Vibrational excitations in glasses show two peculiarities: an excess density of vibrational states with respect to the Debye one in the THz region (the boson peak) and a strong scattering of phonons at frequencies above around 100 GHz. These peculiarities appear at acoustic wavelengths of the order of nanometers and demonstrate themselves, e.g., in the anomalous thermal conductivity and specific heat at low temperatures (5–10 K), and in inelastic neutron and light scattering spectra. Many works over the past two decades have been devoted to the study of these topics, but both the theoretical understanding and the experimental investigation of vibrational properties of glasses are far from being complete. New experimental techniques, like inelastic X-ray scattering (IXS) and small-angle inelastic neutron scattering (INS) open additional possibilities to study acoustic properties in the Brillouin scattering regime and in the frequency range of the boson peak. Together with the picosecond optical technique (POT), the results of these methods encourage further investigations of the dynamic and spatial properties of acoustic excitations in the range of 100–3000 GHz. However, the analysis of the results has been the subject of some controversy, that cannot be resolved at present due to the limited range of spectral resolution of the devices (see, e.g., Refs. 1, 2). Therefore, it would be very useful to obtain additional information about this subject from other experimental methods.

Traditionally, low-frequency Raman scattering is applied to study spectral properties of vibrational excitations in glasses. Usually the momentum dependence of the scattering (q-dependence) is not considered, because the phonon mean free path in the corresponding frequency range is much less than the wavelength of the scattered light. As a result, any q-dependence effect should be very small and difficult to observe experimentally. The q-dependence of light scattering around the frequency of the boson peak has recently been investigated in SiO₂ glass at ambient conditions [1]; no q-dependence was observed, but the accuracy of the measurement allowed an estimation of the upper limit of the localisation length of vibrations.

In the present Letter this approach is refined and extended to lower frequencies and lower temperatures. We present the first observation of a q-dependence effect for low-frequency Raman scattering in glasses. In order to extend the available frequency range of the experiments and to demonstrate the reliability of our results, we use two different, complementary light scattering techniques: conventional Raman spectroscopy (employing a monochromator) and an interferometric technique (employing a tandem Fabry-Perot interferometer). In both cases we use spectrometers with the best elastic line suppression available in their class.

The Raman scattering experiment on a sample of glassy SiO₂ (Heralux, Heraeus, 130 ppm of OH−-groups) was performed using an Ar⁺ laser (514.5 nm, 900 mW) and a five-grating monochromator Z40. The two scattering angles were 20° and 160°; the respective wave vectors were \( q_1 = 0.62 \times 10^{-2} \text{nm}^{-1} \) and \( q_2 = 3.5 \times 10^{-2} \text{nm}^{-1} \) with the refractive index of the sample \( n = 1.46 \). An aperture limiter was placed on the lens in order to collect the scattered light within an angle of \( \sim 14° \). Polarized Raman spectra were measured using spectral slits of 60 GHz (2 cm⁻¹) for the spectral interval 420–3180 GHz (14–106 cm⁻¹) and 45 GHz (1.5 cm⁻¹) for the spectral interval 150–660 GHz (5–22 cm⁻¹). The position of the elastic line was checked for each spectrum with an accuracy of 3 GHz (0.1 cm⁻¹).

One experiment was performed at ambient conditions. The temperature in the illuminated volume of the sample obtained from the Stokes/anti-Stokes ratio was 311.0±1.7 K, and within this precision was the same for experiments in both geometries. The temperature uncertainty leads to a spectral shape uncertainty lower than \( 3 \times 10^{-3} \) over the measured spectral range. In order to obtain spectra with a high accuracy, for each scattering angle we recorded 120 and 36 spectra in the frequency...
ranges 420–2220 GHz and 150–660 GHz, respectively.

An Oxford optical helium cryostat was used for the low-temperature experiments. The incident laser beam entered the cryostat as in a conventional right angle experiment. We used a small mirror within the cryostat in order to have the necessary angle of the incident beam relative to the direction of the scattered light. With this optical scheme we exclude any Raman scattering contribution from cryostat windows that would be difficult to avoid when one uses the same window (or two parallel ones) for the incident laser beam and for the scattered light in the case of a monochromator with slits. The temperature in the illuminated volume of the sample was determined by the Stokes/anti-Stokes ratio to be 33.0±0.5 K. 72 and 40 spectra are accumulated for each scattering angle in the frequency ranges 150–660 GHz and 420–3180 GHz, respectively. We include low-frequency Raman scattering spectra of Heralux and Suprasil measured in previous experiments as right-angle Raman scattering, using the same laser and monochromator. The temperature of the illuminated part of the sample was 7 K in the case of Heralux and 4 K in the case of Suprasil as obtained from the Stokes/anti-Stokes ratio.

Inelastc light scattering spectra of a sample of Suprasil 300 (synthetic silica, Heraeus, <1 ppm of OH− groups) were obtained at temperatures 300, 45 and 6 K (employing a CryoVac dynamic Helium cryostat) using a six-pass Sandercock tandem Fabry-Perot interferometer [12] and an Ar+ laser (514.5 nm, 600 mW). The scattered light was recorded with no selection of polarization; the polarization of the incident beam was perpendicular to the scattering plane leading to a domination of the polarized inelastic light scattering in this experiment due to the low depolarization ratio of silica glass (<0.3 at low frequencies). In this experiment either of two anti-parallel beams of equal intensity was focused onto the same volume of the sample. The direction of the scattered light corresponds to scattering angles of 7° and 173° for the respective beams (\(q_1=0.21 \times 10^{-2} \text{ nm} \) and \(q_2=3.6 \times 10^{-2} \text{ nm} \)), and was collected within an angle of \(\sim 16°\). We used a free spectral range of 500 GHz over two spectral ranges on either side of the elastic line. The position of the elastic line was constantly kept aligned within about 4 GHz. The entrance and exit pinholes of the spectrometer were 450 and 700 µm, respectively, in order to suppress the transmission of higher orders of the tandem interferometer in combination with a prism (the tandem transmits every 20th order of a free spectral range; without suitable suppression this could significantly disturb a broad spectrum) [13]. The experimentally determined finesse was better than 100.

To further validate the absence of possible contributions from the instrumental tail of the elastic line or from higher transmission orders of the tandem, we measured spectra for both geometries at a low temperature, \(T=6\) K. At such a very low temperature the anti-Stokes part of the spectrum should be almost zero because the scattering intensity of the anti-Stokes spectral side is proportional to the Bose factor which is very small for this temperature (in the frequency range where this factor is not very small for this temperature, \(\nu<200\) GHz, the signal itself is very low). Indeed, the anti-Stokes part of the spectrum at this temperature shows no deviations from the dark count level of 2.47 cts/s of our detector, demonstrating the absence of contributions of higher orders or from the elastic line. A quantitative estimation limits any systematic deviations to less than about 0.03 cts/s for the frequency range down to 100 GHz. This value is three orders of magnitude less than the level of the signal at \(T=300\) K which was \(\geq 50\) cts/s. At \(T=45\) K the level of the signal varies from 1.16 cts/s at 100 GHz to 10 cts/s at 1000 GHz. Thus, one can expect that a possible distortion of the experimental spectra is not higher than 0.3% for 1000 GHz and 3% for 200 GHz at 45 K.

A low-frequency light scattering spectrum of glasses consists of two contributions—the vibrational spectrum and a quasielastic one (QES); the latter increases faster than the Bose factor as temperature increases and dominates at low frequencies. Fig. 1 shows the reduced spectra (i.e., \(I/(n(\nu) + 1)\) of the Stokes side, where \(n(\nu)\) is the Bose factor) of the Suprasil sample measured by the Sandercock tandem at \(T=300, 45\) and 6 K in the forward scattering geometry; the right-angle monochromator spectrum recorded at 4 K is also included. At frequencies above some 600 GHz the vibrational contribution dominates and the reduced spectrum does not depend on temperature. At lower frequencies it increases with temperature, since QES becomes significant. At \(T=45\) K the vibrational spectrum dominates at least down to 300 GHz.

![Graph showing reduced light scattering spectra of Suprasil](image)

FIG. 1. Reduced light scattering spectra of Suprasil in the forward scattering experiment measured by the Sandercock tandem at \(T=300\) K (thick line), 45 K (thin solid line), 6 K (dotted line). Symbols corresponds to the right-angle monochromator spectrum at \(T=4\) K.
The ratio of the back- and forward-scattering spectra, $R$, of Suprasil measured with the Sandercock tandem at $T=300$ K is shown in Fig. 2 for the Stokes and anti-Stokes sides. This ratio is a constant at high frequencies; we fix its value as 1 since it is constant up to the optical modes [11]. The figure shows that the ratio deviates from a constant in the frequency range 100–300 GHz, which is a clear demonstration of the $q$-dependence of the light scattering. To improve our statistics, in Fig. 3 (a) we show this ratio $R$ averaged over the Stokes and anti-Stokes sides and smoothed by adjacent averaging over 10 points. Circles in Fig. 3 (a) correspond to the result obtained for Heralux by Raman scattering. We note that in spite of a very weak $q$-dependence (about a few percent) and different experimental techniques being used in these two cases, we find an excellent agreement between the two curves. This is a strong evidence for the reliability of the $q$-dependence effect found in our experiments. Fig. 3 (b) shows the back- to forward scattering ratio $R$ obtained for Suprasil at $T=45$ K and for Heralux at $T=33$ K. Again a clear indication of the $q$-dependence of the light scattering is found. The precision of these curves is lower than in Fig. 3 (a) due to a decrease of the signal at low temperatures; however, the magnitude of the $q$-dependence effect is larger. Again, there is a good agreement between the results obtained by the different experimental techniques. A comparison of these results for the different temperatures with Fig. 2 leads to the conclusion that the $q$-dependence effect increases with a decrease of the quasi-elastic contribution with respect to the vibrational contribution. The deviation of the $q$-dependence from a constant is stronger for lower frequencies; this corresponds to an increase of the vibration correlation length with decreasing frequency, as will be explained in the following.

Let us turn to the interpretation of the experimental data. The $q$-dependence of the inelastic light scattering intensity in the acoustic region is determined by the equation [11]

$$I(q, \nu) \propto F_\nu(q) \langle |\nabla u_\nu(0)|^2 \rangle g(\nu),$$ \hspace{1cm} (1)

where $g(\nu)$ is the vibrational density of states, $u_\nu(r)$ is the amplitude of a vibration of frequency $\nu$ and $F_\nu(q)$ is the spatial Fourier transform of the vibration correlation function

$$F_\nu(r) = \langle \nabla u_\nu(r) \nabla u_\nu(0) \rangle / (|\nabla u_\nu(0)|^2).$$ \hspace{1cm} (2)

At small $q$, $F_\nu(q) \propto 1 - b(ql_\nu)^2$ where $b$ is a constant which depends on a particular form of $F(r)$ and $l_\nu$ is the vibration correlation length [11]. To evaluate the $q$-dependence of the experimental spectra, we use the ratio of $I(q, \nu)$ measured at the larger wavevector, $q_2$ (close to back scattering), to that at the small scattering angle corresponding to the wavevector $q_1$ [14]:

$$R(q_1, q_2, \nu) = I(q_2, \nu) / I(q_1, \nu) \approx 1 - b(q_2^2 - q_1^2)^2 l_\nu^2.$$ \hspace{1cm} (3)

In Ref. [11] it was shown that typical correlation functions (e.g., Gaussian or exponential) lead to a parameter $b$ in the range from 0.1 to 2. In the case of attenuated plane waves the respective expression for $F_\nu(q)$ is more complicated and will be considered in a forthcoming paper. For a rough estimate we follow Shuker and Gammon [15] and approximate $F(r)$ by a step function: $F(r) = \text{const}$ at $r < l_\nu$ and $F(r) = 0$ at $r > l_\nu$. This leads to a value of $b = 0.1$ (see, e.g., Ref. [11]).

The expression (3) corresponds to the vibrational part of the spectrum. At low frequencies (below 300 GHz at 45 K and 600 GHz at 300 K), the QES gives a significant contribution; its $q$-dependence is not known and in principle may be different from that of vibrations as a function of frequency. So, we first consider the part of our spectra which is dominated by vibrations. Our data
at 45 and 33 K show a clear $\mathbf{q}$-dependence in the region between 300 and 600 GHz. To estimate the correlation length $l_\nu$ from the observed $\mathbf{q}$-dependence by Eq. 3, we use our value of $R$ from Fig. 3, at, e.g., 320 GHz. This leads to $l_\nu = 27$ nm at 33 K.

It is interesting to compare $l_\nu$ with the mean free path $L_\nu$ of the acoustic vibrations obtained by POT (1), because it is natural to expect that $L_\nu$ and $l_\nu$ are interrelated. In (7) an estimate $L_\nu = 24$ nm was obtained for $L_\nu$ in silica at 342 GHz and room temperature. Therefore we need to know $l_\nu$ at 300 K, where one should separate the vibrational contribution from that of QES in the data of $R$. We assume that within our accuracy the $\mathbf{q}$-dependence of QES is negligible. This is in accordance with the model of QES developed, e.g., in Ref. (10). In these papers it is argued that the $\mathbf{q}$-dependence of QES is the same as that of the boson peak. However, at the frequencies of the boson peak, as it was already shown in Ref. (11), a $\mathbf{q}$-dependence is absent with a precision of 0.3%, i.e. it is unobservable with our accuracy. The idea that QES is related to relaxational modes that are localized on a short range leads to the same conclusion. Therefore, assuming that $R_{\text{relax}} = 1$, it is easy to show that

$$R(q_1, q_2, \nu) \approx 1 - \frac{b(q_1^2 - q_2^2)}{R_{\text{relax}}},$$

where $\eta = I_{\text{vib}}/I$. Now, using Eq. (4), taking $R$ from Fig. 3 and $\eta$ from Fig. 1 (with the spectrum at $T=4$ K as the vibrational contribution $I_{\text{vib}}$) one obtains $l_\nu = 14$ nm at $T=300$ K and $\nu = 320$ GHz. This estimate is made for a particular choice of the parameter $b$. For different choices of $b$ the magnitude of $l_\nu$ will change as $\sqrt{b}$. The fact that the values of $l_\nu$ and $L_\nu$ have the same order of magnitude may be an additional evidence that the mechanism of the $\mathbf{q}$-dependence we use in this paper is correct.

We note, that at $T=33$ K the correlation length is by a factor of 2 bigger than at room temperature. Our result agrees with the conclusion of Ref. (12) that at least up to frequencies of 400 GHz the vibrational mean free path decreases with increasing temperature up to 100 K. The conclusion of Ref. (12) was based on a comparison of the data for the phonon mean free path from the POT (7), the thermal conductivity of SiO$_2$ (6), and from the tunnel junction technique (8) applied at different temperatures. Our result leads to the same conclusion for $l_\nu$ (independent of the choice of $b$), but is obtained by a single experimental technique. It is interesting to note that the ratio of $l_\nu$ at $T=300$ K to that at 33 K in our case (a factor of 2 for $\nu=320$ GHz) is similar to that obtained by Brillouin scattering at $\nu=35$ GHz (4); this means that the dominating mechanism of the phonon attenuation may be the same at both frequencies at $T>30$ K.

In conclusion, we present the first observation of a $\mathbf{q}$-dependence of the low-frequency (0.1-1 THz) light scattering spectra of silica glasses. This effect provides information on the spatial properties of THz dynamics in glasses. We demonstrate that the estimate of the vibration correlation length found from the $\mathbf{q}$-dependence of light scattering is in a reasonable agreement with the vibrational mean free path found by POT.

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