Quasielastic Scattering of Synchrotron Radiation by Time Domain Interferometry

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We use synchrotron radiation and time resolved x-ray detection to measure structural relaxations of glycerol [$C_3H_5(OH)_3$] having time scales of 30 to 200 ns at 1.5 Å^{-1} momentum transfer. Foils containing ^{57}Fe (14.4 keV nuclear resonance, 141 ns lifetime) are placed before and after the nonresonant sample, and a small difference (~70 MHz) is established in their nuclear response frequencies. Quasielastic scattering from the sample perturbs the 70 MHz quantum beat pattern of the nuclear scattering. A simple model relates the perturbation to the dynamic structure factor of the sample. [S0031-9007(97)04191-4]

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The motion of atoms and molecules on angstrom length scales and few ns time scales is a subject of great interest, providing the possibility to gain insight into many physical processes, including diffusion [1], glass transitions, and the motions of complex biological molecules and polymers [2,3]. Here we introduce a method of measuring quasielastic x-ray scattering from samples having relaxations on time scales of ~15 ns to more than 150 ns (energy scales of ~50 to <5 neV) and at large momentum transfers, in principle up to 14 Å^{-1} (this work is at 1.5 Å^{-1}). The essential idea of this technique is to set up a temporal interference pattern in the nuclear scattering from two foils containing ^{57}Fe (14.4 keV nuclear resonance, 141 ns lifetime) and then see how it is modified by quasielastic scattering from a sample placed between the two foils.

Previously, scattering experiments at large momentum transfers and sub-μeV resolution have largely been the domain of neutron work. The spin echo technique can measure relaxation on few ns (or shorter) time scales (energy transfers of ~100 neV or more) and momentum transfers of a few Å^{-1} [4]. However, high resolution (long time scales) and large momentum transfer are difficult to achieve simultaneously. Light scattering techniques [5] can achieve neV energy resolution (or better), but are limited to low momentum transfers.

In some special cases, when the sample contains a suitable nucleus with a low-lying excited state, it is also possible to do x-ray (or γ-ray) measurements with few neV resolution. The Mössbauer effect allows one to take advantage of the intrinsically small linewidths of nuclear resonances, e.g., 5 neV for the 14.4 keV resonance of ^{57}Fe, to investigate samples either in conventional frequency-domain absorption experiments [6], or, more recently, in time domain measurements [7]. Both frequency [8] and time domain [9] methods have been applied to the study of diffusion. However, these techniques are usually limited in the momentum transfer to exactly that of the absorbed photon (7.3 Å^{-1} for ^{57}Fe). If the sample does not contain a suitable isotope, then either one must be implaned (possibly disturbing the system) or a more complicated and much lower count rate Rayleigh scattering of Mössbauer radiation (RSMR) measurement [10] must be performed. RSMR uses a narrow line source before the sample and a narrow line absorber after the sample to directly measure the frequency distribution of the scattered radiation. We note that there has been one attempt to do an RSMR measurement using synchrotron radiation [11].

We describe this technique as time domain interferometry. The essence of most interferometry measurements is to combine the wave scattered from an object with a reference wave. Usually, one measures the spatial intensity distribution and thus obtains information about the spatial characteristics of the sample. Here we measure a temporal intensity distribution (quantum beats), and obtain information about the temporal characteristics of the scattering from the sample. We use two single line nuclear scatterers (^{57}Fe containing foils) chosen to have different response frequencies (see Fig. 1). After excitation by a pulse of synchrotron radiation, the nuclear scattering from them will show quantum beats (our interference pattern), as the radiation reemitted by the two foils at slightly different frequencies goes in and out of phase. If one places a sample between the two foils, from which the scattering changes on a time scale of the order of the quantum beat period, it will perturb the beats. In essence, after the impulse excitation, the wave from the second foil acts as a reference, allowing the sample-induced modulations of the wave from the first foil to be measured [12].

The amplitude of the quantum beats may be related to the dynamic structure factor of the sample using a semiclassical model. We take the responses of the two ^{57}Fe foils after impulse excitation at $t = 0$ to be $G_1(t)e^{-i(\omega_0+\Omega)t}$ and $G_2(t)e^{-i\omega_0 t}$, where 1 and 2 indicate the foils before and after the sample, respectively. ω_0 is the nuclear response frequency, and Ω is the frequency difference in the response of the two foils (which may be introduced artificially via Doppler shift). G_1 and G_2 are slowly varying functions of time (in the limit of thin

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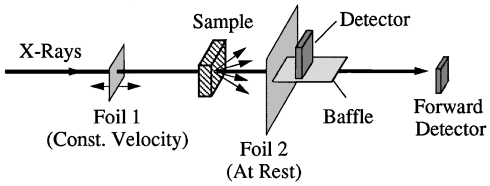

FIG. 1. Experimental setup. ^{57}Fe stainless steel foils were placed before and after the sample, with the first mounted on a Mössbauer drive in constant velocity mode. Detectors measured both the transmitted radiation and that scattered by the glycerol into its structure factor maximum.

foils, $|G_1|^2$ and $|G_2|^2$ will be exponential decays with the natural lifetime, 141 ns for ^{57}Fe).

A pulse of synchrotron radiation excites foil 1, then is scattered by the sample with some finite momentum transfer, $\mathbf{q}$, and excites foil 2. Considering only single scattering from the sample (Born approximation limit), the ratio of the field scattered by the sample to the incident field is proportional to the integral over the electron density ρ of the sample, with appropriate phasing for the momentum transfer. The time dependence of the scattered field (*after* impulse excitation at $t = 0$) is

$$E_m(\mathbf{q}, t) \propto G_1(t) e^{-i(\omega_0+\Omega)t} \int \rho_m(\mathbf{r}, t) e^{i\mathbf{q}\cdot\mathbf{r}}\, d\mathbf{r} + G_2(t) e^{-i\omega_0 t} \int \rho_m(\mathbf{r}, t = 0) e^{i\mathbf{q}\cdot\mathbf{r}}\, d\mathbf{r}\,.$$

The first term is the field from foil 1 after scattering from the sample, while the second is the field from foil 2 (the reference wave). The subscript m indicates that this expression is for some particular microstate of the system and its subsequent evolution. We neglect the influence of the wave from foil 1 on the emission from foil 2, which leads to a convolution term which is small if the frequency shift, Ω, is much larger than the width of the lines used in the experiment. The measured intensity will be the absolute square of E_m, averaged over sample configurations, since the experiment is performed over many successive synchrotron radiation pulses, which are not correlated with the sample microstate. Taking (for simplicity) foils 1 and 2 to be identical ($G_1 = G_2 = G$),

$$I(\mathbf{q}, t) \propto |G(t)|^2 [S(\mathbf{q}, t = 0) + S(\mathbf{q}, t) \cos(\Omega t)]\,,$$

where $S(\mathbf{q}, t)$, the intermediate scattering function, is proportional to the Fourier transform of the dynamic structure factor [13],

$$S(\mathbf{q}, t) = \int d\mathbf{r} \int d\mathbf{r}'\, e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} \langle \rho_m(\mathbf{r}, t) \rho_m(\mathbf{r}', t = 0)\rangle \propto \int d\omega\, S(\mathbf{q}, \omega) e^{i\omega t}.$$

We take f_{qe} to be the ratio of the scattering within our experimental time window to the total scattering [where the total scattering is the integral of $S(\mathbf{q}, \omega)$ over frequency, or $S(\mathbf{q}, t = 0)$]. f_{qe} includes both elastic scattering and quasielastic scattering with time scales greater than about 10 ns (energy scales less than or the order of 75 neV) and is essentially the Debye-Waller factor [14]. One has

$$I(\mathbf{q}, t) \propto |G(t)|^2 \left[1 + f_{\mathrm{qe}}(\mathbf{q}) \cos(\Omega t) \times \int d\omega\, S^n(\mathbf{q}, \omega) e^{i\omega t} \right],$$

where n indicates normalization (division) by the integral of the dynamic structure factor over frequency.

Two effects are clear from the above equation. First, if the amount of quasielastic scattering is small relative to the total scattering ($f_{\mathrm{qe}} \ll 1$), then the amplitude of the beats will be small, and the measured response will be essentially the single foil response. Second, if there is significant quasielastic scattering, then the decay of the quantum beats (the reduction of the contrast of the beats with time) will directly give the Fourier transform of the dynamic structure factor. In particular, structural relaxation around a glass transition is frequently modeled using a Kohlrausch function [15], giving

$$I(\mathbf{q}, t) \propto |G(t)|^2 [1 + f_{\mathrm{qe}}(\mathbf{q}) \cos(\Omega t) e^{-(t/\tau_k)^\beta}]\,,$$

where τ_k and β are the ($\mathbf{q}$-dependent) parameters describing the quasielastic scattering from the sample.

Note that no time domain effects are visible if one, or both, of the foils are removed. Within the above plane wave analysis, this is due to the average over sample microstates. However, in light of recent x-ray intensity fluctuation measurements [16], we examine this in more detail. In particular, if one could observe the x-ray speckle pattern (essentially the exact diffraction pattern of a microstate of the system) from the sample, then one could relate temporal correlations in the speckle intensity of the sample dynamics. However, this typically requires that the incident beam have a size comparable to its transverse coherence length (some few microns) and that the detector size be similarly reduced (to that of a single speckle) resulting in a severe drop in flux. Thus, while x-ray correlation experiments have been extended to times of $\sim$0.1 ms [17], reduction to μs scales will be difficult even at third generation synchrotron radiation sources. In addition, the bandwidth used to gain sufficient flux to achieve event the 0.1 ms resolution limits the range of momentum transfer to less than 10^{-2} Å^{-1}.

Our experiment was performed on the Nuclear Resonance Beamline [18] of the European Synchrotron Radiation Facility (ESRF). The storage ring was run in 16 bunch mode, providing x-ray pulses of about 100 ps duration every 176 ns. The incident radiation was tuned to the 14.4 keV nuclear resonance in ^{57}Fe. The flux was about 10^9 photons/sec in a 6 meV bandwidth, at an average storage ring current of $\sim$70 mA. The beam size was about 0.4×1.5 mm^2.

In order to demonstrate the feasibility of this technique, we choose glycerol as our sample because it has been the subject of many previous investigations. Here, we reference a tiny fraction of the recent work, hoping that the interested reader will look up the references in

the papers. Previous work includes measurements where resonant isotopes were introduced into the sample [19], RSMR experiments [20], and neutron scattering [21]. In particular, our results may be compared to RSMR measurements by Elwenspoek *et al.* [22].

The first foil [stainless steel (SS) 95% enriched in ^{57}Fe] was mounted about 30 cm upstream of the sample on a Mössbauer drive moved at a constant velocity of 6.3 mm/sec ($64.9\Gamma_0$) (see Fig. 1). A second SS foil (nearly identical to the first) was placed, at rest, 60 mm downstream of the sample and intercepted both x rays transmitted directly through the glycerol sample and those scattered at finite angles. Time resolving avalanche photodiode (APD) detectors were placed downstream of the second foil. A small APD was used to measure the forward scattering from the two foils while a larger one, $10 \times 10\ \mathrm{mm}^2$ [23], was placed near the sample in the structure factor maximum for scattering from the glycerol ($q = 1.5\ \mathrm{Å}^{-1}$ or $2\theta \sim 12°$). The acceptances of the detectors, as seen from the sample, were about 2×10^{-5} and 2.4×10^{-2} sr, respectively. A baffle was installed to prevent the detector in the structure factor maximum from seeing scattering from the direct beam hitting the second foil. In addition, Al (120 μm) placed in front of this detector and a high discriminator threshold ensured that background events from 6.4 keV Fe K x-ray fluorescence were not detected (e.g., proceeding from internal conversion in the second SS foil). Count rates in this detector were typically $\sim 2\ \mathrm{s}^{-1}$ in the window of 15–150 ns after the prompt pulse. Prompt rates were $\sim 10^5$ Hz. Count rates in the forward detector were about 2 orders of magnitude larger.

The glycerol sample, 5 mm thick, was mounted in a cryostat with thin kapton windows. Removal of the cryostat from the path of the direct beam showed the background (due, e.g., to air scattering along the beam path) in the detector in the structure factor maximum was about 3%. The contribution from the thin kapton windows of the cryostat was estimated to be an additional 2%. Both backgrounds were ignored in the data analysis.

Figure 2(a) shows the time dependence of the nuclear forward scattering (see [7]) from foil 1, without foil 2 in place. One observes the expected exponential decay modulated by a Bessel function from multiple nuclear scattering [24]. The minimum at $t \sim 75$ ns is not very sharp, indicating the SS foils have a thickness distribution. A good fit to the time response was found taking an average thickness of $T = 27.3$ ($T =$ the number of absorption lengths at resonance) and a distribution of sample thickness of $\pm 15\%$ over the area of the x-ray beam. This thickness corresponds to a linewidth $6\Gamma_0$ in a conventional Mössbauer transmission experiment (neglecting source width). The time response of foil 2 is nearly identical to that of foil 1, with an average thickness of $T = 26.2$ and a distribution of $\pm 17\%$.

Figure 2(b) shows the time dependence of the forward scattering in the direct beam passing through the two foils. The quantum beat at $\sim$70 MHz (13.6 ns period)

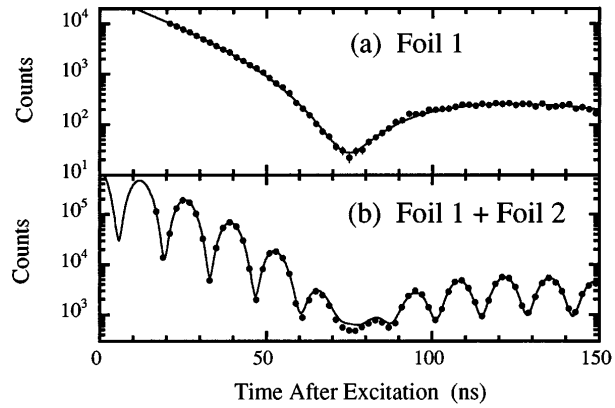

FIG. 2. Forward scattering from (a) foil 1 alone and (b) both foils in series, with foil 1 on the Mössbauer drive at constant velocity (temperature at 200 K). Lines are fits (see text).

introduced from the constant velocity motion of the drive is clear. Note that we used a nitrogen bath cryostat to avoid introducing vibrations (e.g., by the compressor of a closed cycle refrigerator). The fit in the figure uses the parameters found from measurements of the two foils individually and a constant velocity shift corresponding to $64.9\Gamma_0$. In addition, for good agreement, we included a slight broadening of $0.3\Gamma_0$ which is probably caused by imperfect drive motion or residual effects of vibrations. This broadening and the thickness distributions in the foils account for the slight decrease in beat amplitude at later times. The forward time response was constant.

Figure 3 shows the change in the time response in the scattering at the structure factor maximum of the glycerol with temperature. One immediately notes that the contrast in the beats decreases with increasing temperature. In particular, at 263 K, the beat contrast at later times is remarkably reduced from that at early times, corresponding to the expectations for quasielastic scattering. In addition, the amount of inelastic scattering increases with temperature, leading to an overall, time independent, reduction in the beats. (Measurements were also made without foil 2 in place. These always showed just the time response of the first foil [Fig. 2(a)], independent of the glycerol temperature, as expected from the model above.)

The data were well fit using a stretched exponential for $S(\mathbf{q}, t)$. The quality of the data was not sufficient to fit all parameters (β, τ_k, and f_{qe}) independently so we chose $\beta = 0.7$ as was found from neutron measurements [21] and allowed the τ_k and f_{qe} to vary. Fitting gave $\tau_k > 5\ \mu$s, $f_{\mathrm{qe}} = 0.93 \pm 0.06$ at 200 K, $\tau_k = 180 \pm 70$ ns, $f_{\mathrm{qe}} = 0.87 \pm 0.05$ at 250 K, and $\tau_k = 34 \pm 8$ ns, $f_{\mathrm{qe}} = 0.79 \pm 0.05$ at 263 K. (At 276 K, the data quality did not allow unique determination of the parameters—here we show the data are consistent with $\tau_k = 12$ ns, $f_{\mathrm{qe}} = 0.7$.) The results (200–263 K) agree nicely with the RSMR work of Elwenspoek *et al.* [22].

We have demonstrated a new technique that may be used to do time domain measurements of quasielastic scattering with large momentum transfers. In comparison

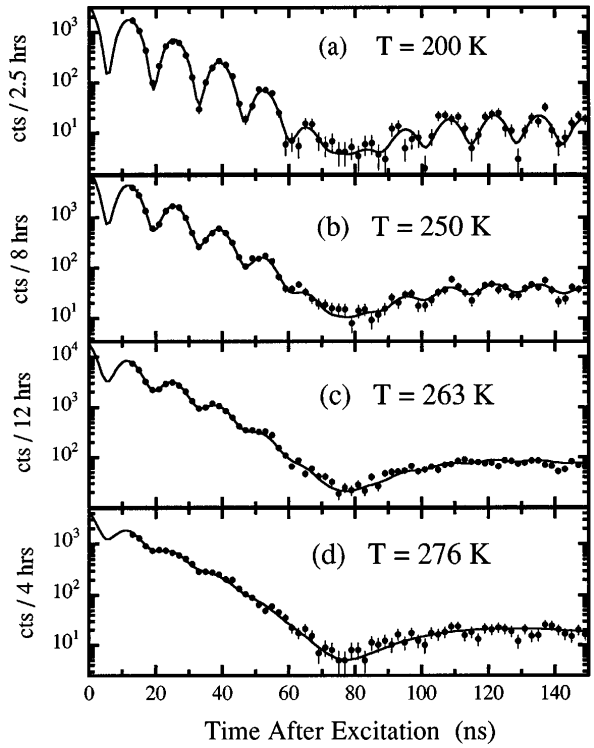

FIG. 3. Scattering from glycerol measured in structure factor maximum at different temperatures. Lines are fits (see text).

to other synchrotron based work, this technique has access to a unique range of momentum and time scales. The time scales here are much longer than the ps time scales of even the highest resolution inelastic x-ray scattering measurements with either crystal analyzers [25] or nuclear absorption techniques [26] and much shorter than the $\sim$0.1 ms scales that have been reached by speckle measurements [17]. Neutron scattering measurements provide more direct competition with this technique, allowing access to similar (or slightly shorter) time scales and momentum transfers. However, they have difficulty simultaneously achieving both high energy resolution and large momentum transfer, and they may suffer from incoherent scattering backgrounds. The last is very different from this work where the dominant channel (Thomson charge scattering) is entirely coherent.

This work is similar to the RSMR technique, and might be thought of as a time domain analog to that method. However, aside from being a direct time domain measurement which might add insight in some cases, this method seems to more easily access longer time scales, which are sometimes obscured by the broad linewidths of the sources and absorbers used in RSMR. Also, the inherent brilliance of synchrotron radiation permits one to do experiments with small ($\sim$1 mm^2) samples and with modest or even extreme (μrad) collimation, such as investigation of quasielastic scattering in the neighborhood of Bragg peaks.

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