Cooperative effects on multiphoton ionization and third-harmonic generation in the region near three-photon resonance

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Three-photon resonance enhancement of third-harmonic generation and multiphoton ionization is treated for a slab geometry configuration. Striking pressure effects which become important at concentrations $n \gtrsim 10^{12}/\text{cm}^3$ for narrow-bandwidth short-pulse lasers are predicted for both the third-harmonic signal and the multiphoton ionization. For example, part of the third-harmonic signal exits the slab simultaneously with the laser pulse while another part is time delayed for small detunings from resonance. At intermediate detuning from the three-photon resonance the two parts can interfere. Multiphoton ionization yields near three-photon resonance are strongly suppressed under certain conditions, and peaks may occur for proper detunings on both sides of the three-photon resonance. A detailed experimental verification is suggested for Xe.

I. INTRODUCTION

In a recent study, Miller *et al.*[1] observed extremely large shifting and broadening of multiphoton ionization signals associated with the three-photon resonance between the $5p^6$ level and the $5p^5 6s\,[^2P_{3/2}]J=1$ level of Xe. Results were obtained with a tightly focused laser beam over the pressure range of 10^{-5} to several Torr. Similar effects were seen in Kr and Ar. Accompanying the increase with pressure in width and shift of the resonance, a strong decrease in ionization yield was simultaneously observed. Payne, Garrett, and Baker[2] accounted for the general trend of these effects in a theoretical model which took account of coherent excitation, ionization, and third-harmonic generation self-consistently in a laser beam propagating through a focal volume. In this treatment it was demonstrated that dramatic effects result from the accumulated influence of the third-harmonic field on the atomic response of atoms along the propagating laser pulse. In the previous theory the beam geometry was greatly simplified and the effect of the π phase change in the laser field in passing through the focus was simulated. The theory contained several approximations which were difficult to evaluate as to their accuracy. Consequently, it is desirable to work out the theory for slab geometry where we shall see that only well-established approximations are required. This simplified treatment also predicts other observable effects which could be observed using commercially available pulsed dye lasers.

II. MODEL DESCRIPTION

We consider a plane wave normally incident on a slab of gas of thickness z_0. Thus, the laser field is of the form

$$E(z,t)=\vec{j}\,E_0(t-z/c)\cos[\omega t-kz+\phi(t-z/c)]\ , \tag{1}$$

where we assume plane polarization in the y direction $\vec{j}$, and $E_0(t-z/c)$ is (on the average) a maximum when its argument is zero and it is very small if $|t-z/c| \gg \tau_0$, where τ_0 is a measure of the pulse length. For transform-limited bandwidth lasers, ϕ will be constant and E_0 will change only over time scales $\sim\tau_0$. However, we can simulate broad bandwidth lasers by considering the occurrence of stochastic fluctuations in E_0 and ϕ. In this case τ_0 is the length of time over which E_0 takes on large values, and both E_0 and ϕ undergo large changes on much shorter time scales $\sim 1/\Gamma_L$, where Γ_L is the laser bandwidth.

In the previous treatment of the present problem (but for pulse propagation through a focal volume), the problem was described by a second quantized effective Hamiltonian which was a function of the position along the laser beam as a result of (1) the focusing of the beam and (2) the progressive influence of atoms within the laser volume with other "downstream" atoms in the direction of propagation of the laser pulse. Here we will adopt a more transparent model which is capable of describing the new cooperative effects while retaining a clear physical picture of the source of various contributions to multiphoton ionization and third-harmonic signals.

Thus, if we consider the propagation of a laser pulse at frequency ω which is near a three-photon resonance between the ground state $|0\rangle$ and an upper level $|1\rangle$ of a target gas, then it is well known from nonlinear optics that in such a situation a polarizability at frequency $\sim 3\omega$ will be generated in the gas.[3] If $\vec{P}_{3\omega}(z,t)$ is this polarizability the resulting field is given classically by

$$\vec{E}_{3\omega}(z,t) = -\vec{j}\,\frac{2\pi}{c}\int_0^{z_0} dz' \frac{\partial \vec{P}_{3\omega}}{\partial t}(z', t - |z-z'|/c) \;. \tag{2}$$

If $\omega_r = \omega_1 - \omega_0$ is the resonance frequency for one-photon excitation of the upper level, we assume that the detuning $\Delta_0 = 3\omega - \omega_r$ from the three-photon resonance is such that $|\Delta_0|$ is small as compared to the detuning from any other three-photon resonance.

An electromagnetic field at frequency 3ω is strongly dispersed. In particular, the wave vector's length is

$$k_{3\omega} = 3\omega/c - 2\pi n\omega_r P_{01}^2/(\hbar c \Delta_0) \;, \tag{3}$$

where P_{01} is the dipole matrix element between the ground state and the near resonance excited state and n is the atomic concentration. It is interesting to note that a wave packet with central frequency near 3ω would propagate at the group velocity $V_g^{-1} = dk_{3\omega}/d(3\omega)$,

$$\begin{aligned} V_g^{-1} &= 1/c + 2\pi n\omega_r P_{01}^2/(\hbar c \Delta_0^2) \\ &= \kappa/\Delta_0^2 + c^{-1} \;, \end{aligned} \tag{4}$$

where

$$\kappa = 2\pi n\omega_r P_{01}^2/\hbar c = (3\pi/2)(c/\omega_r)^2 n\gamma_{01}$$

for a $J=0$ to $J=1$ transition, with γ_{01} being the Einstein A coefficient for the transition. The wave packet would also decrease in amplitude due to near resonant elastic scattering from concentration fluctuations. After a distance z, the decrease in amplitude would be

$$\exp(-n\sigma_e z/2) = \exp(-\gamma_{01}\kappa z/2\Delta_0^2) \;,$$

since

$$\sigma_e = (3\pi/2)(c/\omega_r)^2\gamma_{01}^2/\Delta_0^2 \;.$$

These effects involving the dispersive properties of the medium and the scattering from concentration fluctuations have been reviewed to orient the reader in making connections with standard third-harmonic generation theories and to aid in interpretation of the results which will be derived. We note here that if $\gamma_{01} \simeq 4\times 10^8$/s, $c/\omega_r \simeq 2\times 10^{-6}$ cm, and $n \sim 3\times 10^{16}/\text{cm}^3$, the group velocity becomes much less than c when $|\Delta_0| < 10^{12}$/s ($\lesssim 1$-Å detuning) and the attenuation of the amplitude with z for a wave packet becomes rather rapid. We have it is hoped made the point that the propagation situation with the third-harmonic signal within $|\Delta_0| < 10^{12}$/s is very complex; yet very near to the resonance even a very weak $\vec{E}_{3\omega}$ may change the atomic response considerably, and it is imperative that any treatment of atomic response incorporate the effect of both $\vec{E}_{3\omega}$ and $\vec{E}(z,t)$ self-consistently.[2]

We consider the behavior of an atom at depth z. Let the Hamiltonian be

$$\hat{H}(z) = \hat{H}_0(z) - \hat{P}_y E(z,t) - \hat{P}_y E_{3\omega}(z,t) \;, \tag{5}$$

and $|\Psi(z,t)\rangle$ represents the time-dependent state vector of an atom at z,

$$|\Psi(z,t)\rangle = a_0(z,t)e^{-i\omega_0 t}|0\rangle + a_1(z,t)e^{-i\omega_1 t}|1\rangle + \sum_{n\neq 0,1}\!\!\!\!\!\!\!\int\;\; a_n(z,t)e^{-i\omega_n t}|n\rangle \;, \tag{6}$$

where $\hat{H}(z)$ is the Hamiltonian of the isolated atom, and we include the interaction of the atom with both the laser field and the third-harmonic field. In the following we make a two-state approximation in deriving expressions for ionization and third-harmonic rates. Although the procedure is a familiar one, we resketch it here to keep the physical picture clearly in mind. The unit operator is $\hat{1} \simeq |0\rangle\langle 0| + |1\rangle\langle 1| = \hat{P}_1 + \hat{P}_2$. The field due to the polarizability at 3ω is given by Eq. (2) with

$$\vec{P}_{3\omega}(z,t) = \vec{j}\,n\langle\Psi(z,t)|\hat{P}_y|\Psi(z,t)\rangle \simeq \vec{j}\,n[e^{-i(\omega_1-\omega_0)t}a_1(z,t)a_0^*(z,t) + \text{c.c.}] \;. \tag{7}$$

We endeavor here to treat the situation where $3\omega - \omega_r$ is smaller than a few-hundred wave numbers and $n \lesssim 10^{16}/\text{cm}^3$, so that

$$2\pi(n_\omega - 1)z_0/\lambda_0 << 1 \;,$$

where n_ω is the refractive index at the laser frequency and λ_0 is the laser wavelength. With these restrictions on n and ω the dispersive properties at frequency 3ω will be dominated by the near one-photon resonance, and a two-state plus ionization continuum solution to the problem is appropriate. Further, we can use $\omega/k_\omega=c$ in dealing with the propagation of the laser pulse in situations where n and ω are restricted as described above and power densities in the unfocused laser beam are sufficiently low so that $\int_{-\infty}^{\infty}\Omega_3 dt << 1$, where Ω_3 is the three-photon Rabi frequency at beam center. In the case of the three-photon resonance in Xe studied by Miller and Compton,[1] we estimate that with a beam diameter of 0.1 cm and a pulse length of $\tau\approx 4\times 10^{-9}$ s the energy per pulse would have to be $\epsilon\approx 400$ mJ in order to violate the inequality $\int_{-\infty}^{\infty}\Omega_3 dt << 1$. Thus, with present commercial lasers which have bandwidths of ~ 0.05 cm^{-1}, pulse lengths $\tau\approx 4\times 10^{-9}$ s, and energy per pulse $\epsilon \lesssim 20$ mJ, a linearization in Ω_3 should be an excellent approximation. We will now formulate equations of motion which will permit us to predict the effects of the perturbation $-\hat{P}_y E_{3\omega}(z,t)$ on the atomic response.

We let

$$\hat{V}=-\hat{P}_y E(z,t)-\hat{P}_y E_{3\omega}(z,t)=\hat{V}_1+\hat{V}_2 ,$$

where $\hat{V}_2=-\hat{P}_y E_{3\omega}(z,t)$. The time evaluation of $|\psi(z,t)\rangle$ can be described by

$$|\Psi(z,t)\rangle = e^{-i\hat{H}_0(z)t/\hbar}\hat{S}(z,t)\,|\Psi(z,-\infty)\rangle . \quad (8)$$

Now $\hat{H}\,|\Psi(z,t)\rangle = i\hbar\partial\,|\Psi(z,t)\rangle/\partial t$, which implies that the operator $\hat{S}(z,t)$ satisfies, with

$$\hat{V}_I(z,t)=e^{-H_0 t/\hbar}\hat{V}(z,t)e^{-iH_0 t/\hbar} ,$$

$$i\hbar\partial\hat{S}(z,t)/\partial t=\hat{V}_I(z,t)\hat{S}(z,t)=\hat{V}_I(z,t)\left[\hat{1}+(i\hbar)^{-1}\int_{-\infty}^{t}\hat{V}_I(z,t')\hat{S}(z,t')dt'\right] . \quad (9)$$

Also, we define $a_0(z,t)$ and $a_1(z,t)$ by $[\,|\Psi(z,-\infty)\rangle = |0\rangle]$

$$\begin{aligned}\langle 0|\Psi(z,t)\rangle &= \langle 0|e^{-i\vec{H}_0 t/\hbar}\hat{S}(z,t)\,|\Psi(z,-\infty)\rangle\\ &= e^{-i\omega_0 t}\langle 0|\hat{S}(z,t)|0\rangle\\ &= e^{-i\omega_0 t}a_0(z,t) ,\end{aligned} \quad (10)$$

$$\begin{aligned}\langle 1|\Psi(z,t)\rangle &= e^{-i\omega_1 t}\langle 1|\hat{S}(z,t)|0\rangle\\ &= e^{-i\omega_1 t}a_1(z,t) .\end{aligned}$$

The terms $a_0(z,t)$ and $a_1(z,t)$ are probability amplitudes for atoms at z at time t being in states $|0\rangle$ and $1\rangle$, respectively. To derive an equation of motion for $a_0(z,t)$, we use

$$\begin{aligned}i\hbar\frac{\partial a_0}{\partial t}(z,t) &= i\hbar\frac{\partial}{\partial t}\langle 0|\hat{S}(z,t)|0\rangle\\ &= \langle 0|\hat{V}_I(z,t)\hat{S}(z,t)|0\rangle ,\end{aligned} \quad (11)$$

where we have used Eqs. (9) and (10). We retain only first-order processes involving $\hat{V}_2(z,t)$ since this is very weak light which is nearly resonant with a one-photon dipole-allowed transition,

$$\begin{aligned}i\hbar\frac{\partial a_0}{\partial t}(z,t) &\simeq \langle 0|\hat{V}_{I2}(z,t)(\,|0\rangle\langle 0| + |1\rangle\langle 1|\,)\hat{S}(z,t)|0\rangle + \langle 0|\hat{V}_{I1}(z,t)\hat{S}(z,t)|0\rangle\\ &\simeq \langle 0|\hat{V}_{I2}(z,t)|1\rangle a_1(z,t)\\ &\quad + \left\langle 0\left|\hat{V}_{I1}(z,t)\left[\hat{1}+(i\hbar)^{-1}\int_{-\infty}^{t}\hat{V}_{I1}(z,t')\hat{S}(z,t')dt'\right]\right|0\right\rangle\\ &\simeq \langle 0|\hat{V}_{I2}(z,t)|1\rangle a_1(z,t) + \left\langle 0\left|\hat{V}_{I1}(z,t)\int_{-\infty}^{t}\hat{V}_{I1}(z,t')dt' a_0(z,t')\right|0\right\rangle\Big/(i\hbar)\\ &\quad + \left\langle 0\left|\hat{V}_{I1}(z,t)\int_{-\infty}^{t}\hat{V}_{I1}(z,t')(\hat{1}-|0\rangle\langle 0|)\hat{S}(z,t')dt'\right|0\right\rangle\Big/(i\hbar) .\end{aligned}$$

Using

$$\hat{S}(z,t')\cong\hat{1}+(i\hbar)^{-1}\int_{-\infty}^{t}\hat{V}_{I1}(t'')\hat{S}(z,t'')dt''$$

again and $(\hat{1}-|0\rangle\langle 0|)|0\rangle=0$, we obtain

$$i\hbar\frac{\partial a_0}{\partial t}(z,t)\simeq\langle 0|\hat{V}_{I2}(z,t)|1\rangle a_1(z,t)+\int_{-\infty}^{t}\langle 0|\hat{V}_{I1}(z,t)\hat{V}_{I1}(z,t')|0\rangle a_0(z,t')dt'\Big/(i\hbar)$$
$$+(i\hbar)^{-2}\int_{-\infty}^{t}dt'\int_{-\infty}^{t'}dt''\langle 0|\hat{V}_{I1}(z,t)\hat{V}_{I1}(z,t')(\hat{1}-|0\rangle\langle 0|)\hat{V}_{I1}(z,t'')\hat{S}(z,t'')|0\rangle$$
$$\simeq\langle 0|\hat{V}_{IZ}(z,t)|1\rangle a_1(z,t)+\int_{-\infty}^{t}\langle 0|\hat{V}_{I1}(z,t)\hat{V}_{I1}(z,t')|0\rangle(i\hbar)^{-1}a_0(z,t)$$
$$+(i\hbar)^{-2}\int_{-\infty}^{t}dt'\int_{-\infty}^{t'}dt''\langle 0|\hat{V}_{I1}(z,t)\hat{V}_{I1}(z,t')(\hat{1}-|0\rangle\langle 0|)\hat{V}_{I1}(z,t'')|1\rangle a_1(z,t)\ , \tag{12}$$

where we have used $\hat{1}\approx|0\rangle\langle 0|+|1\rangle\langle 1|$ inserted between $\hat{V}_{I1}(z,t'')$ and $\hat{S}(z,t'')$ with $\langle 0|\hat{V}_{I1}(z,t)\hat{V}_{I1}(z,t')\hat{V}_{I1}(z,t'')|0\rangle=0$. Since $\langle 1|\hat{S}(z,t'')|0\rangle=a_1(z,t'')$, unit operators were inserted between products of interaction representation operators so that the time integrations could be performed. The time integration over t'' in the last term of Eq. (12) involves complex exponential times $a_1(z,t'')$ with the exponential term oscillating with a period $\sim 10^{-15}$ s. Thus, assuming $a_1(z,t)$ changes much slower and integrating by parts permits one to show that $a_1(z,t'')$ can be brought outside the time integrals evaluated at t. The same technique was used to remove $a_0(z,t')$ from the dt' integral in the second term. The equation for $da_0(z,t)/dt$ becomes

$$\frac{\partial a_0}{\partial t}(z,t)=(i\hbar)^{-1}\langle 0|\hat{V}_{I2}(z,t)|1\rangle a_1(z,t)+i\Delta_0^S(t-z/c)a_0(z,t)+ie^{i\Delta_0 t}\Omega_3(t-z/c)a_1\ , \tag{13}$$

where

$$i\Delta_0^S(t-z/c)=(i\hbar)^{-2}\int_{-\infty}^{t}\langle 0|\hat{V}_{I1}(z,t)\hat{V}_{I1}(z,t')|0\rangle dt'\ ,$$
$$ie^{i\Delta_0 t}\Omega_3(t-z/c)=(i\hbar)^{-3}\int_{-\infty}^{t}dt'\int_{-\infty}^{t'}dt''\langle 0|\hat{V}_{I1}(z,t)\hat{V}_{I1}(z,t')(\hat{1}-|0\rangle\langle 0|)\hat{V}_{I1}(z,t'')|1\rangle\ , \tag{14}$$
$$\Delta_0=3\omega-\omega_r\ ,$$

and in evaluating Δ_0^S and Ω_3 only the terms with slow time dependences will be retained. Keeping only those terms which do not oscillate rapidly is analagous to a rotating wave approximation and is also necessary to be consistent with a two-state plus continuum approximation.

To derive an analogous equation for $\partial a_1(z,t)/\partial t$, one begins with $i\hbar\partial a_1(z,t)/\partial t=i\hbar\partial\langle|\hat{S}(z,t)|0\rangle/\partial t$ and proceeds as we did in deriving an equation for $\partial a_0(z,t)/\partial t$. Here, one allows $a_1(z,t)$ to be coupled to $a_0(z,t)$ via $\hat{V}_{I2}(z,t)$ and in third order by $\hat{V}_{I1}(z,t)$. In addition, $\hat{V}_{I1}(z,t)$ couples $a_1(z,t)$ to states in the ionization continuum. If dipole matrix elements between $|1\rangle$ and states in the ionization continuum are slowly varying as a function of the photoelectron energy and if continuum-continuum scattering is neglected, the continuum states can be eliminated in terms of an ionization rate and a principal-value integral contribution to an ac Stark shift. We find

$$\frac{\partial a_1}{\partial t}(z,t)=(i\hbar)^{-1}\langle 1|\hat{V}_{I2}(z,t)|0\rangle a_0(z,t)+i\Delta_1^S(t-z/c)a_1(z,t)$$
$$+ie^{-i\Delta_0 t}\Omega_3^*(t-z/c)a_0(z,t)-\gamma_I(t-z/c)a_1(z,t)/2\ , \tag{15}$$

where

$$i\Delta_1^S(t-z/c)=(i\hbar)^{-2}\int_{-\infty}^{t}\langle 1|\hat{V}_{I1}(z,t)\hat{V}_{I1}(z,t')|1\rangle dt'\ ,$$

and $\gamma_I(t-z/c)$ is the ionization rate of the population of state $|1\rangle$. In evaluating Δ_1^S by inserting a unit operator $\hat{1}=S_n|n\rangle\langle n|$ between $\hat{V}_{I1}(z,t)$ and $\hat{V}_{I1}(z,t')$, the integral over intermediate continuum states is evaluated as a principal value integral (this is dictated by the detailed treatment of the coupling of $|1\rangle$ to the continuum states). The terms Δ_0^S and Δ_1^S are, of course, ac Stark shifts induced in the atom by the laser fields. By considering $\partial(|a_0(z,t)|^2+|a_1(z,t)|^2)/\partial t$, we can show that the rate of change of the ionization probability P_I is

$$\frac{dP_I}{dt}(z,t)=\gamma_I(t-z/c)\,|a_1(z,t)|^2\,, \tag{16}$$

where $a_1(z,t)$ must be obtained by solving simultaneous nonlinear equations for $a_1(z,t)$ and $a_0(z,t)$.

It is of primary importance in this problem to keep track of the phase of $a_0(z,t)$ and $a_1(z,t)$ in detail. We consider first the phase information in Ω_3. Since

$$\hat{V}_1(z,t)=-\hat{P}_y E_0(t-z/c)\cos[\omega t-kz+\phi(t-z/c)]=-\hat{P}_y E(z,t)\,,$$

we have

$$ie^{i\Delta_0 t}\Omega_3(t-z/c)=(i\hbar)^{-3}\int_{-\infty}^{t}dt'\int_{-\infty}^{t'}dt''W\,,$$

where

$$\begin{aligned}W&=\langle 0|\hat{V}_{I1}(z,t)\hat{V}_{I1}(z,t')(\hat{1}=|0\rangle\langle 0|)\hat{V}_{I1}(z,t'')|1\rangle\\&=\sum\!\!\!\!\!\!\int_{n'}\;\sum\!\!\!\!\!\!\int_{\substack{m\\m\neq 0}}\langle 0|\hat{V}_{I1}(z,t)|n'\rangle\langle n'|\hat{V}_{I1}(z,t')|m\rangle\langle m|\hat{V}_{I1}(z,t'')|1\rangle\\&=\sum\!\!\!\!\!\!\int_{n'}\;\sum\!\!\!\!\!\!\int_{\substack{m\\m\neq 0}}\langle 0|\hat{V}_1(z,t)|n'\rangle e^{i(\omega_0-\omega_{n'})t}\langle n'|\hat{V}_1(z,t')|m\rangle e^{i(\omega_{n'}-\omega_m)t'}\langle m|\hat{V}_1(z,t'')|1\rangle e^{i(\omega_m-\omega_1)t''}\,.\end{aligned}$$

In carrying out the integration over t' and t'' the factor $\cos[\omega t''-kz+\phi(t''-z/c)]$ is broken up into a sum of two complex exponentials according to $\cos x=(e^{ix}+e^{-ix})/2$, and several terms with similar amplitudes result after carrying out both the t' and t'' integrations while using the fact that $E_0(t-z/c)$ and $\exp[i\phi(t-z/c)]$ are slowly varying compared with factors such as $\exp[i(\omega_n-\omega_m\pm\omega)t]$. The resonant slowly oscillating term comes from the $\exp(i\omega t'')\exp(i\omega t')\exp(i\omega t)$ term when all three $\hat{V}_1(z,t)$ terms are expressed as complex exponentials. Thus,

$$ie^{i\Delta_0 t}\Omega_3(t-z/c)=\frac{i}{8\hbar^3}e^{-3ikz}e^{3i\phi(t-z/c)}\sum\!\!\!\!\!\!\int_{n'}\;\sum\!\!\!\!\!\!\int_{\substack{m\\m\neq 0}}\frac{P_{0n'}P_{n'm}P_{m1}E_0^3(t-z/c)e^{i(\omega_0-\omega_1+3\omega)t}}{(\omega_m-\omega_1+\omega)(\omega_{n'}-\omega_1+2\omega)}\,.$$

Thus,

$$\Omega_3(t-z/c)=\left[\frac{E_0(t-z/c)e^{i\phi(t-z/c)}}{2\hbar}\right]^3 e^{-3ikz}\sum\!\!\!\!\!\!\int_{n'}\;\sum\!\!\!\!\!\!\int_{\substack{m\\m\neq 0}}\frac{P_{0n'}P_{mn'}P_{m1}}{(\omega_m-\omega_1+\omega)(\omega_{n'}-\omega_1+2\omega)}\,, \tag{17}$$

where $P_{kl}=\langle k|\hat{P}_y|l\rangle$. The evaluation of the ac Stark shifts proceeds in a similar way, and the nonoscillating results in the latter case carry no phase information. We write

$$\Omega_3(t-z/c)=\Omega_{0,3}(t-z/c)e^{3i\phi(t-z/c)}e^{-3ikz}=\Omega_{0,3}(t-z/c)e^{3i\phi(t-z/c)}e^{-3(i\omega/c)z}\,, \tag{18}$$

where we assume that n is small enough so that $k\approx\omega/c$ for the propagation of the laser pulse.

We will now develop a systematic way of solving for $P_I(z,t)$ in the limit where the power density is sufficiently low so that $|a_1(z,t)|$ remains small compared with unity throughout the laser pulse. Consider the system of equations

$$\begin{aligned}\frac{\partial a_1}{\partial t}(\lambda,z,t)&=(i\hbar)^{-1}\langle 1|\hat{V}_{I2}(\lambda,z,t)|0\rangle a_0(\lambda,z,t)+i\Delta_1^S(t-z/c)a_1(\lambda,z,t)\\&\quad-\gamma_I(t-z/c)a_1(\lambda,z,t)/z+i\lambda e^{-i\Delta_0 t}\Omega_3^*(t-z/c)a_0(\lambda,z,t)\,,\\\frac{\partial a_0}{\partial t}(\lambda,z,t)&=(i\hbar)^{-1}\langle 0|\hat{V}_{I2}(\lambda,z,t)|1\rangle a_1(\lambda,z,t)+i\Delta_0^S(t-z/c)a_0(\lambda,z,t)\\&\quad+i\lambda e^{i\Delta_0 t}\Omega_3(t-z/c)a_1(\lambda,z,t)\,,\end{aligned} \tag{19}$$

where $a_0(\lambda,z,-\infty)=1$, $a_1(\lambda,z,-\infty)=0$. Clearly, for $\lambda=1$, Eqs. (19) represent the time evolution of $a_0(z,t)$ and $a_1(z,t)$ if

$$\hat{V}_{I2}(\lambda,z,t)=e^{i\hat{H}_0 t/\hbar}[-\hat{P}_y E_{3\omega}(\lambda,z,t)]e^{-i\hat{H}_0 t/\hbar} ,$$
$$E_{3\omega}(\lambda,z,t)=-\frac{2\pi}{c}\int_0^z dz'\frac{\partial P_{3\omega}}{\partial t}\left[\lambda,z',t-\frac{z-z'}{c}\right] , \tag{20}$$

with

$$\frac{\partial P_{3\omega}}{\partial t}(\lambda,z,t)\simeq -i\omega_r e^{-i\omega_r t} nP_{01}a_0^*(\lambda,z,t)a_1(\lambda,z,t)+\text{c.c.} \tag{21}$$

In order to develop a perturbation-theory solution of these nonlinear coupled equations, we develop $a_0(\lambda,z,t)$, $a_1(\lambda,z,t)$, and $\hat{V}_{I2}(\lambda,z,t)$ as power series in λ. Thus,

$$a_0(\lambda,z,t)=\sum_{n=0}^{\infty} a_0^{(n)}(z,t)\lambda^n ,$$
$$a_1(\lambda,z,t)=\sum_{n=0}^{\infty} a_1^{(n)}(z,t)\lambda^n ,$$

and

$$\hat{V}_{I2}(\lambda,z,t)=\sum_{n=0}^{\infty} \hat{V}_{I2}^{(n)}(z,t)\lambda^n .$$

Substituting the power series into Eq. (19) and equating coefficients of λ^n, we obtain a hierarchy of coupled equations for $a_0^{(n)}(z,t)$, $a_1^{(n)}(z,t)$, and $\hat{V}_{I2}^{(n)}(z,t)$. By using the initial conditions and the hierarchy equations, we find

$$a_0(\lambda,z,t)=a_0^{(0)}(z,t)+\lambda^2 a_0^{(2)}(z,t)+\cdots ,$$
$$a_1(\lambda,z,t)=\lambda a_1^{(1)}(z,t)+\lambda^3 a_1^{(3)}(z,t)+\cdots , \tag{22}$$
$$\hat{V}_{I2}(\lambda,z,t)=\lambda \hat{V}_{I2}^{(1)}(z,t)+\lambda^3 \hat{V}_{I2}^{(3)}(z,t)+\cdots .$$

That is, the equations from equating λ-independent terms are

$$\frac{\partial a_0^{(0)}}{\partial t}(z,t)=i\Delta_0^S(t-z/c)a_0^{(0)}(z,t) ,$$

since with no Ω_3 coupling, $a_1^{(0)}(z,t)=0$. We then have

$$a_0^{(0)}(z,t)=\exp\left[i\int_{-\infty}^{t}\Delta_0^S(t'-z/c)dt'\right] . \tag{23}$$

From the linear in λ equations,

$$\frac{\partial a_1^{(1)}}{\partial t}(z,t)=(i\hbar)^{-1}\langle 1|\hat{V}_{I2}^{(1)}(z,t)|0\rangle a_0^{(0)}(z,t)+i\Delta_1^S(t-z/c)a_1^{(1)}(z,t)$$
$$-\gamma_I(t-z/c)a_1^{(1)}(z,t)/2+ie^{-i\Delta_0 t}\Omega_3^*(t-z/c)a_0^{(0)}(z,t) , \tag{24}$$

where $\hat{V}_2^{(1)}(z,t)=-\hat{P}_y E_{3\omega}^{(1)}$, and

$$E_{3\omega}^{(1)}(z,t)=-\frac{2\pi}{c}\int_0^z dz'\frac{\partial P_{3\omega}^{(1)}}{\partial t}\left[z',t-\frac{z-z'}{c}\right] ,$$
$$\frac{\partial P_{3\omega}^{(1)}}{\partial t}(z,t)=-i\omega_r e^{-i\omega_r t}P_{01}(a_0^{(0)}(z,t))^* a_1^{(1)}(z,t)+\text{c.c.} \tag{25}$$

Up to first order in the three-photon coupling between $|0\rangle$ and $|1\rangle$, one must solve Eqs. (24) and (25) in order to determine the third-harmonic signal and the atomic response. The error in $a_1(z,t)$ obtained by solving Eqs. (24) and (25) will be of third order in the three-photon Rabi frequency. We note that

$$\left[a_0^{(0)}\left[z',t-\frac{z-z'}{c}\right]\right]^* = \left[\exp\left[\int_{-\infty}^{t-(z-z')/c} \Delta_0^S(t'-z'/c)dt'\right]\right]^*$$
$$=\exp\left[-i\int_{-\infty}^{t} \Delta_0^S(t''-z/c)dt'\right],$$

by the substitution $t''=t'-(z-z')/c$. Correspondingly,

$$(i\hbar)^{-1}\langle 1 | \hat{V}_{I2}^{(1)}(z,t) | 0\rangle a_0^{(0)}(z,t) = -\frac{2\pi n\, |P_{01}|^2\omega_r}{\hbar c}\int_0^z dz' e^{i\omega_r(z-z')/c} a_1^{(1)}\left[z',t-\frac{z-z'}{c}\right]. \tag{26}$$

Owing to the fact that $a_0^{(0)}(z',t-(z-z')/c)=a_0^{(0)}(z,t)$, the ac Stark shifts which determine the phase of $a_0^{(0)}(z,t)$ have disappeared from the term which represents the interaction of the third-harmonic field on the downstream atoms. Letting $\kappa=2\pi n\,|P_{01}|^2\omega r/(\hbar c)$, we find with $\lambda=1$,

$$\frac{\partial a_1}{\partial t}(z,t) = -\kappa\int_0^z dz' e^{i\omega_r(z-z'/c)} a_1\left[z',t-\frac{z-z'}{c}\right] + i\Delta_1^S(t-z/c)a_1(z,t)$$
$$-\gamma_I(t-z/c)a_1(z,t)/2 + i\Omega_{03}^*(t-z/c)e^{-3i\phi(t-z/c)}$$
$$\times\exp\left[i\left[-\Delta_0 t + \int_{-\infty}^{t}\Delta_0^S(t'-z/c)dt' + \frac{3\omega z}{c}\right]\right]. \tag{27}$$

To remove the phase factors from the inhomogeneous term, we let

$$a_1(z,t) = A_1(z,t)\exp(-i\Delta_0 t)\exp\left[3i\frac{\omega}{c}z\right]\exp\left[i\int_{-\infty}^{t}\Delta_0^S(t'-z/c)dt'\right].$$

The term $A_1(z,t)$ is also an amplitude for being in the state $|1\rangle$ since it only differs from $a_1(z,t)$ by a phase factor. Substituting into Eq. (27) and finally dividing by the phase factor

$$\exp\left[-i\Delta_0 t + 3i\omega z/c + i\int_{-\infty}^{t}\Delta_0^S(t'-z/c)dt'\right],$$
$$\frac{\partial A_1(z,t)}{\partial t} = -\kappa\int_0^z dz' A_1\left[z',t-\frac{z-z'}{c}\right] + i[3\omega-\omega_r+\Delta_s(t-z/c)]A_1(z,t)$$
$$+ i\Omega_{03}^*(t-z/c)e^{-3i\phi(t-z/c)} - \gamma_I(t-z/c)A_1(z,t)/2, \tag{28}$$

where $\Delta_S(t-z/c)=\Delta_1^S(t-z/c)-\Delta_0^S(t-z/c)$. From Eq. (16), $P_I(z)$ represents the probability of ionizing an atom at z and

$$P_I(z) = \int_{-\infty}^{\infty}\gamma_I(t-z/c)\,|A_1(z,t)|^2 dt. \tag{29}$$

Expressing $E_{3\omega}(z,t)$ in terms of $A_1(z,t)$ and writing an expression for the energy current we show that, with F_γ representing the flux of third-harmonic photons at z and t,

$$F_\gamma = \frac{n\kappa}{4}\left|\int_0^z dz' A_1\left[z',t-\frac{(z-z')}{c}\right]\right|^2. \tag{30}$$

If the integral operator term in Eq. (28) is neglected and Eq. (28) solved for $|\Delta_0| >> \Gamma_I$ and $|\Delta_0| >> |\Delta_T|$, one finds for $P_I(z)$ the standard perturbation-theory result for ionization near a three-photon resonance. Similarly, Eq. (30) leads to the standard result for third-harmonic generation in the same limit. However, we shall see that the integral operator term leads to profound changes in both $P_I(z)$ and F_γ in the region where $\kappa z_0/\Delta_0^2 \gtrsim 1$ (i.e., very near resonance) while producing no effect when $\kappa z_0/\Delta_0^2 << 1$.

In what follows we will use

$$\frac{\partial A_1}{\partial t} = i\Delta A_1 + i\Omega_{03}^*(t-z/c)e^{-3i\phi(t-z/c)} - \kappa \int_0^z A_1\left[z', t-\frac{z-z'}{c}\right]dz' , \quad (31)$$

where

$$\begin{aligned}\Delta &\equiv \Delta(t-z/c)\\ &= \Delta_0 + \Delta_S(t-z/c)\\ &\quad + i[\gamma_{01}+\gamma_I(t-z/c)]/2 ,\end{aligned}$$

and the spontaneous decay rate γ_{01} has been inserted phenomenologically.

III. SOLUTION FOR THE ATOMIC RESPONSE

The most direct way to solve Eq. (31) is to derive a Green's function such that

$$A_1(z,t) = -i\int_{-\infty}^{\infty} \Omega_{03}(t_0)e^{-3i\phi(t_0)} \times G(t,t_0,z)dt_0 . \quad (32)$$

Then $A_1(z,t)$ is a solution to Eq. (31) if $G(t,t_0,z)$ satisfies

$$\frac{\partial G}{\partial t} = i\Delta G - \kappa\int_0^z G\left[t-\frac{(z-z')}{c}, t_0, z'\right]dz' + \delta(t-z/c-t_0) , \quad (33)$$

and $G(t,t_0,z)$ is zero for $t-z/c<t_0$.

Equation (33) can be converted to an integral equation which can be solved by iteration, i.e., through a Born-type series carried to all orders. We find

$$\begin{aligned}G(t,t_0,z) &= H(t-t_0-z/c)\exp\left[i\int_{t_0}^{t-z/c}\Delta(\tau')d\tau'\right]\sum_{n=0}^{\infty}\frac{(-1)^n}{(n!)^2}[\kappa z(t-z/c-t_0)]^n\\ &= H(t-t_0-z/c)\exp\left[i\int_{t_0}^{t-z/c}\Delta(\tau')d\tau'\right]J_0(2[\kappa z(t-z/c-t_0)]^{1/2}) ,\end{aligned} \quad (34)$$

where J_0 is the zero-order Bessel function and $H(x)=0$ if $x<1$ and $H(x)=1$ if $x\geq 0$. Thus, we have an exact solution to Eq. (31). We let $\tau=t-z/c$, $\mu=\kappa z(t-z/c-t_0)$, $u=\kappa z$, $\alpha=3\phi(\tau-\mu/u)$ and find

$$A_1 = -(i/u)\int_0^{\infty}\Omega_{03}(\tau-\mu/u)e^{-i\alpha}\exp\left[i\int_0^{\mu}\Delta(\tau-\mu'/u)d\mu'/u\right]J_0(2\sqrt{\mu})d\mu , \quad (35)$$

$$F_\gamma = \frac{nz}{4u}\left|\int_0^{\infty}\Omega_{03}(\tau-\mu/u)e^{-i\alpha}\exp\left[i\int_0^{\mu}\Delta(\tau-\mu'/u)d\mu'/u\right]J_1(2\sqrt{\mu})\frac{d\mu}{\sqrt{\mu}}\right|^2 . \quad (36)$$

In Eqs. (35) and (36) there are no assumptions about the detailed time structure of Ω_{03}, ϕ, or Δ. Thus, these relations are ideal for making approximations which lead to simple analytical formulas of high accuracy or for carrying out ensemble averages to include finite bandwidth effects. In the following sections we shall see how these analyses proceed.

IV. IONIZATION AND THIRD-HARMONIC GENERATION WITH TRANSFORM-LIMITED PULSES

Equations (35) and (36), if evaluated numerically, can be used in situations where dynamic Stark shifts and ionization rates are large. However, in what follows we will assume that

$$\int_{-\infty}^{\infty}\gamma_I(t-z/c)dt << 1$$

and that $\Delta_S(t-z/c)$ is small. In general, this assumption puts even further restrictions on the power density.

Important analytical results can be derived from Eqs. (35) and (36) if we let $\Delta=\Delta_1+\Delta_0$, where Δ_0 is the detuning (independent of t) and define L by

$$\begin{aligned}L &= 0, \quad \mu<0\\ &= \exp(i\Delta_0\mu/u)J_0(2\sqrt{\mu}), \quad \mu\geq 0 .\end{aligned} \quad (37)$$

The function L can be Fourier analyzed as

$$S = \int_0^{\infty} e^{-W'\mu}e^{i\Delta_0\mu/u}J_0(2\sqrt{\mu})d\mu \quad (38)$$

and

$$L=\frac{1}{2\pi}\int_c e^{-iw'\mu}S\,dW' , \quad (39)$$

where the contour C is a straight line running from $-\infty+i\epsilon$ to $\infty+i\epsilon$ where ϵ is any positive number. Let $\beta=-i(W'+D)$, where $\mathrm{Re}\beta>0$ and $D=\Delta_0/u$. Then,

$$S=\sum_{n=0}^{\infty}\frac{(-1)^n}{(n!)^2}\int_0^{\infty}\mu^n e^{-\beta\mu}d\mu=\frac{i}{W'+D}\exp[-i/(W'+D)] . \quad (40)$$

Using Eq. (39) in Eq. (36) with $\alpha=3\phi=0$,

$$A_1=\frac{1}{2\pi u}\int_c\frac{dW'}{W'+D}\exp[-i/(W'+D)]\int_{-\infty}^{\infty}e^{-iW'\mu}d\mu\,\Omega_{03}(\tau-\mu/u)$$
$$\times\exp\left[i\int_0^{\mu}\Delta_1(\tau-\mu'/u)d\mu'/u\right] . \quad (41)$$

Assuming that Ω_{03} vanishes exponentially or faster at $\pm\infty$, we can define

$$V=\int_{-\infty}^{\infty}e^{-iW'\mu}d\mu\,\Omega_{03}(\tau-\mu/u)\exp\left[i\int_0^{\mu}\Delta_1(\tau-\mu'/u)d\mu'/u\right] , \quad (42)$$

and

$$\Omega_{03}(\tau-\mu/u)\exp\left[i\int_0^{\mu}\Delta_1(\tau-\mu'/u)d\mu'/u\right]=\frac{1}{2\pi}\int_c e^{iW'\mu}V\,dW' . \quad (43)$$

The term Ω_{03} changes only on a time scale τ_0. If $u\,|D|\,\tau_0>>1$ and $|D|\,u/|\Delta_1|>>1$, then for small $|\epsilon|<<|D|$

$$A_1=e^{-i/D}(uD)^{-1}(2\pi)^{-1}\int_c dW'e^{iW'/D^2}V ,$$
$$=(uD)^{-1}e^{-i/D}\Omega_{03}(\tau-1/D^2u)\exp\left[i\int_0^{D^{-2}}\Delta_1(\tau-\mu'/u)d\mu'/u\right] . \quad (44)$$

We have used

$$1/(W'+D)\simeq D^{-1}(1-W'/D)$$

which also requires that the next term in the series plays no role. This more stringent requirement is

$$|D|^3u^2t_1^2>>1 , \quad (45)$$

where $t_1=\min(\tau_0,1/|\Delta_1|)$. The smallest D for which Eq. (44) holds is $|D|>4(ut_1)^{-2/3}$ or $|\Delta_0|>4(u/t_1^2)^{1/3}$. In the region of validity and for small $\gamma_I(\tau-\mu/u)$,

$$|A_1|^2=\Delta_0^{-2}|\Omega_{03}(\tau-u/\Delta_0^2)|^2e^{-\gamma_{01}u/\Delta_0^2} . \quad (46)$$

To get an idea about the ionization rate, consider Xe at $n=3\times10^{16}/\mathrm{cm}^3$ and $z=10$ cm. The value of u is

$$u=\kappa z=z(3\pi/2)(c/\omega_r)^2n\gamma_{01}\simeq2\times10^{15}/\mathrm{s} .$$

Suppose that $t_1\sim10^{-9}$ s. Our approximations dictate that

$$|\Delta_0|>4(2\times10^{15}/10^{-18})^{1/3}\approx4\times10^{11}/\mathrm{s} .$$

At this detuning,

$$u/\Delta_0^2\approx2\times10^{15}/(18\times10^{22})\simeq1\times10^{-8}\ \mathrm{s} .$$

With a pulse length of $\tau_0=4\times10^{-9}$ s, the value of $|A_1|^2$ at $z=10$ and $\tau=0$ would be strongly depressed over the value that would be obtained if the effect of $\vec{E}_{3\omega}$ had been neglected. With $\vec{E}_{3\omega}$ neglected in Eq. (31), we obtain

$$|A_1|^2=|\Omega_{03}(\tau)|^2/\Delta_0^2$$

for Δ_0 this large. When $u/\Delta_0^2<<\tau_0$ and $\gamma_{01}u/\Delta_0^2<<1$, these results become the same and $\vec{E}_{3\omega}$ indeed produces no effect on $|A_1|^2$. The depression starts when

$$|\Delta_0|\lesssim\sqrt{u/\tau_0} ,$$

or

$$|\Delta_0|\lesssim\sqrt{u\gamma_{01}} .$$

Equation (46) suggests that the laser pulse produces almost no $|A_1|^2$ at large u, but that an appreciable wave packet of third-harmonic radiation is produced on the passage of the pulse at $z\simeq0$.

The small third-harmonic pulse propagates down to larger z at the group velocity, and as it propagates it is attenuated by elastic scattering from concentration fluctuations. When this third-harmonic signal reaches z, it produces a value of $|A_1|^2$ given by Eq. (46). The third-harmonic signal resulting from the same approximations is in accord with this interpretation and is given by

$$F_\gamma = \frac{nz}{4u}\left[|\Omega_{03}(\tau)|^2 + |\Omega_{03}(\tau - u/\Delta_0^2)|^2 e^{-\gamma_{01}u/\Delta_0^2} - 2|\Omega_{03}(\tau)\Omega_{03}(\tau - u/\Delta_0^2)|e^{-\gamma_{01}u/2\Delta_0^2}\cos(u/\Delta_0)\right] . \tag{47}$$

A time analysis of the third-harmonic signal for $u/\Delta_0^2 > 2\tau_0$ should show a pulse which exists at z_0 simultaneously with the laser pulse followed by a second smaller pulse time delayed by $\kappa z_0/\Delta_0^2$. The third-harmonic signal is, of course, small here since, in contrast to the earlier study,[2] no π phase change due to focusing occurs, and thus there is no way to compensate for dispersive effects over a sizable distance (i.e., no phase matching). The power densities are also far lower without focusing,[2] further reducing third-harmonic generation (THG).

In Xe the ionization near the three-photon resonance at $\lambda \simeq 4409$ Å requires five laser photons. Thus, if the 4409-Å radiation is achieved by pumping a dye with the radiation from a XeCl exciter laser and a portion of the XeCl radiation is crossed with the dye laser beam at some depth z in the gas, the dominant ionization signal can be almost entirely due to

$$\mathrm{Xe} = 3\hbar\omega + \hbar\omega' \rightarrow \mathrm{Xe}^+ + e ,$$

where $\hbar\omega'$ is the energy of the XeCl photons. The line shape for ionization with simultaneous pulses at ω and ω' and for $n \simeq 3\times10^{16}/\mathrm{cm}^3$ should show nearly zero ion yield for $|\Delta_0| < \sqrt{\kappa z/\tau_0}$. The ionization signal should have peaks at $|\Delta_0| \sim 1.5\sqrt{\kappa z/\tau_0}$ on either side of resonance. At a fixed z the spacing between the peaks increases $\propto \sqrt{n}$ and the peak height is independent of pressure. Once one is at $|\Delta_0| > 3\sqrt{\kappa z/\tau_0}$, the present result merges with the conventional expression for the ion signal neglecting $\vec{E}_{3\omega}$. The same is true of the third-harmonic signal for large $|\Delta_0|$. It would also be interesting to choose $u/\Delta_0^2 \simeq 2\tau_0$ and to study the ionization signal as the ionizing pulse is time delayed. The signal should peak for a time delay of $2\tau_0$. It is clear that very short pulses could be used to great advantage in studying these effects. In the latter case the time delays would be easily achievable by varying the propagation distance. In addition, with large effects being possible for small time delays and relatively large Δ_0, the attenuation of the time-delayed behavior due to scattering should be almost negligible.

At first glance the reader may have been surprised by Eqs. (46) and (47) in which the effects of elastic scattering from concentration fluctuations appear to be present in a treatment in which no explicit consideration of these phenomena was present. However, when one retains for excitation on the far wing of the line an incoherent damping $\gamma_{01}/2$, provisions have been made for an incoherent coupling back to the ground state; and this is just what is required to simulate the effect of scattering. The spontaneous emission term was originally included to provide the proper decay of coherence and the proper line shape for resonance excitation and ionization, but it also simulates an extremely important effect on the line wing.

Before terminating our discussion of transform-limited pulses, we shall specialize to a particular shape of pulse. Let

$$\Omega_{03}(t) = \Omega_{03}(0)\exp(-3t^2/2\tau_0^2) . \tag{48}$$

We shall now discuss an improvement on Eqs. (46) and (47) for this special case. Equation (41) is exact and for this pulse shape,

$$A_1 = \frac{\Omega_{03}(0)}{2\pi u}\int_c \frac{dW'}{W'+D}\exp[-i/(W'+D)]\int_{-\infty}^{\infty} e^{-iW'\mu}d\mu\,\exp[-\gamma_{01}\mu/2u - \tfrac{3}{2}(\tau-\mu/u)^2/\tau_0^2] . \tag{49}$$

The second integral can be done analytically, and the contour integral for $|\Delta_0\tau_0| >> 1$ can be evaluated with $(W'+D)^{-1} \approx D^{-1}(1 - W'/D + W'^2/D^2)$ in the exponential and $(W'+D)^{-1} \approx D^{-1}$ for the resonance factor multiplying the exponential. We get

$$|A_1|^2 \simeq \Delta_0^{-2} |\Omega_{03}(0)|^2 e^{-\gamma_{01} u/\Delta_0^2} R^{-1/2} \exp[-3(\tau/\tau_0 - u/\Delta_0^2\tau_0)^2/R] , \tag{50}$$

where

$$R = 1 + (4u/\Delta_0^3\tau_0^2)^2 . \tag{51}$$

Extensive calculations have been made by numerical integration of Eq. (49) with $\gamma_{01}=0$. In these numerical calculations, $|A_1|^2$ was tabulated as a function of Δ_0 for $\tau_0 u = 10^4$ and 10^5 and for values of τ/τ_0 ranging from 0 to 200. For $\tau/\tau_0=0$ or 1, Eq. (50) is accurate to several significant figures over regions where $|A_1|^2$ is not very small compared with its peak values. For $\tau/\tau_0=200$, the peak position, width, and magnitude of $|A_1|^2$ are predicted to about 30% accuracy over the region near the maximum, even though the peak is at relatively small Δ_0 where the approximations are not clearly accurate. Thus, Eq. (50) can be considered to represent $|A_1|^2$ with good accuracy for $u\tau_0 >> 1$ for the Δ_0 values where $|A_1|^2$ is large for all τ/τ_0.

From Eq. (50) we see that Eq. (46) gives identical results if $|4u/\Delta_0^3\tau_0^2| \lesssim 1/2$ or $|\Delta_0| > 2(u/\tau_0^2)^{1/3}$. If the ionizing laser has γ_I of the form

$$\gamma_I(\tau) = \gamma_I(\tau_0)\exp[-(\tau-\tau_0)^2/\tau_i^2] , \tag{52}$$

then at z,

$$P_I = \gamma_I(\tau_0)\tau_i |\Omega_{03}(0)|^2 \Delta_0^{-2} e^{-\gamma_{01}u/\Delta_0^2} \left[\frac{3\pi\tau_0^2}{3\tau_i^2 + R\tau_0^2} \right]^{1/2} \exp\left[\frac{-3(\tau_0 - u/\Delta_0^2)^2}{3\tau_i^2 + R\tau_0^2} \right] . \tag{53}$$

Above, τ_D is the time delay between exciting and ionizing pulses. Even with non-Gaussian pulse shapes, Eq. (53) can give insight into expected line shapes for ion yield as a function of τ_0, u, and Δ_0. If $\vec{E}_{3\omega}$ is neglected in finding P_I, one obtains, instead of Eq. (53),

$$P_{I0} = \gamma_I(\tau_0)\tau_i |\Omega_{03}(0)|^2 \Delta_0^{-2} [3\pi\tau_0^2/(3\tau_i^2 + \tau_0^2)]^{1/2} \exp[-3\tau_D^2/(3\tau_i^2 + \tau_0^2)] .$$

When $u/\Delta_0^2 << \tau_0$ and $\gamma_{01}u/\Delta_0^2 << 1$, the results are identical.

The inclusion of the $-\hat{P}_y E_{3\omega}$ term in $\hat{H}(z)$ has profound effects on $|A_1|^2$. Since for $z = 10$ cm and $n \approx 3\times10^{16}/\text{cm}^3$, we can easily have $u = \kappa z \approx 3\times10^{15}/\text{s}$, it follows immediately that for $|\Delta| < 10^{12}/\text{s}$, the effect of the integral term at such large z will dominate the effect of $i\Delta A_1$, as implied by Eqs. (46) and (47). The implication of these equations is that for times when the laser pulse is present, we have $A_1 \approx 0$ for large z, and all absorption is converted directly into third-harmonic photons. The latter statement follows because the solution corresponds to

$$-i\Omega_{03}e^{-3i\phi} = \kappa \int_0^z A_1 \left[z', t - \frac{|z-z'|}{c} \right] dz'$$

for times such that the laser field is large and for Δ_0 small enough so that $u/\Delta_0^2 >> \tau_0$.

In our earlier work[2] we suggested a close relation to phenomena which occurs in super radiance[5] in which once there is a macroscopic polarizability and conditions for strong constructive interference, a system of particles can radiate away energy very rapidly. This, in effect, leads to a very short radiative lifetime and makes it difficult to generate a large upper-state population by way of a highly coherent beam of light. Such a picture also explains the time-delayed third-harmonic signal. Those atoms near $z = 0$ have no atoms at smaller z to give a third-signal which balances out against the three-photon excitation. Thus, their excitation proceeds at a level characteristic of isolated atoms subjected to the same laser field. Their excitation produces a polarizability and a packet of third-harmonic photons which propagate downstream at the group velocity. By the time this wave packet reaches large z the laser pulse is absent and a balance occurs (for $\Delta_0\tau_0 >> 1$) in which

$$i\Delta A_1 = \kappa \int_0^z A_1 \left[z', t - \frac{|z-z'|}{c} \right] dz' ,$$

the excitation and $\partial A_1/\partial t$ terms being negligible. In a situation where a laser pulse impinges on a medium in which the concentration of atoms starts out very small and increases with z (as in a pulsed nozzle jet beam where $n \sim 10^{15}/\text{cm}^3$ can be achieved at beam center), the time-delayed third-harmonic signal would not be present and $|A_1|^2$

would be small for large u at all times. In the latter case the ionization signals would be very strongly suppressed, even more so than in the situation described here.

In view of the time structure of the third-harmonic signal, it is interesting to determine the power spectrum of these photons. If $P(\omega')d\omega'$ is the number of photons emerging per pulse per unit area in the frequency range $d\omega'$ around ω' and the transform-limited pulse is Gaussian,

$$P(\omega')=\frac{4\pi}{3\kappa}\,|\Omega_{03}(0)|^2\tau_0^2 n e^{-(\tau_0^2(\omega'-3\omega)^2/6)}\left[1-\exp\left[-\frac{\kappa z_0\gamma_{01}/2}{(\omega'-\omega_r)^2+\gamma_{01}^2/4}\right]\cos\left[\frac{\kappa_0 z_0(\omega'-\omega_r)}{(\omega'-\omega_r)^2+\gamma_{01}^2/4}\right]\right] .$$

The interesting interference effects in the power spectrum might be observable by using mode-locked lasers and allowing the third-harmonic signal to pass through a properly chosen atomic vapor absorption cell where its frequency spectrum could be studied by choosing the peak in power to coincide with the resonance. The absorbing atoms would be ionized by the intense light at ω. Thus, one should be able to pressure tune (via the changes in k) the third-harmonic photon spectrum and the resulting absorption cell through a series of maxima and minima.

V. IONIZATION WITH BROAD-BANDWIDTH LASERS

We assume reasonably good wave-front spacial uniformity with a coherence time which is very short compared with the pulse length. In this situation the laser light will generally undergo both amplitude and phase fluctuations on a time scale of the order of the coherence time. Further, even in situations where the energy per pulse, the length in time of the pulse envelope, and the time-integrated beam intensity profile repeat very well from pulse to pulse, the detailed time structure of the amplitude and phase will not. Thus, averaging over the phase space of the laser field, we obtain[6]

$$\bar{P}_I=\int_{-\infty}^{\infty}\langle\gamma_I(\tau)\rangle\rho_{11}(z,t)d\tau , \tag{54}$$

where

$$u^2\rho_{11}=\int_0^{\infty}d\mu\int_0^{\infty}d\mu'\exp[i(\bar{D}\mu-\bar{D}^*\mu')]J_0(2\sqrt{\mu})J_0(2\sqrt{\mu'})\langle\Omega'^*(\tau-\mu'/u)\Omega'(\tau-\mu/u)\rangle , \tag{55}$$

where we assume that γ_I is dominated by effects due to a second laser beam which is crossed with the first at a distance z after the first enters the medium. Above, $\Omega_3'=\Omega_{03}e^{-3i\phi}$ and $\bar{D}=(\Delta_0+i\gamma_0/2)/u$. We assume a Gaussian line shape for the laser, and in particular, we let

$$\langle\Omega_3'^*(\tau-\mu'/u)\Omega_3'(\tau-\mu/u)\rangle=|\bar{\Omega}_{03}(\tau-\mu/u)|^2(3!)\exp[-\Gamma^2(\mu-\mu')^2/u^2] . \tag{56}$$

Here $\bar{\Omega}_{03}(t)$ is the three-photon Rabi frequency evaluated at the mean intensity at time t, and Γ is a measure of the coherence time of the laser. A rough simulation is achieved if one identifies Γ with about 0.6 of the laser's full width at half maximum bandwidth. The 3! is related to the fact that with incoherent light, photons tend to arrive in bunches; and for high-order processes, these brief periods of constructive interference between different modes during which the field amplitude is much larger tend to dominate.[6] Using the field autocorrelation function in Eq. (56), we can write

$$u^2\rho_{11}=3!\int_0^{\infty}d\mu\,|\bar{\Omega}_{03}(\tau-\mu/u)|^2e^{i\bar{D}\mu}J_0(2\sqrt{\mu})Q , \tag{57}$$

where

$$Q=\int_0^{\infty}d\mu' e^{-i\bar{D}^*\mu'}J_0(2\sqrt{\mu'})\exp[-\Gamma^2(\mu-\mu')^2/u^2] . \tag{58}$$

For a particular situation, Eqs. (57) and (58) can be dealt with numerically.

However, a very useful approximation to the solutions for these equations can be obtained by using Fourier representations of $\exp(-i\bar{D}^*\mu')J_0(2\sqrt{\mu'})$ and $\exp[i(\bar{D}-w')]J_0(2\sqrt{\mu})$ in analogy with Eqs. (38)–(40). Thus, we can transform Eq. (57) to

$$u^2\rho_{11}/3! = -\frac{u}{4\pi^{3/2}\Gamma}\int_{-\infty}^{\infty} dW' \int_{-\infty}^{\infty} dW \exp\{-i[1/(W'-\bar{D}^*)+1/(W+\bar{D}-W')]\}$$
$$\times X \exp(-iu\tau W - u^2W'^2/4\Gamma^2)\,, \tag{59}$$

where

$$X = u\int_{-\infty}^{\infty} |\bar{\Omega}_{03}(\tau')|^2 e^{iuW\tau'}d\tau'\,. \tag{60}$$

Since X is proportional to the Fourier transform of $|\bar{\Omega}_{03}(\tau')|^2$, its width in uW is $\sim 1/(\tau_0)$ or in terms of W it is $\sim(u\tau_0)^{-1}$. Further, it peaks near $W=0$ if $|\bar{\Omega}_{03}(\tau')|^2$ is not too asymmetric about $\tau'=0$. Letting

$$H = \frac{1}{2\pi}\int_{-\infty}^{\infty} \frac{dW}{W+\bar{D}-W'} \exp[-i/(W+\bar{D}-W')]e^{-iu\tau W}X\,, \tag{61}$$

we have

$$u^2\rho_{11}/3! = -\frac{u}{2\Gamma\sqrt{\pi}}\int_{-\infty}^{\infty} \frac{dW'}{W'-\bar{D}^*} \exp[-i/(W'-\bar{D}^*)]e^{-u^2W'^2/4\Gamma^2}H\,. \tag{62}$$

When $u\tau_0 >> 1$ and $|\bar{D}-W'| \gtrsim 3/(u\tau_0)^{2/3}$, we can use $(W+\bar{D}-W')^{-1} \simeq (\bar{D}-W')^{-1}[1-W/(\bar{D}-W')]$ in the exponential term of Eq. (61) and $(W+\bar{D}-W')^{-1} \approx (\bar{D}-W')^{-1}$ in the multiplicative factor. Thus, with these restrictions,

$$H \approx -\frac{1}{W'-\bar{D}} \exp[i/(W'-\bar{D})]\,|\bar{\Omega}_{03}[\tau - 1/u(W'-\bar{D})^2]|^2\,. \tag{63}$$

Furthermore, as $|\bar{D}-W'|$ decreases past $|\bar{D}-W'| \sim 1/\sqrt{u\tau_0}$, H rapidly decreases and by the time $|\bar{D}-W'| = 3/(u\tau_0)^{2/3}$ it has become extremely small. In the region where Eq. (63) does not hold, there is almost no contribution to the integral in Eq. (62). Thus, when $u\tau_0 > 10^3$ or so, Eq. (63) can be used for all $\bar{D}$ for which ρ_{11} is not extremely small. We now have by combining Eqs. (62) and (63) and letting $\beta = uW'/2\Gamma$:

$$u^2\rho_{11}/3! \approx \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty} \frac{e^{-\beta^2}d\beta}{\left|\bar{D}-\frac{2\Gamma\beta}{u}\right|^2} \exp\left[\frac{-\gamma_{01}}{u\left|\bar{D}-\frac{2\Gamma\beta}{u}\right|^2}\right] \left|\bar{\Omega}_{03}\left[\tau - \frac{1}{u\left[D-\frac{2\Gamma\beta}{u}\right]^2}\right]\right|^2\,. \tag{64}$$

Thus, if $|D| \geq 5\Gamma/u$ and $|D| \gtrsim 3/(u\tau_0)^{2/3}$, Eq. (64) becomes

$$u^2\rho_{11}/3! = |\bar{D}|^{-2}\exp(-\gamma_{01}/u\,|\bar{D}|^2)\,|\bar{\Omega}_{03}(\tau - 1/uD^2)|^2\,. \tag{65}$$

Comparing Eqs. (65) and (46), we see that for large $u\tau_0$ and $|D| > 5\Gamma/u$ stochastic light leads to very similar results. Equation (65) will still be valid for $|D| = (u\tau_0)^{-1/2}$ if $(u\tau_0)^{-1/2} \geq 5\Gamma/u$ and that for $|D| < (u\tau_0)^{-1/2}$ the magnitude of ρ_{11} for $\tau=0$ decreases rapidly just as in the case of transform-limited lasers. For $u/\Gamma \geq 100\Gamma\tau_0$, one should be able to observe nearly all of the phenomena described for transform-limited bandwidth lasers. That is, line shapes for multiphoton ionization should (within the limit $u/\Gamma \geq 100\Gamma\tau_0$) be independent of Γ as it is decreased further. Also, ionization signals with time-delayed ionizing pulses should be observable. Similar approximations can be made in carrying out ensemble averages for the third-harmonic signal:

$$\bar{F}_\gamma = \frac{3}{2}\frac{nz}{u}[\,|\bar{\Omega}_{03}(\tau)|^2 + e^{-\gamma_{01}u/\Delta_0^2}|\bar{\Omega}_{03}(\tau - u/\Delta_0^2)|^2 - 2|\bar{\Omega}_{03}(\tau)|^2\exp(-\Gamma^2u^2/\Delta_0^4)\cos(u/\Delta_0)]\,. \tag{66}$$

From Eq. (66) we see that interference effects only occur for $|\Delta_0| \gtrsim \sqrt{u\Gamma}$. The time-delayed pulse of third-harmonic photons is still present.

VI. PREDICTIONS FOR THE $5p^6 \rightarrow 5p^5 6s\,[^2P_{3/2}]J=1$ THREE-PHOTON RESONANCE IN XENON

We consider a slab of Xe gas of thickness ~ 6 cm. A dye laser beam with vacuum wavelength near $\lambda_L \simeq 4409$ Å and a beam diameter ~ 0.1 cm is normally incident on the Xe slab. With reasonable wave-front coherence, we expect to simulate a slab geometry reasonably well since the Fresnel number for this arrangement is large. To give a specific example, we further assume that $\tau_0 \sim 5$ ns and $\Gamma = 1\times 10^{11}$/s. Thus, the laser line width in angstrom units is ~ 0.06 Å. We take $\gamma_{01} \simeq 3\times 10^8$/s for this transition[5] and find κ $(\mathrm{cm}^{-1}\mathrm{s}^{-1}) \simeq 2.5\times 10^{14} P_{\mathrm{Xe}}$ (Torr). The ionization signal is assumed to be produced largely by a second laser pulse of sufficiently short wavelength to ionize $5p^5 6s\,[^2P_{3/2}]J=1$ by one photon. This second laser pulse crosses the dye laser beam over a 0.3-cm region at $z \simeq 5$ cm. Consequently, the relevant value of u is $u = \kappa z \simeq 1.25\times 10^{15} P_{\mathrm{Xe}}$ (Torr). With some of the uv lasers which are commercially available, one should be able to achieve $\gamma_I(0)\tau_0 \simeq 1$ over the 3-mm region where the laser beams overlap.

Predictions can be based on Eqs. (54) and (64) since $u\tau_0$ is very large. For this purpose, we assume that

$$\langle I(\tau)\rangle = \langle I(0)\rangle \exp(-\tau^2/\tau_0^2) ,$$

i.e., a Gaussian envelope for the power density. Most lasers will not have a Gaussian pulse shape in time, but there is relatively little model sensitivity if the average pulse profile has a single nearly symmetric peak. With $\tau_0 = 5$ ns, the full width at half maximum in time is close to 10 ns. When the two lasers are fired simultaneously, the line shape for ionization is very close to that for $\rho_{11}(z,0)$. Thus, a convenient form for Eq. (64) is

$$\frac{u^2 \rho_{11}(z,\tau=0)}{3!\,|\bar{\Omega}_{03}(0)|^2} = \frac{r^2}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{e^{-\beta^2} d\beta}{(\beta-\delta)^2 + E_0^2} \exp\{-2E_0 r/[(\beta-\delta)^2 + E_0^2] - 3(r/s)^2/(\beta-\delta)^4\} , \tag{67}$$

where $\delta = \Delta_0/2\Gamma$, $s = 2\Gamma\tau_0$, $r = u/2\Gamma$, and $E_0 = \gamma_{01}/4\Gamma$. In our example we have $E_0 = 7.5\times 10^{-4}$, $r = 6.25\times 10^3\, P_{\mathrm{Xe}}$, and $s = 1\times 10^3$. Numerical calculation shows that the ionization signal at resonance increases linearly with pressure for $P_{\mathrm{Xe}} < 10^{-3}$ Torr. In the same pressure region the linewidth for ionization is independent of pressure. However, between 10^{-3} and 5×10^{-2} Torr, the $\Delta_0 = 0$ signal starts to increase less rapidly with pressure and by 5×10^{-2} Torr, it is actually smaller than the signal at $\Delta_0 = \pm 3.2\Gamma$. Above 5×10^{-2} Torr the $\Delta_0 = 0$ signal decreases with pressure and the ionization signal is largest (for $P_{\mathrm{Xe}} > 0.1$ Torr) at $\Delta_0 \approx \pm 9.2\Gamma\sqrt{P_{\mathrm{Xe}}\ (\mathrm{Torr})}$. As P_{Xe} is increased, the two side peaks separate proportional to $\sqrt{P_{\mathrm{Xe}}}$, but the peak height of the ionization signal increases very little above $P_{\mathrm{Xe}} = 0.1$ Torr. At $P_{\mathrm{Xe}} = 1$ Torr the peak separation in terms of the dye laser wavelength is ~ 0.6 Å.

With pulse energies for the dye laser of ~ 10 mJ, a few hundred ions will be produced and some form of gas amplification will probably be required to observe them. Due to a lack of phase matching and relatively low-power densities, the THG signal will be a few thousand photons. A good calculation or measurement of $|\bar{\Omega}_{03}(0)|^2$ would be required to make a more accurate estimate.

Equation (67) can be generalized a bit if we assume that the ionizing laser also has a Gaussian pulse shape and may be time-delayed relative to the first by a time τ_D. Taking

$$\langle \gamma_I(\tau)\rangle = \langle \gamma_I(\tau_D)\rangle \exp[-(\tau-\tau_D)^2/\tau_i^2] ,$$

where τ_i is the pulse length of the ionizing laser, we get N_I, the number of ions produced, to be

$$N_I = \frac{3!\,n\Delta V \langle \gamma_I(\tau_d)\rangle \tau_i\, |\bar{\Omega}_{03}(0)|^2}{[1+3(\tau_i/\tau_0)^2]^{1/2}} M , \tag{68}$$

where ΔV is the volume over which the laser beams overlap and

$$M = \int_{-\infty}^{\infty} \frac{e^{-\beta^2} d\beta}{|\bar{D}u - 2\Gamma\beta|^2} \exp\left\{ -\gamma_{01}/u \left| \bar{D} - \frac{2\Gamma\beta}{u} \right|^2 - \frac{3}{1+3(\tau_i/\tau_0)^2} \left[\tau_D/\tau_0 - 1/u\tau_0 \left[D - \frac{2\Gamma\beta}{u} \right]^2 \right]^2 \right\} . \tag{69}$$

The quantity M is relatively easy to evaluate numerically. When $|\Delta_0| > 8\Gamma$, we can use

$$M=\frac{\sqrt{\pi}}{|\Delta_0|^2}\exp\left[-\gamma_{01}/u\,|\bar{D}|^2-\frac{3}{1+3(\tau_i/\tau_0)^2}(\tau_0/\tau-u/\tau_0\Delta_0^2)^2\right]. \tag{70}$$

We will now tabulate M for $\tau_0=0$ (i.e., simultaneous pulses) and $\tau_i=\tau_0$. Letting $\delta=\Delta_0/2\Gamma$, $s=2\Gamma\tau_0$, $r=u/2\Gamma$, and $E_0=\gamma_{01}/4\Gamma$,

$$4\Gamma^2 M=\int_{-\infty}^{\infty}\frac{e^{-\beta^2}d\beta}{(\beta-\delta)^2+E_0^2}\exp\left[-\frac{2E_0 r}{(\beta-\delta)^2+E_0^2}-(3r/4s)^2/(\beta-\delta)^4\right]. \tag{71}$$

Figure 1 shows $4\Gamma^2 P_{\mathrm{Xe}} M$ vs $|\Delta_0|/2\Gamma$ for the values $\tau_0=5\times10^{-9}$ s, $\Gamma=1\times10^{11}$/s, $\gamma_{01}=3\times10^8$/s, and $u=1.25\times10^{14}P_{\mathrm{Xe}}$ (Torr). The evaluation of M for a situation where $\tau_0>0$ can be based on Eq. (69). The computational effort involved with Eq. (69) is nearly one thousand times less than that involved by combining Eqs. (54), (57), and (58) with no approximations. However, detailed numerical checks based on the latter equations were carried out and found to agree very well with Eq. (71) for cases where the peak in M occurs for $|\Delta_0|\gtrsim 3(u/\tau_0^2)^{1/3}$. The latter condition is well satisfied for nearly all experimentally observable effects for $P_{\mathrm{Xe}}>0.05$ Torr.

VII. CONCLUSIONS

A two-state plus ionization continuum model has been developed for multiphoton ionization and third-harmonic generation near a three-photon resonance. The theory is based on the assumptions that (1) there are no other resonances involved; (2) the geometry is well simulated by a plane wave normally incident on a slab of gas or vapor; (3) the concentrations are low and the slab thickness is relatively small so that propagation of the laser pulses are describable by using $k=\omega/c$; (4) the concentration is low enough so that collisional dephasing for $|\Delta_0|\lesssim10^{11}$/s and free-bound absorption by colliding pairs of atoms are unimportant; and (5) the power density $\langle I(0)\rangle\langle 10^{10}\ \mathrm{W/cm^2}\rangle$. For the Xe example discussed in the text, the concentration restrictions mean $Z_0\lesssim5$ cm and $n_{\mathrm{Xe}}\lesssim3\times10^{16}/\mathrm{cm}^3$. The effect of the third-harmonic signal on the atomic response has been included in detail.

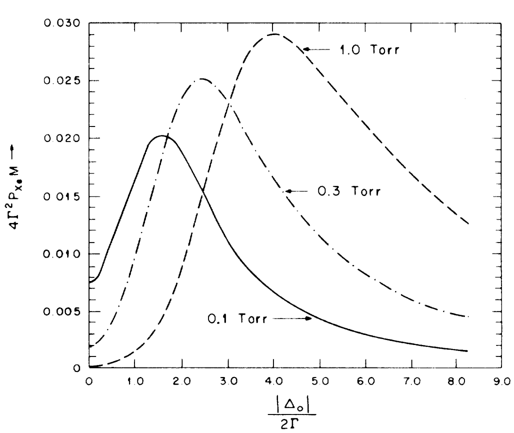

FIG. 1. $4\Gamma^2 P_{\mathrm{Xe}}$ (Torr) M vs $|\Delta_0|/2\Gamma$ for four-photon ionization of Xe near the $5p^6\rightarrow5p\,6s\,[^2P_{3/2}]J=1$ three-photon resonance. Gaussian pulse shapes with pulse length $\tau_0=5\times10^{-9}$ s has been assumed for both the ionizing and the excitation lasers. The two laser beams cross at $Z=5$ cm. The linewidth of the exciting laser is $\Delta\lambda\approx0.06$ Å. ——, $P_{\mathrm{Xe}}=0.1$ Torr, —·—·—·, $P_{\mathrm{Xe}}=0.3$ Torr, and -----, $P_{\mathrm{Xe}}=1.0$ Torr.

As in an earlier study,[2] a strong suppression of the three-photon resonance enhancement of multiphoton ionization has been predicted. In particular, at near zero detuning ($\Delta_0\cong0$) the ion yield is extremely small, with ionization signals having their maxima at symmetrically displaced peaks on either side of the three-photon resonance. The splitting between the ionization maxima above and below the resonance position increases $\propto\sqrt{n}$, and at $n\simeq3\times10^{16}/\mathrm{cm}^3$ the splitting in angular frequency units can be as large as 1×10^{12}/s. With small-bandwidth lasers, large effects on ionization should be observable at $n\simeq3\times10^{12}/\mathrm{cm}^3$, and these phenomena are enhanced by using short pulse lengths. Except for somewhat modified interference, effects and changes in the time of generation spectrum of the third-harmonic photons, harmonic generation is very similar to the results predicted by conventional theories of this process. When $|\Delta_0|>5\sqrt{u/\tau_0}$, the results for multiphoton ionization and third-harmonic generation become identical to the results of conventional theories.

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