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# Theory of third-harmonic generation in metal vapors under two-photon resonance conditions

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The density-matrix formalism is used to develop the theory of two-photon-resonant third-harmonic generation in metal vapors taking into account saturation, ionization, laser-induced Stark shifts, and variations in the wave-vector mismatch as a result of population redistribution. It is shown that for third-harmonic generation in the ultraviolet and the vacuum-ultraviolet regions, where $3\omega$ exceeds the ionization limit of the metal vapor, two-photon-resonant three-photon ionization will be the main limiting process. This will also be true for four-wave parametric processes. For efficient energy conversion, the two-photon-resonant metal vapor must be phase matchable to allow large vapor density and cell length. Otherwise, the low incident intensity limits, set by the saturation and the ionization effects, cannot be efficiently converted in only one coherence length. The theory is applied to two-photon-resonant tripling of the ruby laser in cesium vapor.

## I. INTRODUCTION

Third-harmonic generation in metal vapors has, for many years, been considered as a means of extending the range of available coherent radiation sources beyond the 200-nm absorption limit of nonlinear crystal frequency converters. Harris and co-workers proposed third-harmonic generation in phase-matched alkali metal vapors and have recently reported[1] 10% energy conversion efficiency for tripling of 1.064-$\mu$m radiation in a phase-matched mixture of rubidium and xenon. Since it was a nonresonant process, the achieved high-conversion efficiency required a long vapor cell (1.5 m), high total pressure (1200 Torr), and high incident intensity ($10^{10}$ W/cm$^2$) which caused self-focusing. A different approach[2] that has been suggested is to make use of a two-photon resonance, which enhances the third-order susceptibility by many orders of magnitude, without increasing the absorption either at the incident or at the generated frequency, as is the case for one- and three-photon resonances, respectively. Two-photon-resonant (TPR) third-harmonic generation has been reported recently in cesium,[3] thallium,[4] and strontium.[5] However, the conversion efficiency in all three cases has been very low ($10^{-10}$).

It is the purpose of this paper to examine the limitations[6] and the special problems associated with TPR third-harmonic generation in metal vapors. The density-matrix formalism is used to describe the harmonic generation process in the two-level approximation, which is adequate as long as the incident frequency is far from any one-photon resonance between discrete bound states. We do, however, take into account the loss of atoms due to ionization which inevitably occurs in all three experiments on TPR third-harmonic generation mentioned above. Since the third-harmonic photon will normally exceed the ionization limit of the metal vapor, as in the above three cases,[3-5] the TPR three-photon ionization will be the main limiting process in TPR third-harmonic generation. To indicate the importance of the ionization, we mention here that in cesium under TPR conditions, a 30-nsec 100-MW/cm$^2$ ruby laser pulse will ionize 96% of the interacting atoms. The effect of ionization arises quite naturally in the density-matrix formalism together with saturation and the laser-induced ac Stark effects. In previous papers[3-5] on TPR third-harmonic generation, Stark shifts and ionization have not been taken into account. In Ref. 3 an attempt was made to interpret experimental data solely on the basis of population saturation of the two-photon excited state. As we have shown in an earlier paper,[6] however, the observed intensity dependence of third-harmonic generation can be adequately explained only when ionization and laser-induced Stark shifts are taken into account. The analysis has also considered the effects of population redistribution on the phase matching conditions; the possible influence of stimulated emission from the two-photon excited state; and laser multimode effects.

Sections II–IV are devoted to the development of the theory of TPR third-harmonic generation which is then applied, in Sec. V, to TPR frequency tripling of the ruby laser in cesium vapor. The results of our calculations are compared with experimental data[3] and the limitations in achieving high-energy conversion efficiency are discussed.

## II. DENSITY-MATRIX EQUATIONS

In this section, we derive equations describing TPR third-harmonic generation for the case shown in Fig. 1, that is, when the third-harmonic photon

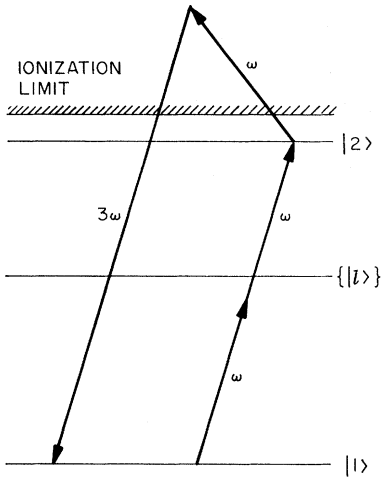


FIG. 1. Schematic diagram of TPR third-harmonic generation with $3\omega$ exceeding the ionization limit. $\{|l\rangle\}$ is the set of all levels, bound or free, with allowed dipole transitions to the TPR levels $|1\rangle$ and $|2\rangle$.

exceeds the ionization limit of the atom. This will usually be the case[3-5] in metal vapors with ruby and optical dye lasers. We begin with the equation of motion for the density-matrix operator $\rho$

$$i\hbar \frac{\partial \rho}{\partial t} = [H_a + H'(t), \rho], \tag{1}$$

where $H_a$ is the unperturbed atomic Hamiltonian and $H'(t)$ is the time-dependent interaction Hamiltonian which in the dipole approximation is given by

$$H'(t) = -\mu E(t), \tag{2}$$

where $\mu$ is the atomic-dipole operator. The incident electric field is as usual written in the form

$$E(t) = \epsilon(t)e^{i\omega t} + \epsilon^*(t)e^{-i\omega t}, \tag{3}$$

where $\epsilon(t)$ is a slowly varying complex amplitude. The generated harmonic field will not be included in the interaction Hamiltonian as it is expected to be negligible in comparison to the incident field. The only density matrix elements which we need to consider are $\rho_{11}, \rho_{22}, \rho_{12}$; the sets $\{\rho_{1l}\}, \{\rho_{2l}\}$; and their complex conjugates. The level $|l\rangle$ stands for any level, bound or free (or even autoionizing), for which the dipole matrix element $\mu_{1l}$ and/or $\mu_{2l}$ is nonzero.

The following equations,

$$\left(\frac{\partial}{\partial t} + \frac{1}{\tau}\right)\rho_{22} = -i\hbar^{-1}E(t)\sum_l (\rho_{2l}\mu_{l2} - \mu_{2l}\rho_{l2}), \tag{4}$$

$$\left(\frac{\partial}{\partial t} + i\omega_{12} + \frac{1}{T}\right)\rho_{12} = -i\hbar^{-1}E(t)\sum_l (\rho_{1l}\mu_{l2} - \mu_{1l}\rho_{l2}), \tag{5}$$

$$\left(\frac{\partial}{\partial t} + i\omega_{1l}\right)\rho_{1l} = -i\hbar^{-1}E(t)\sum_{k=1,2} (\rho_{1k}\mu_{kl} - \mu_{1k}\rho_{kl}), \tag{6}$$

$$\left(\frac{\partial}{\partial t} + i\omega_{2l}\right)\rho_{2l} = -i\hbar^{-1}E(t)\sum_{k=1,2} (\rho_{2k}\mu_{kl} - \mu_{2k}\rho_{kl}), \tag{7}$$

are obtained from Eq. (1) by expanding the commutator and using the eigenvalues of $H_a$, where $H_a|l\rangle \equiv \hbar\omega_l|l\rangle$, $\omega_1 - \omega_l \equiv \omega_{1l}$, etc. In Eqs. (4) and (5), $\tau$ represents the lifetime of level $|2\rangle$ (radiative or collisional, whichever is shorter), and $T$ is the transverse relaxation time. Each matrix element $\rho_{ij}$ is expanded in harmonics of the incident frequency, i.e.,

$$\rho_{ij}(t) = \sigma_{ij}(t) + \sum_{n>0} [\sigma_{ij}^{(n)}(t)e^{in\omega t} + \sigma_{ji}^{(n)*}(t)e^{-in\omega t}], \tag{8}$$

where $\sigma_{ij}$, $\sigma_{ij}^{(n)}$, and $\sigma_{ji}^{(n)*}$ are slowly varying complex amplitudes. Note that $\sigma_{ij}^{(n)}$ and $\sigma_{ji}^{(n)}$ are not complex conjugates of each other. For the diagonal elements $\rho_{11}$ and $\rho_{22}$ we retain only the first term in the expansion, i.e., $\sigma_{11}$ and $\sigma_{22}$, respectively. For the off-diagonal element $\rho_{12}$ and its complex conjugate, owing to the parity selection rule which implies $\mu_{12} = 0$, the first allowed harmonic is the second (only even harmonics allowed) and therefore

$$\rho_{12}(t) = \sigma_{12}^{(2)}e^{i2\omega t} + \sigma_{21}^{(2)*}e^{-i2\omega t}. \tag{9}$$

For the nonresonant elements $\rho_{1l}$, $\rho_{2l}$, coupling levels $|1\rangle$ and $|2\rangle$ with the other levels of the atom, we retain the first and third (odd) harmonics; for example,

$$\rho_{1l}(t) = \sigma_{1l}^{(1)}e^{i\omega t} + \sigma_{l1}^{(1)*}e^{-i\omega t} + \sigma_{1l}^{(3)}e^{i3\omega t} + \sigma_{l1}^{(3)*}e^{-i3\omega t}. \tag{10}$$

Substituting into Eqs. (6) and (7) and neglecting the derivative of the slowly varying amplitudes, we obtain

$$\sigma_{1l}^{(1)} = \frac{\epsilon\sigma_{11}\mu_{1l} + \epsilon^*\sigma_{12}^{(2)}\mu_{2l}}{\hbar(\omega + \omega_{1l})},$$

$$\sigma_{l1}^{(1)*} = -\frac{\epsilon^*\sigma_{11}\mu_{1l} + \epsilon\sigma_{21}^{(2)*}\mu_{2l}}{\hbar(-\omega + \omega_{1l})}; \tag{11}$$

$$\sigma_{1l}^{(3)} = -\frac{\epsilon\sigma_{12}^{(2)}\mu_{2l}}{\hbar(3\omega + \omega_{1l})},$$

$$\sigma_{l1}^{(3)*} = -\frac{\epsilon^*\sigma_{21}^{(2)*}\mu_{2l}}{\hbar(-3\omega + \omega_{1l})}; \tag{12}$$

the equations for $\sigma_{2l}^{(1)}$, $\sigma_{l2}^{(1)*}$, $\sigma_{2l}^{(3)}$, and $\sigma_{l2}^{(3)*}$ can be obtained from Eqs. (11) and (12) by simply interchanging the subscripts 1 and 2. From Eq. (5), we obtain the equation

$$\left(\frac{\partial}{\partial t}+i(2\omega-\omega_{21})+\frac{1}{T}\right)\sigma_{12}^{(2)} = -i\hbar^{-1}\sum_l(\epsilon\sigma_{1l}^{(1)}\mu_{l2}+\epsilon^*\sigma_{1l}^{(3)}\mu_{l2} - \epsilon\mu_{1l}\sigma_{l2}^{(1)}-\epsilon^*\mu_{1l}\sigma_{l2}^{(3)}) \quad (13)$$

for the resonant slowly varying amplitude $\sigma_{12}^{(2)}$. The antiresonant amplitude $\sigma_{21}^{(2)}$ will be neglected. Replacing $\sigma_{1l}^{(1)}$, $\sigma_{1l}^{(3)}$, $\sigma_{l2}^{(1)}$, and $\sigma_{l2}^{(3)}$ by expressions given in Eqs. (11) and (12), the above equation reduces to

$$\left(\frac{\partial}{\partial t}+i(2\omega-\omega_{21})+\frac{1}{T}\right)\sigma_{12}^{(2)} = i\hbar^{-2}\sum_l\left(\frac{\mu_{1l}\mu_{l2}}{\omega+\omega_{l2}}\sigma_{22}+\frac{\mu_{1l}\mu_{l2}}{\omega+\omega_{1l}}\sigma_{11}\right)\epsilon^2 + i\hbar^{-2}\sum_l\left(\frac{|\mu_{2l}|^2}{\omega+\omega_{1l}}+\frac{|\mu_{2l}|^2}{3\omega+\omega_{1l}} + \frac{|\mu_{1l}|^2}{\omega+\omega_{l2}}+\frac{|\mu_{1l}|^2}{3\omega+\omega_{l2}}\right)|\epsilon|^2\sigma_{12}^{(2)}. \quad (14)$$

If we now make use of the TPR condition, $\omega_{21}=2\omega$ (which need not be exact as long as we are far from one-photon resonances) and of identity relations such as $\omega_{1l}=\omega_{12}+\omega_{2l}$, Eq. (14) takes the final form

$$\left[\frac{\partial}{\partial t}+i(2\omega-\omega_{21}-\delta\omega_{21})+\left(\frac{1}{T}+\frac{\gamma}{2}\right)\right]\sigma_{12}^{(2)} = i\hbar^{-2}(\sigma_{22}-\sigma_{11})r_{12}\epsilon^2, \quad (15)$$

where $\delta\omega_{21}$ is the relative laser-induced Stark shift for levels $|1\rangle$ and $|2\rangle$. This shift can be expressed in terms of the real parts of the polarizabilities of these levels as

$$\delta\omega_{21}=\hbar^{-1}(\alpha_1'-\alpha_2')|\epsilon|^2, \quad (16)$$

with the polarizabilities given by

$$\alpha_1=\alpha_1'=\hbar^{-1}\sum_l\frac{2\omega_{1l}|\mu_{1l}|^2}{\omega_{1l}^2-\omega^2}, \quad (17)$$

$$\alpha_2=\alpha_2'-i\alpha_2''=\hbar^{-1}\sum_l\left(\frac{|\mu_{2l}|^2}{\omega_{l2}-\omega}+\frac{|\mu_{2l}|^2}{\omega_{l2}+\omega}\right). \quad (18)$$

The polarizability $\alpha_2$ of level $|2\rangle$ is complex because of the coupling with the continuum. $\gamma$ is the intensity-dependent ionization width, or equivalently, the ionization rate from level $|2\rangle$ which can be written

$$\gamma=2\hbar^{-1}\alpha_2''|\epsilon|^2. \quad (19)$$

The quantity $r_{12}$ (which can be thought of as an equivalent second-order matrix element) is defined by

$$r_{12}\equiv\sum_l\frac{\mu_{1l}\mu_{l2}}{\omega_{l2}+\omega}, \quad (20)$$

with the summation being over all (virtual) intermediate states, bound and free.

In a similar manner we obtain the reduced equation for $\sigma_{22}$,

$$\left(\frac{\partial}{\partial t}+\frac{1}{\tau}\right)\sigma_{22}=-2\hbar^{-2}\,\mathrm{Im}[r_{12}^*\sigma_{12}^{(2)}(\epsilon^*)^2]-\gamma\sigma_{22}, \quad (21)$$

and the obvious equation for the total atomic population

$$\frac{\partial}{\partial t}(\sigma_{11}+\sigma_{22})=-\gamma\sigma_{22}, \quad (22)$$

which takes the place of the usual, but now invalid, normalization condition $\sigma_{11}+\sigma_{22}=1$. It is evident that the loss of atoms due to ionization makes the rotating vector model of Feynman, Vernon, and Hellwarth[7] for the density matrix operator, invalid in this case. The interaction process no longer corresponds to a simple precession of $\rho$ about some torque vector and there are four vector components needed to describe $\rho$, namely, $\mathrm{Re}\sigma_{12}^{(2)}$, $\mathrm{Im}\sigma_{12}^{(2)}$, $\sigma_{11}$, and $\sigma_{22}$, making the three-dimensional visualization of the process impossible.

Note that the formalism developed above can be used to describe any TPR four-wave process of the type $\omega_1+\omega_2\pm\omega_3=\omega_4$. It can also be used to study details of TPR three-photon ionization, as we shall show in a subsequent paper. Similar equations have been obtained for two-photon processes, such as Raman scattering and two-photon absorption by Khronopoulo[8] using the method of averages. One problem which we have not considered in developing this formalism is the possibility of two-photon-pumped lasing from the excited state $|2\rangle$ to some intermediate state of lower energy. This could take place if the gain seen by a fluorescent photon from the two-photon-excited state, as it travels along the vapor cell with the incident beam is high enough to produce stimulated emission. With a typical stimulated emission cross section of $10^{-13}$ cm$^2$ and a vapor cell of a few cm in length, for lasing to take place it would require a population for level $|2\rangle$ of over $10^{14}$ atoms/cm$^3$. In addition, there will be no mirrors to provide feedback. In any case, if lasing did take place it would simply populate an intermediate state which otherwise would not be populated except for the few atoms undergoing spontaneous emission to that state from the two-photon-excited state. As lasing would most likely take place under strong saturation of the TPR transition, which itself limits the harmonic generation, the depopulation of level $|2\rangle$ due to lasing would be favorable. In this sense, lasing has a similar effect with the ionization which we believe is more important, since unlike lasing it is not a threshold process. Lasing will, in fact,

be limited by the ionization process which, by depleting the population of level $|2\rangle$, not only reduces the gain, but also the fluorescence which initiates lasing.

## III. CALCULATION OF THE MEDIUM POLARIZATION

Having obtained the equations for the density-matrix elements, we can now readily calculate the medium polarization resulting from the third-order interaction of the atom with the incident electric field which we now take to be of the form

$$E(z,t) = 2\epsilon(z,t)\cos(\omega t - kz + \phi) \equiv \bar{\epsilon}(z,t)e^{i(\omega t - kz)} + \text{c.c.}, \quad (23)$$

so that it represents a linearly polarized plane-wave pulse and defines $\bar{\epsilon}$. Neglecting the motion of the atoms, the variable $z$ appears as a simple parameter in the density matrix equations. Quantum mechanically, the polarization per atom is defined by

$$P(z,t) \equiv \mathrm{Tr}\rho(z,t)\mu = \sum_i (\rho_{1i}\mu_{i1} + \mu_{1i}\rho_{i1} + \rho_{2i}\mu_{i2} + \mu_{2i}\rho_{i2}), \quad (24)$$

from which we obtain the nonlinear polarization at $3\omega$,

$$P_{3\omega}^{\mathrm{NL}}(z,t) = \sum_i [\sigma_{1i}^{(3)}\mu_{i1} + \mu_{1i}\sigma_{i1}^{(3)} + \sigma_{2i}^{(3)}\mu_{i2} + \mu_{2i}\sigma_{i2}^{(3)}]e^{i(3\omega t - 3kz)} + \text{c.c.}, \quad (25)$$

and the polarization at $\omega$,

$$P_\omega(z,t) = \sum_i (\sigma_{1i}^{(1)}\mu_{i1} + \mu_{1i}\sigma_{i1}^{(1)} + \sigma_{2i}^{(1)}\mu_{i2} + \mu_{2i}\sigma_{i2}^{(1)})e^{i(\omega t - kz)} + \text{c.c.} \quad (26)$$

In Eq. (25), the second and third term inside the square brackets are proportional to the antiresonant amplitude $\sigma_{21}^{(2)}$ and can be neglected. The remaining two terms give

$$P_{3\omega}^{\mathrm{NL}}(z,t) = \sum_i \left(\frac{\mu_{2i}\mu_{i1}}{\omega_{i1} - 3\omega} + \frac{\mu_{2i}\mu_{i1}}{\omega_{i1} + \omega}\right) \times \hbar^{-1}\sigma_{12}^{(2)}(z,t)\bar{\epsilon}(z,t)e^{i(3\omega t - 3kz)} + \text{c.c.} \quad (27)$$

Note that, in general, due to the strong coupling of the atom with the TPR field, one cannot define a third-order susceptibility

$$P_{3\omega}^{\mathrm{NL}}(z,t) \equiv \chi_{3\omega}^{(3)}\bar{\epsilon}^3(z,t)e^{i(3\omega t - 3kz)} + \text{c.c.}, \quad (28)$$

as one can in the case of nonresonant third-harmonic generation. When a TPR is involved, the second-order atomic response represented by $\sigma_{12}^{(2)}$ can saturate and thus limit the third-harmonic generation. We can, however, use Eq. (28) in the weak-field limit in order to assess the potential of a given atom as a TPR third-harmonic generator. In this limit, the peak value of $\chi_{3\omega}^{(3)}$ is

$$\chi_{3\omega}^{(3)} = \sum_i \left(\frac{\mu_{2i}\mu_{i1}}{\omega_{i1} - 3\omega} + \frac{\mu_{2i}\mu_{i1}}{\omega_{i1} + \omega}\right) r_{12}\hbar^{-3}T. \quad (29)$$

Obviously, a strong TPR transition (large $r_{12}$) or a narrow resonance (large $T$) imply a large $\chi_{3\omega}^{(3)}$, but they also imply a low saturation intensity ($S = 4\tau T\hbar^{-4}|r_{12}|^2|\epsilon|^4$). If the coupled third and fourth steps of the third-harmonic generation process are strong, that would imply a large $\chi_{3\omega}^{(3)}$, but it would also imply strong ionization; which means substantial loss of atoms due to ionization by the strong incident beam and also absorption of the generated harmonic.

Abandoning metal vapors and going to noble gases, in order to avoid the ionization, would not help. Noble gases have third-order susceptibilities many orders of magnitude smaller than metal vapors. Thus one may choose to work with metal vapors and do the best one can. One way to reduce the effect of ionization in alkali vapors is to have a TPR between states of the same orbital angular momentum ($S \rightarrow S$), so that every channel out of the two-photon excited state can lead back to the ground state. Ionization will still, of course, take place, but at a weaker rate compared to an $S \rightarrow D$ TPR transition, for neighboring excited $S$ and $D$ states.

The expression for the polarization at the incident frequency given in Eq. (26) reduces to

$$P_\omega(z,t) = [\chi'_\omega(z,t) + i\chi''_\omega(z,t)]\bar{\epsilon}(z,t)e^{i(\omega t - kz)} + \text{c.c.}, \quad (30)$$

where

$$\chi'_\omega(z,t) = \alpha'_1(\omega)\sigma_{11}(z,t) + \alpha'_2(\omega)\sigma_{22}(z,t) + 2\hbar^{-1}\mathrm{Re}[r_{12}^* e^{-i2\phi(z,t)}\sigma_{12}^{(2)}(z,t)] \quad (31)$$

and

$$\chi''_\omega(z,t) = -\alpha''_2(\omega)\sigma_{22}(z,t) + 2\hbar^{-1}\mathrm{Im}[r_{12}^* e^{-i2\phi(z,t)}\sigma_{12}^{(2)}(z,t)]. \quad (32)$$

The linear polarization at $3\omega$ is not included in Eq. (24), because the harmonic field was not included in the interaction Hamiltonian. It can, however, be written easily as

$$P_{3\omega}(z,t) = [\chi'_{3\omega}(z,t) + i\chi''_{3\omega}(z,t)]\bar{\epsilon}_3(z,t)e^{i(3\omega t - k_3 z)} + \text{c.c.}, \quad (33)$$

where

$$\chi'_{3\omega}(z,t) = \alpha'_1(3\omega)\sigma_{11}(z,t) + \alpha'_2(3\omega)\sigma_{22}(z,t)\,, \tag{34}$$

$$\chi''_{3\omega}(z,t) = \alpha''_1(3\omega)\sigma_{11}(z,t) + \alpha''_2(3\omega)\sigma_{22}(z,t)\,, \tag{35}$$

and where the third-harmonic field is

$$E_3(z,t) \equiv \bar{\epsilon}_3(z,t)e^{i(3\omega t - k_3 z)} + \text{c.c.}\,, \tag{36}$$

which defines $\bar{\epsilon}_3$. Note that the susceptibilities at the incident and harmonic frequencies defined above, are all intensity dependent. This gives rise to complications in phase matching and to pulse propagation self-effects[8] which we discuss in Sec. IV.

## IV. WAVE EQUATIONS

The reduced density-matrix equations, obtained in Sec. II, are coupled to the wave equation for the incident field through the polarization at the incident frequency, calculated in Sec. III. In the slowly varying envelope and phase approximation, the second-order wave equation reduces to the first-order wave equations for the envelope and the phase:

$$\frac{\partial \epsilon}{\partial z} + \frac{1}{c}\frac{\partial \epsilon}{\partial t} = \frac{\omega N}{2c\epsilon_0}\chi''_\omega \epsilon\,, \tag{37}$$

$$\frac{\partial \phi}{\partial z} + \frac{1}{c}\frac{\partial \phi}{\partial t} = -\frac{\omega N}{2c\epsilon_0}\chi'_\omega\,, \tag{38}$$

where $N$ is the density of the metal vapor. The index of refraction is set equal to unity everywhere, except in the calculation of the wave-vector mismatch later on. The above equations would have to be solved numerically, together with the reduced density matrix equations; analytical solutions cannot be obtained in a general case. We can, however, study the above equations to investigate what happens to a pulse under TPR propagation and whether this can affect the third-harmonic generation process.

In Eqs. (31) and (32) for the real and imaginary parts of the susceptibility (which appear in the source term of the reduced wave equations), we make the following observations. First, the in-phase component of the TPR transition and the population redistribution produced by the out-of-phase component of the TPR transition and the ionization process, can cause self-phase modulation of the incident wave as well as self-focusing or self-defocusing in the case of Gaussian and focused beams.[8] Second, the ionization and the out-of-phase component of the TPR transition will cause attenuation, pulse reshaping and velocity changes. The third-harmonic generation will be affected by the self-phase modulation in that the phase-matching condition (phase matched or one coherence length) will break. If self-focusing or self-defocusing takes place the harmonic generation will be limited by them. The other effects will not be limiting.

For the third-harmonic field, the reduced wave equation for the complex amplitude is

$$\frac{\partial \bar{\epsilon}_3}{\partial z} + \frac{1}{c}\frac{\partial \bar{\epsilon}_3}{\partial t} = -i\frac{3\omega N}{2c\epsilon_0}\xi\sigma_{12}^{(2)}\epsilon e^{i(\phi - \Delta k z)}\,, \tag{39}$$

where

$$\xi = \hbar^{-1}\sum_l \left(\frac{\mu_{2l}\mu_{l1}}{\omega_{l1} - 3\omega} + \frac{\mu_{2l}\mu_{l1}}{\omega_{l1} + \omega}\right) \tag{40}$$

and

$$\begin{aligned}\Delta k &= 3k - k_3 \\ &= (3\omega N/2c\epsilon_0)\{[\alpha'_1(\omega) - \alpha'_1(3\omega)]\sigma_{11}(z,t) \\ &\quad + [\alpha'_2(\omega) - \alpha'_2(3\omega)]\sigma_{22}(z,t) \\ &\quad + 2\hbar^{-1}\mathrm{Re}[r_{12}^* e^{-i2\phi}\sigma_{12}(z,t)]\}\,.\end{aligned} \tag{41}$$

Since the polarizabilities of levels $|1\rangle$ and $|2\rangle$ are, in general, different, substantial population redistribution and loss of atoms through ionization produce changes in the wave-vector mismatch. Smaller changes are also produced by the third term in the right-hand side of Eq. (41). In phase-matched ($\Delta k = 0$) mixtures of metal vapors and noble gases these changes must be avoided as they will always reduce the conversion efficiency. However, in cases where the metal vapor is normally dispersive ($k_3 > 3k$) and phase matching by means of either a buffer gas or noncollinear incident beams is not possible, the population of level $|2\rangle$, and of other excited levels which may become populated, can play the role of the buffer gas and increase the coherence length ($L_c = \pi/\Delta k$) for third-harmonic generation. One such case is TPR tripling of the ruby laser in cesium vapor which we study in Sec. V. The reduction in the wave-vector mismatch as a result of population redistribution will be maximum when the polarizabilities of levels $|1\rangle$ and $|2\rangle$ have opposite signs and comparable magnitudes. Self-focusing due to population redistribution will not be a problem if the vapor density is low.

If the incident pulse is much longer than the effective length of the vapor cell, which is actually the case for ruby and dye laser pulses, we can neglect the time derivative in Eq. (39) and integrate over $z$ to obtain

$$\bar{\epsilon}_3(L,t) = -i\frac{3\omega N}{2c\epsilon_0}\xi\int_0^L \sigma_{12}^{(2)}(z,t)\epsilon(z,t)e^{i(\phi - \Delta k z)}\,dz\,, \tag{42}$$

where $L$ is the effective length of the vapor cell. Considering the very low efficiency of the multiphoton processes involved, and the fact that self-

phase modulation is a cumulative effect requiring path length, we can make the undepleted pump approximation and neglect self-phase modulation. For short vapor cells we can also neglect the local variations in the wave-vector mismatch. Allowing for time variation in the wave-vector mismatch we calculate the number of third-harmonic photons generated per pulse per unit area

$$N_{3\omega}=\frac{3\omega N^2L^2}{4\hbar c^2\epsilon_0^2}|\xi|^2\int\left(\frac{\sin[\Delta k(0,t)L/2]}{[\Delta k(0,t)L/2]}\right)^2 \times|\sigma_{12}^{(2)}(0,t)|^2I(0,t)\,dt\,, \qquad (43)$$

where $I(o,t)$ is the incident intensity. In the case of a rectangular pulse, we can obtain exact analytical solutions for the density matrix elements. These are decaying solutions of the form

$$\sigma=Ae^{-a_1t}+Be^{-a_2t}+e^{-a_3t}(C\cos bt+D\sin bt)\,. \qquad (44)$$

The reason for the exponentially decaying solutions is of course the loss of atoms due to ionization. The interaction never reaches a steady state and the incident field eventually ionizes all the atoms.

The fraction of atoms ionized per pulse is given by

$$F_{\text{ion}}=\gamma\int_0^{t_p}\sigma_{22}dt\,, \qquad (45)$$

where $t_p$ is the pulse width and $\gamma$ is the one-photon ionization rate from level $|2\rangle$ given in Eq. (19). The ionization is actually a three-photon absorption process from the ground level, but since it is also two-photon resonant, it reduces to a one-photon process feeding on the population of level $|2\rangle$. As a three-photon process, the ionization is stronger than any four-photon process like third-harmonic generation or four-photon parametric processes which take place simultaneously. Moreover, since it is an absorption process it does not require phase matching and at high intensities it can multiply through avalanche ionization, the ultimate catastrophe. But then, it is only a metal vapor.

## V. TWO-PHOTON RESONANT TRIPLING OF THE RUBY LASER IN CESIUM

Cesium has a near TPR with the ruby laser (6943 Å) between the $6s^2S_{1/2}$ and the $9d^2D_{3/2}$ energy levels which are separated by 28 828.9 $cm^{-1}$. This coincidence has been used by Ward and co-workers[3] for TPR tripling of a high-power ruby laser by thermal tuning. The weak-field third-order susceptibility [see Eq. (29)] for cesium under this particular TPR condition is $2.9\times10^{-30}$ esu/atom, assuming a collisional transverse relaxation time $T=2$ nsec. This value is larger, by a factor of $10^9$, than the nonresonant third-order susceptibility of helium at the ruby-laser frequency.[3] The relative laser-induced Stark shift for the $6s^2S_{1/2}$ and $9d^2D_{3/2}$ levels is $27.7I$ $sec^{-1}$ (the levels are pulled together) and the one-photon ionization rate from the excited $9d^2D_{3/2}$ state $2.2I$ $sec^{-1}$, where in both cases the intensity is in $W/cm^2$. In calculating these constants[6] the continuum was properly taken into account using quantum defect theory.

Using the experimental[3] values $\tau=35$ nsec, $T=2$ nsec, the vapor density[9] $N=2.6\times10^{15}$ atoms/$cm^3$ and the corresponding one coherence length $L=6.4$ cm (all atoms in the ground state), we have calculated the number of third-harmonic photons generated per pulse per $cm^2$ [Eq. (43)] as well as the fraction of atoms ionized per pulse [Eq. (45)], assuming a single-mode rectangular pulse of 30 nsec. Figures 2(a) and 2(b) show the dependence of $N_{3\omega}$ (solid line) and $F_{\text{ion}}$ (dashed line) on the detuning of the laser frequency from the Stark shifted two-photon resonance. For comparison we have also plotted the number of third-harmonic photons (dotted-dash line) calculated by neglecting the time variations in the wave-vector mismatch $[\Delta k(0,t)=\pi/L]$. It is clear that population redistribution reduces the wave vector mismatch and enhances the third-harmonic generation. The slight asymmetry of the resonance curves for $N_{3\omega}$ is due to the third term in the right-hand side of Eq. (41).

Note that for the intensities used, 33 and 100 $MW/cm^2$, power broadening has increased the homogeneous width above the Doppler width [0.02-$cm^{-1}$ full width at half-maximum (FWHM)], thus our neglect of the Doppler broadening is justified. For intensities below 33 $MW/cm^2$ the Doppler broadening should be taken into account by numerically averaging Eqs. (43) and (45) as we have done in a previous paper.[6] Figure 2(a) (33 MW/$cm^2$) corresponds to one of the two resonances with the ground-state hyperfine-structure doublet in Fig. 2(g) of Ref. 3. Considering the spectral width of the laser (0.02 $cm^{-1}$) there is very good agreement between theory and experiment. Computer simulation results show that the on-resonance dip in the curves for $N_{3\omega}$, for which there is experimental evidence, is due to saturation of the TPR transition and in addition to the heavy loss of atoms through ionization. Near resonance, however, it is found that the weaker ionization reduces the saturation effect and makes the two peaks higher than what they would be in the absence of ionization.

Shown in Figs. 2(a) and 2(b) is the position (vertical bars) of the unperturbed two-photon resonance relative to the Stark-shifted two-photon resonance. The laser-induced Stark shift together

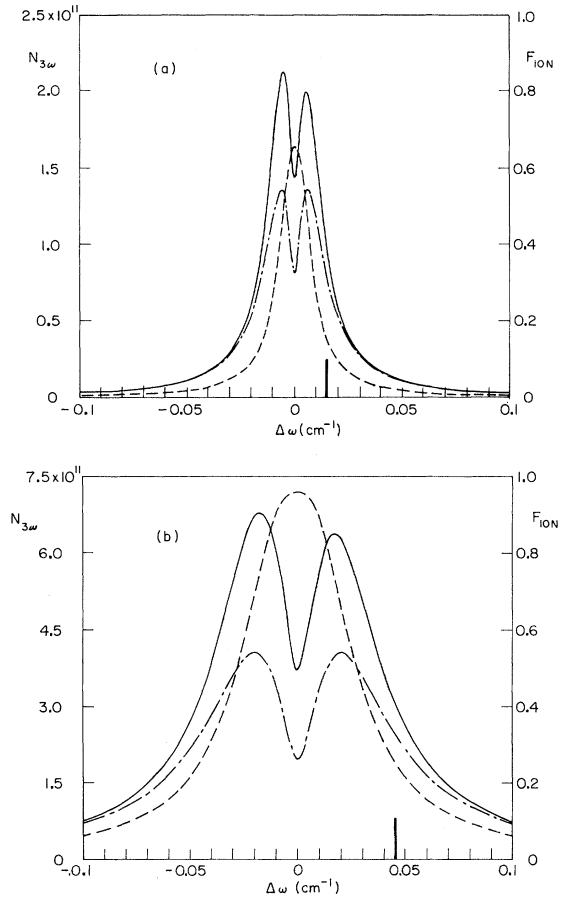


FIG. 2. Resonance curves for the number of third-harmonic photons ($N_{3\omega}$—solid line) generated per pulse per cm$^2$ and the fraction of interacting atoms ionized per pulse ($F_{ion}$—dashed line). The incident intensity is equal to (a) 33 MW/cm$^2$ and (b) 100 MW/cm$^2$; $\Delta\omega$ is the detuning $\omega - \frac{1}{2}(\omega_{21} + \delta\omega_{21})$. The vertical bars are located at the position $\Delta\omega = -\frac{1}{2}\delta\omega_{21}$, which is half the Stark shift. The dash-dot curve represents the number of third-harmonic photons calculated by neglecting the variations in the wave-vector mismatch ($\Delta k = \pi/L$).

with the ionization are responsible[6] for the quadratic intensity dependence of the third-harmonic generation reported in Ref. 3. For intensities greater than 33 MW/cm$^2$ these effects reduce the intensity dependence of $N_{3\omega}$ to about linear. By having the laser tuned to the unperturbed TPR, one avoids the stronger ionization and its complications at the two peaks of the resonance curve for $N_{3\omega}$, without any significant decrease in the conversion efficiency. The peak energy conversion efficiency at the laser intensities used in our calculations has saturated to about $2\times10^{-7}$. Since the hyperfine splitting (0.3 cm$^{-1}$) of the ground state in cesium was resolved in the experiment[3] and thus only half of the atoms were TPR the efficiency is reduced, by a factor of 4, to $5\times10^{-8}$. Ward *et al.* did not report the experimental efficiency in their 1975 work, but in their 1974 work the efficiency was about $10^{-10}$. Optical component absorption and nonuniform vapor density along the cell[3] could explain the discrepancy. Owing to the fact that phase matching in cesium is not possible, as it is normally dispersive at these frequencies, the calculated conversion efficiency of $5\times10^{-8}$ would seem to be the maximum attainable efficiency for tripling of the ruby laser.

In applying our model to TPR tripling of the ruby laser in cesium we have taken into account the dominant effects of ionization, saturation, and laser-induced Stark shifts, and have also allowed for variation in the wave-vector mismatch. From the other processes that could have taken place in the cesium experiment, the most important would be lasing (fluorescence amplification) from the $9D_{3/2}$ state to the $6P_{1/2}$ state. Estimates of the gain for this process show that it should have taken place under saturation of the TPR transition, as indeed has been mentioned in Ref. 3. As we pointed out in Sec. II, the depopulation of level $|2\rangle$ under saturation conditions is favorable to the process of third-harmonic generation. Calculations of the polarizability of the $6P_{1/2}$ state at $\omega$ and $3\omega$ show that populating that state reduces the wave vector mismatch even more than populating the $9D_{3/2}$ state.

The presence of five longitudinal modes in the output of the $Q$-switched ruby laser[3] does not change either the Stark shift or the one-photon ionization rate which were calculated for a single mode. This is because the ruby laser has no one-photon resonances with the cesium atom, and since these effects are linear in the intensity, the contributions from the various modes simply add up. Mode correlation effects would have enhanced the TPR transition[6] but there is no significant phase locking between the modes of a giant-pulse ruby laser. Therefore, except for the fact that the third-harmonic spectrum will be wider than the laser spectrum, the single-mode approximation should provide an adequate description of the experiment in cesium.

## VI. CONCLUSIONS

We have developed a simple formalism to describe TPR third-harmonic generation in metal vapors. The model takes into account saturation, laser-induced Stark shifts, variations in the wave-vector mismatch, and also the ionization process which takes place simultaneously with third-harmonic generation. In addition, the possible effects

of lasing, and of the presence of more than one laser mode have been examined. Applying the model to TPR tripling of the ruby laser frequency in cesium vapor, we find that the process is limited by saturation and ionization. The inability to phase match in cesium limits the conversion efficiency to about $5\times10^{-8}$.

Although efficient TPR tripling of the ruby laser in cesium is not possible, this does not put an end to the expectations[2] for the TPR enhancement approach. It is evident that to fully utilize the potential of TPR enhancement, the metal vapor must also be phase matchable, either by means of a buffer gas or through noncollinear phase matching. With the availability of tunable dye lasers we are not restricted to accidental two-photon resonances with fixed frequency lasers. Furthermore, the use of the two different incident frequencies allows tunable TPR sum generation $(2\omega_1+\omega_2)$ in the vacuum-ultraviolet region of the spectrum.[5] Combining TPR enhancement with phase matching one could construct short practical metal vapor cells with high-energy conversion efficiency and high output power. The incident intensity should be low, about $10^7$ W/cm$^2$, to avoid strong ionization and maintain good beam quality. If the laser-induced Stark shift is large for a particular two-photon resonance it will not necessarily be unfavorable and may not have to be compensated. The reason is that a large Stark shift would probably be connected with either a strong TPR transition, and thus a low saturation intensity, or a strong coupling to the continuum and therefore strong ionization.

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[9]The vapor density can be calculated from the equation of state of an ideal gas: $N=P/KT=9.66\times10^{18}P(\text{Torr})/T(^\circ\text{K})$ atoms/cm$^3$. At the temperature of 483 °K and the corresponding cesium vapor pressure of 0.13 Torr the density is $2.6\times10^{15}$ atoms/cm$^3$.