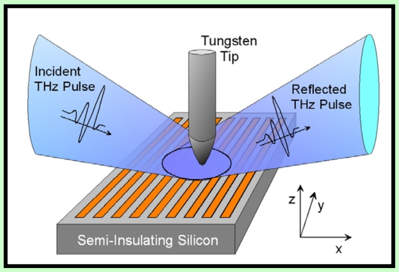
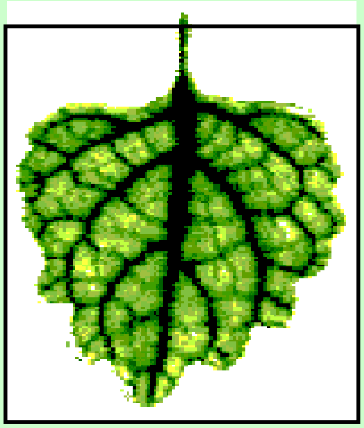
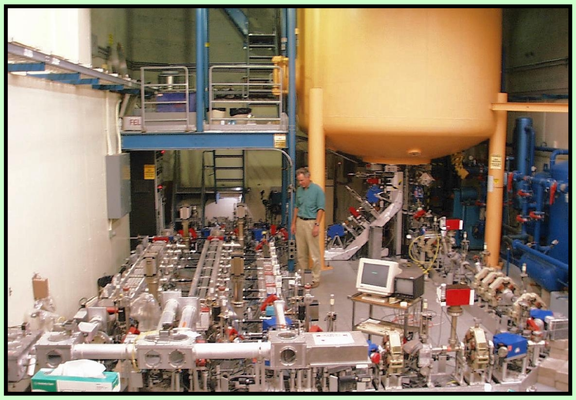
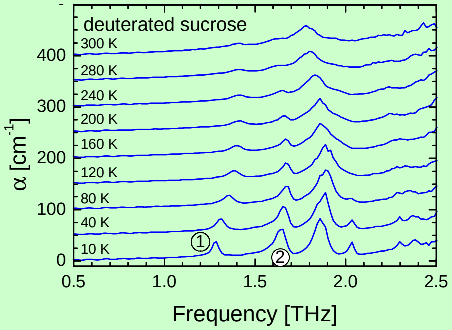
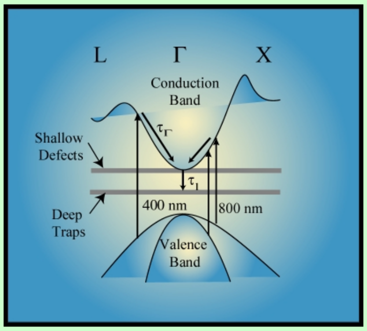
DOE-NSF-NIH Workshop on Opportunities in THz Science
February 12–14, 2004

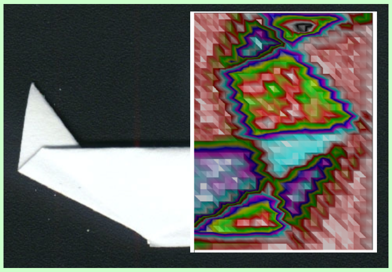


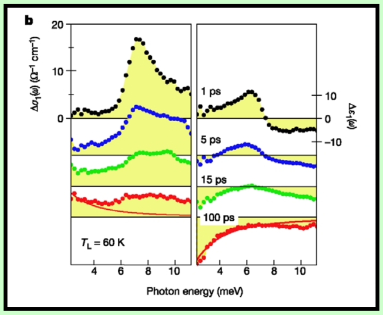


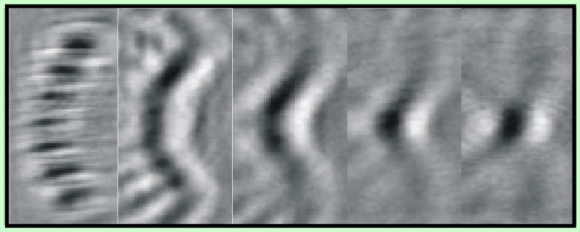


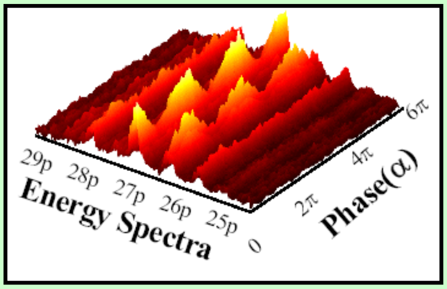


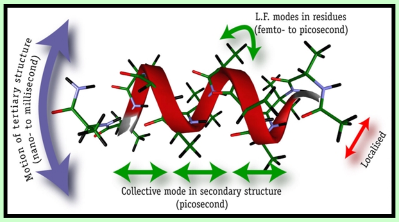


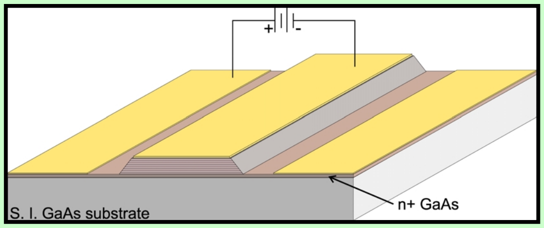


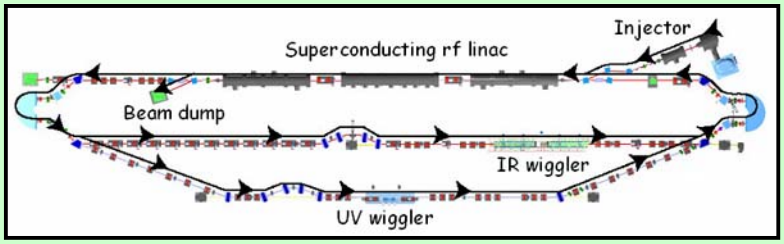


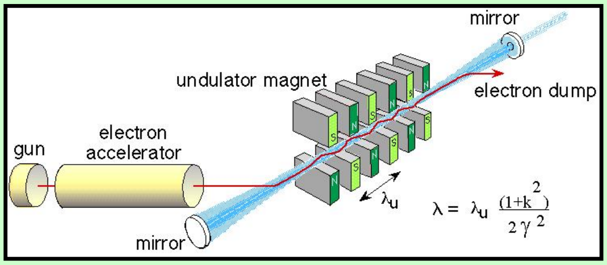












$$\lambda = \lambda_u \frac{(1+k^2)}{2\gamma^2}$$

Opportunities in THz Science

Report of a DOE-NSF-NIH Workshop held February 12 – 14, 2004, Arlington, VA

M. S. Sherwin, C. A. Schmuttenmaer, and P. H. Bucksbaum, Editors

Contributors

Co-Chairs:
Mark Sherwin
Phil Bucksbaum
Charles Schmuttenmaer

Speakers
Jim Allen
Sandra Biedron
Larry Carr
Martyn Chamberlain
Tom Crowe
Frank DeLucia
Qing Hu
Bob Jones
Bart Noordham
Ted Norris
Joe Orenstein
Charles Schmuttenmaer
Karl Unterrainer
Lex Van der Meer
Ingrid Wilke
Gwyn Williams
X.-C. Zhang

Session Chairs
Alan Cheville
Andrea Markelz
Beth Parks
Paul Plancken
Jie Shan

Breakout Session Leaders
Bob Austin
Dimitri Basov
David Citrin
Warren Grundfest
Tony Heinz
Jun Kono
Daniel Mittleman
Peter Siegel
Toni Taylor

Panel Members
Bob Jones
Andrea Markelz
Mike Martin
Keith Nelson
Todd Smith
Gwyn Williams

Other scientific participants
Mark Allen
Rick Averitt
Louis Brunel
Ted Heilweil
James Heyman
Peter Jepsen
Robert Kaindl
Wim Leemans
Laszlo Mihaly
Chitra Rangan
Harry Tom
Vincent Wallace
David Zimdars

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Chapter 1: Executive Summary

1.1 THz research frontiers and opportunities

This is the report of the Workshop on Opportunities in THz Science, held on February 12 – 14, 2004 in Arlington, VA. This workshop brought together researchers who use or produce THz radiation for physics, chemistry, biology, medicine, and materials science to discuss new research opportunities and common resource needs. The charge from the sponsors of the workshop was to focus on basic science questions within these disciplines that have and can be answered using THz radiation. Opportunities in space THz science are discussed in NASA's decadal report, and hence were not strongly represented at the workshop or in this document. The workshop did not focus on the wide range of potential applications of THz radiation in engineering, defense and homeland security, or the commercial and government sectors of the economy. The workshop was jointly sponsored by DOE Basic Energy Sciences, NIH, and NSF.

Consistent with our charge of focusing on science, the first day of the workshop consisted of a series of summary talks on the research fields, followed by an afternoon of breakout sessions where research opportunities were discussed. Given that THz science will not advance without broad access to appropriate sources of THz radiation, the second day consisted of a series of talks on different sources of THz radiation: from small table-top sources to large accelerator-based sources. Further breakout sessions that afternoon helped to define the new source characteristics that could accelerate progress in research. The group reconvened for a panel discussion to consider the size of the field, opportunities for growth, and possible recommendations for actions by the funding agencies in the area of THz science.

1.2 Overview

The region of the electromagnetic spectrum from 0.3 to 20 THz (10 – 600 cm^{-1}, 1 mm – 15 µm wavelength) is a frontier area for research in physics, chemistry, biology, materials science and medicine. Sources of high quality radiation in this area have been scarce (see Figure 1.1), but this gap has recently begun to be filled by a wide range of new technologies. Terahertz radiation is now available in both cw and pulsed form, down to single-cycles or less, with peak powers up to 10 MW. New sources have led to new science in many areas, as scientists begin to become aware of the opportunities for research progress in their fields using THz radiation.

Science at a Time Scale Frontier: THz-frequency electromagnetic radiation, with a fundamental period of around 1 ps, is uniquely suited to study and control systems of central importance: Electrons in highly-excited atomic Rydberg states orbit at THz frequencies. Small molecules rotate at THz frequencies. Collisions between gas phase molecules at room temperature last about 1 ps. Biologically-important collective modes of proteins vibrate at THz frequencies. Frustrated rotations and collective modes cause polar liquids (such as water) to absorb at THz frequencies. Electrons in semiconductors and their nanostructures resonate at THz frequencies. Superconducting energy gaps are found at THz frequencies. An electron in Intel's THz Transistor races under the gate in ~1 ps. Gaseous and solid-state plasmas oscillate at THz frequencies. Matter at temperatures above 10 K emits black-body radiation at THz frequencies. This report also describes a tremendous array of other studies that will become possible when access to THz sources and detectors is widely available. The opportunities are limitless.

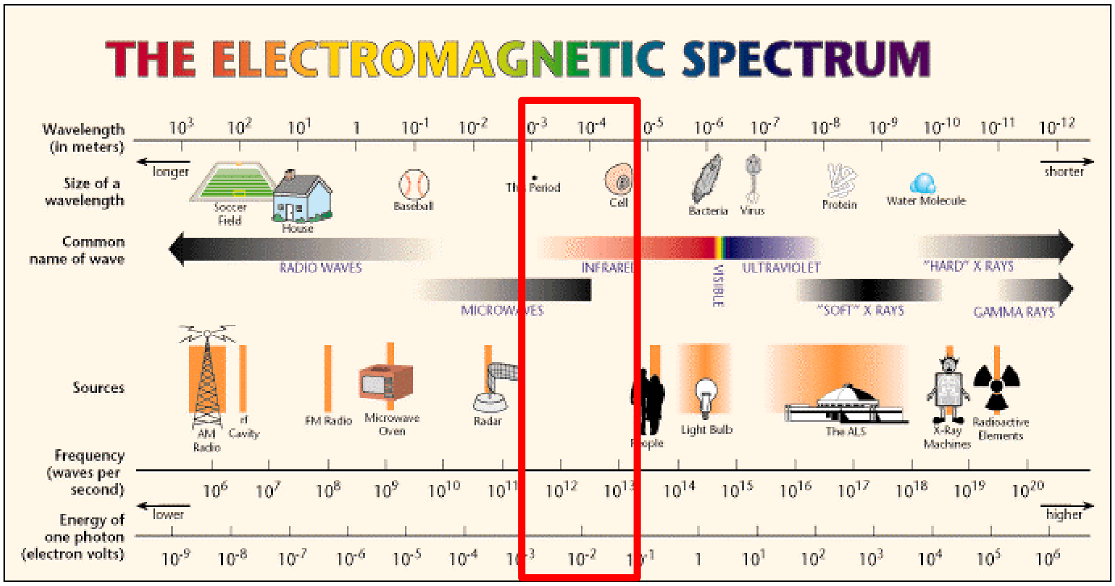


Figure 1.1 The electromagnetic spectrum. The THz frequency range discussed at this workshop lies in the middle of this diagram, between "radar" and "people" and is indicated in red. Diagram from the LBL Advanced Light Source web site (http://www.lbl.gov/MicroWorlds/ALSTool/EMSpec/EMSpec2.html).

Electromagnetic Transition Region: THz radiation lies above the frequency range of traditional electronics, but below the range of optical and infrared generators (see Figure 1.1). The fact that the THz frequency range lies in the transition region between photonics and electronics has led to unprecedented creativity in source development. Solid-state electronics, vacuum electronics, microwave techniques, ultrafast visible and NIR lasers, single-mode continuous-wave NIR lasers, electron accelerators ranging in size from a few inches to a mile-long linear accelerator at SLAC, and novel materials have been combined yield a large variety of sources with widely-varying output characteristics. For the purposes of this report, sources are divided into 4 categories according to their (low, high) peak power and their (small, large) instantaneous bandwidth.

THz experiments: Many classes of experiments can be performed using THz electromagnetic radiation. Each of these will be enabled or optimized by using a THz source with a particular set of specifications. For example, some experiments will be enabled by high average- and peak power with impulsive half-cycle excitation. Such radiation is available only from a new class of sources based on sub-ps electron bunches produced in large accelerators. Some high-resolution spectroscopy experiments will require cw THz sources with kHz linewidths but only a few hundred microwatts of power. Others will require powerful pulses with ≤1% bandwidth, available from free-electron lasers and, very recently, regeneratively-amplified lasers and nonlinear optical materials. Time-domain THz spectroscopy, with its time coherence and extremely broad spectral bandwidth, will continue to expand its reach and range of applications, from spectroscopy of superconductors to sub-cutaneous imaging of skin cancer.

1.3 What is needed

The THz community needs a network: Sources of THz radiation are, at this point, very rare in physics and materials science laboratories and almost non-existent in chemistry, biology and medical laboratories. The barriers to performing experiments using THz radiation are enormous.

One needs not only a THz source, but also an appropriate receiver and an understanding of many experimental details, ranging from the absorption characteristics of the atmosphere and common materials, to where to purchase or construct various simple optics components such as polarizers, lenses, and waveplates (they are not found in the Newport catalog), to a solid understanding of electromagnetic wave propagation, since diffraction always plays a significant role at THz frequencies. There is also significant expense, both in terms of time and money, in setting up any THz apparatus in one's own lab, even if one is the type of investigator who enjoys building things.

Because of the enormous barriers to entry into THz science, the community of users is presently much smaller than the potential based on the scientific opportunities. Symposia on medical applications of THz radiation are already attracting overflow crowds at conferences. The size of the community is increasing with a clear growth potential to support a large THz user's network including user facilities. The opportunities are great. The most important thing we can do is lower research barriers.

A THz User's Network would leverage the large existing investment in THz research and infrastructure to considerably grow the size of the THz research community. The Network would inform the scientific community at large of opportunities in THz science, bring together segments of the community of THz researchers who are currently only vaguely aware of one another and lower the barriers to entry into THz research.

Specific ideas for network activities include disseminating information about techniques and opportunities in THz science through the worldwide web, sponsoring sessions about THz technology at scientific conferences, co-location of conferences from different communities within the THz field, providing funding for small-scale user facilities at existing centers of excellence, directing researchers interested in THz science to the most appropriate technology and/or collaborator, encouraging commercialization of critical THz components, outreach to raise public awareness of THz science and technology, and formation of teams to work on problems of common interest, such as producing higher peak fields or pulse-shaping schemes.

Interagency support is crucial: NIH, NSF, and DOE will all benefit, and all must be involved. Eventually, the network will provide the best and most efficient path to defining what new facilities may be needed. New users of THz methodology will also find it easier to learn about the field when there is a network.

Defining common goals: During the workshop, the community articulated several common and unmet technical needs. This list is far from exhaustive, and it will grow with the network:

1. Higher peak fields.
2. Coverage to 10 THz (or higher) with coherent broad-band sources.
3. Full pulse-shaping.
4. Excellent stability in sources with the above characteristics.
5. Easy access to components such as emitters and receivers, and for time-domain THz spectroscopy.
6. Near-field THz microscopy.
7. Sensitive non-cryogenic detectors.

Chapter 2: Introduction

2.1 Structure of report

A widely-acknowledged “THz gap” exists between about 0.3 and 20 THz. This gap usually refers to the paucity of technology – especially sources and detectors of electromagnetic radiation – available at these frequencies relative to higher and lower frequencies. Below the THz gap, electronics is the dominant paradigm for technology and scientific instrumentation. Above the gap, the paradigm is photonics. Optics and electronics converge in the THz gap, and are currently filling it in a wide variety of very creative ways.

The technological THz gap makes this region of the electromagnetic spectrum a scientific frontier. Critical questions in materials science, physics, chemistry, biology, and medicine cry for answers, or have yet to even be asked, because the requisite technology is currently not accessible to the vast majority of scientists in these fields.

The goals of this report are to inform the reader on the state of the art and opportunities in THz science and the sources which can enable this science, and to make some policy recommendations to grow the field of THz science by lowering barriers to entry.

The report is based on a two-day Workshop on Opportunities in THz Science, sponsored by the DOE, NSF and NIH. The report is organized along the same lines as the workshop. Science was the driver and technology the enabler in the agenda for this workshop. Each of the chapters begins with an *executive summary*, which describes *opportunities*, *status*, and the *potential size of the scientific community and infrastructure needs* that would benefit from easier access to THz technology. An effort has been made to make each chapter relatively self contained, which has led to some redundancies. It was felt that the benefits outweighed the drawback of restating various themes and a slightly longer final report.

The scientific opportunities discussed are presented in Chapters 3 – 7. Chapter 3 is devoted primarily to semiconductors and their nanostructures. Chapter 4 is concerned with metals, correlated electron systems, and insulators. Chapter 5 covers physics, broadly speaking, while Chapter 6 does the same for chemistry and biology. Chapter 7 presents an overview of the fledgling field of THz science in medicine. These were the topics of talks and breakout sessions on the first day of the workshop. Astronomy and astrophysics are some of the biggest users of advanced THz technology. Opportunities in THz space science are discussed in NASA’s decadal report, and hence are not covered in this report.

The science cannot occur without the technology. For many scientific applications, the biggest barrier is an appropriate source of THz radiation. Tremendous ingenuity and creativity, in addition to the ability to combine optics and electronics, have resulted in the development of dozens of types of THz sources. Chapters 8 – 11 are devoted to sources of THz radiation, grouped by similarities in their output characteristics. Chapters 8 and 9 discuss two classes of sources which are suitable for spectroscopy and imaging. Chapter 8 covers continuous wave (cw) sources with extremely narrow linewidths, which are required for high-resolution spectroscopy and are also useful for imaging. Chapter 9 discusses broad-band sources and systems for spectroscopy and imaging. This chapter is dominated by so-called time-domain THz spectroscopy, which has grown in the THz community during the last few years and opened it to ultrafast spectroscopists.

Chapters 10 and 11 are devoted to strong sources of THz radiation – sources of THz radiation that can drive a system into a state far from equilibrium. Chapter 10 covers narrow-band THz sources for nonlinear and non-equilibrium studies. These sources enable studies of nonlinear susceptibilities, energy and phase relaxation times, coherent control, and much more. For ideas of the possibilities, one can look to NMR and ESR, or to nonlinear and ultrafast laser spectroscopy. Chapter 11 is devoted to coherent half- and few-cycle sources for nonlinear and non-equilibrium studies. At THz frequencies, one thing that is easier to do than with higher-frequency radiation is to generate pulses which contain a *fraction* of a cycle of radiation. These sources enable one to drive a system with an impulse, or "kick." For linear systems, the frequency response can be derived from the impulse response. However, no systems in nature are linear to arbitrary field strengths, and for nonlinear excitation the equivalence of time- and frequency-domain measurements breaks down. The response of atomic, molecular, material, biological, and medical systems to powerful THz impulses is, with a very few exceptions, completely unexplored. It is difficult to predict what breakthroughs will result from explorations in this regime. As Nobel Laureate Herb Kroemer enjoys saying, "Each new technology creates its own applications – ones which were not envisioned by the inventor."

The report concludes in Chapter 12 with policy recommendations. The main recommendation is, at this point, to form a THz User's Network which will facilitate the spread of information within and outside of the existing THz community, and grow the research community which uses THz radiation. The most efficient way to grow this community is to lower technological and financial barriers to entry.

2.2 How to use this report

Begin with the Executive Summary and the Introduction, Chapters 1 and 2, respectively. Then read the executive summary for each chapter, and Chapter 12 describing the THz User's Network. Finally, for more detailed information, which at times is quite detailed, read the appropriate chapters in their entirety. Enjoy!

***Disclaimer**:* This is a report on the proceedings of an informal workshop. The focus of the workshop was on scientific opportunities, not on results of past experiments. This report is not a review article (which will be obvious at the outset from the absence of endnotes). Examples of THz science that are reported here are intended to represent the potential and excitement of this field. This report represents the best efforts of the editors and contributors, and any errors are of course our own. Many important contributions to THz science have undoubtedly not been mentioned. The opinions expressed in this report do not necessarily reflect those of the agencies that have generously sponsored the workshop and production of this report.

Chapter 3: Semiconductors and Their Nanostructures

3.0 Executive summary

Opportunities: Exquisite control of semiconductor composition, material heterostructure and nanofabrication present a vast range of opportunities to broadly explore THz dynamics in nanosystems, systems driven far-from equilibrium, coherent control, magnetism, and spin dynamics.

Electronic excitations in systems quantum confined to two, one and zero dimensions have excitations in the THz regime. Well defined collective and single particle excitations emerge as the THz frequency exceeds various relaxation rates and broadening: the response at THz frequencies is dynamic rather than diffusive or relaxed. Fundamental issues include reliable control of carrier injection by doping, electric fields or optical pumping, the relationship between geometry and energy level structure, linewidths of transitions between states, excited state coherence and population lifetimes, superposition states of carriers, and spin excitations. The interband response of single quantum dots at NIR and visible frequencies is currently explored in many groups worldwide, resulting in breakthroughs in quantum optics and condensed matter physics. We are challenged to explore dynamics in single quantum "dots" at THz frequencies, where the opportunities are just as great but the first experiments have yet to be done. Addressing these issues is of fundamental importance, but also critical for applications such as sources, detectors, novel ultrafast electro-optic devices and quantum information processing in semiconductors.

Extreme nonlinear quantum phenomena can be explored using THz electromagnetic fields without exceeding material damage thresholds. Such phenomena occur when the ponderomotive energy (kinetic energy of a conduction electron oscillating in the THz field) or electric dipole coupling strength (THz electric field times dipole moment of a quantum-confined carrier) exceed the photon energy. The photon energy at THz frequencies is large enough to enforce dynamic behavior, but small enough to enter the extreme nonlinear quantum regime with reasonable electric fields.

Coherent quantum control of the orbital and spin states of carriers in semiconductor nanostructures is particularly attractive at THz frequencies. The shape of THz electromagnetic pulses can be controlled exquisitely using a variety of techniques. Strong THz pulses varying in character from a half cycle to several thousand cycles have been demonstrated. Such pulses can lead to Rabi oscillations, photon echoes, and other coherent control of carriers in nanostructures. The properties of semiconductor nanostructures at visible and near-IR wavelengths can also be controlled with THz-frequency electromagnetic radiation.

Status: A THz is a frequency unit that arises naturally in the study of semiconductors and their nanostructures. A rich literature and tradition exists which addresses both linear THz spectroscopy and, more recently, nonlinear and non-equilibrium behavior of semiconductor-based materials at THz frequencies. Fourier transform infrared (FTIR) spectrometers with black-body sources, molecular gas lasers, and, more recently, time-domain THz spectrometers based on ultrafast laser pulses have been used to elucidate the energy levels of electrons and holes weakly bound to dilute impurities, cyclotron resonance, and magnetic polarons in 3-dimensional semiconductors. Low dimensional nanostructures reveal transitions between electric subbands in quantum wells, THz miniband dynamics in superlattices and quantum wire excitations. Free-electron lasers (FELs), powerful molecular gas lasers, and time-resolved visible pump/THz probe methods have been applied to study nonlinear and non-equilibrium phenomena in bulk semiconductors and semiconductor quantum wells. Rabi oscillations, energy relaxation times, extremely large nonlinear optical susceptibilities, many-body effects far from equilibrium, the internal dynamics of excitons and the process of exciton formation have been studied. Photon assisted transport and dynamical localization have appeared in strong THz electric fields. Technology resulting from these fundamental studies includes photoconductors (Ge doped with Ga is widely used in astrophysics) and, most recently, THz quantum cascade lasers.

Potential size of community: A relatively small fraction of semiconductor scientists and engineers have access to THz technology. Several thousand scientists usually attend the biennial International Conference on the Physics of Semiconductors. The proceedings of this conference usually contains close to 1000 papers. This conference is mostly attended by academics from Physics and Materials Science departments. A much larger community of scientists and engineers work on semiconductor devices exists in industry.

Technology and infrastructure needs: In a THz user's network, semiconductor physicists would benefit from wide and easy access to well-maintained and staffed intermediate-scale facilities with a range of capabilities. Many such capabilities already exist, but some only at one or a few locations. Desired capabilities for semiconductor physics include 1 kV/cm – 1 MV/cm peak fields at the sample, flexible bandwidth (pulse durations between half-cycle and cw), pulse-shaping/waveform control, cw sources, THz systems coupled to high magnetic fields, with optical cryostats, synchronized with other lasers, and including high-pressure capabilities.

Also critical is the development of enabling technologies including high-power fiber lasers as optical pumps, and a toolbox of THz optical elements – passive and active, linear and nonlinear, THz antennas, THz near-field techniques (critical for work on quantum dots, which are all different), THz magnetic pulses (~1 T, 1 ps duration), pulse-shaping/waveform control, THz amplifiers, and exploitation of hybrid techniques leveraging off optics and microwaves. Some of the elements of the toolbox could be developed and commercialized by small companies, others would be exchanged among users through a THz user's network.

3.1 Introduction

Terahertz radiation provides a powerful probe into the fundamental excitations in semiconductors and their nanostructures. Terahertz-based studies are needed not only to establish basic material parameters, they are also necessary for the characterization of materials destined for various applications. Apart from providing a probe into excitations, THz radiation can be used to manipulate and control quantum mechanical states in matter. As such, entirely novel applications of semiconductors, such as in spintronics and coherent control, may be enabled.

Broadly speaking THz technology applied to semiconductors will strongly impact the following areas of science:

- *Fundamental properties of semiconductor nanostructures*
- *Fundamental limits of electronic devices*

- *Subwavelength THz spectroscopy*
- *Coherent control and nonlinear THz spectroscopies*
- *Quantum optics*
- *Quantum-information science*
- *Spintronics*
- *High THz electric field physics and quantum nonlinear dynamics*

Semiconductors are materials over which most exquisite control has been developed. Bulk semiconductors have important resonances lying at THz frequencies (phonons, hydrogenic states of impurity-bound carriers, internal transitions of excitons, bulk plasmons in doped material). Quantum wells are structures in which carriers are confined in one direction by a potential whose shape can be controlled with high accuracy. Terahertz linear and nonlinear spectroscopy is more advanced in semiconductors than in any other materials system. This section highlights a variety of different kinds of measurements and phenomena that have already been observed in bulk semiconductors and semiconductor heterostructures, using different techniques, sources and samples.

One of the oldest subjects of study in solid state physics is the spectroscopy of point defects in semiconductors. Figure 3.1 shows the low-lying energy states of Hydrogenic donors in GaAs, which were computed in 1968 and measured in 1969. Although energy levels are well known and understood, lifetimes of these states are not. Figure 3.2 demonstrates Rabi oscillations associated with a 1s-2p transition of an ensemble of Hydrogenic donors, measured using UCSB's FEL. This experiment demonstrates the possibility of coherently controlling the quantum state of such impurities, and also of measuring intrinsic decoherence times in the future with a nonlinear technique such as photon echo.

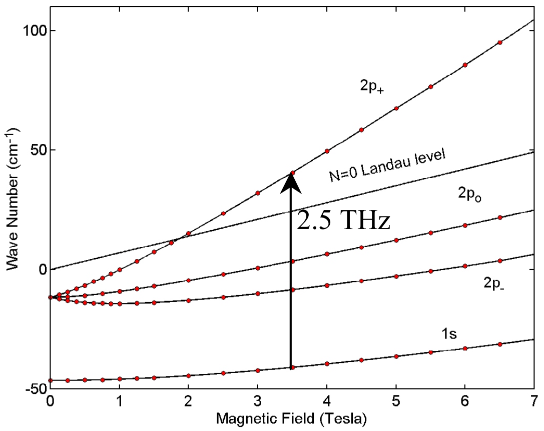


Figure 3.1 Energy level structure of lowest Hydrogenic levels of shallow donors in GaAs. A continuum of states begins at the N=0 Landau level. The experimental data shown in Figure 3.2 was taken using the UCSB FEL tuned to a frequency of 2.5 THz. See Stillman et. al., Solid State Commun. **7**, 921 (1969); J. Larsen, J. Phys. Chem. Solids **29**, 271 (1968).

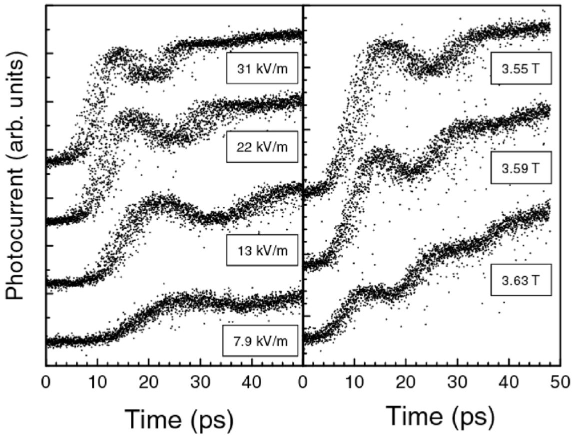


Figure 3.2 Rabi oscillations between the 1s and 2p+ state, as labeled in Figure 3.1. Each point represents a measurement of the integrated photocurrent induced by a pulse of a given duration, and thus is proportional to the number of electrons removed from the 1s state. The positions of the local minima with respect to the onset of photoconductivity represent the period of the Rabi oscillation for a given THz electric field (left panel) and detuning (right panel). See Cole et. al., Nature **410**, 60 (2001); Proc. 25th ICPS, Springer., pp 174-177, 2001.

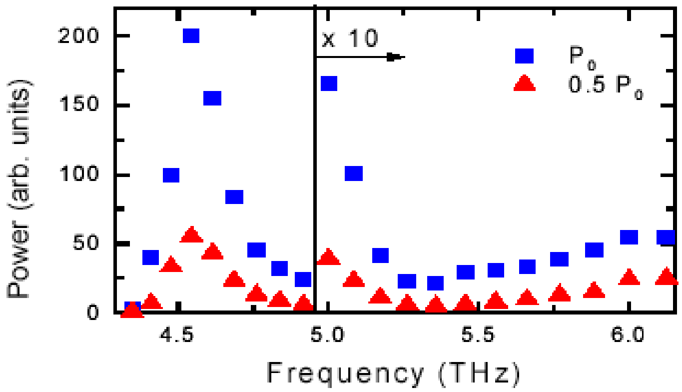


Figure 3.3 Second harmonic power vs. fundamental frequency for two incident power levels. A large peak near 4.5 THz occurs at one half of the transverse optical phonon frequency. The minimum near 5.3 THz is consistent with a predicted zero-crossing of the nonlinear susceptibility, from which important theoretical parameters were evaluated (T. Dekorsy, Phys. Rev. Lett. **90,** 055508 2003))

Besides point defects, semiconductors have phonons at THz frequencies. Non-centrosymmetric semiconductors such as GaAs have relatively large second-order nonlinear susceptibilities, and below the optical phonon frequency, these phonons contribute to the nonlinear optical susceptibility. Recently, using second harmonic generation, the contributions of optical phonons to the nonlinear susceptibility have been observed, and important theoretical parameters in the theory of this nonlinear susceptibility have been evaluated. The experiments were performed at FELIX in the Netherlands.

Excitons in quantum wells have been the subject of thousands of scientific papers. An exciton is a bound electron-hole pair which, like the hydrogenic donor, has a binding energy in the THz frequency range. Recently, time-resolved THz spectroscopy has shed light on the dynamics of exciton formation. Excitons in a quantum well were excited with a ~100 fs visible pulse, and the broad-band ac conductivity at THz frequencies was measured as a function of time after exciton creation. Surprisingly, even immediately after the electrons and holes are injected, before excitons should have had time to form, a peak in the THz conductivity occurs at the frequency of an internal transition of excitons. Results are shown in Figure 3.4.

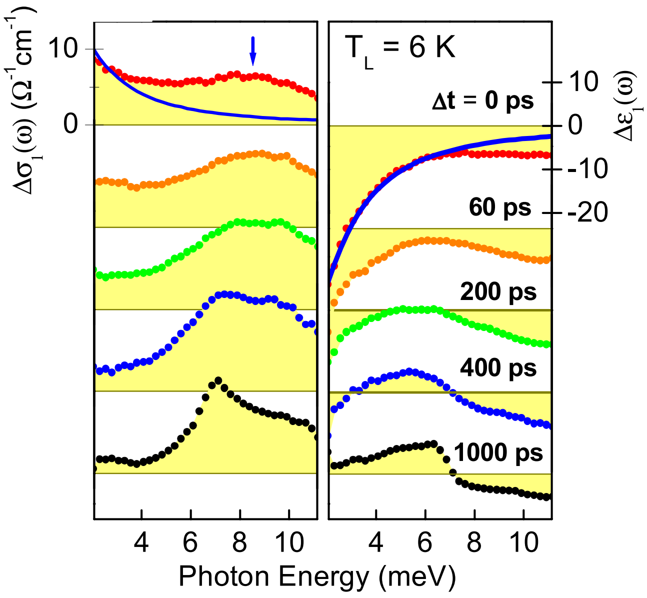


Figure 3.4 Exciton formation in a quasi-2D electron-hole (*e-h*) gas in GaAs quantum wells. Unbound *e-h* pairs excited at $\Delta t = 0$ ps show a broad-band THz response close to a Drude-like conducting state (blue line). As excitons form, the low-frequency conductivity vanishes due to increasingly correlated motion of electrons and holes. The 7 meV peak arises from 1s-2p exciton transitions. Quasi-instantaneous appearance of enhanced absorption around this energy is a surprising consequence of *e-h* pair correlations. (From R. A. Kaindl et al., Nature **423**, 734 (2003)).

The previous experiment demonstrates a visible pump-THz probe experiment. It is also possible to pump a quantum well strongly with THz radiation, and probe the induced excitonic response to THz radiation. In Figure 3.5, the near-IR radiation transmitted through a 4 micron thick layer containing 50 asymmetric coupled GaAs/AlGaAs quantum wells is shown. Terahertz radiation from the UCSB FEL illuminates the edge of the sample. In addition to the laser line at 1.540 eV, sidebands are observed separated by an integer number of THz photons from the main laser line. Figure 3.6 shows data measured in reflection from a different sample in which a front gate and a back gate were placed on either side of the quantum wells, so as to enable Stark-shifting the energy levels by applying a voltage between the gates. The $n = 1$ sideband intensity is displayed in false color as a function of both NIR frequency and dc electric field across the sample. The sidebands are only observed when the NIR frequency or its sideband is resonant with an excitonic transition. The sidebands with n odd are only observed when inversion symmetry is broken. Sidebands provide a new nonlinear spectroscopy tool for semiconductors and other systems, and also are potentially useful for wavelength conversion in telecommunications applications.

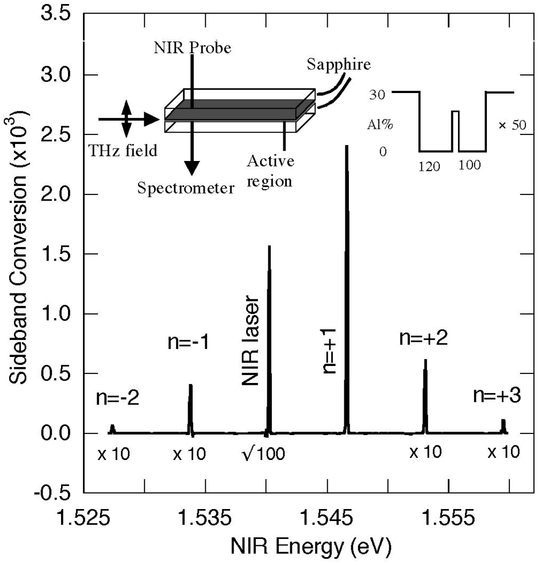


Figure 3.5 Near-IR radiation spectrum transmitted through THz-irradiated multiple quantum wells. Transmitted radiation is observed at the incident laser frequency f_{NIR}, as well as at sidebands $f_s = f_{NIR} + nf_{THz}$, where $f_{THz} = 1.5$ THz is the frequency of the UCSB FEL (power ~ 1 kW) and $n = \pm1, \pm2$, or 3. Insets show schematics of experimental setup (left) and quantum well structure (right). From Carter et. al., Appl. Phys. Lett. **84**, 840 (2004).

The experiments described in the last paragraph were performed on undoped quantum wells, where the THz radiation alone does not excite carriers. In doped quantum wells, THz radiation can directly couple to intersubband transitions if it is polarized in the direction of confinement. Doped quantum wells form the basis for the revolutionary development of the THz quantum cascade laser. The absorption frequency and linewidth of intersubband transitions have been

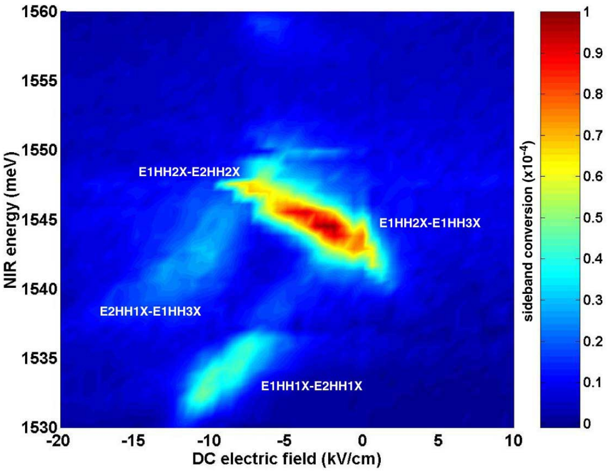


Figure 3.6 Sideband conversion efficiency as function of NIR photon energy and dc electric field for UCSB FEL frequency 2 THz and power~1 kW . This false-color map was taken on a sample containing quantum wells with the same dimensions as those shown in Figure 3.5. A DC voltage was applied between a front and a back gate to tune the energy levels via the DC quantum confined Stark effect. Sideband generation is maximized at excitonic intersubband resonances labeled in white. From M. Su et. al., Appl. Phys. Lett. 81, 1564 (2002)

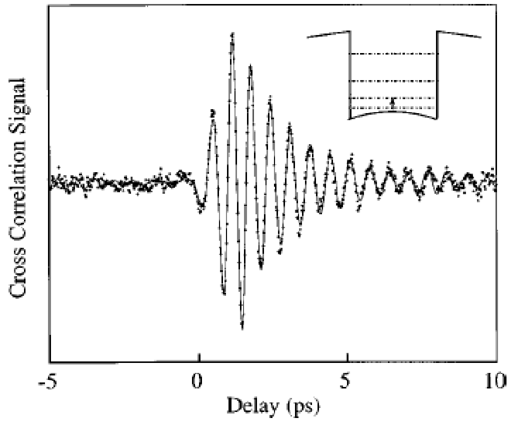


Figure 3.7 Intersubband oscillations in a modulation-doped quantum well recorded in the time-domain. From J. N. Heyman et. al., Appl. Phys. Lett. **72**, 644 (1998).

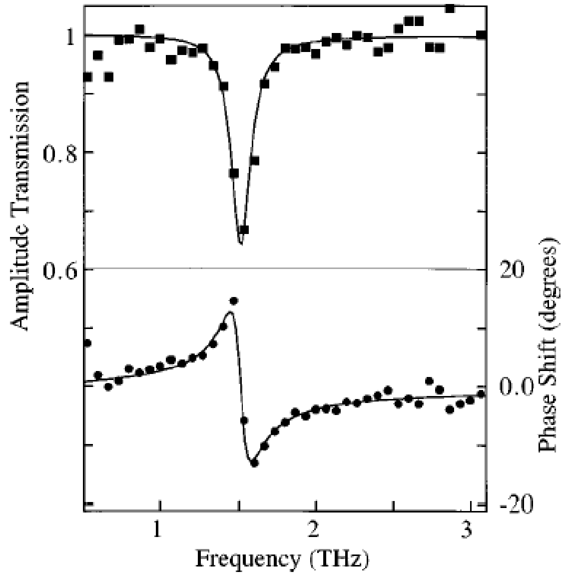


Figure 3.8 Amplitude and phase of transmission after intersubband excitation. Intersubband transition frequency is near 1.5 THz. From J. N. Heyman et. al., Appl. Phys. Lett. **72**, 644 (1998)

investigated using FTIR spectroscopy or, more recently, time-domain THz spectroscopy. Figure 3.7 shows intersubband oscillations in a 510 Å wide doped quantum well excited by a THz impulse. Figure 3.8 shows both amplitude transmission and phase shift extracted from the time-domain data, along with fits to a single oscillator model.

The characteristic time for the intersubband oscillation to decay (T_2) can be extracted directly from the time-domain data of Figure 3.7, or from a linewidth like that shown in Figure 3.8 (intersubband transitions in wide quantum wells are generally believed to be homogeneously broadened). The energy relaxation time T_1, the time required for an electron excited to the second subband to relax to the lower one, is a critical parameter for many applications and is also of fundamental interest. The energy relaxation time may be much longer than T_2 in quantum wells which have intersubband transitions at frequencies smaller than the optical phonon frequency (~9 THz). Several measurements of T_1 have been made using the free-electron lasers FELIX (time-resolved) and the UCSB FEL (quasi-cw). Figure 3.9 shows a measurement of the

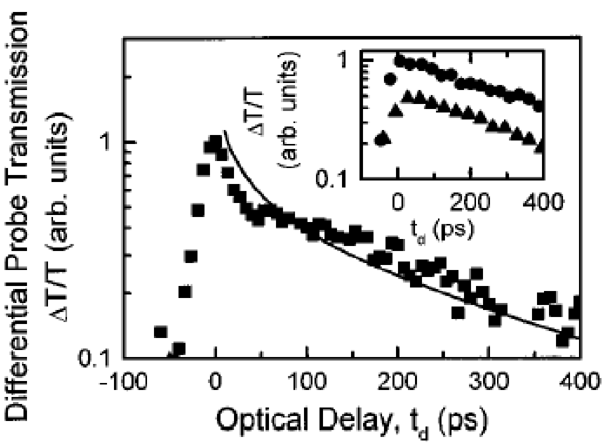


Figure 3.9 Differential probe transmission vs. optical delay. The intersubband absorption is bleached by a 15 ps, 4.7 THz, 6 kW/cm^2 pulse from FELIX, and then probed with a much weaker delayed pulse. Note non-exponential decay. Inset: Differential probe transmission following pump pulses with intensities 40 and 10 W/cm^2. From B. Murdin et. al., Phys. Rev. B. **55**, 5171 (1997).

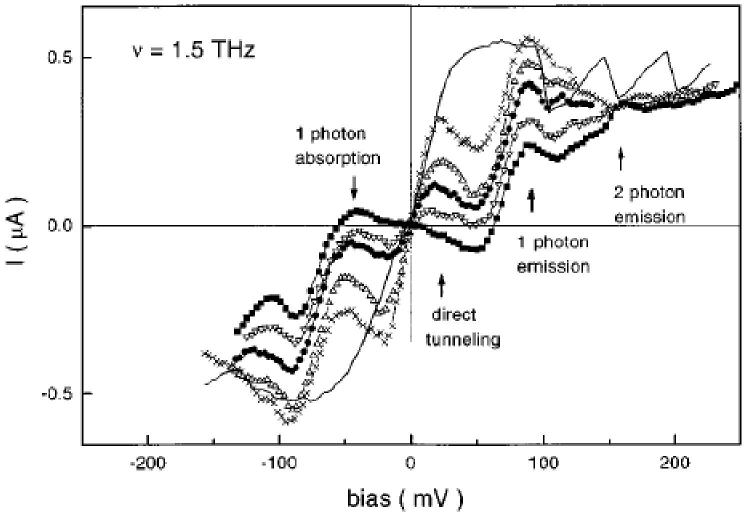


Figure 3.10 I-V curves for through a semiconductor superlattice biased with different intensities of 1.5 THz radiation. Both photon-assisted tunneling and absolute negative resistance are clearly visible. From S. Zeuner et. al., Phys. Rev. B **53**, 1717 (1996).

recovery of intersubband absorption, measured with a weak probe pulse delayed after bleaching with an intense pump pulse. The decay is non-exponential for intense pump pulses.

Finally, we show a remarkable example of non-equilibrium quantum transport through a semiconductor superlattice in the presence of intense THz fields from the UCSB FEL. Figure 3.10 shows a current-voltage curve at various intensities of 1.5 THz radiation. The solid line is the unpumped current-voltage curve. In the presence of a strong THz field, two remarkable features are observed. First, there are peaks associated with photon-assisted tunneling between the ground states of adjacent wells in the superlattice. Second, there are conditions under which the resistance is *absolutely negative*. That is, a positive current flows for a negative voltage drop across the device, and vice-versa. No laws of physics are violated, since energy is being absorbed from the THz field. Nevertheless, this is a truly fascinating and counterintuitive non-equilibrium transport effect, which has excited much theoretical interest.

3.2 Opportunities

The unprecedented ability to engineer semiconductor quantum wells, wires, and dots provides a flexible laboratory for the design of well-defined electromagnetic resonances between quantum mechanical energy levels. Important resonances lying in the few-to-tens of milli-electron-volt, and thus THz, range include hydrogenic states of impurity-bound carriers, internal-exciton and exciton-to-continuum transitions, intersubband transitions, intraband excitations, plasmons, acoustic and optic phonons, Bloch oscillations, and Landau-level splittings in few-Tesla magnetic fields. These transitions involve spectrally sharp optical densities, or optical densities associated with well-defined structured continua.

Interband homogeneous widths in the near infrared can be as small as a few micro-electron volts, while in some cases inhomogeneous broadening can be eliminated entirely by spectroscopies that are sensitive to a single nanostructure. These fundamental parameters remain almost entirely unknown for intraband transitions of quantum wires and dots in the THz regime; the prospect that they are even narrower than the interband case is a distinct and exciting possibility.

While for decades extremely sharp atomic spectroscopic levels have served as a basis for the development of coherent nonlinear spectroscopies and for the study of quantum optics, only recently have the well-defined levels in semiconductor nanostructures been exploited for similar purposes. More specifically, these structures provide a laboratory for the study of coherent nonlinear, ultrafast, and quantum optics. As mentioned above, a natural frequency scale is in the THz range. Extensive study of the coherent nonlinear optical properties of semiconductors nanostructures have identified them as leading candidates to be future building blocks for quantum information science. The requisite manipulations require the use of THz fields for a number of leading implementations.

The high degree of control over growth and ultimately of the energy levels makes semiconductor nanostructures ideal testbeds of ideas related to coherent control, high-field physics, and quantum optics, as well as for testing advanced applications based on these. Unlike atoms, semiconductor nanostructures can be designed to order, and once fabricated they stay put.

Before *control* of quantum states in semiconductor nanostructures can reach its full potential, there is still considerable work that must be carried out to fully characterize the relevant excitations. In achieving this end, THz radiation will serve as a probe into the basic properties of these systems.

Finally, it must be pointed out that semiconductors remain the technological cornerstone of electronics and optoelectronics; the past half century has shown a close give and take between basic science and technology in this area. With the push to frequencies well in excess of 100 GHz, THz and picosecond phenomena come to the fore. Not only are numerous energy splittings in the THz range, many relevant relaxation processes as well as transit times are in the picosecond regime, and thus susceptible to THz probing. Terahertz studies will thus have a large role to play in future generations of high-frequency electronics.

The following have been identified as priority areas:

- *Fundamental properties of semiconductor nanostructures*
- *Fundamental limits of electronic devices*
- *Subwavelength THz spectroscopy*
- *Coherent control and nonlinear THz spectroscopies*
- *Quantum optics*
- *Quantum-information science*
- *Spintronics*
- *High THz electric field physics and quantum nonlinear dynamics*

Fundamental Studies of Nanostructures

Fabrication of semiconductor structures confined in all directions to a few nanometers can be achieved by several means. In these structures, energy-level splittings are often in the THz range. In some cases, impurities provide another means to obtaining atomic-like excitations in semiconductors yielding similar splittings. At THz frequencies, electron interaction with acoustic and optical phonons is small due to the restrictions placed on relaxation by energy and momentum conservation, and extremely narrow linewidths of electronic excitations are found. Application of these phenomenally small linewidths (and correspondingly long relaxation and dephasing times) to various devices, including light emitters, detector and quantum logic devices, has been the focus of intense research. Although interband linewidths in the near infrared as narrow as a few μeV have in some cases been measured, their origins are not in many cases clear. For example, it remains unknown why – despite such apparently narrow linewidths – the linewidths of nanocrystals at very low temperature are as large as they are. In particular, recent careful theoretical work indicates that the zero-phonon line of nanocrystals should remain unbroadened in the presence of phonon anharmonicity in the zero-temperature limit. Moreover, in other cases, only an upper bound to the linewidths has been determined due to limited frequency resolution. The situation for intersubband transitions in the THz regime is even less clear as the intrinsic spectroscopic lineshapes for quantum dots and nanocrystals are entirely unknown. Establishing the intrinsic time scales for dephasing and relaxation are essential to many applications. Coherent nonlinear THz experiments will go a long way to tease out fundamental parameters, such as T_1 and T_2, from largely inhomogeneous distributions of quantum dots or nanocrystals. Such experiments include THz photon echo and intersubband Rabi flopping.

Once such parameters are established, it will be easier to ascertain the degree to which excitations in the THz regime can be coherently manipulated. The ability to induce Rabi flopping in quantum dots will also serve as a prototypical experiment, and will thus help us to ascertain the feasibility of various coherent-control schemes.

Fundamental Limits of Electronic Devices

There is fundamental limit that all high frequency electronics, transistors etc., will encounter as the frequency exceeds scattering times. It appears that the most sophisticated device models do not recognize that at high enough frequencies the inertial effects of the electron will become important when . Dynamics play a more important role compared to diffusion and relaxation. Indeed, that is one area where THz studies are most valuable.

Subwavelength THz Spectroscopy

Better yet would be the ability to carry out nonlinear THz experiments on *single* nanostructures to access the indisputable quantum regime. Near-field THz spectroscopy is in its infancy, and so far, only rudimentary experiments in the linear regime have been carried out. Such techniques may also be a valuable tool for the characterization of high-frequency devices and systems under operating conditions.

An additional approach to subwavelength THz spectroscopy relies on the ability to focus optical beams much more tightly than THz ones. Optical/THz sum and difference frequency generation makes it possible to explore THz dynamics on spatial scales set by the optical probe, leading to resolutions of . Terahertz frequency dependence of the sum and difference frequency sidebands that appear on the optical probe are sensitive only to the overlap region of the optical and THz beams.

Coherent Control and Nonlinear THz Spectroscopies

The ability to manipulate quantum mechanical states of matter in a coherent fashion to attain states that might otherwise be difficult to attain is the aim of coherent control. One class of coherent-control experiments is based on the use of temporally shaped electromagnetic pulses to drive a system in a nonperturbative fashion toward a target state, which may be otherwise difficult to reach via monochromatic or incoherent excitation. Coherent control thus tests the limits to which quantum mechanical states of matter can be manipulated and directed in a coherent fashion.

Quantum Optics

If one can control the quantum state in a single nanostructure, such as a quantum dot or nanocrystal, these processes will involve single THz photons and will thus reveal the quantum nature of the electromagnetic field involved. Already, single quantum-dot spectroscopy has been carried out in the *optical* domain; the THz domain remains unexplored. This is an entirely new area of quantum optics. At THz frequencies, we can almost always think of the electromagnetic field as a classical entity; the demonstration of true quantum optics at THz frequencies will be a new regime, and semiconductor nanostructures may ultimately serve as sources of nonclassical THz light.

Quantum-Information Science

The ability to manipulate quantum mechanical states in a four-dimensional Hilbert space underlies the ability to perform universal quantum logic. Quantum dots or nanocrystals form the basis for several schemes for realizing quantum-logic gates. These manipulations are achieved by controlling the quantum mechanical states of a small number of electrons (usually two) in a quantum-dot structure by various combinations of optical, electrical, and magnetic pulses, depending on the specific scheme. One approach relies on the use of short electric pulses to control the height of a tunnel barrier between two quantum dots to modify transiently the exchange interaction between a pair of electrons. Picosecond gating (read half-cycle THz pulse) is thus desired. In addition, single-qubit manipulations may be achieved by magnetic-field pulses. To carry out the manipulations on the requisite time scale requires in some cases ~1 T picosecond magnetic pulses.

Spintronics

The manipulation of electronic spin as the basis of device operation is known as spintronics. Magnetic level splittings in semiconductor nanostructures in few Tesla fields are frequently in the THz regime. Thus, THz techniques will prove to be central to certain approaches to spintronics in semiconductor nanostructures.

High THz Electric Field Physics and Quantum Nonlinear Dynamics

Electrons in semiconductor nanostructures provide an ideal playground for the exploration of THz *nonperturbative*, *far-from-equilibrium*, and *quantum* dynamics due to their large dipole moments, small effective masses, and high mobilities. Terahertz is the natural frequency range to explore these effects since there exist a large number of single-particle and collective excitations in the THz range – intersubband transitions in quantum dots and wells, internal transitions of donors and excitons, magnetic resonances (cyclotron resonance and electron spin resonance), phonons, plasmons, magnons, … etc. In addition, many-body effects are expected to significantly influence and complicate dynamical processes in these nanostructures, which is another ingredient that differentiates these studies from corresponding efforts in atomic and molecular systems.

Some simple formulas that expose what is meant by strong electric field are:

A: $\frac{e\langle x\rangle E_{AC}}{\hbar} > 1/\tau$ for Rabi oscillations.

B: $\frac{eaE_{AC}}{\hbar\omega} > 1$ for THz photon assisted tunneling. where a is some length, typically the separation between two quantum wells, two quantum dots, or between two quantum systems as in two weakly coupled superconductors. The quantity eaE_{AC} is simply the time varying energy difference between the two quantum systems.

C: $e\frac{eE_{AC}}{m^*\omega^2}E_{AC} > \hbar\omega$ for the dynamical Franz-Keldysh effect. Here the length $a = \frac{eE_{AC}}{m^*\omega^2}$ is the "THz quiver motion" of a free electron in the THz electric field.

The ponderomotive energy E_p of a free electron in a time-oscillatory electromagnetic field is the average classical kinetic quiver energy of the electron induced by the field. Simple mechanics implies that E_p is proportional to ν^{-2}. On the other hand, the photon energy is $h\nu$. Thus, at sufficiently low frequency, the ponderomotive energy exceeds the photon energy. This is the regime of high-field physics where high-order multiphoton processes dominate. Most work on high-field physics has been confined to atomic systems. Here the phenomena of above-threshold ionization and high-field harmonic generation are well known. At optical frequencies, the electric field amplitude where this occurs may exceed the threshold for laser damage in materials, and has therefore largely confined such studies to atoms. At THz frequencies, however, this regime is accessed in the range of a few kV/cm to MV/cm – well below dielectric breakdown in materials. Thus, a new regime of high-field studies in materials is enabled by THz techniques. Low effective masses and giant dipole moments in many cases permit such high-field effects to be accessed at anomalously low fields. Predicted effects include dynamic localization (collapse of the miniband) in superlattices and THz high-field harmonic generation by excitons in quantum wells, wires, and dots.

There has been recent interest in verifying predictions of a chaotic response, as well as other exotic nonlinear behavior, of wide *n*-type quantum wells to strong THz fields. This would be an interesting example of a quantum mechanical system exhibiting a chaotic response.

i. Nonperturbative THz Electro-Optics

The dynamics of effective-mass particles and their complexes in an intense electric field strongly modifies the optical properties of a semiconductor in the vicinity of the absorption edge. In the well-known Franz-Keldysh effect, a strong DC electric field induces absorption below the edge and oscillatory behavior of the absorption above the edge. These electro-optical (EO) effects are well-understood in many bulk and low-dimensional semiconductor systems. The THz frequency range (0.1 to 10 THz) is especially interesting to explore new EO phenomena, since THz electric fields can couple strongly with various elementary and collective intraband excitations in semiconductors. We expect strongly-driven *intra*band excitations to significantly alter *inter*band optical properties. Theoretical studies have predicted fascinating new phenomena for the emission, absorption, and reflection properties of THz-driven semiconductors. However, there have been only a few experimental THz EO studies due to the rarity of sources for strong THz radiation.

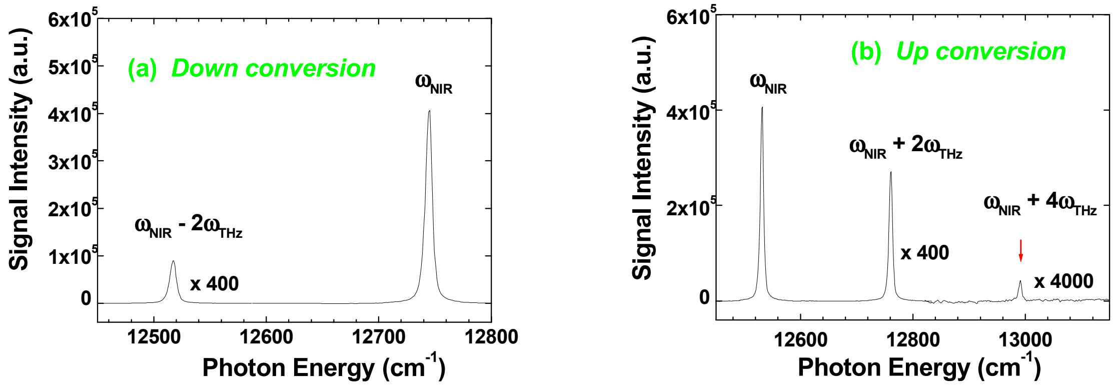


Figure 3.11 a and b Terahertz optical sideband generation in GaAs/AlGaAs quantum wells with electric field polarized in the plane of the quantum well (see Kono et. al., Phys. Rev. Lett. 79, 1758 (1997).

The UCSB FEL group has been studying various THz electro-optical effects in semiconductors. For example, the interaction of intense THz radiation with excitonic internal transitions and intersubband transitions can resonantly produce very strong and narrow near-infrared (NIR) emission lines, or *optical sidebands*, at frequencies $\omega_{NIR} \pm 2n\omega_{THz}$, where ω_{NIR} (ω_{THz}) is the frequency of the NIR (THz) beam and n is an integer. The intensity of the sidebands exhibits pronounced resonances as a function of applied magnetic or electric field. These resonances can be ascribed to virtual internal excitonic transitions. Figures 3.11(a) and 3.11(b) show typical sideband spectra. The frequency of the THz radiation was 115 cm^{-1} for both figures. The intensity of the $+2\omega$ sideband increases *linearly* with NIR power for a constant THz power, whereas it increases *quadratically* with increasing THz power for a constant NIR power. Thus the $+2\omega$ sideband emission can be described as a third-order optical process involving one NIR photon and two THz photons.

ii. Terahertz Extreme Nonlinear Optics

Matter in the presence of a high-intensity time-periodic (AC) electric field exhibits various intriguing phenomena that cannot be understood by treating the field as a small perturbation. For example, the AC Stark effect in atoms, which occurs in the presence of strong driving fields *resonant* (or nearly resonant) with electronic transitions, represents coupled light-matter states (or “dressed” states). In the *non-resonant* (far from resonance) case, laser-driven atoms exhibit other nonperturbative phenomena, such as above-threshold ionization and high-order harmonic generation, when the *ponderomotive potential* (i.e., the time-averaged kinetic energy of an electron in an AC field) is comparable to or greater than the photon energy of the field and/or the relevant energy scale in the system (e.g., ionization energy).

Condensed matter, semiconductors in particular, provides a viable alternative to gases for exploring nonperturbative phenomena. We can expect, e.g., 1) the effect of *quantum confinement*, 2) the explicit coupling of the *spatially periodic* potential of the solid to the *temporally periodic* potential imposed by the AC field, and 3) various *many-body effects* – i.e., phenomena that are difficult or impossible to observe in gases. Theoretical studies have predicted fascinating new phenomena such as band gap oscillations, the appearance of new gaps, field-induced electronic phase transitions, laser-assisted electron-electron attraction, etc. However, such effects have not been observed to date because of the unavoidable sample damage due to the very high intensity required using conventional near-IR (NIR) or visible lasers.

Intense THz radiation solves these problems and allows us to enter the unexplored extreme nonlinear optics regimes in semiconductor systems. The use of long-wavelength light results in 1) an increased ponderomotive potential energy (which is proportional to the *square* of the wavelength), i.e., less intensity is required for observing the predicted effects, and 2) lower probability for multi-photon interband absorption. Both of these help avoid the damage problem. Also, the low dispersion in the THz in semiconductors allows *excellent phase-matching* over long distances. Therefore, the THz is an ideal wavelength range in which to study multi-photon, nonperturbative effects in semiconductors. The intense THz fields *directly*, *coherently* and *strongly* drive charge carriers in semiconductors (sometimes to the regime where the effective mass approximation is no longer valid). The effects of this extreme driving will manifest themselves as dramatic modifications in interband optical properties.

Such research not only provides new insight into the dynamics of strongly-driven systems but also is useful for developing novel semiconductor devices that operate in the frequency range where both field-like and photon-like properties of light are important. Research contributing to the development of new combined electronic/photonic technologies would be extremely useful and valuable.

iii. Coherent Band Structure Distortion

The direct interplay between the spatially periodic lattice potential and the temporally periodic laser field provides unique and fascinating possibilities for strongly-driven solids.

Although this is a rather crude approximation (based on the nearly-free electron model, which treats the lattice potential perturbatively), the main dramatic result here (see Figure 3.12), which is generally true, is that the band gap oscillates as a function of laser intensity and generally *decreases* as the laser intensity increases. Physically, this *laser-induced band-gap shrinkage* may be understood as a consequence of the fact that, with increasing laser intensity, the kinetic

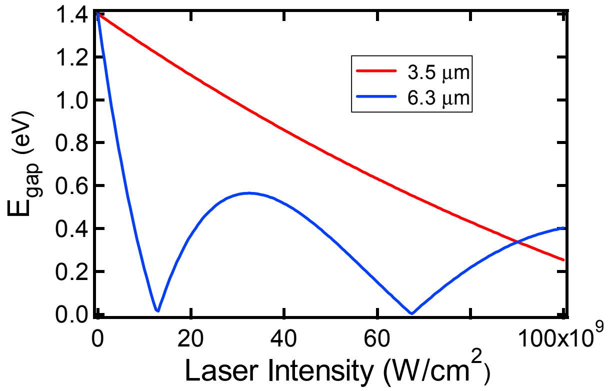


Figure 3.12 Predicted band gap oscillations in GaAs strongly driven by laser fields at 3.5 μm (red line) and 6.3 μm (blue line). (courtesy Junichiro Kono, Rice University)

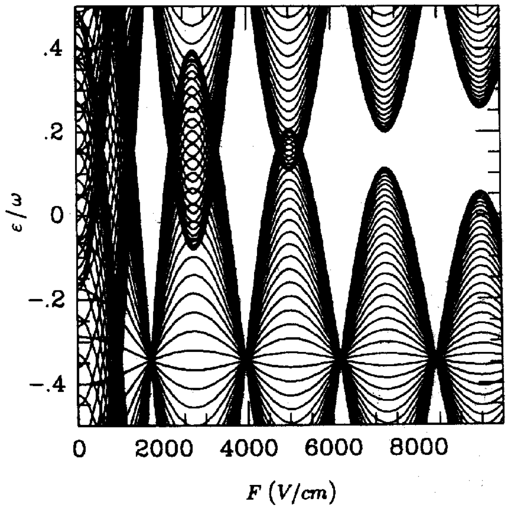


Figure 3.13 Predicted miniband collapse. Miniband width versus THz electric field strength. From M. Holthaus, Phys. Rev. Lett. **69**, 351 (1992).

energy term of the Hamiltonian becomes greater than the lattice potential, such that in the limit of ultra-intense fields ($a \to \infty$) *the electron no longer sees the lattice*. Alternatively, this is equivalent to saying that, upon increasing the laser field strength, the effective lattice potential becomes increasingly small. From either perspective, this suggests the fascinating possibility of coherently controlling the band gap of a semiconductor by simply tuning the intensity of the applied laser field.

It has also been predicted that miniband collapse will occur with sufficiently high electric field strength. Large amplitude THz pulses should allow this phenomenon to be observed (see Figure 3.13).

3.3 Enabling resources and technologies

Currently, a rate-limiting problem is that the same scientists who carry out the experiments in many cases also carry out the source development. This leads to a situation where a state-of-the-art table-top source is developed only to be promptly disassembled. Furthermore, accelerator-based sources of coherent THz radiation in the U. S. have little or no funding dedicated to the support of outside users. To address this we suggest:

- Distributed network of intermediate-scale THz user resources having a range of capabilities. These include 1 kV/cm – 1 MV/cm peak fields at the sample, flexible bandwidth from 1 MHz to 1 THz (quasi-cw to half-cycle), pulse-shaping/waveform control, cw sources, THz systems coupled to high magnetic fields, with optical cryostats, synchronized with other lasers, and including high-pressure capabilities

- Extensive development of enabling technologies including high-power fiber lasers as optical pumps, a toolbox of affordable THz optical elements – passive and active, linear and nonlinear, THz antennas, THz near-field techniques, THz magnetic pulses (~1 T, 1 ps duration), pulse-shaping/waveform control, THz amplifiers, and exploitation of hybrid techniques leveraging off optics and microwaves.

Chapter 4: Metals, Strongly Correlated Electron Systems, and Insulators

4.0 Executive summary

Opportunities: Linear THz spectroscopy under extreme conditions such as high magnetic field, low temperature, or high pressure continues to be a challenge, yet has the potential to bear much fruit. Linear THz spectroscopy of magnetic and spin-related excitations is also a field in its infancy. Terahertz spectroscopy enables one to extract a material's conductivity and dielectric constant without applying electrical contacts.

THz studies of excitation in solids far from thermal equilibrium are also in their infancy. Emerging experiments pump materials with pulses of strong visible or near-IR light and probe their linear THz response with weak delayed THz pulses using time-domain THz spectroscopy. These techniques have recently been applied to insulators, semiconductors and superconductors with fascinating results.

Another class of experiments has been virtually untouched. These explore phenomena resulting from pumping insulators, metals and strongly-correlated electron materials with strong THz pulses. One can imagine accelerating a superconducting condensate past the pair-breaking velocity on sub-ps time scales, inducing structural phase transitions with THz radiation, changing the orientation of ferroelectric or ferromagnetic domains on ps time scales, and inducing novel metastable structural changes, to name just a few exciting possibilities.

Status: Metals are typically very good reflectors of THz radiation. The reflectance of simple metals at THz frequencies is determined by the dc conductivity and the frequency in a relation derived by Hagen and Rubens in 1903. Deviations from this simple relationship indicate physics beyond the simple Drude model.

The investigation of superconductivity was an early application of THz spectroscopy, which was then called far-infrared spectroscopy. Tinkham, Richards and others used FTIR spectrometers with black body sources to the study the onset of absorption in the superconducting states of elemental superconductors. This dramatic deviation from the Hagen-Rubens relation uncovered the existence of an energy gap in the electronic density of states; these results preceded the prediction of such a gap by the Bardeen, Cooper and Schrieffer theory of superconductivity. Phonon-mediated superconductivity is just one of the fascinating phenomena which emerge in solid state materials with strongly-correlated electrons. Other states include giant and colossal magnetoresistance, magnetism, charge and spin density waves, heavy Fermion behavior and superconductivity, and, of course, high-temperature superconductivity. Terahertz spectroscopy continues to be a critical and unique tool for studying the low-lying excitations of correlated electron materials. The advent of time-domain THz spectroscopy, with its superior signal-to-noise ratio and ability to directly measure real and imaginary components of the dielectric response function, has revolutionized the study superconductors at THz frequencies.

Virtually all solids have optical phonons at THz frequencies. Most of these are infrared-active, meaning they can be excited directly by resonant oscillating electric fields. Phonon features are particularly interesting near structural phase transitions, where they become "soft" and move towards zero frequency. Phonons interact strongly with electrons, and, of course, mediate conventional superconductivity.

Conventional FTIR spectroscopy has always been rather awkward below 1 THz, though it is possible with specialized apparatus to reach below 100 GHz with this technique. Time-domain THz spectroscopy has revolutionized linear spectroscopy between 100 GHz and 1 THz. At least two companies are now selling commercial time-domain THz spectrometers – TeraView and Picometrix.

Potential size of community: Almost every solid has interesting excitations at THz frequencies. A reasonable lower bound for the size of the solid state physics community in the U. S. can be derived from the size of the March Meeting of the American Physical Society, which typically attracts over 5,000 registered participants. Only a very small fraction of this community has easy access to any sort of THz infrastructure.

Technology and infrastructure needs:
Broad access to specialized and expensive existing equipment, as well as development of new capabilities, can be supported through a THz User's Network. Highly desirable would be wide access to relatively small-scale facilities for linear THz spectroscopy in extreme conditions (high magnetic fields, high pressure, low and high temperature, small samples). The recent successes in visible pump-THz probe techniques argue in favor of wide access to these facilities as well, also in extreme conditions. Finally, facilities in which samples can be excited far from equilibrium with THz pulses that have peak electric fields up to 1 MV/cm are desirable. After such excitation, the systems can be probed by a variety of means, including optical, transport and, of course, THz. For THz-pump-THz probe experiments (strong THz pump, weak THz probe), it would be useful to have access to a range of bandwidths for the pump. These bandwidths should, ideally, match the linewidth of the excitation. Most excitations in solids have linewidths larger than 1%, so a variable bandwidth that can be as small as 1% would be desirable.

4.1 Introduction

4.1.1 Global science issues

The field of correlated electron systems is the study of materials whose properties cannot be understood by free or independent electron models. These materials were once thought to be isolated special cases because Landau's theory of Fermi liquids predicts that strongly interacting electrons behave like free electrons with renormalized masses. However, in the last fifteen years many systems whose properties defy understanding within Fermi liquid theory have been discovered. Such systems are found in *d*- and *f*-shell metals, organic conductors, semiconductors doped near the metal-insulator transition, and artificial systems with reduced dimensionality, such as quantum dots. The common links among these systems are narrow electronic bands, reduced dimensionality, and low carrier concentration. The latter two properties reduce screening and, hence, increase the inter-electron interactions that lead to strong correlations. The presence of narrow-bands means that the drive to lower kinetic energy is ineffective in destroying such correlations.

The significance of correlated electron physics extends beyond the explanation of the properties of exotic metals. The principles that have emerged from the study of correlated electrons provide the basis for understanding and rational design of new artificial structures – the essence of the emerging field of "nanophysics." A few examples from this list are Kondo effects, the Coulomb blockade in both normal and Josephson tunneling, the Landauer theory for transport in one-dimensional channels, Luttinger liquid theory, and weak localization. These concepts form the language in which the discussion of phenomena in new materials is expressed.

A new and exciting approach to understanding non-Fermi liquid behavior is the theory of quantum phase transitions and criticality. A quantum phase transition is the transformation from a disordered to an ordered phase that takes place at zero temperature as a parameter of the Hamiltonian is varied. Although the existence of such points has been known for a some time, it was not appreciated until recently that their presence at T = 0 can dictate the properties of some materials at much higher temperatures. As shown in the schematic phase diagram below (Figure 4.1), the quantum critical regime encompasses a large, inverted triangle-shaped region in the plane of temperature vs. control parameter.

Within this triangle, the Fermi liquid state is disrupted by strong fluctuations between the competing ordered and disordered phases. Perhaps the most interesting feature of this scenario is the possibility that within a dome-shaped region near the quantum critical, point fluctuations resolve themselves in an entirely new phase, such as superconductivity. Evidence for exactly such a phase diagram has been found recently in the study of the heavy-Fermion compound $CePd_2Si_2$ as function of temperature and pressure (see Figure 4.2).

The phase diagrams for correlated electron materials (CEMs) can be highly complex. Understanding the nature of these phases, as well as the transitions among them, requires detailed characterization of their excited states, or elementary excitations. The most important excitations are those with an energy of order k_BT above the ground state and therefore in the THz region of the electromagnetic spectrum. The excitations that can be studied by THz spectroscopy fall into two main classes: single particle and collective. In the first category, THz

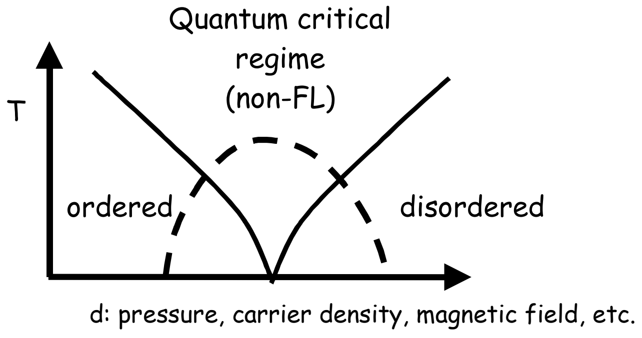


Figure 4.1 Schematic phase diagram of a system with a critical point. Quantum critical point refers to a phase transition at T=0. The horizontal axis is a tuning parameter: doping, pressure, magnetic fields etc.

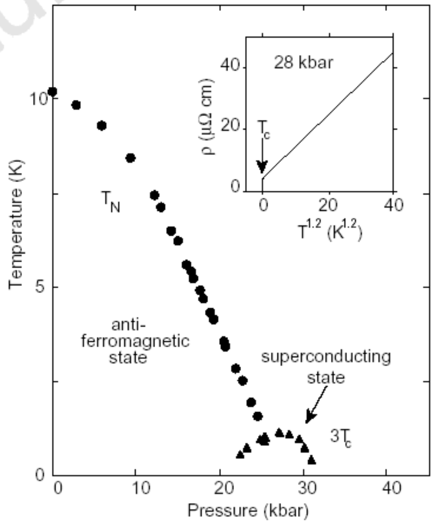


Figure 4.2 Phase diagram for the antiferromagnetic CePd2Si2 as a function of pressure. The superconducting transition induced by pressure at low temperatures. From Julian et al. J. Magn. Magn. Mater. **177**, 265 (1998).

spectroscopy has been used with great success to probe the energy gap in superconductors, the internal transition of excitons, the non-Drude conductivity of correlated metals, intersubband transitions in low dimensional materials, and magnetic dipole transitions in correlated magnets, for example. Terahertz spectroscopy is equally powerful as a probe of collective modes, such as phonons, translational acceleration of a superfluid condensate, antiferromagnetic resonance, the Josephson plasma resonance, cyclotron resonance, and the soft mode in ferroelectrics.

4.1.2 Why THz?

Terahertz spectroscopy provides great flexibility to probe matter in new ways. For example, the THz region of the spectrum is sensitive to all of the thermally accessible excitations that determine the properties of correlated electron systems. Also, the ability to perform spectroscopy in the time as well as frequency-domain provides a unique window on the temporal evolution of optical response functions on time scales between 100 fs and 500 ps. Furthermore, THz methods are compatible with the study of materials under extreme conditions of temperature, electric, and magnetic field. Other critically important factors include the contactless nature of the THz probe, as well as polarization analysis and polarization control. This is important due to the difficulty of forming Ohmic contacts to certain materials or structures, due to the remote location of the material, or to avoid the introduction of extrinsic effects associated with leads. In other cases, the dynamic conductivity itself is of interest. Terahertz probes can also provide detailed information on interface quality or on the presence of buried defects or structures.

Relevant materials include semiconductor heterostructures, colossal magnetoresistive materials, and magnetic/ferroelectric perovskite multilayers. Many classes of microstructured materials are difficult to characterize by other means. Pump-probe experiments that can be readily accomplished using laser-based THz instruments can study the response of correlated systems to high electric fields (of the order of MV/cm) without the risk of excessive heating or electrical breakdown. Electro-optic generation and detection has also proven useful for generating coherent radiation in the 10 – 30 THz range with near-transform limited pulse widths as short as 25 fs.

4.1.3 Examples of impact of THz research on correlated electrons physics.

THz spectroscopy is emerging as a premier experimental tool in the studies of strongly correlated electrons materials. Terahertz methods enable experimental access to the optical constants in the frequency range critical for the understanding of physics underlying strongly correlated phenomena in solids. Below we document several specific examples illustrating unique capabilities and impact of THz methods.

- *Quantum critical power laws*
- *Phase stiffness*
- *Josephson plasma resonance and nanoscale inhomogeneities of the superfluid density*
- *Single molecule magnets*
- *Pair-breaking and condensate recovery in* MgB_2
- *Anti-ferromagnetic resonances.*
- *THz losses and dynamics of vortices in high-Tc superconductors*

4.1.3.1 Quantum Critical Power Laws

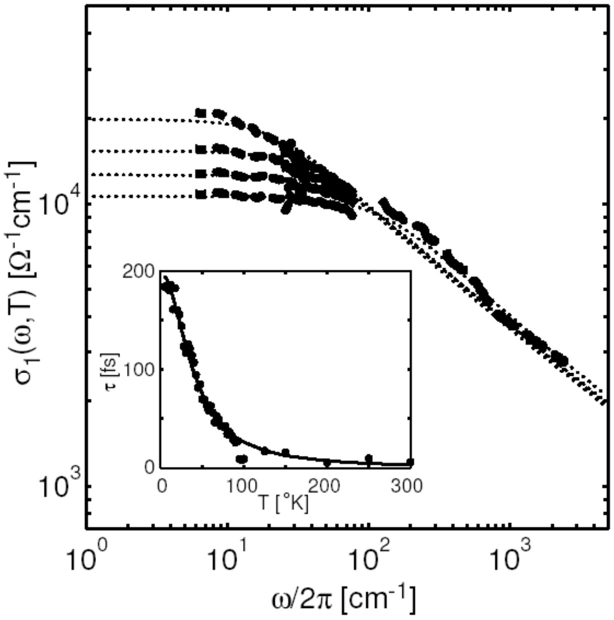


Figure 4.3 Logarithmic plot of the conductivity obtained by a combination of THZ time-domain spectroscopy and infrared interferometer-based spectroscopy for $SrRuO_3$ The conductivity follows a simple phenomenological form, with an analytic structure fundamentally different from that predicted by the standard theory of metals. After J. S. Dodge et al. PRL 85, 4932 (2000)

One of the most striking of the non-Fermi liquid properties of correlated materials is the optical conductivity, whose frequency dependence is strikingly different from a Drude or simple Lorentzian shape. In particular, the Drude model predicts that, for frequencies above the scattering rate, the optical conductivity falls away at a rate given by $1/\omega^2$. However, the optical conductivity of most correlated metals drops off as power of the frequency that is much smaller than two. When these power law conductivities are measured in the infrared frequency regime above the THz regime, the conductivity is typically found to be independent of temperature. This occurs in systems where the zero frequency or dc conductivity is known to increase rapidly with decreasing temperature. Such measurements led to speculation that the non-Drude power laws result from a band to band transition that is not related to the dynamics of the conduction electrons. This speculation was shown to be incorrect in data collected from THz spectroscopy, as illustrated in Figure 4.3. The single set of data points at frequencies above 100 cm^{-1} were measured using conventional FTIR spectroscopy. The four sets of points at frequencies between 5 and 50 cm^{-1} were measured using time-domain THz spectroscopy. The four sets correspond to four different sample temperatures. Combining the data measured by these two techniques provides a unique look at the optical conductivity over three decades of frequency. In this experiment THz spectroscopy is uniquely capable of demonstrating that conductivity over the entire range derives from a single process, i.e., the non-Drude conductivity of the conduction electrons.

4.1.3.2 Phase Stiffness

THz spectroscopy is a powerful probe of superconductivity in correlated electron systems. It is unique in its ability to perform absolute, accurate, and rapid measurements of one of the most important parameters of superconductors, the superfluid condensate density. In two-dimensional superconductors, such as the cuprates, the condensate density is directly related to the phase stiffness, which is the energy required to create distortions of the phase of the superconducting order parameter. Terahertz spectroscopy has the ability to measure the phase stiffness as a function of the frequency of the phase distortion. In the "true" superconducting state the phase

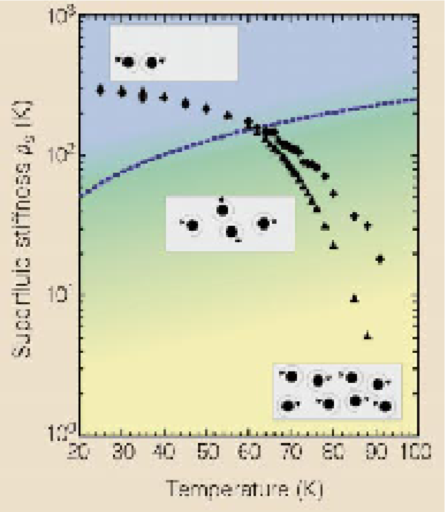


Figure 4.4 Phase stiffness rs as a function of temperature at frequencies of 100 GHz (triangles) and 600 GHz (diamonds) as determined by Corson *et al. Nature 398, 221 (1999)* . Dotted line follows the Kosterlitz–Thouless temperature T_{KT} as a function of phase stiffness. The Kosterlitz– Thouless superconducting transition is predicted to occur when ρ_s intersects this line. Insets show behaviour of vortices in the superfluid phase field. At low temperatures, any vortices present are tightly bound in pairs of opposite circulation, so the phase stiffness is large and frequencyindependent. At TT_{KT} a few unbound vortices are present and ρ_s is non-vanishing at high frequency (short-length scales) but vanishing at low frequency (long-length scales). At $T>>T_{KT}$, a proliferation of vortices causes ρ_s to vanish at all scales.

stiffness is independent of frequency. However, strong superconducting fluctuations can in principle exist above the transition temperature T_c. The signature of such fluctuations is that the phase stiffness can be detected at high frequency, but vanishes in the limit that the frequency goes to zero. Figure 4.4 shows the onset of frequency dependence of the phase stiffness in the cuprate superconductor BSCCO. This is the temperature at which the phase stiffness, measured at two different frequencies, begins to diverge. The dotted line is the famous Kosterlitz-Thouless-Berezinski theory for the relation between the phase stiffness and the temperature at which frequency dependence first appears. The ability to make this direct comparison with theory depends critically on the ability of THz spectroscopy to perform absolute measurements of the frequency-dependent phase stiffness energy.

4.1.3.3 Josephson Plasma Resonance and Nanoscale Inhomogeneities of the Superfluid Density

A Josephson plasma resonance is produced by coherent propagation of Cooper pairs between superconducting "sheets" in layered superconductors. In a variety of layered superconductors this mode falls in THz frequency range. The analysis of the JPR mode provides information on the local variation of the superfluid density within the layers which is particularly valuable in the case of cuprate high-Tc materials. Numerous experiments indicate that charge distribution within the CuO_2 planes is highly non-uniform. In fact, electronic phase separation occurring on diverse length scales appears to be an intrinsic attribute of doped Mott-Hubbard (MH) insulators and also offers new approaches to elucidate high-*Tc* superconductivity. However, until recently

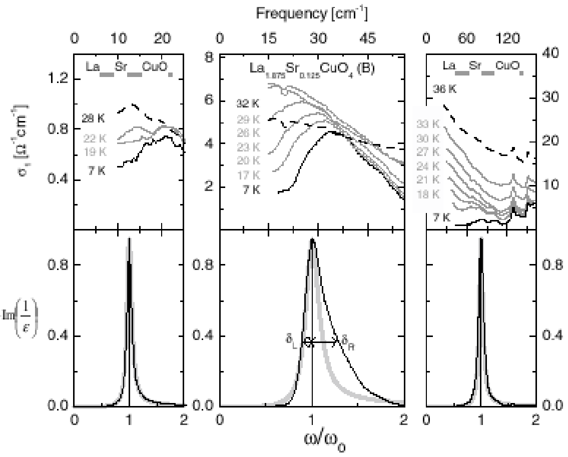


Figure 4.5 Top panels: the optical conductivity (top panels) for crystals of $LaSrCuO_4$ high-Tc superconductors. Bottom panels show the Josephson plasma resonance in the spectra of the loss function. Asymmetric lineshape is a robust indicator of inhomogeneous superconducting condensate in CuO_2 planes occurring on the length scales of 200 Å. After S.Dordevic, Seiki Komiya, Yoichi Ando, and D.N. Basov, PRL 91, 167401, (2003).

it remained unclear if the *superconducting condensate* in cuprates is characterized by similar local disproportions. An examination of the JPR mode offered a tool for ‘‘microscopy’’ on the superconducting condensate. Results displayed in Figure 4.5 uncover the presence of regions with a characteristic length of 100 – 200 Å within which superconductivity is strongly depressed or completely depleted.

4.1.3.4 Single Molecule Magnets

Time-domain THz spectroscopy has shed light on the tunneling mechanism in single molecule magnets. Single molecule magnets are clusters of magnetic ions that are tightly coupled together, acting as a single large spin. The prototypical example is Mn_{12}-acetate, in which each cluster has total spin S = 10. These clusters are arranged on ordered sites a crystalline lattice, but they are well separated from each other so that the inter-cluster interactions are weak. They have been intensely studied since 1996 when quantum tunneling of their magnetic moments was observed. Besides their intrinsic scientific interest, these systems are also interesting because of the possibility of applications in quantum computation.

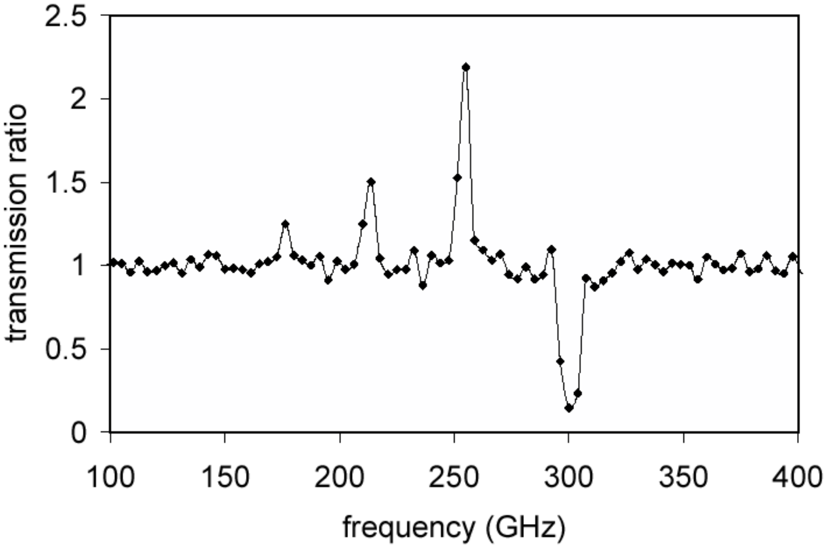


Figure 4.6 The ratio of transmission through Mn_{12}-acetate at 15 K to that at 2 K shows transitions between energy levels within wells. Figure courtesy of E. Parks, Colgate University.

Transitions between spin levels were probed using THz spectroscopy (see Figure 4.6). These transitions were caused by coupling between the *magnetic* field of the THz pulse to the magnetic moment of the clusters (zero-field ESR). The absorption spectrum was measured with 1 GHz resolution, and close examination of these absorption lines provided strong evidence for inhomogeneities in the crystal. The observations of these inhomogeneities is important because they can provide the coupling between spin levels that is required to explain the observed quantum tunneling. This inhomogeneity was quite difficult to observe using other methods such as traditional ESR in which fixed frequencies and swept magnetic fields are used.

4.1.3.5 Pair-Breaking and Condensate Recovery in MgB_2

Optical pump THz probe techniques are proving to be a useful tool to investigate the non-equilibrium dynamics of CEMs. Figure 4.7 shows the temporal evolution (with picosecond resolution) of the real and imaginary conductivity in MgB_2. In this case, the pair-breaking response and the subsequent quasiparticle recombination were simultaneously measured. The

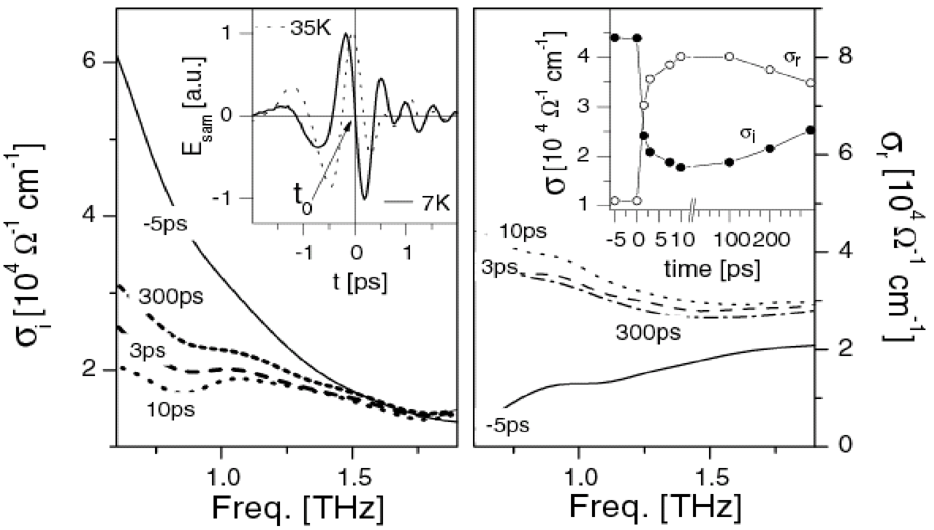


Figure 4.7 Real and imaginary conductivity in MgB_2. Figure courtesy of R. Averitt, Los Alamos National Labs.

beauty afforded by THz measurements such as this is the ability to temporally follow the dynamical evolution of the absolute values of the conductivity.

4.1.3.6 Anti-Ferromagnetic Resonances

Traditional electron spin resonance has been extended in this frequency-domain. The typical high-field ESR instrument uses a fixed frequency source, and the resonance is detected by sweeping the magnetic field. For a large and important class of studies, aiming at the precision measurement of the “g-factor” (the *g* in , $\Delta E = g\mu_B H$) this is indeed the best technique once the measurement is done at the highest possible field nothing new is learned by repeating it at a lower field/frequency. However, in systems with strong spin correlations or order, and/or when the spin-orbit coupling plays a significant role, the spin resonance changes dramatically: resonance may happen in zero field, and the field-dependence is complex, exhibiting several branches of resonance lines. The resonant absorption can be fully mapped over the two-dimensional magnetic field - frequency plane using FTIR spectroscopy and using high intensity white THz radiation. Recent examples for this method include the study of AF resonance in $LaMnO_3$ (see Figure 4.8) and the quantum tunneling transitions on the molecular magnet Mn_{12}.

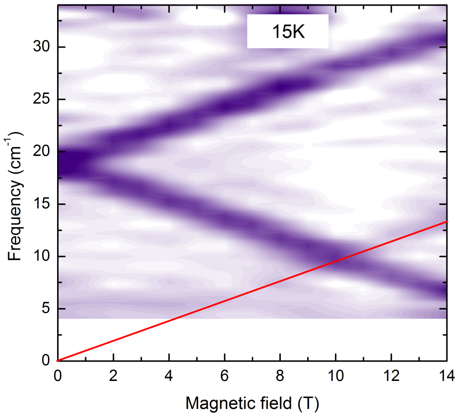


Figure 4.8 Frequency-field map of antiferromagnetic resonance in $LaMnO_3$. Darker shade indicate more absorption. The red line indicates the *g*=2 free spin resonance. After L. Mihaly *et al.*, Phys Rev B, **69** 024414 (2004)

4.1.3.7 THz Losses and THz Dynamics of Vortices in High-Tc Superconductors

A high DC magnetic field puts a large number of vortices in a high-Tc superconductor film.

There are conflicting results on what this does for the THz absorption. Tanner's group at the University of Florida found that the samples were lossless (to the extent they could measure; better to say that the field did not change the loss from the zero field value) whenever the dc resistance was zero in the B,T plane. Louis Brunel also saw this result. Whenever there was a finite dc resistance (i.e., above about 60 K in YBCO at 28 T and above about 35 K in BSCCO at 20 T), then there is a definite increase in absorption in the high-field situation. This can be attributed to the motion of the unpinned vortices. Other groups (Drew, Orenstein, and others) find that the field immediately gives a THz absorption, even at 4.2 K where the vortices are pinned. So there is a difference in the phenomena observed.

To elucidate this discrepancy, and to explore nonlinear/non-equilibrium effects, we propose to go to low T and high B and turn up the THz field until one begins to drive the vortices. Essentially one would want to generate THz currents that approach at their peak values close to the critical current. We can estimate this from the surface impedance and the known j_c, at least in a thin film where the skin depth is not an issue. At 1 THz the conductivity is mostly imaginary (σ_2) and $\sigma_2 \sim 30{,}000$ to 100,000 Ohm^{-1}cm^{-1}. The critical current is in the range of 10^5 to 10^6 A/cm^2 (at zero field). This means electric field strengths between 1 and 30 V/cm, which is achievable with existing narrow-band THz sources.

4.1.4 Other Materials

4.1.4.1 Nonlinear Optical Effect at THz Frequencies

Optical control over coherent lattice responses that are both time-and position-dependent across macroscopic length scales has recently been achieved. In these experiments, spatiotemporal femtosecond pulse-shaping was used to generate excitation light fields that were directed toward distinct regions of crystalline samples, producing THz-frequency lattice vibrational waves that emanated outward from their multiple origins at lightlike speeds. Interferences among the waves resulted in fully specified far-field responses, including tilted, focusing, or amplified wavefronts. Generation and coherent amplification of THz traveling waves and THz phased-array generation also were demonstrated (Figure 4.9). These results also point toward spectroscopic applications,

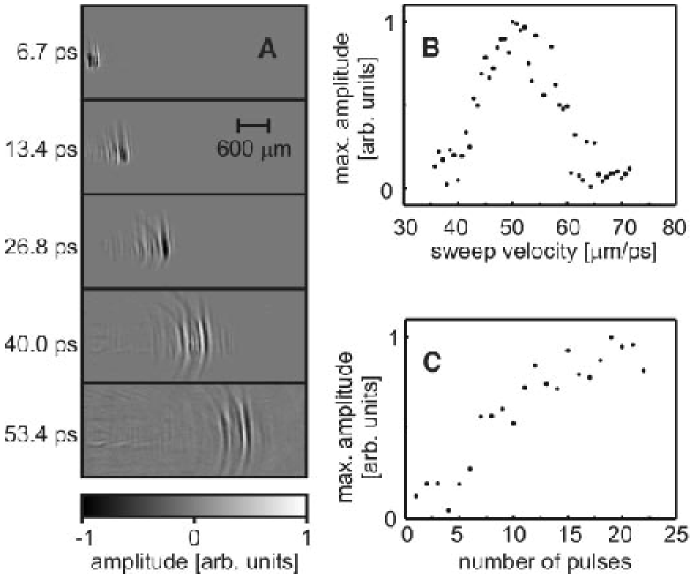


Figure 4.9 Phonon-polariton generation and amplification. **A**) Amplification is realized by a series of “line ” sources moving from left to right at a rate that matches the phonon-polariton group velocity. The last excitation pulse arrives before the fourth frame. Thereafter the amplified response continues moving to the right. Phonon-polariton amplification is shown as a function of **B**) the delay between two regions and **C**) the number of amplifying beams. Figure courtesy of Keith Nelson, MIT.

including the programmable steering of phonon-polaritons into integrated THz waveguide structures for multiplexed, waveguide-based, THz spectroscopy measurements. The generation of amplified and focused high-intensity phonon-polaritons may enable nonlinear THz spectroscopy and control of nonlinear lattice dynamics, anharmonic crystals near structural phase transitions, or liquid-state intermolecular dynamics.

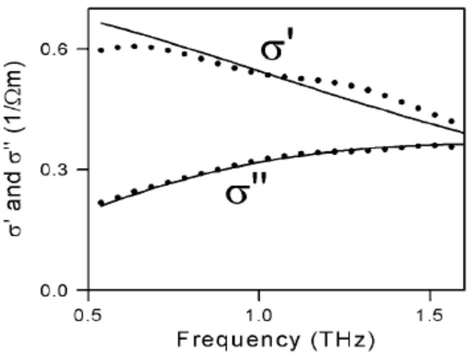


Figure 4.10 Frequency dependence of the real and the imaginary parts of the pump-induced complex conductivity (dots) of sapphire at room temperature. The solid curves represent a fit to the Drude model. After Jie Shan et al. PRL 90, 247401 (2003).

4.1.4.2 THz Dynamics of Photo-Excited Carriers in Insulators

It is possible to examine electron transport in photoexcited single-crystal sapphire using THz time-domain spectroscopy (Figure 4.10). The complex conductivity displays a Drude-type frequency dependence thus enabling direct evaluation of relevant scattering rates and densities. Carrier scattering is dominated by interactions with acoustical and optical phonons at low and high temperatures, respectively, and follows Matthiessen's law over the measured temperature range of 40 – 350 K. The results, including low-temperature mobilities > 10,000 cm^2/Vs , are compatible with a large-polaron description of the conduction electrons. Drude behavior of photoexcited carries has also been observed in n-hexane. These works demonstrate a unique capability of THz TDS to achieve high density of mobile carriers in insulators and also to probe the relaxation processes of photo-generated carriers at ps time scale.

4.2 Opportunities

Pair breaking effects in novel superconductors. It is imperative to carry out systematic investigations of the destruction of superfluid density in a variety of novel superconductors as a function of photon energy. Terahertz experiments are capable of delivering information that is not accessible from other experiments. In unconventional superconductors this would be enormously valuable because there are not clear predictions. This is a form of excitation spectroscopy

Charge and spin dynamics in magnetic semiconductors. Collective quantum-mechanical effects in semiconductors define a vast variety of electronics/optoelectronics device concepts and therefore play a preeminent role in modern technology. Entirely novel functionalities of semiconducting devices may be afforded through a proactive use of magnetic degrees of freedom introduced, for example, by doping of semiconductors with magnetic ions or alternatively through spin injection. The recent discovery of ferromagnetic semiconductors compatible with traditional III-V epitaxy has generated a surge of interest in the possibility of extending the successes of metal-based spintronics into semiconducting materials. Terahertz studies of magnetic semiconductors are capable of addressing the key issues including the nature of electronic and magnetic state produced by Mn-doping, the role that defects play in the electronic transport and magnetism, spin diffusion length in magnetic semiconductors and heterostructures, the role of reduced dimensionality in the formation of the ferromagnetic state.

Probing single quantum dots and nanotubes.

Electron correlations can be very important in nanoscale systems such as quantum dots and carbon nanotubes. However, these samples are not usually monodisperse in size, so observing resonances requires probing single particles. Measuring the response of single particles is limited by the sensitivity of THz spectroscopy. Greatly increased sensitivity or near field techniques would make these measurements possible.

Spin resonance experiments. Recent developments in generating high power electromagnetic pulses in the THz regime bring up the possibility of performing electron pulsed spin resonance in a novel way. The principal characteristics of instruments based on this concept are the use of non-resonant, quasi-optical construction, the real-time (phase sensitive) detection methods, and the ability to excite electron spins over a broad range of frequencies. The key to these measurements is the availability of high-field pulses: typical electric fields in the 10^6 V/cm, corresponding to magnetic fields of 0.3T. The rest of the instrumentation is essentially a standard time resolved THz spectrometer, supplemented with the magnetic field at the sample.

Current pulsed ESR instruments use excitation field H_1 of a few Gauss at most. With this excitation spins can be rotated by a significant angle only if a long train of pulses is applied; the frequency of the pulses should coincide with the Larmor frequency. Naturally, the length of the pulse train limits the work to spin systems with long relaxation times, typically longer than 20ns. In higher excitation field a shorter pulse will achieve a significant spin rotation. The most straightforward application of recent developments in THz sources is using far infrared free electron lasers as an excitation source. The improvement in H_1 is not incremental: for the Santa Barbara FEL, H_1 is on the order of 100 Gauss, and the length of the pulse train can be reduced by a factor of 30 – 100. In the extreme limit of a single pulse with $H_1 >> H_0$ a 90° rotation the pulse length is: , where we assumed $g = 2$, the time is in picoseconds, and the field is in Tesla. Accordingly, with a high-field THz pulse the required pulse length is 20 ps, opening up for research a vast array of spin systems. One can reach the other limit, $H_1 > H_0$, if the field strength of the THz pulse pushed even higher. In $H_0 = 1$T and $H_1 = 10$T a full $\pi/2$ excitation happens in 0.8 ps.

Two limiting cases can be envisioned in terms of the static magnetic field H_0,. For $H_0 > H_1$ a single pulse can not fully excite the spins. Although when the H_1 field is on, the spins precess around the resultant of the H_0 and H_1 vectors, coherent partial excitation is still possible. For $H_1 << H_0$ the excited magnetization is proportional to H_1/H_0 and the required pulse length is (note the H_0 here). This mode of operation is entirely feasible with THz pulses; one can detect free induction decay signals in $H_0 = 3$T with excitation pulses of 3 ps. (A similar “single” pulse excitation with traditional sources would mean $H_0 = 30$G, and spin relaxation would make it impossible to detect anything on most spin systems.)

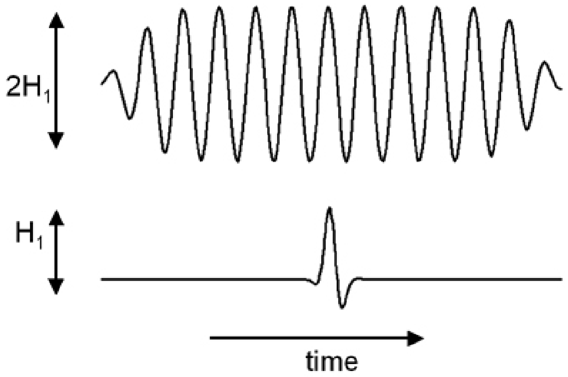


Figure 4.11 Magnetic field as a function of time for narrow-band (upper panel) and broad-band (lower panel) spin excitation. [courtesy of L. Mihaly]

Temporal probe of quasiparticle formation. Understanding the nature of quasiparticles in

CEMs is of fundamental importance. New experimental approaches such as optical-pump THz-probe spectroscopy provide the means for novel investigations of quasiparticles that can directly address such questions by, for example, observing the onset of many-body correlations (e.g. the dressing of an electron by a coherent field of plasmons or phonons). For example – what is the formation time of a polaron or how are phonon excitations triggered and how do they evolve into the correlated phonon cloud of the polaron? Time-resolved THz techniques will enable directly addressing such important questions. Furthermore, such questions map directly onto very recent theoretical advances investigating polarons in the quantum dynamical limit.

Photo-induced phase transitions. While the examples discussed in section 4.1.3 show the potential for utilizing time resolved THz to investigate CEM – it is only the tip of the iceberg. An exciting possibility is photoinducing phase transitions. For example, time-resolved studies have provided insight into the nature of the metal insulator transition in VO_2. In addition to probing optically induced structural phase transitions is the more subtle idea of probing hidden multi-stabilities in CEM that derive from the complex interplay between the charge, orbital, spin, and lattice degrees of freedom. This will provide insight into the ground state properties of CEM and, in addition, offers the potential of creating novel properties in a material that would not otherwise be observed at any temperature.

All-THz time-resolved and nonlinear experiments

Fundamental interactions between quasiparticles, phonons, spin-excitations and other constituents of correlated materials occur on ultrafast time scales. Understanding the microscopic nature of such processes and quantifying the dominant contributions is crucial and holds promise for unraveling basic operating principles behind the unusual material properties. In superconductors, for instance, the coupling of excited quasiparticle states as they “recombine” to form Cooper pairs represents a fundamental interaction. In thermal equilibrium, the rate of recombination is perfectly balanced with the rate of Cooper pair breakup into quasiparticles. However, excitation with a short laser pulse perturbs this balance. Recent experiments in cuprates revealed that subsequent relaxation at low temperatures follows a bimolecular kinetics which yields a measure of the pairwise quasiparticle interaction. In conventional s-wave superconductors these kinetics are masked by a “phonon bottleneck” - its observation in cuprates is surprising and opens the door to basic investigations of quasiparticle interactions.

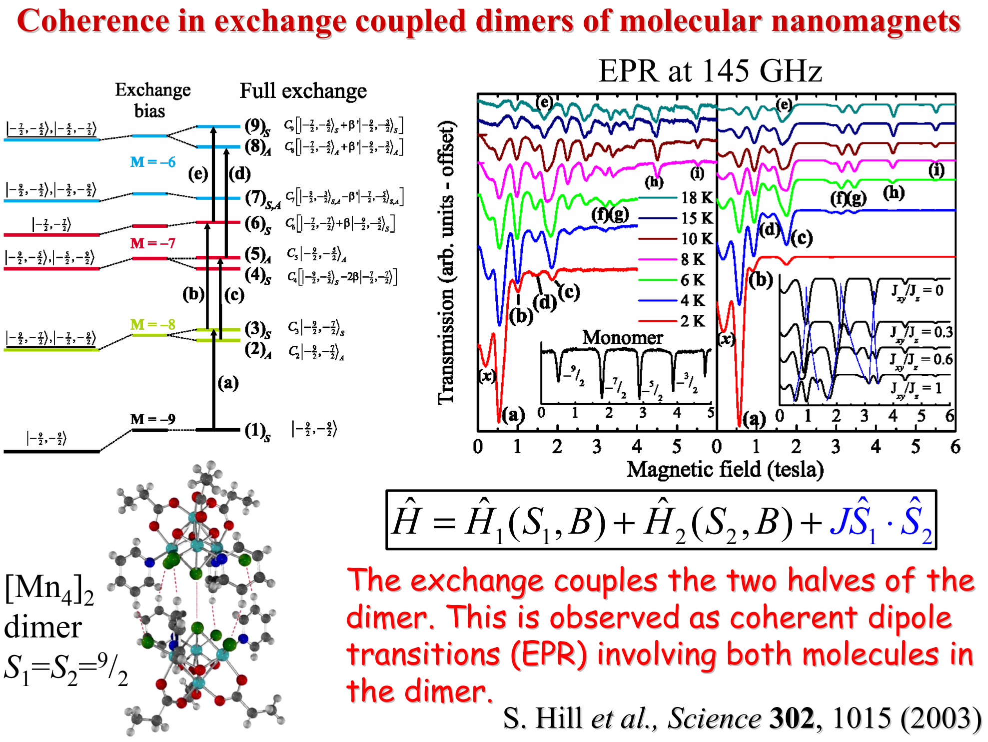
The non-equilibrium dynamics after optical excitation is best monitored by studying the transient THz conductivity that couples directly to quasiparticles and Cooper pairs. First time-resolved studies using such probes have been recently reported for YBCO and Bi-2212 superconductors. However, until now excitation at optical frequencies was employed around ~1.5 eV which is far above the intrinsic excitations and allows no control over the initially excited state. Important insight could be gained if the initial pump energy were tunable in the THz range from ideally ~ 0.5 – 50 THz. Fully tailored to the natural energy scale of these materials, such experiments could selectively generate specific low-energy excitations - such as nodal quasiparticles, phonons or excitations above the mid-infrared conductivity gap - and detect their picosecond relaxation dynamics. Such *all*-THz schemes necessitate a source of intense THz pulses (energies of ≈10 nJ or above) synchronized to a sensitive broad-band THz probe.

Moreover, coherent nonlinear techniques such as optical photon echo experiments form an important part of the ultrafast science arsenal. Extending them towards increasingly lower photon energies can prove fertile to understanding for instance the broadening mechanisms of absorption bands which are linked to interactions that induce the decay of coherent THz polarizations. High intensity THz pulses can also be used to excite superconductors into states far from thermal equilibrium while avoiding excessive heating. Beyond cuprates, applying *all*-THz techniques to other correlated materials such as colossal magnetoresistance manganites, magnetic semiconductors, or nanostructures holds the key to investigating the interactions of their specific low-energy excitations.

Rabi Flopping and Coherent Spin Manipulation in Nanomagnets

There have been recent spectroscopic investigations of single-molecule nanomagnets. In these systems, the crystal field splits the spin states of the molecule. The typical zero-field splittings range from just above 100 GHz to several hundred GHz. Thus, spectroscopy up to 700 GHz in field is necessary. From their work on the dimer (see Figure 4.12), Hill et al. have shown that one can couple molecules via exchange interactions. In principle, it may be possible in future to switch this exchange optically, thus providing fast switching of the exchange interactions within the dimer. Through EPR experiments, they observed coherence associated with the two halves of the dimer, but they need to do time resolved experiments. At present, T_2 is not known precisely, but it is estimated to be in excess of 1 ns. 1 Watt would be necessary for Rabi flopping experiments on this and other related systems.

THz studies of correlated electron issues are intellectually connected to other high priority directions in condensed matter physics and beyond. In fact, there is no simple way to separate work in CEM from research in semiconductors, molecular electronics, quantum manipulation,



Coherence in exchange coupled dimers of molecular nanomagnets

$$\hat{H} = \hat{H}_1(S_1,B) + \hat{H}_2(S_2,B) + J\hat{S}_1 \cdot \hat{S}_2$$

The exchange couples the two halves of the dimer. This is observed as coherent dipole transitions (EPR) involving both molecules in the dimer.

S. Hill *et al., Science* **302**, 1015 (2003)

Figure 4.12 A variety of information regarding molecular magnets. From S. Hill et al., Science **302**, 1015 (2003).

charge transport in nanostructures, spintronics, meta-materials, spin and charge self-organization, magnetism at nano-scales, biological systems such as light harvesting complexes and other areas. Principles that have emerged from investigations in CEM provide basis for the understanding and rational for the design of artificial nano-structures. Approximately, 20 research groups in US pursue THz studies of CEM. Since thousands of investigators work on correlated electron materials and related systems, lowering the barrier for entry into THz investigations has the potential to result in tremendous growth.

Controlled THz-Induced Alteration of Materials

Strong THz fields can drive phonons far into their anharmonic regime, and ultimately lead to structural or chemical changes in materials in a controlled manner along well-defined pathways. These changes may be carried out globally or locally, in ordered, partially ordered, or disordered materials. Other possibilities include driven domain switching in ferroelectrics. Strong fields, as mentioned above, can lead to nonperturbative effects in the electronic structure. For example, associated with the strong-field THz dressing of the bandgap of a semiconductor may be a THz-driven insulator-metal transition. The onset of dielectric breakdown at THz frequencies remains largely unexplored. Terahertz techniques will permit the investigation of the crossover from perturbative to nonperturbative nonlinear phenomena.

4.3 What is needed

A diversity of THz methods is applied to investigate physics of correlated electron systems. These include both laser-based systems, interferometer-based systems, backward wave oscillators, among others. Several groups actively pursue work on THz spectroscopy using synchrotron light sources. The wide spectrum of scientific opportunities and techniques call for a diverse array of experimental setups rather than a single dedicated source. Given the wide variety of THz experiments and materials of interest in CEM studies, the applicability will often depend on optimized combinations of characteristics rather than a single parameter. The THz User's Network described in Chapter 12 is an ideal vehicle for linking experimenters (who do not have their own THz capability) with the most appropriate light source.

Sample environment

In order to capitalize on the unique potential of THz methods in the studies of complex phase diagrams of CEM it is important to develop instrumentation suitable for spectroscopy over a broad temperature range (300 mK – 500 K), with static magnetic field up to 20 T. Development of THz instruments capable of measurements in pulsed magnetic field is essential for the understanding of novel field-induced phases.

Laser based pump-probe THz spectroscopy

Electro-optic generation and detection has also proven useful for generating coherent radiation in the 10 – 30 THz range with near-transform limited pulse widths as short as 70 fs. However, the ease-of-use of such radiation is difficult primarily because of the requirement of facile manipulation of ~10 fs optical pulses that are used for generation, and the phase matching requirement for electro-optic detection at these frequencies (currently (110) ZnTe crystals that are 10 microns thick and gated with 10 fs optical pulses are required for efficient electric-field detection in the 10 – 30 THz range). This makes it difficult to utilize such a source for linear spectroscopy (in comparison to, e.g., a FTIR) – though with improvements in the ease-of-use this could become a desirable tool since, as for the 0.1 – 4 THz range, the electric field is measured allowing for the direct and absolute determination of the complex dielectric function over the bandwidth of the THz pulse. The primary advantage of these mid-THz pulses are for probing the dynamics of photoexcited samples and for investigating nonlinear effects that arise from the electric-field strength of the pulses as discussed below.

For oscillator based THz-TDS, generation of low-power ultra-broad-band pulses in GaSe or ZnTe crystals with a spectrum spanning up to 50 THz has been demonstrated. Use of such sources – which extend continuously into the mid-infrared spectral range – for spectroscopic application is desirable especially in correlated electron materials with broad-band response functions.

Other considerations

Progress in nonlinear and time-resolved experiments can be made using a highly intense, short pulsed tunable THz pump source combined with sensitive synchronized broad-band probes. This source should deliver tunable picosecond pulses with photon energies ideally between 0.3 – 50 THz and energies of ~100 nJ. A minimal thermal load is crucial, average powers should remain well below 100 mW. Control over excitation energies is desirable and can be achieved with spectrally narrow pulses of bandwidths ranging from typically $\Delta\omega/\omega \sim 1 - 10\%$. In addition, improvements in the minimum induced change in the field strength ($\Delta E/E$) that can be detected is an important goal. It has been demonstrated that $\Delta E/E \sim 10^{-4}$ is sufficient to gently probe quasiparticle dynamics in superconductors, for example, but improving $\Delta E/E$ to $\sim 10^{-6}$ would enable entirely new experiment in investigating CEM. This is especially true for materials with low transition temperatures where the primary constraint in optical pump – THz probe (OPTP) experiments is heating due to the excitation pulse. Quite simply, a higher fractional sensitivity permits gentler perturbation with an excitation pulse enabling experiments that do not drive the system above the transition temperature. Optimally, the ability to detect $\Delta E/E \sim 10^{-6}$ over the range from 0.1 – 30 THz would be a powerful enabling capability in CEM research.

Another important avenue involves coupling these THz sources and detectors to other CEM tools such as high magnetic fields. Sample environments with static or pulsed magnetic fields are important for a number of new experiments, including setups for THz-ESR experiments. Variable temperatures (300 mK – 1000 K) are an important ingredient for almost all of the experiments. In addition, the magnetic component of a THz pulse can provide high-field pulses of tuned field (0.1 T – 10 T) and length (10 ps – 0.1 ps), leading to a wide array of thus far unimagined capabilities.

Chapter 5: Physics Applications of THz Radiation

5.0 Executive summary

Opportunities: THz capabilities are important in quantum coherence and control experiments. The THz spectral region is also ideal for investigations in fundamental optical physics, from localization effects to the nonlinear optics of single-cycle pulses. Improvements in spectroscopic capabilities, both in high-resolution cw measurements and in time-domain studies, have also dramatically expanded the impact of THz spectroscopy on astrophysics and atmospheric science, fields that have long exploited the far-infrared for critical spectroscopic signatures. A further section below identifies how advances in THz techniques have also impacted our ability to probe matter under extreme conditions, notably in flames and plasmas.

Within the THz spectrum are rotational excitations in molecules, Rydberg transitions in all Coulomb bound systems, and excitons in solids. Although there has been dramatic progress in our ability to control radiation in the optical part of the electromagnetic spectrum, the THz spectrum offers the highest degree of control and characterization of the electromagnetic field on a subwavelength, sub-period scale, capabilities that have, in turn, been continually enhanced by advances in ultrafast optics.

There will be many new opportunities as the strength and bandwidth of THz pulses increases. For example, above 1 MV/cm, THz pulses can not merely probe, but also pump ion states in gas phase and in solution. Fundamental problems such as the structure of the solvent surrounding a THz-active molecules in solution should become accessible. In addition, we may gain new methods for identifying complex organic molecules in the environment through THz excitation. Expanded access to sources of such radiation are therefore a high priority.

Status: Pulse-shaping is becoming more advanced, using nonlinear generators such as periodically poled lithium niobate, as well as rapidly programmable systems such as mosaic mirrors to modulate the photocurrent in photoconducting THz transmitters. Commercialization of these devices in the near future will expand the research possibilities dramatically. Interactions of strong THz radiation with weakly bound systems such as Rydberg atoms are already quite advanced, with high-field and shaped THz pulses used to demonstrate quantum classical correspondence, quantum algorithms, quantum localization, and quantum chaos. High-field THz is also advancing, both in table-top and machine based sources. The most dramatic example is the recent demonstration of sub-100 fs THz pulses produced by ultra-relativistic (30 GeV) electron beams at SLAC.

Potential size of community, technology and infrastructure needs: Terahertz interactions are a key part of the ultrafast physics research community. In Physical Review A alone, there are several papers each month on THz or half-cycle pulse interactions. Much of the infrastructure is centered on laboratory-scale devices such as amplified ultrafast lasers, FIR interferometers, and bolometers, but there are some needs for larger facilities as well. The IR-FELs, such as the one at Santa Barbara, offer high quality THz radiation for nonlinear and non-equilibrium spectroscopic applications; and the third- and fourth-generation x-ray light sources are also good sources of high brightness THz. These include the Stanford SLAC accelerator, where compressed relativistic electrons have been used recently as sources of sub-100 fs THz radiation, the Jefferson National Lab, Brookhaven National Lab, and the Advanced Light Source at Berkeley, which plans to offer a dedicated FIR facility: the Coherent InfraRed Center, or CIRCE. With many applications in optical, chemical and biological physics, it seems likely that these new sources will be well-utilized.

5.1 Fundamental studies in optical physics

The THz spectral range is characterized by several unique features. It is the highest frequency band where the field can be measured coherently without an interferometer. It has become easy to generate single-cycle pulses, which have unusual optical properties. There are many materials which have well characterized optical properties that can be used in advantageous ways. Here we give a few examples of areas of optical physics for which the THz techniques can have a big impact.

Wave propagation in random media

One long-standing goal in optical physics is the study of Anderson localization in a random medium using photons. This effect has so far only been observed at microwave frequencies, in a waveguide geometry where the number of propagating modes is limited. There have been many attempts to observe such effects using visible or near-infrared radiation in a bulk (three-dimensional) medium, but these results have been controversial because it is difficult to prove that the observed effects are not merely due to residual absorption in the dielectric. At THz frequencies, one can employ materials with more highly characterized optical properties. For example, one can achieve a higher dielectric contrast (e.g., germanium has $n \sim 4$) and at the same time virtually zero absorption (high resistivity material). Localization should therefore be easily observed at THz frequencies in a three-dimensional random medium. These studies will be invaluable for the emerging field of random lasers, where multiply scattered photons play a fundamental role.

Even in a low-contrast regime, where the localization threshold is not achieved, there are many unique opportunities for THz science. Terahertz offers an ideal laboratory for the study of multiply scattered waves, and wave diffusion. Such problems appear in many areas of physics, from medical optics to geophysics. A THz system can serve as a table-top test bed for the study of scattering phenomena. It permits the measurement of complex wave fronts with

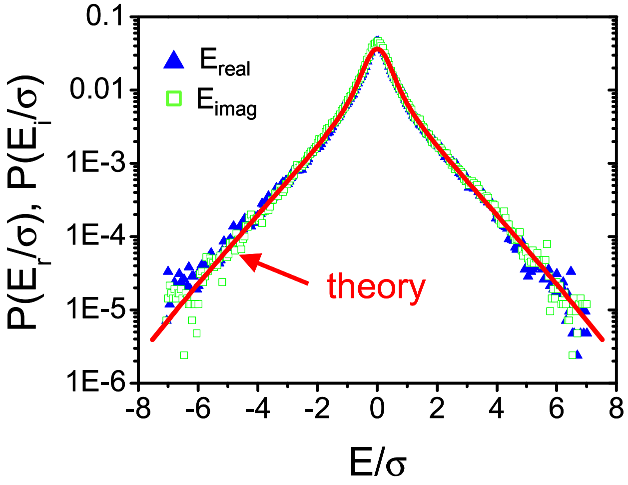


Figure 5.1 Histogram of the amplitudes of the real and imaginary parts of a random broad-band field, normalized to the standard deviation of the field. The departure from Gaussian statistics expected for narrow-band radiation is evident in the wings of the probability histogram. A theoretical model incorporating the frequency-dependent variance, $\sigma \sim I(\omega)^{1/2}$, is shown in red. Figure courtesy of Dan Mittleman, Rice University.

subwavelength spatial resolution, sub-cycle temporal resolution, and coherent detection. Field statistics and field correlations can be studied directly. Already, the distinct nature of these statistics, when broad-band radiation is employed, has been demonstrated (see figure 1). This should lead to a number of important advances, such as new imaging techniques for locating objects immersed in random media.

Metamaterials

Electromagnetic meta-materials are a subset of photonic crystals, artificially structured materials whose electromagnetic properties are distinct from the constituent materials. They offer a range of response that is either difficult or impossible to obtain in naturally occurring materials and composites. A key example of such a meta-material was introduced in 2000 by Professor D. R. Smith and collaborators at UCSD, who demonstrated that a medium composed of conducting elements could exhibit a negative permittivity and a negative permeability, simultaneously, at microwave frequencies. This unconventional electromagnetic behavior termed “left-handed” by V. G. Veselago is yet to be shown to exist in any natural material and so far has been detected only in composite artificial structures. Notably, materials having negative permeability generally require true magnetic materials (i.e., those materials whose magnetic response is related to unpaired spins) that are often heavy, exhibit large losses, and whose response tails off rapidly at higher frequencies. Thus, a medium that exhibits negative permeability using only conducting elements is, itself, an important example of a meta-material. So far, these materials have only been studied at microwave frequencies. There is a clear desire to extend these ideas to other spectral ranges, and the THz regime is the logical next step.

Near-field Electromagnetic Effects

Another area of interest involves near-field optics. Once again, the coherent detection of the radiation provides a great deal of additional information about the nature of the electromagnetic near field, and therefore about the ultimate limits of near-field measurements. In addition, so far there has been no emphasis on the nature of the magnetic component of the field, in the near field regime. Of course, in empty space there is a fixed relationship between E and B, but in the near field the relation is much more complex. Magneto-optic sampling should permit a direct measurement of the transient magnetic field, in principle with the same spatial resolution as has been demonstrated with the electric field component. This will be of particular interest when the sample under study is a magnetically active material. There is a fundamental and unresolved question on the relationship between the magnetic near field and the far field. Terahertz techniques can be used to measure both of these limits, as well as the transition region in between. This should provide a better understanding of all near-field measurements.

Single-cycle Pulses: Linear and Nonlinear Optical Properties

The ability to generate single-cycle pulses also suggests that the THz range is an ideal tool for the study of the propagation of ultra-broadband radiation. In the case of extremely broad-band pulses, the slowly varying envelope approximation no longer applies. Such considerations have become very important in the field of femtosecond optics, where pulses directly generated by mode-locked lasers have already reached durations of 1.5 cycles. In these situations, the propagation, manipulation, and focusing of these pulses are quite distinct from the narrow-band case, and many questions are unresolved. It makes a great deal of sense to use THz techniques to study these questions, since one can readily obtain amplitude and phase information with high resolution. One recent example is the demonstration of single-mode propagation in a waveguide, even when the spectrum of the radiation overlaps many waveguide modes. This has been a somewhat surprising result, which holds promise for the guiding of any short pulses, even those at much shorter wavelengths. In addition, there have been numerous new imaging techniques developed specifically for coherently detected single-cycle pulses. For example, it is possible to perform reflection imaging with sub-coherence length resolution, using careful manipulation of the phase of the light. In tomographic imaging, one of the important parameters is the size of the first Fresnel zone of the propagating wave front, . Short THz pulses have recently been used to demonstrate a rigorous definition of this quantity, in a situation where the wavelength is not unique. These examples demonstrate the complexity of the propagation problem, in the case where the fractional bandwidth approaches unity.

Finally, with the use of intense THz radiation, one could access nonlinear optics. This is of course extremely interesting from the point of view of materials research, as has been discussed elsewhere in this document. Here, we concentrate specifically on the new nonlinear optical physics that could result from the use of extremely broad-band THz pulses. In principle, one could study all of the usual 2nd and 3rd order nonlinear optical effects with radiation that does not have a slowly varying envelope. This is a new regime for nonlinear optics, which is also becoming relevant at optical frequencies, due to the aforementioned advances in short pulse generation. In fact, the long wavelength offers even more opportunities. As pointed out earlier, it is far easier to access a regime of extreme nonlinearity, where the ponderomotive energy approaches or even exceeds the photon energy. In addition, one has the usual advantages of extremely high temporal resolution.

Localizing Energy through Nonlinearity and Discreteness

Highly tunable THz fields of > 10^5 V/cm can drive a new state of matter, namely *intrinsic localized modes*. These occur in electronic and magnetic solids, in microengineered structures including Josephson junctions, in optical waveguide arrays and in laser induced photonic crystals. In solid state physics the phenomenon of localization usually arises from symmetry breaking extrinsic disorder induced by localized impurities, defects, surfaces or artificial boundary conditions in nanostructures. In perfect lattices, electrons and phonons are assumed to exist in extended plane wave states. The surprising discovery that localized modes can be created in such systems jolted well established perceptions. The availability of new sources will enable such studies to search for such modes in many new materials including Bose-Einstein condensates and biopolymers. Hopes are high that these exotic excitations will be useful in all-optical logic and switching devices and in targeted breaking of chemical bonds for example [Campbell 2004].

Spectral characteristics of trains of THz pulses generated by modelocked lasers

In the context of optical physics, one of the most exciting developments of the last few years has been the demonstration of a high-resolution optical frequency comb, based on the highly stable repetition rate of the femtosecond oscillator. This same high stability is mapped onto the spectrum of the THz pulse as well, since it is generated in precise synchronization with the mode-locked laser. As a result, one could imagine using the frequency comb as a local oscillator source at any frequency within the THz bandwidth. Such ideas have already been exploited by De Lucia and colleagues, to perform high resolution spectroscopy using a pulsed source. However, the impact of this tool as a tunable, frequency-agile local oscillator cannot be understated. There are very few LO sources available in the THz band, and this has greatly hampered the accurate characterization of THz sources such as for example quantum cascade lasers.

5.2 Quantum coherence and control

The classical rotation period for a nitrogen molecule with one $\hbar$ of angular momentum is about a picosecond. Likewise, the time of a molecular collision at room temperature (typical velocities of mm/μs) is 0.1 to 1 ps. So THz interactions are ubiquitous in the natural quantum world, and this motivates THz research in this area.

Atomic Systems

To explore quantum dynamics in this time regime, we turn to quantum systems that can be prepared, isolated, and controlled easily, and this motivates the central importance of Rydberg atoms for this research. Rydberg atoms in the $n = 20$ to $n = 60$ range span the spectrum of sensitive response to THz fields. These are model systems for studying many aspects of few body quantum mechanics, including quantum chaos, quantum-classical correspondence, and quantum systems in the presence of strong external fields.

Some examples where THz radiation has already been shown to be quite useful include methods to produce and probe arbitrary wave packets in Rydberg systems consisting of one or two electrons. The most important form of THz radiation for this work has been the half-cycle pulses produced in the near and intermediate field of a photoexcited biased semiconducting switch. Due to the very large spectral bandwidth, these pulses can interact with hundreds of Rydberg levels simultaneously. In regimes where the levels of interest have $n > 30$ or so, the pulses can be modeled as delta function impulses, and this simplifies the analysis of the system considerably.

The critical enabling characteristics of the THz radiation used in these studies is the half-cycle pulse character, coupled to peak fields high enough to transfer momentum to the electron wave packets comparable to the momentum content in the quantum system. So, for example, for $n = 25$, the momentum of the electron distribution has an rms value (derived simply from classical correspondence) of , or approximately .04 atomic units. The characteristic time scale is about 3 ps. To achieve an impulse that can overcome this, the THz radiation must consist of a pulse of much less than 1 ps duration (0.4 ps is commonly used), and a peak field of about 5kV/cm [Bucksbaum, 2000].

Pulses of this character have now been used to analyze the momentum content of the wavepacket, both for analysis of the quantum trajectories, dispersion, and revivals of the wave packet, and also for measurements of the momentum distribution function of eigenstates. One very interesting thing that has already come out of this research is the notion of impulsive ionization of wave packets, which is a new mechanism akin to scattering ionization, and quite distinct from either dc field ionization or photoionization.

This has been utilized to study the scattering problem in a new way. Control of the THz field in impulsive ionization is directly analogous to control of the impact parameter in scattering, which is not generally possible using beam-beam scattering techniques. [Jones 1996].

Rydberg atoms have the rich structure and stability to make them interesting candidates for quantum information processing [Jaksch 2000]. Terahertz radiation can be used to manipulate the quantum states for quantum information processing in a number of ways. An early demonstration of this has been utilizing THz pulses to search a quantum data base [Ahn, 2001]. In this case, the pulse causes intermode interference in the data base that essentially converts phase information (i.e. the presence of a state whose quantum phase is reversed with respect to its neighbors) to amplitude information (i.e. the presence of a highly populated state on among many low population neighbors.) The physics that gives rise to this phase to amplitude conversion is common to many bound systems consisting of "ladders" of neighboring states.

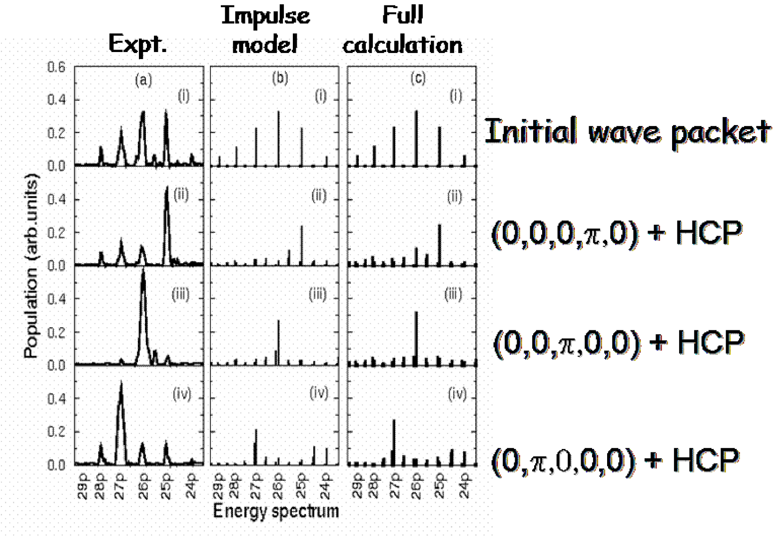


Figure 5.2 Readout of coherently prepared Rydberg in a coherently prepared state using a half-cycle THz pulse. Figure courtesy of Phil Bucksbaum, University of Michigan.

More complex THz interactions are also possible, and successful applications will depend on THz field shaping. A number of promising technologies for this exist now, but the field is still in its infancy. Many of these are based on optical pulse-shaping technologies, which can deliver full amplitude and phase control from DC to more than 10 THz.

Given full control over the shape of the field, then you can define a learning loop to discover optimal paths to quantum "targets." Learning algorithms have been demonstrated for simple quantum systems using optical pulse-shaping, and optimal control fields have been designed for special THz problems such as the quantum search algorithm; but much more sophisticated control methods will be needed for larger molecules or systems with many quantum degrees of freedom.

5.3 Atmospheric science, laboratory astrophysics, and molecular collisions

There are several important scientific questions that couple significant external communities (e. g. astrophysics, atmospheric science, plasmas diagnostics, physical chemistry) with studies that are optimally carried out in the THz spectral region via studies of collisions. Surprisingly, technical limitations have largely precluded experimental studies.

3(a) Atmospheric Science

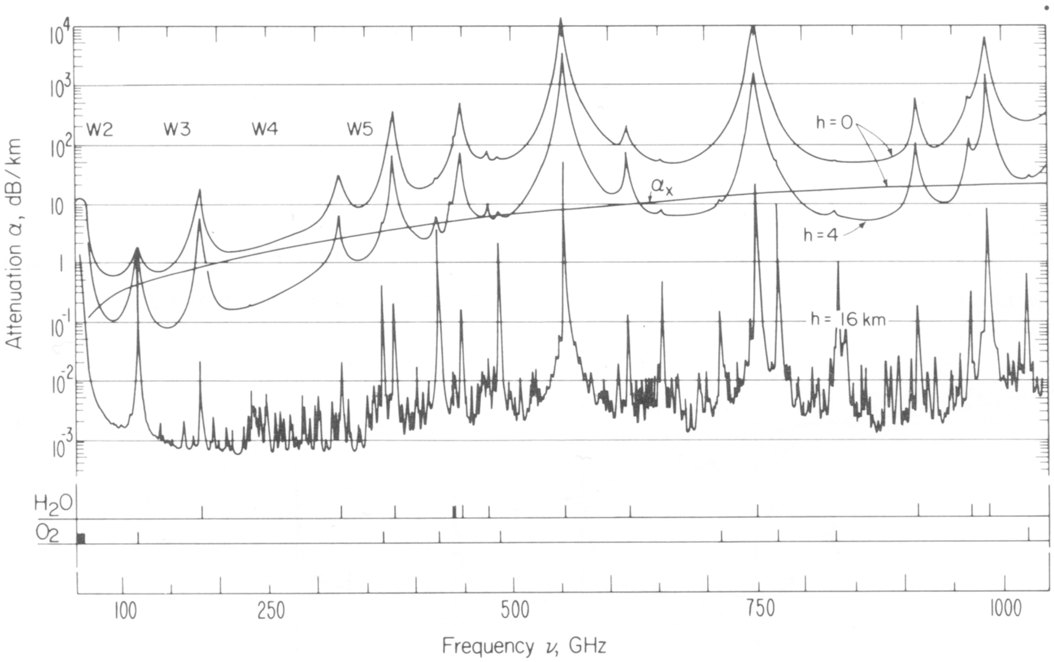


Figure 5.3 courtesy of Frank De Lucia, Ohio State University.

Collisions: The time scale of gas phase collisions is of the order 10^{-12} seconds. This makes the THz a 'natural' regime for such studies. Because collisions are highly nonperturbative and the intermolecular interactions between molecules depend upon largely unknown intermolecular potentials, this is a difficult problem. However, modern quantum chemistry is beginning to impact this problem, especially at low temperatures.

As illustrations, we will focus on three applications: collisions that impact atmospheric propagation, collisions in the interstellar medium, and studies of gas phase dynamics.

The atmospheric continuum: It has been known for many years that atmospheric propagation of THz radiation is a subject of significance for this spectral region because of its strong absorption. Interestingly, while it has been possible to accurately calculate the intensities and the locations of the peaks for many years, the calculations of transmission in the 'windows' is typically in error by > 100%. The solution to this has been to add an empirical 'continuum', the physical origin of which can be controversial. So: a) this is a problem of importance to many communities, b) laboratory experiments have been difficult and in many ways technology limited, and c) while this can be a very interesting scientific question, the experimental data base is so small that it does not constrain these theories very much. In the figure, the smooth curve, labeled α_x, is an empirical correction added to 'well founded' theory to make experiment and theory match. This line is based on only a few data points, most of which are at 300 K.

Quantum collisions at interstellar temperatures: At low temperatures (a few degrees Kelvin) molecular collisions take on an entirely new character. Near ambient (300 K), because many collisional channels are available, collision cross sections tend to vary slowly and are very 'classical'. This can be seen at the right of the two panels of the graph below. However, at low temperature, where the collisional energy is comparable to the rotational energy level spacing,

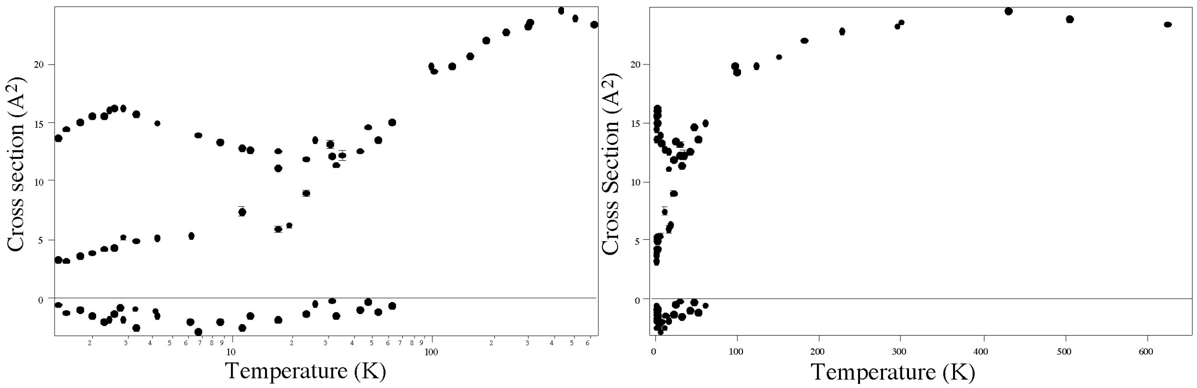


Figure 5.4 Inelastic cross sections (upper points, 1 - 30 K) pressure broadening (1 - 600 K), and pressure shift for the H_2S - He system on linear and logarithmic temperature scales for the 1_{10}-1_{01} transition. Figure courtesy of Frank De Lucia, Ohio State University.

the collision become very quantum mechanical and resonances in their cross sections occur. These can be seen in the second figure below. In addition to being an interesting new scientific regime, these cross sections are vital to the building of the energy transfer models that are needed to convert astronomical observations into astrophysical data.

Gas phase dynamics: The chemists at the workshop mentioned as a 'future desire' the ability to study gas phase dynamics. Terahertz is an excellent way to do this for a wide variety of systems. Because the time scale of these processes is pressure dependent, ~cw (~1 microsecond) techniques are an ideal approach for this.

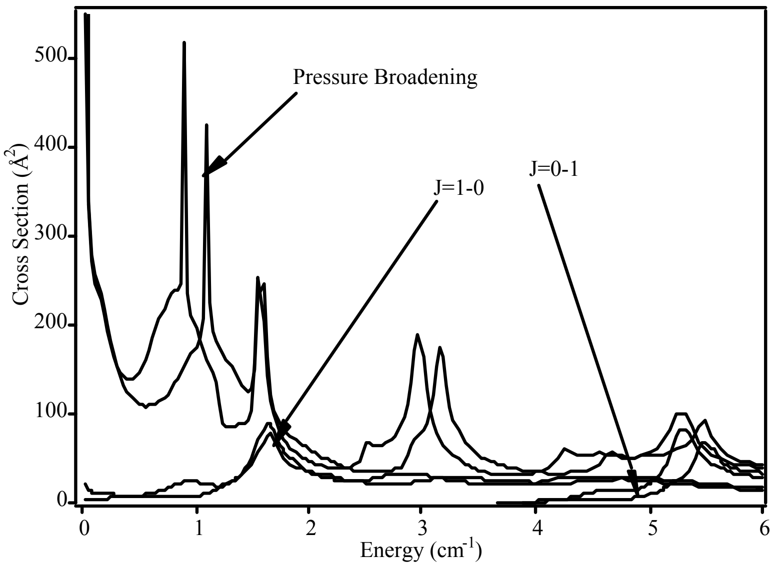


Figure 5.5 Calculated pressure broadening and inelastic cross sections (solid lines) for the CO-He system, along with calculation in which the rotational energy level spacing of CO has been decreased by 5% (dashed lines). The resonances near 1.6 cm^{-1} are the result of a shape resonance and are not shifted by the modification of the rotational energy level structure of CO. On the other hand, the rest of the large resonances are Feshbach resonances, and their energies are shifted according to the rotational levels involved. Figure courtesy of Frank De Lucia, Ohio State University.

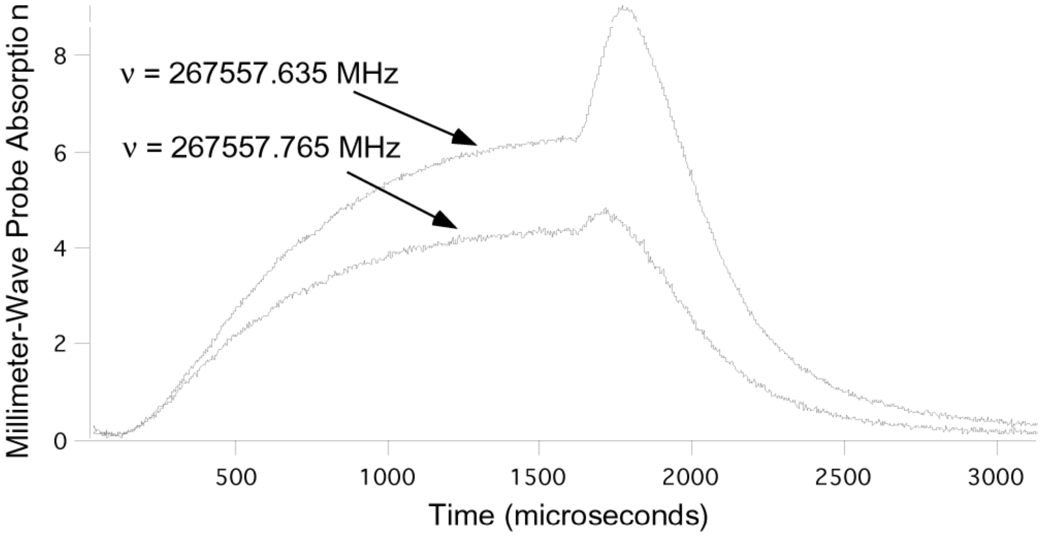


Figure 5.6 The formation and recombination of HCO^+ in an electron beam initiated low temperature plasma at low temperatures. The high resolution make possible time resolved measurements at the center and on the side of the Doppler profile so that the evolution of both the number density and kinetic temperature of the ions can be measured. Figure courtesy of Frank De Lucia, Ohio State University

3(b) High-resolution astronomical science

There are also a number of important high resolution cw applications in physical chemistry, atmospheric science, and laboratory astrophysics. Here we will briefly highlight a few specific scientific problems in the latter.

There are several major ground- and space-based submillimeter/THz telescopes which have recently been completed or will go on line in the near future. Surprisingly, many of these systems will investigate spectral regions for which very incomplete spectral information is available and laboratory experiments are needed in order to understand the origin / identify the carriers of the spectral features. Additionally, large molecules such as (large) poly-aromatic hydrocarbons are probably abundant in interstellar space and believed to be responsible for many of the features. Little spectral information is available for these molecules and molecular clusters in general, especially under conditions relevant for interstellar space: low density, cold and partly ionized. It was shown that a combination of high-intensity, narrow-band THz radiation and ns dye lasers can be a valuable tool for obtaining the fingerprint of such molecules clusters.

3(c) General THz technology requirements for remote spectroscopic investigations

At higher frequencies, currently available sources are far from optimum and not widely available, especially in the academic community. Appropriate goals for this work are:

- Narrow linewidth, continuous-wave sources that are electronically tunable over significant frequency bands (>10%) throughout the 300 GHz – 3 THz range.

- Sensitive and convenient detectors with similar bandwidth and over the same frequency range (0.3-3 THz).
- These should be compact, all-solid-state systems suitable for use in a laboratory or on spacecraft.

One of the most promising types of source that meets these requirements is obtained when difference-frequency mixing two narrow linewidth diode lasers in a photomixer. These sources provide tunable, coherent, narrow-band THz radiation.

Current Status and Limitations: Milliwatt level cw sources with high spectral purity and frequency tunability of about 10 – 20% are presently available to frequencies up to about 600 GHz. These include both tube devices, such as backward wave oscillators (BWOs), and more recently all-solid-state sources based on low frequency oscillators and frequency multiplication. Direct detectors are also available throughout the frequency band. However, room temperature detectors, which are preferred, are available to only about 600 GHz and their sensitivity should be significantly improved.

Future Technology Requirements: The present technology should be extended to at least 3 THz in order to allow the full range of measurements that are desired. Although power levels of 10 – 100 μW are sufficient for many envisioned experiments, more power (up to several mW) would make measurements easier and will facilitate a greater range of measurements. Similarly, an electronically tuned bandwidth of 10 – 20% is sufficient for most measurements, but any improvement in bandwidth will make the systems more versatile. Sensitive, room temperature detectors above 600 GHz are presently not available. Diode detectors with high responsivity and low 1/f noise in the frequency range from 600 GHz – 3 THz are required. Sources that can be rapidly switched (< 0.1μs rise time) should be developed for gas phase dynamics.

5.4 Probing matter under extreme conditions

Recent advances in coherent THz techniques, in both the time and frequency-domain, have now provided bright sources that, unlike conventional approaches to far-infrared spectroscopy, can be used even in the presence of strong thermal backgrounds. This offers new possibilities to exploit the capabilities associated with important spectral range in new contexts, such as studies of flames and combustion processes where the molecular specificity of this spectral range is of enormous value. The method can also be applied, as highlighted elsewhere in this document, to transient systems, we illustrate these capabilities and the promise they hold for studies of ultrafast plasma excitations.

Plasmas created by high-intensity femtosecond lasers are of great interest because of their potential as sources of short x-ray pulses, coherent harmonic radiation, energetic electron and ion beams, plasma-based accelerators, multi-megaGauss magnetic fields. From a fundamental point of view, one can thus explore the interaction of matter with electromagnetic fields that are many orders-of-magnitude stronger than the fields that bind electrons in atoms. In addition, recent work has demonstrated that these plasmas can also serve as a source of intense THz emission. Investigations of this phenomenon in the THz spectral range thus provide both an opportunity to examine plasma dynamics under extreme conditions and, with improved understanding, the possibility of developing novel sources of THz radiation, with possible THz pulse energies approaching a fraction of a mJ within an ultrashort pulse.

The physics knowledge base of such systems is in its infancy, and opportunity exists for developing a complete understanding of the physics of such interactions. The understanding of the emission of THz-modulated far infra-red (FIR) electromagnetic fields from plasmas via laser-matter interactions continues to be an elusive phenomenon. Originally predicted over thirty years ago, only recently have these types of sources been demonstrated in both, gases and solids, over a large range of varying plasma conditions ($n_e \sim 10^{16}$ to 10^{19} cm^{-3}) and laser intensities (10^{13} to 10^{19} W/cm^2). This makes a unifying description of the physical mechanisms difficult. Yet, the most accepted theory for THz production from these plasmas is that the dipole restoring force between the ponderomotively accelerated electrons and "fixed" ions is what produces a current surge as the electrons are damped at the modulating plasma frequency. This description, however, is subject to question, especially at the low intensity regime (~10^{13} W/cm^2) where ponderomotive forces arguably do not dominate. Now the opportunity exists for extending inquiry into the THz portion of the electromagnetic spectrum where intense, coherent, pulsed electromagnetic radiation can be generated by phenomena that include laser-produced electron plasma waves (EPWs), laser wakefield acceleration, and transition radiation at the solid-vacuum boundary.

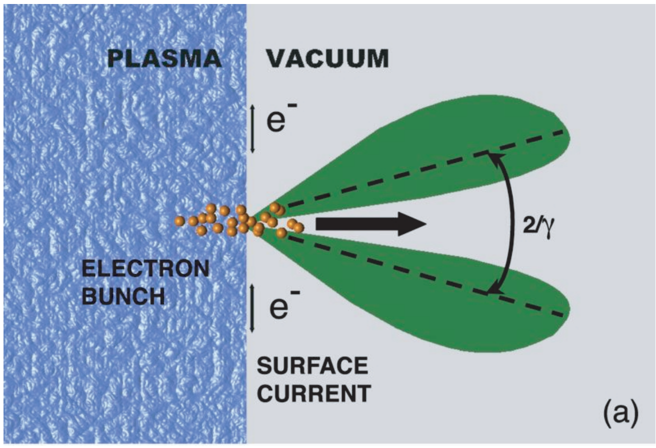


Figure 5.7 Transition radiation production by an ultrafast laser driven electron at the plasma-vacuum boundary. Surface currents are excited at the boundary and generate radiation which peaks at a half angle on the order of $1/\gamma$, where γ is the relativistic factor of the electrons. Figure courtesy of Wim P. Leemans, LBNL

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Chapter 6: Opportunities in Chemistry and Biology for THz Science

6.0 Executive summary

Opportunities: The opportunities for THz science in chemistry and biology are wide ranging. Some will extend work that has been going on for years, many others have not yet been realized but show great promise, and the rest fall somewhere in between.

Gas phase spectra and dynamics, particularly of molecular clusters can be measured. This will lead to significant information on non-covalent interactions in isolated systems. Similarly, low-frequency spectra of liquids characterize their collective (non-covalent) modes, but in a dramatically different environment than the gas phase. The study of liquids will entail both linear and nonlinear spectroscopy, and will reveal both intrinsic properties as well as processes such as solvation.

Membranes, Langmuir-Blodgett (LB) films, and self-assembled monolayers (SAMs) are amenable to THz studies. Membranes are important due to their obvious connection with biological systems, while LB films and SAMs allow a greater amount of control over the constituent species and chemical functionality. For example, the intermolecular interaction among molecules of interest in the field of molecular electronics can be investigated. This will complement infrared studies of the intramolecular properties of these films. More complicated heterostructures can be built and probed as well.

The phonon modes of inorganic and organic crystals fall in the THz region of the spectrum. Equilibrium measurements as well as dynamical processes can be probed. In addition to bulk phonon modes, surface phonons and adsorbate-surface interactions can be measured. In the case of molecular crystals, the low frequency phonon modes are due to non-covalent interactions.

Nonlinear studies in general represent an important and uncharted direction for THz science. Furthermore, the ability to manipulate, rather than just observe, the system under study (coherent control) lends itself to THz spectroscopy since the THz waveform can be controlled by optical pulse-shaping of the driving pulse using standard techniques. Having direct access to the amplitude and phase in a THz pulse is a definite advantage over other methods.

There are opportunities for dramatically advancing electron spin resonance (ESR) spectroscopy. It will be possible to study molecules that have a large zero field splitting which are inaccessible with current techniques; it will be possible to carry out time-resolved studies with sub-picosecond resolution at high-fields; and the magnetic field associated with very intense THz pulses can be used in spin-flip experiments.

THz emission spectroscopy captures the THz pulse emitted when a collection of molecules in a crystal, in a film or monolayer, or oriented in solution, are photoexcited, thereby changing the net polarization of the sample. This differs from the other types of opportunities in that a THz generator is not needed, only a detector, since the sample itself generates a THz pulse. It will be possible to characterize charge transfer and conductivity properties of molecules of interest in molecular electronics. Another important example is the characterization of the primary step in charge transfer in photosynthetic reaction centers. This technique is complementary to other methods for studying charge transfer because the change in polarization of the sample generates the signal, and no other secondary process need be monitored.

There are opportunities with regard to protein structure and dynamics. It is currently possible to distinguish many amino acids based on their THz spectrum, particularly in the crystalline form. Future work will characterize secondary and tertiary structure. There have been many theoretical predictions of the vibrational frequencies of alpha helices, for example, but still no convincing experimental evidence. Linear and nonlinear THz spectroscopy will allow dynamics to be studied on a variety of time scales ranging from milliseconds to sub-picosecond.

Several recent papers have demonstrated the ability to detect single and double stranded DNA sequences. Refinement of this work will lead to label-free sensors based on complementary DNA hybridization. The THz spectra of the individual DNA base pairs have been obtained. There is an extraordinary range of opportunities with regard to DNA dynamics and conductivity.

Ultimately, much larger systems than proteins and DNA strands will be accessible, particularly with the coupling of THz science with near-field probes. One envisions label-free measurement of protein-protein interactions as cellular activity is occurring in live cells.

Status: The great majority of THz studies to date in the chemical and biological communities have been continuous-wave (cw). That is, the linear spectrum of the sample is obtained. It is noted that mm-wave and far-IR spectroscopy, which cover the THz region of the spectrum but are not based on ultrafast lasers or accelerator sources, have been used for many years in the field of gas phase molecular spectroscopy. These "mature" sources are cw and typically narrow linewidth, and are discussed in Chapter 8.

Very recently, non-equilibrium studies have been carried out in which a sample, such as a dye/solvent system or a collection of quantum dots, is photoexcited with an optical pulse and the time-evolution of the low-frequency optical properties are probed with a THz pulse at a variety of delay times after photoexcitation. These studies are inherently non-cw, and must be carried out with systems based on ultrafast lasers or accelerator-based sources. It is expected that many, though obviously not all, future studies in chemistry and biology will involve non-equilibrium systems, and will therefore require pulsed THz sources.

Potential size of community, technology and infrastructure needs: In the realm of chemistry and biology, there are roughly 20 – 30 groups (about 100 people) worldwide who are current practitioners. Given greater access to sources, either at centers of some sort, and by making available "kits" to set it up in one's own lab, the potential community is enormous – on the order of several hundred scientists in the U. S. alone.

Resources should be made available to as many interested people as possible. This would include getting single investigators started, a modest number of small-scale facilities with specialties such as high-field, imaging, near-field, narrow-band, and time-resolved THz science, and access to accelerator-based facilities. A THz user's network will be required to coordinate these efforts.

6.1 Introduction

If one can speak of a grand challenge in chemistry and biology, it is the control of chemical reactions in a highly specific manner. The control of specificity is of course something that biology does exceedingly well, and at present far exceeds the ability of chemists to accomplish. In order to control highly specific chemical reactions, it necessary that the energy put into a molecular system not move into all degrees of freedom ergodically, but instead to be channeled into a specific mode or small subset of modes. A related aspect to this question of mode control is the issue of solvent interactions on a picosecond (ps) time scale, in particular the role of water. We have only begun to explore this exciting area of basic science. It is worth remembering that progress in this broad area will be accomplished through progress in the wide-ranging topics identified above as opportunities.

In order to distinguish this section from others involving materials and medicine, we take the view that chemistry and biology are unified in the sense that they deal with molecular interactions whose microscopic behavior needs to be understood. We can further distinguish between chemistry and biology by proposing that chemistry deals with relatively small molecules (i.e., smaller than a protein) and polymers that are repetitive in composition. These small or homogenous molecular systems can be in the gas phase, liquid phase (either neat or solvated), self-assembled structures, or in a molecular crystal. Biology for our purposes can be considered to exist in the realm of large, complex macromolecules on up through viruses, cells and tissue. Biology can be further characterized as consisting of evolved molecules which have specific functions, often by means of biological networks which involve the highly specific interactions of molecular complexes in a sequential manner.

An example of the interplay of chemical and biological viewpoints to protein motion is described schematically in Figure 6.1 (provided by Klaas Wynne, University of Strathclyde). Vibrational modes localized on particular functional groups in amino acids, such as the carboxyl or amide bands, occur in the infrared region of the spectrum, and are on time scales of femtoseconds to tens of femtoseconds. This might be considered "chemical" information. At the other extreme is tertiary structural dynamics, which occur on time scales of nanoseconds to milliseconds. This might be considered more "biological," given that protein folding and docking have broader consequences – whether or not a protein is active or a cellular signal is received, for example. In between these extremes, there are low-frequency intra and intermolecular modes in and among residues, which occur on time scales of tens of

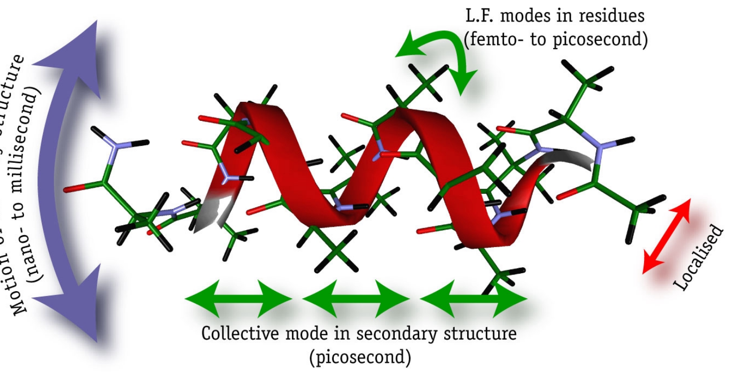


Figure 6.1. Schematic representation of a variety of dynamical time scales in a general biological molecule. Figure courtesy of Klaas Wynne, University of Strathclyde.

femtoseconds to picoseconds, as well as modes in the secondary structure which occurs on a picosecond to tens of picosecond time scale. These intermediate modes fall within the THz region of the spectrum, and bridge the two limiting cases.

The THz region of the spectrum represents the final repository of vibrational energy in a molecular system: a photon of frequency 10^{12} Hz has an energy of 0.004 eV or about 1/6 of the average thermal energy of a degree of freedom at 300 K. Resonances in the THz region are thermally populated, and represent the low frequency collective modes of a molecule involving many atoms which are the gateway to thermalization of higher frequency modes. They are typically highly anharmonic in nature, difficult to compute using molecular dynamic simulations, and lie in a spectral region in which there are few bright conventional sources. Thus, the THz region represents a real frontier in terms of basic chemical science. Further, the fact that biological systems consist of time-varying complexes of macromolecules which interact in highly specific ways presents additional challenges: the local structure of a biological complex, such as a single cell, is exceedingly interesting and changes with time depending on the state of the cell cycle, for example. There are very few ways to measure changes in the chemical state of these networks that do not involve extremely labor-intensive extrinsic labeling technologies. Since the THz region is sensitive to changes in the collective modes of a system it also represents an area where we could imagine that changes in complex molecular interactions could be tracked and imaged within a single cell.

The development of THz sources, including table-top laser-based sources as well as synchrotrons and FELs, with extremely high THz field amplitudes and with considerable control over the field temporal profile are underway. These sources will enable control over motions of molecules and ions, including control over collective structure and dynamics, as well as electronic responses. These features enable THz *excitation* of material responses whose temporal evolution may be probed with additional THz pulses or with light at other wavelengths. Thus nonlinear spectroscopy will be conducted using THz excitation pulses. Initial efforts are under way, with most of the early results coming from the physics community studying systems such as Rydberg states of isolated atoms and intersubband transitions in semiconductor quantum wells or quantum dots.

6.2 Chemistry

Gas Phase

We start with the simplest scenario: individual molecules and molecular clusters in a vacuum. The THz spectral region probes the rotational dynamics of light molecules, the low frequency bending and torsional modes of heavier molecules, and collective intermolecular modes of molecular clusters. The dynamics of these relatively simple systems pose fundamental questions for our understanding of molecules at the basic quantum mechanical level.

Gas phase THz time-domain spectroscopy has been used to study rotational transitions of molecules in flames, has probed the far wings of rotational transitions, and even to probe inversion tunneling in methyl halides. There has been a tremendous amount of gas phase work over the years in the fields of sub-millimeter and far-infrared spectroscopy. This has allowed elucidation of structural and dynamical properties of molecules and clusters.

Cluster Spectroscopy

The next step in complexity is molecular solvation: it is possible using gas phase injection techniques to prepare molecules with progressively larger numbers of solvent "layers" around the molecule or to probe the disappearance of solvent shells. Since molecular clusters have low-frequency, very anharmonic modes, it is necessary to measure their spectra over a broad range of frequencies in order to adequately determine their underlying potential energy surface. This represents a building up or down of the solvation of a molecule from the closest layer of solvent molecules which are highly perturbed by the presence of the solvated molecule ultimately to the bulk phase. We would expect to see changes in the collective THz modes of both the solvated molecule and the solvent molecule with increasing solvation. Additionally, there is a close connection with biology, since the chromophores in a protein are perturbed by the surrounding amino acids which profoundly influence the reaction path that an excited chromophore follows.

Liquids

We now consider the dynamics of molecules in the condensed phase. The THz region is sensitive to the time course the interaction of a molecule with the surrounding solvent on a sub-ps time scale. Viscosity is a macroscopic concept which breaks down at the molecular level and the ps time scale (the THz frequency range). This frequency region represents that at which local vibrational and rotational motions of a molecule which would be underdamped in vacuum now interact with the surrounding solvent molecules, a critical aspect of the loss of coherence in a vibrationally excited state.

On sufficiently short time scales, photon echo, hole-burning, and other time-resolved spectroscopic probes may be possible, thereby enabling study of the dynamics of structural change within selected (more or less homogeneous) subsets of configurations. The time course of vibrational relaxation and the loss of phase coherence can be studied using nonlinear ps THz techniques such as photon echo which measure both longitudinal (T_1) and transverse (T_2) dynamics. In the liquid state, dynamical interconversion among different local structures occurs on picosecond or (for viscoelastic systems) slower time scales. High THz fields will induce molecular orientational motion, or interionic motion, leading to changes in local structure and a non-equilibrium distribution of geometries. Less demanding in terms of time resolution, the

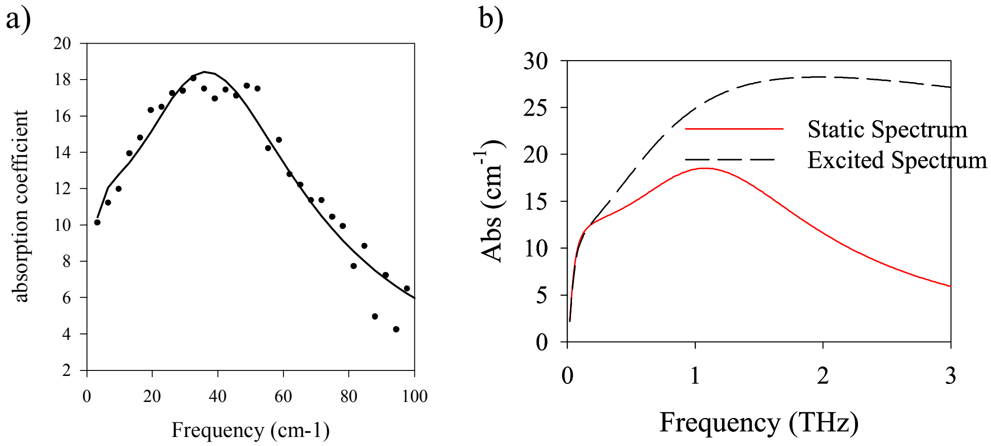


Figure 6.2. Static spectrum of chloroform (part a). Absorption spectrum of collective solvent modes near photoexcited dye molecule (part b). Image courtesy of Charles Schmuttenmaer, Yale University.

dynamics of relaxation back toward equilibrium following a large amplitude deviation from equilibrium also will be observed.

For example, it is possible to monitor the collective solvent response when a chromophore dissolved in solution is photoexcited. Part a) of Figure 6.2 shows the steady-state absorption spectrum of chloroform. There is a slightly underdamped librational mode at 42 cm^{-1}. Upon photoexcitation of 2,11,20,29-tetra-*tert*-2,3-butylnaphthalocyanine (TBNC) dissolved in chloroform, the nearby collective solvent modes are affected, as shown in part b) of Figure 6.2. The underdamped mode becomes highly overdamped for about 1 ps as the surrounding solvent molecules reorient in response to photoexcitation of the TBNC dye molecule.

Self-organized Molecular Structures

Self-assembled monolayers (SAMs), and other self-organized structures such as Langmuir-Blodgett (LB) films, membranes, lipid bilayers, and vesicles, are strongly influenced by intermolecular interactions, and are therefore amenable to THz studies. Membranes are important due to their obvious connection with biological systems, while LB films and SAMs allow a greater amount of control over the constituent species and chemical functionality. For example, the intermolecular interaction among molecules of interest in the field of molecular electronics can be investigated. This will complement infrared studies of the intramolecular properties of these films. More complicated heterostructures can be built and probed as well. The dynamics of these interactions can be probed directly with THz spectroscopy.

THz Emission Spectroscopy

It has been shown that a THz pulse is emitted when a collection of molecules oriented in solution (or in a crystal) are photoexcited, thereby changing the net polarization of the sample. A THz generator is not needed, only a detector, since the sample itself generates a THz pulse. This technique is complementary to other methods for studying charge transfer because the change in polarization of the sample generates the signal, and no other secondary process need be monitored. These studies will be extended to molecular monolayers and SAMs. It will be possible to characterize charge transfer and conductivity properties of molecules of interest in molecular electronics, and even characterization of the primary step in charge transfer in photosynthetic reaction centers.

Partially Disordered Solids

Next, we consider the solid condensed phase, which exists in some form of a lattice (which may be disordered). Many lattice vibrational modes, i.e. phonon modes, lie in the THz frequency range. In the case of disordered molecular solids such as glasses, there is an inherent inhomogeneous broadening of the THz modes; this is particularly strong in the case of biological molecules. Probing with THz fields adds capabilities such as photon echo and related methods that yield line-narrowing in inhomogeneously broadened molecular complexes. In partially disordered systems ranging from mixed ferroelectric crystals to glasses, ions or molecules have hopping and/or tunneling degrees of freedom that give rise to structural changes with varying degrees of collectivity. Simple examples include two-level systems in conventional structural glasses and the flipping of polar nanoregions in mixed ferroelectric dipole glasses. Terahertz fields of large amplitude will induce these motions and the structural rearrangements that arise from them. Measurements of THz hole-burning, photon echo, and higher-order spectroscopic responses in such systems will permit study of the inherent dynamics of localized or collective structural change.

Crystalline Solids

Motions along soft optic phonon coordinates give rise to structural phase transitions and domain switching in many crystals including ferroelectric and other crystalline systems. Terahertz excitation of large-amplitude lattice vibrational coherences can enable direct measurement of lattice anharmonicity in selected modes, with spectroscopy at $\chi^{(3)}$ and higher orders providing information about progressively higher degrees of anharmonicity, representing lattice geometries at progressively larger separations from the equilibrium geometry. In the limit of extremely large-amplitude responses, collective structural change can be monitored in detail and along every step of the transformation. It will also be possible to characterize the coupling of different lattice modes.

At the largest amplitudes, it may be possible to drive collective rearrangements of the lattice structure. Ions may be moved from their initial positions in the lattice, along selected lattice vibrational coordinates, and into positions they occupy in a different phase or domain orientation. In this limit, a perturbative description of the spectroscopy will break down, and it will be more useful to think of the process in terms of THz coherent control over material structure.

THz pulse-induced coherent motion may be monitored with probe light at visible wavelengths through birefringence, interferometric measurements, second harmonic generation, etc. Probing with THz fields adds new capabilities such as photon echo and related methods. In addition, probing THz field-induced structural evolution at x-ray wavelengths should be possible, and is of great interest.

THz Control Over Electron Transfer Chemistry

At sufficiently large amplitudes, THz fields should have a dramatic effect on non resonant electronic responses in a wide range of systems. Here we focus on THz field levels in the 0.1-1 MV/cm level and their effects on photoinduced electron transfer reactions in chemistry and

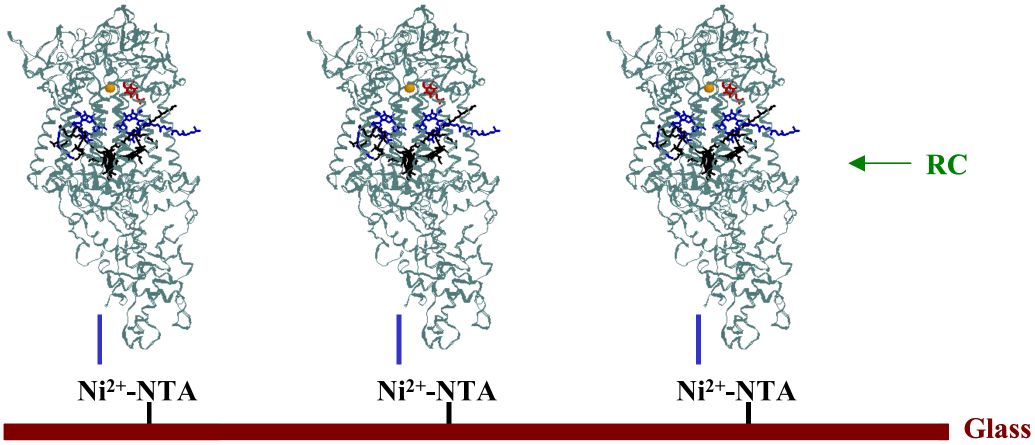


Figure 6.3. Oriented bacterial reaction centers. Image courtesy of K.V. Lakshmi, Yale University.

biology. Fields of this magnitude may influence electron transfer in two ways. First, the transfer rate could be changed drastically, just as it could be by a static field, since the rate increases exponentially with applied potential. This could have important effects on photochemical electron transfer yield, especially in cases where the rate is limited by electronic excited state lifetime. It also could permit directional control over molecular electron transfer in systems with an excited donor and multiple acceptors. Oriented molecular species will be particularly amenable to such control. Second, the THz field amplitude could be comparable to the electrochemical potential difference that drives the electron transfer reaction, i.e., THz effects on energetics as well as dynamics are fully possible. This also could be applied toward direction-selective electron transfer. For example, in oriented photosynthetic reaction centers as shown in Figure 6.3, THz fields with large amplitudes could be used to attempt to drive and control "wrong-way" electron transfer, contrary to the outcome seen in nature.

Magnetic Phenomena

Although emphasis is normally placed upon the electric fields associated with THz radiation, there is of course the accompanying magnetic field. Many molecules represent single molecule magnets (i.e., are paramagnetic), such as the prototypical Mn_{12}-acetate cluster, which is a spin-10 system. Similarly, ESR and time-resolved ESR measurements are of great importance in biology where the spin state of a atom such as iron is closely coupled with its environment and the reactivity of the protein. Also, the zero-field splitting of many species are often in the THz frequency range which makes conventional ESR difficult because of the lack of intense THz light sources. The dynamics of these spin systems are highly sensitive to the local structure of the molecule, and can be studied using THz ESR techniques.

Given very large amplitude THz pulses, the associated magnetic field can be used in spin-flip experiments. For example, for a free electron with $s = 1/2$, a 9 T field is required for a $\pi/2$ pulse if it is 1 ps in duration. This can be achieved with a 1 ps half-cycle pulse of 9 mJ pulse energy, which should be accessible in the near future as high-field THz science progresses.

6.3 Biology

Much of that discussed in the chemistry section can be applied to biology, but with a literal twist. Biological molecules are large, complex and are typically handed. All the naturally occurring chiral amino acids are left-handed and their secondary and tertiary structures are highly chiral in nature. Biological molecules have evolved to perform highly specific functions and bind in a highly specific manner to other molecules. The basic molecular building blocks of biomolecules is now well known: What is far less understood is the specificity and control that biomolecules have as "nanomachines". The dynamics of these nanomachines are important over a huge range of time scales: from the sub-ps time dynamics of the *cis-trans* isomerization of retinol chromophores in vision and the highly specific charge transfer in photosynthesis to the ultra-slow conformational relaxation of the prion proteins from "good" helix structures to plaque forming sheets in the brain. Clearly, the fast (ps) conformational dynamics of proteins are strongly coupled to THz frequencies. Slow processes such as protein unfolding and misfolding are amenable to THz time-domain studies. The conformational flexibility necessary for such dynamics to occur comes from the collective THz frequency modes of the protein. If those modes are frozen out, the ability to change structure is lost; and structural changes are critically

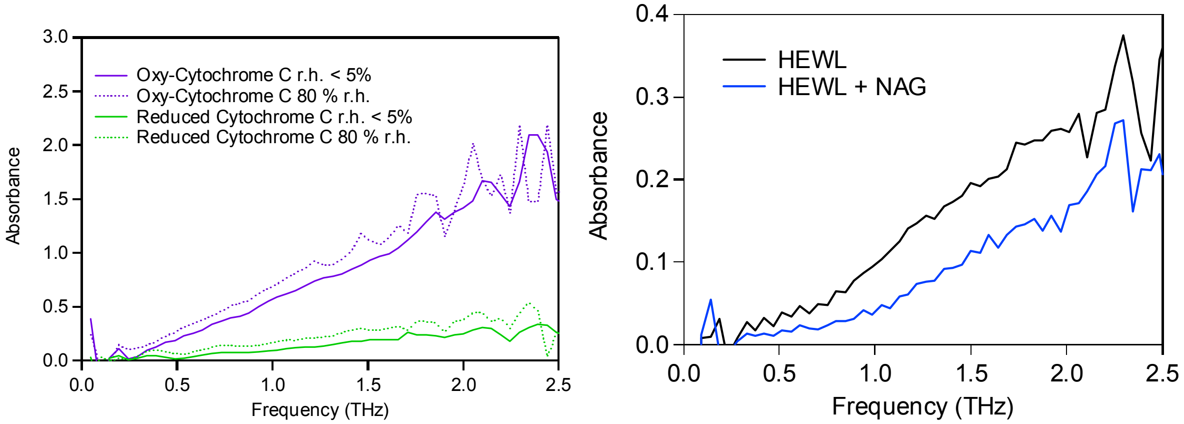


Figure 6.4 Left-hand side compares oxidized (stronger absorbance) and reduced (weaker absorbance) Cytochrome-C. Right-hand side compares hen egg white lysozyme (stronger absorption) and the HEWL/N-acetal glucoseamine complex after binding (weaker absorption). It is clear that the THz spectrum is highly sensitive to the protein conformation. Figures courtesy of Andrea Markelz, University at Buffalo.

important to biological activity. Thus, even the dynamics and progression of protein folding and unfolding will be visible in the THz region.

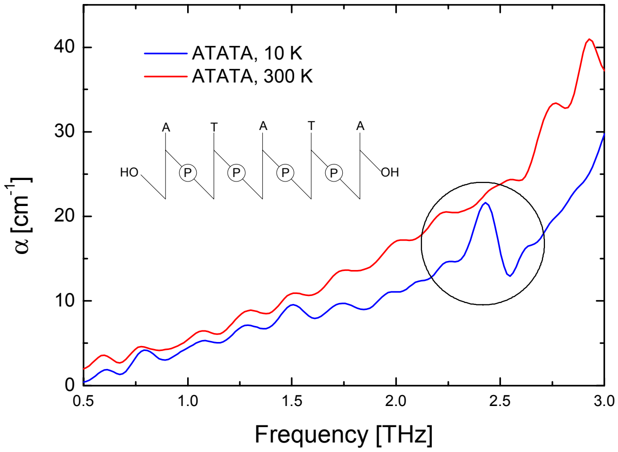


Figure 6.5 Effect of temperature on absorption coefficient of single-stranded DNA pentamer. A mode is present at low temperature, but is washed out due to disorder at room temperature. Figure courtesy of Peter Jepsen, University of Freiburg.

An example of THz measurements of biologically relevant systems is shown in Figures 6.4 and 6.5. The left-hand side Figure 6.4 displays the influence of the oxidation state on the Cytochrome-C spectrum. There is a remarkable difference between the oxidized and reduced forms. The right-hand displays the influence of N-acetyl glucoseamine (NAG) on the hen egg white lysozyme (HEWL) absorption spectrum. It is seen that the absorbance drops significantly when binding occurs. Figure 6.5 displays the absorption coefficient of a single-stranded DNA pentamer at room temperature and at 10 K. A distinct feature is present at 10 K that is absent at room temperature which is due to highly anharmonic vibrations.

Water

A critical aspect of biological molecules is their close coupling with water. Proteins must be in an aqueous environment to function, that is, undergo their conformational switching motions. Bulk water continues to be a difficult substance to understand, particularly in the THz frequency region. It is a highly structured fluid and consists of a flickering set of hydrogen bonds with a deep quantum degeneracy. Protein surfaces interact with this complex and dynamic system, and the induced ordering of hydrogen bonds which in the bulk tunnel rapidly between different degenerate sites gives rise to the hydrophobic effect critical for determining the energy landscape of a protein. It is believed by some that the dynamics of the solvation shells results in broad features centered roughly at 400, 100, and 35 GHz respectively. This assignment is based on comparison to classical MD simulations. Other possibilities are acceptor switching tunneling dynamics and interchange tunneling dynamics of the hydrogen bonds which have been deduced by splittings in high resolution spectra of water dimers. In order to fully understand these features, we need to compare to ab initio molecular dynamics simulations employing larger scale cells (1000 molecules or more) and longer time scales (100 ps) than currently available.

Water in pockets in biological recognition units should have characteristic signatures that are affected by the hydrophobicity of the unit which sets the boundary conditions of the water. Biological function can be linked to the dynamics of water in these pockets. Similarly water in nanopores in porous media and water in micelles should have spectroscopic signatures in the THz which are different from bulk water. Ideally, one would like to know molecular structure and dynamics as a function of distance from the walls of the nanopore. Water in these environments may catalyze chemical reactions or biofunction. In general, water at the air/water, water/solid, and water/membrane interfaces of biology will all differ from bulk liquid water. The water density, pH, orientational order, lateral order, hydrogen-bonding, etc., are all different and vary as a function of distance from the interface. These systems are largely unexplored in the THz regime, and their properties will determine the unique chemistry and biofunction at interfacial water systems. Comparison to ab initio MD simulations is also necessary.

Relevance of THz Science to Biology

Are THz motions functional in biology? As already shown, the answer is yes. Further information will come from two-color experiments that are of a pump-pump nature: energy can be driven into a specific mode at one frequency and tracked versus time, then energy at another mode can be pumped in and changes in the reaction rate observed. There have been preliminary experiments done using visible pump-THz probe techniques, but these were not truly time resolved experiments at the ps time scale and are always open to the question of the difference between local heating effects and true mode-specific coupling effects. These two-color experiments need to be done over a wide range in frequencies. For example, one could envisage performing time-resolved X-ray diffraction experiments in a protein such as myoglobin which is known to have large scale sub-nanosecond dynamics which THz ps synchronous with the X-rays is used to drive specific collective modes of the protein.

Another approach using high power ps THz radiation to enable coherent control of molecular configuration dynamics would be to use a series of THz pulses with the optimal phases and amplitudes to prepare molecular configurations to enhance chemical reaction or biological function. In order to study this, one must not only find ways to characterize the structure but also characterize changes in the reaction rates. In both cases, time-resolved IR in the finger-print vibrational region is essential in understanding changes in structure coherent with the THz excitation and time-resolving the chemical or biological product of reaction. Time-resolved visible absorption and/or fluorescence can also be used as indicators of molecular change and reaction but they are less generally applicable than IR spectroscopy.

Nonlinear Experiments

In addition to probing with other colors, we also envisage two-color mixing spectroscopy experiments. That is, a chromophore could be driven by a ps visible light source while simultaneous THz modes are driven at the ps time scale. If there is nonlinear coupling between the chromophore dynamics and the THz conformational modes they will mix producing side bands in the visible response of the system which could be detected using high resolution spectroscopy. This kind of mixing spectroscopy using a tunable ps THz source could be used to correlate changes in reaction rates with the strength of the THz mode coupling to the chromophore. Such a two color mixing experiment could even be done in the mid-IR, where the "chromophore" simply becomes the amide I band which is sensitive to secondary structure, for example.

Many chromophores of great importance in biology such as the retinol group critical to vision or the heme group exist as molecules relatively weakly coupled to their environment. Terahertz spectroscopy of such isolated molecules is difficult, but by using intense ps THz sources it is possible to climb the collective mode ladder of these systems and ionize them and detect them with great sensitivity. The mode-specific climbing of these collective modes is a form of nonlinear spectroscopy which in combination with quantum chemistry can be used to understand the dynamics of isolated molecules.

Cellular Imaging

Finally, we discuss the issue of imaging in cells. Although this properly belongs in the medicine section, it must be stressed that without an understanding of the basic mechanism of THz contrast, development of this important technology will be hampered. Also, it may well be that THz spectroscopy of molecular complexes in the cell will provide an important window into "label-free" measurements of protein-protein interactions, of vital importance to the exponentially growing field of proteomics, the study of the expressed proteins in a cell and their interactions. The logic is, if in fact protein-protein interactions involve changes in the collective modes of the proteins, as one might expect since the proteins must change their conformations to bind in a specific manner, then differential THz spectroscopy of protein complexes may be sensitive to the binding of proteins to each other. We know very little about this area at present. A key development will be incorporation of an AFM-like tip to selectively probe regions with dimensions of a few tens of nm.

6.4 Terahertz excitation sources: parameters and user needs

For many of the objectives outlined above, THz pulses will be needed that have high-field levels and carefully tailored temporal profiles. Development of methods that achieve excellent control over such fields should be considered a high priority. A concerted effort should be directed toward generation of shaped, large-amplitude THz fields.

Generation of high-fields presently takes several forms. Table-top laser sources are available in individual labs, but at present they demand that the user also be the developer. Other sources are organized around large-scale facilities, and are available to users who are stationed permanently at them or who visit them. We briefly address the issue of high-field THz field generation and accessibility to the broader scientific community, most of which will not be directly involved in THz generation itself.

Table-top sources are of several types. Terahertz generation at semiconductor surfaces produces half-cycle pulses that can reach field levels on the order of 100 kV/cm. Control over the field is possible through temporal shaping of the optical field, although for generation of high-fields, the extent of this control and the limitations that may be imposed by semiconductor recovery times have not been explored fully. Terahertz generation through optical rectification in nonlinear crystals also produces half-cycle to single-cycle pulses. The field strengths reached have not yet been extremely high, but these methods should be scalable through the use of higher optical pulse energies and larger crystals, followed by focusing of the output. In this method, temporal shaping of the excitation light offers possibilities for tailoring of the THz field, without concern for recovery dynamics in the generation crystal. Finally, THz generation through excitation of phonon-polaritons has offered only moderate field levels to date, but have the advantage that extensive control over the field temporal profile is possible through temporal and/or spatial shaping of the optical excitation field. This method will be scalable to larger optical pulse energies and laser crystal sizes, and hence larger shaped THz amplitudes.

A major effort should be launched to generate fields up to roughly 1 MV/cm with fine control over waveform profiles. Field levels of this magnitude have been achieved at Brookhaven and the Jefferson Lab, but they are not yet available in a "user friendly" mode. Laser-based table-top sources will soon reach this objective as well. However, for the near future at least, it is apparent that substantial effort and investment will be required. Single-PI efforts could be sufficient for the development, but the complexity and effort involved will deter those who might wish to be "users" but who are not intimately involved in THz generation. Therefore a network of small-scale user facilities should be supported. At least one such facility should specialize in high-field THz field generation and use for spectroscopy and coherent control. Other important capabilities around which facilities could be centered include narrow-band THz generation and spectroscopy; near-field THz spectroscopy; and THz imaging.

Many of the experiments discussed here, particularly in biology, are sensitive to heat: Terahertz sources which deliver ps pulses of high energy at high repetition rates heat the sample and can destroy it. Thus, there is a need to control the rate at which energy is delivered to the sample, down to the point where a single ps pulses of THz radiation of 10 μJ can be delivered at a rate of 1 Hz or less.

Bandwidth of the pulses is also important. The extent of inhomogeneity of the THz absorption spectrum of biomolecules for example is not well known, so there is a need for the ability to vary the line width of the THz radiation to 1% or better of the central frequency. Some applications, such as THz electromagnetic resonance studies, can utilize cw sources. Continuous-wave THz ESR sources, however, must be of high power, on the order of 1 – 10 W to saturate the system in the ESR experiments.

Quasi-cw FEL sources provide narrow-band fields that reach the 1 – 10 kV/cm level. In some cases, including intersubband transitions in semiconductors, this is sufficient to reach the nonlinear response regime and to permit time-resolved nonlinear spectroscopy and coherent control. Synchrotron sources can provide high-fields, on the order of 1 MV/cm or higher. It is clear that these sources will play an increasingly important role in nonlinear THz spectroscopy and coherent control. Coupling with x-ray probes is also an intriguing possibility.

Coherent synchrotron radiation (CSR) is a recent development. CSR is emitted from accelerated electrons when the electron bunch length is shorter than the wavelengths being emitted. Developments in a variety of accelerators have recently demonstrated sub-ps electron bunches which therefore emit CSR in the THz regime, and the proposed CIRCE facility would focus on this exclusively. This CSR emission is half cycle, high-power (μJ per pulse have been demonstrated with higher powers available in straight-forward extensions), and can be generated with very high repetition rates (100 MHz to 1 GHz) which lead to very high average powers. There are only a few large scale FELs in the world which can generate the high peak power (several megawatts) and ps pulse durations necessary for many of the experiments suggested here. FELs offer a critical advantage: The pulse width and hence the spectral linewidth of the THz pulse can be continuously varied. In inhomogeneously broadened biological systems, large amounts of energy can be put into specific modes for hole burning experiments on the ps time scale.

We believe that both the table-top systems and the FEL sources must develop two-color capabilities over very wide range of photon energies to fully probe the dynamics of complex molecular systems and the coupling of high- and low-frequency modes. While a great deal can be done with table-top systems, many of the most powerful experiments will require some sort of central facility with wide expertise in many different types of powerful ps photon sources, from the X-ray to the FIR. For example, 4th generation light sources such as the upcoming LCLS at SLAC, which will have 1 GW peak power tunable x-rays, 100 fs duration, and could also have concurrent THz generation. The FEL at Jefferson Lab is an example of a high intensity, broadly tunable FEL that simultaneously generates THz pulses.

There also exist efforts to make table-top accelerators which can be efficient generators of THz radiation. Table-top, accelerator-based THz sources are evolving rapidly. They are expected to have powers exceeding the laser-based sources and are tunable in pulse structure, wavelength, and bandwidth. Development of these kinds of sources should be explored.

A final comment: without the encouragement of advances in the theoretical community to calculate the response of molecules and materials to THz radiation, many of the experimental results that flow out of this work will lack a thorough understanding. This is a difficult area for theory: Terahertz modes are collective in nature and involved the cooperative motions of many hundreds of atoms over time scales that from sub-picosecond to nanoseconds (or longer). Currently, molecular dynamics studies are limited in the number of molecules that can be included, and the maximum length of time their dynamics can be followed. New tools and increased computing power necessary for such studies should be developed.

Chapter 7: Medical Opportunities Using THz Radiation

7.0 Executive summary

Opportunities: Major opportunities abound for THz science in medicine. Improving spatial resolution and data acquisition rates are one example. A better understanding of THz pulse propagation through complex media is another. Development of endoscopic ability to provide access to internal epithelial surfaces is a third. After THz methods have been proven and appear likely to be adopted, safety guidelines must be established.

Status: One of the best examples of the current state of the art of THz science in medical applications is shown in Figure 7.1. As described in the caption, and later in the chapter, it is possible to determine the extent and depth of a basal cell carcinoma tumor non-invasively through reflectance mode THz imaging. In addition to imaging features and sub-surface on skin, as shown here, other groups have demonstrated that it is possible to detect dental caries that are not evident in x-ray images, although not *in vivo*. Furthermore, 3-dimensional imaging of bone, again, not *in vivo*, has recently been demonstrated at the level of proof-of-principle.

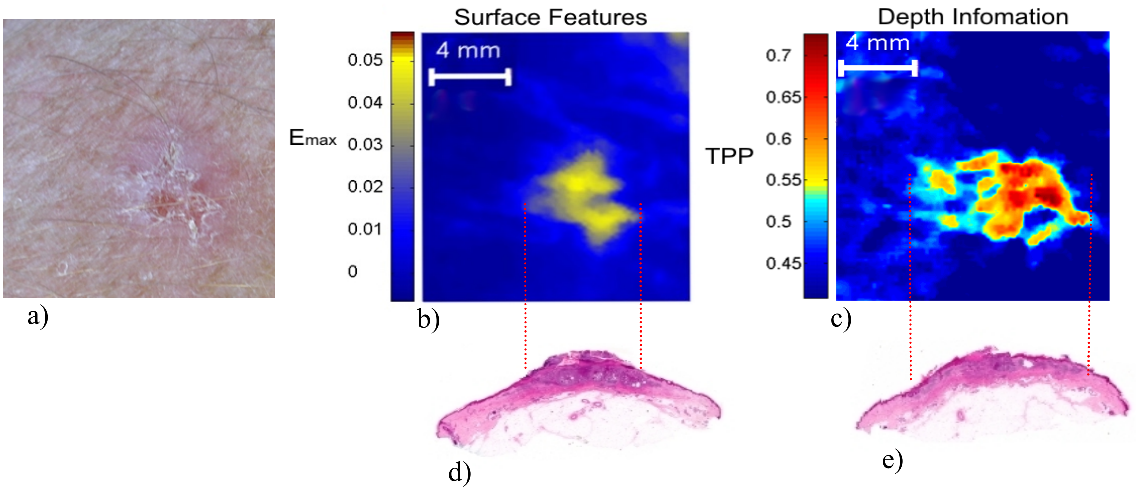


Figure 7.1. An *in vivo* measurement of a nodular BCC with an invasive component. Image a) is a clinical photograph of lesion, b) is a THz image formed by plotting the THz value at E_{min} showing surface features, c) is a THz image that indicates the extent of the tumor at depth (~250μm), d) is a representative histology section showing acute inflammatory crust corresponding to THz image b) and e) is a representative histology section showing lateral extent of tumor corresponding to THz image c). Images courtesy of TeraView Ltd, Cambridge, UK.

Potential size of community, technology and infrastructure needs: It is estimated that 10 to 15 medical groups in the U. S. are interested in the medical applications of THz science and technology, and efforts in THz imaging in the U. S. have been published by 7 different groups.

European based efforts are more developed, approximately 15 groups reporting some form of biological THz applications. Interest in the technology is substantial as evident by the full rooms at recent SPIE conferences. Development of resources at the national, regional and local levels will play a pivotal role in advancing the technology. Opportunities for training are significant.

Much of the interest in commercialization of the capabilities of THz science (TeraView, PicoMetrix, Nikon) is undoubtedly the promise of a huge number of users for a device that could be used in a doctor's office or is transportable throughout a hospital. It is really impossible to quantify the size of that market without input from TeraView or PicoMetrix or Nikon, but none of them are willing to provide information.

The medical community would perhaps benefit even more than those in the natural sciences from a THz Users Network because they simply do not have the expertise to develop new systems. They could carry out preliminary studies at one of the facilities described in Chapter 12.

7.1 Introduction

THz radiation in the 100 GHz to 20 THz range holds promise as a new medical imaging modality. Recent reports have demonstrated a variety of imaging systems using pulsed and cw THz sources. Terahertz radiation is strongly absorbed by water, but differences in tissue water, architecture and chemical content can actually contribute to contrast mechanisms. Early studies of teeth, skin, breast and solid organs suggest that THz imaging can reveal features that are not apparent with other imaging modalities. Figure 7.1, provided by TeraView Ltd, demonstrates the potential of the technology as diagnostic tool. Part a) shows a typical basal cell carcinoma of the skin, it is difficult to determine the extent or depth of this locally invasive tumor. Parts b) and c) represent broad-band reflected THz signals obtained with a photoconductive source and detector. Image b) is optimized for surface detail which allows for orientation, while image c) is optimized for a depth of 200 – 300 microns revealing the extent of the tumor not seen in the clinical photo. As shown in parts d) and e), these images are correlated with standard pathology where the tissue appears colored due to staining with Hematoxlyn and eosin to identify pathologic characteristics. This figure illustrates the potential of THz imaging to scan areas of tissue and obtain images at depth.

The use of THz radiation for imaging requires the efforts of a multidisciplinary team with expertise in ultrafast lasers, THz radiation generators and detectors, imaging algorithms, physics, chemistry, and biology. Preliminary studies have identified several critical areas for scientific investigation and engineering development.

7.2 Rationale

THz radiation has the potential to provide high resolution (100 μm) imaging of biologic materials using contrast mechanism that differ from current imaging techniques. While MRI can image at depth and provide some chemical information it is not well suited to imaging surfaces or thin epithelial layers. Practical considerations including cost, magnet size and long scanning times limit applications. Ultrasound, though widely available, is based on reflection and absorption of sound waves from tissue, and has limited resolution (500 μm) and contrast mechanisms for imaging. Air, internal gas and bone prevent imaging of some tissues and specific patterns of disease are not easily defined. Ultrasound does provide an effective tool for many applications and it may be possible to combine THz and ultrasound imaging techniques.

Optical coherence tomography (OCT) uses femtosecond near-infrared laser pulses to image at or near the surface. High resolution images can be obtained and provide substantial architectural information, but depth of imaging is limited to 1 – 1.25 mm, and contrast mechanisms are based on changes in optical parameters within the tissue. New OCT methods based on polarization or spectral differences in tissue are under development and have the potential to advance applications of OCT. However, tissue absorption of near infrared light, highly scattering surfaces and tissues and a relatively small field of view limit some applications. Other optical techniques using confocal geometries or hyperspectral imaging are also used for tissue characterization. All of these optical techniques are compatible with THz imaging technologies.

THz wavelengths can provide information at depths of 1 – 2 cm in tissue depending on water content. The contrast mechanisms that enable image generation are not well understood. Different wavelengths and pulse structures appear to provide unique information about biologic systems. The contrast mechanisms are related to water content, but influence in the local environment, (bound vs. free water, lipid vs. protein) clearly affect the signal. Considerable progress in THz technology now allows access to the technology for image generation and several companies are selling THz systems. Data presented by TeraView Ltd. suggest that rigorous investigation of the factors which control image generation is feasible and practical. Transmission of THz radiation through waveguides should enable endoscopic applications and improvements in detector technology and imaging algorithms should enhance image quality. Alternatively, endoscopic ability could be achieved by using optical fiber coupled with a miniaturized integrated THz transceiver. Identification of unique biologic signatures of disease may be possible leading to improved techniques for cancer screening and surveillance. While the feasibility of imaging has been demonstrated, selection of optimal parameters for imaging has not been achieved.

To obtain optimal THz images substantial advances in sources, pulse sequences, imaging algorithms, detectors, and an understanding of contrast mechanisms are essential. Sources from 100 GHz to 4 THz are currently readily available, but the power generated, pulse structure and operating parameters can be significantly improved. Current systems generate peak powers of kilowatts and average powers of microwatts. Improvements in pulse structure and operating parameters can be achieved through additional source development using currently available technologies. The use of broad-band sources to identify the most promising areas of study will help the development of the next generation of systems. Current knowledge of THz propagation through tissue is based on water absorption and modeling with Debye theory. The influence of the local chemical environment on signal propagation is not clear. Differences in membrane bound water, intracellular vs. extracellular water and layering appears to influence image generation. With improvement in sources, pulse sequences, and imaging algorithms information from much deeper layers maybe feasible. As sources improve and costs are lowered though technology commercialization, access should improve. Greater system flexibility and improved access will stimulate rapid growth of medical imaging applications.

The choice of imaging modes, the definition of optimal pulse sequences and the identification of optimal detector geometry remains to be determined. The use of multiple wavelengths for differential or spectroscopic imaging may provide significant additional information. The techniques of differential imaging have potential to identify unique biologic signatures. Careful, statistically valid studies in living tissue are an essential part of the scientific investigations necessary to ensure development of a reliable database. As new sources are constructed, improvements in imaging algorithms will be required to extract imaging information. Complex input signals, tissue heterogeneity, and tissue absorption and scattering all affect the energy reaching the detector. Modeling of the propagation processes will allow for more effective image reconstruction. Current imaging rates at a single wavelength allow for scanning of a 5×7 cm area within 3 – 4 minutes with a resolution of 100 μm. Improvements in scanning techniques are feasible and near real time scanning of 20 – 30 cm^2 areas should be achievable with current technology. Investigations of new detectors and improvements in current technology are required. As detectors become more efficient, lower power requirements can be used to achieve the same image quality.

7.3 Other areas applicable to medicine

THz spectroscopy is also poised to contribute substantially to the study of pharmaceutical agents. Using THz spectroscopy, investigators have demonstrated the ability to identify and differentiate drug polymorphs. Polymorphs are various forms of the same compound which have different pharmaceutical or bioavailability activities. Terahertz spectroscopy is complementary to Raman spectroscopy, and spectra can be obtained on short time scales (milliseconds) through plastic packaged materials. Thus the technology may play a role in validating shelf life of drugs and identifying contaminated medicines. This technology may also have implications for the studies of larger biologic molecules such as single lipids and proteins and the development of new drugs. The use of the technology for high throughput screening is currently under investigation. Advances in THz spectroscopy have the potential to significantly improve drug efficacy and identify black market copies of approved pharmaceuticals.

THz pulses generated using time-domain spectroscopy have potential value in scale model measurements of scattering phenomena. The problem of light propagation in highly scattering biologic tissues has been the subject of research for many years. Application of optical methods for imaging diagnostics in optically thick tissues requires an understanding of tissue scattering and absorption that are difficult to obtain with current methods. Using THz radiation, one can study simplified, well-controlled models of millimeter dimensions. These model systems can serve as surrogates and provide insight and guidance for researchers working at near infrared wavelengths. The use of coherent THz radiation may provide the basis for new imaging techniques using time resolved spatial correlations.

7.4 Potential problems

1. The value of the technology is not known. Optimization of numerous THz systems specific to medical imaging is required before comparisons to other imaging systems can take place.
2. THz imaging promises a new modality based on complex contrast mechanisms, understanding the biologic basis of the images is critical to validation. Current published papers are not sufficient to evaluate the potential contributions of THz technology.
3. The technology is currently expensive and requires training to maintain instrumentation. To make efficient use of scarce resources development of a user's network listing instrumentation and expertise would be valuable; as there is not "an ideal system" a variety of approaches are worth considering.

7.5 Suggested areas for focus and development

In order to advance imaging applications of THz radiation in medicine several critical steps should be considered.

1. Multidisciplinary teams with physicists, chemists, engineers, imaging scientists, biologists and pathologists are required for progress.
2. Methodical investigations to optimize sources, pulse sequences, detector and image generation are the key to scientific progress.
3. Exploration of THz propagation through tissue and improved modeling of the propagation process will help optimize instrumentation and improve imaging techniques. Both reflection and transmission measurement will play a role in understanding the basis for biologic contrast mechanisms.
4. Advances in quantum cascade lasers, fiber lasers, multiple wavelength sources and time-domain techniques suggest rapid progress can be expected. Also, advances in high powered tabled top accelerator based systems may prove useful.
5. Development of expertise in imaging can be accomplished at 3 levels a) at large highly specialized centers with dedicated beams lines from synchrotrons or FELs. b) Regional core laboratories with table-top systems supported by local networks of investigators and c) highly focused specific projects at multiple institutions. Large scale facilities can help identify optimal parameters. Regional centers can provide rich resources of both instrumentation and expertise to a broad range of investigators. A network can help link individual investigators and rapidly address common problems. None of theses facilities are mutually exclusive and all can play a role in developing THz imaging.
6. Collaboration with industry should be encouraged, coordination of effort between centers and industry are likely to produce significant progress. Development of turnkey THz imaging systems which can be placed in a broad range of institutions will enlarge the research community and allow access to technology. The growth of the technology maybe similar to that of MRI and OCT instrumentation.
7. Although THz radiation is non-ionizing, safety considerations for both medical imaging and users should be investigated. No specific guidelines exist for THz radiation. European studies have shown that THz radiation has no effect on cell growth or differentiation. However, tissue damage thresholds, and potential impact on biologic systems are not known. These issues should be addressed for both the imaging applications and for investigators who may be exposed to THz radiation.

Chapter 8: Continuous-Wave, Narrow-Linewidth THz Systems for Spectroscopy and Imaging.

8.0 Executive summary

Continuous wave (cw) sources of narrow-band THz radiation are generally used for spectroscopy with very high frequency resolution. Such sources can also can be used for THz imaging. Power levels of a few mW are sufficient for many spectroscopy and imaging applications. Such power levels have been achieved in cw sources in portions of the THz electromagnetic spectrum. However, a cw THz source with mW power levels that can tune, for example, over an octave in the 1 – 10 THz frequency range, remains a technology dream.

This chapter describes briefly existing cw sources of narrow-band THz radiation. Approaches described include

- *Microwave generation followed by frequency multiplication*: These are commercially available, compact, all-solid-state devices. This relatively mature technology is being pushed to higher frequencies and powers. Tuning bandwidths are typically 5 – 10% for highest-power devices, up to 40% with sacrifice of power. Power ranges from 30 mW near 0.2 THz to ~1 μW near 1.6 THz.
- *Backward wave oscillators*. These are commercially available from one supplier in Russia. Power varies from ~100 mW near 0.1 THz to ~1 mW at 1.2 THz. Current designs output multimode beams. The availability of this technology is at risk if the Russian company fails and is not replaced.
- *Photocurrent-based photomixers:* These are not commercially available. Tuning has been demonstrated from 0.1-3 THz in a single device. Power levels are typically below 1 μW at frequencies above 1 THz.
- *Photomixers based on nonlinear optical crystals*. These are not commercially available but the components to make them are. mW of narrow-band THz power have been achieved using high-power pulsed pump lasers. The conversion efficiency is ultimately limited by ratio of THz to visible photon energy.
- *CO_2 laser-pumped molecular gas lasers*. This mature technology is commercially available. These lasers are spot tunable (that is, the frequency cannot be continuously varied). Power levels up to 1 W have been achieved in the laboratory at 2.5 THz.
- *THz quantum cascade lasers*. These are very new, and very rapid progress is being made in their development. This promising new technology is based on all-semiconductor devices. Quantum cascade lasers are well-established at mid-infrared wavelengths. The minimum frequency achieved to date is near ~2 THz. At present, THz quantum cascade lasers must be cooled to temperatures below those achievable with thermo-electric coolers. Output powers are typically a few mW.

Sensors at THz frequencies are in much better shape than sources. However, there is much room for improvement. To bring low-noise THz sensors out of the laboratory, operating temperatures need to be raised from the currently required T<4K. Improvements in speed and the construction of sensitive THz focal plane arrays is also desirable.

The communities which use broad-band pulses generated using ultrafast lasers and those using the cw sources described in this chapter would mutually benefit from enhanced communication, provided, for example, by co-location of conferences.

8.1 Introduction

Continuous-wave (cw) fixed and swept sources for THz applications, and their corresponding narrow-band detectors, have been under development for applications in the molecular spectroscopy, radio astronomy, Earth- and planetary- remote sensing, and plasma fusion communities for almost half a century. The need has focused on sources as drivers for ultra-high sensitivity heterodyne detection systems, as high brightness illuminators for spectroscopic measurements, and as tools for metrology on materials and instrumentation. Expanding interest in THz phenomenology in biology and medicine, chemistry, physics and engineering has stimulated the need for additional varieties of sources as well as sources with specific characteristics that best fit their nominal applications. cw sources with narrow linewidth that can produce tunable power at mW levels throughout the frequency range from 100 GHz to 10 THz are especially desirable. Some of this niche can be filled by reasonable extensions of existing source technology. However complete spectral coverage, especially at the higher THz frequencies is still a technology dream. This section reviews some of the source technology we have today, extensions of this technology that may be available in the near future, and breakthrough developments that are desired for filling the needs of the broader THz community.

Instrumentation and systems for generic THz studies require both a source and a receiver. Depending on the application, either a broad-band direct detector or a narrow-band heterodyne receiver may be most appropriate. Systems using narrow-linewidth cw sources together with the appropriate receiver represent a fundamentally different approach to performing THz metrology and phenomenology than the recently-developed time-domain or pulsed systems discussed in the next chapter. In many cases, a system based on a cw source can perform much higher sensitivity measurements with equivalent integration time. Until the costs of ultrafast lasers come down significantly, systems based on narrow-linewidth cw sources can also be less expensive.

8.2 Sources

Commonly employed millimeter and submillimeter wave cw narrow-band sources and their characteristics are briefly listed below.

Microwave generation followed by frequency multiplication:
By starting at W-band (100 GHz) or below, or alternatively at the highest frequency where mW direct oscillation is available, and following the oscillator with a power amplifier (if available) and a nonlinear solid-state frequency multiplier (typically a Schottky barrier diode or diode array), harmonics of the oscillator can be generated at frequencies in the THz range. Current capabilities allow tunable power generation at the 5-10% bandwidth range from 200 GHz to approximately 1600 GHz with power levels from 30mW (low end) to 1 microwatt at the highest frequencies. The technique involves significant power at the pump frequency and efficiencies are typically below 1 percent for multiple stages. However this technique has been around for as long as microwave spectroscopy (more than 60 years) and is very powerful. With continuing

development in pushing oscillator frequencies up into the submillimeter, or power combining at the pump end, it is possible to generate microwatts of tunable cw power at least up to 2 THz. Also, multiplier based sources optimized for broad electronic tuning bandwidth can achieve up to 40% bandwidth. Although these ultra broad sources tend to have lower efficiency and power handling, they do achieve several mW to hundreds of μW in the 300 – 1,000 GHz range.

Backward Wave Oscillators (BWOs):
Backward wave tubes have been around for more than half a century but are currently only produced in one small remaining arm of a large company, Istok, in Russia. Power levels from 100 mW near 100 GHz to 1mW at 1200 GHz have been commercially achieved in electronically tuned bandwidths from 10 – 25%. However, the expertise for producing tubes from existing designs is rapidly disappearing and replacement technology has not yet materialized. Capabilities from 50 GHz to 200 GHz are likely to remain, but tubes between 200 and 1200 GHz may no longer be procurable once the last members of the production team at Istok have retired. Although these electron sources require high voltages (2 – 10kV) and large magnetic fields (5 – 12 kG), and their output power is multimode, they have been a mainstay for THz cw work for many years. Their potential disappearance is a threat to many groups working in this frequency range. Several US teams, and at least one European group have proposed (and are trying to develop) electron sources using modern microfabrication and cathode technologies, but to date no working oscillators above 300 GHz have been produced. Theoretical projections indicate that BWO sources can work up to at least 2 THz and that advances in cold cathode and MEMS fabrication may yield designs which cost less and use less power. Little funding is going into this area at the current time and it is strongly recommended that this situation be changed for the good of the entire THz community. Tube manufacture in the West at a price accessible to laboratory scientists has been hampered by the extremely small size of the market. Development of an equitable technology transfer with Istok is a possible approach to saving this technology.

Sources based on optical downconversion using nonlinear mixing:
Photomixer sources are based on beating two optical or IR lasers together in a photonic material to generate THz-frequency photocurrents. These photocurrents radiate THz power either directly into free space or onto transmission lines. A photomixer based on semiconducting material with ultrafast carrier recombination times can have a useful tuning range from < 100 GHz to above 3 THz in a single device – a record for a cw THz source. Although the optical to RF efficiency is very low, microwatt power levels can be produced, and rapid tuning over the whole frequency range is possible with simple adjustment to the laser pump. For many THz metrology and phenomenology applications, this low level of power, when coupled with high sensitivity cooled bolometric or heterodyne receivers, is sufficient. Frequency locking has already been demonstrated and MHz line widths are achievable. Pushing the photomixer materials into the 1.5 micron commercial optical band is a major challenge for reducing cost and opening up the market for widespread use of these devices.

Sources based on optical downconversion using a nonlinear-optical crystal:
Optical downconversion using the second-order nonlinear optical ($\chi^{(2)}$) properties of nonlinear crystals has been an active field for many years. Although the inherent conversion efficiency is typically less than 10^{-5}, significant power (mW) has been produced at THz frequencies using pulsed lasers and high power optical beams. Lithium niobate ($LiNbO_3$) and zinc-telluride (ZnTe) crystals have been employed very successfully, and recently line widths in the MHz region have

been obtained by Japanese investigators using an optical laser seeding technique. These sources are also very useful for many spectroscopic and metrology measurements in the THz range. Since they make use of very widely available components from the optical community, cost and availability are much more assured than with the BWO sources.

Far IR Laser pumped sources:
CO_2 pumped far-IR gas lasers have been used for many years as strong cw sources in the THz frequency range. Only a small number of spot frequencies can be covered by commercial systems but power in the tens of mW range or higher are possible. Lab systems have been built with power levels above 1 Watt at the strong methanol line radiating at 2.5 THz. Although these systems are both expensive and bulky, much work has gone into improving efficiency and reducing volume on the CO_2 side. Because the conversion ratio (IR to submillimeter) is much less than with photomixer sources, the inherent efficiencies are significantly better. A space qualified system with 30mW of power at 2.5 THz has been fabricated and draws only 150 W of DC. It should also be mentioned that direct THz lasing is possible from certain excited gases, and there has been some interesting work (late 1970s) on direct water vapor lasers for example.

QC lasers:
The development of far IR and now THz quantum cascade lasers is revolutionizing THz source development in the 2 – 10 THz region. Devices with power levels above 5mW and instantaneous bandwidth below 100 kHz have been measured at 3.5 THz and the lower frequency limit is being pushed down very rapidly. Advantages include solid-state construction, tailorable frequency operation and potentially locked narrow-band output. Disadvantages include cooled operation, but the upper temperature limit for gain is also increasing very quickly and now stands above 140 K.

8.3 Detectors

While cw detectors in the THz range are more mature than most THz sources, they do require significant development. They are very sensitive to thermal background radiation. Detectors for pulsed THz radiation are currently limited to nonlinear crystals such as ZnTe and photoconductive antennas. Combining the exquisite sensitivity of the cw detectors, with the insensitivity to thermal background fluctuations of time-resolved, or gated, detectors must be a top priority.

Near quantum limited superconducting receivers can be built at any frequency between 100 GHz and 1600 GHz with modest bandwidth (> 10%). Above 1600 GHz superconducting bolometers and mixers have been constructed with sensitivities about 10 times the quantum limit. Room temperature receivers based on Schottky diodes are also available up to 2.5 THz with about 10 times poorer performance. Unfortunately commercial sources for these components are not common, although at least one company produces mixers and sources that approach 1 THz and has immediate plans to continue development of such components above 1 THz. These detectors tend to be expensive because of the lack of commercial markets and the expense of fabricating the detector mounts. Quasi-optical circuits that are common in the pulsed TDS systems are also available in the cw world. It would make the detectors needed in pulsed time-domain systems much easier to acquire if a company were to take up the challenge. The bolometric and semiconductor devices however are generally used only in research laboratories and this too must change. The detectors can be used in direct or heterodyne mode (if local oscillator drivers are available) and with radiometric techniques, can integrate down to very low detection limits (mK delta T's).

8.4 Developments needed

The community would like to see more development activity on all the potential sources listed, as each has capability in particular niches. A big hole exists in high power (10 W) pulsed cw THz sources, where micro second switching times and high repetition rates are needed for electromagnetic resonance experiments. Emphasis should be placed on saving technologies that may be disappearing – such as the BWO sources, as well as on pushing commercial development of all source technologies, so that laboratory curiosities can become available community-wide. Oscillator and amplifier technology can certainly be pushed into the low THz range (300 – 600 GHz) which would result in much more available cw power above 1 THz through multiplication techniques. QC lasers offer incredible promise but cooled operation will be a big disadvantage unless operating temperatures are consistent with thermoelectric or inexpensive pulse tube refrigerators. The nonlinear crystal-based sources (especially seeded $LiNbO_3$) are making nice progress and can fill some niches in the spectroscopy arena already. Even gas laser sources are receiving commercial attention, and because of this, cannot be discounted as potential market players.

Although THz detectors are in better shape than sources, developments are needed here as well. The THz direct detectors and heterodyne receivers with lowest noise require cooling to liquid-Helium temperatures or below, restricting them to laboratory use and making them expensive to purchase and complex to operate. Liquid-nitrogen or pulse-tube-cooled detectors with noise comparable to existing, commercial liquid-helium cooled bolometers (10^{-13} W/Hz$^{1/2}$) would be a huge improvement. Many emerging applications also require sensitive detectors that are faster than bolometers. Finally, arrays of THz detectors would greatly enhance THz imaging science.

8.5 Recommendations

Much of the "new" THz community is focused on time-domain pulsed techniques. However there is a great deal of accumulated knowledge and hardware in the older cw spectroscopy and space science fields that can be drawn upon to fill in missing capabilities. In many instances these areas of development are languishing because of small markets and disappearing expertise. By bringing the two communities closer together and funneling some of the development funding into these fields, we can preserve some very necessary and fruitful component research. In addition many of the time-domain applications currently being explored are much better addressed with higher brightness cw source and coupled detector technologies. This is one avenue where a coalescing of workshops and conferences from the two approaches can have high payoff. An overriding problem is the lack of commercial development and availability of source and detector components. In fact the time-domain community is actually better situated in this regard, having now two companies that produce off-the-shelf instruments. In the cw source and detector areas, only a handful of commercial vendors are still in operation and none produce generic instruments above 1 THz. This situation will hopefully change as THz science is pursued by more researchers. In fact a powerful method to spur this commercial development exists in the SBIR programs that are run by the supporting agencies for this workshop.

Chapter 9: Broad-band Sources and Systems for THz Spectroscopy and Imaging

9.0 Executive summary

Opportunities: Given the large amount of currently published work based on broad-band THz spectroscopy and imaging, it is easily understood that many more opportunities remain unexplored. This type of source will continue to be of great value in physics, chemistry, biology, and medicine, as is evident from Chapters 3 – 7 of this report.

Status: There are currently about 30 groups throughout the United States, and at least that many more worldwide with broad-band table-top THz spectrometers based on ultrafast lasers (typically Ti:Sapphire). Some are oscillator-only systems, and some employ a Ti:Sapphire amplifier, depending on the details of the experiments being done. The current availability of broad-band THz radiation at accelerator-based facilities in the U. S. is limited to Brookhaven National Laboratory , the Advanced Light Source at Lawrence Berkeley National Laboratory, and the Jefferson Laboratory. New efforts are proposed for Lawrence Berkeley National Laboratory (see Chapter 11).

There have been well over 1000 papers published on THz spectroscopy and imaging in the last 15 years using broad-band table-top and accelerator-based sources, with a majority of them from table-top sources. These include gas phase spectroscopy, condensed matter spectroscopy, time-resolved studies, THz emission spectroscopy, THz ranging and sensing, and THz imaging (both in transmission and reflection).

Potential size of community, technology and infrastructure needs: The general usefulness of broad-band THz sources ensures a community that will grow as access to these sources grows, both table-top and accelerator-based. A THz user's network is of the utmost importance for opening the door to researchers who are not, and do not wish to be, experts in developing THz source technology. An important part of a user's network would entail access to accelerator-based facilities, centers of excellence where specific types of THz spectroscopy are performed, and "kits" and/or detailed instructions for constructing a table-top apparatus. It is not hard to imagine 500 – 1000 scientists or more (students, postdocs, and faculty) in the U. S. actively carrying out THz spectroscopy and imaging with broad-band sources if the capacity to accommodate them exists.

9.1 Introduction

Systems which can be used for broad-band measurements have played an important role in many of the recent exciting developments in the field of THz science. There is a general consensus that broad-band techniques are crucial for spectroscopy, sensing, and imaging. In many cases, one simply desires to obtain linear spectroscopic information, such as complex dielectric constants or conductivity. In such situations, very broad spectral coverage (extending over more than one order of magnitude in frequency) is necessary for a full understanding of the behavior. For example, it has been pointed out that, in many strongly correlated electron systems, the spectral features are not narrow or resonant, but instead consist of smoothly varying trends. This is true, to a certain extent, in many condensed phase systems as well. In other situations, the broad-band nature of the source can be exploited for novel imaging applications. For example, broad-bandwidths correspond to short coherence lengths, which are required for high resolution time-of-flight imaging or tomography. Finally, although broad-band systems often do not offer the high spectral resolution required for rotationally resolved gas phase spectroscopy of heavy molecules, they can provide a "snapshot" of the spectrum in a fraction of the time. Even a relatively low resolution THz spectrum can serve as a fingerprint of the gas or gas mixture under study, and this capability can be exploited in sensing systems.

9.2 Potential technical developments

Much of the excitement surrounding THz technologies has been inspired by a long list of applications, both ongoing and anticipated. Chapters 3 – 7 of this report allow the reader to appreciate the wide ranging impact of THz technologies. In order to maintain growth comparable to the last ten years, considerable source development activities will be required. Here, we provide a brief list of a few such developments.

- Currently, the combination of broad-bandwidth and high spectral resolution is offered only at the Brookhaven synchrotron light source. This system can attain 0.001 cm^{-1} resolution, using a 6 meter FTIR spectrometer. In contrast, most time-domain systems utilize 15 cm optical delay lines and therefore cannot achieve better than 1 GHz (0.033 cm^{-1}) resolution. In time-domain spectroscopy, is there a possibility to improve the attainable resolution by at least one order of magnitude?

- Several groups have developed techniques for measuring a time-domain waveform in a single shot, using for example chirped pulse electro-optic sampling. These techniques, however, have limitations with respect to both dynamic range and bandwidth, and usually require amplified femtosecond lasers. Is it possible to develop a more robust single-shot imaging technique using a low-power source? This would permit the imaging of extremely fast phenomena such as explosions, which cannot be easily synchronized to an amplified (1 kHz repetition rate) femtosecond laser.

- Currently, one of the great powers (and also limitations) of time-domain techniques is that they can only detect the radiation that is generated in synchronization with a femtosecond oscillator. Is there a method for measuring a THz wave, both amplitude and phase, that is not synchronized with a mode-locked source?

- Is it possible to synchronize a THz wave to an arbitrary external clock? Such synchronization could be important for THz communications (e.g., decoding in CDMA).

- Photoconductive detectors are among the most sensitive sensors for THz radiation. But single-photon detection is currently beyond the capabilities of such systems. Is it possible to detect a single THz photon with high quantum efficiency in a practical detector? This would enable a whole realm of experiments in THz quantum optics.

- One can imagine many imaging applications which require access to restricted environments. Is it possible to perform reflection imaging experiments inside the human body or inside a container with a very small opening? This could enable THz colonoscopy or THz dentistry.

9.3 Requirements

The requirements for a broad-band spectroscopy source are diverse, and no one source offers all of the features necessary for every application. Desirable features include: 1. Broad spectral coverage. 2. High brightness for small samples. 3. Compatibility with coherent detection – this affords both high sensitivity and direct connection to optical constants (absorption coefficient and refractive index). 4. Short pulses (~ 1 ps or less) for time-resolved work.

These requirements are based on the scientific goals of the community articulated elsewhere in this report. In order to achieve or facilitate these goals, we require a number of important advances in the status of THz systems. One primary motivation is to lower the barrier for entry into the field for new users. For table-top systems, this translates into a need for greater simplicity, lower cost, and "kits" and/or step by step instructions for assembling the apparatus. For user facilities, a broader range of capabilities, as well as the creation of a user's network, is required to attract a larger user base.

Spectral Coverage

One immediate need for the community is to increase the range of frequencies over which useful data can be obtained. This could be achieved by a variety of methods, including simply scaling existing systems. This strategy, however, is not likely to be compatible with the ideas of simplicity and low cost since more powerful lasers and larger generation and detection crystals would be required. Rather, further improvements in the *efficiency* of THz generation (and detection) should be pursued.

Currently, most time-domain systems are useful up to a few (3 – 5) THz. Working at higher frequencies (in the range from 5 to 15 THz) is hampered by the fact that virtually all crystalline materials exhibit strong phonon absorption in this range, and a subset of these materials such as GaAs and ZnTe are used as THz generators and detectors. A promising option for accessing this higher frequency range lies in incoherent sources, such as FTIR spectrometers with extremely bright sources such as synchrotron radiation.

Small Samples and Near-Field Methods

Many physical systems of scientific interest have lateral dimensions at or smaller than the diffraction limit. These include systems in the biological sciences (individual cells are ~ 20 microns in size or smaller), environmental sciences (surfaces of small grains), and materials/chemical sciences (small single crystals, nanoparticles). When studying systems that can be spatially isolated, a high-brightness source and far-field method usually offers more directly interpretable information than other approaches. In other situations, near-field methods will be necessary for probing local properties or achieving adequate sensitivity. Since near-field techniques involve coupling the electromagnetic waves into a small structure, the source polarization characteristics become important as well as the available brightness. Waveguide structures are an area of current research activity, and the type of guide (hollow, planar, coaxial) is likely to depend on the type of system to be probed. Therefore, sources of both plane as well as radially polarized light are of interest. Such guide structures offer an opportunity to achieve strong electric fields into very small regions.

To realize this, near-field methods will have to be developed, which allow spectroscopy at frequencies between 0.1 and 50 THz with a spatial resolution of 1 nm or less. This in turn requires further THz source and detector developments.

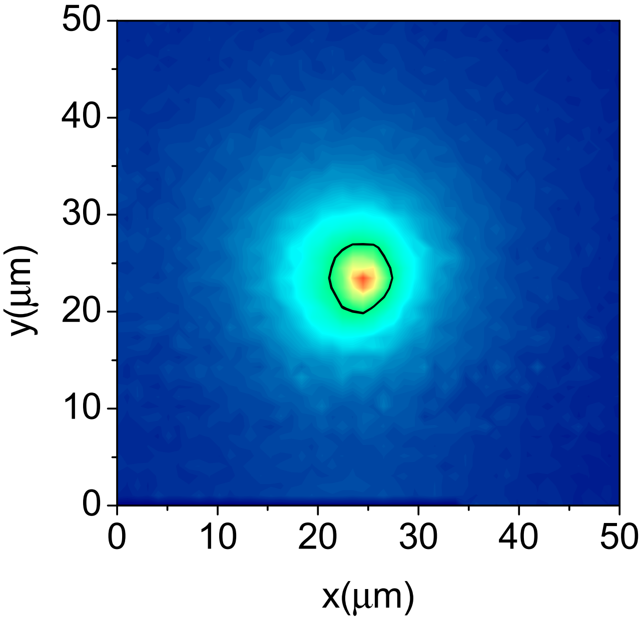


Figure 9.1 THz radiation emitted by a sharp metal tip, with sub wavelength dimensions. Red indicates maximum intensity, dark blue indicates zero intensity. Note that the dimensions of the spot are two orders of magnitude smaller than the wavelengths used. The result shows one of several possible routes to obtain a subwavelength resolution in THz spectroscopy. Figure courtesy of Paul Planckn, University of Delft.

Free-space near-field techniques have been of significant recent interest. The most recent developments in the US and Europe indicate that it will be possible to use near-field techniques to ultimately bring the spatial resolution into the nanometer domain. As the development of other nanoscale techniques has shown, this would open up a whole new avenue of fundamental science. In principle this would allow the study of the fundamental THz properties of a single quantum dot, or small volumes of biologically relevant molecules, or extremely small crystals, etc. For example, it may be possible to look at the low-frequency vibrational spectrum of a single molecule with sub-molecule resolution. In addition, mapping out of the vibrational wavefunction of a delocalized vibrational mode of such a molecule may be a real possibility. This would greatly increase our understanding of the fundamental properties of matter at a truly microscopic level of detail.

Spectroscopic studies under high pressures present stringent requirements with respect to sample geometry. The aperture for a diamond anvil cell varies inversely with the pressure to be achieved, and rapidly falls below the diffraction limit for THz frequencies as the pressure reaches megabar values. In many of these cases, near field techniques will not be practical because of the restricted space near the sample.

Similarly, studies at low temperature and high magnetic field require complex cryostats, and present difficulties in optical throughput. *In situ* (and *in vivo*) biological studies will require waveguides to bring THz to and from the area of interest with an external source/detector, or fiber to transmit the optical beam to and from a localized THz source/detector.

For situations where far-field methods are necessary along with broad spectral coverage, synchrotron radiation provides a solution. These facilities allow standard FTIR spectroscopy methods to be extended into regimes where other methods fail. These are limited resources, but are available for those instances where individual laboratory capabilities are not sufficient. As the table-top techniques evolve, the synchrotron sources will provide a capability for comparative testing and validation. Also, synchrotron radiation is an extremely broad-band source of both high brightness and potentially short pulse duration (tens of picoseconds at present, and a few ps possible in the future) for use in both throughput limited and time-resolved methods.

Optical Components and Waveguides

There is much needed research in the development of optical components for free-space propagation of THz radiation. A device as simple as a variable broad-band attenuator remains unavailable. Free-standing wire grid broad-band polarizers are available, but are quite expensive, and not nearly as efficient as those found in other regions of the spectrum. Many of the useful tools taken for granted at optical frequencies (waveplates, anti-reflection coatings) are simply not available for broad-band THz pulses, and are incompatible with the broad-bandwidth inherent in many types of THz sources. Innovative ideas and the resources to pursue them are required to address these concerns.

Another important consideration is the spatial manipulation of the THz beam. Recent work in the use of quasi-optic waveguides has generated much excitement, as it seems possible to transmit single-cycle pulses with relatively low loss and virtually no dispersion, even though the bandwidth of these pulses overlaps many waveguide modes. Further research in quasi-optic waveguides is critical. With techniques of this sort, one can imagine a system in which the THz beam is delivered to a sample (for imaging or spectroscopy, or both), and then returned to a receiver, without the use of free-space optics. One exciting possibility is a THz endoscope, which would permit imaging or spectroscopy in environments that are otherwise difficult to access.

THz Imaging

It is also clear that many advances are required to further research and development in THz imaging science. With the strong current interest in THz imaging, it is clear that continued development of imaging technologies based on low cost (*i.e.*, unamplified) laser sources will be a strong driving force leading to new results. An important asset of THz imaging is the relative ease at which functional imaging can be performed (see Figure 9.2). This is based on the full characterization of the THz electromagnetic field as it passes through the sample, leading to the underlying spectral signatures of the material in question.

Another direction is to use the inherent high-power and broadband nature of coherent synchrotron radiation (CSR) for THz imaging (see Chapter 11 for more details about CSR sources). This high average power can be used to focus on more difficult samples (i.e. samples inside diamond anvil cells, buried inside a tissue, or small enough to require extremely lossy near-field techniques) or simply to allow illuminating an entire large sample and a CCD-style detection system to enable real-time, full-frame, video-rate THz imaging. This type of development will enable a new class of real-time THz imaging tools, such as video-rate THz imaging of moving parts, proof of concept medical and dental imaging, high photometric accuracy measurements, and linear spectroscopy and imaging of "difficult" samples, such as with near-field microscopy, samples under extreme conditions, and samples with complex geometries, as occurs many biological samples.

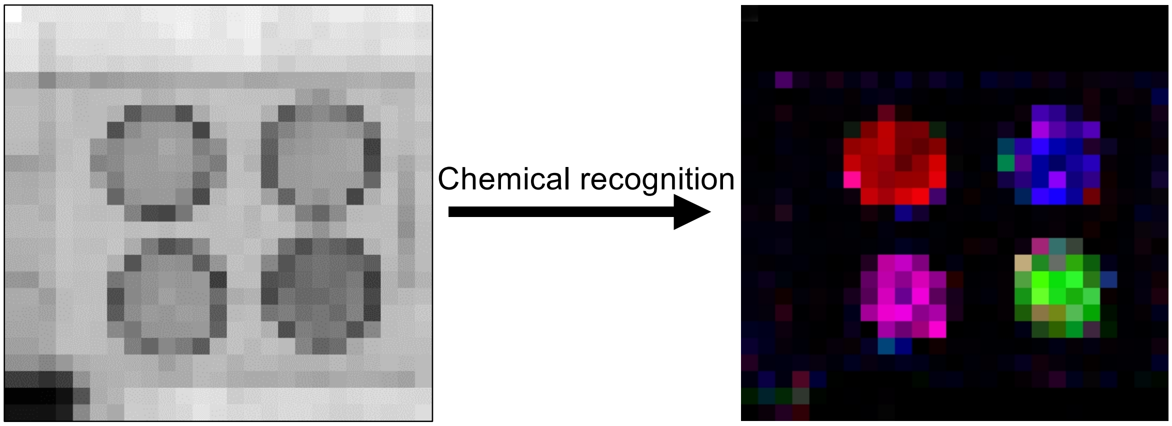


Figure 9.2 The left panel shows a traditional THz transmission image of four pills containing different chemicals (lactose, aspirin, sucrose, and tartaric acid). The right image has color-coded according to the spectral information contained in the full THz trace recorded at each pixel, and is known as "functional imaging". Figure courtesy of Y. Watanabe et al., Yamagata University.

For example, subwavelength imaging using CSR is shown in Figure 9.3. A buried cavity lesion is labeled in both panels, and in the THz image it is seen that it penetrates into the underlying dentin. This image was acquired at 0.3 THz using coherent synchrotron radiation at the BESSY synchrotron, with a 200 micron coaxial wire cone providing better than $\lambda/5$ spatial resolution through the 2.7 mm slab of tooth. The researchers have already demonstrated resolutions to $\lambda/40$ using the intense CSR THz source

Fast, single-shot THz imaging techniques are available using intense THz pulses (as demonstrated by X.-C. Zhang *et al*). However, these are not currently readily implemented with low-power (and therefore relatively inexpensive) THz systems. One route of research will be to develop pulsed THz sources, driven by unamplified lasers, with emitted field strengths at least an order of magnitude higher than what is available today. Such a development will require advances in material technology (e.g. higher mobility, higher breakdown voltages, larger

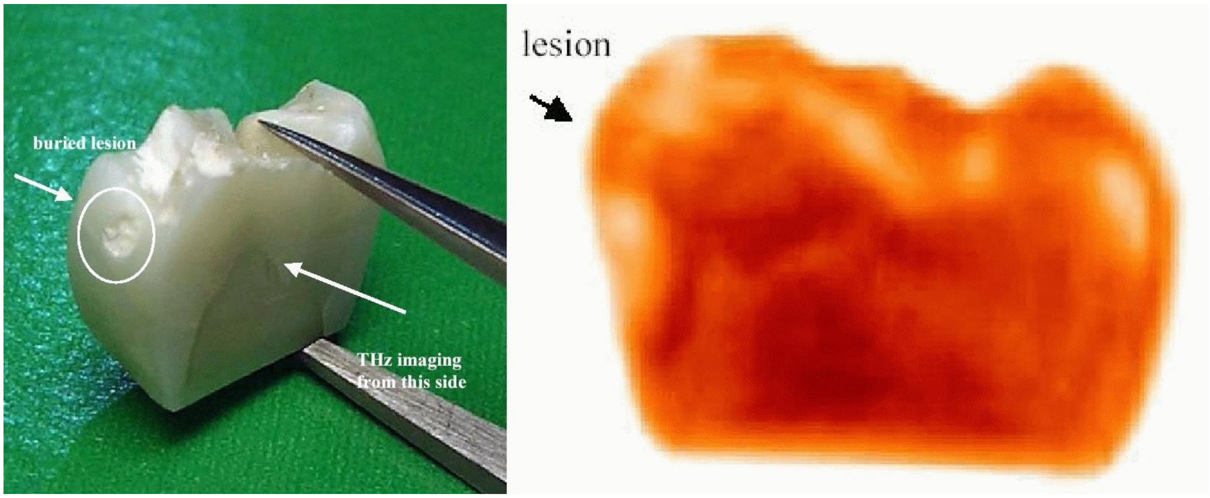


Figure 9.3 Photograph (left) and near-field THz image (right) of a human tooth. Figure courtesy of D. Fried, U.C. San Francisco, and U. Schade and K. Holldack, BESSY Gmbh

electro-optic coefficients, better phase-matching) and possibly micro- or nanostructuring of the antenna surfaces. These strategies must be pursued.

Integrated components offer great promise. This field had its genesis in work involving guided propagation of broad-band waves on coplanar strip lines. The recent work of P. Bolivar and colleagues is a good example. Their group has fabricated coplanar resonator structures and demonstrated that the resonance frequency and quality factor (Q) both shift substantially when they are functionalized with either single-stranded or double-stranded DNA. Indeed, single base-pair mutations in an extended DNA chain can be detected. This work exemplifies the power of THz techniques for sensing, and highlights the need for further work in integrated components. Using a different approach, Nelson's group at M.I.T. has demonstrated a variety of integrated optical components such as diffraction gratings and phased array sources using phonon-polaritons in lithium tantalate.

Another route towards low-power functional THz imaging includes integration of multiple THz field detectors based on photoconductive switching onto a single detector chip. An enabling THz imaging technology required for fast readout of pixel arrays is the development of holographic or micro-optical systems for coupling optical gating beams to the antenna. It will also be necessary to develop low-noise readout electronics and amplifiers, preferably integrated into the active detection area.

9.4 Increasing the size of the community

The evolution and accessibility of table-top systems is a topic of great interest. The THz time-domain spectrometer has proven to be quite versatile for a long list of measurements. However, an important goal is to make this system even simpler. For example, it should be possible to construct a time-domain system with essentially no alignment degrees of freedom. This would have a large impact, as it would dramatically lower the barrier for users who are not extensively trained in the art. To achieve this goal, several substantive research advances are required. For example, the use of a mode-locked fiber laser, rather than the more conventional Ti:Sapphire oscillator, would greatly simplify the generation and delivery of short pulses to the THz transducers. There have been proof-of-principle demonstrations of this idea, but considerable work is still required. Numerous other possibilities exist, and a variety of strategies should be pursued.

The need to establish and develop both table-top and accelerator-based centers of excellence expands on the model described above: Easier, cheaper, and faster (from the user's point of view). These sorts of centers will be critically important to fully harness the utility of broad-band THz sources. These centers will include general spectroscopic capabilities, as well as near-field, far-field, and pump-probe capabilities.

THz imaging presents its own future requirements. The development of low-power, small-footprint, easy-to-operate THz imaging devices will enable users from outside of the traditional field of ultrafast THz optics to benefit from this technology and conduct scientific experiments.

These advances will lead to a larger THz community, where the primary focus is much more on the scientific uses of the technology rather than on the technology itself. This will require support of PI's and table-top experiments, centers of excellence, and accelerator-based sources.

Chapter 10: Narrow-Band THz Sources for Nonlinear and Non-equilibrium Studies

10.0 Executive summary

Opportunities: Scientific opportunities enabled by intense, narrow-band THz radiation in materials science, physics, chemistry, biology and medicine have been described in previous chapters. One need only look at the impact of high-power visible and near-IR lasers, or of microwaves, to get some idea of the possibilities. Sources exist now that can enable many of these experiments, and sources must be developed to enable others.

Status: Many of the most exciting scientific opportunities using THz radiation involve driving systems into a regime in which the response is nonlinear and the system is far from thermal equilibrium. This chapter reviews a variety of methods and sources for generating narrow-band THz radiation with THz electric fields sufficient to produce interesting nonlinear and non-equilibrium effects. We will define as “narrow-band” pulses that have more than 10 cycles of an oscillating electromagnetic field, and “intense” as capable of generating electric fields in excess of 300 V/cm.

Several examples of accomplishments and opportunities have been discussed in previous chapters in which intense, narrow-band THz radiation induces interesting non-equilibrium and nonlinear states of matter. Rabi oscillations of electrons bound to shallow donors in semiconductors, which have small effective masses and enormous dipole moments, have been observed at electric fields of the order of 100 V/cm, or 10 kV/m (see Figures 3.1 and 3.2) with pulses containing ~100 cycles of THz radiation. Terahertz electric fields up to 1 MV/cm are needed for contemplated nonlinear and non-equilibrium studies of electronic transitions with much smaller dipole moments, for example studies of photon echoes in water, collective modes in large molecules and solids, and magnetic transitions.

In any optics experiment, one would like to be able to throw away at least 90% of the power coming out of the source to reflections from windows, surfaces, beam splitters, Fresnel losses, propagation losses, spatial filtering, etc. Thus, in this section, we discuss sources which are capable of generating a minimum of 300 V/cm (~100 W/cm^2) when focused to a diffraction limited spot in air with f/2 optics. For 1 THz, the diffraction limit at f/2 corresponds to a spot with a diameter of approximately 4×300 μm = 1.2 mm. Thus, 100 W/cm^2 can be achieved with a power of 1 W in a ~TEM$_{00}$ mode at 1 THz. An electric field of 3 MV/cm at 1 THz will require a power of 100 MW.

Intense, narrow-band THz electromagnetic radiation can be generated by Free-Electron Lasers (FELs), by molecular gas lasers pumped with powerful CO$_2$ lasers (these are spot tunable) and, more recently, by sources based on amplified ultrafast (<100 fs pulse width) near-IR lasers combined with nonlinear optical materials.

Free-Electron Lasers are extremely flexible sources of electromagnetic radiation, and no two are the same. There are, at present, at least three major FEL facilities in the world at which intense narrow-band THz radiation is available to users. At each of these facilities, in addition to FELs, there is in place an extensive complement of ancillary equipment to enable various classes of experiments. The three operating FEL user facilities are the Free-electron Laser for Infrared experiments (FELIX) in the Netherlands, the Stanford Picosecond FEL Center, and the University of California at Santa Barbara Free-Electron Lasers. At least one more, FELBE in Germany, has recently lased at 15 THz, and is projected to begin operation at frequencies as low as 2 THz in 2006. The Stanford FEL and FELIX can operate at frequencies both above and below 20 THz, and many of their users operate at the higher frequencies. UCSB's FELs tune from 0.12 to 4.8 THz, with extension to 10 THz in progress.

THz sources based on compact electron accelerators are being actively explored, and are discussed in the chapter.

In the last few years, intense, narrow-band THz radiation has been generated using amplified ultrafast visible and near-IR lasers. Two approaches have been taken in a handful of laboratories. One is to send an ultrafast beam through periodically-poled $LiNbO_3$. The number of periods of the THz radiation is then equal to the number of periods in the poled crystal. A second approach has been to shape an ultrafast near-IR laser pulse with a pair of gratings and a phase or amplitude mask, and then send the shaped near-IR pulse into a nonlinear crystal such as $LiTaO_3$. To our knowledge, there are as yet no publications in which intense narrow-band pulses generated by these techniques have been used for nonlinear or non-equilibrium experiments. However, experiments are under way, and both of these methods look extremely promising as relatively small scale sources of intense narrow-band THz radiation.

Recommendations: The barriers to entry into nonlinear and non-equilibrium THz experimentation are, at present, formidable. One either needs access to a Free-Electron Laser, or to build an expensive table-top source based on an amplified near-IR laser which is an emerging technology.

Many investigators in the U. S. travel to the Netherlands to use FELIX for nonlinear and non-equilibrium THz experimentation. FELIX is supported as a user facility, with a staff that maintains and operates the laser, as well as a staff to help visitors set up and perform their experiments. Free-Electron Lasers are all relatively small operations compared to synchrotrons, neutron sources, or the National High Magnetic Field Laboratory. However, they are too large to support with single investigator grants, and support in such a fashion limits the breadth of utilization.

We recommend, within a THz User's Network, funding THz Free-Electron Lasers in the U. S. to support users external to the home institution. In particular, funds for

1. a technical staff member dedicated to supporting external users, similar to a resident scientist responsible for a set of beamlines at a synchrotron.
2. the costs of operating the FELs for external users.
3. costs of user-driven improvements and general-purpose equipment for external users.

Table-top laser-based sources are extremely promising. At this point, the builders are the only ones with access to these sources. Here, we have three recommendations.

1. Fund demonstration experiments, in which table-top laser-based sources are used for new science.

2. Fund investigators who have built these table-top sources, have them working well, and are willing to devote a significant fraction of THz beam time to outside users, as nodes in the THz User's Network, with a post-doc or staff scientist to assist outside users with experiments.
3. Continue to fund source development, with an eye to eventual commercialization. This funding could go both to academic researchers, and to small companies as SBIR or STTR grants.

Further development should occur on compact accelerator-based THz sources targeted at specific applications.

10.1 Introduction

In this section, we review the basic characteristics of existing and prototypical (proof-of-principle) narrow-band THz sources and describe the expected scientific opportunities for such sources. Several examples of accomplishments and opportunities have been discussed in previous chapters in which intense, narrow-band THz radiation induces interesting non-equilibrium and nonlinear states of matter. Rabi oscillations of electrons bound to shallow donors in semiconductors, which have small effective masses and enormous dipole moments, have been observed at electric fields of the order of 100 V/cm, or 10 kV/m (see Figure 3.2) with pulses containing ~100 cycles of THz radiation. THz electric fields up to 1 MV/cm are needed for contemplated nonlinear and non-equilibrium studies of electronic transitions with much smaller dipole moments, for example studies of photon echoes in water, collective modes in large molecules and solids, and magnetic transitions.

10.2 Comparisons of different types of narrow-band THz sources

There exist a number of narrow-band THz sources, including accelerator-based sources from relativistic electrons, table-top nonlinear optical generators, and solid-state quantum cascade lasers. Here we consider only narrow-band THz sources that can produce high-field strengths (over 300 V/cm when focused to near the diffraction limit in free space), which are ideal for nonlinear and non-equilibrium studies.

We note that carefully designed antennas and on-chip waveguiding structures can lead to THz fields greater than 300 V/cm even with modest powers. For example, consider 1 mW traveling along a 50 Ohm microstrip transmission line in which the microstrip is 1 micron above the ground plane. The electric field in between the microstrip and the ground plane will be 3 kV/cm. Of course, engineering such structures, and conducting nonlinear optical experiments in such microscopic geometries, is a tremendous technical challenge. It is much easier, for scientific experiments, to use large samples, not process them extensively, and use a high power source that can generate the requisite fields by focusing in free space. However, this simple calculation shows that applications requiring kV/cm THz field strengths can be accessible, with careful electrical engineering and microfabrication, even with THz powers available from today's THz quantum cascade lasers.

10.2.1 Free-electron lasers

The Free-Electron Laser (FEL) is a unique light source, which converts the kinetic energy of free-electrons into electromagnetic radiation. It is tunable over a wide range of frequencies, from far-infrared to ultraviolet. The type of FEL we consider has an electron gun, an electron accelerator, and a wiggler (or undulator) that is placed inside an "optical" cavity. The wavelength of radiation is determined by three continuously-variable parameters: the acceleration voltage (i.e., the electron kinetic energy), the spatial period of the wiggler, and the strength of the wiggler magnets. Especially in the THz frequency range, because of the lack of efficient nonlinear crystals, FELs have been extremely useful sources for tunable, powerful, and coherent radiation. Table 10.1 summarizes the characteristics of THz free-electron lasers with user facilities.

	Stanford	**UCSB**		**FELIX**	**ENEA Compact FEL**
λ (μm)	15-80	63-340	340-2500	3-250	2000 - 3500
ν (THz)	3.75-20	0.88-4.8	0.12-0.88	1.2-100	0.09 – 0.15
Micropulse width	2-10 ps	-	-	6-100 cycles	50 ps
Micropulse Rep Rate	11.8 MHz	-	-	1000 MHz, 50 MHz, 25 MHz	3 GHz
Micropulse Energy	1 μJ	-	-	1-50 μJ	0.5 μJ
Macropulse Width	0.5-5 ms	1-20 μs	1-6 μs	5 ms	4 μs
Macropulse Rep Rate	0-20 Hz	0-7.5 Hz	0-1.5 Hz	10 Hz	1 -10 Hz
Average Power	< 1 W	5-100 mW	5-100 mW	< 1 W	4 – 40 mW
Peak Power	< 500 kW	< 6 kW	< 15 kW	< 10 MW (@ 20 μm); <1 MW (@ 100 μm)	10 kW (@ 2600 μm)
Peak Field	< 250 kV/cm	< 70 kV/cm	<20 kV/cm	< 10 MV/cm (@ 20 μm); <2 MV/cm (@100 μm)	3.5 kV/cm (@ 2600 μm)

Table 10.1 Characteristics of four operational coherent THz radiation sources.

The four FELs listed in Table 10.1 have evacuated beam transport systems which can steer the beam to one of many experimental stations. Each station is typically instrumented for a different type of experiment at any given time. Some experimental setups remain in place for a few days, others for years.

Very few experiments can be done with only equipment supplied by visiting experimenters. Thus, to be productive a FEL user facility must provide an astonishing variety of support equipment. This equipment ranges from standard laboratory items such as hand tools, multimeters, and oscilloscopes to somewhat more specialized items such as lenses, filters, mirrors, optical tables, mounting hardware, cryogenic detectors, acousto-optic modulators, cryostats, etc. However, far beyond these things, the productivity of the FEL User facilities at Stanford, UCSB, and in the Netherlands has been vastly improved by the provision of many specialized items or systems. These include high resolution FTIR, tunable Ti:Sapphire lasers, regenerative amplifiers, and OPOs which can be synchronized to the FEL pulses, high-resolution monochromators with photomultiplier tubes or CCD cameras, high-field magnets with optically accessible variable-temperature bores, and specialized sample preparation areas. The list can be extended, but it is already long enough to illustrate the often-overlooked point that the investment in facilities to make effective use of the FEL beam is comparable to the investment in the FEL itself.

We now describe in more detail each of the three FEL user facilities listed in Table 10.1. The ENEA Compact FEL is a prototype source, and is discussed in Section 10.3.

1) FELIX

The free-electron laser FELIX, located in the Netherlands at Rinjhuisen, presently covers the spectral range from 1.2 – 100 THz (40 – 3300 cm^{-1}). The output consists of a few-μs long burst (the macropulse) of micropulses. The maximum macropulse repetition rate is 10 Hz while the micropulse repetition rate can be either 25, 50 or 1000 MHz. For experiments that are very susceptible to sample heating, a single micropulse can be sliced out of the pulse train using a fast optical switch. Continuous tuning over an octave is possible in less than a minute. Optical pulses of only 6 cycles, corresponding to a pulse duration of 200 fs at 1000 cm^{-1}, and with peak intensities in excess of 100 MW, can be produced. The maximum micropulse duration is about 100 cycles, which results in a minimum bandwidth of 0.4% (FWHM). The temporal and transverse beam profile are close to being transform- and diffraction- limited.

An evacuated transport system is used to direct the optical beam of the FEL to a diagnostic and beam-handling station from which it is further transported to any of the nine user stations, many of which are equipped with dedicated experimental setups detailed below.

The mode of operation is comprised by two 8-hour shifts per day, from 8:30 a.m. until 4:30 p.m., and 5:00 p.m. until 1:00 a.m., allowing half an hour before each shift for setting-up and optimization of the laser at the requested ‘workpoint,’ i.e., wavelength range and micropulse repetition rate. Under normal running conditions, little interference by the operator is required during the shift. This is a direct result of (a) the reliability of the FEL and (b) the effective computer control the user has over the main characteristics of the laser.

A number of user groups have installed dedicated semi-permanent experimental setups at the facility. For example, the installation of a high-resolution, Fourier Transform Ion Cyclotron Resonance (FTICR) mass-spectrometer, funded by the National Science Foundation in the USA, in collaboration with user groups from the University of Florida and the National High Magnetic Fields Laboratory in Tallahassee, was recently completed.

Apart from the versatile FEL-based mid- and far-IR source, the facility includes the following ancillary equipment:

- A 45 T pulsed-field magnet with flow cryostat. The field can be swept over as much as 10 T during the macropulse of FELIX.
- Two permanent setups for degenerate four-wave mixing experiments (pump-probe, transient-grating, photon-echo) operational in the MIR regime between 3 and 20 μm as well as in the FIR regime from 20 μm up to 250 μm. For pump-probe experiments, using a special compensation technique to suppress the noise due to amplitude fluctuations of the FEL, a resolution in transmission change of $O(10^{-4})$ is achieved.
- A number of external lasers: a ps Nd:YLF laser, a ps Nd:YAG laser, Nd:YAG pumped ns dye lasers, a 25-fs Ti:Sapphire-laser and two -laser-based optical parametric generators, one covering the UV and one the near- and mid-IR regime. As good time resolution is a critical issue in 'two-color' experiments, the short-pulse lasers are all synchronized to the FELIX master clock (jitter ≈ 1 ps).
- A FTICR mass spectrometer, which will be used to obtain IR spectra, and thereby structural information, of large (bio)molecules and clusters by monitoring their dissociation after irradiation with FELIX. The apparatus is now operational in its basic configuration, but will be extended with an ion guiding system shortly to enable the use of a variety of ion sources. Funding has recently been obtained to upgrade the setup in order to allow full control of the experiment via the internet.
- Within the in-house research group "Molecular Dynamics" there are several molecular beam machines operational that enable mass-selected infrared spectroscopic studies of gas-phase molecules, clusters and cluster complexes.
- Several flow cryostats and a bath cryostat with a 16 T superconducting coil.
- A Fourier Transform Infrared (FTIR) spectrometer (50 – 7000 cm^{-1}, 0.1 cm^{-1} resolution) for sample characterization.
- A user interface for beam control and diagnostics: wavelength, spectrum, power, polarization, and pulse slicing.

All the aforementioned infrastructure is available to external users, although sometimes on the basis of a collaboration with the in-house users.

One measure of the integrated scientific productivity of FELIX is its total output of 250 refereed papers, of which 105 papers are at > 20 THz, 75 at < 20 THz and the remaining 70 cross the 20 THz border.

Recently NWO, the major Dutch research funding agency, granted a proposal valid for 5000 kEuro to expand the facility with a new FEL which will be set up in such a way that intra-cavity experiments can be performed, enabling optical studies on molecules and cluster materials throughout the infrared spectral region with unprecedented photon flux. The Free-electron Laser for Intra Cavity Experiments

Figure 10.1 FELIX. Image courtesy of Lex van der Meer.

"FELICE" will generate pulsed infrared radiation tunable in the 3 to 100 μm region, with an intra-cavity energy of some 10 J in a μs duration burst of picosecond pulses. Two dedicated experimental setups, a state-of-the-art FTICR mass spectrometer and a pulsed molecular beam apparatus will be installed inside the optical FEL cavity. Construction of FELICE started a year ago, and will take about three years to be completed. FELICE will be set up with the possibility of full user-control, and the intra-cavity experimental setups will largely be remotely controlled. Interleaved operation between the on-going user experiments with FELIX and FELICE will be possible, effectively doubling the available beam time at the facility. FELICE is expected to open up numerous new possibilities in the field of atomic, molecular and optical physics and to secure and further strengthen the position as a world-leading IR FEL user-facility.

2) UCSB Center for Terahertz Science and Technology

The UCSB Free-Electron Lasers presently cover the spectral range from 0.12 to 4.8 THz. The UCSB FEL facility is the only one of the three FELs discussed here which operates uniquely in the THz frequency range, and the only one to operate below 1 THz. Unlike almost every other FEL in the world, the output consists of a pulse which is a few μs in duration and has no "micropulses." For most experiments, this is a quasi-cw pulse. For experiments which require shorter pulses, a "pulse slicer" has been built which can slice out pulses with continuously variable duration between a few ps and 3.5 ns. The peak power can be in excess of 5 kW. The maximum repetition rate is 7.5 Hz. The transverse beam profile is close to diffraction-limited.

The FELs are tuned by varying the voltage on the terminal of an electrostatic accelerator between 2 and 6 MeV. The accelerator, manufactured by NEC, operates on a principle similar to the familiar Van de Graaff accelerator, with the belt replaced by "pelletron" chains. The electron beam is controlled by a hot-cathode electron gun, which emits 2 A when it is turned on. The electron beam is currently directed to one of two fully operational wigglers, one for lower and one for higher frequencies (see Table 10.1). A third wiggler, designed to extend the frequency range to 10 THz, has been built and has lased. Its use requires extremely fine control over the electron beam. An upgrade to the control system, funded by the NSF, will make the third wiggler, and the entire system much easier to use.

The NEC accelerator and the electronics inside of it are extremely reliable—it recently operated for more than 1 year without opening, and typically operates more than 2000 hours/year. The entire FEL can be operated at any time of day or night by a graduate student or post-doctoral researcher who has been properly trained by the technician who maintains the facility. That being said, the technician is usually desired for experiments that require extensive frequency-tuning.

An evacuated transport system is used to direct the optical beam of the FEL to a diagnostic and beam-handling station from which it is further transported to any of a dozen user stations. Many of these are equipped with specialized, quasi-permanent apparatus, as detailed below.

The UCSB FELs are co-located with world-class semiconductor fabrication and processing facilities. A tremendous synergy has developed among local researchers using the UCSB FELs and local semiconductor materials scientists. This synergy has led to great productivity by local scientists using the UCSB FELs, and has in addition attracted many collaborators from both within and outside of the U. S.

Apart from the FELs, the facility includes the following permanent setups and ancillary equipment:

- A THz electro-optics setup. This setup is used to investigate the response of samples at visible and near-IR frequencies to intense THz radiation. The setup includes an Ar^+ laser, a cw-Ti:Sapphire laser (tunable ~700 – 1000 nm), an acousto-optic modulator to overlap Ti:Sapphire pulses with the FEL pulses, a closed-cycle refrigerator (10 – 300 K), a 0.75 m monochromator with photomultiplier, a smaller monochromator with intensified CCD camera, a wavemeter, and a variety of optics for optical and THz radiation.
- The pulse slicer setup. Pulses are sliced using Si switches activated by intense pulses of near-IR radiation. The pulses to activate the Si switches are generated by a regeneratively-amplified Ti:Sapphire laser, which generates 10 mJ, ~150 fs pulses at a 10 Hz repetition rate. The regenerative amplifier is pumped by a mode-locked Ti:Sapphire laser. The output of the pulse slicer can be directed into the bore of a compact 7 T superconducting magnet that will accept a tightly-focusing ~f/2 beam.
- A 12 T split-coil magnet with variable-temperature insert (1.5 – 300 K)
- A setup for measuring THz-induced semiconductor transport.
- A continuous-wave molecular gas laser which can be coupled into the beam transport system.
- A time-domain THz spectrometer which uses the oscillator from the regenerative amplifier as its pump.
- A Bruker IFS-66v FTIR spectrometer.
- Liquid-He cooled composite bolometers (~1 ms rise time) and hot-electron bolometers (~200 ns rise time)
- Wire-grid polarizers, variable waveplates, variable attenuators based on crossed polarizers, profilers for expanded and focused THz beams, high-pass filters with high contrast for harmonic generation studies.
- A probe station for testing electrical devices.

All the aforementioned infrastructure is available to external users. At this point, all external users by necessity collaborate with local users.

One measure of the integrated scientific productivity of the UCSB FELs is the more than 125 refereed scientific papers published using its output. All of these papers involve frequencies between 0.3 and 4.8 THz.

Recently, the NSF granted a ~$500,000 proposal to enhance the user-friendliness of the UCSB FELs. The proposal consists of two components. One is to enhance the control system to make it more stable, have higher resolution, lower noise, and much-enhanced user-friendliness. The second component is to injection-lock the UCSB FELs to low-power, tunable sources with very narrow linewidth. The second component requires significant research and development. Other possible enhancements to the UCSB FELs include mode-locking and cavity-dumping (demonstrated, but not currently user-friendly).

More than two dozen alumni have completed Ph. D. or post-doctoral research in the last dozen years using the UCSB FELs as a primary research tool. They are now widely distributed across the U. S. and other nations.

The UCSB FELs do not currently have funding as a user facility. The entire facility is, at this time, operated with only two permanent technical staff members. Staff salaries and operating costs are supported by charging grants from local and visiting scientists for THz beam time. The FEL User's lab is entirely staffed by graduate students and post-doctoral researchers. External collaborators are welcomed, encouraged, and often funded by grants held by local PIs. However, the current necessity to charge for beam time, as well as the absence of permanent staff devoted to helping external users with their experiments, are barriers which prevent the optimal utilization of this unique resource in a wide variety of fields by a wide range of investigators.

Figure 10.2 (left) Two free-electron lasers driven by a 6 MeV electrostatic accelerator in a ~1300 ft^2 vault. (right) The Center for Terahertz Science and Technology at UCSB.

3) The Stanford Picosecond FEL Center

The Stanford Picosecond FEL Center presently covers the spectral range from 3.75 – 20 THz, and 25 – 100 THz with two different FELs. A broad-band transition-radiation source is under construction, which is expected to generate half-cycle pulses with bandwidths in excess of 1 THz. The Stanford FELs are powered by a *superconducting* radio-frequency linear accelerator. Like all FELs powered by RF linacs, the output consists of bursts of micropulses. In the case of the Stanford FEL, the macropulses are 5 ms long (as opposed to 5 μs at FELIX), with micropulses variable in duration from 2 – 10 ps on the Far-IR FEL. The macropulse repetition rate is 20 Hz, while the micropulses are spaced by 84.6 ns. FELs with superconducting linacs, with their lower RF losses, are capable of higher macropulse durations and average power. For example, the FEL at the Jefferson Labs in Virginia, using a superconducting linac with electron beam recirculation, has achieved a continuous train of micropulses with kW level average power in the mid-IR.

To provide experimenters with precise and stable beams, feedback loops have been installed to control the optical pulse wavelength and amplitude. Variations in wavelength can be reduced to less than 1 part in 10,000 rms, a small fraction of the transform-limited linewidth. Amplitude variations are reduced to less than 2% rms. The micropulse width can be varied to suit the experiment. Pulse lengths from 700 fs to 3 ps have been delivered to users of the mid-IR FEL. Since the beam is transform-limited the spectral width varies accordingly. A real-time diagnostic display in every lab room shows the pulse length, spectrum, power, beam position and pointing, all of which are critical for crossed-beam nonlinear optics experiments.

There are 10 experimental rooms at the Stanford Center, each provided with an optical bench and some basic electronics. All but 4 rooms have the FIR FEL transported to them at this time. In addition, the following specialized equipment is available:

- A generic pump-probe setup for mid-IR experiments. Optics and data acquisition are provided. The user need only provide the sample and perform final alignment.
- A high resolution FTIR.
- Tunable Ti:Sapphire lasers, regenerative amplifiers, and OPOs which can run in either a picosecond or femtosecond mode while synchronized to the FEL micropulses,
- A scanning near-field infrared microscope.
- An external optical cavity for pulse stacking and cavity ring-down spectroscopy.
- A biomedical laboratory for sample preparation.
- A 9 T magnet with an optically accessible variable temperature bore.
- An FTIR with 0.1 cm^{-1} resolution and step-scan capability.

Recently, funding has become available to install a beamline to deliver coherent transition radiation as an intense (when focused to a 1 mm spot electric fields in the 1 MV/cm and magnetic fields in the 1 T range will be produced) broad-band THz (as a half cycle pulse) source to users. As this pulse will be generated by the same electron beam that powers the FEL, synchronization should be extremely good, allowing for precise multiple color pump-probe or pump-pump experiments. As a result of pressure to provide more beam time, optical and electron beam switching techniques have been developed, which nearly doubled the effective beam time of the facility. It is possible to switch the macropulse between two widely separate and independent accelerator states, which leads to widely different and independently adjustable FEL states. Delivering the two states to two experiments allows each to have full control over its beam and its parameters. It is very much as though there are two separate FELs and accelerators.

The parameters of the Center's FEL and THz beams are presented in Table 10.2.

	Mid-IR (STI)	Far-IR (FIREFLY)	Transition Radiation THz Source*
Frequency	25-100 THz	3.75-20 THz	1-10 THz
Micropulse Width	0.7 – 3 ps	2 – 10 ps	1.0-0.1 ps
Micropulse Repetition Rate	84.6 ns	84.6 ns	84.6 ns
Macropulse Width	5 ms	5 ms	5 ms
Macropulse Repetition Rate	20 Hz	20 Hz	20 Hz
Micropulse Energy	1 μJ	1 μJ	1–10 μJ
Average Power	10 W	10 W	10-100 W
Spectral Bandwidth	Transform-Limited Gaussian	Transform-Limited Gaussian	"HCP"
Spectral Stability	0.01 % rms	0.01 % rms	

Table 10.2 Parameters of the Stanford FELs and the THz transition radiation.
*under construction.

The Stanford Picosecond FEL Center has generated roughly 175 publications in medical science, biology, solid state and surface science, and molecular materials and chemistry. In addition,

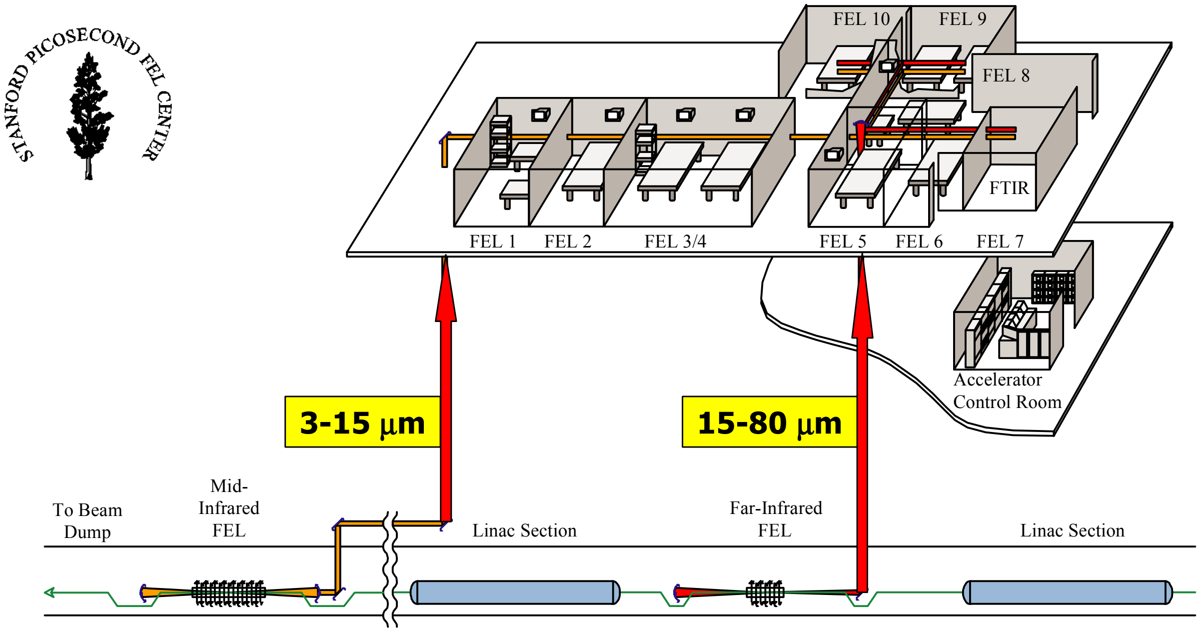


Figure 10.3 The Stanford Picosecond Free-electron Laser Center.

roughly 86 publications on FEL science and 18 about the center itself have been generated. Of these publications, the vast majority have used the original mid-IR FEL.

10.2.2 Compact accelerator-based sources, including "table-top" sources

There also exist accelerator-based THz sources, some of which can fit on or scale to the size of a table-top. Many of them, however, have not been optimized for a specific experiment. They have been proof-of-principle experiments and should be looked upon as ideas that can be specified and/or tailored for particular types of experiments. Funding must be provided for further development work on electron beam based sources as there is great potential to provide users with large amounts of powers in a small size. The RF-gun derived sources (1 and 2) will benefit from ongoing cathode and design work (especially if guns can be made superconducting). Laser wakefield accelerators are actively being researched as possible alternative solutions for high energy systems and are still in the early stages of development. Some of these sources would be able to be designed to also produce half-cycle pulses.

The modulator, klystron, waveguide, cooling, magnets, electron gun, accelerating structure, and all other peripheral accelerator components could be fitted into the space of 3 meters cubed. The Frascati source and the ANL source are examples of this compactness. Although they are not quite this small in the Frascati and ANL prototype systems, in the future everything could be placed into the size described. To eliminate the worry of neutron production, the electron beam energy is kept under 10 MeV. If the electron beam is interlocked to always be directed into a dump with a permanent magnet, the ionizing radiation is contained.

Wavelength	1000 µm – 60 µm
Frequency	0.3 THz - ~5THz
Pulsewidth	1-10 ps
Rep rate	6 Hz (due to timing system)
Pulse energy	depends on mode of operation
Average power	Worst case scenario – thermionic mode; 10 Hz rep rate of the RF; 100 microamps at 2 MeV = 2 mW
Peak power	1 MW
Peak field	depends on mode of operation

Table 10.3 Parameters of the ANL table-top THz source.

This work supported by Contract No. W-31-109-ENG-38 between the United States Government and Argonne National Laboratory and under the Contract Center for Plant Health Science and Technology by the United States Department of Agriculture-Animal and Plant Health Inspection Service (USDA-APHIS) Interagency Agreement No. 0381000826-1A.

1) The coherent prototype radiator at Argonne National Laboratory (ANL).

This source can employ three different cathode types – thermionic, photo-gated thermionic, or photocathode. Even at a low RF repetition rate using a normal conducting accelerator, relatively high average powers are achievable if a laser gates the thermionic cathode. The electron beam pulse length changes depending upon the cathode mode of operation and the degree of compression. Although this source is a prototype, it can be easily adapted to a specific experiment and packaged into a small space. Table 10.3 discusses the present mode of testing. The repetition rate, pulsewidth, average and peak power can be improved significantly.

*2) Frascati FEL CATS – **Prototype** facility.*

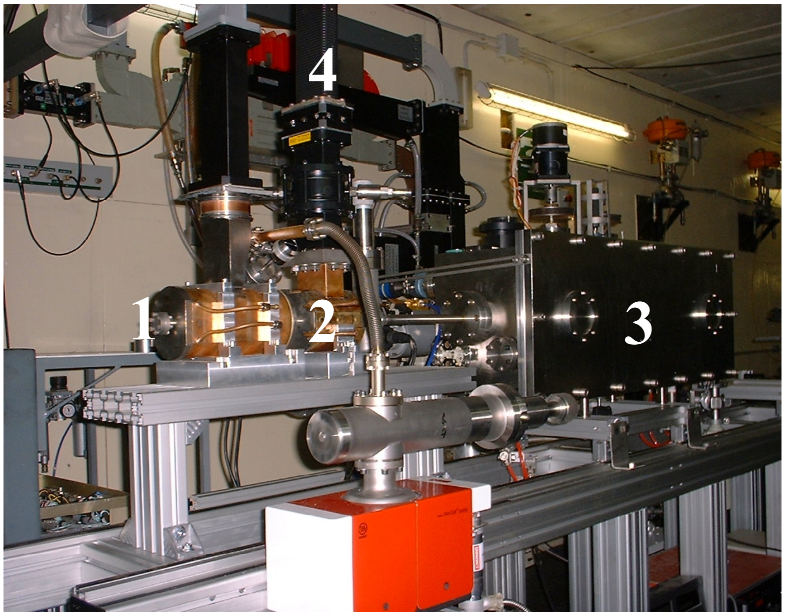


Figure 10.4 Frascati FEL CATS: 1) Linac, – 2) PMD, 3) Vacuum chamber/undulator, 4) RF System. Photo courtesy of G. P. Gallerano.

	ENEA Compact FEL
λ (µm)	2000 - 3500
ν (THz)	0.09 – 0.15
Micropulse width	50 ps
Micropulse Rep Rate	3 GHz
Micropulse Energy	0.5 µJ
Macropulse Widh	4 µs
Macropulse Rep Rate	1 -10 Hz
Average Power	4 – 40 mW
Peak Power	10 kW (@ 2600 µm)
Peak Field	3.5 kV/cm (@ 2600 µm)

Table 10.4 Parameters of Frascati FEL CATS.

A proposal for a full user facility is pending. FEL-CATS utilizes a high-efficiency generation scheme based on the mechanism of coherent spontaneous emission, which allows operation in the frequency range between 70 GHz and 0.7 THz. The electron beam energy is tunable between 2 and 3 MeV. The ENEA Compact FEL has been extensively used for the irradiation ob biological samples in the frame of the European project THz-BRIDGE. The electron beam line has also been used to drive a Cerenkov FEL and a Metal Grating FEL (see below)

3) Modulation of the drive laser pulse for a photocathode-RF gun.

Collaboration between University of Maryland (P. O'Shea and Jonathan Neumann) and the Brookhaven National Laboratory Source Development Laboratory (X Wang, B. Sheehy and G.L. Carr): This is a proof of principle experiment. This device uses a laser to generate a bunch train of electrons through photoemission. Each bunch is about a picosecond long, and they are separated by about a picosecond. An electron accelerator takes these short bunches and accelerates them up to nearly the speed of light. After the electron beam reaches approximately 70 MeV, it is intercepted by a mirror. When the environment around the beam changes from vacuum to metal, transition radiation is emitted. Because of the way the electrons are bunched, there is strong emission in the terahertz frequency range. The frequency spectrum can be controlled by controlling the way the electrons are initially bunched. The result is a tunable terahertz source that could be used for a wide variety of additional experiments. Electron beam energy was between 70 – 72 MeV.

Wavelength	450-100 μm (easily)
Frequency	500 GHz- 3 THz
Pulsewidth	several picosecond electron pulse; light pulse length was not measured
Rep rate	2.5 Hz
Pulse energy	Data undergoing analysis and results will be presented at the 2004 International Free-Electron Laser Conference Trieste Italy.
Average power	Data undergoing analysis and results will be presented at the 2004 International Free-Electron Laser Conference Trieste Italy.
Peak power	Data undergoing analysis and results will be presented at the 2004 International Free-Electron Laser Conference Trieste Italy.
Peak field	Data undergoing analysis and results will be presented at the 2004 International Free-Electron Laser Conference Trieste Italy.

Table 10.5

4) Source Development Laboratory, Brookhaven National Laboratory (H. Loos, B. Sheehy, X. Wang, G.L. Carr).

Linac-based source of coherent THz pulses, operating at the NSLS. Parameters summarized in Table 10.6. Charge per bunch up to ~700 pC, typical bunch length before compression ~5 ps and the repetition rate ~10 Hz. Bunch is compressed to ~300 fs rms. Degree of compression can be varied. Reducing charge should allow for even more compression (100 fs and possibly shorter). Electron bunches produce single-cycle coherent THz as transition radiation or dipole radiation. Demonstrated energy per pulse of ~100 μJ. and E-field to > 1 MV/cm. Method could be improved to produce shorter electron bunches for higher pulses energy and E-field, and broader spectral range. Pulsed laser for linac photocathode provides synchronized IR pulses for electro-optic coherent detection of THz pulses (demonstrated). This is a linac-based source but could be made smaller if need be.

Wavelength	0.1-2 mm
Frequency	Broadband, 0.2 to 2 THz.(present), 5 THz plausible
Pulsewidth	Transform limited ≤ 50 fs
Rep rate	1-10 Hz, can be higher with SC linac
Pulse energy	100 μJ (demonstrated)
Average power	$10^{-4} - 10^{-3}$ W (for 1 – 10 Hz)
Peak power	10^{8} W
Peak field	> 1 MV/cm

Table 10.6

5) Advanced Energy Systems

AES has submitted an NSF Phase II SBIR (first week in February) to develop a multi-watt (50-100 W eventual goal; 5 W in this initial prototype), tunable, compact THz source.

6) Laser wakefield

Intense THz Radiation from ultra-short electron bunches produced by a laser wakefield-based linac at Lawrence Berkeley Laboratory. This source, shown schematically in Figure 10.5, is based on the production of ultra-short (< 50 fs rms), high charge (0.3 – 5 nC) relativistic electron bunches by using a laser excited plasma wave with large enough amplitude to trap background electrons and accelerate them in mm distance to 10's of MeV. As the electrons exit the plasma, a burst of transition radiation is produced. The source performance is controlled by the electron bunch properties and the density and transverse size of the plasma at the exit boundary. Present source characteristics are listed in Table 10.7. The THz radiation is intrinsically synchronized with an external laser and experiments are underway to measure the THz pulse structure with electro-optic sampling. Time averaged spectra have been measured and show that the spectrum with the present configuration is centered around 2 THz. Whereas presently energy

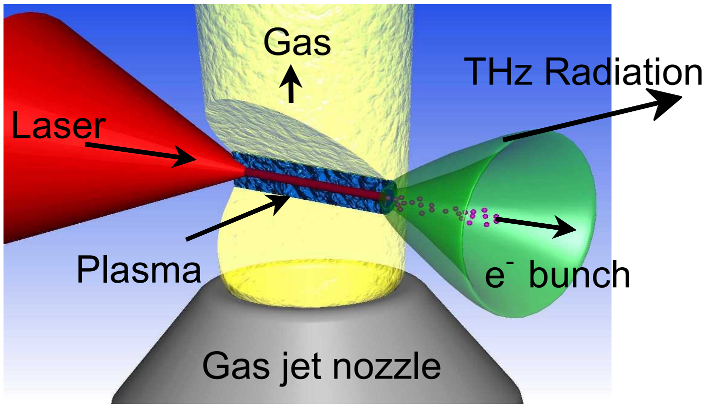


Figure 10.5 Schematic diagram of laser wakefield acceleration.

levels on the order of 0.1 μJ/pulse have been collected, modeling indicates that significantly higher powers can be achieved by optimizing the plasma properties (transverse size and longitudinal profile) and could be as high as 100 μJ/pulse [Ref: W.P. Leemans et al., Phys. Rev. Lett. 91, 074802 (2003)]. Further progress on the laser driven accelerator performance is underway, including the production of quasi-monochromatic (few % energy spread) relativistic electron bunches (100 MeV), which will lead to intense radiation emission from conventional transition radiation foils.

Wavelength	0.01 – 1 mm
Frequency	Peaked in 1 – 10 THz range.
Pulsewidth	Transform limited ≤ 50 fs
Rep rate	10 Hz
Pulse energy	0.10 (present) – 100 μJ (predicted)
Average power	$10^{-6} - 10^{-5}$ W
Peak power	$10^{6} - 10^{8}$ W
Peak field	0.1 – 5 MV/cm

Table 10.7

7) Smith Purcell – Metal Grating.

See Figure 10.6. ENEA- ESSEX-OXFORD collaboration. Wide tunability (700 mm to 3.6 mm) by varying the light collection angle. Low power device (100 mW) useful as electron beam diagnostics. Coherent spontaneous emission due to the short bunch duration (14 ps).

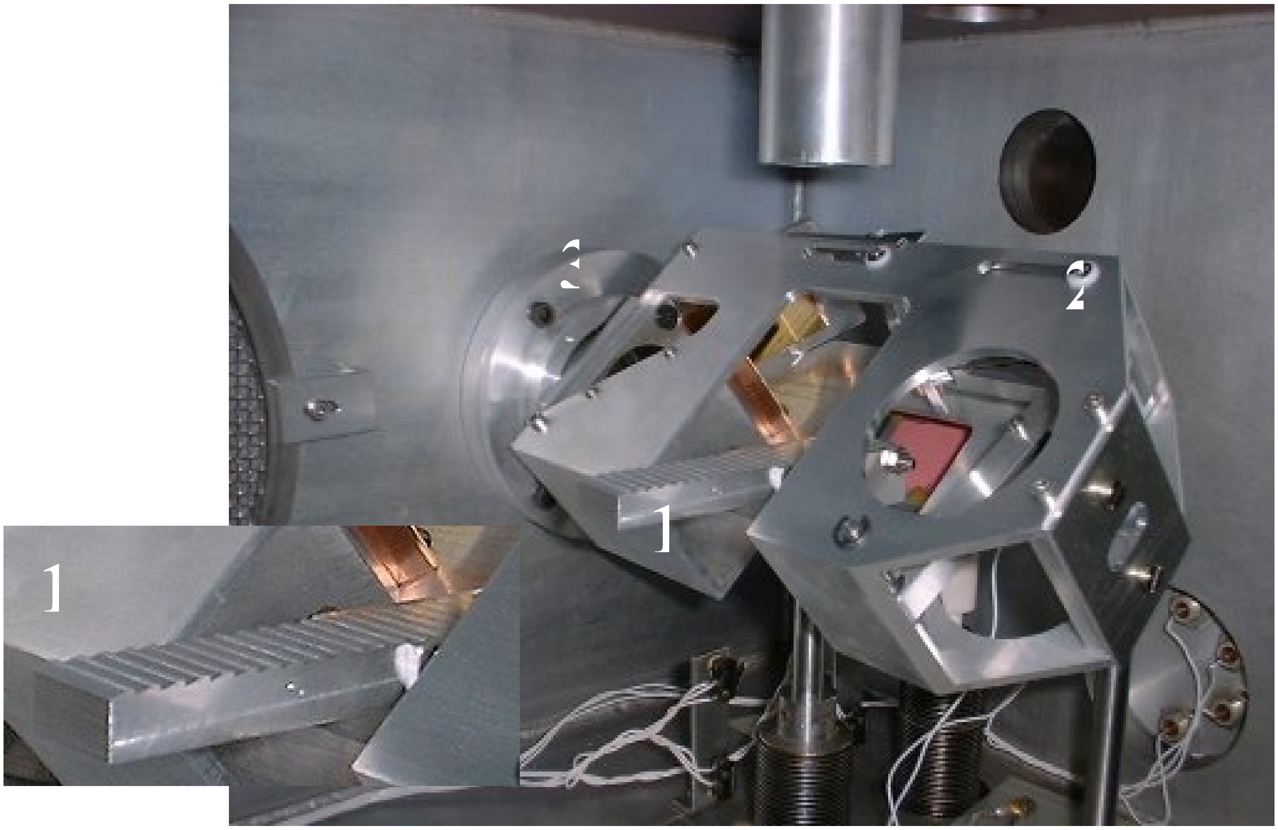


Figure 10.6 1: Grating, 2: Variable angle light collecting system, 3: Light output. Figure courtesy of FEL ENEA-ESSEX-OXFORD.

8) Smith-Purcell and a cw electron microscope gun

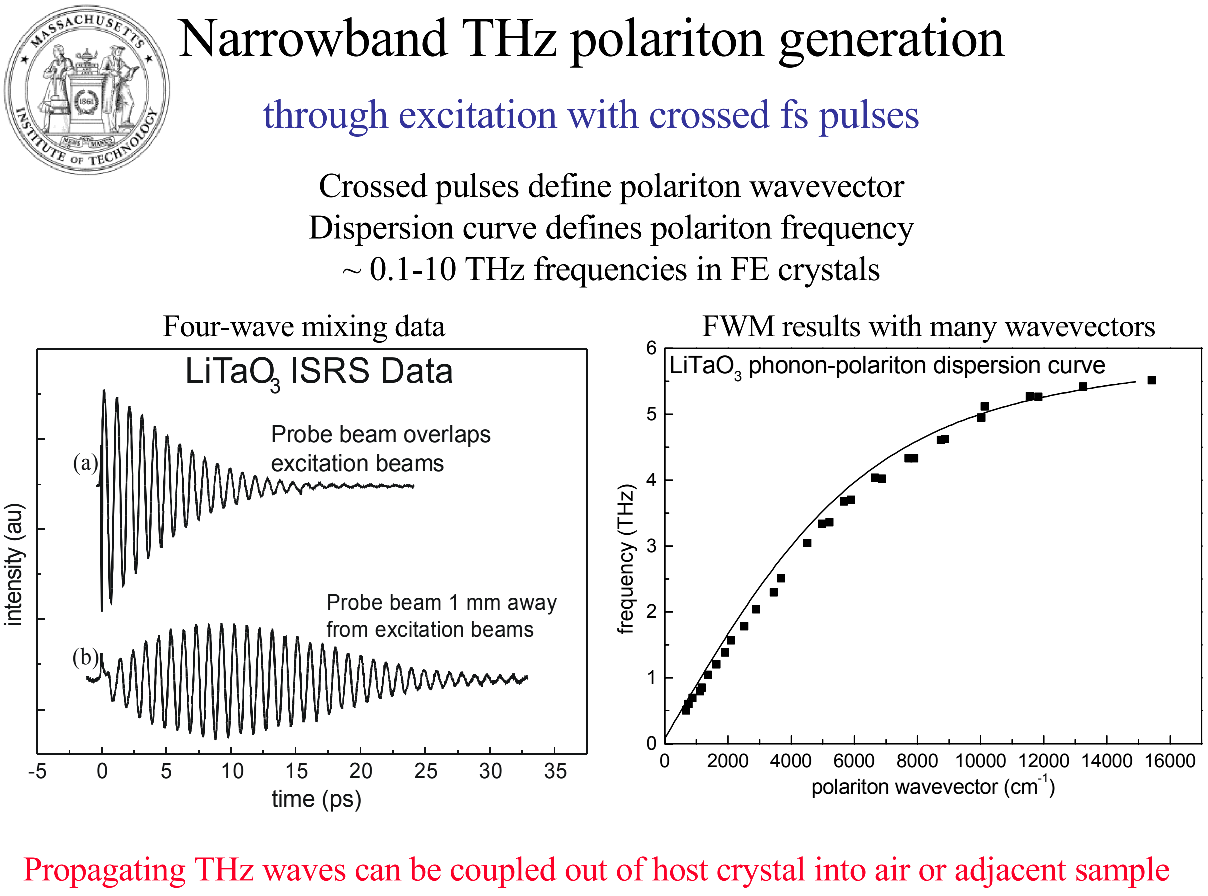
Recently, a tunable THz source (0.3 to 3 THz) based on Smith-Purcell and a cw electron microscope gun has been developed by Michael Mross, Thomas H. Lowell at Vermont Photonics Inc., in collaboration with the Dartmouth group and Maurice F. Kimmitt of the Univ. of Essex

10.2.3 Table-top narrow-band THz sources based on ultrafast lasers

1) 'Polariton' THz Sources

This technique, developed by Nelson's group at MIT, is based on femtosecond optical excitation of lithium niobate or tantalate, or other ferroelectric crystals that support THz phonon-polariton modes. For narrow-band responses, a pair of femtosecond excitation pulses is crossed inside the crystal, creating a short-lived optical interference pattern, and they generate THz waves whose wavelength is given by the interference fringe spacing. The waves are phonon-polaritons, admixtures of transverse optic phonons and electromagnetic waves, with frequencies typically in the range of about 0.3 – 6 THz. The generation mechanism can be thought of as a combination of impulsive stimulated Raman scattering and optical rectification. The THz waves propagate primarily perpendicular to the bisector of the crossed pulses, though there is a small forward wavevector component as well. It is not difficult to couple the waves out of the generation crystal, so this is a source of rather intense THz radiation.

The frequency is tunable by changing the angle between the excitation pulses. As a practical matter, this is now simple to do using diffractive optics, i.e., using a phase grating pattern to



Narrowband THz polariton generation

through excitation with crossed fs pulses

Crossed pulses define polariton wavevector
Dispersion curve defines polariton frequency
~ 0.1-10 THz frequencies in FE crystals

Four-wave mixing data

FWM results with many wavevectors

Propagating THz waves can be coupled out of host crystal into air or adjacent sample

Figure 10.7 Table-top THz sources based on polaritons. Courtesy of Keith Nelson, MIT.

create the two beams that are then crossed in the crystal. Not only does this simplify the generation of the two beams and the tuning of the wavevector/frequency, it also greatly narrows the bandwidth if desired by producing many more interference fringes than could be produced by using reflective optics, i.e., a beamsplitter, to produce the two beams which then would be directed through additional reflectors toward the sample. The number of cycles in the THz wave is simply selected by the number of phase mask periods the optical pulse hits.

One of the advantages of using this approach is that the THz waves can be directly visualized and can be further manipulated through the action of additional excitation pulses or through propagation into patterned structures (waveguides, resonators, gratings, etc.) that can be fabricated within the crystals. Note, too, that resonators generate multiple-cycle waves from a single optical excitation pulse. In the simplest form, with crossed excitation pulses in a bulk unpatterned crystal, we can generate THz radiation whose frequency is simply tunable and whose bandwidth is easily adjusted from single-cycle to many cycles. A single focused pulse in $LiNbO_3$, below the damage or white light threshold, produces a THz field level of a few kV/cm within the crystal. Typically, the highest achievable power is limited by white light or damage, not by excitation pulse energy, or more properly, one expands the spot size so as to stay below the thresholds for anything bad. For narrow-band generation, that means that if the wavevector is in the horizontal plane, one expands the vertical size. Often, using a kHz amplified system, the vertical size is about 5 mm or more. Estimates of maximum field strength in future systems range from 10 kV/cm to 1 MV/cm.

2) THz Generation in Poled Ferroelectric Crystals

This technique, pioneered by Norris's group at Michigan, utilizes optical rectification in ferroelectric crystals, most commonly lithium niobate (LN). The basic idea is very simple. An ultrafast optical pulse (typically a few hundred fs) is incident on a crystal of LN. A nonlinear polarization is generated due to the optical rectification effect, which radiates a THz-bandwidth signal. However, the optical pulse travels faster than the THz field inside the crystal, leading to walk-off of the optical and THz beams. In a bulk crystal, this results in single-cycle THz pulses being generated at the front and exit faces of the crystal, and no net polarization radiated from the interior of the crystal. One may exploit the walk-off effect, however, to generate narrow-band or shaped THz waveforms. If the sign of the second-order optical nonlinear coefficient is reversed after each walk-off length, then the optical pulse will generate a sequence of THz cycles. If the ferroelectric domains are periodic, as in periodically poled lithium niobate (PPLN), then a narrow-band harmonic THz wave can be generated. An illustration of this process, along with a typical THz waveform generated this way, are shown in Figure 10.6.

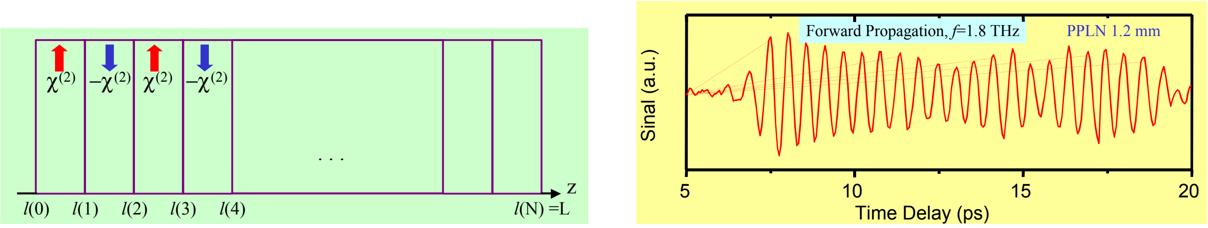


Figure 10.8 Schematic description and measured pulse generated in PPLN. Image courtesy of Ted Norris, University of Michigan.

The PPLN THz source is easily tunable, by poling the LN crystal with a laterally chirped period; simply moving the crystal perpendicular to the optical beam tunes the THz waveform. The relative bandwidth is also easily engineered via the number of poled domains. Data showing the tuning range achieved with a single crystal is shown in Figure 10.9.

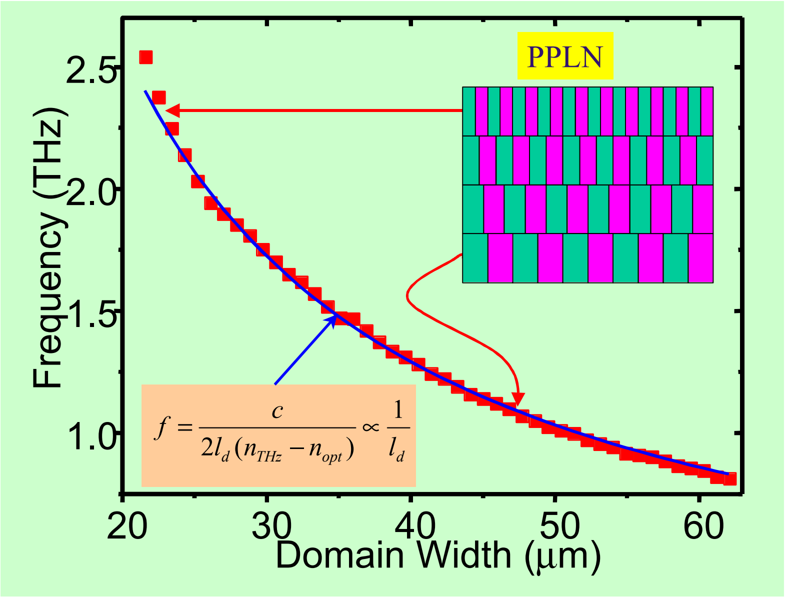


Figure 10.9 Schematic description and measured pulse generated in PPLN. Image courtesy of Ted Norris, University of Michigan.

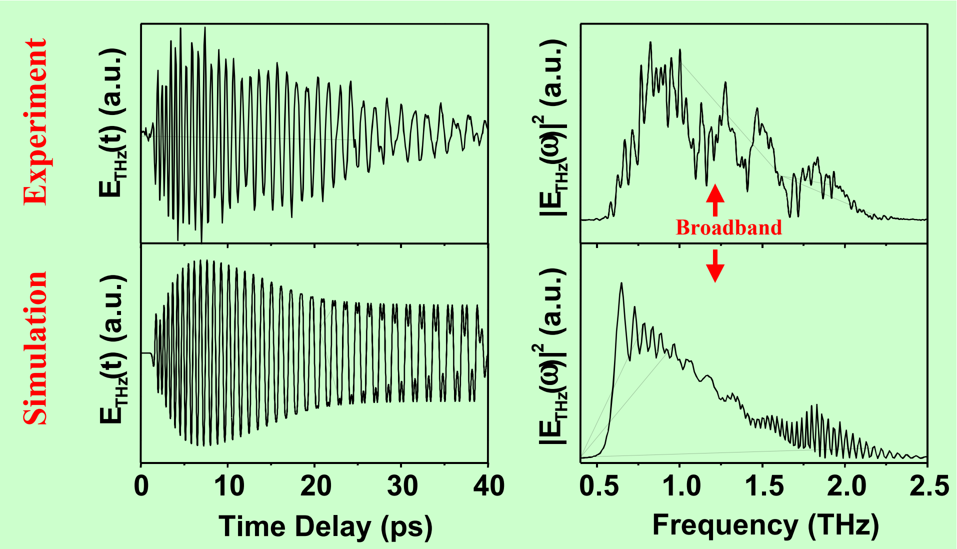


Figure 10.10 Example of downchirped pulse generated in PPLN. Image courtesy of Ted Norris, University of Michigan.

While PPLN is useful as a source of tunable THz pulses of adjustable bandwidth, the use of non-periodically poled LN enables one to generate shaped THz waveforms. In fact, almost arbitrary waveforms may be generated (in the language of pulse-shaping, waveforms with complexity > 100 can be obtained). As an example to show proof of principle, we show in Figure 10.10 data for a downchirped THz pulse.

Such THz sources are expected to be useful for the study of THz coherent control of excitations in molecules (e.g. rotational states), atoms (e.g. Rydberg wavepackets), and semiconductors (e.g. excitonic wavepackets). The field strengths which can be obtained using kHz laser excitation will be up to 100 kV/cm, sufficient for strong-field experiments on these systems. Table 10.8 compares characteristics of these table-top narrow-band THz sources.

	Polaritons (demonstrated)	**PPLN (demonstrated)**
λ (μm)	60-1500	120-3000
ν (THz)	0.2-5	0.1-2.5
Pulse Width	1-many cycles	1-100 cycles
Rep Rate	1 kHz	250 kHz
Pulse Energy	1 nJ	
Average Power	1 μW	<5 mW
Peak Power	< 1 kW	
Peak Field	< 1 kV/cm	<300 V/cm

Table 10.8 Characteristics of typical table-top narrow-band THz sources.

10.3 Recommendations

The barriers to entry into nonlinear and non-equilibrium THz experimentation are, at present, formidable. One needs either access to a Free-Electron Laser or an expensive table-top source .

Although Free-Electron Lasers are relatively small operations (compared to synchrotrons, neutron sources, or the National High Magnetic Field Laboratory), they are too large to support with single investigator grants. The current reliance on multiple single investigator grants limits the breadth of utilization and restricts opportunities for new experiments, forcing many investigators to travel to the Netherlands to use FELIX. Such transatlantic collaboration is to be encouraged, but the Atlantic Ocean is also a formidable barrier for U. S. investigators and inhibits expansion of experimentation in this exciting field. Through a THz User's Network, funding for operating costs and a small number of senior scientists dedicated to supporting users at the existing U. S. THz Free-Electron Lasers would greatly reduce the barrier to entry into this fascinating field.

Table-top sources are extremely promising, but are currently only available to their builders. Their utility for new experimentation will be dramatically enhanced by funding for investigators who have built these sources, have them working well, and are willing to devote a significant fraction of THz beam time to outside users, as nodes in the THz User's Network. Funds for a post-doc or staff scientist to assist outside users with experiments will be essential to making the facilities fully functional. Continued funding of source development, with an eye to eventual commercialization, is important to the growth of THz experimentation. This funding could go both to academic researchers, and to small companies as SBIR or STTR grants.

Chapter 11: Coherent Half- and Few-Cycle Sources for Nonlinear and Non-Equilibrium Studies

11.0 Executive summary

Numerous scientific applications have been listed in the previous chapters requiring high peak powers in half- or few-cycle broadband pulses. Time-domain spectroscopy has recently had a rapid development in large part due to the commercialization of sub-100 fs pulsed near-IR lasers with sufficient powers to drive THz emitters. The typical peak THz field output is < 10 kV/cm with 1 kHz repetition rates, but fields up to 1 MV/cm are feasible with available table-top laser systems at 10 Hz repetition rates, although these are multi-cycle pulses in the > 10 THz spectral range. Electron beam accelerators have demonstrated outputs of coherent THz half-cycle pulses of high power, and offer opportunities for truly high intensity fields (50 MV/cm) at high (MHz) repetition rates with modest development.

Creating nodes within a THz Network that consist of user facilities centered on flexible and well-run THz sources with a range of sample environments available should be a priority. These centers will enable both expert and novice THz users to perform experiments in this otherwise difficult spectral region by using world-class THz pulse sources, instruments, and expertise of the staff running the centers. The sources will be (from the users' point of view) easier, cheaper, and faster, so they can focus their attention on understanding and interpreting the scientific results.

A combination of new dedicated THz user facilities and clever upgrades (optimization of THz production and user support infrastructure) to existing accelerator and laser-based laboratories will lead to a large and rapid growth of the THz community. Expert and perhaps more importantly novice THz users will be able to count on dependable THz sources and equipment so that they can perform rapid, inexpensive and innovative THz science. This will require support of individual scientists, table-top experiments, centers of excellence, and accelerator-based user facilities, all important nodes on a THz user's network.

11.1 Introduction

Previous chapters in this report have discussed the science opportunities in the area of high-field physics and ultrafast science. These research areas have overlapping requirements for sources in the far-infrared. This brief chapter outlines these requirements, and lists the relevant capabilities of laboratory-based or accelerator-based sources.

11.2 Ultrafast time-domain experiments

Ultrafast broad-band pulses in the far-infrared can probe atomic, molecular and solid-state processes on time scales from a fraction of a picosecond to a nanosecond. Phenomena which have been studied in this way include rovibrational motion of simple molecules, and detailed studies of Rydberg wave packets. Far-infrared sources are particularly valuable for these, because they can induce transitions between closely spaced rotational or Rydberg energy levels.

Time-domain experiments are usually performed using a "pump-probe" technique, where the FIR source must be synchronized with an excitation source. This may also be in the far-infrared, but it may also be in any other wavelength regime where ultrafast processes can be initiated. The typical approach to synchronization is to base both the pump and the probe field on the same laser, using nonlinear wavelength conversion to achieve the desired wavelength range. Here is a wish list of the requirements for time-domain experiments:

Ultrafast Requirements:

- THz pulses, tunable (from 0.1 to 50 THz), ultrafast (50 fs), with synchronized ultrafast (50 fs) pulses from mid-infrared to x-ray frequencies.
- The ability to shape the THz pulse pulses with ~100 features over the pulse
- High repetition rate for improved S/N in spectroscopy experiments (10^{-6} peak field to baseline).
- The ability to couple to excitation pulses to special sample environments: low temperatures, static magnetic fields, high-pressure cells, and very small samples (< 0.5 mm).
- Ultrafast magnetic fields: (>1 T, 100 fs) for investigation of transient magnetic phenomena.
- For electron spin resonance experiments, the ability to create π pulses (10 T, 800 fs).

11.3 High-field phenomena

High-field phenomena can be studied when the amplitude of the applied electric or magnetic field greatly exceeds the internal fields in the system of interest. Examples include strongly driven Rydberg systems, and laser-driven plasmas. Optical laser fields can be produced and focused to field amplitudes that greatly exceed the binding fields of atoms and molecules. Far-infrared sources are weaker, and cannot be focused as tightly because of the diffraction limit. Nonetheless, present sources can still achieve the strong field limit for electronic binding energies below 0.01 Rydberg, and stronger fields may be possible with new sources.

High-field experiments requirements:

- High electric fields: >1 MV/cm (10 – 100 kV/cm required for semiconductors).
- Arbitrarily shaped THz pulses (~100 features), with high-fields, and adjustable for specific experiments. The peak fields required for these experiments are again ~1 MV/cm, if the pulse were transform-limited.
- High repetition rate for nonlinear spectroscopies. This requirement is not needed for high-field atomic or molecular physics experiments.
- The ability to couple the THz pulse effectively to the sample without significant loss.

11.4 Optical elements and diagnostic tools

In addition to the source requirements listed above there is the need to develop THz tools to facilitate experiments in the THz frequency regime in the same way experiments are performed in the visible and infrared. These tools go hand-in-hand with the sources: For example, techniques appropriate for waveguide-based THz are often not applicable to freely propagating sources. High efficiency polarizing beamsplitters and reflecting optics already exist, but improvements would be very helpful in high efficiency detectors, bandpass or neutral density filters, beamsplitters, and devices for adjusting dispersion.

11.5 Sources

Ultrafast and high-field THz sources consist of half- and few- cycle THz pulsed output. These kinds of sources can be classed as electron beam based sources and ultrafast laser-based sources. Typically the electron beam based sources are facility-based, while the laser-based sources are typically table-top and found in single investigator laboratories. Some general characteristics of these kinds of sources are described below.

11.5.1 Electron beam based sources

There are several available and proposed THz sources at various electron accelerators and free-electron lasers in the U. S. In many cases these sources were not originally developed or optimized for THz radiation, but they could provide THz pulses for users with other synchronized beams not readily available in single investigator labs, such as picosecond x-ray beams for probing structural transitions driven by THz pulses. The advantages of coherent synchrotron-based FIR include high brilliance, intrinsic polarization, wide spectrum, and broad temporal coherence, i.e. short pulses. Pulse shaping of the THz pulses has been achieved in storage rings by imprinting a shaped laser pulse profile as an energy modulation on the electron beam (laser slicing) [R. W. Schoenlein *et al.*, Science **287** 2237-2240 (2000)].

Accelerator-based FIR sources have the potential of reaching very high-fields. Fields in excess of 1 MV/cm have been demonstrated in electro-optic sampling experiments at SLAC (Coulomb near-field) and BNL (propagating THz radiation field), and these, or even much higher fields, could be used for high-field THz research. The ultrahigh pulsed magnetic field associated with the relativistic electron beam has also been used for high-field experiments [I. Tudosa, et al., Nature **428** 831-833 (2004)]. Accelerator-based THz sources are also useful for their high average power and broad spectrum for linear spectroscopy and imaging of "difficult" samples, such as with near-field microscopy, samples in extreme conditions, video-rate THz imaging, high photometric accuracy measurements, and samples with complex geometries (such as with many biological samples).

The availability of different experimental environments (high magnetic fields, cryogenic temperatures, high pressures) at user facilities for THz experiments would make it possible to extend the range of research at these sources. User facilities will also be important nodes in a THz Network, with infrastructure to allow easy access, support equipment and personnel, on-site housing, and expertise for THz neophytes so that they may rapidly use THz to advance their particular scientific goals.

We now describe in more detail three types of electron accelerator sources exploiting the power of coherent synchrotron radiation, with specific examples of facilities in development or proposed.

1) Normal conducting Linacs

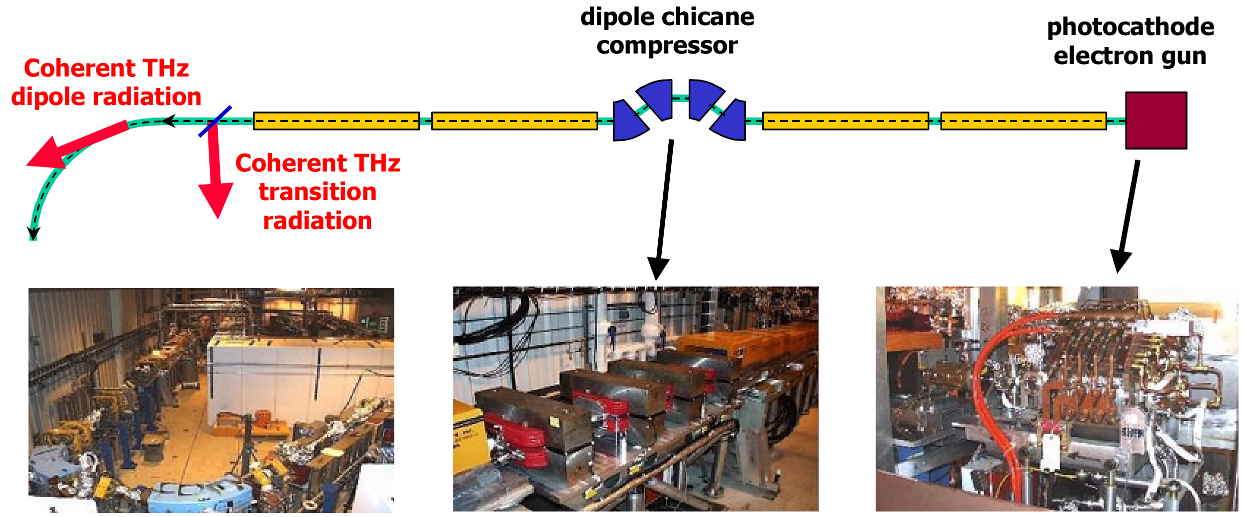


Figure 11.1 Layout of the NSLS Source Development Laboratory LINAC and locations for producing coherent THz radiation. Figure courtesy of G.L. Carr, Brookhaven National Laboratory.

The key ingredient for producing coherent THz pulses from an accelerator is an electron bunch with a density modulation on the same length scale as the desired radiation. FELs induce a periodic density modulation on a bunch by the interaction of the light field and the electrons inside a magnetic undulator, and produce monochromatic light. To produce a single or half-cycle coherent THz pulse, the entire electron bunch must be short (< 1 ps). Several of today's Linacs are capable of producing such short electron bunches. These accelerators typically use photocathode electron guns for producing high-quality, low emittance electron beams. Then, by a technique analogous to chirped-pulse-compression with lasers, the electron bunches are accelerated and compressed, yielding hundreds of pC in a bunch less than 1 mm in length, and in some cases less than 100 μm. The synchrotron radiation produced by such a bunch has many of the attributes of coherent THz pulses produced by laser methods (e.g., photoconductive switches), except that the intensity can be orders of magnitude larger. One example is the NSLS/SDL linac at Brookhaven Lab, where ~100 μJ single-cycle THz pulses have been characterized. When focused, electric field strengths exceeding 1 MV/cm are now achievable. It is worth remembering that an E-field of 3 MV/cm is accompanied by a 1T magnetic field, and these THz pulses can be used for ultra-fast studies of magnetic dynamics.

Linac-based sources offer flexibility in their mode of operation, especially if the spent electrons are not recovered. Because a high energy beam is not needed, energy recovery is probably not an operating requirement. A normal linac can be operated at 10 Hz under these conditions. Since the beam is not stored, greater control over its shape is possible, and in fact the beam can be allowed to strike a metal mirror to produce coherent THz transition radiation, with its unique radial polarization. However, fluctuations in the photocathode laser appear as shot-to-shot intensity fluctuations of a few per cent. For experiments where a higher repetition frequency can be tolerated, it would be advantageous to use a superconducting linac or storage ring. Such accelerators may also offer benefits in the RF stability, helping to stabilize the electron bunch shape and spectral content.

The other benefit of a photocathode gun linac is the intrinsic synchronization of an ultra-fast laser to the electron beam. This synchronized pulsed laser is readily used for coherent detection of the THz pulses by the electro-optic effect in a material such as ZnTe. Coherent EO detection

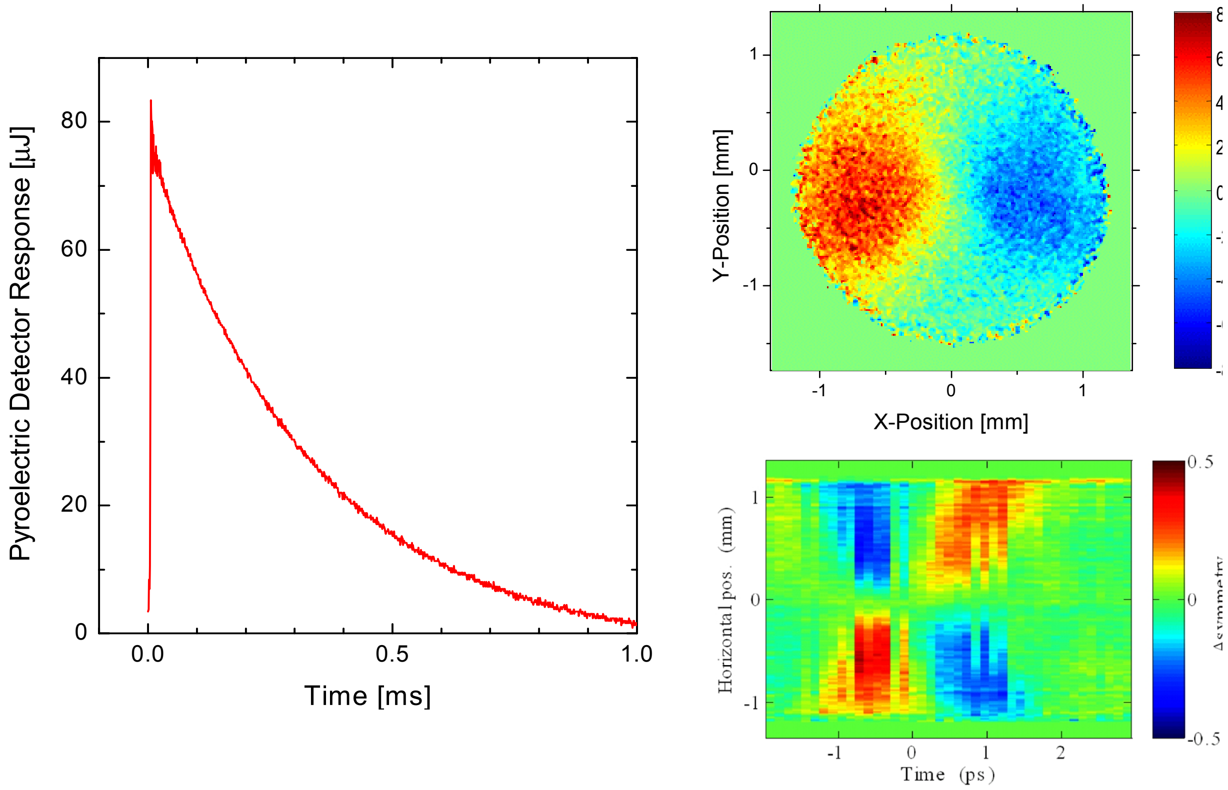


Figure 11.2 Large coherent THz pulse as measured on a calibrated pulse radiometer (left) and images of the coherent THz electric field produced using the electro-optic effect in ZnTe. Figure courtesy of H. Loos et al, Brookhaven National Laboratory.

of propagating THz pulses has now been demonstrated at FELIX (FOM – the Netherlands) and NSLS/SDL (Brookhaven).

We note that the accelerators being used to produce coherent THz pulses were not designed for this purpose. Instead, they were constructed and optimized to drive short wavelength FELs or large storage rings for high-brightness X-rays. It is reasonable to expect that significant advances are possible for this technology. For example, producing THz does not intrinsically require a very high energy electron beam. A 10 to 20 MeV beam would be more than sufficient to produce THz radiation, but other beam dynamics issues may preclude maintaining a large charge in a very short bunch. Controlling the electron beam's longitudinal density and tailoring the resulting electric field waveform will be an important feature of accelerator-produced THz. Efforts are just underway at a few Laboratories to produce bunches with periodic density modulations as a method to produce a second color of coherent light. This is clearly an area where accelerator physics R&D can make important contributions.

2) Superconducting Linacs

Jefferson National Lab has been actively involved in the development of next generation light sources involving ultra-fast energy recovery linacs (ERLs) for mid-IR and UV Free Electron Laser applications. [G. R. Neil, et al., "Sustained Kilowatt Lasing in a Free-Electron Laser with Same-Cell Energy Recovery," Phys. Rev. Let. **84**, 662 (2000)]. These accelerators use superconducting linacs and are able to run in a quasi-cw mode since minimal power is dissipated in the RF cavities. However, they can also be run in pulsed mode and since the beam is produced by a laser-photo-cathode arrangement, considerable variations in pulse repetition frequency and even electron density distribution in the bunches is possible. The Jefferson Lab facility currently operates an ERL that operates at 75 MHz with 135 pC bunches that are 350 fs long. It is planned to take the bunch lengths down to below 100 fs, the repetition rate up to a maximum of 750 MHz and to increase the charge per bunch. Even with the present machine, total power levels of up to 1 kW are possible, which is 6 orders of magnitude higher than table-top sources. Ultimately one may be able to increase this by several more orders of magnitude. Investigations and development of the capabilities of such devices represents one of the scientific frontiers of this field.

Short bunches such as those utilized in the Jefferson Lab ERL produce very high average power pulses of half-cycle THz light via coherent synchrotron radiation [Carol J. Hirschmugl, Michael Sagurton and Gwyn P. Williams, "Multiparticle Coherence Calculations for Synchrotron Radiation Emission", Physical Review **A44**, 1316, (1991) & G.L. Carr, M.C. Martin, W.R. McKinney, K. Jordan, G.R. Neil and G.P. Williams "High Power Terahertz Radiation from Relativistic Electrons", Nature **420** 153-156 (2002)].

The Jefferson Lab Free Electron Laser and THz User Facility

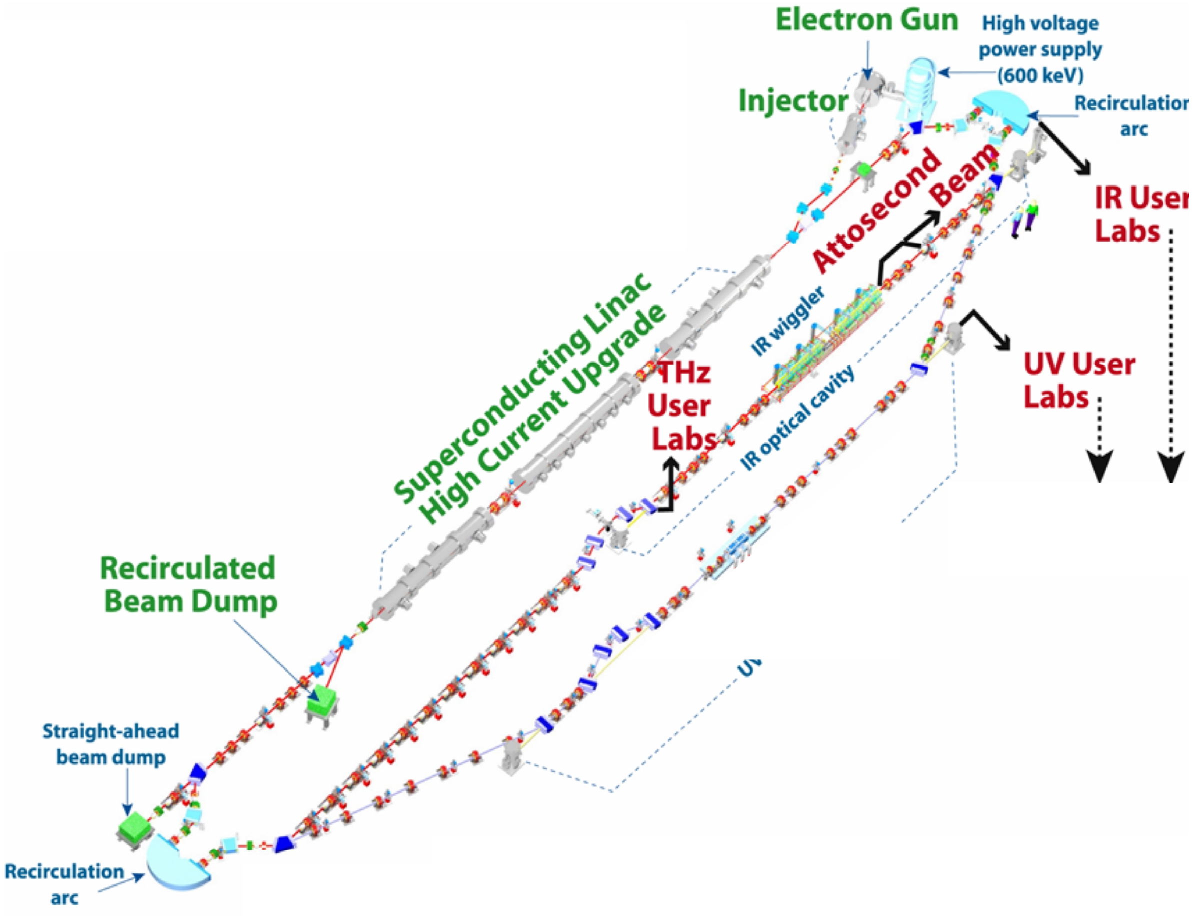


Figure 11.3 Schematic representation of the Jefferson Lab Free Electron Laser and THz User Facility. Figure courtesy of G. Williams, Jefferson Lab.

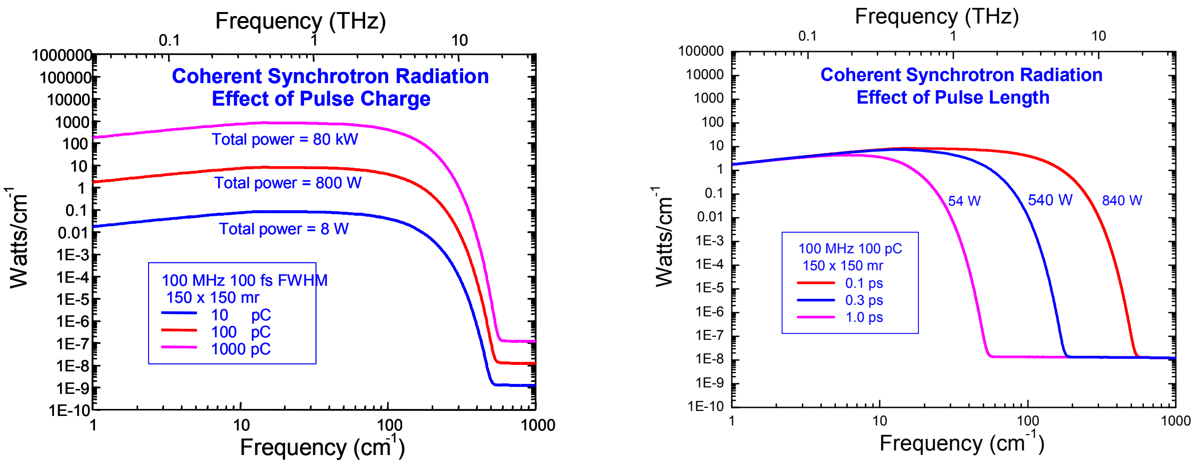


Figure 11.4 Coherent Synchrotron Radiation (CSR) power per cm^{-1} is plotted as a function of frequency for different values of bunch charge and bunch length. Figure courtesy of G. Williams, Jefferson Lab.

The facility is shown schematically in the Figure 11.3. Multiple photon pulses are available from the same facility since the THz pulses are generated simultaneously with the ultrafast tunable IR and UV pulses. In addition sub-picosecond x-ray pulses are produced simultaneously via Thomson scattering within the FEL cavity. Recently a THz beam transport system, which extracts the light from the ERL and transports it to a user laboratory, was added to the facility.

It is possible to illustrate in a device independent fashion, the performance characteristics of coherent synchrotron radiation sources in a manner that is also readily scalable to any other machines of this type. The power per cm^{-1} is plotted as a function of frequency for different values of bunch charge and bunch length in Figure 11.4. The example chosen is for a hypothetical 100 MHz repetition rate. Peak and average power varies linearly with repetition rate, linearly with bunch length and quadratically with bunch charge. Since these sources operate in the diffraction limit, the brightness is given by the above power numbers / λ^2. Thus the brightness advantage and thus the peak fields attainable with these beams is many orders of magnitude higher than conventional sources and these sources are highly suited for nonlinear and imaging applications.

3) Synchrotron storage rings

In recent years, significant progress has been made in understanding Coherent Synchrotron Radiation (CSR) in storage rings: stable CSR was produced in a storage ring [M. Abo-Bakr *et al.*, Phys. Rev. Lett **88**, 254801 (2002) & Phys. Rev. Lett. **90**, 094801 (2003).] and a theoretical model explaining the observation was developed [F. Sannibale *et al.*, Phys. Rev. Lett. *in press* (2004)], and experiments at LBNL demonstrated generation of intense terahertz CSR pulses from “laser-slicing”, based on the energy modulation of a fraction of the electron beam by a femtosecond laser pulse [J. M. Byrd *et al.*, *to be published*].

Based on these results, LBNL is proposing CIRCE (Coherent InfraRed CEnter), a ring based source completely optimized for the generation of coherent terahertz synchrotron radiation exploiting the full complement of CSR production mechanisms mentioned above. The calculated photon flux for CIRCE exceeds by more than 8 orders of magnitude the flux of “conventional” broad-band THz sources. Two modes of operation described below have been optimized in the

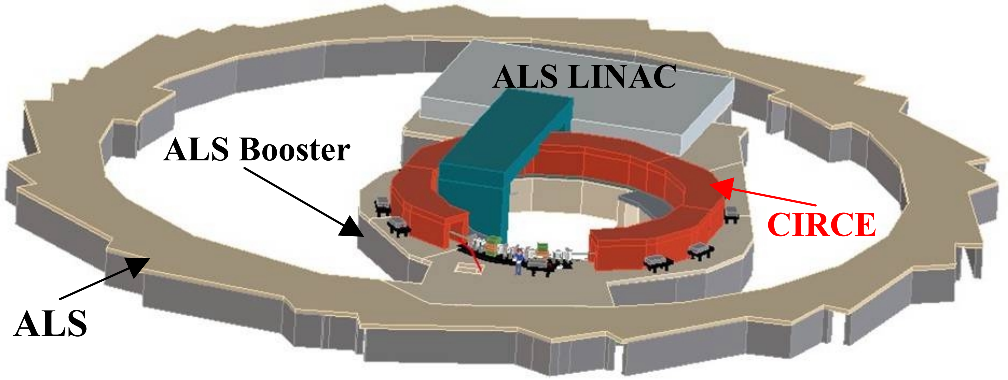


Figure 11.5 The proposed CIRCE coherent THz electron storage ring in the ALS complex, courtesy of M. Martin, Lawrence Berkeley National Lab.

CIRCE design and are based on experimental proof-of-principle demonstrations at BESSY and LBNL. Other possible future upgrades include an infrared FEL in one of the straight sections, and insertion devices for synchronous high-energy photon pulses for pump-probe techniques.

Figure 11.5 shows a 3D layout of the 600 MeV CIRCE ring inside the ALS facility. CIRCE is designed to be located on top of the ALS Booster shielding sharing the injector with the ALS storage ring. The lattice includes six Double Bend Achromat (DBA) cells with ~ 3.5 m straight sections between the arcs. In the optimization of the CSR performance of a storage ring it is very important to have control of its nonlinear dynamics. The CIRCE lattice includes several families of sextupole and octupole magnets specifically for this purpose. The vacuum chamber in the dipole magnets and the first in-vacuum mirror have been designed for a 140 mrad vertical acceptance to optimally couple to the large opening angle of the terahertz synchrotron emissions. Up to 36 beamlines with 100 mrad horizontal and 140 mrad vertical acceptance will be available. Complete cost estimates for CIRCE total to just under $20 M, including contingencies and a first suite of instrumented beamlines. This is relatively inexpensive for a synchrotron source, capitalizing on an existing electron injector, building and utilities, and provides a powerful and flexible THz source for a significant number of users and scientific experiments simultaneously.

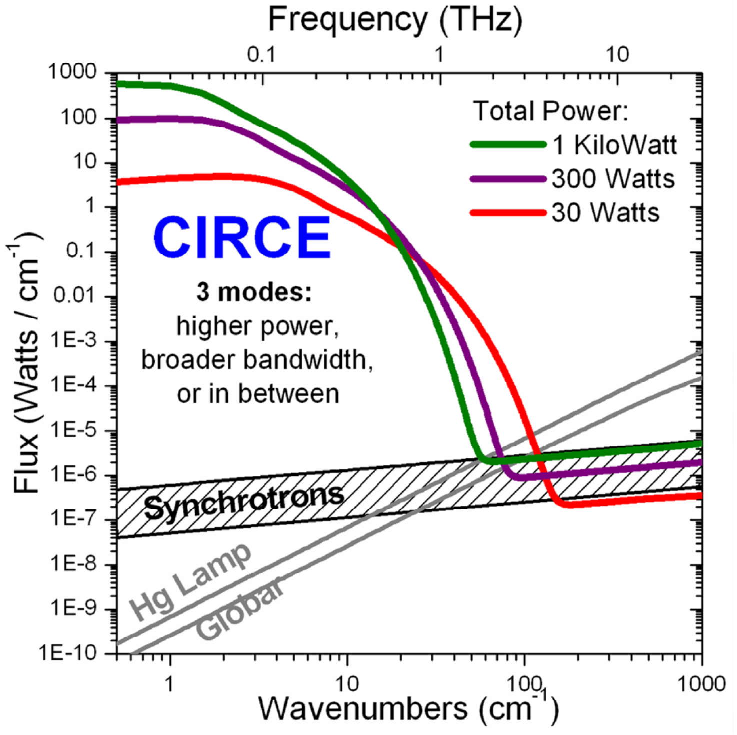


Figure 11.6 CIRCE photon flux in the ultra-stable mode. Flux values are for a single bending magnet port with 300 mrad horizontal acceptance and integrated from 1 to 200 cm^{-1}. Figure courtesy of Lawrence Berkeley National Lab.

One of CIRCE's strengths is its ability to serve a multitude of beamlines simultaneously, with specific beamlines developed specifically for the scientific needs of the users. For example, beamlines can be tailored to samples in high magnetic fields and/or pressures, high resolution spectroscopy, THz magnetic pulses, video-rate full-field THz imaging, two-color pump-probe spectroscopy, nonlinear coherent control applications, time-domain spectroscopy, and more. CIRCE will produce synchronous broadband pulses covering all of the infrared, visible, UV, and VUV regions, and it will be straightforward to synchronize CIRCE to the main ALS ring, allowing the possibility of THz pump, X-ray probe (or vice-versa) experiments with a full suite (> 40) of world class soft and hard x-ray beamlines.

Ultra-stable CSR Mode:

CIRCE's first mode of operation is the ultra-stable CSR mode, featuring a high repetition rate which provide up to kilowatts of very stable THz power, important for many experiments using terahertz radiation. Total power and bandwidth can be traded off as needed, as shown in Figure 11.6 where the flux in the THz region is calculated for three example ultra-stable settings of CIRCE. The field from the synchrotron radiation emitted by the electrons in the bend magnets generates a stable distortion of the longitudinal bunch distribution with a sharp leading edge. Such a distribution radiates CSR at higher frequencies than for the case of a pure Gaussian bunch with same rms length.

This mode of operation is well-suited to not-only half-cycle pulse applications, but also to high average power THz spectroscopy and imaging, important scientific requirements discussed in Chapter 9. Pulse stacking cavities can be implemented on specific beamlines to enable much higher (at least 100 to 1000 times) peak powers and independent beamline controlled repetition rates to suit experimental requirements.

Femtosecond laser slicing CSR:

A wiggler will be installed in one of the CIRCE straight sections to allow imprinting a femtosecond laser modulation onto the electron beam. The first beamline using such a technique,

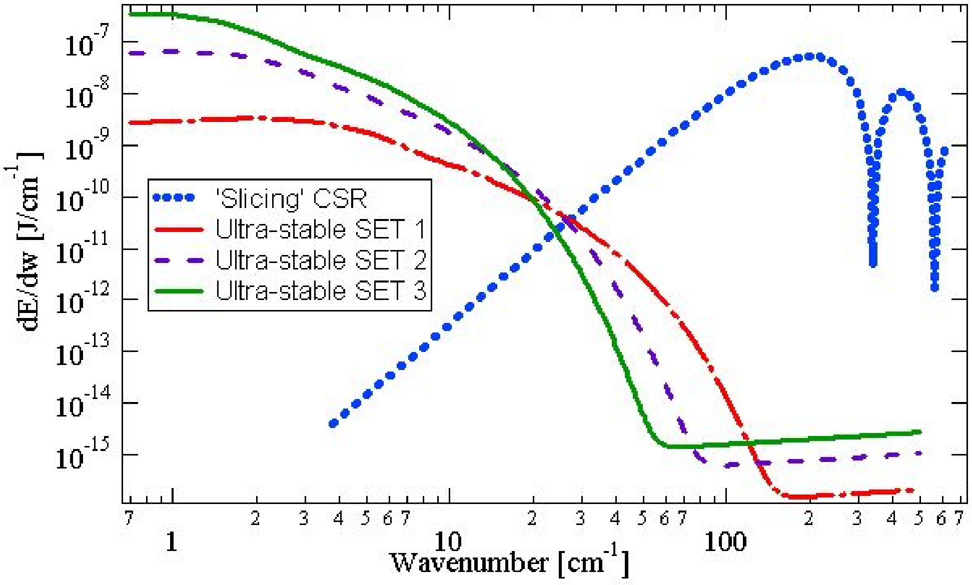


Figure 11.7 Calculated CSR spectrum for a simple configuration of the laser "slicing" mode in CIRCE, compared with the outputs of the ultra-stable modes. Figure courtesy of Lawrence Berkeley National Lab.

commonly referred also as "slicing", has been successfully operating at the ALS since 2001 for the production of femtosecond x-ray pulses [R. W. Schoenlein *et al.*, Science **287** 2237-2240 (2000)]. A short laser pulse is propagated together with the electron beam in a wiggler and modulates the energy of a slice (~ 100 fs) of the electron bunch. Due to the nonzero momentum compaction, a density modulation in the bunch longitudinal distribution is induced when the beam propagates along the storage ring. This density modulation radiates intense CSR pulses with an E-field profile given by the laser pulse structure [J. M. Byrd *et al.*, *to be published*]. These CSR pulses are regularly used at the ALS as a diagnostic for tuning of the slicing interaction and could be used as a terahertz source as well.

Figure 11.7 shows an example of the calculated CSR spectrum for a simple slicing configuration of CIRCE. In this case, the beam is modulated inside a wiggler in a straight section and the CSR is collected from a dipole magnet port 2.5 m downstream. The 50 fs FWHM laser pulse has the intensity necessary for an energy modulation of the electrons as large as six times the beam energy spread (using presently available commercial lasers). The current per bunch is 10 mA and the integrated energy of each CSR pulse over 100 mrad horizontal acceptance is ~ 10 μJ, corresponding to 1 MV/cm on a sample. The repetition rate is limited to 10 – 100 kHz by the laser.

The laser slicing mode can be used to imprint any laser intensity pattern onto the electron beam profile which then radiates it as a high-intensity THz E-field pattern. In this manner, CIRCE builds upon laser pulse shaping technologies and converts the laser pulse envelope into high-power shaped THz pulses for ultrafast nonlinear coherent control experiments, or spectral range and bandwidth selection.

11.5.2 Table-top sources of half and few-cycle THz pulses

Table-top sources of broad-band high-field THz radiation are in general use in a number of single-investigator or small group labs nationally and internationally. The typical output is < 10 kV/cm, but fields up to 1 MV/cm are feasible with available table-top laser systems and current THz emitters. Development of more sophisticated and efficient emitter technology may enable the achievement of even higher field strengths from laser-based THz sources. Figure 11.8 displays a schematic diagram of a generic set up.

A significant advantage of table-top systems is their relative ease of implementation, assuming one already has experience with ultrafast laser technology and the requisite lasers and delay lines. A second advantage is that each system can be customized to the needs of the researcher. For example, THz pulse durations as short as 25 fs, with associated bandwidth reaching 70 THz has been demonstrated and used for time-resolved experiments with exceptionally high temporal resolution. The combination of THz sources with synchronized ultraviolet, visible and infrared sources (with energies of a few hundred μJ) is easily achieved by conversion of the pump pulse that generated the THz pulses to other wavelengths via nonlinear processes. The generation of synchronized x-ray probe pulses, while possible, significantly increases the complexity of the system.

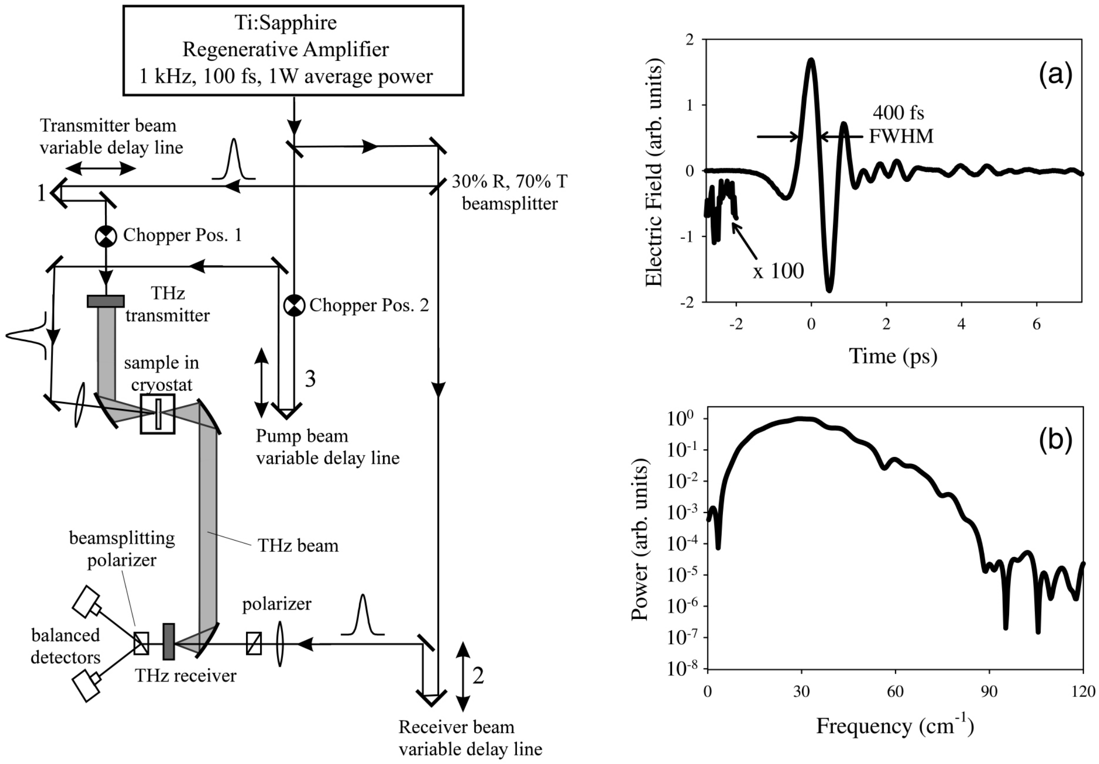


Figure 11.8 Generic experimental set up for table-top THz pulse generation and detection. An additional optional beam (#3) allows for optical excitation of the sample for time-resolved studies. The time-domain pulse is shown in part a), and the power spectrum in part b). Figure courtesy of Charles Schmuttenmaer, Yale University.

Repetition rates of 1 kHz for non-equilibrium pump-probe studies are easily achievable, with rates up to 100 kHz possible depending on the specific requirements. Repetition rates of 10 Hz are more feasible for high-field (1 MV/ cm) sources.

Flexible and adaptable pulse shaping of THz radiation by shaping optical driving pulses has been demonstrated, using several techniques but has not optimized for pump/probe or nonlinear applications. Such optimization is best accomplished while performing specific experiments.

11.6 Summary

Characteristics of available electron beam sources, as well as generic laser-based table-top sources, are shown in Table 11.1. Since the specifics of a particular experiment will dictate the optimal source (laser-based versus accelerator-based), an intriguing possibility promoted by a number of scientists is that the combination of both table-top and electron beam sources be available at user facilities. Such a practice would enable the optimization of experiments and would further serve to promote training of students and postdocs in multiple experimental techniques.

Source type	Band width	Pulse width	Rep Rate	Average power	Pulse Energy	Peak E-field
Table-top lasers existing	~ 5 THz	~ 100 fs	~ 1 kHz	nW to µW	nJ to µJ	~ 10 kV/cm
Table-top lasers anticipated	~ 50 THz	~ 10 fs	~ 10 kHz	µW to mW	µJ to mJ	1 to 10 MV/cm
Linac (normal) existing	~ 2 THz	~ 300 fs	~ 10 Hz	~ mWatts	~ 100 µJ	~ 1 MV/cm
Linac (normal) anticipated	~ 10 THz	~ 50 fs		~ mWatts	~ mJoules	~ 50 MV/cm
Linac (superconducting) existing	~ 2 THz	~ 300 fs	75 MHz	100s Watts	~ µJoules	~ 10 kV/cm
Linac (superconducting) anticipated	~ 10 THz	~ 50 fs	750 MHz	~ kWatts	~ mJoules	~ 50 MV/cm
Storage Ring existing	~ 1 THz	~ 1 ps	500 MHz	~ 1 Watt	~ nJoules	~ 10 V/cm
Storage Ring anticipated*	~ 20 THz	~ 50 fs	1.5 GHz	~ kWatts	~ 10 µJ	~ 1 MV/cm

* Values are given for CIRCE: Maximum bandwidth, short pulse width, and peak E-field values are achieved in "slicing mode" at 100 KHz rep rate; high average power at high rep rate is in the "ultra-stable" mode (see section 11.5.1). Pulse stacking allows significantly (100 – 1000 times) higher pulse energies and fields at lower (but still MHz) repetition rates for individual beamlines independent of other beamline operations.

Table 11.1 Table of typical performance parameters for experimentally realized (existing) and predicted (anticipated) table-top laser and electron accelerator sources of high-field half-cycle THz pulses.

11.7 Recommendations

Numerous examples of science have been described in previous chapters that will rely on sources of high-power coherent half- and few-cycle THz pulses, but the barriers to using these types of sources are particularly steep. Expensive and extensive laser set-ups or access to a new type of electron accelerator operations are required. In both cases, creating nodes within a THz Network that consist of user facilities centered on flexible and well-run THz sources with a range of sample environments available should be a priority. These centers will enable both expert and novice THz users to perform experiments in this otherwise difficult spectral region by using world-class THz pulse sources, instruments, and expertise of the staff running the centers. The sources will be (from the users' point of view) easier, cheaper, and faster, so they can focus their attention on understanding and interpreting the scientific results.

One easy way to approach such a THz center is to "piggy-back" on one of the existing national user facilities that already have infrastructure in place to administer a full user program including receiving and ranking scientific proposals, scheduling beam time, maintaining a high availability of the sources, offering nearby user housing, and having a staff of highly qualified technicians, engineers, scientists, and administrators. Three descriptions of such facilities made by upgrading and optimizing accelerators for THz use at BNL, Jefferson Lab and LBNL were discussed in this chapter, and the FELIX, UCSB and Stanford FEL centers were described in Chapter 10. Including well-run table-top laser THz sources in addition to accelerator-based sources at such centers is an exciting idea. Such a practice would enable the optimization of experiments and would further serve to promote training of students and postdocs in multiple experimental techniques.

Development of THz user facilities will lead to a large and rapid growth of the THz community. At such a facility the user will focus on the wide variety of THz-based science since the functioning of an optimized source will be assured by the professional staff. This mode of operation will require support of individual scientists, table-top experiments, centers of excellence, and accelerator-based user facilities, all important nodes on a THz network.

Chapter 12: Terahertz User's Network

12.0 Executive summary

This report identifies myriad exciting frontiers for "discovery class" THz science. Establishment of a THz user's network at this point is critically important. The current THz community is a reasonably small group with excellent cooperation. Even within this community, a network would help practitioners of different kinds of THz experiments to learn from one another. However, in order to realize the scientific opportunities, we need to greatly expand the user base and bring in scientists who do not have, and do not wish to have, deep THz technical expertise. Centrally organized, a network would nurture and foster partnerships among single investigators and investigators at larger facilities. It is expected that partnerships will not be limited to single-investigator/facility, that is, there will be many opportunities for investigator/investigator and facility/facility partnerships.

The current model is based on single PIs using table-top systems and larger scale accelerator-based facilities. Some of the facilities have permanent technical staff dedicated working with visiting scientists. It will be necessary to add a third component to this model: Centers of excellence, either real or virtual. In order to coordinate all of these efforts, a national steering committee must be organized.

Size of community

It is quite difficult to estimate the current size of the THz science community in the U. S. and its potential for growth. The magnitude of growth will depend a great deal on the extent to which resources are made available. The following figures are based on statements during the panel discussion at the workshop, the sizes of typical meetings in various scientific fields represented at the workshop, and educated guesses.

Discipline	Current size (# of people)	Potential size
Physics	200	3000
Chemistry	50	1000
Biology	20	1000
Medicine	10	1000
Total	**280**	**6000**

12.1 User's network – Overview

At the outset, the network should be established with a clear mission, goals, metrics for success, and a finite but renewable duration (for example, 5 years). The elements of the network, as we envision them now, would include:

- National steering committee
- Full-time coordinator
- Website
- Single investigators
- Centers of excellence

- National labs & other accelerator-based facilities
- Provide expertise to help people get started
- Provide THz generators and receivers at cost
- Provide access to other network members
- Provide limited access to general community to try ideas
- Establish standards (perhaps in collaboration with NIST)
- Repository for spectra
- Interface with industry
- Educational and public outreach components

12.2 User's network – Details

National steering committee: In order to coordinate the growth of THz science, a national steering committee must be established. This will prevent redundancies and will provide a focal point. It should consist of 5 or 6 members, broadly representative of the entire community. This committee will initially organize the THz user's network, and subsequently oversee its development. The committee will clearly establish the mission, goals, and methods to evaluate the success of the network.

Full-time coordinator: The establishment and maintenance of a vital THz User's Network will be a full-time job that no faculty member can afford to take on while maintaining an active research program. A coordinator will be essential to take the recommendations of the steering committee and network members, and implement them in a timely and aggressive fashion. The coordinator will also help to assess and publicize the impact of the Network, and write reports to agencies that fund the Network. The coordinator need not have an advanced degree in science, but should have excellent organizational, writing, and web design skills. A detailed job description for the organizer will be generated by the steering committee.

Website: Much of the coordination will occur through a THz user's network website. There will be sections open to the public for information and outreach, and there will be sections accessible only to network members. As the community grows, a monthly newsletter could be published and archived on the website.

Single investigators: The majority of published THz science has come out of single investigators' groups. This type of work must be more aggressively supported in order to realize the full potential of THz science. There are so many avenues to pursue that it is simply not possible to achieve these goals only at facilities. Furthermore, much important THz science does not require specialized facilities, and would therefore not be the best use of the facilities' time.

Centers of excellence: Modest centers with specific specializations such as high-field studies, THz imaging, near-field studies, narrow-band studies, magnetic field capabilities, and time-resolved THz science should be established. These would be located on the premises of established PIs, and would have 1 to 2 staff members. They could host visits from scientists, as well as make measurements on samples that are sent to them. PI's at centers of excellence must, of course, must be willing to devote a significant fraction of their THz "beam time" and experimental space to outside users.

Accelerator-based THz user facilities at national labs and universities: Currently, there are five of these: Brookhaven National Laboratory, University of California at Santa Barbara, Stanford University, Advanced Light Source at Lawrence Berkeley National Lab, and Jefferson National Lab. Initially, modest funding is needed to allow single investigators and/or their students to travel to one of the 5 centers, and modest funding at the 5 centers in order for them to cover expenses and to provide some support for outside users. The amount of use (and funding) will grow in the out-years through demonstrated excellence in science. Given that the facilities already exist, have accumulated substantial experience, and have not only unique THz sources but also much ancillary equipment, this is an ideal way to benefit significantly from existing infrastructure. The science done at these centers differs from that done in single-investigator labs or at centers of excellence because the capabilities of these sources are unique. After a few years, the community will have a better understanding of the most desirable form for new accelerator-based facilities, such as the CIRCE facility proposed by the ALS.

Provide expertise to help people get started: The network will be a clearinghouse of information. For example, manuals with step by step instructions for building an apparatus with photoconductive antennas, or optical rectification/Free Space Electro-Optic Sampling (FSEOS), or detailed procedures for working up data could be written. Network members could take turns with email correspondence, telephone correspondence, and lab visits to help people get started. Useful information for scientists traveling to centers of excellence or accelerator-based facilities would also be available.

Organize sessions on THz techniques and opportunities at large existing conferences: The American Physical Society, the American Chemical Society, the Materials Research Society, and many other scientific professional societies have large annual conferences. A yearly session at each of these conferences would do much to raise general awareness of the opportunities described in this report. The network coordinator could work with the steering committee and the membership to identify appropriate conferences and speakers for maximum impact. It would be helpful for the Network to fund travel costs of speakers presenting at these conferences, if necessary.

Provide THz generators and receivers at cost: One of the impediments for single investigators who want to begin THz science is the lack of a commercial source of photoconductive antennas. A user's network could provide "kits" for table-top set-ups at cost. This would require that someone design a standardized generator and receiver, and have the lithography performed. The rest of the kits would consist of specific company names and part numbers for the other components that are needed. For those who wish to generate THz pulses via optical rectification, and detect with free space electro-optic sampling (FSEOS), then the "kit" would simply be a list of company names and part numbers.

Provide access to other network members and limited access to general community to try ideas: The issue of access is inherent in the establishment of centers of excellence and existing accelerator-based facilities. A THz user's network would provide access to single-investigator's laboratories to carry out short studies in an area of their specific expertise, or to train personnel who are establishing their own program in THz science. Since the host investigator will be distracted from their own science, a mechanism for "compensation" must be established.

Establish standards (perhaps in collaboration with NIST): There should be some established standards for researchers to verify the performance of their systems. In particular, there is no clear definition of signal-to-noise ratio. By establishing standards, it will be possible to quantitatively compare performance at different labs. Some possibilities are: 1) Gas phase sample, perhaps water vapor at a specified partial pressure and path length, 2) 1 mm path liquid isopropyl alcohol, 3) High resistivity Si wafer.

Repository for spectra: One of the ongoing issues, particularly in studies of biophysical samples, has been consistency and reproducibility of published spectra, or lack thereof. If network members all contributed their spectra to a database, then others could compare their results with those.

Interface with industry: Some commercial products for THz optics and spectroscopy exist. Others are needed. The THz User's Network would serve as a vehicle for letting industry understand potential markets for scientific instruments and components required for THz science, and also make members of the network aware of what is available. The website could also post member-written reviews of products which have been purchased.

Educational/public outreach component: The success of the network requires educating scientists, students, and the general public about THz science. This spans a range of material: There must be something for established single-investigators who are considering embarking on THz studies. There must be material for users who will be traveling to a facility or center of excellence, and there must be general material explaining THz science at an undergraduate level in order to help feed the pipeline. In addition, a network-wide REU program could be established and material for courses on THz science could be made available. The Network would also prepare educational materials and programs aimed at K-12 education and the education of the public at large.

Appendix I: Participants

Organizers

Mark Sherwin	University of California at Santa Barbara
Phil Bucksbaum	University of Michigan
Charles Schmuttenmaer	Yale University
Eric Rohlfing	Department of Energy
Janice Hicks	National Science Foundation
Brenda Korte	National Institutes of Health

Speakers

Jim Allen	University of California at Santa Barbara
Sandra Biedron	Argonne National Lab
Larry Carr	Brookhaven National Lab
Martyn Chamberlain	University of Durham
Tom Crowe	University of Virginia
Frank DeLucia	Ohio State University
Qing Hu	Massachusetts Institute of Technology
Bob Jones	University of Virginia
Bart Noordham	AMOLF FOM Inst. For Atomic & Molecular Physics
Ted Norris	University of Michigan
Joe Orenstein	University of California at Berkeley
Charles Schmuttenmaer	Yale University
Karl Unterrainer	Technical University of Vienna
Lex Van der Meer	FOM Institute Rijnhuizen FELIX
Ingrid Wilke	Rensselaer Polytechnic Institute
Gwyn Williams	Jefferson Laboratory
X.-C. Zhang	Rensselaer Polytechnic Institute

Session Chairs

Alan Cheville	Oklahoma State University
Andrea Markelz	State University of New York at Buffalo
Beth Parks	Colgate University
Paul Plancken	University of Technology Delft
Jie Shan	Case Western Reserve University

Breakout Session Leaders

Bob Austin	Princeton University
Dimitri Basov	University of California at San Diego
David Citrin	Georgia Tech University
Warren Grundfest	University of California at Los Angeles
Tony Heinz	Columbia University

Jun Kono	Rice University
Daniel Mittleman	Rice University
Peter Siegel	California Institute of Technology
Toni Taylor	Los Alamos National Laboratory

Panel Members

Bob Jones	University of Virginia
Andrea Markelz	State University of New York at Buffalo
Mike Martin	Lawrence Berkeley National Laboratory
Keith Nelson	Massachusetts Institute of Technology
Todd Smith	Stanford University
Gwyn Williams	Jefferson Laboratory

Other scientific participants

Mark Allen	Physical Sciences Inc.
Rick Averitt	Los Alamos National Laboratory
Louis Brunel	National High Magnetic Field Laboratory
Ted Heilweil	National Institute of Standards and Technology
James Heyman	Macalester College
Peter Jepsen	University of Freiburg
Robert Kaindl	Lawrence Berkeley National Laboratory
Wim Leemans	Lawrence Berkeley National Laboratory
Laszlo Mihaly	State University of New York at Stony Brook
Chitra Rangan	University of Michigan
Harry Tom	University of California at Riverside
Vincent Wallace	TeraView Ltd.
David Zimdars	Picometrix Inc.

Appendix II: Workshop Agenda

DOE-NSF-NIH Workshop on Opportunities in THz Science
February 12-14, 2004

Agenda
Sheraton National Hotel - Arlington

Scope: Frequencies from 300 GHz to 20 THz; Science; Not engineering, not defense

	Thursday, February 12, 2004 **Talks will be 30 minutes long, with 15 minutes of discussion**	
	Session Chairs: Jie Shan – Morning Andrea Markelz – Afternoon	
8:00 – 8:15am	Continental Breakfast	Assembly Foyer
8:15-8:30am	Introduction by organizers – explaining the workshop's charge Mark Sherwin, Phil Bucksbaum, Charles Schmuttenmaer	Cavalier A/B/C Room
8:30-9:15am	Materials I – semiconductor and insulators – Karl Unterrainer	Cavalier A/B/C Room
9:15-10:00am	Materials II – correlated-electron systems – Joe Orenstein	Cavalier A/B/C Room
10:00-10:30am	BREAK	
10:30-11:15am	Physics – Bob Jones	Cavalier A/B/C Room
11:15-12:00noon	Chemistry and Biology – Charles Schmuttenmaer	Cavalier A/B/C Room
12:00-1:00pm	LUNCH	Assembly Foyer
1:00-1:45pm	Medicine – Martyn Chamberlain	Cavalier A/B/C Room
1:45-3:00pm	Breakout Session #1 Materials I – David Citrin Materials II – Dimitri Basov Physics – Tony Heinz Chemistry and Biology – Bob Austin Medicine – Warren Grundfest	 Mezzanine 1 Room Mezzanine 2 Room East 3 Room Concourse 1 Room Concourse 2 Room
3:00-3:45pm	Interim Reports and Coffee (5-10 minutes each) for the 5 breakout sessions	

3:45-5:00pm	Breakout Session #2 – participants can go to same or different topics Materials I – David Citrin Materials II – Dimitri Basov Physics – Tony Heinz Chemistry and Biology – Bob Austin Medicine – Warren Grundfest	 Mezzanine 1 Room Mezzanine 2 Room East 3 Room Concourse 1 Room Concourse 2 Room
6:00-8:00pm	Working Dinner	Cavailer A/B Room
	Friday, February 13, 2004 **Talks will be 15-40 minutes long, with about 1/3 time devoted for discussion**	
	Sessions Chairs: Paul Plancken – Morning Beth Parks – Afternoon Panel Discussion: Alan Cheville	
7:45-8:00am	Continental Breakfast	Assembly Foyer
8:00-8:40am	“Final” reports of first day’s breakout sessions (5-10 min. each). Should include quantitative appraisal for performance of experimental systems required to achieve scientific goals	Cavalier A/B/C Room
8:40-9:00am	2.1: Incoherent Synchrotron Radiation – Larry Carr	Cavalier A/B/C Room
9:00-9:20am	2.2: Coherent Synchrotron – Gwyn Williams	Cavalier A/B/C Room
9:20-9:40am	2.3: FELs (short pulse) – Lex Van der Meer	Cavalier A/B/C Room
9:40-10:00am	2.4: FELs (quasi-cw) – Jim Allen	Cavalier A/B/C Room
10:00-10:30am	BREAK	
10:30-11:00am	2.5: Time-domain THz Spectroscopy – Ingrid Wilke	Cavalier A/B/C Room
11:00-11:30am	2.6: Time-resolved and High-Field THz Spectroscopy: Table-top Sources of HCP and Few-Cycle Pulses, also, Optical Pump/THz Probe Studies – Bart Noordham	Cavalier A/B/C Room
11:30-11:50am	2.7: Microwave Oscillators and Multplier Chains – Tom Crowe	Cavalier A/B/C Room
11:50-1:00pm	LUNCH	Assembly Foyer
1:00-1:20pm	2.8: THz QCLs – Qing Hu	Cavalier A/B/C Room
1:20-1:40pm	2.9: Photomixers and PPLN (tunable narrow-band) – Ted Norris	Cavalier A/B/C Room
1:40-2:00pm	2.10: High Resolution Applications – Frank DeLucia	Cavalier A/B/C Room
2:00-2:20pm	2.11: THz Imaging – X.-C. Zhang	Cavalier A/B/C Room
2:20-2:35pm	BREAK	

2:35-3:45pm	Breakout Session - #3 Broad-band THz sources and systems for spectroscopy and imaging (primarily 2.1, 2.5 and 2.11) - Daniel Mittleman Coherent half-and few-cycle THz sources for nonlinear and non-equilibrium studies (primarily 2.2 and 2.6) – Toni Taylor Narrow-band THz sources and systems for spectroscopy and imaging (primarily 2.7, 2.8, 2.9, and 2.10) – Peter Siegel Narrow-band THz sources for nonlinear and non-eqiulibrium studies (primarily 2.3 and 2.4) - Jun Kono	Mezzanine 1 Room Mezzanine 2 Room Concourse 1 Room Concourse 2 Room
3:45-4:30pm	Interim reports and coffee (5-10 minutes each) for the 4 breakout sessions	
4:30-5:45pm	Panel discussion to address: 1. Size of community, broken down by scientific field and by technique of choice; 2. Need for and advantages/disadvantages of: user-based facilities, centers of excellence (real or virtual), and single investigators and 3. Need for and useful form of a THz User's Network. Panel Members: Bob Jones; Gwyn Williams; Andrea Markelz; Mike Martin; Todd Smith, Keith Nelson	Cavalier A/B/C Room
6:00-8:00pm	Working Dinner (primarily for people staying on day 3, but everyone is welcome)	North 1 Room
	Saturday, February 14, 2004 Report Writing: Breakout session chairs, scribes, and co-organizers will stay for an additional ½ day. Anyone else who is interested is invited to participate as well.	
7:45-8:00am	Continental Breakfast	Assembly Foyer
8:30-9:30am	Generate 5-8 pages of material per breakout session. The more material that is written during the breakout sessions, the easier this will be to achieve.	Mezzanine 1 Room; Mezzanine 2 Room; East 3 Room; Concourse 1 Room; Concourse 2 Room
9:30-10:30am	Give materials to different group or proofreading and corrections/suggestions	Mezzanine 1 Room; Mezzanine 2 Room; East 3 Room; Concourse 1 Room; Concourse 2 Room
10:30-11:30am	Generate final version	Mezzanine 1 Room; Mezzanine 2 Room; East 3 Room; Concourse 1 Room; Concourse 2 Room
11:30-12:30pm	Co-Organizers and government representatives meet to finalize deadlines and time-tables, etc.	Cavalier A/B/C Room
12:30-1:30pm	LUNCH	
1:30pm	ADJOURN	

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