

Two-color pulsed-laser phase control in dipolar molecules: Rotating-wave approximation versus exact results

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(Received 15 November 2001; published 30 May 2002)

A rotating-wave approximation (RWA) is developed to describe the interaction of a two-level system, which has permanent dipole moments, with two pulsed lasers. The RWA expressions for the time-dependent populations of the molecular states are applied to model laser-molecule interactions and tested by comparison with exact results. The results are used to discuss the pulsed-laser phase control of molecular excitation through the interplay of competing one- and two-photon resonances involving the effects of a nonzero difference d between the permanent dipoles of the two states involved in the transition; the competition vanishes if $d=0$.

DOI: 10.1103/PhysRevA.65.063401

PACS number(s): 32.80.Qk, 33.80.Rv

I. INTRODUCTION

The use of two lasers, or a laser with two frequency components, to excite an atom or molecule provides additional flexibility in extracting information about the system or in modifying the excitation process as compared to single laser excitation. For example, there is a great deal of interest in using two laser fields to control or to modify excitation processes in atoms or molecules by changing the relative phase difference (δ_d) between them [1–6]. Of particular interest here are earlier studies [5,6] of the effects of permanent dipole moments in the one- versus two-photon and one- versus three-photon phase control of molecular excitation. They have utilized both exact two-level model calculations and the harmonic many-resonance rotating-wave approximation developed specifically for studying the interaction of two harmonically linked continuous-wave (cw) lasers with a dipolar molecule. A dipolar molecule refers to a system where there is a nonzero difference d between the diagonal dipole matrix elements (permanent dipole moments) of the initial and final states involved in the transition ($d = \mu_{22} - \mu_{11} \neq 0$). As had been seen previously in one-color cw [7–14], two-color cw [9,15–20], and one-color pulsed [21,22] (and see, more recently published, Ref. [23]) laser-molecule interactions, these effects on the time-dependent and steady-state molecular-state populations can be substantial since, when $d \neq 0$, the selection rules and the molecule-laser(s) coupling can be greatly modified.

The purpose of this paper is to develop a rotating-wave approximation (RWA) for the interaction of two pulsed lasers with a dipolar molecule and then to use the results to discuss the two-color laser phase control of the excitation of the

molecule. While RWAs developed for cw laser-molecule interactions can be used to qualitatively interpret or predict the results for pulsed laser-molecule interactions, see for example [21,24,25], they cannot provide quantitatively reliable results. For example, they cannot provide the pulse characteristics, e.g., durations and intensities of the laser(s), needed to control population transfer between molecular states. This has recently been demonstrated for the interaction of a single pulsed laser with a dipolar molecule [23]. In the present paper, the RWA for the interaction of two pulsed lasers with a dipolar ($d \neq 0$) molecule will be developed and then utilized to illustrate the prediction of optimal pulse parameters for laser phase control involving the simultaneous one- and two-photon excitation of a model two-level dipolar molecule. These results can be compared and contrasted to the parameters obtained qualitatively from calculations involving cw lasers [6]. Through this study, further insight into the effects of permanent dipole moments on laser phase control can be obtained as well as a determination of the limitations of using two-color cw results to predict those for two pulsed lasers.

In Sec. II, the RWA for the two-color pulsed excitation of a dipolar ($d \neq 0$) molecule is developed. For the limit of “infinite” pulse duration, the previously derived two-color cw laser-molecule expressions [5,6,15,16] are obtained. When field two is “turned off,” the recently developed RWA [23] for the interaction of a one-color pulsed laser with a $d \neq 0$ system is obtained. In the limit that $d=0$, the pulsed laser-atom results of Rosen and Zener [26], where only one-photon transitions are allowed, are recovered.

A quantitative assessment of the validity of the RWA, by comparison with exact calculations, is presented in Sec. III. The example chosen involves simultaneous one- and two-photon excitation by Gaussian pulses of a model two-level dipolar molecule. The modification of the selection rules when $d \neq 0$ allows simultaneous two- (a process forbidden for a two-level system if $d=0$) and one-photon excitation to occur. By changing the relative phase difference between the two excitation fields, the time-dependent and, hence, final steady-state molecular-state populations can be controlled. In

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this paper, phase control refers to the process by which the excited state is fully populated for a relative phase difference of zero while it remains unpopulated for a relative phase difference of π . While, in principle, phase control can be achieved at any one specific time during the pulse-molecule interaction, in general, one is most interested in controlling the molecular state populations at the end of the pulse-molecule interaction. Therefore, the RWA expressions developed are used to determine the combination of field strengths and pulse durations needed to maximize the phase control of the steady-state molecular-state populations. However, both the temporal (time-dependent) and final (steady-state) molecular-state populations are considered in the examples in Sec. III. The results for the interaction of pulsed lasers are compared to the analogous cw results that have been discussed previously [6].

Finally, a brief summary of our results for phase control is presented in Sec. IV. We also comment briefly on the applicability of the two-color pulsed RWA to other problems, and, on the extension to many-level systems.

Unless indicated otherwise, atomic units are utilized throughout this paper.

II. THEORY

In matrix form and within the semiclassical dipole approximation, the time-dependent Schrödinger equation for a two-level molecule interacting with a laser field is given by

$$\begin{aligned} i \frac{d}{dt} \begin{pmatrix} a_1(t) \\ a_2(t) \end{pmatrix} &= \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} a_1(t) \\ a_2(t) \end{pmatrix} \\ &= \left[\begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} - \underline{\underline{\varepsilon}}(t) \cdot \begin{pmatrix} \underline{\underline{\mu}}_{11} & \underline{\underline{\mu}}_{12} \\ \underline{\underline{\mu}}_{21} & \underline{\underline{\mu}}_{22} \end{pmatrix} \right] \begin{pmatrix} a_1(t) \\ a_2(t) \end{pmatrix}. \end{aligned} \quad (2.1)$$

Here $\underline{\underline{\mu}}_{jk} = \langle \phi_j | \underline{\underline{\mu}} | \phi_k \rangle$, where $\underline{\underline{\mu}}$ is the dipole moment operator for the system, ϕ_j is the orthonormalized time-independent wave function for the j th stationary state having energy E_j , and $\underline{\underline{\varepsilon}}(t)$ is the total time-dependent electric field. For pulsed two-color excitation, the time-dependent electric field is

$$\underline{\underline{\varepsilon}}(t) = \hat{e}_1 \varepsilon_1 f_1(t) \cos(\omega_1 t + \delta_1) + \hat{e}_2 \varepsilon_2 f_2(t) \cos(\omega_2 t + \delta_2), \quad (2.2)$$

where \hat{e}_i , ε_i , $f_i(t)$, ω_i , and δ_i are, respectively, the polarization vector, field strength, pulse envelope, carrier circular frequency, and carrier phase of laser i . In general, the second laser field could be delayed in time relative to the first laser but here we consider only those situations where the time delay is zero. A special case of Eq. (2.2) that is often of interest involves fields where there is a common pulse envelope, $f(t) = f_1(t) = f_2(t)$, and polarization vector $\hat{e} = \hat{e}_1 = \hat{e}_2$. For this special case of Eq. (2.2), the two frequencies ω_1 and ω_2 are usually the fundamental frequency and one of its higher-order harmonics, often the second or the third, i.e., $\omega_2 = n\omega_1$, $n = 2, 3, \dots$

Following the development of previous rotating-wave approximations (RWAs) including the effects of $d \neq 0$ [6,7,15,23], we transform from the a representation into an interaction representation defined by

$$a_j(t) = b_j(t) \exp \left[-i \left\{ E_j(t-t_0) - \underline{\underline{\mu}}_{jj} \cdot \int_{t_0}^t \underline{\underline{\varepsilon}}(t') dt' \right\} \right], \quad (2.3)$$

where we assume $f_i(t) = 0$ for $t \leq t_0$, i.e., t_0 is the time that the pulse-system interaction begins. The coefficients $b_j(t)$ satisfy

$$i \frac{d}{dt} \begin{pmatrix} b_1(t) \\ b_2(t) \end{pmatrix} = \underline{\underline{H}} \begin{pmatrix} b_1(t) \\ b_2(t) \end{pmatrix}, \quad (2.4)$$

with the diagonal matrix elements of the Hamiltonian $\underline{\underline{H}}$ equal to zero, $H_{11} = H_{22} = 0$, and with the off-diagonal matrix elements given by

$$\begin{aligned} H_{12} = H_{21}^* &= -\underline{\underline{\mu}}_{12} \cdot \underline{\underline{\varepsilon}}(t) \exp \left[-i E_{21}(t-t_0) \right. \\ &\quad \left. + i d \cdot \int_{t_0}^t \underline{\underline{\varepsilon}}(t') dt' \right]. \end{aligned} \quad (2.5)$$

Two useful quantities have been introduced in Eq. (2.5): the energy separation of the stationary states, $E_{21} = E_2 - E_1 > 0$, and the difference between the permanent dipole moments of the excited and ground states, $d = \underline{\underline{\mu}}_{22} - \underline{\underline{\mu}}_{11}$.

The key in making the rotating-wave approximation is to be able to identify the off-resonant or counterrotating terms in the Hamiltonian. By analogy with the recently developed RWA for the interaction of a one-color pulsed laser with a dipolar ($d \neq 0$) molecule [23], the crucial quantity is

$$I = \exp \left[i d \cdot (\hat{e}_1 \varepsilon_1 Q_1 + \hat{e}_2 \varepsilon_2 Q_2) \right], \quad (2.6)$$

where

$$Q_i = \int_{t_0}^t f_i(t') \cos(\omega_i t' + \delta_i) dt'. \quad (2.7)$$

Integrating Eq. (2.7) by parts, each Q_i can be written as

$$Q_i = \frac{1}{\omega_i} f_i(t) \sin(\omega_i t + \delta_i) - \frac{1}{\omega_i} \int_{t_0}^t \frac{df_i(t')}{dt'} \sin(\omega_i t' + \delta_i) dt'. \quad (2.8)$$

In general, the time derivative of the pulse envelope (df/dt) is inversely proportional to the duration of the pulse τ . Therefore, for a pulse whose duration is much longer than the inverse frequency ($1/\omega$), the second term in Eq. (2.8) can be neglected relative to the first term. It is important that the durations of the pulses (τ_1 and τ_2) are long enough such that both conditions $(\omega_1 \tau_1)^{-1} \ll 1$ and $(\omega_2 \tau_2)^{-1} \ll 1$ are satisfied.

Assuming that the second term in Eq. (2.8) can be neglected safely for both field one and field two, Eq. (2.6) can be rewritten as

$$I = \exp[iz_1 f_1(t) \sin(\omega_1 t + \delta_1)] \exp[iz_2 f_2(t) \sin(\omega_2 t + \delta_2)], \quad (2.9)$$

where $z_i = \underline{d} \cdot \hat{e}_i \varepsilon_i / \omega_i$ is a parameter that has been used in previous work examining laser-dipolar molecule interactions [5–7,15,23]. The quantity I can be rewritten as

$$I = \sum_{k=-\infty}^{\infty} \sum_{\ell=-\infty}^{\infty} J_k(z_1 f_1(t)) J_{\ell}(z_2 f_2(t)) \times \exp[ik(\omega_1 t + \delta_1)] \exp[i\ell(\omega_2 t + \delta_2)] \quad (2.10)$$

by using the identity [27]

$$\exp(ix \sin \theta) = \sum_{k=-\infty}^{\infty} J_k(x) \exp(ik\theta), \quad (2.11)$$

where $J_k(x)$ is a Bessel function of integer order k and argument x .

Expanding the cosine functions, occurring in $\varepsilon(t)$, in complex exponential form and using the identity [27]

$$J_n(x) = \frac{x}{2n} [J_{n-1}(x) + J_{n+1}(x)], \quad (2.12)$$

the off-diagonal matrix elements ($H_{12} = H_{21}^*$) are given by

$$H_{12} = -\exp[iE_{21}t_0] \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} J_m(z_1 f_1(t)) J_n(z_2 f_2(t)) \times \left[m\omega_1 \frac{\underline{\mu}_{12} \cdot \hat{e}_1}{\underline{d} \cdot \hat{e}_1} + n\omega_2 \frac{\underline{\mu}_{12} \cdot \hat{e}_2}{\underline{d} \cdot \hat{e}_2} \right] \times \exp[-i(E_{21} - m\omega_1 - n\omega_2)t] \exp[i(m\delta_1 + n\delta_2)]. \quad (2.13)$$

As written, Eq. (2.13) is still exact [within the assumption that the second term of Eq. (2.8) can be neglected for field one and field two] and a closed form expression cannot be derived for the time-dependent state amplitudes $b_j(t)$. However, counterrotating (off-resonant) terms, which have $E_{21} - m\omega_1 - n\omega_2 \neq 0$, can be eliminated by utilizing the rotating-wave approximation. Unlike the one-color pulsed $d \neq 0$ RWA [23], where there is a single N -photon resonance term, two-color resonance terms, which have $E_{21} - m\omega_1 - n\omega_2 \approx 0$, are numerous for a given set of applied frequencies; this is analogous to the discussion for one- versus two-color cw excitation published earlier [15]. The resonance condition

$$E_{21} \approx N_1\omega_1 + N_2\omega_2 \quad (2.14)$$

can be satisfied by a number of (N_1, N_2) combinations, where either N_1 or N_2 can be positive or negative integers, or zero. By making the usual rotating-wave approximation and

neglecting the off-resonant terms in Eq. (2.13), the off-diagonal elements of the Hamiltonian are

$$H_{12} = -\frac{1}{2} \exp[iE_{21}t_0] \sum_{N_1, N_2} C^p(N_1, N_2, t) \times \exp[i(N_1\delta_1 + N_2\delta_2)] \times \exp[-i(E_{21} - N_1\omega_1 - N_2\omega_2)t], \quad (2.15)$$

where $C^p(N_1, N_2, t)$ is the (time-dependent) pulsed laser-molecule coupling for the (N_1, N_2) -photon transition,

$$C^p(N_1, N_2, t) = 2J_{N_1}(z_1 f_1(t)) J_{N_2}(z_2 f_2(t)) \left[N_1\omega_1 \frac{\underline{\mu}_{12} \cdot \hat{e}_1}{\underline{d} \cdot \hat{e}_1} + N_2\omega_2 \frac{\underline{\mu}_{12} \cdot \hat{e}_2}{\underline{d} \cdot \hat{e}_2} \right]. \quad (2.16)$$

The sum in Eq. (2.15) is over all sets of integers (N_1, N_2) such that Eq. (2.14) is obeyed. In general, the solution of Eq. (2.4) with the Hamiltonian given by Eq. (2.15) is not attainable analytically unless the two pulsed lasers are exactly on resonance, i.e., $E_{21} = N_1\omega_1 + N_2\omega_2$, for every significant (N_1, N_2) -photon combination (see below and Refs. [5,6,15,16]). As in the one-color pulsed RWA with $d \neq 0$ [23], it is convenient to define a new independent variable

$$\Omega(\delta_1, \delta_2, t) = \int_{t_0}^t \zeta^p(\delta_1, \delta_2, t') dt', \quad (2.17)$$

where

$$\zeta^p(\delta_1, \delta_2, t) = \sum_{N_1, N_2} C^p(N_1, N_2, t) \exp[i(N_1\delta_1 + N_2\delta_2)]. \quad (2.18)$$

$\zeta^p(\delta_1, \delta_2, t)$ is the overall time-dependent phase-dependent pulsed-laser-molecule coupling. While the sum in Eq. (2.18) is nominally over all (N_1, N_2) combinations that fulfill the resonance condition, usually the sum can be truncated at a small number of (N_1, N_2) combinations due to the decreasing magnitude of the Bessel functions, which occur in the $C^p(N_1, N_2, t)$, with increasing order [15,27]. However, care must be exercised in determining the truncation since the Bessel functions are oscillatory and their arguments are explicitly time dependent. Hence, a coupling may contribute significantly only during certain times of the pulse-molecule interaction. After transforming to the variable $\Omega(\delta_1, \delta_2, t)$, Eq. (2.4) is readily solved as a function of $\Omega(\delta_1, \delta_2, t)$. Assuming that the system is initially in ground state 1, the probabilities $P_j(t)$ of finding the system in states 1 and 2 at time t are given by [26]

$$P_1(t) = |a_1(t)|^2 = |b_1(t)|^2 = \cos^2 \left[\frac{|\Omega(\delta_1, \delta_2, t)|}{2} \right], \quad (2.19)$$

and

$$P_2(t) = |a_2(t)|^2 = |b_2(t)|^2 = \sin^2 \left[\frac{|\Omega(\delta_1, \delta_2, t)|}{2} \right], \quad (2.20)$$

where $|\Omega(\delta_1, \delta_2, t)|$ is defined through Eq. (2.17). In the treatment presented here, relaxation processes that result in a finite lifetime of the excited state are not included. If these are relevant, the results for the temporal evolution of states 1 and 2 would only be valid for times less than the lifetime of the excited state.

As discussed in detail for the two-color cw $d \neq 0$ RWA [15], the condition for the validity of neglecting the counter-rotating terms can be much more stringent in the two-color versus the one-color case. The criterion for the validity of the pulsed two-color RWA will be that $|\zeta^p(\delta_1, \delta_2, t)| \ll \omega_b$ for all time t . Here ω_b is the beat frequency defined as [15,28]

$$\omega_b \equiv \frac{\omega_1}{m_1} - \frac{\omega_2}{m_2}, \quad (2.21)$$

where m_1 and m_2 are the lowest possible integers giving the frequency ratio ω_1/ω_2 . In most instances, where the time delay is zero, both the pulse envelopes $f_i(t)$ achieve their maxima for $t=0$, and, therefore, the overall pulsed-laser-molecule coupling is also maximized at $t=0$. While care must be taken for the oscillatory nature of the Bessel functions, often the criterion for the validity of the pulsed two-color RWA can be applied as $|\zeta^p(\delta_1, \delta_2, t=0)| \ll \omega_b$. When $f_i(t=0) = 1$, this criterion is just the two-color cw condition discussed in Refs. [5,6,15], i.e., $|\zeta(\delta_1, \delta_2)| \ll \omega_b$ when many resonances contribute to the coupling and $|C(N_1, N_2)| \ll \omega_b$ when a single resonance contributes. In addition to the criterion for the overall pulsed-laser-molecule coupling, the pulse durations must be long enough so that the second term in Eq. (2.8) can be neglected safely for both fields, i.e., $(\omega_1 \tau_1)^{-1} \ll 1$ and $(\omega_2 \tau_2)^{-1} \ll 1$.

In general, the evaluation of $\Omega(\delta_1, \delta_2, t)$ will require a numerical integration of Eq. (2.17). However, as discussed for the one-color pulsed RWA with $d \neq 0$ [23], in some situations one can proceed analytically by using the expansion [29]

$$J_{\ell}(zf(t)) = f^{\ell}(t) \sum_{n=0}^{\infty} \frac{[z(1-f^2(t))/2]^n}{n!} J_{\ell+n}(z). \quad (2.22)$$

By utilizing Eq. (2.22) in the expression for $\Omega(\delta_1, \delta_2, t)$ given by Eq. (2.17), and then truncating the infinite series appropriately, various approximations for $\Omega(\delta_1, \delta_2, t)$ can be obtained. Keeping only the first term for each $J_{\ell}(zf_i(t))$ in the (N_1, N_2) sum, $\Omega(\delta_1, \delta_2, t)$ can be rewritten as

$$\Omega(\delta_1, \delta_2, t) = \zeta(\delta_1, \delta_2) \int_{t_0}^t f_1^{N_1}(t') f_2^{N_2}(t') dt', \quad (2.23)$$

where the next correction terms are of order z_i , $(z_i)^2$ ($i=1$ or 2), and $(z_1 z_2)$. In Eq. (2.23), the expression for the cw overall phase-dependent laser-molecule coupling [5,6,16], i.e., the coupling in the limit $f_1(t) = f_2(t) = 1$, has been introduced:

$$\zeta(\delta_1, \delta_2) = \sum_{N_1, N_2} C(N_1, N_2) \exp[i(N_1 \delta_1 + N_2 \delta_2)]. \quad (2.24)$$

The overall cw-laser-molecule coupling includes all (appreciable) individual couplings for the (N_1, N_2) -photon transitions satisfying Eq. (2.14). The individual cw-laser-molecule couplings are given by [5,6,15]

$$C(N_1, N_2) = 2J_{N_1}(z_1) J_{N_2}(z_2) \left[N_1 \omega_1 \frac{\underline{\mu}_{12} \cdot \hat{e}_1}{d \cdot \hat{e}_1} + N_2 \omega_2 \frac{\underline{\mu}_{12} \cdot \hat{e}_2}{d \cdot \hat{e}_2} \right]. \quad (2.25)$$

For many choices of pulse envelopes $f_1(t)$ and $f_2(t)$, the relevant integrals can then be evaluated as a function of t . Starting from Eq. (2.23), literature expressions for the populations of the molecular states can be obtained as special cases. Choosing the cw pulse envelopes, i.e., $f_1(t) = f_2(t) = 0$ for $t \leq 0$ and $f_1(t) = f_2(t) = 1$ for $t > 0$, one obtains $|\Omega(\delta_1, \delta_2, t)| = |\zeta(\delta_1, \delta_2)|t$. If the overall phase-dependent coupling is comprised of a single dominant (N_1, N_2) -photon coupling, $|\Omega(\delta_1, \delta_2, t)| = |C(N_1, N_2)|t$. Substituting this result into Eqs. (2.19) and (2.20), the previously derived dominant-resonance RWA expressions for the molecular-state populations are obtained [15] that are applicable when the laser fields are exactly on resonance, i.e., $E_{21} = N_1 \omega_1 + N_2 \omega_2$. On the other hand, if more than one individual laser-molecule coupling contributes significantly to the overall coupling, one obtains previously derived expressions for the state populations either within the many-resonance RWA for two independent laser fields [15,16], or within the harmonic many-resonance RWA for two harmonically linked fields [5,6].

The previously derived results for pulsed one-color excitation both with $d \neq 0$ [23] and $d = 0$ [26] can also be obtained as limiting cases of the pulsed two-color RWA. In order to obtain the $d \neq 0$ one-color expressions, one must begin at Eq. (2.17) rather than after the approximation Eq. (2.23) has been invoked. If we assume field two is “turned off,” i.e., $\varepsilon_2 = 0$, then the number of photons of frequency two absorbed must be zero ($N_2 = 0$) and the parameter $z_2 = (d \cdot \hat{e}_2 \varepsilon_2 / \omega_2) = 0$. Substituting these results into Eq. (2.16) and then subsequently into Eqs. (2.19) and (2.20) via Eqs. (2.17) and (2.18) yields the $d \neq 0$ pulsed-laser-molecule results derived previously, see Eqs. (16)–(18) of Ref. [23]. Starting from Eq. (2.23) and setting $d = 0$, corresponding to $z_1 = z_2 = 0$, reproduces the original RWA for the state populations for a single pulsed laser-atom interaction [26], which supports only a one-photon transition.

III. NUMERICAL EXAMPLES

In this section, we give numerical examples using the RWA expressions for the molecular-state populations derived in Sec. II. These will be compared with exact results for the populations in order to obtain insights into the reliability and applicability of the pulsed two-color $d \neq 0$ RWA. The explicit

examples considered in this section involve harmonic two-color simultaneous two- and one-photon transitions between two energy levels. The two-level model used in the examples has parameters that are representative of a substituted aromatic molecule [30] and has been utilized in previous theoretical calculations [5,6,15,17,18]. More importantly, the two-level model chosen has been used to discuss the role of permanent dipole moments in the phase control of simultaneous one- versus two-photon excitation involving cw lasers [6], and, hence, the results for pulsed lasers can be directly compared with these previous cw calculations. The relevant system properties are $E_{21}=0.10$ a.u. ($21\,947\text{ cm}^{-1}$), $\underline{\mu}_{12}=\underline{\mu}_{21}=\underline{\mu}=3.0$ a.u. ($7.62D$), and $\underline{d}=\underline{\mu}_{22}-\underline{\mu}_{11}=6.5$ a.u. ($16.52D$). The transition and permanent dipole moments are taken to be aligned ($\underline{\mu}\parallel\underline{d}$).

The two fields are harmonically related, i.e., the second field is generated from the first field, so we are considering a special case of the electric field given in Eq. (2.2) with $\omega_2=2\omega_1$, $f(t)\equiv f_1(t)=f_2(t)$, and $\hat{e}\equiv\hat{e}_1=\hat{e}_2$. Here the fundamental laser frequency is denoted by the subscript 1 and corresponds to the two-photon transition while its second harmonic is denoted by the subscript 2 and corresponds to the one-photon transition. Due to the harmonic nature of the frequencies, the fundamental frequency is also equivalent to the beat frequency ($\omega_1=\omega_b$). The pulsed laser is assumed to have a Gaussian envelope,

$$f(t)=\exp[-t^2/\tau^2], \quad (3.1)$$

where τ is the characteristic pulse duration ($\tau\equiv\tau_1=\tau_2$). The analogous cw [$f(t)=1$] problem for competing two- and one-photon excitations has been discussed previously [6].

For the case of explicit interest, i.e., simultaneous two- and one-photon excitation, the dominant individual pulsed-laser-molecule couplings are $C^p(2,0,t)$ and $C^p(0,1,t)$. From Eq. (2.18), the magnitude of the overall pulsed-laser-molecule coupling can be reduced to

$$|\zeta^p(\delta_1,\delta_2,t)|= [|C^p(2,0,t)|^2+|C^p(0,1,t)|^2+2|C^p(2,0,t)||C^p(0,1,t)|\cos(\delta_2-2\delta_1)]^{1/2}. \quad (3.2)$$

Clearly, the overall laser-molecule coupling, and, therefore, the dynamics, are functions of the phase difference ($\delta_d=\delta_2-2\delta_1$) between the two fields. For the calculations presented here, the phase difference is generated by varying the phase of the one-photon field, δ_2 , with the phase of the two-photon field set to zero, $\delta_1=0$. Within the RWA, the dynamics only depend upon the phase difference between the two fields, and not upon the absolute carrier phases used to generate this difference. However, it is well known [31–35] for one-color cw fields, and has been shown recently for one-color pulses [36], that for strong enough laser fields the exact dynamics and, more importantly, the steady-state molecular-state populations, can be functions of the absolute carrier phase of the laser field. For two-color cw fields, the state populations have been shown [37] to be functions of the absolute carrier phases of the two fields in addition to depending on the

relative phase difference. The dependence on absolute carrier phase applies for two-color pulses but discussion of this phenomenon will be reserved for a future publication. For the field strengths considered here, the exact results are (essentially) independent of the absolute carrier phases from which the relative phase difference is determined.

In previous studies of phase control for dipolar molecules interacting with cw lasers [5,6], the key to maximizing control was to choose the field strengths such that the cw laser-molecule couplings, see Eq. (2.25), for the two most important (N_1,N_2)-photon transitions were approximately equal, e.g., for simultaneous two- and one-photon excitation, the fields were chosen such that $C(2,0)\approx C(0,1)$. However, for pulsed laser-molecule interactions, the laser-molecule couplings are explicitly time dependent, see Eq. (2.16), and hence a different control condition must be utilized. From Eqs. (2.19) and (2.20), the molecular-state populations depend upon the value of $|\Omega(\delta_1,\delta_2,t)|$ defined by Eq. (2.17). For phase control involving simultaneous two- and one-photon excitation, $\Omega(\delta_1,\delta_2,t)$ is given explicitly by

$$\begin{aligned} \Omega(\delta_1,\delta_2,t) &= e^{i2\delta_1}\int_{t_0}^t C^p(2,0,t')dt' + e^{i\delta_2}\int_{t_0}^t C^p(0,1,t')dt' \\ &= e^{i2\delta_1}\bar{C}^p(2,0,t) + e^{i\delta_2}\bar{C}^p(0,1,t), \end{aligned} \quad (3.3)$$

and, therefore,

$$\begin{aligned} |\Omega(\delta_1,\delta_2,t)| &= [\bar{C}^p(2,0,t)^2 + \bar{C}^p(0,1,t)^2 \\ &\quad + 2\bar{C}^p(2,0,t)\bar{C}^p(0,1,t)\cos(\delta_2-2\delta_1)]^{1/2}. \end{aligned} \quad (3.4)$$

In order to maximize control at time t during the pulse, one would like the population of the excited state $P_2(\delta_d,t)$ to vary between 100% and 0% as the relative phase difference $\delta_d=\delta_2-2\delta_1$ changes from 0 to π . Substituting Eq. (3.4) for the relative phases 0 and π into the expression for the excited-state population, Eq. (2.20), and then determining the conditions for which $P_2(\delta_d=0,t)=1$ and $P_2(\delta_d=\pi,t)=0$, we obtain the following general conditions to maximize control at time t during the pulse,

$$\begin{aligned} \bar{C}^p(2,0,t) &= (n+m+\frac{1}{2})\pi, \\ \bar{C}^p(0,1,t) &= (n-m+\frac{1}{2})\pi, \end{aligned} \quad (3.5)$$

where n,m ($n\geq m$) are the integer number of full Rabi cycles that the excited state has completed for the relative phase differences 0 and π , respectively. If $\bar{C}^p(2,0,t)$ and $\bar{C}^p(0,1,t)$ are interchanged in Eq. (3.5), the conditions for control are also achieved. In general, one is interested in controlling the molecular-state populations after the interaction of the pulse with the molecule is complete, i.e., for $t\rightarrow\infty$, which for the calculations performed here corresponds numerically to $t=4\tau$.

Assuming one is interested in controlling the excited-state population within the first Rabi cycle for both the relative

phase differences $\delta_d = \delta_2 - 2\delta_1 = 0$ and π , one has $n = m = 0$ in Eq. (3.5) and the conditions for maximal control can be expressed as

$$\bar{C}^p(2,0,t=\infty) = \bar{C}^p(0,1,t=\infty) = \frac{\pi}{2}. \quad (3.6)$$

Using these two control conditions, the field strengths ε_1 and ε_2 along with the pulse duration $\tau (= \tau_1 = \tau_2)$ needed to maximize phase control can be determined. Often, at least one of ε_1 , ε_2 , or τ will be fixed. For example, experimentally the one-photon field strength ε_2 may be set by the efficiency of the second-harmonic generation process [38]. Once one of the variables is set, the other two variables can be iterated until Eq. (3.6), as determined using the expressions derived in Sec. II, is satisfied.

Due to the phase dependence of the laser-molecule coupling, see Eq. (3.4), the period of the Rabi cycle is different for each relative phase difference. Therefore, although one can refer to a common “first Rabi cycle,” once the system has passed through one Rabi cycle for the maximal coupling, the number of Rabi cycles will be different for each relative phase difference. In what follows, unless indicated otherwise, the number of Rabi cycles refers specifically to those for a relative phase difference $\delta_d = 0$, i.e., for the maximal laser-molecule coupling. Generally, controlling the excitation within the first Rabi cycle for maximal coupling will be of most interest, but, in principle, one should be able to control the excitation for any number of Rabi cycles. For example, limits on the pulse duration and the field strengths could force phase control to have to be optimized beyond the first Rabi cycle. After the first Rabi cycle, the control condition Eq. (3.5) must be considered more carefully as a variety of n, m combinations can produce complete control. As an example, if the time-dependent population for a relative phase difference of zero will pass through one full Rabi cycle ($n = 1$) and for $\delta_d = \pi$ will go through zero cycles ($m = 0$), the control condition becomes

$$\bar{C}^p(2,0,t=\infty) = \bar{C}^p(0,1,t=\infty) = \frac{3\pi}{2}, \quad (3.7)$$

where $|\Omega(\delta_1, \delta_2, t=\infty)|$ ranges between 3π and 0.

These two possible control scenarios, control within the first Rabi cycle, see Eq. (3.6), and control after one Rabi cycle, see Eq. (3.7), will be examined in Secs. III A and III B, respectively. We shall demonstrate that while, in principle, the molecular-state populations can be controlled for the system passing through any number of Rabi cycles, in general in order to maximize phase control the excitation should be limited to within the first Rabi cycle.

The exact solution to Eq. (2.1) for the state amplitudes, for the two-level model, is obtained by using the Crank-Nicholson method [39–41]. For a small time step dt , over which the pulses can be considered constant, the state amplitudes and hence state populations, can be determined from

$$a(t+dt) = \exp\left[-iHdt\right] \underline{a}(t) \approx \left[\frac{1 - iH(dt/2)}{1 + iH(dt/2)} \right] \underline{a}(t). \quad (3.8)$$

The state amplitudes for all times of interest can be obtained by applying Eq. (3.8) repeatedly given the appropriate initial conditions. For all examples considered in the paper, the system is in the ground state initially, i.e., $a_1(t = -4\tau) = 1$ and $a_2(t = -4\tau) = 0$. For the exact calculations reported here, a time step of 0.001 fs has been employed. This time step gives results converged to three or four decimal places as verified by comparison with results computed utilizing a time step of 0.0001 fs. As mentioned in Sec. II, the variable $\Omega(\delta_1, \delta_2, t)$ needed for determining the state populations within the RWA must be evaluated through numerical integration. $\bar{C}^p(2,0,t)$ and $\bar{C}^p(0,1,t)$ needed to determine the control conditions must also be calculated numerically. In the RWA calculations presented here, $\Omega(\delta_1, \delta_2, t)$, $\bar{C}^p(2,0,t)$, and $\bar{C}^p(0,1,t)$ are evaluated by employing a simple trapezoidal scheme. For the RWA calculations, an integration time step of 0.1 fs gives results converged to 11 or 12 decimal places as verified by comparison with results calculated using a time step of 0.01 fs. These choices of time step for the exact versus the RWA calculations illustrate the computational efficiency of the RWA, in addition to its utility for interpreting the exact results. For excited-state populations that, in general, range from 0 to 1, the time steps utilized provide results to better than graphical accuracy.

A. Phase control within the first Rabi cycle

Following previous studies involving cw laser fields, the field strength for the one-photon transition is chosen to be $\varepsilon_2 = 1 \times 10^{-6}$ a.u. (3.51×10^4 W/cm²). Initially, the goal is to optimize phase control within the first Rabi cycle, where “first Rabi cycle” refers to the numbering of the Rabi cycle for the relative phase differences $\delta_d = 0$. Since the laser-molecule coupling is strongest for $\delta_d = 0$, see Eq. (3.2), the time-dependent population evolves most rapidly for this relative phase difference. Therefore, if one is within the first Rabi cycle for $\delta_d = 0$, one is within the first Rabi cycle for all relative phase differences. Hence, this is the simplest case to consider for pulsed phase control. Using numerical iteration, based on Eq. (3.6) and the relevant RWA expressions derived in Sec. II, the best choices of ε_1 and τ for achieving phase control are determined to be 1.475×10^{-4} a.u. (7.64×10^8 W/cm²) and 7.15 ps, respectively. For these choices of field strengths and pulse duration, $\bar{C}^p(2,0,t=\infty) = \bar{C}^p(0,1,t=\infty) = 0.50028\pi$, thus fulfilling the two control conditions corresponding to a final steady-state excited-state population that will vary between 100% and 0% within the first Rabi cycle, see Eq. (3.6).

For the field strengths in question, the maximal individual pulsed-laser–molecule couplings, i.e., the couplings at $t = 0$, are $C^p(2,0,t=0) = 4.242 \times 10^{-6}$ and $C^p(0,1,t=0) = 3.000 \times 10^{-6}$. The next largest individual laser-molecule couplings are $C^p(-2,2,t=0) = 2.241 \times 10^{-15}$ and $C^p(4,-1,t=0)$

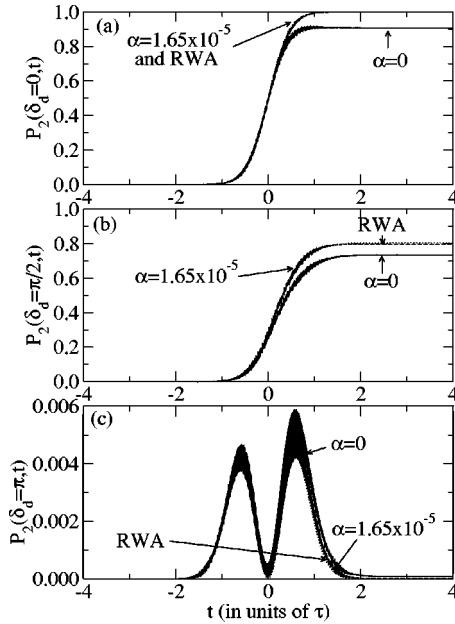


FIG. 1. Plots of the populations of the excited state as a function of t/τ with $\tau = 7.15$ ps for competing one- and two-photon resonances (see text) as a function of the relative phase ($\delta_d = \delta_2 - 2\delta_1$) of the two fields: (a) $\delta_d = 0$, (b) $\delta_d = \pi/2$, and (c) $\delta_d = \pi$. The field strengths are $\varepsilon_1 = 1.475 \times 10^{-4}$ a.u. (7.64×10^8 W/cm 2) and $\varepsilon_2 = 1.0 \times 10^{-6}$ a.u. (3.51×10^4 W/cm 2). In each plot, there are three curves: the exact calculation with $\alpha = 0$ (solid line), the exact calculation with $\alpha = 1.65 \times 10^{-5}$ (dashed line), and the two-color pulsed $d \neq 0$ RWA result (dotted line). Note the change of scale for a relative phase difference $\delta_d = \pi$.

$= 1.056 \times 10^{-15}$, and, therefore, only the two desired coupling terms dominate. Using the dominant $C^p(0,1,t=0)$ and $C^p(2,0,t=0)$ couplings in Eq. (3.2), the overall pulsed-laser-molecule couplings at $t=0$ for the relative phase differences 0, $\pi/2$, and π are $|\zeta^p(0,0,t=0)| = 7.242 \times 10^{-6}$, $|\zeta^p(0,\pi/2,t=0)| = 5.196 \times 10^{-6}$, and $|\zeta^p(0,\pi,t=0)| = 1.243 \times 10^{-6}$. Clearly, the criteria for the validity of the RWA, $|\zeta^p(\delta_1, \delta_2, t=0)| \ll \omega_b$, $(\omega_1 \tau_1)^{-1} = 6.76 \times 10^{-5} \ll 1$, and $(\omega_2 \tau_2)^{-1} = 3.38 \times 10^{-5} \ll 1$, are obeyed for all three relative phase differences, and we expect the RWA expressions to be valid for predicting the dynamical behavior of the two-level system. However, in order to determine the utility of the RWA for interpreting exact results and its ability to predict optimal field strengths and pulse durations for maximizing control, we now consider the time-dependent behavior of the excited-state population as computed using both the two-color pulsed $d \neq 0$ RWA and exact techniques for the choice of pulse duration $\tau = 7.15$ ps and with the field strengths $\varepsilon_2 = 1 \times 10^{-6}$ a.u. and $\varepsilon_1 = 1.475 \times 10^{-4}$ a.u.

The RWA and the exact results ($\alpha = 0$ in the figure) for the time-dependent excited-state population as a function of (t/τ) are illustrated in Figs. 1(a)–1(c) for the relative phase differences $\delta_d = \delta_2 - 2\delta_1 = 0, \pi/2$, and π , respectively. For both the RWA and the exact ($\alpha = 0$) results, the frequencies are set equal to their weak-field on-resonance values, i.e., $\omega_1 = 0.05$ a.u. and $\omega_2 = 0.10$ a.u. Since ω_1 and ω_2 are harmonically connected ($\omega_2 = 2\omega_1$) and both are related to the

beat frequency, i.e., $\omega_1 = \omega_b$ and $\omega_2 = 2\omega_b$, in all further discussions we will not refer to the two frequencies but rather to a single frequency—the beat frequency. For example, the weak-field on-resonance frequency is given by $\omega_b = 0.05$ a.u. Even though all three of the criteria for the validity of the RWA are obeyed for all three relative phase differences, the RWA and the exact results exhibit significant discrepancies for $(t/\tau) > 0$. The discrepancies arise because the RWA resonance frequency ($\omega_b = 0.05$ a.u.) is not the exact resonance frequency except for extremely weak laser-molecule couplings, i.e., in the wings of the pulse where the field strengths are small. As has been discussed extensively for two-color cw calculations [5,6,15], the exact resonance frequency is shifted away from the weak-field (RWA) resonance value; for one-color fields, this is referred to as the Bloch-Siegert shift [42]. The magnitude of the frequency shift depends upon the strength of the applied field, or fields. As the instantaneous field strength(s) is (are) a function of time for pulsed lasers, the frequency shift will also be a function of time. Since in this study we consider only time-independent frequencies, i.e., there is no chirping (for example, see Ref. [43]), one needs to find an average (time-independent) “resonance” frequency by using a shifted frequency. A similar procedure has been discussed for the one-color $d \neq 0$ pulsed RWA [23]. The use of frequency shifts to attain agreement between RWA and exact results has also been discussed in the context of both one-color and two-color cw laser-molecule interactions [5,6,15,44]. In particular, for the simultaneous two- and one-photon transition considered here, the cw resonance frequency shift of $\Delta\omega_b = \Delta\omega_1 = 0.286$ cm $^{-1}$ ($\Delta\omega_2 = 2\Delta\omega_1$) needs to be taken into account [6] in order for the RWA and the exact time-dependent state populations to agree.

Unlike one-color cw excitation [44], there is no analytical expression available for the frequency shift in two-color cw laser-molecule interactions, let alone for pulsed-laser interactions. Therefore, an effective resonance frequency can only be found by utilizing a brute force method. We define a parameter α by the relation $\omega_b = (1 + \alpha)E_{21}/2$, which gives the beat frequency. The frequencies of the two- and one-photon fields are obtained through the relationships $\omega_1 = \omega_b$ and $\omega_2 = 2\omega_b$. The exact solution for the population of the excited state is calculated as a function of α , and then the α that has a steady-state excited-state population $P_2(t = \infty)$ that comes closest to the RWA result is taken to correspond to the resonance shift. For phase control problems, an effective resonance frequency can be found for each relative phase difference. By computing the steady-state population as a function of α , the best choices were determined to be $\alpha = 1.65 \times 10^{-5}$ ($\Delta\omega_b = 0.181$ cm $^{-1}$), 1.56×10^{-5} ($\Delta\omega_b = 0.171$ cm $^{-1}$), and 1.03×10^{-5} ($\Delta\omega_b = 0.113$ cm $^{-1}$) for the relative phases 0, $\pi/2$, and π , respectively. As expected, the pulsed resonance shift is less than the shift (0.286 cm $^{-1}$) obtained for cw lasers. For these choices of α , the exact (RWA) steady-state excited-state populations are 1.0000 (1.0000) for $\delta_d = 0$, 0.7977 (0.8033) for $\delta_d = \pi/2$, and 0.0000 (0.0000) for $\delta_d = \pi$.

While a different resonance frequency can be determined for each relative phase difference, in practice, the laser fre-

quencies would be set and then the relative phase difference would be scanned without modifying the frequencies. Therefore, as an example, we have chosen α for the relative phase difference of zero ($\delta_d=0$) to determine the effective resonance frequency and have then computed the time-dependent excited-state populations for the relative phase differences 0, $\pi/2$, and π . The exact results obtained using the value of $\alpha=1.65\times 10^{-5}$ ($\Delta\omega_b=0.181\text{ cm}^{-1}=\alpha E_{21}/2$) are included in Figs. 1(a)–1(c) for comparison with the exact $\alpha=0$ and the two-color pulsed $d\neq 0$ RWA results. With the use of this value of the parameter α , the modified exact results for the time-dependent excited-state populations match the RWA results quite well. The RWA (exact, $\alpha=1.65\times 10^{-5}$) steady-state excited-state populations are 1.0000 (1.0000), 0.8033 (0.7975), and 0.0000 (0.0000) for the relative phases 0, $\pi/2$, and π as shown in Figs. 1(a)–1(c), respectively. Note that the steady-state populations for this choice of α are nearly identical to those determined for the best choice of α for the relative phases $\pi/2$ and π ; in fact for $\delta_d=\pi$, the two results are identical within the numerical accuracy of the exact calculations, i.e., four decimal places.

In addition to the large discrepancies between the exact and the RWA results that are attributable to the resonance frequency shift, the exact results exhibit small oscillations (amplitude less than 0.01) in the molecular-state populations that are not seen in the RWA results; the RWA results are smooth. These undulations occur with a period of $\pi/\omega_b \approx 1.5$ fs and superimposed on these undulations is an even smaller oscillation (amplitude less than 0.002) with a period of $\pi/\omega_2 \approx 0.75$ fs (not illustrated). The oscillations may not appear periodic in the figures due to the sampling used to generate the plots (every 10 fs). These undulations have been observed previously in both one-color pulsed [45,46] and one-color cw calculations [24,32,47]. Their presence is due to the counter-rotating terms that have been neglected in the RWA and their positions correspond to the zeros in the electric fields, i.e., when either $\cos(\omega_1 t + \delta_1)=0$ or $\cos(\omega_2 t + \delta_2)=0$. Therefore, the location of the oscillations depends on the absolute carrier phases (δ_1 and δ_2) used to generate the relative phase difference (δ_d). While these small oscillations depend of the absolute phases, the global behavior of the time-dependent populations depends solely on the relative phase difference (for the relatively weak field exact results presented here and within the RWA).

Although the time-dependent behavior of the state populations behaves as predicted by the RWA, one may wonder why there exist two “periods,” albeit with small amplitudes, for a relative phase difference of π , see Fig. 1(c). These result from the fact that the control conditions, see Eq. (3.6), are chosen such that phase control is optimized at the end of the pulse-molecule interaction ($t=\infty$) and not for all times within the pulse envelope. Figure 2 illustrates the time dependence of individual contributions $\bar{C}^p(2,0,t)$ and $\bar{C}^p(0,1,t)$, see Eq. (3.4), to $\Omega(\delta_1, \delta_2, t)$, which determines the molecular-state populations, see Eqs. (2.19) and (2.20). For $-2 \leq (t/\tau) \leq 0$, $\bar{C}^p(0,1,t)$ exceeds $\bar{C}^p(2,0,t)$ while for $0 \leq (t/\tau) \leq 2$, $\bar{C}^p(2,0,t)$ exceeds $\bar{C}^p(0,1,t)$. The different time dependence for these two terms results in small excited-

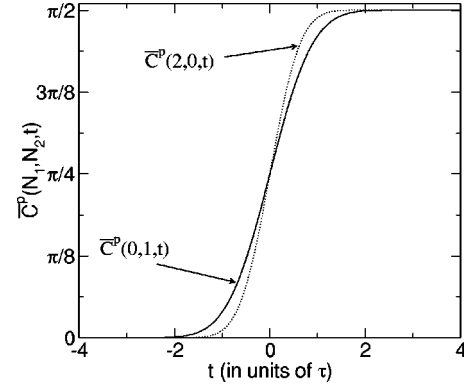


FIG. 2. Plots of the individual contributions $\bar{C}^p(2,0,t)$ (dotted line) and $\bar{C}^p(0,1,t)$ (solid line) to $\Omega(\delta_1, \delta_2, t)$, see Eq. (3.3), as a function of t/τ with $\tau=7.15$ ps. The field strengths are $\epsilon_1=1.475\times 10^{-4}$ a.u. (7.64×10^8 W/cm²) and $\epsilon_2=1.0\times 10^{-6}$ a.u. (3.51×10^4 W/cm²).

state populations within these time ranges for a relative phase difference of π since the interference is not “perfect” for these times. So even though the desired excited-state population of zero for a relative phase difference of π is achieved at the end of the pulse-molecule interaction, the population does not remain exactly zero during the entire interaction time.

From the three choices of phase difference considered here (0, $\pi/2$ and π), it is clear that a great deal of phase control can be exerted over the dynamics and, therefore, the steady-state populations of the molecular states. While the RWA expression for the overall laser-molecule coupling suggests that the relative phase differences of 0 and π correspond to the extremes, i.e., the maximum and the minimum, respectively, in the associated steady-state populations, it is interesting to consider the final excited state populations as a (continuous) function of the phase difference between the laser fields for the pulse duration of 7.15 ps and with the one- and two-photon field strengths set at $\epsilon_2=1\times 10^{-6}$ a.u. and $\epsilon_1=1.475\times 10^{-4}$ a.u., respectively. By considering the steady-state population as a function of relative phase, we can determine if these choices of phase do correspond to the extremes even when the true laser-molecule couplings are functions of time, and, we can also determine if a single resonance-frequency shift is adequate for all relative phase differences regarding the control of the steady-state populations. The RWA and the exact ($\alpha=0$ and $\alpha=1.65\times 10^{-5}$) results for the steady-state excited-state populations as a function of the relative phase difference between the fields are illustrated in Fig. 3. Clearly, the relative phase differences 0 and π correspond to the extremes as predicted by the two-color pulsed $d\neq 0$ RWA and a single frequency shift, while not corresponding to the best choice of shift for each individual δ_d , is more than adequate for all relative phases regarding the control of the steady-state molecular-state populations. Also, one can achieve “perfect” control over the final population of the excited state with the RWA (exact, $\alpha=1.65\times 10^{-5}$) population varying between 1.0000 (1.0000) for $\delta_d=0$ and 0.0000 (0.0000) for $\delta_d=\pi$.

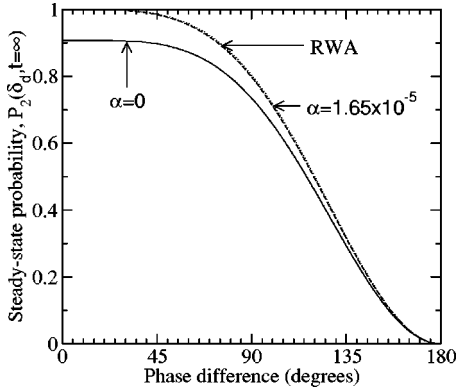


FIG. 3. Plot of the steady-state population of the excited state, $P_2(\delta_d, t=\infty)$, as a function of the relative phase difference ($\delta_d = \delta_2 - 2\delta_1$) for competing one- and two-photon resonances (see text) and for a pulse duration $\tau=7.15$ ps. The field strengths are $\varepsilon_1=1.475 \times 10^{-4}$ a.u. (7.64×10^8 W/cm²) and $\varepsilon_2=1.0 \times 10^{-6}$ a.u. (3.51×10^4 W/cm²). There are three curves: the exact calculation with $\alpha=0$ (solid line), the exact calculation with $\alpha=1.65 \times 10^{-5}$ (dashed line), and the RWA result (dotted line).

It is useful to compare these pulsed results with the previous results [6] for two- versus one-photon phase control for cw lasers. For cw fields, complete control, i.e., $P_2(\delta_d=0, t) \approx 1$ and $P_2(\delta_d=\pi, t) \approx 0$ for a fixed choice of t , is obtained using the field strengths $\varepsilon_1=1.25 \times 10^{-4}$ a.u. and $\varepsilon_2=1.00 \times 10^{-6}$ a.u. for the simultaneous two- and one-photon transitions [6]. For these field strengths, if one considers the time-dependent population at $t=12.6$ ps, the excited-state population for a relative phase difference of $\delta_d=0$ is 0.9999 while that for $\delta_d=\pi$ is 0.0002; this time represents the “best” phase control obtainable within the first Rabi cycle. When utilizing pulsed lasers, and with the one-photon field strength fixed at $\varepsilon_2=1.00 \times 10^{-6}$ a.u., the two-photon field strength must be increased to $\varepsilon_1=1.475 \times 10^{-4}$ a.u. and the first instance of “complete” (100%) phase control occurs for a pulse duration $\tau=7.15$ ps. So while the cw results provide a reasonable guide to the choices of field strengths and pulse duration needed to achieve phase control, the newly developed two-color pulsed $d \neq 0$ RWA is an excellent predictor of the field strengths and pulse durations necessary for phase control using pulsed lasers.

B. Phase control beyond the first Rabi cycle

The only pulse duration considered explicitly so far has been one for which the excited-state steady-state population was first maximized for a relative phase difference of zero. However, as discussed previously, in principle, phase control can be achieved for the system passing through any number of Rabi cycles for $\delta_d=0$. In order to facilitate comparison with the results of Sec. III A, we consider the situation where the one-photon field strength is again fixed at $\varepsilon_2=1.0 \times 10^{-6}$ a.u. Let us assume that a pulse duration of 7.15 ps is unachievable and thus one considers the next possible phase control condition, i.e., the time-dependent population for a relative phase difference of zero will pass through one full Rabi cycle. The new control conditions are given by Eq. (3.7).

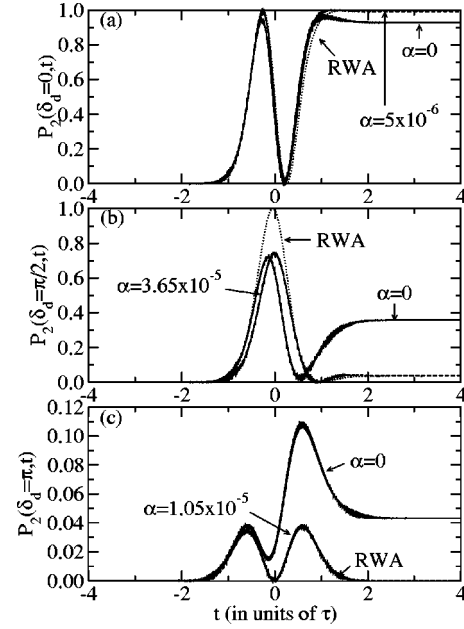


FIG. 4. Plots of the populations of the excited state as a function of t/τ with $\tau=21.45$ ps for competing one- and two-photon resonances (see text) as a function of the relative phase ($\delta_d = \delta_2 - 2\delta_1$) of the two fields: (a) $\delta_d=0$, (b) $\delta_d=\pi/2$, and (c) $\delta_d=\pi$. The field strengths are $\varepsilon_1=1.475 \times 10^{-4}$ a.u. (7.64×10^8 W/cm²) and $\varepsilon_2=1.0 \times 10^{-6}$ a.u. (3.51×10^4 W/cm²). In each plot, there are three curves: the exact calculation with $\alpha=0$ (solid line), the exact calculation with the “best” choice of α (dashed line), and the two-color pulsed $d \neq 0$ RWA result (dotted line). Note the change of scale for a relative phase difference $\delta_d=\pi$.

We proceed exactly as was done when examining phase control within the first Rabi cycle. With the one-photon field strength set at $\varepsilon_2=1.0 \times 10^{-6}$ a.u., the best choices of ε_1 and τ for achieving phase control are determined using numerical iteration of the pulsed two-color RWA control expressions given by Eq. (3.7). With the values of 1.475×10^{-4} a.u. (7.64×10^8 W/cm²) and 21.45 ps, respectively, the control condition is fulfilled as $\bar{C}^P(2,0, t=\infty) = \bar{C}^P(0,1, t=\infty) = 1.5008\pi$. Note that the two-photon field strength required to obtain phase control after the first Rabi cycle is the same as that needed to obtain phase control within the first Rabi cycle; for multiple Rabi cycles and stronger applied fields, this will not generally be the case.

For these choices of field strength and for $\tau=21.45$ ps, the RWA and the exact results ($\alpha=0$ in the figure) for the excited-state population as a function of (t/τ) are illustrated in Figs. 4(a)–4(c) for the relative phase differences $\delta_d = \delta_2 - 2\delta_1 = 0, \pi/2$, and π , respectively. For both the RWA and the exact ($\alpha=0$) results, the frequencies are set equal to their weak field on-resonance values, i.e., $\omega_1=0.05$ a.u. and $\omega_2=0.10$ a.u. As expected from the results of Sec. III A, the exact ($\alpha=0$) and the RWA results exhibit significant differences due to the (time-dependent) shift of the exact resonance frequency. By computing the steady-state population as a function of α , we determined the time-independent frequency shift that produced the best agreement between the RWA prediction and the exact excited-state steady-state

population. The best α 's, as defined by the agreement of the steady-state populations, are 0.50×10^{-5} ($\Delta\omega_1 = 0.055 \text{ cm}^{-1}$), 3.65×10^{-5} ($\Delta\omega_1 = 0.401 \text{ cm}^{-1}$), and 1.05×10^{-5} ($\Delta\omega_1 = 0.115 \text{ cm}^{-1}$) for the relative phases 0, $\pi/2$, and π , respectively. For these choices of α , the exact (RWA) steady-state excited-state populations are 0.9895 (1.0000) for $\delta_d = 0$, 0.0367 (0.0366) for $\delta_d = \pi/2$, and 0.0001 (0.0000) for $\delta_d = \pi$. The exact time-dependent excited-state populations obtained using these values of α are included in Figs. 4(a)–4(c) for comparison with the exact $\alpha = 0$ and the two-color pulsed $d \neq 0$ RWA results. From Fig. 4, it is clear that although the steady-state populations can be matched quite well through the use of the frequency shift α , the agreement between the exact and RWA results for the corresponding time-dependent behavior is not as good as for the shorter pulse durations, see Fig. 1. More importantly, if the frequency shift for the relative phase difference of 0 is utilized for both $\delta_d = \pi/2$ and π , as was done in Sec. III A, significant differences occur between the exact and the RWA results for the steady-state excited-state populations in addition to the time-dependent populations. The exact ($\alpha = 5.0 \times 10^{-6}$) steady-state excited-state populations of 0.9895, 0.2539, and 0.0044 for the relative phases 0, $\pi/2$, and π , can be compared to the RWA predictions of 1.0000, 0.0366, and 0.0000, respectively. Therefore, while the RWA predicts “perfect” control of the steady-state population, the exact results illustrate that this is no longer attainable for a single fixed resonance frequency beyond the first Rabi cycle (Sec. III A).

It is clear from the results presented in Fig. 4 that if longer pulse durations are considered, or more specifically, pulse durations and field strengths such that more than a single Rabi cycle is revealed in the time-dependent behavior, the agreement between the two-color pulsed $d \neq 0$ RWA and the exact results for the time-dependent behavior of the excited-state population becomes poorer relative to shorter pulse durations. Similar behavior has been seen in the multiphoton ($N > 1$) one-color case [23], where, for example, excellent agreement between the one-color pulsed $d \neq 0$ RWA and exact results can be obtained over the first Rabi cycle for a two-photon absorption but the agreement becomes poorer for pulse durations such that two Rabi cycles occur. Since the field strengths change during the pulse, the resonance frequency shift is a function of time, whereas we have used a constant (time-independent) frequency shift throughout the pulse duration in order to (partially) compensate for the time-dependent shift of the resonance frequency away from the weak-field value. As the pulse duration gets longer, a constant frequency shift is less able to compensate completely since the shift is a function of time. Also, as the pulse duration increases, the bandwidth of the laser decreases along with the possibility that this frequency bandwidth can help compensate for the frequency shift. For phase-control problems involving two-color excitation, the success, or failure, of a constant frequency shift to compensate for the time-dependent frequency shift depends upon the relative phase difference between the fields. When there is constructive interference ($\delta_d = 0$), the laser-molecule coupling is maximized. The maximal laser-molecule coupling results in the

widest two-color cw resonance profile [6,15], and, hence, if considering this effect alone, the consequences of missing the resonance frequency should be less pronounced when compared to those for all other phase differences. However, the best agreement between RWA and exact temporal behavior occurs for $\delta_d = \pi$, i.e., the weakest laser-molecule coupling. It is clear that the strength of the laser-molecule coupling is not the only factor that must be considered when assessing whether a constant frequency shift will suffice for a fixed relative phase difference. In general, the RWA's ability to predict the exact results depends upon the interplay between three properties: (1) the magnitude of the time-dependent frequency shift, (2) the strength of laser-molecule coupling (applied fields) and therefore, for phase control problems, on the relative phase difference between the fields, and (3) the pulse durations that determine the frequency bandwidth of the applied fields. However, while the two-color pulsed $d \neq 0$ RWA is not able to reliably predict the time-dependent behavior beyond the first Rabi cycle, it is still very successful at predicting the field strengths and pulse durations required to maximize phase control of the steady-state molecular-state populations provided both relative phase difference and laser frequency are varied.

These results suggest that, if one is limited by pulse duration, the field strengths should be attenuated such that control occurs within the first Rabi cycle ($\delta_d = 0$). For example, for $\tau = 21.45 \text{ ps}$, if the one- and two-photon field strengths are set to $\varepsilon_1 = 3.33 \times 10^{-7} \text{ a.u.}$ and $\varepsilon_2 = 8.52 \times 10^{-5} \text{ a.u.}$, the control conditions within the first Rabi cycle, see Eq. (3.6), $\bar{C}^p(0,1,t=\infty) = 0.4998\pi$ and $\bar{C}^p(2,0,t=\infty) = 0.5008\pi$ are satisfied. Using these new field strengths and a single frequency shift ($\alpha = 4.50 \times 10^{-6}$, i.e., the phase shift for $\delta_d = 0$) “perfect” control can be obtained for the pulse duration 21.45 ps as verified by computing the exact steady-state molecular-state populations. As well as obtaining the desired steady-state populations, i.e., 1.0000 for $\delta_d = 0$ and 0.0000 for $\delta_d = \pi$, with the single frequency shift, the RWA correctly predicts the time-dependent dynamics for all three relative phase differences.

IV. SUMMARY

RWA formulas for the time-dependent molecular-state populations for the interaction of two pulsed lasers with a model two-level dipolar molecule ($d \neq 0$) have been developed. The derivation requires that both pulse durations are larger than the inverse of their respective carrier frequencies, i.e., $(\omega_1 \tau_1)^{-1} \ll 1$ and $(\omega_2 \tau_2)^{-1} \ll 1$. Also, the overall pulsed-laser-molecule coupling must be smaller than the beat frequency for all times t during the pulse duration, i.e., $|\zeta^p(\delta_1, \delta_2, t)| \ll \omega_b$. Since most pulse envelopes $f(t)$ are maximal at $t = 0$, one can often simplify the second condition for the applicability of the pulsed two-color $d \neq 0$ RWA to $|\zeta^p(\delta_1, \delta_2, t = 0)| \ll \omega_b$ although this condition is normally more stringent than necessary. As this only represents the criteria for maximal coupling, for most other times where $|\zeta^p(\delta_1, \delta_2, t)| < |\zeta^p(\delta_1, \delta_2, t = 0)|$, $|\zeta^p(\delta_1, \delta_2, t)| \ll \omega_b$ can readily be achieved.

Numerical examples have been presented comparing re-

sults for the molecular-state populations obtained using the two-color pulsed $d \neq 0$ RWA and exact calculations for the simultaneous one- and two-photon excitation of a model two-level molecule where the relative phase difference between the two fields ($\delta_d = \delta_2 - 2\delta_1$) has been used to control the excitation process. These results have also been compared to the previously discussed [6] results for the simultaneous one- and two-photon excitation of a two-level molecule using cw lasers. The RWA and the exact results agree very well for the pulsed laser-molecule interaction but account must be taken of the (time-dependent) shift of the resonance frequency away from the weak-field value ($\omega_b = \omega_1 = 0.05$ a.u.; $\omega_2 = 2\omega_1$) in the exact calculations. An effective (time-independent) frequency shift was found by utilizing a brute force method, where the exact steady-state population was determined as a function of the frequency shift $\Delta\omega_b = \Delta\omega_1 = \alpha E_{21}/2$ and compared to the RWA prediction under long-time steady-state conditions. Using a time-independent frequency shift becomes less effective as the pulse duration increases. Most importantly, the RWA expressions developed can be used to predict the field strengths and pulse duration needed to maximize the phase control of the excitation, i.e., to vary the steady-state excited-state population between 100% and 0% as the relative phase difference is varied between 0 and π . Maximal phase control for the steady-state molecular-state populations was only achievable within the first Rabi period ($\delta_d = 0$), unless both the relative phase difference and beat frequency were simultaneously varied, i.e., beyond the first Rabi cycle one had to determine a resonance frequency for each relative phase difference. Since, in practice, one would like to fix the frequency and then just vary the relative phase difference to obtain control,

pulse parameters should be chosen such that excitation does not continue beyond the first Rabi cycle. However, while the RWA expressions were no longer quantitatively reliable for predicting time-dependent populations beyond the first Rabi cycle ($\delta_d = 0$), the RWA expressions were still useful in determining field strengths and pulse durations needed to obtain control beyond the first Rabi cycle; the caveats being that maximal (100%) phase control cannot be achieved and that optimization of control involves scanning the relative phase difference and the beat frequency simultaneously.

The two-color pulsed $d \neq 0$ RWA developed here has been applied to the phase control of the time-dependent evolution of the state populations of a two-level dipolar system. However, as presented, the RWA is quite general and, therefore, can be applied to various problems involving the two-color pulsed laser excitation of dipolar molecules. For example, it could be used to discuss pulsed (1+1)-photon excitation, where the presence of permanent dipoles greatly enhances the excitation process [15,17–19], or excitation related to two-color molecular beam electric resonance experiments [16]; these are problems that to date have been discussed only for cw laser fields. Two-level models are useful in many-level problems especially in instances where the two-levels of interest interact relatively weakly with the manifold of other states [9]. Also, the two-level model developed here provides a basis for constructing a generalized rotating-wave approximation [48–53] for the interaction of two pulsed lasers with a many-level system.

ACKNOWLEDGMENT

A.B. and W.J.M. thank the Natural Sciences and Engineering Research Council of Canada for financial support.

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