

# Hyper-Raman scattering by polaritons in fused quartz

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The first observation of volume polaritons in an amorphous substance—quartz glass—is reported. It is established that the spatial length of the optical vibrational modes is at least  $1\ \mu\text{m}$ .

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It is now customary to assume<sup>1,2</sup> that optical vibrations in glasses are highly localized, i.e., the extent  $\Delta x$  of the excited mode is small<sup>3</sup> ( $\Delta x \sim 10\text{--}100\ \text{\AA}$ ). This assumption has been used to construct a widely used theory of the intensity of Raman scattering of light in glasses.<sup>3,4</sup> Such small  $\Delta x$  values correspond to large uncertainties in the values of the wave vector  $\mathbf{k}$  of the excited vibration— $\Delta k \approx 1/\Delta x = 10^6\text{--}10^7\ \text{cm}^{-1}$  which greatly exceed the values of the wave vector  $k_i$  of the exciting photons ( $k_i \sim 10^5\ \text{cm}^{-1}$ ). There are no wave-vector selection rules in glasses (violation of the quasi-momentum conservation law).<sup>1-4</sup> A corollary of this would be an absence of noticeable variation in the scattering spectra of glasses as the scattering angle  $\theta$  decreases from  $90$  to  $0^\circ$ . It is known that polariton effects—a dependence of the dipole vibration frequency on the angle  $\theta$  or on the wave vector of the vibration—can be observed in the scattering spectra of crystals as  $\theta$  decreases.<sup>5</sup> It is easy to see that, because of nonconservation of quasi-momentum in glasses, the polaritons can be observed at any angles  $\theta$  in the form of low-frequency wings of the transverse vibrational lines, i.e., the entire polariton tuning region  $\omega(k)$  can be simultaneously observed at any  $\theta$ . A study of volume polaritons in glasses could therefore confirm or refute the validity of the assumptions that are used to construct the modern theories of Raman scattering of light in glasses and the physical models of glass.

We have investigated the hyper-Raman scattering (HRS) in fused quartz at small angles  $\theta$ . The HRS spectra were recorded by means of a multichannel photoelectric spectrometer.<sup>6</sup> We used the same experimental setup with annular diaphragms as in Ref. 7 to observe the scattered light at small angles  $\theta$ . The collection angles  $\Delta\theta$  of scattered light that passed through the annular diaphragm and the divergence angle of the exciting radiation were each  $\sim 1^\circ$ .

We had established earlier<sup>8</sup> that for scattering at an angle  $\theta = 90^\circ$  there are four pairs of transverse-longitudinal (*TO-LO*) splitting components of the dipole oscillations in the HRS spectra of fused quartz:  $470\ (TO)\text{--}530\ (LO)$ ,  $820\ (TO)\text{--}825\ (LO)$ ,  $\sim 1180\ (TO)\text{--}\sim 1180\ (LO)$ , and  $1065\ (TO)\text{--}1250\ (LO)\ \text{cm}^{-1}$  (Fig. 1a). The HRS spectrum for forward observation ( $\theta = 0^\circ$ ,  $\Delta\theta \approx 14^\circ$ ) (Fig. 1b) differs greatly from the spectrum at  $\theta = 90^\circ$ : the  $470\text{-cm}^{-1}$  line is missing, and a broad band appears at  $\sim 600\text{--}1050\ \text{cm}^{-1}$  instead of the  $\sim 820\text{-cm}^{-1}$  line. These differences in the HRS spectra as  $\theta$  changes indicate that the intensity of the fused-quartz lines depends on the wave vector  $\mathbf{k}$ .

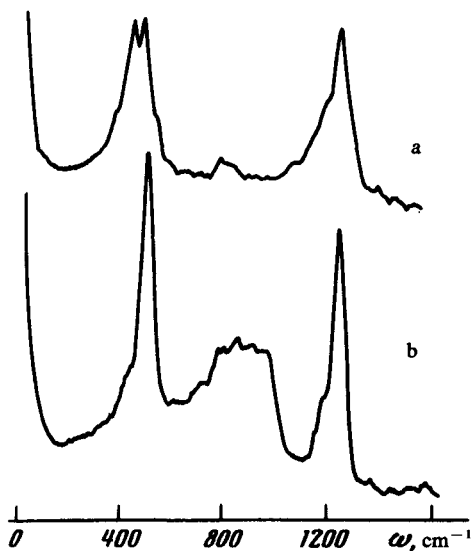


FIG. 1. HRS spectra of fused quartz: (a)  $\theta = 90^\circ$ ; (b) forward scattering ( $\theta = 0^\circ$ ,  $\Delta\theta \approx 14^\circ$ ).

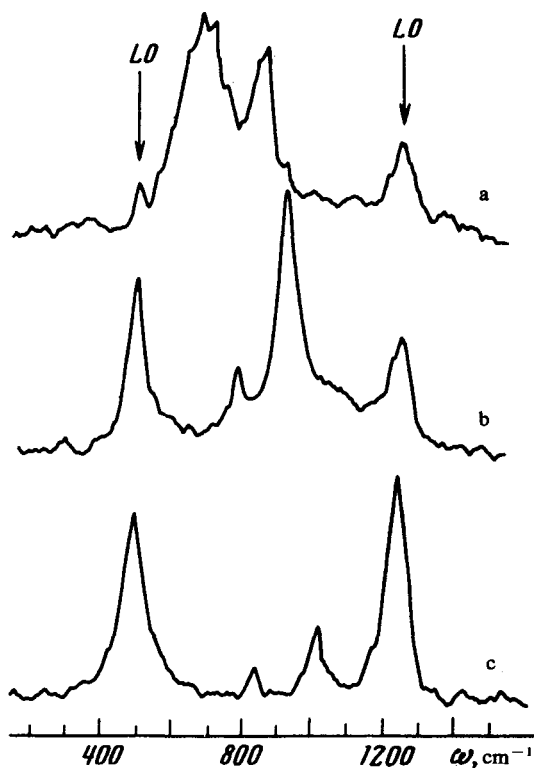


FIG. 2. Polariton HRS spectra of fused quartz at certain scattering angles  $\theta$ : (a)  $1.4^\circ$ ; (b)  $3.3^\circ$ ; and (c)  $6.1^\circ$ .

Figure 2 shows the HRS spectra for some of the angles  $\theta$  produced by the annular diaphragms with an angular width  $\Delta\theta \approx 1^\circ$ . We can see that two narrower bands, whose location of the maxima depends on the angle  $\theta$ , appear in each spectrum at the location where the broad 600 to 1050- $\text{cm}^{-1}$  band is usually present at  $\theta = 0^\circ$  and  $\Delta\theta \approx 14^\circ$  (Fig. 1b). As  $\theta$  increases, the frequencies of the narrow bands increase from 670 to 820  $\text{cm}^{-1}$  and from 840 to 1015  $\text{cm}^{-1}$ , respectively.

We note that the intensities of the 530 and 1250- $\text{cm}^{-1}$  *LO* lines and of the examined bands in the 600 to 1050- $\text{cm}^{-1}$  region depend differently on the scattered-light collection angle  $\Delta\theta$ : the intensities of the *LO* lines are proportional to the angle  $\Delta\theta$ , but the bands in the 600 to 1050- $\text{cm}^{-1}$  region, similarly to the polariton lines in cubic crystals, are broadened as  $\Delta\theta$  increases.

These unique features of small-angle scattering indicate that the narrow bands in the 600 to 1050- $\text{cm}^{-1}$  region correspond to polaritons that are associated with the 820 and 1065- $\text{cm}^{-1}$  *TO* oscillations, respectively.

The dispersion dependences  $\omega(k)$  (points in Fig. 3) of the polaritons in fused quartz were determined from the experimental  $\omega(\theta)$  dependences. We were interested in comparing the experimental  $\omega(k)$  dependences with those calculated for glass using the method<sup>7</sup> which has heretofore been used only for crystals. By using the above mentioned *TO* and *LO* frequencies and  $\epsilon_\infty = 2.1$ , we were able to calculate the predicted shape of the polariton curves (solid lines in Fig. 3).

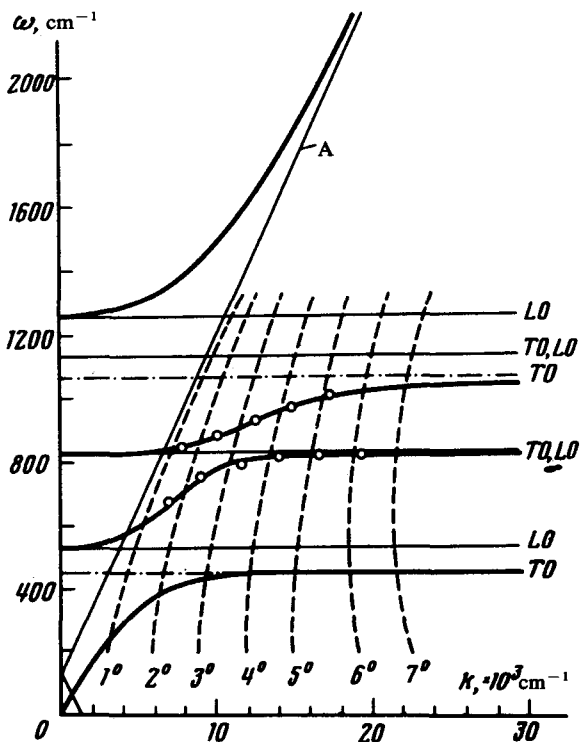


FIG. 3. Dispersion dependences of polaritons in fused quartz: the solid lines represent the calculated  $\omega(k)$  curves and the points denote the experimental  $\omega(k)$  values. Line A is  $\omega(k)$  dependence for  $\theta = 0^\circ$ .<sup>7</sup> The dashed curves represent a family of calculated  $\omega(k)$  curves for other angles  $\theta_i = \text{const}$ .

HRS can occur only in those polaritons whose  $k$  and  $\omega$  values lie on the right-hand side of the  $\omega(k)|_{\theta=\sigma}$  line (line A in Fig. 3). The polaritons of the upper branch are forbidden in HRS, and the frequencies of the three lower *TO*-polariton branches are expected to shift considerably. The intensity of polariton scattering on the lowest branch turned out to be very small. We therefore investigated only the higher frequency branches, which are associated with the 820 and 1065-cm<sup>-1</sup> *TO* oscillations. A satisfactory agreement between the experimental  $\omega(k)$  points and the calculated curves indicates that the method of calculating  $\omega(k)$ , which is usually used for crystals, can also be used for glasses.

In the measurements we could differentiate the frequencies of those volume polaritons whose wave vectors differed by  $(2-3) \times 10^3$  cm<sup>-1</sup> (points in Fig. 3). In addition, according to our measurements at the 900-cm<sup>-1</sup> frequency, the polariton line width in  $k$  space is  $\sim 2 \times 10^3$  cm<sup>-1</sup>. We can therefore assume that the polariton wave vector in fused quartz is conserved within an accuracy of at least  $\Delta k \sim 2 \times 10^3$  cm<sup>-1</sup>. It therefore follows from the uncertainty relation that the polariton mode in this glass is localized in a volume whose linear dimension  $\Delta x$  is at least 1  $\mu$ m.

This experimental result is inconsistent with the value  $\Delta x \sim 10-100$  Å obtained by model calculations.<sup>1,3</sup> We can conclude that the polaritons in fused quartz "do not see" the uncertainties caused by the topological and angular disorders characteristic of glasses, probably because of the long wavelength of a polariton as compared with the dimensions of the uncertainties; hence, the correlation region of the atomic shifts produced as a result of optical vibrations in glass must be large, just as in a crystal.

In conclusion, we note that the small-angle HRS analysis makes it possible to reconstruct the dispersion dependences of polaritons in glass and to establish a correlation between the lines of the HRS spectrum and the *TO* or *LO* oscillations, which cannot be done by using other methods.

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