Inelastic Ultraviolet Scattering from High Frequency Acoustic Modes in Glasses

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The dynamic structure factor of vitreous silica and glycerol has been measured as a function of temperature and of the momentum transfer up to $Q = 0.105\ \mathrm{nm}^{-1}$ using a novel experimental technique, the inelastic ultraviolet scattering. As in the case of Brillouin light scattering and ultrasonic measurements, the temperature dependence of the acoustic attenuation shows a plateau below the glass transition whose amplitude scales as Q^2. Moreover, a slight temperature dependence of attenuation has been found in vitreous silica at about 130 K, which seems to be reminiscent of the peak measured at lower Qs. These two findings strongly support the idea that anharmonicity is responsible for sound attenuation at ultrasonic and hypersonic frequencies. Finally, we demonstrate that the attenuation mechanism should show a change of regime between 0.105 and 1 nm^{-1}.

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The nature of acoustic excitations and of the acoustic absorption is a central issue in the physics of glasses and, more generally, of disordered materials [1]. The acoustic absorption of glasses is strongly enhanced compared to crystals and a broad absorption maximum occurs in many systems at temperatures higher than 10 K. The peak intensity scales as the momentum transfer Q, while the high temperature side, almost constant with temperature, exhibits a quadratic Q dependence [2]. This behavior is well documented up to $Q \approx 0.04\ \mathrm{nm}^{-1}$, typical of Brillouin light scattering (BLS) experiments [3,4].

A Q^2 dependence of attenuation has been also widely discussed in the 1–10 nm^{-1} range investigated by inelastic x-ray scattering (IXS) [5] and by numerical calculations [6–8], up to a region where a Q^4 behavior is found, possibly due to Rayleigh scattering of acoustic waves [9,10]. At even higher Qs a region of strong scattering is eventually observed as the Ioffe-Regel limit is reached [9].

Different models have been proposed to account for these experimental findings. The interpretation of the sound absorptions in terms of Debye relaxation alone is questionable because unrealistic distributions of relaxation times have to be assumed especially at high temperature and Q where the maximum of absorption tends to degenerate into a shoulder [2]. A model has been recently proposed suggesting that anharmonicity, i.e., the coupling of acoustic modes with thermal vibrations, can induce sound attenuation at ultrasonic and hypersonic frequencies, explaining both the T independence of attenuation above the peak and the Q^2 behavior [11]. The validity of this model is supposed not to extend up to IXS frequencies, being limited to the so-called Akiezer regime [12], below ≈ 100 GHz. The Q^2 behavior in the THz region, obtained also in harmonic simulations of the glass, has been attributed to the topological disorder [5–8]. A crossover regime in the attenuation mechanism can be thus inferred between $Q = 0.04$ and $Q = 1\ \mathrm{nm}^{-1}$ [3]. In this critical region little data on sound attenuation of glasses can be found, obtained by a picosecond optical technique (POT) [13], and these data seem to be inconsistent with BLS results [3].

In the present Letter we report an inelastic ultraviolet scattering (IUVS) study on the damping of acoustic waves in two prototypical glasses: vitreous silica and glycerol. This novel technique is used to gain information on the dynamic structure factor of the investigated glasses in the mesoscopic Q range from 0.078 to 0.105 nm^{-1}, never investigated before by scattering techniques.

The experiment was performed at the new IUVS beam line at the Elettra Synchrotron light laboratory in Trieste. This instrument allows one to work both with undulator and UV laser sources. In the first case the incident radiation can be tuned from 240 to 110 nm. The undulator radiation must be monochromatized and, for this purpose, an 8 m Czerny-Turner normal incidence monocromator is used [14]. The laser is a 488 nm single mode 95 second harmonic generator Lexel Ar^+ laser whose frequency is doubled by an intracavity system equipped with nonlinear beta barium borate single crystals. Independent of the configuration chosen, the beam is focused onto the sample to a spot size of about $200 \times 200\ \mu\mathrm{m}^2$. The incident flux on the sample is $\approx 10^{13}$ photons/s when operating with synchrotron radiation and $\approx 10^{17}$ photons/s in the laser mode. A spherical mirror collects the scattered radiation over a solid angle of $40 \times 40\ \mathrm{mrad}^2$ close to backscattering and sends it onto the entrance slit of a 8 m Czerny-Turner spectrograph used to energy analyze the signal coming from the probe [14]. The photons are detected by a 13.5 μm pixel charge-coupled device detector that allows one to collect the inelastic spectrum in one single shot, thus avoiding long-lasting monochromator scans of the diffraction

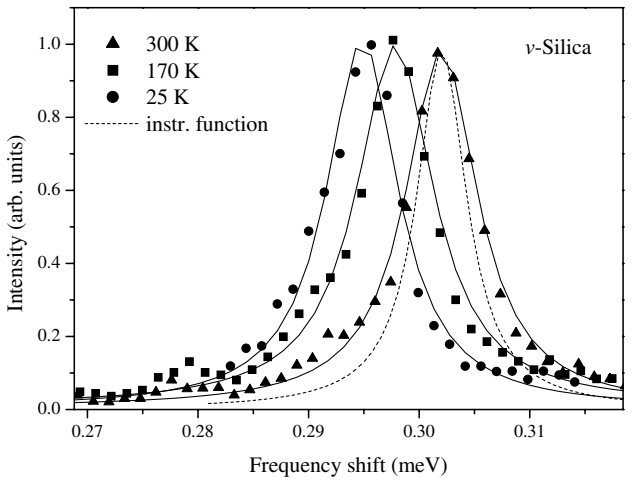

FIG. 1. Inelastic ultraviolet scattering spectrum of vitreous silica at the indicated temperatures. The full lines are the best fit to the data as discussed in the text. The dashed line represents the instrumental function.

angle. The IUVS total resolving power was measured to be 5×10^5 using the undulator beam and 1.1×10^6 in the laser configuration. The momentum transfer can be varied by changing the scattering angle ϕ and depends on the refraction index of the sample n via the formula $Q = 4\pi n/\lambda \sin(\phi/2)$, where λ is the incident photons wavelength. In the present case we fixed the scattering angle to $\phi = 175°$. The laser intensity was set to 5 mW in order to operate well below the damage threshold of our samples.

Representative IUVS spectra of vitreous silica and supercooled and glassy glycerol obtained using the UV laser source are shown in Figs. 1 and 2 at different temperatures. The full lines are fits to the data, obtained using a model function made by the convolution of the experimental resolution function with a damped harmonic oscillator model for the inelastic peaks [15]. This model for the $S(Q, \omega)$ gives an appropriate estimate of the linewidth Γ of the Brillouin line both in the liquid and in the glassy state of matter [16]. Γ is simply related to the acoustic attenuation coefficient α through the relation $\alpha = 2\pi\Gamma/hc$.

Glycerol (Fig. 2) shows a marked temperature variation of both frequency position and linewidths of Brillouin lines at temperatures higher than $T_g = 187$ K. In fact, above the glass transition temperature the structural relaxation starts to play a relevant role in the damping of acoustic waves, as recently shown in a BLS investigation of glycerol [17]. This is not the case for v-silica, since the glass transition is located at a much higher temperature ($T_g \approx 1500$ K) and only a slight temperature variation can be observed in Fig. 1.

The values of Γ/Q^2 resulting from the fit of the IUVS data of Figs. 1 and 2 are displayed as a function of T in Figs. 3 and 4, respectively. In the same figures are also shown the values of Γ/Q^2 taken from literature.

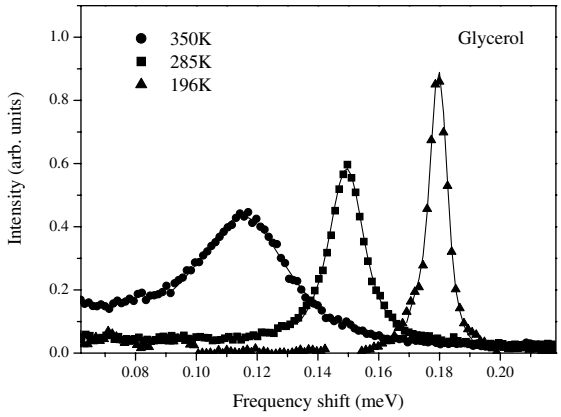

FIG. 2. Inelastic ultraviolet scattering spectrum of glycerol at the indicated temperatures. The full lines are the best fit to the data.

Figure 3 demonstrates that the high temperature side of IUVS and BLS data rescales into a single master plot when Γ is normalized to Q^2. Moreover $\Gamma(T)$ as measured by IUVS shows a slight temperature dependence below $\approx$ 200 K and a broad maximum can be inferred at $T \approx$ 130 K. These results are in good agreement with the model for acoustic attenuation in amorphous systems of Fabian and Allen based on the coupling of acoustic phonons with thermal vibrations (see Ref. [11], Fig. 2). The smearing out of the peak at 130 K can be ascribed to the less pronounced Q dependence of its intensity with respect to the high temperature plateau [2].

This picture for the sound attenuation obtained in v-silica is further endorsed by the results obtained in glycerol. In Fig. 4 the $\Gamma(T)/Q^2$ for glycerol is displayed, together with previous BLS results [17–19]. BLS $\Gamma(T)$ values increase with temperature up to $\approx$ 100 K, where they stay almost constant up to the glass transition temperature. The further increase above T_g is the contribution

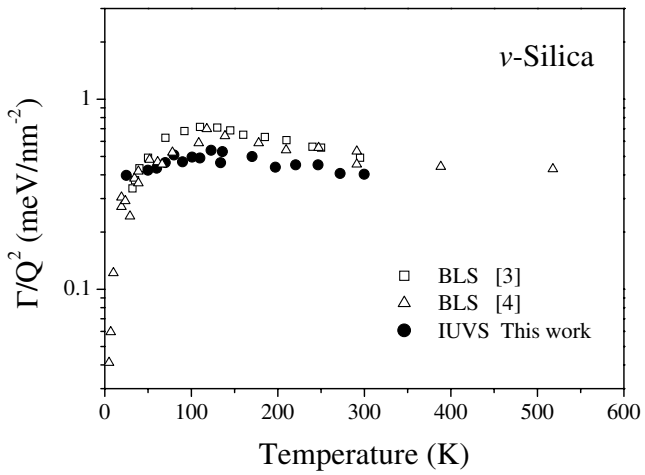

FIG. 3. Temperature dependence of Γ/Q^2 in v-silica at $Q = 0.08$ nm^{-1} (full symbols) and $Q = 0.035$ nm^{-1} (empty symbols).

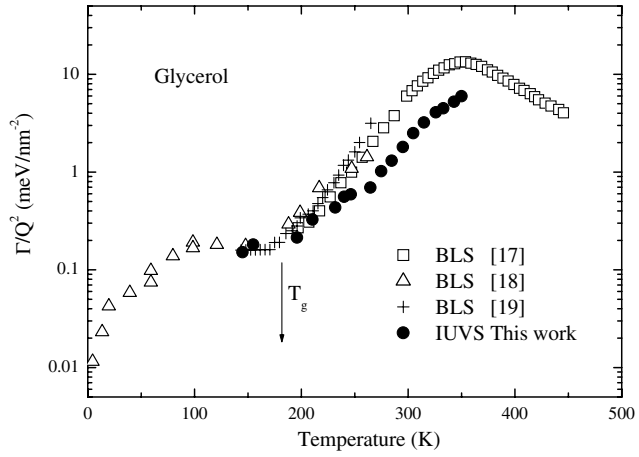

FIG. 4. Temperature dependence of Γ/Q^2 in glycerol at $Q \approx 0.08$ nm^{-1} (full symbols) and $Q = 0.035$ nm^{-1} (empty symbols). The vertical dashed line indicates the glass transition temperature, $T_g = 187$ K.

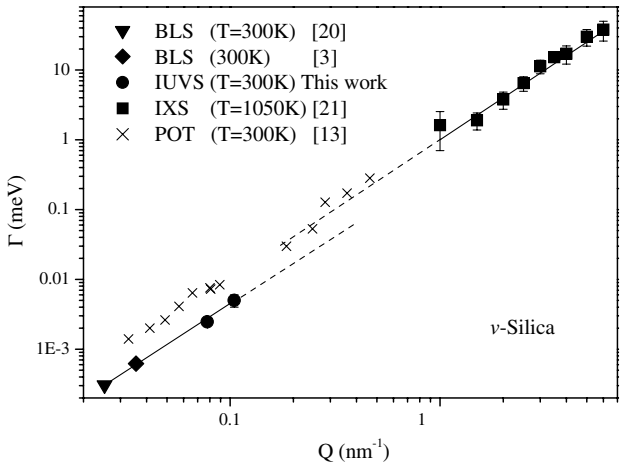

FIG. 5. Q dependence of the linewidth parameters Γ for v-silica at the indicated temperatures. The full lines represent the two distinct Q^2 behaviors, which are the best fit to $\Gamma(Q)$ at high and low Q, respectively. Also shown in the figure are extrapolations of the Q^2 laws in the intermediate Q range (dashed lines).

to the damping arising from the structural relaxation process. IUVS data conform to this behavior and the values of $\Gamma(T)$ obtained between 100 K and T_g scales as Q^2, consistent with the above cited model.

The similarities between v-silica and glycerol are in favor of a common origin of attenuation in the BLS-IUVS range. The important question now arises if the same mechanism is also responsible for attenuation in the THz range covered by IXS. To investigate this point we extended our measurements on v-silica up to $Q = 0.105$ nm^{-1} using the tunable synchrotron source. Our data now cover a relevant portion of the gap existing between traditional low frequency techniques and IXS.

We report in Fig. 5 $\Gamma(Q)$ obtained by laser IUVS and synchrotron IUVS, compared with previous BLS [3,20], POT [13], and IXS [21] results. It can be seen that our data are interpolated by a single Q^2 behavior which extends towards lower Q values to encompass BLS data. As a consequence a single attenuation mechanism, namely, nonlinear coupling of acoustic modes with thermal vibrations [11], can be invoked to account for $\Gamma(Q)$ in the whole range up to 0.105 nm^{-1}. It must be noticed that our data are systematically shifted towards lower values with respect to those obtained by POT. This result helps to clarify some important questions arising from previous studies of attenuation in the mesoscopic Q regime of v-silica [3]. It is now evident from Fig. 5 that the Q^2 behavior found at low Qs does not extrapolate up to IXS points, which exhibit a higher attenuation. In fact, the contribution to attenuation from nonlinear effects should reach a plateau above some 0.1 nm^{-1} [11], while the attenuation in the high Q regime should be dominated by topological disorder [21]. The results of Fig. 5 give the first clear experimental evidence for the existence of such a change in the attenuation mechanism between $Q = 0.1$ and 1 nm^{-1}. The apparent Q^2 behavior joining POT and IXS data led one to infer that the same mechanism should be responsible for attenuation in the whole range between 0.04 and 10 nm^{-1} [22]. Contrary to this, our results suggest that some extra contribution must exist in the attenuation values measured by POT. Notice that the existence of some spurious effect was hypothesized by the same authors [13] and tentatively attributed to the corrugation of the surface of their samples. As a matter of fact, the phonon mean free path obtained by POT data was at least 3 times smaller than that estimated from the thermal conductivity of bulk SiO_2 [13], also suggesting the existence of a spurious contribution to attenuation. It is interesting to observe that IUVS technique is insensitive to spurious surface effects since, similar to BLS, it deals with a scattering process occurring in the bulk of the sample. Moreover our results for Γ in Fig. 5 are $\approx$ 2.6 times smaller than POT ones, thus being in better agreement with thermal conductivity data.

In conclusion, we have reported an inelastic ultraviolet scattering investigation of sound wave attenuation in v-silica and glycerol glasses. Attenuation shows a plateau below T_g which scales as Q^2 and, in v-silica, a bump below ≈ 200 K, reminiscent of the maximum at about 100 K observed by ultrasonic measurements. These features can be consistently explained in terms of nonlinear coupling of acoustic waves with thermal vibrations [11]. Finally, from a comparison of our results with previous IXS investigations, evidence is given for the existence of a change of attenuation mechanism located between $Q = 0.105$ and 1 nm^{-1}.

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