Femtosecond far-infrared pump–probe spectroscopy: a new tool for studying low-frequency vibrational dynamics in molecular condensed phases

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Received 4 December 1996; in final form 5 June 1997

Abstract

Low-frequency (terahertz) motions that play an important part in reactive processes in condensed phases are directly probed, following an optical excitation. A voltage-biased semiconductor wafer, excited with a 70 femtosecond laser pulse, is employed as a source for intense terahertz pulses, which are used as the probe arm of a pump–probe experiment. Difficulties in using terahertz probe pulses are discussed. We then demonstrate the method with two examples. In the first, a terahertz signal is shown to follow the solvent response to charge transfer in betaine. In the second example, relaxation of sapphire lattice phonons, excited impulsively by a 405 nm pulse, is observed. © 1997 Published by Elsevier Science B.V.

1. Introduction

Vibrational modes in the 5–200 cm−1 spectral region have been implicated as important in a large variety of chemical processes, from solvation [1] to mediation of conformational changes in proteins [2]. A variety of techniques can be used to measure the vibrational spectrum in this very low-frequency spectral region. Among these are FT-FIR spectroscopy [3] and Raman scattering [4] which are both frequency domain methods. Several time-domain techniques were developed for the same purpose, based on impulsive stimulated Raman scattering [5]. Each of these methods can yield in principle the spectrum of low-frequency vibrations of a liquid or a solid.

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These time domain methods measure directly vibrational dephasing times, but do not readily measure vibrational energy relaxation. In recent years, femtosecond terahertz pulses generated by semiconductor devices (see below) were used as a broad band spectral source for low-frequency vibrational spectroscopy [6–9].

Many of the situations where low-frequency vibrational modes might have important role actually involve non-equilibrium processes. For example, when a change occurs in the charge distribution of a molecule during a chemical reaction, the solvent responds by rearranging around the new distribution [10]. Such solvent motion is expected to lead to time-dependent changes in the low-frequency vibrational spectrum of the solvent. In order to be able to follow such changes as they occur, a method is required for recording transient spectra at short times.

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PIT S0009-2614(97)00705-7
after initiation of the pertinent process. The aim of this Letter is to describe the development of such a method, where ultrafast terahertz pulses are used to probe the far-infrared spectrum of a sample after the initiation of a chemical reaction.

It was shown by several groups in recent years that terahertz pulses can be generated by exciting a semiconductor wafer (such as GaAs or InP) or a photoconducting antenna structure with a femtosecond pulse. The excitation leads to a burst of far-infrared (far IR) radiation from the semiconductor [11–14]. Biasing a semiconductor wafer with an external electric field (1–10 kV/cm) leads to the most efficient production of far-IR light [15], but the pulses obtained in this way are relatively narrow-band (≈ 50 cm⁻¹ FWHM, peaked at 15 cm⁻¹) and long (≈ 500 fs). Excitation of an unbiased wafer [16] or a photoconducting antenna [17] leads to far-IR pulses almost as short as the exciting pulse, but with low energy. Such pulses can have a bandwidth larger than 100 cm⁻¹ and peak at ≈ 50 cm⁻¹. The mechanism for far IR light generation can range from optical rectification in the case of an unbiased semiconductor wafer, to radiation by ultrafast photocarrier acceleration in the case of a biased wafer or a photoconducting antenna [18].

In this Letter we discuss the development of a femtosecond terahertz pump–probe spectrometer, utilizing the above ideas. Two examples are presented for the application of terahertz pulses to the study of the dynamics of non-equilibrium processes in molecular condensed phases. The first example demonstrates the response of the solvent to the shift of a charge in the molecule betaine, while the second example involves the measurement of energy relaxation of excited phonons in a sapphire crystal. We have carried out experiments with proteins that will be published elsewhere.

2. Technique

The femtosecond far-IR spectrometer (Fig. 1A) was based on a home-built chirped-pulse Ti:Sapphire regenerative amplifier, which produces 70 fs pulses with energy of 250 µJ at a repetition rate of 2 kHz [19]. For sample excitation at 810 nm, the amplified beam was split into two parts. The first was sent through a delay line and used as an excitation ('pump') source, while the second was expanded to a diameter of ≈ 1 cm, and then used to excite a (100) GaAs wafer, biased with a 10 kV/cm electric field [15]. For sample excitation at 405 nm, the output of the regenerative amplifier was sent through a 2 mm BBO crystal, and the generated second harmonic at 405 nm was separated with a dichroic mirror, sent through a delay line and used as an excitation ('pump') source for the sample. The remaining 810 nm light was expanded as above, and used to excite the GaAs wafer. The far-IR light emitted by the wafer, which was essentially collimated, was focused by a parabolic mirror onto the sample, to serve as an interrogating ('probe') pulse.

In one mode of our ultrafast far-IR spectrometer, the far-IR light transmitted through the sample was detected with a liquid helium-cooled silicon bolometer (Infrared Laboratories). The pump beam was chopped at half the repetition rate of the laser. The
signal from the bolometer was averaged by a lock-in amplifier referenced to the chopper frequency, the output of which was therefore proportional to the difference between transmission of the far IR light through a pumped and unpumped sample. Since all samples used in this study were isotropic, we do not expect the pump beam to be rectified by the samples, thereby producing THz radiation that can interfere with that of the probe beam.

In a second mode, the time-dependence of the electric field of the transmitted far-IR light was measured using a free-space electro-optic detector (Fig. 1B), following the design of Zhang and coworkers [20]. This detector consisted of a 1 mm ZnTe crystal, on which the far-IR beam was focused. The electric field of the far-IR beam induced birefringence in the ZnTe crystal through the Pockels effect. This birefringence rotated the polarization direction of a weak 810 nm beam which was also sent through the crystal, and this polarization rotation was recorded by a balanced photodetector. By scanning the time delay between the far-IR and 810 nm beams it was possible to map the electric field of the terahertz pulse. The result of such a measurement is shown in Fig. 2A. In this case the terahertz pulse was sent directly into the detector after its generation. The pulse is seen to be highly asymmetric, with a positive lobe having a FWHM width of \( \approx 700 \) fs, and a broader negative lobe. The power spectrum of the pulse, obtained by a Fourier transformation of the signal of Fig. 2A, is shown in Fig. 2B. The spectrum peaks at \( 5 \) cm\(^{-1} \) and has a width of \( \approx 5 \) cm\(^{-1} \), but its spectral content goes up to 30–35 cm\(^{-1} \).

The long wavelength of the focused probe beam leads to some interesting behavior; Due to diffraction, the longer wavelength components of the pulse will have a larger waist size after the parabolic mirror. Thus, while the measured focus size is 3–4 mm, shorter wavelength components will have more intensity at the center of the focused beam. A pinhole can therefore be used as a spectral filter, shifting the wavelength distribution of the terahertz pulse to shorter wavelengths. This effect can be calculated quantitatively using Gaussian beam propagation techniques [21] as discussed recently by You and Bucksbaum [22]. In our experiment we use a 1 mm pinhole at the focus of the terahertz beam. The spectrum of the beam after passing through the pinhole was calculated from the measured spectrum, and is given as a dotted line if Fig. 2. It is seen that the spectrum is indeed shifted to shorter wavelengths, peaking at 10 cm\(^{-1} \), with a width of \( \approx 10 \) cm\(^{-1} \).

The 1 mm pinhole served a second purpose. Since rather small signals are expected and observed for the experiments reported below, it was essential to improve the signal/noise ratio by matching the sizes of the pump and probe spots on the sample. On the other hand, it was also important to keep a high pump energy density. We therefore used an unfocused, 1 mm pump beam, which was made to overlap with the terahertz beam through the 1 mm pinhole, at an angle of \( \approx 20^\circ \). At 810 nm, the pump energy density at the sample was 50 mJ/cm\(^3 \), while at 405 nm it was 10 mJ/cm\(^3 \).
3. Solvation dynamics of betaine in chloroform

The dynamics of solvation processes have been extensively studied in recent years, typically by measuring the dynamic Stokes shift of a fluorescent dye (see e.g. Ref. [23] for a recent example), or by measuring the influence of solvent reorganization on charge transfer phenomena [10]. The lowest energy absorption band of betaine has a strong charge transfer character, and is therefore very sensitive to solvent properties, which made it the basis for the popular solvent polarity scale ET$_{30}$ [24]. The internal conversion from excited to ground state, which also involves charge transfer, was studied by Barbara and coworkers ([25] and references therein) in a series of solvents, and the rate was shown to depend on the characteristic time for solvation. To understand the type of solvent motion involved in charge solvation, it will be useful to develop methods to directly follow the solvent coordinate responsible for the process. As this coordinate may involve collective, low-frequency modes of the liquid, ultrafast far-IR spectroscopy is ideal for studying it.

We performed an 810 nm pump/far-IR probe experiment on a solution of betaine in chloroform. The betaine solution was flowed through a 50 μm cell equipped with 0.5 mm sapphire windows. The betaine concentration was adjusted to give an optical density of 1 in the flow cell. The flow rate was fast enough to replace the sample between consecutive laser pulses. The betaine molecules were excited with 70 fs pulses at 810 nm, and probed with terahertz pulses generated by a biased GaAs wafer. A silicon bolometer enabled detection of the undispersed terahertz pulse. The signal was recorded with a lock-in amplifier, as discussed in the Technique section. The resultant transient is shown in Fig. 3A, where a positive signal is due to increased absorption.

Around time zero the signal shows a pulse-width limited spike. This spike can either be a coherent four-wave mixing signal, with the terahertz light acting on the sample before the 810 nm light, or a solvent response faster than the terahertz pulse. The spike-subtracted signal shows a pulse-width limited growth of a negative (bleach) signal, which is due to the impulsive change of the magnitude of the electric field sensed by the solvent molecules after excitation of the betaine molecules. This signal is seen to decay with a time constant of 1.7 ps, leading to the appearance of an absorptive signal.

To further elucidate the source of the dynamics observed in the far-IR signal, we performed an 810 nm degenerate pump/probe experiment on betaine in chloroform, using 70 fs pulses. The result (together with a theoretical fit) is shown in Fig. 3B, and is similar to results discussed by Barbara et al. [10], although they did not report the dynamics of betaine in chloroform. A large bleach signal appears, and is due to the loss of ground-state absorption. The absorption is regained in a non-exponential process, starting with a very fast, 120 fs component (not previously reported in betaine studies, presumably due to lack of sufficient time resolution) and continuing with a 2.7 ps component. Hot ground-state molecules are formed after the back electron transfer process, leading to an increased absorption signal, which decays with the cooling of the molecules, in ≈ 18 ps.

Thus, the rise in the far-IR signal follows the electron transfer reaction of the solute, reporting directly on solvent motions involved in the process.
The signal remains at a positive level for at least 60 ps (data not shown), which we ascribe to heating of the solvent vibrational modes. In fact, the long time signal hints at a slow rise which parallels the cooling of the betaine molecules. However, the signal/noise ratio is not good enough to assign this rise unequivocally.

This is the place to note that in fitting femtosecond far-IR signals the rotating wave approximation should not be used, but we have found that this has only a quantitative, rather than a qualitative, effect on the calculated result. Even more important is the fact that the field (Fig. 2) is not simply a symmetric envelope times a sine or a cosine wave, as one is used to encounter in optical spectroscopy. This means that in general the generated field should be calculated from Maxwell’s equations numerically, leading to results that could be qualitatively different from those obtained with optical pulses. However, since we used a square-law detector in this experiment, the signal (apart from the spike at time zero) should probably be proportional to the intensity profile of the terahertz pulse. The latter has a very similar shape to the envelope of a typical optical pulse, and can therefore be deconvoluted from the signal using standard methods, as was done above.

In this work, a single 405 nm pulse is used to excite phonons in a 1 mm thick sapphire crystal (which was not crystallographically oriented), by a mechanism to be discussed below. Following excitation, the transient absorption of a terahertz pulse is measured at variable delay times. The result of a 405 nm pump/far-IR probe experiment on the sapphire crystal is shown in Fig. 4. The absorptive signal does not appear immediately, but rises with a time constant of 1.5 ps. It then decays with a time constant of 10 ps. A study of the dependence of the signal on the pump intensity shows it to be quadratic (inset to Fig. 4).

What is the excitation mechanism in our experiment? The quadratic dependence on pump intensity can be consistent with impulsive stimulated Raman scattering, two-photon absorption above the band-gap, or two photon absorption by impurities and/or color centers. Since pumping the sapphire crystal at 810 nm does not lead to a far-IR signal equivalent to the one shown in Fig. 4, it is quite unlikely that the signal actually arises from a Raman process. Also, since the absorption edge of sapphire is at 142.5 nm (8.7 eV) under ambient conditions [30,31], a two-photon excitation at 405 nm will not lead to absorption above the band-gap. Color centers in either irradiated [32] or unirradiated [33] sapphire crystals

4. Relaxation of lattice vibrations in a sapphire crystal

Measurements of dephasing of phonons can be achieved by Raman techniques, the impulsive version of which has been used frequently in recent years [26–28]. A general experimental method for the measurement of energy (or population) relaxation of lattice vibrations, which is the microscopic equivalent of heat transfer, has not been described. Phonon population relaxation is especially difficult to follow in the low-frequency regime. One method to study this process was developed by Yen and coworkers, who excited phonons in a doped crystal at low temperatures using a narrow-band far-IR laser, and then probed the time-dependent phonon spectrum using side-band spectroscopy of the dopant [29]. We show here that terahertz pulses can serve as very useful probes of phonon relaxation, when coupled with a suitable excitation method.

![Fig. 4. Pump–probe signal from a sapphire crystal.](image-url)
have been extensively studied. In particular, a strong absorption band near 200 nm was assigned to anion vacancy (F-type) color centers [33]. Since the optical absorption spectrum of the sapphire material we used displays this band (data not shown), it seems likely that two photon absorption by anion vacancy centers is the excitation mechanism in our experiment. Fast electronic relaxation of the excited centers and dissipation of the energy will lead to a temperature jump [34], i.e. excitation of lattice phonons. This is the most likely source of the far-IR signal. Only phonons directly coupled to the anion vacancy sites will be excited at first. We suggest that relaxation of these into lower-energy phonons is the cause of the finite-time rise of the far-IR signal. Further relaxation by energy transfer to unexcited regions of the crystal or by emission leads to the 10 ps decay of the signal. A full transient spectrum is required to elucidate the couplings responsible for the relaxation. The capability to obtain it is now being developed in our lab.

From the known response of our lock-in amplifier we can estimate the maximum signal in this experiment to be equivalent to an increase of 2–3 mOD in the absorption of the crystal. The increase in absorption at low frequencies can be predicted on the basis of a simple Debye model for the phonon density of states. Under such a model, an increase of the lattice temperature can lead to a reduction in the Debye cut-off frequency and hence to an increase of the density of states at low frequencies, and so to an increased absorption. The absorption of a 1 mm thick sapphire crystal at 10 cm\(^{-1}\) is \(\approx 10\) mOD, as estimated from the absorption spectra of Thomas et al. [35]. Thus the signal in our experiment corresponds to an increase of 20–30% in absorption.

5. Conclusion

We have shown in this work that the application of ultrafast far-IR spectroscopy can lead to new and interesting results on non-equilibrium chemical processes involving collective motions in a liquid or a crystal. A fuller picture of the discussed processes will be obtained by measuring transient changes in the far-IR spectrum, in addition to the intensity measurements presented here. We are in the process of adapting the free-space electrooptic detector as a transient spectrometer. Another direction to pursue would be to increase the bandwidth of the far-IR light used in the experiment. By improving the signal to noise ratio in our setup we hope to be able to use unbiased terahertz sources for this purpose.

Acknowledgements

We would like to acknowledge the ongoing support of Dr. Benjamin Greene from Bell Labs Lucent technologies with both advice and equipment for our terahertz spectrometer.

References