

On the effects of absolute laser phase on the interaction of a pulsed laser with polar versus nonpolar molecules

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The absolute laser phase dependence of the time-dependent populations of the molecular states, including the steady-state (long time) populations of the states, associated with the interaction of a molecule with a pulsed laser is investigated using illustrative two-level examples. One-photon transitions, including the effects of permanent dipoles, are discussed as a function of the pulse duration, intensity, and (absolute) laser phase, for selected laser frequencies. The effects of laser phase can be large, depending on the values of the pulse duration for a given frequency and intensity. The effects of permanent dipoles, relative to no permanent dipoles, are significant for large laser field strengths ϵ^0 . When the laser-molecule coupling parameter $b = \mu_{12}\epsilon^0/E_{21} \geq 0.2$, where μ_{12} and E_{21} are the transition dipole and energy difference between the ground and excited states, respectively, the dynamics of the pulse-molecule interaction are (strongly) phase dependent, independent of pulse duration, whereas the corresponding steady-state populations of the molecular states may or may not be phase-dependent depending on the pulse duration. Analytical rotating wave approximations for pulsed laser-molecule interactions are useful for interpreting the dynamics and the steady-state results as a function of field strength and pulse duration, including the effects of permanent dipole moments. The results reported in this paper are based on molecular parameters associated with an $S_0 \rightarrow S_1$ electronic transition in a dipolar molecule. However, they are presented in reduced form and therefore can be scaled to other regions of the electromagnetic spectrum. Short, intense pulses at or beyond the limits of current laser technology will often be required for the types of absolute laser phase effects of this paper to be appreciable for electronic excitations. The discussion, in the UV-VIS, also suffers from the use of a two-level model and from the requirement of field intensities that can be beyond the Keldysh limit. For other spectral regions, these absolute laser phase effects will be much more readily applicable. © 1998 American Institute of Physics. [S0021-9606(98)00945-3]

I. INTRODUCTION

The purpose of this paper is to discuss, with illustrative two-level examples, the (absolute) laser phase dependence of the dynamics, and the steady-state populations of the molecular states, associated with the interaction of a molecule with a single pulsed laser. This dependence is discussed for one-photon transitions, including the explicit role of the effects of permanent dipole moments on the observables.

The effects of absolute laser phase for the interaction of a molecule with a continuous wave (cw) laser are well documented.¹⁻⁸ In such cases, the phase dependence of the populations of the atomic or molecule states is negligible for weak applied electromagnetic fields (EMFs), such that the molecule-EMF coupling strength parameter $b = \mu_{12}\epsilon^0/E_{21} \ll 1$, where μ_{12} and $E_{21} = E_2 - E_1$ are the transition dipole moment and the energy level separation, respectively, for the two-level $1 \rightarrow 2$ transition of interest and ϵ^0 is the electric field amplitude. On the other hand, if the field strength is increased so $b \leq 1$ (e.g., $b \approx 0.2$),^{5,6} the populations of the atomic or molecular states can be strongly phase dependent and it is important to take these effects into account when

performing calculations of the observables associated with the interactions of cw lasers with atoms or molecules.¹⁻⁸

Interestingly, apparently little explicit attention has been given to the role of (absolute) laser phase in interactions involving a pulsed laser with a molecule. Notable exceptions include a (perturbatively based) study of the effects of laser phase on the time-dependent dipole moment induced in two-level system by an intense laser pulse, by Ivanov *et al.*,⁹ an investigation including a study of the role of the phase of a dissociating laser pulse on laser-controlled dissociation from a selectively prepared vibrational state, by Korolkov *et al.*,¹⁰ and a paper by Griffith *et al.*,¹¹ that became available during the review of the present paper, involving a combined theoretical and experimental study of absolute laser phase effects in the response of a two-level system to radio-frequency pulses. It appears that most single pulsed laser atom or molecule calculations in the literature correspond to setting the phase of the carrier wave equal to zero; see, however, Refs. 9-12.

The relatively little amount of work on absolute phase effects is in contrast to the attention given to relative phase effects for interactions involving atoms or molecules and more than one pulsed (or cw) laser. Here much work has been done on the effects of varying the relative phases of the

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lasers, including studies of the (relative) phase control of molecular excitations through the use of both simultaneously applied, and delayed, phase-related pulses (see, for example, Refs. 13–33). In these studies, as in the case of single laser-molecule interactions,^{5,6,34} there is a strong analogy between optical and NMR spectroscopies.^{14,15,18}

In this paper, we consider a model two-level molecule characterized by a transition dipole, and a difference $d = \mu_{22} - \mu_{11}$ between the permanent dipoles of the excited and ground states 1 and 2, respectively, interacting with a pulsed (Gaussian) laser of duration τ_p , (circular) carrier frequency ω , (absolute) phase δ , and field amplitude ϵ^0 . The effects of laser phase δ , as a function of τ_p and ϵ^0 , for selected laser frequencies ω , on the time-dependent populations of the molecular states are examined in Secs. III A and III B for $d=0$ and $d \neq 0$, respectively; the comparison of the results augments previous discussions³⁵ of the importance of permanent dipoles on pulsed laser-molecule interactions. For example, for a given field strength ϵ^0 , the effects of changing δ on the time evolution of the molecular states, and on the (steady-state) populations of these states after the pulse-molecule interaction is completed, can be large depending on the values of τ_p for a given ω . The numerical results reported in Sec. III are based on molecular parameters characteristic of the $S_0 \rightarrow S_1$ electronic transition in 1-[*p*-(*N,N*-dimethylamino)phenyl]-4-(*p*-nitrophenyl)-1,3-butadiene since this model was involved in an earlier study³⁵ of the effects of permanent dipoles on pulsed laser-molecule interactions for $\delta=0$. However, all the results are presented in terms of the dimensionless parameter b and time and pulse durations in units of $(2\pi/\omega)$, and so can be scaled to other regions of the electromagnetic spectrum. For electronic transitions, many of the effects of absolute laser phase discussed in Sec. III will require short, intense laser pulses, with intensities often at or beyond the Keldysh limit, at or beyond current laser technology. The discussion, for electronic transitions, also suffers from the use of a two-level model. For other spectral regions, these absolute laser phase effects will be much more readily applicable. Even in the UV-VIS, the results of this paper should nevertheless be suggestive of absolute laser phase effects in many-level molecules and these effects will manifest themselves, in one way or another, in the electronic excitation of real molecules. The techniques used to obtain the exact two-level results of Sec. III, in the semi-classical dipole approximation, are reviewed in Sec. II which also contains a review of the analytic rotating wave approximation (RWA), for pulsed laser-molecule interactions,^{36–41} which is used to help interpret the exact results of Sec. III. Finally, Sec. IV contains a discussion of the more general conclusions of this work.

Atomic units are used in this paper. The units of energy E , the transition and permanent dipole moments μ_{jk} , the carrier frequency ω , time t , and field strength ϵ^0 are E_H , ea_0 , $E_H \hbar^{-1}$, $\hbar E_H^{-1}$, and $E_H (ea_0)^{-1}$, respectively, where E_H is the Hartree of energy, e is the absolute value of the charge of an electron, a_0 is the Bohr radius, and \hbar is the reduced Planck constant. The following conversion factors may be useful in what follows: $ea_0 \approx 2.5415$ D, $\hbar E_H^{-1} \approx 2.4189 \times 10^{-17}$ s (10^{15} fs = 10^{12} ps = s), and the field inten-

sity corresponding to a cw electric field is $I \approx 3.509 \times 10^{16} [\epsilon^0(\text{au})]^2 \text{ W/cm}^2$.

II. THEORY AND COMPUTATIONAL METHODS

The time-dependent wave function for a two-level molecule, interacting with a time-dependent field electric field $\epsilon(t)$, can be written as $\Psi(\mathbf{r}, t) = a_1(t)\phi_1(\mathbf{r}) + a_2(t)\phi_2(\mathbf{r})$ with $|a_1(t)|^2 + |a_2(t)|^2 = 1$ and where $\phi_j(\mathbf{r})$ is the time-independent wave function for the j th stationary state of the unperturbed molecule with energy E_j , $j=1,2$, $E_2 > E_1$. In the dipole approximation, the time-dependent coefficients $a_j(t)$ satisfy the system of coupled first order differential equations

$$i \frac{d\mathbf{a}(t)}{dt} = \mathbf{H}(t)\mathbf{a}(t) = [\mathbf{E} - \boldsymbol{\mu} \cdot \boldsymbol{\epsilon}(t)]\mathbf{a}(t). \quad (1)$$

Here $\mathbf{a}(t)$ 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 $(\boldsymbol{\mu})_{jk} = \langle \phi_j | \boldsymbol{\mu} | \phi_k \rangle$, where $\boldsymbol{\mu}$ is the dipole moment operator for the molecule. The electric field is taken to be linearly polarized, $\boldsymbol{\epsilon}(t) = \hat{e} \epsilon^0 f(t) \cos(\omega t + \delta)$, where $f(t)$ is a time-dependent pulse envelope which modulates the sinusoidal (continuous wave, cw) field having an amplitude ϵ^0 , polarization vector \hat{e} , circular frequency ω , and phase δ . The Gaussian pulse envelope, which is of particular interest later, corresponds to $f(t) = \exp(-t^2/\tau_p^2)$, where τ_p is a measure of the pulse duration; the spectral and temporal full widths at half-maximum for the Gaussian pulse are $\Delta\omega = 4(\ln 2)^{1/2} \tau_p$ and $\Delta t = 2\tau_p (\ln 2)^{1/2}$.

Transforming (1) to an interaction representation, defined by $b_j(t) = a_j(t) \exp(-iE_j t)$, and eliminating the counterrotating terms (rotating wave approximation), one obtains^{1,36–41}

$$\begin{aligned} i \frac{db_1(t)}{dt} &= -\frac{\boldsymbol{\mu}_{12} \cdot \hat{e} \epsilon^0}{2} f(t) e^{-i(E_{21} - \omega)t} e^{i\delta} b_2(t), \\ i \frac{db_2(t)}{dt} &= -\frac{\boldsymbol{\mu}_{12} \cdot \hat{e} \epsilon^0}{2} f(t) e^{i(E_{21} - \omega)t} e^{-i\delta} b_1(t), \end{aligned} \quad (2)$$

where $E_{21} = E_2 - E_1$. In obtaining (2), the effects of permanent dipoles, μ_{ii} , have been neglected; this is not always valid,^{7,35,42,43} see also Sec. III. Although Eq. (2) has a simple form, the general solution, for any $f(t)$, is only known when the detuning is zero, $\Delta = E_{21} - \omega = 0$, i.e., the on-resonance solution. By transforming to the variable

$$z = \int_{-\infty}^t f(t') dt' \quad (3)$$

and utilizing the initial conditions $a_j(-\infty) = b_j(-\infty) = \delta_{j1}$, the following well-known solutions are obtained^{36,37,40,41,44–46}

$$\begin{aligned} b_1(t) &= \cos\left(\frac{\boldsymbol{\mu}_{12} \cdot \hat{e} \epsilon^0}{2} \int_{-\infty}^t f(t') dt'\right), \\ b_2(t) &= \sin\left(\frac{\boldsymbol{\mu}_{12} \cdot \hat{e} \epsilon^0}{2} \int_{-\infty}^t f(t') dt'\right), \end{aligned} \quad (4)$$

where we have omitted phase factors of modulus unity which are unimportant in the context of this paper. When the detuning is nonzero, $\Delta = E_{21} - \omega \neq 0$, Eqs. (2) can apparently be solved for only one time-dependent symmetric pulse shape, the secant pulse shape $f(t) = \text{sech}(t/\tau_p)$, where τ_p is a measure of the pulse duration.³⁶ The solution was obtained for all times by Rosen and Zener³⁶ but is of particular interest in the present context for $t = \infty$. Using their result, the solution for the excited state steady-state population $P_2(\infty) = |b_2(\infty)|^2$ i.e., the population after the pulse has passed through the system, for the secant pulse shape is given by

$$P_2(\infty) = \sin^2 \left[\frac{\mu_{12} \cdot \hat{e} \epsilon^0}{2} \int_{-\infty}^{\infty} f(t') dt' \right] \text{sech}^2 \left[\frac{(E_{21} - \omega) \pi \tau_p}{2} \right] \\ = \sin^2 \left[\frac{\mu_{12} \cdot \hat{e} \epsilon^0}{2} \pi \tau_p \right] \text{sech}^2 \left[\frac{(E_{21} - \omega) \pi \tau_p}{2} \right]. \quad (5)$$

This solution lead Rosen and Zener³⁶ to conjecture that for any pulse shape, a possible general form for the excited state steady-state population, $P_2(\infty)$, is given by

$$P_2(\infty) = \frac{\sin^2 A}{A^2} \left| \frac{\mu_{12} \cdot \hat{e} \epsilon^0}{2} \int_{-\infty}^{\infty} f(t) e^{i\Delta t} dt \right|^2 \\ = \frac{\sin^2 A}{A^2} |\mathfrak{J}(\Delta)|^2, \quad (6)$$

where A is the so-called pulse ‘‘area’’ defined by $A = (\mu_{12} \cdot \hat{e} \epsilon^0 / 2) \int_{-\infty}^{\infty} f(t) dt$ and $\mathfrak{J}(\Delta)$ is the Fourier transform of the pulse shape evaluated at $\omega = \Delta$. This was deduced from the secant pulse shape solution which depends upon the $\Delta = E_{21} - \omega = 0$ solution, i.e., $\sin^2 A$, and the normalized Fourier transform of the pulse shape, i.e., $|\mathfrak{J}(\Delta)|^2 / A^2 = \text{sech}^2[(E_{21} - \omega) \pi \tau_p / 2]$. For the Gaussian pulse, with $f(t) = \exp(-t^2/\tau_p^2)$, which is considered here, the Rosen–Zener conjecture can be written as³⁷

$$P_2(\infty) = \sin^2 \left(\frac{\mu_{12} \cdot \hat{e} \epsilon^0}{2} \sqrt{\pi} \tau_p \right) \exp \left[- \frac{\{(E_{21} - \omega) \tau_p\}^2}{2} \right]. \quad (7)$$

Although the conjecture has been shown to be quantitatively unreliable for $\Delta \neq 0$, it is ‘‘exact’’ for $\Delta = 0$ and is qualitatively reliable for $\Delta \leq \frac{1}{2} E_{21}$.^{46–48} Here ‘‘exact’’ means only within the same approximations which lead to any RWA being quantitatively reliable, i.e., that the elimination of the counterrotating terms is a valid approximation. Although these analytical expressions will be useful in helping to suggest or interpret numerical calculations, for intense laser fields, RWAs are not reliable and exact numerical calculations must be performed to obtain reliable results for steady-state and time-dependent populations.

In principle, the duration of the pulse is $-\infty < t < \infty$, but for numerical computational purposes an effective pulse duration of $-\alpha \tau_p \leq t \leq \alpha \tau_p$ can be employed, where α is a constant such that $f(t = \pm \alpha \tau_p)$ is very small ($< 10^{-6}$) and the perturbation of the molecule by the field for $|t| > \alpha \tau_p$ is negligible.

The exact (numerical) solution of (1) can be written in terms of the evolution operator $\mathbf{U}(t, t_0)$, $\mathbf{a}(t) = \mathbf{U}(t, t_0) \mathbf{a}(t_0)$, where $\mathbf{U}(t, t_0)$ satisfies

$$i \frac{d\mathbf{U}(t, t_0)}{dt} = \mathbf{H}(t) \mathbf{U}(t, t_0) \quad (8)$$

subject to the initial conditions $\mathbf{U}(t_0, t_0) = \mathbf{I}$, where \mathbf{I} is the unit matrix. The numerical evaluation of the evolution operator for pulsed molecule-EMF interactions can be carried out by application of the Riemann product integral (RPI) method.^{49–52} In order to solve Eq. (8) with this technique, the time interval $[t_0, t]$ is subdivided into m small intervals, the evolution operator $\mathbf{U}(t, t_0)$ is evaluated for each subinterval, and the group property of the evolution operator over adjoining subintervals utilized to yield $\mathbf{U}(t, t_0) = \mathbf{U}(t, t_m) \mathbf{U}(t_m, t_{m-1}) \dots \mathbf{U}(t_2, t_1) \mathbf{U}(t_1, t_0)$. The time divisions are assumed to be sufficiently small (m sufficiently large) that $\mathbf{H}(t)$ is (essentially) constant over each subinterval. Application of the mean value theorem^{51,53} then leads to an expression for the evolution operator for the s th time subinterval,

$$\mathbf{U}(t_s, t_{s-1}) = \exp \left[-i \int_{t_{s-1}}^{t_s} \mathbf{H}(t) dt \right]. \quad (9)$$

The RPI method is equivalent to using the first Magnus approximation to $U(t_s, t_{s-1})$ with the neglect of higher order Magnus terms being justified by the choice of large m .^{49,50} The number of Riemann intervals used was 180 per cw field period ($2\pi/\omega$). Utilizing this number of intervals provided results to at least graphical accuracy.

III. RESULTS AND DISCUSSION

The two-level system used in the calculations in this paper is modeled after the $S_0 \Rightarrow S_1$ transition in 1-[*p*-(*N,N*-dimethylamino)phenyl]-4-(*p*-nitrophenyl)-1,3-butadiene. This molecule has been used to help investigate the effects of permanent dipoles in single- and multi-photon^{43,54} molecular spectra and, more recently, on the dynamics of pulsed laser-molecule interactions.³⁵ In atomic units, the molecular parameters are $E_{21} = 0.0859$, $\mu_{12} = 3.93$, and $d = \mu_{22} - \mu_{11} = 11.8$; the transition moment μ_{12} and permanent moments μ_{jj} are taken to be aligned with the direction of polarization of the applied electric field. In order to facilitate the investigation of the role of permanent moments in the dynamics, the pseudo-molecule with $d = 0$ is also considered.

The starting point for this study is a previous investigation³⁵ of the effects of permanent dipoles on the dynamics of pulsed laser-molecule interactions which focused, in large part, on the effect of a molecule-EMF coupling minimum induced by the presence of permanent dipoles. Exact cw phase-averaged calculations of the time-dependent population of the excited state 2 were carried out for a variety of field strengths until evidence for a one-photon molecule-EMF coupling minimum was discovered. The results for a field strength of $\epsilon^0 = 0.0677 (1.61 \times 10^{14} \text{ W cm}^{-2})$ were chosen in Ref. 35 to illustrate some of the effects of $d \neq 0$ vs $d = 0$ on the temporal evolution of the excited state. For this field strength, the resonance period of the exact phase-averaged time-dependent excited state population, that is, twice the time required for the excited state

population to vary from its minimum to its maximum value, is on the order of 1 fs when $d=0$ and is on the order of 1×10^2 fs when $d \neq 0$; in each case, the calculations were carried out for a frequency set equal to the resonance frequency corresponding to the phase-averaged one-photon resonance profile of the two-level model molecule ($\omega=0.8329E_{21}$ and $\omega=1.205E_{21}$ for $d \neq 0$ vs $d=0$).

In the associated Gaussian pulsed laser-molecule calculations of Ref. 35, the phase of the sinusoidal part of the EMF was fixed at $\delta=0$, and, to help interpret the pulsed results, the cw calculations for $d \neq 0$ and $d=0$ were repeated for $\delta=0$ (no phase averaging) with the frequencies set equal to the fixed-phase ($\delta=0$) continuous wave resonance frequencies for the field strength of $\epsilon^0=0.0677$ which are $\omega=0.835E_{21}=0.0717$ and $\omega=1.67E_{21}=0.1438$, respectively. From these fixed-phase ($\delta=0$), time-dependent cw calculations, the exact resonance periods were determined to be 0.54 fs when $d=0$ and 150 fs when $d \neq 0$. For a pulse, the field strength is a function of time and therefore the Bloch–Siegert shift, which is the shift of the resonance frequency from the weak field result of E_{21} (for a one-photon transition), can change as a function of time and so the phrases on- and off-resonance should be utilized with due caution.

For large field strengths, the fixed phase and the phase-averaged time-dependent population of the excited state are very different for the interaction of an atom or molecule with a continuous wave laser.^{1,5–8} In order to understand the effects of laser phase in intense field pulse-molecule interactions, the dynamics of the excited state are re-examined here for pulses of various widths (τ_p) and phases (δ) with the field strength set to $\epsilon^0=0.0677(1.61 \times 10^{14} \text{ W cm}^{-2})$. In the calculations reported here, the results for the temporal and the steady-state populations of the excited state are symmetric, with respect to the phase δ , about $\delta=\pi/2$ for $d=0$, that is $P_2(\delta,t)=P_2(\pi-\delta,t)$, and about $\delta=\pi$ for $d \neq 0$, that is, $P_2(\delta,t)=P_2(2\pi-\delta,t)$. To help interpret the phase-dependent results, cw calculations were carried out for the fixed phases $\delta=\pi/4$ and $\pi/2$ for $d=0$, and for the fixed phases $\delta=\pi/4$, $\pi/2$, $3\pi/4$, and π for $d \neq 0$, to determine the corresponding resonance frequencies; these calculations augment the $\delta=0$ results³⁵ referred to in the last paragraph. For the field strength of $\epsilon^0=0.0677$, the resonance frequencies for $d=0$ and $d \neq 0$ are $\omega=2.81E_{21}=0.2416$ and $\omega=0.796E_{21}=0.0684$, respectively, when $\delta=\pi/4$ and they are $\omega=3.29E_{21}=0.2830$ and $\omega=0.835E_{21}=0.0717$, respectively, for $\delta=\pi/2$. Also, for $d \neq 0$, the resonance frequencies are $\omega=0.836E_{21}=0.0718$ and $\omega=0.829E_{21}=0.0712$ for $\delta=3\pi/4$ and $\delta=\pi$, respectively. Fixed-phase, time-dependent cw calculations were carried out for selected frequencies as needed to help interpret the associated Gaussian pulsed laser-molecule calculations of Secs. III A and III B. The case where the permanent moments are taken to be zero, $d=0$, will be considered first and then the effects of permanent moments, $d \neq 0$, will be considered.

The calculations that follow are based on the one-photon electronic transition associated with the two-level model molecule with field strengths, pulse durations, and frequencies partly chosen to illustrate the dramatic effects arising from changes in laser-molecule couplings due to permanent

dipoles by comparison of Sec. A ($d=0$) with those of Sec. B ($d \neq 0$). However, the numerical results are presented in dimensionless form, that is, in terms of the molecule-electric field coupling parameter $b=\mu_{12}\epsilon^0/E_{21}$, and time and pulse durations in units of $(2\pi/\omega)$. This allows the numerical results to be used for other transitions in the UV-VIS, and for other regions of the electromagnetic spectrum, by using scaling techniques; illustrative examples are discussed later.

A. $d=0$

Figure 1 illustrates the exactly calculated time-dependent, phase-dependent excited state population, $P_2(\delta,t)$, for the model ($d=0$) molecule interacting with a Gaussian pulsed laser of varying pulse width. Each part of the figure contains three curves which correspond to a specific laser phase of $\delta=0$ (—), $\delta=\pi/4$ (---), and $\delta=\pi/2$ (⋯). In Fig. 1(a) the frequency is set to the weak field one-photon resonance frequency, $\omega=E_{21}=0.0859$, while in Fig. 1(b) it is set to the fixed-phase ($\delta=0$) continuous wave resonance frequency of $\omega=0.1438$ corresponding to $\epsilon^0=0.0677$. Each section of the figure contains three parts, (i)–(iii), which illustrate the effects of an increase in pulse duration for $\tau_p/(2\pi/\omega)=1, 1.6$ and 2 , that is for $\tau_p=73.145$ (1.7693 fs), 117.032 (2.8688 fs), and 146.291 (3.5386 fs) when $\omega=0.0859$ in Fig. 1(a) and $\tau_p=43.694$ (1.0569 fs), 69.910 (1.6910 fs), and 87.388 (2.1138 fs) when $\omega=0.1438$ in Fig. 1(b). Calculations have been carried out for $\tau_p/(2\pi/\omega)=1.2, 1.4$, and 1.8 but are omitted here for reasons of graphical clarity. Both parts of Fig. 1(a) and (b) clearly demonstrate that both the dynamics of the excited state and the steady-state population, i.e., $P_2(\infty)$, depend on the phase of the sinusoidal field contained within the pulse envelope. However, the phase dependence of the steady-state population diminishes as the pulse duration increases, while the dynamics within the pulse can still retain their phase dependence. Also, of course,^{35,51} the value of $P_2(\infty)$ for a fixed phase clearly depends on the pulse duration, τ_p , with this dependence vanishing for large enough τ_p for $\omega=0.1438 \neq E_{21}$ where $P_2(\infty)$ approaches zero for all phases.

Since the steady-state excited state population is of considerable interest, i.e., it gives the population of the excited state after the pulse has completely interacted with the system, it is shown as a function of increasing pulse duration in Fig. 2. Each part of the figure contains three curves which correspond to $\delta=0$ (—), $\delta=\pi/4$ (---), and $\delta=\pi/2$ (⋯). In Fig. 2(a) the resonance frequency is set to the weak field resonance frequency, $\omega=0.0859$ while in Fig. 2(b) it is set to the fixed-phase ($\delta=0$) continuous wave resonance frequency of $\omega=0.1438$.

When the frequency equals the weak field resonance value of $\omega=0.0859$ [Figs. 1(a) and 2(a)], the steady-state population essentially varies between zero and one. Aside from a phase dependence, which can be strong for small τ_p and which vanishes as τ_p increases (see below), this population variation is qualitatively predicted by Eq. (7), which indicates whenever the pulse area, A , is an integer multiple of π , the steady-state population will be zero. Note that in Fig. 1(a)(iii) the steady-state population being approximately zero is fortuitous and the steady-state population will again

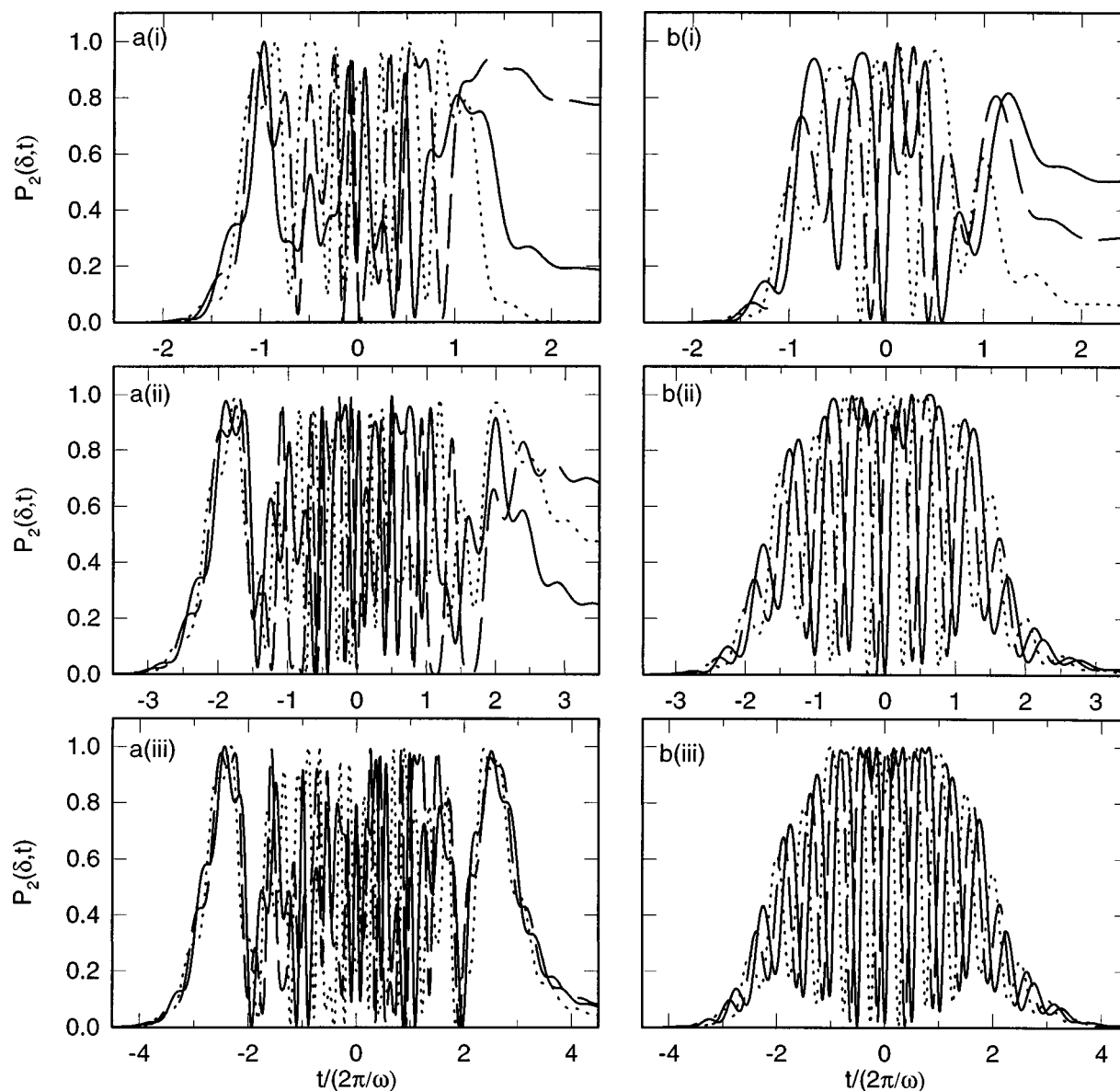


FIG. 1. Time-dependent, phase-dependent excited state population, $P_2(\delta, t)$, versus time in units of $(2\pi/\omega)$, for the model $d=0$ molecule interacting with a pulsed laser of varying pulse width τ_p : (i) $\tau_p/(2\pi/\omega)=1$; (ii) $\tau_p/(2\pi/\omega)=1.6$; and (iii) $\tau_p/(2\pi/\omega)=2$. The molecular and field parameters are $E_{21}=0.0859$, $d=0$, $\mu_{12}=3.93$, $\epsilon^0=0.0677$, with (a) $\omega=E_{21}=0.0859$ and (b) $\omega=0.1438$; with $\delta=0$ (—), $\delta=\pi/4$ (---), $\delta=\pi/2$ (···).

increase to unity as the pulse duration is increased [see Fig. 2(a)]. If the expression for $P_2(\infty)$ for the interaction of a Gaussian pulse, Eq. (7), is utilized, it predicts a period of oscillation which is too short, $0.182 \times 2\pi/\omega$ (13.3 au), as compared to the exact period of oscillation, $0.330 \times 2\pi/\omega$ (24.1 au). The probable causes of this failure of Eq. (7) are the neglect of counterrotating terms in its derivation and the fact that Eq. (7) assumes monochromatic radiation while short pulses can contain many frequency components in addition to the carrier frequency. Thus for example, not all the intensity of the laser drives the one-photon transition when $\omega=E_{21}$ and the molecule-laser coupling for the exact calculation is weaker than that implied in the pulsed $d=0$ RWA result of Eq. (7) corresponding to a larger period of oscillation for $P_2(\infty)$ vs τ_p for the exact versus the RWA calculations.

When $\omega=E_{21}$ and the pulse duration is short

($\tau_p/(2\pi/\omega) < 2$), there can be a large dependence of the steady-state excited state population on phase, for example, when $\tau_p/(2\pi/\omega)=1$, $P_2(0, \infty)=0.20$, $P_2(\pi/4, \infty)=0.78$, and $P_2(\pi/2, \infty)=0.02$; see Fig. 1(a)(i) and Fig. 2(a). However, as the pulse duration increases ($\tau_p/(2\pi/\omega) > 4$), the phase differences become essentially zero; see Fig. 2(a). When partial or few cw field periods are contained within the pulse envelope, i.e., when $\tau_p/(2\pi/\omega)$, or more succinctly $\omega\tau_p$, is small, there is a large phase dependence of the maximum field strength, which is given by $\epsilon^{\max} = \epsilon^0 \exp\{-[\delta/(\omega\tau_p)]^2\}$ where $0 \leq \delta \leq 2\pi$. If the field strength ϵ^0 is such that phase effects are important, i.e., the RWA is no longer applicable, large differences in $P_2(\infty)$ are expected due to variations of phase for very short pulse durations where $\omega\tau_p \leq 2\pi$. However, as the pulse duration increases, two important effects take place: (1) $\epsilon^{\max} \rightarrow \epsilon^0$, so the phase dependence of the maximum field strength is lost and

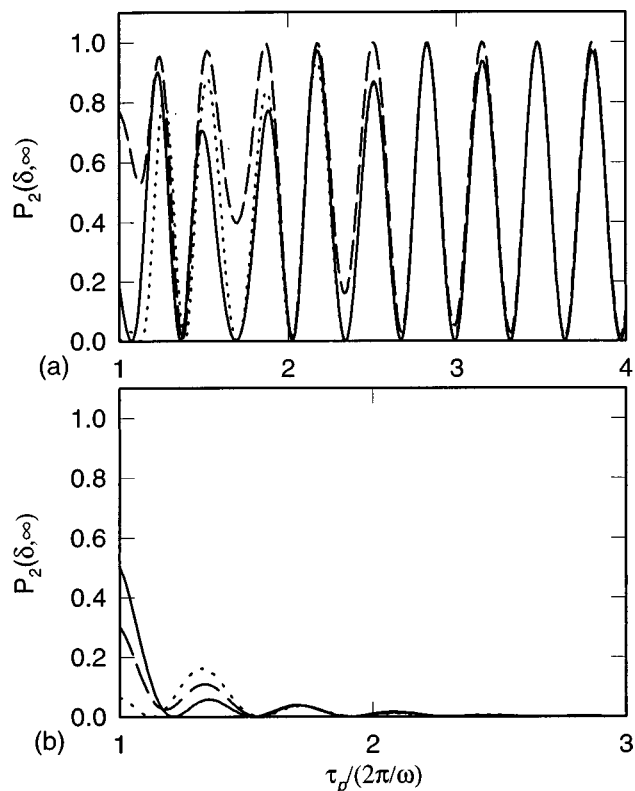


FIG. 2. Steady-state, phase-dependent excited state population, $P_2(\delta, \infty)$, versus pulse duration, $\tau_p/(2\pi/\omega)$, for the model molecule interacting with a pulsed laser. The molecular parameters are as in Fig. 1 while the field parameters are $\epsilon^0 = 0.0677$, with (a) $\omega = E_{21} = 0.0859$ and (b) $\omega = 0.1438$; with $\delta = 0$ (—), $\delta = \pi/4$ (---), $\delta = \pi/2$ (···).

(2) a greater number of cw field periods are contained within the pulse envelope and, more importantly, contained within the wings (weak field areas) of the pulse. When the field is weak, there is little phase dependence⁵⁻⁷ and when the number of field periods in the weak field areas is large, the loss of phase dependence for $P_2(\infty)$ is therefore expected, while the excited state dynamics within the middle of the pulse envelope (strong field area) still retain their phase dependence.

In order to help clarify the above discussion on pulse duration and its effects on the absolute laser phase dependence of the temporal and steady-state molecular populations, we show the time-dependent electric field associated with the Gaussian pulse as a function of $[t/(2\pi/\omega)]$ for $[\tau_p/(2\pi/\omega)] = 1, 2,$ and 5 and for $\delta = 0, \pi/4,$ and $\pi/2$ in Fig. 3. It is clear that the number of optical cycles supported by the pulse increases markedly as τ_p increases. For a Gaussian pulse of the type considered here, where the pulse duration controls both the rise and fall times of the pulse and the number of optical cycles supported by the pulse, it is relatively easy to see why laser phase effects are more appreciable for short relative to long pulses. However, it is relevant to comment in general that it is the rise (and fall) time of the pulse which is crucial and not the number of optical cycles supported by the pulse. This can be rationalized by considering a pulse made up of a Gaussian rise, followed by a constant amplitude field of duration ΔT , which is followed by a Gaussian fall. As long as the Gaussian rise (and fall) time is sufficiently short, and b is such that cw results related

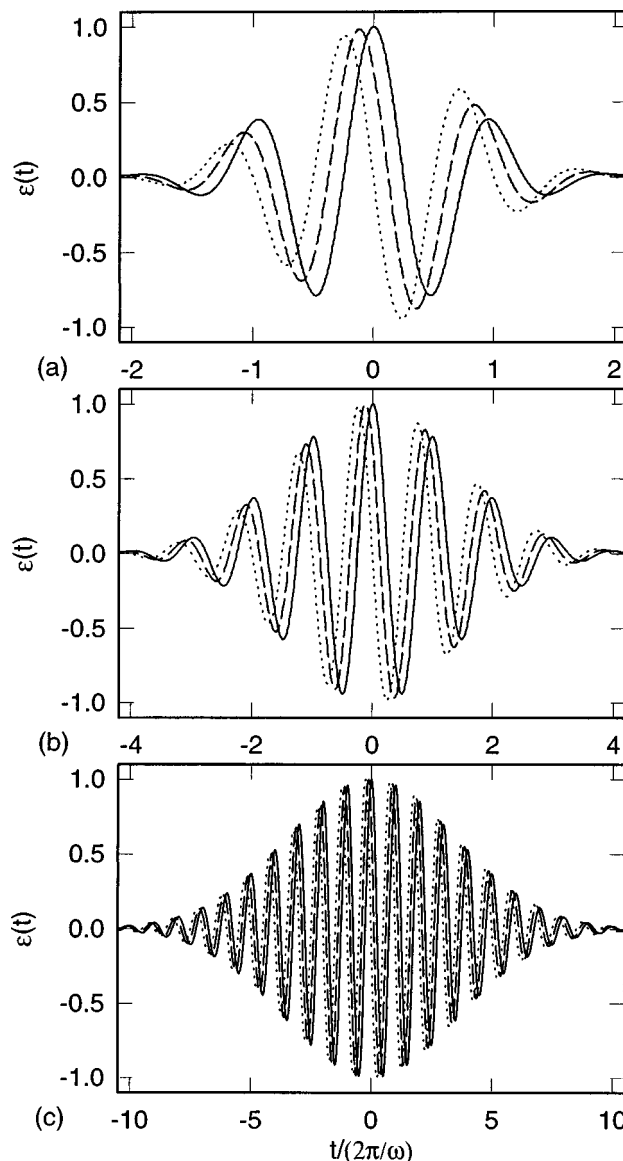


FIG. 3. The temporal dependence, in units of $(2\pi/\omega)$, of a Gaussian pulse, $\exp(-t^2/\tau_p^2)\cos(\omega t + \delta)$, as a function of $\tau_p/(2\pi/\omega)$, for (a) $\tau_p/(2\pi/\omega) = 1$, (b) $\tau_p/(2\pi/\omega) = 2$, and (c) $\tau_p/(2\pi/\omega) = 5$; $\delta = 0$ (—), $\delta = \pi/4$ (---), $\delta = \pi/2$ (···).

to ΔT have phase dependencies ($b > 0.2$), then the phase effects of the pulse will be maintained for any number of optical cycles which can be selected by the choice of ΔT . The actual values of the laser intensity associated with a given b , or the pulse duration associated with a given $[\tau_p/(2\pi/\omega)]$, depend markedly on the region of the electromagnetic spectrum of interest. This will be explicitly illustrated by some of the discussion of Sec. IV; see also Ref. 11.

When the frequency is set at the exact $\delta = 0$ continuous wave resonance value of $\omega = 0.1438$ [Figs. 1(b) and 2(b)], the steady-state population decreases rapidly to zero for increasing pulse duration. This reduction of the steady-state excited state population for an "off-resonance" frequency ($\omega \neq E_{21}$) is predicted by the Rosen-Zener conjecture for a Gaussian pulse, Eq. (7). Here the term "off-resonance" will be utilized for any frequency which is not the weak field resonance value of $\omega = E_{21} = 0.0859$. Although the con-

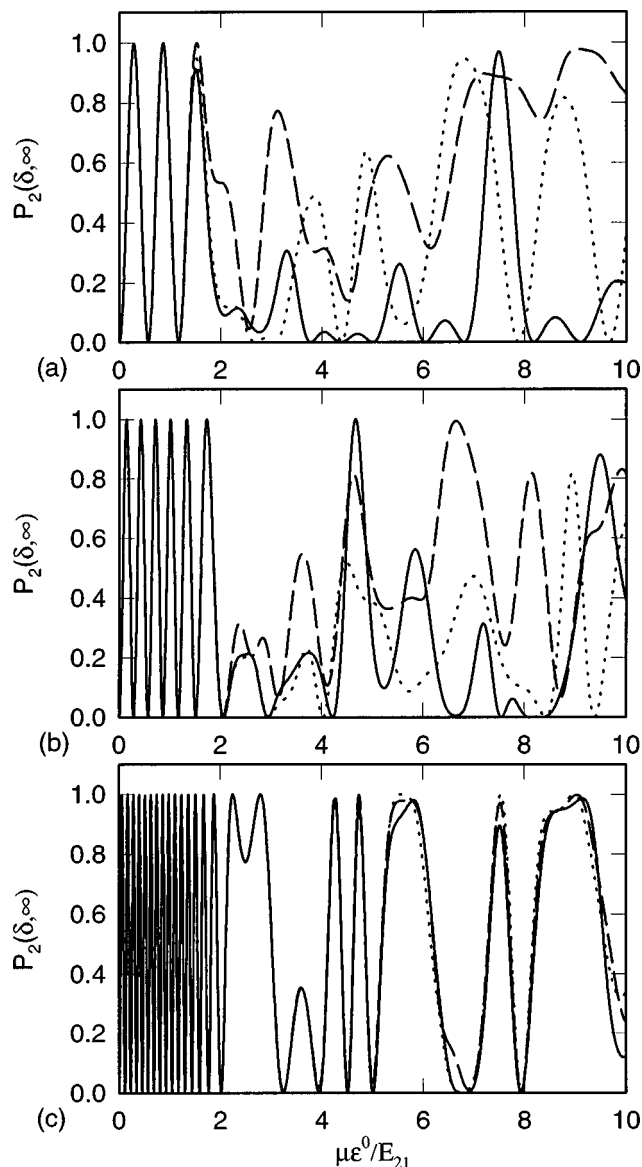


FIG. 4. Steady-state, phase-dependent excited state population, $P_2(\delta, \infty)$, versus scaled peak field strength, $\mu\epsilon^0/E_{21}$, for the model molecule interacting with a pulsed laser. The molecular parameters are as in Fig. 1 while the field parameters are $\omega=0.0859$, with (a) $\tau_p/(2\pi/\omega)=1$, (b) $\tau_p/(2\pi/\omega)=2$, and (c) $\tau_p/(2\pi/\omega)=5$; with $\delta=0$ (—), $\delta=\pi/4$ (---), $\delta=\pi/2$ (···).

ture gives the decay of the steady-state population of the excited state as a function of increasing pulse duration, the result is only qualitatively reliable. For example, similarly to the weak field resonance case of Fig. 2(a), i.e., $\omega=0.0859$, the period predicted by the pulsed RWA for $\omega=0.1438$, $0.305 \times 2\pi/\omega$ (13.3 a.u.), as compared to the exact “period” of oscillation, $\approx 0.380 \times 2\pi/\omega$ (16.6 a.u.), is too short. Note that the exact steady-state population does not vary in a totally periodic manner, i.e., the distance between the zeroes in Fig. 2(b) varies from $0.320 \times 2\pi/\omega$ to $0.410 \times 2\pi/\omega$. Also, of course, the Rosen–Zener result for $P_2(\infty)$ is independent of phase δ whereas the exact results of Figs. 1(b) and 2(b) show a phase dependence for small τ_p .

Figure 4 shows the steady-state, phase-dependent, excited state population as a function of increasing

molecule-cw electric field strength coupling parameter $b = \mu_{12}\epsilon^0/E_{21}$ with the laser frequency set at its weak field one-photon resonance value, $\omega=E_{21}=0.0859$, for three pulse durations: (a) $\tau_p/(2\pi/\omega)=1$; (b) $\tau_p/(2\pi/\omega)=2$; and (c) $\tau_p/(2\pi/\omega)=5$; the temporal behavior of the corresponding Gaussian pulses is given in Fig. 3 for the relevant choices of laser phase. As the coupling parameter (field strength) increases, the effects of phase become more pronounced for fixed τ_p . The phase effects are more important for a given field strength for shorter pulse durations. For example, for $b=2$, $P_2(\delta, \infty)$ is phase dependent when $\tau_p/(2\pi/\omega)=1$ while the steady-state excited state population is phase independent for $\tau_p/(2\pi/\omega)=5$. On the other hand, for $\tau_p/(2\pi/\omega)=5$, when the molecular coupling parameter is increased to $b \geq 5$ (small) phase dependencies occur in the steady-state excited state population; for $\tau_p/(2\pi/\omega)=1$ and 2, the phase dependencies are large for $b \geq 5$. While the phase dependence of the steady-state excited state population varies with pulse duration for a fixed field strength (molecule-EMF coupling strength parameter), the phase dependence of the dynamics, contained within the pulse envelope, is determined largely by the laser-molecule coupling strength parameter. The criteria for the phase dependence or phase independence of the dynamics in pulsed laser-molecule interactions and in cw laser-molecule interactions are essentially the same. That is, if $b \ll 1$, the time-dependent, and also the associated steady-state, populations will be phase independent. However, for $b \geq 0.2$, the dynamics associated with the pulsed laser-molecule interaction will be phase dependent while the phase dependence of the steady-state excited state population must be examined for every pulse duration of interest

For weak field strengths, Eq. (7) correctly predicts the oscillations of $P_2(\infty)$ as a function of increasing field strength for fixed τ_p as well as its phase independence but, as ϵ^0 increases, the predictions of the RWA become less reliable. For example, the RWA, i.e., Eq. (7), and the exact results agree over the first one and a half periods of oscillation in Fig. 4(a), the first three periods in Fig. 4(b), and the first six periods in Fig. 4(c). The pulsed RWA predicts the periods of oscillation to be 0.564, 0.282, and 0.113 for $\tau_p/(2\pi/\omega)=1, 2$, and 5, respectively while, for the exact calculations, the “period” generally increases with increasing field strength, more so for small τ_p values. For the exact results, the distances between the zeros of $P_2(\infty)$ in Fig. 4 are $\approx 0.567, 0.599, \dots, \approx 0.284, 0.284, 0.293, 0.307, \dots$, and remain at ≈ 0.114 for the first six oscillations, before increasing to 0.119, 0.128, \dots , as ϵ^0 increases, for $\tau_p/(2\pi/\omega)=1, 2$, and 5, respectively. Graphically the occurrence of phase dependence lags behind the variable “period” dependence of the exact calculations as $\mu_{12}\epsilon^0/E_{21}$ increases for a given τ_p . The steady-state excited state population as a function of increasing coupling parameter $\mu\epsilon^0/E_{21}$ is not illustrated or discussed for the fixed-phase ($\delta=0$) resonance frequency, $\omega=0.1438$, since it quickly approaches zero for pulses of any appreciable duration [see Fig. 1(b), Fig. 2(b), and previous discussion].

Next we consider the real molecule ($d \neq 0$), in order to determine the effects of the presence of permanent dipole

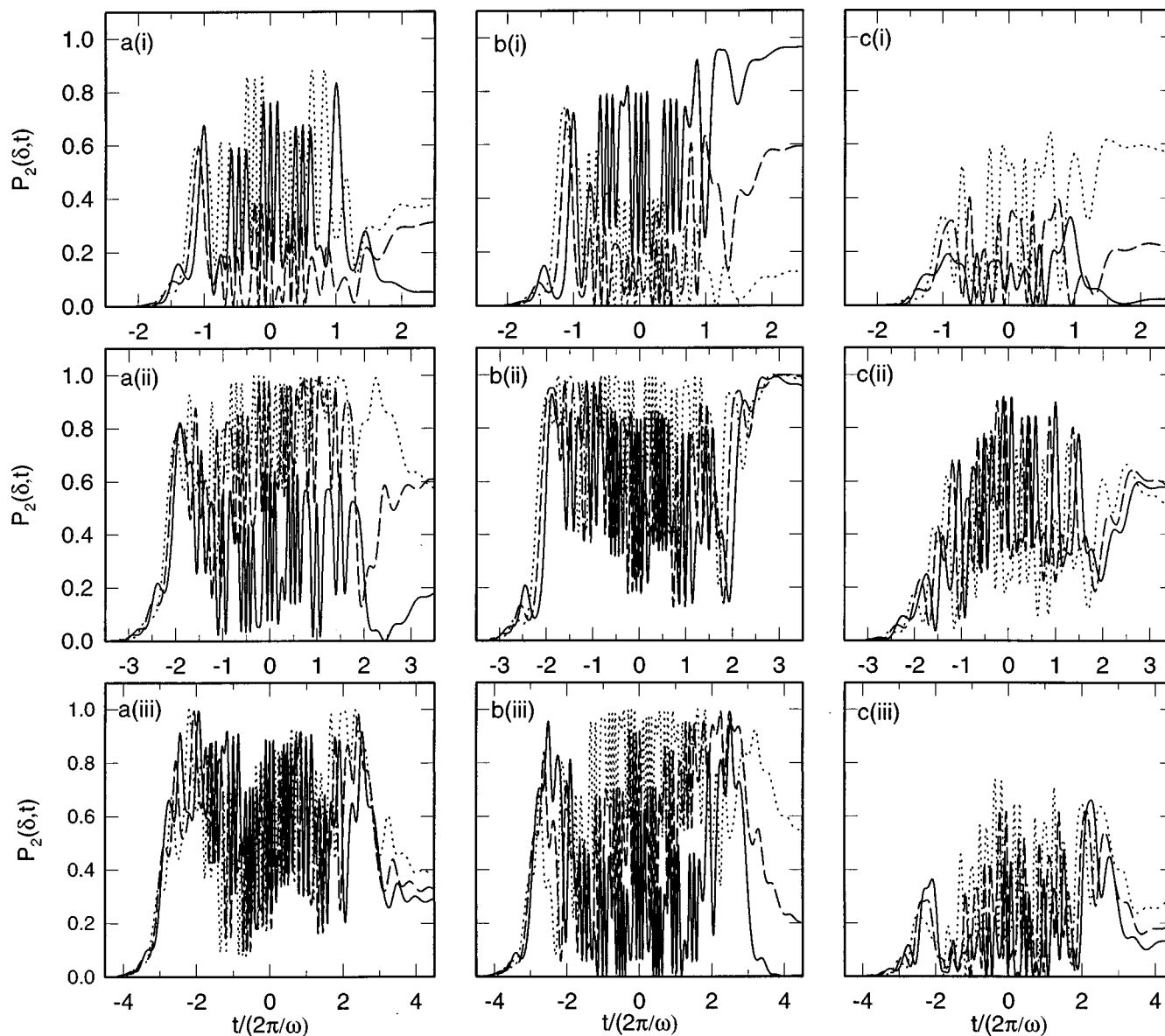


FIG. 5. Time-dependent, phase-dependent excited state population, $P_2(\delta, t)$, versus time in units of $(2\pi/\omega)$, for the model $d \neq 0$ molecule interacting with a pulsed laser of varying pulse width τ_p : (i) $\tau_p/(2\pi/\omega) = 1$; (ii) $\tau_p/(2\pi/\omega) = 1.6$; and (iii) $\tau_p/(2\pi/\omega) = 2$. The molecular and field parameters are $E_{21} = 0.0859$, $d = 11.8$, $\mu_{12} = 3.93$, $\epsilon^0 = 0.0677$, with (a) $\omega = 0.0859$, (b) $\omega = 0.0717$, and (c) $\omega = 0.1438$; with $\delta = 0$ (—), $\delta = \pi/4$ (---), $\delta = \pi/2$ (···).

moments on the dynamics and steady-state molecular populations associated with ultra-short intense phase-dependent pulsed laser-molecule interactions.

B. $d \neq 0$

A rotating wave approximation solution for the interaction of a cw electric field with a two-level system, including the effects of permanent dipoles has been obtained previously.^{7,42,43,52} For one-photon transitions, the usual atom(molecule)-EMF coupling ($\mu_{12} \cdot \hat{\epsilon} \epsilon^0$) is replaced by a frequency dependent effective molecule-EMF coupling $C(1) = 2\omega J_1(\mathbf{d} \cdot \hat{\epsilon} \epsilon^0 / \omega) (\mu_{12} / d)$, where $J_1(z)$ is the first-order Bessel function of argument z . Qualitatively, the effects of $d \neq 0$ on the pulsed laser-molecule RWA results of Sec. II can be obtained by replacing ($\mu_{12} \cdot \hat{\epsilon} \epsilon^0$) by $C(1)$ in Eqs. (4)–(7) and the effects of $d \neq 0$, relative to $d = 0$, on the dynamics of the excited state, $P_2(t)$ vs t including “ $t = \infty$,”

will be of particular interest later. More details on the molecular $d \neq 0$ RWA for pulse-molecule interactions will be provided in a subsequent paper.

Figure 5 gives illustrative examples of the exactly calculated time-dependent, phase-dependent excited state population, $P_2(\delta, t)$, versus time for the model ($d \neq 0$) molecule interacting with a Gaussian pulsed laser of varying pulse duration. Each part of the figure contains three curves which correspond to $\delta = 0$ (—), $\delta = \pi/4$ (---), and $\delta = \pi/2$ (···); for $d \neq 0$, the results for $P_2(\delta, t)$ are not symmetric about $\delta = \pi/2$ (see Figs. 6 and 7, and their discussion). In Fig. 5(a) the laser frequency is set to the weak field resonance frequency, $\omega = E_{21} = 0.0859$; in Fig. 5(b) it is set to the fixed-phase ($\delta = 0$) continuous wave resonance frequency of $\omega = 0.0717$; and in Fig. 5(c) it is set to the $d = 0$ fixed-phase ($\delta = 0$) continuous wave resonance frequency of $\omega = 0.1438$. Each section of the figure contains three parts,

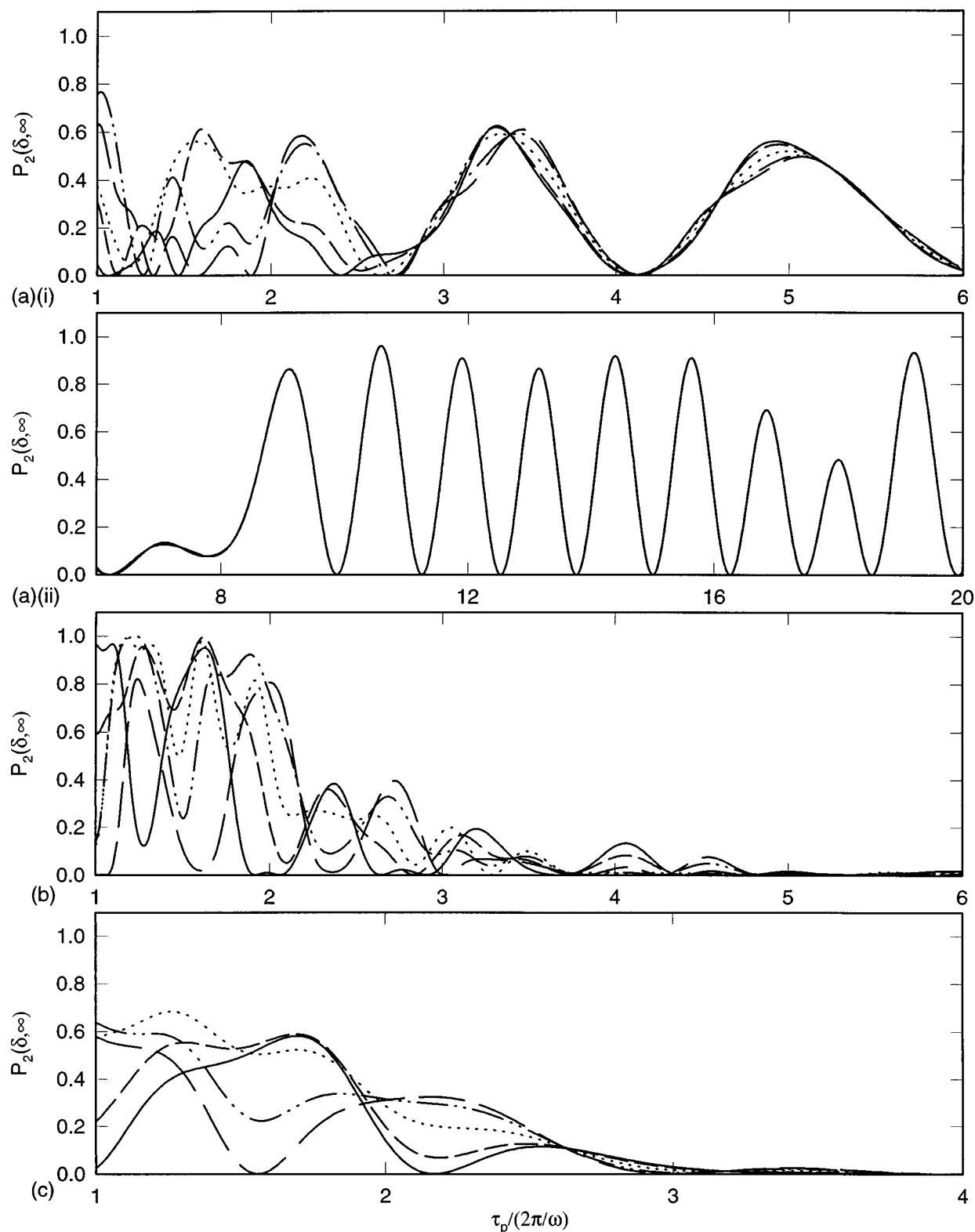


FIG. 6. Steady-state, phase-dependent excited state population, $P_2(\delta, \infty)$, versus pulse duration, $\tau_p/(2\pi/\omega)$, for the model molecule interacting with a pulsed laser. The molecular parameters are as in Fig. 5 while the field parameters are $e^0=0.0677$, with (a) $\omega=0.0859$, (b) $\omega=0.0717$, and (c) $\omega=0.1438$; with $\delta=0$ (—), $\delta=\pi/4$ (---), $\delta=\pi/2$ (···), $\delta=3\pi/4$ (-·-·-), $\delta=\pi$ (- - -). Part (a) of this figure is presented in two portions, (i) and (ii), in order to illustrate the phase dependence of the steady-state population of the excited state with clarity for $\tau_p/(2\pi/\omega) \leq 6$.

(i)–(iii), which show the effects of an increase in pulse duration for $\tau_p/(2\pi/\omega)=1, 1.6$, and 2 , that is, τ_p is the same for Fig. 5(a) as in Fig. 1(a), the same for Fig. 5(c) as in Fig. 1(b), while for Fig. 5(b) when $\omega=0.0717$, $\tau_p=87.632$

(2.1197 fs), 140.211 (3.3915 fs), and 175.263 (4.2394 fs). Calculations have been carried out for $\tau_p/(2\pi/\omega)=1.2, 1.4$, and 1.8 but are omitted here for reasons of graphical clarity. All three parts of Fig. 5(a), (b), and (c), clearly illustrate that

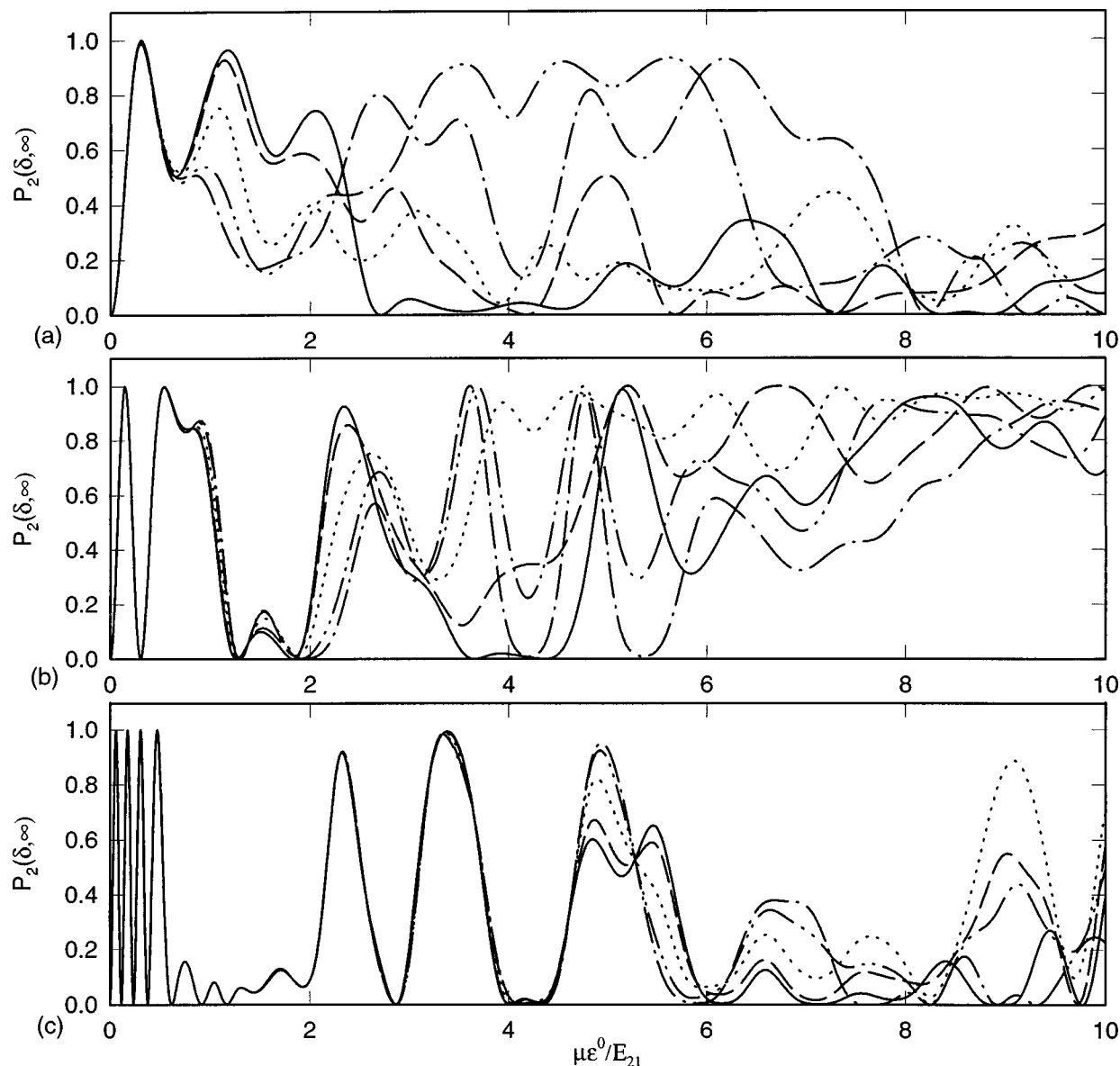


FIG. 7. Steady-state, phase-dependent excited state population, $P_2(\delta, \infty)$, versus scaled peak field strength, $\mu_{12}\epsilon^0/E_{21}$, for the model molecule interacting with a pulsed laser. The molecular parameters are as in Fig. 5 while the field parameters are $\omega=0.0859$, with (a) $\tau_p/(2\pi/\omega)=1$, (b) $\tau_p/(2\pi/\omega)=2$, and (c) $\tau_p/(2\pi/\omega)=5$; with $\delta=0$ (—), $\delta=\pi/4$ (---), $\delta=\pi/2$ (···), $\delta=3\pi/4$ (-·-·-), $\delta=\pi$ (- - -).

both the dynamics and the steady-state population of the excited state depend on the phase of the sinusoidal field contained within the pulse envelope for the τ_p considered in the figure. The steady-state excited state population, $P_2(\delta, \infty)$, which is of particular interest, is shown as a continuous function of increasing pulse duration in Fig. 6(a), (b), and (c) for $\omega=0.0859$, 0.0717, and 0.1438, respectively, for $\delta=0, \pi/4, \pi/2, 3\pi/4$ and π . Note the change in the pulse duration scales for the three parts of the figure. The results of Fig. 6 illustrate the lack of symmetry of the calculations about $\delta=\pi/2$, for $d\neq 0$, mentioned previously.

When the frequency equals the weak field resonance value of $\omega=0.0859$ [Figs. 5(a) and 6(a)], the steady-state population oscillates between zero and a value less than unity for the values of τ_p considered in the figures. As the pulse duration increases, the maximum value of $P_2(\delta, \infty)$ approaches one; calculations extending Fig. 6(a) to $\tau_p\leq 40$

yield a total of 17 peaks between $20\leq\tau_p\leq 40$ with maxima ranging from $P_2(\delta, \infty)=0.77-1.00$ and averaging ≈ 0.94 [excluding a peak at $\tau_p=20.4$ where $P_2(\delta, \infty)=0.20$]. Relative to the analogous $d=0$ results of Fig. 2(a), the attainment of a maximum steady-state population of unity for $d\neq 0$ requires much longer pulse durations ("times"). Excitation on the very leading edge of the pulse is similar for both the $d=0$ and the $d\neq 0$ molecule [compare Figs. 1(a) and 5(a)] since for one-photon transitions the effects of $d\neq 0$ only become appreciable for stronger field strengths.^{7,42,43,52} Therefore, the differences between the $d\neq 0$ and the $d=0$ results can qualitatively be explained by considering the strong field part of the pulse. For the interaction of a cw laser, relative to $d=0$, there is always a reduced one-photon molecule-EMF coupling due to the presence of permanent dipoles ($d\neq 0$) which is reflected in a longer period in the cw temporal behavior.^{42,43,52} In general, for pulse-molecule interactions,

the excited state cannot become fully populated for pulse durations shorter than the Rabi half-period of the underlying cw temporal behavior of $P_2(\delta, t)$.^{35,51,55} For example, when $\omega = 0.0859$ and the field strength $\epsilon^0 = 0.0677$, the exactly calculated $d \neq 0$ resonance period is τ_E is ≈ 8.8 fs, $\tau_E/(2\pi/\omega) \approx 5$, for all phases δ , while for $d=0$, the resonance period is < 1 fs for all phases δ . Therefore, $P_2(\infty)$ does not reach unity for short pulse durations when $d \neq 0$ [see Fig. 6(a)] but does reach unity for $d=0$ [Fig. 2(a)]. These observations reinforce earlier work³⁵ emphasizing that ultra-short to short pulses can be used to monitor temporal, as well as steady-state, effects of $d \neq 0$. Note, however, that for this strong field strength, arguments based on the cw behavior are only qualitatively reliable due to four main effects:³⁵ (i) the bandwidth of the laser may allow frequencies other than the carrier frequency to induce transitions; (ii) cw resonance frequencies depend on the field strength which is a function of time for pulses; (iii) the available cw calculations assume an initial zero population of the excited state while for the associated pulse calculations the excited state may be populated when the cw pattern begins to appear around the center of the pulse; and (iv) when $d \neq 0$, the one-photon cw molecule-EMF coupling, while always less than the corresponding $d=0$ molecule-EMF coupling, may decrease (increase) with increasing (decreasing) field strength ϵ^0 due to its (damped) oscillatory nature as a function of increasing field strength (for further discussion, see Refs. 7, 35, 42, 43, 52).

When $\omega = E_{21}$, the one-photon transition is readily driven at the weak field resonance frequency during the weak field part of the pulse and the excited state *can* become fully populated if the duration of the pulse is long enough. However, during the strong field part of the pulse, the one-photon transition is not driven very efficiently since the weak field frequency is off-resonance compared to the Bloch–Siegert shifted $\delta=0$ (or $\delta=\pi/4$ and $\pi/2$) cw resonance frequency, $\omega = 0.0859$ versus $\omega = 0.0717$ (or 0.0684 and 0.0717), respectively, and the population is “trapped” in (or out of) the excited state. See, for example, Fig. 5(a)(ii) where for $-1 \leq t/(2\pi/\omega) \leq 1$, the population varies between zero and 0.6 for $\delta=0$ (“trapping” out of the excited state), while the excited state population varies between 0.8 and unity for $\delta = \pi/2$ (“trapping” in the excited state). The relative weakness of the $d \neq 0$ one-photon molecule-EMF coupling where there is population trapping [Fig. 5(a)] can be compared with the correspondingly strong $d=0$ coupling where the excited state is more readily populated and depopulated [Fig. 1(a)] during the strong field part of the pulse. Finally, on the trailing edge of the pulse, the one-photon transition is again driven efficiently and, as a result, the excited state can be readily depopulated (or populated) by laser-molecule interactions; see, for example, Fig. 5(a)(iii) where the excited state is readily depopulated for all δ . As with the $d=0$ results, when the pulse duration is short, $\tau_p/(2\pi/\omega) \leq 3$, there can be a large dependence of the steady-state excited state population on phase, for example, when $\tau_p/(2\pi/\omega) = 1.6$, $P_2(0, \infty) = 0.20$, $P_2(\pi/4, \infty) = 0.61$, $P_2(\pi/2, \infty) = 0.58$, $P_2(3\pi/4, \infty) = 0.11$, and $P_2(\pi, \infty) = 0.00$; see Fig. 5(a)(ii) and Fig. 6(a)(i). However, as the pulse duration increases,

the phase dependence vanishes; see Fig. 6(a)(ii). Although the phase effects occur at approximately the same pulse durations for both the $d \neq 0$ molecule [see Fig. 6(a)(i)] and the $d=0$ molecule [see Fig. 2(a)], these phase dependencies bear little resemblance to one another.

When the frequency equals the exact ($d \neq 0$) $\delta=0$ continuous wave resonance value of $\omega = 0.0717$ [Figs. 5(b) and 6(b)], the steady-state population decreases to zero relatively rapidly for increasing pulse duration, this is more clearly illustrated in Fig. 6(b). The reduction of the steady-state excited state population for an “off-resonance” frequency is in agreement with the Rosen–Zener conjecture. Interestingly, unlike the results for the weak field resonance frequency, for short pulses before the damping effect becomes relevant ($\tau_p/(2\pi/\omega) \leq 2$), $P_2(\infty)$ oscillates between zero and unity, compare Figs. 6(a) and (b) for small τ_p . Except for the very large discrepancy in the steady-state populations, the excited state dynamics for the weak field resonance frequency and the cw resonance frequency [see Fig. 5(a) and (b), respectively] contain similarities: ready excitation on the leading and trailing edges of the pulse and population “trapping.” The similarities can probably be attributed to the fact that the frequencies essentially overlap due to the spectral bandwidth associated with a pulse of duration of τ_p which has a full width at half-maximum $\Delta\omega = 4(\ln 2)^{1/2}/\tau_p$: for the pulse durations and frequencies considered, i.e., for $1 \leq \tau_p/(2\pi/\omega) \leq 2$ with $\omega = 0.0859$ and $\omega = 0.0717$, $0.010 \leq \Delta\omega \leq 0.023$.

When the frequency equals the exact ($d=0$) $\delta=0$ continuous wave resonance value of $\omega = 0.1438$ [Figs. 5(c) and 6(c)], $P_2(\infty)$ decreases to zero rapidly for increasing pulse duration, more clearly illustrated in Fig. 6(c). Note that $P_2(\infty)$ decreases to zero more rapidly for this further off-resonance frequency, than when $\omega = 0.0717$, as predicted by the Rosen–Zener conjecture. The excited state dynamics in Fig. 5(c) where $\omega = 0.1438$ are quite distinct from those of Fig. 5(a) and (b). Unlike when $\omega = 0.0859$ and $\omega = 0.0717$, there is a reduced overlap of frequencies due to the spectral bandwidth of the laser; see above and for $1 \leq \tau_p/(2\pi/\omega) \leq 2$ when $\omega = 0.1438$, $0.038 \leq \Delta\omega \leq 0.076$. Also, when $\omega = 0.1438$, the frequency is off-resonance in both the weak and the strong field parts of the pulse and the main reason there is any appreciable excitation is probably due to power broadening effects because of the strength of the molecule-EMF coupling.

It is interesting to compare $P_2(\delta, \infty)$, for the common frequency $\omega = 0.1438$, for the $d \neq 0$ [Fig. 6(c)] versus the $d=0$ [Fig. 2(b)] molecule. The smaller number of increasing damped oscillations in $P_2(\delta, \infty)$ as a function of increasing $\tau_p/(2\pi/\omega)$, for $d \neq 0$ relative to $d=0$, is consistent with the RWA based Rosen–Zener conjecture, Eq. (7), with a reduced molecule-EMF coupling for the $d \neq 0$ relative to the $d=0$ molecule, as predicted by the RWA for cw laser-molecule interactions. As discussed in Sec. III A for $d=0$, Eq. (7) is only qualitatively reliable and fails to predict the phase dependence in $P_2(\delta, \infty)$ for $d \neq 0$ as well as $d=0$.

Figure 7 illustrates the steady-state, phase-dependent excited state population as a function of increasing molecule-cw electric field coupling parameter $\mu_{12}\epsilon^0/E_{21}$ with the laser frequency set at its weak field one-photon reso-

nance value, $\omega = E_{21} = 0.0859$, for three pulse durations: (a) $\tau_p/(2\pi/\omega) = 1$; (b) $\tau_p/(2\pi/\omega) = 2$; and (c) $\tau_p/(2\pi/\omega) = 5$. $P_2(\delta, \infty)$ is shown as a function of $\mu_{12}\epsilon^0/E_{21}$ in order to compare Figs. 3 and 7 on the same scale. In this regard it is important to recognize that $P_2(\delta, \infty)$ for $d \neq 0$ is not a simple sinusoidal function of increasing $\mu_{12}\epsilon^0/E_{21}$ as it is for $d = 0$. For example, within the RWA, for $d \neq 0$, $(\mu_{12} \cdot \hat{e} \epsilon^0)$ is replaced, in Eq. (7), by $C(1) = 2\omega J_1(d\epsilon^0/\omega)(\mu_{12}/d)$, which is a nonlinear function of field strength; J_1 is the first-order Bessel function of argument $(d\epsilon^0/\omega)$. The steady-state behavior for $d \neq 0$ (Fig. 7) and $d = 0$ (Fig. 3) is quite similar at relatively weak field strengths, $\mu_{12}\epsilon^0/E_{21} < 0.2$, since for these field strengths the effects of $d \neq 0$ are small and $C(1) \approx (\mu_{12}\epsilon^0)^{7,35,42,43,52}$. For larger field strengths, $C(1)$, which involves the Bessel function, exhibits much different behavior than the linear behavior of the $d = 0$ molecule-EMF coupling: it is, in general, much weaker and is an oscillatory function of increasing field strength (see Fig. 2 of Ref. 52). The differences between Fig. 4 and Fig. 7 as $\mu_{12}\epsilon^0/E_{21}$ increases are due to the effects of permanent dipoles in the latter results. These generally are not well represented by the pulsed RWA, Eq. (7) with $E_{21} - \omega = 0$ and with $(\mu_{12} \cdot \hat{e} \epsilon^0)$ replaced by $C(1)$, since the RWA, with or without $d \neq 0$, fails with increasing field strength. As with the $d = 0$ results, the effects of phase, not predicted in the RWA, increase with increasing ϵ^0 for fixed τ_p , and are more pronounced for fixed ϵ^0 for decreasing τ_p . As pointed out previously, the results for $d \neq 0$ are not symmetric about $\delta = \pi/2$ (see Fig. 7) while those for $d = 0$ are symmetric about $\delta = \pi/2$.

IV. CONCLUDING REMARKS

The effects of (absolute) laser phase δ , and permanent molecular dipoles, in (Gaussian) pulse-molecule interactions have been investigated using a two-level molecular model, characterized by a transition dipole moment $\mu_{12} = 3.93$, an energy level separation $E_{21} = 0.0859$, and a dipole moment difference $d = \mu_{22} - \mu_{11} = 11.8$, based on the electronic $S_0 \rightarrow S_1$ transition in 1-[*p*-(*N,N*-dimethylamino)phenyl]-4-(*p*-nitrophenyl)-1,3-butadiene. Both effects can be large, depending on the values of the laser field strength ϵ^0 and the pulse duration τ_p , and those for $d = 0$, relative to $d \neq 0$, are investigated by ‘‘artificially’’ setting $d = 0$ in the real molecule to model a transition involving states with no permanent dipoles or the situation of interpreting the $S_0 \rightarrow S_1$ transition in the dipolar molecule without realizing the importance of the permanent dipoles in such a transition.

For the $d = 0$ molecule, both the time-dependent and the steady-state populations of the excited state, $P_2(\delta, t)$ and $P_2(\delta, \infty)$ respectively, are investigated for the laser frequencies $\omega = E_{21}$ and $\omega = 1.674E_{21}$ as a function of τ_p , $1 \leq \tau_p/(2\pi/\omega) \leq 4$, varying from approximately 1 fs to 7 fs, for a fixed peak laser field strength of $\epsilon^0 = 0.0677$, corresponding to a peak field intensity of 1.6×10^{14} W/cm² (Figs. 1 and 2). Both $P_2(\delta, t)$, and its steady-state value $P_2(\delta, \infty)$, can exhibit strong phase dependence with that for the steady-state population decreasing as τ_p increases [so that $\tau_p/(2\pi/\omega) \geq 2.5$ for $\omega = E_{21}$] even though the phase dependence in the dynamics of the excited state can still persist as τ_p increases. The steady-state value of $P_2(\delta, t)$, for a given

δ , depends on τ_p for both choices of frequency until, in the case of the ‘‘off-resonance’’ frequency $\omega = 1.674E_{21}$, the pulse duration becomes sufficiently large that $P_2(\delta, \infty) \rightarrow 0$ [as predicted by Rosen and Zener’s steady-state pulsed RWA result of Eq. (7)]. The disappearance of the laser phase dependence of $P_2(\delta, \infty)$ for increasing pulse duration is apparently due to the decreasing phase dependence of the maximum laser field strength $\epsilon^{\max} = \epsilon^0 \exp\{-\delta/(\omega\tau_p)\}^2$, and to the increase in the duration of the weak field strength regions of the pulse, as τ_p increases. For the Gaussian pulse envelopes considered here, where the pulse duration controls both the pulse rise (fall) time and the number of optical cycles within the pulse, pulses with relatively few total optical cycles are required to see absolute phase effects. While this is not a difficulty in some regions of the electromagnetic spectrum,^{11,56–59} it is for frequencies associated with electronic transitions.^{58–60} However, as discussed in Sec. III A, the requirement of a few optical cycles is not needed in general. In fact, as long as b is such that absolute laser phase effects are seen in the corresponding cw laser-molecule interaction (i.e., $b > 0.2$), it is the rise and fall times of the pulse which are crucial, and not the total number of optical cycles; see also Ref. 11.

The phase dependence of $P_2(\delta, \infty)$, for fixed values of τ_p , $\tau_p/(2\pi/\omega) = 1, 2$, and 5, has also been investigated as a function of the laser-molecule coupling strength parameter $b = \mu_{12}\epsilon^0/E_{21}$ for values of b ranging from zero to 10 with $\omega = E_{21}$ (Fig. 4). The phase dependence of the steady-state population of the excited state increases, for fixed τ_p , as b increases, in agreement with previous cw work,^{5,6} and decreases, for fixed b , as τ_p increases. When the cw RWA ‘‘fails,’’ i.e., when $b \geq 0.2$, and the cw temporal results for the population of the excited state are phase dependent, the dynamics in a corresponding pulsed calculation will be phase dependent, independent of the pulse duration, while the corresponding steady-state population of the excited state may or may not be phase dependent, depending on the pulse duration. As illustrated in Sec. III, for both the $d = 0$ and the $d \neq 0$ results, to interpret the phase dependence of $P_2(\delta, t)$ and its steady-state value, it is important to recognize that the field strength for pulsed laser-molecule interactions is a function of time and therefore the shift of the resonance frequency from the weak field resonance result of $\omega = E_{21}$, the Bloch–Siegert shift, changes with time as the pulse interacts with the molecule.

All the calculations just discussed above are repeated in Sec. III B for the real ($d \neq 0$) molecule with an additional frequency $\omega = 0.835E_{21}$, and a larger range of pulse durations in the analysis of the steady-state results, included in the calculations. The presence of the permanent dipoles has two pronounced effects relative to the $d = 0$ situation; (1) the laser-molecule coupling is markedly reduced and (2) the phase dependence of the excited state populations is symmetric about $\delta = \pi$ rather than $\delta = \pi/2$. Aside from the difference in δ symmetry, the phase dependence of the dynamics of the excited state, $P_2(\delta, t)$, and of the steady-state population $P_2(\delta, \infty)$, are analogous to that discussed for $d = 0$ if due account is taken of the considerably weaker molecule-laser couplings for the $d \neq 0$ problem. All differ-

ences between the two sets of results, which are significant, are of course due to the presence of permanent dipoles in the real versus the “artificial” molecule.

The time evolution of the excited state, and the steady-state value of the population of the excited state, show pronounced laser phase dependencies for all values of τ_p , and for the three values of ω , considered in Fig. 5. Relative to $d=0$, the weakness of the $d\neq 0$ one-photon molecule-EMF coupling causes population trapping, either in or out of the excited state, which depends intimately on the laser phase and the pulse duration; for $d=0$, the excited state is much more readily populated and depopulated during the strong field part of the pulse. The relatively small $d\neq 0$ molecule-EMF coupling, resulting in a longer period of the underlying cw temporal behavior of the excited state population relative to $d=0$, is also reflected in the long times (large τ_p), relative to $d=0$, required to observe large values, approaching unity, of $P_2(\delta, \infty)$ for $\omega = E_{21}$ [Fig. 6(a) versus Fig. 2(a)]. For the “off-resonance” frequencies, $\omega = 0.835E_{21}$ and $\omega = 1.674E_{21}$, the steady-state population $P_2(\delta, \infty)$ rapidly approaches zero for increasing pulse duration (Fig. 6) with the approach to zero being more rapid for the further “off-resonance” frequency in agreement with the pulsed RWA result [Eq. (7)] for the steady-state population of the excited state. The dynamics of the excited state for the two “off-resonance” frequencies are also quite different [compare Fig. 5(b) and (c)] since for $\omega = 1.674E_{21}$ the frequency of the laser is off-resonance in both the weak and the strong field parts of the pulse whereas $\omega = 0.835E_{21}$ is “near-resonance” and on-resonance, respectively. As with the $d=0$ results, the laser phase dependence of $P_2(\delta, \infty)$ for $d\neq 0$ is large for relatively small values of $\tau_p/(2\pi/\omega)$, for example, ≤ 5 for $\omega = E_{21}$ and $\omega = 0.835E_{21}$, and ≤ 3 for $\omega = 1.674E_{21}$; the phase dependencies for the three sets of calculations bear little resemblance to each other.

The steady-state population of the excited state for $d\neq 0$ and $d=0$ are essentially identical for small enough $b = \mu_{12}\epsilon^0/E_{21}$, since the molecule-EMF coupling $C(1)$, including the effects of $d\neq 0$, is approximately equal to the $d=0$ result, $\mu_{12}\epsilon^0$, for small b (Fig. 7 versus Fig. 4, $\omega = E_{21}$). Differences occur as b increases and strong phase effects in the $d\neq 0$ results occur as b increases with higher b values being required as the pulse duration increases, for example, $b \geq 0.7$, $b \geq 1.5$, and $b \geq 4.7$ for $\tau_p/(2\pi/\omega) = 1, 2$, and 5, respectively. Specific comparisons between the $d=0$ and the $d\neq 0$ results are complicated by the fact^{42,43,52} that the molecule-EMF coupling for $d\neq 0$ is not a linear function of ϵ^0 , whereas it is for $d=0$. The massive differences between the $d\neq 0$ and the $d=0$ results for $P_2(\delta, \infty)$, for all δ , with increasing ϵ^0 are due to permanent dipole effects in the laser-molecule interactions.

While the pulsed RWA results reviewed in Sec. II are very useful in helping to explain some of the effects discussed in this paper involving the variation of $P_2(\delta, \infty)$ as a function of τ_p and ϵ^0 , the predictions of the RWA are qualitative, at best, for most values of $b = \mu_{12}\epsilon^0/E_{21}$. Also, since the RWA is independent of the laser phase, none of the phase effects discussed in this paper can be predicted by the results reviewed in Sec. II.

The phase dependence of the population of excited state 2 can, in principle, be examined in several ways. For example, this state can be probed with a second laser and the phase dependence studied by monitoring the resulting population in a “third” state. The study of the phase dependence of the dynamics, that is, $P_2(\delta, t)$, requires having a probe laser with a duration less than the original pump laser and so the pump laser would probably need to be of at least picosecond duration rather than of the femtosecond duration studied explicitly here. On the other hand, a probe laser of a duration appropriately greater than that of the pump laser, yet shorter than the lifetime of excited state 2, could be used to monitor the phase dependence of the steady-state population of this state; indeed the phase dependence of the excited state will also be reflected in the observed decay from this state. Similar comments apply to the observation of the effects of permanent dipoles on laser-molecule interactions and this has been discussed previously in the literature.³⁵

For electronic transitions, such as those associated explicitly with our two-level model molecule, many of the effects of absolute laser phase discussed in Sec. III A, and summarized briefly in this section, will require short, intense laser pulses which are at or beyond the limits of current laser technology in the UV-VIS spectral region.⁶⁰ Also, since the intensities used are often at or beyond the Keldysh limit,^{61–63} the molecule would ionize and so a two-level model would not be directly applicable. For example, the laser intensity associated with Fig. 1, which corresponds to $b = 3.1$, is 1.6×10^{14} W/cm² which is at the Keldysh limit for the model molecule and therefore as b increases the calculations become more unrealistic. On the other hand, the effects of laser phase can become important for $b > 0.2$ and for $b = 0.2$ the intensity is 6.6×10^{11} W/cm². Similar comments apply for the $d\neq 0$ results of Sec. III B with the proviso that, for most laser intensities, the laser-molecule coupling is much reduced for the real $d\neq 0$ molecule relative to the $d=0$ molecule. Indeed the laser intensities of Figs. 1 and 5 are associated with near nodal one-photon laser-molecule couplings for the model dipolar molecule employed for the calculations.^{35,64} In general, the results of this paper, insofar as electronic transitions are concerned, must be used with caution with respect to interpreting absolute laser phase effects for many-level laser-molecule interactions. Nevertheless, they should be suggestive of such effects that will manifest themselves, in one way or another, in the pulsed laser excitation of real molecules. For other spectral regions, these absolute laser phase effects will be much more directly applicable using current laser technology, see below.

The importance of two-level models for laser-molecule and laser-atom interactions has been well documented in the literature. These models have their limitations and are directly useful as models, in many-level contexts, only if the effects of other energy levels, on the two-level transition of interest, are minimal. An example of the use of two-level models for dipolar molecules, in the laser excitation of a two-level system embedded in a many-level environment, in the context of the effects of permanent dipoles, can be found in the literature.⁶⁵ An example of the effects of laser phase in many-level vibrational systems, referred to in Sec. I, has

been discussed previously.¹⁰ The two-level model studied here has been selected, in part, because of its relevance in the study of the effects of permanent dipoles in laser-molecule interactions involving electronic transitions.^{35,43,54,64} In this context, vibrational and rotational structure is neglected and each electronic state is effectively represented by one energy level. In some cases the two levels can be intrinsically isolated from other energy levels of the system, for example, Refs. 9 and 66; another example is contained in the discussion below.

As pointed out earlier, while the numerical results of Sec. III are based on molecular parameters characteristic of the $S_0 \rightarrow S_1$ electronic transition in a particular dipolar molecule, they are presented in terms of the dimensionless laser-molecule coupling parameter $b = \mu_{12} \epsilon^0 / E_{21}$, and with both time and pulse duration in units of $(2\pi/\omega)$, and so can be scaled to other frequency and time regimes. Thus for example, to obtain absolute laser phase effects like those associated with Fig. 1 for infrared, microwave, and radiofrequency transitions, characterized by frequencies on the order of THz, GHz, and 300 MHz, will require pulse durations on the order of picoseconds, nanoseconds, and again nanoseconds, which are available in these frequency regimes.^{11,56,57,67} Also, the relatively large laser-molecule coupling parameter b associated with this figure, and larger, can be obtained in these spectral regions using lasers of much less intensity than is required for electronic transitions due to the inverse dependence of b on E_{21} . This is illustrated in a paper that became available while the present paper was under review. Griffith *et al.*¹¹ have reported absolute laser phase effects associated with the pulsed radiofrequency excitation of the anti-crossing of the potassium $21s-19f$ states. The paper contains both experimental results and a theoretical analysis, based on a two-level model, which is in agreement with these experimental results. The paper shows that absolute laser phase effects can be obtained using pulses of any number of optical cycles provided that the laser rise and fall times are not appreciable. Other related precursor work can be found in Watkins *et al.*⁵⁶ and Baruch and Gallagher.⁶⁷ These papers and Ref. 11, as well as that of Xu *et al.*,⁵⁹ illustrate the current experimental interest in the development of laser pulses with specified phases.

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