PHYSICAL REVIEW B VOLUME 54, NUMBER 18 1 NOVEMBER 1996-II

Time-domain observation of nuclear contributions to the optical nonlinearities of glasses

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(Received 6 September 1996)

Time-resolved measurements of nonlinear refraction and two-photon absorption in glasses directly exhibit the effects of nuclear vibrational motion in addition to the electronic response. Time-domain observation of the Raman response of optical glasses allows us to determine the relative contributions of the electronic and nuclear mechanisms to the nonlinear response. [S0163-1829(96)51842-4]

Optical glasses can be fabricated with large refractive nonlinearities and reasonably small two-photon absorption, and thus have become strong candidate materials for optical switching applications.[1] In particular, sulfide glasses and heavy-metal oxide glasses are found to have among the largest nonresonant third-order nonlinearities reported to date.[2,3] At the other extreme, glass fibers with the smallest possible nonlinearities are desired for dispersive pulse transmission, where nonlinearities lead to pulse distortion.

An unresolved issue is the magnitude of the nuclear contribution to the nonlinear response function of glasses. Working in the Born-Oppenheimer approximation, the third-order nonlinear polarization can be written

$$P_i(t)=E_j(t)\int_{-\infty}^{t}dt'[\sigma_{ijkl}\delta(t-t')E_k(t')E_l(t')$$
$$+R_{ijkl}^{\mathrm{nuc}}(t-t')E_k(t')E_l(t')].$$

The first and second terms on the right side are the electronic and nuclear contributions to the nonlinear polarization, and $R_{ijkl}^{\mathrm{nuc}}(t)$ is the nuclear response function. By analyzing Raman-scattering spectra along with intensity-induced polarization changes, Hellwarth *et al.* estimated the relative contributions of electronic and nuclear mechanisms to the third-order polarization of a number of glasses.[4] These workers concluded that the nuclear contribution is 15–20% of the total response for fused silica, for example. Although the Raman spectra of most optical glasses indicate substantial nuclear polarizabilities, other measurements of the third-order nonlinearities,[5] even those made with short (50–100 fs) pulses,[3,6,7] have shown no conclusive evidence of a nuclear contribution.

More generally, much attention has been paid to the implications of the Raman response function of glasses for pulse propagation in optical fibers,[8,9] the performance of Raman amplifiers,[10] and the squeezing of optical solitons.[11] Despite the importance of the Raman response of glasses, there is no prior report of a direct time-domain observation of a Raman response function. Thus the expected connection between the light-scattering spectra and the time-domain response has not been established for glasses.

Here we report the time-domain observation of nuclear vibrational motion in optical glasses. We find that coherent nuclear motion is induced by pulses much shorter than the period of dominant vibrational modes, i.e., when the excitation is ‘‘impulsive.’’[12] The time-domain responses are consistent with the Raman spectra, and we discuss the assignment of the observed motions to specific vibrational modes of structural groups in the glasses. Finally, the relative contributions of the nuclear and electronic mechanisms to the nonlinear response are estimated from the time-domain data.

In the last ten years there has been considerable interest in the use of femtosecond-duration light pulses to induce and detect nuclear vibrational motion in the ground state[13] and excited states[14] of molecules. An optical pulse with a frequency bandwidth spanning two or more vibrational levels creates a superposition of vibrational eigenstates, which evolves with frequencies determined by the energy level differences. The motion of the photoexcited wave packet is detected as an oscillatory modulation (or quantum beat) in the transient optical properties. Raman-active vibrational modes have been driven and detected in molecules in solution as well as molecular crystals. The same basic physics underlies the observation of coherent optical phonons in semiconductor crystals,[15] although the details of the excitation and detection processes differ.

The situation appears to be more complex in glasses. Disorder causes a breakdown of the $\mathbf{k}=\mathbf{0}$ selection rule, so all modes are allowed to participate in Raman scattering. Shuker and Gamon showed that light scattering in disordered materials is first-order Raman scattering,[16] so the nuclear response in the time domain should in fact be simply related to the Fourier transform of the light-scattering spectrum. The vibrational density of states of glasses are often structureless or exhibit only broad features. It is reasonable to expect that the nuclear contribution will be difficult to observe due to rapid dephasing of localized vibrations in the inhomogeneous structure of a glass. Banet and Nelson attribute the failure to observe oscillatory signals from lead oxide glasses in four-wave mixing experiments[7] to rapid inhomogeneous vibrational dephasing.

We studied a variety of sulfide glasses and heavy-metal oxide glasses designed to have large third-order nonlinearities. The compositions of the glasses are listed in Ref. 3.

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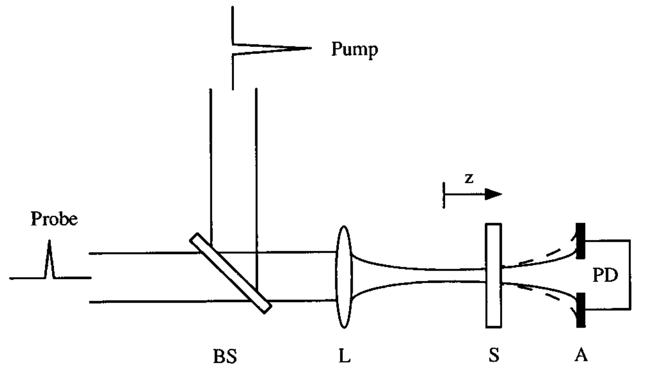

FIG. 1. Schematic of the experimental setup. BS: beam splitter; L: lens; S: sample; A: aperture; PD: photodiode. Pump and probe beams are orthogonally polarized and a polarizer (not shown) in front of the photodiode rejects the pump beam. The dashed line indicates the probe beam in the absence of the positive nonlinear refraction induced by the intense pump beam.

Time-resolved two-photon absorption and nonlinear refraction of the glasses were measured using the z-scan technique. The time-integrated z scan[17] is a simple, single-beam technique: the sample is translated through the focus of a Gaussian beam, and the nonlinear absorption or phase shift of light traversing the sample is detected as a fractional change in the transmittance ($\Delta T/T$) through an aperture in the far field. Nonlinear (i.e., two-photon) absorption is measured when the aperture is fully open. Nonlinear refraction produces a change of the beam divergence, and thus the transmittance through the aperture when it is partially closed. The magnitude of the nonlinearity is determined by analyzing the variation of $\Delta T/T$ with sample position, z, relative to the focal plane. For time-resolved z scans[18] an excitation beam is added to the apparatus in a standard pump-probe arrangement, allowing the determination of the temporal response of the nonlinearities. A schematic of the experimental setup is shown in Fig. 1.

Excitation and probe pulses with energies of ~1 nJ and centered at 825 nm were obtained from a mode locked Ti:sapphire laser, and for these experiments the pulse duration was 35 fs. To conveniently vary either the sample position (z) or the time delay, we employed collinear and orthogonally polarized pump and probe beams. The nonlinear response tensor of an isotropic medium has two independent elements; in this configuration the experiment probes the off-diagonal element of the response function R_{1122}.

Qualitatively similar traces were recorded from several sulfide and lead oxide glasses; results obtained from a Ge-Ga-S glass (Corning XT) will be discussed in detail. Time-resolved nonlinear refraction was measured in a closed-aperture scan with 35-fs pulses. The results are shown in Fig. 2(a); in addition to a sharp spike near zero delay, there is a damped oscillation with a period of 98 fs. By recording the trace shown in Fig. 2(a) with $|z|$ large compared to the confocal parameter of the beams, the contribution of two-photon absorption to the signal is kept small; the magnitude of the peak of the open-aperture scan is only a few percent of that of the closed-aperture scan at this value of z. The measured trace thus represents the refractive nonlinear response of the glass. The absorptive nonlinearity (measured using an open-aperture scan) exhibits similar oscillations but with a relative phase shift of ~90°, as expected between the absorptive and refractive parts of a response function.

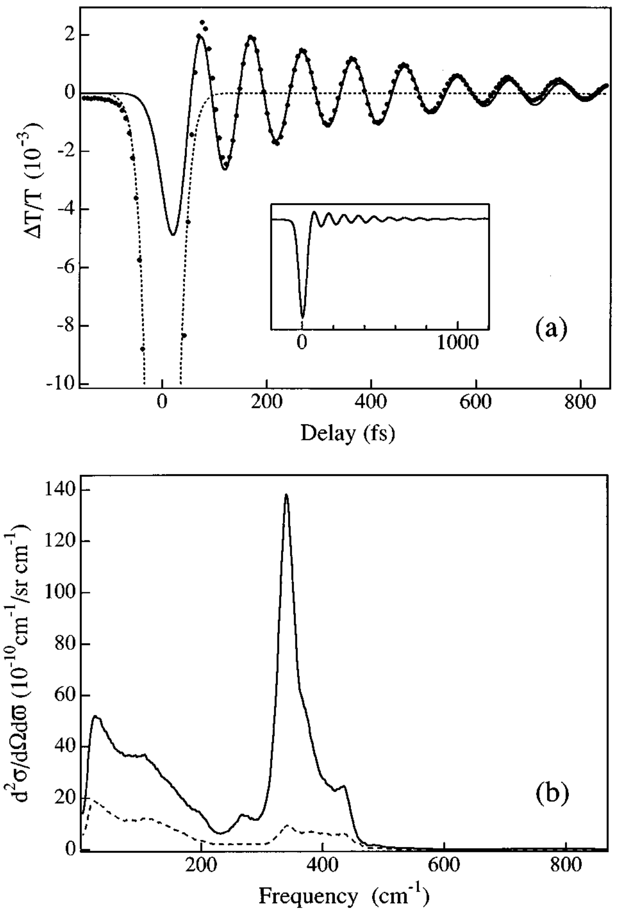

FIG. 2. (a) Time-resolved z scan of the Ge-Ga-S glass XT. The relative change in transmittance $\Delta T/T$ of the probe beam was recorded with closed aperture at a fixed value of z. Filled circles: experimental data; solid line: nuclear contribution calculated from the Raman spectra; dotted line: electronic contribution. The total experimental signal is shown in the inset. (b) Polarized (solid line) and depolarized (broken line) Raman spectra of XT glass versus the Raman shift $\overline{\omega}$ in wave numbers. The spectra were recorded in backscattering geometry with excitation at 633 nm.

The sharp feature near zero delay includes the electronic nonlinear response but the width is very close to that of the pulse autocorrelation recorded after propagation through the sample. This experiment is unable to time-resolve the electronic response, which is expected to occur on the ~1-fs time scale.

We attribute the oscillatory decay to the excitation of vibrations on the basis of the Raman spectra of XT glass, which are shown in Fig. 2(b). The polarized spectrum exhibits a strong peak near 340 cm^{-1}, along with weaker peaks at 267 and 433 cm^{-1}. The peak at 340 cm^{-1} has a linewidth of ~35 cm^{-1}, which corresponds to a 10.2-THz sinusoid exponentially damped with a time constant of ~300 fs, similar to the time-domain data.

A more-detailed analysis is based on the analytic relationship between the light-scattering spectra and the time-domain response function. The nuclear contribution to the

χ_{1122} element of the third-order susceptibility tensor can be obtained from the polarized and depolarized Raman spectra:[4]

$$\mathrm{Im}\{\chi^{\mathrm{nuc}}_{1122}(\omega)\} \propto \frac{1}{\hbar\omega_L(\omega_L-\omega)^3}\left(\frac{d^2\sigma_{hh}}{d\Omega d\omega}-2\frac{d^2\sigma_{hv}}{d\Omega d\omega}\right) \times(e^{-\hbar\omega/k_BT}-1).$$

Here $d^2\sigma_{hh/hv}/d\Omega d\omega$ denotes the polarized/depolarized differential scattering cross section, ω is the vibrational frequency, and ω_L is the frequency of the laser radiation. A Fourier transform of the imaginary part of the susceptibility with the additional condition that the response function must be real and causal yields the time-domain response function for the nuclear contribution.[8] This response function is then convolved with the excitation and probe pulse intensities and the overall scale is adjusted to fit the z-scan signal. The nuclear response function obtained from the Raman spectra is shown as the solid line in Fig. 2(a) and agrees well with the experimental results. In this case subtracting the depolarized cross section from the polarized cross section eliminates most of the broad features in the spectrum. A single peak dominates the resulting difference spectrum and the time-domain signal is approximately a single damped sinusoid. By measuring the diagonal element $R^{\mathrm{nuc}}_{1111}(t)$ (which is determined by the polarized spectrum alone) in other glasses it should be possible to determine whether all peaks in the Raman spectrum contribute to the time-domain signal.

We now turn to the nature of the vibrational modes responsible for the observed signals. Modes with the largest differential polarizabilities will contribute most to the time-domain response, and these will be the totally symmetric modes. A fairly sharp peak in the Raman spectrum indicates that the mode responsible for that peak is not influenced strongly by the disorder of the glass. Based on these arguments, it is clear that the possible candidates are either localized modes or symmetric ring-breathing modes.

The structure of Ga-containing Ge sulfide glasses is thought to be a network of corner-sharing GeS_4 tetrahedra similar to the SiO_4 network in silica glasses, with Ga substituting for Ge on some sites. $Ge_{1-x}S_x$ glasses exhibit a strong and polarized Raman peak at 340 cm^{-1}, and this has been assigned to the A_1 breathing mode of the tetrahedral GeS_4 group.[19] Corning XT glass is 87% GeS_2 and 13% Ga_2S_3, so we attribute the 340-cm^{-1} peak in the Raman spectrum to this mode. Similar time-resolved and light-scattering experiments on materials which exist in both crystalline and glass phases would allow further investigation of whether the experimental results are due to localized modes (present only in the glass) or ring-breathing modes (present in both phases).

The Ge-Ga-S glass XT is a natural candidate for the time-domain observation of the nuclear response function, because the Raman spectrum is dominated by a relatively narrow peak, i.e., it does not appear to be ''glasslike.'' We have observed similar oscillatory signals from a Pb- and Bi-rich borate glass (Corning PbBi1) that has a typical glasslike Raman spectrum: one or more low-frequency ($\sim$100 cm^{-1}) features superposed on a broad background. The composition and structure of PbBi1 are very similar to those of the Pb-Bi-O glass studied in Ref. 7. The time-resolved nonlinear refraction of PbBi1 is shown in Fig. 3(a) along with the response inferred from the Raman spectra of Fig. 3(b). The 237-fs period corresponds to the Raman peak at 130 cm^{-1}, which has been assigned to a Pb-O stretch mode[20] in gallate glasses with similar Pb concentration.

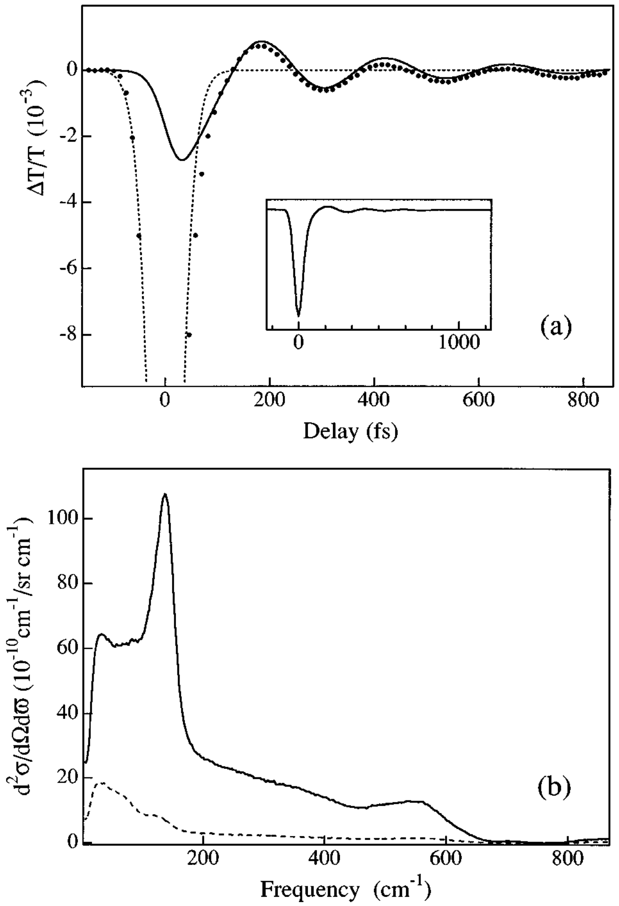

FIG. 3. (a) Time-resolved z scan of the Pb-Bi-O glass PbBi1. All curves and symbols have the same meaning as in Fig. 2(a). (b) Raman spectra of PbBi1 glass. Curves have the same meaning as in Fig. 2(b).

Since the electronic and nuclear contributions to the nonlinear response can be separated so simply in the time domain, it is possible to make a direct estimate of their relative strengths. The absolute nonlinearities can then be obtained by either quantitative analysis of the time-resolved z scan or by using the total nonlinear response obtained with a time-integrated z scan. We assumed that all of the signal left after subtraction of the nuclear response is due to the electronic response [indicated by the dotted lines in Figs. 2(a) and 3(a)] and not other physical processes, and integrated the time-resolved signal to find that (13±5)% of the (R_{1122}) nonlinear refraction of Corning XT glass is due to the nuclear contribution. For PbBi1, we obtained (12±5)% for the fractional nuclear contribution. These values are comparable to those obtained for the R_{1111} tensor elements of other glasses, from their Raman-scattering spectra and intensity-induced polarization changes.[4] However, a more systematic study is needed to determine the significance of obtaining similar values for different materials and tensor elements.

Although it is implied in the analysis above, it is worth mentioning that these experiments are not vibrationally selective, i.e., they do not provide information on the origin of the vibrational dephasing. Determination of the homogeneous dephasing time of a vibrational mode requires either an infrared photon echo or an optical experiment relying on fifth- or higher-order nonlinearities, such as the Raman echo.[21]

In conclusion, we have shown that it is possible to observe the nuclear response of an optical glass in the time domain. From the time-domain data we estimate the relative contributions of nuclear and electronic mechanisms to the nonlinear refraction. With shorter pulses it may be possible to resolve the electronic response directly but it will still have to be separated from the Raman response of the glass.

We thank M. L. Powley for assistance in preparing the glass samples. Portions of this work were supported by the National Science Foundation under Grant No. DMR-9321259. T. Krauss acknowledges the support from New Focus Research.

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