Theory of four-photon resonant vacuum-ultraviolet generation with reabsorption via resonant two-photon process

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Motivated by the recent experiments of Vallee *et al.* [IEEE J. Quantum Electron. **QE-19**, 1331 (1983)], we formulate the theory of the four-photon resonant VUV generation in a media that is positively dispersive. Dispersion characteristics of the medium change as the refractive index becomes intensity dependent. The phase-matching conditions for the third-harmonic generation through a five-photon process are derived. The blue shifts as observed by Vallee *et al.* are explained as due to the interaction of generated VUV via a two-photon process. Finally the renormalization of the fifth-order polarization due to the generated fields is also considered.

1. INTRODUCTION

Multiphoton excitation and nonlinear mixing in atomic vapors have become standard methods of producing VUV radiation over a range of frequencies. Much of the experimental work has used the VUV generation via a $\chi^{(3)}$ process.[1] The theoretical framework for such studies is well established. Recently Valle *et al.*[2] demonstrated how the higher-order nonlinear process involving six-wave mixing can be used to produce VUV radiation in a positively dispersive medium. This experiment is important from several viewpoints—it shows (1) how to isolate the effects due to the $\chi^{(5)}$ process; (2) how the resonant four-photon process can lead to VUV generation; and (3) the reabsorption of the generated VUV, which could lead to blue shifts. The last aspect is especially significant. It may be added that the interference effects and the reabsorption of the generated VUV were the key to the understanding of the disappearance of the resonant multiphoton ionization signal in Xe gas at high pressures.[3–7] Interference effects in other vapors have also been demonstrated. Normand *et al.*[3] used different transitions in Hg to study the enhancement of third-harmonic generation by both three-photon and four-photon resonance. Another quantity worth investigating in this system is fluorescence or ionization following resonant four-photon excitation. This quantity should exhibit the effect of interference that is due to two channels.

The organization of this paper is as follows: In Section 2 we examine the phase-matching conditions for the generation of VUV through a fifth-order process described by $\chi^{(5)}$ (ω, ω, ω, ω, $-\omega$) assuming that the incident beam has Gaussian shape. Analytic result for the phase-matching condition in the tight focusing limit is given. Efficient VUV generation is shown to take place in the negatively dispersive medium. In Section 3 we present a general theory of the four-photon resonant VUV generation. The formulation incorporates the effect of the VUV through a resonant two-photon process. In section 4 we discuss the application of the formalism of Section 3 to the recent experiments of Vallee *et al.* A remarkable result that emerges from our formulation is the possibility of the change in the dispersion characteristic of the medium due to the reaction of VUV photons. Finally, in Section 5 we present general considerations that lead to the renormalization of the generated polarization that is due to the reabsorption of the VUV. In particular we show how the $\chi^{(5)}$ process is renormalized owing to lower-order processes described by $\chi^{(1)}$ and $\chi^{(3)}$.

2. PHASE-MATCHING CONSIDERATIONS FOR THE VUV GENERATION THROUGH $\chi^{(5)}$

In this section we consider the generation of the VUV radiation at 3ω that is due to the fifth-order nonlinearity of the medium, i.e., we examine for simplicity the generation that is due to the process $\omega + \omega + \omega + \omega - \omega$. We calculate in detail the phase-matching conditions for the efficient generation through the $\chi^{(5)}$ process assuming that the beam at ω has the Gaussian form,[8] i.e., we take the incident field as

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

where

$$\epsilon = \epsilon_0(1 + i\beta)^{-1} \exp\left[-\frac{k(x^2 + y^2)}{b(1 + i\beta)}\right]. \tag{2.2}$$

Here $\beta = 2(z - f)/b$, $b = (2\pi/\lambda)\overline{\omega}_0{}^2$ and $\overline{\omega}_0$ is the beam waist. For simplicity, we ignore the vector character of the fields. The induced polarization due to the fifth-order process mentioned above will be

$$P = P(3\omega)\exp(3ikz - 3i\omega t) + \text{c.c.}, \tag{2.3}$$

$$P(3\omega) = \chi^{(5)}(\omega, \omega, \omega, \omega, -\omega)\epsilon\epsilon\epsilon\epsilon\epsilon^*. \tag{2.4}$$

On substituting Eq. (2.2) into Eq. (2.4) we get

$$P(3\omega) = \chi^{(5)}\epsilon_0{}^4\epsilon_0{}^*(1 + \beta^2)^{-1}(1 + i\beta)^{-3} \times \exp\left[-\frac{k(x^2 + y^2)}{b}\left(\frac{4}{1 + i\beta} + \frac{1}{1 - i\beta}\right)\right], \tag{2.5}$$

where for the sake of brevity we have not written the argument of $\chi^{(5)}$. It should be remembered that β is z dependent.

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The generated VUV field E_V at ω_V is determined from

$$-\nabla^2 E_V - \frac{\tilde{\epsilon}_V \omega_V^2}{c^2} E_V = +\frac{4\pi}{c^2}\omega_V^2 P(\omega_V), \qquad (2.6)$$

while the driving polarization P is given by Eqs. (2.3) and (2.5). Here $\tilde{\epsilon}_V$ is the dielectric function of the vapor at the frequency ω_V. Let k_V be the propagation vector of $E_V = \epsilon_V \exp(ik_V z - i\omega_V t)$ + c.c. Then, on making a slowly varying envelope approximation, Eq. (2.6) can be reduced to

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\epsilon_V + 2ik_V \frac{\partial}{\partial z}\epsilon_V = -\frac{4\pi\omega_V^2}{c^2} P \exp[-i(k_v - 3k)z]. \qquad (2.7)$$

In order to solve Eq. (2.7), we use two-dimensional Fourier transforms with respect to x and y,

$$\epsilon_V = \int \epsilon_V(z, \mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} d^2 q,$$

$$P(3\omega) = \int P(z, \mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} d^2 q, \qquad (2.8)$$

which lead to

$$\left(q^2 - 2ik_V \frac{\partial}{\partial z}\right)\epsilon_V(z, \mathbf{q}) = \frac{4\pi\omega_V^2}{c^2}\exp[-i(k_V - 3k)z] P(z, \mathbf{q}), \qquad (2.9)$$

whose integral is

$$\epsilon_V(z, \mathbf{q}) = \frac{4\pi\omega_V^2}{c^2(-2ik_V)} \int_0^z \mathrm{d}z' \exp\left[-\frac{i\mathbf{q}^2}{2k_V}(z - z')\right] \times \exp(-i\Delta k z') P(z', \mathbf{q});$$

$$\Delta k = k_V - 3k. \qquad (2.10)$$

On changing the variable of integration to $\beta' = 2(z' - f)/b$ and defining $+\xi = 2f/b$, Eq. (2.10) reduces to

$$\epsilon_V(z, \mathbf{q}) = \frac{i\pi\omega_V^2 b}{c^2 k_V} \int_{-\xi}^{\beta} \mathrm{d}\beta' \times \exp\left[-\frac{ibq^2}{4k_V}(\beta - \beta') - \frac{b\Delta k i}{2}\beta'\right] P(\beta', \mathbf{q}). \qquad (2.11)$$

The inversion of Eq. (2.11) involves Gaussian integrals over q, which can be done with the result that

$$\epsilon_V(x, y, z) = \frac{i\pi b \chi^{(5)} \omega_V^2 \epsilon_0^4 \epsilon_0^*}{k_V c^2} I, \qquad (2.12)$$

where

$$I = \int_{-\xi}^{\beta} \frac{\exp\left(-\frac{i\beta'\Delta k b}{2}\right)\exp\left[-\frac{k(x^2 + y^2)}{b\psi(\beta', \beta)}\right]}{(1 + i\beta')^3 (5 - 3i\beta')\psi(\beta', \beta)} \mathrm{d}\beta'$$

and

$$\psi(\beta', \beta) = \frac{1 + \beta'^2}{5 - 3i\beta'} - \frac{i(\beta' - \beta)k}{k_V}. \qquad (2.13)$$

The integral in Eq. (2.12) is to be evaluated numerically. The structure Eq. (2.12) of the generated field via $\chi^{(5)}$ is to be compared with the one generated via the $\chi^{(3)}$ process[9]:

$$\epsilon_V(x, y, z) = \left[\frac{i\pi b \chi^{(3)} \omega_V^2 \epsilon_0^3}{k_V c^2}\right] \frac{1}{(1 + i\beta)} \exp\left[-\frac{3k(x^2 + y^2)}{b(1 + i\beta)}\right] \times \int_{-\xi}^{\beta} \mathrm{d}\beta' \frac{\exp\left[-\frac{ib}{2}\Delta k(\beta' - \beta)\right]}{(1 + i\beta')^2}. \qquad (2.14)$$

The phase matching depends on the poles in the integrand of Eqs. (2.12) and (2.14). Since the nature of the poles in the two cases is different, it is obvious that the phase-matching conditions for the generation through the $\chi^{(3)}$ and $\chi^{(5)}$ processes will be different.

In the tight focusing limit the integrals can be evaluated in the closed form as follows: We approximate k_V by $3k$ in Eq. (2.13) and let $\beta \rightarrow \infty$; then

$$\psi(\beta', \beta) \sim i \frac{\left(\beta - \frac{5}{3}i\right)}{3}. \qquad (2.15)$$

In the limit $b \rightarrow 0$, the integral I becomes

$$I \simeq \frac{\exp\left[-\frac{3k}{ib}\frac{(x^2 + y^2)}{(\beta - 5/3i)}\right]}{i^3\left(\beta - \frac{5}{3}i\right)} \int_{-\infty}^{\infty} \frac{\exp\left(-\frac{i\Delta k b}{2}\beta'\right)\mathrm{d}\beta'}{(\beta' - i)^3\left(\beta' + \frac{5}{3}i\right)}, \qquad (2.16)$$

which on using methods of contour integration reduces to

$$I = -\frac{2\pi i}{\left(\beta - \frac{5}{3}i\right)} \exp\left[-\frac{3k}{ib}\frac{(x^2 + y^2)}{\left(\beta - \frac{5}{3}i\right)}\right] \exp\left(-\frac{5\Delta k b}{6}\right)\left(\frac{3}{8}\right)^3 \quad \text{if } \Delta k b > 0 \qquad (2.17)$$

$$= -\frac{2\pi i}{\left(\beta - \frac{5}{3}i\right)} \exp\left[-\frac{3k}{ib}\frac{(x^2 + y^2)}{\left(\beta - \frac{5}{3}i\right)} + \frac{\Delta k b}{2}\right] \times \left[\frac{3(\Delta k b)^2}{64} - \frac{9\Delta k b}{128} + \frac{27}{512}\right] \quad \text{if } \Delta k b < 0. \qquad (2.18)$$

The integrated intensity of the VUV will be

$$W = \iint_{-\infty}^{+\infty} |\epsilon_V|^2 \,\mathrm{d}x\mathrm{d}y, \qquad (2.19)$$

which can be written as

$$W = \frac{\pi^3 b^3 (\chi^5)^2 \omega_V^4 |\epsilon_0|^{10}}{k_V^2 c^4 (10)k} F, \qquad (2.20)$$

where

$$F = \left(\frac{10k}{\pi b}\right) \iint_{-\infty}^{+\infty} dxdy |I|^2. \qquad (2.21)$$

On using Eq. (2.17) and (2.18), we find that in the tight focusing limit F is given by

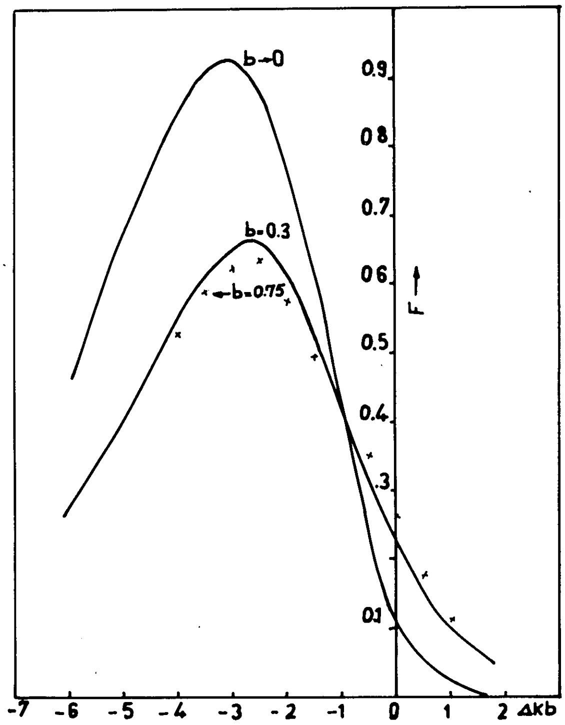

Fig. 1. The behavior of the function F [defined by Eq. (2.21)] as a function of $b\Delta k$ for various values of b/L and for $f/L = 0.5$.

$$F = 4\pi^2 \left(\frac{3}{8}\right)^6 \exp\left(-\frac{5}{3}\Delta kb\right) \qquad \text{if } \Delta kb > 0$$

$$= 4\pi^2 \left[\frac{3(\Delta kb)^2}{64} - \frac{9\Delta kb}{128} + \frac{27}{512}\right]^2 e^{\Delta kb} \qquad \text{if } \Delta kb < 0. \tag{2.22}$$

A simple analysis shows that the maximum of F lies at

$$\Delta kb = -3.104. \tag{2.23}$$

An interesting point that emerges from the above study is that the non-phase-matched VUV generation through the $\chi^{(5)}$ process is possible in a positively dispersive medium, i.e., for the case $\Delta kb > 0$. This is in contrast to the VUV generation through the $\chi^{(3)}$ process, which in the tight focusing limit is possible only in the negatively dispersive medium.[9] Our result, Eq. (2.23), concerning the position of the maximum of F is also in contrast to that mentioned in Ref. 1. It also turns out (see Fig. 1) that the values of F in the negatively dispersive region $\Delta kb < 0$ are generally much higher than in the region $\Delta kb > 0$, leading to the result that the efficient VUV generation through the $\chi^{(5)}$ process also occurs in the negatively dispersive medium. In Fig. 1, we also display the results, outside the tight focusing limit, obtained by using fast-Fourier-transformation technique. For finite b/L, L being the length of the sample, the maximum shifts toward the origin and the values in the region $\Delta kb > 0$ also start becoming significant.

3. THEORY OF FOUR-PHOTON RESONANT VUV GENERATION WITH BACKREACTION OF THE GENERATED VUV

In Section 2 we have seen that VUV generation through a fifth-order process $\omega + \omega + \omega + \omega - \omega = 3\omega$ is significant only in the negatively dispersive medium. However, in the negatively dispersive media even the VUV generation through $\omega + \omega + \omega = 3\omega$ is significant. Thus in a medium with negative dispersion the process $\chi^{(3)}$ will dominate, and there is little chance for observing the $\chi^{(5)}$ process unless there is resonant enhancement of the $\chi^{(5)}$ process. In the experiment of Vallee *et al.*, four-photon resonant enhancement of $\chi^{(5)}$, coupled with the positive dispersion of the medium, was used to observe VUV generation through the $\chi^{(5)}$ process. The observation of Vallee *et al.* suggests that the backreaction of the generated VUV must be significant, for they found that the excitation spectrum of the generated VUV was considerably blue shifted even when the Xe medium was made positively dispersive by the addition of Ar. Again it should be borne in mind that one has to have a situation in which the VUV generation through the third-order process $\omega + \omega + \omega \rightarrow 3\omega$ is kept to the minimum, and thus one has to avoid the resonance of 3ω radiation with the atomic medium. Of course if this resonance is avoided, then at first sight it would appear that the backreaction of the generated 3ω (i.e., absorption of 3ω) will be insignificant. We will, however, show that the absorption of the generated 3ω is significant through the two-photon process $3\omega + \omega$ with the atom going to the excited state $|e\rangle$, which is four-photon resonant with the initial $|i\rangle$ (ground) state. We will show that the two-photon process has two effects: (1) it modifies the dispersive properties of the medium through the intensity-dependent refractive index, which as we will see is crucial in determining the efficiency of VUV generation through the $\chi^{(5)}$ process, and (2) the population in the state that is close to four-photon resonance does depend on the imaginary part of $\chi^{(5)}$. This population governs the multiphoton ionization that is essentially an incoherent process. Thus in our analysis both real and imaginary parts of $\chi^{(3)}$, calculated from considerations involving the absorption of two photons, 3ω and ω, play a significant role.

Let $|i\rangle$ and $|e\rangle$ represent the initial and the four-photon resonant excited states. Let ω and ω_{ei} represent, respectively, the frequency of the exciting radiation and the energy separation between $|e\rangle$ and $|i\rangle$ with $\omega_{ei} \sim 4\omega$. The four-photon interaction between $|e\rangle$ and $|i\rangle$ can be represented by an effective Hamiltonian,

$$H_4 = -\mathbf{M}.\epsilon\epsilon\epsilon\epsilon|e\rangle\langle i| + \text{H.c.},$$

$$= -m|e\rangle\langle i| + \text{H.c.}, \tag{3.1}$$

where M denotes the four-photon matrix element. The incident field has been taken to be a traveling wave

$$\mathbf{E} = \epsilon \exp[i(kz - \omega t)] + \text{c.c.} \tag{3.2}$$

The generated third harmonic is written as

$$\mathbf{E}_V = \epsilon_V \exp[i(k_V z - 3\omega t)] + \text{c.c.} \tag{3.3}$$

As mentioned above, we have to take into account the reabsorption of 3ω via a two-photon process through intermediate states $|j\rangle$. This two-photon absorption is described by H_2:

$$H_2 = -\sum_j \mathbf{d}_{ej}\mathbf{E}|e\rangle\langle j| - \sum_j \mathbf{d}_{ji}\cdot\mathbf{E}_V|j\rangle\langle i| + \text{H.c.} \tag{3.4}$$

The two processes described by the Hamiltonians H_4 [Eq. (3.1)] and H_2 [Eq. (3.4)] are shown schematically in Fig. 2. Note that one can also write an effective Hamiltonian instead of Eq. (3.4). Such an effective Hamiltonian will involve the

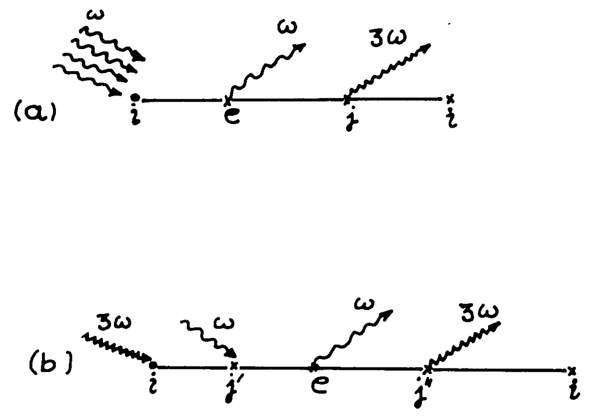

Fig. 2. Two different pathways (channels) for the excitation of the system to the state $|e\rangle$, which is four-photon resonant with $|i\rangle$. $|j\rangle$'s represent intermediate states. The VUV photon is represented by 3ω. The transitions from $|e\rangle$ to $|i\rangle$ via the stimulated four-photon emission are not shown.

product of $\mathbf{E}$ and $\mathbf{E}_V$. The density matrix equations can now be obtained. In what follows we ignore the saturation effects as these are not important in the experiments of Vallee *et al.* Thus the induced polarization at 3ω will be calculated only to first order in the index M. In first order in M, the relevant density matrix equations in rotating-wave approximation are found to be

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_{ie}^{(1)} = -[-i(\omega_{ei} - 4\omega) + \Gamma_{ge}]\rho_{ie}^{(1)} + \frac{m^*(-i)}{\hbar} - \sum_j \frac{id_{ej}^*\epsilon^*}{(\hbar)}\rho_{ij}^{(1)}, \tag{3.5}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_{ej}^{(1)} = -[i(\omega_{ej} - \omega) + \Gamma_{je}]\rho_{ej}^{(1)} + \sum_{j'} id_{ej'}\epsilon\rho_{j'j}^{(1)}, \tag{3.6}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_{ij}^{(1)} = -[-i(\omega_{ji} - 3\omega) + \Gamma_{ji}]\rho_{ij}^{(1)} - \frac{id_{ji}^*}{\hbar}\epsilon_V^* - \frac{id_{ej}}{\hbar}\epsilon\rho_{ie}^{(1)}, \tag{3.7}$$

where we have also introduced the decay constants Γ_{ij} associated with the off-diagonal element ρ_{ij}. In obtaining Eqs. (3.5)–(3.7) we have also used the fact that the generated field ϵ_V is of first order in M. Steady-state solutions of these equations are easily found. For example,

$$\rho_{ei}^{(1)} = \left\{\Gamma_{ei} + i(\omega_{ei} - 4\omega) + \sum_j \frac{|d_{ej}\epsilon|^2}{\hbar^2} \times [\Gamma_{ji} + i(\omega_{ji} - 3\omega)]^{-1}\right\}^{-1} \times \left\{+\frac{im}{\hbar} - \frac{1}{\hbar^2}\sum_j \frac{(d_{ej}\cdot\epsilon)(d_{ji}\cdot\epsilon_V)}{[\Gamma_{ji} + i(\omega_{ji} - 3\omega)]}\right\}, \tag{3.8}$$

$$\rho_{ji}^{(1)} = [\Gamma_{ji} + i(\omega_{ji} - 3\omega)]^{-1}\left[\frac{id_{ji}\cdot\epsilon_V}{\hbar} + \frac{id_{je}\cdot\epsilon^*}{\hbar}\rho_{ei}^{(1)}\right]. \tag{3.9}$$

The induced polarization at 3ω will be

$$P(3\omega) = \sum_j n d_{ij}\rho_{ji}^{(1)} + P^{\mathrm{NR}}. \tag{3.10}$$

Here P^{NR} is the nonresonant contribution to polarization and n the density of atoms. The equation of motion for the generated VUV follows from Maxwell's equations in slowly varying envelope approximation:

$$\left[\frac{\partial}{\partial z} + \frac{3\omega}{c^2 k_V}\frac{\partial}{\partial t} + \frac{1}{2ik_V}\left(-k_V^2 + \frac{9\omega^2}{c^2}\right)\right]\epsilon_V = \frac{18\pi i\omega^2 P(3\omega, t)}{c^2 k_V}, \tag{3.11}$$

where we drop transverse derivatives involving $\partial/\partial x$, $\partial/\partial y$, i.e., we ignore the Gaussian beam character. The induced polarization is to be obtained from the solution of Eqs. (3.5)–(3.7). The steady-state solution for the field will be simple, as then $\partial/\partial t \sim 0$ and Eqs. (3.8)–(3.10) can be used. Since the generated polarization has a wave vector $3k$, we will put $k_V = 3k \sim 3\omega/c$, where we have taken $\epsilon(\omega) \simeq 1$ at the fundamental frequency ω. However, we do not put $\epsilon(3\omega)$ equal to unity. This will lead to the free-wave generation with wave vector different from $3k$ [cf. the contribution that arises from $\psi^{(1)}$ in Eq. (3.17)]. On substituting Eqs. (3.8) and (3.9) in Eq. (3.10), we write the induced polarization in the form

$$P(3\omega) = \psi^{(1)}\epsilon_V + \psi^{(5)}\epsilon^3|\epsilon|^2 + \psi^{(3)}\epsilon_V|\epsilon|^2 + \tilde{\psi}^{(3)}\epsilon^3, \tag{3.12}$$

where

$$\psi^{(1)} = \frac{in}{\hbar}\sum_j d_{ji}d_{ij}[\Gamma_{ji} + i(\omega_{ji} - 3\omega)]^{-1}, \tag{3.13}$$

$$\psi^{(3)} = \left(\frac{i}{\hbar}\right)^3 n \sum_j d_{ij}d_{je}[\Gamma_{ji} + i(\omega_{ji} - 3\omega)]^{-1} \times \sum_{j'} \frac{d_{ej'}d_{j'i}}{[\Gamma_{j'i} + i(\omega_{j'i} - 3\omega)]} \times \left\{\Gamma_{ei} + i(\omega_{ei} - 4\omega) + \sum_j \frac{|d_{ej}\epsilon|^2}{\hbar^2}[\Gamma_{ji} + i(\omega_{ji} - 3\omega)]^{-1}\right\}^{-1}, \tag{3.14}$$

$$\psi^{(5)} = \left(\frac{i}{\hbar}\right)^2 n \sum_j d_{ij}d_{je}M[\Gamma_{ji} + i(\omega_{ji} - 3\omega)]^{-1} \times \left\{\Gamma_{ei} + i(\omega_{ei} - 4\omega) + \sum_j \frac{|d_{ej}\epsilon|^2}{\hbar^2}[\Gamma_{ji} + i(\omega_{ji} - 3\omega)]^{-1}\right\}^{-1}. \tag{3.15}$$

In Eq. (3.12) $\tilde{\psi}^{(3)}$ is related to the nonresonant part of $\chi^{(3)}$. The quantities $\psi^{(i)}$'s are related to the nonlinear susceptibilities specialized to the present model—$\psi^{(1)}$ gives just the first-order susceptibility at the frequency of the VUV. If we ignore the Stark-shift terms, then $\psi^{(5)}$ is essentially the fifth-order susceptibility $\chi^{(5)}$ $(\omega, \omega, \omega, \omega, -\omega)$, whereas $\psi^{(3)}$ corresponds to the third-order susceptibility characterizing the absorption of two-photon $-\chi^{(3)}$ $(\omega, -\omega, 3\omega)$. The denominator in Eq. (3.14) can be cast in terms of the Stark-shifted frequencies if we ignore all the damping terms and certain approximations are made; for example,

$$\sum_j \frac{|d_{ej}\epsilon|^2}{\hbar^2}[\Gamma_{ji}+i(\omega_{ji}-3\omega)]^{-1} \approx \sum_j \frac{|d_{ej}\epsilon|^2}{\hbar^2 i}[(\omega_{ji}-3\omega)]^{-1}$$
$$= \sum_j \frac{|d_{ej}\epsilon|^2}{\hbar^2 i}(\omega_{je}+\omega_{ei}-4\omega+\omega)^{-1}$$
$$\sim \sum_j \frac{|d_{ej}\epsilon|^2}{\hbar^2 i}(\omega-\omega_{ej})^{-1},$$

if we put $\omega_{ei} \sim 4\omega$. Thus the Stark shift of the excited state is obtained. The terms involving ϵ_V do not appear as we are calculating the induced polarization only to first order in ϵ_V. The generated VUV field in the steady state is obtained from Eqs. (3.11) and (3.12):

$$\epsilon_V(z) = \frac{6\pi i\omega}{c}[\psi^{(5)}\epsilon^3|\epsilon|^2 + \Psi^{(3)}\epsilon^3](1-e^{-\alpha z})/\alpha, \quad (3.16)$$

where

$$\alpha = -\frac{6\pi i\omega}{c}[\psi^{(1)} + \psi^{(3)}|\epsilon|^2]. \quad (3.17)$$

The Im α corresponds to the dispersion of the wave in the medium. It determines the phase mismatch and is responsible for Maker fringes. The real part of α corresponds to the absorption of the wave. The absorption has two contributions: (1) the usual linear part $[\psi^{(1)}]$ and (2) a nonlinear part $\psi^{(3)}$, which arises since the generated VUV is absorbed owing to a resonant two-photon absorption process. Note also that if the absorption of the generated VUV is ignored, then

$$\epsilon_V(z) \approx -\psi^{(5)}\epsilon^3|\epsilon|^2/\psi^{(1)}. \quad (3.18)$$

The generated field intensity will be

$$I_V(z) = |\epsilon_V(z)|^2 = \frac{36\pi^2\omega^2}{c^2}\frac{|\psi^{(5)}|^2|\epsilon|^{10}}{|\alpha|^2} \times [1 + e^{-2\,\mathrm{Re}\,\alpha} - 2e^{-\mathrm{Re}\,\alpha}\cos(\mathrm{Im}\,\alpha z)], \quad (3.19)$$

where we have put $\Psi_3 = 0$.

The dependence of I_V on the excitation frequency and other system parameters will be examined in Section 4. Note that if Re $\alpha = 0$, then I_V is maximum when Im $\alpha = 0$.

We close this section by examining the population distribution in the state $|e\rangle$. This population distribution determines, among other things, ionization from $|e\rangle$ by another laser. We thus will be able to answer questions regarding the influence of the backreaction of the VUV on the ionization. The equation of motion for ρ_{ee} can be obtained from Eq. (3.1). The long-time solution of the resulting equation for ρ_{ee} shows that

$$\rho_{ee}^{(2)} = \frac{i}{\hbar\kappa}\{m\rho_{ie}^{(1)} - m^*\rho_{ei}^{(1)}\}, \quad (3.20)$$

where κ is the net decay constant of the level $|e\rangle$. The density matrix element $\rho_{ie}^{(1)}$ is given by Eq. (3.8). We substitute Eq. (3.16) into expression (3.8) and simplify by assuming a thick sample so that $e^{-\alpha z} \sim 0$. This yields

$$-\frac{im^*}{\hbar\kappa}\rho_{ei}^{(1)} = \frac{|m|^2}{\hbar^2\kappa}\frac{\psi^{(1)}}{[\psi^{(1)}+\psi^{(3)}|\epsilon|^2]}\Bigg\{\Gamma_{ei}+i(\omega_{ei}-4\omega) + \sum_j \frac{|d_{ej}\cdot\epsilon|^2}{\hbar^2}[\Gamma_{ji}+i(\omega_{ji}-3\omega)]^{-1}\Bigg\}^{-1}. \quad (3.21)$$

Note further that if we had ignored the backreaction of VUV, then in place of Eq. (3.21) we would have obtained

$$-\frac{im^*}{\hbar\kappa}\rho_{ei}^{(1)} = \frac{|m|^2}{\hbar^2\kappa}[\Gamma_{ei}+i(\omega_{ei}-4\omega)]^{-1}. \quad (3.22)$$

The population of the level $|e\rangle$ and hence the ionization signal, etc. will be $\psi^{(1)}/\{\psi^{(1)}+\psi^{(3)}|\epsilon|^2\}$ times that produced if the reabsorption of VUV were ignored. The term $\psi^{(1)}$ by itself is quite small since it essentially gives the nonresonant susceptibility of the atomic vapor. Therefore the ionization will be considerably reduced if $\psi^{(3)}|\epsilon|^2 \gg \psi^{(1)}$. We will see in Section 4 that the experiments of Vallee *et al.* have in fact been done under the condition such that $\psi^{(3)}|\epsilon|^2 \gg \psi^{(1)}$.

In the foregoing analysis we have ignored the saturation effects. However, if the saturation effects become important, then the underlying density matrix equations given in Appendix A are to be used.

4. EXCITATION SPECTRUM OF THE GENERATED VUV

In this section we examine in detail the frequency dependence of Eq. (3.19) and connect the results to recent experiments of Vallee *et al.* For a given length of the sample and for a given density, we have to find the peak of I_V as the excitation frequency ω is varied. A simplified expression for α can be obtained by noticing that the only resonance that we have to consider is $4\omega \sim \omega_{ei}$. Thus the damping terms such as Γ_{ji} can be ignored, as the corresponding detuning factor in the denominator is large. Thus from Eqs. (3.13) and (3.14) we find the approximate results

$$\psi^{(1)} \approx \frac{n}{\hbar}\sum_j |d_{ji}|^2(\omega_{ji}-3\omega)^{-1} \equiv \frac{n}{\hbar}\gamma \quad (4.1)$$

$$\psi^{(3)} \approx \frac{n}{\hbar^3}\sum_j d_{ij}d_{je}(\omega_{ji}-3\omega)^{-1}\sum_{j'} d_{ej'}d_{j'i}(\omega_{j'i}-3\omega)^{-1} \times \left[\omega_{ei}-4\omega-i\Gamma_{ei}-\sum_j\frac{|d_{ej}\epsilon|^2}{\hbar^2}(\omega_{ji}-3\omega)^{-1}\right]^{-1} \quad (4.2)$$

$$\equiv \frac{n}{\hbar^3}\overline{\beta}(\delta'-i\Gamma_{ei})^{-1}, \quad (4.3)$$

where δ' represent the Stark-shifted detuning parameter

$$\delta' = \omega_{ei} - 4\omega - \sum_j \frac{|d_{ej}\epsilon|^2}{\hbar^2}(\omega_{ji}-3\omega)^{-1} \quad (4.4)$$

and $\overline{\beta}$ represents the rest of the terms on the right-hand side of expression (4.2). For making an order-of-magnitude estimate, we take δ'^s to be real, and thus we can write

$$\mathrm{Re}\,\alpha = \frac{6\pi\omega n}{c\hbar^3}\frac{\Gamma_{ei}\overline{\beta}|\epsilon|^2}{(\Gamma_{ei}^2+\delta'^2)}, \quad (4.5)$$

$$\mathrm{Im}\,\alpha = -\frac{6\pi\omega n}{c}\left[\frac{\gamma}{\hbar}+\frac{\overline{\beta}\delta'|\epsilon|^2}{\hbar^3(\delta'^2+\Gamma_{ei}^2)}\right]. \quad (4.6)$$

The parameter $\overline{\beta}$ is expected to be positive. If the medium is positively dispersive, then $\gamma > 0$. It is clear from Eq. (4.6) that it is possible for the medium to become negatively dispersive if δ' is negative and such that the term in the square bracket in Eq. (4.6) is negative. We give a rough estimate to demonstrate that the term in the square bracket in Eq. (4.6)

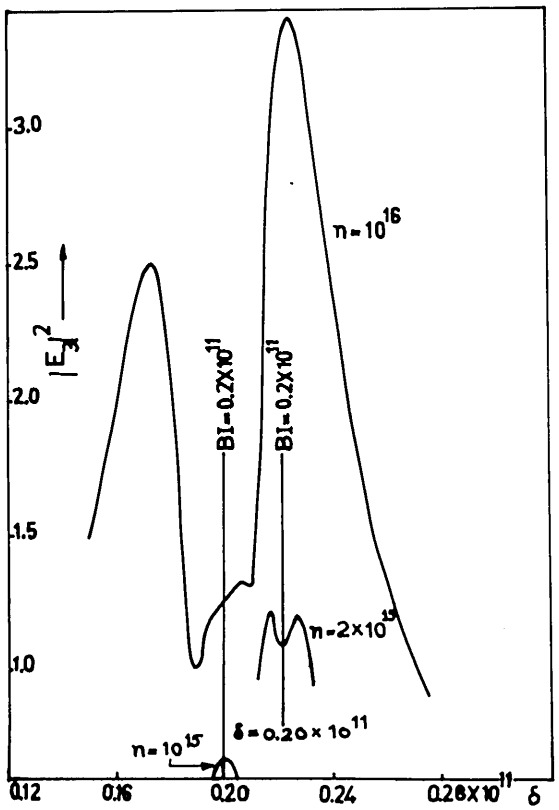

Fig. 3. The excitation spectra of the VUV in the plane-wave approximation; curves are labeled by the densities of the atomic system. Other parameters are given in the text. For clarity the curve for $n = 2 \times 10^{15}$ is shifted parallel to the δ axis.

can indeed be negative. We use $d_{ij} \simeq ea_0$, a_0 being Bohr radius, and replace $\omega_{jg} - 3\omega$ by an optical frequency so that the positive dispersion may be determined by

$$\frac{\gamma}{\hbar} \simeq \frac{e^2 a_0^2}{\hbar 10^{15}} = 5.5 \times 10^{-24} \text{ cgs esu},$$

and second term in the square bracket in Eq. (4.6) is

$$\frac{\bar{\beta}|\epsilon|^2}{\delta' \hbar^3} \approx -20 \times 10^{-24} \text{ cgs esu}$$

at $\delta' = -1\ \text{cm}^{-1}$ and at laser flux $10^{10}\ \text{W/cm}^2$. Thus the term in the square brackets at certain negative detunings can become negative.

These estimates are rather crude as determined by atomic parameters. It is well established that Xe at high pressures forms strong diatomic molecules in its excited states. The parameters γ and $\bar{\beta}$ in particular should therefore be strongly influenced by the contribution from the diatomic potential curves for some of the excited levels of Xe_2. A detailed analysis for a Xe experiment could not be attempted here because of nonavailability of relevant data. Our analysis shows that the dispersive character of the medium changes from *positive to negative because of the intensity-dependent changes in refractive index.* We have already seen in Section 2 that the phase-matching conditions really require the medium to be sufficiently negatively dispersive so that efficient generation of VUV takes place. From the above analysis leading to negative values of δ, it is evident that the peak of I_V will be blue shifted, i.e., ω will be on the higher side from the Stark-shifted resonant frequency $\frac{1}{4}[\omega_{ei} - \Sigma_j(|d_{ei}\epsilon|^2/\hbar^2)(\omega_{ji} - 3\omega)^{-1}]$. Using the formulas of Section 3 and the phase-matching conditions of Section 2, we have thus been able to explain the observed behavior of the VUV generated through the $\chi^{(5)}$ process in a positively dispersive medium.

We conclude this section by examining the behavior of the intensity I_V as given by Eq. (3.19) as a function of δ for various densities of the atomic system. The density appears through α. The collisional parameter Γ_{ei} is also density dependent. We show in Fig. 3 the behavior of $I_V(x)/|\epsilon|^{10}|M|^2$ for various densities assuming a cell length of, say, 10 cm, and other parameters are determined by constant

$$B = \frac{e^2 a_0^2}{\hbar^2 10^{15}} = 5 \times 10^3$$

according to $\gamma = \hbar B$, $\bar{\beta} = \hbar^4 B^2$, and $\Delta_S = BI$ at $I \approx 2\ \text{GW/cm}^2$. The intensity as a function of the excitation frequency starts showing a doublet structure as the density is increased by an order of magnitude, i.e., roughly for $n = 10^{15}$–10^{16} atoms/cm^3. Note that the excitation spectra are all centered at $\delta' = 0$ rather than blue shifted. This is because of the plane-wave approximation used in obtaining these results.

5. RENORMALIZATION OF THE $\chi^{(5)}$ PROCESS DUE TO $\chi^{(1)}$ AND $\chi^{(3)}$ PROCESSES

In this section we present general considerations that are model independent and that show the net effect of the back-reaction of the generated VUV. These considerations are somewhat similar to those used by Wynne[5] and Jackson and Wynne,[6] although the spirit is quite different as we are dealing with excitations near four-photon resonance.

According to the microscopic theory the induced polarization in a system with inversion symmetry can be written as

$$P(\omega) = \chi^{(1)}(\omega)\bar{\epsilon}(\omega) + \sum_{\Sigma\omega_i=\omega} \chi^{(3)}(\omega_1, \omega_2, \omega_3)\bar{\epsilon}(\omega_1)\bar{\epsilon}(\omega_2)\bar{\epsilon}(\omega_3) + \sum_{\Sigma\omega_i=\omega} \chi^{(5)}(\omega_1, \omega_2, \omega_3, \omega_4, \omega_5)\bar{\epsilon}(\omega_1)\bar{\epsilon}(\omega_2)\bar{\epsilon}(\omega_3)\bar{\epsilon}(\omega_4)\bar{\epsilon}(\omega_5) + \ldots \quad (5.1)$$

In a dilute system, the field $\bar{\epsilon}$ is the incident field. However, in a dense medium it is well known that the field acting on a molecule or atom is not the incident field but the local field. The local field takes into account the field generated by all other molecules in the system. The local field in turn depends on the induced polarization, and the corrections to the susceptibilities arising from local fields have been studied at great length.[10] The backreaction of the generated VUV is similar to the local-field problem. The effective field in Eq. (5.1) should be replaced by the sum of the incident field and the field generated, i.e.,

$$\bar{\epsilon}(\omega) = \epsilon(\omega) + \epsilon_V(\omega). \quad (5.2)$$

On substituting Eq. (5.2) and using the fact that $\epsilon_V(\omega)$ is related to the nonlinear polarization,

$$\epsilon_V(\omega) = R(\omega)P^{\text{NL}}(\omega), \quad (5.3)$$

we can rewrite the series in Eq. (5.1) as

$$P(\omega) = \tilde{\chi}^{(1)}(\omega)\epsilon(\omega) + \sum_{\substack{\Sigma\omega_i=\omega \\ i}} \tilde{\chi}^{(3)}(\omega_1, \omega_2, \omega_3)\epsilon(\omega_1)\epsilon(\omega_2)\epsilon(\omega_3)$$
$$+ \sum_{\Sigma\omega_i=\omega} \tilde{\chi}^{(5)}(\omega_1, \omega_2, \omega_3, \omega_4, \omega_5)\epsilon(\omega_1)\epsilon(\omega_2)\epsilon(\omega_3)\epsilon(\omega_4)\epsilon(\omega_5). \quad (5.4)$$

The new susceptibilities $\tilde{\chi}'^s$, which take into account the backreaction of the generated VUV, can be calculated from Eqs. (5.1)–(5.4).

As an application we consider the problem discussed in Section 3. The induced polarization at 3ω can be written as

$$P(3\omega) \cong \chi^{(1)}(3\omega)\epsilon_V(3\omega) + \chi^{(3)}(3\omega, \omega, -\omega)\epsilon_V(3\omega)|\epsilon(\omega)|^2$$
$$+ \chi^{(3)}(\omega, \omega, \omega)\epsilon^3(\omega) + \chi^{(5)}(\omega, \omega, \omega, \omega, -\omega)\epsilon^3(\omega)|\epsilon(\omega)|^2. \quad (5.5)$$

The contribution coming from the term $\chi^{(3)}\epsilon^3(\omega)$ is expected to be very small. We are assuming that the ϵ_V is not strong enough so that the nonlinear generation of ω can be ignored, i.e.,

$$P(\omega) \approx \chi^{(1)}(\omega)\epsilon(\omega). \quad (5.6)$$

Writing Eq. (5.3) as

$$\epsilon_V(3\omega) = R(3\omega)[\chi^{(5)}\epsilon^3(\omega)|\epsilon(\omega)|^2 + \chi^{(3)}\epsilon^3(\omega)], \quad (5.7)$$

we get from expression (5.5)

$$P(3\omega) = \{[\chi^{(1)}(3\omega) + \chi^{(3)}(3\omega, \omega, -\omega)|\epsilon(\omega)|^2]R(3\omega) + 1\}$$
$$\times [\chi^{(5)}\epsilon^3(\omega)|\epsilon(\omega)|^2 + \chi^{(3)}(\omega, \omega, \omega)\epsilon^3(\omega)]. \quad (5.8)$$

The function R is to be found from Maxwell's equations. Assuming that the boundary term is not important, i.e., retaining only the particular solution of Maxwell's equations, we find that

$$R(3\omega) = 4\pi\{\tilde{\epsilon}(\omega) - 1 - 4\pi[\chi^{(1)}(3\omega) + \chi^{(3)}(3\omega, \omega, -\omega)|\epsilon(\omega)|^2]\}^{-1} \quad (5.9)$$

Note the appearance of the $\chi^{(3)}$ term in the denominator. Thus the net polarization at 3ω becomes

$$P(3\omega) = \frac{[\tilde{\epsilon}(\omega) - 1][\chi^{(5)}\epsilon^3(\omega)|\epsilon(\omega)|^2 + \chi^{(3)}(\omega, \omega, \omega)\epsilon^3(\omega)]}{\{\tilde{\epsilon}(\omega) - 1 - 4\pi[\chi^{(1)}(3\omega) + \chi^{(3)}(3\omega, \omega, -\omega)|\epsilon(\omega)|^2]\}}. \quad (5.10)$$

For the four-photon resonant medium both $\chi^{(5)}$ and $\chi^{(3)}$ are resonantly enhanced [cf. Eqs. (3.14) and (3.15)]. Note also that $\epsilon(\omega) \sim 1$, since ω is far removed from any resonance in the medium, which leads to small values of $P(3\omega)$ unless $\chi^{(3)}|\epsilon|^2 \approx \chi^{(1)}$. Thus if there are quantities that depend directly on $P(3\omega)$ such quantities will be negligibly small because of the interference effects due, for example, to two processes shown in Fig. 2. Note, however, that the fluorescence or ionization for the present system is determined not by $P(3\omega)$ but by the considerations of the excited-state population as discussed at the end of Section 3.

The above analysis can be generalized to more-general cases, for example, to those involving fundamental beams at several different wave vectors. The analysis can also be carried out for the cases when the k dependence of the nonlinear susceptibilities is important, for example in crystals.

In summary, we have (1) shown that for tightly focused Gaussian beams efficient VUV generation by the fifth-order process, i.e., via $\chi^{(5)}(\omega_{VUV}; \omega + \omega + \omega + \omega - \omega)$, occurs dominantly in a negative dispersive medium, (2) developed the theory for VUV generation via four-photon resonant $\chi^{(5)}$, (3) demonstrated that the blue shifts observed in the experiments by Vallee *et al.*[2] can be understood by taking into account the reabsorption of the generated VUV via a two-photon resonant absorption process, and (4) considered the backreaction of generated VUV field as a local-field problem leading to renormalization of the generated polarization.

APPENDIX A

Here we give for completeness the optical Bloch equations for the four-photon resonant plus two-photon resonant process envisaged in the text. The four-photon resonance between the levels $|i\rangle$ and $|e\rangle$ of an atom is due to the field E, at the fundamental frequency ω. The generated third-harmonic field, E_V, together with one photon of the fundamental frequency, induces simultaneously the two-photon resonant transition between the same levels $|i\rangle$ and $|e\rangle$. The interaction Hamiltonian in a dipole approximation may be written as

$$H = -\mathbf{d} \cdot \mathbf{E} - \mathbf{d} \cdot \mathbf{E}_V, \quad (A.1)$$

where the fields E and E_V are given by Eqs. (2.1) and (2.7), respectively. The resonant interaction between the resonant levels going through a series of virtual transitions can be described by an effective two-level Hamiltonian that gives the optical Bloch equations. This effective Hamiltonian can be obtained by standard methods[12] and is given by

$$H_{\text{eff}} = \frac{\hbar\tilde{\omega}_{ei}}{2}(|e\rangle\langle e| - |i\rangle\langle i|) - \mathbf{M}^{(4)}\mathbf{:EEEE}$$
$$\times |e\rangle\langle i| - \mathbf{M}^{(2)}\mathbf{:EE}_V|e\rangle\langle i| + \text{c.c.}, \quad (A.2)$$

where $\tilde{\omega}_{ei}$ is the Stark-shifted energy difference between the resonant levels given by

$$\tilde{\omega}_{ei} = \frac{1}{\hbar}(E_e - E_i) + \Delta_S, \quad (A.3)$$

where

$$\Delta_S = \sum_m \frac{2|d_{im}|^2}{\hbar^2}\omega_{mi}\left[\frac{|\epsilon|^2}{\omega_{mi}^2 - \omega^2} + \frac{|\epsilon_V|^2}{\omega_{mi}^2 - (3\omega)^2}\right]$$
$$- \sum_m \frac{2|d_{em}|^2}{\hbar^2}\omega_{me}\left[\frac{|\epsilon|^2}{\omega_{me}^2 - \omega^2} + \frac{|\epsilon_V|^2}{\omega_{me} - (3\omega)^2}\right] \quad (A.4)$$

and $M^{(2)}$ is the effective two-photon absorption matrix element given by (see Ref. 12 for comparison)

$$\mathbf{M}^{(2)} = \frac{1}{\hbar}\sum_m \frac{d_{im}d_{me}}{2}[(\omega_{me} + 3\omega)^{-1} + (\omega_{me} + \omega)^{-1}$$
$$+ (\omega_{mi} - 3\omega)^{-1} + (\omega_{mi} - \omega)^{-1}]. \quad (A.5)$$

The four-photon absorption resonant matrix element $M^{(4)}$ may be symbolically written as

$$\mathbf{M}^{(4)} = \left(\frac{-i}{\hbar}\right)^3 \sum_{j,n,m} \frac{(-\mathbf{d}_{ej})(-\mathbf{d}_{jn})(-\mathbf{d}_{nm})(-\mathbf{d}_{mi})}{(\omega_{ji} - 3\omega)(\omega_{ni} - 2\omega)(\omega_{mi} - \omega)}. \quad (A.6)$$

Using Eq. (A.2) we can obtain the equation of motion for density matrix ρ in space consisting of two states $|e\rangle$ and $|i\rangle$:

$$\dot{\rho}_{ei} = -i(\tilde{\omega}_{ei} - 4\omega)\rho_{ei} - \frac{i}{\hbar}(\mathbf{M}^{(4)}:\epsilon\epsilon\epsilon\epsilon + \mathbf{M}^{(2)}\epsilon\epsilon_V)(\rho_{ee} - \rho_{ii}) - \Gamma_{ei}\rho_{ei}, \quad (A.7)$$

$$(\dot{\rho}_{ee} - \dot{\rho}_{ii}) = \frac{2i}{\hbar}\mathbf{M}^{(4)}\epsilon\epsilon\epsilon\epsilon\rho_{ie} + \frac{2i}{\hbar}\mathbf{M}^{(2)}\epsilon\epsilon_V\rho_{ie} - \frac{1}{T_1}[-\eta + (\rho_{ee} - \rho_{ii})] + \text{c.c.}, \quad (A.8)$$

where η is the equilibrium population difference $\rho_{ee} - \rho_{ii}$. These are the effective Bloch equations for the present problem. The induced polarization problem can be calculated in terms of ρ_{ee}, ρ_{ei} in the usual way.

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