Nonlinear optical processes in xenon and krypton studied by two-color multiphoton ionization

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Multiphoton ionization (MPI) and third-harmonic generation (THG) in xenon and krypton have been studied via three-photon resonance with the xenon $6s'[\frac{1}{2}]_1^0$ and krypton $5s[\frac{3}{2}]_1^0$ states. A second, tunable dye laser is used to couple these states to higher-lying even-parity states. Observations are reported regarding the third-harmonic related cancellation of the intermediate s-state population and the mechanisms of population of the final states. Effects of the four-photon resonance on THG are detailed. Changes induced by the second laser reduce THG in normally favorable regions and enable it in otherwise forbidden regions. Striking effects in the MPI spectra due to the changes induced in THG are reported.

INTRODUCTION

The rare gases have been actively studied in experiments detailing laser-matter interactions. In particular, they rapidly assumed prominent roles in studies of MPI (Ref. 1) and THG (Refs. 2 and 3). The high energy of rare-gas excited electronic states makes it necessary to study them at vacuum ultraviolet (vuv) wavelengths or through high-order multiphoton excitation. Study of such multielectron atoms also presents a significant challenge to theoretical calculation. Nonetheless, it is precisely these difficulties which make the rare gases interesting subjects of study which continue to provide many fascinating results. Several new results relevant to previous and ongoing studies are presented in this article. Aron and Johnson published the first comprehensive results on MPI in xenon.[4] They observed many sharp atomic lines, broad "molecular" features, and atomic excited-state transitions due to "hybrid resonances" involving dissociation of molecular xenon. The broad, molecular features were found to be highly pressure dependent and are now well understood to involve excitation by third-harmonic light.[5] It was noted that the parity-allowed transition to the $6s[\frac{3}{2}]_1^0$ level was missing while that to the $6s'[\frac{1}{2}]_1^0$ level showed a pressure-dependent shift and broadening.

Compton *et al.*[6] and Miller *et al.*[7,5] completed more extensive investigations in which they confirmed that ionization at the xenon $6s$ position is null at high pressures, but very strong under low-pressure beam conditions. They noted the occurrence of strong, forward-directed THG under the higher-pressure conditions and postulated that the THG may be involved in depopulating the $6s$ level. Further evidence for the interplay between THG and MPI was provided by Glownia and Sander.[8] Theoretical descriptions of this "cancellation effect" were given by Payne *et al.*[9] and Payne and Garrett.[10] Additional treatments of this problem have appeared.[11,12] In particular, the treatment by Jackson and Wynne yielded the simple model of destructive interference of the coherent pathways to the excited states.[11] The general results indicate that an atomic state which is connected to the ground state by odd-photon multiphoton excitation as well as by one-photon excitation can show an interference between the two pathways. This interference results when the atomic density becomes large enough to produce a macroscopic polarization of the medium at the sum frequency, i.e., harmonic generation. The ionization at the exact resonance frequency will be quenched, and, for focused laser beams, harmonic generation will occur to the high-energy side of the resonance, often engendering strong ionization of the background gas. In the rare gases, this occurs at the dipole-allowed, odd-parity, $J=1$ states.

Compton and Miller published a detailed two-color study of xenon.[13] They used one laser to achieve three-photon excitation at and near the xenon $6s$ state and a second laser to excite to a higher p level. By detuning the first laser slightly to the blue of the resonance, they were able to establish that excitation of the upper state occurs via two distinct mechanisms: (1) an "energy conserving" mechanism in which $3\omega_1+\omega_2$ reaches the energy of the upper state (as generally expected), and (2) an "incoherent" or dissociative mechanism in which xenon collision complexes (dimers) at higher energy than the $6s$ resonance produce a $6s$ atom and a ground-state atom; the second laser then excites the $6s \rightarrow np$ state transition. That the two mechanisms occur is clear from the fact that the detuning of the first laser to higher energy than $3\hbar\omega_1 = E(6s)$ results in two ionization peaks when tuning the second laser near the $6s \rightarrow np$ transition. One peak in the doublet, that due to mechanism (2), remains fixed at the $6s \rightarrow np$ transition energy. The position of the other peak, due to mechanism (1), changes with the detuning of the first laser such that $3\hbar\omega_1+\hbar\omega_2$ always equals the energy of the upper state: Mechanism (2) occurs strongly to the blue of the $6s$ resonance due to the fact that THG occurs there, and the third harmonic is strongly absorbed

by the collision complexes to produce dissociation. We note that by the term *collision complex* we mean two xenon atoms in the act of colliding—i.e., on the inner repulsive wall of an essentially unbound potential curve.[13] At 1 Torr, approximately 10% of the molecules are best represented as such collision complexes at some time within the 10-ns laser pulse. In contrast, the number of bound dimers would be considerably less.

A major point of interest in this work concerns whether the addition of the second, resonant laser field serves to disturb the cancellation of the two pathways (three photon and one photon) to the three-photon resonance. Based on this, Tewari and Agarwal have calculated the changes in phase matching of a medium toward THG that can be induced by the addition of a second, resonant laser field.[14] Here we present additional two-color experiments in krypton and xenon which help elucidate the phenomena due to concurrent MPI and THG. Several major results of the present study have been published separately[15] and are not presented here.

EXPERIMENT

The experimental apparatus was described previously.[15] Briefly, the pulsed output of a xenon-chloride excimer laser at 308 nm is split and used to pump two tunable dye lasers. The two beams from the dye lasers are focused into a stainless-steel ionization cell, through windows mounted on opposite sides, to achieve temporal and spatial overlap of the light pulses. Laser one, with a uv output of ~ 1 mJ per 10-ns pulse is focused to a power density of $\sim 5\times 10^8$ W/cm^2 to give three-photon excitation and harmonic generation. Laser two, of higher power, is focused to $\sim 10^9$ W/cm^2 for use as the strong probe laser. Ionization is detected by collecting electrons on a positively biased collection wire in the cell and amplified by a charge-sensitive preamplifier. The signal is averaged with a gated integrator and displayed on an x-y recorder. Vacuum ultraviolet (vuv) THG could be detected by direct photoionization of nitric oxide in a second ionization cell attached to the first via a common magnesium fluoride window. A schematic diagram of the apparatus is shown in Fig. 1.

RESULTS

In our arrangement, one laser beam ("laser one") achieves three-photon excitation of a potentially canceled, $J=1$ resonance associated with THG. Here, this was either the krypton $5s[\frac{3}{2}]_1^0$ state at 370.6 nm or the xenon $6s'[\frac{1}{2}]_1^0$ state at 388.6 nm. The second laser beam is tuned to the energy of the one-photon transition from the three-photon level to an allowed state at higher energy. The generalized energy level diagram for these schemes is given in Fig. 2. Since cancellation means that the three-photon resonance remains effectively unpopulated, a transition to a higher level might be regarded as a nonresonant, two-color, four-photon process rather than a one-photon excited-state transition from the three-photon level. However, many of the results to be discussed entail excitation at energies higher than the three-photon resonance. In such a case, when a second laser is tuned to excite to a higher, allowed state, strong excitation of the upper state is achieved. This occurs not by a four-photon mechanism, but by a two-photon mechanism due to one generated third-harmonic photon and one photon from the second laser. The large enhancement in ionization is obtained, not by an intermediate resonance *per se* but, by the strong TH flux. The only criterion for

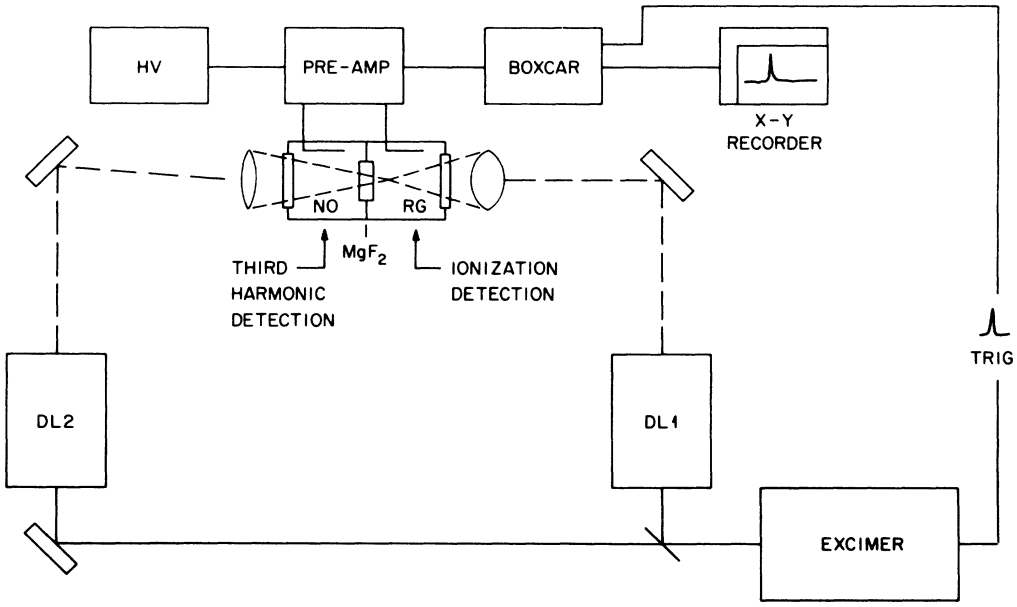

FIG. 1. Schematic diagram of the apparatus used to detect two-color MPI and THG. The output of an excimer laser is split and used to pump two dye lasers, DL1 and DL2. The two dye-laser outputs are focused into a rare-gas cell with a biased wire to collect electrons. A second such cell attached to the first via a common MgF_2 window allows third-harmonic detection from the photoionization of nitric oxide.

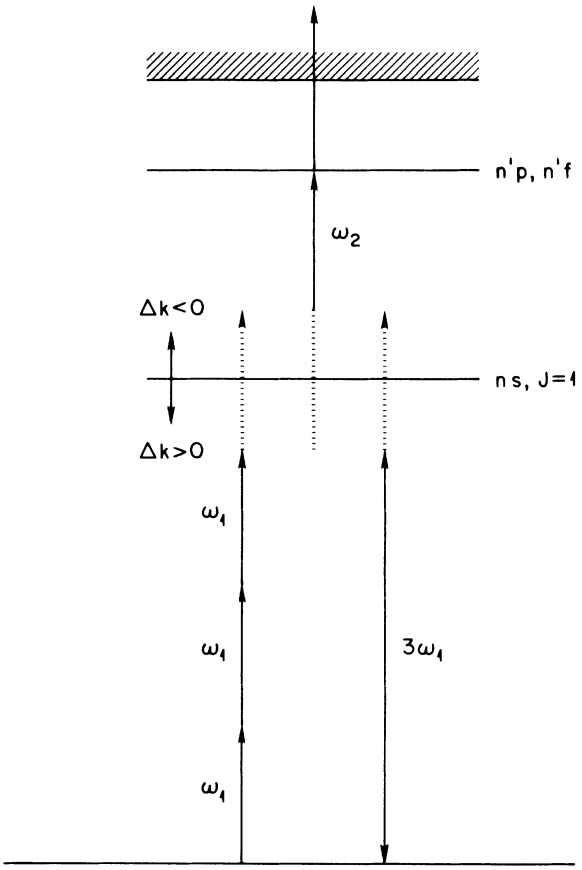

FIG. 2. Generalized energy-level diagram for the MPI of rare gases reported in this paper. Three photons reach the vicinity of a $J=1$ resonance and a fourth couples to an upper, allowed state. The sign of the wave-vector mismatch of $3\omega_1$ and ω_1 is indicated by arrows pointing away from the three-photon resonance. Third-harmonic generation normally occurs for focused beams where $\Delta k<0$. The extent of detuning near the ns state is exaggerated in the figure.

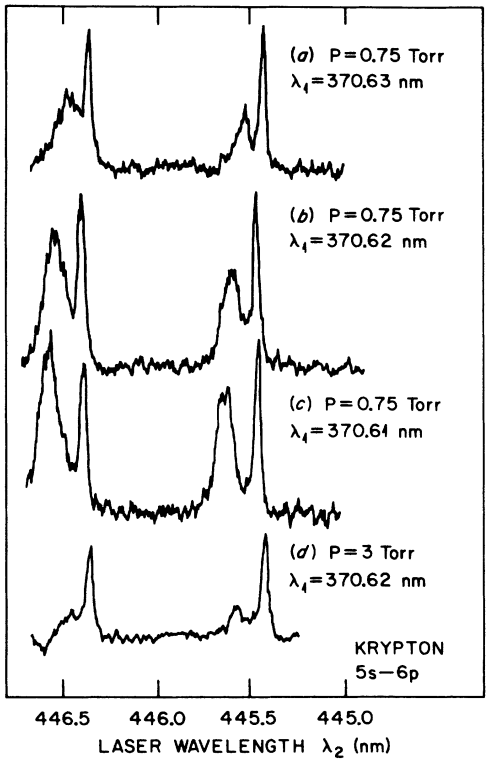

FIG. 3. Two-color excitation of the krypton $6p$ resonances. The first laser is detuned to the blue of the $5s$ state as in Fig. 2, while the second laser is scanned over the $6p[\frac{3}{2}]_1$ and $6p[\frac{3}{2}]_2$ states. Spectra (a)–(c) are from progressive detunings to the blue of the $5s$ state, while (d) is for the same detuning as in (b) but at higher pressure.

high-ionization rates is $3\hbar\omega_1+\hbar\omega_2=E(\text{res})$ over the region to the blue of the three-photon resonance where THG occurs. This region is "negatively dispersive" for phase matching for THG ($\Delta k<0$, Fig. 1) and its extent is dependent upon the conditions of focusing of the laser beam, the gas pressure, and the composition of the medium (if not a neat gas).

KRYPTON $5s[\frac{3}{2}]_1^0$

In the present work the previous two-color observations near the xenon $6s[\frac{3}{2}]_1^0$ state[13] have been extended to three-photon excitation near the krypton $5s[\frac{3}{2}]_1^0$ states. Figure 3 shows a series of spectra obtained by setting the laser-one wavelength to the blue of three-photon resonance with the krypton $5s$ level and scanning the laser-two wavelength over the transitions to the $6p[\frac{3}{2}]_1$ and $6p[\frac{3}{2}]_2$ states. Two doublets are seen in the scan. The spectra given in Figs. 3(a)–3(c) demonstrate the characteristics of the doublets in the two-color spectra with respect to detuning. As the frequency of laser one is moved slightly to the blue in the progression 3(a), 3(b), and 3(c), the broader, lower-energy components track to the red in the laser-two scan such that $3\hbar\omega_1+\hbar\omega_2$ is conserved. These features are due to the coherent excitation of the $6p$ states. The sharp, higher-energy peaks remain constant in position. These are due to dissociation of krypton collision complexes by third-harmonic light to yield $5s$ atoms, which undergo subsequent excitation and ionization via the atomic $5s$-$6p$ transitions with laser two. Scan 3(d) shows the effect of increasing the krypton pressure. Comparison of scan 3(d) with 3(b), taken at the same laser-one detuning, indicates an increase in the intensities of the sharp components of the doublets with respect to the broader peaks at increased pressure. This is supportive of a dimer mechanism producing the sharp peak and an atomic mechanism the broad one. Note that the apparent signal level in scan 3(d) cannot be compared directly to that in 3(a)–3(c) due to changes in gain in the cell with pressure.

We have also studied the krypton $5s$-$6p$ double resonance with the goal of further clarifying the role of a canceled resonance in a double-resonance experiment. In the earlier experiments it was noted that admission of a second, resonant laser beam could restore ionization at

the position of the canceled xenon 6s state, but an increase in pressure could again cause the signal to disappear.[13] Two ways were suggested in which the second laser might act to restore the ionization: (1) by opening the resonance ionization pathway, it might allow more sensitive detection of some excited atoms that are invariably produced or, (2) the addition of a new wave might act in some way to partly destroy the cancellation. The latter mechanism is suggested by noting that retroreflection of the exciting laser tuned to a canceled resonance dramatically restores the ionization signal for both circularly polarized[8] and linearly polarized light.[11] In a further effort aimed at clarifying the mechanisms of this type of "double-resonant" excitation, we have compared the effects of retroreflection of the ω_1 beam and addition of the resonant (or nearly resonant) ω_2 beam on the signal obtained when $3\omega_1+\omega_2 \rightarrow$Kr 6$p$ and $3\omega_1$ falls on or near the krypton 5s state.

Figure 4 shows a series of such spectra. Laser two, when used, is set to 445.4 nm or further to the red to excite the $6p[\frac{3}{2}]_2$ state via either of the two mechanisms discussed previously when the first laser is scanned to the blue of the $5s[\frac{3}{2}]_1^0$ state at 370.6 nm. Figure 4(a) shows the result of scanning the first laser over the krypton 5s region without a second laser present. Retroreflection of the laser beam yields some ionization at the position of three-photon resonance with the 5s state. The peak at the right-hand end of the scan is due to the unavoidable [3+1] ionization of trace xenon via the $5d[\frac{3}{2}]_3^0$ state. This peak is useful as a reference for intensity and wavelength throughout the scans. In Fig. 4(b), the retroreflection of the first laser is maintained and a second laser beam is overlapped with the first to excite the $6p[\frac{3}{2}]_2$ state. This gives rise to the new peak displaced from the 5s resonance. This peak is due to the coherent excitation of the 6p state (i.e., that which corresponds to the broad components of the doublets in the ω_2 scans of Fig. 3). In addition, the ionization at the position of the 5s state is dramatically increased. In Fig. 4(c), the second laser is tuned to excite the 6p state nearer the 5s resonance. The intensities of the two krypton resonances are the same as in 4(b). (Since this scan did not include the xenon resonance, it has been added as a dotted line in the figure.) In 4(d) the ω_2 wavelength is left the same as in 4(c) but the ω_1 retroreflection is blocked. The ionization at the 5s position disappears completely whereas that due to the coherent excitation of the 6p by $[3\omega_1+\omega_2]$ is unchanged. In 4(e) ω_2 is tuned to exact resonance with the 5s-6p transition (retroreflection still blocked) and the ionization largely disappears. Restoration of the retroreflection of the ω_1 beam in 4(f) restores the ionization at the resonance position to the level in 4(b) and 4(c). The broad background due to the dissociation of collision complexes is too weak to be observed here.

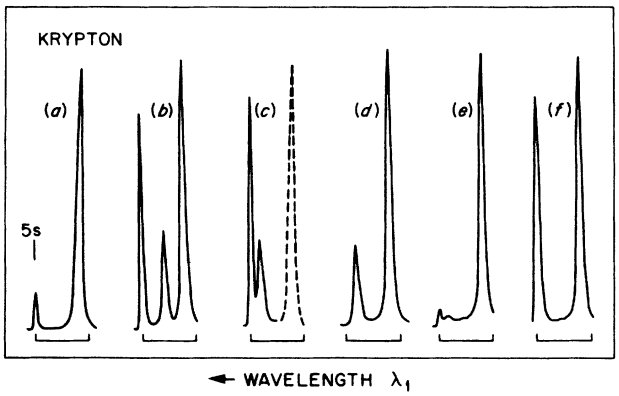

FIG. 4. Laser-wavelength scans over the region where three photons can excite the 5s state in krypton at 370.7 nm. Comparisons are made of the ionization signals obtained by the retroreflection of the excitation laser with those from coupling to the $6s[\frac{3}{2}]_2$ state with a second laser. In spectrum (a), no second laser is present and three-photon laser is retroreflected giving ionization at the position of the 5s state. The tall peak at the end of the scan is due to trace xenon. In scans (b)–(d) a second laser also excites the 6p state off of the 5s resonance. Scan (d) is as (c) without retroreflection. In (e) and (f) the 6p state is resonantly excited from 5s, without and with retroflection, respectively. The pressure is 4 Torr. The ordinate scale is constant for all the spectra and spans roughly 2 Å.

Comparison of the spectra presented in 4(b) and 4(c) with that in 4(a) strongly suggests that the second laser acts to more efficiently ionize 5s atoms produced, but not ionized, by laser one. This is because the cross section for ionization of 5s atoms is large near resonance with the 6p state. Without the second laser present, the ionization of the 5s atoms take place with much lower cross section. In the absence of the retroreflection as in 4(d), no ionization is seen at the 5s wavelength, indicating that the retroreflection is necessary for the population of the 5s state. To the blue of the 5s state, excitation of the 6p state is dominated by the two-photon, third-harmonic mechanism. In 4(e) where the resonant excitation of the 6p state is attempted through the 5s state, no third-harmonic flux is generated and the two-photon mechanism disappears. When the retroreflection is restored as in 4(f), it is the strong, resonant ionization of the 5s atoms produced by $3\omega_1$ that is seen as in 4(b) and 4(c).

XENON $6s'[\frac{1}{2}]_1^0$

Just as for the krypton 5s and xenon 6s states, excitation of the xenon $6s'[\frac{1}{2}]_1^0$ state exhibits interference effects which were demonstrated in Ref. 5. In a recent communication we outlined several striking effects in double-resonant MPI and THG near the 6s' state.[15] In the earliest experiments, unusual behavior of the ionization signals at "accidental" four-photon resonances was observed when the resonances fall in a wavelength region where THG occurs.[5,7] There is a background of nonresonant ionization in xenon and krypton over the regions in which THG occurs. When the laser wavelength is tuned to reach an "accidental" four-photon resonance, a strong peak is seen in the ionization signal. However, when the background ionization is very large, the resonance may appear as a *dip* in the background. In our recent communication,[15] we studied this further by utilizing the 6s'-5f double resonance in xenon with two independently

tunable lasers. We have explained the dips as being due to the spoiling of phase matching for THG due to the dispersive changes induced in the medium by the coupling to the upper resonance. The data may be interpreted in terms of an ac Stark shift of the intermediate level which results in a modification of the dispersion. We also examined the excitation of the $5f$ levels from the regions to the red of the $6s'$ state. On the low-energy side of the resonance, the medium is "positively dispersive" ($\Delta k > 0$) and does not allow THG to occur in a focused configuration. We observed that the coupling to the four-photon state could modify the dispersion on the low-energy side of the resonance thus enabling THG. Here, we present several details of this investigation omitted in the earlier brief report.

Figure 5 shows the xenon $5f$ transitions excited by tuning laser one slightly to the red of three-photon resonance with the xenon $6s'$ state and scanning a second laser over the $5f$ levels. The spectrum consists of four peaks due to states of different total angular momentum. In this region, no THG normally occurs. However, when the first laser is tuned to higher energy than the $6s'$ resonance, THG occurs and the spectrum obtained by scanning a second laser over the $5f$ levels takes on a different appearance. Figure 6 shows another such spectrum where in this case laser one is scanned while laser two is fixed. The bottom trace shows that strong peaks in the ionization are seen at only two of the $5f$ levels—the $5f[\frac{5}{2}]_2$ and $5f[\frac{3}{2}]_2$ levels which are two-photon allowed from the ground state. The upper trace monitors the vuv third-harmonic light from the cell and shows that the TH is strongly absorbed in exciting those two resonances. The small peak at the resonance is attributed to fluorescence from $6s'$ atoms created by the dissociative mechanism. Phase matching cannot be achieved for THG at the resonance wavelength.

We have reported that the ion signals at the resonances diminish in intensity and change into dips in the background as they are moved to the center of the THG profile.[15] This can be accomplished by changing the wavelength of laser two or by changing the gas pressure, which determines where THG occurs. Near optimal phase matching, the coupling of the $6s'$ level to a $5f$ level by the second laser, deoptimizes phase matching thereby reducing the TH flux. Since the ionization is dominated by third-harmonic excitation, the reduction in THG

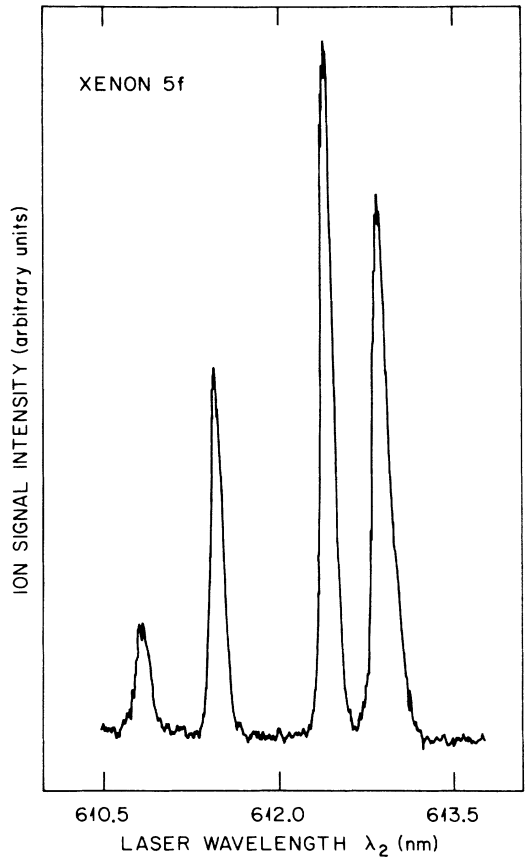

FIG. 5. Xenon $5f$ levels excited by a scheme as shown in Fig. 2, with laser one detuned to the red of the xenon $6s'$ level. The peaks, from left to right, are the $5f[\frac{7}{2}]_4$, $5f[\frac{5}{2}]_2$, $5f[\frac{9}{2}]_4$, and the $5f[\frac{3}{2}]_2$ resonances. The pressure is 24 Torr.

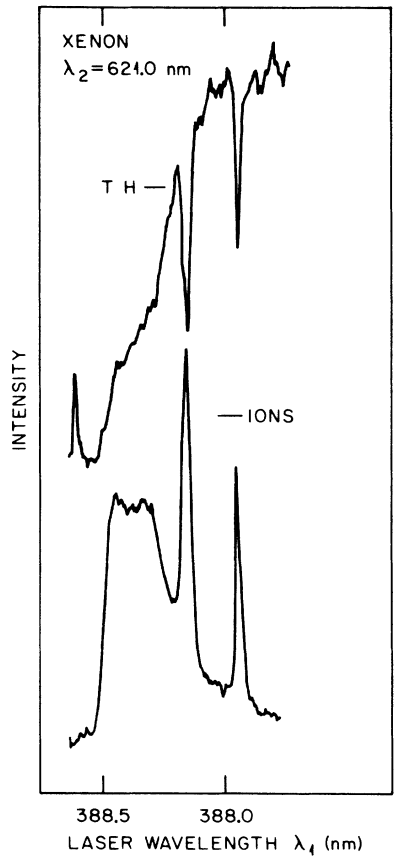

FIG. 6. Scan of laser one over the xenon $6s'$ region while laser two excites transitions to the $5f$ states. The top trace shows third-harmonic yield and the bottom, ion yield. The xenon pressure is 10 Torr.

yields decreased ionization. Another example is shown in Fig. 7 where the laser-two wavelength is fixed to achieve off-resonant excitation of the $5f$ levels in xenon when laser one is tuned to the blue of the $6s'$ state. In 7(a), the scan of laser one over the region to the blue of the $6s'$ state yields the hump of background ionization with the two peaks due to the $5f$ levels superimposed. In 7(b)–7(d), changes are made in the laser-two wavelength such that the $5f$ levels are excited near the maximum of the background ionization. The peaks shrink and turn into dips as they are "moved" to the red through the maximum. In 7(d), the second peak has turned into a dip and the first has disappeared near the red edge of the third-harmonic produced ionization.

Figure 8 shows these dips in another way. Laser one is set to the maximum in THG and ionization, and the second laser is scanned across the $5f$ resonances. The xenon is "phase matched" with the addition of excess argon buffer gas to allow more efficient THG. A decrease in the background ionization in excess of 50% occurs at the positions of the two-photon resonances.

Another way to effect the transition from peaks to dips in the ion signal is through the degree of focusing of the laser beam. This is shown in Fig. 9 for the xenon $5f'$ and $6p$ "accidental" (one-laser) four-photon resonances that lie in the wavelength region to the blue of the $6s'$ state. The lower trace shows clear peaks in the ion signal when the laser is focused with a 100-mm focal length lens. In the upper trace, focusing with a 50-mm lens gives dips at the resonances. Here, the shorter focal length changes the experiment in two important ways. (1) It changes the phase-matching parameter $b\Delta k$ due to the three-photon resonance, and (2) it changes the coupling of the intermediate and upper states through the one-photon transition.

Odd behavior of the $5f$ ionization signals has been characterized when they are excited to the red of the $6s'$ state.[15] Unusual dependences on the xenon pressure and detuning of the first laser from the $6s'$ resonance are observed. An example of this is shown in Fig. 10. The spectrum of four peaks is obtained by fixing the laser-one wavelength 0.05 nm to the red of the $6s'$ resonance and scanning laser two over the $5f$ levels. Figure 10(a) was

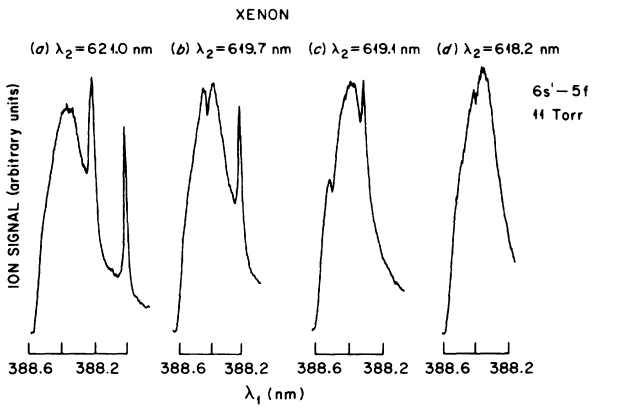

FIG. 7. Ionization spectra showing excitation of the $5f$ states by third-harmonic light from the blue of the $6s'$ state. Spectra (a)–(d) are obtained by setting laser two to progressively shorter wavelengths so that the $5f$ resonances are excited progressively closer to the $6s'$ state. When the resonances are "moved in" over the maximum of THG, they turn from peaks to dips in the ionization.

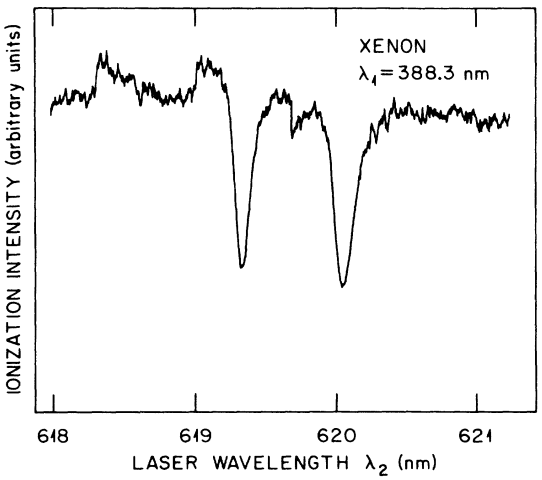

FIG. 8. Xenon $5f$ resonances from 25 Torr of xenon in 150 Torr of argon. Laser one is fixed to a wavelength where dips occur as in the previous figure, and laser two is scanned.

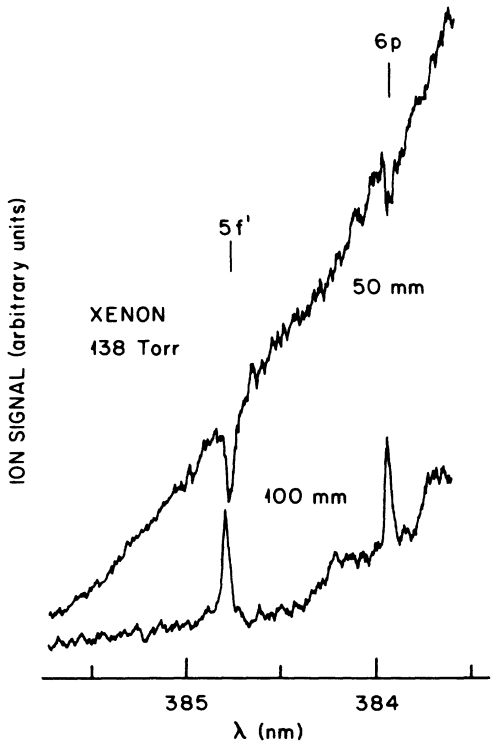

FIG. 9. "Accidental" (one-laser) excitation of the xenon $5f'$ and $6p$ states. The use of a shorter focal length lens causes the resonances to turn to dips.

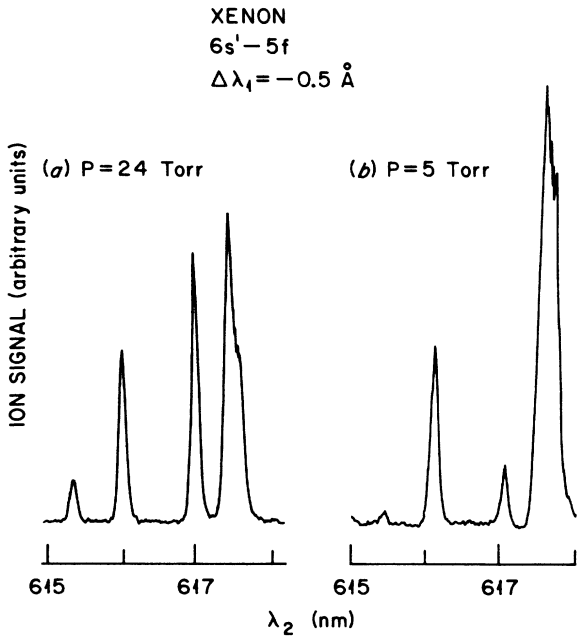

FIG. 10. Two-color scans over the xenon $5f$ levels with laser one detuned 0.5 Å to the red of the $6s'$ level. Only the xenon pressure has been changed from (a) to (b). Marked differences in the relative intensities of the peaks are seen.

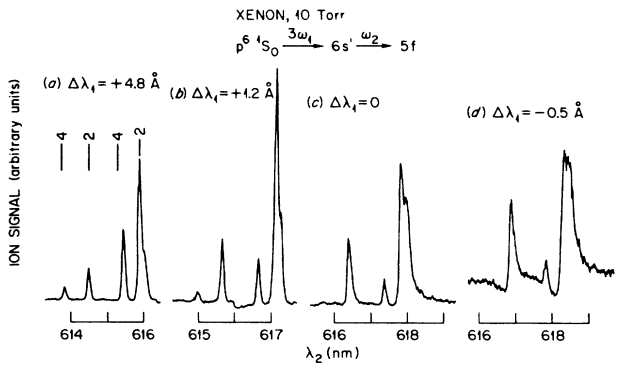

FIG. 11. Series of laser-two scans over the xenon $5f$ levels excited near $6s'$-$5f$ double resonances. Detuning of the first laser from the red of the $6s'$ state over to the blue yields a smooth, continuous change in the appearance of the spectrum. Here we define $\Delta\lambda_1$ as positive for a detuning to the red of the $6s'$ state

obtained at a gas pressure of 24 Torr while (b) is from 5 Torr of xenon. A striking difference in the relative intensities of the peaks between the two spectra is evident. This can be explained as being due to the involvement of THG in the excitation of the $5f$ levels.[15] THG is normally forbidden to the red of the $6s'$ state where the medium is positively dispersive, but it is enabled through the phase-matching changes induced in the medium by the coupling to the $5f$ levels with the second laser. The same laser-induced changes in phase matching produce the ionization dips seen to the blue of the $6s'$ state. Here, THG is evident in Fig. 9(b) where the peaks due to $J=2$ states become intense. These are the resonances which are two-photon allowed from the ground state and which are excited so strongly to the blue of the $6s'$ state where THG normally occurs. We have previously demonstrated the direct detection of the red-side THG.[15] An additional investigation of the $5f$ resonances is shown in Fig. 11. A series of spectra obtained at constant pressure is shown at several detunings of laser one to the red of the $6s'$ state, near the $6s'$ state, and to the blue of it. In tuning from the red to the blue of the $6s'$ state, the intensities of the two $J=2$ peaks gradually increase with respect to the intensities of the other two peaks. No sudden turn-on of third-harmonic excitation is noted to the blue of the $6s'$ state. The intensity pattern associated with TH excitation has already developed to the red of the resonance. At other pressures, different intensity patterns are seen (Fig. 10) due to the different locations of optimal phase matching for THG.

DISCUSSION

Studies of the role of THG in MPI have appeared in the literature.[16] Resonance effects on THG have also been studied. At first, the effects of a two-photon resonance in THG and other third-order sum- and difference-frequency generation were investigated.[17–19] More recently, attention has focused on the role of four-photon resonances in THG. Generally, it is found that two-photon resonances give rise to large nonlinear susceptibilities in the medium reflected in dramatic increases in THG. Similar effects can occur for a four-photon resonance. However, the main effect of a four-photon resonance is to alter the dispersion of the medium at the third-harmonic frequency. Several experimental studies involving THG at four-photon resonance have appeared. The earliest report shows the dips in third-harmonic output and ionization intensity which can occur at accidental four-photon resonances.[5] Enhancement of THG in mercury was reported by Normand *et al.*[20] These results were extended by Smith who suggested that nonlinear contributions to the refractive index become important at the four-photon resonance.[21] Valée *et al.* used two untunable dye lasers to study sum-frequency generation in xenon.[22] Their observations include that of the production of tunable vuv light in the mildly, positively dispersive regions between adjacent three-photon resonances. This can occur through a fifth-order process ("up and down") which generates a wave at the same frequency as the concurrent third-order process.

Ganeev *et al.* have also studied the occurrence of THG in positively dispersive media under rather different circumstances.[23] They used a high-intensity focused beam (power density $>10^{12}$ W/cm^2) to enable THG in krypton and xenon in positively dispersive wavelength regions. These results are interpreted in terms of Kerr nonlinearities offsetting the phase shift which normally cancels THG from a focused beam in a positively dispersive medium.

In our experiments, one laser excites near a three-photon transition, and a second laser provides an addi-

tional photon for excitation to a second excited state. For such a situation (nearly) resonant at two steps, $\chi^{(3)}(-3\omega_1;\omega_1,\omega_1,\omega_1)$ and $\chi^{5}(-3\omega_1;\omega_1,\omega_1,\omega_1,\omega_2,-\omega_2)$ become similarly important, or in fact, can no longer be considered separate and distinct quantities. In other words, the second laser field modifies $\chi^{(3)}$ by mixing it with higher-order susceptibilities. More importantly, the dispersion of the medium at the third-harmonic wavelength is altered such that[15,24]

$$\Delta k = \frac{\Delta k_0(\delta_1)}{1-|\Omega_{12}|^2/\delta_1(\delta_2+i\Gamma_2)} ,$$

where $\Delta k_0(\delta_1)$ is the wave-vector mismatch in the absence of the second beam $=k(3\omega_1)-3k(\omega_1)$, δ_1 is the detuning of the three-photon resonance δ_2 is the detuning of the four-photon energy $3\hbar\omega_1+\hbar\omega_2$ from the upper resonance, Ω_{12} is the Rabi rate between the upper states, and Γ_2 is the width of the state at the four-photon level.

When the first laser is detuned to slightly lower energy than the three-photon state, the medium is very positively dispersive and unfavorable for the occurrence of THG. However, the introduction of the second laser field alters the dispersion through the ac Stark shift of the level and THG can occur. These results are in contrast to those of Valée *et al.* wherein the three-photon level is far from resonance, so the harmonic generation occurs via a simpler $\chi^{(5)}$ process in a less positively dispersive medium. Third-harmonic generation in both situations involving a four-photon resonance has been studied theoretically by Agarwal and Tewari[12] and Tewari and Agarwal.[14] An independent treatment of our results has been done by Payne and Garrett.[24]

CONCLUSION

Multiphoton ionization experiments using two lasers have been done in the rare gases. Once again, THG is shown to play an important role in the signals observed when three photons reach an energy somewhat higher than that of a $J=1$ resonance. The use of two lasers unravels the mechanisms of third-harmonic assisted ionization which occur. Observations are made of the ionization signals near the canceled $J=1$ resonances. The coupling of third harmonic to an upper state with a second laser field yields strong excitation of the upper state when it is two-photon allowed from the ground state. Furthermore, interesting behavior of the ionization signals can result from the dispersive changes induced in the medium by the second laser. These dispersive changes modify the production of third-harmonic light and the resultant ionization. Such a scheme can be used to enable THG in the positively dispersive regions of the medium.

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