Four-photon-resonant third-harmonic generation in Hg

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A tunable resonant enhancement of third-harmonic and sum-frequency generation is observed at four-photon resonance with the 7^1S, 6^1D, and 6^3D levels and at five-photon resonance with 9^1P levels of atomic mercury. The causes of this resonant enhancement are examined and appear to include a nonlinear refractive index and nonlinear mixing of order 5 and higher. A perturbative treatment of the nonlinearities is found to be inadequate.

Recent reports[1,2] have described resonant enhancements of third-harmonic generation near four-photon resonances between the ground and a bound excited state. In one case,[1] the incident photon energy was one fourth of the Hg $6S$–$6D$ transition frequency. In another case,[2] two input frequencies were used, and the third harmonic, $3\nu_1$, was enhanced when the level $E(3S) + 3h\nu_1$ in the ionization continuum of atomic Na was coincident with $E(5S) + h\nu_2$ (Fig. 1). Such schemes may provide tunable resonances for sum-frequency mixing and so may have implications for efficient generation of coherent, tunable UV light.[3] In this Letter we report our observations on sum-frequency generation near four-photon resonances with the Hg ($6S$–$6D$) and Hg ($6S$–$7S$) transitions (Fig. 1).

The types of nonlinearity involved in Refs. 1 and 2 are not immediately obvious. In the case of Hg, perhaps the most straightforward explanation for third-harmonic generation is that the process is mediated by the fifth-order nonlinearity $\chi_5(-3\omega; \omega, \omega, \omega, \omega, -\omega)$. Other possibilities must be considered, however. One is that the four-photon resonance makes it possible to generate the third harmonic through $\chi_3(-3\omega; \omega, \omega, \omega)$. Although third-harmonic generation normally does not occur in a tight focus if $\Delta k > 0$ ($\Delta k = k_{3\omega} - 3k_\omega$) owing to destructive interference of the harmonic generated in the regions before and after the focal plane,[4] any perturbation of the isotropic symmetry of the nonlinear medium in the region of the focus or of the focal parameters could cause incomplete cancellation, leading to the appearance of third-harmonic generation. In Hg, for example, four-photon-resonant absorption could destroy the symmetry by depleting the ground-state population near the focus.[5] Similarly, four-photon-resonant ionization could deplete the ground state, or the resulting ions and electrons could produce local electric fields,[6] permitting second- or fourth-harmonic generation with subsequent mixing to generate the third harmonic. The role of an intensity-dependent refractive index must also be considered. Self-focusing or self-defocusing would upset the destructive interference, as would the intensity-dependent change in dispersion or Δk.[7] We examine each of these possible contributors to the observed emission of third-harmonic light.

Other mechanisms involving higher-order nonlinearities are also considered. One is direct third-harmonic generation through $\chi_5(-3\omega; \omega, \omega, \omega, \omega, -\omega)$ and similar terms of higher order. This process is not limited to regions of negative Δk, as Fig. 2 shows. Here we have plotted the index-matching factor (calculated by the methods outlined in Ref. 8) for third-harmonic generation by means of third- and fifth-order mixing.

Indirect or cascade processes are another mechanism involving higher-order mixing. For example, a fifth-harmonic wave generated directly could be mixed with the fundamental to produce the third harmonic. This can occur when Δk is slightly positive for fifth-harmonic generation, since there can be a strong fifth-harmonic wave near the focus even though none is emitted because of destructive interference.

In order to illuminate the nature of four-photon-resonant third-harmonic generation, we have reexamined third-harmonic and sum-frequency mixing in Hg near the $6S$–$6D$ four-photon resonance and have studied a similar effect on another resonance, the $6S$–$7S$ Hg transition.
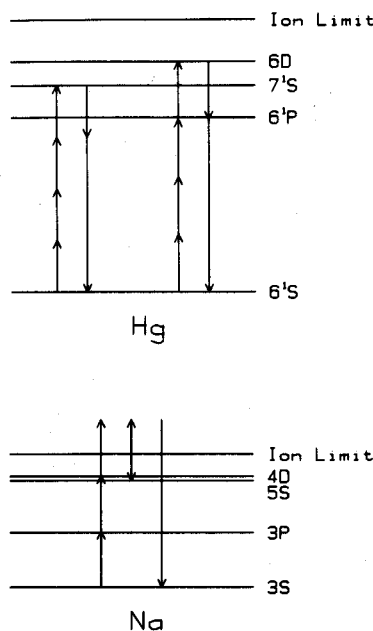
The experimental apparatus consists of two Nd:

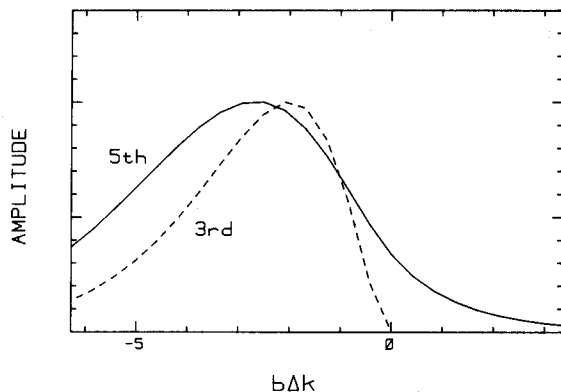Fig. 1. Energy levels of Hg and Na.

Fig. 2. Shapes of the index-matching factors for third-harmonic generation through $\chi_3(-3\omega; \omega, \omega, \omega)$ (dashed line) and $\chi_5(-3\omega; \omega, \omega, \omega, \omega, -\omega)$ (solid line) for a tight focus in an isotropic medium. The shape of the observed resonances should be determined by the product of the index-matching factor and the appropriate $|\chi|^2$.

YAG-pumped dye lasers with pulse energies up to 60 mJ in pulses of 8-nsec duration and linewidths of approximately 0.5 cm^{-1}. The beams are combined on a beam splitter and then focused by a 20-cm focal-length lens (focal diameter ~ 30 μm) into the center of a cell containing 25-Torr He buffer gas and 10^{-3}–10 Torr of atomic-Hg vapor. Peak intensities lie in the range 10^{10}–10^{12} W/cm^2. The output is dispersed with a prism or, when necessary, by a 0.3-m vacuum monochromator and detected by a solar-blind photomultiplier.

Third-harmonic intensities in the vicinity of the two four-photon resonances are shown in Fig. 3. Here a single laser with linear polarization is used. Most features of these resonance profiles can be accounted for qualitatively by considering ac Stark shifts and the role of dispersion in harmonic generation. Stark shifts create asymmetry in the 6^1D peak owing to spatial and temporal variations of light intensity. Likewise, the 6^1P resonance is blue shifted, but, in addition, the role of dispersion prevents third-harmonic generation through a third-order process on the low-frequency side of 6^1P and contributes to the asymmetric shape characteristic of third-harmonic generation through $\chi_3(3\omega; \omega, \omega, \omega)$. In Figure 3(b), the 7^1S resonance is also shifted and broadened by an ac Stark shift. For both the $6D$ and $7S$ resonances, $\Delta k_3 = k_3\omega - 3k_\omega > 0$.

We consider now each of the processes that could contribute to third-harmonic generation. We have looked for photoionization, fifth-harmonic generation, and fluorescence from 7^1S under conditions that produce a strong third-harmonic signal on the 7^1S resonance. A voltage-biased thin-wire electrode inside the grounded stainless-steel Hg cell was used to measure photoionization at 0.3-Torr Hg. The collected charge was amplified by a low-noise electronic preamplifier with a noise-limited sensitivity of about 10^4 electrons per laser shot. With a positive voltage bias, a substantial signal is observed with a line shape like that of the third harmonic. This is evidently due to photoemission from the windows or walls of the cell since the signal disappears for negative electrode bias. The upper limit of ionization in the focal region is 1 atom in 10^5 for a light input of 20 mJ. This level of ionization

is too low to account for the intensity of the observed third harmonic through local electrical fields. The measurement was repeated at much lower Hg density using a channeltron detector and 40-mJ light with similar results.

Fluorescence from 7^1S was below our detection limit, so the 7^1S to 6^1S population ratio in the focal volume is less than 10^{-5} for 40-mJ input energy.

We looked for fifth-harmonic generation near the 7^1S resonance at a wavelength near 125 nm by using an ionization chamber separated from the Hg cell by a LiF window and filled with 0.3 Torr of NO. There was no detectable signal near the 7^1S resonance. From the known NO photoionization cross section and the sensitivity limit set by detector noise, we conclude that there are fewer than 2×10^6 fifth-harmonic photons generated for a 40-mJ fundamental. Since $b\Delta k_5 (\Delta k_5 = k_{5\omega} - 5k_\omega)$ is estimated as +6.0 at 1-Torr Hg (using the f values of Ref. 9) near the 7^1S resonance, we should not expect much fifth-harmonic output. However, since the fifth harmonic is at least an order of magnitude weaker than the third harmonic, it is reasonable to argue that the observed third harmonic is not generated by difference frequency mixing of ω and 5ω, at least for the 7^1S associated peak.

Next we consider the influence of nonlinear refractive indices. The change in refractive index at the fundamental frequency ω is too small to contribute to harmonic generation. The nonlinear contribution to the refractive index at 3ω owing to $\chi_3(-3\omega; \omega, -\omega, 3\omega)$, on the other hand, is substantial. For the nonlinear contribution to $b\Delta k$ at the focus for 1-Torr Hg and 40 mJ‘
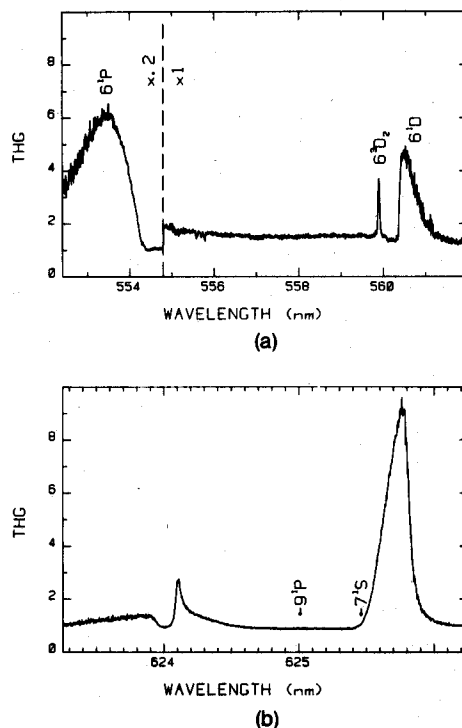

(a)

(b)

Fig. 3. (a) Third-harmonic intensity versus input wavelength near $6D$ four-photon and 6^1P three-photon resonances. Input energy 0.5 mJ. (b) Same as (a) near 7^1S resonance. Arrows indicate unshifted positions of the 7^1S four-photon level and the 9^1P five-photon level. Input energy 30 mJ.
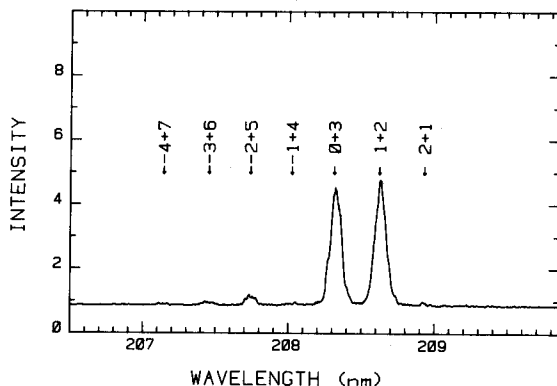
Fig. 4.   Sum-frequency spectrum for input frequencies ν_1 and ν_2, where $h\nu_1 + 3h\nu_2 = E(7^1S) - E(6^1S)$. The arrows indicate possible output frequencies in terms of combinations of the input frequencies. For example, the arrow at $(-2 + 5)$ points to the peak at the frequency $(-2\nu_1 + 5\nu_2)$.

of input light, we calculate that

$$b\Delta k_{\mathrm{NL}} = 14/\Delta,$$

where Δ is the detuning from the 7^1S resonance in inverse centimeters. The sign is negative on the blue side of the resonance and positive on the red side. This compares with an estimated linear $b\Delta k$ of $+0.11$ at 1 Torr (400 K). In fact, there is also a large contribution to $b\Delta k_{\mathrm{NL}}$ from the 9^1P five-photon resonance, also negative on the blue side and positive on the red. This indicates that the nonlinear refractive index must play a major role in four-photon-resonance third-harmonic generation, at least near the 7^1S resonance. We would expect from the calculated values that no matter what order nonlinearities are involved, the harmonic signal would be strongest on the blue side of the 7^1S and 9^1P Stark-shifted positions (see Fig. 2) and should shift to the blue with increasing Hg density. This is in qualitative agreement with our observation of a blue shift in the 7^1S peak with increasing Hg density.

So far we have ruled out several candidate processes and have shown that the nonlinear refractive index is important, but the question remains: What is the nature of the nonlinear mixing involved in four-photon-resonant third-harmonic generation? When we attempt to calculate the nonlinear susceptibility of 3ω near the 7^1S resonance by using the customary perturbation expansion, we find that near the four-photon resonance, and for the intensities encountered in our experiments, the expansion does not converge. For example,

$$\chi_5(-3\omega; \omega, \omega, \omega, \omega, -\omega)/\chi_3(-3\omega; \omega, \omega, \omega)$$
$$= 1.1 \times 10^{-9} I/\Delta,$$

where $\Delta = \Omega_{7s} - 4\omega$ and I is the applied optical intensity in watts per square centimeter ranging from 10^{10} to 10^{12} W/cm^2 in our measurements. Thus it may be more appropriate to discuss the frequency mixing in terms of an induced or dressed state at the three-photon level. Third-harmonic generation is then three-photon resonant with this induced level. If the laser dressing the 7^1S level is tuned, then of course there is a tuned resonant enhancement of the third-harmonic mixing of a

second laser. We have demonstrated a tunability of this enhancement over several thousand wave numbers.

In order to obtain direct evidence of the importance of high-order mixing, we have also analyzed the output frequencies near the third harmonic when two lasers of nearly equal intensity and frequency were combined and focused into the Hg. For the two input frequencies $\nu_1 = 15\,924$ cm^{-1} and $\nu_2 = 15\,994$ cm^{-1}, so $h\nu_1 + 3h\nu_2 = E(7^1S) - E(6^1S)$, the output wavelength spectrum displayed in Fig. 4, was obtained. While the two prominent peaks at $3\omega_2$ and $(\omega_1 + 2\omega_2)$ are those favored by χ_5 and also by the lowest-order contributions to the nonlinear refractive index, other frequencies are clearly present and for other input frequencies can be made more prominent. The presence of these frequencies supports the conclusion that high-order mixing is important. Generation of light of frequency $(7\omega_2 - 4\omega_1)$, for example, involves an eleventh- or higher-order process. These secondary peaks extend to the blue much more than to the red in all observed cases, as would be favored by the influence of the nonlinear refractive index, which is lower on the blue side. Similar experiments near the $6D$ resonance yielded similar results.

In conclusion, we have reexamined the process of third-harmonic generation near Hg $6D$ four-photon resonance and have demonstrated the same effect at the 7^1S four-photon resonance. Photoionization, population transfer, and fifth-harmonic generation followed by mixing to 3ω are shown to be relatively unimportant here. Instead, we believe that the process is dominated by the nonlinear contributions to the refractive index of the third-harmonic frequency and by high-order mixing. These nonlinearities are not adequately treated by a conventional perturbative expansion since the expansions diverge near the four-photon resonances. A better treatment, perhaps involving dressed or induced states, is needed.

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