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The size effect on the infrared spectra of condensed media under conditions of 1D, 2D and 3D dielectric confinement

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Abstract

A general expression for the dielectric loss spectrum of an absorbing composite medium was obtained from a Maxwell-Garnett general equation. This expression was simplified for the cases of one, two and three dimensional dielectric confinement in both ordered and disordered thin layers, rods (wires) and spheres of absorbing medium which are considered as mesoparticles or mesoscopic molecules.

This theoretical approach was verified experimentally using high purity organic liquids with strong absorption bands in the infrared range. Three organic liquids, namely benzene, chloroform and carbon disulphide, were measured in various dielectric confinement configurations using Fourier Transform Infrared (FTIR) spectroscopy with a Grazing Angle attachment GATR^{TM}. A significant shift of the resonant absorption band of liquid mesoparticles was observed for various dielectric confinement geometries which is in good agreement with theoretical predictions. Possible applications of this work include investigations of industrial smoke, toxic aerosols and liquid droplets.

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1. Introduction

At present, a great deal of attention is paid to the investigation of the optical properties of various types of condensed matter experiencing quantum confinement at sizes significantly smaller than the wavelength of the probe beam. This has been enabled by rapid development of the fabrication technology used to construct nanostructures and parallel developments in the application of these structures to areas such as life sciences and computing.

Decreasing the characteristic size of materials results in a dramatic alteration in the optical properties of crystalline as well as non-crystalline media and enables the fabrication of materials with new and unique properties. These changes in the optical properties of materials as a result of reducing their characteristic size are related to a quantum confinement effect as well as to the effect of dielectric confinement. The quantum confinement effect which is related with the change zone structure of material and plays a significant role in semiconductor nano-crystalsis not being considered here. The dielectric confinement effect is due to the sharp changes in the intensity of the internal effective electric field $E_{eff}(\nu)$, causing significant changes in the spectroscopic characteristics. The effect depends on the direction of the external field $E(\nu)$ and the size and shape of the submicron sized particles or micro-objects. Note that these micro-objects are often called mesoparticles or mesoscopic molecules [1].

In the long wavelength limit, $d<<\lambda$, for determination of the spectroscopic characteristic of micro-particles with size d in the direction of dielectric confinement, one can use an effective media theory model, while taking account of the dispersive local field [2-4]. For prediction of the optical properties of binary composite media the Maxwell-Garnett and Bruggeman models are used [5-8]. Dielectric confinement occurs when the absorbing material consists of micro-particles with characteristic sizes significantly smaller than the wavelength of the probe beam. These particles are generally embedded in a transparent dielectric matrix or deposited on a transparent substrate as a super-thin film. A good analogy to these systems is that of an aerosol suspended in air. As mentioned earlier, dielectric confinement is accompanied by a strong

local-field effect, resulting in a modification of the spectral properties of the medium in the direction of the size confinement, compared to the properties of the bulk.

For strong absorption bands, this effect is quite large, even if the dielectric permittivity of the matrix, ε_h, is close to the background dielectric permittivity ε_h of the particle itself. The influence of the effective local field on the infrared spectra of small particles in the limited case of 1D, 2D and 3D dielectric confinement has been analysed in Ref. [9]. It was shown that when the particle size in the direction of confinement, d, satisfies the condition $d<<\lambda$, the dielectric loss properties of the particles can be described by the spectrum $\hat{\varepsilon}_2^{micro}(v)$, which is related to the dielectric loss spectrum $\hat{\varepsilon}_2^{bulk}(v)$ of the bulk counterpart via the internal effective field factor $\theta(v)=|E(v)/E_{eff}(v)|^2$.

Since the average value of $\theta(v)$ significantly deviates from 1, the factor itself has a strong dispersion within the absorption band. So the spectrum $\hat{\varepsilon}_2^{micro}(v)$ for particles in the direction of dielectric confinement differs in all respects, viz. peak position, peak intensity and band shape, from the $\hat{\varepsilon}_2^{bulk}(v)$ spectrum. The expressions obtained in Ref. [9] are applicable only to the limited cases of 1D, 2D and 3D dielectric confinement, and ignore the particle shape.

In this study, we develop theory to describe the absorption spectra of particles experiencing dielectric confinement, taking into account the geometry of the ellipsoidal particles over a wide range of semi-axis ratios. The theory is experimentally verified in materials experiencing dielectric confinement for liquid absorbing media in the infrared range.

2. Theoretical considerations

We model the particle as an ellipsoid of revolution with depolarisation factors L_z and $L_x=L_y$. In the case of 1D, 2D and 3D dielectric confinement, these factors can be described as $L_z=1$ and $L_x=L_y=0$ for 1D, $L_z=0$ and $L_x=L_y=1/2$ for 2D, and a $L_x=L_y=L_z=1/3$ for 3D confinement. In order to calculate the absorption spectra for composite media, containing ellipsoidal particles with a wide range of depolarisation factors, we use a

generalised equation for the dielectric function of binary dielectric media, obtained by combining the Maxwell-Garnett equation with a phenomenological theory of the effective medium [2,3] :

$$\frac{\hat{\varepsilon}_i(v) - \varepsilon_h}{L_i\hat{\varepsilon}_i(v) + (1 - L_i)\varepsilon_h} = \frac{f \cdot (\hat{\varepsilon}(v) - \varepsilon_h)}{L_i\hat{\varepsilon}(v) + (1 - L_i)\varepsilon_h}, \qquad (1)$$

where L_i is the corresponding component of the depolarisation factor, $\hat{\varepsilon}_i(v)$ is the component of the tensor of the effective dielectric permittivity of the medium, ε_h is the dielectric permittivity of the matrix, $\hat{\varepsilon}(v)$ is the dielectric permittivity of the bulk material of the embedded particles and f is the relative volume concentration, the filling factor, of the embedded particles. At $L = 1/3$ expression (1) can be converted to the typical form of the Maxwell-Garnett equation

$$\frac{\hat{\varepsilon}_i(v) - \varepsilon_h}{\hat{\varepsilon}_i(v) + 2\varepsilon_h} = \frac{f \cdot (\hat{\varepsilon}(v) - \varepsilon_h)}{L_i\hat{\varepsilon}(v) + 2\varepsilon_h} \qquad (2)$$

These expressions have been widely used in the past for modelling the spectral properties of granular metallic films. The depolarisation factor L_i for ellipsoidal particles is defined by the ratio of the semi-axes of the ellipsoid shown schematically in Fig. 1a. For two orientations of the electric field vector E, viz; parallel or perpendicular to the rotation axis of the ellipsoid, the corresponding depolarisation factors, L_z and $L_{x,y}$, are determined by the following expressions [10]:

$$L_z = [\ 1 - P \cdot \{\arcsin(1 - P^2)^{1/2}/(1 - P^2)^{1/2}\}]/(1 - P^2) \quad \text{(Vasily-Check!!!)} \qquad (3)$$

$$L_{x,y} = \frac{1 - L_z}{2}, \qquad (4)$$

where $P = \dfrac{dz}{dx} = \dfrac{dz}{dy}$ and dz and $dx = dy$ are the sizes of the corresponding semi-axes of the ellipsoid.

We note that the limits of applicability of this approximation are defined by the applicability of the electrostatic model of the effective medium, since this approximation does not take into account the size of the particles under consideration. A more precise

approach is required to take account of so-called dynamic polarisation, which takes into consideration the size of the particle and its interaction time with the field of the electromagnetic wave [11,12].

It is reasonable to assume that the dynamic polarisation is significant only in the visible range, playing only a minor role in the mid-infrared range, to a first approximation. Solving expression (1) for the desired value, we obtain the following expression for the dielectric permittivity spectrum of composite media

$$\hat{\varepsilon}_i = \frac{f(\hat{\varepsilon}(v) - \varepsilon_h)\,\varepsilon_h\,(1 - L_i) + \varepsilon_h\left[L_i\hat{\varepsilon}(v) + (1 - L_i)\varepsilon_h\right]}{L_i\hat{\varepsilon}(v) + (1 - L_i)\varepsilon_h - f\cdot(\hat{\varepsilon}(v) - \varepsilon_h)L_i} \qquad (5)$$

Here $\hat{\varepsilon}_i(v)$ is the component of the complex dielectric permittivity spectrum of the composite medium, L_i is the corresponding value of the depolarisation factor, $\hat{\varepsilon}(v)$ is the complex dielectric permittivity of the bulk material with filling factor f, impregnated in the transparent medium with permittivity ε_h. It should be noted that expressions (1) and (5) refer to the case when the ellipsoids, which model the shape of the impregnated particles, are oriented in the same direction. That corresponds to the cases shown in Figs. 1 b and 1 c.

At L_i=1/3 the composite medium is isotropic and the expression (5) corresponds to the typical Maxwell-Garnett expression for spherical particles. When L_i=0, expression (5) reduces to

$$\hat{\varepsilon}_i(v) = f\hat{\varepsilon}(v) + (1 - f)\varepsilon_h \qquad (6)$$

which describes the component of the spectrum $\hat{\varepsilon}_i(v)$ of the composite medium under no dielectric confinement. The contribution of the individual components of the composite medium in this case is proportional to their volume fraction. This expression is valid for a medium containing long columns with E parallel to their length and $d_z \gg \lambda$. It is also valid for a super-thin layer stack (with $d_z \ll \lambda$), or for a stack of parallel oriented strongly oblate disks (with $d_z \ll \lambda$ and $d_{x,y} \gg \lambda$) with the vector E oriented parallel to their plane. With L_z=1 (E||Z) the component of the spectra of the composite medium $\varepsilon_Z(v)$, corresponding to the case shown in Fig. 1b, is described by

$$\hat{\varepsilon}_z(v) = \frac{\varepsilon_h \hat{\varepsilon}(v)}{\hat{\varepsilon}(v) \cdot (1-f) + f\varepsilon_h} \qquad (7)$$

When $L_x = L_y = 1/2$ (E⊥Z), expression (5) reduces to expression (8) below, describing the structure shown in <mark>Fig. 1c</mark>

$$\hat{\varepsilon}_{x,y} = \frac{f(\hat{\varepsilon}(v) - \varepsilon_h)\,\varepsilon_h + \varepsilon_h[\hat{\varepsilon}(v) + \varepsilon_h]}{\hat{\varepsilon}(v) + \varepsilon_h - f \cdot (\hat{\varepsilon}(v) - \varepsilon_h)} \qquad . \quad (8)$$

We note that expressions (7) and (8) were obtained in our previous work [9] by taking account of the dispersion of the internal field factor, $\theta_i\,(v)$, under conditions of 1D and 2D size confinement.

For a random particle orientation, the initial situation is that their average polarisability is determined by the expression

$$\langle \alpha \rangle = \frac{1}{3}(\alpha_x + \alpha_y + \alpha_z), \qquad (9)$$

where α_i is the component of the polarisability along the main axes of the ellipsoid [13]. A similar approach can be used in order to average the components of the spectra of the dielectric permittivity of the composite medium. Using this approach, the effective dielectric permittivity spectrum is given by

$$\varepsilon_{eff}(v) = \frac{1}{3}(\varepsilon_z + 2\varepsilon_{x,y}(v)) \qquad (9a)$$

It follows, from expression (9a), that two absorption bands will appear in the absorption spectrum of the isotropic composite medium. One of these bands corresponds to the peak position of the bulk medium, while the other is related to the contribution from the components of the dielectric loss spectrum in the direction of 1D and 2D dielectric confinement.

The corresponding components of the effective dielectric loss spectrum of such a composite medium $\mathrm{Im}(\hat{\varepsilon}_i(v))$ following from expression (5), has the form

$$\mathrm{Im}(\hat{\varepsilon}_i(v)) = \frac{A_1 B_2 - A_2 B_1}{B_1^2 + B_2^2}, \qquad (10)$$

where
$$A_{1i}(v) = \{(1-f)(1-L_i) + [f(1-L_i) + L_i]\hat{\varepsilon}_1(v)\}\varepsilon_h$$
$$A_{2i}(v) = [f(1-L_i) + L_i]\varepsilon_h \hat{\varepsilon}_2(v)$$

$$B_{1i}(v) = (1 - L_i)\varepsilon_h + f\varepsilon_h L_i + L_i(1 - f)\hat{\varepsilon}_1(v)$$

$$B_{2i}(v) = L_i(1 - f)\hat{\varepsilon}_2(v)$$

Here $\hat{\varepsilon}_1(v)$ and $\hat{\varepsilon}_2(v)$ are the real and imaginary parts of the dielectric permittivity spectrum of the particle material in the bulk state $\hat{\varepsilon}(v) = \hat{\varepsilon}_1(v) - i\hat{\varepsilon}_2(v)$ respectively. In the case of strongly diluted composite material (f << 1), containing particles satisfying the conditions required for dielectric confinement to be apparent, expressions (7) and (10) can be simplified to a form more suitable for spectrum modelling. This simplified expression was obtained in earlier work [9] and can be described as

$$\text{Im}(\hat{\varepsilon}_j(v)) = f\varepsilon_2(v)\theta_{iD}(v),\tag{11}$$

where $\theta_{iD}(v)$ is the correction factor for the internal effective field, acting on the particles under 1D, 2D and 3D dielectric confinement

$$\theta_{iD}(v) = \left(\left|1 + \frac{\hat{\varepsilon}(v) - \varepsilon_h}{m_i \varepsilon_h}\right|\right)^{-2},\tag{12}$$

where $m_i = 1, 2, 3$ for 1D, 2D and 3D confinement, respectively.

Thus, in accordance with equations (9a), (11) and (12), we obtain the following expressions for randomly oriented, strongly oblate ellipsoids of revolution ($L_z = 1$), rod-like ($L_{x,y} = 1/2$) and spherical particles ($L = 1/3$) respectively, in an infinitely dilute solution ($f < 0.01$)

$$\hat{\varepsilon}_{2eff}(v) = \frac{1}{3}f\varepsilon_2(v)\left[\varepsilon_h^2 \cdot |\varepsilon(v)|^{-2} + 2\right],\tag{13}$$

$$\hat{\varepsilon}_{2eff}(v) = \frac{1}{3}f\varepsilon_2(v)\left[8\varepsilon_h^2 \cdot |\hat{\varepsilon}(v) + \varepsilon_h|^{-2} + 1\right],\tag{14}$$

$$\hat{\varepsilon}_{2eff}(v) = \frac{1}{3}f\varepsilon_2(v)\left[27\varepsilon_h^2 \cdot |\hat{\varepsilon}(v) + 2\varepsilon_h|^{-2}\right]\tag{15}$$

It can be easily shown that expressions (13)-(15) can be generalised to the following form

$$\hat{\varepsilon}_{2eff}(v) = \frac{1}{3}f\varepsilon_2(v)\left[3 - m_i + m_i^3\varepsilon_h^2 \cdot |\hat{\varepsilon}(v) + (m_i - 1)\varepsilon_h|^{-2}\right]\tag{16}$$

where $m_i = 1, 2$ and 3.

It is worth noting that expressions (13)-(16) are valid only for strongly diluted composites, when the resonance dipole-dipole interaction between the particles themselves can be neglected. Depending on the intensity of the absorption band, or oscillator strength, the resonant interactions between the particles become noticeable when the volume fraction of the particles is in the range $f = 1\text{-}10\%$. In this case, the $\theta_{iD}(v)$ factor of the effective field is becoming dependent on the concentration of the particles [9] and expression (16) is transformed to the following

$$\hat{\varepsilon}_{2eff}(v) = \frac{1}{3} f \varepsilon_2(v)\Big[3 - m_i + m_i^3 \varepsilon_h^2 \cdot \big|(\hat{\varepsilon}(v) - \varepsilon_h)(1 - f) + m_i \varepsilon_h\big|^{-2}\Big] \qquad (16a)$$

As was shown in reference [9], the difference between the spectral characteristics of bulk materials and those from a composite of micro-particles can be very significant. In the case of the intense absorption bands, the shift in the peak position due to the dielectric confinement effect can be substantially greater than the linewidth of the absorption band observed in the bulk material. The peak position, or maximum frequency, for isolated particles in the case of 3D confinement (v_{3D}) is close to the Fröhlich's frequency (v_F) [14], or to the frequency of intrinsic vibration of the crystalline lattice (v_0), calculated from the elastic constants of the crystal.

The maximum shift in the peak position of the absorption spectrum occurs in the case of 1D confinement. The peak position obtained in this case from calculations for polar crystals coincides with the frequency of the corresponding band of LO-phonon vibrations. The maximum frequency of the spectrum from a composite medium in the case of 2D confinement lies between the frequencies for 1D and 3D dielectric confinement, i.e. $v_{3D} < v_{2D} < v_{1D}$. A similar splitting of the absorption spectra can be expected for liquid and amorphous media.

The absorption spectra of ionic micro-crystallites embedded in transparent media have been intensively studied [15-20]. A shift in the position of the fundamental lattice vibrations to the higher frequency side was observed in all of these investigations. In many cases, the peak position of the observed bands coincided well with Fröhlich's frequency, v_F. Some deviations of the experimental spectra from v_F were also observed. This deviation was explained by the larger particle size and their shape, as well as by a particle conglomeration effect, resulting in a deviation of the shape of the particles from

the modelled spheres [18,19]. LO-TO splitting in the spectra of the amorphous media was also discussed in numerous papers [20-25], including our work [9,24]. A conclusion on the size dependent nature of this effect was made earlier in the theoretical work of Lehmann [25]. We would like to emphasise that we cannot discuss longitudinal phonons in amorphous solids and, especially, in liquids, since the observed new bands arise as a result of the interaction of the transverse electromagnetic wave with a condensed medium under dielectric confinement, when the contribution of the surface vibrations becomes equal to or greater than the bulk properties of the material.

3. Experimental and discussion

The objective of this paper is to demonstrate theoretically and experimentally the role of various types of dielectric confinement on the absorption spectra of liquids in the infrared range. Three organic liquids of spectroscopic grade viz. C_6H_6, $CHCl_3$ and CS_2 were selected for these investigations, since they have strong absorption in the infrared range and also because their optical characteristics are well characterised [26-28]. In Fig. 2, sample calculations of the dielectric loss spectrum of a hypothetical composite system, containing particles (or droplets) of CS_2, satisfying the criteria necessary to experience dielectric confinement and embedded in a silicon matrix with $\varepsilon_h = 11.56$, are presented. The results of the calculations for all the model composites are summarised in Table 1, together with spectroscopic experimental data obtained under various dielectric confinement conditions for these liquids.

The infrared absorption spectra were measured on an FTS 6000 Fourier Transform Infrared (FTIR) spectrometer using a UMA microscope in one experimental set up and a GATR attachment in another set up. In order to achieve dielectric confinement of these liquids, two methods were used. Absorption measurements were made on a thin layer of liquid as well as on the adsorbed liquid. In the first case, absorption spectra were measured using a commercially available Grazing Angle Attenuated Total Reflection, GATR[TM] ,attachment from the Harrick Scientific Corporation. A thin film of liquid was obtained by liquid compression between the Ge ATR prism and a 4 mm thick silicon top window. Both elements were new and of excellent optical quality. The strength of

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window compression was changed using the GATR pressure applicator control. Measurements were performed in both polarized and non-polarized infrared light at a 60° angle of incidence.

The absorption spectra obtained for three of the liquids under investigation are shown in Fig. 3 (*a,b,c*). From Fig. 3a, one can see that in case of a thick chloroform layer, an absorption band with a peak position at $v =753$ cm^{-1}, corresponding to the bulk mode, is observed. With further compression, the peak position is shifted to $v=760$ cm^{-1} with a simultaneous increase in the linewidth. Finally, at the maximum possible compression, when the layer is only $\sim$100-200 nm thick, the absorption peak is shifted to $v = 771$ cm^{-1}. This value agrees very well with the results of calculations of the dielectric loss spectrum of liquid CHCl$_3$ under 1D dielectric confinement. We believe the line width increase observed for the absorption band at 760 cm^{-1} is due to the fact that the absorption band for this intermediate case is a superposition of the absorption bands obtained in the presence and absence of the dielectric confinement effect. We would like to emphasise that the position and the shape of the weaker absorption band, observed for CHCl$_3$ at v $=1215$ cm^{-1}, remained unchanged as expected.

Similar behaviour was observed for liquid benzene (see Fig. 3b), where the frequency of the spectrum maximum for the bulk liquid initially observed at $v=671$ cm^{-1} was shifted under strong compression to $v=679$ cm^{-1}, corresponding to 1D dielectric confinement of a very thin layer of C$_6$H$_6$. The same effect was demonstrated for liquid CS$_2$ (see Fig. 3c) with a frequency shift from $v=1498$ cm^{-1}, observed for the bulk mode, to $v=1530$ cm^{-1}, measured under 1D confinement.

In order to measure the vibrational spectra of these liquids under 2D/3D dielectric confinement, we modified the experimental setup as follows. The top silicon window was replaced with a 5 mm thick glass plate, coated with an Al layer $\sim$ 0.1 μm thick. The coating was applied by evaporation of Al wire in a bell jar evaporator. Under these evaporation conditions the Al film consists of pores, with diameters ranging from a few microns to several tens of nanometers. A small drop of liquid was placed on the top of the ATR Ge prism, then the Al coated glass plate was placed on top and the experiment was immediately run as the compression of the top glass window was increased. The effects of compression on the spectral position were practically identical to those described

earlier, with the exception of the final stage. When the thin layer of liquid evaporated completely, the maximum frequency in the spectrum shifted to 760 cm^{-1} for CHCl$_3$, 677 cm^{-1} for C$_6$H$_6$ and to 1514 cm^{-1} for CS$_2$. These measured frequencies are in excellent agreement with calculated data for 2D or 3D dielectric confinement. This can be seen in Table 1 and from Figs. 3 and 4. Note that the infiltration of the liquid into the pores in the Al layer was confirmed by the fact that the spectra related to 2D/3D confinement were still observed when the thin layer between the Ge prism and Al coated substrate had evaporated. Since the porous Al layer deposited in this experiment is too thin to be utilised as a matrix for fabricating liquid wires, the diameter/length ratio of the pores suggests that liquid spheres are embedded in the porous Al matrix situated on the top of the Ge prism.

From Table 1, the peak positions for 2D and 3D confinement are quite close to each other which makes it difficult to draw definitive conclusions, but based on the explanation above, we believe that with this experiment we can obtain information on the absorbance spectra of these liquids when they are experiencing 3D confinement.

Another experimental method for exploring dielectric confinement effects is based on the use of a macro-porous silicon matrix with liquid infiltrated into the pores. In our experiment, porous Si samples were fabricated by electrochemical etching of single-crystal (100) n-type Si wafers in a HF(48%):H$_2$O=2:3 solution. Etching was performed for 30 minutes using a current density of 16 mA/cm^2. The pore diameter was about 1 μm and all three liquids evaporated completely from the pores approximately 30 - 40 minutes after infiltration. Therefore, in-situ FTIR measurements were carried out immediately after liquid infiltration with a registration time of ~ 20 sec and a dwell time of ~ 5 sec.

Fig. 5 a,b,c shows the behaviour of the absorption spectra of benzene registered at various times using this method. The position of the absorption band for benzene immediately after infiltration was quite close to the frequency of the bulk mode of C$_6$H$_6$ (v= 675 cm^{-1}). During evaporation, the peak position shifted to the higher-frequency side, with v= 683 cm^{-1} at the end of the registration process.

We believe that at the beginning of the registration process all the pores were entirely filled with liquid benzene. Since the pore diameter is larger than that required for dielectric confinement, the absorption spectrum observed is that of the bulk liquid.

During the evaporation process, the liquid bulk phase of the C_6H_6 evaporates and only a thin layer of adsorbed liquid is left on the surface of the pores. When the electric field of the incident light is parallel to the sample surface, registration of spectra under 1D dielectric confinement is possible (see Fig. 4).

A similar situation was observed for a super-thin benzene layer using a grazing angle ATR method. With this set up, the bulk mode of the benzene spectrum ($v = 673$ cm^{-1}) is observed in S-polarisation, while in P-polarisation, which satisfies the conditions for 1D dielectric confinement, the absorption band is shifted to $v = 680$ cm^{-1}. This shift is in good agreement with our calculations. Similar results were obtained for $CHCl_3$ and for CS_2, these results are summarized in Table 1.

In conclusion, we would like to note that due to the fact that the exact value of the layer thicknesses and the sphere diameter distribution was not known, we were not able to calculate the imaginary part of the dielectric function from the experiment in order to compare it with the calculated values $\hat{\varepsilon}_{2eff}(v)$. Therefore, the position of the absorption spectra were used for this comparison. However, it is known that for strong and narrow isolated absorption bands, the peak positions of $\varepsilon''(v)$, $\alpha(v)$ and, therefore, absorbance, $A(v)$, are close to each other. Our experiments allow us to estimate the deviation to be less than 1-2 cm^{-1} .

4. Conclusion

In conclusion, we note that the experimental results obtained in this work verify the dielectric confinement effect, manifested in the strong absorption bands of dielectric media, including crystalline and amorphous structures as well as liquids. The results obtained are in good agreement with analytical expressions obtained in this work for the description of dielectric permittivity spectra under dielectric confinement.

Although the expressions obtained correlate with the theory of light absorption by small particles, this theory cannot be applied to the description of the absorption spectra of small particles of arbitrary shape, since these expressions deal only with isolated particles of spheroidal shape and are valid only when the spheroidal semi-axes in one or two directions are satisfied by the conditions $d_z \ll \lambda$ or $d_x = d_z \ll \lambda$. Therefore, the approach

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suggested in the form presented here cannot be used as a general description of the spectral characteristics of any sub-micron particles under dielectric confinement and further development in both the theory and experimental verifications is required.

The local-field effect, used in the approach presented here, is widely used at present for the analysis of the spectral characteristics of condensed matter under dielectric confinement. In particular, in Ref. [29] the description of the distribution of the *p*-component of the effective electric field, E_{eff} within a quantum well in GaAs-Al$_x$Ga$_{1-x}$As multi-quantum well structures and the absorption band for the intersubband transition has been obtained, based on the self-consistent integral equation for the local field.

The development of the approach described in this paper for the analysis of features in the spectra of materials based on porous structures is of particular importance [4,8,12,29]. The aim of these investigations is the further development of the models used in the effective medium theory. For example, in Ref. [4], hybrid models combining aspects of both phenomenological and statistical theories of the dielectric function of dielectric media were used for modelling the infrared spectra of porous silicon carbide films. In Ref. [7] an analysis of the accuracy of the modified Maxwell-Garnett equation, taking account of multiple scattering of light by the composite medium with spherical inclusions, has been carried out.

It is clear that further development of simple models for the description of the spectral properties of composite media, including meso-composites based on porous semiconductors as well as other porous media with absorbent inclusions is required. One of the important aspects of these studies is the prediction of the absorption spectra of industrial smokes, toxic aerosols and liquid drops of various types (see Ref. [31], for example).

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