

Research Accomplishments
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The majority of my research effort continues to revolve around a goal – and now a realization – of opening the far-infrared region of the spectrum to time-resolved studies through the development of time-resolved THz spectroscopy (TRTS). A detailed account of the evolution of THz spectroscopy in my group at Yale can be found in "THz Spectroscopy" by Beard, Turner, and Schmuttenmaer.¹ Here I will only summarize.

To varying degrees, I have established five related research areas which are described in more detail below. Briefly: 1. We have devoted much effort to developing our new method for studying rapid intramolecular electron transfer based on THz emission. 2. We have been leaders in the development of optical pump – THz probe spectroscopy. Using our amplified system, we have completed time-resolved studies of solvation dynamics in liquids as well as transient photoconductivity in semiconductors: bulk, nanocrystalline, and quantum dots. 3. We expend the requisite theoretical/computational effort required to fully understand our data. We have developed a numerical method for pulse propagation of arbitrary pulse shapes through media with arbitrary optical properties to attain full understanding of the results of the time-resolved experiments. We have also developed an analytical form of the theory. 4. We have carried out steady state, equilibrium measurements of binary liquid mixtures of water and methanol with each other and non-hydrogen bonding solvents with our unamplified THz system. The work on binary liquid mixtures has led to the study of librational band dynamics of water and methanol confined within reversed micelles. 5. We have begun to carry out THz imaging experiments. Because THz radiation penetrates many materials that visible and infrared light does not, it can be used in imaging applications where standard techniques fail.

THz pulses have spectral bandwidth from 3 cm^{-1} to about 100 cm^{-1} (or .09 THz to 3 THz), and temporal duration on the order of 400 fs. Terahertz pulse spectroscopy is the only possible way to carry out time-resolved studies in the far-infrared (FIR) region of the spectrum with sub-picosecond temporal resolution. One of the unique characteristics of THz spectroscopy is that the electric field of the pulse, not merely its intensity, is measured. This allows both the absorption coefficient and index of refraction of the sample to be determined simultaneously, without any approximations, assumptions, or the use of a Kramers-Kronig analysis. It is essential to characterize the full complex permittivity (obtained from α and n) in order to relate the measured quantities to chemical dynamics or different models of conductivity. It is easy enough to build an experimental setup to generate and detect THz pulses, and then photoexcite a sample and observe the distortion of the THz waveform. It is quite a different matter to do so reproducibly and quantitatively in order to unravel the meaning of the changing waveform and extract information about the underlying causes for a change in absorption and refractive index. The time-resolved aspect of THz spectroscopy has been the driving force behind the majority of my group's work, but about 20% of our work involves non-time-resolved studies as well.

1. Intramolecular electron transfer

We have developed a completely novel method for measuring intramolecular charge transfer,^{2,3} based on THz emission spectroscopy. Typically, one measures changes in fluorescence intensity from the donor or acceptor portion of the molecule, or sometimes transient absorption studies can be employed to track the charge transfer. Using our method, no external

probe need be used. Instead, we measure the electromagnetic pulse that accompanies the acceleration of charge. Therefore we can study species that do not fluoresce or show a change in their transient absorption spectrum upon electron transfer. We demonstrated this technique on dye molecules as a proof-of-principle, and are now in the process of applying it to the primary step of charge transfer in bacterial photosynthetic reaction centers (in collaboration with Gary Brudvig).

2. Time-resolved THz spectroscopy

One of the truly unique aspects of THz spectroscopy is the fact that it is *time-resolved*. It should be noted that there is simply no other way to generate FIR pulses of sub-picosecond duration – even free electron lasers or synchrotron sources have pulse durations of several ps. Therefore, we have devoted significant effort towards developing TRTS. The configuration of interest has been visible pump / THz probe, although a small amount of effort has gone into THz pump / visible probe and THz pump / THz probe adaptations. The underlying philosophy is that time-resolved studies have proven to be very valuable in general during the last 2 or 3 decades, and we now have the opportunity to extend these concepts into the FIR region of the spectrum.

We have made the greatest strides in developing TRTS through the study of time-resolved photoconductivity in bulk GaAs.^{4,5} We chose this system to benchmark TRTS because it has been extensively studied by other techniques, and a great deal is known about the carrier dynamics. Broadly speaking, we find that one can not make approximations when analyzing the pulse propagation through a photoexcited medium. That is, complex-valued transmission coefficients must be used, and sample interfaces must be included in order to extract the complex permittivity of the medium. The GaAs results led to transient photoconductivity studies in three other materials: Low-temperature grown GaAs (LT-GaAs),⁵ CdSe quantum dots,⁶ and nanocrystalline TiO₂.⁷

The study of transient photoconductivity in LT-GaAs clearly demonstrated the utility of TRTS as a non-contact electrical probe with sub-picosecond temporal resolution. LT-GaAs is a material grown using molecular beam epitaxy of GaAs in an excess As flux. Upon annealing, the As atoms form metallic clusters which act as deep traps for photoexcited electrons. Thus, the material is only conductive for 1 – 2 ps after excitation. We were able to determine the mobility of the carriers during the brief period after photoexcitation before they encountered the deep traps. The CdSe and TiO₂ studies showed how the mobility of carriers within a very small particle could be measured. It is very difficult to attach electrical leads to objects that are only a few nanometers in dimension, and it is even more difficult to make ohmic contacts. However, this was not an issue for us since TRTS is a non-contact electrical probe. Not surprisingly, we find that the mobility in CdSe quantum dots is strongly influenced by the particle size. In TiO₂, we find the unexpected result that the carriers undergo strong backscattering which leads to a high AC mobility, but low DC mobility.

Another type of process that can be probed in this fashion is solvation dynamics.⁸⁻¹¹ The static FIR spectra of liquids contains information about their collective dynamics and structure. Photoexcitation of a solvated dye molecule causes a perturbation in the FIR spectrum of the surrounding solvent due to changes in the liquid's local structure and dynamics. We have shown that probing the FIR spectrum as a function time after the initial photoexcitation event provides detailed information about solvation dynamics that is unavailable through conventional time-resolved fluorescence Stokes shift experiments.

3. Theoretical/computational advances

My group has made some notable theoretical/computational advances over the past few years. A THz pulse has a duration of 200 fs to 400 fs, an optical excitation pulse is 100 fs or

less, and the intrinsic response times for the systems we study are on the timescale of several fs to several ps. This brings up some interesting issues with regard to interpreting our results. That is, the response of the system is evolving and changing as different parts of the THz pulse pass through it. We have developed a method to extract the time-dependent response function from visible-pump/THz-probe experiments, even with these apparent complications. We have treated the time-dependent response function both analytically¹² and numerically.¹³

The analytical treatment has the advantage that it is analytic, but can suffer from limitations when trying to apply it to actual data because of various experimental details. The numerical approach is based on finite-difference time-domain (FDTD) electromagnetic field propagation methods, and has the advantage that no assumptions regarding the dispersive medium need be made. One must be able to parameterize the response by using some sort of model – but that is not much of a limitation since models such as Drude, Debye, Lorentz, etc., are quite general and flexible. Use of FDTD methods is absolutely essential in analyzing and understanding our experimental data because the slowly varying envelope approximation (SVEA) and rotating wave approximation (RWA) are not valid for single-cycle pulses. Pulse propagation techniques commonly used, based on Fourier transform methods, are not applicable for our experiments because the absorption properties of the medium change *while* the THz pulse is propagating through it. That is, the leading edge of the pulse will travel through non-photoexcited sample, while the trailing edge will travel through a photoexcited sample. The numerical methodology presented in Ref. 13 is used for our studies of liquids, semiconductors, and THz pulse generation experiments.

4. Binary liquid mixtures

It is hardly surprising that binary liquid mixtures of small, polar molecules behave non-ideally. Our work has led to quantifying the degree of non-ideality. We have studied the following mixtures:¹⁴⁻¹⁷ acetonitrile/water, acetone/water, methanol/water, acetonitrile/methanol, acetone/methanol, and acetone/acetonitrile. The deviations from ideality were sometimes striking; the Debye relaxation time constant for some compositions of acetone/water is a factor of two longer than that expected for an ideal mixture.¹⁵ In addition to THz spectroscopy, we have also carried out low frequency IR absorption spectroscopy from 400 cm^{-1} to 1000 cm^{-1} using a commercial FTIR, and have also employed molecular dynamics (MD) simulations. These additional studies were initiated in an effort to understand whether or not these mixtures exhibit clustering or microheterogeneity. The MD simulations have been particularly helpful in answering this type of question. While our experimental results provide assessment of the overall timescale of relaxation, they can not directly address the issue of microheterogeneity. Our approach has therefore been to compare the simulated spectra with the measured spectra, and if they agree sufficiently well, to extract greater detail from the simulation results.^{15,17}

The studies of binary liquid mixtures demonstrated the sensitivity of the OH librational motion (670 cm^{-1}) to the hydrogen bonding environment. More recently, we have measured the librational band of water and methanol confined within reverse micelles with a range of sizes.¹⁸ We find that the data are well fit by a two-state model consisting of bulk-like and "bound" liquid.

5. THz imaging

Many common materials such as plastics and paper are transparent in the far-IR but are opaque in the visible or IR regions of the spectrum. An increasing amount of work carried out in THz community is directed toward 2- and 3-dimensional imaging. Very recently, my group has begun development of an imaging spectrometer. For initial characterization and benchmarking,

we have obtained 2-dimensional images of the structure inside a sunflower seed.¹⁹ We were able to clearly distinguish the shell, the kernel, and the gap that surrounds the kernel within the shell.

One of the most important characteristics of THz imaging is that the measurements are made in the time-domain, and both the pulse arrival time and amplitude provide valuable information. Were this not the case, this type of experiment could be carried out on a standard Fourier transform FIR spectrometer fitted with a pair of focusing mirrors around the sample. We have shown that by being able to divide the scan into regions, and measuring the peak height and arrival time within each region reveals a detailed picture of the sample under study.

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