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Models of the delayed nonlinear Raman response in diatomic gases

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We examine the delayed response of a diatomic gas to a polarizing laser field with the goal of obtaining computationally efficient methods for use with laser pulse propagation simulations. We demonstrate that for broadband pulses, heavy molecules such as O_2 and N_2, and typical atmospheric temperatures, the initial delayed response requires only classical physics. The linear kinetic Green's function is derived from the Boltzmann equation and shown to be in excellent agreement with full density-matrix calculations. A straightforward perturbation approach for the fully nonlinear, kinetic impulse response is also presented. With the kinetic theory a reduced fluid model of the diatomic gas' orientation is derived. Transport coefficients are introduced to model the kinetic phase mixing of the delayed response. In addition to computational rapidity, the fluid model provides intuition through the use of familiar macroscopic quantities. Both the kinetic and the fluid descriptions predict a nonlinear steady-state alignment after passage of the laser pulse, which in the fluid model is interpreted as an anisotropic temperature of the diatomic fluid with respect to motion about the polarization axis.

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I. INTRODUCTION

In the presence of a laser electric field the electron clouds of atoms comprising a molecule become deformed. The deformation provides an induced electrical dipole moment, through which the laser pulse acts to provide a net force and/or torque on the molecule with associated potential $V = -\frac{1}{2}\vec{p}\cdot\vec{E}$, where p is the induced dipole moment and $\vec{E}$ the laser electric field. The molecule undergoes both an instantaneous and delayed response in the electric field of the laser pulse. The instantaneous response results from the laser-induced separation between the electron cloud and nucleus of the atoms within the molecule. The delayed response involves the rotation of the molecular axes and occurs over a longer time scale due to the molecular inertia. The cross attraction between the electron clouds and nuclei on opposite sides of the molecule results in a torque which aligns the molecules along the laser polarization axis. In the case of a linear molecule (such as a diatomic molecule) the applied potential takes the form

$$V_L(\theta,t) = -\tfrac{1}{4}[\alpha_\perp + \Delta\alpha\cos^2\theta]|\vec{E}(t)|^2, \tag{1}$$

where $\vec{E}$ is now the electric field amplitude of the laser, polarized along the vertical axis in Fig. 1, $\Delta\alpha = \alpha_\parallel - \alpha_\perp$, $\alpha_\parallel$ and $\alpha_\perp$ are the parallel and perpendicular molecular polarizabilities respectively defined with respect to the symmetry axis of the molecule, which makes an angle θ with respect to the electric field, and $V(\theta,t)$ has been cycle averaged.

The delayed molecular alignment induced by the laser electric field results in a polarization current [1], $\vec{P} = \rho[\alpha_\perp + \Delta\alpha\langle\cos^2\theta\rangle]\vec{E}$, where ρ is the number density of molecules and the pointy brackets represent an ensemble average over all molecules (or in a quantum mechanical description an average over the angle dependent wave function). The polarization current feeds back onto the laser pulse affecting propagation. Defining $\chi \equiv 4\pi\rho\alpha_\perp$ and $\Gamma(\vec{x},t:\vec{E}) = \rho\Delta\alpha\langle\cos^2\theta\rangle$, the propagation of the laser obeys the wave equation

$$\left[\nabla^2\vec{E} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}(1+\chi)\vec{E}\right] = \frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\Gamma(\vec{x},t:\vec{E})\vec{E}. \tag{2}$$

As seen from Eq. (1), Γ is a function of $\vec{E}$, which can result in self-focusing of the laser pulse [2–5] and potentially filamentation. Filamentation occurs when a defect on the phase front of the laser pulse causes different transverse locations of the laser pulse to focus at different positions due to the differential polarization current. The higher intensity regions of the pulse (the filaments) have an extended focal length, while the low-intensity regions diffract. As a result, the high-intensity regions can propagate over distances much longer than a Rayleigh range. However, if the high-intensity regions focus too strongly, the intensity can reach the ionization threshold of the air, causing enhanced diffraction. This potential for propagating laser pulses over long distances in atmosphere has led to several investigations into filamentation, both theoretical and experimental [5–10].

For accurate simulations of laser propagation over long distances, accurate models of the delayed molecular response are critical. First-principle models of the molecular response involve quantum-mechanical density-matrix theory in which the diatomic molecule is treated as quantum rotor with discrete rotational frequencies. In fact, the density-matrix theories were successful in predicting the rotational revivals associated with diatomic molecules, a strictly quantum-mechanical effect [1,11–16]. However, the computational requirements of a full density-matrix theory make iterated density-matrix, laser-propagation simulations impractical with current computing capabilities. This is exacerbated by the interest in propagation over distances of meters to kilometers in atmosphere [17,18]. In particular, at every point in space, a $\sim\ell_{\max}^4$ calculation must be done, where $\ell_{\max}$ is the maximum rotational quantum number excited. For broadband or high-intensity pulses, $\ell_{\max}$ can be quite large. As we will see, however, broadband pulses are where classical treatments are the most accurate.

Several authors have considered the classical response of a diatomic gas and comparisons to quantum-mechanical theory [19–24]. Khodorkovsky and Gershnabel and Averbukh present a classical and quantum comparison of molecules in strong laser fields and weak laser fields, respectively [23,24], but stop short of full analytic calculations of the time-dependent classical response function, both linearly

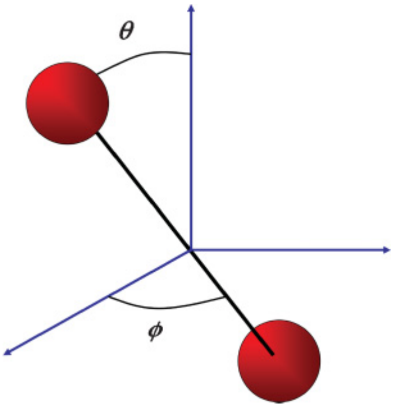

FIG. 1. (Color online) Coordinate system for molecular alignment. The vertical axis represents the polarization axis of the polarizing laser pulse.

and nonlinearly. Khodorkovsky does present full nonlinear Monte Carlo calculations. Monte Carlo methods, however, are not computationally ideal, as they would require separate calculations for each point in space and time along a laser pulse's propagation path. M. S. Child presents a semiclassical rotational model utilizing Sommerfeld quantization but does not examine thermal effects or the correspondence with a full classical theory [20]. Finally, Iñarrea *et al.* present a single molecule analysis of the classical rovibrational trajectories in a laser field, but do not consider ensemble effects [22].

Here we present full kinetic calculations of the time-dependent response of a diatomic gas and derive an analytic expression for the linear Green's function from the Boltzmann equation. A simplified method for determining the full nonlinear impulse response is also presented from which we find an analytic expression for the second-order polarizability. With the kinetic equations we derive a set of fluid equations which include phase mixing through transport coefficients, following the procedure popularized in plasma physics by Hammet *et al.* [25,26]. For calculating the molecular response, the fluid equations offer a computational savings of $\sim\ell_{\text{max}}^3/N$, where N is a numerical factor on the order of ten, over the full density-matrix calculation. The fluid model also provides intuition by casting the problem in terms of the familiar macroscopic quantities of density, momentum flow, temperature, and heat.

An estimate of the circumstances under which the quantum and classical descriptions of the molecules' rotation should correspond is given as follows. First it is required that the typical quantum state involved be high order. Specifically, we require $\ell_{\text{th}} \gg 1$, where ℓ_{th} is the total angular momentum quantum number for a thermal molecule, defined by $T = E_\ell = \hbar\Omega_\ell = \hbar\Omega_0\ell_{\text{th}}(\ell_{\text{th}}+1)$, where $E_0 = \hbar\Omega_0$ are the ground state energy and Ω_0 the ground state frequency. Second, the correspondence will apply only for times shorter than the Heisenberg time: $t_H \equiv 2\pi/(\Omega_{\ell_{\text{th}}+1} - \Omega_{\ell_{\text{th}}}) \simeq 2\pi/(2\ell_{\text{th}}\Omega_0)$. For times longer than t_H the discreteness of the energy spectrum cannot be ignored and the recurrences in the response of the molecules occur. For nitrogen at room temperature we find $\ell_{\text{th}} \sim 10$ and $t_H \sim 0.84$ ps.

This paper is organized as follows. In Sec. II we describe the single-molecule trajectories in field-free conditions and the full nonlinear trajectory in an impulsive laser field. After the single molecule analysis, we derive the fully kinetic linear response function and Green's function for the molecular ensemble, and a simplified nonlinear approach for obtaining the impulse response to all orders. In Sec. III, we derive the fluid moments and determine which closures are required to accurately model the kinetic phase mixing of the diatomic gas and nonlinear effects. At the end of Sec. III, we examine the time asymptotic behavior of fluid response. In Sec. IV we present our conclusions.

II. KINETIC RESPONSE MODEL

A. Classical diatomic molecule

We begin by considering the motion of a classical rigid body. The body consists of two masses connected by a rigid rod. Each mass represents an atom in the diatomic molecule. Our classical molecule has three translational degrees of freedom and two rotational degrees of freedom. The moment of inertia around the molecular axis, the axis parallel to the rigid rod, is much smaller than the moment of inertia around the perpendicular axis and is neglected. The field free Hamiltonian can then be written as

$$H = \frac{\vec{p}_K \cdot \vec{p}_K}{2m} + \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2\theta}, \tag{3}$$

where I is the moment of inertia, $\vec{p}_K$ is the translational momentum (configuration space momentum), and $p_\theta = I\omega_\theta$ and $p_\phi = I\omega_\phi \sin^2\theta$ are the rotational momenta in the plane of the vertical axis and around the vertical axis, respectively. Here $\omega_\theta = \dot{\theta}$ and $\omega_\phi = \dot{\phi}$ are the rotational frequencies associated with the momenta. The Hamiltonian has no explicit dependence on time or ϕ and thus both H and p_ϕ are constants of motion. The geometry of the rotor is depicted in Fig. 1.

We assume the laser intensity is uniform in space so that the applied potential does not couple the translational degrees of freedom, and we only need consider the rotational Hamiltonian. We define K as the kinetic energy in configuration space, $K \equiv \vec{p}_K \cdot \vec{p}_K/2m$, and R as the rotational Hamiltonian, $R \equiv H - K$:

$$p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta} = 2IR. \tag{4}$$

The field free orbits can be solved for exactly. After integrating Hamilton's equations that follow from Eq. (4), we find

$$\begin{aligned}\cos\theta &= \tfrac{1}{2}(1 - \Omega_{\theta,0})\cos[\theta_0 - \omega_R t]\\ &\quad + \tfrac{1}{2}(1 + \Omega_{\theta,0})\cos[\theta_0 + \omega_R t],\end{aligned} \tag{5}$$

where $\theta_0 = \theta(t_0)$, $\Omega_{\theta,0} = \omega_{\theta,0}/\omega_R$, and $\omega_R \equiv (2R/I)^{1/2}$. We note that $|\Omega_{\theta,0}| \leqslant 1$. Equation (5) demonstrates that the motion is completely characterized by the constants of motion and the initial conditions.

B. Classical molecular trajectory in an impulsive laser pulse

If the duration of the laser pulse is much shorter than the response time of the molecules the torque may be treated as an impulse. In this case, the full nonlinear molecular trajectory can be determined. The impulsive torque imparted by the polarizing field will result in a jump discontinuity in the momentum, p_θ, of the molecule while keeping the angular precession continuous in time. We write the rotational Hamiltonian as follows:

$$p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta} - \tfrac{1}{2} I\sigma[\alpha_\perp + \Delta\alpha\cos^2\theta]E_0^2\delta(t - t_I) = 2IR, \tag{6}$$

where σ is the time constant associated with the impulse and t_I is the time at which the impulse occurs. From the equations of motion we obtain the relation $\omega_{\theta,>}(t_I) = \omega_{\theta,<}(t_I) - \frac{1}{4}\sigma\,\Delta\alpha\,E_0^2\sin[2\theta_I]$, where the subscripts $<$ and $>$ distinguish the trajectory before and after the impulse, respectively, and $\theta_I = \theta_<(t_I) = \theta_>(t_I)$. Both before and after the impulse the molecule follows its field-free trajectory. For $t < t_I$ the trajectory evolves as described by Eq. (5). For $t \geqslant t_I$ we have

$$\begin{aligned} \cos\theta_> = {} & \tfrac{1}{2}(1 - \Omega_{\theta,I})\cos[\theta_I - \omega_R(t - t_I)] \\ & + \tfrac{1}{2}(1 + \Omega_{\theta,I})\cos[\theta_I + \omega_R(t - t_I)], \end{aligned} \tag{7}$$

where $\Omega_{\theta,I} = \omega_{\theta,>}(t_I)/\omega_R$. The polarizing impulse modifies the rotational frequency of the molecules based on their angular orientation at the moment of the impulse. In particular, molecules get pushed toward the pole to which they are closest providing an overall aligning of the diatomic gas.

C. Ensemble of classical diatomic molecules

We now consider the phase space evolution of a distribution of classical molecules. The four-dimensional phase space is defined by the variables θ, p_θ, ϕ, and p_ϕ. The evolution of the distribution function is governed by the collisionless Boltzmann equation

$$\left[\frac{\partial}{\partial t} + \frac{\vec{p}}{I}\cdot\overrightarrow{\nabla} - \overrightarrow{\nabla}V(\theta,t)\cdot\overrightarrow{\nabla}_p\right] f(\theta,\phi,p_\theta,p_\phi,t) = 0, \tag{8}$$

where $\vec{p}\cdot\overrightarrow{\nabla} \equiv p_\theta\partial_\theta + (\sin^{-2}\theta)p_\phi\partial_\phi$ and $\nabla_p \equiv \hat{\theta}(\partial/\partial p_\theta) + \hat{\phi}(\partial/\partial p_\phi)$. If there is no external potential, the only condition on the distribution function is $(\vec{p}\cdot\nabla - \nabla I V_{\mathrm{eff}}\cdot\nabla_p)f = 0$, where $\hat{\theta}\cdot\nabla V_{\mathrm{eff}} = -p_\phi^2\cos\theta/I\sin^3\theta$ is the effective torque due to the explicit θ dependence of the Hamiltonian. The thermal distribution in the absence of an external potential is then

$$f(\theta,p_\theta,p_\phi) = \frac{1}{8\pi^2 IT}\exp\left[-\frac{p_\theta^2}{2IT} - \frac{p_\phi^2}{2IT\sin^2\theta}\right], \tag{9}$$

where the equilibrium density, n_0, is defined to be $(\sin\theta)^{-1}\int f(\theta,p_\theta,p_\phi)dp_\theta dp_\phi = 1/4\pi$ and $\int f(\theta,p_\theta,p_\phi)d\theta d\phi\, dp_\theta dp_\phi = 1$.

D. Classical, kinetic linear polarizability

We first consider the linear response of the diatomic gas to the applied potential. The distribution function is written as the sum of an equilibrium and response contribution

$$f(\theta,\phi,p_\theta,p_\phi,t) = f_0(\theta,p_\theta,p_\phi) + \delta f(\theta,\phi,p_\theta,p_\phi,t). \tag{10}$$

Inserting Eq. (10) into Eq. (8) and linearizing we find

$$\frac{d}{dt}\delta f = \overrightarrow{\nabla}V_L(\theta,t)\cdot\overrightarrow{\nabla}_p f_0. \tag{11}$$

From Eq. (11), we see that the component of potential proportional to the perpendicular polarizability will not contribute to the evolution of the perturbed potential: $\overrightarrow{\nabla}\alpha_\perp|\vec{E}|^2 = 0$. As a result we do not consider this component of the distribution function when evaluating the linear response.

Noting that $\overrightarrow{\nabla}IV_L\cdot\overrightarrow{\nabla}_p = (\vec{p}\cdot\overrightarrow{\nabla}V_L)\partial_R$ and $(d_t - \partial_t)IV_L = \vec{p}\cdot\overrightarrow{\nabla}V_L$, Eq. (11) can be integrated to provide

$$\delta f(\theta,t) = V_L(\theta,t)\frac{\partial f_0}{\partial R} - \int_{-\infty}^{t} dt'\left[\frac{\partial}{\partial t'}V_L(\theta,t')\right]\frac{\partial f_0}{\partial R}, \tag{12}$$

where we have used $\delta f(\theta,t \to -\infty) = 0$. The first term represents the adiabatic response of the diatomic gas to the applied potential, which we denote $\delta f_A \equiv V_L\partial_R f_0$. This is the only contribution to the perturbed distribution function for time-independent applied potentials. The second term, which we denote δf_{NA}, represents the nonlocal time response of the distribution function to the applied potential and includes the contributions of the individual orbits for the diatomic molecules.

Evaluating f_{NA} requires integrating the equilibrium orbits through the first-order potential. In other words, we perform an ensemble average of all initial conditions that end at the angle θ at time t. Upon expressing $|\vec{E}(t)|^2$ in the frequency domain, which we denote with a "hat," and inserting Eq. (5) for $\cos^2\theta$, we write $\delta f_{NA}(\theta,t)$ as follows:

$$\begin{aligned} \delta f_{NA} = -i\frac{\Delta\alpha}{8}\int_{-\infty}^{0}\int \Bigg[& \cos\theta\cos(\omega_R\zeta) - \left(\frac{p_\theta}{I\omega_R}\right) \\ & \times \sin\theta\sin(\omega_R\zeta)\Bigg]^2 \widehat{|\vec{E}|}^{\,2} e^{-i\omega(\zeta+t)}\frac{\partial f_0}{\partial R}d\omega^2 d\zeta, \end{aligned} \tag{13}$$

where ζ is now a dummy integration variable and the inner integration is over all frequencies. Performing the integral over ζ, we have

$$\begin{aligned} \delta f_{NA} = {} & -\frac{\Delta\alpha\cos^2\theta}{4T}f_0 \\ & \times \int\left[\frac{\omega^2 + A(\theta)\omega - B(\theta)}{\omega^2 - 4\omega_R^2}\right]\widehat{|\vec{E}|}^{\,2} e^{-i\omega t}d\omega, \end{aligned} \tag{14}$$

where $A(\theta)=2i(p_\theta/I)\tan\theta$, $B(\theta)=2[\omega_R^2 + (p_\theta/I)^2\tan^2\theta]$, and we have used the fact that $\partial_R f_0 = -f_0/T$.

To find the perturbation on the dielectric response of the gas, we need to multiply Eq. (14) by $\cos^2\theta$ and integrate over phase space. Before integrating we transform variables from p_θ to ω_R. In particular $p_\theta = I(\omega_R^2 - p_\phi^2/I^2\sin^2\theta)^{1/2}s_R$, $s_R \equiv \mathrm{sgn}(\omega_R)$, $dp_\theta = (I^2\omega_R/p_\theta)d\omega_R$, and we define $\omega_T =$

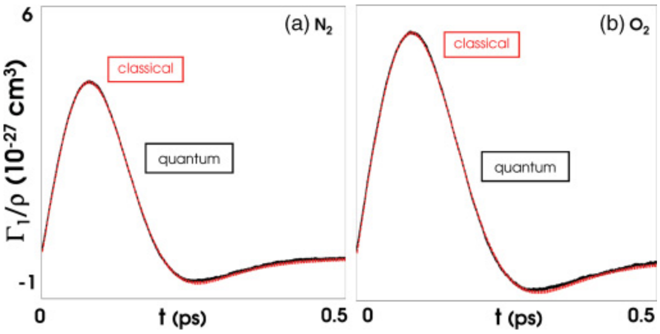

FIG. 2. (Color online) Comparison of the classical theory in red (dashed) with a full quantum-mechanical density-matrix calculation in black (solid). In (a) nitrogen is considered while in (b) oxygen is considered.

$(2T/I)^{1/2}$. Upon integrating over p_ϕ, ϕ, and θ, we find the nonadiabatic, nonlinear polarizability as follows:

$$\Gamma_{NA} = -\frac{4\pi^2 I\rho(\Delta\alpha)^2}{5\omega_T^2}\int\int s_R\omega_R\left[1+\frac{4}{3}\left(\frac{\omega_R^2}{\omega^2-4\omega_R^2}\right)\right] \times |\widehat{\vec{E}}|^2\, e^{-i\omega t} f_0(\omega_R)\,d\omega\, d\omega_R, \tag{15a}$$

where $f_0(\omega_R) = (8\pi^2 IT)^{-1}\exp[-\omega_R^2/\omega_T^2]$. Similarly, one can show that the adiabatic response is

$$\Gamma_A = \frac{2}{5}\frac{\pi\rho(\Delta\alpha)^2}{I\omega_T^2}|\vec{E}(t)|^2, \tag{15b}$$

which cancels the first term within square brackets Eq. (15a). From here on, we consider the total polarizability $\Gamma_T = \Gamma_A + \Gamma_{NA}$.

Equation (15) is in the form of a product of Fourier transforms, thus by considering an impulse for $|\vec{E}(t)|^2$, we can obtain the linear time domain Green's function, G, for the molecular response: $\Gamma_T(t) = \int G(t-t')|\vec{E}(t')|^2 dt'$. From Eq. (15a) we find the Green's function in the frequency domain to be

$$G(\Omega) = -g_0\int s_R\left(\frac{\Omega_R^3}{\Omega^2-4\Omega_R^2}\right)e^{-\Omega_R^2}d\Omega_R, \tag{16a}$$

while in the time domain

$$G(\tau) = \frac{g_0}{2}\int s_R\Omega_R^2\sin(\Omega_R\tau)e^{-\Omega_R^2}d\Omega_R, \tag{16b}$$

where we have defined $\Omega = \omega/\omega_T$, $\Omega_R = \omega_R/\omega_T$, $\tau = 2\omega_T t$, and $g_0 = 8\pi\rho(\Delta\alpha)^2/15I\omega_T^2$. Equations (16) demonstrate that the shape of classical linear response depends on only one parameter: ω_T. Performing the integration over Ω_R we find

$$G(\tau) = \frac{g_0}{4}\left[\tau + \pi^{1/2}\left(1-\frac{\tau^2}{2}\right)e^{-\tau^2/4}\mathrm{erfi}\left(\frac{\tau}{2}\right)\right], \tag{17}$$

where erfi is the imaginary error function. In Appendix A, we examine limits of Eq. (16a).

Figures 2(a) and 2(b) show a comparison of $\Gamma_1 = \omega_T\sigma E_0^2 G(\tau)$ with the full quantum mechanical result obtained by solving for the evolution of the density matrix (details of the quantum mechanical calculation can be found in Ref. [15]) for N$_2$ and O$_2$ respectively. Here we use a laser pulse intensity of $I = 1\times 10^{12}$ W/cm^2, duration $\sigma = 20$ fs, and $T = 294$ K.

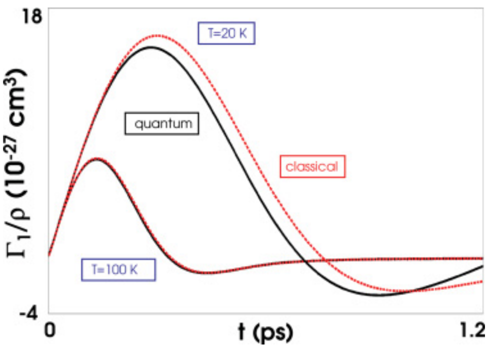

FIG. 3. (Color online) Comparison of the classical theory in red (dashed) with a full quantum-mechanical density-matrix calculation in black (solid) for nitrogen at $T = 20$ K and $T = 100$ K.

The results are almost exactly identical, implying that the dominant quantum effect is that of rotational recurrences. For lower temperatures we may expect the classical and quantum response functions to diverge. In particular, when the thermal energy approaches the fundamental rotational eigenfrequencies, $T \sim 4\pi c\hbar B$, where B is the rotation constant, only a few states are populated in equilibrium and the discrete nature of the rotational eigenstates become important. As an example, we consider nitrogen at $T = 20$ K and $T = 100$ K. Figure 3 shows a comparison of the classical response function with the density-matrix calculation. From Fig. 3 it is clear that the accuracy of the classical model relies on the number of states populated. The condition $T \sim 4\pi c\hbar B$ also depends on the rotational constant, which is inversely proportional to the moment of inertia: For nitrogen $B \simeq 1.99$ cm^{-1}, for oxygen $B \simeq 1.44$ cm^{-1}, while for hydrogen $B \simeq 59.3$ cm^{-1}. The response of diatomic gases such as hydrogen, which have less inertia, exhibit quantum properties at higher temperatures. Figure 4 shows a comparison of $\Gamma_1 = \omega_T\sigma E_0^2 G(\tau)$ with the density-matrix calculation for hydrogen at $T = 294$ K. Clearly, our classical model is insufficient for modeling the initial response of hydrogen gas at atmospheric temperatures. Furthermore, for times approaching a quarter of the recurrence period $T \sim 1/8cB$, the presence of quantum recurrences can affect the polarizability, and the classical model is no longer applicable.

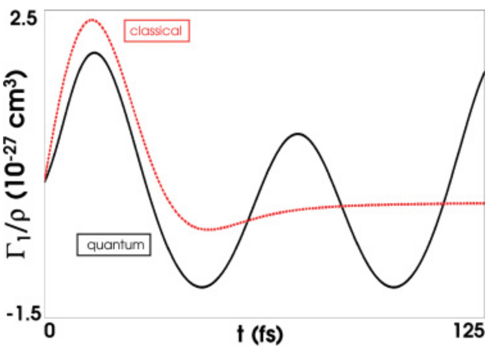

FIG. 4. (Color online) Comparison of the classical theory in red (dashed) with a full quantum-mechanical density-matrix calculation in black (solid) for hydrogen at $T = 294$ K.

E. Classical, kinetic nonlinear polarizability

As demonstrated in Sec. II B above, the nonlinear molecular trajectories can be determined when the polarizing field takes the form of an impulse. This allows us to write an expression for the full nonlinear response to the impulsive field for which a simple Taylor expansion provides the response at each order in $|E|^2$. Right after the impulse the distribution can be written as

$$f(\theta_I,p_{\theta I},p_\phi) = \frac{1}{8\pi^2 IT}\exp\left[-\frac{(p_{\theta I}-A\sin 2\theta_I)^2}{2IT}-\frac{p_\phi^2}{2IT\sin^2\theta_I}\right], \tag{18}$$

where the subscript I denotes quantities just after the impulse and $A=\frac{1}{4}I\sigma\Delta\alpha E_0^2$. Because the Hamiltonian phase space volume is conserved $f(\theta_I,p_{\theta I},p_{\phi I})d\mathrm{P}_I = f(\theta,p_\theta,p_\phi)d\mathrm{P}$, where $d\mathrm{P}=d\theta d\phi dp_\theta dp_\phi$, and $\langle\cos^2\theta\rangle$ can be written as an integral over phase space quantities immediately after the impulse as follows:

$$\langle\cos^2\theta\rangle = \int\left[\cos\theta_I\cos(\omega_R t)-\left(\frac{p_{\theta I}}{I\omega_R}\right)\sin\theta_I\sin(\omega_R t)\right]^2 \times f(\theta_I,p_{\theta I},p_{\phi I})d\mathrm{P}_I. \tag{19}$$

Upon transforming from p_ϕ to ω_R using $p_\phi = s_R I(\omega_R^2 - p_\theta^2/I^2)^{1/2}\sin\theta$ and $dp_\phi = (I^2\omega_R\sin^2\theta/p_\phi)d\omega_R$ the integral over $p_{\theta I}$ and ϕ can be performed. The resulting expression can then be Taylor expanded to any order desired in the parameter $A\propto E_0^2$. Writing $\Gamma=\sum_i\Gamma_i$, we find, as expected, to lowest order $\Gamma_0=\frac{4\pi}{3}\rho\Delta\alpha$ and $\Gamma_1=\omega_T\sigma E_0^2 G(\tau)$, where $G(\tau)$ is given in Eq. (17). To next order in E_0^2 we find the following:

$$\Gamma_2 = \frac{1}{210}\pi^{3/2}\rho\Delta\alpha\left(\frac{\sigma\Delta\alpha E_0^2}{I\omega_T}\right)^2\tau e^{-\tau^2/4}\mathrm{erfi}\left(\frac{\tau}{2}\right). \tag{20}$$

Equation (20) has the interesting property that it does not phase mix to zero as $\tau\to\infty$. Thus, at second order, the laser pulse leaves behind a steady-state alignment in the diatomic gas with a time asymptotic polarizability of $\Gamma_2=\pi\rho\Delta\alpha(\sigma\Delta\alpha E_0^2/I\omega_T)^2/105$.

Figure 5 shows a comparison of the fully nonlinear quantum-mechanical treatment with the classical analytic expressions for the first- and second-order polarizability of nitrogen derived above: $\Gamma_1+\Gamma_2$. The first-order classical response is also plotted for reference. For these calculations, we considered a laser pulse intensity of $I=1\times10^{14}$ W/cm^2, duration $\sigma=20$ fs, and $T=294$ K. The inset shows a zoomed-in region of the response detailing the steady-state alignment left behind by the pulse before the quarter recurrence. Again the results are almost identical. The second-order polarizability is clearly sufficient for capturing the full response up to intensities of 1×10^{14} W/cm^2. This is particularly remarkable: Beyond these intensities, we reach the ionization threshold for nitrogen, $\sim2\times10^{14}$ W/cm^2 [27] and thus higher order treatments may be unnecessary for propagation simulations in which both molecular alignment and ionization play a role.

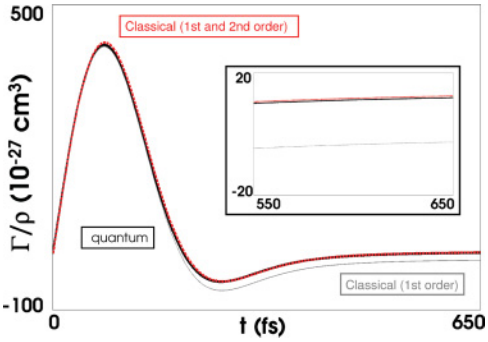

FIG. 5. (Color online) Comparison of the fully nonlinear quantum theory in black (solid) and the first- and second-order classical theory in red (dashed) for nitrogen at $T=294$ K. The fist-order classical theory is plotted for reference in gray (thin line). The inset shows a zoomed-in region detailing the constant offset in the molecular alignment.

III. FLUID RESPONSE MODEL

While evaluation of the linear Green's function in kinetic theory is tractable, full nonlinear treatments can become cumbersome due to the four-dimensional phase space. Here we derive a set of fluid equations for describing the evolution of the macroscopic rotation frequency by taking moments of Eq. (8), which simplifies nonlinear calculations of the response. In particular, we define the following: $n=(\sin\theta)^{-1}\int d\vec{p}f$, $n\vec{P}=(\sin\theta)^{-1}\int\vec{p}d\vec{p}f$, $\Pi_{\theta\theta}=\int(p_\theta-P_\theta)^2d\vec{p}f$, $\Pi_{\phi\phi}=(\sin\theta)^{-2}\int(p_\phi-P_\phi)^2d\vec{p}f$, and $\Pi_{\theta\phi}=(\sin\theta)^{-1}\int(p_\theta-P_\theta)(p_\phi-P_\phi)d\vec{p}f$, which represent the density, momentum density, and three elements of the pressure tensor ($\Pi_{\theta\phi}=\Pi_{\phi\theta}$) in molecular orientation space. We note that, in general, the pressure can be anisotropic, corresponding to a distribution function that is not separable in momentum, which provides the off-diagonal elements, $\Pi_{\theta\phi}$. The potential due to the laser pulse is independent of ϕ, and any derivative with respect to ϕ can be ignored. The resulting fluid equations are then

$$\frac{\partial n}{\partial t}+\vec{\nabla}\cdot\left(\hat{\theta}n\frac{P_\theta}{I}\right)=0, \tag{21a}$$

$$\frac{d}{dt}P_\theta = \frac{1}{In\sin\theta}\left[\cot\theta\,\Pi_{\phi\phi}-\frac{\partial\Pi_{\theta\theta}}{\partial\theta}\right] + \frac{\cot\theta}{I\sin^2\theta}P_\phi^2-\frac{\partial}{\partial\theta}V, \tag{21b}$$

$$\frac{d}{dt}P_\phi = -\frac{1}{In}\vec{\nabla}\cdot\Pi_{\theta\phi}, \tag{21c}$$

where $d_t=\partial_t+(P_\theta/I)\partial_\theta$ and $\vec{\nabla}\cdot\hat{\theta}=(\sin\theta)^{-1}\partial_\theta\sin\theta$. The absence of convection in ϕ and the conservation of P_ϕ up to the anisotropic pressure are results of the potential being independent of ϕ. If P_ϕ and $\Pi_{\theta\phi}$ start as zero, they will remain so for all time.

When the applied potential is independent of time, corresponding to an infinitely long laser pulse, and the temperature is uniform, Bernoulli-like steady-state equations can be derived using the ideal gas law, $\Pi_{\theta\theta} = \Pi_{\phi\phi} = nT\sin\theta$, namely,

$$\alpha = nP_\theta \sin\theta, \tag{22a}$$

$$\beta = \frac{1}{2}\left[\frac{P_\theta^2}{I} + I\omega_T^2 \log_e(n)\right] + V, \tag{22b}$$

where α and β are independent of θ and we have taken $P_\phi = \Pi_{\theta\phi} = 0$. Any isothermal equilibrium of the system must satisfy Eqs. (22a) and (22b). The most straightforward equilibrium is that for which $V = 0, n = (4\pi)^{-1}$, and $P_\theta = 0$. In the presence of a potential and with $P_\theta = 0$ the equilibrium density is $n = n_0 \exp[-2V/I\omega_T^2]$, where n_0 is the density where the potential is zero.

A. Fluid linear polarizability

To obtain the polarizability from the fluid theory we must evaluate the quantity $\langle \cos^2\theta \rangle = \int n(\theta)\sin\theta\cos^2\theta d\theta d\phi$. The diatomic gas starts in the equilibrium with $V = 0, n = (4\pi)^{-1}$, and $P_\theta = 0$ and is perturbed by the presence of the laser pulse. We denote the first-order perturbations as n_1 and $P_{\theta,1}$. Using the equation of state (EOS) closures $\Pi_{\phi\phi} = c_\phi \sin\theta n^\alpha$ and $\Pi_{\theta\theta} = c_\theta \sin\theta n^\gamma$, where the c_ϕ and c_θ are constants, the linearized versions of Eqs. (15a) and (15b) can be expressed as the following second-order differential equation:

$$\left[\frac{\partial^2}{\partial\theta^2} + A\cot\theta\frac{\partial}{\partial\theta} - (2 - A)\frac{1}{\sin^2\theta} - \frac{2}{\gamma\omega_T^2}\frac{\partial^2}{\partial t^2} + (1 - A)\right] \times P_{\theta,1} = \frac{I\Delta\alpha}{2\gamma\omega_T^2}\sin 2\theta\frac{\partial}{\partial t}|\vec{E}(t)|^2, \tag{23a}$$

where $A = \gamma + (1 - \alpha)/\gamma$. For the special case of $A = 1$, Eq. (23a) simplifies to the driven, modified Legendre differential equation

$$\left[L^2 - \frac{2}{\omega_T^2}\frac{\partial^2}{\partial t^2}\right] P_{\theta,1} = \frac{I\Delta\alpha}{2\omega_T^2}\sin 2\theta\frac{\partial}{\partial t}|\vec{E}(t)|^2, \tag{23b}$$

where we have defined $L^2 = \partial_\theta^2 + \cot\theta\partial_\theta - \sin^{-2}\theta$. The situation of $A = 1$ corresponds to the condition that $\gamma = \frac{1}{2}[1 + (5 - 4\alpha)^{1/2}]$, and thus the only integer solution is $\alpha = \gamma = 1$ corresponding to an isothermal EOS, $T = \text{const}$. The general solution to Eq. (23b) can be expressed as $P_{\theta,1}(\theta,t) = \sum_\ell P_\ell(t)M_\ell^1(\cos\theta)$, where M_ℓ^1 is the modified Legendre polynomial (we use M for the Legendre polynomials as opposed to the traditional P to distinguish the momentum). The exact solutions for the momentum and density are then

$$P_{\theta,1}(\theta,t) = -i\frac{I\Delta\alpha}{4}\sin 2\theta \int \frac{\omega}{\omega^2 - 3\omega_T^2}\widehat{|\vec{E}|}^2 e^{-i\omega t}d\omega, \tag{24a}$$

$$n_1(\theta,t) = -\frac{\Delta\alpha}{16\pi}[1 + 3\cos 2\theta]\int \frac{1}{\omega^2 - 3\omega_T^2}\widehat{|\vec{E}|}^2 e^{-i\omega t}d\omega. \tag{24b}$$

As in the previous section, we look for the impulse response to determine the Green's function for which we find

$$G(\Omega) = -g_0\left[\frac{1}{\Omega^2 - 3}\right], \tag{25a}$$

$$G(\tau) = \frac{g_0}{\sqrt{3}}\sin\left[\frac{\sqrt{3}}{2}\tau\right]. \tag{25b}$$

We note that for large Ω and small τ the fluid and kinetic Green's functions are identical. However, for large τ the fluid Green's function does not damp away due to phase mixing like the kinetic Green's function. This is not surprising as momentum space phase mixing is a strictly kinetic phenomenon.

B. Phase mixing in fluid response

Because the lack of phase mixing can diminish the utility of a pure fluid treatment, we follow the technique outlined by Hammett *et al.* for including phase mixing [25,26]. The general procedure involves choosing a closure to the fluid equations that damps away any initial perturbation. The transport coefficients associated with the closure are found by fitting the damping to the kinetic result to ensure similar time behavior. The type of closure introduced determines which conservation laws apply. For instance, including a diffusion closure $\overset{\leftrightarrow}{\Pi} = n\overset{\leftrightarrow}{T} - (\nu/I)\overrightarrow{\nabla}\vec{P}$ to the angular momentum equation would conserve momentum but not energy.

Previous work using the two-pole approximation for the response function [10,28] can be expressed within the formalism of fluid closures. In particular, the two-pole approximation is equivalent to adding a viscosity, ν, to Eq. (21b) and allowing for variation in the "natural" frequency $\sqrt{3}\omega_T$. In the original method described by Hammett *et al.* ν is an integral operator representing a convolution with respect to the spatial variable. However, for the polarizing field of the laser pulse, the spatial form of the potential is known and thus only one spatial mode need be considered. As a result, ν is simply an algebraic coefficient. Specifically, Eqs. (21b), (25a), and (25b) take the form

$$\frac{d}{dt}P_\theta = \frac{\nu}{12\pi n}L^2 P_\theta + \frac{1}{In\sin\theta} \times \left[\cot\theta\,\Pi_{\phi\phi} - \frac{\partial\Pi_{\theta\theta}}{\partial\theta}\right] - \frac{\partial}{\partial\theta}V, \tag{26a}$$

$$G(\Omega) = -g_0\left[\frac{1}{\Omega^2 + 2i\Omega\hat{\nu} - 3}\right], \tag{26b}$$

$$G(\tau) = g_0\frac{\sin\left(\frac{1}{2}\hat{\omega}_{T\nu}\tau\right)}{\hat{\omega}_{T\nu}}e^{-\frac{1}{2}\hat{\nu}\tau}, \tag{26c}$$

where ν is the rate of momentum loss associated with viscosity, $\hat{\nu} = \nu/\omega_T$, and $\hat{\omega}_{T\nu} = (3 - \hat{\nu}^2)^{1/2}$. We note that the kinematic viscosity is given by $\nu/12\pi n$. The value of ν is typically determined by fitting Eq. (26c) to experimental data or a full quantum-mechanical density-matrix calculation. It is clear that Eq. (26b) does not preserve the zero-frequency limit of the kinetic Green's function. However, matching the low-frequency limits of Eq. (26b) to Eq. (A3) is not required to ensure similarity of the fluid and kinetic response functions in the time domain. Because the response is damped for large times, matching the zero-frequency behavior is not critical. On the other hand, the small time (large frequency limit) limit of Eq. (26c) is independent of ν but still has the same functional behavior as Eq. (16a). A clear difference of the fluid response function is that the imaginary component drops as Ω^{-3} for large frequencies, whereas the kinetic response drops much more rapidly.

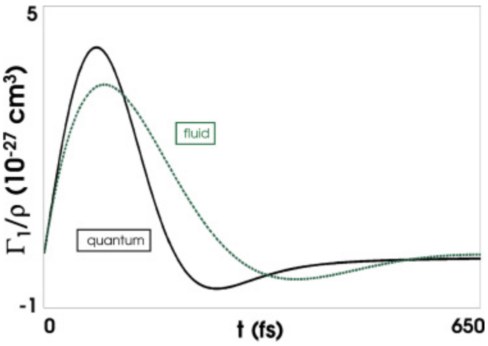

FIG. 6. (Color online) Comparison of the fully nonlinear quantum theory in black (solid) and the two-moment fluid response with viscosity in green (dashed) for nitrogen at $T = 294$ K.

The value of ν can be chosen in a variety of ways to match features of the kinetic response in either the time or frequency domain. In general, choice of the transport coefficient ν depends on the problem being solved. For short laser pulses, matching the initial behavior of the response is critical, while for long pulses matching the total integral of the response function may be important. Here we focus on capturing time domain features of the response function by finding the minimum with respect to ν of the integral $I(\nu) = \int [G_k(t) - G_f(\nu,t)]^2 dt$, where the subscripts k and f refer to the kinetic and fluid responses, respectively. In other words, we look for the least-squares fit with the parameter $\hat{\nu}$. With the least-squares fit we find that $\hat{\nu} = 0.95$; thus, the viscosity is similar to the thermal time scale. The results for a laser pulse with an intensity of $I = 1 \times 10^{12}$ W/cm^2 and duration $\sigma = 20$ fs in nitrogen at $T = 294$ K are shown in Fig. 6. While the fit is reasonable, it is not as accurate as desired and we next examine how to improve upon the fluid model by introducing additional fluid moments and transport coefficients.

C. Pressure equations

The traditional two-pole approximation presented above provides a reasonable fit to the kinetic response, but inclusion of more fluid moments can provide better approximations to the kinetic response function. Hammett *et al.* achieved a close representation of the kinetic response function of a plasma with four fluid moments. Here we follow a similar procedure and examine how our approximation of the kinetic response improves as we include additional moments. The inclusion of additional moment equations increases the maximum order of the pole approximation. For instance, adding the pressure equations allows a three-pole approximation, adding the heat flux equation allows for a four-pole approximation, etc. In addition, using a closure relation at higher moments can ensure conservation of the intuitive macroscopic quantities of momentum and energy. As we will see, inclusion of the pressure equation is necessary to capture the nonlinear behavior of the kinetic response as it involves conservation of energy.

We first define the heat flux moments as follows: $Q_{\theta\theta\theta} = \int (p_\theta - P_\theta)^3 d\vec{p} f$, $Q_{\phi\phi\theta} = (\sin\theta)^{-2} \int (p_\phi - P_\phi)^2 (p_\theta - P_\theta) d\vec{p} f$, $Q_{\phi\phi\phi} = (\sin\theta)^{-3} \int (p_\phi - P_\phi)^3 d\vec{p} f$, and $Q_{\phi\theta\theta} = (\sin\theta)^{-1} \int (p_\phi - P_\phi)(p_\theta - P_\theta)^2 d\vec{p} f$. We then rewrite the elements of the pressure tensor in terms of temperature, $\Pi_{ab} = nT_{ab}\sin\theta$, and the heat flux as $Q_{abc} = Inq_{abc}\sin\theta$. While the general equations for the temperature elements can be quite complicated (as shown in Appendix B), here we consider the situation of $T_{\theta\phi} = P_\phi = q_{\phi\theta\theta} = q_{\phi\phi\phi} = 0$. This situation is equivalent to disallowing off-diagonal elements of the pressure tensor to develop and is consistent with the conservation of P_ϕ. The equations for the temperature take the form

$$\begin{aligned}\frac{d}{dt}T_\theta &= -\frac{2}{I}T_\theta\frac{\partial P_\theta}{\partial\theta} - \frac{\nu}{6\pi I n}P_\theta L^2 P_\theta \\ &\quad - \frac{1}{n}\overleftrightarrow{\nabla}\cdot(\hat{\theta} n q_{\theta\theta\theta}) + 2\cot\theta\, q_{\phi\phi\theta},\end{aligned} \tag{27a}$$

$$\frac{d}{dt}T_\phi = -\frac{2}{I}T_\phi P_\theta\cot\theta - \frac{1}{n\sin^2\theta}\overleftrightarrow{\nabla}\cdot(\hat{\theta} n q_{\phi\phi\theta}\sin^2\theta). \tag{27b}$$

From here on we use the shorthand $q_\phi = q_{\phi\phi\theta}$ and $q_\theta = q_{\theta\theta\theta}$ since we are only interested in these two elements of the heat flux tensor. If the heat flux is identically zero, one can show that the linear temperature perturbations can be expressed as $T_{\theta,1} = \hat{T}_{\theta,1}(t)\cos 2\theta$ and $T_{\phi,1} = \hat{T}_{\theta,1}(t)\cos^2\theta$, implying that both temperatures have the same time dependence but different spatial dependence.

There are several choices for the heat flux closure, each of which will result in a different relationship between T_θ and T_ϕ. Here we focus on one closure and note that the response functions resulting from other closures are only trivially different. We consider another closure in Appendix C and show that the resulting response functions are only trivially different. We choose closures on q_θ and q_ϕ of the form

$$\begin{aligned}&\frac{1}{n}\overleftrightarrow{\nabla}\cdot(\hat{\theta} n q_\theta) - 2\cot\theta\, q_\phi \\ &\quad = -\frac{\mu}{4}\frac{\partial^2 T_\theta}{\partial\theta^2} - \frac{\varpi}{2I}T_\theta\frac{\partial P_\theta}{\partial\theta} + \frac{\varsigma}{12n}\frac{\partial^2 n}{\partial\theta^2},\end{aligned} \tag{28a}$$

$$\begin{aligned}&\frac{1}{n\sin^2\theta}\overleftrightarrow{\nabla}\cdot(\hat{\theta} n q_\phi\sin^2\theta) \\ &\quad = \frac{1}{4}\cot\theta\frac{\partial}{\partial\theta}\left[\frac{\mu}{4}\frac{\partial^2 T_\theta}{\partial\theta^2} + \frac{\varpi}{2I}T_\theta\frac{\partial P_\theta}{\partial\theta} - \frac{\varsigma}{12n}\frac{\partial^2 n}{\partial\theta^2}\right].\end{aligned} \tag{28b}$$

The terms on the right-hand side of Eq. (28a) can be interpreted as thermal conduction, modifications to the adiabaticity, and modifications to the compressibility of the diatomic fluid. The utility of these closures is demonstrated below. For now we note that μ, ϖ, and ς need not be independent.

We write the first-order quantities as $n_1 = \hat{n}_1(t)(1 + 3\cos 2\theta)$, $P_{\theta,1} = \hat{P}_{\theta,1}(t)\sin 2\theta$, $T_{\theta,1} = \hat{T}_{\theta,1}(t)\cos 2\theta$, and $T_{\phi,1} = \hat{T}_{\theta,1}(t)\cos^2\theta$. Upon linearing Eqs. (27a) we have the following:

$$\frac{\partial}{\partial t}\hat{T}_{\theta,1} = -(4 - \varpi)\frac{T_0}{I}\hat{P}_{\theta,1} - \mu\hat{T}_{\theta,1} + 4\pi\varsigma\hat{n}_{1,\theta}. \tag{29}$$

The resulting response function is

$$G(\Omega) = -g_0\left[\frac{\Omega + i\hat{\mu}}{\Omega^3 + i\Omega^2(2\hat{\nu}+\hat{\mu}) - \Omega\left(2\hat{\mu}\hat{\nu} - \frac{5}{4}\varpi + 8\right) - i\left(3\hat{\mu} + \frac{5}{2}\hat{\varsigma}\right)}\right], \tag{30}$$

where $\hat{\mu} = \mu/\omega_T$ and $\hat{\varsigma} = \varsigma/\omega_T^3$. For $\hat{\mu},\hat{\varsigma} = 0$ and $\varpi = 4$ [which eliminates the first term in Eq. (29)] we recover Eq. (26b). From Eq. (30) it is clear that the parameter ϖ provides the freedom to choose the "natural" frequency of the mode. There are, however, constraints on how the transport coefficients can be chosen. The response function in the time domain must be damped as a function of time; thus, all the roots of the denominator in the Eq. (30) must be complex with negative imaginary components. Given this condition, one can show that the denominator in Eq. (30) has two possibilities for the set of three roots: $\Omega = [\omega_1 - i\nu_1, -\omega_1 - i\nu_1, -i\nu_2]$ or $\Omega = [-i\nu_1, -i\nu_2, -i\nu_3]$. Furthermore, the physical argument that thermal conduction and compressibility must be diffusive: $\mu,\varsigma > 0$, precludes the second set of roots above. Fortuitously, the first choice of roots has more correspondence with the response function found in Sec. III B. We see in the next section that a nonzero value of the coefficient ς can lead to unphysical equilibria and time asymptotic behavior; thus, we choose to set it to zero.

We can rewrite Eq. (30) using our choice of root set as

$$G(\Omega) = -g_0\left[\frac{-i\hat{\nu}_2\left(1 - \frac{1}{3}\hat{\omega}_1^2\right)}{\hat{\nu}_2^2 + \hat{\omega}_1^2 - 2\hat{\nu}_1\hat{\nu}_2}\right] \times \left[\frac{\Omega + i\Psi}{\Omega^2 + 2i\hat{\nu}_1\Omega - \hat{\omega}_1^2} - \frac{1}{\Omega + i\hat{\nu}_2}\right], \tag{31a}$$

where $\Psi = \hat{\omega}_1^2(1 + \frac{1}{3}\hat{\nu}_2^2 - \frac{2}{3}\hat{\nu}_1\hat{\nu}_2)/\hat{\nu}_2(1 - \frac{1}{3}\hat{\omega}_1^2)$, and $\hat{\omega}_1$, $\hat{\nu}_1$, and $\hat{\nu}_2$ are related to the transport coefficients via the equations: $\hat{\mu} = \frac{1}{3}\hat{\omega}_1^2\hat{\nu}_2$, $2\hat{\nu} + \hat{\mu} = 2\hat{\nu}_1 + \hat{\nu}_2$, and $2\hat{\nu}\hat{\mu} + 8 - \frac{5}{4}\varpi = 2\hat{\nu}_1\hat{\nu}_2 + \hat{\omega}_1^2$. The variables $\hat{\omega}_1$, $\hat{\nu}_1$, and $\hat{\nu}_2$ will be chosen to match the kinetic response function in the time domain. Rewriting Eq. (31a) in the time domain we have the following:

$$G(\tau) = -g_0\left[\frac{\hat{\nu}_2\left(1 - \frac{1}{3}\hat{\omega}_1^2\right)}{\hat{\nu}_2^2 + \hat{\omega}_1^2 - 2\hat{\nu}_1\hat{\nu}_2}\right]\left[\left(\frac{\Psi - \hat{\nu}_1}{\hat{\omega}_1}\right)\sin\left(\tfrac{1}{2}\hat{\omega}_1\tau\right) \times e^{-\frac{1}{2}\hat{\nu}_1\tau} + \cos\left(\tfrac{1}{2}\hat{\omega}_1\tau\right)e^{-\frac{1}{2}\hat{\nu}_1\tau} - e^{-\frac{1}{2}\hat{\nu}_2\tau}\right]. \tag{31b}$$

As with the two-moment model, we use the method of nonlinear least squares to find the values of $\hat{\omega}_1$, $\hat{\nu}_1$, and $\hat{\nu}_2$. The process involves minimizing the integral $I(\vec{R}) = \int[G_k(t) - G_f(\vec{X},t)]^2dt$, where the elements of the vector $\vec{X}$ are $\hat{\omega}_1$, $\hat{\nu}_1$, and $\hat{\nu}_2$. From the values of $\hat{\omega}_1 = 2.37$, $\hat{\nu}_1 = 1.27$, and $\hat{\nu}_2 = 3.28$ that minimize $I(\vec{R})$, we find $\hat{\mu} = 6.16$, $\varpi = -6.45$, and $\hat{\nu} = -0.17$. While a negative value of viscosity may seem strange, it provides a linearly stable solution. The stability of the response is determined by the roots of the denominator of Eq. (30), not the value of the transport coefficients. Figure 7 shows the results for the same laser parameters and temperature used in Fig. 6. The fluid response function matches the quantum response function quite well. By including the heat flux equations we could improve upon this result, but this will be considered in subsequent publications.

D. Nonlinear time asymptotic behavior

In the previous section we found that adding the pressure moment with additional transport coefficients provided a simple way to model kinetic phase mixing. In addition to providing an accurate response function, the pressure moment also provides energy conservation. A result of this is a steady-state alignment, as found in the quantum and classical kinetic calculations. Here we consider the time asymptotic behavior of the second-order quantities after the presence of the polarizing impulse. The second-order equations are driven by terms involving products of the first-order quantities, which damp away due to phase mixing. Furthermore, the effect of phase mixing should eliminate any macroscopic flow in the system: Directed energy imparted by the polarizing field is converted to thermal energy. In particular, we can write the conservation of energy after passage of the laser pulse as $\int n(T_{\theta\theta} + T_{\phi\phi} + P_\theta^2/I)dV = \text{const}$. At first order one can show that $\int[n_0(T_{\theta,1} + T_{\phi,1})dV = 0$; thus, there is no global gain in thermal energy at first order, and a second-order treatment is necessary for energy conservation.

For long times, the equations for the second-order quantities reduce to the following:

$$\varsigma\frac{\partial^2 n_2}{\partial\theta^2} - \frac{3\mu}{4\pi}\frac{\partial^2 T_{\theta,2}}{\partial\theta^2} = 0, \tag{32a}$$

$$\frac{\partial T_{\theta,2}}{\partial\theta} + (T_{\theta,2} - T_{\phi,2})\cot\theta + 4\pi T_0\frac{\partial n_2}{\partial\theta} = 0. \tag{32b}$$

Equation (32a) guarantees the heat flux is eliminated in equilibrium while Eq. (32b) is the steady-state equation for momentum density. The transport coefficient ς allows a gradient in $T_{\theta,2}$ in equilibrium. As shown in Appendix D, this is an unconventional equilibrium; thus, we continue considering the situation of $\varsigma = 0$. Multiplying Eq. (32b)

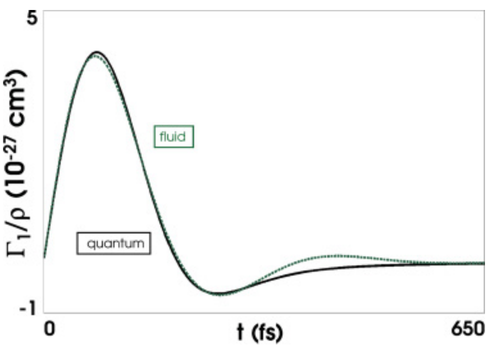

FIG. 7. (Color online) Comparison of the fully nonlinear quantum theory in black (solid) and the three-moment fluid response in green (dashed) for nitrogen at $T = 294$ K.

by $\frac{1}{3}\cot\theta\cos^2\theta$ and integrating by parts the asymptotic second-order polarizability is

$$\Gamma_2 = \frac{2\pi\rho\Delta\alpha}{3T_0}\int (T_{\theta,2} - T_{\phi,2})\cos^2\theta\sin\theta d\theta, \tag{33}$$

where we have used that n is symmetric about $\theta = \pi/2$ and $4\pi n_2(\theta = 0) = -\frac{1}{2T_0}\int(T_{\theta,2} - T_{\phi,2})\cos\theta\cot\theta d\theta$ [found by multiplying Eq. (30b) by $\cos\theta$]. Equation (33) demonstrates that a modified steady-state polarizability requires $T_{\theta,2} \neq T_{\phi,2}$. In terms of kinetic theory, this implies the distribution function is not just a function of the Hamiltonian, but also has dependence on the constant of motion p_ϕ (see Appendix D).

Upon using the condition of energy conservation, $\int I(T_{\theta,2} + T_{\phi,2})_{t\to\infty}dV \simeq \int(P_{\theta,1}^2)_{t=0}dV$, and writing $T_{\phi,2} = T_{\theta,2} - T_{\theta,2}\sin^2\theta$ we find

$$T_{\theta,2}(t \to \infty) = \frac{T_0}{20}\left(\frac{\sigma\Delta\alpha E_0^2}{I\omega_T}\right)^2. \tag{34}$$

With Eqs. (33) and (34) the time asymptotic second-order polarizability can be calculated, for which we find

$$\Gamma_2(t \to \infty) = \pi\rho\Delta\alpha\left(\frac{2}{225}\right)\left(\frac{\sigma\Delta\alpha E_0^2}{I\omega_T}\right)^2, \tag{35}$$

nearly the same value found from the kinetic theory.

IV. SUMMARY AND CONCLUSIONS

We have considered the delayed response of a diatomic gas to an ultrashort laser pulse using both classical kinetic and fluid theory. A classical kinetic model was developed for the evolution of the molecular distribution function in the presence of a polarizing laser pulse. An analytic expression was derived for the linear response function. For heavy molecules such as nitrogen and oxygen at atmospheric temperatures, the analytic expression was shown to be in excellent agreement with full quantum-mechanical density calculations of the molecular response before the quarter recurrence time.

For impulse laser pulses we formulated a fully nonlinear approach for determining the response function to any desired order in the electric field strength. Using this approach, we derived an analytic expression for the second-order polarizability. The classical expression for the polarizability including the second-order correction was again in excellent agreement with the full quantum-mechanical calculations. An interesting effect of the second-order polarizability was a modified steady-state alignment after passage of the laser pulse. We concluded that the second-order polarizability was sufficient as the differences between the nonlinear quantum calculation and the classical kinetic theory were negligible up to the intensity threshold for ionization.

From the Boltzmann equation used for the classical kinetic theory, we derived fluid moment equations. In doing so, we lost the ability to capture the phase mixing of the molecular gas. To model phase mixing with fluid equations, we used the approach of Hammett *et al.* [25,26] previously considered in plasma physics. The method involves defining a closure for the fluid equations with transport coefficients that provide linear damping. The linear damping provides the same physical result as phase mixing. We considered this approach for both a two-moment model (continuity and momentum) and a three-moment model (continuity, momentum, and energy). The transport coefficients were found using nonlinear least squares on the linear fluid time domain response and the quantum-mechanical response. The results for the three-moment model were in good agreement.

Aside from providing an accurate response function, the three-moment model also provides energy conservation. In the absence of net equilibrium momentum, the kinetic energy is proportional to the square of the first-order momentum. Thus, to consider energy conservation, we had to consider the fluid equations at second order in the laser intensity. While energy conservation was necessary to capture the modified steady-state alignment at second order, it was not sufficient. The steady-state alignment required an anisotropic temperature. We showed that not only was the temperature anisotropic but the ϕ component of the temperature was a function of θ in the modified equilibrium.

The main result of the paper was to derive a computationally expedient model for determining the molecular response. In the linear kinetic case this was done by determining the Green's function of the gas: For any pulse shape the response of the gas can be determined through a convolution in time. The convolution, however, is an expensive operation $\sim N_t^2$, where N_t is the number of numerical time steps and cannot capture nonlinear effects. The fluid equations provide an efficient method for determining the response. The linear time domain response is completely separable with respect to time, and thus a convolution only requires $\sim N_t$ operations. For the nonlinear response, a system of four coupled first-order partial differential equations must be solved.

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APPENDIX A: LIMITS OF THE KINETIC RESPONSE FUNCTION

In Sec. II C, we derived the kinetic response function of the molecular gas to the perturbing potential. Here we examine properties of this function. We begin by considering the small argument limit, for zero frequency we have

$$G(0) = \tfrac{1}{4}g_0. \tag{A1}$$

One can show that $G(\Omega)$ satisfies the differential equation

$$\left[\Omega\frac{d^2}{d\Omega^2} + (\Omega^2 - 1)\frac{d}{d\Omega} + \frac{1}{4}\Omega^3\right]G = -\frac{1}{8}g_0\Omega; \tag{A2}$$

however, $d_\Omega^2 G$ has a logarithmic divergence as $\Omega \to 0$; thus, the Frobenius method is not an option for determining the low-frequency behavior. One can write an alternative low-frequency expansion of the form $G(\Omega) = \sum[\alpha_n +$

$\beta_n \log_e(\Omega)]\Omega^n$, for which we find the first few coefficients to be

$$G(\Omega) = \frac{1}{4}g_0\left[1 + i\pi s_\Omega\left(\frac{\Omega}{2}\right)^2 e^{-\Omega^2/4} - \frac{1}{4}\Omega^2\log_e|\Omega| + \frac{1}{16}\Omega^4\log_e|\Omega| - \frac{3}{64}\Omega^4\cdots\right]. \tag{A3}$$

In the large argument limit we can simply Taylor expand the denominator of Eq. (16a) to find

$$G(\Omega) = \frac{1}{4}g_0\left[i\pi s_\Omega\left(\frac{\Omega}{2}\right)^2 e^{-\Omega^2/4} - \sum_{n=1}\Gamma(n+1)\left(\frac{2}{\Omega}\right)^{2n}\right], \tag{A4}$$

where Γ is the Γ function and s_Ω represents the sign of Ω.

APPENDIX B: GENERAL TEMPERATURE EQUATIONS

In Sec. III, we introduce simplified versions of the temperature equations. The general equations before simplification are shown below:

$$\frac{d}{dt}T_\theta = -2\frac{T_\theta}{I}\frac{\partial P_\theta}{\partial\theta} + \frac{4}{I}\frac{\cot\theta}{\sin\theta}P_\phi T_{\theta\phi} - \frac{\nu}{6\pi In}P_\theta L^2 P_\theta + 2\cot\theta q_{\phi\phi\theta} - \frac{1}{n}\vec{\nabla}\cdot(\hat\theta n q_{\theta\theta\theta}), \tag{B1}$$

$$\frac{d}{dt}T_\phi = -2T_\phi P_\theta\cot\theta - \frac{2T_{\theta\phi}}{I\sin\theta}\frac{\partial P_\phi}{\partial\theta} - \frac{1}{n\sin^2\theta}\vec{\nabla}\cdot(\hat\theta n q_{\phi\phi\theta}\sin^2\theta), \tag{B2}$$

$$\frac{d}{dt}T_{\theta\phi} = -\frac{T_{\theta\phi}}{I}\frac{\partial P_\theta}{\partial\theta} - \frac{T_{\theta\phi}P_\theta}{I}\cot\theta + \frac{2}{I}\frac{\cot\theta}{\sin\theta}T_\phi P_\phi - \frac{\nu}{6\pi In}P_\phi L^2 P_\theta - \frac{T_\theta}{I\sin\theta}\frac{\partial P_\phi}{\partial\theta} - \frac{1}{n\sin\theta} \times \vec{\nabla}\cdot(\hat\theta n q_{\phi\theta\theta}\sin\theta) + \cot\theta q_{\phi\phi\phi}. \tag{B3}$$

APPENDIX C: ANOTHER CLOSURE CHOICE FOR THE HEAT FLUX

In Sec. III we considered a closure that resulted in $T_{\theta,1}$ and $T_{\phi,1}$ having the same temporal dependence but different spatial dependence. Here we consider an additional closure on q_ϕ that allows for different time dependence of $T_{\theta,1}$ and $T_{\phi,1}$ as follows:

$$\frac{1}{n\sin^2\theta}\vec{\nabla}\cdot(\hat\theta n q_\phi\sin^2\theta) = -\frac{\mu}{4}\frac{\partial^2 T_\theta}{\partial\theta^2} - \frac{\varpi}{2I}T_\theta\frac{\partial P_\theta}{\partial\theta} + \frac{\varsigma}{12n}\frac{\partial^2 n}{\partial\theta^2}. \tag{C1}$$

We write the first-order temperatures as $T_{\theta,1} = \hat T_{\theta,1}(t)\cos 2\theta$ and $T_{\phi,1} = \hat T_{\theta,1}(t)\cos^2\theta + \delta\hat T(t)\sin^2\theta$, where $\delta\hat T$ represents the difference in time dependence between $T_{\phi,1}$ and $T_{\theta,1}$. From the linearized equations for continuity, momentum density, and temperature we have

$$\frac{\partial}{\partial t}\delta\hat T = -\varpi\frac{T_0}{I}\hat P_{\theta,1} + \mu\hat T_{\theta,1} - 4\pi\varsigma\hat n_{1,\theta}, \tag{C2}$$

where the equation for $\hat T_{\theta,1}$ is Eq. (29). Equations (C2) and (29) are different due to the first term in Eq. (27b) not contributing to the evolution of $\delta\hat T$, implying that $\hat T_{\theta,1}$ and $\hat T_{\phi,1}$ do not have identical time dependence. Although Eqs. (C1) and (30) are different, the resulting response function is surprisingly similar:

$$G(\Omega) = -g_0\left[\frac{\Omega + i\hat\mu}{\Omega^3 + i\Omega^2(2\hat\nu + \hat\mu) - \Omega(2\hat\mu\hat\nu - \varpi + 9) + i(5\hat\mu + 2\hat\varsigma)}\right]. \tag{C3}$$

The similarity between Eqs. (C1) and (30) indicates that the linear response function is insensitive to the closure chosen.

APPENDIX D: KINETIC EQUILIBRIA

Here we discuss kinetic equilibrium and show that T_θ has no gradient for conventional equilibria. This is the primary justification for setting the transport coefficient $\varsigma = 0$ in Sec. III. As discussed in Sec. II the equilibrium distribution function must satisfy the equation $(\vec p\cdot\vec{\nabla} - \vec{\nabla} I V_{\text{eff}}\cdot\vec{\nabla}_p)f = 0$, where $\hat\theta\cdot\nabla V_{\text{eff}} = -p_\phi^2\cos\theta/I\sin^3\theta$. The most general solution to this equation is $f = f(R,p_\phi)$, which is a function only of the constants of motion. Equation (9) is one such solution. Taking the pressure moments of Eq. (9), one can show that $T_\theta = T_\phi$, where both are independent of angle. In Sec. III, we also showed that in order for a laser pulse to leave behind a modified equilibrium polarizability $T_\theta \neq T_\phi$. The simplest equilibrium distribution function allowing this is

$$f \propto \exp\left[-\frac{1}{2IT}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) - \delta\frac{p_\phi^2}{2IT}\right], \tag{D1}$$

for which $T_\theta = T$ is independent of θ, and δ parametrizes the difference between T_θ and T_ϕ. Because there is no first-order correction to the equilibrium (all first-order quantities phase mix away) δ must be a quartic function of the laser pulse's electric field: $\delta \sim (\Delta\alpha)^2\sigma^2 E_0^4$. Upon taking the moment $\Pi_{\phi\phi} = \sin^{-2}\theta\int p_\phi^2 f\,d\vec p/\int f\,d\vec p$ we have

$$T_\phi - T_\theta = -\delta T_\theta\frac{\sin^2\theta}{1 + \delta\sin^2\theta}; \tag{D2}$$

thus, equilibrium differences between the temperatures are a result of even orders in the perturbation expansion. Noting that the modifications to the temperature are also proportional to δ, we can write $T_{\theta,2} \sim \delta T_0$; thus, $T_{\phi,2} - T_{\theta,2} = -\delta T_0\sin^2\theta$.

[1] C. H. Lin *et al.*, Phys. Rev. A **13**, 813 (1976).
[2] J. H. Marburger, Prog. Quantum Electron. **4**, 35 (1975).
[3] A. Braun *et al.*, Opt. Lett. **20**, 73 (1995).
[4] G. Fibich *et al.*, Opt. Express **13**, 5897 (2005).
[5] P. Sprangle *et al.*, Phys. Rev. E **66**, 046418 (2002).
[6] A. Couairon and A. Mysyrowicz, Phys. Rep. **441**, 47 (2007).
[7] A. Ting *et al.*, Appl. Opt. **44**, 1474 (2005).
[8] S. Eisenmann *et al.*, Opt. Express **15**, 2779 (2007).
[9] S. Varma *et al.*, Phys. Rev. Lett. **101**, 205001 (2008).
[10] Y.-H. Chen *et al.*, Phys. Rev. Lett. **105**, 215005 (2010).
[11] H. Stapelfeldt and T. Seideman, Rev. Mod. Phys. **75**, 543 (2003).
[12] E. Hamilton *et al.*, Phys. Rev. A **72**, 043402 (2005).
[13] M. S. Molodenskiy and O. V. Tikhonova, Laser Phys. **17**, 401 (2007).
[14] Y.-H. Chen *et al.*, Opt. Express **15**, 11341 (2007).
[15] A. J. Pearson and T. M. Antonsen, Phys. Rev. A **80**, 053411 (2009).
[16] A. York and H. M. Milchberg, Opt. Express **16**, 10557 (2008).
[17] G. Méchain *et al.*, Appl. Phys. B **79**, 379 (2004).
[18] G. Méchain *et al.*, Phys. Rev. Lett. **93** 035003 (2004).
[19] M. E. Sukharev and V. P. Krainov, Zh. Eksp. Teor. Fiz. **113**, 573 (1998).
[20] M. S. Child, Mol. Phys. **101**, 637 (2003).
[21] M. S. Molodenskiy and O. V. Tikhonova, Laser Phys. **14**, 1191 (2004).
[22] M. Iñarrea *et al.*, Phys. Lett. A **374**, 457 (2010).
[23] E. Gershnabel and I. Sh. Averbukh, Phys. Rev. A **82**, 033401 (2010).
[24] Y. Khodorkovsky, Phys. Rev. A **83**, 023423 (2011).
[25] G. W. Hammett *et al.*, Phys. Fluids B. **4**, 2055 (1992).
[26] G. W. Hammett and F. W. Perkins, Phys. Rev. Lett. **64**, 3019 (1990).
[27] A. Talebpour *et al.*, Opt. Commun. **163**, 29 (1999).
[28] J. R. Penano *et al.*, Phys. Rev. E **68**, 056502 (2003).