Two-color pulsed laser excitation of dipolar molecules: Absolute laser carrier-phase effects

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The excitation of a two-level dipolar ($d \neq 0$) molecule with two Gaussian pulsed lasers is examined theoretically for the case where one laser's frequency is tuned close to the energy level separation (pump laser) while the second laser's frequency is extremely small (probe laser). The final excited state populations are shown to depend on the probe laser's absolute carrier phase while remaining independent of the pump laser's absolute carrier phase. They do not depend on the relative phase difference between the two laser fields as in many other pump-probe scenarios. The absolute carrier-phase effect is negligible for nondipolar ($d=0$) molecules. The probe laser absolute carrier-phase effect arises through the coherent excitation of multiple optical paths from the initial to the final state containing a common number of pump photons ($N_{\text{pump}}=1$) and a varying number of probe photons. Excited state populations, after the interaction of the pulses with the molecule is complete, are examined as a function of the probe laser's absolute carrier phase for varying field strengths, frequencies, and pulse durations in order to verify the source of the probe laser absolute carrier-phase effect and to determine the conditions needed to most readily detect it.

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I. INTRODUCTION

The use of the relative phase difference between two laser fields to modify (control) excitation processes in atoms or molecules has been well established both theoretically and experimentally, for example, see Refs. [1,2]. More recently, the possibility of accessing the absolute carrier phase of a single pulsed laser and then using it to modify excitation processes has been proposed [3–16]. For single-pulse (one-color) excitation, the time-dependent electric field, i.e., the laser field, can be represented by

$$\varepsilon(t)=\varepsilon_0 f_0(t)\cos(\omega_0 t+\delta), \tag{1}$$

where ε_0 is the peak field strength, $f_0(t)$ is the pulse envelope, ω_0 is the carrier frequency, and δ is the absolute carrier phase. The field depends very sensitively on the absolute carrier phase if only a few optical cycles are contained within the pulse envelope; a condition now experimentally achievable. Brabec and Krausz [17,18] have shown that the description of the laser field ''in terms of carrier and envelope is self-consistent, unambiguous, and hence legitimate, for pulse durations down to the carrier oscillation cycle.'' Since the original proposal [3], experimental efforts to stabilize an absolute carrier phase [4–6,19–21] and theoretical predictions for physical observables depending on absolute carrier phase [7–16,22] have been carried out in concert. As intuitively predicted, most have the requirement of ultrashort pulse duration such that only a few optical cycles are contained within the pulse envelope (e.g., ≈ 5 fs for $\lambda = 800$ nm). Additionally, in order for absolute phase effects to manifest themselves, many of the proposed schemes require lasers of high intensity ($>10^{14}$ W/cm^2). While these two requirements are true of most proposed mechanisms involving a single laser field (and all involving infrared fields), Brown and Meath [14] have discussed frequency and intensity scaling as it pertains to absolute phase effects in one-photon excitations and Gallagher and co-workers [15] have demonstrated absolute carrier phase effects in the multiphoton excitation of potassium-atom Rydberg states using much weaker radio-frequency fields.

In this paper, the pump-probe excitation of a model two-level dipolar ($\vec{d} \neq \vec{0}$) molecule involving a pump laser frequency tuned close to the energy level separation of the stationary states ($\omega_{\text{pump}} \approx E_{21}=E_2-E_1>0$) and a probe laser frequency that is small compared to the energy level separation ($\omega_{\text{probe}} \ll E_{21}$) is examined (see Fig. 1). A dipolar molecule refers to a system where there is a nonzero difference $\vec{d}$ between the permanent dipole moments $\vec{\mu}_{jj}$ of the initial and final states involved in the transition ($\vec{d}=\vec{\mu}_{22}-\vec{\mu}_{11}$). Recently, we have shown that this two-laser pump-probe scenario can be used to access the absolute carrier phase of the probe field [23]. These results are expanded upon in this paper. Brumer, Frishman, and Shapiro [24] have also predicted an absolute laser phase effect in a multiple-pulse excitation scheme. They have predicted chiral selection, within a minimal four-level model for excitation of L and D enantiomers, that depends on the absolute phase of one laser in a three-laser excitation scheme [24].

In order to determine the conditions where the dependence on the probe laser's absolute carrier phase is strongest

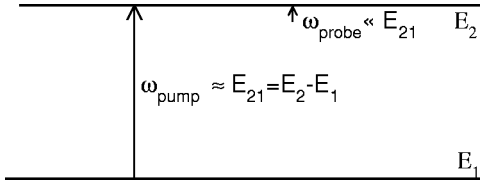

FIG. 1. Schematic of the two-level system interacting with pump ($\omega_{\text{pump}} \approx E_{21}$) and probe ($\omega_{\text{probe}} \ll E_{21}$) lasers.

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in our pump-probe excitation scheme, the final excited state population, i.e., the population of the upper level after both pump and probe lasers have interacted with the system, is carefully examined as a function of the most important pump and probe laser parameters, i.e., field strengths, durations, and frequencies. Through exact calculations, and aided by rotating wave approximation (RWA) analytic expressions for the laser-molecule couplings and corresponding time-dependent state populations, the source of the absolute carrier-phase effect is attributed to interference between multiple excitation paths from the initial to the final state. We demonstrate that a nonzero difference $\vec{d}=\vec{\mu}_{22}-\vec{\mu}_{11}$ between the permanent dipole moments $\vec{\mu}_{jj}$ of the two electronic molecular states involved in the transition is crucial for the appearance of absolute phase effects. The absolute carrier phase effect is negligible for nondipolar ($\vec{d}=\vec{0}$) systems. Most interestingly, the effect occurs for weaker fields than those required to see an absolute phase effect in single-pulse excitation and it survives into the multicycle regime where the probe pulse duration τ_{probe} is much greater than the optical period ($\tau_{\text{probe}} \gg T_{\text{probe}}=2\pi/\omega_{\text{probe}}$).

While most studies emphasize the use of few cycle pulses to obtain absolute carrier-phase effects, it is not the total number of optical cycles that is crucial, but rather it is the rise and fall times of the pulse that are most important. This has been convincingly demonstrated by Gallagher and coworkers [15]. However, for the commonly considered pulse envelopes, e.g., Gaussian, Lorentzian, and hyperbolic secant, the total number of optical cycles and the rise and fall times are intrinsically connected due to symmetry and thus a short rise/fall time implies a short total pulse duration. But, as we shall demonstrate in this paper, one can access the absolute carrier phase δ for long symmetric (Gaussian) pulses provided the excitation scheme is judiciously chosen.

Section II A provides a review of RWA analytic expressions for molecular state populations and molecule-laser couplings for the interaction of two pulsed or two continuous wave (cw) lasers with a two-level dipolar system. While the RWA results will help in qualitatively describing the effects of absolute carrier phase, the RWAs are no longer quantitatively reliable for most of the field strengths and pulse durations under consideration in Secs. III and IV. The exact computational technique used to determine the time-dependent state amplitudes and the molecular model chosen for the application are outlined in Secs. II B and II C, respectively. The use of permanent dipoles and absolute carrier phase to modify final excited state populations in a two-level system is described qualitatively using the RWA results in Sec. III. In Sec. IV, the results of exact calculations of the final excited state populations are presented as a function of many of the variables controlling the excitation process: field strengths, carrier frequencies, and pulse durations. Finally, in Sec. V, we draw some brief conclusions. Atomic units are utilized throughout this paper.

II. THEORY

Within the semiclassical dipole approximation, the time-dependent wave equation for an N-level system interacting with an electric field (laser or lasers) is given in matrix form by

$$i\frac{\partial \underline{a}(t)}{\partial t}=\underline{\underline{H}}(t)\underline{a}(t)=[\underline{\underline{E}}-\underline{\underline{\vec{\mu}}}\cdot\vec{\varepsilon}(t)]\underline{a}(t). \tag{2}$$

Here $a(t)$ is the column vector defined by $[a(t)]_j=a_j(t)$, the square energy and dipole moment matrices are defined by $(E)_{jk}=E_j\delta_{jk}$ and $(\vec{\mu})_{jk}=\langle\phi_j|\vec{\mu}|\phi_k\rangle$, where $\vec{\mu}$ is the dipole moment operator, ϕ_j are the orthonormalized time-independent wave functions for the stationary states having energy E_j, and $\vec{\varepsilon}(t)$ is the total time-dependent electric field. In the present study, we are concerned with a two-level ($N=2$) system interacting with two linearly polarized pulsed lasers (two-color excitation), where

$$\vec{\varepsilon}(t)=\hat{e}_1\varepsilon_1 f_1(t)\cos(\omega_1 t+\delta_1)+\hat{e}_2\varepsilon_2 f_2(t-t_d)\times\cos[\omega_2(t-t_d)+\delta_2]. \tag{3}$$

The variables $\hat{e}_i$, ε_i, $f_i(t)$, ω_i, and δ_i correspond to the polarization vector, peak field strength, pulse envelope, carrier circular frequency, and absolute carrier phase of laser i, respectively. The time delay between the pulses is given by t_d. In Sec. IV, we consider Gaussian pulse envelopes where

$$f_i(t)=\exp(-t^2/\tau_i^2), \tag{4}$$

τ_i is the pulse duration, and $i=$ pump or probe. The spectral and temporal full widths at half maximum for a Gaussian pulse are $\Delta\omega_i=4(\ln 2)^{1/2}/\tau_i$ and $\Delta t_i=2\tau_i(\ln 2)^{1/2}$. We are interested in the case where one laser frequency is tuned close to the energy level separation of the stationary states and the second laser frequency is small compared to the energy level separation (see Fig. 1). The two laser fields will be referred to as the pump ($\omega_{\text{pump}}\approx E_{21}$) and probe ($\omega_{\text{probe}}\ll E_{21}$) fields, respectively. The terms "pump" and "probe" refer to the relative magnitudes of the frequencies rather than to their time order since the time delay is set to zero ($t_d=0$) for all calculations considered in this paper. The effects of time delay will be examined in a forthcoming publication.

A. Analytical solutions

A rotating wave approximation, for a two-level system interacting with two pulsed lasers including the effects of permanent dipoles, has recently been derived [25]. Only the expressions relevant to the present study are given here. Assuming that the system is initially in ground state 1, the probability that the system is in excited state 2 at time t is given by

$$P_2(t)=|a_2(t)|^2=\sin^2\left[\frac{|\Omega(\delta_1,\delta_2,t)|}{2}\right]. \tag{5}$$

In this paper, the population of the excited state at the end of the pulse-molecule interaction, i.e., at $t=\infty$, is of most interest. $P_2(t=\infty)=|a_2(t=\infty)|^2$ will be referred to as the steady-state (or final) excited state population. In Eq. (5), $\Omega(\delta_1,\delta_2,t)$ is the variable

$$\Omega(\delta_1,\delta_2,t)=\int_{t_0}^{t}\zeta^p(\delta_1,\delta_2,t')dt', \tag{6}$$

where

$$\zeta^p(\delta_1,\delta_2,t)=\sum_{N_1,N_2}C^p(N_1,N_2,t)\exp[i(N_1\delta_1+N_2\delta_2)] \tag{7}$$

and t_0 is the time the pulse-molecule interaction begins. $\zeta^p(\delta_1,\delta_2,t)$ is the overall time-dependent phase-dependent pulsed laser-molecule coupling. $C^p(N_1,N_2,t)$ is the (time-dependent) pulsed laser-molecule coupling for an individual (N_1,N_2)-photon transition,

$$C^p(N_1,N_2,t)=2J_{N_1}(z_1f_1(t))J_{N_2}(z_2f_2(t))\times\left[N_1\omega_1\frac{\vec{\mu}_{12}\cdot\hat{e}_1}{\vec{d}\cdot\hat{e}_1}+N_2\omega_2\frac{\vec{\mu}_{12}\cdot\hat{e}_2}{\vec{d}\cdot\hat{e}_2}\right], \tag{8}$$

where $z_i=(\vec{d}\cdot\hat{e}_i)/\omega_i$ and $J_N(x)$ is a Bessel function of integer order N and argument x. The pulse-molecule coupling is explicitly time dependent since the field strengths are explicitly time dependent [25]. The sum in Eq. (7) is over all appreciable (N_1,N_2) combinations that satisfy the resonance condition $E_{21}=N_1\omega_1+N_2\omega_2$. For long laser pulses, where the frequency bandwidths of the lasers are narrow, the resonance terms are readily identified, and one can use the RWA for quantitative predictions of the time-dependent populations [25]. However, for short laser pulses, as are considered in this paper, where the frequency bandwidths of the lasers are large, single carrier frequencies may be insufficient to describe the resonance terms and the RWA will no longer be quantitatively reliable. However, the RWA will still prove useful for the qualitative interpretation of the results.

In order to determine the origin of the absolute carrier phase effect, it will also prove useful to examine the interaction of two cw lasers $[f_i(t)=1]$ with the two-level system. The interaction of two cw lasers with a two-level dipolar system has been discussed extensively elsewhere [26–29]. The relevant RWA results are presented below and they are very similar to the analogous expressions for pulsed lasers.

When only one (N_1,N_2)-photon resonance term dominates, i.e., its laser-molecule coupling is much greater than all other possible contributing couplings, the steady-state (long-time averaged) excited state population is given by [26]

$$\overline{P}_2^{N_1,N_2}=\lim_{\tau\to\infty}\frac{1}{\tau}\int_0^{\tau}P_2^{N_1,N_2}(t)dt=\frac{|C(N_1,N_2)|^2}{2[|C(N_1,N_2)|^2+(E_{21}-N_1\omega_1-N_2\omega_2)^2]}. \tag{9}$$

$\overline{P}_2^{N_1,N_2}$, as a function of ω_1 and ω_2, is the (N_1,N_2)-photon absorption spectrum or resonance profile for the two-level system in the dominant-resonance rotating wave approximation (DR-RWA). In Eq. (9), the individual cw laser molecule coupling is given by [26–28]

$$C(N_1,N_2)=2J_{N_1}(z_1)J_{N_2}(z_2)\times\left[N_1\omega_1\frac{\vec{\mu}_{12}\cdot\hat{e}_1}{\vec{d}\cdot\hat{e}_1}+N_2\omega_2\frac{\vec{\mu}_{12}\cdot\hat{e}_2}{\vec{d}\cdot\hat{e}_2}\right], \tag{10}$$

which is simply the pulsed laser-molecule coupling with $f_i(t)=1$. If more than one cw laser-molecule coupling contributes to the excitation process, the RWA expressions for the time-dependent and associated steady-state populations can only be determined in certain instances: exactly on resonance if the fields are independent of each other [26,29], or, as a function of frequency, provided the two fields are harmonically connected to a generating frequency [28,27].

For a single (N_1,N_2)-photon resonance, the associated full width at half maximum (FWHM) of the absorption profile, under the assumption that the coupling $C(N_1,N_2)$ does not vary appreciably over the width of the resonance, when one frequency is held fixed while the other is varied, is

$$\mathrm{FWHM}=\frac{2|C(N_1,N_2|)}{N_i}, \tag{11}$$

where N_i is the frequency being changed.

Although these analytic expression will be useful in helping to interpret numerical calculations, including the origin of the absolute carrier phase effect, RWAs are not reliable for intense and/or temporally short (frequency bandwidth broad) laser fields. Therefore, exact numerical calculations must be performed to obtain the state amplitudes and corresponding state populations.

B. Exact solutions

The exact state amplitudes $a_j(t)$ are obtained by using the Cranck-Nicholson method [30–32] to solve Eq. (2). For a small time step dt, over which the total electric field can be considered constant, the state amplitudes can be determined from

$$\underline{a}(t+dt)=\exp[-i\underline{\underline{H}}dt]\underline{a}(t)\approx\left[\frac{1-i\underline{\underline{H}}(dt/2)}{1+i\underline{\underline{H}}(dt/2)}\right]\underline{a}(t). \tag{12}$$

The state amplitudes for all times of interest can be obtained by applying Eq. (12) repeatedly given the appropriate initial conditions. Here the molecule is taken to be in the ground state initially, i.e., $a_1(t_0)=1$ and $a_2(t_0)=0$. Once the state amplitudes are known, the state populations can be determined via $P_j(t)=|a_j(t)|^2$. By using a time step of 0.001 fs, state populations converged to three or four decimal places are obtained.

In principle, the durations of the pulses are $-\infty<t<\infty$, but for numerical purposes the effective time domain is taken as $-\alpha\tau_g\leqslant t\leqslant\alpha\tau_g$, where τ_g is the greater of τ_{pump} and τ_{probe}. The constant α is chosen such that $f_i(t=\pm\alpha\tau_g)$ are

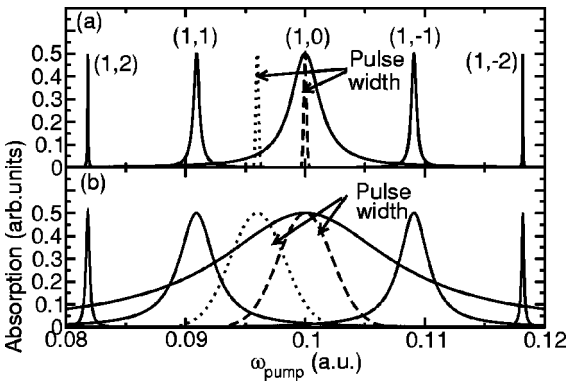

FIG. 2. The simulated DR-RWA absorption profiles (solid lines) as a function of ω_{pump} with $\omega_{\text{probe}}=E_{21}/11$ and $\varepsilon_{\text{probe}}=5\times10^{-4}$ a.u. illustrating the adjacent $(N_{\text{pump}},N_{\text{probe}})$-photon resonances. Superimposed are the frequency bandwidths of Gaussian pump pulses centered at $\omega_{\text{pump}}=E_{21}$ (dashed line) and $\omega_{\text{pump}}=0.0960$ a.u. (dotted line). (a) $\varepsilon_{\text{pump}}=5\times10^{-4}$ a.u. and $\tau_{\text{pump}}=152$ fs$\approx100(2\pi/\omega_{\text{pump}})$ and (b) $\varepsilon_{\text{pump}}=3.00\times10^{-3}$ a.u. and $\tau_{\text{pump}}=15.2$ fs$\approx10(2\pi/\omega_{\text{pump}})$.

very small and the perturbation of the molecule by the field for $|t|>\alpha\tau_{\text{g}}$ is negligible. For all calculations reported here, $\alpha=4$, although convergence has been checked on sample calculations by increasing α.

C. The model system

The two-level model used in the examples is representative of a substituted aromatic molecule [33]. The model has been used previously for studying the role of permanent dipole moments in two-color excitation processes [26–28,34,35] including investigations of the process illustrated in Fig. 1. However, except for the recent preliminary publication of these results [23], in these previous studies the emphasis has been on studying and enhancing transition rates rather than on the roles played by relative or absolute laser carrier phases. For the system of interest, the energy level separation is $E_{21}=0.10$ a.u. (21 947 cm^{-1}), the transition dipole moment is $\vec{\mu}_{12}=\vec{\mu}_{21}=\vec{\mu}=3.0$ a.u. (7.62 D), and the difference between the permanent dipole moments of states 1 and 2 is $\vec{d}=\vec{\mu}_{22}-\vec{\mu}_{11}=6.5$ a.u. (16.52 D). The transition and permanent dipole moments are taken to be aligned with each other and with the pump and probe fields $(\vec{\mu}\parallel\vec{d}\parallel\hat{e}_{\text{probe}}\parallel\hat{e}_{\text{pump}})$ and, therefore, only the magnitudes of the dipoles d and μ are indicated subsequently. In order to investigate the role of the permanent dipole moments, the pseudomolecule with $d=0$ is also considered.

III. ORIGIN OF THE ABSOLUTE PHASE EFFECT

In order to predict the origin of a probe laser absolute carrier-phase effect in the pump-probe pulsed excitation of a two-level system, the results from considering the interaction of two cw $[f_i(t)=1]$ lasers can be utilized. In Fig. 2, the simulated DR-RWA absorption profiles, as a function of the frequency of the pump laser with the frequency of the probe laser set at $\omega_{\text{probe}}=E_{21}/11$, are shown for $\varepsilon_{\text{probe}}=5.0\times10^{-4}$ a.u. and two choices of pump field strength: (a) $\varepsilon_{\text{pump}}=5\times10^{-4}$ a.u. and (b) $\varepsilon_{\text{pump}}=3.00\times10^{-3}$ a.u. The conversion factor from field strength to intensity is $3.5095\times10^{16}\varepsilon^2$ (in a.u.) $=I$ (in W/cm^2). As the pump laser frequency is scanned with the probe laser frequency held fixed, the system passes through resonances, where $E_{21}=N_{\text{pump}}\omega_{\text{pump}}+N_{\text{probe}}\omega_{\text{probe}}$, corresponding to the absorption of different numbers of pump and probe photons $(N_{\text{pump}},N_{\text{probe}})$. In Fig. 2, the system passes through five major resonance transitions corresponding to the (1,2)-, (1,1)-, (1,0)-, (1,−1)-, and (1,−2)-photon transitions as ω_{pump} is scanned between 0.08 a.u. (17 558 cm^{-1}) and 0.12 a.u. (26 337 cm^{-1}). For a nondipolar ($d=0$) two-level system, only transitions containing an odd total number of photons are allowed, i.e., the (1,1)- and (1,−1)-photon resonance peaks corresponding to the absorption of even numbers of photons would be absent. The illustrated absorption spectrum has been determined using the DR-RWA and thus it consists of a series of ''isolated'' Lorentzian peaks, i.e., the laser-molecule coupling for a particular (N_1,N_2)-photon resonance has been calculated using Eq. (10) and its individual absorption profile has been determined as a function of ω_{pump} using Eq. (9). For relatively weak pump-probe field strengths, the individual $(N_{\text{pump}},N_{\text{probe}})$-photon resonances are narrow and well separated [see Fig. 2(a)]. As the field strengths of the pump and/or probe lasers are increased, the widths of the individual $(N_{\text{pump}},N_{\text{probe}})$ absorption profiles generally increase (see Ref. [26] for a complete discussion of resonance width as a function of field strength). In Fig. 2(b), where the pump field strength has been increased, this has resulted in regions of frequency space where there is strong overlap between the individual resonances. While the DR-RWA assumption of isolated resonance is no longer valid, the picture will prove useful in elucidating the probe laser absolute phase effect.

These overlapping regions of frequency space may be sampled by tuning the frequency of the pump laser field and/or by using a short pump pulse with a correspondingly large frequency bandwidth. In Figs. 2(a) and 2(b), the corresponding frequency spreads for Gaussian pulsed lasers with $\tau_{\text{pump}}\approx100(2\pi/\omega_{\text{pump}})$ and $\tau_{\text{pump}}\approx10(2\pi/\omega_{\text{pump}})$ with $\omega_{\text{pump}}=E_{21}$ and $\omega_{\text{pump}}=0.0960$ a.u. are illustrated. Clearly, in Fig. 2(a), the couplings are not strong enough and the pump pulse used is not short enough to cause an interference between the adjacent $(N_{\text{pump}}=1,N_{\text{probe}})$-photon couplings, i.e., the different paths from the initial to the final state. However, in Fig. 2(b), where the increased pump field strength has overlapped adjacent resonances, the interfering regions can be sampled using a temporally short (frequency broad) laser pulse as illustrated, or, in fact, using a longer (frequency narrow) laser pulse whose frequency is tuned appropriately.

Hence, by applying lasers with appropriate field strengths and pulse durations, multiple optical paths from the initial state to the desired final state can be simultaneously excited—a condition required in well-known control scenarios. For example, when $d=6.5$ and $\omega_{\text{pump}}=E_{21}$, the (1,1)-, (1,0)-, and (1,−1)-photon resonances can readily be overlapped for moderately intense fields and for pump pulse

durations on the order of 10–50 fs. On the other hand, when $d=0$, the (1,1)- and (1,−1)-photon resonances are absent. Thus, significant interference will be much more difficult to achieve for nondipolar ($d=0$) molecules since the adjacent resonances are further away from each other. Also, the laser-molecule couplings for adjacent resonances will be different by orders of magnitude. For example, the (1,2)- and (1,−2)-photon resonances will be much weaker than the (1,0)-photon resonance, due to the need to absorb two photons of probe frequency; within time-dependent perturbation theory, the strength of the (1,0)-photon absorption scales as $\varepsilon_{\text{pump}}$ while those of the (1,2)- and (1,−2)-photon absorptions scale as $\varepsilon_{\text{pump}}\varepsilon_{\text{probe}}^2$.

When a single $(N_{\text{pump}},N_{\text{probe}})$-photon transition contributes to the excitation process, the overall coupling and hence the dynamics are phase independent. On the other hand, when there are multiple $(N_{\text{pump}},N_{\text{probe}})$-photon transitions contributing to the excitation process, the overall laser-molecule coupling, which determines the temporal evolution of the molecular states and hence the final state populations, depends on the phases of the pump and probe lasers and on the relative numbers of pump and probe photons absorbed in the competing processes, see Eq. (7). For example, in the commonly discussed one-photon versus three-photon process [see, for example, [1,27]], the interference term depends on the relative phase difference between the two fields, $\delta_1-3\delta_3$. However, in our pump-probe scenario, all processes which contribute to the excitation process involve the absorption of a single photon of the pump frequency, i.e., $N_{\text{pump}}=1$. Therefore, the overall laser-molecule coupling can be reduced to

$$|\zeta^p(\delta_{\text{probe}},t)|=\left|\sum_{N_{\text{probe}}} C^p(1,N_{\text{probe}},t)\exp[iN_{\text{probe}}\delta_{\text{probe}}]\right|, \tag{13}$$

or, expanding Eq. (13) for the (1,1)-, (1,0)-, and 1,−1)-photon transitions,

$$\begin{aligned}|\zeta^{\text{p}}(\delta_{\text{probe}},t)|=[&|C^{\text{p}}(1,0,t)|^2+|C^{\text{p}}(1,1,t)|^2+|C^{\text{p}}(1,-1,t)|^2\\&+C^{\text{p}}(1,0,t)C^{\text{p}}(1,1,t)\cos(\delta_{\text{probe}})\\&+C^{\text{p}}(1,0,t)C^{\text{p}}(1,-1,t)\cos(\delta_{\text{probe}})\\&+C^{\text{p}}(1,1,t)C^{\text{p}}(1,-1,t)\cos(2\delta_{\text{probe}})]^{1/2}.\end{aligned} \tag{14}$$

Provided more than one $(1,N_{\text{probe}})$-photon combination can be excited simultaneously, the overall laser-molecule coupling, and the dynamics that arise, depend on three incoherent terms and three coherent, interference terms which depend on the absolute phase of the probe laser and are independent of the pump laser's phase. As will be shown in Sec. IV, excitation of multiple $(1,N_{\text{probe}})$-photon combinations can be achieved through the application of fields with short enough pulse durations and/or high enough field strengths (intensities).

IV. RESULTS AND DISCUSSION: PULSED LASERS

From the discussion of the cw absorption profiles, the absolute probe laser phase control that can be achieved is expected to be dependent on several laser parameters: field strengths, pulse durations, and frequencies. While the effects of these pulse parameters are strongly interconnected, the major effects of each can be partially delineated by varying them individually. The field strengths of the two lasers determine the strengths of the $(N_{\text{pump}}=1,N_{\text{probe}})$-photon laser-molecule couplings that interfere. With the application of pulsed lasers, the pulse durations that determine the bandwidths of the laser fields must also be considered when examining which resonances will be successfully overlapped. Following from Fig. 2, for a long pulse, the pump frequency must be carefully chosen to be within the interfering region of frequency space due to the narrow frequency bandwidth of the laser. On the other hand, for a short pump pulse with a correspondingly greater frequency bandwidth, the choice of pump frequency may not be as critical. The choice of pump pulse frequency determines the extent to which the overlapping resonances are sampled. For example, if $\omega_{\text{pump}}=E_{21}$, one samples at the center of the (1,0)-photon resonance and in the wings of the (1,1)- and (1,−1)-resonances. However, if the pump laser frequency is tuned away from the (1,0)-photon resonance, the relative contributions of the (1,0)-, (1,1)-, and (1,−1)-photon transitions will be modified. For example, if the pump laser frequency is set to $\omega_{\text{pump}}=0.096$ a.u., one samples in the wings of both the (1,0)- and (1,1)-photon resonances, and in the far wing of the (1,−1)-photon resonance. Thus, the interference can be controlled via the pump laser frequency. For $\omega_{\text{pump}}=E_{21}$ and $\omega_{\text{probe}}\ll E_{21}$, as is considered here, the probe frequency dictates how close the adjacent $(N_{\text{pump}}=1,N_{\text{probe}})$-photon resonances are spaced and thus controls how these competing resonances interfere.

In the following sections, the effects of the choices of field strengths, frequencies, and corresponding pulse durations, on the expression of the probe laser absolute carrier-phase dependence of the final excited state populations are considered. In doing so, we confirm that the absolute carrier-phase effect results from the interference of multiple optical paths from the initial state to the desired final state.

In all calculations presented here, the pump laser's absolute carrier phase has been fixed at $\delta_{\text{pump}}=0$. For the pulse parameters considered in Secs. IV A and IV B, the final excited state populations do not change as a function of pump laser absolute carrier phase as verified by comparison with calculations with $\delta_{\text{pump}}=\pi/6$, $\pi/3$, $\pi/2$, and π (not explicitly presented). The fact that the results are independent of the pump laser's absolute carrier phase implies that they do not depend on the relative phase difference between the two laser fields.

A. Effects of field strength

As discussed in Sec. III, the overlap of the adjacent resonances depends strongly on the pump and probe field strengths (see Fig. 2). Initially, the final state populations are determined as a function of the pump field strength in order

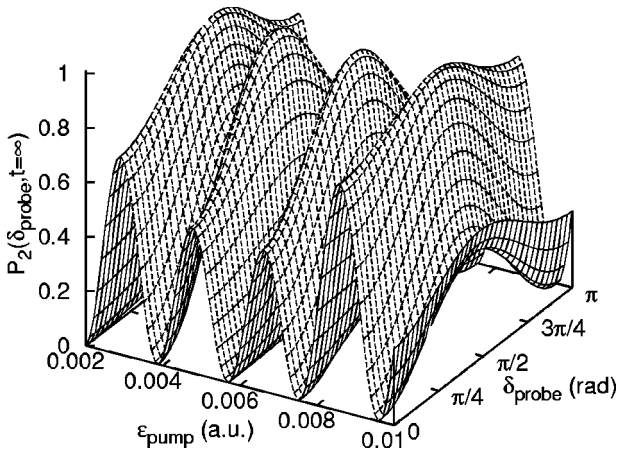

FIG. 3. The steady-state population of the excited state, $P_2(\delta_{\text{probe}}, t=\infty)$, as a function of the probe laser's absolute carrier phase and the pump laser's field strength for $d=6.5$. The other pulse characteristics are $\varepsilon_{\text{probe}}=5.0\times10^{-4}$ a.u., $\tau_{\text{pump}}=15.2$ fs $=10(2\pi/\omega_{\text{pump}})$, $\tau_{\text{probe}}=250$ fs$\approx15(2\pi/\omega_{\text{probe}})$, $\omega_{\text{pump}}=E_{21}$, and $\omega_{\text{probe}}=E_{21}/11$.

to determine the minimum pump field strength needed to express the probe laser absolute carrier-phase effect for a fixed probe field strength. These results are then utilized as a starting point for optimizing the probe field strength to produce the greatest effect of absolute probe laser phase for a fixed pump field strength.

Figures 3 and 4 illustrate the final excited state population as a function of the probe laser's absolute carrier phase and the field strength of the pump laser for the pump-probe laser interaction with dipolar ($d=6.5$) and nondipolar ($d=0$) two-level systems, respectively. The frequency of the pump laser is set to the energy level separation ($\omega_{\text{pump}}=E_{21}$) and its duration is $\tau_{\text{pump}}=15.2$ fs$=10(2\pi/\omega_{\text{pump}})$. Hence, the FWHM frequency bandwidth of the pump laser is very broad ($\Delta\omega_{\text{pump}}=0.0053$ a.u.$=1163$ cm^{-1}). Following previous calculations of the analogous two-color process involving cw lasers [26], the frequency of the probe laser is set to ω_{probe} $=E_{21}/11$. The probe laser has a peak field strength of 5×10^{-4} a.u. (8.77×10^{9} W/cm^2) while its duration is set to $\tau_{\text{probe}}=250$ fs$\approx15(2\pi/\omega_{\text{probe}})$. The frequency bandwidth of the probe laser ($\Delta\omega_{\text{probe}}=3.21\times10^{-4}$ a.u.$=71$ cm^{-1}) is much smaller than that of the pump laser, and, therefore, all further discussion of the effects of laser bandwidth focuses on the pump laser field. Since the pump laser is tuned to the (1,0)-photon resonance, the interference will occur when the pump field strength is sufficiently strong such that the (1,1)- and (1,−1)-photon resonances can be sampled. When $d=6.5$ and the pump field strength exceeds 2.0×10^{-3} a.u., the probe laser absolute carrier-phase dependence of the final excited state population begins to manifest itself (see Fig. 3). For example, when $\varepsilon_{\text{pump}}=\varepsilon_{\text{probe}}=5\times10^{-4}$ a.u., the final excited state population of 0.5227 is independent of the probe laser's phase. However, when the pump laser's field strength is increased to, say, $\varepsilon_{\text{pump}}=3.9\times10^{-3}$ a.u., the final excited state population varies from 0.0025 to 0.6664 to 0.0009 as the probe laser's absolute carrier phase is changed from 0 to $\pi/2$ to π. On the other hand, when $d=0$, the final excited state populations are independent of the probe laser's absolute carrier phase for the same range of pump field strengths (5.0×10^{-4} a.u.$\leqslant\varepsilon_{\text{pump}}\leqslant1.0\times10^{-2}$ a.u.) (see Fig. 4). The lack of probe laser phase dependence for $d=0$ is expected from the interpretation based on the cw resonance profiles. When $d=0$, the (1,1)- and (1,−1)-photon absorptions are not allowed. Since it is the interference of these two pathways with each other and the (1,0)-photon absorption, see Eq. (14), that is the source of the absolute probe laser phase effect for $d=6.5$, the variation of final excited state population with δ_{probe} is absent for $d=0$. For all the results discussed here and in subsequent sections, the absolute probe laser phase effect is negligible for all nondipolar systems, i.e., the steady-state populations vary by less than 0.001 as a function of probe laser phase. Therefore, only the $d\neq0$ results are discussed below.

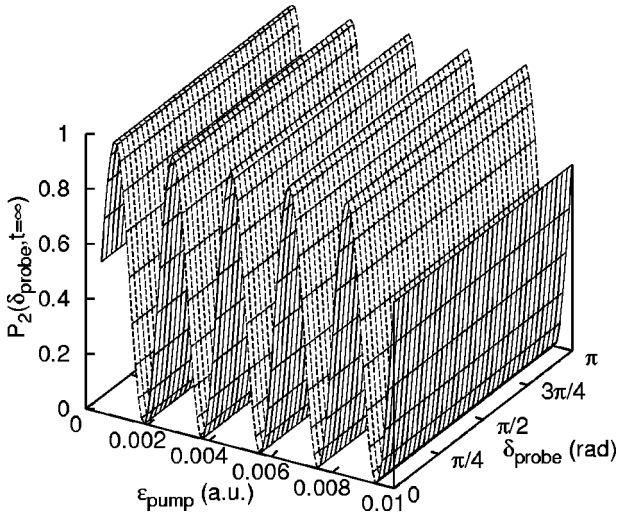

FIG. 4. Same as Fig. 3 but with $d=0$.

While the steady-state excited state populations for a fixed absolute probe phase changed markedly for large changes in pump field strength, they are fairly insensitive to small changes in the pump laser field strength. For example, for field strengths approximately 5% lower (higher) than $\varepsilon_{\text{pump}}$ $=3.9\times10^{-3}$ a.u., i.e., $\varepsilon_{\text{pump}}=3.7\times10^{-3}$ a.u. and 4.1×10^{-3} a.u., the steady-state populations vary as 0.0463 (0.0912) to 0.6591 (0.7662) to 0.0549 (0.0784) as the absolute probe laser phase changes from 0 to $\pi/2$ to π.

The probe laser field strength can also be changed to modify the overlap (interference) between adjacent resonances. In general, the probe laser's field strength and duration should be chosen such that negligible population transfer occurs between the ground and excited state without the presence of the pump laser. For the probe frequency considered here, this is readily achieved as excitation from the ground to excited state requires 11 probe frequency photons.

Figure 5 illustrates the final excited state population as a function of the probe laser's absolute carrier phase and the field strength of the probe laser. The pulse durations and laser frequencies are the same as those of Fig. 3. The pump field strength is set at $\varepsilon_{\text{pump}}=3.9\times10^{-3}$ a.u.; a field strength such that absolute carrier phase effects are strongly exhibited

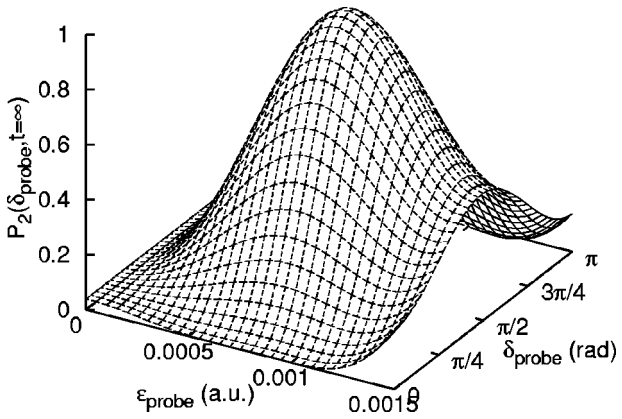

FIG. 5. The steady-state population of the excited state, $P_2(\delta_{\text{probe}},t=\infty)$, as a function of the probe laser's absolute carrier phase and the probe laser's field strength for $d=6.5$. The other pulse characteristics are the same as those in Fig. 3 except with the pump field strength fixed at $\varepsilon_{\text{pump}}=3.9\times10^{-3}$ a.u.

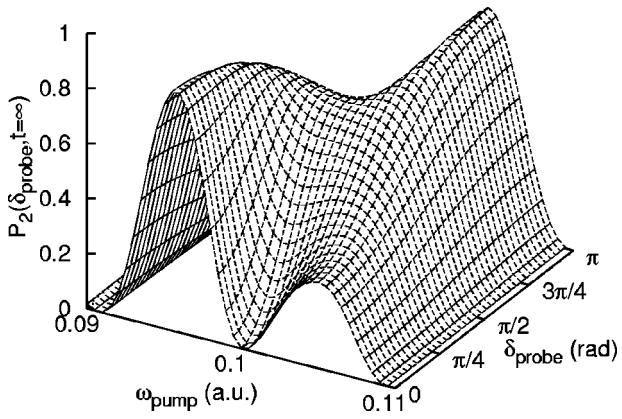

FIG. 6. The steady-state population of the excited state, $P_2(\delta_{\text{probe}},t=\infty)$, as a function of the probe laser's absolute carrier phase and the pump laser's frequency for d=6.5. The other pulse characteristics are $\varepsilon_{\text{probe}}=5.0\times10^{-4}$ a.u., $\varepsilon_{\text{pump}}=3.9\times10^{-3}$ a.u., $\tau_{\text{pump}}=15.2$ fs, $\tau_{\text{probe}}=250$ fs$=15(2\pi/\omega_{\text{probe}})$, and $\omega_{\text{probe}}=E_{21}/11$.

for $\varepsilon_{\text{probe}}=5.0\times10^{-4}$ a.u.. As the probe field strength is increased, the magnitude of the absolute phase effect begins to increase until a 100% effect is exhibited, i.e., $\Delta P_2=P_2^{\max}-P_2^{\min}\approx1$, and then decreases again. When $\varepsilon_{\text{probe}}=8.5\times10^{-4}$ a.u., the steady-state population changes from 0.0000 to 0.9998 to 0.0031 as the probe laser's absolute carrier phase changes from 0 to $\pi/2$ to π.

While a 100% effect is exhibited for these choices of pump and probe laser parameters, it is not guaranteed to occur when maximizing the absolute phase effect as a function of probe field strength with all other pump and probe laser parameters held fixed. If the pulse durations and laser frequencies are the same as those of Fig. 5 but the pump field strength is changed from $\varepsilon_{\text{pump}}=3.9\times10^{-3}$ a.u., the absolute phase effect can be optimized as a function of probe field strength relative to its value for $\varepsilon_{\text{probe}}=5.0\times10^{-4}$ a.u. but it may not reach 100%. For example, if the pump field strength is set at $\varepsilon_{\text{pump}}=3.0\times10^{-3}$ a.u., the maximum steady-state population difference as a function of probe laser absolute phase is $P_2(\delta_{\text{probe}}=\pi/2)-P_2(\delta_{\text{probe}}=0)=0.7449-0.2140=0.5309$ for a probe field strength of $\varepsilon_{\text{probe}}=9.5\times10^{-4}$ a.u. (not illustrated). The absolute phase effect is much larger than that for the original probe field strength of $\varepsilon_{\text{probe}}=5.0\times10^{-4}$ a.u. where $P_2(\delta_{\text{probe}}=\pi/2)-P_2(\delta_{\text{probe}}=0)=0.9999-0.6989=0.3010$, but it is not a 100% effect, i.e., $\Delta P_2\neq1$. So it is clear that for each choice of pulse durations and frequencies, the absolute phase effect must be considered as a function of both pump and probe field strengths in order to maximize its value and only for specific choices will a 100% effect be achieved.

B. Effects of frequency

The absolute probe laser phase effect has only been considered for excitations where the pump pulse is tuned exactly to the energy level separation ($\omega_{\text{pump}}=E_{21}$) and the probe pulse has a frequency of $\omega_{\text{probe}}=E_{21}/11$. As discussed in Sec. III, the interference of adjacent resonances should be able to be controlled via the tuning of either the pump or probe frequency. In order to assess the role frequency plays in the interference process, the pump and probe field strengths must be sufficiently strong so that the absolute phase effect occurs. Using Fig. 3 as a guide, the pump and probe field strengths are set at 3.9×10^{-3} a.u. and 5.0×10^{-4} a.u., respectively. The final excited state population as a function of the probe laser's absolute carrier phase and the frequency of the pump laser is illustrated in Fig. 6 for $\tau_{\text{pump}}=15.2$ fs $\approx10(2\pi/\omega_{\text{pump}})$ and in Fig. 7 for $\tau_{\text{pump}}=152$ fs $\approx100(2\pi/\omega_{\text{pump}})$. In both figures, the frequency of the probe laser is $\omega_{\text{probe}}=E_{21}/11$ and its pulse duration is $\tau_{\text{probe}}=250$ fs.

When $\tau_{\text{pump}}=15.2$ fs, the probe laser absolute carrier-phase effect is large over much of the range of illustrated frequencies. It is interesting to consider the three extreme (maximum or minimum) final excited state populations for $\delta_{\text{probe}}=0$, i.e., $P_2(\delta_{\text{probe}}=0,t=\infty)=0.8689$, 0.0023, and 0.3125 for $\omega_{\text{pump}}=0.0960$ a.u., 0.1000 a.u., and 0.1050 a.u., respectively. For $\omega_{\text{pump}}=E_{21}=0.1000$ a.u., the final excited state population is (essentially) symmetrical about $\delta_{\text{probe}}=\pi/2$; with $P_2(\delta_{\text{probe}}=0,t=\infty)$ changing from 0.0025 to 0.6664 to 0.0009 as the probe laser's absolute carrier phase

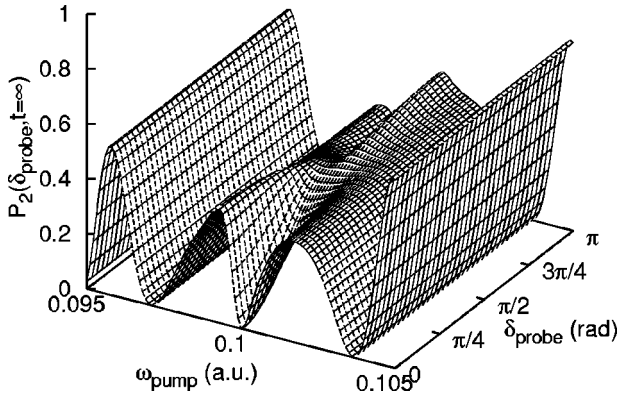

FIG. 7. Same as Fig. 6 but with $\tau_{\text{pump}}=152$ fs.

varies from 0 to $\pi/2$ to π. On the other hand, the steady-state excited state populations for $\omega_{\text{pump}}=0.0960$ a.u. and 0.1050 a.u. do not exhibit this symmetry about $\delta_{\text{probe}}=\pi/2$; rather they both exhibit symmetry about $\delta_{\text{probe}}=\pi$. When $\omega_{\text{pump}}=0.0960$ a.u. the final excited state population changes from 0.8689 to 0.6980 to 0.2886 as δ_{probe} varies from 0 to $\pi/2$ to π; the corresponding results for $\omega_{\text{pump}}=0.1050$ a.u. are 0.3065, 0.6274, and 0.8034.

The behavior of the final excited state population as a function of δ_{probe} can be rationalized using the RWA expression for the overall laser-molecule coupling [see Eq. (14)]. When $\omega_{\text{pump}}\approx E_{21}$, the interference is between the $C(1,0)$, $C(1,1)$, and $C(1,-1)$ resonances and, thus, the three interference terms will be $C(1,0)C(1,1)\cos(\delta_{\text{probe}})$, $C(1,0)C(1,-1)\cos(\delta_{\text{probe}})$, and $C(1,1)C(1,-1)\cos(2\delta_{\text{probe}})$. Note that the explicit time dependence of the individual couplings, $C(1,N_{\text{pump}},t)$, has been dropped for convenience. An important consideration is that the $C(1,0)C(1,1)\cos(\delta_{\text{probe}})$ and the $C(1,0)C(1,-1)\cos(\delta_{\text{probe}})$ interference terms contribute in opposite senses since $C(1,N_{\text{probe}})\propto J_1(z_{\text{pump}})J_{N_{\text{probe}}}(z_{\text{probe}})$ and $J_{-N}(z)=(-1)^N J_N(z)$. Thus, when $\omega_{\text{pump}}=E_{21}=0.1000$ a.u. and, correspondingly, $|C(1,1)|\approx|C(1,-1)|$, these terms (approximately) cancel leaving the $C(1,1)C(1,-1)\cos(2\delta_{\text{probe}})$ term as the only interference term. The resulting steady-state excited state population is symmetric about $\delta_{\text{probe}}=\pi/2$ rather than $\delta_{\text{probe}}=\pi$. On the other hand, when ω_{pump} is tuned away from the energy level separation, one reduces the magnitude of either the $C(1,1)$ or the $C(1,-1)$ laser-molecule coupling. Therefore, the only non-negligible interference term is either $C(1,0)C(1,1)\times\cos(\delta_{\text{probe}})$ or $C(1,0)C(1,-1)\cos(\delta_{\text{probe}})$ depending on if the probe frequency is tuned below ($\omega_{\text{pump}}=0.0960$ a.u.) or above ($\omega_{\text{pump}}=0.1050$ a.u.) the energy level separation. This manifests itself in the δ_{probe} dependence of the steady-state population which is now symmetric about $\delta_{\text{probe}}=\pi$.

When the duration of the pump laser is increased from 15.2 fs to 152 fs, the probe laser absolute carrier-phase effect persists, but the magnitude of the effect and the spread of pump frequencies over which it occurs are much reduced; compare Fig. 6 and Fig. 7. However, the δ_{probe} dependence of the final excited state population is very similar to that observed when $\tau_{\text{pump}}=15.2$ fs. For example, when $\omega_{\text{pump}}=E_{21}=0.1000$ a.u., the final excited state populations vary from 0.0017 to 0.3549 to 0.0013 as the probe laser's phase is changed from 0 to $\pi/2$ to π. If the pump frequency is tuned away from the energy level separation, in this case to $\omega_{\text{pump}}=0.0993$ a.u. and 0.1017 a.u. the steady-state excited state population varies as 0.4141, 0.3492, and 0.2236 and 0.2542, 0.3734, and 0.4561 as δ_{probe} changes from 0 to $\pi/2$ to π, respectively. Although for all pump laser frequencies the magnitude of the final state population variation is reduced, it exhibits the same δ_{probe} dependence as was seen when $\tau_{\text{pump}}=15.2$ fs.

It is interesting to consider the effects of changing pump laser frequency for other field strength combinations. We have calculated results analogous to those presented in Figs. 6 and 7 for the optimized probe field strength $\varepsilon_{\text{probe}}=8.5\times10^{-4}$ a.u. with all other pulse parameters held fixed (not illustrated). When $\tau_{\text{pump}}=15.2$ fs, the steady-state populations for the new probe laser field strength are globally very similar to those presented in Fig. 6, i.e., they exhibit the same δ_{probe} dependence as a function of frequency. When $\omega_{\text{pump}}=E_{21}$, the steady-state population changes from 0.0013 to 0.9996 to 0.0078 as δ_{probe} varies from 0 to $\pi/2$ to π. On the other hand, when the pump frequency is tuned away from the energy level separation to higher ($\omega_{\text{pump}}=0.1045$ a.u.) and lower ($\omega_{\text{pump}}=0.0960$ a.u.) frequency, the populations vary as 0.6452, 0.9320, 0.9834, and 0.9454, 0.9100, 0.5742, respectively, as δ_{probe} changes from 0 to $\pi/2$ to π.

Unlike for $\varepsilon_{\text{probe}}=5.0\times10^{-4}$ a.u., when the pump pulse duration is increased to $\tau_{\text{pump}}=152$ fs with $\varepsilon_{\text{probe}}=8.5\times10^{-4}$ a.u., the final steady-state populations are independent of the pump laser phase. Results as a function of pump pulse duration (between 15.2 fs and 152 fs) show that by increasing the pulse length the spread of frequencies over which absolute probe phase effect occurs narrows. For $\tau_{\text{pump}}\geqslant 50$ fs and with $\varepsilon_{\text{pump}}=3.9\times10^{-3}$ a.u. and $\varepsilon_{\text{probe}}=8.5\times10^{-4}$ a.u., the effects of probe laser phase are negligible. Clearly, one cannot achieve a significant absolute phase effect that persists to ''long'' pulse durations simply by increasing the magnitudes of the applied fields. The source of this effect may lie in the two-color Bloch-Siegert shift [26] which is not accounted for in our interpretation based on RWA arguments, or in the ''saturation'' of the transition. As the field strengths are increased, the positions of the $(N_{\text{pump}},N_{\text{probe}})$-photon absorptions shift to higher (or lower) frequencies; see Ref. [26] for a discussion of $(1,N_{\text{pump}})$-photon results. The shift in the resonance position causes an additional modification of the interference. It could be the Bloch-Siegert shift in the resonance position, which will change as the pulses interact with the system since the field strengths are explicitly time dependent, that removes the absolute phase effect when $\tau_{\text{pump}}=152$ fs for $\varepsilon_{\text{probe}}=8.5\times10^{-4}$ a.u. relative to the analogous results for $\varepsilon_{\text{probe}}=5.0\times10^{-4}$ a.u. However, there are no analytical expressions available for the two-color Bloch-Siegert shift comparable to those for the one-color Bloch-Siegert shift [36–39]; thus, it is not possible to introduce empirically the effect of a field-strength-dependent frequency shift into the RWA results used to interpret qualitatively the absolute phase effect. Alternatively, the absolute phase effect may disappear due to ''saturation'' of the transition (defined as follows). The increase in the probe field strength causes a correspondingly large increase in the magnitudes of the $C(1,1)$ and $C(1,-1)$ couplings and a relatively small decrease in the $C(1,0)$ coupling. For $\varepsilon_{\text{probe}}=8.5\times10^{-4}$ a.u. and $\varepsilon_{\text{pump}}=3.9\times10^{-3}$ a.u., the couplings are 3.697×10^{-3}, 3.090×10^{-3}, and 1.056×10^{-2} for $C(1,1)$, $C(1,-1)$, and $C(1,0)$, respectively, as compared to 2.242×10^{-3}, 1.874×10^{-3}, and 1.124×10^{-2}, when $\varepsilon_{\text{probe}}=5.0\times10^{-4}$ a.u. Note that since the couplings are time dependent, we can only quote values that correspond to the peak values, i.e., at $t=0$. The increase in the individual laser-molecule couplings causes an increase in the overall coupling [see Eq. (7)] and, thus, a decrease in the period of the time-dependent oscillations of the state

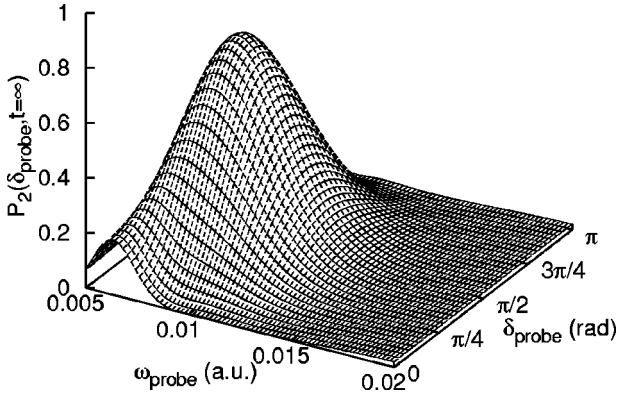

FIG. 8. The steady-state population of the excited state, $P_2(\delta_{\text{probe}},t=\infty)$, as a function of the probe laser's absolute carrier phase and the probe laser's frequency for $d=6.5$. The other pulse characteristics are $\varepsilon_{\text{probe}}=5.0\times10^{-4}$ a.u., $\varepsilon_{\text{pump}}=3.9\times10^{-3}$ a.u., $\tau_{\text{pump}}=10(2\pi/\omega_{\text{pump}})=15.2$ fs, $\tau_{\text{probe}}=250$ fs, and $\omega_{\text{pump}}=E_{21}$.

populations [see Eq. (5)]. Therefore, there is rapid oscillation of the populations caused by incoherent excitation, i.e., the $|C(1,0)|^2$, $|C(1,1)|^2$, and $|C(1,-1)|^2$ terms of Eq. (14), and a ''long'' pulse may not be able to sample the absolute phase-dependent oscillations which arise due to the coherent excitation. In this sense, the transition is ''saturated.''

While the pump frequency can be used the modify which resonances, $(1,-1)$, $(1,0)$, and/or $(1,1)$, contribute to the excitation process, the probe frequency changes the frequency separation between the adjacent $(N_{\text{pump}}=1,N_{\text{probe}})$-photon resonances. As with examining the effects of the pump frequency, the pump and probe field strengths must be sufficiently strong so that the absolute phase effect occurs. Using Fig. 3 as a guide, the pump and probe field strengths are set at 3.9×10^{-3} a.u. and 5.0×10^{-4} a.u., respectively. The frequency of the pump laser is $\omega_{\text{pump}}=E_{21}$ and its pulse duration is $\tau_{\text{pump}}=15.2$ fs. The duration of the probe laser is set to 250 fs. The final excited state population as a function of the pump laser's absolute carrier phase and the frequency of the probe laser is illustrated in Fig. 8. Unlike varying the pump laser frequency, which changes the δ_{probe} dependence of the final state populations, changing the probe frequency simply modifies the magnitude of the absolute phase effect. For example, for large probe frequencies, the phase effect is quite small or zero as the $(1,1)$-, $(1,0)$-, and $(1,-1)$-photon resonances are far apart relative to the bandwidth of the pump laser. As the probe frequency is reduced, the absolute phase effect becomes larger, i.e., as the resonance get closer together, it becomes easier to overlap them and thus generate interference. However, when the probe frequency becomes too small relative to the bandwidth of the pump laser field, the absolute phase effect loses its simple δ_{probe} dependence and begins to diminish in magnitude as other additional resonances, e.g., $(1,2)$ and $(1,-2)$, begin to contribute to the excitation process.

The arguments above for the effects of changing the probe frequency hold for situations where $\omega_{\text{pump}}=E_{21}$ and $\omega_{\text{probe}}\ll\omega_{\text{pump}}$. The roles of absolute and relative laser phases can be changed if one modifies the probe frequency and the relative magnitudes of the pump and probe field strengths, e.g., all examples considered in the paper involve $\varepsilon_{\text{probe}}\leqslant\varepsilon_{\text{pump}}$. In the examples considered above, the interference depends on the absolute phase of the probe laser since the interference arises between pathways containing a common number of pump photons, i.e., (1,1)-, (1,0)-, and $(1,-1)$-photon transitions. The same dependence on absolute probe laser phase would manifest itself in all situations where the number of pump photons in the interfering processes is fixed. On the other hand, the final state populations will depend on relative phase, or, more precisely, on the absolute phases of the pump and probe lasers, if two or more excitations containing different numbers of both pump and probe photons can interfere. In general, the situation where $\omega_{\text{pump}}=E_{21}$ and $\omega_{\text{probe}}=E_{21}/N_{\text{probe}}^{\text{res}}$ is of interest where $N_{\text{probe}}^{\text{res}}$ is the number of probe photons required to satisfy the resonance condition, e.g., $N_{\text{probe}}^{\text{res}}=11$ in most of the examples considered in this paper. The largest couplings containing different numbers of both pump and probe photons are $C(1,0)$ and $C(0,N_{\text{probe}}^{\text{res}})$. As $N_{\text{probe}}^{\text{res}}$ is decreased, and the number of photons required to satisfy the resonance condition decreases accordingly, the magnitude of $C(0,N_{\text{probe}}^{\text{res}})$ increases. If the pump and probe field strengths are chosen such that $C(0,N_{\text{probe}}^{\text{res}})$ becomes similar in magnitude to $C(1,0)$ then the final state populations will depend on the relative phase difference $\delta_{\text{pump}}-N_{\text{probe}}^{\text{res}}\delta_{\text{probe}}$, which is the common example of interference involving the fundamental frequency and a low-lying harmonic; see, for example, [1,27,28].

All of the pulsed calculations presented have been for a probe pulse duration of $\tau_{\text{probe}}=250$ fs. We have seen that the pump pulse duration is critical in determining the probe laser's absolute carrier-phase effects, and, therefore, one may wonder if the probe pulse duration also plays an important role. Calculations have shown that for the field strengths and frequencies considered above, the effects of changing the probe pulse duration are negligible provided $\tau_{\text{probe}}\geqslant\tau_{\text{pump}}$ and that $P_2(t)$ does not vary significantly from zero under the influence of the probe laser alone. For example, when $\varepsilon_{\text{probe}}=3.9\times10^{-3}$ a.u., $\varepsilon_{\text{pump}}=5.0\times10^{-4}$ a.u., $\tau_{\text{probe}}=15.2$ fs, and $\tau_{\text{pump}}=250$ fs, the steady-state excited state population for the probe laser phase of $\pi/2$ is 0.6664 (see Fig. 1). The final steady-state excited state population is within 1% of this value for probe pulse durations 65 fs $\leqslant\tau_{\text{probe}}\leqslant$250 fs and within 5% of this value for 30 fs $\leqslant\tau_{\text{probe}}\leqslant$65 fs (probe pulse durations longer than 250 fs have not been considered).

V. CONCLUSIONS

In this paper, a method for determining the absolute carrier phase of a multicycle pulsed laser (probe) using a second femtosecond laser (pump) has been demonstrated using a two-level model. The absolute carrier phase of the probe laser can then be utilized to control the final excited state population. In distinction to other two pulse (two-color) laser control methods, the final excited state populations do not depend on the relative phase difference between the two

fields since they are independent of the pump laser's absolute carrier phase.

Analytical rotating wave approximation expressions for the overall laser-molecule couplings, which determine the time-dependent and steady-state populations, have been used to qualitatively explain the dependence of the results on the absolute laser carrier phase of the probe laser. It is shown that the absolute carrier phase control arises due to the simultaneous excitation of multiple optical paths from the initial to the final state. Multiple paths can be excited by applying pulses of appropriately high enough intensity, such that power broadening overlaps the adjacent resonances, and/or short enough pulse duration, such that the pump laser's frequency bandwidth overlaps the adjacent resonances. Since all paths contributing to the excitation process, i.e., (1,1)-, (1,0)-, and $(1,-1)$-photon absorptions, involve the absorption of one photon of the pump frequency ($N_{\mathrm{pump}}=1$), the overall laser-molecule coupling, and corresponding state populations, do not depend on the phase of the pump laser but depend only on the absolute carrier phase of the probe laser.

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