Harmonic generation at high field strengths. Frequency shifts and saturation phenomena*

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(Received 28 May 1974)

Optical harmonic generation and mixing in the gas phase has been proposed as a technique for the generation of coherent radiation in the vacuum ultraviolet and soft x-ray spectral region. At the high field strengths required by these processes the interaction between atoms and the electromagnetic field shows intensity-dependent resonances. In this paper we modify harmonic generation theory to include the effect of these frequency shifts. Closed-form expressions for generated dipole moment, absorption probability, and coherence length are presented. The most important consequences of frequency shifts on resonantly enhanced processes are that the pump laser must be tuned away from the small-field resonance frequency, that the conversion efficiency may saturate, and that the dispersion of the medium may change sign. As an example, the generation of 198-Å radiation by a five-photon mixing process in Li^+ is considered.

I. INTRODUCTION

It is known[1-4] that at high field strengths the resonances of interactions between atoms and electromagnetic fields show intensity-dependent shifts. In two recent papers[5,6] Harris discussed harmonic generation and mixing processes which may be used for the generation of coherent radiation in the 100-Å region. These processes require high intensities, and in this paper we discuss how his results are modified when frequency shifts are taken into account. We proceed by solving the density-matrix equations for a collection of atoms interacting with two electromagnetic fields: a strong incident pump field at frequency ω and a much weaker generated field at frequency $n\omega$. (In what follows we limit ourselves to harmonic generation; extension of the results to mixing processes is straightforward.) The reason why frequency shifts will appear in our results is that we do not solve the equations independently, as is usually done in the calculation of nonlinear susceptibilities (e.g., Ref. 7), but consider feedback of the higher orders in the perturbation sequence to the lower orders. We demonstrate the technique with the example of third-harmonic generation in a four-level system. Generalized closed-form expressions for generated dipole moment, absorption probabilities and coherence length are presented in the Appendix.

II. DERIVATION OF FREQUENCY SHIFTS

The off-diagonal elements of the density matrix between the ground level and some other level, for a four-level system, satisfy the following equations (the levels are labeled from 0 to 3):

$$\begin{aligned}
\frac{d\rho_{01}}{dt} &= i\omega_{10}\rho_{01} + \frac{i}{\hbar}(\rho_{00}H'_{01} + \rho_{02}H'_{21}) - \frac{\rho_{01}}{T_{01}}, \\
\frac{d\rho_{02}}{dt} &= i\omega_{20}\rho_{02} + \frac{i}{\hbar}(\rho_{01}H'_{12} + \rho_{03}H'_{32}) - \frac{\rho_{02}}{T_{02}}, \\
\frac{d\rho_{03}}{dt} &= i\omega_{30}\rho_{03} + \frac{i}{\hbar}(\rho_{02}H'_{23} + \rho_{00}H'_{03}) - \frac{\rho_{03}}{T_{03}},
\end{aligned} \tag{1}$$

where $\omega_{i0} = (E_i - E_0)/\hbar$, $H'_{ij} = -\mu_{ij}\times$(electric field), and T_{0i} is the atomic dephasing time for the $0 \rightarrow i$ transition. We assume that the fields are limited to a value such that the change of the population of the ground level due to absorption to other levels during the time the fields are on is small, i.e., ρ_{00} is essentially constant. (This assumption is discussed in Sec. III for various kinds of absorption processes.) Other on-diagonal elements and off-diagonal elements between levels neither of which is the ground level are left out because for the processes considered they are usually far from resonance and hence have little effect. The fields are taken to be sinusoidal:

$$\begin{aligned}
E(t;\omega) &= Ee^{i\omega t}/2 + \text{c.c.}, \\
E'(t;3\omega) &= E'e^{i3\omega t}/2 + \text{c.c.}
\end{aligned} \tag{2}$$

The solution to the set of equations (1) can then be written as

$$\rho_{0k}(t;k\omega) = \rho_{0k}e^{ik\omega t}, \quad k = 1, 2, 3. \tag{3}$$

In the transient regime the ρ_{0k} are functions of time, slowly varying compared to the period of the applied field. We are interested, however, in interaction times which are long compared to the decay times of these transients. If, as is explained in Sec. III, the power density is limited such that the change of the population of the ground state due to absorption processes is small during the inter-

action time, then the set of equations (1) can be solved treating ρ_{00} as a constant (quasistatic approach). The quantities ρ_{0k} will, however, be modulated by a very slowly varying envelope as a result of the changing occupation of the ground state. Substitution of (2) and (3) into (1) yields, by harmonic balance, the following system of linear algebraic equations for the case where the generated field is much smaller than the pump field:

$$\begin{aligned}(\Delta\omega_1 + i/T_{01})\rho_{01} &= \alpha_{21}\rho_{02} + \alpha_{01}\rho_{00}\,,\\ (\Delta\omega_2 + i/T_{02})\rho_{02} &= \alpha_{12}\rho_{01} + \alpha_{32}\rho_{03}\,,\\ (\Delta\omega_3 + i/T_{03})\rho_{03} &= \alpha_{23}\rho_{02} + \alpha'_{03}\rho_{00}\,,\end{aligned} \tag{4}$$

where

$$\Delta\omega_j = \omega_{j0} - j\omega\,,$$

$$\alpha_{ij} = \mu_{ij}E/2\hbar,\quad i,j = 1,2,3\,,$$

$$\alpha'_{ij} = \mu_{ij}E'/2\hbar.$$

The solution of these equations is discussed in Sec. III. The resonances of this third-harmonic process are defined by setting the real part of the determinant of the set of equations (4) equal to zero, i.e., $D_r = 0$, where

$$D_r = \Delta\omega_1\Delta\omega_2\Delta\omega_3 - |\alpha_{12}|^2\Delta\omega_3 - |\alpha_{23}|^2\Delta\omega_1\,. \tag{5a}$$

The zeros of this polynomial in ω are intensity dependent. For small intensities, D_r reduces to $D_r = \Delta\omega_1\Delta\omega_2\Delta\omega_3$, which is the well-known form of the denominator of the third-order nonlinear susceptibility. The intensity dependence of the widths of the resonances is found from the imaginary part of the determinant, i.e., D_i, where

$$D_i = \frac{\Delta\omega_1\Delta\omega_3}{T_{02}} + \frac{\Delta\omega_1\Delta\omega_2 - |\alpha_{12}|^2}{T_{03}}\,. \tag{5b}$$

Although the intensity dependence of the widths of the resonances of the physical quantities studied in Sec. III could be calculated from the set of equations (4), we will not study it in detail in this paper. This dependence was taken into account, however, in the example discussed in Sec. IV.

III. CONVERSION EFFICIENCY OF HARMONIC GENERATION PROCESSES IN THE PRESENCE OF FREQUENCY SHIFTS

In an earlier work[5] Harris has derived an expression for the conversion efficiency of an nth harmonic generation process where the generated frequency comes close to a single-photon–allowed transition. He shows that if the coherence length is dominated by the nearby transition and if the pump power is limited by n-photon absorption to that level, the conversion efficiency is given by

$$\mathcal{E} = \frac{2\hbar n\omega}{\sigma_{0n}}\frac{1}{J_i/A}\,, \tag{6}$$

where σ_{0n} is the single-photon cross section for absorption to the nth atomic level (this level is by definition the level closest to the generated frequency), and J_i/A is the energy density in the incident pulse. To obtain this result the pump-power density is chosen such that the product of the absorption probability per second and the pulse length is 0.5, in which case about 70% of the atoms are still in the ground state at the end of the interaction. (This limit is somewhat arbitrary, it is used here to be consistent with Refs. 5 and 6.)

Using the solution of the system of equations (4), we find the following expressions for generated dipole moment at frequency 3ω, single-photon absorption probability per second to level 3, three-photon absorption probability per second to level 3, and coherence length:

$$\langle\mu(t;3\omega)\rangle = \frac{2\alpha_{01}\alpha_{12}\alpha_{23}\mu_{30}}{D_r^2 + D_i^2}(D_r\cos 3\omega t + D_i\sin 3\omega t)\,, \tag{7}$$

$$W^{(1)} = \frac{2}{T_{03}}|\alpha'_{03}|^2\left(\frac{\Delta\omega_1\Delta\omega_2 - |\alpha_{12}|^2}{D_r}\right)^2, \tag{8}$$

$$W^{(3)} = \frac{2}{T_{03}}\frac{|\alpha_{01}|^2|\alpha_{12}|^2|\alpha_{23}|^2}{D_r^2 + D_i^2}\,, \tag{9}$$

$$L_c = \frac{h}{3\omega\eta_0|\mu_{03}|^2N}\frac{D_r}{\Delta\omega_1\Delta\omega_2 - |\alpha_{12}|^2}\,, \tag{10}$$

where N is the density of atoms and η_0 is 377 Ω.

For small field strengths these expressions reduce to those calculated without considering feedback effects. Substitution of Eqs. (7)–(10) into the expression for the power density generated in one coherence length,

$$\frac{P(3\omega)}{A} = \frac{\eta_0(3\omega)^2|\langle\mu(3\omega)\rangle|^2(NL_c)^2}{2\pi^2}\,, \tag{11}$$

together with the requirement $W^{(3)}\times$(pulse length) $= 0.5$, yields an expression for the efficiency of the process which is the same as in the small-field case, i.e.,

$$\mathcal{E} = \frac{(2\hbar)(3\omega)}{\sigma_{03}}\frac{1}{J_i/A}\,,$$

where σ_{03} is now defined, however, in terms of a modified detuning from level 3:

$$\sigma_{03} = \frac{3\omega\eta_0}{\hbar}\frac{|\mu_{03}|^2}{T_{03}}\left(\frac{1}{\Delta'\omega_3}\right)^2, \tag{12}$$

where

$$\Delta'\omega_3 = \Delta\omega_3 - \frac{|\alpha_{23}|^2\Delta\omega_1}{\Delta\omega_1\Delta\omega_2 - |\alpha_{12}|^2}$$

$$= \frac{D_r}{\Delta\omega_1\Delta\omega_2 - |\alpha_{12}|^2}.$$

So the earlier result is correct if one replaces the detuning from the third level in the expression for the single-photon cross section by a modified detuning which depends on the intensity of the applied field.

Harris has also shown[6] that the conversion efficiency of an nth harmonic generation process (or n-photon mixing), where $n-1$ photons are resonant with a single-photon nonallowed transition to the ground state, such that the power density of the pump is limited by $(n-1)$-photon absorption to that level, is given by

$$\mathcal{E} = \frac{T_{02}}{T_1}\frac{|\mu_{n-1,n}|^2}{|\mu_{0,n}|^2}, \tag{13}$$

where T_1 is either the pulse length or the lifetime of the absorbing level, whichever is shorter.

Using the solution of the set of equations (4), and taking into account the fact that the sum of two pump photons can come close to level 2 such that the linewidth $2/T_{02}$ can no longer be neglected, the two-photon absorption probability per second is given by

$$W^{(2)} = \frac{2}{T_{02}}|\alpha_{01}|^2|\alpha_{12}|^2\frac{\Delta^2\omega_3}{D_r^2 + D_i^2}. \tag{14}$$

Substitution of Eqs. (7), (14), and (10) into Eq. (11), together with the requirement $W^{(2)}T_1 = 0.5$, yields the following expression for the efficiency:

$$\mathcal{E} = \frac{T_{02}}{T_1}\frac{|\mu_{23}|^2}{|\mu_{03}|^2}\left(1 - \frac{|\alpha_{23}|^2\Delta\omega_1}{\Delta\omega_1\Delta\omega_2\Delta\omega_3 - |\alpha_{12}|^2\Delta\omega_3}\right). \tag{15}$$

For small field strengths the factor in parentheses reduces to 1. If one limits the shifts to values which are small compared to the atomic level spacings, the allowed power densities are usually smaller than those found from the limitation on multiphoton absorption. At such lower power densities the factor in parentheses reduces to 1, but the efficiency of the process is reduced by another factor which is given by

$$\left(\frac{\text{power density applied}}{\text{power density as limited by } (n-1)\text{-photon absorption}}\right)^{n-1}$$

IV. EXAMPLE

As an example we consider a five-photon mixing process in Li^+:

$$4\times 816\ \text{Å} + 6745\ \text{Å} \rightarrow 198\ \text{Å}.$$

The path used is: $1s^2 \rightarrow 1s2p \rightarrow 1s^2 \rightarrow 1s2p \rightarrow 1s2s \rightarrow 1s2p$. Level positions and oscillator strengths were taken respectively from Refs. 8 and 9. The pump frequencies were chosen such that the detuning from the unshifted four-photon resonance was 1250 cm^{-1} (below the resonance) while the detuning from the unshifted five-photon resonance was 3750 cm^{-1} (above the resonance). The laser pulse length was assumed to be 30 psec and the linewidth 1 cm^{-1}. Figure 1 shows how at a power density of 2×10^{14} W/cm^2 the system becomes four-photon resonant and also how, at higher power densities, the efficiency saturates; here the efficiency was defined, consistent with Ref. 5, as the ratio of the generated power and the power at 6745 Å. Figure 1 was computer-generated and takes into account the intensity-dependent widths. At the high intensities involved, five-photon ionization by the pump field at 816 Å has to be considered. From Refs. 11 and 12 an approximate value for the ionization probability can be calculated. If the expressions in Refs. 11 and 12 are adjusted for shifts, a limiting intensity of about 2×10^{14} W/cm^2 is found, i.e., if a pulse with this intensity is applied, then about 50% of the Li^+ ions will be ionized during the pulse, and also the broadening of the four-photon resonance due to ionization will be comparable to the laser linewidth. It should be noted that if shifts were not taken into account, the limiting power density (as calculated by the formulas of Bebb and Gold in Ref. 11) would be about a factor of 17 higher. At the intensity of 2×10^{14} W/cm^2 the four-photon absorption is well below the maxi-

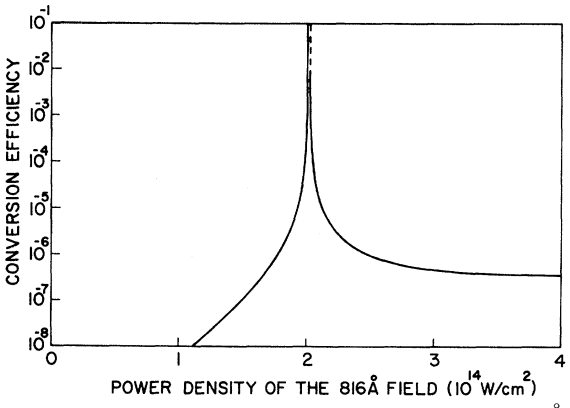

FIG. 1. Conversion efficiency for generation of 198-Å radiation using a five-photon mixing process. In the dashed region the medium is positively dispersive.

mum allowed value. To keep the coherence length short (about 1 cm at a pressure of a few Torr), the power density of the 6745-Å field has to be limited to about one part in ten thousand of the density of the 816-Å field. It is also indicated in Fig. 1 that in certain regions of the intensity the dispersion of the medium can change sign. This is important because harmonic generation with a focused Gaussian beam in an infinite positively dispersive medium is impossible.[10] It should also be noted that the width of the resonance in Fig. 1 is quite small, and hence a stable laser is required, typically around 1%.

We conclude that, taking into account frequency shifts, harmonic generation is a promising means of generating wavelengths in the vacuum-uv and soft x-ray spectral region. The most important consequences of frequency shifts are that the pump laser has to be tuned to a wavelength different from that required to bring the system into resonance at small field strengths, that the conversion efficiency may saturate, and that the dispersion of the medium may change sign.

ACKNOWLEDGMENTS

The author acknowledges many stimulating discussions with S. E. Harris and A. H. Kung. He also wishes to thank the European Space Research Organization for granting him a fellowship.

APPENDIX

Using the technique explained in Sec. I it can be shown that for an nth harmonic process (or n-photon mixing), the generated dipole moment at frequency $n\omega$, the single-photon absorption probability per second to the nth level, the multiphoton absorption probabilities per second to the $(n-1)$th and nth level, and the coherence length, are given by:

$$\langle \mu(n\omega) \rangle = 2\mu_{n0} \prod_{k=1}^{n} \frac{\alpha_{k-1,k}}{D_k} ,$$

$$W^{(1)} = \frac{2}{T_{0n}} \frac{|\alpha'_{0n}|^2}{D_n^2} ,$$

$$W^{(n-1)} = \frac{2}{T_{0n-1}} \left(\prod_{k=1}^{n-2} \left| \frac{\alpha_{k-1,k}}{D_k} \right|^2 \right) \times \frac{|\alpha_{n-2,n-1}|^2}{[D_{n-1} - |\alpha_{n-1,n}|^2/(\omega_{n0} - n\omega)]^2} ,$$

$$W^{(n)} = \frac{2}{T_{0n}} \prod_{k=1}^{n} \frac{|\alpha_{k-1,k}|^2}{D_k^2} ,$$

$$NL_c = \frac{h}{n\omega\eta_0 |\mu_{0n}|^2} D_n .$$

The efficiencies for the processes discussed in Sec. III are as follows.

Case A[5]*:*

$$\mathcal{E} = \frac{2\hbar n\omega}{\sigma_{0n}} \frac{1}{J_i/A} ,$$

where σ_{0n} is defined in terms of the single-photon absorption probability per second to level n.

Case B[6]*:*

$$\mathcal{E} = \frac{T_{0n-1}}{T_1} \frac{|\mu_{n-1,n}|^2}{|\mu_{0,n}|^2} \left(1 - \frac{|\alpha_{n-1,n}|^2/(\omega_{n0} - n\omega)}{D_{n-1}} \right) .$$

In these expressions D_k is defined by

$$D_k = \omega_{k0} - k\omega - |\alpha_{k-1,k}|^2/D_{k-1} , \quad k \neq 1 ,$$

$$D_1 = \omega_{10} - \omega .$$

Note that in all these expressions the linewidth was neglected.

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*Work supported by the U. S. Office of Naval Research and by the National Aeronautics and Space Administration.

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