Phase-modulation effects on the spectrum of third-harmonic generation

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(Received 6 June 1990)

We calculate the spectrum of third-harmonic generation (THG) for multimode fundamental input fields. We consider input fields from (1) a laser with gain on several cavity modes, (2) pulses with short temporal duration, and (3) frequency-modulated input fields. The effects of phase modulation in the nonlinear medium on the spectrum of the THG field are considered. Using the estimates by Miles and Harris [IEEE J. Quantum Electron. **QE-9**, 470 (1973)] for the nonlinear susceptibilities $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ and $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ in alkali-metal vapors, we find that phase modulation can profoundly affect the efficiency and the spectrum of the THG. Generally, the self-phase modulation of the fundamental will tend to reduce the phase matching of an intense fundamental field and the third harmonic and thereby lower the conversion efficiency. New frequencies not contained in the set of frequencies $\omega_{1i}+\omega_{1j}+\omega_{1k}$, where $\{\omega_{1i}\}$ are frequencies in the fundamental laser spectrum, are created even at relatively low conversion due to phase modulation. Effects of cross phase modulation are also studied.

The theory of wave mixing [sum-frequency generation (SFG), difference-frequency generation, second-harmonic generation (SHG), parametric oscillation, third-harmonic generation (THG)] for cw fields was formulated over 25 years ago[1] and descriptions of these processes are available in many fine texts.[2-4] A theoretical description of three-wave mixing for multimode time-dependent input fields (as opposed to cw single-frequency time-independent input fields) has recently been presented.[5,6] Analytic solutions were developed for the time-dependent intensities of the output fields. These solutions differ dramatically from those for single-mode fields. New frequencies in the sum-frequency output spectrum and in the input-field output spectrum are created and grow in magnitude as the input intensities are increased. The output spectrum broadens under conditions of strong nonlinear coupling, ultimately reaching the phase-matched bandwidth limit of the nonlinear crystal. For SHG, the growth of the bandwidth with increasing input intensity of the fundamental and with increasing nonlinear coupling strength is very much reduced compared with the SFG case. At the highest conversion strengths the spectral bandwidth of the second harmonic actually shrinks.[6] In previous studies of SHG and SFG, the bandwidth of the output in these processes have been assumed to be the sum of the bandwidth of the fundamental fields. These estimates were based upon perturbation theory. Generally, the bandwidth of SHG and SFG depend on the intensity, spectral character of the input fields, and the conversion strength of the nonlinear medium.

Here we present results of calculations for THG for multimode fields. In particular, we study the effects of the interplay of third-harmonic generation and phase modulation (due to the quadratic Kerr susceptibility of the nonlinear medium) on the resulting spectrum of the THG. The nonlinear susceptibilities for THG and phase modulation, $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ and $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ are of the same order of perturbation theory in the fundamental field, and therefore one might expect that, for arbitrary frequency ω, the effects of both phenomena should be simultaneously considered. Resonance with energy-level differences in the medium may, however, make one of these susceptibilities larger than the other. Using estimates from the classic work of Miles and Harris[7] for the third-order susceptibilities for THG and self-phase modulation in alkali-metal vapors at Nd:YAG (neodymium-doped yttrium aluminum garnet) and ruby frequencies, we find that phase modulation can profoundly affect the efficiency and the spectrum of THG. Our calculations do not include considerations of beam profile and self-focusing, as they are plane-wave calculations. However, our conclusions should remain valid when such effects are included.

Third-harmonic generation has distinct advantages over other methods presently available for generation of light in the uv. Generally, light sources in the vacuum uv (e.g., resonance discharge lamps) are cw sources (with the exception of synchrotron radiation). The bandwidths of these sources are difficult to control and their intensities are generally low. Moreover, light obtained by SHG of the fundamental, or by SFG with the second harmonic with the fundamental, in nonlinear crystals, is limited to wavelengths longer than 200 nm because of absorption in the available nonlinear crystals in the vacuum uv spectral region. Even the new nonlinear crystal BBO (β-barium borate) is limited to wavelengths larger than 205 nm. In contrast, THG in gases has been successfully employed to produce light at the Lyman-alpha transition (121.6 nm) to detect hydrogen atoms as reactants and products in elementary reactions, e.g., $H+D_2 \rightarrow D+HD$, $F+H_2 \rightarrow H+HF$, etc.[8,9] Bandwidth control of the third harmonic allows Doppler studies of the laser-induced fluorescence or multiphoton ionization signal. The velocity distribution of the hydrogen atoms or molecules involved in the reaction can be deduced from the second moment of the fluorescence excitation versus frequency. Frequency and bandwidth control also allows the study of isotopic substitution (H and D). Use of light pulses of a few nanoseconds or less duration allows the study of molecular dynamics under collisionless conditions. When employing THG in gases to produce uv light, the bandwidth and temporal duration of the pulses might be better controlled.

The dynamical equations governing phase-matched THG for plane waves are given in the slowly-varying-envelope approximation by

$$\partial E_1(z,\tau)/\partial z = -i\omega_1[\chi E_3(E_1^*)^2+\xi(E_1)^2E_1^* + \zeta|E_3|^2E_1^*] , \tag{1}$$

$$\partial E_3(z,\tau)/\partial z = -i\omega_1[\chi E_1^3+\xi'|E_3|^2E_3+\zeta'|E_1|^2E_3] . \tag{2}$$

Here E_1 and E_3 are the slowly varying field envelopes of the fundamental and third-harmonic fields, respectively; τ is the local pulse time ($\tau=t-z/c$); z is the distance in the medium; χ, ξ, ξ', ζ, and ζ' are the nonlinear polarization coefficients for the four-wave-mixing processes involving the fields E_1 and E_3. The last two terms on the right-hand sides of Eqs. (1) and (2) are self- and cross-phase modulation terms, respectively. The coefficients χ, ξ, ξ', ζ, and ζ' depend on the nonlinear medium and the frequency.

Reference 7 presented results of calculations for the coefficients $\chi^{(3)}(3\omega)\equiv\chi$ and $\chi^{(3)}(\omega)\equiv\xi$ for alkali-metal vapors at the wavelengths 1064 and 694 nm. For Li at $\lambda=1064$ nm, $\chi^{(3)}(3\omega)=1.25\times10^{-34}$ esu and $\chi^{(3)}(\omega)=6.7\times10^{-34}$ esu, so $\chi^{(3)}(\omega)/\chi^{(3)}(3\omega)=5.4$. For Li at $\lambda=694$ nm, $\chi^{(3)}(3\omega)=3.00\times10^{-34}$ esu and $\chi^{(3)}(\omega)=3.2\times10^{-32}$ esu, so $\chi^{(3)}(\omega)/\chi^{(3)}(3\omega)=107$. For K at $\lambda=1064$ nm, $\chi^{(3)}(3\omega)=2.61\times10^{-34}$ esu and $\chi^{(3)}(\omega)=1.7\times10^{-32}$ esu, so $\chi^{(3)}(\omega)/\chi^{(3)}(3\omega)=65$. For K at $\lambda=694$ nm, $\chi^{(3)}(3\omega)=6.17\times10^{-35}$ esu and $\chi^{(3)}(\omega)=-2.8\times10^{-32}$ esu, so $\chi^{(3)}(\omega)/\chi^{(3)}(3\omega)=-454$. For the sake of simplicity, and because we do not have estimates of the susceptibilities ξ', ζ, and ζ', we will assume that they are zero. We present results of calculations with the ratio $\chi^{(3)}(\omega)/\chi^{(3)}(3\omega)$ equal to zero and to 100, and are thereby able to clearly see the effects of phase modulation on the spectrum of THG. Then, we point out the effects of cross-phase modulation by including a nonzero value for the cross-phase modulation susceptibility $\zeta'\equiv\chi^{(3)}(-3\omega;\omega,-\omega,3\omega)$.

We shall present calculations of the spectra and temporal dependence of the third-harmonic output and the fundamental output upon THG of a multimode fundamental field in the very low, low, and medium conversion regimes. We consider three types of fundamental fields. The first type is where the fundamental field originates from a laser emitting light at several cavity mode frequencies. The temporal dependence of the input electric field, $F_1(0,\tau)$, can then be written as

$$F_1(0,\tau)=\exp(i\omega_1\tau)E_1(0,\tau)+\text{c.c.}$$
$$=\exp(i\omega_1\tau)\sum_{j=-n}^{n}E_{1,j}\exp[i(\Delta j\tau+\phi_{1,j})]+\text{c.c.} , \tag{3}$$

where we have defined the cavity mode frequencies as $\omega_{1j}\equiv\omega_1+\Delta j$, Δ is the mode frequency spacing of the cavity, and $\phi_{1,j}$ are the phase shifts for the different modes. We let the input beam contain three equal intensity modes, i.e., $n=1$, with equal amplitudes, $E_{1,-1}=E_{1,0}=E_{1,1}=\frac{1}{3}$, and phases $\phi_{1,-1}=\phi_{1,0}=\phi_{1,1}=0$. The slowly varying envelope is then given by

$$E_1(0,\tau)=[1+2\cos(\Delta\tau)]/3 . \tag{4}$$

The second type of field is a short-duration pulse with a Gaussian envelope. The slowly varying envelope is given by

$$E_1(0,\tau)=\exp[-(\tau-t_0)^2/2\sigma^2] . \tag{5}$$

The third type is a frequency-modulated field with slowly varying envelope given by

$$E_1(0,\tau)=\exp[iF_0\cos(\Delta\tau)] . \tag{6}$$

We define the (dimensionless) coupling strength parameter u as $u\equiv\sup_\tau[I_1(\tau)]\omega_1\chi L$, where L is the length of nonlinear crystal through which the light propagates, and $I_1(\tau)$ is normalized to $|E_1(\tau)|^2$. In what follows we designate very low, low, and medium conversion strengths as follows: $u=5\times10^{-3}$, 5×10^{-2}, and 0.5, respectively. For each type of field, we perform calculations with these conversion strengths.

Let us first consider the input fundamental field with slowly varying envelope $E_1(0,\tau)=E_0[1+2\cos(\Delta\tau)]/3$ of Eq. (4). In the very low and low conversion cases the temporal dependence of the fundamental output is virtually indistinguishable in appearance from the input fundamental field because very little of the fundamental is converted to the third harmonic. The conversion efficiency to the third harmonic for the very low, low, and medium conversion cases corresponds to 1.5×10^{-5}, 1.5×10^{-3}, and 0.14, respectively when no phase modulation is present. Figure 1 shows the temporal dependence of the fundamental output and the THG output for the medium conversion case without any phase modulation. Here the depletion of the fundamental is clearly evident. Figure 2 shows the intensity of the THG versus frequency for the very low conversion case, without and with self-phase modulation of the fundamental included. In this figure, the central frequency labeled 0 actually has a frequency of $3\omega_1$ and the frequency scale is in units of Δ. The calculated spectrum in Fig. 2 is a series of Δ functions at frequencies $3\omega_1+m\Delta$, $m=0,\pm1,\pm2$, etc. (the electric field goes on forever so no linewidth is present), and therefore the width of the lines at frequencies $3\omega_1+m\Delta, m=0,\pm1,\pm2$, etc. are arbitrarily included. We see that the spectrum of the third harmonic is somewhat broadened as a result of the phase modulation. Note that the ordinate of Fig. 2 is plotted on a log scale, and the total intensity in the additional harmonics intro-

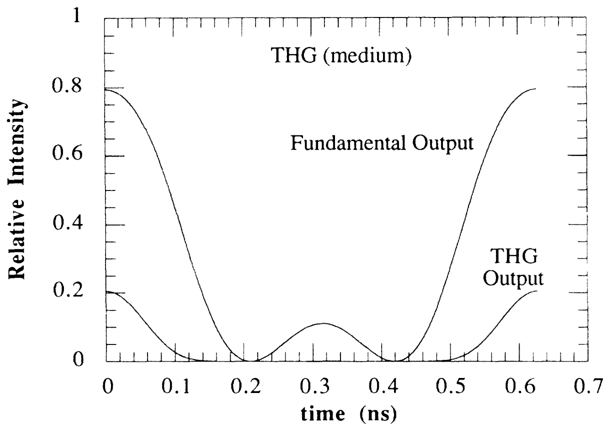

FIG. 1. Temporal dependence of the fundamental output at frequencies around ω_1 and the THG output at frequencies around $3\omega_1$ for an input fundamental field with three modes in the medium conversion case without phase modulation. The temporal dependence of the field is periodic and recurs outside the period plotted in the figure.

duced by the phase modulation is not large. Figure 3 shows the intensity versus frequency for the low-conversion case. We see that, in this case, the spectrum is significantly broadened by the phase modulation in that there is a long progression of higher harmonics that are created. Moreover, the intensity of the third harmonic is significantly reduced relative to the non-phase-modulated case. This results because the fundamental field is self-phase modulated and therefore steps out of phase with the third harmonic, which is not phase modulated. We now introduce a cross-phase modulation of the third harmonic via the nonlinear susceptibility ξ', which is taken arbitrarily to equal 3ξ. The temporal intensity pattern obtained for the third harmonic without any phase modulation of the fundamental is thereby recovered; however, the frequency spectrum of the third harmonic is as shown in Fig. 3(c) and is very different from that without phase modulation. This cross-phase modulation compensates the phase of the third harmonic so that it keeps up with the self-phase modulation of the fundamental. The total integrated intensity is then the same as in the case of no phase modulation whatever. Figure 4 shows the intensity versus frequency for the medium conversion case. In Fig. 4(c) we have not drawn the intensity at frequencies away from $3\omega_1+m\Delta$, $m=0,\pm1,\pm2$, etc., equal to zero because this would make the figure unreadable. Again, inclusion of phase modulation of the fundamental reduces the intensity of the third harmonic. This is clearly shown in Fig. 5, which plots the temporal dependence of the fundamental output and the THG output in the medium conversion case with phase modulation. In fact, the total third-harmonic intensity is less

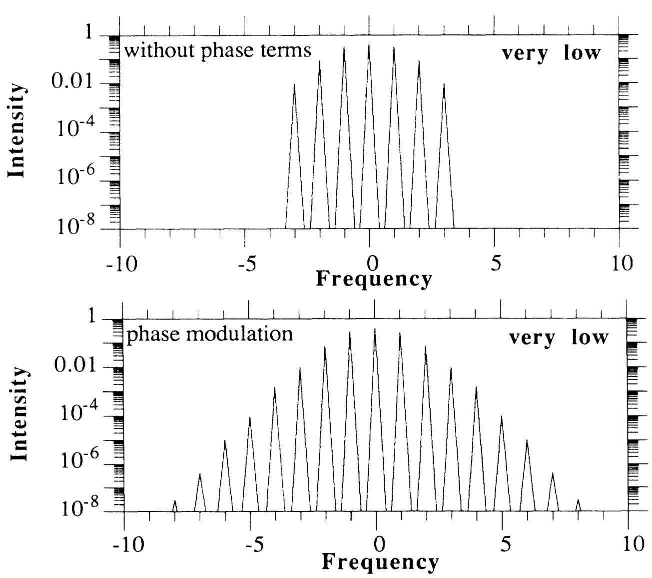

FIG. 2. Intensity of the THG vs frequency for an input fundamental field with three modes in the very low conversion case, without and with phase modulation included. The central frequency labeled 0 actually has frequency $3\omega_1$ and the frequency scale is in units of Δ.

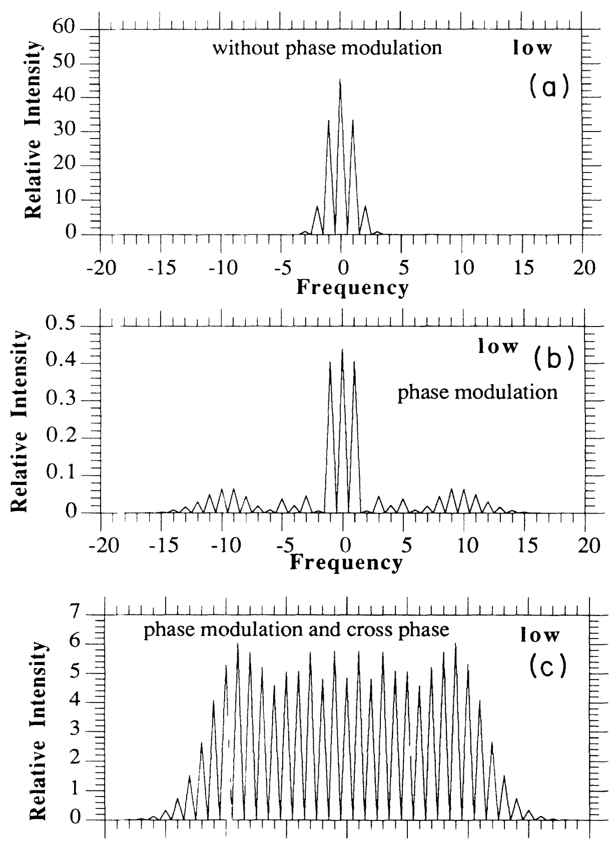

FIG. 3. Intensity of the THG vs frequency for an input fundamental field with three modes in the low conversion case: (a) without phase modulation included, (b) with phase modulation of the fundamental, and (c) with phase modulation of the fundamental and cross-phase modulation of the third harmonic. The central frequency labeled 0 actually has frequency $3\omega_1$ and the frequency scale is in units of Δ.

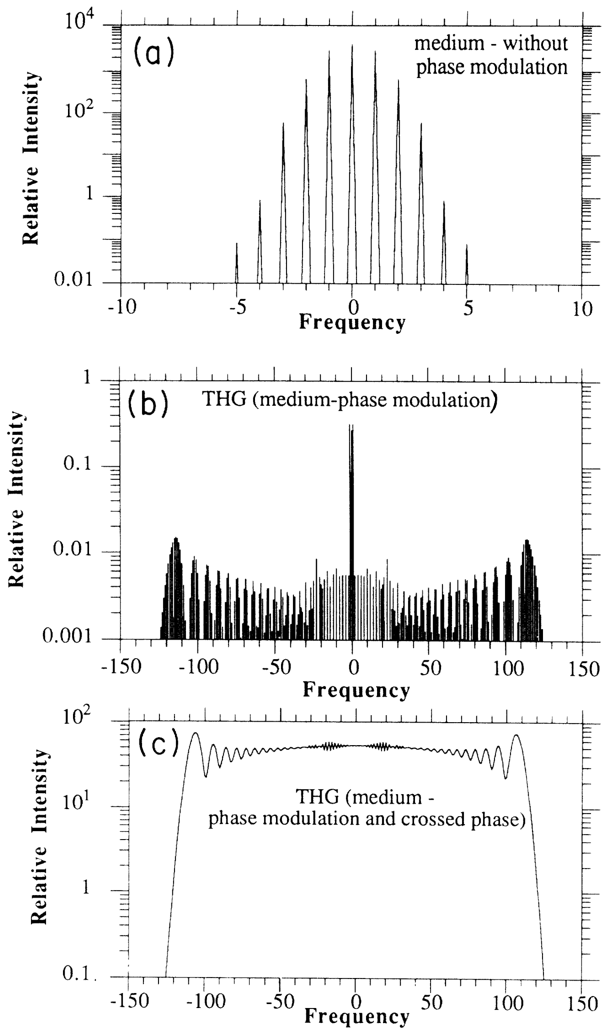

FIG. 4. Intensity of the THG vs frequency for an input fundamental field with three modes in the medium conversion case: (a) without phase modulation included, (b) with phase modulation of the fundamental, and (c) with phase modulation of the fundamental and cross-phase modulation of the third harmonic.

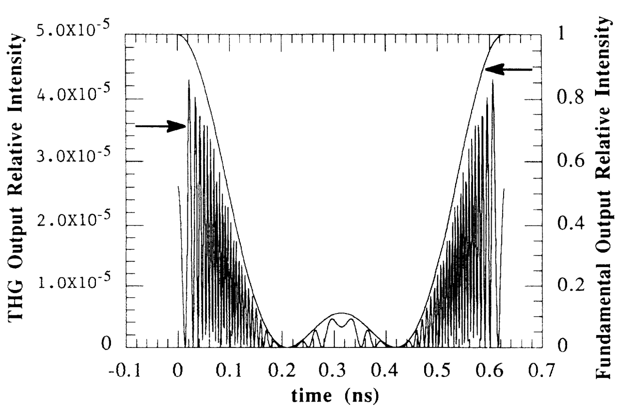

FIG. 5. Temporal dependence of the fundamental output at frequencies around ω_1 and the THG output at frequencies around $3\omega_1$ for an input fundamental field with three modes in the medium conversion case with phase modulation.

than that for the low-conversion case. Adding the cross-phase modulation to the third harmonic restores the integrated intensity and the temporal pattern is just as in the case without any phase modulation (Fig. 1).

We now consider the short-duration pulse input field, $E_1(0,\tau)=E_0\exp[-(\tau-t_0)^2/2\sigma^2]$. Figure 6 shows the temporal dependence of the fundamental output and the THG output for a short-pulse-duration input fundamental field [full width at half maximum (FWHM) ~ 400 ps] in the medium conversion case without phase modulation. Figure 6(a) shows the output intensities of the fundamental and the THG on scales with their peaks overlapped, thereby demonstrating the pulse shortening of the THG, and Fig. 6(b) shows the relative intensities of the fields plotted on the same scale. The conversion efficiency to the third harmonic for the very low, low, and medium conversion cases corresponds in the short pulse case to 1.5×10^{-5}, 1.5×10^{-3}, and 0.12, respectively, when no phase modulation is present. Figure 7 shows the intensity versus frequency for the very low conversion case (a) without phase modulation, (b) with phase modulation, and (c) with phase modulation of the fundamental and cross-phase modulation of the third harmonic ($\zeta'=3\xi$ as above). Figure 8 shows the intensity versus frequency for the low conversion case. Again, inclusion of phase modulation of the fundamental reduces the intensity of the third harmonic. Note that the phase modulation result was multiplied by a factor of 50 so that it

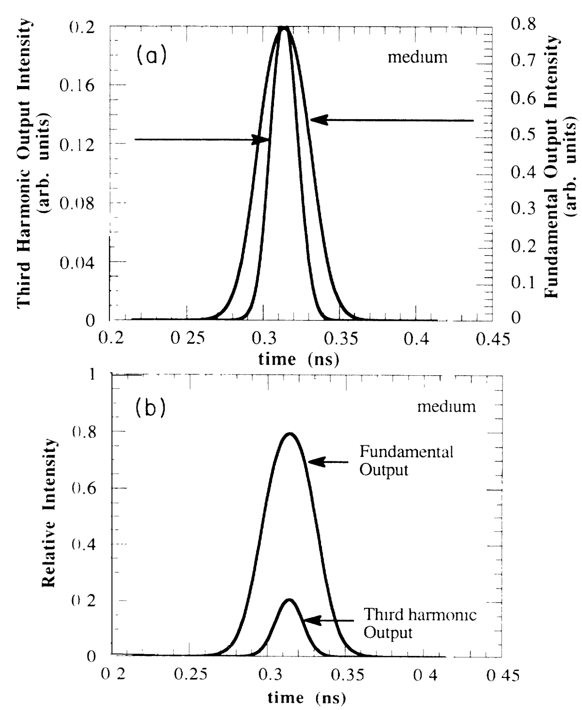

FIG. 6. Temporal dependence of the fundamental output at frequencies around ω_1 and the THG output at frequencies around $3\omega_1$ for a short-pulse-duration input fundamental field in the medium conversion case without phase modulation. (a) shows the output intensities on a scale which demonstrates the pulse shortening of the THG, and (b) shows the relative intensities of the fields.

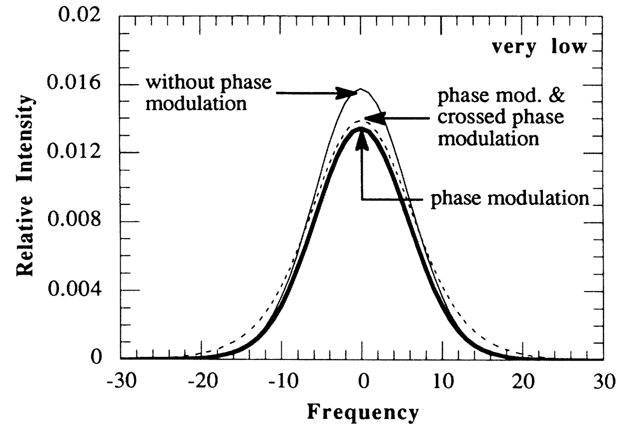

FIG. 7. Intensity of the THG vs frequency for a short-pulse-duration input fundamental field in the very low conversion case.

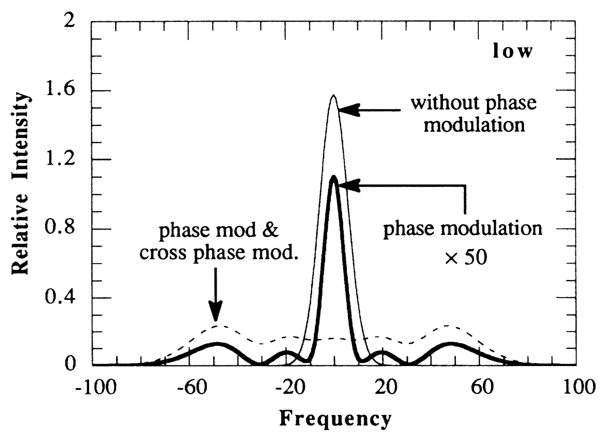

FIG. 8. Intensity of the THG vs frequency for a short-pulse-duration input fundamental field in the low conversion case.

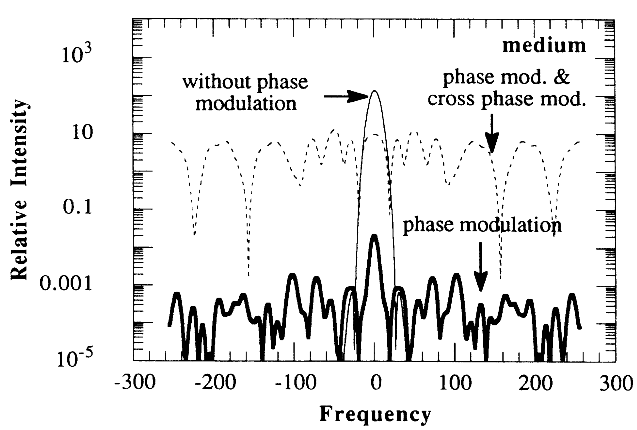

FIG. 9. Intensity of the THG vs frequency for a short-pulse-duration input fundamental field in the medium conversion case.

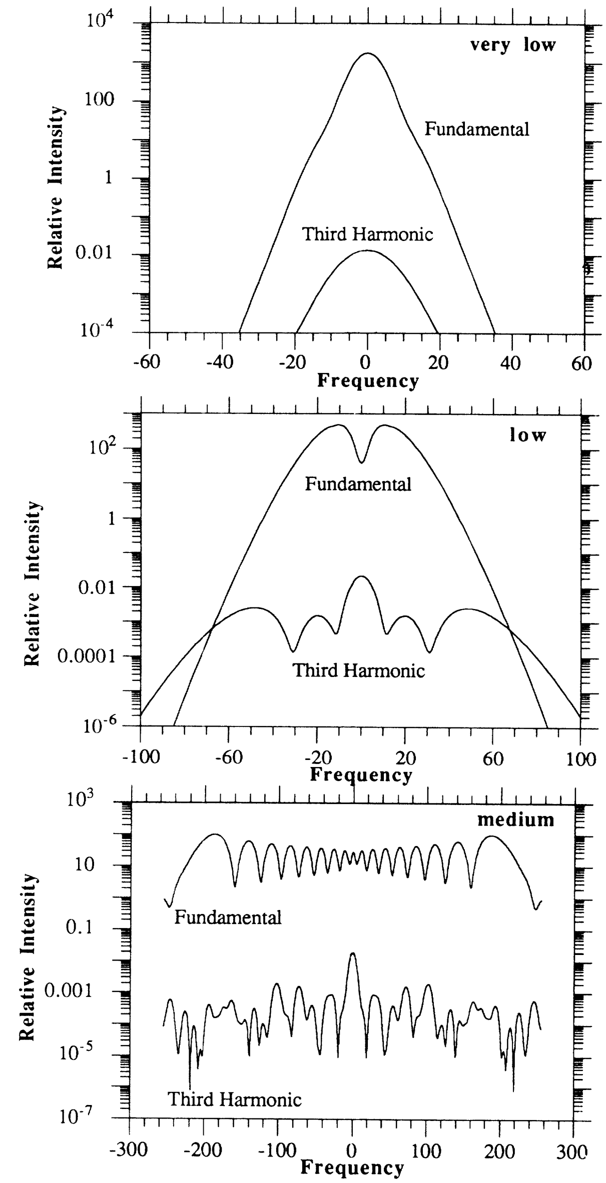

FIG. 10. Intensity of the fundamental and the third harmonic vs frequency (centered around ω_1 and $3\omega_1$, respectively) for very low, low, and medium conversion.

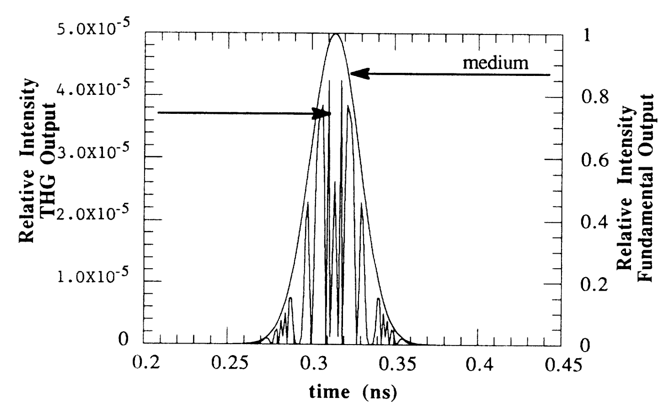

FIG. 11. Temporal dependence of the fundamental output at frequencies around ω_1 and the THG output at frequencies around $3\omega_1$ for a short-pulse-duration input fundamental field in the medium conversion case with phase modulation.

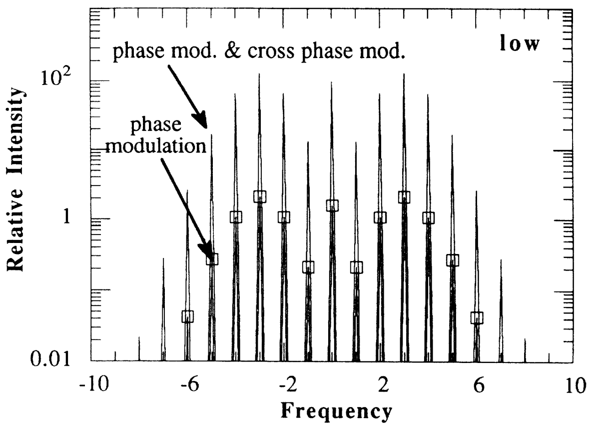

FIG. 12. Intensity of the THG vs frequency for the frequency modulated input fundamental field $\exp[i1.4\cos(\Delta\tau)]$, without and with cross-phase modulation included. The central frequency labeled 0 actually has frequency $3\omega_1$ and the frequency scale is in units of Δ.

could be easily seen in the figure. With cross-phase modulation, the total integrated intensity and the temporal shape of the third harmonic is then the same as in the case of no phase modulation whatever. Figure 9 shows the intensity versus frequency for the medium conversion case. The spectra of the third-harmonic radiation without and with phase modulation are dramatically different. In order to observe the effects of phase modulation as the conversion strength increases we have plotted the spectrum of the fundamental and the third harmonic for the very low, low, and medium conversion cases in Fig. 10. We see that for the low and medium conversion cases, phase modulation introduces oscillations in the spectrum of the fundamental. As the intensity of the fundamental or the propagation length increases, phase modulation shifts intensity away from the central frequency ω_1 and spreads it into surrounding frequencies in a well-known manner.[10] The temporal pattern of the fundamental intensity is unaffected by the phase modulation (phase modulation affects the frequency, not the amplitude). Figure 11 plots the temporal dependence of the fundamental output and the THG output in the medium conversion case with phase modulation. The reduction of the intensity of the third harmonic due to phase modulation of the fundamental is clearly evident but there is no effect of the phase modulation on the intensity of the fundamental versus time.

We now consider a frequency-modulated input field, $\exp[iF_0\cos(\Delta\tau)]$, and arbitrarily take $F_0=1.4$. The intensity of the input field is constant with time, and the fundamental and third-harmonic output intensities are also constant. The conversion efficiency in the very low, low, and medium cases is 2.58×10^{-5}, 2.58×10^{-3}, and 0.205, respectively, without phase modulation. With phase modulation the conversion efficiency is 2.12×10^{-5}, 4.22×10^{-5}, and 2.62×10^{-5}, respectively. With both phase modulation and cross-phase modulation ($\zeta'=3\xi$ as above) the percent conversion is the same as without phase modulation. Figure 12 shows the intensity versus frequency with and without cross-phase modulation for the low conversion case. Note that the relative intensities with cross-phase modulation are significantly increased (by a factor of 61) relative to the case without cross-phase modulation.

In summary, we have seen that the effects of self- and cross-phase modulation of the nonlinear medium on the spectrum of the THG can be quite dramatic. Generally, the self-phase modulation of the fundamental will tend to reduce the phase matching of an intense fundamental field and the third harmonic, and thereby lower the conversion efficiency for THG. Using the estimates of Miles and Harris[7] for the nonlinear susceptibilities $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ and $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ in alkali-metal vapors, we find that phase modulation can profoundly affect the efficiency and the spectrum of THG. We have seen that the cross-phase modulation of the third harmonic by the fundamental may compensate for the self-phase modulation of the fundamental, depending, of course, on the value of the cross-phase modulation susceptibility, $\chi^{(3)}(-3\omega;\omega,-\omega,3\omega)$ and its relation to $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$. We believe that, generally, the effect of the cross-phase modulation of the fundamental field by the third harmonic will be much less significant, because the intensity of the third harmonic is generally much smaller than that of the fundamental. We have calculated the spectrum of THG for multimode input fields (i) originating from a laser with gain on several cavity modes, (ii) of the form of pulses with short temporal duration, and (iii) frequency-modulated input fields. We have shown that new frequencies not contained in the set of frequencies $\omega_{1i}+\omega_{1j}+\omega_{1k}$ are created even at relatively low conversion due to the effect of phase modulation. We conclude that great care must be exercised if we want to control the spectrum and the bandwidth of the THG in gas media and that the effects of self-phase modulation of the fundamental may significantly lower the conversion efficiency of intense fundamental beams.

Note added. After submission of this manuscript, Professor S. E. Harris made me aware of a paper by Zych and Young,[11] which reports THG experiments in Xe-Ar mixtures that indicate that cross-phase modulation, $\chi^{(3)}(-3\omega;\omega,-\omega,3\omega)$, alters the index of refraction of the third harmonic of 354.7-nm radiation.

I thank R. Bavli and B. Katz for useful discussions. This work is supported in part by a grant from the U.S.-Israel Binational Science Foundation.

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