Direct extraction of intense-field-induced polarization in the continuum on the attosecond time scale from transient absorption

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A procedure is suggested for using transient absorption spectroscopy above the ionization threshold to measure the polarization of the continuum induced by an intense optical pulse. In this way transient absorption measurement can be used to probe subfemtosecond intense field dynamics in atoms and molecules. The method is based on an approximation to the dependence of these spectra on time delay between an attosecond XUV probe pulse and an intense pump pulse that is tested over a wide range of intensities and time delays by all-electrons-active calculations using the multiconfiguration time-dependent Hartree-Fock method in the case of neon.

I. INTRODUCTION

Recent experiments [1–6] have revealed how the dynamics of photon coupling between states of the target atom or molecule are manifested in attosecond transient absorption spectra. In most such studies to date, an intense femtosecond near-infrared (NIR) or visible (VIS) pulse is applied to probe or modify the dynamics initially driven by a weak and much shorter extreme ultraviolet (XUV) pulse [7,8]. In this study, we propose a different transient absorption experiment in which a weak and ultrashort XUV pulse is used to probe the continuum dynamics driven by an intense pump pulse in the NIR or by a low harmonic (e.g., 400 or 266 nm) of such a pulse. Based on an approximation to these spectra tested by *ab initio* solutions of the time-dependent Schrödinger equation on neon, we demonstrate an all optical procedure whereby the subfemtosecond response of the system, i.e., polarization of the continuum induced by an intense pump field, could be directly extracted from this kind of transient absorption measurement.

The induced polarization of the continuum is a subfemtosecond response of the system to an intense driving field. Using an ultrafast variant of Stark spectroscopy to measure that response, Neidel *et al.* reported the observation of attosecond time scale electron dynamics in neutral molecules [9]. In this experiment, by monitoring the time-dependent variations of the parent molecular ion yield, it was shown that the time-dependent dipole induced by a moderately strong near-infrared (NIR) laser field can be probed by an attosecond XUV pulse. The key ingredient of the experiment in Ref. [9] for real-time probing of polarization can be understood as the nonresonant dynamic Stark effect (NRDSE) [10]. The NRDSE is conventionally defined in the intermediate strength regime, i.e., nonperturbative but also nonionizing, where two limiting cases exist: the dipole coupling regime and the Raman regime. In the dipole case, the system's response closely follows the instantaneous electric field, which is what Neidel *et al.* [9] observed. In the Raman case, the field envelope is followed [11]. These effects are the result of a slow response of the system to a moderately strong driving field which does not depopulate the ground state appreciably.

However, the much faster response of the system at frequencies in the XUV spectral region that becomes prominent as the intensity of the driving field grows is also interesting, because it contains much of the physics responsible for high harmonic generation (HHG), for example. It is this nonlinear, high frequency response of the system on which we focus here. In this study we suggest a method for extracting this response on the attosecond time scale directly, including the associated phase information, from transient absorption measurements.

Although we suggest that this type of measurement might be possible in the general case of a transient absorption experiment with a probing XUV attosecond pulse and a longer driving NIR/VIS pulse, the calculations that are within reach of all-electrons-active calculations require that we consider cases in which fewer photons are involved. We consider an example in neon in which the relevant processes nominally involve five or seven photons. In these calculations we employ a recently developed implementation of the multiconfiguration time-dependent Hartree-Fock (MCTDHF) method [12,13]. The calculations we present here include competing effects, including ionization of the target, that might obscure such an observation. Even though we consider an example in which only relatively low harmonics are generated, these calculations suggest that this approach to investigating the response of atoms and molecules to intense laser pulses might be fruitful in situations where many more photons are absorbed or emitted.

This paper is organized as follows. In Sec. II, we review the theory of transient absorption and describe the proposed procedure for extracting the continuum polarization from transient absorption spectra. In Sec. III we discuss the computational approach to compute the transient absorption signals for neon, and in Sec. IV we describe the extracted induced polarizations in both the frequency and the temporal domain. In Sec. V, we discuss the feasibility of the measurement of continuum polarization by this approach, and we offer concluding remarks in Sec. VI.

II. TRANSIENT ABSORPTION AND CONTRIBUTIONS TO INDUCED POLARIZATION

In the pulse configuration we consider, a time-delayed isolated XUV attosecond pulse is used to probe the polarization in the continuum induced by an intense pump pulse. To

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describe the resulting spectrum we start from a familiar expression for the single atom response function. If the time-dependent Hamiltonian can be expressed as $H = H_0 - \hat{d}\mathcal{E}(t)$, where H_0 is the field-free Hamiltonian, $\hat{d}$ is the dipole operator, and $\mathcal{E}(t)$ is the electric field of the applied laser pulses, the single-atom response function can be expressed as [14–16]

$$\tilde{S}(\omega, \tau_d) = 2\mathrm{Im}[\tilde{d}(\omega, \tau_d)\tilde{\mathcal{E}}^*(\omega, \tau_d)], \tag{1}$$

where $\tilde{d}(\omega, \tau_d)$ and $\tilde{\mathcal{E}}(\omega, \tau_d)$ are the Fourier transform of the time-dependent induced dipole, $d(t) \equiv \langle\Psi(t)|\hat{d}|\Psi(t)\rangle$, and the total electric field, $\mathcal{E}(t)$, respectively, and where we explicitly note the dependence on the time delay, τ_d. We use Eq. (1) in this study together with *ab initio* calculations of the electron dynamics to compute the absorption signals.

In the example we describe in detail below, a weak 1-fs XUV probe pulse centered at 23.13 eV is applied to the neon atom together with a time-delayed, much more intense 12-fs-long pump pulse centered at 266 nm (the third harmonic of a 800-nm laser). We observe in these calculations that at frequencies in the XUV spectral region (above the ionization potential of the atom) an "additive approximation" can be made to describe the combined field-induced polarization when the field-induced polarizations by the pump and probe fields are comparable or when the polarization induced by the pump field is larger than that induced by the XUV probe,

$$
\begin{aligned}
d(t; t_d) &\approx d_{\mathrm{pr}}(t) + d_{\mathrm{pu}}(t; t_d) \\
&= d_{\mathrm{pr}}(t) + d_{\mathrm{pu}}(t - t_d; 0),
\end{aligned} \tag{2}
$$

where $d_{\mathrm{pr}}(t)$ and $d_{\mathrm{pu}}(t; t_d)$ are the time-dependent polarizations induced solely by the probe pulse and by the pump pulse, respectively, in separate calculations, and where t_d is the time delay between these two pulses. This is the point of departure for using a delayed attosecond XUV pulse to read out intense-field-induced polarization, $d_{\mathrm{pu}}(\omega)$. In the case where the two pulses are nonoverlapping, the polarization in the unstructured continuum induced by the first pulse decays rapidly during the time delay, and the approximation described by Eq. (2) would be unsurprising for any intensities. In the case of overlapping pulses we observe Eq. (2) to hold nonetheless for the range of intensities in which particular frequency-mixing processes can be neglected.

The additive approximation observed to describe the results of the *ab initio* calculations can be understood schematically as follows. Remembering that we are considering only contributions at XUV frequencies, we consider the processes that can reach those continuum states of the atom. If the XUV probe can reach the portion of atomic spectrum in the continuum near that accessed by N (odd) pump photons, those processes are the ones allowed within the bandwidths of the pulses. In the example we consider computationally, the bandwidth of the pump is relatively narrow, but the XUV probe has a bandwidth that spans roughly the energy of two pump photons. Focusing on the contribution in perturbation theory of the energy range of the continuum states of the atom that can be populated near N times the central frequency of the pump pulse and within its bandwidth, which we denote $|\Psi_f(t)\rangle$, we might write the contributions from the relevant orders of perturbation theory and from the range of continuum states that contribute to the

full wave function, $|\Psi(t)\rangle$, as

$$
\begin{aligned}
|\Psi(t)\rangle \approx |\Psi_0(t)\rangle &+ \left|\Psi_f^{(1\mathrm{pr})}(t)\right\rangle + \left|\Psi_f^{(N\mathrm{pu})}(t)\right\rangle \\
&+ \left|\Psi_f^{(1\mathrm{pr}\pm 2\mathrm{pu})}(t)\right\rangle + \text{other.}
\end{aligned} \tag{3}
$$

Here $|\Psi_0(t)\rangle = |\Psi_0\rangle e^{-i\,E_0 t/\hbar}$ is the wave function for the initial (ground) state (assumed for the moment not to be significantly depopulated), and $|\Psi_f^{(1\mathrm{pr})}(t)\rangle$, $|\Psi_f^{(N\mathrm{pu})}(t)\rangle$, and $|\Psi_f^{(1\mathrm{pr}\pm 2\mathrm{pu})}(t)\rangle$ are the contributions to the perturbation expansion of $|\Psi_f(t)\rangle$ of the processes involving 1 probe, N pump, and 1 probe $\pm$ 2 pump photons, respectively. The time-dependent induced polarization is $d(t) = \langle\Psi(t)|\hat{d}|\Psi(t)\rangle$, and the portion of it in this region of the spectrum can thus be approximated as

$$
\begin{aligned}
d_f(t) &\approx \langle\Psi_0(t)|\hat{d}\left|\Psi_f^{(1\mathrm{pr})}(t) + \Psi_f^{(N\mathrm{pu})}(t) + \Psi_f^{(1\mathrm{pr}\pm 2\mathrm{pu})}(t)\right\rangle + \text{c.c.} \\
&\approx \langle\Psi_0(t)|\hat{d}\left|\Psi_f^{(1\mathrm{pr})}(t)\right\rangle + \langle\Psi_0(t)|\hat{d}\left|\Psi_f^{(N\mathrm{pu})}(t)\right\rangle \\
&\quad + \langle\Psi_0(t)|\hat{d}\left|\Psi_f^{(1\mathrm{pr}\pm 2\mathrm{pu})}(t)\right\rangle + \text{c.c.,}
\end{aligned} \tag{4}
$$

where the first and the second terms correspond to $d_{\mathrm{pr}}(t)$ and $d_{\mathrm{pu}}(t; t_d)$ in Eq. (2), respectively.

When the energy bandwidths of both fields, probe and pump, are narrow, the third pathway is negligible and can be safely neglected. However, when the probe (XUV) field has a wide energy bandwidth and, most importantly, also is sufficiently intense, this additional third pathway can cause the additive approximation to break down. Our proposed extraction procedure, which is entirely based on the additive approximation in Eq. (2), is effective when this third contribution to polarization is significantly smaller than the first two contributing terms in this analysis. For combinations of intensities for which such frequency mixing in the ionization continuum is not negligible, in particular, for an overly intense probe pulse, this approximation would be expected to fail.

This limited analysis is admittedly insufficient to completely explain the robustness of this approximation as we observe it in the numerical simulations presented here. It appears to be accurate even when the initial state of the atom is significantly depopulated by the pulses through multiphoton ionization. In exploratory calculations on the hydrogen and nitrogen atoms with 400-nm pump pulses, in which the continuum polarization corresponding to the absorption of five pump photons was probed by the XUV pulse, results were observed similar to the ones we report in detail for neon.

We now turn to the consequences of the approximate additive property we observe in Eq. (2). The central result comes essentially from substituting the Fourier transform of Eq. (2) into Eq. (1). The electric field for ω in the XUV spectral region is mainly due to the probe field, because those frequencies are outside the bandwidth of the pump pulse, $\tilde{\mathcal{E}}_{\mathrm{pu}}(\omega) \ll \tilde{\mathcal{E}}_{\mathrm{pr}}(\omega)$. That fact, together with the identity $\int_{-\infty}^{\infty} d(t - t_d) \exp[i\omega t]dt = \exp[i\omega t_d] \int_{-\infty}^{\infty} d(t) \exp[i\omega t]dt$ and the additive approximation allows Eq. (1) to be simplified to

$$
\begin{aligned}
\tilde{S}(\omega; t_d) &= 2\mathrm{Im}[\tilde{d}(\omega; t_d)\tilde{\mathcal{E}}^*(\omega)] \\
&\approx \tilde{S}_{\mathrm{pr}}(\omega) + 2\mathrm{Im}[\tilde{d}_{\mathrm{pu}}(\omega; t_d)\tilde{\mathcal{E}}_{\mathrm{pr}}^*(\omega)] \\
&\approx \tilde{S}_{\mathrm{pr}}(\omega) + 2\mathrm{Im}[\tilde{d}_{\mathrm{pu}}(\omega; t_d = 0)e^{i\omega t_d}\tilde{\mathcal{E}}_{\mathrm{pr}}^*(\omega)].
\end{aligned} \tag{5}
$$

Equation (5) is the key result showing that the time-delay dependence of this transient absorption spectrum is contained only in the exponential factor, $\exp[i\omega t_d]$. If the probe field is well characterized, this equation provides the ingredients for a heterodyne detection of the continuum polarization induced by the pump, $\tilde{d}_{pu}(\omega)$. Given knowledge of the probe field $\tilde{\mathcal{E}}_{pr}(\omega)$ and the values of $\tilde{S}(\omega; t_d)$ for three time delays, the approximate expression in Eq. (5) can be used to solve at each value of ω for three unknowns: the probe-only absorption spectrum, $\tilde{S}_{pr}(\omega)$, and the real and imaginary components of the pump-field-induced polarization, $\mathrm{Re}[\tilde{d}_{pu}(\omega; t_d = 0)]$ and $\mathrm{Im}[\tilde{d}_{pu}(\omega; t_d = 0)]$. In Eq. (5) the probe-only absorption is given by $\tilde{S}_{pr}(\omega) = 2\mathrm{Im}[\tilde{d}_{pr}(\omega)\tilde{\mathcal{E}}_{pr}^*(\omega)]$.

To test this procedure for extracting the real and imaginary parts of the pump-field-induced polarization, we also calculate it separately from a pump-only *ab initio* calculation. The induced polarization as a function of time at frequencies in the continuum is given by the Fourier transform $\tilde{d}_{pu}(\omega; t_d = 0)$:

$$d_{continuum}(t) \equiv \frac{2}{\sqrt{2\pi}} \mathrm{Re}\left[\int_{I_p}^{\infty} \tilde{d}_{pu}(\omega; t_d = 0)e^{-i\omega t} d\omega\right], \quad (6)$$

where I_p is the ionization potential (IP). The induced polarization in the continuum is a measure of the established superposition of the ground state and continuum-state states of the atom and is transient in nature because the ionized electrons quickly leave the vicinity of the atom. The continuum polarization differs in that sense from the induced polarization below the IP, which can persist until dephasing or spontaneous emission extinguishes it. The procedure we describe here allows the extraction of both the magnitude and the phase of the field-induced polarization directly from measured absorption spectra.

III. COMPUTATIONAL APPROACH

To demonstrate the extraction of the field-induced polarization, we study the transient absorption spectrum of the atomic neon system using the MCTDHF method to solve the time-dependent Schrödinger equation with all ten electrons active. This method has been previously explored and developed by several groups [17–23] and by two of the present authors [12,13] at length. As more orbitals are included, the MCTDHF wave function formally converges to the exact many-electron solution. It rigorously treats the ionization continua for both single and multiple ionization using exterior complex scaling of the electronic coordinates. The results presented here were calculated using 9 time-dependent orbitals represented using grid methods in full dimensionality, which can be initially labeled as $1s$, $2s$, $2p$, $3s$, and $3p$. These calculations have a spin-adapted singlet configuration space of dimension 4116. We performed calculations similar to the ones reported here using 10-orbital (configuration space of dimension 12 656) and 12-orbital wave functions (137 196 configurations) which are considerably more computationally demanding. The MCTDHF results shown here were thereby verified to be converged with respect to the number of orbitals.

In all the calculations reported in this study, the weak XUV probe pulse is an isolated 1-fs pulse with a $\sin^2$ envelope centered at 23.13 eV (corresponding to a period of 0.179 fs) and with an intensity of 1.6×10^{10} W/cm^2. The intense

12-fs-long pump pulse is centered at 266 nm (corresponding to 4.65 eV and a period of 0.887 fs) which is the third harmonic of an 800-nm laser. The intensities of the pump pulses were varied in the calculations as reported below. Using Eq. (1), we first computed the probe-only absorption spectrum which is shown by the dashed lines in Fig. 1(a). The direct photoionization cross section can be computed from that absorption spectrum using $\sigma(\omega) = 4\pi\alpha\omega\tilde{S}(\omega)/|\tilde{\mathcal{E}}(\omega)|^2$ and agrees well with the measurement in Ref. [24]. The computed energy-dependent photoelectron angular anisotropy parameter agrees with the measurements in Refs. [25,26].

IV. NUMERICAL EXTRACTION OF CONTINUUM POLARIZATION FROM TRANSIENT ABSORPTION

We first study the transient absorption spectra using a pump pulse with an intermediate strength of $I_{pump} = 1 \times 10^{14}$ W/cm^2. At this pulse intensity the ionization probability is nearly zero and the system is mostly unexcited largely after the pulse ends. To solve for the unknowns in Eq. (5), three different time delays near zero are chosen, $t_d = -0.092$, 0, and 0.092 fs, where the two pulses have maximal temporal overlaps. The resulting transient spectra from MCTDHF calculations are shown in Fig. 1(a). The associated electric fields for these three pump pulses in relation to a fixed probe pulse are shown in the inset. These computed spectra, $\tilde{S}(\omega; t_d)$, are used as input for Eq. (5) to solve for $\mathrm{Re}[\tilde{d}_{pu}(\omega; t_d = 0)]$ and $\mathrm{Im}[\tilde{d}_{pu}(\omega; t_d = 0)]$.

In Fig. 1(b), we show the real components of both the extracted and the MCTDHF computed $\tilde{d}_{pu}(\omega)$, which agree well with each other. At this intensity, the cutoff energy of harmonics is at $\omega = 27.9$ eV and thus the fifth harmonic centered around 23.3 eV is significantly larger than the seventh harmonic centered around 32.6 eV, and the extraction of the continuum polarization in the region of both harmonics is seen to be effective. The duration of the polarization induced by the fifth harmonic shown in Fig. 1(c) is about half the 12-fs duration of the pump pulse, and this is consistent with the fact that it scales with the fifth power of the electric field, $\mathcal{E}(t)$, which has a $\sin^2$ envelope.

The pump-field-induced polarization in the continuum, $d_{extracted}(t)$, can then be computed using Eq. (6) and is compared in Fig. 1(c) with $d_{continuum}(t)$ computed with Eq. (6) directly from the MCTDHF wave function. The two curves are almost graphically indistinguishable, and measuring their relative proximity by the root-mean-square deviation divided by the maximum value of $d_{continuum}(t)$ gives 1% for the data shown in Fig. 1(c). We must note however, that in an experimental implementation of the procedure in this example, the bandwidth of the short XUV pulse and its characterization would be limitations, and it is likely that a pulse shorter than the 1-fs duration used in this computational demonstration would be necessary.

V. FEASIBILITY OF MEASUREMENT OF CONTINUUM POLARIZATION

It is important to note that the pump-field-induced polarization in the continuum, $d_{continuum}(t)$, is not a measure of the NRDSE [10]. As shown in the inset of Fig. 1(c), which
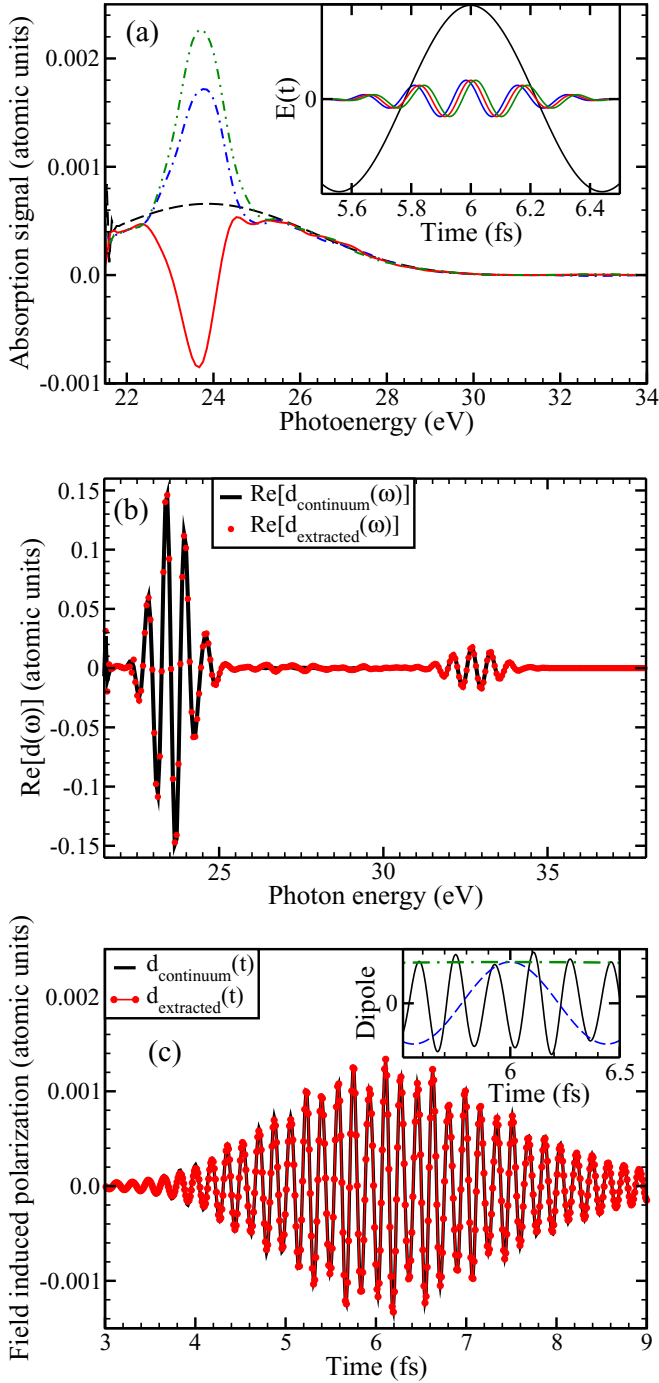
FIG. 1. (a) Energy-resolved absorption signals for the probe-only (dash) and pump-probe cases with time delays of −0.092 fs (dash-dot line), 0 fs (solid line), and +0.092 fs (dash-dot-dot line). Inset: Schematic of timing of the associated electric fields of the 12-fs 266-nm pump and the delayed 1-fs XUV probe. Comparison of the extracted (dots) and the computed (solid) induced polarization by the pump field ($I_{\mathrm{pump}} = 1 \times 10^{14}$ W/cm²) in the continuum in the (b) frequency and (c) temporal domains. Inset: A schematic comparison of the field-induced polarization (solid line) and instantaneous electric field of the pump field (dashed line) and its envelope (dash-dot line).

magnifies the time scale around the middle of the 266-nm pulse, the induced polarization in the continuum follows neither the instantaneous electric field nor its envelope. Instead,
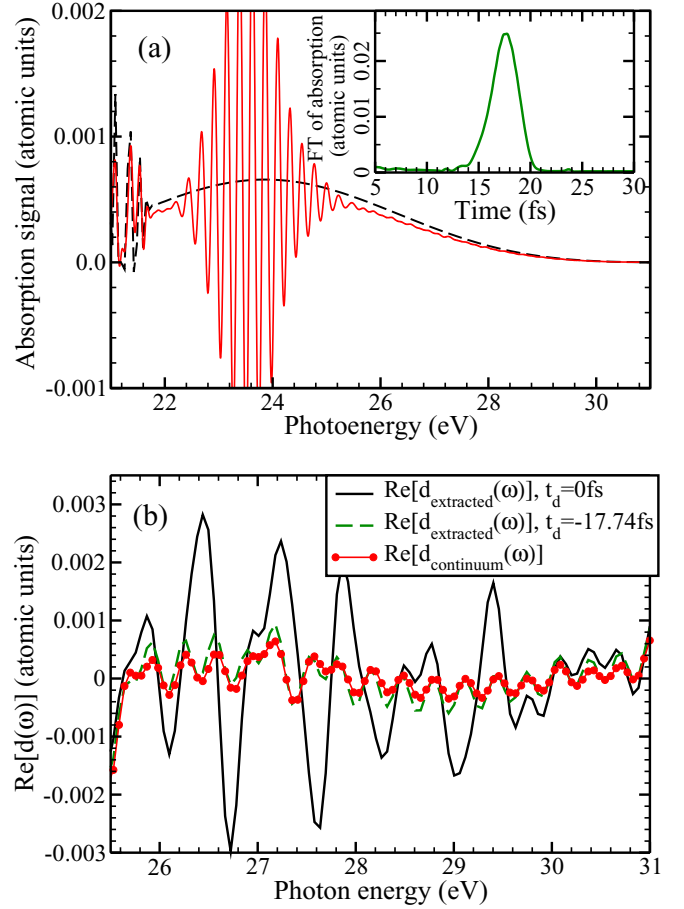

FIG. 2. (a) Energy-resolved absorption signals for the probe-only (dashed line) and pump-probe case with a time delay of −17.74 fs (solid line) with its Fourier-transform (FT) in the inset. (b) Comparison of the extracted polarization for two different time delays, $t_d = 0$ fs (black solid line) and $t_d = -17.74$ fs (green dashed line), with the MCTDHF computed polarization in continuum (red dots).

$d_{\mathrm{continuum}}(t)$ is a nonlinear response to its driving field (pump) and oscillates at a much higher frequency, i.e., $\omega \gg \omega_{\mathrm{pump}}$. Below, we apply this extraction procedure in the case of a much more intense pump field that can completely ionize the system, well beyond the intermediate strength regime where the NRDSE is relevant.

In the intermediate pulse strength regime, with $I_{\mathrm{pump}} = 1 \times 10^{14}$ W/cm², we can also investigate the applicability of this extraction procedure for two nonoverlapping pulse configurations: the pump-first and probe-first cases. At this intensity, the pump pulse does not lead to appreciable ionization or excitation after it is over. The same is true of course for the weaker probe pulse, and one therefore expects the additive approximation to hold for both pulse orders. In Fig. 2(a), we show the MCTDHF computed spectrum with a time delay of −17.74 fs compared with the probe-only spectrum. To verify these arguments, four pulse configurations, $t_d \approx -17.74, -8.87, +8.87$, and $+17.74$ fs (20 optical cycles), were tested. The values of $d_{\mathrm{continuum}}(t)$ extracted using Eq. (1) and computed from the MCTDHF wave function are almost identical to those shown in Fig. 1(b) for $t_d = 0$ fs and are

therefore not shown here. Note, in the probe-first case, the transient absorption spectrum is always measured after both of the pulses are over. Therefore, the success of extraction with this *counterintuitive* pulse sequence, probe-first, does not conflict with causality.

Another difference between the nonoverlapping (e.g., pump first probe later) and overlapping pulse configurations is that the additional pathway discussed above involving absorption of one probe (XUV) photon plus two pump (NIR/VIS) photons, which corresponds to the third contributing term to the total polarization in Eq. (4), would have minimum effect in the nonoverlapping case (particularly in the continuum). Hence, to investigate the potential limit of the additive approximation and thus the limit of this proposed extraction procedure, we compared the extracted polarization in the continuum for two cases at $t_d = 0$ fs and $t_d = -17.74$ fs with the MCTDHF computed one. The largest difference between these two extracted polarizations is in the range from 26.5 to 30.5 eV as shown in Fig. 2(b). It is clear that when $t_d = -17.74$ fs the extraction is more effective because the additive approximation still holds: the additional contribution [the third term in Eq. (4)] to the polarization is minimal when the pump field is applied well before the probe field.

Next we investigate the range of applicability of the extraction procedure as a function of the pump field intensity. As the pump field intensity increases, more complex dynamics are induced. The inset of Fig. 3 displays the time-dependent population of the ground state for three pump field intensities. As mentioned above, at $I_{pump} = 1 \times 10^{14}$ W/cm^2, the pump field is nonionizing and leaves the atom mostly unexcited. However, at $I_{pump} = 5 \times 10^{15}$ W/cm^2, the pump field completely depopulates the ground state, transferring 13.6% to excited states and 86.4% to ionization. We studied a wide range of pump field intensities, with I_{pump} between 5×10^{13} and 5×10^{15} W/cm^2, as well as pulse sequences with t_d between -17.74 and 17.74 fs. We found the relative proximity

FIG. 4. Comparison of the extracted (dots) and the computed (solid) induced polarization by the pump field ($I_{pump} = 1 \times 10^{14}$ W/cm^2) in the continuum with a 30% error in the measured spectra shown in the inset [cf. Fig. 1(a)].

of $d_{extracted}(t)$ and $d_{continuum}(t)$ (by the measure described above) to be 2.0% and 6.5% for $I_{pump} = 1 \times 10^{15}$ W/cm^2 and $I_{pump} = 5 \times 10^{15}$ W/cm^2, respectively. For the most intense pulses studied, with $I_{pump} = 5 \times 10^{15}$ W/cm^2, $d_{pr}(t)$ in Eq. (2) is effectively negligible, and Eq. (5) simply becomes $\tilde{S}(\omega; t_d) \approx 2\text{Im}[\tilde{d}_{pu}(\omega; t_d = 0)e^{i\omega t_d}\tilde{\mathcal{E}}_{pr}^*(\omega)]$. Heterodyne detection of $\tilde{d}_{pu}$ therefore succeeds even at this intensity in these calculations, even though our theoretical justification of the additive approximation upon which it is based is insufficient to completely explain why.

It is important to understand the degree to which error in measuring the intensity of the transient absorption spectrum might limit the practicality of the proposed extraction procedure. In the inset of Fig. 4, a spectrum with zero time delay and a 30% measurement error on average is compared with the computed spectrum. The result of using three such noisy spectra with different time delays in Eq. (5) to produce $d_{extracted}(t)$ is compared with $d_{continuum}(t)$ in Fig. 3. The relative proximity of $d_{extracted}(t)$ and $d_{continuum}(t)$ is calculated to be 17.5%. Additional studies showed that the error in the extraction of $d_{continuum}(t)$ is statistically a linear function of the error in the measured spectra $\tilde{S}(\omega)$.

In solving for the polarization $\tilde{d}_{pu}$ using Eq. (5), the absolute time delay t_d between the probe and pump pulses was assumed to be known accurately. By artificially shifting the value of t_d by values of Δt_d of up to 2 fs, we verified that, as Eq. (5) suggests, the extracted polarization is simply shifted by $-\Delta t_d$ in time t without changing its shape.

The form of Eq. (5) also suggests a way to determine t_d experimentally if the probe pulse is well characterized, at least in principle. The only dependence on t_d of $\tilde{S}(\omega; t_d)$ appears in the exponential factor, $\exp[i\omega t_d]$, indicating that, for a specific t_d, the transient absorption signal would show a fast oscillation as a function of the photon energies with a period of $2\pi\hbar/t_d$. In Fig. 2, we show the MCTDHF computed spectrum with a time delay of -17.74 fs compared with the probe-only spectrum. This fast oscillation is most clearly exhibited above the IP
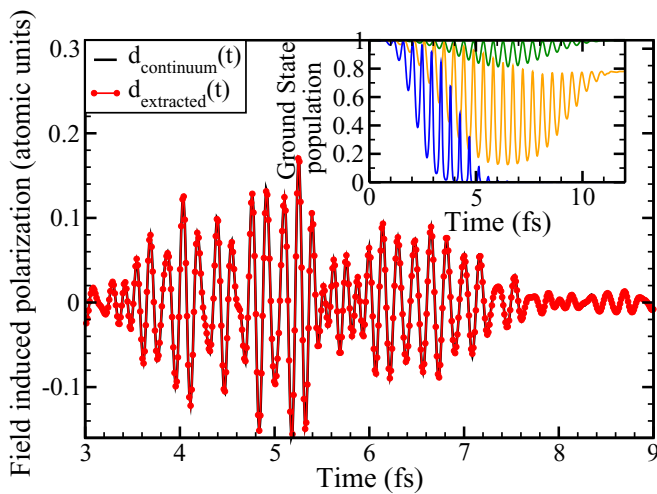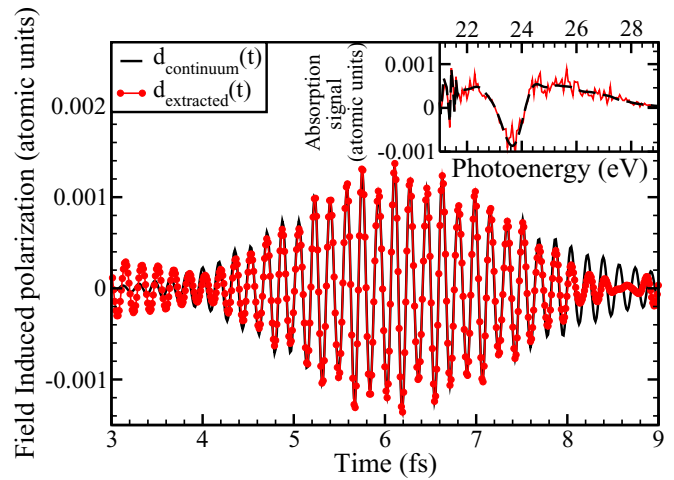

FIG. 3. Comparison of the extracted (dots) and the MCTDHF computed (solid) induced polarization by the pump field ($I_{pump} = 5 \times 10^{15}$ W/cm^2) in the continuum. Inset: The time-dependent population of the ground states for $I_{pump} = 1 \times 10^{14}$ W/cm^2 (green, top line), 1×10^{15} W/cm^2 (orange, middle line), and 5×10^{15} W/cm^2 (blue, bottom line).

where the absorption signals are continuous as a function of photon energy. The Fourier transform of the absorption signal over the photon energies is plotted in the inset of Fig. 2, which shows a clear maximum at 17.60f s. This Fourier transform of the absorption signal can be used to determine t_d with a deviation of 0.14 fs from its true value in this case, simulating a direct measurement of the absolute time delay with a subcycle and subfemtosecond resolution [27].

The fast oscillation with photon energy with a period of $2\pi\hbar/t_d$ as shown in Fig. 2 implies a practical limit of the longest time delay at which Eq. (5) is useful. When the energy resolution of the measured spectra is comparable with $2\pi\hbar/t_d$, it will be difficult to resolve these fast oscillations and thus the extraction of the field-induced polarization in the continuum will necessarily fail. For a 10-meV resolution this upper limit of t_d is estimated to be 100 fs.

At high intensities, the pump field (NIR/VIS) generates harmonics, and it is reasonable to ask whether those harmonics at frequencies within the bandwidth of the probe pulse might obscure the transient absorption signal. At a specific time delay, the input electric field strength is the sum of that of the two pulses, $\tilde{\mathcal{E}}_{in}(\omega) = \tilde{\mathcal{E}}_{pr}(\omega) + \tilde{\mathcal{E}}_{pu}(\omega; t_d)$. We estimate the electric field strength of the generated harmonics from the wave equation in the slowly evolving wave approximation, which in the frequency domain reads as [28,29]

$$\nabla_\perp^2 \tilde{\mathcal{E}}(\omega) - \frac{2i\omega}{c}\frac{\partial \tilde{\mathcal{E}}(\omega)}{\partial z} = -\frac{\omega^2}{\epsilon_0 c^2}[\tilde{P}(\omega)]. \tag{7}$$

In the limit of perfect phase matching, we can estimate an upper limit for the electric field strength of the harmonics propagating through a medium of length L:

$$\tilde{\mathcal{E}}_{HG}(\omega) = \frac{i\omega}{2\epsilon_0 c}\tilde{d}(\omega)nL. \tag{8}$$

To complete the estimate we take $n = 1 \times 10^{17}/cm^3$ as the atomic density and $L = 0.1$ mm as the medium length. The comparison of $\tilde{\mathcal{E}}_{in}(\omega)$ and $\tilde{\mathcal{E}}_{HG}(\omega)$ is shown in Fig. 5(a). In these calculations the Fourier transform, $\tilde{d}(\omega)$, is computed from $d(t)$ using a windowing function, $\cos(t\pi/2T_{max})$, with the window having a width of $T_{max} = 3000$ atomic time units, for a 266-nm pulse duration of 500 atomic units.

We also estimated the output electric field strength for the probe pulse by employing the Beer-Lambert law as done in Ref. [30]:

$$\tilde{\mathcal{E}}_{out}(\omega) = \tilde{\mathcal{E}}_{in}(\omega)\exp\left\{i\frac{2\pi\omega}{c}\frac{\tilde{d}(\omega)}{\tilde{\mathcal{E}}_{in}(\omega)}nL\right\}. \tag{9}$$

We compare $\tilde{\mathcal{E}}_{in}(\omega)$, $\tilde{\mathcal{E}}_{out}(\omega)$, and $\tilde{\mathcal{E}}_{HG}(\omega)$ in Fig. 5(b) for photon energies in the range of 21–30 eV, which is spectrally covered by the 1-fs probe pulse. This comparison strongly suggests that the contribution to the change of the XUV intensities due to harmonics is significantly smaller than the transient absorption signals and thus can be safely neglected here.

In general, for the extraction of polarization in the continuum from transient absorption it appears that several conditions should hold. First, the probe XUV pulse should not be so intense as to lead to an appreciable contribution from additional pathways to the induced polarization so that the additive approximation breaks down. Second, an estimate
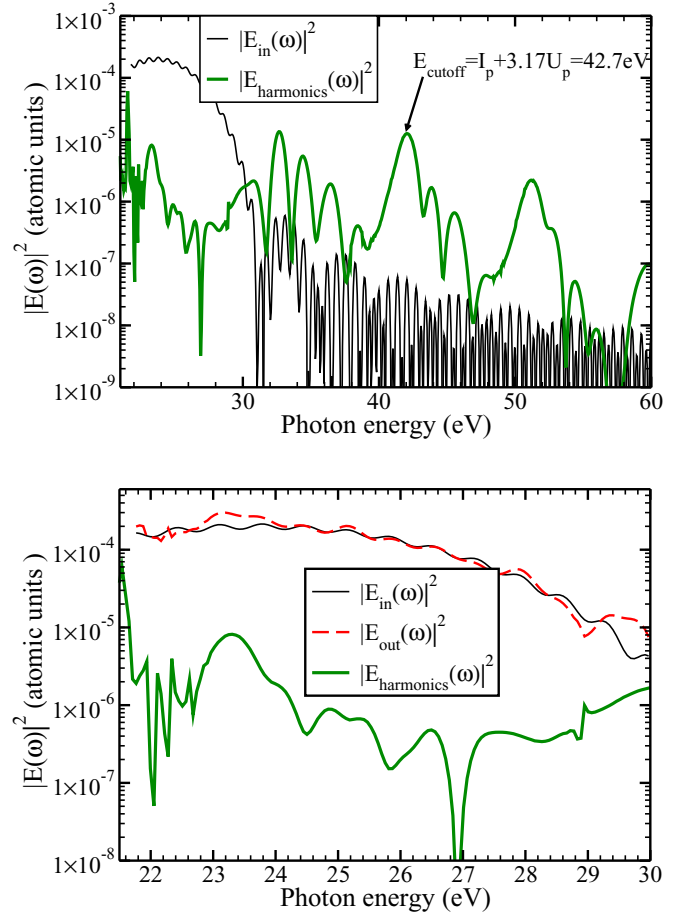

FIG. 5. At $I_{pu} = 1 \times 10^{15}$ W/cm^2: (a) Comparison of the input electric field magnitude (black thin-solid line), $|\tilde{\mathcal{E}}_{in}(\omega)|^2$, and the electric field magnitude for the generated harmonics (green thick-solid line), $|\tilde{\mathcal{E}}_{HG}(\omega)|^2$. (b) Comparison of the input electric field magnitude (black thin-solid line), $|\tilde{\mathcal{E}}_{in}(\omega)|^2$, output electric field magnitude (red dashed line), $|\tilde{\mathcal{E}}_{out}(\omega)|^2$ as computed via Eq. (9), and the electric field magnitude for harmonics (green thick-solid line), $|\tilde{\mathcal{E}}_{HG}(\omega)|^2$.

should be made to ensure that the pump field does not produce harmonics so intense that they overwhelm the transient absorption signals. In the example of atomic neon with the 266-nm pump laser, however, for the range of intensities for which we could perform numerically stable MCDTHF calculations we did not find this upper limit of the pump field intensities where the extraction procedure becomes impractical. Finally, although our tests in this example succeeded with a 1-fs probe pulse, in order to probe the polarizations for higher harmonics induced by a very intense pump field, the probe field should be temporally short enough to cover the entire spectral range of the higher harmonics.

In this study, where the time delay between the two pulses is varied, the carrier envelope phases (CEP) of the pulses are assumed locked. Additionally, we investigated a scheme where only the CEP of the pump pulse is varied and the time delay is fixed at zero. The MCTDHF computed spectra show five cycles of oscillation as the CEP$_{pump}$ changes by 2π, as one would expect in the variation with t_d over one optical period of the pump from the $\exp[i\omega t_d]$ factor when $\omega = 5\omega_{pump}$.

Thus, we notice a mirroring between the $\tilde{S}(\omega; t_d; \text{CEP} = 0)$ and $\tilde{S}(\omega; t_d = 0; \text{CEP} = -t_d \, \omega_{266nm})$ which demonstrates a clear one-to-one mapping between changes in the transient absorption spectrum from manipulating time delay or from manipulating the CEP of the pump pulse. Thus one could use experiments with several CEP choices instead of several time delays to accomplish the same extraction of continuum polarization demonstrated here.

VI. CONCLUSION

The calculations presented here test a proposed direct method for measuring the polarization in the continuum, both modulus and phase, induced on the attosecond time scale by an intense optical pump field by using transient absorption spectroscopy above the ionization potential of the system. The procedure was tested for all possible pulse sequences, pump first, probe first, and coincident. In addition, the main characteristics of the intense-field-induced polarization remain extractable in the presence of a 30% measurement error in the transient absorption spectrum. We also addressed the question of whether the transient absorption signal might be masked by the harmonics generated by the pump pulse by estimating their intensity in these calculations.

These results suggest that such a measurement may be possible in the cases where, for example, intense NIR pulses are used to generate high harmonics in other systems. While the all-electrons-active MCTDHF calculations we present are for processes involving only five to seven photons from the probe pulse, they nonetheless have allowed us to explore the proposed method for extracting the continuum polarization in detail. Computational tests of the basic idea presented here for the case of intense NIR pulses generating high harmonics will necessarily make use of more approximate methods.

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