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Thin-sample limit for time-resolved terahertz spectroscopy

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The retrieval of the primary (subpicosecond) photoproducts in small-band two-dimensional time-domain terahertz spectroscopy has succeeded only in a few model systems, due to the complicated correlation between the two time parameters. We show that the nature of the primary photoproducts is revealed upon differentiating the measured time-domain spectra with respect to the pump-probe delay. An analytical treatment is given in the thin-sample limit, which distinguishes unambiguously between excitons and free charge carriers. This treatment gives a fair description of the data even for thick samples, including the subpicosecond timescale. © *2010 American Institute of Physics*. [doi:10.1063/1.3505340]

Two-dimensional (2D) time-resolved terahertz (THz) spectroscopy is rapidly imposing as a technique to determine the mobility of optically excited carriers in condensed matter and biomaterials.[1,2] Even though the technique has ultrashort capability (100 fs pulsed lasers are commercially available since decades), it is mostly used as a method to determine conductivities on the subnanosecond timescale. In the fewer cases that subpicosecond dynamics are addressed, the theoretical framework is either too complex[3] or insufficient (in the sense that the 2D-correlated data are described in terms of uncorrelated one-dimensional stacks[2,4,5]) to provide a satisfactory description of the measured data. There is one notable exception as follows: Beard and Schmuttenmaer[6] were able to give a beautiful simulation of their measurements on a dye (tetra-butyl-naphtalocyanine) in toluene, a simulation that was later fine-tuned by Nemec and co-workers.[7]

It is remarkable that up to date hardly any 2D contour plots have been published in the literature, and on those rare occasions the meanders observed at (sub)picosecond pump-probe delays are left without explanation.[5,8] Numerical simulations of the full Maxwell equations have the drawback of being very time consuming, and they are useful only if one knows the nature of the primary photoproducts on forehand. Yet even for model systems like bulk GaAs, with enormous signal levels, the primary photoproducts remain elusive: Beard and co-workers write that they were not able to account for differences between simulation and experiment in the first picosecond after excitation.[3]

An important step forward was done by Nemec *et al.* in 2002,[9] who derived an analytical solution in the perturbative limit. This solution has the advantage of simplification without loss of applicability (in the large majority of experiments one is specifically interested in the perturbative regime), and calculations need much less computing time.[7,10] However, the major issue, that of the immediate assessment of the primary photoproducts, remained unsolved.

In this letter, we elaborate on previous work[11] by deriving a simple expression in the thin-film limit. Preliminary measurements on a GaAs wafer demonstrate that the thin-film-limit is applicable in the case of thick samples, too: apparently, the thin-film limit does not throw out the bay with the bathwater. Moreover, the thin-film expression shows that a pump-induced representation of the 2D time-domain data is required in order to assess the nature of the primary photoproducts. This new representation paves the way to exploiting the full time-resolving capability of pump-probe THz spectroscopy, and effectively assessing the nature of the primary photoproducts as well as their subsequent reactions.

Starting points are Eqs. (7) and (46) of Ref. 11. In the twofold approximation of vanishing sample thickness ($L \rightarrow 0$) and lack of dispersion the pump-induced field reads

$$\Delta E(t,\tau) = -\nu_{tf}\theta(\tau)e^{-\Gamma\tau}\int_{t-\tau}^{t} dt' E_0(t')\Delta\dot{G}(t-t'),$$

$$\nu_{tf} \equiv \frac{q^2\rho L}{2nm\varepsilon_0 c}. \tag{1}$$

Here, $E_0(t)$ represents the THz electric field in the absence of the exciting pump pulse, $\Delta E(t,\tau)$ the pump-induced THz electric field. The initial population fraction, effective charge, and mass of the excited carrier species are represented by ρ, q, and m, respectively. The index of refraction is represented by n. The fields depend parametrically on the delay times t_p, t_g, and t_d, for the pump, generation, and detection delays, respectively, with the definitions $t = t_d - t_g$ and $\tau \equiv t_d - t_p$. The response to an instantaneous acceleration of a given carrier species is represented by the Green function $G(t)$; in case of harmonic motion it obeys the well-known second order equation

$$\left(\frac{\partial^2}{\partial t^2} + \gamma\frac{\partial}{\partial t} + \omega^2\right)G(t) = \delta(t). \tag{2}$$

Here, γ represents the damping coefficient and ω the resonance frequency of the carrier in question. The pump-induced response $\Delta G(t) = G_{\mathrm{free}}(t) - G_{\mathrm{bound}}(t)$ is the difference between the responses of the excited (G_{free}) and ground states (G_{bound}); i.e., ground state depletion and the concomitant decrease in polarizability following excitation are included in the here presented treatment.

Consider $\Delta E(t,\tau)$ as a function of the first time parameter (t) only, i.e., for a fixed value of the second one (τ). From Eq. (1) one may see that for a Drude response, $\dot{G}_{\mathrm{free}}(t) = e^{-\gamma t}\theta(t)$, the pump-induced field lags the driving

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field. Conversely, for a bound charge, $G_{\text{bound}}(t) = \gamma^{-1} \sin \omega t e^{-\gamma t} \theta(t)$, the pump-induced field leads the driving field, the lead angle increasing with the resonance frequency. In the high-frequency limit $\omega \gg \gamma$ the pump-induced field is proportional to the derivative of the driving field, as can be appreciated in measurements of exciton polarizability.[12]

Due to the lower limit of the temporal integral in Eq. (1) a rapidly oscillating response implies an equally rapidly oscillating pump-induced field along the τ-axis. This is never observed because the duration of the pump pulse always largely exceeds the period of a tightly bound electron. The pump-induced field in Eq. (1) must therefore be generalized by means of a convolution along the τ-axis $(\otimes)$ with the pump pulse as follows:

$$\Delta E''(t,\tau) \equiv \Delta E'(t,\tau) \otimes \frac{\xi(\tau)}{\Delta t_p} = -\frac{\nu_{tf}}{\Delta t_p} \int dt'' \xi(\tau - t'') \theta(t'') e^{-\Gamma t''} \times \int_{t-t''}^{t} dt' E_0(t') \Delta \dot{G}(t-t'). \tag{3}$$

Here. the function $\xi(\tau)$ stands for the envelope of the pump pulse, with a duration Δt_p. When the duration of the pump pulse is much shorter than the lifetime of the population $(\Delta t_p \ll 1/\Gamma)$, the exponential $e^{-\Gamma t''}$ in Eq. (3) can be approximated by $e^{-\Gamma \tau}$. A change in order of integration results in

$$\Delta E''(t,\tau) \approx -\frac{\nu_{tf}}{\Delta t_p} e^{-\Gamma \tau} \int_{-\infty}^{t} dt' E_0(t') \Delta \dot{G}(t-t') \times \int_{-\infty}^{\infty} dt'' \xi(\tau - t'') \theta(t'' - t + t'). \tag{4}$$

The twofold integral Eq. (4) can be simplified to a single integral by taking the partial τ-derivative as follows:

$$\frac{\partial}{\partial \tau} e^{\Gamma \tau} \Delta E''(t,\tau) \approx -\frac{\nu_{tf}}{\Delta t_p} \int_{-\infty}^{t} dt' E_0(t') \Delta \dot{G}(t-t') \times \xi(\tau - t + t'). \tag{5}$$

In the most common case that the scattering time exceeds the duration of the pump pulse, it follows

$$\gamma^{-1} \gg \Delta t_p \quad \frac{\partial}{\partial \tau} e^{\Gamma \tau} \Delta E''(t,\tau) \approx -\frac{\nu_{tf}}{\Delta t_p} E_0(t-\tau) \times \int dt' \Delta \dot{G}(t') \xi(\tau - t'). \tag{6}$$

It is useful to introduce the so-called "disturbance" $K(t,\tau)$ and the "characteristic function" $J(\tau)$ as follows:

$$K(t,\tau) \equiv \frac{\partial}{\partial \tau} e^{\Gamma \tau} \Delta E''(t,\tau) \equiv -\nu_{tf} E_0(t-\tau) \Delta J(\tau),$$

$$J(\tau) \equiv \Delta t_p^{-1} \int dt' \dot{G}(t') \xi(\tau - t'). \tag{7}$$

Assuming a Gaussian temporal profile of the pump pulse, $\xi(t) = e^{-(t/\Delta t_p)^2}$, the characteristic functions for free and bound charges read

$$J_{\text{free}}(\tau) = \frac{\sqrt{\pi}}{2} \left[1 + \text{erf}\left(\frac{\tau}{\Delta t_p} - \frac{1}{2} \gamma \Delta t_p \right) \right] e^{(\gamma \Delta t_p / 2)^2 - \gamma \tau},$$

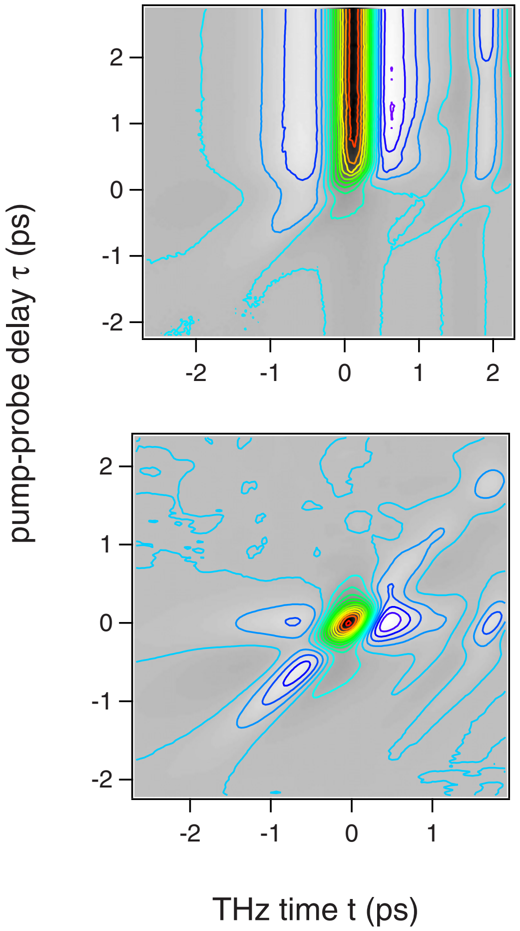

FIG. 1. (Color online) Experimental data for GaAs excited at 800 nm at room temperature. Upper pane: pump-induced field $\Delta E(t,\tau)$. Lower pane: $\partial / \partial \tau \Delta E(t,\tau)$.

$$J_{\text{bound}}(\tau) = -\frac{2\tau}{\gamma \omega \Delta t_p^3} e^{-(\tau/\Delta t_p)^2}. \tag{8}$$

These expressions hold in the limiting case $\Gamma \ll \gamma \ll \Delta t_p^{-1} \ll \omega$. If the binding energy of the bound state is low, such that the oscillation period of the bound electron $(2\pi/\omega)$ does not exceed the duration of the pump pulse by more than an order of magnitude, the characteristic function for the bound state does not permit the simple analytical form displayed in Eq. (8); terms of higher order in the oscillation period should then be taken into account [these terms can be derived by repeated partial integration of the characteristic function in Eq. (7)].

The two characteristic functions of Eq. (8) are typically revealed by measurements on a 300 μm thick GaAs wafer, excited by 800 nm pulses (<100 fs) at room temperature (see Fig. 1). The same data set is displayed twice as follows: the upper pane shows the pump-induced electric field $\Delta E(t,\tau)$, and the lower pane its (slightly smoothed) derivative to the pump-probe delay $\partial / \partial \tau \Delta E(t,\tau)$. The latter expression may be identified with the disturbance defined in Eq. (7) given the long life time of the free charges in GaAs $(\Gamma \rightarrow 0)$. The diagonal nodal lines in the disturbance (lower pane) imply that the electronic scattering time probably exceeds the duration of the pump pulse, such that the approximation of Eq. (6) applies, resulting in the factoring out of the pump-induced electric field $E_0(t-\tau)$ in the disturbance [Eq.

(7)]. The horizontal nodal line in the contour plot of the disturbance indicates that not only free charges but also bound charges are involved in the signal. Since free charges have a positive characteristic function [Eq. (8)], and bound charges a bimodal one, with the positive lobe at shorter times, the experimental data show that the bound charges participate with opposite sign. This must be expected to be the case, as the disturbance arises from a pump-induced signal difference $\Delta E = E_{\text{pump}} - E_{\text{no pump}}$; for every photon absorbed in the crystal from the pump beam there is one free charge *more* contributing to the disturbance, and one bound charge *less*. Earlier attempts to reproduce the measured 2D contour plots for GaAs probably failed (at subpicosecond pump-probe delays) due to the reasonable yet not allowed approximation $\Delta G(t) \approx G_{\text{free}}(t)$. In particular, detection response and THz propagation effects need not be invoked to account for the data.

Close inspection of the disturbance data shows oscillations in the characteristic function of the ground state of a period of 1.3 ps. Hence, the high-frequency limit proposed in Eq. (8) is not optimal, and the more general expression of Eq. (7) should be used instead. A detailed discussion of the GaAs data is left for a forthcoming report dedicated to semiconductor crystals.

Summarizing, we showed (i) that the experimental data reveal the nature of the primary photoproducts when displayed as a disturbance (i.e., the derivative to the pump-probe delay time of the pump-induced electric field) rather than the traditional way (the pump-induced electric field); (ii) that ground state depletion must be taken into account to describe the experimental data for GaAs, where the simple Drude model (or modifications of it) would fail, and (iii) that in the absence of resonances, the thin-sample limit is general enough to account for the principal features of THz spectroscopical data on thicker, dispersive samples, too: apparently, the thin-sample limit throws out the bathwater without losing the baby.

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