Theory of the effect of third-harmonic generation on three-photon resonantly enhanced multiphoton ionization in focused beams

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Multiphoton ionization in the region near a three-photon resonance is treated for focused, plane-polarized Gaussian beams with diffraction-limited beam divergence. In this situation, a third-harmonic field is generated within the laser beam. At, and very near, three-photon resonance the driving rate for the upper-state probability amplitude due to one-photon absorption of third-harmonic light becomes nearly equal to the corresponding three-photon rate due to the laser field, but these effects are 180° out of phase. As a consequence of this cancellation between two pumping terms, the three-photon resonance line essentially disappears at moderate concentrations and the observed ionization has a line shape that is close to the phase-matching curve for third-harmonic generation. The ionization signal, near but not on the resonance, is due almost entirely to absorption of third-harmonic photons plus other laser photons; three-photon resonantly enhanced multiphoton ionization by the laser is much weaker. This is particularly true on the blue side of the three-photon resonance at detunings where phase matching occurs. The problem is treated quite generally with predictions of the full line shape for n-photon ionization and third-harmonic light generation near three-photon resonance, including the rather strong influences of positively dispersive buffer gases. We also show that the cancellation between the one-photon and the three-photon process is partially spoiled in the presence of a counterpropagating beam at the same frequency.

I. INTRODUCTION

Studies of third-harmonic generation (THG) in gases were initiated by New and Ward[1]; later the same individuals[2] presented a theory of odd-harmonic generation in the gas phase. This theory drew heavily on the theory of Kleinman *et al.*[3] for second-harmonic generation in solids by focused Gaussian beams. Recently a number of studies[4] have demonstrated the utility of gas phase THG or four-wave mixing in generating vacuum ultraviolet (vuv) light.

Multiphoton ionization (MPI) is currently of much interest. References to experimental work on this subject before 1978 can be found in an article by Mainfray.[5] Theoretical developments prior to 1976 have been reviewed by Lambropoulos.[6] Recent developments in theory have been made by many workers.[7] Resonantly enhanced MPI is currently being used both for spectroscopy[8] and as a state-selective detection method.[9]

Almost all of the work on MPI referenced above deals with situations where concentrations of the target species are very small and all atoms or molecules can be considered to interact independently with the laser field. However, Compton *et al.*[10] and Miller *et al.*[11] observed very striking pressure effects when three-photon resonantly enhanced MPI of argon, krypton, and xenon was studied for concentrations $>10^{15}/\text{cm}^3$. If in the latter situation the atoms interacted independently with the laser field, the resonance signal should increase linearly with pressure until the pressure-broadened linewidth becomes comparable with the laser bandwidth. In the Miller *et al.* study, the linear increase in ionization signal should have continued[10,11] up to $N>10^{18}/\text{cm}^3$. Further, with self-broadening in rare gases, the pressure-broadened lines should be symmetric about the resonance except on the far wing of the line. The Miller *et al.* study[11] showed, however, that the ionization signal actually decreased with increasing N for $N>10^{16}/\text{cm}^3$ and that the observed line shape for ionization appeared to shift strongly toward the blue side of the unperturbed resonance. With a lens of ~ 5-cm focal length and an initial beam size ~ 0.1 cm, the observed shifts were of the order $\Delta\omega_s \approx 10^{-4}N$, where $\Delta\omega_s$ is the shift in the laser angular frequency from the unperturbed resonance frequency in sec^{-1} and N is the concentration in cm^{-3}. These shifts depend, of course, on the focal length of the lens used to focus the beam since they will be seen to be initiated by the absorption of third-harmonic (TH) light.

An explanation for the strong suppression of the resonant enhancement at the three-photon resonance was provided in a theoretical formulation of the problem by Payne, Garrett, and Baker[12] in which the atoms interacted with the laser field and with each other via the TH radiation field which was generated in the interaction volume. Though the early theory was very approximate in the treatment of the beam geometry, it nevertheless showed that inclusion of the TH field in a self-consistent way led to a great reduction in the probability of exciting the resonance state and, moreover, it showed that above a critical concentration which depends on (1) the magnitude of the a.c. Stark shift, (2) the laser bandwidth, (3) the diameter of the unfocused beam, and (4) the focal length of the lens, the peak height of observed near-resonance ionization decreases in proportion to NF^2, where F is the focal length of the lens used to focus the laser light. The magnitude of the predicted shifts was close to what was observed experimentally,[10,11,13] and it was pointed out that the only observed ionization had a line shape closely corresponding to the phase-matching curve for TH generation.

In a subsequent paper on resonantly enhanced ionization near three-photon resonances, Payne and Garrett[14] gave a very detailed *ab initio* treatment of the resonance suppression effect in the simpler geometry of unfocused beams. At the power densities of interest there (and here) the three-photon Rabi frequency is so low that depletion of the ground state is negligible,[14] and stimulated processes out of the upper state at three-photon resonance are of no importance. Yet the coupling between three- and one-photon pumping (by the TH field) of the resonance level is so strong that one cannot assume that the near-resonant TH field is the same as that produced in the absence of the new effect. Thus, the present authors treated the problem as follows: (1) by deriving the equivalent of Bloch equations for a two-state plus ionization continuum representation of the system where the ground and excited states of an atom at position $\vec{r}$ in a laser pulse of arbitrary time profile were coupled by three-photon absorption and stimulated emission as well as by one-photon absorption and stimulated emission driven by the TH field; (2) Maxwell's equations were written for the propagation and generation of the TH field with the source term for the TH field being written in terms of the components of the Bloch vector, and with the solution for the TH field, $\vec{E}_{3\omega}$, being obtained by a Green's-function method and written as an integral operator operating on components of the Bloch vector; (3) the integral expression for $\vec{E}_{3\omega}$ in terms of Bloch vector components was used to replace $E_{3\omega}$ in Bloch's equations. The Bloch equations were then self-consistently linearized in the three-photon Rabi frequency Ω_3 and the ionization continuum was eliminated in terms of a damping rate and an a.c. Stark shift. This analysis led to a linear inhomogeneous integro-differential equation for the probability amplitudes or for the polarizability from which the ionization yield and the TH field could be determined within the linearized approximation. The resulting integro-differential equations for the polarizability contained a conventional three-photon term due to the interaction with laser photons and an integral term due to the TH field. Explicit solutions of the equations of motion showed that, except for the region near the entrance to the gas cell, the contributions to the time evaluation of the polarizability from the three-photon and one-photon process *exactly cancel* as the resonance is approached. The complete line shape was given as a function of pressure, laser bandwidth, and oscillator strength for transform-limited and broad-bandwidth pulsed lasers. The cancellation effect persisted even with very nonideal characteristics of the exciting laser.

In another recent MPI study involving the TH cancellation effect, Jackson and Wynne[15] treated the problem on resonance with a simple perturbation treatment for a plane-wave approximation to a focused geometry and in a steady-state approximation to pulsed laser excitation. They also made the *ad hoc* assumption that the TH field could be written in terms of the nonlinear susceptibility at 3ω as would obviously be valid in the absence of the rather striking coupling effect. This latter assumption is essentially correct, as was shown in Ref. 14, but it was not obvious until proven. Finally, the authors added a semi-empirical width to the resonance as opposed to the more exact treatment in Ref. 14 through the Bloch equations. With this great simplification of the problem, a fifth-order perturbation analysis of the five-photon ionization problem showed that the three-photon and one-photon contributions to resonant excitation are 180° out of phase, which the authors designated as an interference effect. Thus, they arrived at the same result which was obtained in the more general and more exact treatment of Ref. 14 though the latter was more complex due to the inclusion of pulse effects and due to a treatment in which $E_{3\omega}$ and the atomic response were derived self-consistently without assuming that ionization could be dramatically altered while $E_{3\omega}$ is completely unchanged. Thus, Ref. 14 was less transparent than the treatment based on the Fermi "golden rule" approach.[15]

In the present study we present a detailed treatment of the MPI problem near a three-photon resonance for focused diffraction-limited Gaussian beams. In Sec. II we consider a simplified perturbation approach wherein the physical effects are handled from first principles but within a picture which provides a clear illustration of the rather dramatic effect under investigation, with a slight generalization of earlier treatments to include the effect of a buffer gas. Then, in Sec. III, we present a more exact treatment of the less tractable exact resonance region where a perturbation approach could be flawed, but where we prove that the behavior tracks smoothly through the resonance as would be inferred from the simpler treatment of the problem. Thus, we obtain the complete ionization signal line shape in the resonant region, including the influence of a phase-matching buffer gas on the observed resonance profile. In Sec. IV we briefly discuss the partial reappearance of a resonance signal in the presence of a counterpropagating portion of the laser beam and, in Sec. V, we present some conclusions.

II. PERTURBATION TREATMENT OF THE NEAR-RESONANT FOCUSED BEAM PROBLEM

We consider a gas with concentration N in the presence of a focused diffraction-limited Gaussian laser beam. We will later consider the additional effect of a buffer gas which has no resonances that are close to either the laser or TH frequencies. The laser light is plane polarized in the direction of the y axis, and the optical axis of the lens corresponds to the z axis with the origin being the focal point. We follow Kleinman *et al.*[3] in writing the laser field in the form

$$\begin{aligned}\vec{E}(\vec{r},t)=&\frac{\vec{e}_y}{2}(A(z,\rho)\exp\{-i[\omega t+\phi(t-z/c)]\}\\&+A^*(z,\rho)\exp\{i[\omega t+\phi(t-z/c)]\})\\&\times E_0(t-z/c)\,,\\A(z,\rho)=&e^{ikz}(1+2iz/b)^{-1}\exp[-k\rho^2/b(1+2iz/b)]\,,\end{aligned}\tag{1}$$

where k is given by $k = n(\omega)\omega/c$. Here $n(\omega)$ is the index of refraction of the gas (or gas mixture when a buffer gas is present) at frequency ω, and $b = kw^2$, where $w = \lambda F/\pi d$. Also, w is the beam waist at $z = 0$, d is the beam diameter just before the lens, F is the focal length, b is the confocal parameter, and ρ is the radial distance from the z axis. Equation (1) applies to cases where $d/F \ll 1$ so that a paraxial approximation applies in the development of the equation. The time dependence of the pulse, $E_0(t - z/c)$, will be restricted only by the condition that its time derivative be small as compared to ω. Finite bandwidth effects will be included for the pulsed laser by assuming that $E_0(t - z/c)$ and $\phi(t - z/c)$ undergo fluctuations during a laser pulse, as would be the case if there were a very large number of longitudinal modes present with each having independent phases. The amplitude of $E(r,t)$ before focusing can be related to $E_0(t - z/c)$ by evaluating Eq. (1) at $z = -F$ and by assuming that F/b is very large. Thus, the on-axis power densities before and after focusing are related by having I_0 equal to the focused power density which is equal to $(2F/b)^2 I_u = (d/w)^2 I_u$, where I_u is the unfocused power density on axis.

In the following we repeat some well-known material in order to show clearly the effect of THG on MPI in the region very near a three-photon resonance. We define the detuning $\Delta_0 = 3\omega - \omega_r$, where ω_r is the frequency of light emitted in spontaneous emission between the excited state $|1\rangle$ and the ground state $|0\rangle$. When $\Delta_0 = 0$ we have three-photon resonance. In all that follows we assume $|\Delta_0| \ll \omega_r$ and that $|\Delta_0|$ is also very small compared to the detuning from any other three-photon resonance.

A. Perturbation equations for the bound-state probability amplitudes

It is well known[2] that in the region near a three-photon resonance having $\Delta J = 1$, plane-polarized light generates a polarizability at frequency 3ω and that this effect leads to a TH electric field. Consider an atom at position $\vec{r}$ and time t. The response of the atom to the TH field $\vec{E}_{3\omega}(\vec{r},t)$ and the laser field $\vec{E}(\vec{r},t)$ is determined by the time-dependent Schrödinger equation

$$\hat{H}(\vec{r},t)\,|\psi_{\vec{r}}(t)\rangle = i\hbar\frac{\partial}{\partial t}\,|\psi_{\vec{r}}(t)\rangle \tag{2}$$

or equivalently in a time-evolution operator form[16]

$$|\psi_{\vec{r}}(t)\rangle = e^{-i\hat{H}_0 t/\hbar}\hat{S}(\vec{r},t)\,|\psi_{\vec{r}}(0)\rangle \,, \tag{3}$$

where $t = 0$ corresponds to the time when the laser is triggered. If the Hamiltonian in the absence of the laser field is H_0, then in a dipole approximation the Hamiltonian for the present problem is given by

$$\hat{H}(\vec{r},t) = \hat{H}_0 - \hat{\mathscr{D}}_y[\vec{E}(\vec{r},t) + \vec{E}_{3\omega}(\vec{r},t)]\cdot\vec{e}_y \,, \tag{4}$$

where the $\hat{\mathscr{D}}_y$ is the atomic dipole operator and the laser is polarized in the y direction $\vec{e}_y$. Then, from Eqs. (2)–(4),

$$i\hbar\frac{\partial}{\partial t}\hat{S}(\vec{r},t) = \hat{V}_I(\vec{r},t)\hat{S}(\vec{r},t) \,, \tag{5}$$

where for any operator $\hat{A}$ we define the interaction representation of $\hat{A}$ as

$$\hat{A}_I = \exp(i\hat{H}_0 t/\hbar)\hat{A}\exp(-i\hat{H}_0 t/\hbar) \,.$$

In the following analysis we separate the atom field interaction term $\hat{V}_I$ into a component due to the TH field and another due to the laser field according to

$$\hat{V}_I(\vec{r},t) = \hat{V}_{I1}(\vec{r},t) + \hat{V}_{I2}(\vec{r},t) \,, \tag{6}$$

where

$$\hat{V}_{I1}(\vec{r},t) = -\hat{\mathscr{D}}_{Iy}(t)E(\vec{r},t) \tag{7a}$$

and

$$\hat{V}_{I2}(\vec{r},t) = -\hat{\mathscr{D}}_{Iy}(t)E_{3\omega}(\vec{r},t) \,. \tag{7b}$$

The operator $\hat{\mathscr{D}}_{Iy}(t)$ is just $\hat{\mathscr{D}}_y$ in the interaction representation. Initially, all atoms are assumed to be in their ground state and $|\psi_{\vec{r}}(0)\rangle = |0\rangle$. Defining eigenstates of $\hat{H}_0$ by $\hat{H}_0|n\rangle = \hbar\omega_n|n\rangle$, we can write $1 = \sum\!\!\!\!\!\int |n\rangle\langle n|$, where the $\sum\!\!\!\!\!\int$ indicates a sum over discrete states and integration over continuum states. Inserting $\hat{1}$ between $\exp(-i\hat{H}_0 t/\hbar)$ and $S(\vec{r},t)$ in Eq. (3),

$$\begin{aligned} |\psi_{\vec{r}}(t)\rangle &= \sum\!\!\!\!\!\!\int_n e^{-i\omega_n t}\langle n\,|\hat{S}(r,t)|0\rangle\,|n\rangle \\ &= \sum\!\!\!\!\!\!\int_n e^{-i\omega_n t}a_n(\vec{r},t)\,|n\rangle \end{aligned} \tag{8}$$

with $a_n(\vec{r},t) = \langle n\,|\hat{S}(\vec{r},t)|0\rangle$, which is the probability amplitude for atoms at $\vec{r}$ and t being in state $|n\rangle$. If we use the simple properties of $\hat{S}(r,t)$, $\hat{S}(r,0) = 1$, and the fact that the laser is triggered at $t = 0$, we can integrate Eq. (5) and obtain the well-known result

$$\hat{S}(\vec{r},t) = \hat{1} + (i\hbar)^{-1}\int_0^t \hat{V}_I(\vec{r},t')\hat{S}(\vec{r},t')dt'$$

which when iterated n times leads to a time-dependent perturbation series[16]:

$$\begin{aligned} \hat{S}(\vec{r},t) = 1 &+ (i\hbar)^{-1}\int_0^t dt_1\,\hat{V}_I(\vec{r},t_1) + (i\hbar)^2\int_0^t dt_1\int_0^{t_1} dt_2\,\hat{V}_I(\vec{r},t_1)\hat{V}_I(\vec{r},t_2) \\ &+ \cdots + (i\hbar)^{-n}\int_0^t dt_1\int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n\,\hat{V}_I(\vec{r},t_1)\hat{V}_I(r,t_2)\cdots\hat{V}_I(\vec{r},t_n)\hat{S}(\vec{r},t_n) \,. \end{aligned}$$

With this expansion in the equation $a_n(\vec{r},t) = \langle n\,|\hat{S}(\vec{r},t)|0\rangle$, we get a similar perturbation series for $a_n(\vec{r},t)$ in the form[16]

$$a_n(\vec{r},t)=\delta_{n,0}+(i\hbar)^{-1}\int_0^t\langle n\,|\,\hat{V}_I(\vec{r},t_1)\,|\,0\rangle dt_1+(i\hbar)^{-2}\int_0^t dt_1\int_0^{t_1}dt_2\langle n\,|\,\hat{V}_I(\vec{r},t_1)\hat{V}_I(\vec{r},t_2)\,|\,0\rangle$$
$$+(i\hbar)^{-3}\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3\langle n\,|\,\hat{V}_I(\vec{r},t_1)\hat{V}_I(\vec{r},t_2)\hat{V}_I(\vec{r},t_3)\,|\,0\rangle+\cdots \,. \quad (9)$$

The perturbation series of Eq. (9) can be used if $|\Delta_0|$ is large compared with the resonant linewidth, the a.c. Stark shifts in $|0\rangle$ and $|1\rangle$, the laser linewidth, and the ionization rate of $|1\rangle$. Since we will use Eq. (9) in our present discussion, the theory developed in this section will not hold at, or extremely close to, the resonance because at zero detuning $\vec{E}_{3\omega}$ is in one-photon resonance between $|0\rangle$ and $|1\rangle$ and is very strongly absorbed. Also, since we assume that $|\Delta_0|$ is small enough so that the three-photon resonance dominates the ionization signal, we cannot be too far from resonance. In the Miller *et al.* study[11] with xenon and with $I_0<10^9$ w/cm^2, a region with $|\Delta_0|<1\times10^{12}$/sec must be excluded and $|\Delta_0|$ must be $<5\times10^{13}$/sec. A more exact treatment appropriate to the resonance situation will be presented in Sec. III.

In the interaction term $\hat{V}_I=\hat{V}_{I1}+\hat{V}_{I2}$ of Eq. (9) the magnitude of $\hat{V}_{I1}$, due to the laser field, is much larger than $\hat{V}_{I2}$, which is due to the TH field. However, since it is near three-photon resonance, $\hat{V}_{I1}$ is only important in third order. On the other hand, the TH light is near one-photon resonance and is important in first order but negligible in higher order. Also, as indicated above, we consider a regime which is far below saturation such that $a_0(\vec{r},t)$ remains almost unaffected, $a_0(\vec{r},t)\sim1$, and where the only near-resonant condition is that between $|0\rangle$ and $|1\rangle$. Thus, we consider Eq. (9) for $a_1(\vec{r},t)$, where we include terms through third order in the laser field $\vec{E}$ but include only first-order contributions from $\vec{E}_{3\omega}$. We get

$$a_1(\vec{r},t)\cong(i\hbar)^{-1}\int_0^t dt_1\langle1\,|\,\hat{V}_{I1}(\vec{r},t_1)+\hat{V}_{I2}(\vec{r},t_1)\,|\,0\rangle$$
$$+(i\hbar)^{-3}\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3\langle1\,|\,\hat{V}_{I1}(r,t_1)\hat{V}_{I1}(\vec{r},t_2)\hat{V}_{I1}(\vec{r},t_3)\,|\,0\rangle+\cdots \,. \quad (10)$$

To evaluate Eq. (10), unit operators $\hat{1}$ are inserted between each of the interaction terms and use is made of dipole selection rules. Also, for convenience the laser field of Eq. (1) is written in the simple form

$$E(\vec{r},t)=\vec{e}_yE^0_\omega(\vec{r},t)\cos[\omega t+\mu(\vec{r},t)]\,,$$

where the time dependencies of the pulse shape function $E^0_\omega(\vec{r},t)$ and of the phase change in $\exp[i\mu(\vec{r},t)]$ are very slow as compared to $\exp(3i\omega t)$. The terms $E^0_\omega(\vec{r},t)$ and $\mu(\vec{r},t)$ are related to the amplitude and phase of Eq. (1) through the relations

$$E^0_\omega(\vec{r},t)=\frac{E_0(t-z/c)}{(1+4z^2/b^2)^{1/2}}\exp[-k\rho^2/b(1+4z^2/b^2)]$$

and

$$\mu(\vec{r},t)=-kz+\phi(t-z/c)+\tan^{-1}(2z/b)-2k\rho^2z/b^2(1+4z^2/b^2)\,.$$

Additionally, the TH field $\vec{E}_{3\omega}(\vec{r},t)$, in a nearly paraxial focused beam, will be of the form

$$\vec{E}_{3\omega}(\vec{r},t)=\vec{e}_yE^0_{3\omega}(\vec{r},t)\cos[3\omega t+\theta(\vec{r},t)]\,,$$

where again $E^0_{3\omega}$ and $\exp[i\theta(\vec{r},t)]$ are slowly varying as compared to $\exp(3i\omega t)$. The expression for $a_1(\vec{r},t)$ becomes

$$a_1(\vec{r},t)=\frac{M_{1,0}}{2\hbar}e^{i(\omega_1-\omega_0)t}\left[E^0_{3\omega}(\vec{r},t)\left[\frac{e^{-i(3\omega t+\theta)}}{\omega_1-\omega_0-3\omega}+\frac{e^{i(3\omega t+\theta)}}{\omega_1-\omega_0+3\omega}\right]+E^0_\omega(r,t)\left[\frac{e^{-i(\omega t+\mu)}}{\omega_1-\omega_0-\omega}+\frac{e^{i(\omega t+\mu)}}{\omega_1-\omega_0+\omega}\right]\right]$$
$$+\left[\frac{E^0_\omega(\vec{r},t)}{2\hbar}\right]^3\Delta_0^{-1}\sum_m\!\!\!\!\!\!\int\;\sum_n\!\!\!\!\!\!\int\;\frac{M_{1,n}M_{n,m}M_{m,0}}{(\omega_n-\omega_0-2\omega)(\omega_m-\omega_0-\omega)}\exp\{-i[(\omega_1-\omega_0-3\omega)t-3\mu(\vec{r},t)]\}\,, \quad (11)$$

where here and below we define the dipole matrix element $M_{n,m}=\langle n\,|\,\mathscr{D}_y\,|\,m\rangle$; thus, $M_{1,0}=\langle1\,|\,\mathscr{D}_y\,|\,0\rangle$. In Eq. (11) the last term will be recognized as the three-photon Rabi frequency Ω_3 for the $|0\rangle$ to $|1\rangle$ transition:

$$\Omega_3(\vec{r},t)=[E^0_\omega(\vec{r},t)/2\hbar]^3\sum_n\!\!\!\!\!\!\int\;\sum_m\!\!\!\!\!\!\int\;M_{1,n}M_{n,m}M_{m,0}/(\omega_n-\omega_0-2\omega)(\omega_m-\omega_0-\omega)\,. \quad (12)$$

Thus, Eq. (11) can be written in the form

$$a_1(\vec{r},t)=\frac{M_{1,0}}{2\hbar}e^{i(\omega_1-\omega_0)t}\left[\frac{E^0_{3\omega}e^{-i(3\omega t+\theta)}}{\omega_1-\omega_0-3\omega}+\frac{E^0_{3\omega}e^{i(3\omega t+\theta)}}{\omega_1-\omega_0+3\omega}+\frac{E^0_\omega e^{-i(\omega t+\mu)}}{\omega_1-\omega_0-\omega}+\frac{E^0_\omega e^{i(\omega t+\mu)}}{\omega_1-\omega_0+\omega}\right]$$
$$+\frac{\Omega_3(\vec{r},t)}{\Delta_0}\exp\{i[(\omega_1-\omega_0-3\omega)t-3\mu(\vec{r},t)]\}\,, \quad (13)$$

where $\Delta_0 = 3\omega - \omega_r$ is the detuning from three-photon resonance between $|0\rangle$ and $|1\rangle$.

For all $a_n(\vec{r},t)$ with $n > 1$, the third-order term involving Ω_3 is quite small as compared to its value in Eq. (13). Thus, we can neglect the third-order contribution in all other amplitudes and write

$$a_n(\vec{r},t) = e^{i(\omega_n-\omega_0)t}\frac{M_{n,0}E^0_{3\omega}(r,t)}{2\hbar}\left[\frac{e^{-i(3\omega t+\theta)}}{\omega_n-\omega_0-3\omega}+\frac{e^{i(3\omega t_1+\theta)}}{\omega_n-\omega_0-3\omega}\right]+e^{i(\omega_n-\omega_0)t}\frac{M_{n,0}E^0_{\omega}}{2\hbar}(\vec{r},t)\left[\frac{e^{-i(\omega t+\mu)}}{\omega_n-\omega_0-\omega}+\frac{e^{i(\omega t+\mu)}}{\omega_n-\omega_0+\omega}\right], \tag{14}$$

for all $n > 1$.

In order to evaluate these expressions for the amplitudes $a_n(\vec{r},t)$ we must know the TH field:

$$E_{3\omega}(\vec{r},t) = E^0_{3\omega}(\vec{r},t)\{\exp[-i(3\omega t+\theta)]+\exp[i(3\omega t+\theta)]\}/2 .$$

But the TH field is determined by the atoms themselves as they respond in a cooperative manner both to the laser field and to the TH field due to other atoms further upstream in the laser beam. The electric dipole polarization at a point $\vec{r}$ and time t is given by the expectation value of the dipole operator $\hat{\mathscr{D}}_y$:

$$\vec{\mathscr{P}}(\vec{r},t) = N\langle\psi_{\vec{r}}(t)|\hat{\mathscr{D}}_y|\psi_{\vec{r}}(t)\rangle\vec{e}_y = \vec{e}_y N \sum_n \sum_m e^{i(\omega_n-\omega_m)t}a_n^*(\vec{r},t)a_m(\vec{r},t)M_{n,m} . \tag{15}$$

To the same order of approximation as that of Eqs. (13) and (14) we can use the results of these equations for $a_j(\vec{r},t)$ and write the local polarization in the form

$$\begin{aligned}\vec{\mathscr{P}}(\vec{r},t) &= N\sum_n \frac{|M_{n,0}|^2}{\hbar}\left[\frac{1}{\omega_n-\omega_0-\omega}+\frac{1}{\omega_n-\omega_0+\omega}\right]\vec{\mathrm{E}}(\vec{r},t)+N\sum_n\frac{|M_{n,0}|^2}{\hbar}\left[\frac{1}{\omega_n-\omega_0-3\omega}+\frac{1}{\omega_n-\omega_0+3\omega}\right]\vec{\mathrm{E}}_{3\omega}(\vec{r},t)\\ &\quad+N\left[\frac{\Omega_3(\vec{r},t)}{\Delta_0}M_{0,1}\exp\{-3i[\omega t+\mu(\vec{r},t)]\}+\text{c.c.}\right]\\ &= \chi(\omega)\vec{\mathrm{E}}(\vec{r},t)+\chi(3\omega)\vec{\mathrm{E}}_{3\omega}(\vec{r},t)+\left[\frac{\Omega_3(r,t)}{\Delta_0}M_{0,1}N\exp\{-3i[\omega t+\mu(\vec{r},t)]\}+\text{c.c.}\right]\vec{e}_y .\end{aligned} \tag{16}$$

Thus, the polarization has the usual component $\chi(\omega)\vec{\mathrm{E}}(\vec{r},t)$ which oscillates at the laser frequency ω where

$$\chi(\omega) = 2N\sum_j |M_{j,0}|^2(\omega_j-\omega_0)/\hbar[(\omega_j-\omega_0)^2-\omega^2] \tag{17}$$

is the linear susceptibility at ω. This term leads to a modified phase velocity for the laser field which is already included in Eq. (1), where $n^2(\omega)=1+4\pi\chi(\omega)$ and $k=n(\omega)\omega/c$. Note for later reference that the presence of a buffer gas of number density N_B would simply add a term similar to Eq. (17) to give an additional nonresonant contribution to $\chi(\omega)$.

The polarization has two additional components that oscillate at the TH frequency 3ω. The first of these, $\chi(3\omega)\vec{\mathrm{E}}_{3\omega}$, is proportional to the TH field where the linear susceptibility at $\chi(3\omega)$ is again

$$\chi(3\omega) = 2N\sum_j |M_{j,0}|^2(\omega_j-\omega_0)/\hbar[(\omega_j-\omega_0)^2-(3\omega)^2] . \tag{18}$$

We rewrite this only to comment that at near zero detuning the $j=1$ term of $\chi(3\omega)$ in Eq. (18) becomes very large; thus, it may not be proper to cast the polarization in the present form exactly on resonance. (We consider this situation in Sec. III.) Note again that a buffer gas would add another nonresonant contribution to $\chi(3\omega)$ similar to Eq. (18). The other 3ω component of $\vec{\mathscr{P}}$ is that due to the three-photon Rabi oscillation Ω_3 which is third order in the laser field.

In Eq. (16) the susceptibilities, the Rabi term, and the laser field are known or calculable, but the TH field $\vec{\mathrm{E}}_{3\omega}(\vec{r},t)$ is unknown since, as noted above, it is contained in the expressions for $a_n(\vec{r},t)$ which are to be evaluated. However, the relation between $\vec{\mathscr{P}}$ and $\vec{\mathrm{E}}$ is governed by Maxwell's equations; thus, we can solve Maxwell's equations for the TH frequency components of Eq. (16) and obtain $\vec{\mathrm{E}}_{3\omega}$ in terms of a spacial integral over the polarization sources of this field. For convenience we define the components of $\vec{\mathscr{P}}$ from Eq. (16):

$$\begin{aligned}\vec{\mathscr{P}}(\vec{r},t) &= \chi(\omega)\vec{\mathrm{E}}(\vec{r},t)+\chi(3\omega)\vec{\mathrm{E}}_{3\omega}(\vec{r},t)+\mathscr{P}^{\Omega}_{3\omega}(\vec{r},t)\\ &= \vec{\mathscr{P}}_{\omega}(\vec{r},t)+\vec{\mathscr{P}}_{3\omega}(\vec{r},t) ,\end{aligned} \tag{19}$$

where

$$\vec{\mathscr{P}}_{3\omega}(r,t) = \chi(3\omega)\vec{\mathrm{E}}_{3\omega}(r,t)+\vec{\mathscr{P}}^{\Omega}_{3\omega}(\vec{r},t) \tag{20a}$$

and

$$\mathscr{P}^{\Omega}_{3\omega}(\vec{r},t) = \Omega_3(\vec{r},t)\Delta_0^{-1}M_{0,1}N\exp\{-3i[\omega t+\mu(\vec{r},t)]\}+\text{c.c.} \tag{20b}$$

B. Expression for the third-harmonic field

In order to evaluate the TH field in terms of the laser field and relevant atomic transition moments, we solve Maxwell's equations for $E_{3\omega}$ with the polarization terms of Eqs. (16) and (20), where the polarization becomes a spatially distributed source term for the TH field. Thus, in Maxwell's equations we have

$$\rho(r,t)=-\vec{\nabla}\cdot\vec{\mathscr{P}}_{3\omega}(\vec{r},t)$$

and

$$\vec{J}=\partial\vec{\mathscr{P}}_{3\omega}(\vec{r},t)/\partial t\ ,$$

where ρ and $\vec{J}$ are effective charge and current densities, respectively. Very succinctly, we Fourier transform Maxwell's equations, e.g.,

$$\int_0^\infty[\partial\vec{\mathscr{P}}_{3\omega}(\vec{r},t)/\partial t]e^{ist}dt=-is\vec{\mathscr{P}}_{3\omega}(\vec{r},s)=\vec{J}(\vec{r},s)\ ,$$

etc., and manipulate the transformed equations into the form

$$\nabla^2\vec{E}_{3\omega}(\vec{r},s)+\frac{s^2}{c^2}[1+4\pi\chi(3\omega)]\vec{E}_{3\omega}(\vec{r},s)=-4\pi\frac{s^2}{c^2}\vec{\mathscr{P}}^{\,\Omega}_{3\omega}(\vec{r},s)-\frac{4\pi\vec{\nabla}[\vec{\nabla}\cdot\vec{\mathscr{P}}^{\,\Omega}_{3\omega}(\vec{r},s)]}{1+4\pi\chi(3\omega)}\ . \tag{21}$$

This is a wave equation with the nonlinear Ω_3 term of $\mathscr{P}_{3\omega}$ as source terms for $E_{3\omega}$. We solve by a Green's-function method where the Green's function appropriate to Eq. (21) is just

$$G(\vec{r},\vec{r}')=-\frac{e^{is|\vec{r}-\vec{r}'|/v}}{4\pi|\vec{r}-\vec{r}'|}\ ,$$

where we have defined $v=c/[1+4\pi\chi(3\omega)]^{1/2}$. After solving Eq. (21) and taking the inverse transform (which produces the usual retarded time variables), we get the TH field in terms of an integral over source terms:

$$\vec{E}_{3\omega}(\vec{r},t)=\int\frac{d^3\vec{r}'}{|\vec{r}-\vec{r}'|}\left[-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{\mathscr{P}}^{\,\Omega}_{3\omega}\left[\vec{r}',t-\frac{|\vec{r}-\vec{r}'|}{v}\right]\cdot(\vec{\mathbb{1}}-\vec{R}_I\vec{R}_I)-\frac{(\vec{\mathbb{1}}-3\vec{R}_I\vec{R}_I)}{1+4\pi\chi(3\omega)}\cdot\left[\frac{\vec{\mathscr{P}}^{\,\Omega}_{3\omega}\left[\vec{r}',t-\frac{|\vec{r}-\vec{r}'|}{v}\right]}{|\vec{r}-\vec{r}'|^2}+\frac{1}{v}\frac{\frac{\partial}{\partial t}\vec{\mathscr{P}}^{\,\Omega}_{3\omega}\left[\vec{r}',t-\frac{|r-r'|}{v}\right]}{|\vec{r}-\vec{r}'|}\right]\right]\ , \tag{22}$$

where $\vec{\mathbb{1}}$ is the unit dyad and

$$\vec{R}_I=(\vec{r}-\vec{r}')/|\vec{r}-\vec{r}'|\ .$$

When $|z-z'|$ is larger than a few wavelengths and the paraxial approximation is used, Eq. (22) simplifies to

$$\vec{E}_{3\omega}(\vec{r},t)=-\frac{1}{c^2}\int\frac{d^3\vec{r}'}{|\vec{r}-\vec{r}'|}\frac{\partial^2}{\partial t^2}\vec{\mathscr{P}}^{\,\Omega}_{3\omega}\left[\vec{r}',t-\frac{|\vec{r}-\vec{r}'|}{v}\right]\simeq\frac{\omega_r^2}{c^2}\int\frac{d^3\vec{r}'}{|\vec{r}-\vec{r}'|}\vec{\mathscr{P}}^{\,\Omega}_{3\omega}\left[\vec{r}',t-\frac{|\vec{r}-\vec{r}'|}{v}\right]\ . \tag{23}$$

Since the beam waist $w=\lambda F/\pi d\gg\lambda$, because $F\gg d$, it can be shown that Eq. (23) can be used with no restriction on $|z-z'|$. Here $b\gg w$ and there is a lengthy region, as compared with the beam waist, over which the photon flux is nearly constant. Thus, contributions from $|z-z'|\gg w$ are of more importance than those from $|z-z'|<w$ in the calculation of $\vec{E}_{3\omega}(\vec{r},t)$. Consequentially, Eq. (23) is equivalent to the approximations $k_x^2+k_y^2\ll k_z^2$ which are made in the elegant Fourier transform method used to evaluate $\vec{E}_{3\omega}$ in the work of Ward and New.[2] We write

$$\vec{E}_{3\omega}(\vec{r},t)=\tfrac{1}{2}[E^+_{3\omega}(\vec{r},t)+E^-_{3\omega}(\vec{r},t)]\vec{e}_y\ ,$$

use Eq. (20b) in (23), and get

$$E^+_{3\omega}(\vec{r},t)=\frac{N\omega_r^2M_{0,1}}{c^2\Delta_0}\int\frac{d^3\vec{r}'}{|\vec{r}-\vec{r}'|}\Omega_3(r',t-|\vec{r}-\vec{r}'|/v)\exp\{-3i[\omega t+\mu(\vec{r}',t-|\vec{r}-\vec{r}'|/v)]\}e^{3i\omega|\vec{r}-\vec{r}'|/v} \tag{24}$$

with $E^-_{3\omega}(\vec{r},t)$ the complex conjugate of Eq. (24). If b/v is small compared to the inverse laser bandwidth, we can go further than replacing $|\vec{r}-\vec{r}'|$ by $|z-z'|$ when $F\gg d$ and replace $|\vec{r}-\vec{r}'|$ by $|z|$ in the slowly varying quantities such as μ and Ω_3. Thus,

$$E^+_{3\omega}(\vec{r},t)=\frac{NM_{0,1}\omega_r^2}{c^2\Delta_0}e^{-3i\omega t}\int\frac{d^3\vec{r}'}{|\vec{r}-\vec{r}'|}\Omega_3(\vec{r}',t-|z|/v)e^{-3i\mu(\vec{r}',t-|z|/c)}e^{3i\omega|\vec{r}-\vec{r}'|/v}\ . \tag{25}$$

The expression of $\vec{E}_{3\omega}(\vec{r},t)$ as an integral over source points is being used here because it is most useful for dealing with an extension of the theory to cases where Δ_0 can be small. We evaluate Eq. (25) for a laser beam whose intensity is independent of the azimuthal angle ϕ in cylindrical coordinates z, ρ, and ϕ. We note that, with the laser field of Eq. (1), $\Omega_3(\vec{r},t)$ can be written as (in a rotating-wave—type approximation)

$$\Omega_3(\vec{r},t)=\Omega_3(0,0,t)\frac{e^{-3k\rho^2/b(1+4z^2/b^2)}}{(1+2iz/b)^3}e^{3i\tan^{-1}(2z/b)} , \tag{26}$$

where $\Omega_3(0,0,t)$ is the three-photon Rabi frequency at $\rho=0$ and $z=0$.

In the Appendix, expression (25) is explicitly reduced to the form

$$E^+_{3\omega}(\vec{r},t)=\frac{i\pi Nb\omega_r M_{0,1}v}{\Delta_0 c^2}\frac{\Omega_3(0,0,t-|z|/c)}{1+2izv/bc}\exp\{-3i[\omega t-kz+\phi(t-|z|/c)]\}$$
$$\times\exp\{-3\omega\rho^2/[bc(1+2izv/bc)]\}g\left[\frac{2z}{b},\frac{\Delta k\, b}{2}\right] , \tag{27}$$

where $\Delta k=3(k-\omega/v)$, $\rho^2=x^2+y^2$, $v=c/[1+4\pi\chi(3\omega)]^{1/2}$, b is the confocal parameter of Eq. (1), $\Delta_0=3\omega-(\omega_1-\omega_0)$, and

$$g(u,v)=\int_{-\infty}^{u}\frac{e^{iv(u'-u)}}{(1+iu')^2}du' . \tag{28}$$

The TH field is thus expressed in terms of atomic matrix elements and a single closed form quadrature, $g(2z/b,\Delta k\, b/2)$. The total field is $E_{3\omega}(r,t)=\frac{1}{2}(E^+_{3\omega}+E^-_{3\omega})$, where the $E^+_{3\omega}$ term makes the major contribution in considerations below. Note that $E_{3\omega}$ has the same confocal parameter as the laser field, but the beam waist is smaller by about a factor of $\sqrt{3}$.

With the expression for $E_{3\omega}$ we return to Eq. (13) and, in a rotating-wave approximation where only near-resonant denominators and slowly varying exponentials are retained, we substitute $E_{3\omega}$ from Eq. (27) for the TH field and the expression (26) for the three-photon pumping component $\Omega_3(r,t)$ and get

$$a_1(\vec{r},t)=e^{-i\Delta_0 t}\exp\{-3\omega\rho^2/[vb(1+2iz/b)]\}\exp\{3i[kz-\phi(t-|z|/c)]\}$$
$$\times\frac{\Omega_3(0,0,t)}{(1+2iz/b)\Delta_0}\left[\frac{-i\kappa b}{2\Delta_0}g\left[\frac{2z}{b},\frac{\Delta kb}{2}\right]+\frac{1}{(1+2iz/b)^2}\right] , \tag{29}$$

where, for convenience and physical implications to be discussed below, we have defined

$$\kappa=\frac{2\pi|M_{0,1}|^2\omega_r N}{\hbar c} . \tag{30}$$

Also, we have restricted the analysis to the region not too near $\Delta_0=0$ such that the phase velocity of the TH field, v, is not too different from c, i.e., $v=c\pm\delta$, where $\delta/c<1$.

Before we go on to calculate the resonantly enhanced ionization probabilities we pause to note some features of the expression for the probability amplitude $a_1(r,t)$ for the one- and three-photon allowed excited state $|1\rangle$. First we note that inside the brackets of Eq. (29) there are two terms that contribute to the probability amplitude for the excited state, the magnitudes and phases of which were important in the analysis leading to the equation. The first term involving the integral $g(2z/b,\Delta k\, b/2)$ is produced by the TH field $E_{3\omega}$, while the second term is due to three-photon pumping by the laser field. As was shown in Ref. 14 for unfocused geometry, these terms tend to cancel each other as $\Delta_0\to 0$. We can easily establish the same behavior here from Eq. (29) where the result is more transparent than was the case in the integro-differential equation for $a_1(\vec{r},t)$ in Ref. 14.

To establish the behavior of a_1 in Eq. (20) as the resonance is approached, we must evaluate $g(2z/b,\Delta k\, b/2)$ in this frequency region. First we note a feature of $\Delta k=3(k-w/v)$ in Eq. (27) where

$$v^{-1}=c^{-1}[1+2\pi\chi(3\omega)] ,$$

v is the phase velocity of the TH field, and the susceptibility $\chi(3\omega)$ was defined in Eq. (18). Since Δ_0 is restricted to stay very small as compared to the detuning from any *other* three-photon resonance, all terms in $\chi(3\omega)$ are almost independent of Δ_0 except for the term associated with $|1\rangle$, i.e., the $j=1$ term in Eq. (18),

$$N|M_{1,0}|^2/\hbar(\omega_1-\omega_0-3\omega)=-N|M_{1,0}|^2/\hbar\Delta_0 .$$

Thus, we write Δk as the sum of a part which is almost frequency independent and a frequency-dependent part by separating the $j=1$ term from the expression for $\chi(3\omega)$ to get

$$\Delta k=3k-3\omega/v=3k-\frac{3\omega}{c}[1+2\pi\chi(3\omega)]=3k-\frac{3\omega}{c}\left[1+4\pi N\sum_{j(\neq 1)}\frac{|M_{j,0}|^2(\omega_j-\omega_0)}{\hbar[(\omega_i-\omega_0)^2-(3\omega)^2]}\right]+\frac{3\omega}{c}\frac{2\pi N|M_{1,0}|^2}{\hbar\Delta_0}$$
$$\simeq\Delta k_0+2\pi\omega_r N|M_{1,0}|^2/\hbar c\Delta_0 \tag{31a}$$

or

$$\Delta k = \Delta k_0 + \kappa/\Delta_0 , \tag{31b}$$

where κ is given in Eq. (30). For convenience we define

$$v_S = \Delta k_0 b/2 \tag{32a}$$

and

$$v_R = \kappa b/2\Delta_0 \tag{32b}$$

and note that v_R becomes large as the resonance is approached, whereas v_S remains essentially constant. In these variables, and with $u = 2z/b$, the terms inside the brackets in Eq. (29) become

$$I(u, v_R + v_S) = \left[\frac{1}{(1+iu)^2} - iv_R g(u, v_R + v_S) \right] . \tag{33a}$$

We want to evaluate g of Eq. (28) when $|v_R + v_S| \gg 1$. We can repeatedly integrate Eq. (28) by parts to get an asymptotic expansion

$$g(u, v_R + v_S) = \frac{-i}{v_R + v_S} \left[\frac{1}{(1+iu)^2} + \frac{2}{(v_R + v_S)} \frac{1}{(1+iu)^3} + \cdots \right] . \tag{34}$$

Thus, to first order the two terms in the parentheses of Eq. (33a) cancel as v_R becomes large. That is

$$I \sim \left[\frac{1}{(1+iu)^2} - \frac{v_R}{v_R + v_S} \frac{1}{(1+iu)^2} \right]$$

$$\cong (1+iu)^{-2} \frac{\Delta k_0 \, \Delta_0}{\kappa} \tag{33b}$$

which approaches zero as Δ_0 approaches zero.

Thus, we conclude that the single-photon pumping by the TH field and the three-photon pumping by the laser field strongly cancel at small Δ_0, leading to a greatly reduced probability of populating $|1\rangle$. This same conclusion was reached in the earliest treatment by Payne, Garrett, and Baker of this effect[12] and in the more detailed analysis of Payne and Garrett.[14] In the perturbation treatment the effect is easily described in a physical picture wherein $E(\vec{r},t)$ (the laser field) and $E_{3\omega}(\vec{r},t)$ (the third-harmonic field) each drives the transition from $|0\rangle$ to $|1\rangle$ with equal Rabi frequencies, but the effects become 180° out of phase as the resonance is approached. The more recent and more simplified perturbation treatment of Jackson and Wynn[15] exhibited the same effect. We return to this point again below, where we obtain the total line shape for MPI near the three-photon resonance.

C. Ionization probability: line shapes for n-photon ionization and third-harmonic photon output

With the above expressions for $\vec{E}_{3\omega}(\vec{r},t)$ and $a_1(\vec{r},t)$ we now consider ionization in the presence of both the TH and laser fields. Let $C_\mu(\vec{r},E,t)$ be a continuum amplitude of the atom in state $|E,\mu\rangle$, where $H_0|E,\mu\rangle = E|E,\mu\rangle$. The continuum states, along with the discrete states, are contained in $\hat{1} = \sum\!\!\!\!\!\!\int |n\rangle\langle n|$ and are involved in the implied integration over continuum and sum over discrete states. We have simply labeled the continuum states differently here to designate continuous energy eigenvalues. The normalization is such that $\langle E,\mu | E',\mu' \rangle = \delta(E-E')\delta_{\mu,\mu'}$, where the μ quantum numbers label angular momenta. The explicit expression for $C_\mu(\vec{r},E,t)$ analogous to Eq. (7) is

$$\begin{aligned} C_\mu(\vec{r},E,t) &= \langle E,\mu | \hat{S}(\vec{r},t) | 0 \rangle \\ &= (i\hbar)^{-1} \int_0^t dt_1 \langle E,\mu | \hat{V}_I(\vec{r},t_1) | 0 \rangle + (i\hbar)^{-2} \int_0^t dt_1 \int_0^{t_1} dt_2 \langle E,\mu | \hat{V}_I(\vec{r},t_1) \hat{V}_I(\vec{r},t_2) | 0 \rangle \\ &\quad + (i\hbar)^{-3} \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \langle E,\mu | \hat{V}_I(\vec{r},t) \hat{V}_I(\vec{r},t_2) \hat{V}_I(\vec{r},t_3) | 0 \rangle \\ &\quad + (i\hbar)^{-4} \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \langle E,\mu | \hat{V}_I(r,t_1) \hat{V}_I(\vec{r},t_2) \hat{V}_I(\vec{r},t_3) \hat{V}_I(\vec{r},t_4) | 0 \rangle + \cdots . \end{aligned} \tag{35}$$

Near the three-photon resonance the dominant terms are those already considered which are near resonance between $|0\rangle$ and $|1\rangle$ either with one TH photon or with three laser photons. We will assume here that one more photon can ionize $|1\rangle$, but it is trivial to generalize the results to situations where two or more photons are required to ionize $|1\rangle$. The first- and third-order terms adiabatically follow the perturbations and lead to no final-state ionization (except for the third order with absorption of one laser photon plus two third harmonics—the latter, being second order in a weak field, is neglected). Thus, if we retain only the second- and fourth-order terms in $\hat{V}_I$ and in these if we keep only terms with a near resonance between $|0\rangle$ and $|1\rangle$, we get

$$\begin{aligned} C_\mu(\vec{r},E,t) &\simeq (i\hbar)^{-2} \int_0^t dt_1 \int_0^{t_1} dt_2 \langle E,\mu | \hat{V}_{I1}(\vec{r},t_1) | 1 \rangle \langle 1 | \hat{V}_{I2}(\vec{r},t_2) | 0 \rangle \\ &\quad + (i\hbar)^{-4} \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \langle E,\mu | \hat{V}_{I1}(\vec{r},t_1) | 1 \rangle \langle 1 | \hat{V}_{I1}(\vec{r},t_2) \hat{V}_{I1}(\vec{r},t_3) \hat{V}_{I1}(\vec{r},t_4) | 0 \rangle . \end{aligned} \tag{36}$$

In deriving this expression, the unit operator was inserted into Eq. (35) at the positions where $|1\rangle\langle 1|$ appears in Eq. (36). However, all other terms which result from the expansion of the unit operator are far off resonance and are negligible as compared to the highly resonant contribution resulting from the $|1\rangle\langle 1|$ term. Thus, only the latter is retained. Also, in the second-order term the product $\hat{V}_{I1}(t')\hat{V}_{I2}(t'')$ was neglected because it corresponds to absorbing a laser photon first so that no near resonance is achieved. We can rewrite Eq. (36) as

$$C_\mu(\vec{r},E,t)=(i\hbar)^{-1}\int_0^t dt_1\langle E,\mu\,|\,\hat{V}_{I1}(\vec{r},t_1)\,|\,1\rangle\left[(i\hbar)^{-1}\int_0^{t_1}dt_2\langle 1\,|\,\hat{V}_{I2}(\vec{r},t_2)\,|\,0\rangle\right.$$
$$\left.+(i\hbar)^{-3}\int_0^{t_1}dt_2\int_0^{t_2}dt_3\int_0^{t_3}dt_4\langle 1\,|\,\hat{V}_{I1}(\vec{r},t_2)\hat{V}_{I1}(\vec{r},t_3)\hat{V}_{I1}(\vec{r},t_4)\,|\,0\rangle\right]. \quad (37)$$

For brevity we have given a word description of the mathematical steps that lead from Eq. (36) to Eq. (37). As before, the expression (37) has a simple physical picture which results from the steps just described. The first term inside the parentheses corresponds to the amplitude for excitation from $|0\rangle$ to $|1\rangle$ by a TH photon; the second term represents the amplitude for excitation of the same level by three laser photons; and the term multiplying the material in parentheses leads to promotion by a single photon from $|1\rangle$ to the continuum $|E,\mu\rangle$.

Each of the terms within the large parentheses was evaluated above in the analysis of Eq. (10). When $\Delta k \ll 3k$ we obtain

$$C_\mu(\vec{r},E,t)=\frac{e^{3ikz}\exp[-3k\rho^2/b(1+2iz/b)]}{\Delta_0(1+2iz/b)}$$
$$\times(i\hbar)^{-1}\int_0^t\Omega_3(0,0,t'-|z|/c)e^{-3i\phi(t'-|z|/c)}e^{-i\Delta_0 t'}\langle E,\mu\,|\,\hat{V}_{I1}(\vec{r},t')\,|\,1\rangle I\left[\frac{2z}{b},\frac{\Delta k\, b}{2}\right]dt', \quad (38)$$

where, from the previous analysis,

$$I\left[\frac{2z}{b},\frac{\Delta k\, b}{2}\right]=\frac{1}{(1+2iz/b)^2}-\frac{i\kappa b}{2\Delta_0}g\left[\frac{2z}{b},\frac{\Delta kb}{2}\right] \quad (39)$$

and we had defined $\kappa=2\pi|M_{0,1}|^2\omega_r N/\hbar c$. We note here again that the first term in the expression (39) represents the contribution to the continuum amplitude through three-photon excitation to the resonance level and the second term is that from single-photon excitation by the TH field. The probability of ionizing an atom at $\vec{r}$ sometime during the laser pulse is

$$P_I(\vec{r})=\sum_\mu\int dE\,|C_\mu(\vec{r},E,\infty)|^2$$
$$=\frac{\exp[-8k\rho^2/b(1+4z^2/b^2)]}{(1+4z^2/b^2)^2}\frac{1}{4\hbar^2\Delta_0^2}\left|I\left[\frac{2z}{b},\frac{\Delta k\, b}{2}\right]\right|^2$$
$$\times\sum_\mu\int dE\int_0^\infty\Omega_3(0,0,t')e^{-4i\phi(t')}e^{i(\omega_E-\omega_0-4\omega)t'}M(E,\mu;1)E_\omega^0(0,0,t')dt'$$
$$\times\int_0^\infty\Omega_3^*(0,0,t'')e^{4i\phi(t'')}e^{-i(\omega_E-\omega_0-4\omega)t''}M^*(E,\mu;1)E_\omega^0(0,0,t'')dt'', \quad (40)$$

where $M(E,\mu;1)=\langle E,\mu\,|\,\hat{\mathscr{D}}_{Iy}\,|\,1\rangle$ is the dipole matrix element from $|1\rangle$ to $|E,\mu\rangle$, the continuum at E. Consider the $dE=\hbar d\omega_E$ integration. When $\omega_E-\omega_0-4\omega$ is much larger than the laser bandwidth, the contribution adiabatically follows the laser field and gives no final-state contribution. Thus, the $d\omega_E$ integral is carried out between $\omega_0+4\omega-\delta\le\omega_E\le\omega_0+4\omega+\delta$, where $\delta\gg$ laser bandwidth but is small compared with the frequency range over which $M(E,\mu;1)$ changes appreciably. Thus, if $M(E,\mu;1)$ is slowly varying,

$$\int dE\,|M(E,\mu;1)|^2\exp[i(\omega_E-\omega_0-4\omega)(t'-t'')]\cong\hbar|\langle\hbar(4\omega+\omega_0),\mu\,|\,\hat{\mathscr{D}}_y\,|\,1\rangle|^2\int_{-\delta}^{\delta}e^{i\epsilon(t'-t'')}d\epsilon$$
$$\cong 2\pi\hbar|\langle\hbar(4\omega+\omega_0),\mu\,|\,\hat{\mathscr{D}}_y\,|\,1\rangle|^2\delta(t''-t').$$

This decreases sharply for $(t-t')\sim\pi/\delta$. Thus, it behaves like a Dirac delta function in time for functions like Ω_3 and

$$E_0(0,0,t')\exp[4i\phi(t')].$$

Accordingly, we identify in Eq. (40) the conventional expression for the ionization rate $\gamma_I^{(1)}$ for photoionization out of state $|1\rangle$ by a single photon:

$$\gamma_I^{(1)}(0,0,t')=\frac{\pi}{2\hbar}\sum_\mu|\langle\hbar(\omega_1+\omega),\mu\,|\,\hat{\mathscr{D}}_y\,|\,1\rangle|^2[E_\omega^0(0,0,t')]^2$$
$$=\frac{4\pi^2\omega}{c}\sum_\mu|\langle\hbar(\omega+\omega_1),\mu\,|\,\hat{\mathscr{D}}_y\,|\,1\rangle|^2\mathscr{F}(0,0,t), \quad (41)$$

where $\mathscr{F}(0,0,t)$ is the photon flux at the focal point and

$\gamma_I^{(1)}(0,0,t')$ is the ionization rate of state $|1\rangle$ at the focal point. Then, using the delta function property in the above approximation where the continuum dipole matrix element is a slowly varying function of E, we get

$$P_I(\vec{r})=\frac{\exp[-8k\rho^2/b(1+4z^2/b^2)]}{(1+4z^2/b^2)^2}\times\frac{\left|I\left[\frac{2z}{b},\frac{\Delta k\,b}{2}\right]\right|^2}{\Delta_0^2}\times\int_0^\infty |\Omega_3(0,0,t')|^2\gamma_I^{(1)}(0,0,t')dt' . \quad (42)$$

The number of ions per pulse is

$$N_I=2\pi N\int_{-\infty}^{\infty}dz\int_0^\infty d\rho\,\rho P_I(\vec{r})=\frac{\pi Nbw^2}{16\Delta_0^2}\int_0^\infty dt\,\gamma_I^{(1)}(0,0,t)\,|\Omega_3(0,0,t)|^2\times\int_{-\infty}^{\infty}\frac{du}{(1+u^2)}\left|I\left[u,\frac{\Delta k\,b}{2}\right]\right|^2 , \quad (43)$$

where $u=2z/b$. Equation (43) is easily generalized to the case where two or more photons are required to ionize $|1\rangle$. Let $\gamma_I^{(m)}(0,0,t)$ be the ionization rate for $|1\rangle$ in the case where m photons are required. Equation (43) in this case (m-photon ionization) becomes

$$N_I=\frac{\pi Nbw^2}{4(m+3)\Delta_0^2}\int_0^\infty dt\langle\gamma_I^{(m)}(0,0,t)\,|\Omega_3(0,0,t)|^2\rangle\times\int_{-\infty}^{\infty}\frac{du}{(1+u^2)}\left|I\left[u,\frac{\Delta k\,b}{2}\right]\right|^2 . \quad (44)$$

In the discussion of Sec. II B we explored the behavior of the expression $I(2z/b,\Delta k\,b/2)$ of Eq. (39). Here we extend this discussion to see in more detail what the line shape for MPI should be in the presence of the cancellation effect involving the TH field. In terms of the reduced variables $v_R=\kappa b/2\Delta_0$ and $v_S=(\Delta k_0\,b)/2$, introduced earlier, we write the number of ions per pulse as

$$N_I=\frac{\pi Nw^2}{(m+3)b\kappa^2}M^{(m)}(v_R,v_S)\times\int_0^\infty dt\langle\gamma_I^{(m)}(0,0,t)\,|\Omega_3(0,0,t)|^2\rangle , \quad (45)$$

where

$$M^{(m)}(v_R,v_S)=v_R^2\int_{-\infty}^{\infty}\frac{du}{(1+u^2)^m}\left|\frac{1}{(1+iu)^2}-iv_Rg(u,v_R+v_S)\right|^2=v_R^2\int_{-\infty}^{\infty}\frac{du}{(1+u^2)^m}|\mathcal{M}_L+\mathcal{M}_{\rm TH}|^2 . \quad (46)$$

All of the information about the line shape for the ionization is contained in $M^{(m)}(v_R,v_S)$. Thus, we examine the line-shape function in some detail.

Note that we have written the first term of the complex function inside the absolute value signs as $\mathcal{M}_L$ since it comes from the three-photon process involving laser photons, and the second $\mathcal{M}_{\rm TH}$, is contributed by the one-photon excitation process involving the TH field. With reference to Eq. (30) or (46) we see that neglecting the effect of the TH field is achieved by setting $v_Rg(u,v_A+v_S)=0$ in Eq. (46) which gives a function

$$M_0^{(m)}(v_R,v_S)=v_R^2\int_{-\infty}^{\infty}\frac{du}{(1+u^2)^{m+2}}=\frac{\pi}{2^{2m+2}}\frac{(2m+2)!}{[(m+1)!]^2}v_R^2 . \quad (47)$$

In our earliest treatment of this problem[12] we showed that, as the resonance is approached (i.e., as v_R becomes very large), N_I becomes much smaller than would be expected if the effect of the TH field were neglected. Here this property is much more explicit. Note again that when $|v_R+v_S|\gg 1$ we can repeatedly integrate Eq. (28) by parts to get the asymptotic expansion of Eq. (34). Thus, as the resonance is approached, where v_R becomes very large (v_R is inversely proportional to the detuning Δ_0), Eq. (34) can be used in Eq. (46) with the immediate result that the two contributions to the ionization signal *cancel exactly to first order* in $1/(v_R+v_S)$, and

$$M^{(m)}(v_R,v_S)\to\left[\frac{v_S}{v_R+v_S}\right]^2M_0^{(m)}(v_R,v_S)\times\left[1+\frac{4(1-v_S)}{v_S^2}\left[\frac{m+\frac{3}{2}}{m+2}\right]\right] . \quad (48)$$

We see that the reduction in the ionization signal due to the TH field can be very large indeed. Note that $v_R=\kappa b/2\Delta_0$ is proportional to the gas number density N through κ. Thus, at low pressure the asymptotic expansion (34) will not be well represented by the first terms and the cancellation is not very effective. However, as N increases, the cancellation between the two terms that contribute to the ionization becomes more and more effective. In the region which is relevant to the experimental studies on xenon, $|v_R+v_S|\gg 1$, and the line shape (i.e., number of ions at detuning Δ_0) for an $(m+3)$ photon ionization signal takes the form

$$N_I \cong \frac{\pi N w^2}{(m+3)b\kappa^2} \frac{M_0^{(m)}(v_R,v_S)v_S^2}{(v_R+v_S)^2}\left[1+\frac{4(1-v_S)}{v_S^2}\left[\frac{m+\frac{3}{2}}{m+2}\right]\right]\int_0^\infty dt\langle\gamma_I^{(m)}(0,0,t)\,|\,\Omega_3(0,0,t)\,|^2\rangle$$

$$=\frac{\pi^2 N w^2 b(2m+2)!}{2^{2m+2}(m+3)[(m+1)!]^2(\kappa b+2\Delta_0 v_S)^2}\left[v_S^2+4(1-v_S)\left[\frac{m+\frac{3}{2}}{m+2}\right]\right]\int_0^\infty dt\langle\gamma_I^{(m)}(0,0,t)\,|\,\Omega_3(0,0,t)\,|^2\rangle \;. \quad (49)$$

Typically, for a strong transition, $\kappa(\text{cm}^{-1})\sim 10^{14}P$, where P is the partial pressure in Torr of the atomic species which exhibits the three-photon resonance. If $b\approx 0.2$ cm, a pressure of $P>0.2$ Torr may be required in order for the limit in Eq. (48) to be approached before Δ_0 becomes too small for our treatment of the resonance to be valid. This conclusion is arrived at by noting that $|v_R+v_S|>20$ is required for Eq. (34) to be valid [Eq. (34) uses only the first term in the asymptotic series]. Thus, $b/2$ must be large enough for $|v_R+v_S|>20$ to be achieved while $|\Delta_0|>5\times 10^{11}$/sec. As we described above, N_I is greatly reduced near the resonance because $\vec{E}(\vec{r},t)$ (the laser field) and $\vec{E}_{3\omega}(\vec{r},t)$ (the TH field) are driving the transition with equal Rabi frequencies, but the effects are of opposite sign, i.e., 180° out of phase. A nonperturbation extension of these results is required to generalize such a statement to exact resonance.

In our earlier theoretical studies on this subject, we described the suppression of the resonant enhancement of the ionization process as a cooperative effect[12,14] since (a) individual atoms are coupled together by the radiation field with a long-range r^{-1} functional form, (b) the effect builds coherently with number density N, and (c) this language provided a connection with superfluorescence and other similar phenomena in which strong interatomic interactions influence the physical process of interest. We use the term cancellation effect here simply because the physical picture is better described by this choice. Jackson and Wynne have chosen to call it an interference.[15] We will return to this point in our final comments.

To facilitate tracing of the line-shape function $M^{(m)}(v_R,v_S)$, we note that analytic function theory can be used to derive a number of useful properties of $g(u,v)$. We have demonstrated some of these properties in Appendix B. Equations (46) and (49) tell us that N_I is strongly suppressed on either side of the resonance. On the $\Delta_0<0$ side of the line as one moves away from resonance, N_I always decreases as $|\Delta_0|$ becomes larger. However, on the $\Delta_0>0$ side of the line N_I initially increases as $|\Delta_0|$ becomes larger. The function $M^{(m)}(v_R,v_S)/v_R^2$ is bounded above for any v_R or v_S. Consequently, for large $|\Delta_0|$ the value of $M^{(m)}(v_R,v_S)$ approaches zero for either sign of v_R. The fact that N_I initially increases as v_R decreases from a very large value, while still approaching zero as $v_R\to 0$, implies that $M^{(m)}(v_R,v_S)$ has a *peak* on the blue side of the resonance.

For completeness we note that a similar expression for the number of TH photons that exit the system (at large z) can be obtained if we note that the number of photons per (cm^2 sec) is equal to $c\vec{E}_{3\omega}^{\,2}/(4\pi\hbar\omega_r)$ and we use Eq. (27) for $E_{3\omega}^{+}(r,t)$, where $E_{3\omega}(\vec{r},t)=\frac{1}{2}(E_{3\omega}^{+}+E_{3\omega}^{-})$. This gives zero for $v_R<0$ and for $v_R>0$,

$$N_\gamma \cong \frac{N w^2\pi^3}{6\kappa}|v_R|^2|v_R^2+v_S^2|e^{-2|v_R+v_S|}\times\int_0^\infty |\Omega_3(0,0,t)|^2 dt \;, \quad (50)$$

where N_γ is the total number of TH photons per pulse.

We will apply the results of the present analysis to calculate line shapes for four-photon ionization near a three-photon resonance, and the line shape for the TH photon output. First, we note a feature of the above treatment that was mentioned in the course of the discussion. Namely, the addition of a positively dispersive buffer gas, which is very nonresonant for frequencies ω or 3ω, will simply modify $\chi(\omega)$ and $\chi(3\omega)$. Note particularly that in Eqs. (31a) and (31b) the presence of a buffer gas will modify the Δk_0 term but will leave κ unchanged. Thus, the theory is applicable directly to the situation involving a nonabsorbing buffer gas, with apporpriate modification of the reduced variable v_S.

In Figs. 1–3 we show graphs of the ionization line-shape function $M^{(1)}(v_R,v_S)$ as a function of v_R^{-1} and the (normalized) curve for the corresponding TH signal for three different values of $v_S=(\Delta k_0 b)/2$. Here $v_S=0$ corresponds to no buffer gas, $v_S=-1$ corresponds to a mixture of target gas plus a proper amount of positively dispersive buffer gas to yield the corresponding Δk_0 value, and finally $v_S=-2$ corresponds to even higher number

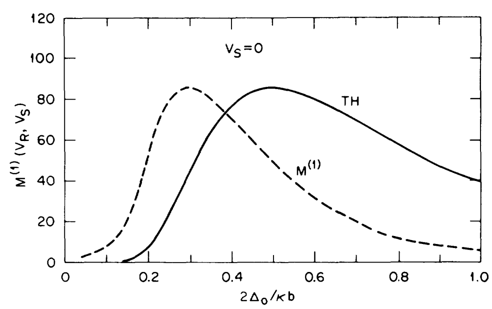

FIG. 1. Ionization line shape $M^{(1)}(v_R,v_S)$ vs $v_R^{-1}=2\Delta_0/\kappa b$ for $v_S=0$. This would correspond to a situation where there was no buffer gas and the pressure of the target species is relatively low. The phase-matching curve for the corresponding third-harmonic signal is shown for reference and is normalized to have the same peak height as $M^{(1)}$ so that an easy comparison can be made. This is also done in Figs. 2 and 3. Ionization near its maximum is totally dominated by absorption of one third-harmonic photon plus added photons to ionize, but $M^{(1)}$ peaks at smaller Δ_0 due to the fact that even though $E_{3\omega}$ is larger at increased Δ_0, the detuning from resonance is also larger and the signal is correspondingly depressed.

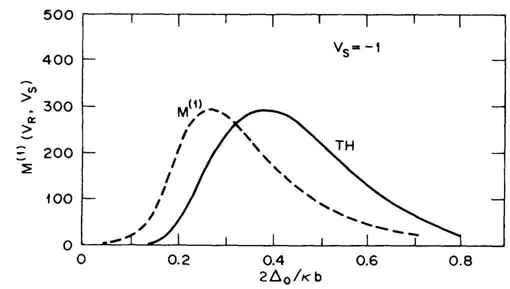

FIG. 2. Ionization line-shape function $M^{(1)}(v_R,v_S)$ vs $v_R^{-1}=2\Delta_0/\kappa b$ for $v_S=-1$. Here $v_S=-1$ corresponds to adding a proper amount of positively dispersive buffer gas which enhances the third-harmonic signal and moves its peak to smaller Δ_0, thus enhancing $M^{(1)}(v_R,v_S)$ by almost a factor of 3 over the $v_S=0$ case.

density of a positively dispersive buffer gas.

In order to understand the shape of $M^{(m)}(v_R,v_S)$, we note that Eqs. (B6) and (B8) determine $g(0,v)$. Since

$$g(u,v)=g(0,v)+\int_0^u \frac{e^{iv(u'-u)}du'}{(1+iu')^2} ,$$

we can write for $|u| \ll 1$, $(1+iu')^{-2}\approx\exp(-2iu')$. Thus, for small $|u|$,

$$g(u,v)=g(0,v)-ie^{-ivu}(e^{i(v-2)u}-1)/(v-2) .$$

When $0<v<3$, $|g(u,v)|$ increases nearly linearly as u increases; while, when $u<0$, $|g(u,v)|$ initially decreases linearly and approaches a small value by $u=-1$. Stationary phase occurs for $v=2$, and the relationship $g(u,2)=g(0,2)+u$ remains fairly accurate at positive v for $|u|<0.5$. When $|u|\geq 1$ and $0\leq v<3$, the value of $|g(u,v)|$ is close to

$$|g(\infty,v)|=2\pi v\exp(-v)$$

and the effect of the TH field is larger than the three-photon term but no longer 180° out of phase, as is the case near the resonance. Consequently, $M^{(m)}(v_R,v_S)$ has a v_R dependence somewhat similar to that of the TH signal.

When a substantial amount of a positively dispersive buffer gas is added so that with a long focal length lens $|v_S|\gg 1$ but $v_S<0$, the shifts and widths become smaller, the reduction in signal is much less due to the smaller shifts and a resulting enhancement in $E_{3\omega}$, and the ionization signal starts to have a line shape that looks even more like the phase-matching curve for the TH signal. In particular, in the latter case, if F, the focal length, is increased sufficiently the ionization signal becomes sharply peaked with a cutoff for $\Delta_0=-\kappa b/2v_S=2\pi|P_{01}|^2\omega_r N/(\hbar c\Delta k_0)$ (independent of F). An example of this type will be discussed in Sec. IV.

In Sec. III we show that within the type of dominant resonance treatment given here there is no residual peak at the unperturbed resonance when $\kappa b/2\gg$ laser bandwidth or a.c. Stark shift. However, the nonlinear susceptibility has a small contribution from further off-resonance levels which has been ignored here, and this contributes an uncancelled contribution to $E_{3\omega}$ which may leave a small residual peak at the resonance. Thus, e.g., as compared to the xenon 6*s* study, a residual peak might be more likely to appear if the effect were studied for the 4*s* level in argon where the fine-structure constant is smaller and the uncancelled part of $E_{3\omega}$ is more significant.

The cancellation of the effects of $E_{3\omega}$ and three-photon excitation on the resonance at first seems strange since no TH light exits from the cell. However, one must remember that at $z=0$, $E_{3\omega}$ for small Δ_0 is large, but at larger z the π phase change associated with focusing the light leads to destructive interference. In fact, in the focal region, $E_{3\omega}$ is also significant for $\Delta_0<0$ (i.e., the red side of the resonance) and could contribute to the ionization of an impurity with a one-photon resonance on the red side of the resonance. On the blue side of the resonance, impurities with a one-photon resonance which can be ionized by a single additional photon from the laser should exhibit a phenomenal enhancement in resonance ionization signal due to two-photon ionization involving one TH photon and a laser photon. Such effects are presently under theoretical and experimental investigation by the present authors and some colleagues.[13–21]

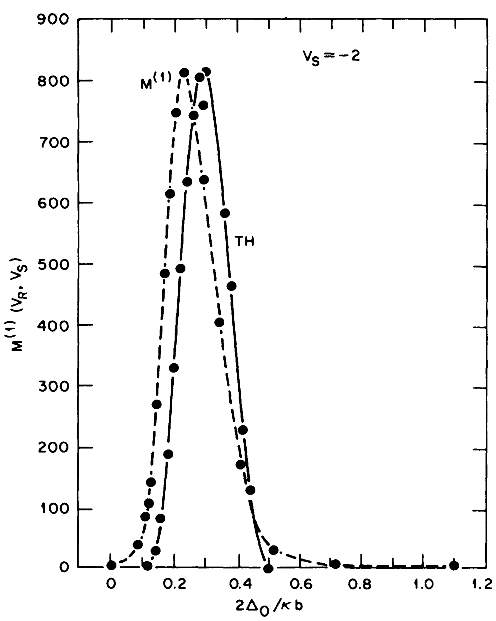

FIG. 3. Ionization line-shape funtion $M^{(1)}(v_R,v_S)$ vs $v_R^{-1}=2\Delta_0/\kappa b$ for $v_S=-2$. Here $M^{(1)}(v_R,v_S)$ is enhanced by almost a factor of 10 over the $v_S=0$ case and the shape of the ionization function is much closer to that for the third-harmonic phase-matching curve. With $v_S<-2$, the third-harmonic signal will be enhanced even more than a factor of 10 and will peak at even smaller values of $2\Delta_0/\kappa b$, thereby yielding even larger enhancements to the ionization signal.

III. HIGHER-ORDER APPROXIMATION TO INCLUDE EXACT RESONANCE

In Sec. II we derived the line shape for the TH field and for the *n*-photon ionization signal, but we carefully avoided application of the perturbation method in the region of zero detuning from three-photon resonance. Indeed, one cannot argue for the appropriateness of a formulation involving the nonlinear susceptibility on resonance, and it is not evident that strong coupling effects can be handled by replacing denominators by terms involving a complex width.[15] Our initial short treatment of the present problem[12] did not involve the perturbation limitation of Sec. II, though the geometry was treated approximately and the analysis was limited to concentrations where $|\Delta k_0 b/2| = |v_S| \ll 1$. Nevertheless, the result for the number of excited atoms at time t [Eq. (9) of Ref. 12] did approach zero as $|\Delta_0| \to 0$. Our subsequent more detailed Bloch equation treatment of the problem for unfocused beams,[14] with proper account of the geometry and pulse characteristics, again gave complete cancellation on resonance. In this section we also follow a Bloch equation approach to analyze the present focused Gaussian beam problem. We generalize the earlier treatment and solve the focused geometry problem in an *ab initio* manner to allow the line-shape determination to pass through the resonance. We include not only the effect of a buffer gas, but we also deal with the linewidth and shift effect in the region near the resonance.

We follow along lines similar to those in Ref. 14 to derive equations of motion for the amplitudes $a_0(r,t)$ and $a_1(r,t)$, though here we make the conventional choice of defining

$$Z(\rho,z,t) = a_0^*(\rho,z,t)a_1(\rho,z,t)$$

and obtaining an equation for $Z(\rho,z,t)$ which contains an integral over the TH source term.

Without belaboring the details of a standard procedure, we note that within the usual rotating-wave approximation and with the inclusion of terms through third order in $\vec{E}_\omega$ but only first order in $\vec{E}_{3\omega}$, we get equations of motion for a_0 and a_1 in a two-state plus ionization continuum model[17] as was done earlier.[14] Substitution of the expanded form of $\psi_{\vec{r}}(t)$ from Eq. (8) into the time-dependent Schrödinger equation gives

$$\begin{aligned}\frac{\partial}{\partial t}a_0(\vec{r},t) &= (i\hbar)^{-1}\langle 1|\hat{V}_{I2}(\vec{r},t)|0\rangle a_1(\vec{r},t)\\ &\quad + (i\hbar)^{-1}\langle 1|\hat{V}_{I1}(\vec{r},t)|0\rangle\\ &\quad + i\Delta_0^s(t-z/c)a_0(\vec{r},t)\\ &\quad + ie^{i\Delta_0 t}\Omega_3(\vec{r},t-z/c)a_1(\vec{r},t)\end{aligned} \tag{51}$$

and

$$\begin{aligned}\frac{\partial}{\partial t}a_1(\vec{r},t) &= (i\hbar)^{-1}\langle 1|\hat{V}_{I2}(\vec{r},t)|0\rangle a_0(\vec{r},t)\\ &\quad + (i\hbar)^{-1}\langle 1|\hat{V}_{I1}(\vec{r},t)|0\rangle\\ &\quad + [i\Delta_1^s(t-z/c) - (\gamma_I^{(m)}+\gamma_{10})/2]a_1(\vec{r},t)\\ &\quad + i\Omega_3(\vec{r},t-z/c)a_0(\vec{r},t)\ ,\end{aligned} \tag{52}$$

where the a.c. Stark shift Δ_n^s which we will take to be independent of ρ and z, is defined as

$$\Delta_m^s(t-z/c) = (i\hbar)^{-2}\int_{-\infty}^{t}\langle n|\hat{V}_{I1}(\vec{r},t)\hat{V}_{I1}(r,t')|n\rangle dt'\ . \tag{53}$$

The spontaneous emission rate out of state $|1\rangle$ is γ_{10}.

In these equations $\hat{V}_{I2}$ is the perturbation due to the TH field which again must be derived from the spatially distributed polarization $\mathscr{P}(r,t)$. However, since we want to consider the resonant situation, it is not feasible to write the polarization in the same manner as in Eqs. (15) through (18), since the $j=1$ term for $\chi(3\omega)$ of Eq. (18) diverges as $\Delta_0 \to 0$. In Sec. II, $a_1(\rho,z,t)$ was broken into one part due to three-photon excitation by the laser field and a second part due to one-photon excitation by $\vec{E}_{3\omega}$. The part due to $\vec{E}_{3\omega}$ was incorporated into $\chi(3\omega)\vec{E}_{3\omega}(\vec{r},t)$ and contributed to the phase velocity v in Maxwell's equations. But in the present situation we cannot write $a_1(\rho,z,t)$ as a term proportional to $\vec{E}_{3\omega}$ plus a second simple term. Instead we leave all of the contribution to the polarizability involving $a_1(\rho,z,t)$ as a source term by separating off the $j=1$ term in the expression for $\chi(3\omega)$. That is, we omit the term

$$2N|M_{0,1}|^2(\omega_1-\omega_0)/\{\hbar[(\omega_1-\omega_0)^2-(3\omega)^2]\}$$

from Eq. (18) and define $\chi_1(3\omega)$ as the sum of the remaining nonresonant terms. Thus we now write the 3ω frequency component of the polarizability in a manner analogous to Eq. (20a), but here we subdivide the contributions into a form

$$\begin{aligned}\vec{\mathscr{P}}_{3\omega}(\vec{r},t) &= \vec{e}_y\chi_1(3\omega)E_{3\omega}(\vec{r},t)\\ &\quad + \left[e^{-i(\omega_1-\omega_0)t}M_{0,1}Z(\rho,z,t) + \text{c.c.}\right]\\ &= \vec{e}_y\chi_1(3\omega)E_{3\omega}(\vec{r},t) + \vec{\mathscr{P}}_{3\omega}^{(1)}(\vec{r},t)\ ,\end{aligned} \tag{54}$$

where

$$Z(\rho,z,t) = a_0^*(\rho,z,t)a_1(\rho,z,t)\ . \tag{55}$$

Thus, we treat the contributions to $\vec{\mathscr{P}}(r,t)$ from all states except $|0\rangle$ and $|1\rangle$ just as they were done in Sec. II. Here $\chi_1(3\omega)$ can also have added to it a nonresonant contribution from a buffer gas.

We let $v_1^2 = c^2[1+4\pi\chi_1(3\omega)]^{-1}$ and again solve Maxwell's equations as was done in Sec. II. Source terms now become $\rho = -\vec{\nabla}\cdot\vec{\mathscr{P}}_{3\omega}^{(1)}$ and $\vec{J} = \partial\vec{\mathscr{P}}_{3\omega}^{(1)}/\partial t$. This results in an equation for $\vec{E}_{3\omega}$ similar to Eq. (21). In the paraxial approximation we have, as before,

$$\vec{E}_{3\omega}(\vec{r},t) = \frac{\omega_r^2}{c^2}\int\frac{d^3\vec{r}\,'}{|\vec{r}-\vec{r}\,'|}\mathscr{P}_{3\omega}^{(1)}\left[\vec{r}\,',t-\frac{|\vec{r}-\vec{r}\,'|}{v_1}\right]\ . \tag{56}$$

Thus, if we again define

$$E_{3\omega}(\vec{r},t) = \tfrac{1}{2}[E_{3\omega}^{+}(\vec{r},t) + E_{3\omega}^{-}(\vec{r},t)]\ ,$$

then in the present case

$$E^{+}_{3\omega}(\vec{r},t)=\frac{\vec{e}_y N\omega_r^2 M_{0,1}}{c^2}\times\int\frac{d^3\vec{r}\,'}{|\vec{r}-\vec{r}\,'|}Z\left[\rho',z',t-\frac{|\vec{r}-\vec{r}\,'|}{v}\right]\times\exp\left[i(\omega_1-\omega_0)\left[\frac{|\vec{r}-\vec{r}\,'|}{v_{1_1}}-t\right]\right] \quad (57)$$

with $E^{-}_{3\omega}$ the complex conjugate of (57).

If we neglect the ρ and z dependence of the a.c. Stark shifts Δ_n^s, the solution to equation of motion for $Z(\rho,z,t)$, which follows from Eqs. (51) and (52), can be written as a product of a ρ- and a z-dependent function. That is, we can write

$$Z(\rho,z,t)=\frac{1}{(1+2iz/b)}\times\exp\left[i(3kz-\Delta_0 t)-\frac{3\rho^2}{w^2(1+2iz/b)}\right]\times Y(z,t) \quad (58)$$

in which case Eq. (57) for $E_{3\omega}$ can be reduced to

$$E^{+}_{3\omega}(\vec{r},t)=\frac{\vec{e}_y 2\pi i\omega_r N M_{0,1}}{c(1+2iz/b)}\times\exp\left[-3\omega\left[t-\frac{z}{v_1}\right]-\frac{3\rho^2}{w^2(1+2iz/b)}\right]\times\int_{-\infty}^{\infty}Y\left[z',t-\frac{z-z'}{v_1}\right]\times\exp[3iz'(k-\omega/v_1)]dz' . \quad (59)$$

From Eqs. (51) and (52) one readily obtains an equation for $Z(\rho,z,t)$ containing a matrix element for $\hat{V}_{I2}$ (i.e., the TH field). We utilize the result of Eq. (57) in this matrix element and convert the product

$$(i\hbar)^{-1}\langle 1|\hat{V}_{I2}(\vec{r},t)|0\rangle Z(\vec{r},t)$$

into an integral expression as was done in Ref. 14. The resultant equation for $Z(\rho,z,t)$ can be made independent of ρ, by the substitution of Eq. (58), to yield

$$\frac{\partial Y(z,t)}{\partial t}=i\{\Delta_0+\Delta_S(0,0,t-z/c)+i[\gamma_0+\gamma_I^{(m)}(0,0,t-z/c)]/2\}Y(z,t)-\kappa\int_{-\infty}^{z}dz'\exp[-3i(z-z')(k-\omega/v_1)]Y\left[z',t-\frac{z-z'}{v_1}\right]+\frac{i\Omega_3^*(0,0,t-z/c)e^{-3i\phi(t-z/c)}}{(1+2iz/b)^2} . \quad (60)$$

Equation (60) is linearized in Ω_3^* [i.e., we assume $|Z(\rho,z,t)|\ll 1$ and $|a_0(\rho,z,t)|\approx 1$], the identity of Eq. (26) was used for $\Omega_3(r,t-z/c)$, and we have approximated Δ^s and $\gamma_I^{(m)}$ by their values at beam center. Also, we have defined $\Delta_s=\Delta_1^s-\Delta_0^s$. For three-photon transitions in inert gases, power densities $\geq 10^{11}$ W/cm^2 are required to cause a breakdown of the linearization approximation. The type of approximation involved in Eq. (60), which allows for either three-photon excitation by the laser field or one-photon excitation by the TH field (i.e., the integral term) is described in more detail in Ref. 14. The number of ions generated in an $(m+3)$ photon ionization process is

$$N_I^{(m)}=2\pi N\int_{-\infty}^{\infty}dz\int_0^{\infty}d\rho\rho\int_0^{\infty}dt\langle\gamma_I^{(m)}(0,0,t)|Z(\rho,z,t)|^2\rangle . \quad (61)$$

The neglect of the ρ and z dependence in the a.c. Stark shift will not significantly modify the diffraction effects in the propagation of $\vec{E}_{3\omega}$ if

$$\Delta_s(0,0,t-z/c)b/2c\ll 1 .$$

When the latter condition is strongly violated, Eq. (60) is no longer a reasonable approximation and Y depends on both ρ and z. It is important to note that for a given laser output Δ_s varies as F^{-2}, while $b\propto F^2$. Therefore, changing to a longer focal length lens will not restore the validity of Eq. (60) if the laser output is too high for the original lens. Three-photon transitions between the ground state and the lowest s states of inert gases have $\Delta_s(0,0,t)\sim(\alpha_s)I_0$, where Δ_s is in sec^{-1}, I_0 is the power density at the focal point in W/cm^2, and $\alpha_s\sim 1$ to 10. Thus, for $I_0\lesssim 5\times 10^{10}$ W/cm^2 we have $\Delta_s b/2c<(0.8$ to $8)b$. Except for very long focal length lenses, the neglect of ρ and z dependence does not affect propagation. For five-photon ionization near three-photon resonances in rare gases, the ionization comes from the regions of very highest power where Δ_s is indeed nearly equal to $\Delta_s(0,0,t-z/c)$. Consequently, we believe that the approximations involved in deriving Eq. (55) are sufficiently good to warrant a careful study of its solution.

Before proceeding to obtain properties of the solution to Eq. (60) we note briefly that this equation is very similar in form to that found in our first treatment of this problem, i.e., Eq. (3) of Ref. 12. In the latter equation, $\Gamma_c/b=0$ K, $\Delta_T=\Delta_s$, and $3\omega_L-\omega_r=\Delta_0$ in the present notation, and the transformation (58) above causes the present definition of the dependent variable Y to differ by $(1+2iz/b)^{-1}$ from the earlier form.[18] Thus, the equations are the same but for the TH source term inside the integral of each integro-differential equation. These differ due to the more approximate treatment of the beam geometry in the earlier study. Note, however, that in the region of largest contribution to the integral, where $z'\cong z$, the integrals in these two equations also become the same. Since the physical content in the earlier treatment is the same as in the present study, we expect this result. The physical picture for the resulting diminution of the upper state probability is clearer here where the cancellation effect was illustrated in Sec. II. We now consider solutions of Eq. (60) above in a form which still exhibits the origin of the cancellation, as was shown in Sec. II.

In order to solve Eq. (60) we let

$$\bar{\Delta}=\Delta_0+i\gamma_0/2 \tag{62}$$

and

$$\Delta_1(t-z/c)=\Delta_s(0,0,t-z/c)+i\gamma_I^{(m)}(0,0,t-z/c)/2 . \tag{63}$$

We define the function $R(z,t)$ by

$$Y(z,t)=e^{ig_0(t-z/c)}R(z,t) , \tag{64}$$

where

$$g_0(t-z/c)=\int_0^t \Delta_1(t'-z/c)dt'=\int_0^{t-z/c}\Delta_1(\tau)d\tau ,$$

and in the last step we use $\Delta_1(\tau)=0$ before the laser is triggered (i.e., $\tau<0$). We note that $g_0(t-z/c)$ has the property that if we replace z by z' and t by $t-(z-z')/v_1$ [we also use $z'(1/c-1/v_1)\approx 0$], we get $g_0(t-z/c)$ again. We obtain

$$\frac{\partial R(z,t)}{\partial t}=i\bar{\Delta}R(z,t)-\kappa\int_{-\infty}^{z}\exp[-3i(z-z')(k-\omega/v_1)]R\left[z',t-\frac{z-z'}{v_1}\right]dz' + i\frac{\Omega_3^*(0,0,t-z/c)}{(1+2iz/b)^2}e^{-3i\phi(t-z/c)}e^{-ig_0(t-z/c)} . \tag{65}$$

We Fourier transform both sides of Eq. (65), letting

$$W(\epsilon)=\int_0^\infty e^{i\epsilon(t-z/c)}\Omega_3(0,0,t-z/c)e^{-3i\phi(t-z/c)}e^{-ig_0(t-z/c)}dt \tag{66}$$

and

$$Q(z,\epsilon)=\int_0^\infty e^{i\epsilon t}R(z,t)dt . \tag{67}$$

Following the transform we differentiate both sides of the transformed equation with respect to z and obtain

$$\frac{\partial Q(z,\epsilon)}{\partial z}+\left[\frac{i\kappa}{\epsilon+\bar{\Delta}}+3i(k-\omega/v_1)\right]Q(z,\epsilon)=-i\frac{W(\epsilon)}{\epsilon+\bar{\Delta}}e^{i\epsilon z/c}\left[\frac{3(k-\omega/v_1)}{(1+2iz/b)^2}-\frac{4}{b(1+2iz/b)^3}\right] . \tag{68}$$

After integrating Eq. (68) and rearranging, we find Q. By carrying out the inverse transform,

$$R(z,t)=-\frac{1}{2\pi}\int_{-\infty}^{\infty}d\epsilon\frac{W(\epsilon)}{e+\bar{\Delta}}e^{-i\epsilon(t-z/c)}\left[\frac{1}{(1+2iz/b)^2}-i\left[\frac{\kappa b/2}{\epsilon+\bar{\Delta}}-\frac{\epsilon b}{2}\right]g\left[\frac{2z}{b},\frac{\kappa b/2}{\bar{\Delta}+\epsilon}+v_S-\frac{\epsilon b}{2c}\right]\right] , \tag{69}$$

where $g(u,v)$ is the same function defined by Eq. (28). Thus,

$$Y(z,t)=-\frac{e^{ig_0(t-z/c)}}{2\pi}\int_{-\infty}^{\infty}d\epsilon\frac{W(\epsilon)}{\epsilon+\bar{\Delta}}e^{-i\epsilon(t-z/c)}\left[\frac{1}{(1+2iz/b)^2}-i\left[\frac{\kappa b/2}{\epsilon+\bar{\Delta}}-\frac{\epsilon b}{2c}\right]g\left[\frac{2z}{b},\frac{\kappa b/2}{\epsilon+\bar{\Delta}}+v_S-\frac{\epsilon b}{2c}\right]\right] . \tag{70}$$

The reader should note the similarity between the function $I(2z/b,\kappa b/2)$ defined by Eq. (33a) and the quantity in square brackets above. Indeed, we have a solution to the integral equation which again exhibits the cancellation property in an explicit form.

We now consider two limiting cases of Eq. (64). First, note that $w(\epsilon)$ has its peak location determined by the magnitude of the a.c. Stark shift and that the width of this peak is dictated by the largest of the a.c. Stark shift, the laser bandwidth, and the ionization width. Our first limit is $|\bar{\Delta}|\gg|\epsilon_{\max}|$, where $\epsilon_{\max}$ is the largest ϵ for which $w(\epsilon)$ is appreciable. In this situation, everywhere that $\epsilon+\bar{\Delta}$ appears, the ϵ can be neglected. Also, if $|\epsilon_{\max}|b/2c<1$ we obtain

$$Y(z,t)=-\frac{\Omega_3^*(0,0,t-z/c)}{\bar{\Delta}}e^{-3i\phi(t-z/c)} \times\left[\frac{1}{(1+2iz/b)^2}-\frac{i\kappa b/2}{\bar{\Delta}}g\left[\frac{2z}{b},\frac{\kappa b/2}{\bar{\Delta}}+v_S\right]\right] . \tag{71}$$

Combining Eqs. (59), (70), and (61), we obtain Eq. (45) as we should since this is the adiabatic limit where our earlier analysis is valid.

Our second limit is to show that once $\kappa b/2\gg|\epsilon_{\max}|$, as $\Delta_0\to 0$ Eq. (A9) remains valid. Clearly, when

$|\Delta_0| \lesssim |\epsilon_{\max}|$ and $\kappa b/2 \gg |\epsilon_{\max}|$ the integral over ϵ all comes from regions where

$$\left|\frac{\kappa b/2}{\epsilon+\bar{\Delta}}\right| \gg 1 \; .$$

If $|v_S|$ is not extremely large, we will also have

$$\left|\frac{\kappa b/2}{(\epsilon+\bar{\Delta})}+v_S-\frac{\epsilon b}{2c}\right| \gg 1 \; ,$$

and an asymptotic formula like Eq. (34) can be used for g. Consequentially, as $\Delta_0 \to 0$ we obtain from the asymptotic formula and Eq. (42)

$$N_I^{(m)}=\frac{\pi N w^2}{(m+3)b\kappa^2}\int_0^\infty dt \langle \gamma_I^{(m)}(0,0,t)\,|\,\Omega_3(0,0,t)\,|^2\rangle \times \frac{\pi}{2^{2m+2}}\frac{(2m+2)!}{[(m+1)!]^2} \times \left[v_S^2+2(1-v_S)\left[\frac{m+\frac{3}{2}}{m+2}\right]\right] \tag{72}$$

which is the $v_R \to \infty$ limit from Eqs. (32) and (A9). Note that in this limit there is no peak at the position of the three-photon resonance.

There are two approximations which we have made that may result in a residual peak at the resonant frequency even in this limit of $\kappa b/2 \gg |\epsilon_{\max}|$. The first has to do with neglecting all of the nonlinear susceptibility except for the resonant terms. The part of $\vec{E}_{3\omega}$ due to the neglected part of the susceptibility is not cancelled, and there is a residual, nonzero (but small), TH field in the focal region which can drive the transition. This residual resonance will typically be several orders of magnitude smaller than the signals seen by Glownia and Sander[19] when the three-photon transition is pumped by counterpropagating circularly polarized beams with excitation only being possible (due to angular momentum selection rules) by absorption of photons from each of the counterpropagating beams. In the latter situation there is no TH field, even in the focal region, to cancel out the three-photon pumping of the resonance. It may also occur that at very high-power densities where $\Delta_s(0,0,t)b/c \gg 1$, the effect of the position-dependent phase of the atomic dipoles due to the a.c. Stark shift will distort the propagation of $\vec{E}_{3\omega}$ so that the one-photon Rabi frequency due to $\vec{E}_{3\omega}$ and the three-photon Rabi frequency due to the laser do not tend to cancel on a point-by-point basis. Thus, at power densities as high as $I_0 \gtrsim 10^{11}$ W/cm^2 for $F=5$ cm and $d=0.1$ cm, the resonance may be increased relative to the ionization predicted in the phase-matched frequency region. This power-dependent resurrection of the resonance, if present at all, would persist for longer focal length lenses as well since $\Delta_s(b/c) \gg 1$ will also be true for other focal lengths. However, such effects are expected to be very small as compared to that which occurs when a counterpropagating beam is present. We discuss this briefly below.

IV. UNCANCELLED THREE-PHOTON CONTRIBUTION TO RESONANCE EXCITATION IN THE PRESENCE OF A COUNTERPROPAGATING BEAM

In an elegant experimental test of the effect of the presence or absence of a TH field on resonantly enhanced five-photon ionization of xenon near three-photon resonance between the ground-state and 6s levels, Glownia and Sander[19] recently carried out an experiment in which counterpropagating circularly polarized laser beams were used to show that the three-photon resonance between the ground state and 6s levels of xenon was readily apparent in the absence of TH generation. The TH signal was missing in the latter situation due to the necessity of absorbing from both beams in order to satisfy $\Delta J=1$, in the $J=0$ to $J=1$ transition, and this precludes phase matching. Their result was completely consistent with the present theoretical picture.[12,14] However, even more recently, Jackson and Wynne[15] have found experimentally that with counterpropagating plane-polarized beams the same resonance is greatly enhanced relative to a single beam with twice the laser power. This observation is also precisely what is to be expected within the present model. We give a brief description of this effect here. In a separate study[20] we obtain analytic results for the complete line shape and signal strength for the counterpropagating *unfocused* beam geometry of arbitary relative beam intensities, with detailed comparison with unfocused beam experimental results.[21–23]

To see the effect on the resonance counterpropagating beam of the same frequency ω as that of the original beam (the original plane-polarized beam paritally or totally reflected back on itself), note that in the latter situation the perturbation in Eq. (4) becomes

$$\hat{V}(\vec{r},t)=-\hat{\mathscr{D}}_y[E_+(\vec{r},t)+E_-(\vec{r},t)+E_{3\omega(+)}(\vec{r},t) +E_{3\omega(-)}(\vec{r},t)] \; , \tag{73}$$

where E_+ is the laser field propagating in the positive z direction and E_- is the laser field propagating in the negative z direction. $E_{3\omega(+)}$ is the TH field propagating in the positive z direction and $E_{3\omega(-)}$ propagates in the negative z direction. Let

$$\hat{V}_1(\vec{r},t)=-\hat{\mathscr{D}}_y[E_+(\vec{r},t)+E_-(\vec{r},t)] \; . \tag{74}$$

Now the three-photon Rabi frequency is given by[14,16] the low-frequency part of the three-photon terms involving $\hat{V}_{I1}$, i.e.,

$$ie^{i\Delta_0 t}\Omega_3(\rho,z,t-z/c)=(i\hbar)^{-3}\int_0^t dt'\int_0^{t'}dt''\langle 0\,|\,\hat{V}_{I1}(\vec{r},t)\hat{V}_{I1}(\vec{r},t')\hat{V}_{I1}(\vec{r},t'')\,|\,1\rangle \; . \tag{75}$$

But here,

$$\hat{V}_{I1}(\vec{r},t)=e^{i\hat{H}_0 t/\hbar}\hat{V}_1(r,t)e^{-i\hat{H}_0 t/\hbar}$$

is made up of the sum of two terms, one due to E_+, the beam propagating in the positive z direction, and the other due to E_- which propagates in the negative z direction. Thus, there are *eight* terms in the product

$$V_{I1}(\vec{r},t)V_{I1}(\vec{r},t')V_{I1}(\vec{r},t'')$$

that appears in the expression for Ω_3. The $\exp[i\omega(t+t'+t'')]$ part of the term involving

$$E_+(\vec{r},t)E_+(\vec{r},t')E_+(\vec{r},t'')$$

is all that contributes to $E_{3\omega(+)}$, and at the resonance the corresponding part of Ω_3 and the one-photon Rabi frequency due to $E_{3\omega(+)}$ cancel each other. Correspondingly, the part of Ω_3 involving

$$E_-(\vec{r},t)E_-(\vec{r},t')E_-(\vec{r},t'')$$

is solely responsible for $E_{3\omega(-)}$, and the part of the one-photon Rabi frequency due to $E_{3\omega(-)}$ again cancels with the related part of Ω_3 (these becoming equal but 180° out of phase near the resonance). However, with counterpropagating beams there are six terms in Ω_3 which involve the absorption of photons with both directions of propagation which remain uncancelled, and a large portion of the three-photon pumping of the resonance remains. That is, these terms [e.g., $E_+(\vec{r},t)E_+(\vec{r},t')E_-(\vec{r},t'')$] provide an excitation route from $|0\rangle$ to $|1\rangle$ that is not offset by a corresponding one-photon driving term involving the TH field, leading to reappearance of the three-photon resonance in counterpropagating beam geometries. The reader should note that some of the same type of effect is present if the effect is studied with a single laser beam having a beam divergence much larger than the diffraction limit. Thus, a laser with poor wave-front coherence, so that it has a low conversion efficiency relative to the power densities generated near the focus, could leave a signal at resonance which is disproportionately large compared with the ionization signal predicted on the blue side of resonance. We defer more quantitative treatment of the uncancelled three-photon pumping component in a counterpropagating geometry to later papers.[20–22]

V. COMMENTS AND CONCLUSIONS

The strong influence that TH fields can have on near-resonant three-photon excitation of an optically allowed state and on MPI in regions of phase matching near such resonances is quite dramatic with surprising features in a number of the aspects of the phenomenon. It is useful to summarize the results of the present and earlier theoretical studies of this problem taken in the context of available experimental results.

First we note a very important point about the cancellation phenomenon. The effect involves a very exact cancellation between two resonant or near-resonant pumping terms, each of which can be rather large. Thus, small inaccuracies in a description of the phenomenon might be significant. In order to be able to make meaningful comparisons with experiments, we have treated the problem very generally. That is, we find that with a very nonidealized pulsed laser having finite bandwidth, arbitrary time dependence, and Gaussian spacial beam intensity, and with a properly described spacial intensity profile through the focal volume, the cancellation behavior *still persists*—even at appreciable number density and/or in the presence of a large buffer gas concentration. Thus, we have shown that this is not one of those effects which, though strongly present for an idealized laser, washes out in a realistic experimental situation. This is in agreement with experiments wherein no ionization signal is observed at three-photon resonances in xenon, krypton, and argon studies, focused and unfocused, with and without buffer gases, and with dye lasers of vastly different performance (being pumped in various instances by nitrogen, XeCl, and YAG pumps).[11,15,20–22]

Since we have formulated a rather general treatment of the present problem, the analysis was unavoidably lengthy. However, the treatment has revealed considerable detail about the near-resonant MPI problem. The perturbation treatment in Sec. II retained a clear physical picture of the problem and clearly revealed the source and analytic behavior of the cancellation effect as the resonance is approached, giving the ionization line shape and the TH line shape with and without a positively dispersive buffer gas. A more exact treatment of the problem at and near zero detuning revealed the behavior in the strongly dispersive on-resonance region. We also showed that the resulting integral equation was similar to those obtained in our earlier treatments of the focused and unfocused problem and, moreover, that a solution to the integral equation could be cast in a form which again clearly illustrated the cancellation between two contributing terms. This feature was apparent in our first treatment of the problem[12] only in the bottom line—that is, the diminution of the number of excited states. It was explicit in our subsequent detailed treatment of the unfocused beam geometry,[14] but not as transparent analytically. Also, we have earlier referred to the phenomenon as a cooperative effect wherein the atoms respond to the laser field and with each other through the long-range interaction mediated by the TH field, involving competition between excitation by three-photon and excitation and deexcitation by one-photon processes. (In this language the generation of TH light is a cooperative effect.) Thus, we did not assume that the TH field, on resonance, would be the same as that which would be generated in the absence of the strong coupling between the three-photon and one-photon processes. As we have seen here and in Ref. 14, the TH field itself is indeed the same as it would be without the effect and, on resonance, it drives the equation for a_1 in the direction exactly opposite to that due to three-photon excitation, *point by point everywhere within the focal region.*

We can also make some useful and fairly quantitative comments about the line shape for ionization. Note that the number of TH photons exiting the cell in the absence of absorption (other than by the resonance) is given by Eq. (50) when $v_R+v_S>0$. If $v_R+v_S<0$, then $N_I=0$. The line shape for N_I is rather similar to that of N_γ. This reflects the fact that in the region of phase matching the dominant ionization mechanism is the absorption of a TH photon followed by absorption of further laser photons to ionize. For $|v_S|<1$, N_I peaks at slightly smaller Δ_0 than N_γ, but when v_S is negative due to a positively dispersive buffer gas and $|v_S|\gg 1$, the appearance of the line shapes N_γ and N_I become very similar, and the addition of the buffer gas increases both. This behavior is demonstrated in the figures. In any case, a study of the line shape of N_γ gives a good estimate of the expected line shape of N_I. Since Eq. (52) is very simple, this observation is quite useful. From Eq. (50) we can estimate that N_I will be small for $|v_S|\gg 1$ and $v_S<0$ unless

$$\Delta_0<\kappa b/(z\,|v_S|)\ .$$

Further, N_I should peak near

$$\Delta_0=\frac{\kappa b/2}{1-v_S/2+(1+v_S^2/4)^{1/2}}\cong\frac{\kappa b/2}{1+|v_S|}\ . \tag{76}$$

In this limit of large negative v_S we see that $\kappa b/2|v_S|$ is *independent of focal length.* Thus, with a buffer gas, increasing the focal length of the lens does not change the position of the maximum in N_I or N_γ appreciably. This effect has been demonstrated experimentally both qualitatively and quantitatively.[13]

In the absence of a buffer gas and at relatively low concentrations ($n\lesssim 10^{16}/\text{cm}^3$), the shape of N_I is given more appropriately by Fig. 1. Thus, N_I peaks when

$$\Delta_0\simeq 0.5\kappa b/2\cong 0.05\left[\frac{2\pi|M_{0,1}|^2\omega_r N}{\hbar c}\right]\left[\frac{n(\omega)\omega}{c}\right]\left[\frac{\lambda^2F^2}{2\pi^2d^2}\right]$$

providing $\kappa b/2\gg|\epsilon_{\max}|$. Thus, with pure xenon gas at room temperature, $\kappa(\text{cm}^{-1}\text{sec}^{-1})\simeq 2.4\times 10^{14}P_{\text{Xe}}$, where P_{Xe} is the pressure in Torr. If $d=0.1$ cm and $\gamma_{\text{Xe}}\cong 4400$ Å, then for a diffraction-limited Gaussian beam, $b\simeq 3\times 10^{-3}F^2$. Thus, $\kappa b/2\simeq 3.6\times 10^{11}P_{\text{Xe}}F^2$, or in terms of the detuning of the laser from resonance in angstroms,

$$(\Delta\lambda)_{\max}\cong -0.06P_{\text{Xe}}F^2\ .$$

For instance, at $P_{\text{Xe}}=0.5$ Torr and $F=10$ cm the peak should occur about 3 Å on the blue side of the resonance. When $\kappa b/2\gg|\epsilon_{\max}|$ and $|v_S|\ll 1$, the peak height should decrease as P_{Xe}^{-1} as concentration is increased. The drop in signal and the near vanishing of the on-resonance signal should begin when $\kappa b/2\approx|\epsilon_{\max}|$. In the very low concentration the resonance has a width ~ 0.3 Å (i.e., $|\epsilon_{\max}|\simeq 1\times 10^{12}/\text{sec}$), and we see that strong effects should occur in xenon when

$$P_{\text{Xe}}F^2>1.5\ .$$

Thus, for $F=10$ cm the resonance signal should stop increasing proportional to P_{Xe} at pressures $P_{\text{Xe}}>1.5\times 10^{-2}$ Torr. With $F=20$ cm, the effects begin at 3×10^{-3} Torr. In experiments on noble gases the pressure region where the effect *first* begins to dominate is difficult to observe because the number density is low and the ionization signal is not easy to measure.

In the present treatment of the MPI problem we have tried to be rather general in our formulation. However, we have still neglected an important contribution to the observed ionization when either N is large or when there is a large concentration of a buffer gas. In this high concentration limit there is often dimer absorption on the blue wing of a resonance which can play a key role in determining the observed ionization signal. As a rather obvious example consider a mixture of xenon and krypton with $P_{\text{Xe}}=2$ Torr and $P_{\text{Kr}}=15$ Torr. With the laser tuned to 3880.4 Å the TH light will be attenuated about 50% in 10 cm by dimer absorption.[18] This absorption is from a bound dimer state to a repulsive excited state of xenon-krypton which dissociated to yield a xenon atom in the $6s^1$ state. Similar effects occur in mixtures of xenon with argon, krypton, and neon near both the $6s$ and $6s^1$ resonances. If the absorption coefficient of the gas mixture is 2β and the distance from the focal point to the cell window is L, atoms in the resonance state are produced at the rate

$$R_c(t)=(1-e^{-2\beta L})\frac{\pi^3Nw^2}{6\kappa}|v_R|^2|v_R+v_S|^2$$

$$\times e^{-2(v_R+v_S)}|\Omega_3(0,0,t)|^2\ . \tag{77}$$

In particular, with long focal length lenses used near the $6s^1$ state of xenon the power density remains high enough to yield nearly 100% ionization of the resulting resonance state population for several centimeters past the focal point. This absorption-related contribution to the ionization signal has a line shape determined by phase matching and the wavelength dependence of β. This aspect of MPI near a three-photon resonance will be quantitatively explored in a separate study.[20]

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APPENDIX A

We want to evaluate the integral of Eq. (25) in cylindrical coordinates z,ρ,ϕ where the laser field intensity is independent of azimuthal angle ϕ and where the three-photon Rabi frequency $\Omega_3(\vec{r},t)$ is given by Eq. (26). It is useful to employ the identity

$$\frac{e^{3i\omega v^{-1}|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}=\frac{3\omega}{v}\sum_{n=-\infty}^{\infty}e^{in(\varphi-\varphi')}\left[\int_1^\infty J_n(3\omega v^{-1}\rho s)J_n(3\omega v^{-1}\rho' s)\exp[-(s^2-1)^{1/2}3\omega v^{-1}|z-z'|]\frac{s\,ds}{(s^2-1)^{1/2}}\right]$$
$$+\left[i\int_0^1 J_n(3\omega v^{-1}\rho s)J_n(3\omega v^{-1}\rho' s)\exp[i(1-s^2)^{1/2}3\omega v^{-1}|z-z'|]\frac{s\,ds}{(1-s^2)^{1/2}}\right]. \quad \text{(A1)}$$

With this identity and Eq. (26) we get Eq. (25) in the following form:

$$E^+_{3\omega}(\vec{r},t)\cong\frac{2\pi N M_{0,1}\omega_r^3}{c^2 v\Delta_0}\exp\{-3i[\omega t+\phi(t-|z|/c)]\}\Omega_3(0,0,t-|z|/c)$$
$$\times\int_{-\infty}^{\infty}\frac{e^{3ikz'}dz'}{(1+2iz'/b)^3}\int_0^\infty \rho' d\rho' \exp\left[\frac{-3k\rho'^2}{b(1+2iz/b)}\right]$$
$$\times\left[\int_1^\infty J_0(3\omega v^{-1}\rho s)J_0(3\omega v^{-1}\rho')\exp[-(s^2-1)^{1/2}3\omega v^{-1}|z-z'|]\frac{s\,ds}{(s^2-1)^{1/2}}\right.$$
$$+i\int_0^1 J_0(3\omega v^{-1}\rho s)J_0(3\omega v^{-1}\rho' s)$$
$$\left.\times\exp[i(1-s^2)^{1/2}3\omega v^{-1}|z-z'|)]\frac{s\,ds}{(1-s^2)^{1/2}}\right]. \quad \text{(A2)}$$

We must evaluate

$$\int_0^\infty \exp\{-3\rho'^2/[w^2(1+2iz'/b)]\}J_0(3\omega v^{-1}\rho' s)\rho' d\rho'=\frac{w^2}{6}(1+2iz'/b)\exp\left[\frac{-3w^2s^2\omega^2}{4v^2}\left[1+2i\frac{z'}{b}\right]\right], \quad \text{(A3)}$$

where $w=\lambda F/\pi d$ which equals the beam waist at the focus, and $b=kw^2$ which equals the confocal parameter. Since $w\omega/v$ is very large, the integration over s comes from very small s. The integral over s from 1 to ∞ is extremely small, and the integral from zero to unity can be replaced by an integral from 0 to ∞ with the integral converging at such small s values that $(1-s^2)^{1/2}\simeq 1-s^2/2$. The s integration is of the same form as that in Eq. (A3), and we find

$$E^+_{3\omega}(\vec{r},t)\cong\frac{2\pi N M_{0,1}\omega_r v}{c^2\Delta_0}\Omega_3(0,0,t-|z|/c)$$
$$\times\exp\{-3i[t+\phi(t-|z|/c)]\}i\int_{-\infty}^{\infty}\frac{e^{3ikz'}e^{3i\omega|z-z'|/v}}{(1+2iz'/b)^2}\exp\left[\frac{-3\omega\rho^2}{vb(1+2iz'/b+2i|z-z'|/b)}\right]dz'. \quad \text{(A4)}$$

The contribution to the z' integral from $z'>z$ is small for all ω/v. Letting $\Delta k=3(k-\omega/v)$, $x'=2z'/b$, and defining

$$g(x,y)=\int_{-\infty}^{x}\frac{e^{iy(x'-x)}}{(1+ix')^2}dx' \quad \text{(A5)}$$

we can write

$$E^+_{3\omega}(\vec{r},t)=\frac{i\pi N b\omega_r M_{0,1}v}{c^2\Delta_0}\frac{\Omega_3(0,0,t-|z|/c)}{1+2iz/b}\exp\{-3i[\omega t-kz+\phi(t-|z|/c)]\}$$
$$\times\exp\{-3\omega\rho^2[vb(1+2iz/b)]\}g\left[\frac{2z}{b},\frac{\Delta kb}{2}\right]. \quad \text{(A6)}$$

From our earlier definition

$$E^+_{3\omega}(\vec{r},t)=E^0_{3\omega}(\vec{r},t)\exp\{-i[3\omega t+\theta(\vec{r},t)]\}. \quad \text{(A7)}$$

The TH field has the same confocal parameter as the laser field, but its beam waist is smaller by about a factor of $\sqrt{3}$. The equation for $E^+_{3\omega}(\vec{r},t)$ is obvious from earlier work, but it is of extreme importance that the approximations made in deriving this result be fully appreciated in evaluating the effect of $E^+_{3\omega}(\vec{r},t)$ on the resonantly enhanced MPI. The TH field, from our original definition, is

$$\vec{E}_{3\omega}(\vec{r},t)=\tfrac{1}{2}[E^+_{3\omega}(\vec{r},t)+E^-_{3\omega}(\vec{r},t)]\vec{e}_y=\vec{e}_y E^0_{3\omega}(\vec{r},t)\cos[3\omega t+\theta(\vec{r},t)],$$

where $E^-_{3\omega}$ is the complex conjugate of Eq. (A2).

APPENDIX B

It is useful to summarize some of the properites of $g(u,v)$ as defined by Eq. (28) and of $M^{(m)}(v_R,v_S)$ of Eq. (46). Thus, we have

$$g(u,v)=\int_{-\infty}^{u}\frac{e^{iv(u'-u)}}{(1+iu')^2}du'$$

and if $H(x)=0$ for $x<0$ and $H(x)=1$ for $x>0$, we have for $|u|>0$

$$g(u,v)=2\pi vH(u)H(v)e^{-v(1+iu)}-ih(u,v)\ , \tag{B1}$$

where

$$h(u,v)=v\int_0^\infty\frac{e^{-y}dy}{[y-v(1+iu)]^2} \tag{B2}$$

and for all v and $|u|>0$,

$$|h(u,v)|<u^{-2}|v|^{-1}\ . \tag{B3}$$

Thus, at large $|u|$ the function $g(u,v)$ approaches the limit

$$2\pi|v|H(u)H(v)\exp[-|v|(1+i|u|)]\ .$$

We can also prove the following relationship between $g(u,v)$ for positive u and $g(-u,v)$. For $u>0$

$$g(u,v)=2\pi vH(v)e^{-v(1+iu)}-g^*(-u,v)\ . \tag{B4}$$

Consequently, the value of $g(u,v)$ at negative u determines through Eq. (38) the value at positive u. For $v<0$ the following inequality holds for $g(u,v)$

$$|g(u,-|v|)|<\frac{1}{|v|(1+u^2)}\ . \tag{B5}$$

A more useful relationship which is valid for $v<-3$ is

$$|g(u,-|v|)|\cong\frac{1}{(1+iu)[2+|v|(1+iu)]}\ . \tag{B6}$$

Some exact properties which help to visualize $g(u,v)$ are

$$g(u,0)=i/(1+iu)\ , \tag{B7}$$

$$g(0,|v|)=\pi ve^{-|v|}+i[1-|v|e^{-|v|}E_i(|v|)]\ , \tag{B8}$$

and

$$g(0,-|v|)=ie^{|v|}E_2(|v|)\ . \tag{B9}$$

Also, for very large $|v|$ we have the asymptotic expansion of Eq. (34):

$$g(u,v)\cong-\frac{i}{v}\left[\frac{1}{(1+iu)^2}+\frac{2}{v}\frac{1}{(1+iu)^3}+\cdots\right]. \tag{B10}$$

Using asymptotic relations like Eq. (B6), we find that if $v=v_S+v_R<-6$, or if $v>15$,

$$\begin{aligned}M^{(m)}(v_R,v_S)&\cong\frac{v_R^2}{(v-2)^2}\frac{\pi}{2^{2m+2}}\frac{(2m+2)!}{[(m+1)!]^2}\times\left[v_S^2+4(1-v_S)\left[\frac{m+\frac{3}{2}}{m+2}\right]\right]\\&\cong M_0^{(m)}(v_R,v_S)\frac{1}{(v-2)^2}\times\left[v_S^2+4(1-v_s)\left[\frac{m+\frac{3}{2}}{m+2}\right]\right].\end{aligned} \tag{B11}$$

Another important check on the numerical evaluation of $M^{(m)}(v_R,v_S)$ follows from Eq. (B6):

$$M^{(m)}(v_R,-v_R)=\frac{\pi}{2^{2m+2}}\frac{(2m+2)!}{[(m+1)!]^2}v_R^2\times\left[(1+V_R)^2+\frac{V_R^2}{2m+1}\right]. \tag{B12}$$

The easiest way to generate a table of $M^{(m)}(v_R,v_S)$ may be to note that

$$\frac{dg}{du}(u,v)=\frac{1}{(1+iu)^2}-ivg(u,v)$$

and to define $g(u,v)=R(u,v)+iJ(u,v)$ such that

$$\frac{dR}{du}=\frac{(1-u^2)}{(1+u^2)^2}+vJ\ ,$$

$$\frac{dJ}{du}=\frac{-2u}{(1+u^2)^2}-vR\ .$$

Thus, we can use an asymptotic formula to calculate $g(u,v)$ for large negative u. The solution of the simultaneous equations are then marched along in u, and $M^{(m)}(v_R,v_S)$ is evaluated by numerically integrating in Eq. (46) as new values of $g(u,v)=R(u,v)+iJ(u,v)$ are generated.

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$$\frac{\partial\mathscr{Y}(z,t)}{\partial t}=i[(3\omega-\omega_r)-\Delta_T+i(\gamma_0+\gamma_I)]\mathscr{Y}(z,t)-\frac{\Gamma_c}{b}\int_{-\infty}^{z}\exp[-3i(z-z')(k-\omega/v_1)]\times\frac{(1+2iz'/b)}{(1+2iz/b)}\times\mathscr{Y}(z,t-|z-z'|/v_1)dz'+\frac{i\Omega_3e^{-3i\phi}}{(1+2iz/b)^3}\,.$$

[In Eq. (3) of Ref. 12 the constant γ_0 is misprinted as y_0.] The largest contribution to the integrals here and in Ref. 12 comes from the region $z'\sim z$, and at $z=z'$ the integrals in Eq. (60) and in Eq. (3) of Ref. 12 are equal.

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