

# Finite-difference time-domain simulation of ultrashort pulse propagation incorporating quantum-mechanical response functions

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A semiclassical implementation of the finite-difference time-domain method is used to simulate coherent linear propagation of ultrashort mid-infrared pulses through optically dense samples of isotopically diluted liquid water. Bloch equations for the density matrix are used as a simple model of the O—H oscillator relaxation, and the algorithm is extended to other response functions. Sensitivity of the field to the form of the response function is demonstrated, and the results are compared with experimentally determined electric fields in the same media [Rev. Sci. Instrum. **73**, 2227 (2002)]. © 2003 Optical Society of America

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When pulses of duration comparable to the dephasing time of a resonance propagate through an optically dense sample, distortions of the pulse electric field occur as a result of destructive interference between the pulse field and the free-induction decay(s) (FIDs) that it drives.<sup>1</sup> Recently this effect was demonstrated for the propagation of ultrashort mid-infrared (mid-IR) pulses through samples of isotopically diluted water at a series of optical densities.<sup>2</sup> The field intensity and phase were determined by cross-correlation frequency-resolved optical gating (XFROG). These results demonstrated the importance of simulating propagation effects on spectroscopic measurements, as has also been noted by others.<sup>3–5</sup> These effects are of particular relevance to ultrafast mid-IR spectroscopy, as the small transition dipole moments of vibrational modes often necessitate the use of samples with optical densities larger than the standard value of 0.3 employed in nonlinear optical experiments.

Traditionally, pulse propagation effects have been modeled with only the field envelope taken into consideration and with the assumption that the rotating wave and slowly varying envelope approximations are valid.<sup>6</sup> However, given the current technological feasibility of generating few-cycle pulses and the ability to measure or determine the electric fields of spectroscopic signals, it is desirable to utilize a full-field technique, such as the finite-difference time-domain (FDTD) method,<sup>7</sup> to model the effects of propagation on experimental results. The FDTD method holds great promise for modeling ultrafast spectroscopic measurements, but until recently<sup>8,9</sup> had received little attention. A major issue is proper modeling of the material response through the polarization term in Maxwell's equations; it would be advantageous to use a method that treats the medium quantum mechanically and allows for the incorporation of complicated response functions.

In this Letter we present a corrected and extended version of a semiclassical FDTD method first introduced by Ziolkowski et al.<sup>10</sup> for modeling the resonant

propagation of ultrashort mid-IR pulses. The algorithm is applied to the OH-stretch spectral region of isotopically diluted liquid water. The Bloch model for a two-level system is introduced by means of equations for the density matrix, and the resulting set of equations is solved with a predictor–corrector (PC) algorithm. Because this method treats the density matrix directly, complex relaxation functions can be incorporated. The extension reported herein is to a Gaussian response function.

The PC FDTD algorithm is based on finite differencing of Maxwell's curl equations.<sup>7</sup> Consider linearly polarized fields traveling in one dimension (along  $z$ ): The curl equations are

$$\begin{aligned}\frac{\delta H_y}{\delta t} &= -\frac{1}{\mu_0} \frac{\delta E_x}{\delta z}, \\ \frac{\delta E_x}{\delta t} &= -\frac{1}{\epsilon} \frac{\delta H_y}{\delta z} - \frac{1}{\epsilon} \frac{\delta P_x}{\delta t},\end{aligned}\quad (1)$$

where the medium is assumed to carry no electric or magnetic currents and  $H$  represents the magnetic field. The permeability in all regions is that of free space, and the permittivity is that of the medium in which the pulse is propagating, either free space or a liquid. The polarization of the two-level medium is determined by the relation  $P_x(t) = -N\gamma\rho_1(t)$ , where  $\rho_1$  represents the dispersive component of the polarization,  $\gamma$  is the transition dipole moment, and  $N$  is the number density of two-level absorbers. The Bloch model's phenomenological decay constants are  $T_1$  (population relaxation time) and  $T_2$  (dephasing time). The equations for all density matrix elements—including  $\rho_2$  (the absorptive component) and  $\rho_3$  (the inversion)—as well as the electric and magnetic fields, are developed in detail in Ref. 10. However, the finite-difference equations in the appendix of that paper contain a number of errors; the corrected equations needed for the PC FDTD calculation are

$$H_y\left(m + \frac{1}{2}, n + \frac{1}{2}\right) = H_y\left(m + \frac{1}{2}, n - \frac{1}{2}\right) - \frac{\Delta t}{\mu_0 \Delta z} [E_x(m+1, n) - E_x(m, n)], \quad (2)$$

$$E_x(m, n+1) = E_x(m, n) - \frac{\Delta t}{\epsilon \Delta z} \left[ H_y\left(m + \frac{1}{2}, n + \frac{1}{2}\right) - H_y\left(m - \frac{1}{2}, n + \frac{1}{2}\right) \right] - \Delta t A \left(n + \frac{1}{2}\right) \times \frac{1}{2} [u_1(m, n+1) + u_1(m, n)] + \Delta t B \left(n + \frac{1}{2}\right) \frac{1}{2} [u_2(m, n+1) + u_2(m, n)], \quad (3)$$

$$u_1(m, n+1) = u_1(m, n) + \Delta t \omega_0 \frac{1}{2} [u_2(m, n+1) + u_2(m, n)], \quad (4)$$

$$u_2(m, n+1) = u_2(m, n) - \Delta t \omega_0 \frac{1}{2} [u_1(m, n+1) + u_1(m, n)] + \Delta t \frac{1}{2} [E_x(m, n+1) + E_x(m, n)] \left\{ C_+ \left(n + \frac{1}{2}\right) \frac{1}{2} [u_3(m, n+1) + u_3(m, n)] + D \left(n + \frac{1}{2}\right) \right\}, \quad (5)$$

$$u_3(m, n+1) = u_3(m, n) - \Delta t C_- \left(n + \frac{1}{2}\right) \times \left\{ \frac{1}{2} [E_x(m, n+1) + E_x(m, n)] \times \frac{1}{2} [u_2(m, n+1) + u_2(m, n)] \right\}. \quad (6)$$

The variables  $u_1$ ,  $u_2$ , and  $u_3$  are reduced forms of density matrix elements  $\rho_1$ ,  $\rho_2$ , and  $\rho_3$  as given in Ref. 10, and  $\Delta z$  and  $\Delta t$  are the space and time step sizes, respectively. The time-dependent coefficients appearing in Eqs. (3)–(6) are

$$A(n) = \frac{N\gamma}{\epsilon T_2} \exp\left(-\frac{n\Delta t}{T_2}\right),$$

$$B(n) = \frac{N\gamma\omega_0}{\epsilon} \exp\left(-\frac{n\Delta t}{T_2}\right),$$

$$C_{\pm}(n) = 2 \frac{\gamma}{\hbar} \exp\left[\mp n\Delta t \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right],$$

$$D(n) = 2 \frac{\gamma}{\hbar} \rho_{30} \exp\left(\frac{n\Delta t}{T_2}\right). \quad (7)$$

As in the Yee cell representation, the time and space grids are shifted by one half-step between the electric and magnetic fields.<sup>7</sup> In Eqs. (2)–(7),  $m$  and  $n$  denote the space and time step indices, respectively, and  $\omega_0$  is the transition frequency. Equations (7) are discretized in time. Equation (2) for the magnetic field is updated in the usual manner. However, Eqs. (3)–(6) for the electric field and density matrix elements mix past and current time steps and are solved by use of a PC algorithm.<sup>10</sup> All simulations presented in this Letter were performed with  $\Delta z = \lambda/100$  and  $\Delta t$  at half of the Courant stability criterion.<sup>7</sup>

The quantities required for the PC FDTD simulation were estimated from a combination of literature values and experimentally determined parameters. The experimental details are provided in Ref. 2. The number density of O—H oscillators was determined from the concentration of the 1:50 HDO:D<sub>2</sub>O sample modeled herein to be  $\sim 6.7 \times 10^{26} \text{ m}^{-3}$ . The transition dipole moment was first estimated from the integrated absorption coefficient<sup>11</sup> by means of the Einstein B coefficient for absorption. The permittivity of the solution was that of neat D<sub>2</sub>O at  $3400 \text{ cm}^{-1}$ ,<sup>12</sup> near the OH-stretch transition maximum. In addition, all molecules were initially in the ground vibrational state. The pulse parameters (electric field intensity and phase) were obtained from XFROG measurements of the instrument response and pulse after propagation through the D<sub>2</sub>O solvent.<sup>2</sup> The initial pulses had a Gaussian envelope and carrier frequency matched to that of the mid-IR pulse, which was resonant with the OH-stretch transition. The pulse field duration was 88 fs and had  $\sim 7 \times 10^{-6} \text{ fs}^{-2}$  of chirp, which assumed propagation through neat D<sub>2</sub>O and the CaF<sub>2</sub> windows before the PC-FDTD calculation.

Figure 1A shows the experimental field as determined from the amplitude and phase obtained from XFROG analysis,<sup>2</sup> and Figure 1B shows the simulated field arising from interaction with a 1:50 HDO:D<sub>2</sub>O solution modeled as a homogeneously broadened Bloch medium.<sup>13</sup>  $T_1$  was set to 700 fs,<sup>14</sup> and  $T_2$  was established from the transition bandwidth as  $\sim 43$  fs. Simulations of pulse propagation through 1:200 and 1:100 solutions were also performed, as well as chirp-dependent simulations. The simulated fields show the same trends as those observed in the experiment: The FID beat grows in magnitude with increasing OH concentration: a second FID beat was spawned in the most concentrated sample (1:50). Increases in chirp led to incomplete destructive interference in the nodal regions.<sup>13</sup> Although the agreement between experiment and simulation is fairly good, the simulation does not quantitatively account for the observed fields. Three issues may contribute to the discrepancy between simulation and experiment: the treatment of the solvent's nonresonant response to the pulse field, (quasi-)inhomogeneous broadening in the relaxation, the Gaussian inertial relaxation.<sup>15</sup> The response of D<sub>2</sub>O is approximated by a constant permittivity, but the increase in pulse duration and chirp observed in experiments after pulses have passed through neat D<sub>2</sub>O indicate that it is dispersive. One should incorporate this dispersion

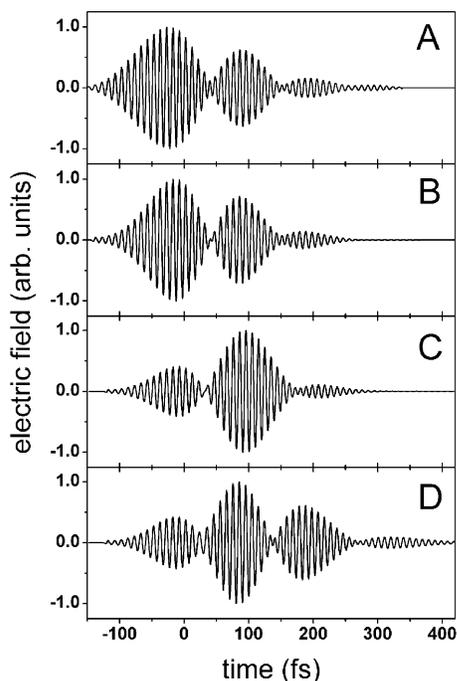


Fig. 1. Dependence of simulated fields on response functions for 1:50 HDO:D<sub>2</sub>O solution: A, experimentally determined field, B, Bloch relaxation; C, inhomogeneous broadening; D, Gaussian response. In each case the experimental and simulated fields were normalized. Response function parameters were set to match the FWHM transition spectral width.

into the simulations instead of chirping the pulse before propagation and allowing  $\epsilon$  to be constant. This dispersion would likely account for the pulse broadening observed in the driving field.

Another consideration is the response function itself. Mid-IR photon echo experiments have shown that the OH-stretching band of HDO in D<sub>2</sub>O is not homogeneously broadened.<sup>14,16</sup> To examine the intermediate response function, we treated the transition as an inhomogeneous line by fitting the absorption band with a set of seven Lorentzian lines. Each Lorentzian had a 126-cm<sup>-1</sup> FWHM, corresponding to  $T_2^* = 90$  fs and  $T_1 = 700$  fs.<sup>14</sup> Each transition was simulated separately, and a weighted sum of the fields was used as a model of the total field. Figure 1C shows the same initial pulse as in Fig. 1B after the pulse has traversed the inhomogeneously broadened medium. There are large discrepancies from the experiment: while a second FID beat is observed in simulations with single Lorentzians near the absorption maximum (not shown), it is largely canceled out in the sum because of destructive interference between the fields from the detuned Lorentzians.

As the early time relaxation of a transition is often modeled as Gaussian in shape,<sup>15</sup> a Gaussian response function was incorporated into the algorithm.<sup>13</sup> The relaxation time was set such that the bandwidth matched that of the transition. The result of the simulation is shown in Fig. 1D. The Gaussian response weights the beat magnitudes differently from those in Fig. 1C: Although the first FID beat is overesti-

mated in both, the Gaussian response enhances the second beat. Furthermore, the Gaussian function captures the beat duration more successfully than does the inhomogeneous simulation. The difference in the beat magnitudes between the Bloch and the Gaussian treatments suggests that a Kubo response, treating the relaxation as Gaussian at early times and as Lorentzian at later times, may be more successful in modeling the fields. Implementation of this response function in the PC FDTD algorithm is in progress.<sup>13,17</sup> Future goals include extensions to a three-level medium and incorporation of non-Markovian response functions, both of which are critical to the proper modeling of the nonlinear infrared spectroscopy of water. Extensions to nonlinear response functions are anticipated.

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