Conical Harmonic Generation in Isotropic Materials

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A novel class of nonlinear optical processes is described in which radiation at the nth harmonic is generated through the use of a $(2n + 1)$-order nonlinearity. Utilizing an odd-order nonlinearity, this process allows for the generation and amplification of both odd- and even-order harmonics in isotropic materials. Additionally, this process can always be phase matched in normal-dispersion materials without the use of birefringence. Experimental results are presented in which conical third-harmonic emission is generated from a sapphire sample.

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Since the birth of nonlinear optics [1], researchers have been exploring novel techniques for generating the harmonics of a laser field. For example, recent work using hollow waveguides has successfully produced the ~31st harmonic [2] of a Ti:sapphire laser beam, and soft x rays have been created by focusing into a gas jet [3]. There are several issues that must be taken into account in the generation of harmonic radiation. For example, it is commonly accepted knowledge in nonlinear optics that it is not possible to generate or amplify a second-harmonic (SH) signal (or other even-order harmonics) in a bulk isotropic material because symmetry conditions require the even-order nonlinear susceptibilities to vanish identically [4]. Second-harmonic generation (SHG) in fibers has been observed, but this noninstantaneous process relies on a permanent static field developing in the fiber which couples through $\chi^{(3)}$ to generate the SH signal [5]. Even harmonics may also be generated at the surface of an isotropic material; however, only the atomic layer at the interface contributes, which results in extremely weak signals [6]. Recent experiments [7] have demonstrated SHG in a centrosymmetric material if the material is antiferromagnetic.

Another important requirement for the efficient generation of harmonics is that the process be phase matched over an appreciable interaction length. Since most materials are normally dispersive in the visible and infrared, phase matching can be achieved only through the use of birefringence [4] or by the use of periodically poled materials [8]. More recent experiments have demonstrated phase matching by adjusting the coupled mode of the input beam and the gas pressure inside a hollow waveguide [9]. Even in the limit of perfect phase matching, tightly focused beams in bulk materials are problematic since the light generated prior to the focus destructively interferes with that generated beyond the focus [10–12]. This symmetry can be broken by nonlinear refractive index changes, by plasma generation [13], or by focusing the beam near the surface of the sample [14]. In the latter case, the generated third harmonic (TH) light can be monitored to detect interfaces [15], to produce third-order intensity autocorrelations [16], or to perform optical microscopy [17].

In this Letter, we present a class of nonlinear optical processes that allows for any order harmonic to be generated or amplified in an isotropic material by utilizing higher-order nonlinearities. Phase matching is achieved automatically by emitting the generated light in the form of a cone. If the process is externally seeded, the angle between the pump and signal can be adjusted to achieve phase matching. This process could play an important role, particularly in the case where the perturbative limit of the nonlinear susceptibility becomes invalid, and higher-order processes are as probable as the lower-order process.

For illustration, we analyze the specific example of SH amplification in an isotropic medium. We initially assume that two monochromatic beams are present and decompose the electric field E into the fundamental and SH components

$$E(t) = E(\omega)e^{-i\omega t} + E(2\omega)e^{-2i\omega t} + \text{c.c.}, \qquad (1)$$

where $E(\omega)$ is the electric field of the fundamental and $E(2\omega)$ is the electric field of the SH. We have neglected the vector nature of the fields by assuming that the incident fields are all polarized along the same direction. The nonlinear polarization P^{NL} produced by these fields in the perturbative limit can be expressed as

$$P^{\text{NL}}(t) = \chi^{(3)}E^3(t) + \chi^{(5)}E^5(t) + \ldots, \qquad (2)$$

where $\chi^{(n)}$ is the nth order nonlinear susceptibility, and all even-order susceptibilities have been omitted because the nonlinear material is assumed to be isotropic.

Substituting the form of the electric field given by Eq. (1) into Eq. (2), we separate the resulting nonlinear polarization into terms that oscillate at frequencies ω and 2ω,

$$P^{\mathrm{NL}}(\omega) = 3\chi^{(3)}_{\mathrm{spm}}|E(\omega)|^2E(\omega) + 10\chi^{(5)}_{\mathrm{spm}}|E(\omega)|^4E(\omega), \tag{3a}$$

$$P^{\mathrm{NL}}(2\omega) = 6\chi^{(3)}_{\mathrm{xpm}}|E(\omega)|^2E(2\omega) + 30\chi^{(5)}_{\mathrm{xpm}}|E(\omega)|^4E(2\omega) + 5\chi^{(5)}_{\mathrm{shg}}E^4(\omega)E^*(2\omega), \tag{3b}$$

where we have expanded up to fifth order and made the undepleted-pump/weak-probe approximation [i.e., neglecting terms of order $E^2(2\omega)$], and $\chi^{(n)}_{\mathrm{spm}}$, $\chi^{(n)}_{\mathrm{xpm}}$, and $\chi^{(n)}_{\mathrm{shg}}$ represent the nth order nonlinear susceptibilities responsible for self-phase modulation, cross-phase modulation, and second-harmonic generation, respectively. Of particular interest is the term

$$P^{\mathrm{NL}}_{\mathrm{shg}} \sim \chi^{(5)}_{\mathrm{shg}}E^4(\omega)E^*(2\omega)e^{-2i\omega t} \tag{4}$$

that potentially leads to the transfer of energy between the fundamental and the SH. This lowest order process was first investigated by Andrews [18], and a variation of this six-wave mixing process was used to explain the time-dependent growth of a second-harmonic signal in an organic dye [19]. The remaining terms in Eq. (3) represent self- and cross-phase modulation contributions. Figure 1(a) depicts the Manley-Rowe photon diagram for $P^{\mathrm{NL}}_{\mathrm{shg}}$. It is apparent that such a wave-mixing interaction can be phase matched via the wave vector diagram as shown in Fig. 1(b). Neglecting the effects of self- and cross-phase modulation, the phase-matching diagram suggests that the process will be phase matched if the fundamental wave and SH seed propagate at an angle θ such that $\cos\theta = n(\omega)/n(2\omega)$ where $n(\omega)$ is the linear index of refraction of the material at the frequency ω.

To determine the propagation characteristics of this process, we perform a plane-wave analysis with light fields corresponding to the geometry suggested by Fig. 1(b) such that

$$E(\omega) = A_p(z)e^{ik_1z}, \tag{5a}$$

$$E(2\omega) = A_s(z)e^{i(k_{2z}z+k_{2x}x)} + A_i(z)e^{i(k_{2z}z-k_{2x}x)}, \tag{5b}$$

where $k^2_{2z} + k^2_{2x} = k^2_2$, $k_m = m\omega n(m\omega)/c$ is the wave vector, $m = 1, 2$, and $A_p(z)$, $A_s(z)$, and $A_i(z)$ are the amplitudes of the pump, signal, and idler waves, respectively. By substituting these fields into the wave equation and making the slowly varying envelope approximation, we

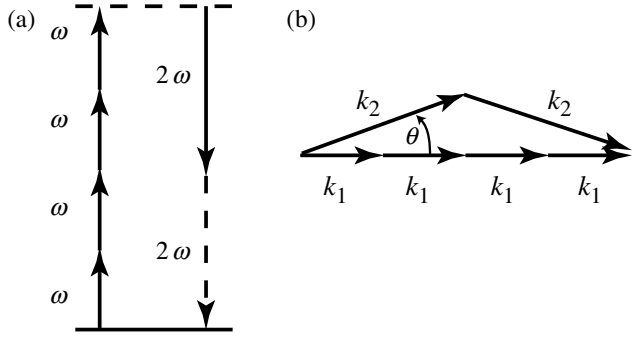

FIG. 1. (a) Manley-Rowe photon picture and (b) phase-matching diagram of the $\chi^{(5)}$ process responsible for second-harmonic amplification. $k_m = n(m\omega)m\omega/c$ is the wave vector of a beam propagating through the material with frequency $m\omega$.

derive three coupled-amplitude equations that govern the propagation of the fields:

$$2ik_1\frac{dA_p}{dz} = \frac{-4\pi\omega^2}{c^2}(3\chi^{(3)}_{\mathrm{spm}}|A_p|^2A_p + 10\chi^{(5)}_{\mathrm{spm}}|A_p|^4A_p), \tag{6a}$$

$$2ik_{2z}\frac{dA_s}{dz} = \frac{-16\pi\omega^2}{c^2}(6\chi^{(3)}_{\mathrm{xpm}}|A_p|^2A_s + 30\chi^{(5)}_{\mathrm{xpm}}|A_p|^4A_s + 5\chi^{(5)}_{\mathrm{shg}}A^4_pA^*_ie^{2iz(2k_1-k_{2z})}), \tag{6b}$$

$$2ik_{2z}\frac{dA_i}{dz} = \frac{-16\pi\omega^2}{c^2}(6\chi^{(3)}_{\mathrm{xpm}}|A_p|^2A_i + 30\chi^{(5)}_{\mathrm{xpm}}|A_p|^4A_i + 5\chi^{(5)}_{\mathrm{shg}}A^4_pA^*_se^{2iz(2k_1-k_{2z})}). \tag{6c}$$

In separating these three equations, we neglect wave components that propagate in directions other than those of the three waves we are considering since these fields are not phase matched.

The pump-field amplitude A_p is decoupled from the other fields, and its solution is given in terms of its initial amplitude, $A_p(0)$, by

$$A_p(z) = A_p(0)e^{i(\Delta k^{NL}_p)z}, \tag{7}$$

where $\Delta k^{\mathrm{NL}}_p = \frac{2\pi\omega^2}{k_1c^2}[3\chi^{(3)}_{\mathrm{spm}}|A_p(0)|^2 + 10\chi^{(5)}_{\mathrm{spm}}|A_p(0)|^4]$ represents the nonlinear wave vector contribution experienced by the pump beam.

Substituting $A_p(z)$ into the differential equations for $A_s(z)$ and $A_i(z)$ yields two linear, coupled differential equations,

$$\frac{dA_s}{dz} = i(\Delta k^{\mathrm{NL}}_s)A_s + i\beta e^{2i(\Delta k_{\mathrm{eff}}+\Delta k^{\mathrm{NL}}_s)z}A^*_i, \tag{8a}$$

$$\frac{dA_i}{dz} = i(\Delta k^{\mathrm{NL}}_s)A_i + i\beta e^{2i(\Delta k_{\mathrm{eff}}+\Delta k^{\mathrm{NL}}_s)z}A^*_s, \tag{8b}$$

where $\Delta k^{\mathrm{NL}}_s = \frac{8\pi\omega^2}{k_{2z}c^2}[6\chi^{(3)}_{\mathrm{xpm}}|A_p(0)|^2 + 30\chi^{(5)}_{\mathrm{xpm}}|A_p(0)|^4]$ is the nonlinear wave vector contribution to the amplitude experienced by the second-harmonic beams, $\Delta k_{\mathrm{eff}} = 2[\Delta k^{\mathrm{NL}}_p + k_1] - [\Delta k^{\mathrm{NL}}_s + k_{2,z}]$ is the effective wave vector mismatch between the fundamental and second-harmonic waves, and $\beta = \frac{8\pi\omega^2}{k_{2z}c^2}[5\chi^{(5)}_{\mathrm{shg}}A_p(0)^4]$ is the gain parameter that leads to growth of the second-harmonic signal.

Under the assumption that the idler beam is initially absent, the intensities of the signal and idler as a function of propagation distance are given by

$$\frac{I_s(z)}{I_s(0)} = \cosh^2(gz) + \frac{(\Delta k_{\mathrm{eff}})^2}{g^2}\sinh^2(gz), \tag{9a}$$

$$\frac{I_i(z)}{I_s(0)} = \frac{|\beta|^2}{g^2}\sinh^2(gz), \tag{9b}$$

where $g = \sqrt{|\beta|^2 - (\Delta k_{\mathrm{eff}})^2}$. The maximum exponential gain is achieved when $\Delta k_{\mathrm{eff}} = 0$, and when $|\Delta k_{\mathrm{eff}}| > |\beta|$

oscillatory, rather than exponential, behavior is observed. A similar calculation was performed for the nondegenerate case in which four photons at the fundamental wavelength produce photons at frequencies $2\omega + \Delta$ and $2\omega - \Delta$ instead of two photons at frequency 2ω. Exponential growth also occurs for the nondegenerate case, but the gain coefficient β is maximum when $\Delta = 0$ (the degenerate case).

This type of interaction is not limited solely to SH generation. Detailed calculations similar to those above were performed for third-harmonic generation (THG) through a $\chi^{(7)}$ process in which case six pump photons are annihilated to create two TH photons. Even though the calculations have been done under the assumption that the process is seeded by an external beam, these processes may grow from quantum fluctuations. In addition, in the case of odd-harmonic generation, radiation from the mismatched $\chi^{(n)}$ process is able to seed the $\chi^{(2n+1)}$ process. For example, a small signal generated through phase-mismatched $\chi^{(3)}$ THG or surface THG would greatly increase the output signal resulting from the $\chi^{(7)}$ phase-matched TH process.

In addition to the plane-wave analysis, we show results of numerical simulations of focused monochromatic Gaussian beams for THG under the assumption of radial symmetry. All terms up to seventh order are included in addition to the terms that generate the harmonic. We observe exponential growth of the TH wave as a function of the input power of the fundamental beam and conical emission at the harmonic. Figure 2 shows results for a simulation of THG. The parameters (with the exception of $\chi^{(7)}$) are chosen to simulate a laser at 1500 nm being focused into sapphire such that the diffraction angle is 2°. The TH seed is generated by the phase-mismatched $\chi^{(3)}$ process. The incident power of the pump is kept less than the critical power for self-focusing ($P_{\rm cr} \approx 1.9\lambda^2/[4\pi n_0 n_2]$ where $n_2 = 12\pi^2\chi^{(3)}_{\rm spm}/[n(\omega)^2 c]$ is the nonlinear index of refraction [4,20]); otherwise, the radial profile would collapse to a singularity. For the results in Fig. 2, we assume the pump power was $0.6P_{\rm cr}$ and that $\chi^{(7)}$ is larger than might be assumed from an estimation [4] of a purely nonresonant electronic nonlinearity since in the experiment the pump power can be much larger than $P_{\rm cr}$. The far-field diffraction pattern is shown in Fig. 3. As can be seen, two components propagating off axis are generated with a cone angle of $\theta \sim 10°$ in agreement with the predictions based on the linear indices of refraction and a plane-wave geometry. If the diffraction angle of the input beam is increased so that it is comparable to the expected cone angle of the TH, a significant on-axis component of the TH is also observed. This results from the component of the fundamental beam that is traveling in the direction of the expected cone angle pumping the on-axis components of the TH beam.

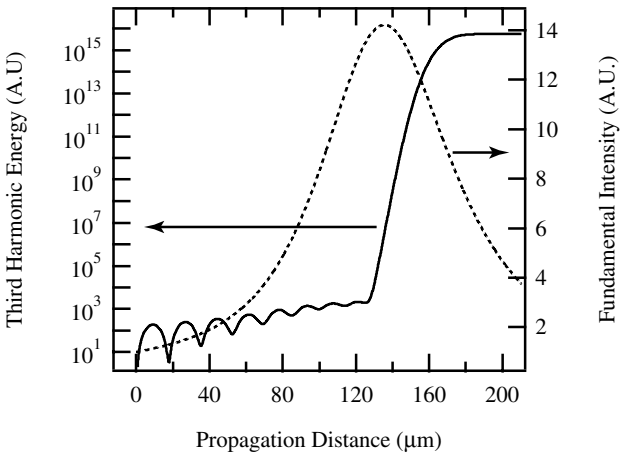

FIG. 2. The energy in the third harmonic (TH) wave (solid line) and the intensity of the fundamental (dotted line) as the two beams focus. Phase mismatched $\chi^{(3)}$ TH generation is observed at weak intensities of the fundamental beam, and exponential growth occurs at the focus where the $\chi^{(7)}$ process becomes important.

We have observed this process experimentally using the same values for wavelength and indices of refraction as in the above theoretical calculation. Pulses at 1500 nm with energies of 10 μJ and 50 fs duration are generated by an optical parametric amplifier operating at a 1-kHz repetition rate and are focused into a sapphire sample by a 10× microscope objective with a numerical aperture (NA) of 0.16. A picture of the TH output ring and a plot of the corresponding spectrum are shown in Fig. 4. We believe the SH is not observed since phase-mismatched $\chi^{(2)}$ harmonic generation is not possible in isotropic materials, and the growth from quantum fluctuations requires substantially larger gain for the observation of the SH signal. Strong continuum generation is sometimes seen to accompany the conical THG depending on the input power and focusing conditions. The output angle ($\theta \sim 12°$) is nearly equal to the value expected from the above analysis, with the inclusion of refraction at the output surface of the sample. The output angle is experimentally observed to change with the NA of the lens, in qualitative agreement with the numerical simulations. There are two reasons that higher-NA objectives result in larger cone angles. First, the tighter focusing conditions result in a larger distribution of propagation directions. Second, the higher-NA objectives result in

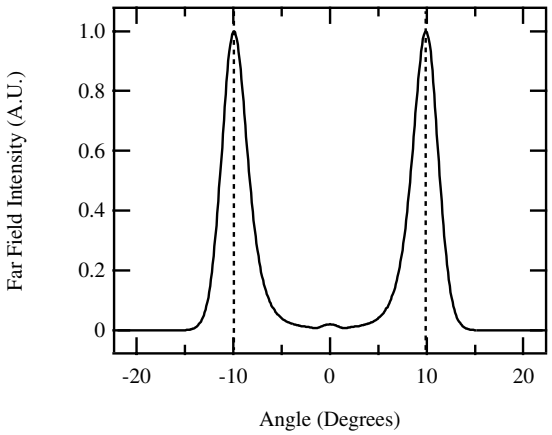

FIG. 3. The far-field diffraction pattern of the third-harmonic wave generated through a $\chi^{(7)}$ process. The cone angle is ~10° as predicted by the plane-wave analysis.

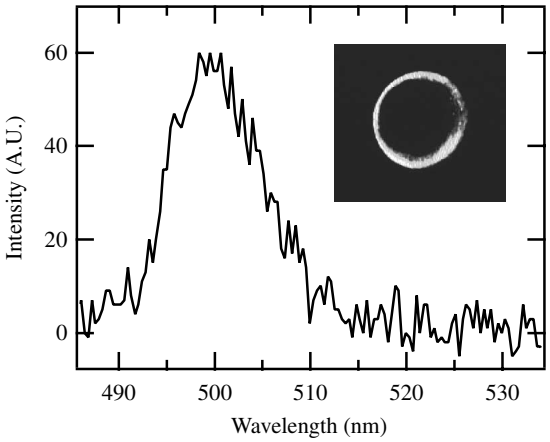

FIG. 4. Experimental spectrum of conical third-harmonic emission from sapphire and the corresponding photograph of the output ring (inset) for the case in which the wavelength of the input pulse is centered at 1500 nm. The spectral width results from the bandwidth of the fundamental pulse. The cone angle is $\sim 12°$ and the conversion efficiency is $\sim 10^{-6}$.

higher intensities and thus larger Δk_s^{NL} and Δk_p^{NL}. In order to satisfy the phase-matching condition $\Delta k_{\mathrm{eff}} = 0$, the angle must be larger. This process is observed in a single shot and thus is not a result of damage induced in the material, which supports the instantaneous nonlinear interaction proposed here. We have also observed conical emission in fused-silica glass. However, the spectrum in this case is considerably more complicated which we believe is partly a result of higher-order hyper-Raman scattering; the Raman scattering cross section for sapphire is over an order of magnitude smaller than that of fused silica [21].

For purely nonresonant electronic nonlinearities the magnitude of these higher-order processes is expected to be small relative to the lower-order counterparts. However, there are several situations where we expect these processes to play an important role. The first is in the case of a resonant interaction. For example, if the material chosen for SHG is such that the band gap is smaller than the energy of four photons at the fundamental wavelength, the $\chi^{(5)}$ process depicted in Fig. 1(a) will be resonantly enhanced. In addition, since the band gap will be larger than the energy of a single SH photon, the material will be transparent at the pump and signal wavelengths. This process may be inhibited by nonlinear absorption, but explicit knowledge of the $\chi^{(5)}$'s is necessary to make a determination. These processes will also be relevant to experimental conditions experienced during high-harmonic generation. In these situations, the perturbative limit of expanding the nonlinear polarization is violated, and these higher-order processes may be as probable as the direct process. However, since the index of refraction at the harmonic frequency is less than the index at the fundamental, the conventional noncollinear phase-matching geometry must be used. Although this process offers no advantage over the lower-order process for odd-harmonic generation, the higher-order process presented here would allow even harmonics to be generated. In addition, since the dispersion of gases is small, the output generated from these higher-order processes will be nearly on axis.

In conclusion, we describe a class of higher-order nonlinear processes that allow for the production of harmonics of any order in normal-dispersion materials regardless of the symmetry. Phase matching is automatically satisfied at a suitable angle between the pump and signal waves which results in the harmonics to be emitted in the form of a cone. We believe that these higher-order terms could play an important role in very intense interactions when the perturbative expansion of the polarizability is no longer valid or when these higher-order processes are resonantly enhanced. We have observed experimental evidence of a $\chi^{(7)}$ process generating third-harmonic radiation in agreement with our theory.

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