Third- and fifth-harmonic generation at the interfaces of glass and liquids

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We observe optical third- and fifth-harmonic generation to wavelengths of ultraviolet and vacuum ultraviolet at an unconventional vacuum-glass interface without plasma formation. We extend this harmonic-generation technique to various other interfaces and suggest that odd-multipole harmonic generation at an interface by a focused light beam is a general phenomenon. [S1050-2947(96)05512-6]

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Third- and fifth-harmonic generation (THG and FHG) at an air-solid interface, using a laser oscillator, has recently been observed and is believed to be a general phenomenon due to the action of an effective third-order surface nonlinear susceptibility [1]. It was found that although the odd-multiple order nonlinear optical processes are weak, they are much enhanced at an interface when it is excited by a focused laser beam, giving an adequate number of harmonic photons even when a mode-locked laser oscillator is employed. Although a quantitative interpretation on the mechanism of the surface-enhanced THG is still being developed, our results suggested that a new source of nonlinearity arises at a boundary due to the dispersive nature of a wave vector, i.e., nonlocal characteristic, which depends not only on the electric field at the interface but also on the spatial derivative of the electric field there, that is, the field gradient. In this Brief Report we provide further experimental results supporting our original findings. Specifically, we demonstrate the THG process at an interface using three different wavelengths, ruling out the possibility of any resonance enhancement, and we further show that this nonlinear process occurs at various strengths at the boundary of essentially all materials of any or no crystal structure, including liquids. But unlike high-order harmonics generation in noble gases, where the nonlinear process is nonperturbative above the intensity of $\sim 10^{14}$ W/cm^2, these surface odd-multiple harmonic processes are perturbative and occur at a much lower fluence of $\sim 10^{11}$ W/cm^2.

The light sources were the outputs of a Q-switched 50-ns pulsed Nd:YAG laser (1064 nm) (where YAG denotes yttrium aluminum garnet), a self-mode-locked femtosecond Ti:sapphire laser oscillator (780 nm), and the frequency-doubled of the Ti:sapphire laser (390 nm). Except for one set of results where THG was shown at the infrared wavelength of 1064 nm, all others were performed using the self-mode-locked Ti:sapphire laser oscillator. This laser oscillator has an output average power of 300 mW in ~100-fs duration at a repetition rate of ~100 MHz. The pulses were focused by a 20× microscope objective onto the surface of a 160-μm-thick glass slide placed as an entrance window of a 0.5-m focal length vacuum monochromator. The monochromator was maintained at the vacuum level of 5×10^{-4} Torr by a molecular adsorption pump that would not introduce any mechanical vibration during measurements. A 5-cm focal length MgF_2 convex lens was placed after the sample to collimate the harmonics. A 1200-groove/mm grating dispersed the photons and the harmonics were detected by an uv-sensitive photomultiplier tube (PMT) (Hamamutsu R1220). The harmonic photons were identified for correct wavelengths and the order of the nonlinear process was confirmed by the power-law behavior: an increase of harmonic signals with input intensities to powers of 3 and 5 for the THG and FHG, respectively.

Figure 1 displays the normalized THG signals at the three different excitation wavelengths when a glass slide is traversed across the beam focus. The width of the signal peaks are limited to ~6 μm by the depth of focus of the 20× microscope objective. It is evident that the source of nonlinearity is localized at the interface but not in the bulk, and since the nonlinear process is a surface phenomenon, the resulting wavelength is therefore not limited by the optical transmittance of the bulk material. Hence two THG sources were actually observed in the data of the 355-nm run, one from the air-glass interface and the other from the vacuum-glass interface, where glass is still largely transparent at this wavelength. Third-harmonic conversion efficiencies of

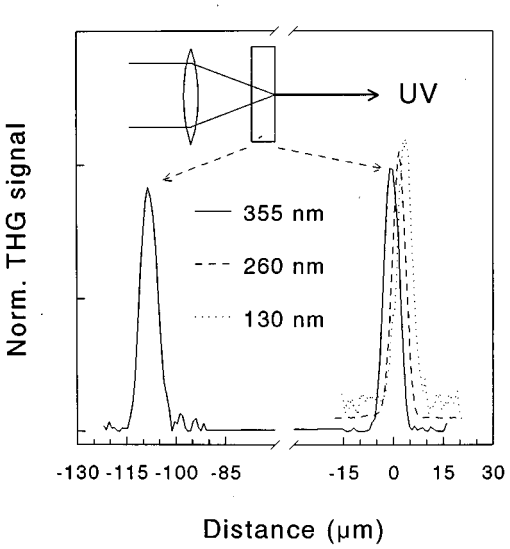

FIG. 1. Normalized THG signal as a function of the position of the focal plane at three different excitation wavelengths: 1064 nm (solid curve), 780 nm (dashed curve), and 390 nm (dotted curve). The dashed and dotted curves are shifted off center for clarity. The inset shows the experimental arrangement.

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1.67×10^{-8}, 5.7×10^{-7}, and 8.5×10^{-10} at the fluences of 45×10^{9}, 3×10^{11}, and 11.5×10^{9} W/cm^2 were measured at the wavelengths of 355, 260, and 130 nm, respectively. It is interesting to note that they all extrapolate to a photon conversion efficiency of $\sim$ $(6–7)\times10^{-7}$ if they were at the intensity of 3×10^{11} W/cm^2, indicating that the nonlinear process is insensitive to a phase matching and resonance enhancement is absent. Therefore, one can conceivably obtain tens of nanowatts of vacuum ultraviolet (vuv) photons at 130 nm by focusing the output of a 300-mW frequency-doubled femtosecond Ti:sapphire oscillator onto a piece of glass. We noted that no plasma was formed at these intensities nor optical damage initiated. Also self-focusing at these intensities was not induced on solids as noted by the lack of a threshold behavior or signal saturation for the harmonic generation. However, near the intensity of 100 GW/cm^2 self-focusing was initiated in liquids and was avoided by lowering the laser fluence. Although both the surface second-harmonic generation (SHG) due to the broken symmetry of an interface and the bulk contribution of THG exist, these nonlinear processes are found to be much weaker than the surface THG and their signals fall below the sensitivity of the present detector.

Because the odd-multiple order nonlinear process is dipole allowed and the process is enhanced at an interface, the next high-order process, FHG, can now be generated using a laser oscillator. Figure 2(a) depicts the spectrum and the normalized strength of the THG and FHG utilizing the full beam output of the Ti:sapphire laser oscillator. The signal level of the FHG, after being normalized to that of the THG, has been corrected for loss in the optics and the quantum yield of the PMT; it was then normalized to the signal level of the THG. It is found that FHG to the wavelength of 153 nm is $\sim10^{-5}$ less efficient than THG, strongly favoring a perturbative behavior. Unlike high-order harmonic generation in reflection on glass using intense laser beams [2], where plasma was formed on the glass surface and became the nonlinear medium, a very different nonlinear optical process was in action at this low-intensity regime and is quite general. We have also examined the dependence of these harmonics on the polarization and ellipticity of the driving fields. Unlike harmonic generation in the bulk of nonlinear crystals where the strength of the harmonic signal depends strongly on the polarization of the driving field owing of a phase-matching condition, the surface THG and FHG have no s- or p-polarization dependence, but cease on an elliptically polarized beam. The ellipticity ϵ is introduced by rotating a zeroth-order $\lambda/4$ waveplate placed before the focusing lens. It is defined as the ratio of the two axes of the polarization ellipse ($\epsilon=E_y/E_x$) such that $\epsilon=0$ and 1 correspond, respectively, to linear and circular polarizations. The results are shown in Fig. 2(b). Both the third and fifth harmonics exhibit the close conformity of the general bell-shape response behavior: $\cos(\pi\epsilon/2)$, solid curve in Fig. 2(b). This response arises because harmonic radiation is mainly polarized along the major axis of the polarization ellipse and the major axis of the incident polarization rotates as the cosine of the ellipticity. The inability of an elliptical beam to produce odd-multiple harmonics has been investigated and was attributed to a symmetry argument that circularly polarized light cannot produce odd-multiple harmonics in an isotropic medium [3].

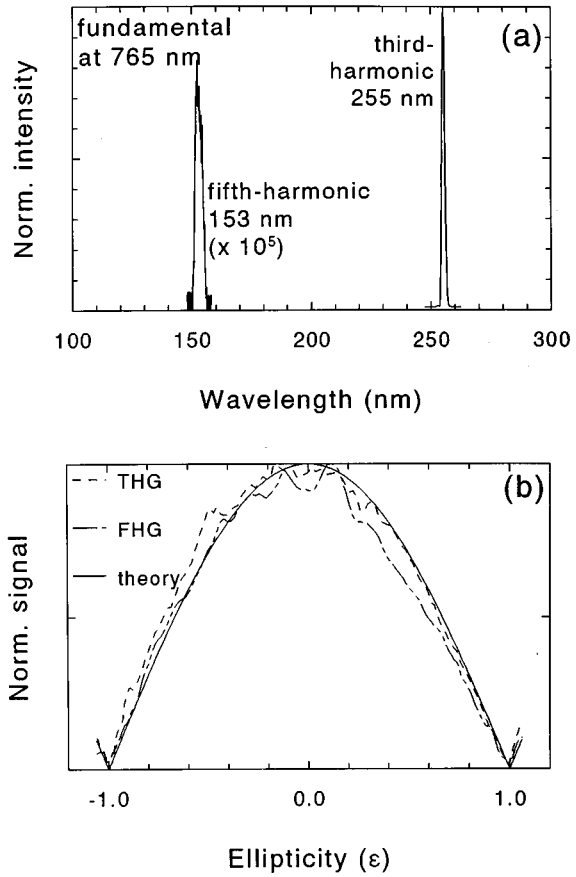

FIG. 2. (a) Spectrum and (b) ellipticity dependence of third- and fifth-harmonics generated at a vacuum-glass interface. The solid curve in (b) is the calculation.

The odd-multiple harmonic generation is not limited to air-solid interfaces but occurs at all interfaces, such as solid-solid, solid-liquid, and liquid-liquid interfaces. Figure 3 shows the strength of THG at some selected interfaces. Table I tabulates the experimental results and the literature values [4–6] of other liquids. The relationship of the THG signal equal to $(\chi^{(3)}_{\text{surface}}E^3)^2$ was used, where E is the laser field.

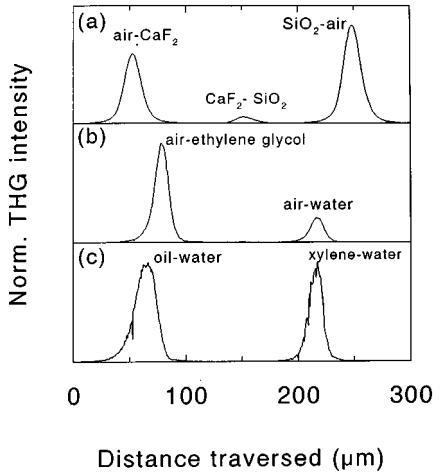

FIG. 3. Same as Fig. 1, but for other interfaces: (a) air-solid and solid-solid, (b) air-liquid, and (c) liquid-liquid interfaces. The peaks were plotted separately at an arbitrary distance for clarity.

TABLE I. Comparison on the values of $\chi^{(3)}$ in liquids. The values of liquid-air interfaces were measured by dispensing the solutions on a fused silica dish, while the values of liquid-SiO_2 interfaces were measured with the solutions placed in a 1-mm optical path-length cuvette.

Liquid \ Interface $\chi^{(3)}$ (esu)	Experiment: liquid-air (units of 10^{-11})	Experiment: liquid-SiO_2 (units of 10^{-11})	Experiment: bulk (units of 10^{-11})	Refs. [3–5] bulk (units of 10^{-11})
SiO_2 (solid)	1.0			0.0031
CH_3OH	1.29	0.57		0.0030
H_2O	1.38	0.40		0.0028
C_2H_5OH	1.47	0.67		0.0035
CH_2Cl_2	1.59	0.93	0.0010	0.0061
CCl_4	1.76	1.09		0.0080
CS_2	3.34	2.61		0.190
air (gas)			10^{-17} esu	$\sim 10^{-17}$ esu

The large third-order nonlinear susceptibility of dichloromethane, together with a good transparence to an uv beam, allows one to make a direct comparison of its measured bulk nonlinearity to a literature value. Agreement to within an order of magnitude was found and a $\sim 10^3$ increase of $\chi^{(3)}$, that is, 10^6 in THG signal strength, was measured generally at the interfaces of all solutions, except CS_2, which is one of the largest $\chi^{(3)}$ solutions. We note that our experimental values were deduced by selectively focusing the excitation beam at an interface or in the bulk of a solution, while the literature values were obtained (at the 1.064 μm) from experiments in which the solutions were normally dispensed in test cells, which were then placed within the confocal length of an excitation beam. In doing so, the distinction between the bulk and the interface contributions may have been lost. However, the agreement on the value of air, which, of course, has no interface contribution, was good. Since the structural symmetry of an isotropic cubic CaF_2 crystal has been successfully probed using surface THG [1] and the liquid-liquid interface has a rotational invariant about the surface normal, it is conceivable that interfacial ordering at a liquid-liquid interface may be probed using the polarization dependence of the surface THG as opposed to the weaker SHG process that was normally used [7]. Also, because of the instantaneous nature of the surface THG process, the dynamics of the interfacial ordering can be studied using the conventional pump-probe technique by monitoring the noninstantaneous component of the third harmonic due only to interfacial ordering.

One of the simple applications of this surface THG phenomenon is for ultrashort laser pulse characterization using the intensity and/or interferometric autocorrelations. Because of the third-order nonlinearity, the time symmetry of a pulse electric field is broken in an autocorrelation measurement. Recently, using this surface THG technique, combined with a frequency-resolved optical gating (FROG) measurement, the direction-of-time ambiguity that is inherently presented in SHG FROG measurements has been removed [8]. This unambiguous surface THG FROG technique may provide a method for ultrashort-pulse characterization of laser oscillators to below the 10-fs regime at various wavelengths. We note that this surface THG is dipole allowed and does not rely on the efficient phase-matching condition nor does it strongly depend on wavelengths. Thus it can potentially be applied to ultrashort-pulse lasers of all classes when suitable SHG materials are lacking. Therefore, the simplicity of a THG autocorrelation technique is particularly useful in the far infrared and at wavelengths below the ultraviolet, where only complicated methods have recently come into existence [9,10].

In conclusion, it was found that the surface odd-multiple order harmonic generation does not have a strong frequency or polarization dependence on the driving fields. Despite the weak nonlinearity of THG and FHG, uv to vuv beams are now readily generated using laser oscillators. The general nature of the phenomenon allows one to study and utilize the nonlinear process at the interface of all optical materials: solids and liquids. Although the physical interpretation of the nonlinear process still remains to be clarified, nevertheless, surface THG has found a unique application in ultrashort-laser-pulse characterization.

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