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Rate equations versus Bloch equations in multiphoton ionization*

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The Wilcox-Lamb method of deriving rate equations from Bloch equations is outlined using as an example a two-level atomic model. Computer-generated plots directly comparing solutions of these rate equations and of Bloch equations for a three-level atomic model are illustrated. Two cases of interest are discussed: copropagating and counterpropagating laser beams. Some comments concerning collisional accessing and ionizing of atoms in a very broad Doppler profile are made.

I. INTRODUCTION

The dynamics of atomic excitation under the influence of radiation has traditionally been described by rate equations which balance population gains and losses. For elementary radiative processes the rate coefficients are the familiar Einstein A and B coefficients for spontaneous and stimulated emission.[1]

With the introduction of lasers, intense sources of coherent nearly monochromatic light, new classes of phenomena became apparent. The Schrödinger equation is commonly used to describe details of time-dependent behavior in which coherence of the radiation-atom interaction dominates the dynamics.

The rate equation and the Schrödinger equation are usually viewed as two extremes of a more general dynamics expressed through the Liouville or Bloch equations[2] for the density matrix ρ. The diagonal elements of ρ provide the population variables of the rate equation, and off-diagonal elements of ρ contain phase information as do the Schrödinger amplitudes.

For an N-level atom the rate equations comprise N equations for N real variables; the Schrödinger equation yields N equations for N complex variables; whereas, the Bloch equations deal with N real and $N(N-1)/2$ complex variables. Thus rate equations are attractive for physical as well as computational simplicity. Under what conditions can rate equations be used with confidence for modelling multiphoton ionization dynamics? As a rule,[3] if the coherence-preserving stimulated rates are much slower than incoherent rates, such as spontaneous emission, collisional phase interruption, or ionization, then coherence can be expected to pay a minor role in the excitation dynamics. However, even when these intuitive inequalities fail and coherent population pulsations occur, it may still be possible to obtain reliable population averages from rate equations.

Recently some work on multiphoton ionization of atoms and molecules has shown specific cases where Schrödinger-equation or Bloch-equation solutions are identical with rate-equation solutions.[4] For two-photon interaction, these regimes correspond to very weak or very intense laser intensities (compared with the ionization rate).[4(a)] For multilevel excitation leading to ionization, it was shown that a very large ionization rate can totally dominate the dynamics, thereby making each successive transition of the excitation ladder describable by successively increasing stimulated emission rate.[4(b)]

The purpose of this paper is to study for very general parameter choices (not simply expected rate limits) the agreement between the Bloch-equation solutions and rate-equation solutions in multiphoton ionization. The agreement will be considered good if the rate-equation solutions represent the time-averaged Bloch-equation solutions, meaning that the gross features of population flow from the initially totally populated ground state up through the excited bound levels into the continuum are accurately described. Some analytic calculations along these lines have been done in the context of excitation transport and laser-induced rate processes in gases.[5]

A well-defined method for deriving rate equations from Bloch equations was outlined in 1960 by Wilcox and Lamb.[6] Their formal technique is based on the assumption that the off-diagonal density matrix elements relax very rapidly to steady-state values. Their method yields an explicit form for the absorption cross section.

Section II of this paper illustrates the Wilcox-Lamb method applied to a two-level atomic model. In Sec. III we show, for a more interesting three-level atomic model, some computer plots comparing rate- and Bloch-equation solutions for co-propagating the counter propagating laser beams. In the concluding sections, we summarize our results and find that we can make some comments on collisional accessing of atoms within a very broad Doppler profile.

II. WILCOX-LAMB METHOD

In 1960, Wilcox and Lamb proposed a method for deriving rate equations from Bloch equations.[6] In this section we will outline their general approach using a two-level model atom.

The equations of motion describing the interaction of light with a two-level atom are well known[7]:

$$\dot{\rho}_{11}=\tfrac{1}{2}i\Omega(\rho_{12}-\rho_{21}), \tag{1}$$

$$\dot{\rho}_{22}=\tfrac{1}{2}i\Omega(\rho_{12}-\rho_{21}), \tag{2}$$

$$\dot{\rho}_{12}=i\Delta\rho_{12}-\tfrac{1}{2}i\Omega(\rho_{22}-\rho_{11}), \tag{3}$$

where the ground state (excited state) is indicated by the index 1 (2). Here $\rho_{ij}=\rho_{ji}^*$ is the atomic density matrix element coupling the states i and j. Δ is the detuning frequency between the atom and the laser. Ω is the on-resonance Rabi frequency which describes the rate of coherent population cycling between the two atomic levels.

The introduction of homogeneous rates into the Bloch equations can be accomplished with a first-principles calculation. However, for simplicity we will introduce them in the standard way[8] and write

$$\dot{\rho}_{11}=\tfrac{1}{2}i\Omega(\rho_{12}-\rho_{21})+(1/\tau)\rho_{22}, \tag{4}$$

$$\dot{\rho}_{22}=-\tfrac{1}{2}i\Omega(\rho_{12}-\rho_{21})-(1/\tau)\rho_{22}-R\rho_{22}, \tag{5}$$

$$\dot{\rho}_{12}=-i\Delta\rho_{12}-\tfrac{1}{2}i\Omega(\rho_{22}-\rho_{11})-(1/2\tau)\rho_{12}-\tfrac{1}{2}R\rho_{12}-(1/2T_I)\rho_{12}, \tag{6}$$

where $1/\tau$ is the spontaneous emission rate, R is the ionization rate, and $1/T_I$ is the collisional phase destruction rate. Spontaneous emission and ionization affect both level populations and atomic coherence, whereas collisions in this model only affect atomic coherence by relaxing the off-diagonal density matrix elements. For simplicity, we shall assume the laser intensities to be sufficiently large such that spontaneous emission can be neglected ($1/\tau=0$).

The first step of the Wilcox-Lamb procedure is to set the time derivatives of the off-diagonal density matrix elements to zero. We can then solve these algebraic equations for the off-diagonal density matrix elements in terms of only diagonal density matrix elements. For our two-level atomic model we obtain

$$i\rho_{12}\simeq\frac{\tfrac{1}{2}\Omega}{+i\Delta+\tfrac{1}{2}R+1/2T_I}(\rho_{22}-\rho_{11})=\frac{\tfrac{1}{2}\Omega(\tfrac{1}{2}R+1/2T_I-i\Delta)}{(\tfrac{1}{2}R+1/2T_I)^2+\Delta^2}(\rho_{22}-\rho_{11}). \tag{7}$$

By substituting these solutions for the off-diagonal density matrix elements into the differential equations for the diagonal density matrix elements, we obtain the desired rate equations,

$$\dot{\rho}_{11}=R_s(\rho_{22}-\rho_{11}), \tag{8}$$

$$\dot{\rho}_{22}=-R_s(\rho_{22}-\rho_{11})-R\rho_{22}, \tag{9}$$

where the stimulated emission rate R_s for this two-level model is

$$R_s=\frac{\tfrac{1}{4}\Omega^2(R+1/T_I)}{(\tfrac{1}{2}R+1/2T_I)^2+\Delta^2}. \tag{10}$$

If we define the photon frequency to be ω and the magnitude of the transition dipole matrix element to be d, then the photon flux is

$$\frac{c}{8\pi}\frac{\Omega^2}{\omega d^2}. \tag{11}$$

By substituting (11) into (10) and defining the stimulated rate to equal the flux multiplied by the absorption cross section σ, we find[9]

$$\sigma=\frac{(2\pi\omega d^2/c)(R+1/T_I)}{(\tfrac{1}{2}R+1/2T_I)^2+\Delta^2}. \tag{12}$$

The form of the cross section is a Lorentzian broadened by all the homogeneous broadening mechanisms in the model. Note that the laser power does not appear in the cross section.

III. COMPUTER SOLUTIONS

It is not difficult to generalize the two-level equations, particularly for a system wherein the laser interaction links only successive levels along an excitation ladder. Diagonal elements of ρ evolve according to the equation

$$\dot{\rho}_{mm}=-i\tfrac{1}{2}\Omega_m(\rho_{m-1,m}-\rho_{m,m-1})+\tfrac{1}{2}i\Omega_{m+1}(\rho_{m,m+1}-\rho_{m+1,m})-\left(\sum_{k<m}^{N}\frac{1}{\tau_{mk}}+R\delta_{mN}\right)\rho_{mm}+\sum_{k>m}^{N}\frac{1}{\tau_{km}}\rho_{kk}, \tag{13}$$

where $1/\tau_{km}$ is the spontaneous emission rate from the state k to the state m, Ω_m is the Rabi frequency for the transition m, and R is the ionization rate loss from the highest bound level N. Off-diagonal elements obey the equation

$$\dot{\rho}_{mn}=-\left(i\Delta_{mn}+\sum_{k<m}\frac{1}{2\tau_{mk}}+\sum_{k<n}\frac{1}{2\tau_{nk}}+\frac{R}{2}\delta_{Nn}+\frac{1}{2T_I}\right)\rho_{mn}+\tfrac{1}{2}i\Omega_n\rho_{m,n-1}-\tfrac{1}{2}i\Omega_m\rho_{m-1,n}+\tfrac{1}{2}i\Omega_{n+1}\rho_{m,n+1}-\tfrac{1}{2}i\Omega_{m+1}\rho_{m+1,n}, \tag{14}$$

$m<n$, where Δ_{mn} is the laser-atom detuning between levels m and n. $1/T_I$ is the collision phase destruction rate which is assumed constant independent of m and n.

As discussed in the previous section, we obtain rate equations by setting off-diagonal time derivatives (14) to zero, solving (14) for off-diagonal elements, and substituting the result into Eq. (13). Although this prescription has been followed analytically by several authors,[3,6] the resulting formulas are quite complicated, even for a three-level atom. We have instead constructed solutions numerically. The following paragraphs examine some of our results for a three-level atom.

The Rabi frequencies, Ω_1 and Ω_2, and the ionization rate R will be fixed parameters: $\Omega_1=\Omega_2=1$ and $R=0.5$. We will vary both the collisional phase interruption time and the detuning independently for the two cases of copropagating and counterpropagating lasers. If the lasers are copropagating, then a laser-atom detuning of Δ_1 for the first transition implies a laser-atom detuning of $2\Delta_1$ for the two-photon transition. If the lasers are counterpropagating, then we have the two-photon, Doppler-free case: a detuning of Δ_1 for the first transition is cancelled by the detuning Δ_2 of the second transition, such that the two-photon transition is always resonant.

We would expect that the Wilcox-Lamb rate equations are exact if $1/T_I$ is very large. In this case, the off-diagonal density matrix elements relax very rapidly to their steady-state values, making their derivatives exactly zero. We have used this information to check our computer code.

Figure 1 shows the Bloch and rate solutions on-resonance with no collisional phase interruption. The agreement appears very good in this case, since the rate curves roughly represent the time-averaged Bloch solutions. By turning on the collisions, we notice in Fig. 2 the damping out of the Rabi oscillations, and after the initial transients decay, the solutions for the lower populations and for the ions become essentially identical. On this time scale, the total ions produced are almost the same in Figs. 1 and 2, implying that on-resonance for $1 \geq 1/T_I \geq 0$ the ion production is independent of $1/T_I$. On-resonance there is no difference between copropagating and counterpropagating laser beams.

In Fig. 3, we choose a laser-atom detuning for each successive transition equal to the Rabi frequency and have no collisional relaxation. The rate-equation solutions have no obvious relation to the Bloch-equation solutions. In particular, the rate equations do not predict any ionization, while the Bloch-equation solutions on this time scale predict roughly 20% ionization. If we keep the detuning fixed, but introduce collisional relaxation equal to the Rabi frequency, then in Fig. 4 we find very good agreement between the rate- and Bloch-equation solutions after the initial transients decay. The off-resonance ionization with collisional re-

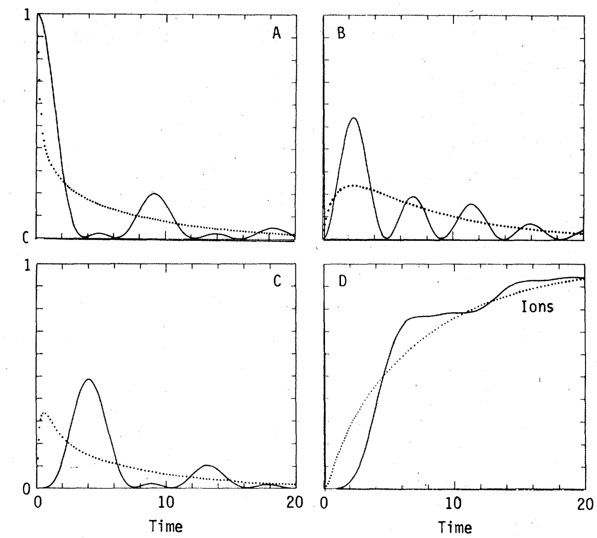

FIG. 1. Atomic level populations versus time (in units of inverse Rabi frequency) obtained as solutions to Bloch equations (solid line) and to rate equations (dotted line): A = level 1; B = level 2; C = level 3; D = ions. Parameters are Rabi frequencies $\Omega_1=\Omega_2=1$ and ionization rate $R=0.5$. Both lasers are resonant (either collinear or counterpropagating); there is no collisional phase interruption: $1/T_I=0$.

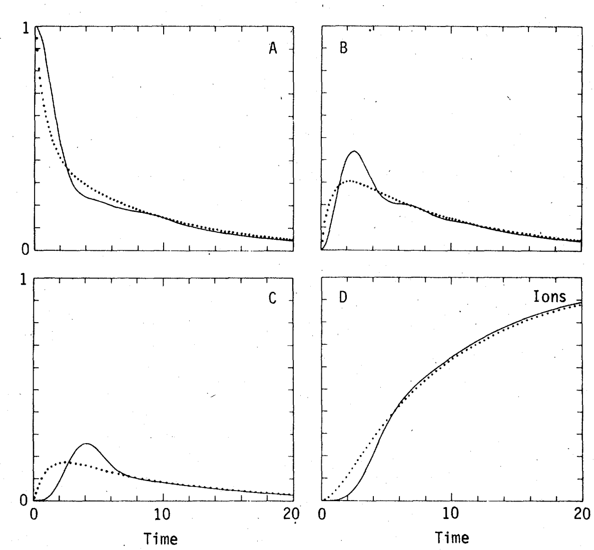

FIG. 2. Same as in Fig. 1 ($\Omega_1=\Omega_2=1$; $R=0.5$; $\Delta=0$) but with relaxation rate equal to the Rabi frequency, $1/T_I=1$.

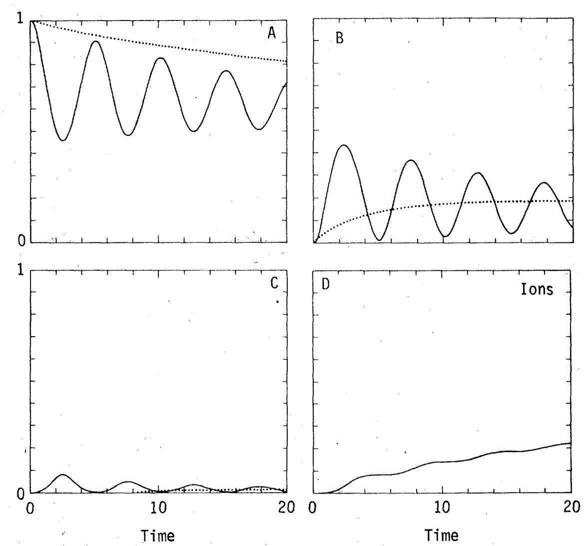

FIG. 3. Atomic populations versus time obtained as solutions to Bloch equations (solid line) and rate equation (dotted line): A = level 1; B = level 2; C = level 3; D = ions. Parameters are $\Omega_1 = \Omega_2 = 1$ and $R = 0.5$; lasers are collinear and are detuned by one Rabi frequency, $\Delta = \Omega_1 = 1$; no relaxation, $1/T_I = 0$.

laxation on this time scale is roughly 65%.

We are observing pressure broadening as a means of ionizing atoms off-resonance. The atomic levels are effectively broadened by the collisions, allowing the detuned lasers to effectively resonantly excite and ionize many atoms. For the two-level model, Eq. (12) shows the broadening effect of collisions on the absorption cross section.

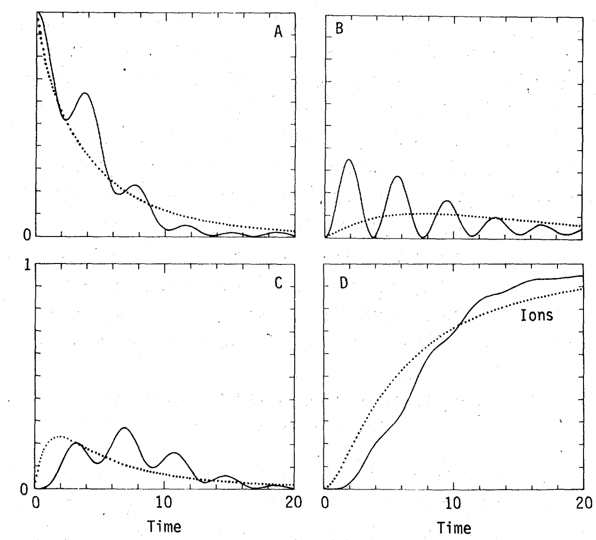

FIG. 5. Same as in Fig. 3 ($\Omega_1 = \Omega_2 = 1$; $R = 0.5$; detuned $\Delta = 1$; no relaxation, $1/T_I = 0$) but with counterpropagating lasers.

If we would continue to broaden the transition by increasing $1/T_I$, we would find that the number of ionized atoms decreases. The optimum can be shown to be in this case nearly unity.

In Fig. 5 we consider counterpropagating laser beams where the intermediate-level detuning equals unity, but the two-photon transition is resonant. Collisional relaxation is negligible. We see very good agreement between rate-equation solutions and Bloch-equation solutions. We suspect the two-photon resonance is the origin of this

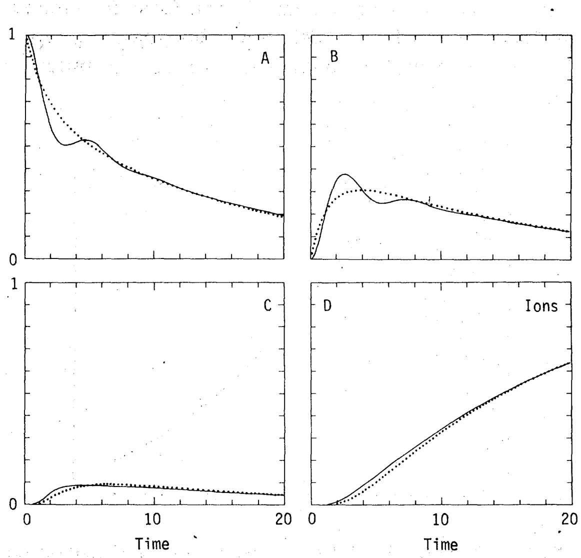

FIG. 4. Same as Fig. 3 ($\Omega_1 = \Omega_2 = 1$; $R = 0.5$; $\Delta = 1$, collinear lasers) but with relaxation rate equal to Rabi rate, $1/T_I = 1$.

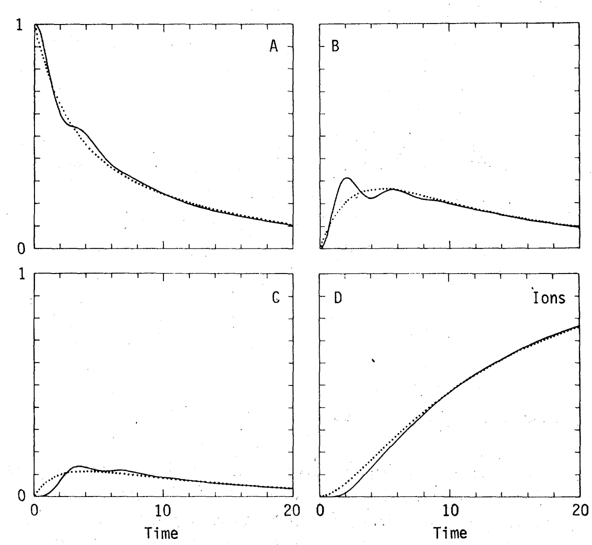

FIG. 6. Same as in Fig. 5 ($\Omega_1 = \Omega_2 = 1$; $R = 0.5$; detuned $\Delta = 1$ counterpropagating) but with relaxation $1/T_I = 1$. (Same as in Fig. 4 but counterpropagating.)

agreement, since Fig. 1 shows that resonance allows rate-equation solutions to be the time averages of the Bloch-equation solutions. The number of ions collected on this time scale is almost identical to that collected in Fig. 1, where the intermediate level is resonant. We see a very uniform ionization, which is very large and independent of the intermediate-level detuning. If we increase the collisional relaxation as shown in Fig. 6, the ionization on this time scale decreases. As expected, the rate- and Bloch-equation solutions are identical after the initial-time transients decay.

IV. COMMENTS ON COLLISION OR PRESSURE BROADENING

The implications of our results with respect to multiphoton ionization of atoms which are substantially Doppler broadened is that for copropagating lasers a collision bandwidth on the order of the Rabi frequency can substantially improve the off-resonance ion output, while not significantly reducing the on-resonance ion output. In Fig. 7, we see overall ion output within the Doppler profile as a function of time and detuning. On the same time scale, Fig. 7(b) shows the increase in the ion output with collisions as compared to Fig. 7(a). However, Fig. 7(c) shows that if the collision width becomes much larger than the Rabi frequency, overall ion output is reduced. The unequal increase in the ion output with time in Fig. 7(a) is a result

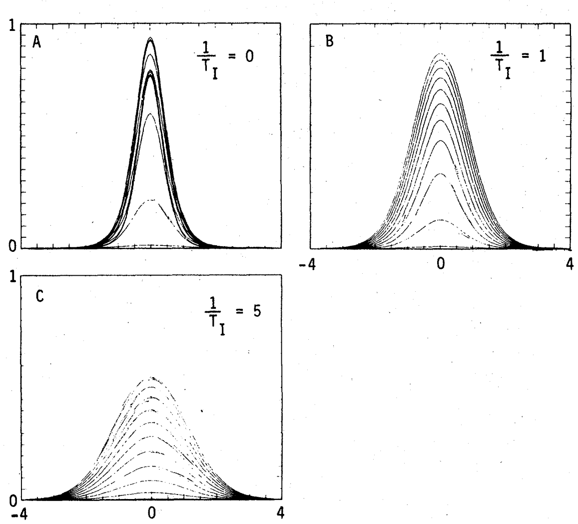

FIG. 7. Distribution of ions at successively later times (solid curves) within a Doppler profile: relative ion probability versus detuning in units of Rabi frequency Ω_1. Parameters are Rabi frequencies $\Omega_1 = \Omega_2 = 1$; ionization rate $R = 0.5$; collinear lasers. (a) No relaxation, $1/T_I = 0$. (b) Relaxation rate equal to Rabi frequency, $1/T_I = 1$. (c) Relaxation rate much larger than Rabi frequency, $1/T_I = 5$.

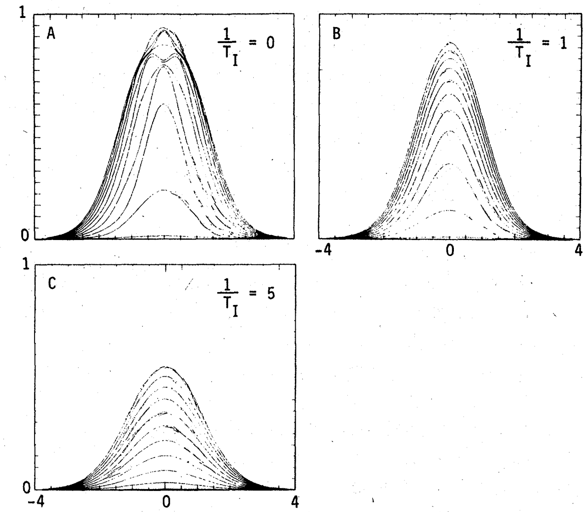

FIG. 8. Same as Fig. 7 ($\Omega_1 = \Omega_2 = 1$; $R = 0.5$) but with counterpropagating lasers. (a) $1/T_I = 0$; (b) $1/T_I = 1$; (c) $1/T_I = 5$.

of Rabi oscillations. We can see this by comparing Fig. 1 with the resonant-ion production in time in Fig. 7(a). The collisions act to reduce the coherence and, therefore, the Rabi oscillations. The roughly uniform increase in the ion output with time is shown in Figs. 7(b) and 7(c). The resonance portion of Fig. 7(b) can be compared with Fig. 2.

In Fig. 8, we illustrate the case where the lasers are counterpropagating. The ion output with an increasing collision bandwidth continually decreases. We see this effect by comparing Fig. 8(a) with Fig. 8(b) and Fig. 8(c). For a collision bandwidth greater than or proportional to the Rabi frequency, we find essentially no difference between copropagating and counterpropagating lasers: compare

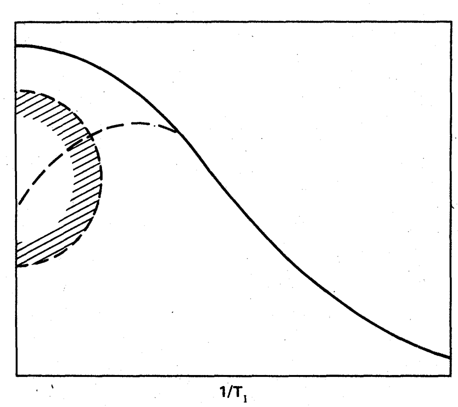

FIG. 9. Schematic plot of Doppler-averaged ionization versus collision width $1/T_I$ for collinear lasers (dashed line) and counterpropagating lasers (full line). Shaded region indicates region where rate equations fail.

Figs. 7(b) and 7(c) with Figs. 8(b) and 8(c). The collision broadening has become sufficiently large such that the concept of resonance is no longer meaningful. Off-resonance atoms are now as resonant as resonantly pumped atoms. In general, counterpropagating lasers and no collisions maximizes ion output.

V. SUMMARY

We found that without any collisional phase interruption, the rate-equation solutions represent the time-averaged Bloch-equation solutions if we are on-resonance. Agreement is also good if we tune our lasers to a two-photon resonance, but allow intermediate-state detuning. The comparison between rate-equation solutions and Bloch-equation solutions off-resonance is poor if we have our lasers copropagating. Therefore, rate equations cannot be used with confidence to model a system of atoms which have a large Doppler profile if the lasers are copropagating. If the lasers are counterpropagating, however, such that we have a two-photon resonance over the entire Doppler profile, then rate equations can be used with confidence.

If we introduced a collisional- or pressure-broadened width on the order of the Rabi frequency, then in all cases after the initial transient period rate-equation solutions and Bloch-equation solutions become identical. As expected, rate equations can be used with confidence. In addition, ion output off-resonance is significantly improved by pressure broadening if the lasers are copropagating. Figure 9 shows the Doppler-averaged ionization as a function of the collision width $1/T_I$ and the region where rate equations are not valid.

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