Theory of the cancellation of four-photon resonances by an off-resonance three-photon cancellation

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We present a complete account of our recent work [Phys. Rev. A 44, 31 (1991)] in which we investigate the theory of cancellation by interference between the absorption of three fundamental laser photons and one third-harmonic photon. The theory is formulated in terms of the density matrix so as to take detunings, dephasing, and laser bandwidth into account. The result is a theory of cancellation for finite detuning that explains how four-photon resonances can be canceled by a three-photon mechanism if there is an atomic level at near-three-photon resonance. The treatment is extended to focused beams and the interplay between phase matching and cancellation is investigated. We obtain explicit conditions for cancellation to occur, and perform calculations pertaining to a recent experiment where cancellation of 4+1 resonantly enhanced multiphoton ionization has been observed.

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I. INTRODUCTION

A. History

In the study of nonlinear processes, the possibility of harmonic generation through multiphoton absorption and subsequent harmonic reemission has been known for a long time. In the past ten years, though, a new possibility for testing the understanding of the processes has emerged. In a series of elegant experiments, Compton *et al.* [2] and Miller *et al.* [3,4] demonstrated how an apparently missing 3+2 resonantly enhanced multiphoton ionization (REMPI) peak from the Xe 6*s* level was restored when going to very low pressures. Their explanation was that a generated third harmonic somehow obliterated the peak at higher pressures, at which a prominent harmonic was seen. Later, Glownia and Sander [5] supported this interpretation by a dramatic restoration of the signal when using a setup of circularly polarized beams, in which harmonic generation was forbidden.

Another important contribution came from Jackson and Wynne [6–8], who showed experimentally that the ionization could be restored by a simple counterpropagating geometry. A very simple and intuitive theoretical picture was given, in which it was shown that the two pathways, three fundamental or one harmonic photon, leading to the 6*s* state could be seen to interfere exactly destructively. Such interference effects had been anticipated in a theoretical paper by Manykin and Afanas'ev [9]. Other theoretical approaches by Payne, Garret, and collaborators [10], Normand, Morellec, and Reif [11], Poirier [12], and Agarwal and Tewari [13] have added much insight by handling the full system as opposed to the simple susceptibility picture used by Jackson and Wynne.

B. Aspects of cancellation

All the previous work has dealt with the cancellation of a three-photon resonance (e.g., 6*s* state in Xe). Recently, though, experiments have been performed that show the fingerprints of cancellation in 4+1 REMPI of 4*f* and 5*f* in Xe [14]. By fingerprints we mean the (partial) disappearance of the resonance peaks with increasing pressure and the restoration of these in a counterpropagating (standing-wave) laser beam. It is not obvious how this type of cancellation can take place. Fourth-harmonic generation is forbidden by parity, so the direct interference between the effect of four fundamental photons and one photon cannot take place. Previous sources have, indeed, used the four-photon peaks as a calibration of three-photon cancellation [3].

In view of recent results on cancellation of four-photon resonances this is still justifiable, since the cancellation of the four-photon resonances is seen at much higher pressure than that of three-photon cancellation [1].

C. Proposed mechanism

Working under the reasonable assumption that the deenhancement of the 4+1 REMPI peaks is due to cancellation (involving somehow the generated third harmonic), the question now is exactly which mechanism causes the deenhancement. One could imagine a complicated set of interfering processes in which the total sum of paths going from the ground state to the four-photon state (all combinations of one fundamental and one third-harmonic photons going through all intermediate states of the atom) would somehow cancel.

There is a conceptually simpler and theoretically easier possibility, though. It has been established that cancellation on resonance of a three-photon state is due to the lack of excitation of the three-photon state. This, in turn, is due to the disappearance of the coupling between the ground state and the three-photon state. Imagine now, that one attempted to see a four-photon resonance, for which three photons were at exact resonance with the discussed three-photon state. Because of cancellation, there is no coupling from the ground state to the three-photon state, and consequently *continuing with one pho-*

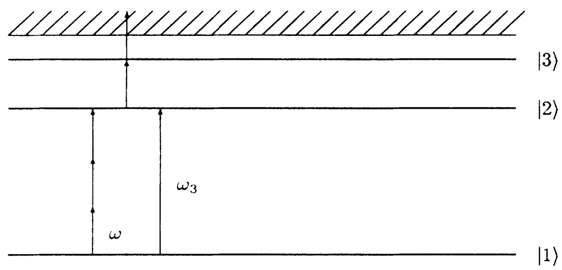

FIG. 1. The excitation of $|2\rangle$ is gone due to the interference of the two processes leading from the ground state to $|2\rangle$. The subsequent (one-photon-resonant) two-photon ionization cannot take place, since no population is present in $|2\rangle$.

ton to the four-photon state will not be possible. (See Fig. 1.) In this picture, the four-photon resonance will disappear from the spectra, but *all the cancellation takes place at the three-photon level.*

The experiments did not have the four-photon resonances at a position that would cause exact (three-photon) resonance with a three-photon state [14] (in Xe this could be 6*s*), but still the three-photon state is at reasonably close resonance. Depending on how close this three-photon resonance is, one might still expect the mechanism sketched above (three-photon mechanism cancels four-photon resonances) to be responsible for the deenhancement of the four-photon peaks. The present work addresses this possibility in the following way: While paying strong attention to the question of how a finite detuning affects the possibility of cancellation, we reformulate the theory of three-photon cancellation in a way resembling that of Jackson and Wynne in the physical picture, but in a more complete (density-matrix) formalism. This allows one to see exactly why and how a simple picture based on susceptibilities works even though the system inherently has strong interferences disturbing the dynamics of the interaction between the ground state and 6*s*. From this comes a series of conditions showing when a cancellation at the three-photon level is possible. Most notably, it turns out that for cancellation to work, it is of extreme importance that only one state dominates all the processes (ionization, refractive index, and harmonic generation).

We cast the theory in a form that handles a focused beam and show that the interplay between pressure and phase-matching considerations are rather different in a cancellation picture than for ordinary harmonic generation. We find the surprising result that for cancellation to take place, the harmonic profile must be shifted not over, but completely away from, the desired cancellation detuning. And for the first time, we present actual calculations of the atomic parameters, allowing us to establish the validity of the various conditions.

II. SYSTEM DESCRIPTION

To give the basic description, one imagines a Xe gas driven by two fields—one at angular frequency ω and one at frequency $\omega_3=3\omega$. The ω_3 field will be provided by the gas itself through harmonic generation.

A. Fields

The two fields are described by

$$E=\mathcal{E}\exp(i\omega t-ikz)+\text{c.c.}=\overline{\mathcal{E}}\exp(i\omega t)+\text{c.c.}\ , \tag{2.1}$$

$$E_3=\mathcal{E}_3\exp(i3\omega t-ik_3z)+\text{c.c.}$$
$$=\overline{\mathcal{E}}_3\exp(i3\omega t)+\text{c.c.} \tag{2.2}$$

The complex amplitudes $\mathcal{E}$ and $\mathcal{E}_3$ are taken to be slowly varying functions of space and time. In this way, they can contain both phases (that eventually lead to interference) and any amplification or attenuation of the third harmonic field. And later, it will be possible to let $\mathcal{E}$ describe a focused (Gaussian) beam.

B. Atomic system

For the atomic system, Xe is chosen with the laser tuned close to resonance with the ground-state to 6*s* transition. The two states are taken explicitly into account, and an adiabatic elimination of all the other atomic states is performed (including those in the continuum), thus obtaining effective three-photon matrix elements, ac Stark shifts, and the ionization width of the 6*s* state in the description.

C. Dynamics

It is not our purpose here to rigorously derive the density-matrix equations. The techniques used and results obtained are merely stated. Consider Fig. 2. It has the two states and the fields that couple them to one another and to the continuum. This system will be considered in the dipole approximation, with a Hamiltonian

$$H=H^{\text{atom}}+H^{\text{interaction}}\ . \tag{2.3}$$

H^{atom} is the usual atomic Hamiltonian and $H^{\text{interaction}}$ is the interaction with the field given by

$$H^{\text{interaction}}=-\mu E\ , \tag{2.4}$$

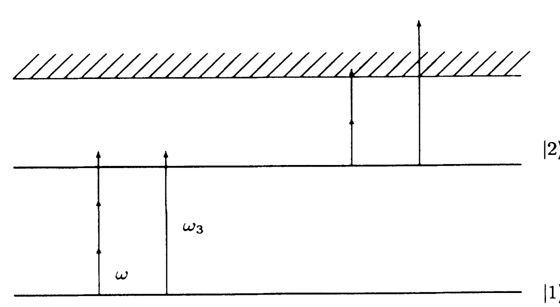

FIG. 2. The two levels, ground state and 6*s*, of Xe together with the continuum. Three fundamental photons or one third-harmonic photon are at (near) resonance with the transition. Note that one photon of the fundamental cannot go into the continuum.

μ being the dipole operator $-e\epsilon\cdot\mathbf{r}$ with ϵ being the unit polarization vector of the field.

The idea is now to use the time evolution of the density operator

$$\dot{\rho}=-i[H,\rho] \tag{2.5}$$

(having set $\hbar=1$). This time evolution is used on the matrix elements of ρ, after expansion of these in harmonics of the fundamental laser frequency

$$\rho_{ij}=\sigma_{ij}+\sum_{n(>0)}[\sigma_{ij}^{(n)}\exp(in\omega t)+\sigma_{ji}^{(n)*}\exp(-in\omega t)] . \tag{2.6}$$

For the diagonal elements it is assumed that the populations vary on a time scale much larger than the laser frequency, i.e., one takes $\rho_{11}\simeq\sigma_{11}$, $\rho_{22}\simeq\sigma_{22}$. All matrix elements σ_{ij} with indices i,j that do not refer to 1 or 2 are nonresonant and will be eliminated. Concerning ρ_{12}, it is noted that in a first approximation, off-diagonal elements rotate with a frequency $(E_2-E_1)/\hbar$. Thus $\rho_{12}\simeq\sigma_{12}^{(3)}\exp(i3\omega t)$.

Now one can systematically use (2.5) to perturbatively expand the time evolution of the three main matrix elements σ_{11}, σ_{22}, and $\sigma_{12}^{(3)}$. By picking only lowest-order paths connecting the three main matrix elements, one arrives at three independent differential equations for the atomic system (note that as only the lowest-order resonant paths have been included, the rotating-wave approximation has been made),

$$[\partial_t-i(\omega_{21}+\delta\omega_{21}-3\omega)+1/T+\tfrac{1}{2}(\gamma+\gamma_3)]\sigma_{12}^{(3)} =i(\overline{\mathcal{E}}_3\mu_{12}+\overline{\mathcal{E}}^{\,3}\mu_{12}^{(3)})(\sigma_{22}-\sigma_{11}) , \tag{2.7}$$

$$\partial_t\sigma_{11}-\frac{1}{\tau}\sigma_{22}=2\,\mathrm{Im}[(\overline{\mathcal{E}}_3^*\mu_{12}^*+\overline{\mathcal{E}}^{*3}\mu_{12}^{(3)*})\sigma_{12}^{(3)}] , \tag{2.8}$$

$$[\partial_t+1/\tau+(\gamma+\gamma_3)]\sigma_{22} =-2\,\mathrm{Im}[(\overline{\mathcal{E}}_3^*\mu_{12}^*+\overline{\mathcal{E}}^{\,*3}\mu_{12}^{(3)*})\sigma_{12}^{(3)}] , \tag{2.9}$$

where

$$\partial_t(\sigma_{11}+\sigma_{22})=-(\gamma+\gamma_3)\sigma_{22} . \tag{2.10}$$

Of course, all the symbols need to be defined. (In the following the summation indices $l,m,n,\ldots$ cover all atomic states including the continuum. The sums are therefore generalized—they include summation over discrete states and integration over continuum states.)

The matrix elements multiplying the fields are one- and three-photon dipole matrix elements, the latter given by

$$\mu_{12}^{(3)}=\sum_{m,l}\frac{\mu_{1m}\mu_{ml}\mu_{l2}}{(\omega+\omega_{1m})(2\omega+\omega_{1l})} . \tag{2.11}$$

One obtains the polarizabilities

$$\alpha_1=-\sum_l\left[\frac{|\mu_{l1}|^2}{\omega_{1l}-\omega}+\frac{|\mu_{l1}|^2}{\omega_{1l}+\omega}\right] , \tag{2.12}$$

$$\alpha_2=-\sum_l\left[\frac{|\mu_{l2}|^2}{\omega_{2l}-\omega}+\frac{|\mu_{l2}|^2}{\omega_{2l}+\omega}\right] , \tag{2.13}$$

α_1 denoting the polarizability of level $|1\rangle$ and α_2 the polarizability of level $|2\rangle$ with respect to the fundamental field at ω. Similarly at ω_3 one has the polarizabilities

$$\beta_1=-\sum_{l(\neq 2)}\frac{|\mu_{l1}|^2}{\omega_{1l}+3\omega}-\sum_l\frac{|\mu_{l1}|^2}{\omega_{1l}-3\omega} , \tag{2.14}$$

$$\beta_2'-i\beta_2''=-\sum_{l(\neq 1)}\frac{|\mu_{l2}|^2}{\omega_{2l}+3\omega}-\sum_l\frac{|\mu_{l2}|^2}{\omega_{2l}-3\omega} . \tag{2.15}$$

These resemble the polarizabilities with respect to ω. Note that β_2 has been split in two. This is due to the fact that the third-harmonic photon can actually go into the continuum. This gives a singularity in the sum or integration over l that can be handled by a principal-value technique. The result of this is an imaginary part of the result, being the ionization width of state $|2\rangle$ due to the harmonic field. The ionization rate from level $|2\rangle$ due to 3ω is

$$\gamma_3=2\beta_2''|\overline{\mathcal{E}}_3|^2 . \tag{2.16}$$

Note that there was no imaginary part in the polarizabilities with respect to the fundamental frequency. This is because one photon cannot go from $|2\rangle$ to the continuum, and the polarizabilities arise from a second-order process, involving the vertical emission and absorption of photons (see Fig. 3).

However, the two-photon ionization is needed, so a fourth-order process is included to account for that (see Fig. 3)

$$\gamma=2|\overline{\mathcal{E}}|^4\mathrm{Im}\left[\sum_{lm}\frac{|\mu_{2l}|^2}{(4\omega+\omega_{1l})}\frac{|\mu_{lm}|^2}{(5\omega+\omega_{1m})}\right] . \tag{2.17}$$

The polarizabilities give rise to ac Stark shifts of the states, where

$$\delta\omega_{21}=-(\alpha_2-\alpha_1)|\overline{\mathcal{E}}|^2-(\beta_2'-\beta_1)|\overline{\mathcal{E}}_3|^2 \tag{2.18}$$

is the difference between the ac Stark shifts of the states $|1\rangle$ and $|2\rangle$.

Finally, $1/\tau$ represents spontaneous decay from $|2\rangle$ to $|1\rangle$, and $1/T$ represents *coherence decay* or dephasing due to effects other than ionization,

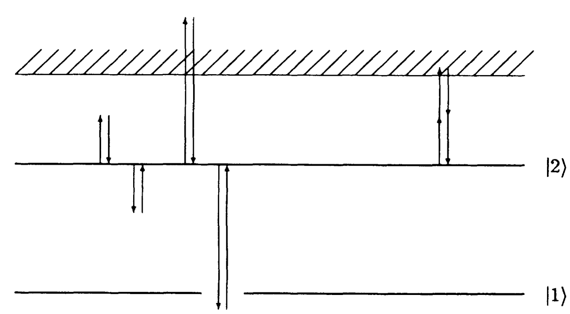

FIG. 3. The two levels, ground state and 6s, of Xe and the continuum. Three fundamental photons or one third-harmonic photon are at (near) resonance with the transition. Note that one photon of the fundamental cannot go into the continuum.

$$\frac{1}{T}=\tfrac{1}{2}(1/\tau+3\gamma_{\text{laser}})+(\text{other dephasings}) . \quad (2.19)$$

The γ_{laser} is the bandwidth of the laser and the factor of 3 is included because it is a third-order process. The other dephasings are mainly due to collisions and will be proportional to N, N being the pressure.

The model accounting for the laser bandwidth in Eq. (2.19) is based on the assumption that the laser exhibits amplitude fluctuations. The total off-diagonal dephasing can be shown to reduce to the above form when the three-photon Rabi frequency is much smaller than the ionization width and the laser bandwidth, which certainly has been the case in the experimental situation analyzed in this paper. It is also true that the laser exhibited amplitude fluctuations. In addition to the bandwidth due to stochastic fluctuations, a pulsed laser has a Fourier bandwidth due to the finite duration of the pulse. In the case of our calculations with pulses of the order of 10 nsec, this bandwidth is totally negligible compared to the stochastic one. In general, however, the two bandwidths have different origins and are present at the same time when the differential equations are solved with a given pulse shape. The larger of the two will dominate. It is needless to add that the total bandwidth cannot be smaller than the Fourier width, irrespective of the stochastic properties of the field.

III. GENERATED FIELD

This section is devoted to the mechanism that generates and sustains the third-harmonic field. Eventually, this will give a wave equation for the third-harmonic field. With the density-matrix equations this will form the full description of the system. But first how is the harmonic field generated?

A. Polarization

As the gas is pumped with the fundamental frequency, the atoms will be deformed and will be sources of the electromagnetic field as oscillating dipoles. As usual in electrodynamics, one has

$$P=N\mu \ , \quad (3.1)$$

P denoting the polarization. This is easy to translate to quantum mechanics in the density-operator formalism

$$\frac{1}{N}P=\langle\mu\rangle=\text{Tr}[\rho\mu] \ . \quad (3.2)$$

In expanding the trace in the previous equation, a perturbation expansion is again needed. The guiding line is to pick the lowest-order paths that describe the phenomena under consideration. Expanding Eq. (3.2) and projecting on the 3ω component of the polarization, one has

$$\frac{1}{N}P_{3\omega}\simeq\left[\left[\sum_{(l,m)\neq(1,2)}\sigma_{lm}^{(3)*}\mu_{ml}\right]e^{-i3\omega t}+\text{c.c.}\right]+(\sigma_{12}^{(3)*}\mu_{21}e^{-3i\omega t}+\text{c.c.}) \ . \quad (3.3)$$

Notice that one term has explicitly been taken out of the trace summation. The complex conjugates are in order to be consistent with the definition of the fields (2.1) and (2.2).

The final expression must contain only the three main elements (σ_{11}, σ_{22}, and $\sigma_{12}^{(3)}$), since they are the only nonvanishing components of the density matrix. In eliminating all the σ_{ij} that are not the three main types, one again uses the adiabatic approximation. For instance, using the time-development of ρ, (2.5), one obtains (considering for simplicity only the field $\overline{\mathcal{E}}$):

$$i(\partial_t+n\omega+\omega_{1l})\sigma_{1l}^{(n)}=i\sum_m(-\overline{\mathcal{E}}\sigma_{1m}^{(n-1)}\mu_{ml}-\overline{\mathcal{E}}^*\sigma_{1m}^{(n+1)}\mu_{ml}+\overline{\mathcal{E}}\mu_{1m}\sigma_{ml}^{(n-1)}+\overline{\mathcal{E}}^*\mu_{1m}\sigma_{ml}^{(n+1)}) \ . \quad (3.4)$$

The adiabatic approximation now consists in ignoring the time derivative, thereby obtaining

$$\sigma_{1l}^{(n)}\simeq\sum_m\frac{-\overline{\mathcal{E}}_{1m}^{(n-1)}\mu_{ml}-\overline{\mathcal{E}}^*\sigma_{1m}^{(n+1)}\mu_{ml}+\overline{\mathcal{E}}\mu_{1m}\sigma_{ml}^{(n-1)}+\overline{\mathcal{E}}^*\mu_{1m}\sigma_{ml}^{(n+1)}}{n\omega+\omega_{1l}} \ . \quad (3.5)$$

One now finds all the lowest-order contributions obtained by picking successively one of the four terms in the previous equation as an expansion for σ_{lm}, until ending up on σ_{11}, σ_{22}, or $\sigma_{12}^{(3)}$.

Formally, the result is

$$P_{3\omega}=[\chi'^{(1)}(3\omega)\overline{\mathcal{E}}_3+\chi'^{(3)}(\omega)\overline{\mathcal{E}}^3+\sigma_{12}^{(3)}\mu_{21}]e^{i3\omega t}+\text{c.c.} \quad (3.6)$$

It is important at this point to note, though, that only the last term containing σ_{12} has any resonant effects in it. So, the $\chi'^{(1)}(3\omega)$ represents nonresonant polarization at 3ω, and $\chi'^{(3)}(\omega)$ represents nonresonant harmonic generation at 3ω.

A more direct way would have been to use single-sided, non-time-ordered Feynman diagrams for finding the total χ [15]. This would be a good approximation for the nonresonant χ, but for the resonant ones, we prefer to investigate the conditions for the validity of this approach much more carefully. Finally, we will end up with expressions resembling the ones obtained through the susceptibility approach, but with complete control over the regime of its validity.

B. Wave equation—plane waves

Now knowledge of the sources of the third-harmonic field is used to obtain its wave equation. To begin with, the problem is analyzed for plane waves with slowly varying amplitudes of the form

$$E=E_1+E_3\ , \tag{3.7}$$

where

$$E_1=\mathcal{E}e^{i(\omega t-kz)}+\text{c.c.}\ ,$$
$$E_3=\mathcal{E}_3e^{i(\omega_3 t-k_3 z)}+\text{c.c.}\ , \tag{3.8}$$

$k=n\omega/c$ is the wave vector of the fundamental laser frequency, n being the refractive index at ω. For k_3, the exact size is not yet decided—it is still a free parameter. A choice of k_3 will affect how the phase varies in the slowly varying amplitude $\mathcal{E}_3$, and all one needs to demand of k_3 is that it is close to $3k$. As the wave equations are derived, the obvious choice for k_3 will be clear.

One now starts out from the wave equation for the electromagnetic field projected down on the third harmonic, given by

$$\nabla^2\mathbf{E}_3(\mathbf{r},t)-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{E}_3(\mathbf{r},t)=\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{P}_3(\mathbf{r},t)\ . \tag{3.9}$$

The interaction volume is approximated by a long pipe, and the wave by a plane propagating wave. The equation thus reduces to

$$\partial_z^2E_3-\frac{1}{c^2}\partial_t^2E_3=\frac{4\pi}{c^2}\partial_t^2P_3\ . \tag{3.10}$$

Assuming that $\mathcal{E}_3$ varies slowly in time and space, all second derivatives are neglected (the slowly varying amplitude approximation), and one arrives at

$$-k_3^2\mathcal{E}_3-2ik_3\partial_z\mathcal{E}_3-\frac{1}{c^2}(-\omega_3^2\mathcal{E}_3+2i\omega_3\partial_t\mathcal{E}_3)(1+4\pi\chi'^{(1)})=\frac{4\pi}{c^2}[-\omega_3^2\chi'^{(3)}e^{-i3kz}\mathcal{E}^3(-\omega_3^2N\sigma_{12}^{(3)}+i\omega_3\partial_t\sigma_{12}^{(3)})\mu_{21}]e^{ik_3z}\ . \tag{3.11}$$

It is to be noted that time derivatives of χ' have been ignored, even though they still formally contain the time-dependent populations. However, the time derivatives will be small corrections to a perturbation and can be ignored. Moreover, in the following χ will be approximated by constant susceptibilities, which is consistent with ignoring the derivatives at this point.

Collecting terms in the above equation, one has the equation

$$-\left[k_3^2-\frac{(1+4\pi\chi'^{(1)})\omega_3^2}{c^2}\right]\mathcal{E}_3-2ik_3\partial_z\mathcal{E}_3-\frac{2i\omega_3(1+4\pi\chi'^{(1)})}{c^2}\partial_t\mathcal{E}_3$$
$$=\frac{\omega_3^2 4\pi}{c^2}\left[\chi'^{(3)}e^{-i3kz}\mathcal{E}^3+N\left[\sigma_{12}^{(3)}-\frac{i}{\omega_3}\partial_t\sigma_{12}^{(3)}\right]\mu_{21}\right]e^{ik_3z}\ . \tag{3.12}$$

As promised, it is now obvious that choosing

$$k_3=n_3\frac{\omega_3}{c},\quad n_3^2=1+4\pi\chi'^{(1)} \tag{3.13}$$

simplifies the equation greatly, since the first term vanishes. This amounts to including all nonresonant polarization effects on $\mathcal{E}_3$ in k_3. Finally one has the wave equation for the slowly varying amplitude for the third-harmonic field:

$$\frac{\partial\mathcal{E}_3}{\partial z}+\frac{n_3}{c}\frac{\partial\mathcal{E}_3}{\partial t}=-i\frac{2\pi\omega_3}{n_3c}\left[\chi'^{(3)}e^{-i3kz}\mathcal{E}^3+N\left[\sigma_{12}^{(3)}-\frac{i}{\omega_3}\partial_t\sigma_{12}^{(3)}\right]\mu_{21}\right]e^{ik_3z}\ . \tag{3.14}$$

Here, as before, the term containing $\chi'^{(3)}$ gives nonresonant pumping of the third-harmonic field by the fundamental laser. The term containing $\sigma_{12}^{(3)}$ and its derivative gives all resonant effects—pumping and polarization. Note that the nonresonant polarization at ω_3 has been absorbed in the dispersion $k_3=n_3\omega_3/c$.

This gives all the equations needed to describe the coupled system atoms plus the field. The atomic response is described by the density-matrix equations (2.7) through (2.10) and the field by the above equation. The density-matrix equations are stated again in a slightly more compact form:

$$(\partial_t-i\Delta+\Gamma/2)\sigma_{12}^{(3)}=i(\mathcal{E}_3e^{-ik_3z}\mu_{12}+\mathcal{E}^3e^{-i3kz}\mu_{12}^{(3)})$$
$$\times(\sigma_{22}-\sigma_{11})\ , \tag{3.15}$$

$$\partial_t\sigma_{11}-\frac{1}{\tau}\sigma_{22}=2\,\text{Im}[(\mathcal{E}_3^*e^{ik_3z}\mu_{12}^*+\mathcal{E}^{*3}e^{i3kz}\mu_{12}^{(3)*})\sigma_{12}^{(3)}]\ , \tag{3.16}$$

$$\partial_t(\sigma_{11}+\sigma_{22})=-(\gamma+\gamma_3)\sigma_{22}\ , \tag{3.17}$$

$$\Delta=\omega_{21}+\delta\omega_{21}-3\omega,\quad \Gamma=2\frac{1}{T}+\gamma+\gamma_3\ , \tag{3.18}$$

Δ now denoting the total detuning (including ac Stark shift) and Γ all decay of the coherence of the system (radiative, collisional, laser broadening, etc.).

C. Rate approximation

Looking at the equations for the density-matrix elements, it is clear that there can be a special situation, if the field $\mathcal{E}_3$ is of a phase and magnitude, so that the sum of fields and matrix elements (the coupling) in Eq. (3.15) vanishes. In the following the wave equation will be examined more closely, and an expression for the third-harmonic field will be derived that will eventually lead to this situation. To decouple the field and density-matrix equations, one does the familiar rate approximation in the density-matrix equations. This basically means ignoring the time derivative in the differential equation for $\sigma_{12}^{(3)}$ (3.15), thus allowing $\sigma_{12}^{(3)}$ to be eliminated from the wave equation. The approximation will be valid under the condition that $\sigma_{11}-\sigma_{22}$ is slowly varying compared to the total dephasing time. One way of satisfying this condition is to have Γ much greater than the Rabi frequency [16]. Whether this is satisfied or not will have to be investigated for each experimental choice of atom, resonant energy levels (leading to atomic parameters), and laser (intensity and statistics). For the experiment relating to this paper [14], it turns out that the laser coherence time, $\tau_{\text{laser}}=1/\gamma_{\text{laser}}$ is by far the shortest of all relevant times in the system. The laser bandwidth is reported to be $\simeq 0.2\ \text{cm}^{-1}$, and the Rabi frequency is calculated (at an intensity of $6\times 10^9\ \text{W/cm}^2$) to be on the order of 0.001 cm^{-1}. The ionization width is even lower ($\simeq 0.0001\ \text{cm}^{-1}$). So the total Γ is, in fact, dominant, and the rate approximation is valid. We emphasize that the rate approximation in this case can be made because of a dominant laser bandwidth.

The validity of the rate approximation will allow us, as will be seen, to handle the theory in a very simple susceptibility approach, analogous to previous treatments. We must stress, though, that not all experiments can be handled by this approach, and it is still an open question what will happen to cancellation if the rate approximation breaks down.

Under the rate approximation, one has

$$(-i\Delta+\Gamma/2)\sigma_{12}^{(3)}\simeq i(\mathcal{E}_3 e^{-ik_3 z}\mu_{12}+\mathcal{E}^3 e^{-i3kz}\mu_{12}^{(3)})\times(\sigma_{22}-\sigma_{11}) \tag{3.19}$$

or

$$\sigma_{12}^{(3)}\simeq\frac{\mathcal{E}_3 e^{-ik_3 z}\mu_{12}+\mathcal{E}^3 e^{-i3kz}\mu_{12}^{(3)}}{(\Delta+i\Gamma/2)}n(z)\ , \tag{3.20}$$

where $n(z)=\sigma_{11}-\sigma_{22}$ is the slowly varying difference in populations.

D. Wave equation in rate approximation

The calculated $\sigma_{12}^{(3)}$ can now be fed back into the wave equation. One assumes further that the pulse is so long that time effects are ignorable and that the field is steady-state in the interaction volume:

$$\partial_z\mathcal{E}_3\simeq -i\frac{2\pi\omega_3}{n_3 c}\left[\left[\chi'^{(3)}+\frac{\mu_{12}^{(3)}\mu_{21}Nn(z)}{\Delta+i\Gamma}\right]e^{i\Delta k^{\text{NR}}z}\mathcal{E}^3+\frac{\mu_{12}\mu_{21}Nn(z)}{\Delta+i\Gamma}\mathcal{E}_3\right]\ , \tag{3.21}$$

with Δk^{NR} defined as k_3-3k. The quantity $\chi'^{(3)}+\mu_{12}^{(3)}\mu_{21}/\Delta+i\Gamma Nn(z)$ is the *total susceptibility for harmonic generation,* $\chi^{(3)}$. When eliminating σ_{12} by the rate approximation, the expression for $\chi^{(3)}$ becomes the familiar nonlinear susceptibility expression and is in a non-time-ordered approach given by [17,15]

$$\chi^{(3)}=N\sum_{n,m,l;i=1,2}\left[\frac{\mu_{il}\mu_{lm}\mu_{mn}\mu_{ni}}{(\varpi_{li}+3\omega)(\varpi_{mi}\pm 2\omega)(\varpi_{ni}\pm\omega)}+\frac{\mu_{il}\mu_{lm}\mu_{mn}\mu_{ni}}{(\varpi_{li}\mp\omega)(\varpi_{mi}\pm 2\omega)(\varpi_{ni}\mp\omega)}\right]\sigma_{ii}\ . \tag{3.22}$$

The $\pm$ is shorthand for either taking the upper sign in the whole denominator or taking the lower sign. In actual calculations of $\chi^{(3)}$, it is assumed, that only $i=1$ (the ground state) contributes. It is furthermore noticed that in the above expression, two paths corresponding to $l=2$, $i=1$ and $l=1$, $i=2$ are resonant. This is the resonant contribution from $\sigma_{12}^{(3)}$ and must be handled with special care. All the ϖ_{ij} contain a dephasing $i\Gamma_{ij}$, but since all but two are nonresonant, one can ignore these dephasings except in ϖ_{21}. From (3.20) it is seen that ϖ_{21} should be $\omega_{21}+\delta_{21}+i\Gamma/2$. The focus will be on the effects of the balance between resonant (R) and nonresonant (NR) effects, so the susceptibility is split into two:

$$\chi^{(3)}=\chi^{\text{NR}(3)}+\frac{\mu_{12}^{(3)}\mu_{21}Nn(z)}{\Delta+i\Gamma/2}\ , \tag{3.23}$$

the second term being the above-discussed resonant pathways. In complete analogy to the discussion of $\chi^{(3)}$, in these approximations, one has

$$\chi^{(1)}=\chi^{\text{NR}(1)}+\frac{\mu_{12}\mu_{21}Nn(z)}{\Delta+i\Gamma}\simeq\sum_{l,i=1,2}\frac{\mu_{il}\mu_{li}Nn(z)}{(\varpi_{li}\pm 3\omega)}\sigma_{ii}\ . \tag{3.24}$$

In (3.13) one takes $\chi'^{(1)}=\chi^{\mathrm{NR}(1)}$.

Defining $\chi^{\mathrm{R}(1)}=\mu_{12}\mu_{21}N/\Delta+i\Gamma$ and $a=2\pi\omega_3/n_3c$ finally gives the reduced wave equation

$$\partial_z\mathcal{E}_3\simeq -ia(\chi^{(3)}e^{i\Delta k^{\mathrm{NR}}z}\mathcal{E}^3+\chi^{\mathrm{R}(1)}\mathcal{E}_3)\ . \qquad (3.25)$$

This is a first-order inhomogeneous differential equation, and it can be solved analytically. With the boundary condition that $\mathcal{E}_3|_{z=0}=0$, one obtains

$$\mathcal{E}_3=-ia\frac{e^{i\Delta k^{\mathrm{NR}}z}\mathcal{E}^3-e^{-ia\chi^{\mathrm{R}(1)}z}}{i(a\chi^{\mathrm{R}(1)}+\Delta k^{\mathrm{NR}})}\chi^{(3)}$$
$$\simeq -\frac{\chi^{(3)}}{\chi^{(1)}}(e^{i\Delta k^{\mathrm{NR}}z}\mathcal{E}^3-e^{-ia\chi^{\mathrm{R}(1)}z})\ . \qquad (3.26)$$

Since

$$\chi^{\mathrm{R}(1)}\propto\frac{1}{\Delta+i\Gamma/2}=\frac{\Delta-i\Gamma/2}{\Delta^2+\Gamma^2/4}\ ,$$

the second exponential will decay as z increases, and if

$$z\gg\frac{1}{\mathrm{Im}(a\chi^{\mathrm{R}(1)})}=\frac{n_3c}{2\pi\omega_3}\frac{\Delta^2+\Gamma^2/4}{|\mu_{12}|^2Nn(z)\Gamma/2}\ , \qquad (3.27)$$

the second exponential will have totally dampened out.

Now the solution simplifies even further

$$\mathcal{E}_3\simeq -\frac{\chi^{(3)}}{\chi^{(1)}}\mathcal{E}^3e^{i\Delta k^{\mathrm{NR}}z}\ . \qquad (3.28)$$

Since the process is near resonant it is a reasonable assumption (which will be discussed in detail later) that $\chi^{(3)}\simeq\chi^{\mathrm{R}(3)}$ and $\chi^{(1)}\simeq\chi^{\mathrm{R}(1)}$. Inserting the expressions for the resonant χ, one has

$$\mathcal{E}_3\simeq -\frac{\mu_{12}^{(3)}}{\mu_{12}}e^{i\Delta k^{\mathrm{NR}}z}\mathcal{E}^3\ . \qquad (3.29)$$

This is a very important result. It shows how the third-harmonic field settles at a magnitude and phase determined by the quotient between the one- and three-photon matrix elements.

E. The cancellation

With the rate approximation (3.20), one obtains the rate equations

$$\partial_t\sigma_{11}-\frac{1}{\tau}\sigma_{22}=2\,\mathrm{Im}\left[\frac{|\mathcal{E}_3e^{-ik_3z}\mu_{12}+\mathcal{E}^3e^{-i3kz}\mu_{12}^{(3)}|^2}{\Delta+i\Gamma/2}n(z)\right], \qquad (3.30)$$

$$\partial_t(\sigma_{11}+\sigma_{22})=-(\gamma+\gamma_3)\sigma_{22}\ . \qquad (3.31)$$

The quantity involving the fields is now the effective coupling element from $|1\rangle$ to $|2\rangle$, and that will subsequently give rise to ionization. Using the expression for $\mathcal{E}_3$, which was just obtained, one finds:

$$\mathcal{E}_3e^{-ik_3z}\mu_{12}+\mathcal{E}^3e^{-i3kz}\mu_{12}^{(3)}=0\ . \qquad (3.32)$$

This expression is what underlies the cancellation. The two resonant terms representing the coupling due to the third harmonic and laser fields have exactly the same magnitude and phase except for a difference in signs. The third-harmonic field settles at a value that, combined with the fundamental field through the appropriate matrix elements, *cancels the resonant contribution* of both fields. The rate equations end up being

$$\partial_t\sigma_{11}-\frac{1}{\tau}\sigma_{22}=0\ , \qquad (3.33)$$

$$\partial_t(\sigma_{11}+\sigma_{22})=-(\gamma+\gamma_3)\sigma_{22}\ . \qquad (3.34)$$

There is no resonant coupling between $|1\rangle$ and $|2\rangle$ left, and the system is frozen in the ground state.

F. Discussion of conditions

Taking the general set of equations that describe the system, some approximations were made (rate approximation), the equations were rewritten in a form that could be analytically solved, and cancellation under certain conditions was shown to exist. These conditions will be inspected a little more systematically.

(1) Single-state condition. It is a demand that $\chi^{\mathrm{R}(1)}\gg\chi^{\mathrm{NR}(1)}$ and that $\chi^{\mathrm{R}(3)}\gg\chi^{\mathrm{NR}(3)}$. If the resonant parts of χ are not the dominant ones, an examination of the detailed expressions for the coupling (3.32) shows that one will not in general have cancellation. The cancellation comes about because the quotient in (3.28) between the two χ reduces to the quotient in (3.29) between the two matrix elements. We will provide an even more convincing way of seeing this necessity of one state being absolutely dominant in the harmonic generation and the refractive index. Note, that the "uniqueness" of state $|2\rangle$, because it was included explicitly in the formalism is not relevant—in the end coherence effects of state $|2\rangle$ were eliminated by going to the rate approximation. It is, therefore, not an artifact of the choice of formalism that one needs state $|2\rangle$ to be dominant.

(2) Single-state condition. One thing that has not at all been taken into account is the direct five-photon ionization from the ground state to the continuum. It has been demonstrated how the 3+2 REMPI process is cancelled by harmonic, but the nonresonant five-photon process will remain unaffected. So, once more, one must demand that the resonant 3+2 process be much stronger than the nonresonant five-photon process for the cancellation to be observable. Again this can be called a single-state condition.

(3) Pressure condition. It is necessary that

$$z\gg\frac{n_3c}{2\pi\omega_3}\frac{\Delta^2+\Gamma^2/4}{|\mu_{12}|^2Nn(z)\Gamma/2}\ . \qquad (3.35)$$

This is to say that the interaction volume must be much longer than the linear absorption depth of third harmonic *if there were no interference.* Notice how width, detuning, and pressure enter in a delicate balance to give the condition. As long as the single-state conditions are satisfied, (3.35) allows for cancellation detuned as far from state $|2\rangle$ as desired, as long as the pressure is increased quadratically in the detuning. This condition provides in a quantitative way the reason why cancellation is seen at high pressure. Later, in the focused-beam treatment, we will discuss the nature of this condition in more detail.

Note that for cancellation on resonance (which is the case that has been discussed in the literature previously), one knows that for some (high) pressure, cancellation *will* take place. This is seen from the pressure condition. And since the single-state conditions are automatically satisfied on resonance, these do not provide any limit to the cancellation effect. Cancellation off resonance, as discussed in the present treatment, will *always* require one to perform a calculation to assess in a quantitative way if the single-state conditions are satisfied. These depend on the atomic parameters and are pressure independent, as opposed to the pressure condition.

G. Second cancellation

The cancellation manifests itself as an interference between the driving field $\mathcal{E}$ and the harmonic field $\mathcal{E}_3$ through the three- and one-photon matrix elements, respectively, to state $|2\rangle$. The third-harmonic field adjusts by itself to this cancellation field. Looking back, it is clear that in the rate approximation the cancellation takes place already in the field parts of $\sigma_{12}^{(3)}$ [as seen by Eqs. (3.20) and (3.32)]. Since the main contributions to the polarization P_3 also come from $\sigma_{12}^{(3)}$, the *cancellation also takes place with respect to the sources and/or losses of the third-harmonic field.* This is very important. Previously, the pressure condition stated that "the medium must be optically thick at 3ω." This is misleading, since once cancellation is obtained, the medium is totally passive towards the third-harmonic field due to cancellation—the medium is, in fact, totally thin at this frequency. All the optically thick medium needs to do is to establish the balance; then it becomes inoperative.

H. Single-state condition reinvestigated

In this section we will provide a more intuitive way of seeing why cancellation must demand a single-state condition to hold. First, we construct a self-consistent description of how cancellation works.

Self-consistency: Assuming throughout that cancellation *does* exist for a specific system and pressure, we get the following chain (see Fig. 4).

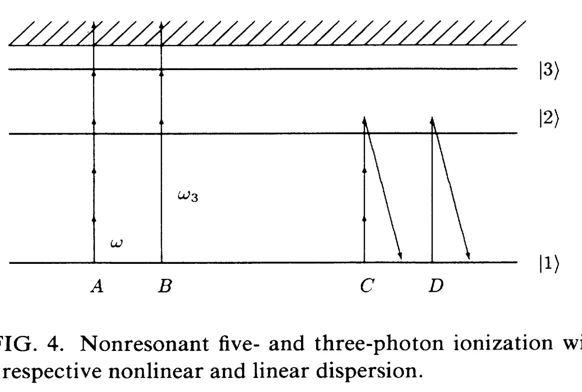

FIG. 4. Nonresonant five- and three-photon ionization with the respective nonlinear and linear dispersion.

(1) $\mathcal{E}_3$ settles fast (due to the pressure condition that makes transients die out fast). The adjustment is accomplished by some small amount of ionization.

(2) Ionization stops due to cancellation.

(3) The harmonic field must now stay constant (or cancellation will break down).

(4) $\mathcal{E}_3$ comes from $C+D$.

(5) If there is a steady production of harmonic from condition (4), then the harmonic must be drained continuously to stay constant.

(6) The only way to drain the harmonic is by ionization.

We have now closed the circle. We see that we have a problem if there is a continuous production of harmonic from condition (4), since it must lead to ionization, i.e., breakdown of cancellation.

We can now conclude that cancellation *must* depend on two simultaneous effects: (i) cancellation of ionization (referred to as cancellation); (ii) cancellation of third-harmonic generation (THG) (referred to as second cancellation—we now see that it was not accidental; the second cancellation took place). In addition, $\mathcal{E}_3$ must be such that both are satisfied.

An investigation of these two simultaneous conditions will show us why the single-state conditions are important for χ. In a very symbolic notation, one has the following.

(i) $A+B=0$ implies $(i,j,k,l$ denoting intermediate atomic states and c the final continuum state),

$$\sum_{i,j,k,l}\frac{\mu_{1i}\mu_{ij}\mu_{jk}\mu_{kl}\mu_{lc}}{\Delta_i\Delta_j\Delta_k\Delta_l}\overline{\mathcal{E}}^{\,5}+\sum_{k,l}\frac{\mu_{1k}\mu_{kl}\mu_{lc}}{\Delta_k\Delta_l}\mathcal{E}_3\overline{\mathcal{E}}^{\,2}=0 \ .$$

(ii) $C+D=0$ implies

$$\sum_{i,j,k}\frac{\mu_{1i}\mu_{ij}\mu_{jk}\mu_{k1}}{\Delta_i\Delta_j\Delta_k}\overline{\mathcal{E}}^{\,3}+\sum_{k}\frac{\mu_{1k}\mu_{k1}}{\Delta_k}\overline{\mathcal{E}}_3=0 \ .$$

The k summation is the summation at the three-photon level and contains the $6s$ state near resonance. The two conditions have only one variable: $\mathcal{E}_3$. The rest depends on the atomic parameters in a far from obvious way. It seems that for cancellation to work, one has to demand that $\mathcal{E}_3$ satisfies two conditions simultaneously, which shows that in the general case, one cannot expect cancellation by the three-photon mechanism. One has to find circumstances under which the two conditions will automatically be satisfied. And one such circumstance is if $6s$ is so resonant that the k summation can be ignored by only taking the $6s$ state at the three-photon level. Then the two conditions read as follows.

(i) $A+B=0$ implies

$$(\mu_{12}^{(3)}\overline{\mathcal{E}}^{\,3}+\mu_{12}\overline{\mathcal{E}}_3)\frac{1}{\Delta+i\Gamma/2}\sum\frac{\mu_{2l}\mu_{lc}}{\Delta_l}=0 \ .$$

(ii) $C+D=0$ implies

$$(\mu_{12}^{(3)}\overline{\mathcal{E}}^{\,3}+\mu_{12}\overline{\mathcal{E}}_3)\frac{\mu_{21}}{\Delta+i\Gamma/2}=0 \ ,$$

which is actually only one condition that is satisfied by the cancellation field already found. This provides very strong evidence that to cancel higher resonances by means of an underlying three-photon cancellation, the single-state conditions cannot be violated.

I. Imperfect cancellation

It has been shown that cancellation demands χ to be totally dominated by its resonant parts. If it is not, one will expect some ionization to take place (since the coupling between $|1\rangle$ and $|2\rangle$ is nonvanishing). What is the physical interpretation for this ionization? The explanation is straightforward for the importance of nonresonant harmonic generation. It is clear that when the harmonic field reaches a steady-state balance, it is a balance between all generation and loss channels of harmonic. However, only the resonant balancing gives cancellation. If now one generates some excess harmonic through nonresonant processes (that do not cancel), this excess harmonic will have to be absorbed or removed somehow. This must be through ionization. It is now clear that ionization is needed to remove excess nonresonant harmonic.

It is not immediately obvious why a nonresonant refractive index ($\chi^{NR(1)}$) will lead to ionization. One can find the clue, though, by inspection of (2.1) and (3.29) which show that

$$E_3=\frac{\mu_{12}^{(3)}}{\mu_{12}}e^{i(3\omega t-3kz)}+\text{c.c.} \tag{3.36}$$

The third harmonic actually propagates with the group velocity of the fundamental $3k/\omega_3$. A free ω_3 wave would propagate with a velocity determined by $\chi^{(1)}$. However, the effect of $\chi^{R(1)}$ in $P_{3\omega}$ will vanish due to cancellation, and we will only have to account for the discrepancy due to Δk^{NR} coming from $\chi^{NR(1)}$. The picture now is that a harmonic wave, left alone, will propagate with a velocity determined by $\chi^{NR(1)}$. Since it is actually propagating with the velocity of the fundamental one has to find the mechanism that adjusts it. The adjustment takes place by absorbing (by ionization) some third harmonic that is getting out of phase and then emitting some of the proper phase.

Now that we have provided a physical interpretation of why nonresonant effects in χ will cause ionization (imperfect cancellation) let us see what the quantitative effect is. In (3.28) one can assume that both $\chi^{(1)}$ and $\chi^{(3)}$ have small nonresonant contributions. To lowest order in these, one gets

$$\mathcal{E}_3=-\frac{\mu_{12}^{(3)}}{\mu_{12}}\left[1+\frac{\chi^{NR(3)}}{\chi^{R(3)}}-\frac{\chi^{NR(1)}}{\chi^{R(1)}}\right]\mathcal{E}^3e^{-3ikz}\,. \tag{3.37}$$

Looking once more at the coupling between $|1\rangle$ and $|2\rangle$, (3.32) gives

$$\mathcal{E}_3e^{-ik_3z}\mu_{12}+\mathcal{E}^3e^{-i3kz}\mu_{12}^{(3)}=\mu_{12}^{(3)}\left[\frac{\chi^{NR(3)}}{\chi^{R(3)}}-\frac{\chi^{NR(1)}}{\chi^{R(1)}}\right]\mathcal{E}^3e^{-3ikz}\,. \tag{3.38}$$

In the total absence of harmonic generation, this coupling would be

$$\mu_{12}^{(3)}\mathcal{E}^3e^{-i3kz}\,. \tag{3.39}$$

It is now seen how the natural coupling is suppressed by the interference going to zero, if the single-state condition is perfectly fulfilled.

Note, too, that these last expressions show how phase matching or lack of same affects the system. In conventional treatments, one looks at the total phase mismatch. It is seen that in the cancellation picture, the phase mismatch (or $\chi^{(1)}$) must be divided in a resonant and a nonresonant part, and *the ratio of these* will determine the behavior of the system.

J. Cancellation in a focused beam

All the previous work was done in the geometry of an infinite plane wave. Most experiments, however, are performed in a focused geometry. It turns out that cancellation works just as well here, under exactly the same conditions. Having gone through the transition from the complete density-matrix formalism to the much simpler susceptibility approach and discussed the validity and conditions for this transition, we shall now continue in the susceptibility picture without further discussion.

Using the same notation as before, the fundamental is taken to be the Gaussian beam

$$\mathcal{E}(z)=\mathcal{E}_0e^{-ikz}(1-i\xi)^{-1}\exp\left[\frac{-k(x^2+y^2)}{b(1-i\xi)}\right], \tag{3.40}$$

b being the confocal parameter (roughly the interaction length) and ξ a reduced z variable, $\xi=2(z-f)/b$. f is the position of the focus. Note, that due to the choice of sign of ωt and kz in (2.1), the above $\mathcal{E}$, and in the following, these fields will be the complete conjugates of those of Refs. [18,19]. Ward and New and Bjorklund find [18,19] that the third harmonic field at (x,y,z), $\xi=2(z-f)/b$ (see Fig. 5) is given by the expression

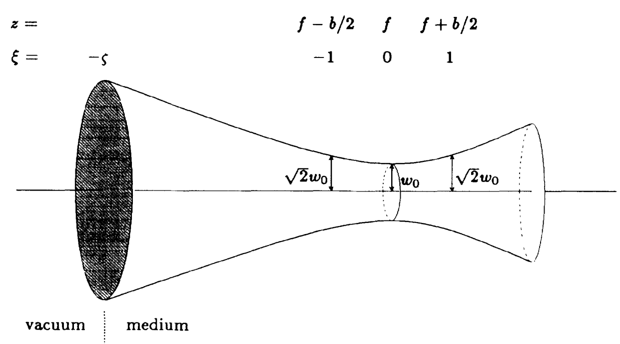

FIG. 5. The setup of the Gaussian beam. The vacuum-medium interface is at $\xi=2(z-f)/b=-\zeta$, the focus at $\xi=0$, and the focal region is roughly contained in $\zeta=\pm1$. ω_0 is the beam waist.

$$\mathcal{E}_3(z)=\frac{-i\pi(k_0)^2 b\chi^{(3)}}{k_3}\mathcal{E}_0^3 e^{-i3kz}(1-i\xi)^{-1} \times\exp\left[\frac{-3k(x^2+y^2)}{b(1-i\xi)}\right] \times\int_{-\zeta}^{\xi}\frac{\exp\left[\frac{ib}{2}\Delta k(\xi'-\xi)\right]}{(1-i\xi')^2}d\xi' , \quad (3.41)$$

$$\Delta k=k_3-3k . \quad (3.42)$$

In the following, k_3 is taken to contain both $\chi^{\mathrm{NR}(1)}$ *and* $\chi^{\mathrm{R}(1)}$ and k_0 is the wave vector for a harmonic wave in vacuum ($=3\omega/c$). The integral is strongly dependent on Δk and is responsible for all the phase-matching effects.

In the absence of ionization (Δk real), the generated power of harmonic peaks for Δk satisfying $\Delta kb\simeq -2$. We will now investigate what happens when Δk has a large imaginary part, as was the requirement in the plane-wave case. Letting $\Delta k=\Delta k_1+i\Delta k_2$, the integral is

$$\int_{-\zeta}^{\xi}\frac{\exp\left[\left[\frac{\Delta k_2 b}{2}-i\frac{\Delta k_1 b}{2}\right](\xi-\xi')\right]}{(1-i\xi')^2}d\xi' . \quad (3.43)$$

Since

$$k_3=\frac{\omega_3}{c}[1+4\pi\chi^{(1)}(3\omega)]^{1/2} , \quad (3.44)$$

and since the resonant part contributes strongly,

$$\chi^{(1)}\simeq\chi^{\mathrm{R}(1)}\propto\frac{1}{\Delta+i\Gamma/2}=\frac{\Delta-i\Gamma/2}{\Delta^2+\Gamma^2/4} , \quad (3.45)$$

so $\Delta k_2<0$. That means that the exponential in the numerator will only be important for $\xi'\simeq\xi$, and if the denominator varies slowly, it can be approximated by $(1-i\xi)^{-2}$. This is possible if

$$\left|\frac{2}{\Delta k_2 b}\partial_z(1-i\xi')^2|_{\xi'=\xi}\right| \ll |(1+i\xi)^2| \quad (3.46)$$

or

$$|\Delta k_2 b(1-i\xi)/4| \gg 1 . \quad (3.47)$$

Since $\xi\simeq 1$ inside the focusing region, the condition roughly says that

$$-\Delta k_2 b \gg 1 . \quad (3.48)$$

Explicitly written out, (3.48) gives

$$b \gg \frac{c}{2\pi\omega_3}\frac{\Delta^2+\Gamma^2/4}{|\mu_{12}|^2 N n(z)\Gamma/2} . \quad (3.49)$$

Equation (3.49) is exactly equivalent to the pressure condition of the plane-wave analysis, with the confocal parameter b now taking the role of the interaction length.

Taking the denominator outside the integral, one finds

$$\int_{-\zeta}^{\xi}\frac{\exp\left[\left[\frac{\Delta k_2 b}{2}-i\frac{\Delta k_1 b}{2}\right](\xi-\xi')\right]}{(1-i\xi')^2}d\xi' \quad (3.50)$$

$$\simeq\frac{1}{(1-i\xi)^2}\int_{-\zeta}^{\xi}\exp[\tfrac{1}{2}(\Delta k_2 b+i\Delta k_1 b)(\xi-\xi')]d\xi' \quad (3.51)$$

$$=\frac{1}{(1-i\xi)^2}\frac{1}{-b/2(-i\Delta k)} \times\{\exp[b/2(-i\Delta k)(\xi-\xi')]\}_{-\zeta}^{\xi}$$

$$\simeq\frac{1}{(1-i\xi)^2}\frac{-2i}{b\Delta k} . \quad (3.52)$$

Inserting (3.50)–(3.52) in the expression for $\mathcal{E}_3$ yields

$$\mathcal{E}_3=\frac{-2\pi(k_0)^2\chi^{(3)}}{\Delta k k_3}\mathcal{E}_0^3\exp(-i3kz)\frac{1}{(1-i\xi)^3} \times\exp\left[\frac{-3k(x^2+y^2)}{b(1-i\xi)}\right] =-\frac{2\pi(k_0)^2\chi^{(3)}}{k_3\Delta k}\mathcal{E}^3 , \quad (3.53)$$

and we have the desired result. It will be seen that the factor in front of the cube of the fundamental is exactly what is needed for cancellation. Using

$$\Delta k=k_3-3k=k_0[1+4\pi\chi^{(1)}(3\omega)]^{1/2}-3k \simeq k_0 2\pi\chi^{(1)} , \quad (3.54)$$

we find

$$\mathcal{E}_3\simeq-\frac{\chi^{(3)}}{\chi^{(1)}}\mathcal{E}^3 e^{i\Delta k^{\mathrm{NR}}z} , \quad (3.55)$$

which is exactly the result from the plane-wave analysis, only now in a focused beam. It is actually an expected result; the most dominant feature of harmonic generation in this treatment is that the transient regime is short, and the harmonic field settles quickly at a steady-state value. Therefore, the harmonic field at any point relates only to the fundamental and the atomic response in a small slice of the interaction region. If this slice is thin enough, even the Gaussian beam will look like a plane wave, and the result will be the same. Cancellation has remarkable stability due to the pressure condition.

Using again the single-state assumption (for both polarization and harmonic generation at ω_3) to find

$$\chi^{(1)}\simeq\chi^{\mathrm{R}(1)}=\frac{N\mu_{12}^{(3)}\mu_{21}}{\Delta+i\Gamma/2} \quad (3.56)$$

and

$$\chi^{(3)}\simeq\chi^{\mathrm{R}(3)}=\frac{N\mu_{12}\mu_{21}}{\Delta+i\Gamma/2} , \quad (3.57)$$

we once more have

$$\mathcal{E}_3 = -\frac{\mu_{12}^{(3)}}{\mu_{12}} \mathcal{E}^3 \ . \tag{3.58}$$

The result is exactly the same as the one for the plane wave. In short, the above derivation shows that a focused beam does not really introduce any complications; the cancellation will still work as in a plane wave. It does, however, give one a much more satisfying way of discussing the interplay between cancellation and phasematching, as will be explored below.

K. Phase-matching considerations

As noted in the end of the plane-wave analysis, phase matching takes on a slightly different form when working with cancellation. Usually, one looks for the peak intensity of the generated harmonic. This will (for weak ionization) be at a detuning satisfying $\Delta k b \simeq -2$ (real),

$$\Delta k_1 + i\Delta k_2 \simeq 3k 2\pi N \frac{\mu_{12}\mu_{21}(\Delta - i\Gamma/2)}{\Delta^2 + \Gamma^2/4} \ , \tag{3.59}$$

so for a reasonably large detuning $\Delta \gg \Gamma$, one has $\Delta k \propto N/\Delta$, and the peak of harmonic will shift towards larger and larger detunings for larger pressures. This is in perfect accord with the conventional view of harmonic generation.

At the detuning corresponding to the harmonic peak, $\Delta \gg \Gamma$ and therefore $b|\Delta k_2| \ll b|\Delta k_1| \simeq 2$ in violation of (3.48), so cancellation cannot take place at the peak of harmonic, but requires a much smaller detuning. The overall picture is then that one will have a harmonic profile peaking at some detuning, and the cancellation regime will be at a much smaller detuning. Or, another way of saying this is that one has to shift the harmonic profile well past the detuning where cancellation is desired. It is seen that the object of large pressure is definitely not to generate a sufficient amount of harmonic, but rather to make phase matching demand that there be almost no harmonic generated.

Notice another very surprising effect of the focused-beam cancellation result. Imagine that the desired cancellation refers to the ionization of a state placed at four-photon resonance, and the energy is such that three photons fall just *below* the 6*s* state. Conventionally, one would say that on the red side of a three-photon resonance, no global harmonic is generated (due to phase-matching considerations in a focused beam) and therefore the harmonic will not be able to interfere with the fundamental, and cancellation should not take place.

The argument is flawed, though, in that existence of global harmonic output and cancellation are not necessarily connected. In the present treatment, the conditions for cancellation are symmetric in $\pm\Delta$, so the cancellation is here predicted to work equally well for four-photon resonances that correspond to a detuning to the red of the 6*s* as for the ones that correspond to a detuning to the blue of 6*s*. An intuitive way to explain this is that for cancellation to work, the harmonic field must behave as though it is locally generated and immediately absorbed again, thus giving only the driven harmonic field at any point in the interaction volume. The reason for the harmonic to be absent on the red side of a generating state is a global interference between a harmonic generated symmetrically around the focus. Obviously under cancellation conditions, the field is determined and used for cancellation completely locally, and cancellation should not be affected by large-scale interference effects.

IV. CALCULATIONS

A calculation of the atomic parameters of Xe has been performed to examine the various conditions with respect to whether cancellation is possible in a three-photon picture for the resonances 4*f* and 5*f* at four photons. For these states, three fundamental photons are detuned, respectively, $\simeq 100\ \text{cm}^{-1}$ and $2000\ \text{cm}^{-1}$ to the blue of the 6*s* state. It would seem that quite different behavior could be expected, since the single-state assumption calls for 6*s* to be entirely dominant in all aspects when trying to excite the higher states.

The calculations are based on the work of L'Huillier, Tang, and Lambropoulos [20]. By use of their multichannel quantum-defect theory (MQDT) program and fitted quantum defects for Xe, dipole matrix elements could be calculated for bound-bound and bound-continuum transitions. All multiphoton matrix elements are calculated by a truncated summation method excluding the continuum. The $J=0,1,2,3$ series were included with, respectively, 15, 49, 48, and 41 states. Convergence tests were performed by truncating the number of atomic states to approximately half the above-mentioned size, without any considerable change in the multiphoton matrix elements. The results are as follows.

A. Susceptibility for harmonic generation

The susceptibility was calculated according to (3.22) and (3.23) including all four non-time-ordered diagrams. The effect of Γ has not been included; therefore, a singularity arises at the 6*s* position. Since the importance in the cancellation theory is placed upon the relative magnitudes between (6*s*-)resonant processes and all others, $\chi^{(3)}$ has been explicitly split in a resonant and nonresonant part. Figure 6 shows the result. It is seen that the resonant 6*s* feature is very prominent, superseding the back-

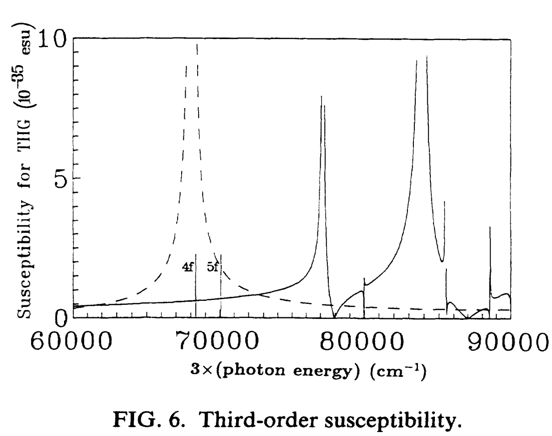

FIG. 6. Third-order susceptibility.

ground out to a detuning of $\simeq 3500\ cm^{-1}$ from the 6s state ($68\,045\ cm^{-1}$). For four photons resonant with the 4f states, the third photon is completely within the 6s feature, whereas for the 5f states, the third photon is in a region where the 6s is still rather prominent, but not all dominating. It seems that the single-state condition is extremely well satisfied for the 4f states, and reasonably well for 5f, with respect to $\chi^{(3)}$.

B. Polarizability at 3ω

The polarizability is calculated from (3.24). Again the resonant path involving 6s is separated from all the other ones. The results are seen in Figs. 7 and 8. In the first figure the absolute value of $\chi^{(1)}$ is shown for better comparison between the resonant and background part. It is seen that the picture is very similar to the one for $\chi^{(3)}$ concerning the region of dominance for 6s.

On the second graph, the total absolute value of $\chi^{(1)}$ is shown. As the dispersion changes sign when passing from one side of a resonance to the other, the path from resonant 6s and the path from resonant 6s′ (the singularity to the right of the 6s feature) will interfere destructively at some frequency between the two. Zero is seen to be at $\simeq 73\,500\ cm^{-1}$. From comparisons with known oscillator strengths of Xe [21], it has been found that the dipole matrix element from the ground state to the 6s state in the calculation is a factor of $\sqrt{2}$ too large. This means that the whole 6s-resonant feature is a factor of 2 too large. Consequently, the above zero in dispersion is probably closer to $71\,500\ cm^{-1}$.

As $\Delta k^{R+NR} \propto \chi^{(1)} \propto N/(\Delta + i\Gamma/2)$, the phase-matching requirement that $\Delta k^{R+NR} b \simeq 2$ will be satisfied for increasing pressure by the maximum-generated harmonic shifting towards larger detunings, thus keeping $\chi^{(1)}$ constant. However, since $\chi^{(1)}$ and therefore Δk goes to zero and then becomes positive at the above-discussed frequency, the harmonic maximum will eventually reach this point and not be able to shift any further, thus presenting an effective cutoff frequency for harmonic generation from 6s. This is in excellent agreement with an observed third-harmonic cutoff at $140\ nm \simeq 71\,400\ cm^{-1}$ [14].

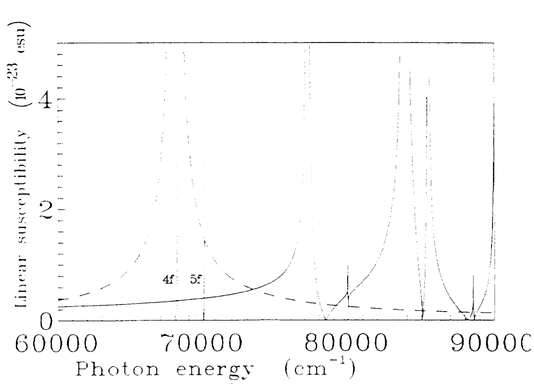

FIG. 7. $\chi^{(1)}$ separated (due to the near-resonant state 6s alone).

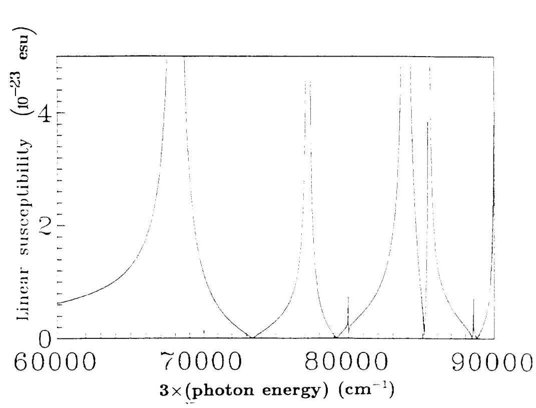

FIG. 8. $\chi^{(1)}$ total.

C. The importance of 6s in reaching the four-photon resonances

As a final test of the validity of the single-state condition, one has to test whether or not the pathway through 6s in reaching the higher states truly dominates the non-6s-resonant paths. It turns out that for both the $4f_{5/2}$ and $4f_{3/2}$, the resonant path is barely important at the three-photon energy corresponding to four-photon resonance with the 4f states. It seems to indicate that a three-photon cancellation is not really possible even for the 4f states, for which three photons are only detuned on the order of $100\ cm^{-1}$ from the 6s state. This is an extremely narrow dominance of the 6s state and is caused by the very low matrix elements from 6s to 4f.

However, an inspection of the 6s state in the MQDT calculation shows that the 6s state has 97.5% s character. Previous work has suggested that the d character of the 6s should be far larger—close to 30% [22,23]. An increased d character of the 6s state would increase the coupling between the 6s and 4f states and in this way make the resonant path more dominant. One could examine what the effect of a stronger d character of the 6s state would be by adding 30% d character by hand to the 6s state. The 6s state has a $^2P_{3/2}$ designation, so for the d waves, the two channels $^2P_{3/2}d_{3/2}$ and $^2P_{3/2}d_{5/2}$ will dominate the channel $^2P_{1/2}d_{3/2}$ in the mixing. To exam-

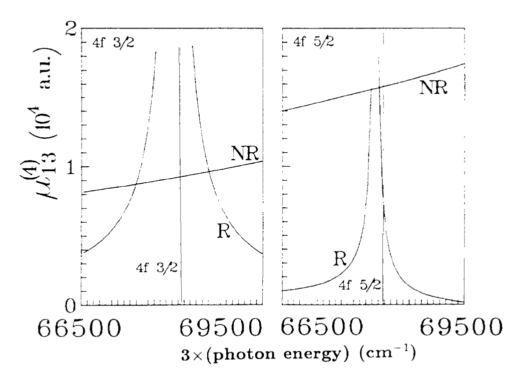

FIG. 9. Four-photon matrix element for modified 6s to 4fs.

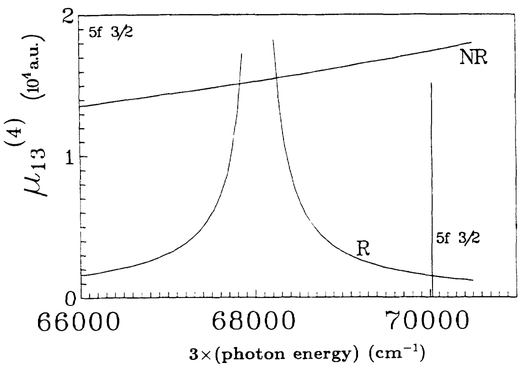

FIG. 10. Four-photon matrix element to $5f$.

ine the magnitude of the effect, the two d waves were included with 15% each, either with same or opposite sign in the $6s$ state.

Figure 9 shows the result obtained by using opposite signs for the two d waves. $4f_{3/2}$ now has a very strong and dominating resonant path at the detuning required for four-photon resonance, while $4f_{5/2}$ has a very small resonant path (only half the nonresonant). Taking the same sign for the two d waves gives the exact opposite picture with respect to which of the $4f$ states has the strong resonant path and which has the vanishing one.

In the experiment [14], the $4f_{3/2}$ was indeed seen to have a very strong peak that would cancel at high pressure. $4f_{5/2}$ has a small resonance peak, and it would not cancel. We can get total consistency with the experiment by this manual addition of two d waves of opposite sign to $6s$ (giving the results in Fig. 9). We believe this provides sufficient evidence that the cancellation of the $4f$ peaks in Xe can be understood and explained by the three-photon mechanism proposed in this paper.

Figure 10 shows the four-photon matrix element leading from the ground state to the $5f_{3/2}$. (The result is similar for $5f_{5/2}$.) It seems that here the nonresonant path is really dominant. The experiments, though, see weak cancellation of the $5f$ states. Figure 10 shows a four-photon matrix element, which means that an error of 2 in some crucial matrix element could give an error of an order of magnitude. This is what is needed to again make the resonant paths dominant, and the three-photon mechanism provides the explanation for the observed cancellation.

D. Interpretation

Charalambidis *et al.* [14] have obtained spectra that show how the four-photon resonances gradually cancel as one increases the pressure. They have taken scans of the third-harmonic profile for these increasing pressures as a function of detuning from the $6s$. In light of the theoretical treatment given in our paper, we interpret the spectra as follows. For very low pressure, the harmonic generation has a very low efficiency, and the observed ionization peaks are mostly the results of 4+1 REMPI. As shown, $4f_{3/2}$ sees the intermediate $6s$ state and is enhanced tremendously by it.

As the pressure is increased, the harmonic profile slowly grows and shifts over the three-photon position corresponding to resonance with the four-photon states. This gives a tremendous enhancement of the $4f_{3/2}$ peak, since one laser photon and one fundamental are near-resonant processes going to the $4f$ state. Note that the theory predicted that cancellation would not take place if the harmonic profile peaked at the resonance position. As the ionization peak is enhanced, a dip is observed in the harmonic profile from depletion of the harmonic due to this ionization. The coupling between $6s$ and $4f_{5/2}$ is very small, and consequently there is no intermediate resonance here to enhance the peak or cause a dip in the harmonic.

As the pressure is increased further, the harmonic shifts through and away from the $4f$ states and is now controlled (at a three-photon frequency corresponding to $4f$ resonance) by the large imaginary part of the resonant phase mismatch. This leads to a totally flat harmonic structure, an almost complete absence of harmonic. And at this point, suddenly the size of $4f_{3/2}$ goes dramatically down (compared to the $J=4$ states, which are not affected by a harmonic), and finally settles at a level much below the low-pressure size and close to the size of $4f_{5/2}$. It is as the theory predicts—the pressure condition for cancellation that the harmonic profile is far from the desired resonance. It is also in good agreement with the fact that the $4f_{5/2}$ peak is always a non-$6s$-resonant process, and that the effect of cancellation is to remove the resonant process from the $4f_{3/2}$ process.

V. CONCLUSION

We have shown theoretically that a cancellation of ionization of four-photon resonances, by means of a slightly off-resonant version of three-photon cancellation, is possible. A number of conditions were derived, and these have been investigated by means of a MQDT calculation of the multiphoton matrix elements. By comparison with recent experiments, we concluded that the proposed three-photon mechanism can explain the observed deenhancement of the resonance peaks.

The treatment of cancellation in a focused beam allowed us to explain in great detail how the phase-matching considerations from conventional treatments of THG have to combine with the theory of cancellation. We were able to completely explain the pressure dependence of the harmonic profile and the total lack of harmonic at the three-photon position under cancellation conditions. We stress the fact that cancellation exactly on three-photon resonance (as has been treated before) only has one condition to fulfill, that is the pressure condition. It can always be fulfilled, no matter what the atomic parameters are, as long as one goes to high enough pressure. Off-resonance cancellation (as discussed here), however, places very specific demands on the atomic parameters, and they are completely pressure independent. To assess the question of whether or not an off-resonance cancellation is possible, one will then be unable to ignore the question of atomic structure.

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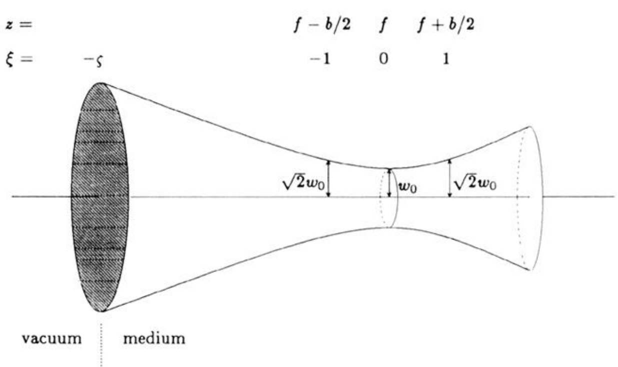

FIG. 5. The setup of the Gaussian beam. The vacuum-medium interface is at $\xi = 2(z-f)/b = -\zeta$, the focus at $\xi = 0$, and the focal region is roughtly contained in $\zeta = \pm 1$. ω_0 is the beam waist.