Parametric mixing in monolayers deposited on thin-film waveguides

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We analyze the parametric mixing of light by molecular monolayers deposited on a thin-film dielectric waveguide. It is shown that large signal levels are possible, even with cw lasers.

In a beautiful series of experiments,\textsuperscript{1,2} Shen and coworkers have shown that molecules can be detected on the surfaces of transparent and metallic media by second-harmonic generation and parametric mixing.\textsuperscript{3} The essential concept is that a surface breaks inversion symmetry for the molecules at the surface and hence the molecules exhibit second-order nonlinearities.\textsuperscript{3} By illuminating the surface from above, Shen and his colleagues were able to predict theoretically and show experimentally that signal levels of $10^9-10^7$ photons/sec are feasible with pulsed lasers for power densities at the surface of 1-100 MW/cm\textsuperscript{2}. Their signal $S \propto A I^2 T$, where $A$ is the surface area, $I$ is the power density, and $T$ is the pulse duration. For illumination from above, the required power densities make experiments with the most powerful dye lasers marginal at best. Furthermore, achieving 100-MW/cm\textsuperscript{2} power densities with Q-switched lasers requires 10-mJ pulses over $10^{-2}$-cm\textsuperscript{2} areas. Thus tunable pulsed-laser energy availability will ultimately limit sensitivities.

A desirable solution would be to find another geometry that requires less power to produce the same surface power density. This can be achieved by guiding light in thin-film optical waveguides, and indeed such enhanced surface fields have been used to demonstrate efficient second-harmonic generation by copropagating\textsuperscript{4,5} and counterpropagating\textsuperscript{6} guided waves, parametric mixing,\textsuperscript{7} and coherent anti-Stokes Raman spectroscopy.\textsuperscript{8} In this Letter we analyze second-order nonlinear mixing by molecules on the surface of thin-film waveguides and show that this geometry can be used both to dramatically increase the signal levels and to reduce the energies required.

The two interaction geometries that we analyze are shown in Fig. 1. In the first, Fig. 1(a), two guided waves mix to produce a phase-matched second-harmonic guided wave in an amorphous waveguide with molecules on top. Because of the phase-matched nature, this case produces the largest signal levels. In the second, Fig. 1(b), two oppositely directed (but not necessarily collinear) waves of frequency $\omega_1$ and $\omega_2$ mix to produce a signal at $\omega_1 + \omega_2$ that is radiated at some angle to the surface. This geometry produces signal levels comparable with those of Shen and his colleagues\textsuperscript{1,2} but with smaller energies required to produce the same surface power densities. The value assumed for the monolayer nonlinear coefficient is $10^{-11}$ m/V.\textsuperscript{1,2}

To produce an efficient interaction through $d_{zzz}$, we
consider TM guided waves, i.e., waves for which $H$ lies in the plane of the surface. For a wave of frequency $\omega_1$ guided by a film of thickness $h$ and refractive index $n_f$ (cladding and substrate indices $n_c$ and $n_s$, respectively), the field distributions are

$$ H = \frac{i}{2} j C_{Tm} \exp[i(\omega_1 t - \beta_1 x)] f_i(x) a_i(x) + c.c., \quad (1) $$

where

$$ n_c: f_i(x) = \exp(S_i x), \quad S_i^2 = \beta_i^2 - n_c^2 k^2, \quad (2) $$

$$ n_f: f_i(x) = \left[ \cos(\kappa_i x) + \frac{S_i}{\kappa_i} \sin(\kappa_i x) \right], \quad (3) $$

$$ n_s: f_i(x) = \left[ \cos(\kappa_i x) + \frac{S_i}{\kappa_i} \sin(\kappa_i x) \right] \exp[-P_i(x - h)], \quad (4) $$

with $S_i^2 = S_i n_f^2/n_c^2$ and $P_i = P_i n_f^2/n_s^2$. The fields are normalized so that $|a_i(x)|^2$ is the guided-wave power in watts per meter of wave front and

$$ C_{Tm} = 2 \kappa_i [S_i^2 + S_i^2] h_{eff} \beta_i/\omega_1 e_0 \omega_1^{-1/2}, \quad (5) $$

with

$$ h_{eff} = h + \frac{1}{n_f^2} + \frac{S_i^2}{S_i n_f^2} \frac{1}{\kappa_i^2 + P_i^2} \frac{1}{S_i n_c^2} \frac{\kappa_i^2 + P_i^2}{P_i n_s^2}. \quad (6) $$

In our calculations we assume that the monolayer does not perturb these three-media field solutions, a reasonable assumption since $h \approx 0.1 \rightarrow 1.0 \mu m$ compared to $d \approx 5 \AA$ for a monolayer. For a given thickness $h$, a discrete number of modes labeled $TM_m$ can be guided with $eta(m = 0) > \beta(m = 1) > \beta$.

It is first second-harmonic generation Fig. 1(a). Assuming TM incident and scattered guided waves, the nonlinear polarization is

$$ P_z(\omega_3) = 2 \epsilon_0 d_{zzz} \delta(z - 0^+) E_z(\omega_1) E_z(\omega_2), \quad (7) $$

where we use two incident fields ($\omega_1 = \omega_2$) since phase matching requires a specific angle between two input fields. From Maxwell's equation ($\nabla \times H = -\partial D/\partial t$),

$$ E_z(\omega_1) = -\frac{1}{2} k \frac{\beta_i}{\omega_1 e_0 n_f^2} C_{Tm} \times \exp[i(\omega_1 t - \beta_1 x)] f_i(x) a_i(x) + c.c. \quad (8) $$

Assuming low-loss waveguides, coupled mode theory gives

$$ \frac{d}{dx} a_3(x) = \frac{\omega_3}{4} \int P_z \frac{\beta_3}{\omega_3 e_0 n_f^2} C_{TM3}(3) dz \quad (9) $$

for the phase-matched case. Evaluating Eq. (9) for an overlap area $LH$, where $L$ is the interaction distance,

$$ P_3 = D_{NL} \frac{L^2}{H} P_1 P_2, \quad (10) $$

with

$$ D_{NL} = \left[ \frac{d_{zzz} C_{TM1} C_{TM2} C_{TM3} \beta_1 \beta_2 \beta_3}{2 \omega_1 \omega_2 e_0^2 n_c^2 n_s^2} \right] d^2 \quad (11) $$

Here $P_1$, $P_2$ and $P_3$ are the total input and scattered powers, respectively.

The mixing of oppositely propagating guided waves [Fig. 1(b)] may be easier to implement experimentally because there is no phase-matching requirement. From simple geometric considerations (wave-vector conservation in the plane of the surface), the sum-frequency radiation is emitted into the cladding at the angle $\theta_c$ from the normal to the surface where $\sin \theta_c = c(\beta_1 - \beta_2)/n_c \omega_3$. [When the radiation is emitted into the substrate, $\sin \theta_s = c(\beta_1 - \beta_2)/n_s \omega_3$]. The nonlinear polarization is given by Eq. (7), and the calculation of the radiated power is a straightforward application of Maxwell's equation and boundary equations to a polarization source on top of a thin film. For an overlap area $LH$,

$$ P_3 = D_{NL} \frac{L^2}{H} P_1 P_2. \quad (12) $$

Here

$$ D_{NL} = \frac{4 \epsilon_0 \omega_3^2 d_{zzz} \beta_1 \beta_2 \beta_3 C_{TM1}^2}{2 \omega_1^2 \omega_2^2 e_0^2 n_c^4 n_s^4} \frac{1 + \mathcal{R}^2}{d^2} \times \tan^2 \theta_c \cos \theta_c, \quad (13) $$

where

$$ \mathcal{R} = \frac{1}{r_s} + \exp(2i\hbar \omega_3 / \omega_2) / \exp(2i\hbar \omega_3 / \omega_2) \quad (14) $$

and $r_s$ and $r_f$ are the usual $p$-polarized Fresnel coefficients for the cladding $\rightarrow$ film and film $\rightarrow$ substrate interfaces. Note the dependence on $\theta$, hence the variation with $s$. For $\beta_1 = \beta_2$, there is no signal that is due to the $d_{zzz}$ component. (However, signals can be obtained from the terms $d_{zzz}$, $d_{zz}$, and $d_{xx}$ for this geometry.)

We now illustrate the signal levels available from

![Fig. 2. Nonlinear cross-section coefficients $D_{NL}$ for the harmonic mixing of two guided waves by means of a monolayer deposited on a Ta2O5 waveguide versus film thickness using cw laser excitation. Solid curve (left-hand scale), generation of a harmonic wave radiated out of the waveguide.](image-url)
guided waves of frequencies mixing in a monolayer of two oppositely propagating signal of $9.3 \times 10^9$ photons/pulse. This corresponds to beam. This small energy input still produces a peak signal this requires only 0.4 pJ of energy in each input the monolayer is fixed at 100 angles between the incident laser beams of 0° to 40°, these two geometries for two cases of laser excitation, TM$_0$(co) + TM$_0$(2co) yields good cross sections and was used in Fig. 2. Phase matching is obtained for 0.225 < h < 0.35 μm; dashed curve (right-hand scale), radiation of the sum frequency out of the waveguide with $\lambda_1 = 0.53$ μm and $\lambda_2 = 1.06$ μm.

We have also studied numerically the parametric mixing in a monolayer of two oppositely propagating guided waves of frequencies $\omega_1$ and $\omega_2$. The signals are lower ($\sim k^2L$) than for the phase-matching case ($\sim k^4L^2$), where $k$ is the sum-frequency wave vector. For mixing a 2-W beam at $\lambda = 0.488$ μm with a 100-mW beam of $\lambda = 0.65$ μm (from an argon-ion and a dye laser, respectively, both cw), the cross section $D_{\text{NL}} \approx 10^{11}$. The variation in $D_{\text{NL}}$ with film thickness (Fig. 2) exhibits oscillations resulting from interference effects in the film. Here we use TM$_0$(2co) + TM$_0$(co), and a peak signal of $1.2 \times 10^7$ photons/sec is predicted. This is less than for the phase-matched case but still represents a very large signal.

Finally, we consider mixing fundamental and doubled Nd:YAG pulses (15-nsec duration) in the geometry of Fig. 1(b). Here $H = L = 5$ mm and TM$_0$(co) + TM$_0$(2co). The signal in photons per pulse is shown in Fig. 3. As in the cw case, it oscillates with film thickness because of signal-interference effects in the film. When the power density at the monolayer is fixed at 100 MW/cm², the peak signal levels become comparable with those obtained by Shen and his colleagues for external illumination, namely, $\approx 4 \times 10^9$ photons/pulse. The principal difference is that only 2.5 and 0.7 μJ of energy are required in the input beams, versus tens of millijoules for external illumination.

In summary, we have analyzed nonlinear mixing of light by monolayers placed on the surface of a thin-film waveguide. We find that the large field enhancements available with guided waves reduce the incident laser power requirements by orders of magnitude over the case of illumination by plane waves from above the surface. Conditions also exist for phase matching the signals parallel to the surface, which increases signal levels up to conversion efficiencies as high as 0.1%. Experiments are currently under way to verify these predictions.

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References


![Fig. 3. Sum-frequency signal in photons per pulse generated by monolayers on a Ta$_2$O$_5$ waveguide versus waveguide film thickness. Pulsed-laser excitation (15-nsec duration) is assumed with 100 MW/cm² power density at the monolayer. Solid curve (left-hand scale), generation of a phase-matched second harmonic at $\lambda = 0.53$ μm; dashed curve (right-hand scale), radiation of the sum frequency out of the waveguide with $\lambda_1 = 0.53$ μm and $\lambda_2 = 1.06$ μm.](image-url)