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Multiphoton ionization spectra and tunable fifth-harmonic production near five-photon resonances in Xe and Ar

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Through multiphoton ionization measurements, we have observed the interference of five-photon and internally generated fifth-harmonic excitation processes in $\Delta J = 1$ even-odd parity resonant transitions in Xe and Ar. In agreement with theory, these five-photon resonances are not observable in single-pass laser beams, but are convincingly observed in counterpropagating beams. In the negatively dispersive regions of the $5d[3/2]^0 J = 1$ level of Xe, tunable fifth-harmonic light is generated by phase matching with various buffer-gas mixtures. The fifth-harmonic profiles are in good agreement with calculated phase-matching curves.

I. INTRODUCTION

Since the experimental discovery[1] and initial theoretical description of the effect,[2,3] several studies have been made[4–12] of the cancellation of three-photon resonance excitation of an atomic state which can also be excited by a one-photon transition under circumstances (sufficient number density) where one-photon excitation by the coherently generated field at the three-photon sum frequency can interfere with resonant three-photon excitation. The cooperative response of the atoms along a laser beam is such that excitation by the internally generated field at the sum frequency is 180° out of phase with the three-photon pumping of a given level by the laser photons.[3,6–12] Subsequent studies of the phenomenon have established the theoretical and experimental generality of the effect.[10–12] In complete conformance with theoretical predictions it has been shown, in resonance ionization experiments, that with linearly polarized laser excitation three-photon resonances are "unobservable" at elevated atomic densities. With circularly polarized light[5] or with counterpropagating beams where no accompanying third-harmonic fields are generated, the cancellation effect is thwarted and three-photon resonances reappear as predicted.[6,11,12] The effect has been shown experimentally and theoretically to persist with broadband pulsed laser sources, in the presence of high-pressure self-broadening or foreign-gas broadening in noble gases,[10,11] and in Hg, at all laser intensities[13] and all pressures above the threshold region. The effect has recently been shown to hold in experiments involving the more general case of four-wave mixing,[12] and in the case of parametric four-wave mixing in the presence of amplified spontaneous emission.[14]

In the present study, we observe the predicted interference effect in five-photon excitation of the $5d[3/2]^0 J = 1$ state of Xe and in a similar five-photon process involving the $5s[3/2]^0\ J = 1$ state of Ar. The effect was investigated through resonance ionization measurements in a proportional counter system involving single-pass and counterpropagating linearly polarized laser beams.

We also observe phase-matched fifth-harmonic production in the negatively dispersive region of the $5d$ state of Xe. The results are shown to be in quantitative agreement with theoretical analysis.

II. EXPERIMENTAL METHOD

The basic experimental apparatus used in the present study has been described previously.[10,11] It is depicted schematically in Fig. 1. A Lumonics 861 excimer laser operated at 308 nm in 80 mJ pulses of 4 nsec duration pumped a Lumonics EPD 330 dye laser. The dye laser was operated with Rhodamine B at 3 mJ/pulse in the experiments on Xe and with Coumarin 440 at 4.8 mJ/pulse in the Ar study. A short ionization cell (9 cm window-

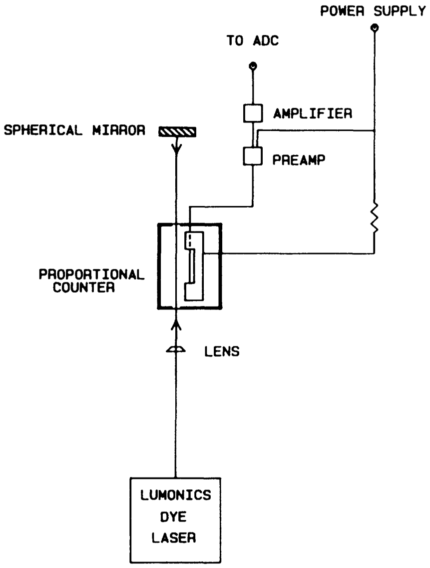

FIG. 1. Schematic diagram of experimental setup.

to-window) contained a proportional counter with a shielded charge collection region of 4 cm length. An internal x-ray source (^{55}Fe) provided absolute ionization signal calibration of the proportional counter.[10] The laser beam was operated in single-pass configuration with a 7.5-cm focal length lens and in counterpropagating geometry through insertion of a spherical mirror of 15 cm radius of curvature which reflected the beam back on itself. Data were recorded as described previously.[10,11]

III. RESULTS

A. Cancellation effect in five-photon excitation of Xe $5d[3/2]^0$ $J=1$

As already mentioned, the rather general theoretical treatment of the interference effect between three-photon resonant excitation of a dipole-allowed transition by photons of frequencies ω_1,ω_2, and ω_3, and the internally generated field at the sum frequency $\omega_s=\omega_1+\omega_2+\omega_3$, also predicts the same result for all higher-order odd-photon processes. It is easy to extend previous results[7,10] to show that the same cancellation effects as those demonstrated in three-photon processes will occur, e.g., in the five-photon process depicted in Fig. 2 for transitions from the ground state to the $5d[3/2]^0$ $J=1$ state in Xe. If we denote the difference between ground- and excited-state energies as $\hbar\omega_r=\hbar(\omega_1-\omega_0)$, then at laser frequencies such that $\delta=5\omega-\omega_r$ is positive (high-energy or negatively dispersive side of five-photon resonance) fifth-harmonic generation can be achieved. With a focused laser beam the phase mismatch between laser field and the fifth-harmonic field, $\Delta k=k_{5\omega}-5k_\omega$ can be compensated in traversing the focal region resulting in fifth-harmonic production of predictable form. The presence of a positively dispersive buffer gas (Ar or Kr in the present instance) aids in phase matching and influences fifth-harmonic production again in a predictable manner (see below).

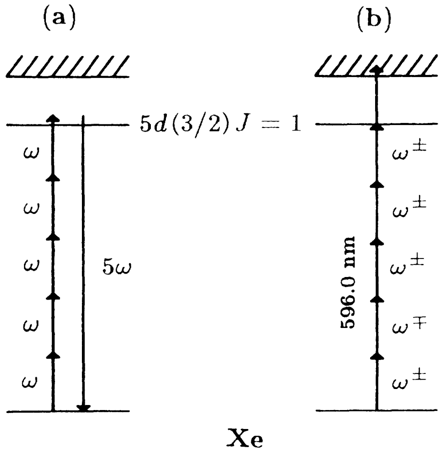

FIG. 2. Energy-level depiction of (a) fifth-harmonic production near the $5d[3/2]^0$ $J=1$ level of Xe and (b) one mode of resonant five-photon excitation of Xe $5d$ by counterpropagating laser beams in which no fifth-harmonic field is generated.

If the laser is tuned onto exact resonance such that $\delta=5\omega-\omega_r=0$, then a large phase mismatch, Δk, occurs, and production of fifth-harmonic photons becomes extremely inefficient and negligibly small. Photons that are generated are strongly absorbed by the medium which is essentially opaque at ω_r. On the other hand, five-photon excitation of the resonant state would ordinarily be expected to produce resonant enhancement of, e.g., six-photon ionization of Xe through the $5d$ level. Any photons emitted at 5ω would be quickly reabsorbed and thus leave enhanced ionization undiminished. However, on the basis of previous work, we can make a firm theoretical prediction that, at exact resonance, excitation through the internally generated fifth-harmonic field interferes with direct five-photon excitation of the state (the two Rabi pumping terms are 180° out of phase), resulting in no population of the resonant state and no resonantly enhanced ionization through the level. The interference effect is absent at very low pressure, where the coherently generated sum frequency fields are negligible. But under circumstances such that the product of number density, N_0, and square of dipole matrix element $|D_{01}|^2$ connecting $|0\rangle$ and $|1\rangle$ in the combination $\kappa=2\pi N_0|D_{01}|^2\omega_r/\hbar c$ exceed a predictable value,[10] the population of the resonant level decreases as $1/N_0$ as pressures are elevated. It is interesting that the conditions for cancellation of n-photon resonant excitation by an internally generated field at the sum frequency are the same for all odd-photon excitations, and always independent of laser intensity. Specifically, theory predicts that the effect becomes significant if $|\kappa/\Delta k_0|\gg\frac{1}{2}\gamma_{01}+\Gamma_c$ and $\kappa z(\Gamma_c+\frac{1}{2}\gamma_{01})/[S_m^2+(\Gamma_c+\gamma_{01}/2)^2]\gg 1$ are satisfied, where γ_{01} is the spontaneous emission width of the resonance level and Γ_c is its collision-induced width. The parameter Δk_0 is the nonresonant contribution to the phase mismatch,[3,7,10] S_m is proportional to the laser bandwidth[10] and z is the distance traversed by the laser beam in the nonlinear medium. In experiments performed with narrow-band lasers at low buffer-gas pressures involving strong dipole-allowed transitions in a sample of several centimeters thickness, the cancellation effect becomes very effective at concentrations as low as $10^{12}/\text{cm}^3$. The same criterion applies for any N-photon excitation process where N is odd (but greater than 1).

However, if counterpropagating beams are utilized in the excitation process, the cancellation effect is partially spoiled through all combinations of n-photon excitation in which at least one photon from each beam is absorbed. In the five-photon process illustrated in Fig. 2, we denote by $\omega^{\pm}$ photons which are traveling in the $+z$ or $-z$ direction. (In the figure the second photon from the bottom is traveling opposite the other four.) No coherent field at the sum frequency is present for these components of the total excitation probability, thus no cancellation effect exists in the corresponding terms in the total transition probability. The result is that the n-photon excitation process is present again and enhanced ionization, e.g., can again be observed at resonance.

In Fig. 3 we show the results of an experiment in which

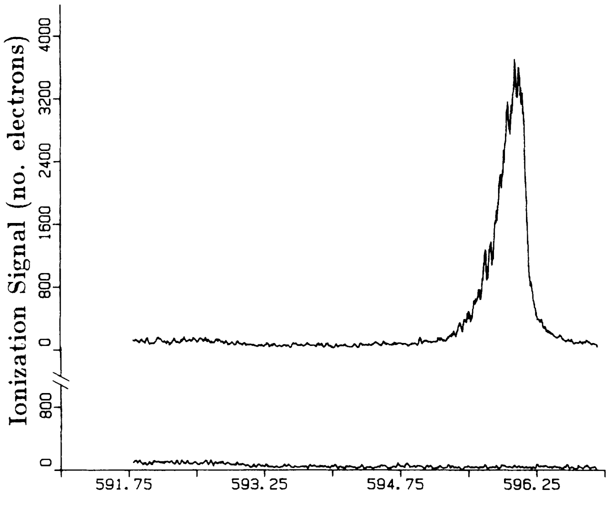

FIG. 3. Bottom trace—ionization signal in the region of five-photon resonance with Xe $5d[3/2]^0$ $J=1$ with single laser beam showing no resonant enhancement at $\lambda=596.01$ nm. Upper trace—same experiment but with counterpropagating beams. Strong resonant signal is present.

a focused laser beam, as shown in Fig. 1, is tuned through the five-photon $5d[3/2]^0 J=1$ resonance in Xe. In the bottom trace we show that the six-photon ionization signal for Xe as the five-photon resonance at $\lambda=596.01$ nm is traversed with a single-pass beam. No enhancement is visible in this experiment at 40 Torr Xe with 3.6 mJ pulse energy (R590 dye). The top trace depicts the ionization signal with counterpropagating beams produced by introducing a 15 cm radius reflecting mirror at 1.8 mJ/pulse. The $5d$ resonance is observed as a strong five-photon resonant enhancement at $\lambda \simeq 596.1$ nm. In the example shown, 100 Torr of Ar buffer gas was also present. Identical behavior was found, as predicted, for Xe pressures from 5 through 400 Torr, with various buffer-gas concentrations from zero to 1000 Torr of Ar and Kr. In every case no enhanced resonant signal could be seen in a unidirectional beam, and resonant five-photon excitation was again observable in every case with the use of counterpropagating beams.

B. Phase-matched fifth-harmonic production near Xe $5d$

In the same experimental setup, using counterpropagating geometry, we performed a set of experiments in which the laser was tuned over the negatively dispersive region on the short-wavelength side of the $5d[3/2]^0$ $J=1$ resonance with increasing buffer-gas pressures added to a constant pressure of Xe. Under these conditions we know that phase-matched fifth-harmonic photons can be produced over a limited region where the range of wavelengths and the peak position, with respect to the $5d$ resonance, of the fifth-harmonic profile is determined by the focal length of the lens, the absolute Xe and buffer-gas pressures, and the indices of refraction of the medium at ω and 5ω. We also know from previous analyses and experiments[7,10–12] in noble gases, that in frequency regions where phase-matched third-harmonic photons are produced, the multiphoton ionization process is totally dominated by dimer absorption of the generated third-harmonic photons, as opposed to direct three-photon excitation and subsequent ionization by the laser photons. In these previous studies it has been shown that, except for the enhancement at exact resonance (with counterpropagating beams), the frequency profile of multiphoton ionization signals in an arrangement such as that in Fig. 1, is the result of phase-matched four-wave mixing at the sum frequency. Thus, the enhanced ionization signals have been shown to mimic the third-harmonic output as a function of laser frequency.

The previous analysis of the relationship between observed enhanced ionization signals and third-harmonic production also holds for fifth-harmonic production and concomitant multiphoton ionization yields. This circumstance is rather fortunate in the present instance since it allows for the simultaneous production and detection of fifth-harmonic photons in a gas cell which also serves as a proportional counter.

Since the formalism is well established[15,16] for describing phase-matched fifth-harmonic production in a focused laser beam, we will not repeat the development. The phase-matching curve for producing 5ω in a beam focused far from any windows is determined primarily by the phase-matching integral $F(\Delta kb)$, where

$$\begin{aligned} F(\Delta kb) &= \left| \int_{-\infty}^{\infty} \frac{e^{i\Delta kbz'/2}}{(1+iz')^4} dz' \right|^2 \\ &= \frac{\pi^2}{9} \left[\frac{\Delta kb}{2} \right]^6 e^{\Delta kb}, \quad \Delta k < 0 \\ &= 0, \quad \Delta k > 0 \, . \end{aligned}$$

Here $b=(2\lambda/\pi)(f/d)^2$, where f is the focal length of the lens, d is the initial beam diameter, and λ is the laser wavelength. The phase mismatch, between the laser and fifth-harmonic fields, Δk, is defined as $\Delta k = k_{5\omega} - 5k_{\omega}$, where k_{ω} is the wave vector for the laser field and $k_{5\omega}$ that for fifth-harmonic propagation.[17] In the present experiment, $f=7.5$ cm, $d=0.15$ cm, and $b=5000\lambda/\pi \simeq 0.1$ cm for the Xe studies near 600 nm. At 290° K we have $N=3.27\times 10^{16}P$ Torr and we can write

$$\begin{aligned} b\Delta k = 1.63\times 10^{21} \{ & P_{\mathrm{Xe}}[\eta_{\mathrm{Xe}}(5\omega) - \eta_{\mathrm{Xe}}(\omega)] \\ & + P_B[\eta_B(5\omega) - \eta_B(\omega)] \} \, , \end{aligned}$$

where $\eta_{\mathrm{Xe}}(5\omega)$ is the index of refraction per atom for Xe at 5ω, $\eta_B(5\omega)$ that for the buffer gas, etc. We have used available oscillator strengths for Xe, Ar, and Kr to evaluate Δk and the resultant phase-matching curve for fifth-harmonic production under each of our experimental conditions. Fifth- and higher-harmonic production have been experimentally investigated under various conditions,[16,18–20] but the general behavior of fifth-harmonic generation with tunable light under controlled phase matched has not heretofore been quantitatively demonstrated.

In Figs. 4(a) and 4(b) we show ionization signals that result from tuning the focused, counterpropagating laser beam over the short-wavelength side of the $5d[3/2]^0\ J=1$ five-photon resonance of Xe. As described above, enhanced ionization signals result from five-photon excitation of the $5d$ state and from phase-matched fifth-harmonic production. A series of experiments was conducted in which increasing quantities of Ar buffer gas were added to 40 Torr of Xe. For pure Xe [bottom trace in Fig. 4(a)] no fifth-harmonic signal is visible in the region scanned. However, with 200 and 400 Torr of Ar, fifth-harmonic light is produced with peaks at 591.8 and 592.8 nm, respectively. The dashed lines represent the theoretical fifth-harmonic profiles. In Fig. 4(b) the series is continued with 600, 800, and 1000 Torr of Ar buffer gas. Again, the predicted profiles match observations closely, except for an additional width in the fifth-harmonic profiles at the highest buffer-gas pressures. We note that, as fifth-harmonic photons are produced closer to the atomic resonance, the absorption coefficient for the generated photons increases. As discussed earlier by Payne, Garrett, and Ferrell,[10] the absorption produces an added width to the fifth-harmonic profile, which agrees qualitatively with the present observation. [Also note that the bottom trace of Fig. 4(b) shows no resonance signal at 596.0 nm. This trace was run *without* the reflecting mirror, thus only the fifth-harmonic enhancement is present, as expected.] Finally, we note that the small peak at the laser wavelength of 591.6 nm in Fig. 4 is due to resonant excitation of the $4f'$ autoionizing state of Xe.[21] Excitation of this high-lying level is primarily due to absorption of one fifth-harmonic photon plus one laser photon, as opposed to direct six-photon excitation.[11]

In Fig. 5 are shown results from a similar set of experiments with 40 Torr Xe but with Kr buffer gas. The profiles again conform to predicted behavior for phase-matched fifth-harmonic profiles under the conditions illustrated. Note that fifth-harmonic wavelengths in these data are in the range of 117–119 nm.

In the data shown in Figs. 4 and 5, we noted that no fifth-harmonic signal was observable in pure Xe. However, we know that with a focused beam, phase-matched fifth-harmonic generation can be achieved in the pure gas also. As the number density of pure Xe is increased, the profile of any fifth harmonic that is produced moves to shorter wavelengths and away from the resonance, toward the wavelengths where $\Delta k=0$. This predicted behavior is again observed in pure Xe at increased pressure. In Fig. 6 we show a trace of the enhanced ionization signals in 400 Torr of Xe over a wavelength region from 584.9 to 596.5 nm. On the left is the $7s[3/2]^0\ J=1$ photon resonance, and on the right is the $5d[3/2]^0\ J=1$ resonance, where both are excited by five photons with counterpropagating beams. In the region near 587.5 nm is the fifth-harmonic profile, which is in the vicinity of the point at which $\Delta k=0$. In every instance the tunable fifth-harmonic production closely follows simple theoretical predictions.

C. Results for Ar $5s[3/2]^0\ J=1$

We also demonstrate the fifth-order interference effect in another system, namely, Ar. The Ar $5s[3/2]^0\ J=1$

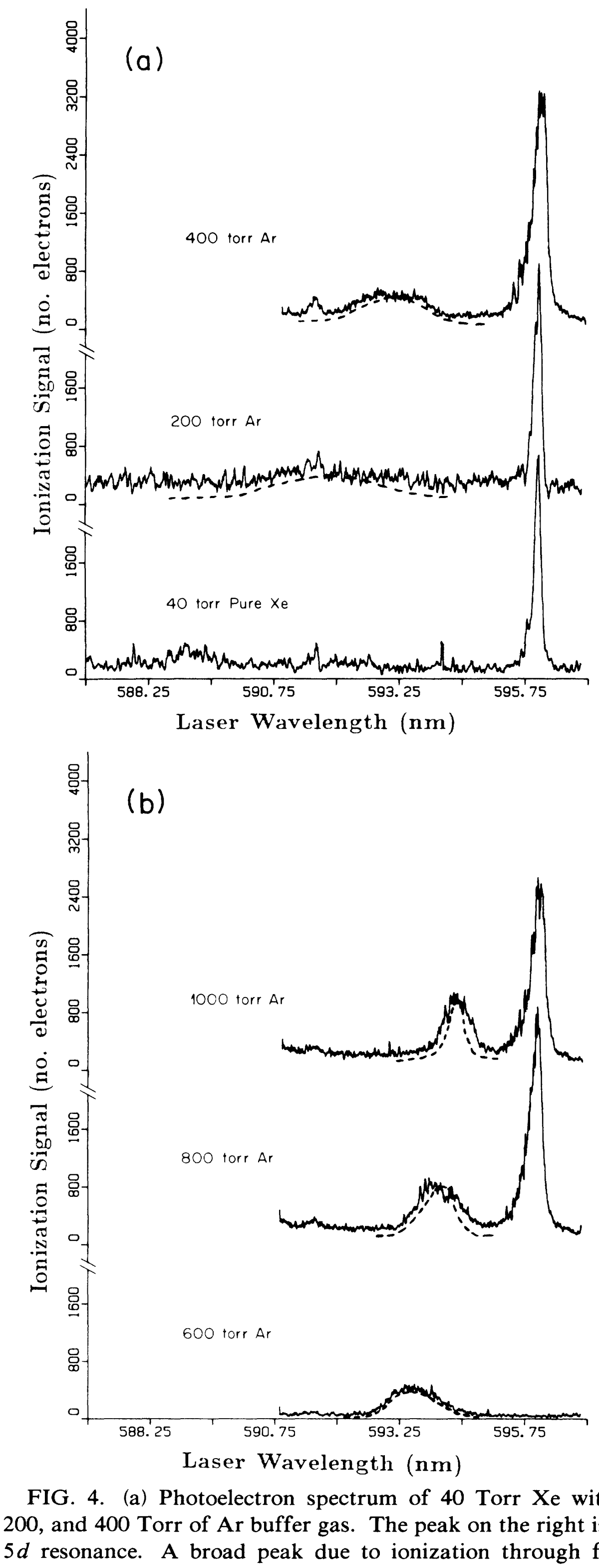

FIG. 4. (a) Photoelectron spectrum of 40 Torr Xe with 0, 200, and 400 Torr of Ar buffer gas. The peak on the right is the $5d$ resonance. A broad peak due to ionization through fifth-harmonic production becomes evident as more positively dispersive buffer gas is added. The dashed curve is the theoretically predicted fifth-harmonic profile under the conditions of the experiment ($f=7.5$-cm lens). (b) Same as (a) but with higher buffer-gas pressure. Dashed line is again the theoretical prediction.

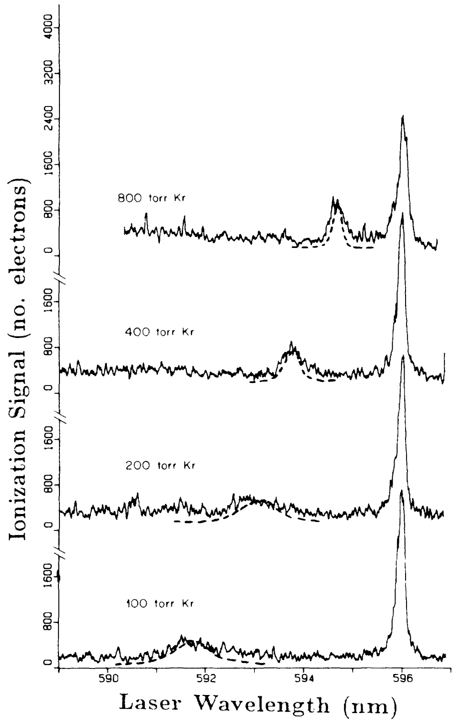

FIG. 5. Same as Fig. 4(a) but with Kr buffer gas.

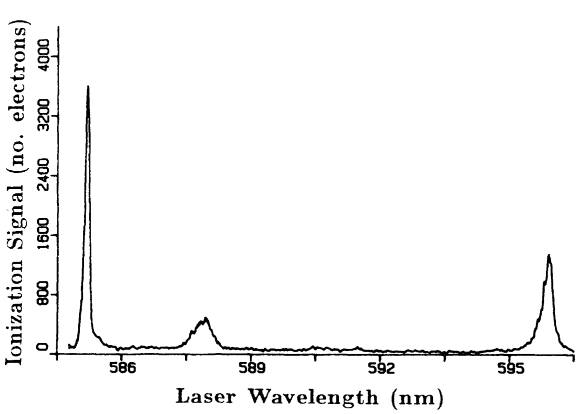

FIG. 6. Photoionization spectrum of 400 Torr of pure Xe. On the left and right are the $7s[3/2]^0\ J=1$ and $5d[3/2]^0\ J=1$ resonances, respectively (counterpropagating geometry). Between the two resonances is the fifth-harmonic peak near the position where $\Delta k=0$.

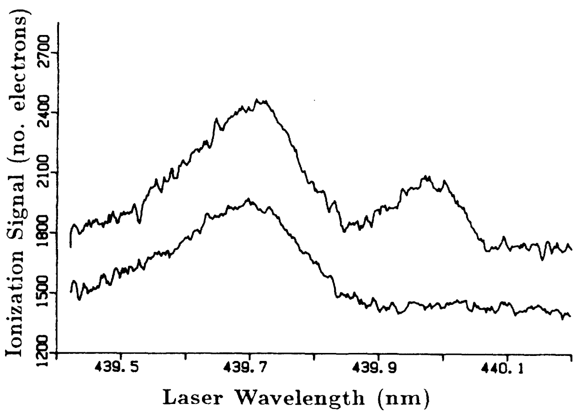

FIG. 7. Multiphoton ionization spectrum of Ar in the region of $3d[5/2]J=3$ and $5s[3/2]^0\ J=1$ five-photon resonances. Bottom curve is single pass. Top curve is counterpropagating beams at same total intensity.

state can be reached from the ground state by five photons or by a one-photon transition, and thus should exhibit the interference effect (at a laser wavelength of 439.97 nm). Very close to this state in energy is the $3d[5/2]^0\ J=3$ state which can be pumped from the ground state by five photons but not by a single photon. Thus, this resonance should not exhibit an interference effect between the five-photon and one-photon processes. (It is at a laser wavelength of 439.69 nm.) In Fig. 7 we show the multiphoton ionization spectrum of Ar in the region from 439.5—440.1 nm. The sample consists of 136 Torr of Ar and 14 Torr of CH_4 plus 1 Torr of Kr. Ionization signals were exceedingly weak in Ar. Additionally, pure Ar is a poor "counting gas" in a proportional counter operating at high gain. Success in detecting the six-photon ionization processes was achieved by using the classic 90% Ar—10% CH_4 gas mixture[22] which produces stable counter performance at high gain. Sensitivity was increased by addition of 1 Torr of Kr which can be Penning ionized by Ar* (5*s*). This mode of producing ions operates in addition to photoionization of the excited state by an additional laser photon. It increases the sensitivity for detecting excited Ar atoms in the proportional counter. With these refinements, the Ar $5s[3/2]^0\ J=1$ and Ar $3d[5/2]^0\ J=3$ states both showed resonantly enhanced ionization signals in the expected laser wavelengths as shown in the top trace of Fig. 7 where counterpropagating beams were present. In the bottom trace, where only a unidirectional beam was used, the 5*s* resonance is absent due to the expected interference between five-photon and one-photon excitation of the state.

IV. CONCLUSIONS

We have experimentally demonstrated the predicted behavior of five-photon excitation of dipole-allowed transitions in Xe and Ar, wherein the internally generated fifth-harmonic field totally suppresses five-photon excitation in a unidirectional laser beam over a wide range of pressures, with and without the presence of another gas, independent of laser intensity. With counterpropagating beams the cancellation effect is partially spoiled and resonantly enhanced ionization signals are readily observed. Also, we have shown that tunable phase-matched fifth-harmonic production in the negatively dispersive region of the $5d[3/2]^0\ J=1$ level of Xe closely follows standard perturbation theoretical predictions of the phase-matching curves in Xe-AR and Xe-Kr mixtures.

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