PHYSICAL REVIEW A VOLUME 18, NUMBER 2 AUGUST 1978

ac Stark splitting in doubly resonant three-photon ionization with nonmonochromatic fields

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(Received 27 January 1978)

We present a theory of Stark splitting in doubly resonant three-photon ionization (three-level system) with nonmonochromatic fields. The asymmetry of the peaks of the resonance curve due to Stark splitting is shown to be reversed when the laser bandwidth is larger than the width of the atomic transitions of the resonant states. It is further shown that ionization as well as the probe field have a significant effect on the features of the splitting. Similar effects are found with monochromatic fields in the presence of an additional level near the initial level (four-level system). The results of the analysis are in general qualitative agreement with existing observations.

I. INTRODUCTION

Optical double resonance provides a simple technique for the study of intense field effects on atomic transitions. As is well known, an atomic transition undergoes Stark splitting under the influence of a (near-) resonant intense field. One way of interpreting this effect is to consider the atom and quantized radiation field as a single quantum system.[1] If the lower and upper atomic states $|1\rangle$ and $|2\rangle$, respectively, have energies $\hbar\omega_1$ and $\hbar\omega_2$, and the (near-) resonant incident radiation contains n photons of frequency ω, the uncoupled states $|A\rangle \equiv |1\rangle|n\rangle$ and $|B\rangle \equiv |2\rangle|n-1\rangle$ have energies $\hbar\omega_A = \hbar\omega_1 + n\hbar\omega$ and $\hbar\omega_B = \hbar\omega_2 + (n-1)\hbar\omega$ which are (nearly) degenerate if $\omega \cong \omega_2 - \omega_1$. The degeneracy is removed when one includes the interaction V coupling the field to the atom. In the simplest case of exact resonance ($\omega = \omega_2 - \omega_1$), the "new" energies of the states of the coupled systems (dressed states) are given by $\hbar\omega^{\pm} \equiv \frac{1}{2}\hbar(\omega_A + \omega_B) \pm \frac{1}{2}\langle B|V|A\rangle$ and are separated by $\langle B|V|A\rangle$ which is referred to as the dynamic (or ac) Stark splitting or the Rabi frequency. For this splitting to be observable, it must of course be larger than the natural width of level $|2\rangle$. It can then be detected through the observation of a weak transition from level $|2\rangle$ such as spontaneous emission or a weakly driven induced transition to a third level (double optical resonance in a three-level system). The effect of ac Stark splitting on the frequency spectrum of resonance fluorescence has been studied in considerable detail in the last two years. As for its effect on double optical resonance, measurements of the absorption spectrum by Bonch-Bruevich *et al.*[2] seem to be one of the first observations. More recently, Stark splitting effects have been observed in two additional types of experiments on three-level systems: Spontaneous emission experiments,[3,4] in which the fluorescence from the uppermost (third) level was used as the signal for the detection of the Stark splitting of the transition $|1\rangle \longleftrightarrow |2\rangle$. Ionization experiments[5-7] in which the splitting was detected through the observation of the total ionization from the uppermost level. Thus not only can ionization be used for the observation of Stark splitting effects but conversely such effects do influence resonant multiphoton ionization.

Theoretical papers on double resonance have been concerned with either the absorption or emission spectrum and the analysis has been mainly limited to steady-state solutions.[8-13] In this paper we present a theory of Stark splitting effects in doubly resonant three-photon ionization. The presence of ionization which constantly depletes the uppermost level introduces a qualitative new feature with a significant effect on the dynamics of the system. As a result, no steady state exists and the behavior is inherently time dependent which requires the complete solution of the differential equations for the density matrix or the probability amplitudes. Because of the number of equations involved, the solution is of course obtained numerically. Moreover, ionization has a number of further consequences on the dynamics. The widths of the peaks resulting from the Stark splitting are profoundly influenced by the strength of ionization. In fact, the peaks may be obliterated if the ionization becomes too strong. Also the heights of the peaks are affected by ionization. Owing to the absence of a steady state, most of the features of the peaks depend on the interaction time. As the interaction time increases, the peaks broaden and in the limit of long times—strictly speaking infinite—the peaks will disappear since all atoms are ionized independently of the probe frequency. Thus a three-level system with ionization exhibits several new interesting features which in addition to their relevance to Stark splitting experiments are of relevance to processes related to possible applications such as isotope separation.

As already implied above, in a double resonance of the type

$$|1\rangle \xrightarrow{\omega_a} |2\rangle \xrightarrow{\omega_b} |3\rangle,$$

the total signal of ionization from level $|3\rangle$—as a function of the second photon frequency ω_b—exhibits two peaks when the intensity of the beam of photons ω_a is sufficiently large to cause Stark splitting. The shape and detailed structure of the two-peaked curve depend on the atomic parameters, and the strength and stochastic properties of both the strong field (ω_a) and the weak probe field (ω_b). A nonresonant n-photon process depends only on the nth-order correlation function of the field where all field factors are evaluated at equal times. In a resonant process, however, because of the highly nonlinear nature of the saturation, the interaction depends on multitime field correlation functions of all orders.[10] Thus the Stark splitting in a double resonance experiment contains information about all stochastic properties of the field and provides its unique signature with many possible applications in the laboratory.

In Sec. II we consider the familiar three-level system,[8-12] appropriately extended to include ionization. We employ the density matrix in the semiclassical formalism with the fields treated as stochastic processes. The fields are here assumed to have constant amplitudes but phases fluctuating with Wiener-Levy statistics. The fluctuation of the phase gives the field a finite bandwidth. Note that certain aspects of the effect of nonmonochromatic fields on three-level systems have been discussed in Refs. 8–10 whereas Refs. 11 and 12 deal with monochromatic fields. A number of other papers[14-26] have in the last decade or so discussed the effect of nonmonochromatic fields on various resonance processes. In Sec. III we study the behavior of a four-level system with ionization in a monochromatic field. This is similar to the three-level system except that now the ground state is assumed to consist of two closely spaced levels both of which are dipole-connected to the intermediate level. Coupling these three levels with a strong field and probing—with a weak field—the transition from the intermediate to the upper level, the total ionization exhibits three peaks. Although the behavior of this system is substantially different, under certain circumstances certain of its Stark splitting features can be mistaken as those of a three-level system in a nonmonochromatic field. Moreover, a four-level system of this type can be found in real atoms. In Sec. IV we present representative results of numerical calculations. The emphasis is on the effects of the finite bandwidth of the fields, the strength of the probe, and of ionization on the process under consideration. Finally, in Sec. V we discuss approximate analytic solutions that can be obtained if one assumes weak ionization. Then a steady-state approximation can be made which enables one to exhibit certain results in closed form. These results provide additional insight into the physical interpretation of the role played by the laser bandwidth.

II. THREE-LEVEL SYSTEM WITH IONIZATION

We consider an atomic system with a ground state $|1\rangle$, two excited states $|2\rangle$ and $|3\rangle$, and an ionization continuum denoted by $|l\rangle$, with respective energies $\hbar\omega_i, i=1,2,3,l$ ($\omega_1<\omega_2<\omega_3<\omega_l$). The transitions $|1\rangle \leftrightarrow |2\rangle$ and $|2\rangle \leftrightarrow |3\rangle$ are assumed to be dipole allowed while $|1\rangle \leftrightarrow |3\rangle$ is dipole forbidden. In view of existing relevant experimental results, we also discuss the case of an electric quadrupole $|2\rangle \leftrightarrow |3\rangle$ transition. The atom is assumed to interact with two linearly polarized nonmonochromatic fields written as

$$\vec{E}_a(t)=\hat{e}_a[\epsilon_a(t)e^{i\omega_a t}+\text{c.c.}], \tag{1a}$$

$$\vec{E}_b(t)=\hat{e}_b[\epsilon_b(t)e^{i\omega_b t}+\text{c.c.}], \tag{1b}$$

where $\hat{e}_a$ and $\hat{e}_b$ are unit polarization vectors, ω_a and ω_b the center frequencies of the respective spectra, and $\epsilon_a(t)$ and $\epsilon_b(t)$ fluctuating complex amplitudes representing stochastic processes. The mathematical treatment in this paper is rigorous when the field undergoes phase fluctuations. As discussed later on, the quantitative treatment of amplitude fluctuations is extremely difficult and only partially understood. Their effect will be compared qualitatively to that of phase fluctuations.

In the case of phase fluctuations we write

$$\epsilon_a(t)=\epsilon_a e^{i\phi_a(t)}, \quad \epsilon_b(t)=\epsilon_b e^{i\phi_b(t)}, \tag{2}$$

where ϵ_a and ϵ_b are real constant amplitudes with $\phi_a(t)$ and $\phi_b(t)$ being fluctuating phases assumed to be uncorrelated Wiener-Levy stochastic processes. Note that a Wiener-Levy process—also known as Brownian motion—is a normal process with independent increments and as such is a special case of a Markov process.[27] For this type of process we have the autocorrelation functions

$$\langle e^{i[\phi_a(t_1)-\phi_a(t_2)]}\rangle = e^{-\gamma_a|t_1-t_2|/2}, \tag{3}$$

and

$$\langle e^{i[\phi_b(t_1)-\phi_b(t_2)]}\rangle = e^{-\gamma_b|t_1-t_2|/2}, \tag{4}$$

where γ_a and γ_b are the full widths at half maximum (FWHM) of the spectrum of $\vec{E}_a(t)$ and $\vec{E}_b(t)$, respectively. The angular brackets in Eqs. (3) and (4) indicate stochastic averages. The center frequencies ω_a and ω_b of the Lorentzian spectra are here assumed to be in (near) resonance with the transitions $|1\rangle \leftrightarrow |2\rangle$ and $|2\rangle \leftrightarrow |3\rangle$, respectively. The detunings from resonance are defined as $\Delta_1 \equiv \omega_a - \omega_{21}$ and $\Delta_2 \equiv \omega_b - \omega_{32}$, where $\omega_{ij} \equiv \omega_i - \omega_j$. It is also assumed that the states $|1\rangle$, $|2\rangle$, and $|3\rangle$ are chosen so that either (or both) of the near-resonant frequencies ω_a and ω_b have sufficient energy to ionize state $|3\rangle$ by the absorption of a single photon.

The observed quantity is the total ionization during the time of interaction between atoms and radiation. The probability of ionization during time t, averaged over the field fluctuations, is given by

$$P_{\text{ion}}(t) = 1 - \sum_{i=1}^{3} \langle \rho_{ii}(t) \rangle , \tag{5}$$

where $\langle \rho_{ii}(t) \rangle$, $i = 1, 2, 3$ are the diagonal density matrix elements averaged over the fluctuations of the fields. We consider the equation of motion for $\rho(t)$ in the rotating-wave approximation and introduce the slowly varying amplitudes $\sigma_{ij}(t)$ defined by

$$\rho_{12}(t) = \sigma_{12}(t) e^{i\omega_a t}, \quad \rho_{23}(t) = \sigma_{23}(t) e^{i\omega_b t},$$

$$\rho_{13}(t) = \sigma_{13}(t) e^{i(\omega_a + \omega_b)t}, \quad \rho_{ii}(t) = \sigma_{ii}(t).$$

The resulting equations are

$$\left(\frac{d}{dt} + i\Delta_1 + \frac{1}{2}\Gamma_{21}\right)\sigma_{12}(t) = -\frac{i}{2}[\sigma_{11}(t) - \sigma_{22}(t)]\omega_{Ra} e^{i\phi_a(t)} - \frac{i}{2}\sigma_{13}(t)\omega_{Rb} e^{-i\phi_b(t)} , \tag{6}$$

$$\left(\frac{d}{dt} + i\Delta_2 + \frac{1}{2}(\Gamma_{32} + \gamma)\right)\sigma_{23}(t) = -\frac{i}{2}[\sigma_{22}(t) - \sigma_{33}(t)]\,\omega_{Rb} e^{i\phi_b(t)} + \frac{i}{2}\sigma_{13}(t)\omega_{Ra} e^{-i\phi_a(t)} , \tag{7}$$

$$\left(\frac{d}{dt} + i(\Delta_1 + \Delta_2) + \frac{1}{2}(\Gamma_{31} + \gamma)\right)\sigma_{13}(t) = -\frac{i}{2}\sigma_{12}(t)\omega_{Rb} e^{i\phi_b(t)} + \frac{i}{2}\sigma_{23}(t)\omega_{Ra} e^{i\phi_a(t)} , \tag{8}$$

$$\frac{d}{dt}\sigma_{11}(t) = \Gamma_2\sigma_{22}(t) + \text{Im}[\sigma_{12}(t)\omega_{Ra} e^{-i\phi_a(t)}] , \tag{9}$$

$$\left(\frac{d}{dt} + \Gamma_2\right)\sigma_{22}(t) = \Gamma_3\sigma_{33}(t) - \text{Im}[\sigma_{12}(t)\omega_{Ra} e^{-i\phi_a(t)} - \sigma_{23}(t)\omega_{Rb} e^{-i\phi_b(t)}] , \tag{10}$$

$$\left(\frac{d}{dt} + \Gamma_3 + \gamma\right)\sigma_{33}(t) = -\text{Im}[\sigma_{23}(t)\omega_{Rb} e^{-i\phi_b(t)}] , \tag{11}$$

where Γ_2 and Γ_3 are the spontaneous decay rates of levels $|2\rangle$ and $|3\rangle$, respectively; Γ_{21}, Γ_{32}, and Γ_{31} are transverse relaxation rates which are assumed here to be purely radiative ($\Gamma_{21} = \Gamma_2$, $\Gamma_{32} = \Gamma_3 + \Gamma_2$, $\Gamma_{31} = \Gamma_3$). γ is the one-photon ionization rate[28] from level $|3\rangle$, which is linear in the intensity of the fields and independent of their phases; the parameters $\omega_{Ra} = 2\hbar^{-1}\vec{\mu}_{12}\cdot\hat{e}_a\epsilon_a$ and $\omega_{Rb} = 2\hbar^{-1}\vec{\mu}_{23}\cdot\hat{e}_b\epsilon_b$ are the Rabi oscillation frequencies of the transitions $|1\rangle \leftrightarrow |2\rangle$ and $|2\rangle \leftrightarrow |3\rangle$ with $\vec{\mu}_{12}$ and $\vec{\mu}_{23}$ being the respective electric-dipole vector matrix elements.

When $|2\rangle \leftrightarrow |3\rangle$ is an electric quadrupole transition—as has been the case in a relevant experiment[5,6]—we replace the dipole interaction $-\vec{\mu}_{23}\cdot\hat{e}_b\epsilon_b$ by the quadrupole interaction

$$\frac{i}{2} e\omega_b c^{-1} \sum_{j=1}^{3} Q_{j3}\hat{x}_3 \cdot \hat{e}_b\epsilon_b ,$$

where e is the electronic charge, c the speed of light, Q the quadrupole dyadic, and $\hat{x}_3$ the unit vector in the direction of propagation of the field which is assumed to be a plane wave. In this case, the term $\Gamma_3\sigma_{33}(t)$ will not appear in the right-hand side of Eq. (10); because if $|2\rangle$ and $|3\rangle$ are connected through a quadrupole transition, state $|3\rangle$ does not decay to $|2\rangle$ spontaneously. Depending on the angular momenta of the states $|1\rangle$, $|2\rangle$, and $|3\rangle$, state $|3\rangle$ may decay to $|1\rangle$ in which case $\Gamma_3\sigma_{33}(t)$ will appear in the right-hand side of Eq. (9). An example of this case would consist of the states $|1\rangle = |3S\rangle$, $|2\rangle = |3P_{3/2}\rangle$, and $|3\rangle = |5P_{3/2}\rangle$ in sodium. On the other hand, one could have $|3\rangle = |4F_{5/2}\rangle$ instead; in which case $|4F\rangle$ does not decay spontaneously either to $|3S\rangle$ or to $|3P\rangle$ except via cascade transitions. If the interaction time is sufficiently short, these cascade decays can be neglected and $\Gamma_3\sigma_{33}(t)$ does not appear in the right-hand side of either Eq. (9) or Eq. (10). For interaction times long compared to the longest lifetime in the cascade, one must consider the relevant branching ratios and insert part of $\Gamma_3\sigma_{33}(t)$ in Eq. (9) and part of it in Eq. (10).

To calculate the average probability of ionization [Eq. (5)], we perform a statistical average on the stochastic differential equations (6)–(11) for the density matrix elements. Taking a formal stochastic average of Eqs. (9)–(11) over the fluctuating phases we obtain,

$$\frac{d}{dt}\langle\sigma_{11}(t)\rangle=\Gamma_2\langle\sigma_{22}(t)\rangle+\mathrm{Im}[\langle\sigma_{12}(t)\omega_{Ra}e^{-i\phi_a(t)}\rangle], \quad (12)$$

$$\left(\frac{d}{dt}+\Gamma_2\right)\langle\sigma_{22}(t)\rangle =\Gamma_3\langle\sigma_{33}(t)\rangle-\mathrm{Im}[\langle\sigma_{12}(t)\omega_{Ra}e^{-i\phi_a(t)}\rangle -\langle\sigma_{23}(t)\omega_{Rb}e^{-i\phi_b(t)}\rangle], \quad (13)$$

$$\left(\frac{d}{dt}+\Gamma_3+\gamma\right)\langle\sigma_{33}(t)\rangle=-\mathrm{Im}[\langle\sigma_{23}(t)\omega_{Rb}e^{-i\phi_b(t)}\rangle]. \quad (14)$$

We now need to calculate the correlations $\langle\sigma_{12}(t)\omega_{Ra}e^{-i\phi_a(t)}\rangle$ and $\langle\sigma_{23}(t)\omega_{Rb}e^{-i\phi_b(t)}\rangle$. Integrating formally Eqs. (6)–(8) and then eliminating $\sigma_{13}(t)$, we obtain

$$\begin{aligned}\sigma_{12}(t)=&-\frac{i}{2}\int_0^t \exp\{[i\Delta_1+\tfrac{1}{2}\Gamma_{21}](t'-t)\}\,\omega_{Ra}\exp[i\phi_a(t')][\sigma_{11}(t')-\sigma_{22}(t')]\,dt'\\ &-\frac{1}{4}\int_0^t \exp\{[i\Delta+\tfrac{1}{2}\Gamma_{21}](t'-t)\}\,dt'\int_0^{t'}\exp\{[i(\Delta_1+\Delta_2)+\tfrac{1}{2}(\Gamma_{31}+\gamma)](t''-t)\}\\ &\times(\omega_{Rb}^2\exp\{i[\phi_b(t'')-\phi_b(t')]\}\sigma_{12}(t'')\\ &-\omega_{Ra}\omega_{Rb}\exp\{i[\phi_a(t'')-\phi_b(t')]\}\sigma_{23}(t''))\,dt''\ ,\end{aligned} \quad (15)$$

$$\begin{aligned}\sigma_{23}(t)=&-\frac{i}{2}\int_0^t \exp\{[i\Delta_2+\tfrac{1}{2}(\Gamma_{32}+\gamma)](t'-t)\}\,\omega_{Rb}\exp[i\phi_b(t')][\sigma_{22}(t')-\sigma_{33}(t')]\,dt'\\ &-\frac{1}{4}\int_0^t \exp\{[i\Delta_2+\tfrac{1}{2}(\Gamma_{32}+\gamma)](t'-t)\}\,dt'\int_0^t\exp\{[i(\Delta_1+\Delta_2)+\tfrac{1}{2}(\Gamma_{31}+\gamma)](t''-t')\}\\ &\times(\omega_{Ra}\omega_{Rb}\exp\{i[\phi_b(t'')-\phi_a(t')]\}\sigma_{12}(t'')\\ &-\omega_{Ra}^2\exp\{i[\phi_a(t'')-\phi_a(t')]\}\sigma_{23}(t''))\,dt''\ .\end{aligned} \quad (16)$$

Next, we multiply both sides of Eq. (15) by $\omega_{Ra}\exp[-i\phi_a(t)]$ and Eq. (16) by $\omega_{Rb}\exp[-i\phi_b(t)]$ and take the stochastic average over the phases ϕ_a and ϕ_b

$$\begin{aligned}\langle\sigma_{12}(t)\omega_{Ra}\exp[-i\phi_a(t)]\rangle=&-\frac{i}{2}\int_0^t \exp\{[i\Delta_1+\tfrac{1}{2}(\Gamma_{21}+\gamma_a)](t'-t)\}\,\omega_{Ra}^2[\langle\sigma_{11}(t')\rangle-\langle\sigma_{22}(t')\rangle]\,dt'\\ &-\frac{1}{4}\int_0^t \exp\{[i\Delta_1+\tfrac{1}{2}(\Gamma_{21}+\gamma_a)](t'-t)\}\,dt'\int_0^{t'}\exp\{[i(\Delta_1+\Delta_2)+\tfrac{1}{2}(\Gamma_{31}+\gamma+\gamma_a+\gamma_b)](t''-t')\}\\ &\times\{\omega_{Rb}^2\langle\sigma_{12}(t'')\omega_{Ra}\exp[-i\phi_a(t'')]\rangle\\ &-\omega_{Ra}^2\langle\sigma_{23}(t'')\omega_{Rb}\exp[-i\phi_b(t'')]\rangle\}\,dt''\ ,\end{aligned} \quad (17)$$

$$\begin{aligned}\langle\sigma_{23}(t)\omega_{Rb}\exp[-i\phi_b(t)]\rangle=&-\frac{i}{2}\int_0^t \exp\{[i\Delta_2+\tfrac{1}{2}(\Gamma_{32}+\gamma+\gamma_b)](t'-t)\}\,\omega_{Rb}^2[\langle\sigma_{22}(t')\rangle-\langle\sigma_{33}(t')\rangle]\,dt'\\ &-\frac{1}{4}\int_0^t \exp\{[i\Delta_2+\tfrac{1}{2}(\Gamma_{32}+\gamma+\gamma_b)](t'-t)\}\,dt'\int_0^{t'}\exp\{[i(\Delta_1+\Delta_2(\Gamma_{31}+\gamma+\gamma_a+\gamma_b)](t''-t)\}\\ &\times\{\omega_{Rb}^2\langle\sigma_{12}(t'')\omega_{Ra}\exp[-i\phi_a(t'')]\rangle\\ &-\omega_{Ra}^2\langle\sigma_{23}(t'')\omega_{Rb}\exp[-i\phi_b(t'')]\rangle\}\,dt''.\end{aligned} \quad (18)$$

In obtaining the equations above, we have used relations of the type

$$\langle \sigma_{11}(t')\exp\{-i[\phi_a(t)-\phi_a(t')]\}\rangle = \langle \sigma_{11}(t')\rangle \langle \exp\{-i[\phi_a(t)-\phi_a(t')]\}\rangle \quad (19)$$

and

$$\begin{aligned}\langle \sigma_{12}(t'')\exp[-i\phi_a(t)]\rangle &= \langle \sigma_{12}(t'')\exp[-i\phi_a(t'')]\exp\{-i[\phi_a(t)-\phi_a(t'')]\}\rangle \\ &= \langle \sigma_{12}(t'')\exp[-i\phi_a(t'')]\rangle \\ &\quad \times \langle \exp\{-i[\phi_a(t)-\phi_a(t'')]\}\rangle , \end{aligned} \quad (20)$$

where $t>t'>t''$. These decorrelations are valid because a Wiener-Levy process, such as $\phi_a(t)$, is a process with independent increments.[27] Functions of different independent increments can be decorrelated rigorously.

A few parenthetical remarks concerning the above decorrelation are perhaps in order at this point. The decorrelation of atomic and field variables is not valid in the general case, but often is made as an approximation. It can be shown[29] that the decorrelation is valid only for fields whose nth-order correlation function satisfies the relation

$$\langle \epsilon(t_1)\epsilon^*(t_2)\cdots\epsilon(t_{2n-1})\epsilon^*(t_{2n})\rangle = \langle \epsilon(t_1)\epsilon^*(t_2)\rangle \cdots \langle \epsilon(t_{2n-1})\epsilon^*(t_{2n})\rangle , \quad (21)$$

where $t_1>t_2>\cdots>t_{2n-1}>t_{2n}$. Fields with constant amplitudes and Wiener-Levy statistics for their phases, as the ones discussed here, satisfy the above relation. The other well-known model field, the chaotic field, does not satisfy Eq. (21) and cannot be decorrelated from the density matrix elements rigorously.[26] Actual laser fields which exhibit amplitude, frequency and phase fluctuations, and whose stochastic properties are unknown, could not be expected to satisfy Eq. (21). The correlation between fluctuations of the perturbing field and fluctuations of the unknown atomic response is the heart of the problem in studying resonant processes with nonmonochromatic fields. Exact solutions to such problems cannot be found, in general. The decorrelation approximation, although very good when the bandwidth of the radiation field exceeds the natural atomic widths and the average Rabi oscillation frequency (below saturation), is very inadequate for a general stochastic field of high intensity (above saturation).[29] In the decorrelation approximation, one effectively neglects higher-order correlations of the field and thus cannot distinguish between fields with entirely different stochastic properties. Higher-order field correlations play a very important role in the intensity regime above saturation and because of this any theory that makes the decorrelation approximation is inherently a weak-field theory. Since Stark splitting is a high-intensity effect, the decorrelation approximation for a general field, in either double resonance or resonance fluorescence, can lead to erroneous results.

One can consider special cases, mathematically simplified, for which closed-form solutions for the density matrix can be obtained. The stochastic average over the field can then be carried out on the solutions rather than the equations of motion. In such cases of course the problem of decorrelation does not arise. Such models have been considered by Przhibelskii and Khodovoi[9] and also by Zusman and Burshtein.[10] These authors assume that only $\vec{E}_b(t)$ is strong and nonmonochromatic while $\vec{E}_a(t)$ is a weak monochromatic probe. Note that the role of $\vec{E}_a$ and $\vec{E}_b$ is exactly the inverse of that assumed in the present paper. They assume further that $\sigma_{11}(t)\simeq 1$ and $\sigma_{22}(t)\simeq\sigma_{33}(t)\simeq 0$. These assumptions allow them to obtain in closed form a stochastic expression for the absorption spectrum of the $|1\rangle\to|2\rangle$ transition and to compare results for phase and amplitude fluctuations. Their assumptions, however, are not satisifed in recent experiments on double resonance.[3-7] Thus these simplified models do not shed much light on these experiments.

If we examine the equations for the density matrix elements averaged over phase fluctuations, we see that they are equivalent to the equations for the same atomic system, but with effective transverse relaxation rates $\Gamma_{21}^*=\Gamma_{21}+\gamma_a$, $\Gamma_{32}^*=\Gamma_{32}+\gamma_b$, and $\Gamma_{31}^*=\Gamma_{31}+\gamma_a+\gamma_b$, interacting with two monochromatic fields of the same average power as the nonmonochromatic ones.

Note that amplitude fluctuations would have a more complicated effect on Stark splitting. In the case of amplitude fluctuations, the Rabi frequencies ω_{Ra} and ω_{Rb} themselves are fluctuating quantities which effectively broaden the transitions. Since the Rabi frequencies are intensity dependent, this broadening is also intensity dependent and it can exceed the laser width. This is unlike phase fluctuations where the broadening is equal to the laser width. The exact shape of the split double-resonance curve in the case of amplitude fluctuations would depend on the particular stochastic properties of the fields.

The average probability of ionization [Eq. (5)] can be evaluated using the equivalent monochromatic model mentioned above. Separating the real and imaginary parts of the off-diagonal density matrix elements of the equivalent monochromatic model, the differential equations can be written in matrix notation

$$\frac{d}{dt} S_i(t) = \sum_{j=1}^{9} M_{ij} S_i(t), \quad i = 1, \ldots, 9 \tag{22}$$

where S_i and M_{ij} are real quantities. The solution of Eq. (22) can be written analytically

$$S_i(t) = \sum_{j=1}^{9} \sum_{k=1}^{9} R_i^{(k)} L_i^{(k)} S_i(t=0) e^{\lambda_k t} , \tag{23}$$

where λ_k are the eigenvalues of the square matrix M and $R^{(k)}$ and $L^{(k)}$ the corresponding eigenvector and reciprocal eigenvector. Using Eqs. (5) and (23) we can calculate numerically the average probability of ionization for arbitrary interaction parameters. Results of such calculations are presented in Sec. IV.

III. FOUR-LEVEL SYSTEM WITH IONIZATION

This section is devoted to the analysis of the effect of Stark splitting on a system not directly related to recent experiments. Under certain conditions, however, its peak asymmetries for monochromatic light could be mistaken as those of a three-level system with nonmonochromatic light. There are of course fundamental differences between the two systems and it is only under particular experimental circumstances that they may exhibit some resemblance. In addition, it is possible to envision experiments in actual atoms to which the model would be applicable. In this paper, we are interested mainly in the theoretical aspects of its behavior.

Consider an atomic system similar to that of Sec. II except for the initial state which is assumed to consist of two states denoted by $|\pm 1\rangle$ and with an energy separation $\hbar\delta$. An example would be a pair of hyperfine levels. The other states of the system are denoted by $|2\rangle$ and $|3\rangle$ as in the three-level system of Sec. II.

We shall also use this section to illustrate the use of the resolvent operator in the study of Stark-splitting problems. This has the advantage of a smaller number of equations—four in this case—as compared to the density matrix which would lead to 16 coupled differential equations. However, the resolvent operator—which is equivalent to working with the Schrödinger equation—has the disadvantage of not allowing the correct treatment of spontaneous decay. Although it can account for the spontaneous depopulation of excited states, it can not account easily for the repopulation of the lower states. As a result, this formalism is valid only as long as the interaction time is shorter than the spontaneous lifetimes of the states involved. This of course is not a serious limitation in a number of experiments with pulsed lasers. Moreover, in ionization experiments the probability of ionization can exceed the probability of spontaneous decay thus minimizing its importance.

In this section, the fields are assumed to be monochromatic since our aim is to show how the presence of a second initial state causes the same reversal of the asymmetry as the nonmonochromatic field in a three-level system. The radiation field is quantized in this formalism and the total Hamiltonian of the system "atom plus field" is written

$$H = H_0 + V = H_a + H_r + V ,$$

where H_a is the atomic Hamiltonian, H_r the Hamiltonian of the radiation field, and V the interaction between the two. The eigenstates of H_0 which are important in the resonant interaction of the atom and the field are

$$|A\rangle = |-1\rangle |n_a\omega_a, n_b\omega_b\rangle , \tag{24a}$$

$$|B\rangle = |+1\rangle |n_a\omega_a, n_b\omega_b\rangle , \tag{24b}$$

$$|C\rangle = |2\rangle |(n_a - 1)\omega_a, n_b\omega_b\rangle , \tag{24c}$$

$$|D\rangle = |3\rangle |(n_a - 1)\omega_a, (n_b - 1)\omega_b\rangle , \tag{24d}$$

$$|E\rangle = |l\rangle |(n_a - 2)\omega_a, (n_b - 1)\omega_b\rangle , \tag{24e}$$

$$|F\rangle = |l\rangle |(n_a - 1)\omega_a, (n_b - 2)\omega_b\rangle , \tag{24f}$$

where n_a and n_b are the initial numbers of photons with frequency ω_a and ω_b, respectively. The detunings from resonance in this case are defined as $\Delta_1 \equiv \omega_a - (\omega_2 - \omega_{-1} - \frac{1}{2}\delta)$ and $\Delta_2 \equiv \omega_b - \omega_{32}$.

At time $t=0$ the system is assumed to be in the state $|I\rangle = 2^{-1/2}(|A\rangle + |B\rangle)$, with the atomic population divided equally between the two states of the doublet ground state. We will use the resolvent operator

$$G(z) = 1/(z - H) , \tag{25}$$

to calculate the time evolution operator

$$U(t) = \frac{1}{2\pi i} \int e^{izt} G(z)\, dz , \tag{26}$$

and from it calculate the probability of ionization.

Writing Eq. (25) in the form

$$(z - H_0 - V) G(z) = 1 , \tag{27}$$

and taking matrix elements between the initial state and the eigenstates of H_0 given in Eqs. (24a)–(24f), we obtain

$$(z - \omega_A) G_{AI} - V_{AC} G_{CI} = 2^{-1/2} , \tag{28}$$

$$(z - \omega_B) G_{BI} - V_{BC} G_{CI} = 2^{-1/2} , \tag{29}$$

$$(z-\omega_C)G_{CI}-V_{CA}G_{AI}-V_{CB}G_{BI}-V_{CD}G_{DI}=0\,, \tag{30}$$

$$(z-\omega_D)G_{DI}-V_{DC}G_{CI} - \int (V_{DE}G_{EI}+V_{DF}G_{FI})g(\omega_l)\,d\omega_l=0\,, \tag{31}$$

$$(z-\omega_E)G_{EI}-V_{ED}G_{DI}=0\,. \tag{32}$$

$$(z-\omega_F)G_{FI}-V_{FD}G_{DI}=0\,. \tag{33}$$

In Eq. (31), $g(\omega_l)$ is the density of the continuum states. Substituting the values of G_{EI} and G_{FI} from Eqs. (32) and (33) into Eq. (31), that equation becomes

$$(z-\omega_D')G_{DI}-V_{DC}G_{CI}=0\,, \tag{34}$$

where

$$\begin{aligned}\omega_D'&=\omega_D+\int\left(\frac{|V_{ED}|^2}{z-\omega_E}+\frac{|V_{FD}|^2}{z-\omega_F}\right)g(\omega_l)\,d\omega_l\\ &\simeq\omega_D+\int\left(\frac{|V_{ED}|^2}{\omega_A-\omega_E}\;\frac{|V_{FD}|^2}{\omega_A-\omega_F}\right)g(\omega_l)\,d\omega_l\\ &\simeq\omega_D+\Delta\omega_3-\tfrac{1}{2}i\gamma\,,\end{aligned} \tag{35}$$

where the integral has been evaluated at $z=\omega_A$. The parameters $\Delta\omega_3$ and γ are the energy shift and the ionization width of level $|3\rangle$ owing to coupling with the continuum. The energy shift $\Delta\omega_3$ will be neglected here. Although it is relatively easy to calculate and include in the treatment, it does not add to the physics of the problem at hand.

Using the relations $\omega_B=\omega_A+\delta$, $\omega_C=\omega_A+\frac{1}{2}\delta-\Delta_1$, $\omega_D=\omega_A+\frac{1}{2}\delta-\Delta_1-\Delta_2$ and letting $z=x+\omega_A$, we can write Eqs. (28)–(30) and (34) in matrix form:

$$\begin{bmatrix} x & 0 & -V_{AC} & 0\\ 0 & x-\delta & -V_{BC} & 0\\ -V_{CA} & -V_{CB} & x-\frac{1}{2}\delta+\Delta_1 & -V_{CD}\\ 0 & 0 & -V_{DC} & x-\frac{1}{2}\delta+\Delta_1+\Delta_2+\frac{1}{2}i\gamma\end{bmatrix}\begin{bmatrix}G_{AI}\\ G_{BI}\\ G_{CI}\\ G_{DI}\end{bmatrix}=\begin{bmatrix}2^{-1/2}\\ 2^{-1/2}\\ 0\\ 0\end{bmatrix}\,. \tag{36}$$

The probability of ionization is given by

$$P_{\text{ion}}(t)=1-\sum_{S=A,B,C,D}|U_{SI}(t)|^2\,. \tag{37}$$

The probability amplitudes $U_{SI}(t)$ are obtained from the resolvent operator using Eq. (26) and have a time dependence of the form

$$U_{SI}(t)=e^{-i\omega_A t}\sum_{K=1}^{4}C_{SK}e^{-ix_K t}\,, \tag{38}$$

where x_K are the four eigenvalues of the square matrix in Eq. (36). If levels $|2\rangle$ and $|3\rangle$ are coupled very weakly ($|V_{CD}|\ll|V_{AC}|,|V_{BC}|$), then $x_4\simeq\omega_D'-\omega_A=\frac{1}{2}\delta-\Delta_1-\Delta_2-\frac{1}{2}i\gamma$ which is independent of $|V_{AC}|$, $|V_{BC}|$, and $|V_{CD}|$. The other three eigenvalues are functions of δ, Δ_1, $|V_{AC}|$, and $|V_{BC}|$. The ionization as a function of Δ_2 will have three resonances at $\Delta_2=\frac{1}{2}\delta-\Delta_1-x_i$, $i=1,2,3$, corresponding to the condition $\mathrm{Re}(x_4)=x_i$. Numerical results are presented in Sec. IV.

IV. NUMERICAL CALCULATIONS AND DISCUSSION

A. Three-level system

1. Monochromatic fields ($\gamma_a=\gamma_b=0$)

We present now typical results of numerical solutions corresponding to incident fields that are synchronized rectangular pulses of duration T. If $\omega_{Ra}\gg\omega_{Rb},\gamma,\Gamma_2,\Gamma_3$, the probability of ionization as a function of Δ_2 has two peaks at $\Delta_2\simeq\frac{1}{2}[-\Delta_1\pm(\Delta_1^2+\omega_{Ra}^2)^{1/2}]$, just as the absorption and emission[11,12] lines. For $\Delta_1=0$ the resonance curve is symmetric while for $\Delta_1\neq0$ it is asymmetric. Depending on whether Δ_1 is positive or negative the peak which occurs at the negative or positive value of Δ_2, respectively is larger. In the limit $\Delta_1\gg\omega_{Ra}$ the dominant peak occurs at $\Delta_2=-\Delta_1$ which is the condition for two-photon resonance at weak fields. In the same limit, the other peak at $\Delta_2=0$ vanishes. Note that this vanishing peak corresponds to a one-photon resonance in the $|2\rangle\leftrightarrow|3\rangle$ transition. Whereas the separation of the two peaks for a given detuning Δ_1 is almost entirely dependent on ω_{Ra}, the asymmetry of the peaks depends on many other parameters, such as, the probe interaction ω_{Rb}, the ionization rate γ, the natural decay rates Γ_2 and Γ_3, and also on the interaction time T. As we shall see in Sec. IV A 2, the asymmetry also depends dramatically on the spectral widths of the fields. In real atoms the asymmetry should also depend on the structure and degeneracy of the states. In view of all these factors, it is not surprising that while there is good agreement between theory and experiment in regard to the magnitude of the splitting, the same cannot be said about the asymmetry. The asymmetry depends on the details of the over-

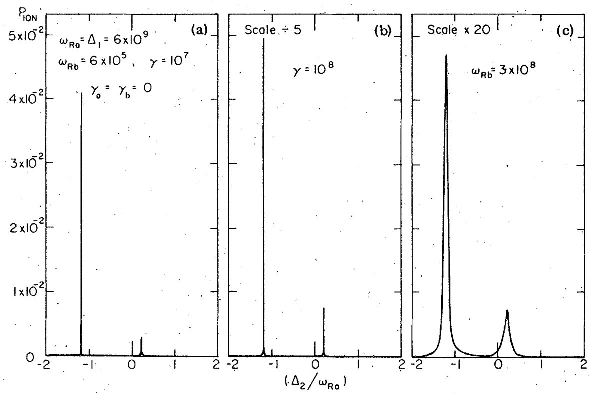

FIG. 1. Probability of ionization for a three-level system vs detuning of the probe laser. The laser fields are monochromatic.

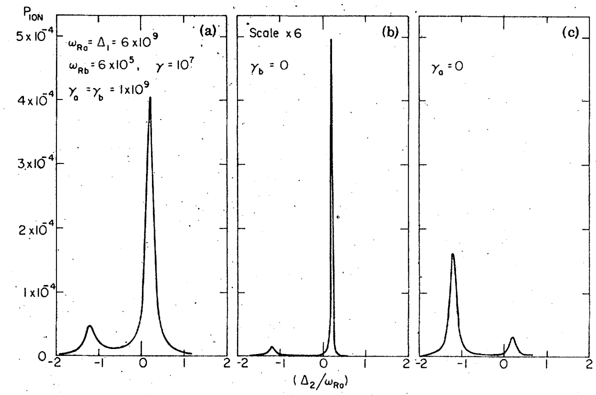

FIG. 2. Probability of ionization for a three-level system vs detuning of the probe laser. The laser fields are nonmonochromatic.

all interaction while the splitting depends only on the strongly driven transition.

Figure 1 shows the dependence of the asymmetry on γ and ω_{Rb}. In these calculations we have taken $T=600$ nsec and $\Gamma_2=6.3\times10^7$ sec^{-1}. Γ_3 has been assumed to be much less than γ and has been neglected. The other parameters are as specified in Fig. 1. Comparing Figs. 1(a) and 1(b) we see that as γ is increased by a factor of 10 the asymmetry ratio decreases by about a factor of 2 while at the same time the peak ionization decreases. Comparing Figs. 1(a) and 1(c) we see that by increasing ω_{Rb} by a factor of 500 the asymmetry ratio is also decreased by about a factor of 2. At the same time the increase in the probe interaction causes broadening of the resonances.

2. *Nonmomochromatic fields*

As we saw in Sec. II, the effect of the phase fluctuations, when averaged, is equivalent to changing the effective transverse relaxation rates from Γ_{21}, Γ_{32}, and Γ_{31} to $\Gamma_{21}^*=\Gamma_{21}+\gamma_a$, $\Gamma_{32}^*=\Gamma_{32}+\gamma_b$, and $\Gamma_{31}^*=\Gamma_{31}+\gamma_a+\gamma_b$. Therefore, since the asymmetry depends on the transverse relaxation rates, we expect it to be affected by the widths of the fields. Figure 2 shows how dramatic this effect is, when we compare it with Fig. 1. Making both fields broad and leaving all other parameters the same as in Fig. 1(a) the asymmetry reverses [Fig. 2(a)]. The reason for this reversal is that while both the one-photon and the two-photon resonances are broadened by the spectral width of the fields, the broadening of the $|1\rangle \rightarrow |2\rangle$ transition, which is nonresonant ($\Delta_1\neq0$), favors the resonance which corresponds to the one-photon resonance in the $|2\rangle \rightarrow |3\rangle$ transition. In Fig. 2(b) where the probe field $\vec{E}_b(t)$ is monochromatic, the asymmetry remains reversed and increases compared to the case in Fig. 2(a). However, in Fig. 2(c) where only the probe field is broad the asymmetry is the "normal" asymmetry as in Fig. 1 where both fields are monochromatic. This clearly shows that it is the broadening of the strongly driven $|1\rangle \rightarrow |2\rangle$ transition which reverses the asymmetry.

The reversed asymmetry for nonmonochromatic fields has been observed in recent experiments on doubly resonant three-photon ionization.[5-7] In the initial experiments of Moody and Lambropoulos,[5,6] the observed asymmetry was reversed, but their measurements were limited to small detunings ($|\Delta_1|\lesssim\gamma_a$). More recently Hogan and Smith[7] continuing their work have reported that for large detunings ($|\Delta_1|>4\gamma_a$) the asymmetry reverts to normal, as for monochromatic fields. In the model used in this paper with the assumed Lorentzian spectra the reversed asymmetry is found to persist for detunings of several hundred laser widths (γ_a). This is owing to the long wings of the Lorentzian line shapes whose contribution turns out to be comparable to the off-resonance two-photon absorption. This suggests that the actual line shapes in the experiment decreased much more rapidly in the wings. In fact they are expected to have a cutoff. Under such conditions of course the asymmetry reverts to normal as soon as the atomic line is outside the laser line shape. Note that for small detunings the actual line shape is not very important. Owing to the lack of a realistic model for the line shapes of the lasers used in the experiments,[5-7] we have not attempted quantitative comparisons especially in connection with the return of the asymmetry to normal. All other parameters used in our calculations, however, correspond to the experimental conditions. Thus we can obtain several of the qualitative features of the experiment including the reversed asymmetry for small detunings. We do not of course expect the single-mode field with

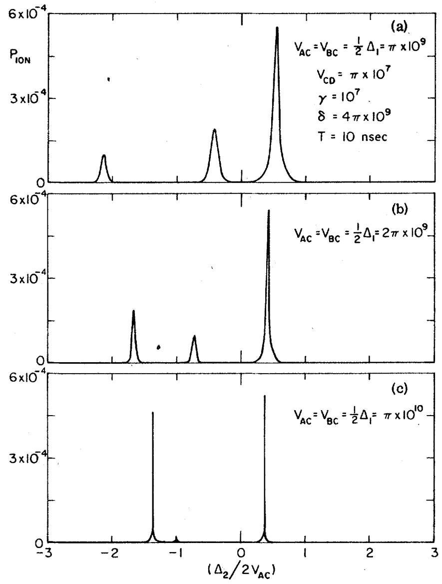

FIG. 3. Probability of ionization for a four-level system vs detuning of the probe laser. The laser fields are monochromatic.

phase fluctuations to represent the actual pulsed dye lasers which most likely exhibited significant amplitude and frequency fluctuations as well. We expect to present the results of more realistic calculations in a future publication.

B. Four-level system

The results presented in this subsection illustrate the behavior of the four-level system and show how the presence of an additional state—near the ground state—modifies the resonance curve of the three-level system. In Fig. 3 we show the ionization as a function of probe frequency for three cases. As expected the strong field gives rise to three peaks, that is as many as there are (near-) degenerate states of the system "atom-field." Note that in all three cases the asymmetry is opposite to that found in a three-level system interacting with monochromatic fields. It is possible in an experiment one of the three peaks to be small and undectable. The remaining peaks would then exhibit what we have called reversed asymmetry thus mimicking a three-level atom under nonmonochromatic fields. Recall that for the three-level system, the asymmetry reverses when Δ_1 changes sign. For the four-level system, the relative spacing of the peaks as well as their relative heights depends on the magnitude of V_{AC}, V_{BC}, and Δ_1 relative to δ. For V_{AC}, V_{BC}, Δ_1 much larger than δ the central peak moves toward one of the side peaks and becomes vanishingly small [Fig. 3(c)]. In this limit the four-level system tends to behave like a three-level system. For $V_{AC} = V_{BC}$, and $\Delta_1 = 0$ the central peak disappears apparently owing to interference effects.

The different behavior of the four-level system as compared to the three-level system points to the important role that the hyperfine structure of atomic states can play in experiments of this type.

V. STEADY-STATE APPROXIMATION FOR THE THREE-LEVEL SYSTEM

As pointed out in Secs. I and II, the probability of doubly resonant three-photon ionization has to be calculated numerically, in general, if a quantitative comparison between theory and experiment is to be achieved. It turns out however that certain qualitative features can be exhibited analytically if judiciously chosen approximations are introduced. A case in point is the effect of the finite laser bandwidth on the peak asymmetry. To obtain a manageable analytical expression, we consider a special case in which ionization is sufficiently weak to be negligible, as a first approximation. Then one can neglect the derivatives $d\langle\sigma_{ij}\rangle/dt$, which is equivalent to exploring steady-state solutions of the system. As we shall see below, even with this approximation, the relation between peak asymmetry and laser bandwidth remains the same as in the rigorous solutions of the previous sections. solutions of the previous sections.

Introducing the approximation $d\langle\sigma_{ij}\rangle/dt = 0$, the populations of the three levels can be written

$$\langle\sigma_{11}\rangle = 1 - \langle\sigma_{22}\rangle - \langle\sigma_{33}\rangle\,, \tag{39}$$

$$\langle\sigma_{22}\rangle = (1/\Gamma_2)\,\mathrm{Re}(i\langle\sigma_{12}\rangle\omega_{Ra})\,, \tag{40}$$

$$\langle\sigma_{33}\rangle = (1/\Gamma_3)\,\mathrm{Re}(i\langle\sigma_{23}\rangle\omega_{Rb})\,, \tag{41}$$

where, after some algebra, $\langle\sigma_{12}\rangle$ and $\langle\sigma_{23}\rangle$ can be cast in the forms

$$\langle\sigma_{12}\rangle = \frac{-i/2\omega_{Ra}(ST + 1/4\omega_{Ra}^2)T(\langle\sigma_{11}\rangle - \langle\sigma_{22}\rangle) - i/8\omega_{Ra}\omega_{Rb}^2 T(\langle\sigma_{22}\rangle - \langle\sigma_{33}\rangle)}{(RT + 1/4\omega_{Rb}^2)(ST + 1/4\omega_{Ra}^2) - (1/4\omega_{Ra}\omega_{Rb})^2} \tag{42}$$

and

$$\langle\sigma_{23}\rangle = \frac{-i/2\omega_{Rb}(RT + 1/4\omega_{Rb}^2)T(\langle\sigma_{22}\rangle - \langle\sigma_{33}\rangle) - i/8\omega_{Ra}^2\omega_{Rb} T(\langle\sigma_{11}\rangle - \langle\sigma_{22}\rangle)}{(RT + 1/4\omega_{Rb}^2)(ST + 1/4\omega_{Ra}^2) - (1/4\omega_{Ra}\omega_{Rb})^2} \tag{43}$$

with

$$R = i\Delta_1 + \tfrac{1}{2}(\Gamma_{21} + \gamma_a),$$

$$S = i\Delta_2 + \tfrac{1}{2}(\Gamma_{32} + \gamma_b),$$

and

$$T = i(\Delta_1 + \Delta_2) + \tfrac{1}{2}(\Gamma_{31} + \gamma_a + \gamma_b).$$

These coupled equations are still too complicated to allow one to recognize the effect of γ_a and γ_b on $\langle\sigma_{33}\rangle$. Further simplification is obtained if we introduce the weak-probe approximation, i.e., assume

$$\omega_{Rb}^2 \ll \omega_{Ra}^2, (\Gamma_{21} + \gamma_a)^2, (\Gamma_{32} + \gamma_b)^2, (\Gamma_{31} + \gamma_a + \gamma_b)^2.$$

Then we can write $\langle\sigma_{33}\rangle$ as

$$\langle\sigma_{33}\rangle = \left(\frac{1/4\omega_{Ra}^2}{RR^* + \omega_{Ra}^2(R + R^*)/2\Gamma_2}\right) \times \left(\frac{R^* + [(R+R^*)/\Gamma_2]T}{ST + 1/4\omega_{Ra}^2} + \text{c.c.}\right)\frac{1/4\omega_{Rb}^2}{\Gamma_3}. \tag{44}$$

This expression is similar to Eq. (3) of Ref. 11 which was derived for monochromatic fields. The quantity in the square brackets is independent of Δ_2 and is equal to the population of level $|2\rangle$ for $\omega_{Rb} = 0$. The quantity in the curly brackets is a resonant function of Δ_2 with two peaks at the roots of the quadratic equation

$$\Delta_2^2 - \Delta_1\Delta_2 - 1/4\omega_{Ra}^2 + (\Gamma_{32} + \gamma_b)(\Gamma_{31} + \gamma_b) = 0.$$

The peaks are better resolved for Rabi frequencies large compared to the various widths. Let us then assume $\omega_{Ra}^2 \gg (\Gamma_{32} + \gamma_b)(\Gamma_{31} + \gamma_a + \gamma_b)$ in which case the peaks occur at

$$\Delta_2^{\pm} = -\tfrac{1}{2}[\Delta_1 \pm (\Delta_1^2 + \omega_{Ra}^2)^{1/2}], \tag{45}$$

where the signs of the square root are chosen so that $|\Delta_2^+| \geq |\Delta_2^-|$, for both positive and negative values of Δ_1. Note in passing that for $\Delta_1^2 \gg \omega_{Ra}^2$ the two roots are

$$\Delta_2^+ = -\Delta_1 \quad\text{and}\quad \Delta_2^- = \tfrac{1}{4}\omega_{Ra}^2/\Delta_1.$$

Thus, for $\Delta_1^2 \gg \omega_{Ra}^2$ the peak at Δ_2^+ corresponds to a two-photon resonance in the $|1\rangle \to |3\rangle$ transition, while the peak at Δ_2^- (in the limit $\Delta_2^- \to 0$) corresponds to a one-photon resonance in the $|2\rangle \to |3\rangle$ transition.

The peak values $\langle\sigma_{33}(\Delta_2^{\pm})\rangle$ for arbitrary values of Δ_1 are given by

$$\langle\sigma_{33}(\Delta_2^{\pm})\rangle = \left(\frac{1/4\omega_{Ra}^2}{RR^* + \omega_{Ra}^2(R+R^*)/2\Gamma_2}\right)\left(\frac{1 + [(\Delta_1 + \Delta_2^{\pm})/\Delta_2^{\pm}](\gamma_a/\Gamma_2)}{(\Gamma_3 + \gamma_a + \gamma_b) + [(\Delta_1 + \Delta_2^{\pm})/\Delta_2^{\pm}](\Gamma_3 + \Gamma_2 + \gamma_b)}\right)\frac{\omega_{Rb}^2}{\Gamma_3}. \tag{46}$$

From Eq. (46) we see that for $\Delta_1 = 0$ the two peaks have equal heights. For $\Delta_1 \neq 0$ we have $(\Delta_1 + \Delta_2^{\pm})/\Delta_2^+ < (\Delta_1 + \Delta_2^-)/\Delta_2^-$ and the relative heights of the two peaks depend on the value of the ratio γ_a/Γ_2. If $\gamma_a < \Gamma_2$, the peak at Δ_2^+ is higher than the peak at Δ_2^-. This is in agreement with the predictions of monochromatic theory ($\gamma_a = \gamma_b = 0$). If $\gamma_a = \Gamma_2$, the two peaks are equal independently of Δ_1. Finally, if $\gamma_a > \Gamma_2$ the peak at Δ_2^+ is smaller than the peak at Δ_2^-. A physical interpretation of this effect can be given by considering energy conservation in the $|1\rangle \to |3\rangle$ transition in the limit $\Delta_1^2 \gg \omega_{Ra}^2$. In that case Eq. (46) reduces to

$$\langle\sigma_{33}(\Delta_2^+)\rangle = \left[\frac{1/4\omega_{Ra}^2}{\Delta_1^2 + 1/2\omega_{Ra}^2(1 + \gamma_a/\Gamma_2)}\right] \times \frac{\omega_{Rb}^2}{\Gamma_3 + \gamma_a + \gamma_b}\,\frac{1}{\Gamma_3} \tag{47}$$

and

$$\langle\sigma_{33}(\Delta_2^-)\rangle = \left[\frac{1/4\omega_{Ra}^2}{\Delta_1^2 + 1/2\omega_{Ra}^2(1 + \gamma_a/\Gamma_2)}\right] \times \left[\frac{\omega_{Ra}^2}{4\Delta_1^2}\left(1 + \frac{\gamma_a}{\Gamma_2}\right) + \frac{\gamma_a}{\Gamma_2}\right] \times \frac{\omega_{Rb}^2}{\Gamma_3 + \Gamma_2 + \gamma_b}\,\frac{1}{\Gamma_3} \tag{48}$$

The forms of Eqs. (47) and (48) show that the peak at Δ_2^+ corresponds to off-resonance two-photon excitation

$$|1\rangle \xrightarrow{\omega_a} \xrightarrow{\omega_b} |3\rangle,$$

while the peak at Δ_2^- corresponds to two-step excitation

$$|1\rangle \xrightarrow{\omega_a} |2\rangle \xrightarrow{\omega_b} |3\rangle.$$

For $\gamma_a = 0$, the nonresonant excitation of level $|2\rangle$ goes as $(1/4\omega_{Ra}^2/\Delta_1^2)^2$, which is quadratic in the intensity of the strong field. This nonlinear intensity dependence has to do with the fact that the excitation of level $|2\rangle$ with nonresonant photons comes from the mixing of levels $|1\rangle$ and $|2\rangle$ by the strong field, even if nonresonant. Equations (47) and (48) correspond to the limit of such mixing for $\Delta_1^2 \gg \omega_{Ra}^2$. As this limit is approached, the two-photon nonresonant excitation

$$|1\rangle \xrightarrow{\omega_a} \xrightarrow{\omega_b} |3\rangle$$

becomes increasingly stronger than the two-step excitation. The latter can not conserve energy for large detunings Δ_1. For $\gamma_a \neq 0$, however, photons with frequencies in the tail of the Lorentzian are in resonance with the $|1\rangle \rightarrow |2\rangle$ transition. The excitation of level $|2\rangle$ by these resonant photons goes as $\frac{1}{4}(\omega_{Ra}^2/\Delta_1^2)(\gamma_a/\Gamma_2)$ which, as expected, is linear in the intensity. It is this resonant excitation of level $|2\rangle$ that enhances the two-step excitation and for $\gamma_a > \Gamma_2$ makes it stronger than the two-photon excitation thus reversing the peak asymmetry. Moreover, Eqs. (47) and (48) show that is is the bandwidth γ_a of the strong laser and not that of the probe laser (γ_b) that causes the reversal. These results are of course in accordance with the more rigorous calculations of the previous sections.

Similar peak asymmetry effects owing to the finite bandwidth of an intense field with a Lorentzian spectrum have been discussed recently in connection with resonance fluorescence.[23,25] In that case, the finite bandwidth of the field causes the three peak resonance fluorescence spectrum to become asymmetric for off-resonance excitation. The physical interpretation of this effect is similar to the interpretation given above for double resonance. Photons in the tail of the Lorentzian spectrum are in resonance with the atomic transition and excite atoms which subsequently emit within the natural line. This contribution to resonance fluorescence makes the side peak which is closer to the atomic transition frequency more intense than the other side peak, and even the central peak in extreme cases. We should point out, however, that such effects in either double resonance or resonance fluorescence depend significantly on the line shape of the field spectrum. A field whose line shape falls off faster than a Lorentzian will appear monochromatic to the atom beyond a certain detuning. The asymmetry is then expected to revert back to normal as in the recent experiments of Hogan and Smith.[7]

VI. CONCLUDING REMARKS

Doubly resonant three-photon ionization has been shown to lead to several interesting effects related to the Stark splitting of an atomic transition under a strong field. When contrasted to similar Stark-splitting problems involving spontaneous emission, the presence of ionization introduces new features to the behavior of a three-level system. As we have seen, the problem becomes inherently time dependent and the time of interaction is now an important parameter. Owing to the nonlinear nature (saturation) of the process—a result of the strong field—the dependence of the interaction time is not straightforward as in the case of nonresonant multiphoton ionization. It is the same combination of ionization and saturation that causes the intricate behavior of the widths, heights, and asymmetries of the peaks. This behavior is intricate even when the radiation is monochromatic. The presence of nonmonochromatic radiation introduces another level of complexity. We have dealt, in this paper, with one particular cause of nonmonochromaticity, namely, fluctuating phases modeled as a Wiener-Levy stochastic process. The effect of the finite bandwidth on several aspects of the system has been found to be quite significant. It must be emphasized, however, that the above model does not enable one to predict the complete behavior of the system in the presence of field-amplitude fluctuations. The mathematical complexity is in that case enormous and very little has been done on the problem. However, preliminary and qualitative arguments show that even more significant effects are to be expected. Progress on this problem will be necessary before one can interpret quantitatively experiments performed with pulsed lasers which in most cases exhibit amplitude fluctuations. Nevertheless, our results show that one can obtain a useful qualitative picture even on the basis of phase fluctuations alone.

We chose to study ionization because of the existing experimental results. As we saw, the problem is of interest in its own right. One must remember, in addition, that ionization is apt to be a significant factor whenever strong optical radiation interacts with an atom. How significant it is does of course depend on the particular atom and the details of the experiment. But in most experiments with, for example, atoms such as alkali or alkali earths, ionization more often than not has been found to play its role.

ACKNOWLEDGMENTS

We are grateful to Dr. P. Hogan, Dr. M. Lambropoulos-Reading, Dr. S. E. Moody, and Dr. S. J. Smith for many discussions and communications over the last three years. Their generosity and patience in making available to us a wealth of experimental data have been extremely valuable to this work. This work has been supported by a grant from the National Science Foundation PHY 76-23163.

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