TIME-RESOLVED FAR-INFRARED EXPERIMENTS AT
THE NATIONAL SYNCHROTRON LIGHT SOURCE

Final Report

D.B. Tanner and D.H. Reitze

Department of Physics, University of Florida, Gainesville, FL 32611-8440

G.L. Carr

National Synchrotron Light Source, Brookhaven
National Laboratory, Upton, NY 11973-5000

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Summary

A facility for time-resolved infrared and far-infrared spectroscopy has been built and commissioned at the National Synchrotron Light Source. This facility permits the study of time dependent phenomena over a frequency range from 2–8000 cm$^{-1}$ (0.25 meV–1 eV). Temporal resolution is $\sim 200$ psec and time dependent phenomena in the time range out to $\gtrsim 100$ nsec can be investigated.

Contact: David B. Tanner
Tel: 904-392-4718
Fax: 904-392-3591
Email: tanner@phys.ufl.edu
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I. INTRODUCTION

A facility for time-resolved infrared and far-infrared spectroscopy has recently been commissioned at beamline U121R at the National synchrotron Light Source (NSLS). The VUV ring at the National Synchrotron Light Source is the cradle of synchrotron-based infrared spectroscopy. Experiments performed there have demonstrated that the brightness of the source makes certain type of far-infrared measurements uniquely possible. The NSLS VUV ring is the world's brightest source of infrared, due to the high stored beam currents. In addition, a global orbit feedback system provides extremely high beam stability, crucial for Fourier-transform infrared measurements. Because the trend of new synchrotron development is towards higher energies, the leading role of the VUV ring in the low end of the spectral range will remain unchallenged.

A key difference between the synchrotron infrared source and conventional blackbody lamps is that the electrons in the synchrotron ring exist in bunches, so that the light is pulsed. Of all the aspects of synchrotrons radiation, this time structure is the least exploited. However, the present authors believe that the existence of this pulse structure makes the synchrotron able to do a class of very important experiments that cannot be done in any other way: infrared time-resolved or pump-probe spectroscopy.\(^1\) We exploit this feature to do pump-probe studies of solids, using a short-pulse laser as pump and the synchrotron radiation as probe. Synchronization between laser and infrared pulses gives the ability to study transient behavior on timescales from 0.5 to \(\sim\)100 nsec.

II. THE FACILITIES AT U121R

A. Advantages of pump-probe spectroscopy with synchrotron radiation

The spectral, temporal, and spatial characteristics of the NSLS make it a unique source for performing transient response (pump-probe) spectroscopy in a spectral region (mid-infrared and far infrared) not accessible by conventional pump-probe spectroscopy. The implementation of this capability at NSLS is shown schematically in Fig. 1, with a cartoon of the timing sequence shown in Fig. 2. A material sample is irradiated with a short, relatively high-power light pulse (the "pump" pulse) which initiates the physical process to be investigated (e.g., the creation of electron hole pairs in a semiconductor or quasiparticles in a superconductor). The subsequent dynamics modify the frequency-dependent optical properties of the material; these changes are detected using a second pulse (the "probe" pulse), which irradiates the material at some time delay with respect to the pump pulse. The time-dependent optical properties can be determined by varying the time delay of the probe pulse with respect to the pump pulse.

The time resolution of a pump-probe experiment is determined by the cross correlation (controlled by the pulse widths and their degree of synchronization) of the pump and probe pulses. Adjustment of time delay between the pump and the probe is achieved using optical delay lines. This eliminates the need for fast photodetectors and permits the experiment to be performed in a time-integrated manner. At a fixed time delay with respect to the pump, the change of the probe is averaged over multiple shots (typically in excess of one million for high repetition rate sources such as the NSLS).
Fig. 1. Apparatus for time-resolved pump-probe measurements.

Fig. 2. Cartoon view of time-resolved pump-probe spectroscopy. The laser pulse creates excitations in the sample prior to the arrival of the infrared pulse (upper panel). The photoexcitations evolve for a time, after which the infrared pulse arrives and probes the excited state (middle panel). The infrared pulse is detected and analyzed (lower panel).
the probe interrogates the same excited-state configuration on every shot. The time delay is then adjusted and the experiment is repeated to build up the time-resolved response curve.

At the NSLS, a mode-locked laser operating in the visible and near infrared (described below) is the excitation source; the synchrotron source delivers the probe pulses. The broad spectral coverage of the two spectrometers at the beamline (2-8000 cm\(^{-1}\); 0.25 meV–1 eV) permits measurements of the time-dependent spectrum of the photoexcited material in spectral regions previously inaccessible to time-resolved methods. The duration of the synchrotron pulses (\(-200\) psec) determines the temporal resolution of the pump-probe measurements. The shot-to-shot stability of the synchrotron combined with conventional noise reduction techniques permits a detection capability of \(10^{-5}\) above \(1000\) cm\(^{-1}\) and \(10^{-4}\) in the 2–1000 cm\(^{-1}\) spectral window. When the synchrotron operates in single bunch mode, measurements with subnanosecond resolution are possible over 170 nsec, the single-bunch interpulse period.

The use of synchrotron radiation as a probe has advantages not found in other sources with time resolution in the 100 psec–1 \(\mu\)sec range. The spectral coverage of the synchrotron exceeds that from any other available source, including the competing technologies of coherent THz spectroscopy,\(^2\) nonlinear frequency mixing techniques,\(^3\) and free electron lasers.\(^4\) Time-domain THz spectroscopy has the potential to become a powerful spectroscopic tool and has been demonstrated in the 2–200 cm\(^{-1}\) range\(^2,5\) However, the prospects for extending the frequency range much further are limited because the generation is governed by the time decay of a photocurrent in a semiconductor, typically occurring on 100 fsec or longer time scales. Nonlinear mixing techniques work well at near- and midinfrared wavelengths (down to 500 cm\(^{-1}\)), but crystals which phase match at longer wavelengths have not been found. In addition, multi-phonon absorption effects in nonlinear crystals compromise the tunability at the longer wavelengths. Free electron lasers offer very short-pulsed infrared light, but are not readily tuned across the complete spectrum of interest.

B. Technical characteristics of the pump-probe instrumentation

1. The beamline

Our equipment is part of the U121R beamline of the NSLS. The basic construction is similar to the existing U41R beamline, with a large 90 mrad\(\times\)90 mrad port needed for efficient extraction of the far infrared. Whereas the U41R line is instrumented for surface science, the U121R facility is dedicated to solid state physics investigations, with emphasis on the very far infrared. Two other infrared ports (U10A and U10B), located adjacent to the U121R beamline, are operational and may also be used for pump-probe studies. In particular, an infrared microspectrometer will be located at U10B, and will therefore be readily accessible for this program.

2. Pulse structure details

The time structure of the pulses from the NSLS VUV ring depends on the electron bunch pattern. The ring supports 9 RF “buckets,” with each bucket separated in time by the RF period of 18.9 ns. Electrons are put into one or more of the 9 RF buckets, with the bunch pattern repeating at the ring’s orbital period of 170 ns. Normally, the pattern has 7 adjacent buckets filled and the remaining 2 empty, allowing 1 A of current
Fig. 3. The synchrotron pulses are shown as the solid line. Note the two empty bunches in the pattern. The laser pulses are shown as the dashed line. The synchrotron pulses always see the system in a state $\Delta t$ after the laser excitation.

in combination with a long on-orbit lifetime. This pattern is illustrated in Fig. 3, which shows as a solid line the synchrotron radiation as detected by a fast photodiode near the beamline. Other patterns are injected to meet specific user needs, such as for these timing experiments. Useful electron bunch patterns are one- and three-bunch modes. One bunch allows the greatest time (170 ns) between pulses but at the cost of lower ring current (400 mA maximum) and short on-orbit lifetime. Three-bunch mode, a compromise between one- and seven-bunch modes, provides about 57 ns between pulses at nearly the full ring current.

3. Pump laser

The laser is a commercially available (Coherent, Inc.) mode-locked Ti:sapphire laser, pumped by a doubled Nd:VO$_4$ laser. It produces 750 mW average power, tunable over wavelengths of 0.7–1.0 µm at a repetition rate of 105.7 MHz (corresponding to 9.5 ns interpulse spacing). This repetition rate was chosen to be exactly twice the repetition rate of the synchrotron operating in multi-bunch mode, greatly simplifying synchronization of the optical and synchrotron pulses. (Two vendors attempted to design and build a laser operating at the synchrotron RF frequency of 52.8 MHz but for technical reasons were not successful.) Optical pulse duration of 2 ps (transform-limited) is typical from this laser, well in excess of the temporal resolution of the NSLS. The laser includes a “synchro-lock” accessory, to phase-lock the Ti:sapphire laser to the synchrotron RF frequency. Currently, the laser operates at its fundamental wavelength range (700–1000 nm).
4. Synchronization and operation of the pump-probe system

The synchronization of the synchrotron radiation and the optical pulse is accomplished by slaving the Ti:sapphire laser to the synchrotron. Because the Ti:sapphire laser operates at exactly twice the synchrotron RF frequency, it can be locked directly to the synchrotron RF signal, producing two optical pulses for every possible synchrotron pulse (nine bunches in 170 ns). To match the synchrotron pulse train, an electro-optic pulse picker (Conoptics Model 350-80) operating at 52.9 MHz is employed to select every other optical pulse. We have found it possible to use a short delay line and some optics to re-inject the de-selected pulses in step with the following selected ones, thereby nearly doubling the optical power in the pump pulse train and using almost all of the available laser power. The laser and synchrotron pulses are shown together in Fig. 3.

When lower synchrotron repetition rates are called for, a second pulse picker operating at up to 20 MHz is used, giving the capability to synchronize the optical pulse to the synchrotron pulse at any operational frequency of the synchrotron. Fine control of the Ti:sapphire pulses relative to the synchrotron pulses is achieved by the synchro-lock electronics.

5. Infrared spectrometers

A commercial rapid-scan Michelson interferometer (Bruker IFS-113v) is used for the 50–8000 cm\(^{-1}\) regime. Presently a lamellar grating interferometer\(^6\) is used for the very far infrared (2-60 cm\(^{-1}\)). During the first year of the project we will replace this instrument with a polarizing Michelson interferometer which covers a similar spectral range but with 10-times higher spectral resolution. NSF funding for this upgrade has already been granted.

A direct comparison of the power spectra from the synchrotron and a high-pressure mercury arc lamp (GE model UA3, 1.2 cm diameter, emitting into f/1.7)\(^6\) finds that the synchrotron provides more energy than the arc lamp below about 20 cm\(^{-1}\). Only one other infrared beamline (BL6A1 at UVSOR in Japan) utilizes such a spectrometer with high efficiency in the far infrared, so this superiority is just beginning to be exploited for linear far-infrared spectroscopy as well as for the pump-probe experiments.

Detectors include cooled bolometer detectors for the far infrared and either Ge:Cu, or InSb (which has better linearity than HgCdTe) in the midinfrared. Cryostats permit any sample temperature between 1.7 K (immersed in liquid Helium) and 400 K. Samples may be studied either in transmission or reflection.

6. Safety

Both the Ti:sapphire laser and infrared beamline are operated according to NSLS and BNL safety requirements. The laser (class IV) is located in a hutch near beamline U6 of the NSLS VUV ring—a short distance from U12IR. Light is brought to the experiment by an optical fiber. Laser safety glasses appropriate for both the doubled Nd:NV04 (532nm) pump laser and the Ti:sapphire laser are located at the hutch. An interlock system on all doors prevents accidental exposure to unauthorized personnel entering the room.
C. Performance

1. Semiconducting $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$

A study of the photoconductive detector material $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ demonstrates the performance of the U12IR time-resolved spectroscopy facility and illustrates a key advantage of the pulsed synchrotron source—namely its extremely broad spectral coverage. The specimen consisted of a $\sim 10$ $\mu$m layer of $x = 0.35$ material on a Cd(Zn)Te substrate; it was unpassivated, yielding a fast carrier relaxation due to a high surface recombination rate. The photoinduced absorption, defined as $-\Delta \mathcal{I}/\mathcal{I}$ where $\mathcal{I}$ is the transmittance with the pump beam off and $\Delta \mathcal{I}$ is the difference between the transmittance with pump on and with pump off, was measured.

Figure 4 shows the far infrared photoinduced absorption at a variety of pump-to-probe delay times. The absorption by the photogenerated mobile carriers fits the Drude formula,

$$\sigma_1(\omega) = \frac{\sigma_{dc}}{1 + (\omega/\gamma)^2}$$

where $\sigma_{dc}$ is the DC conductivity, and $\gamma$ is determined by electronic scattering rates. Typical values of $\gamma$ for electrons in crystalline semiconductors require measurements in the very far infrared, where the synchrotron source and its interferometer have high performance. The data are fitted by a constant (in time) $\gamma = 16$ cm$^{-1}$, in good agreement with the mobility.

![Fig. 4. Far-infrared photoinduced spectra of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ at 5 K along with fits to the Drude conductivity.](a)
Changes in the optical properties also occur at the interband absorption edge near 3000 cm⁻¹. Figure 5 shows the midinfrared $-\Delta \mathcal{I}/\mathcal{I}$ for the same sample. In a reversal of the behavior in the far infrared, photocarriers cause a bleaching near the band edge, essentially a time-dependent Burstein-Moss shift⁸,⁹ (a shift of the interband absorption edge with carrier density). The $-\Delta \mathcal{I}/\mathcal{I}$ spectrum closest to coincidence shows absorption extending above the band edge, possibly evidence for residual hot carrier effects.

![Figure 5. Time resolved infrared spectra near the bandgap of Hg₁₋ₓCdₓTe.](image)

Besides demonstrating the technique’s sub-nanosecond time resolution, the Hg₁₋ₓCdₓTe data illustrate the value of a wide spectral range. The oscillator strength sum rule is

$$\int_0^\infty \sigma_1(\omega) \, d\omega = \frac{\pi ne^2}{2m},$$

where $n$ is the electron density, $e$ the electronic charge, and $m$ the electronic mass. Because the number of electrons in the semiconductor is not changed by the photoexcitation, this equation implies that

$$-\int_0^\infty \frac{\Delta \mathcal{I}}{\mathcal{I}} \, d\omega = \int_0^\infty \Delta \sigma \, d\omega = 0$$

at each instant of time. This fact can be shown by integrating $-\Delta \mathcal{I}/\mathcal{I}$ at each time interval for both the far and mid IR measurements. The two curves, shown in Fig. 6, are essentially equal and opposite, indicating that all the photoinduced oscillator strength has been accounted for.
2. Superconducting Pb

A second time-resolved measurement is a study of quasiparticle recombination in thin superconducting Pb films. The quasiparticle recombination in metallic superconductors has been studied both theoretically\textsuperscript{10–13} and through tunneling and transport experiments.\textsuperscript{14–16} Only one study\textsuperscript{16} directly sensed a time-dependent quantity (the resistance). Absorption of a visible photon produces a pair of highly excited quasiparticles; these relax via electron-electron scattering (breaking many more pairs) and phonon emission to energies near the superconducting gap edge, eventually recombining into Cooper pairs with the emission of a phonon. This recombination time is governed by the strength of the electron-phonon coupling and, as well, by phonon trapping effects in the metal films.

Figure 7 shows the change in far-infrared transmission due to a laser pulse for a thin Pb film at $T = 3.6$ K. as a function of the time delay of the infrared probe pulse. The probe pulse had spectral content spanning the $2\Delta = 22$ cm$^{-1}$ energy gap of Pb. The photoinduced $\delta T$ is sensitive to changes in the superfluid density and the associated gap renormalization. The signal was largest near coincidence and dropped rapidly within a few hundred picoseconds. This fast decay is associated with the actual pair-breaking and recombination process. After this point the excess energy has been thermalized over all the degrees of freedom, and the extended decay “tail” is due to the flow of heat from the film. This interpretation was confirmed by comparing the magnitude of the extended decay tail with the temperature-dependent transmission.

Figure 8 shows two determinations of the quasiparticle recombination time as a function of the temperature. The points are from fits to the time-dependent data of Fig. 7. We used a two-exponential decay and Gaussian probe pulse to model the time-dependent decay. The points show the results for the fast component. (The slow component is attributed
Fig. 7. Time-dependent change in far-infrared transmission due to a laser pulse. The sample is a Pb thin film at $T = 3.6$ K.

Fig. 8. The quasiparticle recombination time as a function of the temperature for a Pb thin film.

above to thermal effects.) The solid curve is simply the magnitude of the time-differential transmission at coincidence. Here we assume that the transmission change is proportional to the quasiparticle density and that the probe pulse is longer than the decay time, making this signal proportional to the quasiparticle decay time. We measure an effective recombination time of 230 ps at a temperature of 3.65 K. This value is comparable to the 180 ps estimated by Parker and Williams\textsuperscript{14} in measurements employing tunnel junctions. Note that in our
study the effective lifetime was directly determined. Also, our spectra clearly show the gap shift downwards in accord with the calculation of Owen and Scalapino. A quantitative value for the gap shift gives us a direct measure of the number density of excited quasiparticles. With this, we can determine when we are in the “weak” and “strong” perturbation regimes.

References


7. The transmittance with pump beam off is $\mathcal{T} \approx \exp(-\alpha d)$ while the transmittance with pump beam on is $\mathcal{T} + \Delta \mathcal{T} \approx \exp[-(\alpha + \Delta \alpha)d]$ with $\alpha$ the ordinary absorption coefficient, $\Delta \alpha$ the photoinduced change in absorption coefficient, and $d$ the sample thickness, yielding $-\Delta \mathcal{T}/\mathcal{T} = \Delta \alpha d$. The photoinduced conductivity is then $\Delta \sigma \propto \Delta \alpha$, ignoring the small change in refractive index.


III. PUBLICATIONS


IV. BEAMLINE ORGANIZATION

A memorandum of understanding (MOU) between the NSLS and the U12IR Participating Research Team (PRT) was signed in May 1998. The MOU covers the research goals, PRT membership, beamline management, and facility operation. The initial membership consists of the following personnel (and institutions): D.B. Tanner, D.H. Reitze (both University of Florida), and G.L. Carr (Brookhaven National Laboratory). In the next year we expect that both C.J. Stanton (Florida) and Laszlo Mihaly (SUNY Stony Brook) will join the PRT. The governance of the beamline follows the principles described in the MOU, with the PRT administered by one or two voting representatives from each PRT institution, with votes weighted in terms of each institution’s contribution. The principal investigator of this grant and PRT spokesperson has responsibility for monitoring the progress of the research and to organize the PRT meetings as well as all required reports to the NSLS and the DOE. The beamline manager has the responsibility to respond to all issues of beamline operations, including hardware, software, and safety. To date, the PRT Spokesperson and grant principal investigator has been D.B. Tanner (Florida). The beamline manager has been G.L. Carr (NSLS).

Beamtime on the U12IR beamline, using either the Bruker 113v or the far infrared interferometers, will be divided as follows: 45% U12IR PRT members, 30% U10A PRT members (Stony Brook, BNL Physics Department, NSLS) and 25% General User Requirement. (There is a reciprocal beamtime agreement between U10A and U12IR wherein the U12IR PRT has access to 30% of the beam time on the Bruker 66vs spectrometer at U10A.) General User beamtime will be allocated through the NSLS General User Program, including reviews by the Proposal Study Panel and allocation by the General User Oversight Committee. These fractions are subject to revision at each annual meeting of our PRT.