

# TIME-RESOLVED TERAHERTZ SPECTROSCOPY OF CONDENSED PHASE REACTIONS

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Ultrafast time-resolved visible-pump, far-IR (THz) probe spectroscopy has been developed in our lab and has been applied to study carrier dynamics in photoexcited GaAs and dipole solvation dynamics in betaine and *p*-nitroaniline. This type of spectroscopy enables us to study for the first time the nonequilibrium interaction between excited electronic states and low frequency vibrational modes.

*Keywords:* Ultrafast; spectroscopy; condensed phase; dynamics; terahertz; semiconductors

Ultrafast optical Kerr effect and photon echo experiments [1] have shown that there is a correlation between the rates of simple chemical reactions and low frequency ( $10-100\text{ cm}^{-1}$ ) librational modes present in polar solvents and proteins. However, no true microscopic identification of the relevant modes has been made, as these experiments are only sensitive to the **equilibrium** solvent spectrum. Time-resolved THz pump-probe spectroscopy may be more suitable, as it is in principle sensitive to the **non-equilibrium dynamics** of the solvent modes. We have developed a system for ultrafast visible/near-UV pump, THz-probe spectroscopy. Pump-probe experiments were performed on the carrier dynamics of photoexcited SI GaAs and the dynamic dipole solvation of two different dyes in polar solution.

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Femtosecond pulses are generated by a Coherent Mira/RegA laser system resulting in 120 fs pulses at 800 nm with  $4 \mu\text{J}/\text{pulse}$  at a repetition rate of 250 kHz. Nearly single cycle THz pulses with a 200 fs cycle length, a peak frequency of  $50 \text{ cm}^{-1}$  and a usable bandwidth from 1 to  $85 \text{ cm}^{-1}$ , are generated and electro-optically detected in ZnTe [2, 3]. The experimental setup has two optical delay lines, one for the pump-probe delay and one for the gate delay, *i.e.*, the time delay within the THz probe pulse. At each pump-probe delay, the gate delay line can be scanned and the data Fourier transformed to obtain a transient spectrum. Pump-probe experiments were performed on SI GaAs with the pump centered at 800 or 400 nm (see Fig. 1). The creation of carriers by the pump pulse gives rise to a transient absorption over the entire accessible frequency range that can be described by a modified Drude-Lorentz model based on a generalized Langevin equation (see Fig. 1). Pumping SI GaAs at 400 nm forces the

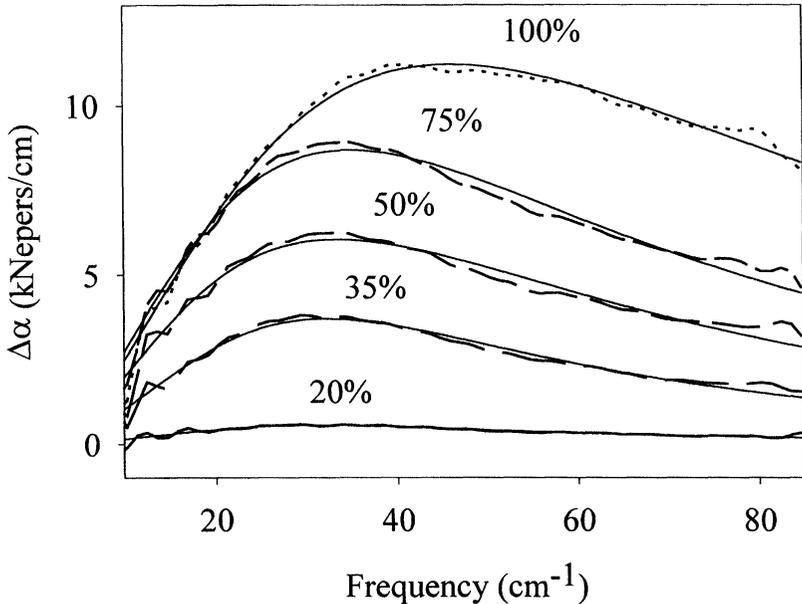


FIGURE 1 Transient spectra due to free carrier absorption photoinduced by an 800 nm pump pulse in SI GaAs. The spectra were taken at a pump-probe delay of 20 ps and at pump powers varying from full to 20%. All traces were fitted to a modified Drude-Lorentz absorption model.

carriers into the L and X valleys; Relaxation, due to the emission of phonons, back into the main  $\Gamma$  valley is observed to take place in  $1.35 \pm 0.06$  ps.

As model systems for condensed phase chemical reactions, the electron-transfer reaction in betaine [4] and the charge-shift reaction in *p*-nitroaniline (PNA) were used. Betaine undergoes an electron-transfer reaction in *circa* 1 ps from  $S_1$  back to  $S_0$  in which the dipole moment changes by 9D [5]. PNA has a dipole moment that increases by 7.3 D upon photoexcitation [6] and an excited state lifetime of *circa* 25 ps in *m*-dichlorobenzene. Figure 2 shows the change in the *m*-dichlorobenzene far-IR absorption after excitation of PNA at 400 nm [7]. In both betaine and PNA an oscillatory component is seen with a frequency of  $4.0 \pm 0.7 \text{ cm}^{-1}$  and a decay time of  $2.0 \pm 0.8$  ps. The data taken in PNA show a bleach of the ground state absorption that grows with  $6.9 \pm 3.3$  ps and that does not decay within the observed time window. Static absorption spectra of betaine and PNA in various

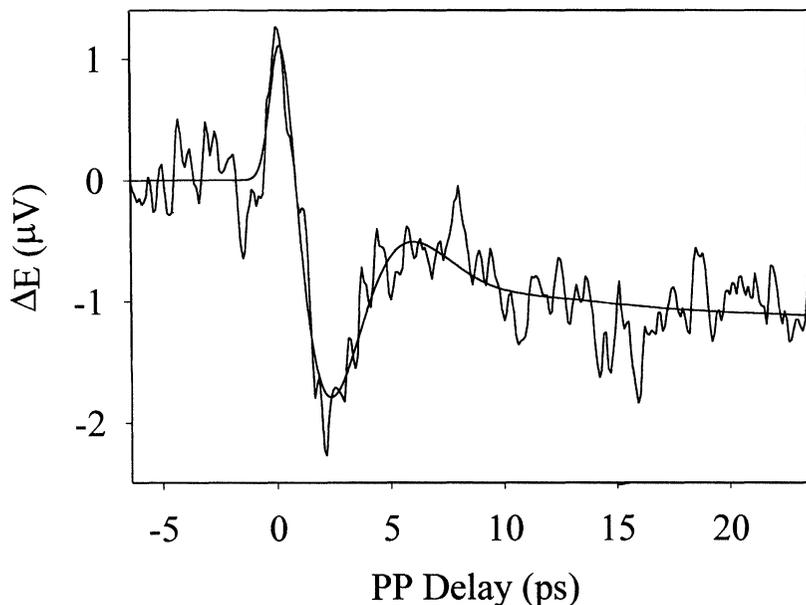


FIGURE 2 Transient pump-probe signal taken in *p*-nitroaniline in *m*-dichlorobenzene. The pump is at 400 nm (resonant with  $S_1 \leftarrow S_0$  transition of PNA) and the probe is a THz pulse monitored at its peak for various pump-probe delays.

polar solvents show that there is a small blue shift of the far-IR absorption band due to the presence of the dyes. Hence, the persistent bleach observed in the pump-probe signal in PNA may be due to a semi-permanent rearrangement of the solvent molecules around the solute in its polar excited state. Within the signal-to-noise, no such persistent signal is observed in betaine consistent with its short 4.3 ps excited state lifetime in *m*-dichlorobenzene [4]. We surmise that the oscillatory signal is an impulsive response of the solvent molecules in the first solvation shell to the sudden dipole moment change upon photoexcitation of the solute.

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