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Final Report: Stanford Free Electron Laser Materials Research: Picosecond nonlinear Studies of Condensed Matter Systems

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The Stanford SCA/FEL is a powerful took which provides unique capabilities for conducting materials research. The FEL can be used to obtain information of fundamental importance on a wide variety of materials such as high temperature superconductors; semiconductors, including amorphous materials and multi-quantum well structures; inorganic and organic crystals and glasses; biological materials, for example, hemoglobin, proteins, DNA, and membranes; surfaces and molecules on surfaces; polymeric solids and liquids. In all cases it is the unique operating characteristics of the SCA/FEL, providing single, high powered, picosecond pulses tunable across the IR spectrum, which makes it possible to probe matter with methods that have previously been impossible.

In the last thirty years, lasers have gone from being intriguing new devices to the status of powerful instruments for probing matter. In particular, picosecond pulses of light have made it possible to examine dynamically interatomic and intermolecular interactions on the timescales of fundamental events. While lasers are capable of producing ultrashort pulses, usable systems have operated until now in the visible and near ultraviolet spectral regimes. There are lasers which can generate light in the IR, however, these are frequently fixed-frequency devices which produce long duration pulses. Techniques which can produce psec pulses in the IR generally are low in power and limited to the shorter wavelength portion of the IR.

In the visible, psec optical experiments have become highly sophisticated, using pulse sequences which are composed of a number of laser beams impinging on the sample from a variety of directions with precise time control and frequency control. Many modern experiments are nonlinear techniques in which the signal is a high power of the intensity of the laser. The requirements of modern ultrafast experiments place extreme demands on the laser source.

The first photon echo experiments ever performed with a free electron laser as the source were conducted at Stanford using the SCA/FEL.[1] The photon echo is a nonlinear experiment which involves three interactions of the sample with the radiation field.[2] The incoming pulses generate a polarization in the sample which gives rise to an outgoing coherent pulse of light propagating in a unique direction. This outgoing pulse is the signal, and is referred to as the echo. As the time between the incoming pulses is delayed, the echo signal becomes smaller. This is called the echo decay. It contains detailed information on the dynamics and the intermolecular interactions in the medium. By measuring the echo decay as a function of temperature, the extent of the fluctuations of the medium and the nature of the motions and interactions can be determined.[3]

Unlike many experiments conducted with FELs to date, which involve essentially pointing the FEL beam at the sample, the photon echo experiment is very demanding. it requires precise control of the timing between pulses, the wavevector of the pulses, the intensities of the pulses, and the spot size of the pulses. The experiments are conducted in a liquid helium dewar, which gives precise control of temperature from 1.5 K to 300 K. The multiple pulse sequence must pass through 14 optical surfaces (windows) on the way in and out of the Dewar. This results in literally hundreds of reflections against which the very weak coherent echo signal must be detected. The timing between the pulses must be controlled and varied by a fraction of a picosecond. It is necessary to select a limited number of single micropulses from each FEL macropulse. In addition, the experiments were performed with the second harmonic of the FEL operating wavelength. This means that the signal depended on the 6th power of the FEL intensity.

These experiments (described in more detail below) placed severe demands on the FEL and on the coordination of the FEL operation and the experimental users. The FEL had to provide pulses of stable intensity, stable frequency, stable direction, and stable pulse duration. A number of single micropulses were acousto-optically selected from each macropulse. This was possible with the SCA/FEL because the pulses are separated by 85 nsec. This is in contrast to a short pulse linac driven FEL in which the pulses are too close together (e.g. 350 psec) to select single pulses, and the frequency slews across the macropulse by more than 1 %. It was also necessary to develop special electronics and computer software to detect and process the signal. Frankly speaking, it would seem that if this experiment can be done with Stanford SCA/FEL, there is essentially no limit to the nature of experiments which can use the FEL as a source!

The actual photon echo experiments examined the molecule HITCI in a polymeric glass, PMMA [poly(methyl methacrylate)]. HITCI is a large organic dye molecule which absorbs in the new IR. It has a very extended conjugated π electron system. Previously smaller, more compact molecules have been studied in a variety of glasses, [4] including PMMA. The important question is how does the structure of a molecule influence its intermolecular interactions and the way it senses the dynamics of the media?

In the HITCI\PMMA experiments photon echo decays were measured at 15 temperatures from 1.5 K to over 15 K. Figure 1a shows a decay curve at 1.5 K. The signal-to-noise ration is excellent and actually exceeds that taken on molecules which absorb in the visible using conventional lasers. Figure 1b displays a log plot of the same data. The echo decay is 284 psec, and is a single exponential. The exponential form of the decay can only arise from a dipole-dipole interaction between the molecules and the environment.[5]

Figure 2a shows the experimentally determined temperature dependence on a log plot. At low temperature the temperature dependence is a power law, $T^{1.4}$. This is consistent with theories of glass dynamics and provides detailed information on the energy levels associated with structural rearrangements in the glass. At the higher temperatures the data is exponentially activated as is shown in Figure 2b. The measured activation energy is 15.3 cm^{-1}. This is the energy of a very low frequency optical phonon mode in the PMMA.

Measurements at each temperature required several hours. The complete study was conducted over many days of experimentation, with the FEL operating at 1.54 μm. The FEL performed well, day after day, making it possible to do this set of difficult experiments. This successful set of experiments came after developing the techniques during several previous FEL runs. The methodology which was developed will make future complex experiments more doable. Of great importance is that these experiments demonstrate that the SCA/FEL can be used in a manner analogous to the conventional laser systems, i.e., as tools for doing detailed scientific studies. We are past the stage in which is necessary to tailor an experiment to the FEL. Rather the FEL can be tailored to perform the important experiments of interest.

Preliminary experiments for performing photon echoes between 3 and 4 μm on vibrational modes of molecules in glasses were conducted. All previous nonlinear optical experiments on glasses (photon echoes and other pulse sequences) have involved looking at a solute molecule in a glassy solvent, such as the HITCI/PMMA experiments described above. The solute molecule is used as a probe to study the glass. By moving into the IR it will be possible to do the same type of studies by looking at the vibrational modes of the glass. This will be a dramatic departure from previous studies, and is made possible because of the short pulse and high peak power capability of the SCA/FEL, combined with its wavelength stability and the wide temporal spacing between micropulses.

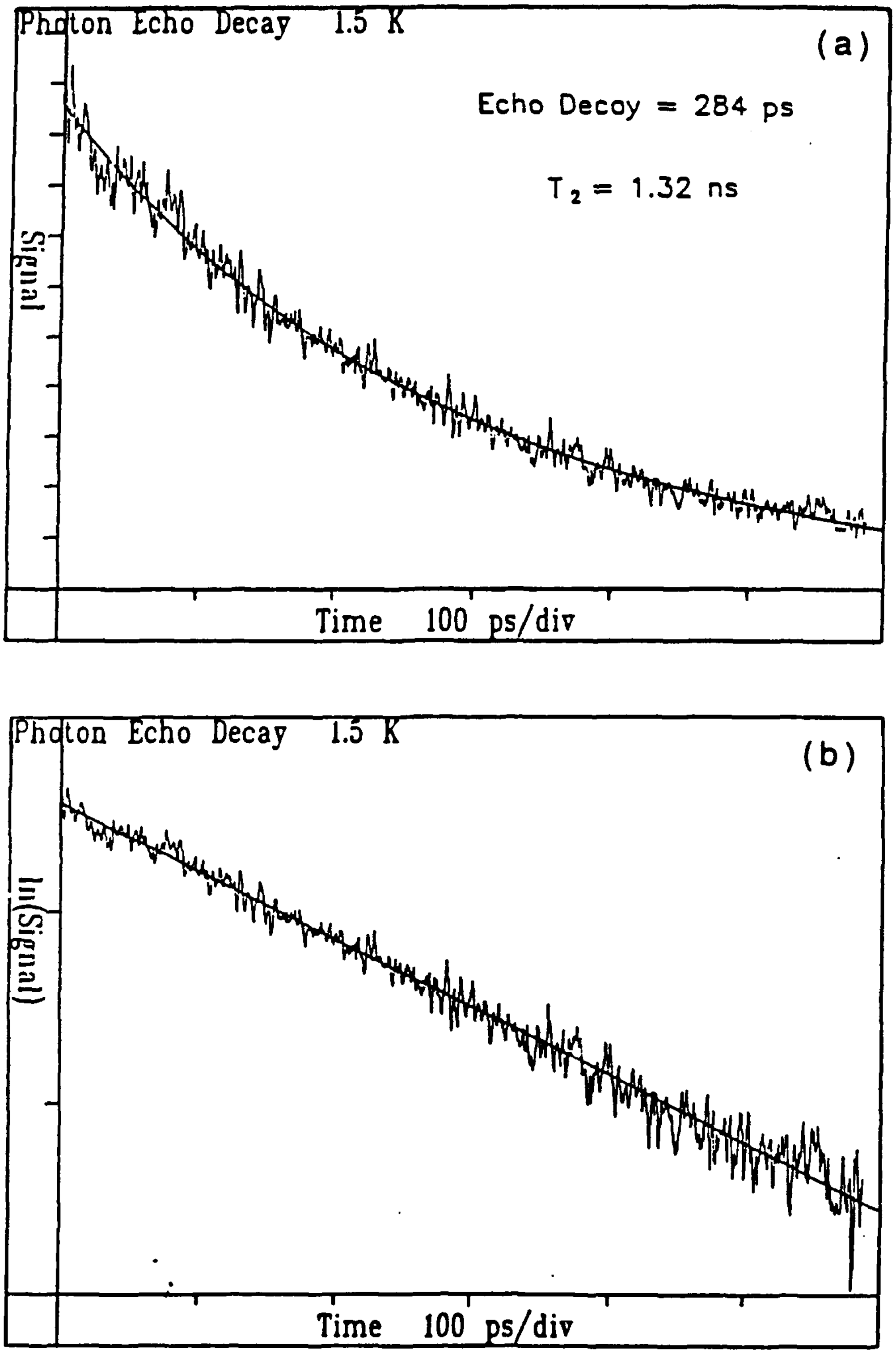
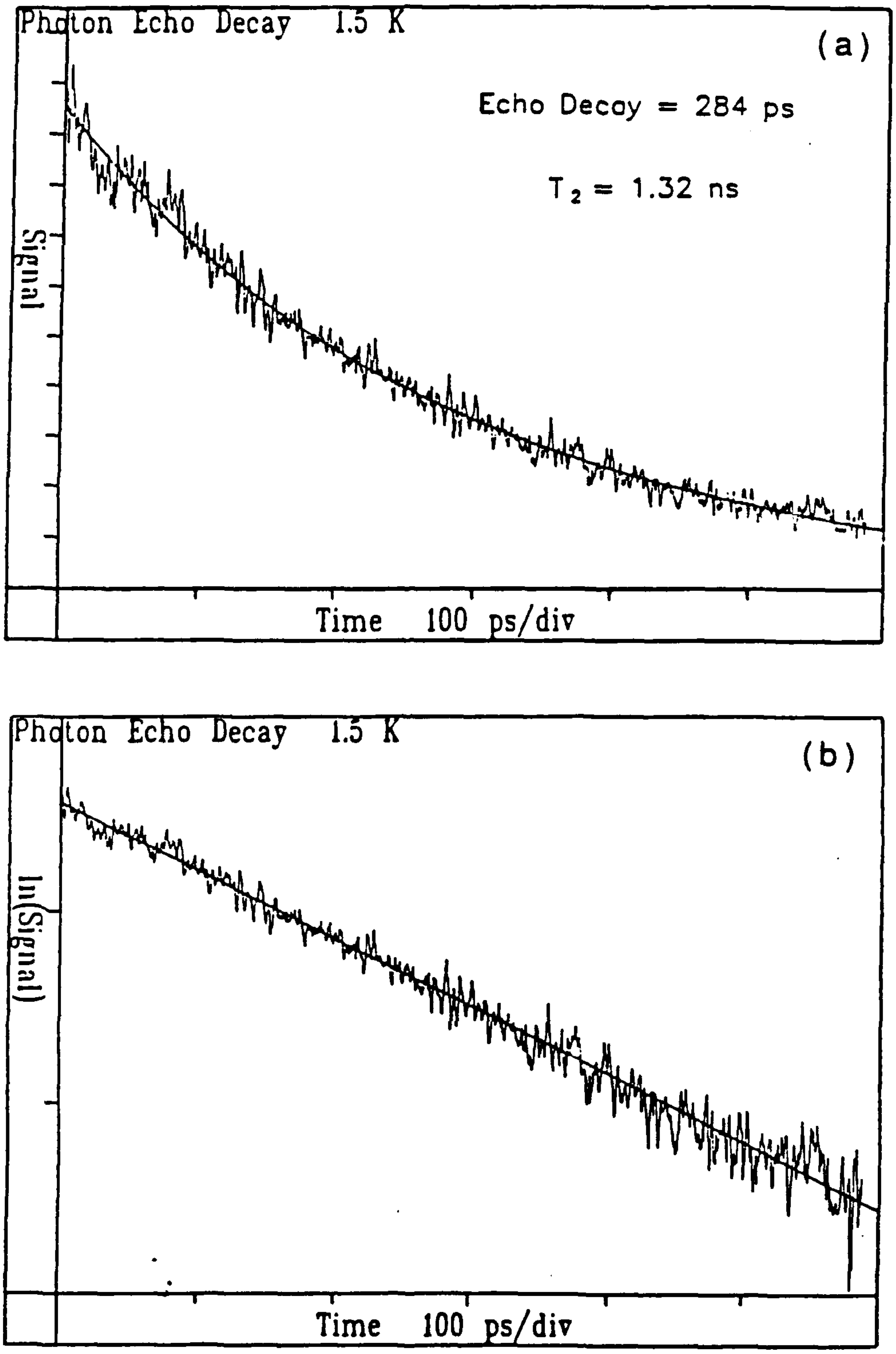


Fig 1. a) Photon echo decay of molecule HITCI in polymethyl methacrylate glass.
b) Logarithmic plot of Fig 5a, showing one-exponential decay character.



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