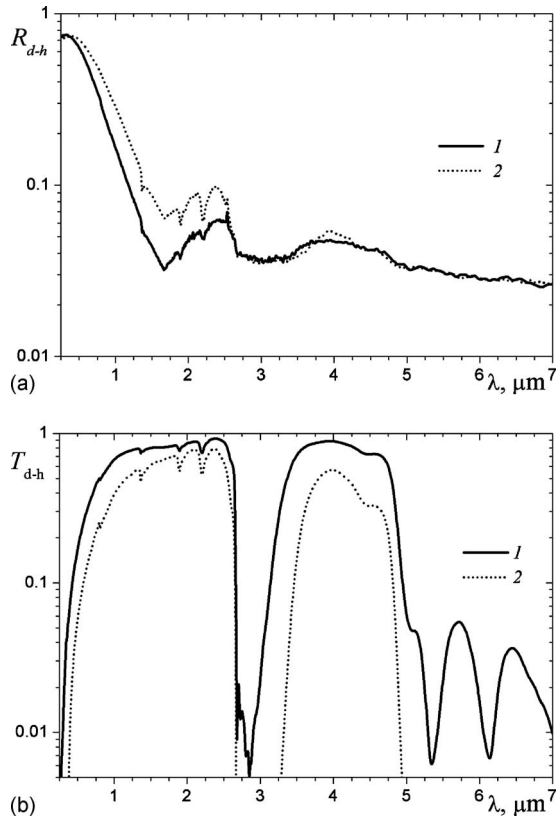


FIG. 2. Directional-hemispherical (a) reflectance and (b) transmittance spectra of two samples made of HDK-T30 powder: 1- $h=2$  mm, 2- $h=5$  mm.

morphology of the nanoporous material under investigation should be taken into account in analysis of the experimentally obtained radiative properties. In addition to the parameters of powders, some characteristics of the samples are also presented in Table I. In this paper, we consider only one representative sample for every powder. But two samples of different thickness were really examined for HDK and COK powders. Figure 2 shows the spectra of directional-hemispherical reflectance ( $R_{d-h}$ ) and transmittance ( $T_{d-h}$ ) obtained for two samples of thicknesses 2.0 and 5.0 mm made of the Wacker HDK-T30 powder. One can find more details of the experiment in recent paper by Lallich *et al.*<sup>11</sup>

Once we obtained the reflectance and transmittance spectra, we aim at identifying the radiative properties of these media. To do so, we use a method based on the inversion of the radiative transfer equation (RTE) (Ref. 11) described below. To compute the theoretical data used in the parameter identification process, we have to solve the RTE. The assumptions of our model are as follows: we consider one-dimensional radiative transfer within a homogeneous absorbing and scattering medium using the transport approximation. We neglect also the self-emission term and consider azimuthal isotropy. Under these assumptions, the RTE can be written as follows<sup>9,18</sup>

$$\mu \frac{\partial I_\lambda(z, \mu)}{\partial z} + \beta_\lambda^{tr} I_\lambda(z, \mu) = \frac{\sigma_\lambda^{tr}}{2} \int_{-1}^1 I_\lambda(z, \mu) d\mu, \quad (2)$$

where  $I_\lambda(z, \mu)$  is the spectral space and direction dependent intensity field,  $z$  is the spatial coordinate,  $\mu$  is the cosine of

the polar angle of the scattering direction,  $\beta_\lambda^{tr} = \alpha_\lambda + \sigma_\lambda^{tr}$  is the transport extinction coefficient. As we have experimental values of  $R_{d-h}$  and  $T_{d-h}$ , we are able to determine  $\alpha_\lambda$  and  $\sigma_\lambda^{tr}$  using the parameter identification method.<sup>2</sup> As long as the boundary conditions are concerned, first our samples being very porous, the refraction index contrast at their boundary is very weak and so we can consider the boundaries fully transparent. Second, we consider a collimated illumination of the sample along the normal. To summarize, we use the following boundary conditions:

$$I_\lambda(0, \mu) = I_e \delta(1 - \mu) \quad I_\lambda(h, -\mu) = 0 \quad \mu > 0, \quad (3)$$

where  $h$  is the sample thickness. Following the usual technique,<sup>9,18</sup> we express the radiation intensity  $I_\lambda$  as a sum of diffuse component  $J_\lambda$  and a term corresponding to the collimated external radiation

$$I_\lambda = J_\lambda + I_e \exp(-\beta_\lambda^{tr} z) \delta(1 - \mu). \quad (4)$$

The mathematical problem statement for the diffuse component of radiation intensity is as follows:

$$\mu \frac{\partial J_\lambda(z, \mu)}{\partial z} + \beta_\lambda^{tr} J_\lambda(z, \mu) = \frac{\sigma_\lambda^{tr}}{2} \left[ \int_{-1}^1 J_\lambda(z, \mu) d\mu + I_e \exp(-\beta_\lambda^{tr} z) \right], \quad (5)$$

$$J_\lambda(0, \mu) = 0 \quad J_\lambda(h, -\mu) = 0 \quad \mu > 0. \quad (6)$$

The problem in Eqs. (5) and (6) can be solved numerically using the discrete ordinate method (DOM).<sup>18</sup> Remember that the DOM consists in replacing the angular term of the RTE by a quadrature and further solving the coupled algebraic equations for the corresponding set of angles. Once the radiation intensity field is known, the directional-hemispherical reflectance and transmittance can be calculated as follows:

$$R_{d-h} = \frac{1}{I_e} \int_0^1 J_\lambda(0, -\mu) \mu d\mu \quad T_{d-h} = \exp(-\beta_\lambda^{tr} h) + \frac{1}{I_e} \int_0^1 J_\lambda(h, \mu) \mu d\mu. \quad (7)$$

The whole procedure described above, which allows the evaluation of the directional-hemispherical reflectance and transmittance of our samples from the knowledge of their radiative properties ( $\alpha_\lambda$  and  $\sigma_\lambda^{tr}$ ), must be regarded as the direct problem; the inverse problem is numerically solved using a method based on the Newton–Raphson algorithm.

It is important to note that an alternative identification procedure based on the modified two-flux approximation (instead of complete RTE) suggested by Dombrovsky *et al.*<sup>12</sup> was also employed in the present study. It was found that this simplified analytical approach gives exactly the same results as the procedure based on high-order DOM calculations. The latter can be considered as a verification of the mathematics of the inverse problem solution and confirms that the spectral values of both absorption coefficient and transport scattering coefficient presented in Fig. 3 are reliable.

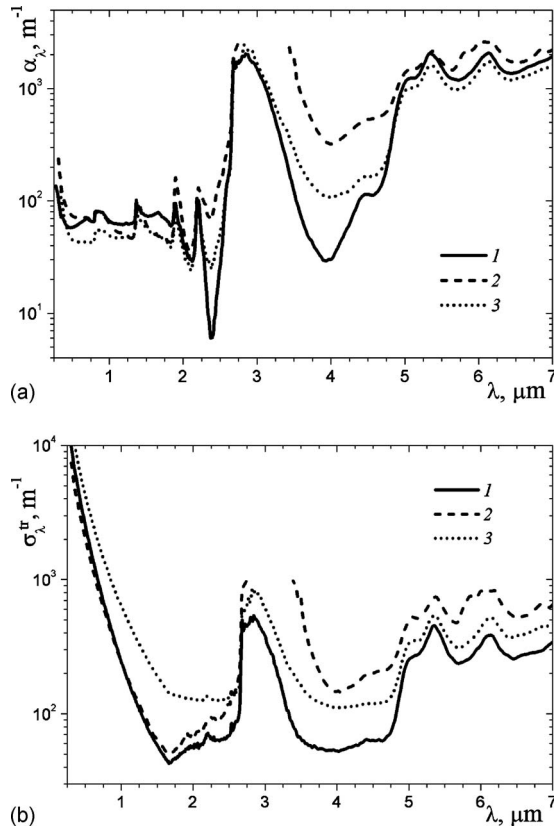


FIG. 3. Spectral dependences of absorption coefficient (a) and transport scattering coefficient (b) of samples prepared from various powders: 1—HDK-T30, 2—COK84, 3—EH5.

### III. ANALYSIS OF ABSORPTION

The specific process of silica powders preparation makes very problematic a determination of the bulk material optical constants. The simplest way is to use the optical constants of pure silica from the literature.<sup>19–21</sup> As for index of refraction, it can be really done because this physical quantity is weakly sensitive to water content and small impurities in the material. In contrast to the index of refraction, the index of absorption is much more sensitive to water content and internal hydroxylation of the highly porous matrix. Small absorbing additives of another nature may also yield significant contribution to the material absorption, especially in the short-wave range where pure silica is a weakly absorbing substance.

It seems to be more realistic to use our experimental data for absorption coefficient of nanoporous matrix to estimate an equivalent index of absorption of a conventional bulk material. This procedure is based on approximate Eq. (1) and the known relation between absorption coefficient and index of absorption of a homogeneous medium<sup>22</sup>

$$\alpha_{\lambda}^0 = 4\pi\kappa/\lambda. \quad (8)$$

Obviously, this approach yields us an upper estimate of the value of  $\kappa$  because the material is not optically soft over the whole spectrum. The term “optically soft” is used when condition of  $|m-1| \ll 1$  is satisfied, where  $m=n-i\kappa$  is the complex index of refraction of the medium. The specific properties of large optically soft particles have been analyzed in the

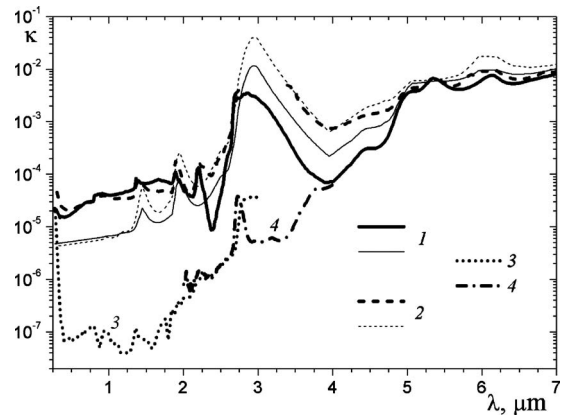


FIG. 4. Spectral index of absorption of silica determined from the experimental data for absorption coefficient: 1—HDK-T30, 2—EH5 (theoretical estimates based on the Maxwell-Garnett mixing rule are shown by the corresponding thin lines), 3, 4—experimental data for pure silica [3—Khashan and Nassif (Ref. 20), 4—Dombrovsky *et al.* (Ref. 6)]

greatest detail by van de Hulst.<sup>8</sup> One can also refer to recent monograph<sup>23</sup> on this subject. But the resulting spectral dependences  $\kappa(\lambda)$  are expected to be sufficiently accurate for further computational analysis. The values of the index of absorption determined for samples made of silica powders HDK-T30 and EH5 are presented in Fig. 4. The values of  $\kappa$  appear to be much greater than the known data for pure silica. One can try to explain so large absorption by the presence of water molecules in the nanoporous samples by using theoretical estimates based on the Maxwell-Garnett mixing rule.<sup>18,22</sup> It was done using the values of water content of 2% and 8% for the samples made of HDK and EH5 powders, correspondingly. Figure 4 indicates that this approach is too crude to obtain correct values of the absorption index. Nevertheless, it is clear that molecular water and silanol groups are really responsible at least for high infrared absorption. As for abnormally high level of short-wave absorption, especially in the visible range, it is not explained so simple by high water content in the samples and may be a subject of a separate study based on detailed chemical analysis. Generally speaking, it seems natural that the role of water is much greater in the case of nanoporous silica matrices than it has been observed earlier for ordinary silica materials.

### IV. ANALYSIS OF SCATTERING

#### A. The visible range

It has been already shown by Lallich *et al.*<sup>11</sup> that relatively high short-wave scattering of radiation by nanoporous silica is a result of dependent scattering of radiation by primary nanoparticles collected in large aggregates. The known discrete-dipole approximation (DDA) (Refs. 24–27) was employed in paper<sup>11</sup> to calculate the radiative characteristics of these aggregates. This method allows computation of the absorption and scattering properties of irregular particles of complex shapes and clusters of spheres approximated by arrays of point dipoles. DDA calculations require a prior step consisting of the localization of dipoles in space and the evaluation of their polarizabilities. Concerning the polarizabilities, since we apply the DDA on a cluster of spherical

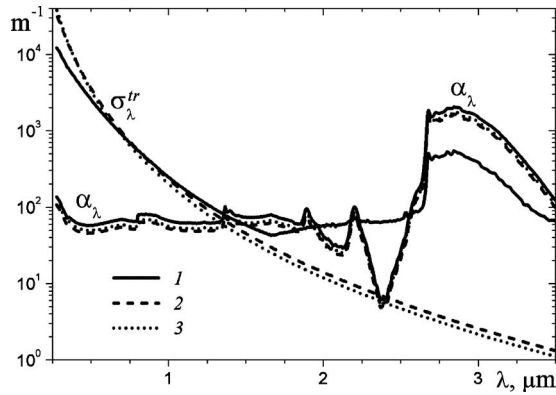


FIG. 5. A comparison of the experimental data (1) and theoretical predictions based on (2) detailed modeling of nanoparticle aggregates and (3) simplified physical model of thin-wall hollow spheres.

particles that are small compared to the wavelength, we may treat each particle as a single dipole. This method has been shown to be superior to the other polarizability prescriptions for a cluster of spherical monomers replaced by single dipoles.<sup>28</sup> The dipole moments within the cluster result, on the one hand, from an incident electromagnetic field that activates them, and on the other hand, from the interaction between them; once these dipole moments are solved, it is possible to determine the radiative properties of the cluster. In order to obtain valuable results, the material structures on which DDA calculations are performed must be representative of our nanoporous matrix in terms of porosity, specific surface area, and fractal dimension, which is equal to about 1.8.<sup>29</sup>

In this paper, we repeat the DDA calculations of paper<sup>11</sup> by using the above determined index of absorption. Of course, the role of the absorption index is very small because the scattering by particle aggregates depends mainly on index of refraction. It is assumed that short-wave index of refraction is insensitive to water content and the spectral dependence  $n(\lambda)$  can be calculated by the known three-term Sellmeier equation suggested by Malitson.<sup>30</sup> A comparison of the computational results with experimental data for a sample made of silica powders HDK-T30 is presented in Fig. 5. One can see that theoretical model yields the transport scattering coefficient which is very close to the experimental data in the wavelength range  $\lambda < 1.4 \mu\text{m}$  but the high scattering at larger wavelengths cannot be treated as a scattering by the nanoparticle aggregates. Note that a good agreement of the calculated absorption coefficient with the experimental data confirms the hypothesis of additive absorption formulated by Eq. (1).

As an alternative of the detailed scattering model of paper,<sup>11</sup> we suggest a simplified physical model. It is supposed that radiative properties of complex aggregates of particles randomly oriented in space are similar to the properties of hollow microspheres of wall thickness equal to the diameter  $d$  of the primary particles. The external radius of these microspheres is determined by the value of characteristic aggregate length

$$a = \frac{l}{2\pi}. \quad (9)$$

Equation (9) means that long aggregates of the same length are treated as circular chains forming the hollow microsphere. The volume fraction of hollow microspheres  $f_v$  is calculated by taking into account the own particle “porosity”  $p_1 = (1 - \delta)^3$ , where  $\delta = d/a$  is the relative thickness of the particle wall. The resulting relation for the particle volume fraction is as follows:

$$f_v = \frac{1 - p}{1 - p_1}, \quad (10)$$

and the equation for transport scattering coefficient is

$$\sigma_\lambda^{tr} = 0.75 \frac{1 - p}{1 - p_1} \frac{Q_s^{tr}}{a}, \quad (11)$$

where  $Q_s^{tr}$  is the transport efficiency factor of scattering.<sup>9</sup> Obviously, we can consider only the microspheres with  $p_1 < p$  but this condition is satisfied in our problem. One can see in Fig. 5 that the approximate model gives practically the same results as the detailed DDA calculations.

It is important that the above approximate model is physically sound and there are no any free/fitting parameters in the model. Moreover, one can use only very simple analytical equation for the efficiency factor of Rayleigh scattering for hollow spherical particles<sup>8,9</sup>

$$Q_s^{tr} = Q_s = \frac{8}{3} x^4 \left| \frac{m^2 - \xi}{m^2 + 2\xi} \right|^2 \quad \xi = \frac{1 + \delta^3 M}{1 - 2\delta^3 M}$$

$$M = \frac{m^2 - 1}{1 + 2m^2} \quad x = \frac{2\pi a}{\lambda}. \quad (12)$$

It goes without saying that this approach is much simpler than DDA calculations for complex aggregates of nanoparticles. It means that this approximation can be recommended for engineering estimates of intense scattering typical of pressed nanoporous silica in the range of about  $0.3 < \lambda < 1.4 \mu\text{m}$ . Unfortunately, the both models of radiation scattering by aggregates of nanoparticles do not explain the observed behavior of scattering at wavelength greater than about  $2 \mu\text{m}$ .

## B. The near-infrared range

We were trying to find some micron-size morphological objects (single cavities, hollow particles, or cracks) which might be responsible for high scattering in the near-infrared. Thin cracks at the side surface of some samples were really observed. That is why we have analyzed the radiation scattering (reflection) by polydisperse parallel cracks at normal incidence. Obviously, the material including some cracks oriented parallel to the sample surface is anisotropic. Nevertheless, having in mind a predominant role of radiation propagating in the normal direction to the sample surface, we consider only the scattering characteristics in this direction. The relations for the normal reflection coefficient of a thin plane-parallel gap inside a homogeneous absorbing and refracting medium are well known.<sup>18,22</sup> These general relations

take into account the effect of interference. Let us consider a plane parallel gap of thickness  $t$  with a complex index of refraction  $m_2$  embedded between two media of complex indices of refraction  $m_1$  and  $m_3$ . Using designation  $r_{ij}=(m_i - m_j)/(m_i + m_j)$ , one can express the complex reflection coefficient and the reflectance of a slab as follows:

$$r_{slab} = \frac{r_{12} + r_{23} \exp(-4i\pi t m_2/\lambda)}{1 + r_{12} r_{23} \exp(-4i\pi t m_2/\lambda)} \quad R = r_{slab}^* r_{slab}. \quad (13)$$

One should remind also the relation between the reflectance of a single crack and transport efficiency factor of scattering:  $Q_s^{tr} = 2R$ . The reflectance of polydisperse cracks of various thicknesses  $\Delta$  can be calculated as follows:

$$\bar{R} = \int_0^{\Delta_{\max}} R(\Delta) F(\Delta) d\Delta. \quad (14)$$

Where  $F(\Delta)$  is the normalized distribution of the gap thickness. The choice of the lower limit of integration is explained by the fact that every long crack of variable thickness can be considered as a polydisperse system of relatively short cracks and the minimum thickness is very small. It is also clear that the physical result should not depend on the details of the gap size distribution. Assuming the simplest size distribution of the gaps

$$F(\Delta) = \frac{\Theta(\Delta) - \Theta(\Delta_{\max} - \Delta)}{\Delta_{\max}}, \quad (15)$$

where  $\Theta$  is the Heavyside function, one can write:

$$\bar{R} = \frac{1}{\Delta_{\max}} \int_0^{\Delta_{\max}} R(\Delta) d\Delta. \quad (16)$$

In the calculations, we used the subtractive Kramers–Krönig analysis<sup>31</sup> to determine the spectral dependence of index of refraction  $n(\lambda)$  of silica in the nanoporous silica matrix under investigation. This analysis is based on the following equation for the difference between  $n(\lambda)$  and the reliable measured value of refractive index at a certain wavelength  $\lambda_1$ :

$$n(\lambda) - n(\lambda_1) = \frac{2(\lambda_1^2 - \lambda^2)}{\pi} \int_0^{\infty} \frac{\lambda' \kappa(\lambda') d\lambda'}{(\lambda^2 - \lambda'^2)(\lambda_1^2 - \lambda'^2)}. \quad (17)$$

For numerical integration over a limited spectral range Eq. (17) has been rearranged to

$$n(\lambda) = n(\lambda_1) + \frac{2(\lambda_1^2 - \lambda^2)}{\pi} \left( \int_{\lambda_{\min}}^{\lambda_1 - \varepsilon} f d\lambda' + \int_{\lambda_1 + \varepsilon}^{\lambda - \varepsilon} f d\lambda' + \int_{\lambda + \varepsilon}^{\lambda_{\max}} f d\lambda' \right) + O(\varepsilon), \quad (18)$$

where

$$f = f(\lambda, \lambda') = \frac{\lambda' \kappa(\lambda')}{(\lambda^2 - \lambda'^2)(\lambda_1^2 - \lambda'^2)}, \quad (19)$$

$\varepsilon$  is a small parameter and the choice of  $\lambda_{\min}$  and  $\lambda_{\max}$  is determined by the location of the main absorption bands in the spectrum. The calculations are based on Eqs. (18) and (19) with  $\lambda_{\min} = 0.28 \mu\text{m}$  and  $\lambda_{\max} = 7.1 \mu\text{m}$ . It is assumed  $n(\lambda_1) = 1.488$  at  $\lambda_1 = 0.3 \mu\text{m}$  (from the dispersion relation by

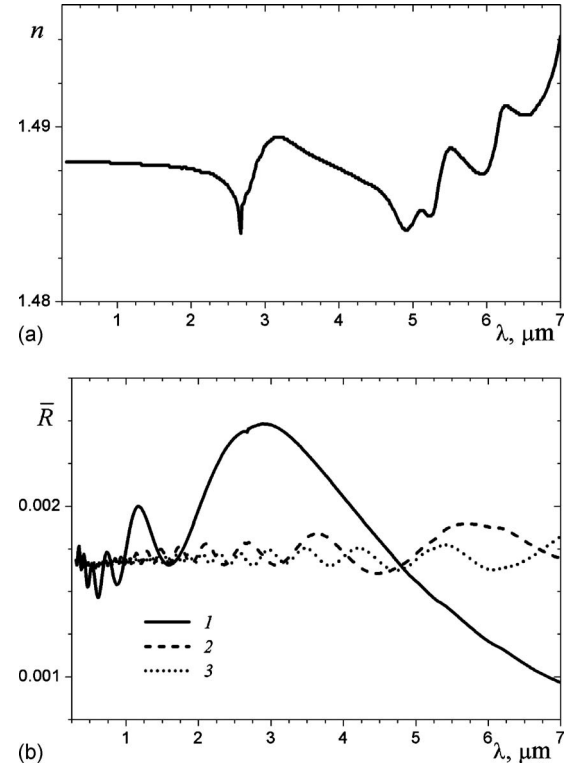


FIG. 6. Spectral dependences of (a) the index of refraction and (b) reflection coefficient of polydisperse cracks in nanoporous silica at normal incidence: 1— $\Delta_{\max} = 1 \mu\text{m}$ , 2— $\Delta_{\max} = 5 \mu\text{m}$ , 3— $\Delta_{\max} = 10 \mu\text{m}$ .

Malitson<sup>30</sup> for pure silica). The results of calculations are shown in Fig. 6(a). One can see that strong absorption bands of hydroxylated silica lead to nonmonotonic spectral variation in the refractive index and the local maxima of the index of refraction appear at the wavelength corresponding to the absorption peaks. At the same time, the amplitude of the oscillations of  $n(\lambda)$  is very small and one cannot expect a considerable effect of these spectral variations in index of refraction on scattering characteristics of some particles.

The calculations of reflectance of polydisperse cracks within nanoporous silica matrix [see Fig. 6(b)] indicate smooth spectral dependences without strong peaks observed in the experimental scattering curves. There is practically no effect of small spectral variations in the index of refraction [Fig. 6(a)]. The latter is an additional confirmation of the above formulated statement that a weak uniform absorption cannot yield a considerable contribution to scattering in disperse/porous media. Of course, the cracks of volume fraction  $f_{v,cr}$  give a contribution to the transport scattering coefficient in the near infrared according to the following obvious equation (see Ref. 9)

$$\sigma_{\lambda,cr}^{tr} = 2f_{v,cr} \bar{R} / \bar{\Delta} \approx 0.0035 f_{v,cr} / \bar{\Delta} \quad \bar{\Delta} = \Delta_{\max} / 2, \quad (20)$$

but the spectral dependence of  $\sigma_{\lambda,cr}^{tr}$  has no strong maxima in the absorption bands. The expected maximum value of the ratio of  $f_{v,cr} / \bar{\Delta} \sim 10^4$  can be obtained from the minimum experimental values of  $\sigma_{\lambda}^{tr} = 43 \text{ m}^{-1}$  at  $\lambda \approx 1.7 \mu\text{m}$  and  $\sigma_{\lambda}^{tr} = 53 \text{ m}^{-1}$  at  $\lambda \approx 4.0 \mu\text{m}$  for the sample made of HDK powder. In the case of  $\bar{\Delta} \sim 1 \mu\text{m}$ , one can find a realistic value of  $f_{v,cr}^{\max} \approx 1\%$ .

Let us focus on the observed physical effect: a correlation between the scattering and absorption peaks (note that both absorption and scattering peaks are really strong: it seems to be not evident in the logarithmic scale). One can remember similar behavior of scattering in the case of non-refracting but absorbing particles. This effect is described by the Mie theory for single spherical particles. Particularly, it was discussed in details in the book<sup>9</sup> and called there “the scattering by absorption.” The physical explanation of the scattering by absorption is quite clear: the local absorption leads to deformation of the wave front. It means that the electromagnetic wave near this local region does not propagate in the original direction and there is a scattering. It is well-known that direct Mie calculations for particles at complex index of refraction  $m=1-i\kappa$  yield a nonzero scattering which depend on diffraction parameter  $x$  and absorption index  $\kappa$ .

As applied to our problem, one can imagine that there is an absorbing substance (like water or something else) which is not uniformly distributed in nonabsorbing (or weakly absorbing) matrix but it is concentrated in some local regions. These local regions (quasi-particles) may have practically the same index of refraction as the index of refraction of ambient host medium but the index of absorption of the quasi-particles is greater than the index of absorption of the host medium. It is obvious, that our quasi-particles will scatter the radiation and this scattering is directly proportional to the absorption of the quasiparticle material.

The scattering by absorbing quasi-particles can be estimated using the known modification of the Mie theory for the case of refracting but nonabsorbing ambient medium. It is sufficient to use the relative complex index of refraction  $\bar{m}=1-i\kappa_*/n$ , where  $\kappa_* \gg \kappa$  is the index of absorption of quasi-particle,  $n$  is the ambient medium index of refraction. The calculations should be performed at the modified value of the diffraction parameter  $\bar{x}=nx$ , where  $x=2\pi a_*/\lambda$  and  $a_*$  is the quasi-particle radius. For an equivalent optically soft refracting medium, which represents highly porous material, we have  $n \approx 1$  and there is no need in account for the refraction of the ambient medium. The results of calculations using the Mie theory are presented in Fig. 7. One can see that the value of  $Q_s^{tr}$  increases very fast with the diffraction parameter and reaches approximately constant value at  $x \sim 1$ . Moreover, the dependence of  $Q_s^{tr}$  on  $\kappa_*$  is almost linear and we can use the following approximate relation in further estimates:

$$Q_s^{tr} = \xi \kappa_* \quad \xi \approx 0.35. \quad (21)$$

We assume that absorption is localized mainly in quasiparticles and Eq. (1) is correct. It enables us to obtain the volume fraction of quasiparticles:

$$f_{v,*} = (1-p)\kappa/\kappa_*. \quad (22)$$

Having substituted Eqs. (21) and (22) in the known formula for transport scattering coefficient of a monodisperse system<sup>9</sup> we obtain

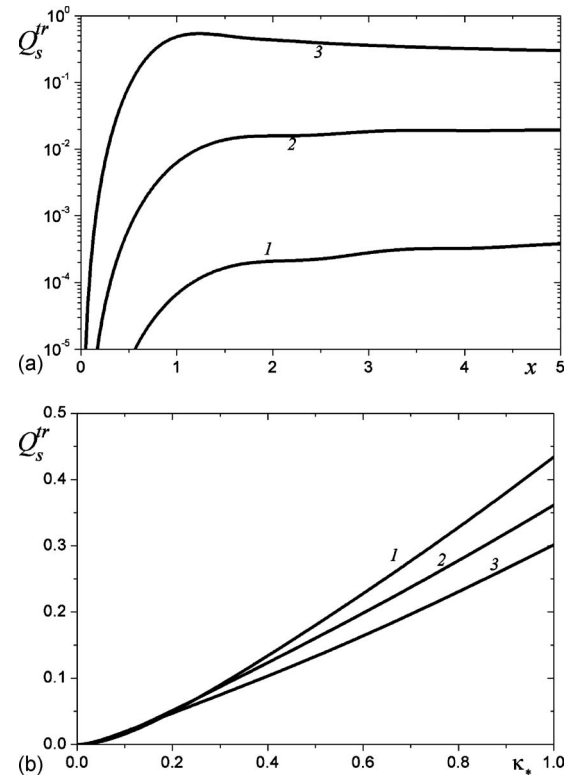


FIG. 7. Transport efficiency factor of scattering for nonrefracting particles as a function of diffraction parameter (a,  $1-\kappa_*=0.01$ ,  $2-\kappa_*=0.1$ ,  $3-\kappa_*=1$ ) and index of refraction (b,  $1-x=2$ ,  $2-x=3$ ,  $3-x=5$ ).

$$\sigma_\lambda^{tr} = 0.75 f_{v,*} Q_s^{tr} / a_* = 0.75 \xi (1-p) \kappa / a_* \quad \text{or}$$

$$\sigma_\lambda^{tr} = 0.375 \xi \alpha_\lambda / x. \quad (23)$$

One can see that transport coefficient of scattering is directly proportional to the absorption coefficient and the important ratio  $S_\lambda = \sigma_\lambda^{tr} / \alpha_\lambda = \omega_\lambda / (1-\omega_\lambda)$  ( $\omega_\lambda$  is the albedo) does not depend on the material porosity and optical constants. Equation (23) yields  $S_\lambda \approx 0.13$  at  $x=1$  ( $a_*=1 \mu\text{m}$  and  $\lambda \approx 6.3 \mu\text{m}$ ). In terms of order of magnitude, this result agrees well with the experimental data. For the sample made of HDK powder we have (see Fig. 3) experimental value of  $S_\lambda \approx 0.22$  at the absorption peak of  $\lambda=5.34 \mu\text{m}$  and  $S_\lambda \approx 0.19$  at the peak of  $\lambda=6.14 \mu\text{m}$ . Of course, the above comparison is not quite correct because one should consider not the total values of the absorption and scattering coefficients but only their parts related with hydroxylation. In addition, our assumption on spherical shape of quasi-particles is not justified and one can consider some longitude quasi-particles oriented mainly along the sample surfaces. In other words, we obtained a physical estimate only. But it is important that our hypothesis of scattering by absorption gives a qualitative explanation of the experimental results.

It is clear at the moment that there are two major effects which contribute to the radiation scattering in nanoporous silica in the visible and near-infrared: (1) the scattering by submicron aggregates of primary nanoparticles in the range of  $\lambda < 1.4 \mu\text{m}$  and (2) the scattering by micron-size local

regions (quasi-particles) of relatively high absorption (mainly by silanol groups) which is the main mode in the infrared range of  $\lambda > 2.5 \mu\text{m}$ .

## V. CONCLUSIONS

The spectroscopic experimental data for absorption and scattering characteristics of nanoporous silica in the wavelength range from 0.25 to 7  $\mu\text{m}$  are presented in the paper. The spectral behavior of both absorption coefficient and transport scattering coefficient of several samples of matrices made of various silica powders is analyzed. It was found that an equivalent index of absorption of bulk material is very high. In the near-infrared, this effect is explained by adsorption of water from the ambient air and high concentration of silanol groups in the nanoporous matrix.

The spectral behavior of transport scattering coefficient appears to be much more complex. The relatively high scattering in the short-wave range from 0.25 to 1.4  $\mu\text{m}$  is well described by formation of long chainlike aggregates of primary nanoparticles observed at microphotographs of the samples. An approximate physical model of scattering by the particle aggregates is suggested in this paper. It is considered as an alternative of the recently developed detailed model based on the DDA. Both approximate and detailed models yield the results which are very close to the experimental data in the above mentioned spectral range.

It is shown that the aggregates and micron-size cracks observed at side wall of the samples are not responsible for unusual behavior of scattering in the long-wave part of the spectral range under investigation. The main attention of the authors is focused on understanding the observed scattering peaks appeared at exactly the same wavelengths as the infrared absorption peaks of bulk silica: at  $\lambda = 2.9, 5.3,$  and  $6.1 \mu\text{m}$ . The known physical effect of scattering by absorption is considered as a source of these scattering peaks. It means that absorption centers are assumed to be not uniformly distributed in the nanoporous matrix but collected in some micron-size regions called quasi-particles. The estimates based on this hypothesis are supported by the fact that the absorption peaks in the near-infrared are produced by silanol groups and other types of bound water which may be nonuniformly distributed in the hydroxylated nanoporous silica. The theoretical predictions based on the Mie calculations for quasi-particles showed similar scattering behavior with approximately the same values of the medium albedo as that observed in the experiments. To the best of our knowledge, it is the first case when the effect of scattering by

absorption appears to be important for the near-infrared properties of a semitransparent thermal insulation.

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