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Optical third-harmonic generation using ultrashort laser pulses

D. Stoker,[1,2,*] M. F. Becker,[2,3] and J. W. Keto[1,2]
[1]*Department of Physics, The University of Texas at Austin, 1 University Station C1600, Austin, Texas 78712–0264, USA*
[2]*Center for Nano and Molecular Science and Technology and the Texas Materials Institute, The University of Texas at Austin, Building ETC, Room 8.102, Campus Mail Code C2201, Austin, Texas 78712-1063, USA*
[3]*Electrical and Computer Engineering, The University of Texas at Austin, 1 University Station C0803, Austin, Texas 78712–0240, USA*
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To better predict optical third-harmonic generation (THG) in transparent dielectrics, we model a typical ultrashort pulsed Gaussian beam, including both group velocity mismatch and phase mismatch of the fundamental and harmonic fields. We find that competition between the group velocity mismatch and phase mismatch leads to third-harmonic generation that is sensitive only to interfaces. In this case, the spatial resolution is determined by the group velocity walk-off length. THG of modern femtosecond lasers in optical solids is a bulk process, without a surface susceptibility, but bears the signature of a surface enhancement effect in *z*-scan measurements. We demonstrate the accuracy of the model, by showing the agreement between the predicted spectral intensity and the measured third-harmonic spectrum from a thin sapphire crystal.

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I. INTRODUCTION

Third-harmonic generation (THG) in thin, transparent materials has been interpreted in a variety of ways recently [1–5]. Some have attributed it to a surface-effect or surface-enhanced effect, and others stated that their measurements are consistent with traditional models of bulk nonresonant harmonic generation. Common among all of these experiments is the use of ultrashort laser pulses to achieve the required high intensities, but none model the time dependence of third-harmonic production.

It is important to understand third-harmonic production in transparent dielectrics, because they are typical substrates for the manufacture of more advanced materials and devices. To measure nonlinear optical properties of a film, it must be isolated from any background, requiring precise knowledge of how the substrate contributes to the signal. Tsang *et al.* state that third-harmonic generation in typical glasses has a surface enhancement effect [3]. Trebino used frequency-resolved optical gating (FROG) to study surface THG, and attributed the observed, minimal phase distortion to the surface effect [6]. Barad *et al.* claim their measurements are consistent with the Gaussian harmonic treatment and disagree with the surface enhancement explanation [2,7]. We show here that the results measured by Tsang and Trebino are compatible with a bulk susceptibility when a full time dependence is included in the model. We also show that the observed harmonic signal is only generated within one group velocity walk-off length of the interface. This apparent third-harmonic source is significantly shorter than previously reported [2,4].

II. EXPERIMENT

Our measurements and model are based on the *z*-scan THG technique that has been introduced elsewhere [2–4]. Our laser pump source was an unamplified Ti:Sapphire oscillator (KMLabs), with an 800-nm central frequency, λ_0. The pulses are 40 fs, 30 nm full width at half maximum (FWHM), 7.5 nJ/pulse with an 85-MHz repetition rate. A piece of sapphire was translated through the focus of the laser at $z=0$, and the THG spectrum was measured for each position, z, using a monochrometer connected to an optical multichannel analyzer. We focused the laser using a 2-cm focal length (f.l.) lens to a measured waist radius, $\omega_1 = 4.4\ \mu$m, from a measured input waist, $\omega_0 = 600\ \mu$m. We measured the depth of focus, z_r, to be 75 μm in air, somewhat smaller than the calculated value. We correct for the index of refraction of sapphire, $n(\lambda_0)=1.76$, through $z_r = \pi\omega_1^2 n(\lambda)/\lambda$. The quantity, $I_{3\omega}(z)$, determines the intensity at the third harmonic produced by the material, as a function of position, z. Phase matching in the Gaussian beam geometry has been formalized for continuous-wave (CW) beams as

$$I_{\lambda/3}(z,\lambda) \propto |\chi^{(3)}(\lambda/3;\lambda,\lambda,\lambda) J_p(z)|^2 \tag{1a}$$

$$J_p(z,\lambda) = \int_{z-L/2}^{z+L/2} \frac{e^{i\Delta k(\lambda) z'}}{\left[1 + i\left(\frac{z'}{z_r}\right)\right]^2} dz', \tag{1b}$$

where J_p is the phase-matching integral [7]. The material thickness is L, and the limits of integration track the input and output surface of the nonlinear medium for a fixed laser focus at $z=0$. $\Delta k = 3k_\omega - k_{3\omega}$. Equation (1a) is explicitly wavelength dependent through $k = 2\pi n(\lambda)/\lambda$.

Z-scan THG measurements cannot easily distinguish between surface and bulk effects. As such, interpretations of *z*-scan measurements have not given a clear impression of the harmonic generation mechanism [1–3]. To illustrate this point, Fig. 1 compares a surface generation model, approximated as thin nonlinear material at each interface, and a bulk CW generation model for THG from a thin, sapphire (Al_2O_3) crystal. They are qualitatively similar. Both exhibit a peak in the signal when the laser focus is placed at the interface, but

*Electronic mail: stoker@mail.utexas.edu

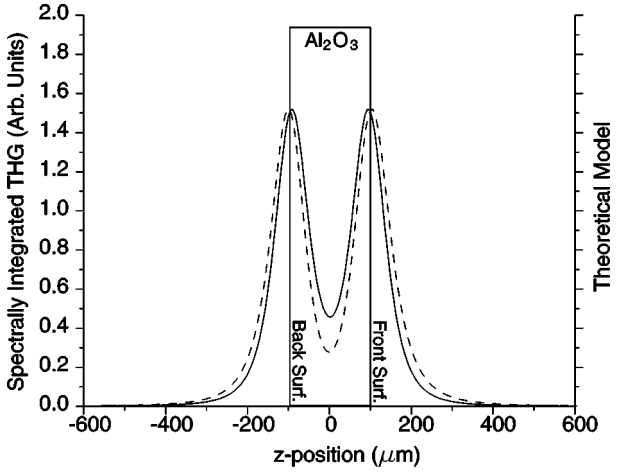

FIG. 1. Comparison of surface and bulk models of THG in transparent media. The solid line shows the theoretical surface effect. The dashed line shows the theoretical bulk effect of Eq. (1a) and integrates the contributions of all modes within the bandwidth. Distances have been scaled by 1.76; the index of refraction of Al_2O_3 at the pump wavelength.

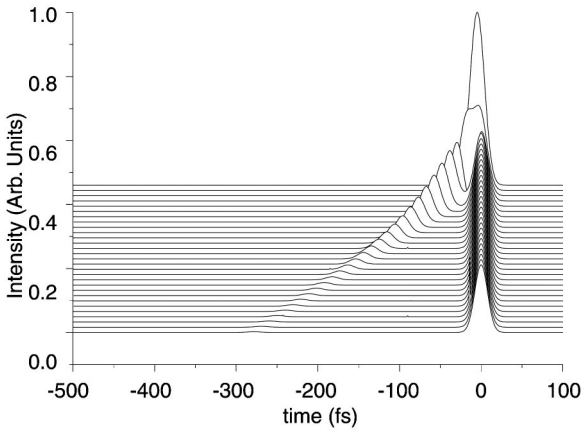

FIG. 2. Time-dependent third-harmonic field radiated from Al_2O_3 of various thicknesses ranging from $0.1z_r$ in the highest curve to $3z_r$ in the lowest curve in steps of $0.1z_r$. The signal is plotted in the rest frame of the harmonic pulse, relative to the time of detection.

THG efficiency decreases when the laser focus is placed in the center of the sample.

A close inspection of Fig. 1 shows differences. CW lasers generate a third harmonic less efficiently when focused in the bulk of the sample, because the photons generated after the focus are out of phase with those generated prior to it [7,8]. However, ultrashort pulsed lasers suffering from a group velocity mismatch of the harmonic and the fundamental do not spatially overlap through the entire focus. As a result, a *z*-scan measurement done with ultrashort laser pulses will appear as a surface effect. We will show how this apparent surface effect is obtained through a bulk susceptibility if group velocity mismatch is included. This requires modifying Eq. (1a) to account for the time dependence of third-harmonic generation. Not accounting for the full time dependence of THG will lead to erroneous interpretations of *z*-scan measurements.

Although the time average of Gaussian pulse propagation is equivalent to Gaussian CW beam propagation, harmonic generation using ultrashort pulses exhibits important differences. For pulses, coherent transfer of energy between the fundamental and harmonic fields can not occur for all times, because of group velocity walk off. Accurate models for group velocity mismatch in second-harmonic production are known [9–12]. However, the effect is relatively unexplored in the case of third-harmonic generation using ultrashort pulses. Group velocity mismatch of the harmonic and fundamental laser pulses can be added to Eq. (1a). The new phase-matching integral can be written as

$$J_p(t,L) \equiv \int_0^L \frac{\tilde{E}^3[t-\tau(z)]e^{i\Delta kz}}{\left(1+i\dfrac{(z-\xi)}{z_r}\right)^2}dz \tag{2a}$$

$$\tau(z) = [\beta_1(\lambda) - \beta_1(\lambda/3)]z, \tag{2b}$$

where ξ is the distance from the entrance surface of the nonlinear medium to the laser focus, and the fundamental field is written as

$$\tilde{E}(t) = e^{-\tilde{\Gamma}_0(t)^2}. \tag{3}$$

Time, $\tau(z)$, accounts for the separation of the pulses as they propagate some distance, *z*, through the material in terms of the inverse group velocity, $\beta_1(\lambda) = \partial k/\partial\omega)_{\lambda_0}$. The length, *L*, is the total thickness of the nonlinear material, and $\tilde{\Gamma}_0$ is the complex Gaussian beam parameter [13,14].

III. RESULTS

Changes in the spectral intensity of the third-harmonic signal are used to monitor the time profile of the radiated field. The ability to accomplish this is derived from the phase-matching integral for Gaussian beams, J_p, which is proportional to $e^{i\Delta k(\lambda)z}$, shown in Eq. (1b). Phase dispersion accumulates rapidly as *L* increases. Equation (1a) predicts spectral modulation will develop within the bandwidth of the laser after just a few coherence lengths. This can be verified by including the dispersion of Al_2O_3 in the calculation of J_p, and so counting the spectral oscillations is a natural gauge for the depth over which a harmonic is produced. However, this method is limited for materials much thicker than the Rayleigh range of the focus. This is because the ability to resolve any spectral modulation decreases, independent of z_r, beyond the resolving limit of instrumentation as *L* becomes very large.

Equation (2a) can be used to predict the time-dependent third-harmonic field radiated from a transparent material. In Fig. 2, the radiated fields are computed numerically for various propagation lengths with the laser waist at the input surface as the output surface is placed sequentially further away. The interplay of the phase mismatch and group velocity dispersion causes the third-harmonic pulse to split. As the non-

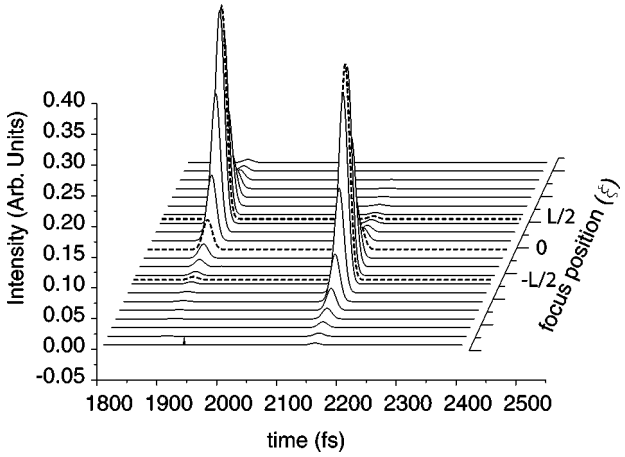

FIG. 3. Time-dependent harmonic field radiated from 330-μm-thick Al_2O_3 as a function of the focal position, ξ. The dashed curves emphasize THG for focusing at either surface, as well as in the center.

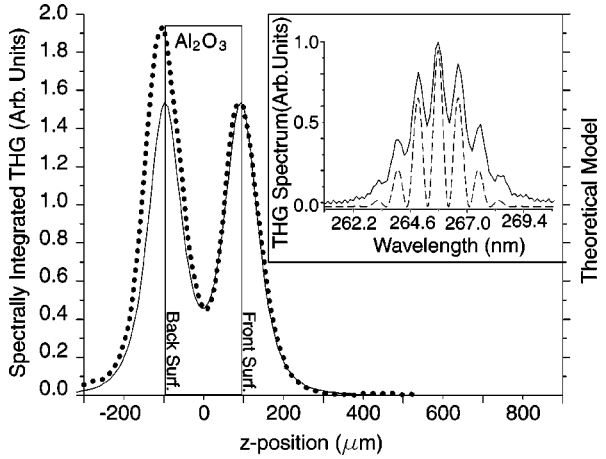

FIG. 4. Comparison of temporally integrated z scan calculation of Eq. (2a) for the 330-μm sapphire sample, solid line, and experimental data. Also shown (inset) is the transform of the calculated time-dependent fields, shown as a dashed line, and the observed spectrum, shown as a solid line.

linear material increases in thickness, the harmonic pulse produced by the fundamental beam steadily declines over the Rayleigh length of the laser focus, so that for the case of an infinitely long medium, the output pulse is just what was created at the input surface. The effect on the spectral intensity due to this is consistent with the previous discussion of phase-mismatched THG over large distances. We measured the third-harmonic spectrum in this limiting case, from a sapphire crystal with $L=3$ mm, and observed a smooth spectral intensity.

It is interesting to consider this effect in the context of the measurement done by Trebino and Tsang, who saw that surface third-harmonic generation displays minimal phase distortion in FROG [6]. Our analysis predicts this to occur, not because the harmonic generation is due to any $\chi^{(3)}_{surface}$, but because the active region of the crystal is small compared to the interaction length required to modulate the spectral intensity. Figure 2 shows how temporally, and as well spatially, the large phase mismatch and considerable group velocity mismatch cause the harmonic pulse to remain short. The very short distance over which the interaction occurs leaves the phase of the pulse undistorted. We emphasize that this is not really an "enhancement," because the $\chi^{(3)}$ value is not changing in a fundamental way at the surface. The amplitude of the radiated third harmonic grows solely through a coherent process.

Using Eq. (2a) it is possible to calculate the time-dependent, radiated fields when the focus is placed at an arbitrary position, ξ, relative to the original beam waist. We calculate these fields for various focal positions in Fig. 3. We find that the radiated field can be approximated as the sum of two Gaussian pulses, where each pulse is generated within one coherence length of each surface, and the pulses are separated in time by $\tau(L)=[\beta_1(\lambda)-\beta_1(\lambda/3)]L$. In reality, third-harmonic light is being generated in all regions of the crystal, but phase matching is so poorly satisfied, there is no chance for the field to amplify. In CW Gaussian optics, the Guoy effect manifests itself as a reduction in the efficiency of THG when the fundamental beam is focused in the center of isotropic media [8]. This remains true even when spatiotemporal overlapping is no longer satisfied, but the dominant mechanism for the disappearance of the harmonic field upon focusing at the center of the crystal is not Guoy, which is commonly understood as "light generated prior to the focus destructively interferes with that generated beyond the focus" [1]. Group velocity mismatch eliminates such a long-range coherent effect, so the z-scan will always resemble a surface effect.

We z scanned a 330-μm sapphire substrate, shown in Fig. 4, spectrally resolving the signal for each position ξ, and obtained a series of spectra that are conjugate to the time-domain fields in Fig. 3. Equation (2a) predicts the radiated third-harmonic field is approximately a Gaussian pair, separated by τ, with field strengths, $E_{3\omega}(z_{surface}) \propto E_{\omega}(z_{surface})^3$. Using the Fourier transform,

$$|\tilde{E}(\Omega)|^2 = \left| \int_{-\infty}^{\infty} \tilde{E}(t) e^{-i\Omega t} dt \right|^2 \tag{4a}$$

$$\tilde{E}(t) = e^{-\Gamma_0 t^2} + e^{-\Gamma_0 (t-\tau)^2}, \tag{4b}$$

the spectrum can be computed. This is a standard integral which is solved analytically. It has the solution given by

$$|\tilde{E}(\Omega)| = \left| \sqrt{\frac{\pi}{\Gamma_0}} e^{-(\pi^2\Omega^2)/\Gamma_0} (1 + e^{i\tau\Omega}) \right|, \tag{5}$$

where the electric field is in the form of Eq. (3). The result is in good agreement with what we observe experimentally in the 330-μm substrate, when the focus is placed at $\xi=0$. Figure 4 demonstrates how a z-scan experiment cannot be distinguished from a surface enhancement effect. The temporally integrated fields of Fig. 3, when plotted as a function of ξ, produce a curve identical to the surface model in Fig. 1. This is a result of the third-harmonic's origination from a thin layer near the dielectric interface. The experimental data fit this model well at the first surface. At the second surface

the signal is stronger, plausibly resulting from an overcompensation of group velocity dispersion in our experimental setup.

IV. DISCUSSION

Third-harmonic generation in transparent materials is a bulk process. The same $\chi^{(3)}$ that is used for CW measurements applies to measurements done using ultrashort pulsed lasers. However, there are significant differences in the coherent nature of the harmonic process, due to the group velocity mismatch of the pump and harmonic, which causes a *z*-scan measurement to indicate a surface susceptibility, rather than a bulk susceptibility. We have shown how to model the time dependence of third-harmonic generation to account for this. Since the frequency domain and time domain are related by a Fourier transform, the appearance of spectral modulation in a short pulse laser indicates either phase modulation of the pulse, or multiple pulses without phase modulation [14,15]. We observe spectral modulation due to pulse breakup. The origin of this phenomena is the group velocity mismatch of the fundamental and harmonic light pulses. This can be understood as follows: As the harmonic pulse begins to fall behind the fundamental in such a way that in one group velocity walk-off length of the nonlinear interaction, the initial harmonic pulse is no longer spatially overlapped with the instantaneous harmonic relative to the fundamental, the effect of phase matching is to cut the pulse into two separate pulses. For a thin optical material, the frequency domain of the third-harmonic signal can interpret the time separation of the signal pulses generated at dielectric interfaces. This time separation is directly proportional to the length, L, of the nonlinear medium.

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