

Low-Frequency Raman Scattering from Fractal Vibrational Modes in a Silica Gel

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The intensity of the Raman light scattered from localized vibrational modes in a disordered material is expressed as a function of frequency shift and fractal and spectral dimensions. This expression which is obtained interprets the low-frequency Raman scattering from a silica gel and clearly shows the fractal structure of this material.

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Since the work of Shuker and Gammon,¹ the low-frequency Raman scattering in glasses has stimulated many experiments.² Recently, Raman scattering from vibrational modes localized on nuclei in a nucleated glass was observed.³ Because of disorder which destroys the translation symmetry, it is possible to observe in glass an inelastic light scattering from acoustical phonons. The intensity $I(\omega)$ of light scattered with a frequency shift $\pm \omega/2\pi$ is determined by the Raman tensor $I_{ij}(\omega)$. From Shuker and Gammon,¹

$$I_{ij}(\omega) = C_{ij}(\omega)g(\omega)[n(\omega) + 1]/\omega. \quad (1)$$

The Bose factor $n(\omega) + 1$ for Stokes scattering has to be replaced by $n(\omega)$ for antiStokes scattering; $g(\omega)$ is the phonon density of states, and $C_{ij}(\omega)$ describes the coupling of the vibrational modes of frequency $\omega/2\pi$ to the light for a particular polarization geometry. From the Martin-Brenig model,⁴ the coupling constant $C_{ij}(\omega)$ is proportional to the square of frequency ω , and when $\omega \ll v/\sigma$ (v being the sound velocity and 2σ the correlation length in glass) we can write

$$C_{ij}(\omega) \propto \omega^2. \quad (2)$$

At low energy $g(\omega)$ is proportional to ω^2 , and the intensity of scattered light $I(\omega)$ becomes

$$I(\omega) \propto \omega^3[n(\omega) + 1]. \quad (3)$$

Such a frequency variation is well obeyed in amorphous silicon⁵ and amorphous As_2S_3 , GeS_2 , and GeSe_2 .⁶ The situation is much less clear in vitreous silica obtained from fusion.

Alexander *et al.*⁷ suggested that some glasses could have a fractal structure. Obviously this suggestion is not relevant for the amorphous materials cited above, which obey the Martin-Brenig model, but it is still valid for glasses like fused silica. The fractal structure is physically more likely in (aero)gels or sol-gel glasses than in fused glasses.

According to the relaxation theory of Alexander, Entin-Wohlman, and Orbach^{8,9} for localized electronic centers in disordered materials, it is possible to determine the frequency variation of Raman scattering from fractal vibrational modes. The Raman tensor $I_{ij}(\omega, r)$ at the point r in a material is proportional to the oscillating dielectric susceptibilities $\chi_i(\omega, r)$ and $\chi_j(\omega, r)$:

$$I_{ij}(\omega, r) \propto \chi_i(\omega, r)\chi_j(\omega, r). \quad (4)$$

The susceptibilities are linearly related to the elastic local strains $e_k(\omega, r)$ and $e_l(\omega, r)$ induced by the localized vibrations:

$$\chi_i(\omega, r) \propto p_{ik}e_k(\omega, r), \quad \chi_j(\omega, r) \propto p_{jl}e_l(\omega, r). \quad (5)$$

The elasto-optic tensor p_{ik} is considered as r independent. Then we can write

$$I_{ij}(\omega, r) \propto e_k(\omega, r)e_l(\omega, r). \quad (6)$$

Alexander, Entin-Wohlman, and Orbach^{8,9} assume for the amplitude, at the point r , of the normalized wave function associated with the a th fracton located at a distance L from this point, the following form:

$$\phi_a(\omega_a, L) \propto (l_{\omega_a})^{-D/2} \exp[-\frac{1}{2}(L/l_{\omega_a})^{d_\phi}], \quad (7)$$

where l_{ω_a} is the localization length, D the Hausdorff dimension of the fractal, and d_ϕ a geometrical exponent describing the localization in real space. They express the energy dependence of the fracton localization length as

$$l_{\omega_a} \propto \omega_a^{-\tilde{d}/D}, \quad (8)$$

where \tilde{d} is the spectral or fracton dimension.

The local strain induced by the a th fracton is proportional to the gradient of the wave function $\phi_a(\omega_a, L)$. From (6)–(8) it is deduced that the Raman tensor $I_{ij}(\omega, L)$ giving the intensity of light scattered at a point

by fracton localized at a distance L varies like

$$I_{ij}(\omega, L) \propto \omega^{2q-1} l_\omega^{-D} [n(\omega) + 1] \times \sigma^{-1} \exp[-(L/l_\omega)^{d^*}], \quad (9)$$

where $q = \tilde{d}(d_\phi/D)$. The factor δ represents the energy width of the fracton state.

The observed intensity of light scattered with a frequency shift $\pm \omega/2\pi$ is given by $I_{ij}(\omega)$ calculated by averaging of the Fermi "Golden Rule" expression for $I_{ij}(\omega, L)$ over all fracton modes:

$$I_{ij}(\omega) \propto \omega^{2q-1} g(\omega) [n(\omega) + 1], \quad (10)$$

where $g(\omega)$ is the fracton vibrational density of states.

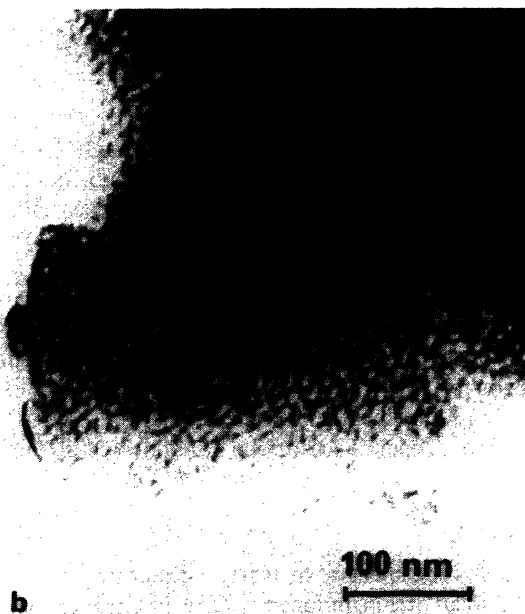
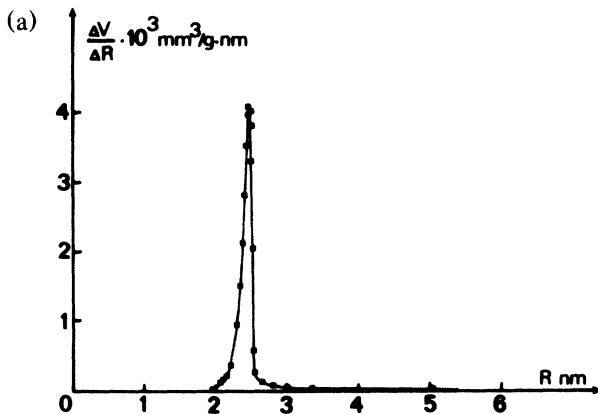


FIG. 1. (a) Pore distribution as function of their radius R as obtained by thermoporometry (Ref. 11). (b) Transmission electron microscope image of gel.

From Alexander and Orbach,¹⁰

$$g(\omega) \propto \omega^{\tilde{d}-1}, \quad (11)$$

so that

$$I_{ij}(\omega) \propto \omega^{(\tilde{d}/D)(2d_\phi+D)-2} [n(\omega) + 1]. \quad (12)$$

This last equation will interpret our experimental results which will now be described.

The silica gel¹¹ studied by Raman scattering was obtained by hydrolysis and condensation of a mixture containing 25% (by volume) of $(C_2H_5O)_4Si$, 20% of H_2O , and 55% C_2H_5OH . The pH of the solution is adjusted at a value of 2. This mixture was placed in an open vessel where polymerization and simultaneous evaporation of solvent occurred. The gel obtained is hard (Young modulus $\sim 10^9$ N/m²), brittle, and transparent. The density of the water-saturated gel is 1.7 g/cm³.

The comparison between fusion and solidification thermograms measured by thermoporometry¹¹ allows us to deduce a pore form factor equal to 1.7, which suggests that the pores are interconnected cylinders (spherical pores give 1 and cylindrical pores give 2). The pore size distribution is narrow [Fig. 1(a)] and gives a mean radius around 25 Å: This does not mean that the distribution of cylinders inside the gel is uniform, but only that all cylinders have the same radius. The total pore volume was determined to be 740 mm³/g of dried matter. These textural characteristics were confirmed by electron microscopy [Fig. 1(b)].¹²

The experimental configuration to observe Raman

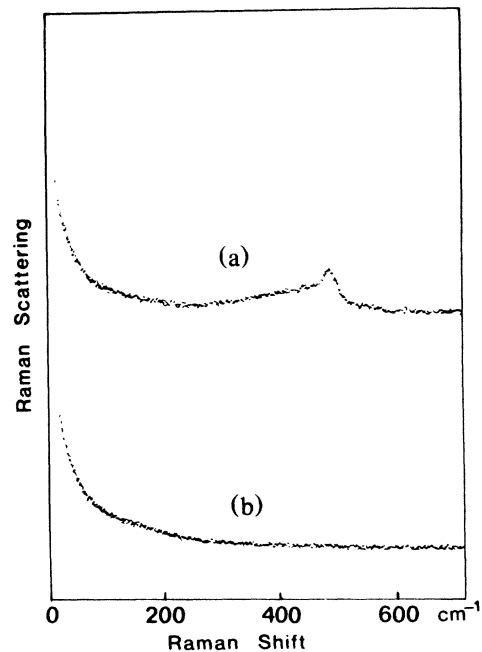


FIG. 2. Stokes-polarized Raman scattering of silica gel: (a) V-V polarization. (b) H-V polarization (incident light parallel and scattered light perpendicular to the scattering plane).

scattering from the gel was conventional.³ The incident light was emitted from a 4-W argon laser. Various lines were used, but mainly the 4880- and 5145-Å lines with a mean power of 300 mW. A Jobin Yvon model U1000 spectrograph and a photon counting system are used to study the scattered light.

The Raman spectrum at room temperature is shown in Fig. 2. The low-frequency part is totally different from the Raman spectrum of fused silica.¹³ Instead of our observing a "boson peak" at 60 cm⁻¹, a broad scattering band is seen to extend up to the Rayleigh line.¹⁴ The relatively intense line at 480 cm⁻¹ shows that the gel is not completely dried.¹⁵ The depolarization ratio at low frequency is very large (~0.7).

The more exciting experimental fact is shown in Fig. 3. The normalized intensity, i.e., $I(\omega)\omega/[n(\omega)+1]$ is represented in log-log coordinates from 10 to 180 cm⁻¹. From 20 to 180 cm⁻¹ the normalized Raman-scattering intensity obeyed the equation

$$I(\omega)\omega/[n(\omega)+1] \propto \omega^\nu, \quad (13)$$

where ν is the slope of the straight line in Fig. 3. Experimental results agree with Eq. (12),

$$\nu = (\tilde{d}/D)(2d_\phi + D) - 1, \quad (14)$$

and it was found that

$$\nu = 1.39 \pm 0.02.$$

This value is very far from the value 4 which would be found for a nonfractal material obeying the Debye model.

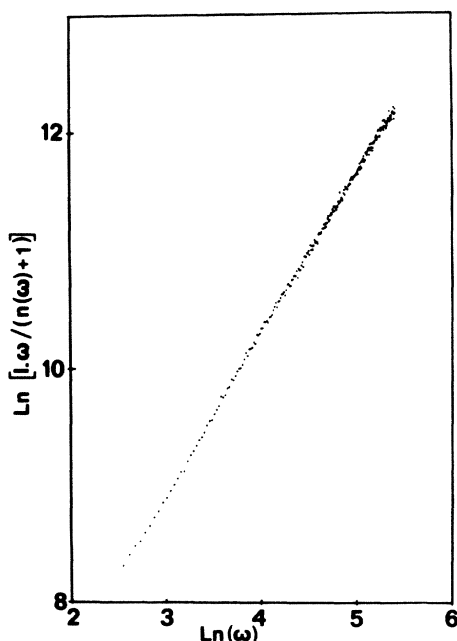


FIG. 3. Curve $\ln\{I(\omega)\omega/[n(\omega)+1]\} = \nu \ln(\omega)$ for ω varying between 10 and 187 cm⁻¹ for silica gel; $\nu = 1.39$.

The coefficient ν depends on fractal and spectral dimensions D and \tilde{d} , respectively. For a fixed value of ν , \tilde{d} varies slowly with D from (14): The coefficient ν depends much more on \tilde{d} than D . Experimentally, the fractal dimension for gels^{16,17} or porous silica¹⁷⁻²⁰ is higher than 1.75 and smaller than 3. These materials are different in composition or density from the silica gel studied herein as they are prepared by different methods and have different structure. They can nevertheless be considered to test the \tilde{d} value. If the more simple hypothesis is chosen for the localization factor taking $d_\phi = 1$, for $D = 3$ we find from our experimental value of ν , $\tilde{d} = 1.43$, and for $D = 1.75$, $\tilde{d} = 1.11$. The two extreme values for the spectral dimension \tilde{d} are in fair agreement with the theory.^{10,21}

If the theoretical value 2.5 for percolation¹⁰ is chosen for D , it is interesting to notice that the value obtained for \tilde{d} is very close to the universal one,^{10,22} which is $\frac{4}{3}$.

The Raman scattering from fractal vibrational modes is clearly demonstrated for our studied silica gel. However, the experimental coefficient ν equal to 1.39 fits the experimental data for energies higher than ≈ 20 cm⁻¹. This means that the fractal regime is effective at length scales shorter than ≈ 50 Å.

Similar experimental results have been obtained by use of low-frequency Raman scattering from porous Vycor. On the assumption that $D = 1.75$ for this material, as given by Even *et al.*,¹⁹ it was found, with the same model, that $\tilde{d} = 1.11$. This value for the spectral dimension is in agreement with the experimental results of Kopelman, Parus, and Prasad.²³

This work shows for the first time that low-frequency Raman scattering reveals clearly the fractal structure of disordered materials. This technique, completed by small-angle x-ray scattering, would allow us to determine precisely D and \tilde{d} . Similar measurements are in progress on other gels and other materials.

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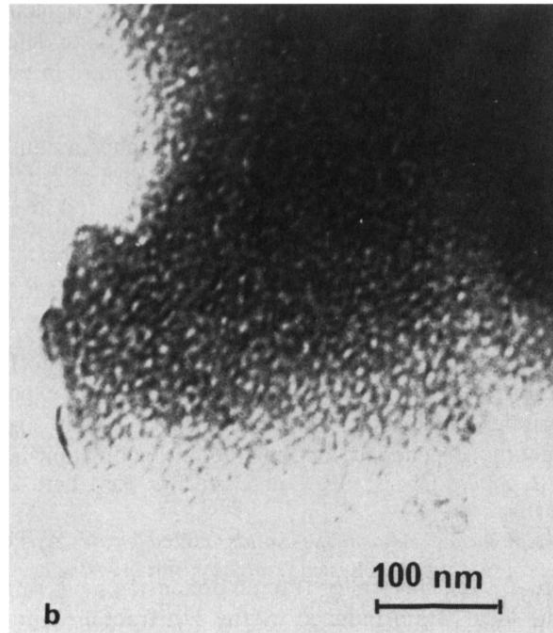
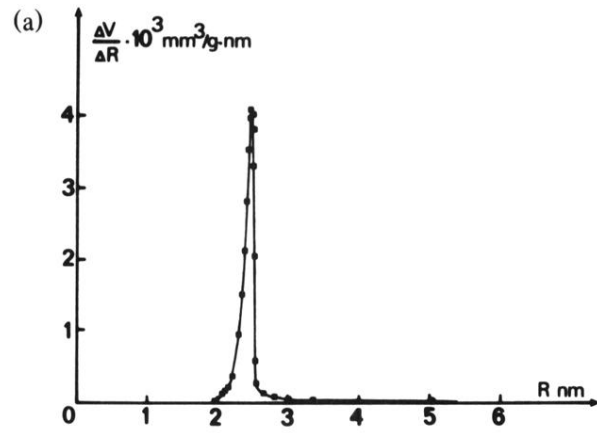


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