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Theory for determination of the low-frequency time-dependent response function in liquids using time-resolved terahertz pulse spectroscopy

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With the current rapid improvement in techniques for generating and detecting femtosecond terahertz (fs-THz) pulses, it is now possible to detect time-dependent perturbations to low-frequency intermolecular far-infrared modes during solvation events. The interpretation of these time-resolved terahertz spectroscopy experiments has generally relied on a collapse of the information available in the fs-THz pulse to give a one-dimensional time-dependent function, whose physical significance is not well defined. We describe a method to exploit the full electric field profile of the pulse as a function of pump/probe delay time to obtain a two-dimensional function that describes the system's time-dependent dielectric response. We discuss the physical significance of this response function in terms of the time evolution of solute/solvent modes following photoexcitation, and give examples to show how its qualitative features relate to the measurable signal. © *1999 American Institute of Physics.* [S0021-9606(99)51417-7]

I. INTRODUCTION

A longstanding goal of ultrafast spectroscopy has been the elucidation of solvation dynamics,[1] that is, the response of solvent to a perturbation in a solute, generally delivered as a photoinduced change in the electronic state of a dissolved dye molecule. Traditional solvation dynamics experiments, including time-dependent Stokes shift[2] and photon echo[3] experiments, measure the changing environment around the solute via its electronic transitions. The use of a probe pulse that directly responds to dipolar reorientation, with a far-infrared frequency range matching that of typical solvent responses, is now possible owing to developments in the generation and detection of femtosecond terahertz (fs-THz) pulses. This technique involves the generation and free-space propagation of a subpicosecond electric field pulse having a broad frequency spectrum (50 GHz–5 THz), followed by the measurement of its time-dependent electric field amplitude.[4–6] In addition to the use of fs-THz pulses as a broadband source of far-infrared radiation for spectroscopy in a wide range of systems, their potential as an ultrafast far-infrared probe has been exploited in time-resolved terahertz spectroscopy (TRTS).[7–21]

Several reports have been published on the application of TRTS to solvation dynamics.[16–18] In each case, the data have been presented in terms of a single measure of THz transmittance, either the change in total power absorbance or the change in amplitude at the peak of the THz pulse, as a function of time following the pump pulse. While this treatment allows assignment of a general time scale to the dynamic response, it does not provide specific insight into the nature of the solvent or solute modes involved. To fully exploit the potential of this method requires that a full profile of the THz pulse—which encodes the dielectric response of the sample during its passage—be measured for each point on a closely spaced two-dimensional grid of pump-probe delay times. Such an endeavor is a difficult challenge with the present state of stability and sensitivity of fs-THz pulse instrumentation, but will soon become practical given the rate of technical progress.

Apart from the experimental challenge, the interpretation of results for such an experiment is not intuitive. The equilibrium frequency-domain concepts of absorption and refractive index make little sense when the medium's properties are changing quickly with respect to the period of the radiation. Instead, we will show that TRTS results can be used to generate a two-dimensional time-domain response function that is well-defined and physically meaningful at all times during a solvation event. The purpose of this report is to describe how this response function can be derived from experimental TRTS results, to discuss the treatment of data and related issues of experimental setup, and to present simulated data for simple models as a demonstration of the insights into solvation dynamics this method promises.

The following section will be devoted to reviewing the relationship, for a classical system at equilibrium, between the dynamical response of a material and the change in a low-frequency electromagnetic pulse propagating through it. The subsequent section will raise the issue of complications that occur when the response is rapidly changing, and propose a method to account for these complications in interpreting two-dimensional TRTS data. The final sections will discuss experimental factors due to finite sample thickness, multiple reflections, and detector response; give examples of simulated data based on simple models for several qualitatively different varieties of response in a solution system; and extend our discussion to applications of time-resolved femtosecond THz pulse spectroscopy to the electronic properties of semiconductors and to the ultrafast dynamics of photoexcited molecules in the gas phase.

II. DIELECTRIC RESPONSE IN A MEDIUM AT EQUILIBRIUM

The classical linear response of a medium to any time-dependent electric field is determined by a memory kernel or response function $\chi(t-t')$, which gives the contribution to the medium's polarization at any time t resulting from the electric field at prior time t'. The response function can be defined in terms of the polarization caused by a delta-function electric field impulse at t',[22] with the result that $\chi(t-t')$ is zero for $t-t' \leqslant 0$, starts off positive and eventually decays back to zero at long times (with or without oscillations passing through zero). Integrating over all prior times gives the polarization at time t:

$$P(t)=\varepsilon_0 \int_{-\infty}^{t} E(t')\chi(t-t')dt'. \tag{1}$$

The time-domain response function can be related, via its Fourier transform $\tilde{\chi}(\omega)$, to the more familiar frequency domain dielectric properties, the complex dielectric constant $\tilde{\varepsilon}(\omega)$ and index of refraction $\tilde{n}(\omega)$:[23]

$$1+\tilde{\chi}(\omega)=\tilde{\varepsilon}(\omega)=\tilde{n}^2(\omega). \tag{2}$$

We proceed to show how a small change $\Delta\chi(t-t')$ to the equilibrium response function corresponds to a change in the E-field profile of a transmitted pulse. An infinite planar thin sheet of thickness s undergoing a time-dependent polarization in vacuum radiates plane waves, with electric field proportional to the negative of the time derivative of polarization, from either side of the plane:[24]

$$E(t)=-\frac{\mu_0 cs}{2}\frac{\partial}{\partial t}P(t). \tag{3}$$

If the sheet is replaced by a slab embedded in a dielectric medium with frequency-dependent complex index of refraction $\tilde{n}(\omega)$, solution of Maxwell's equations shows that an external perturbation to the polarization of the form $\Delta P(t)$ yields plane waves propagating in the medium according to

$$\Delta E(t)=-\frac{\mu_0 cs}{2}\int_{-\infty}^{\infty} i\omega \frac{\Delta\tilde{P}(\omega)}{\tilde{n}(\omega)}\exp(i\omega t)d\omega. \tag{4}$$

The time derivative of the polarization can be recovered by convolution of the generated electric field $\Delta E(t)$ with the Fourier transform of $\tilde{n}(\omega)$. Alternatively, when there is little dispersion in the medium and the index of refraction is dominated by the high-frequency, electronic response (i.e., $\tilde{n}(\omega) \approx n_\infty$ for all frequencies of interest), Eq. (4) reduces to

$$\Delta E(t)=-\frac{\mu_0 cs}{2n_\infty}\frac{\partial}{\partial t}\Delta P(t). \tag{5}$$

In the following, we will assume that dispersion is minimal and that Eq. (5) is a good approximation, which is a valid assumption for weakly absorbing liquids such as chloroform in the 100 GHz–2 THz range. Substituting the derivative of Eq. (1) into Eq. (5), given that $\epsilon_0\mu_o=c^{-2}$, yields

$$\Delta E(t)=-\frac{s}{2n_\infty c}\int_{-\infty}^{t} E(t')\frac{\partial}{\partial t}\Delta\chi(t-t')dt'. \tag{6}$$

Using Eq. (6), the time derivative of an equilibrium perturbation to the response function can be obtained from the deconvolution of the change in electric field signal, $\Delta E(t)$, from the original signal, $E(t)$ (assuming reflection effects can be ignored). Equation (6) holds only when $\Delta E(t)$ is a small perturbation to $E(t)$, that is when for all frequency components of the reference and perturbation signals,

$$\exp(\Delta\tilde{E}(\omega)/\tilde{E}(\omega)) \approx 1+\Delta\tilde{E}(\omega)/\tilde{E}(\omega). \tag{7}$$

III. TIME-DEPENDENT RESPONSE FUNCTION

If the system is not at equilibrium, but rather is evolving as a function of time with respect to some event, such as the photoexcitation of a chromophore, a response function can still be defined to relate the polarization at time t to the applied electric field at earlier times t'. It becomes a function of two dimensions, however,

$$P(t'',t)=\varepsilon_0 \int_{-\infty}^{t} E(t')\chi(t-t'',t-t')dt', \tag{8}$$

with t'' marking the time of the event. The time-dependent electric field in Eq. (8) refers only to the field of the fs-THz pulse and not to the much higher-frequency field of the photoexciting pump pulse, whose influence is folded into the t'' dependence of the response function. An implicit assumption is that the presence of the fs-THz pulse field does not significantly alter the effect of the photoexcitation pulse on the electronic state of the sample.

We will treat the time-dependent component of the two-dimensional response function as a perturbation to the native material response,

$$\chi(t-t'',t-t')=\chi_0(t-t')+\Delta\chi(t-t'',t-t'), \tag{9}$$

with the $\Delta\chi$ term vanishing for $t<t''$. The measured change in electric field will likewise gain an additional dependence on t'', as seen by substituting Eq. (8) in Eq. (5):

$$\Delta E(t'',t)=-\frac{s}{2n_\infty c}\int_{\infty}^{t} E(t')\frac{\partial}{\partial t}\Delta\chi(t-t'',t-t')dt'. \tag{10}$$

Unlike Eq. (6), Eq. (10) is not a convolution of two one-dimensional functions, and therefore cannot be solved for fixed t''. In other words, the fact that the end of the THz pulse can experience a different response than the beginning of the pulse complicates the analysis. An implication is that frequency components related to the $t-t''$ dependence of the response function, that were not present in the initial pulse, are introduced into the response signal; the response is now nonlinear in this respect, although a given linear combination of input THz pulses will result in the same linear combination of output pulses and difference signals.

The way to resolve the problem is to consider, instead of a single propagating THz pulse with a fixed pump time t'', a set of data points taken from different pulses, all measured at the same delay with respect to the pump pulse. Collecting data in this arrangement is easy to achieve experimentally in a system with gated detection. Referring to the experimental scheme in Fig. 1, instead of fixing the relative arrival of the pump pulse and the probe pulse at the sample by fixing delay

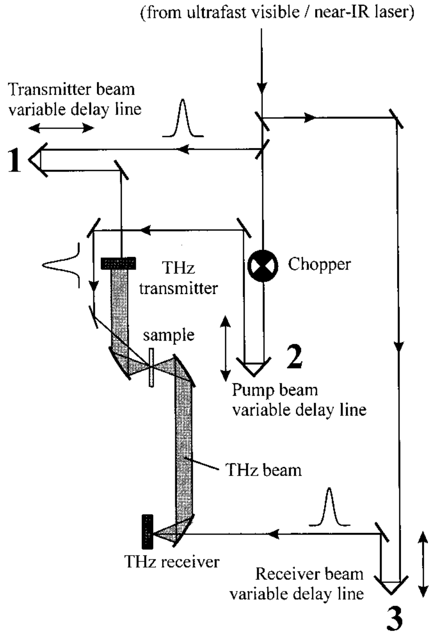

FIG. 1. Schematic diagram of time-dependent THz pulse spectroscopy setup, showing delay lines **1**, **2**, and **3** that can be fixed or scanned during data acquisition to vary the arrival times of visible and fs-THz pulses. (Optical components such as lenses and polarizers are omitted.)

lines **1** and **2** and increasing **3** to measure the THz pulse, it requires that data be acquired at a fixed relative delay of the pump pulse at the sample and the gating pulse at the detector, fixing delay lines **2** and **3** and decreasing **1**. In either scenario, the THz profile must be measured repeatedly over a range of incremental delays of the pump pulse, **2**. Furthermore, both methods of data acquisition yield the same ΔE when the delay time after photoexcitation is long compared to the THz pulse and the response timescale.

This change corresponds to a different projection along the two-dimensional ΔE response, fixing $u=t-t''$, so that the analysis is of a composite series of data points measured at a constant delay from the pump pulse event. Now, each point in the measured waveform has passed through the sample after the same amount of time from the photoexcitation event:

$$\Delta E(t-u,t)=-\frac{s}{2n_{\infty}c}\int_{\infty}^{t}E(t')\frac{\partial}{\partial t}\Delta\chi(u,t-t')dt'. \tag{11}$$

Since u is held constant, $\Delta E(t-u,t)$ can be deconvolved from $E(t)$ to yield $(\partial/\partial t)\Delta\chi(u,t-t')$. This is the time derivative of a two-dimensional function that has time in both its arguments:

$$\begin{aligned}\frac{\partial}{\partial t}\Delta\chi(u,t-t')&=\frac{\partial}{\partial t}\Delta\chi(t-t'',t-t')\\&=\left[\frac{\partial\Delta\chi}{\partial(t-t'')}\right]_{(t-t')}+\left[\frac{\partial\Delta\chi}{\partial(t-t')}\right]_{(t-t'')}.\end{aligned} \tag{12}$$

Solving for $\Delta\chi(t-t'',t-t')$ given $(\partial/\partial t)\Delta\chi(u,t-t')$ therefore requires integrating on a diagonal *across u*, at constant t'', as shown in Fig. 2(c).

The steps connecting a set of time-dependent difference signals with the corresponding response function are illustrated in Fig. 2. The first step, from a two-dimensional data set of E-field difference signals arranged by pump-THz probe delay time [Fig. 2(a)] to one arranged by pump-THz receiver delay time [Fig. 2(b)], is simply a change of axes (conveniently achieved by the experimental set-up shown in Fig. 1). The second step, deconvolution of the difference profile at each $t-t''$ value from the transmitted probe pulse E-field profile, yields the negative of the time derivative of the two-dimensional response function [Fig. 2(c)]. Integrating with respect to t, that is, along on the diagonal as represented by the dashed arrow in Fig. 2(c), and reversing the sign yields the actual time-dependent change in the response function. We do not include an absolute scale for either the difference signal or the response function; their relative scale will depend on the sample thickness, index of refraction, and THz probe pulse magnitude, while the absolute scale of the response function will depend on the pump pulse magnitude.

The most distinctive feature of Fig. 2 is that at small values of $t-t''$, the difference signal in panel (b) and its deconvolution in panel (c) look qualitatively different than their long-time limits, whereas the actual response function in panel (d) increases in magnitude but does not change form during this same time period. It is vital to recognize that a rapid change in the response function will cause this type of transient feature in the measured THz difference signal.

We note that an assumption of this treatment is that the high-frequency index of refraction remains constant. Small changes in n_{∞} of the solution will manifest themselves as spikes in $\Delta\chi(t-t'',t-t')$ at small values of $(t-t')$, with duration limited by the time interval of sampling, as appropriate for a polarization that is for practical purposes instantaneous with respect to the THz pulse.

IV. LIMITS TO TIME RESOLUTION

The time resolution achievable in the response function along the $t-t'$ axis will depend, just as in the equilibrium case, on the bandwidth of the pulse detected at the receiver, which is a convolution of the THz pulse generated and the detector response, with losses from the sample and windows factored in. The time resolution along the other axis depends on the pump pulse duration, on the detector response, and on the dispersion and thickness of the sample. If the index of refraction of the sample is significantly different in the visible and far-infrared regions of the spectrum, the time resolution will be degraded further. We note that neither aspect of the time resolution depends on the *duration* of the THz probe pulse. While these factors favor a short sample pathlength with low loss, complications caused by multiple reflections are fewest with thick, highly absorbing samples, in which multiple reflections are either largely quenched or sufficiently delayed that they do not interfere with the main signal, just as in the equilibrium case.

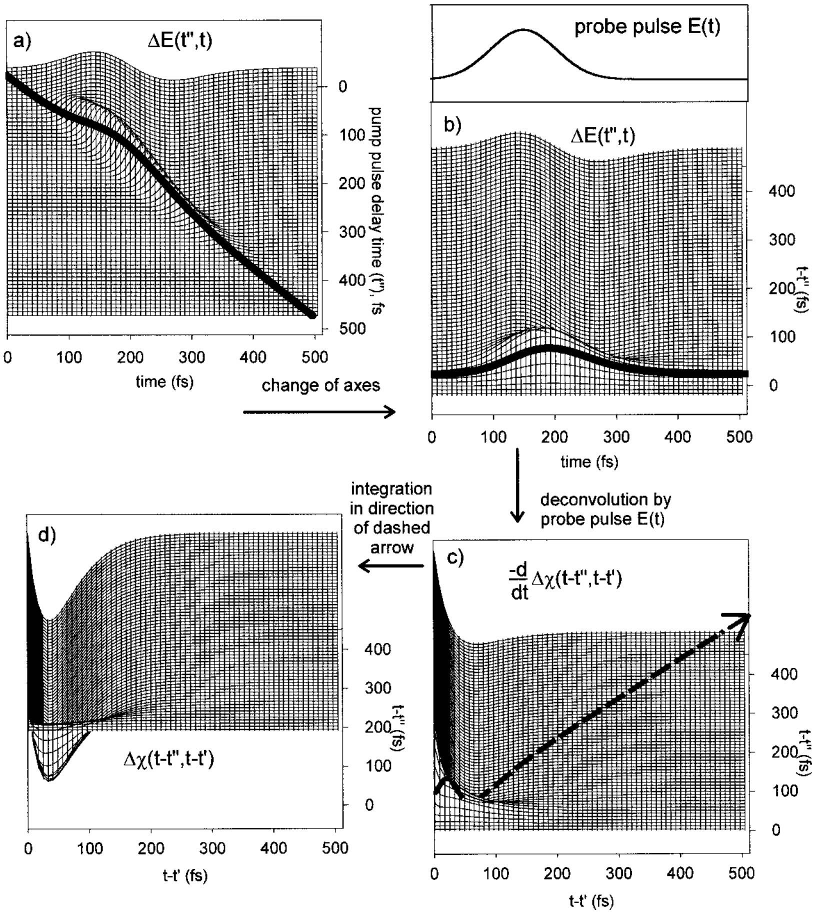

FIG. 2. Illustration of procedures in analysis of time-dependent THz difference signal to yield the time-dependent response function. A simulated THz pulse difference signal acquired as a function of pump pulse-probe pulse delay time in (a) is transformed by a change of axes to the same signal arranged as a function of pump pulse-receiver pulse delay time in (b), with the heavy diagonal line in (a) shown mapped onto (b) for illustrative purposes. The time-resolved difference signals in (b) are deconvolved from the reference transmitted THz probe pulse (inset) at each value of $t-t''$ to yield the negative time derivative of the two-dimensional response function in (c). Integration of the two-dimensional function in (c) in the direction indicated by the dashed line, followed by negation, yields the time-dependent perturbation to the response function, $\Delta\chi(t-t'',t-t')$, and is shown in (d).

V. MODELS FOR THE TIME-DEPENDENT RESPONSE FUNCTION IN SOLVATION DYNAMICS

The optical pump pulse leads to immediate changes in the electronic distribution of the system and, indirectly, to slower changes in the molecular arrangement. Both types of structural changes can alter the low-frequency dielectric response by changing the interaction potentials in which the solute and solvent move, and by changing the dipole moments (both permanent and induced) that couple their motion to the probe pulse. If we make the approximation that the average solute/solvent dielectric response can be represented by a few independent harmonic modes, each with a damping term representing dephasing and dissipation by the surrounding bath (i.e., the multimode Brownian oscillator model[25]), then these changes can be expressed in terms of a time-dependent component to the parameters that dictate each mode's dynamics and coupling to the external *E*-field. While the true microscopic solute/solvent modes are both anharmonic and coupled to one another, the mean linear dielectric response can often be represented by as few as two uncoupled damped oscillators, even for a structured liquid like water.[26] The solvent dynamics close to a solute will not in general be identical to the bulk modes; the difference in equilibrium dielectric response between a solution and pure solvent should allow identification of modes specifically related to the presence of the solute. For simplicity, in the following discussion we will assume that only one mode is affected by the solute photoexcitation.

The time evolution of a given damped harmonic mode, expressed in terms of a dimensionless macroscopic mode coordinate s (which actually represents an expectation value over all microscopic orientations and phases of the mode), satisfies the differential equation

$$\ddot{s}(t)=-ks(t)-\gamma\dot{s}(t)+\mu E(t), \tag{13}$$

while its contribution to the macroscopic polarization is given by

$$P(t)=\mu s(t). \tag{14}$$

The parameters k and γ are the force constant and damping constant of the oscillator, and μ is the coupling of the mode to the field, i.e., the first derivative of the net dipole moment with respect to the mode coordinate. We neglect nonlinearities both in the potential and in the expansion of the dipole moment with respect to s. As mentioned in Sec. II, the linear dielectric response function $\chi(t-t')$ is equivalent to the polarization response at time t from a delta-function E-field impulse at time t', which sets the mode—originally at its equilibrium position, with no polarization—in motion with velocity $\dot{s}(t')=\mu$. For the equilibrium case, where the parameters are not time dependent, the solution becomes[27]

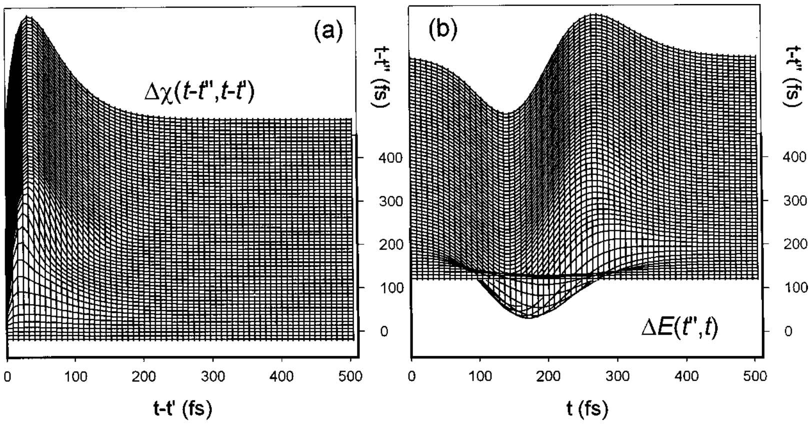

FIG. 3. Time-dependent perturbation to response function (a) and simulated difference signal (b) for a single slightly underdamped harmonic mode ($k=4.24\times10^{-4}$ fs^{-2}, $\gamma=5.76\times10^{-2}$ fs^{-1}) undergoing a 50% increase in μ over the duration of a 42 fs full width at half maximum (FWHM) Gaussian pump pulse. The THz probe pulse used to generate the difference signal is a Gaussian (FWHM=125 fs) centered at 150 fs, and is shown in the inset of Fig. 2(b).

$$\chi(t-t')=\frac{\mu^2}{\sqrt{\gamma^2-4k}}\left[\exp\left(\frac{-\gamma+\sqrt{\gamma^2-4k}}{2}t\right)-\exp\left(\frac{-\gamma-\sqrt{\gamma^2-4k}}{2}t\right)\right],\qquad t\geqslant t'. \tag{15}$$

Equation (15) can describe both underdamped harmonic motion resulting in coherent oscillations($\gamma^2<4k$) and overdamped motion characterized at long times by exponential relaxation ($\gamma^2>4k$); the special case of critical damping ($\gamma^2=4k$) gives a different functional form for $\chi(t-t')$, but one which is approached smoothly from either of the other two cases.

Our interest here is the calculation of the response function when the parameters themselves become explicitly time dependent. Given some event initiating a change in parameters at or around time t'', we can rewrite Eqs. (13) and (14) as

$$\ddot{s}(t)=-k(t-t'')s(t)-\gamma(t-t'')\dot{s}(t)+\mu(t-t'')E(t), \tag{16}$$

$$P(t)=\mu(t-t'')s(t). \tag{17}$$

To calculate $\chi(t-t'',t-t')$ given a set of time-dependent parameters, we numerically solve Eqs. (16) and (17) for $P(t)$ over a range of t'', subject to an initiating delta-function E-field impulse at time t', either before or after time t''. The time-dependent perturbative component of the response function, $\Delta\chi(t-t'',t-t')$, is then assigned according to Eq. (14).

We now consider a few simple cases to determine how the form of the two-dimensional response function will reflect the short-time dynamics of a photoexcited solute-solvent system. The first example is a change in a mode's transition dipole moment, μ, leaving the frequency and damping parameters unchanged. This corresponds to a change in the magnitude (or even the sign or direction) of the mode's coupling to the external field, with no change to the intrinsic dynamics. Such a situation is interesting both as a simple limiting case, and also because many of the dye molecules previously studied in ultrafast solvation dynamics experiments were chosen because photoexcitation dramatically changes their dipole moment. A change in solute dipole can contribute not only to a change in μ for modes directly involving solute reorientation, but also, via the change in electronic polarization the solute induces in its neighborhood, to a change in μ for nearby solvent modes.

Figure 3(a) shows $\Delta\chi(t-t'',t-t')$ corresponding to a mode in which μ is increased by 50% of its original value, μ_0 over the duration of a 42 fs [full width at half maximum (FWHM)] Gaussian pump pulse to its excited state value, $\mu_e=1.5\mu_0$. The interesting result is that the response function continues to change even after μ has reached its final value. At long pump-probe delay times $t-t''$ the difference in the response function is simply a scalar times the mode's original contribution to the response function. More precisely, since according to Eq. (15) the contribution of a time-independent mode to χ is proportional to μ^2,

$$\Delta\chi(t-t'',t-t')_{t\gg t''}=\frac{\mu_e^2-\mu_0^2}{\mu_0^2}\chi_0(t-t'). \tag{18}$$

For shorter times following photoexcitation, however, there will be a memory from the oscillator's response to the electric field of the THz pulse while the oscillator was still responding with its ground state dipole. This contribution to the polarization will be proportional to the product of the original coupling μ_0, which determined the magnitude and direction of the response to the electric field at t', and the new value μ_e, which relates the response (the mode's position) to the polarization at the current time t:

$$\Delta\chi(t-t'',t-t')_{\substack{t>t''\\ t'<t''}}=\frac{\mu_0\mu_e-\mu_0^2}{\mu_0^2}\chi_0(t-t'). \tag{19}$$

The transition between the initial phase in the response and the long-time response is evident in Fig. 3(a) along the diagonal $t-t'=t-t''$. In this case, for a 50% increase in μ, the long-time response of Eq. (18) is 2.5 times as large as the initial response given by Eq. (19). The extension to a vector μ, which can rotate an arbitrary angle as well as change in magnitude, is achieved by replacing $\mu_0\mu_e$ in Eq. (19) with a dot product. Even though the change in μ occurs simultaneously with the pump pulse, the response function continues to evolve due to this memory effect, linking the dynamics of the mode before and after the photoexcitation.

Simulated time-dependent (two-dimensional) THz difference signals, corresponding to this time-dependent re-

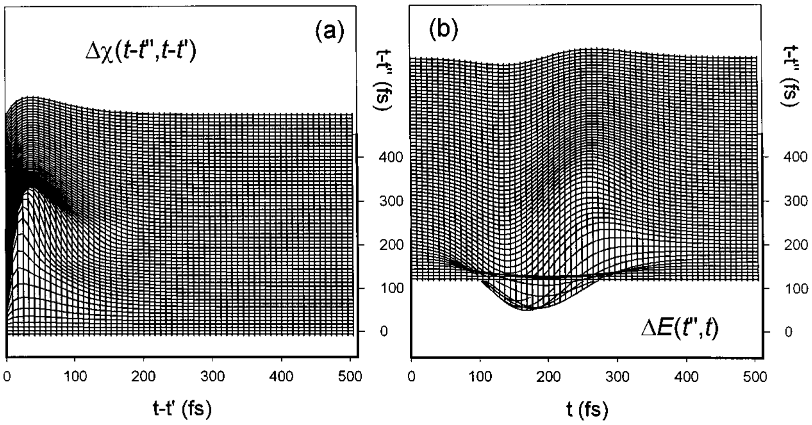

FIG. 4. Time-dependent perturbation to response function (a) and simulated difference signal (b) for a single damped harmonic mode ($k=4.24\times10^{-4}$ fs^{-2}, $\gamma=5.76\times10^{-2}$ fs^{-1}) undergoing undergoing a 100% increase in μ over the duration of a 42 fs full width at half maximum (FWHM) Gaussian pump pulse, with μ subject to an exponential decay ($\tau=500$ fs) to a net 50% increase. The THz probe pulse shape is as in Figs. 2 and 3.

sponse function probed by a Gaussian THz probe pulse, are shown in Fig. 3(b), arranged with constant pump-receiver delay. At short pump-receiver delay times $t-t''$, the difference signal has a shape similar to the negative of the convolution of the input signal and the response function. This reflects the contribution to the change in polarization from the increase in magnitude of dipoles already oriented by the pulse. At long pump-receiver delay times, there is no longer any change in dipole strength and the only contribution to $\partial P/\partial t$ is from the dipoles in their photoexcited state responding to the external electric field. As in the equilibrium case, the difference signal takes the approximate form of the convolution of the external signal and the time derivative of the response function with respect to $t-t'$.

Figure 4(a) shows the time-dependent response function that results when μ for a given mode has a slower time-dependent evolution in addition to its rapid transition during the pump pulse. This is one way in which solvent reorientation around a photoexcited solute might manifest itself. If we envision a dipolar solute surrounded by a solvent shell with a net dipole moment oriented either with or against that of the solute, then the effective combined dipole moment of the solute and the solvent shell will continue to change after photoexcitation as the solvent shell reorganizes to adapt to the new electronic structure of the solute.[28] This process will affect the effective dipole of the solute modes and, through shielding, the induced dipoles of surrounding solvent molecules. To generate the response function in Fig. 4, the transition dipole moment of the same mode appearing in Fig. 3 is first doubled, then scaled back exponentially to a 50% net increase with a 500 fs time constant. The difference signal shown in Fig. 4(b) shows qualitatively a fast rise and slower decay, but is not merely a replica of Fig. 3(b) with an exponential decay in the $t-t''$ coordinate; the exponential decay of the polarization is fast enough to contribute significantly to $\partial P/\partial t$ and thus contributes to the change in E-field.

In general, photoexcitation of the solute is as likely to change the dynamics of solution intermolecular modes as it is to change their coupling to the external field, so time-dependent dynamics will now be considered. Again, memory effects from modes propagating on changing potentials will be manifested in the response function at short times, although the result is less clear-cut because the intrinsic dynamics are changing. As an example, we simultaneously decrease both μ by 5% and γ by 25%, and present the resulting change to χ in Fig. 5(a). At long $t-t''$ times, the response function has structure corresponding to the difference between the response functions of the new mode and the old mode. At the very shortest times (less than 80 fs), because the new potential has not been in effect for long, the response function primarily reflects the decrease in dipole moment. Convolution of the time derivative with a Gaussian THz probe pulse gives a fairly complex result, shown in Fig. 5(b). No possible one-dimensional representation of this difference signal could adequately represent the evolution of modes from which it is generated.

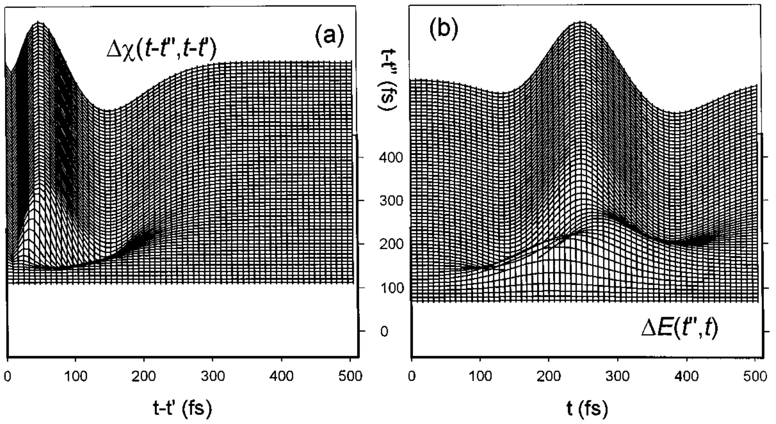

FIG. 5. Time-dependent perturbation to response function (a) and simulated difference signal (b) for a single damped harmonic mode ($k=4.24\times10^{-4}$ fs^{-2}, $\gamma=5.76\times10^{-2}$ fs^{-1}) simultaneously undergoing a 25% decrease in γ and a 5% decrease in μ over the duration of a 42 fs full width at half maximum (FWHM) Gaussian pump pulse. The THz probe pulse profile is as in Figs. 2 and 3.

Even these simple models, involving only a single mode, produce complicated response functions. Interpreting real experimental data, which might involve multiple electronic states and several solvent modes (or for which the concept of modes might not be applicable) will require careful attention to the results of other experiments: time-dependent fluorescent Stokes shift data, all available information about the solute electronic states and relaxation rates involved, and a thorough understanding (from equilibrium THz spectroscopy) of how the solute in its ground state contributes to the solution response function. With this in mind, the fact that the TRTS signal depends both qualitatively and quantitatively on which modes are affected by photoexcitation, in what manner they are affected, and the timescale on which they evolve promises that a picture of the underlying dynamics will be accessible.

VI. IMPLICATIONS FOR TRTS IN OTHER SYSTEMS

TRTS has attracted most attention thus far in studies of the dynamics of photogenerated charge carriers in semiconductors,[7–9,11,12,19–21] several of which have gone beyond a one-dimensional analysis and reported time-dependent changes in the THz absorption spectrum.[19,20] The analysis of pump-probe data for conductive samples follows that described in Sec. III, with the substitution of $\sigma(t-t'',t-t')$ for $(\partial/\partial t)\chi(t-t'',t-t')$, removing the need for the last step of integration. As the time-dependent conductivity response and its Fourier transform $\sigma(t-t'',\omega)$ have been calculated by Vengurlekar and Jha[29] for the photoexcitation of GaAs under diverse conditions of temperature and pump excitation energy, conditions are ripe for a careful comparison between theory and experiment.

Equilibrium time-domain THz spectroscopy has been applied to gas phase rotational spectroscopy as well.[30] As gas phase far-infrared spectra exhibit narrow lines, gas phase response functions generally decay over a very long time, often exhibiting many coherent recurrences. While this long decay would seem to prohibit any notion of using fs-THz pulses as a probe of ultrafast dynamics, the time resolution does not depend on the duration of the probe pulse, as described above. By photoexciting a gas phase molecule with a pump laser pulse and collecting THz probe data with fixed pump-receiver delay time, it may very well be possible to extract information about the evolution of the response function—and from thence the dipole moment and moment of inertia tensor—at subpicosecond times following ultrafast optical or infrared excitation.

VII. CONCLUSIONS

The time-dependent dielectric response function of a system undergoing changes that are rapid with respect to the response timescale can be obtained, via an analysis described above, from time-resolved THz pulse spectroscopy. This information will be valuable in describing details of solvation dynamics, as features of this response function at short times reflect the evolution of solvent and solute modes from their behavior in the ground state to their new behavior in the perturbed excited state. The analysis is applicable with some modification to the study of ultrafast charge carrier dynamics, and may prove useful in studies of ultrafast dynamics in the gas phase. Future extensions of this work will include alternative methods of generating two-dimensional response functions based on alternative models of solute-solvent interactions[31] instead of Brownian harmonic oscillators, recasting the analysis in terms of quantum observables, and developing a method to derive the two-dimensional response function from molecular dynamics simulations of solute photoexcitation.

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