PHYSICAL REVIEW A VOLUME 34, NUMBER 6 DECEMBER 1986

Laser-induced third-harmonic generation in forbidden regions

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(Received 5 May 1986)

New observations are reported of tunable vacuum ultraviolet light generated in the forbidden region to the red of the xenon $6s'[\frac{1}{2}]_1^0$ state due to the introduction of a second, resonant laser field. Striking observations of double-resonant ionization signals on the blue side of the xenon $6s'$ level are also reported. Both sets of data are interpreted in terms of the changes in phase matching and the nonlinear susceptibility induced in the medium by the second laser. These changes are successfully analyzed in terms of the ac Stark effect in the three-photon level due to the second laser field.

Optical frequency conversion by nonlinear processes was realized soon after the development of high-power lasers. In particular, laser third-harmonic (TH) generation in gaseous media has long been established as a practical method for the generation of short wavelength radiation.[1] The necessary criteria for the production of third-harmonic light have been thoroughly studied and are well understood.[1,2] In particular, for a tightly focused configuration, such third-harmonic production occurs only for those wavelengths at which the gas is negatively dispersive, i.e., $\Delta k < 0$, where Δk is the wave-vector mismatch, $k(3\omega) - 3k(\omega)$, between the incident and generated waves.[2] In the rare gases, these negatively dispersive regions are on the high-energy side of ("to the blue of") the accessible $J = 1$ resonances.

A very general theoretical treatment predicts that the introduction of a second laser field in near resonance with a one-photon allowed transition between the three-photon level and some higher level should influence the generation of third-harmonic light. Specifically, it predicts third-harmonic generation in normally positively dispersive regions, and under the same conditions, changes in the third-harmonic yield in the negatively dispersive regions. An independent treatment of some aspects of this problem was very recently published by Tewari and Agarwal.[3]

In an earlier paper, Compton and Miller studied two-color multiphoton ionization through $6s[\frac{3}{2}]_1^0$ state of xenon[4] using weaker lasers than those of the present study.

In the present work, we have investigated in detail modifications of third-harmonic generation by a second strong laser. We report the observation of *tunable* third-harmonic light in the positively dispersive region on the low-energy side of ("to the red of") the xenon $6s'[\frac{1}{2}]_1^0$ state induced upon introduction of a second, strong laser field. We also report observations of strong, systematic increases and decreases in ionization signals generated to the blue of the $6s'$ level.

Effects of a four-photon resonance on third-harmonic production in mercury have been seen by Normand, Morellec, and Reif[5] and by Smith[6] when they tune near the three-photon allowed 6^1P transition and a fourth photon is resonant with some higher level. These single-laser studies are limited to a few "accidental" four-photon resonances. Vallée, DeRougemont, and Lukasik[7] have also employed a two-laser scheme to access four-photon resonances in xenon to generate a third frequency $(2\omega_1 + \omega_2)$ by four-wave mixing in a positively dispersive region. This region is roughly midway between the xenon $6s$ and $6s'$ resonances and has been described as a $\chi^{(5)}$ process resonant in the fourth photon rather than a laser-modified $\chi^{(3)}$ process.[8]

In our experiments, the output of a Lambda Physik EMG101 excimer laser (XeCl) was split and used to pump two dye lasers. A Molectron DL-II dye laser ("laser one") was operated with the dye QUI (Lambda Physik) near 388 nm. The output pulses (≤ 1.0 mJ, ~ 15 ns) were focused with a 50- or 75-mm focal length lens into a cell containing xenon gas to induce the three-photon absorption near the xenon $6s'[\frac{1}{2}]_1^0$ level. The output of a Lambda Physik FL2000 dye laser ("laser two") operated with Rhodamine B (≤ 5 mJ per pulse) was focused colinearly into the same cell with a 100-, 75-, or 50-mm focal length lens such that the focal regions spatially coincided. Both copropagating and counterpropagating modes were investigated. Absorption of an additional photon from laser two excites xenon to one of its $5f[K]_J$ sublevels. Subsequent absorption of a photon from either laser then ionizes the excited atom.

Ionization is detected in a stainless-steel cell with a positively biased collection wire. The signal is detected with a charge-sensitive preamplifier and averaged over several laser shots with a gated integrator (Stanford Research Systems).

For direct detection of vacuum ultraviolet (vuv) light, a second ionization cell was attached such that the two cells had a magnesium fluoride window in common. Vacuum ultraviolet light between 9.26 eV (nitric oxide ionization potential) and 11.00 eV (MgF_2 cutoff) was detected by the one-photon ionization of nitric oxide. Further experimental details may be found in previous publications.[9]

The energy levels appropriate to our experiment are depicted in Fig. 1. In a typical double-resonance experiment, the first dye laser is used to excite xenon near the $6s'[\frac{1}{2}]_1^0$ level and a second dye laser further excites the atom to one of the allowed J components of the $5f[K]_J$ levels. In the experiments described here, the first laser is detuned such that $3\omega_1$ falls either to the red or to the blue of the $6s'$ resonance and the second laser is tuned to reach a $5f$ level,

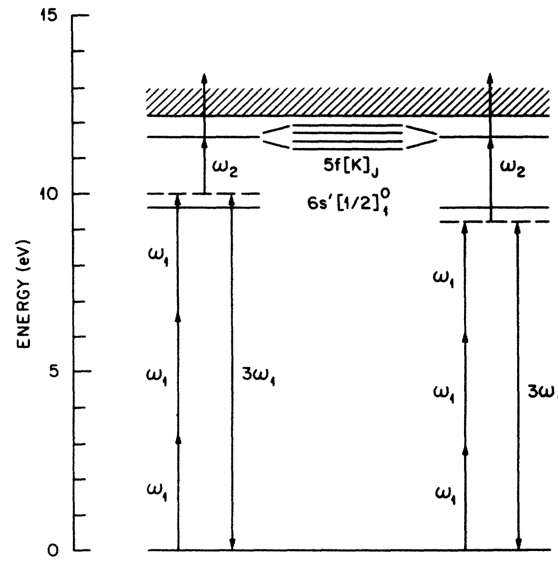

FIG. 1. Energy level diagram for xenon $6s'$-$5f$ double resonant ionization. Left: laser one detuned such that $3\hbar\omega_1 > E(6s')$ where third harmonic is normally produced. Right: laser one detuned such that $3\hbar\omega_1 < E(6s')$; laser two *induces* third-harmonic production. Magnitude of detunings is exaggerated. Center shows $5f$ level in expanded scale as consisting of four pairs (each pair unresolved) of J sublevels. Energies and state labeling as in Moore (Ref. 10).

i.e., $3\hbar\omega_1 + \hbar\omega_2 = E(5f)$. Such a "pseudo-double resonance" is strong when the first laser is tuned to the blue of the $6s'$ level (left-hand side of Fig. 1) because of the production of third-harmonic light. A xenon atom in the interaction region can absorb a third-harmonic photon plus a photon from the second laser to effect a strong two-photon excitation to a $5f$ level.[4,9]

When third-harmonic light is present, this excitation mechanism of the $5f$ level dominates the direct $(3\omega_1+\omega_2)$ mechanism, as evidenced by the relative intensity of the ionization. When laser one is tuned to the blue of the $6s'$ level, a scan of the laser-two wavelength yields two strong peaks. These two peaks result from excitation of overlapping J components of the $5f$ level, in particular, the $J=1$ and $J=2$ components, the only sublevels which are one-photon allowed from the $6s'$ state. In contrast, when the laser-one wavelength is fixed red of the $6s'$ level and laser two is scanned over the $5f$ levels, essentially no signal is seen at the same level of sensitivity. At higher gain, under some conditions of pressure and detuning of laser one, a spectrum of four peaks is obtained. These are due to four allowed transitions to sublevels in the $5f$: $J=1,2$ $(\omega_{TH}+\omega_2)$ and $J=4$ $(3\omega_1+\omega_2)$. These differences in appearance and intensity of the spectra obtained from opposite detunings from the $6s'$ resonance indicate the dominant role third-harmonic light plays in the blue-side excitation. The role of third-harmonic excitation in double-resonant ionization near the $6s$ level in xenon has previously been discussed in detail.[4,9,11] In the following, we will discuss the effect of the second resonant field on the generated third harmonic and ionization, first on the blue side (normally negatively dispersive) and then on the red side (normally positively dispersive) of the $6s'$ level.

By setting laser two at an energy lower than the $6s'$-$5f$ transitions, a wavelength scan of laser one across the region of the third-harmonic production yields a "hump" of ionization signal due to vuv-assisted ionization of xenon collision complexes. Two strong peaks are superimposed due to two-color excitation of $5f$ levels from the virtual level (or collision-complex level) at the third-harmonic energy. At various xenon pressures and detunings of laser two, these $5f$ ionization signals could be made to appear as enhanced ionization above the large background or as *dips* within it. Some of these data are summarized in Fig. 2.

Figure 2(b) is typical of what is seen whenever the $5f$ resonances are induced on the blue tail of the region in which third-harmonic light is produced. The resonances appear as two large positive peaks. Figure 2(a) is taken with laser two set at the same wavelength, but at a higher xenon pressure when the wavelength for optimum phase matching of third-harmonic production is shifted further to the blue.[9] Here the redder of the two $5f$ resonances is now nearer the maximum of the third harmonic and appears as a negative peak or dip in the ionization. At this same pressure, laser two can be reset so that the resonances are further blue shifted as in Fig. 2(c). Once again, with the resonances induced from the blue tail of the third harmonic they appear as peaks in the ionization spectrum. But at this *same* detuning, the xenon pressure can again be increased to yield the results in Fig. 2(d). Again, with the third harmonic shifted "under" the resonances, they can be induced as dips in the background ionization. Here the redder resonance is again a dip and the second an attenuated peak.

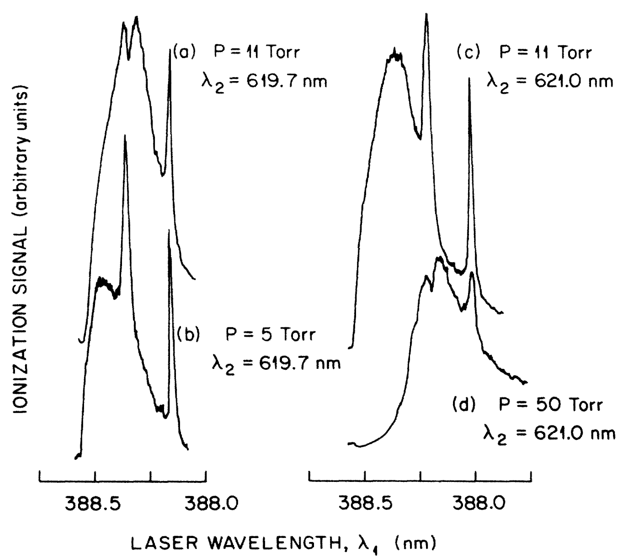

FIG. 2. Multiphoton ionization blue of the xenon $6s'$ level. Hump of ionization is due to third-harmonic excitation and subsequent ionization. Two resonances are superimposed because of excitation by a second laser to $5f[2\frac{1}{2}]J=2$ and $5f[1\frac{1}{2}]J=1,2$ (overlapping) sublevels. Here in a given figure, ω_2 is fixed and ω_1 is scanned. Resonances appear as peaks on the blue side of third-harmonic profile and dips near maximum or redder. See text for details.

To summarize, combinations of xenon pressure and laser-two detuning may be used to induce two peaks, a peak and a dip, or two dips. In general, the resonances will appear as peaks in ionization when the phase matching is such that $|b\Delta k| < |b\Delta k_{opt}|$, where b is the confocal parameter and $b\Delta k_{opt}$ is the criterion for optimal third-harmonic generation. As the resonances are "moved" toward the maximum of third-harmonic production, either by resetting the laser-two wavelength or by increasing the xenon pressure to shift the third-harmonic production to the blue, the ionization at the resonances decreases until it is actually a dip in the level of background ionization. These dips then occur when $|b\Delta k| > |b\Delta k_{opt}|$ and shrink as they are moved further down the red falling edge of the third harmonic. At low enough pressure, where a critical third-harmonic intensity is not produced, the peaks decrease in size as moved over the third-harmonic region but never turn to dips. The same is true when a longer focal length lens is used to focus laser two. Similar effects were observed in one-color spectra where an "accidental" four-photon resonance condition was met.[9] This enhancement or depletion of the TH yield which depends only on the magnitude of $b\Delta k$ relative to $b\Delta k_{opt}$ appears to be quite general. Characterization of this effect is dependent upon using two independently tunable lasers, and the effect has not been described by previous theory.

We also examined the xenon ionization through the $5f$ levels when induced to the red of the $6s'$ resonance, where phase-matching considerations normally preclude the generation of third-harmonic light. Marked changes in absolute intensity and relative intensities of the four peaks ($J=2,4$) vis a vis each other were observed with detuning of laser one from the $6s'$ level. In particular, the intensities of the two $J=2$ resonances increase much more rapidly than those of the other two $J=4$ resonances as laser one is tuned closer to the $6s'$ resonance. In fact, if a series of laser-two scans of the double resonance are made at different laser-one detunings, starting well red of the $6s'$ and continuing over and to the blue of the resonance position, a smooth, continuous increase of the two $J=2$ peak intensities relative to the other two is observed. Restated, the double resonance induced just to the red (1–2 Å) of the $6s'$ has the same characteristics as when induced on the blue side where the third-harmonic light plays the dominant role in the ionization.

In order to examine more carefully the possibility that the second laser is inducing the generation of third harmonic of the first-laser frequency, we sought to directly detect vuv light when laser one was detuned to the red of the $6s'$ level. The paired arrangement of ionization cells was used in which photoionization of nitric oxide in the second cell resulted from third-harmonic production in the first cell.

Figure 3 shows excitation spectra due to ionization and third-harmonic production resulting from pumping the $5f$ levels from the virtual level to the red of the $6s'$. The laser-one wavelength is fixed, and the spectrum results from tuning laser two. The ionization spectra show four peaks due to the allowed transitions to J sublevels of the $5f$. As laser one is moved from a larger detuning as in Fig. 3(b) and closer to resonance as in Fig. 3(a), the magnitude of the ionization signal increases and, particularly in the $J=1,2$ peak at 617.0 nm in Fig. 3(a), broadens to the red. The same scans detecting vuv light clearly show peaks associated with the $J=1$ and 2 resonances only. Thus, tunable vuv light is being induced in normally positively dispersive regions by the introduction of the second-laser beam. It should be noted that the induced third-harmonic generation occurs with the two laser beams either counterpropagating or copropagating.

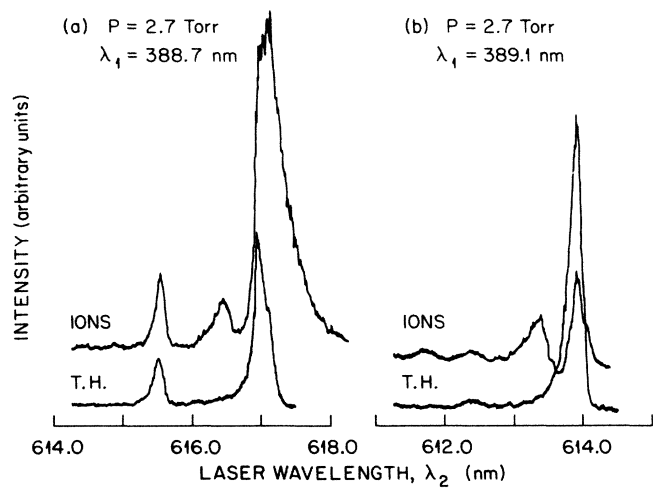

FIG. 3. Xenon $5f$ resonances induced from the red of xenon $6s'$. Traces show xenon ionization signal and third-harmonic light intensity. Here, a spectrum is obtained by fixing ω_1 and scanning ω_2. See text.

We have analyzed our data on the blue and red sides of the $6s'$ resonance in terms of intensity-dependent changes in the susceptibilities of the medium introduced by the second, strong laser field. In our analysis, the introduction of a second-laser field resonant with the $6s'$-$5f$ transition introduces an ac Stark shift of the $6s'$ level. As the laser pulse grows in intensity, it shifts the $6s'$ level increasingly, thereby changing the dispersive characteristics of the gas in a time-dependent fashion. The detailed analysis yields[12]

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

where δ_1 is the detuning from the intermediate three-photon resonance $|1\rangle$; $\hbar\delta_1 = 3\hbar\omega_1 - E(1)$, and δ_2 is the detuning of the four-photon energy from the upper state $|2\rangle$; $\hbar\delta_2 = 3\hbar\omega_1 + \hbar\omega_2 - E(2)$. $\Delta k_0(\delta_1)$ is the phase mismatch at detuning δ_1 in the absence of the second laser, Ω_{12} is the one-photon Rabi frequency between states $|1\rangle$ and $|2\rangle$ and Γ_{12} is a line-shape parameter, generally dominated by the ionization rate out of state $|2\rangle$. In our experiments, $|1\rangle$ and $|2\rangle$ correspond to the $6s'$ and $5f$ states, respectively.

Red of the $6s'$ resonance, we have $\delta_1 < 0$. This is the positively dispersive region where $\Delta k > 0$ so no third harmonic is normally produced. From Eq. (1), one may determine what changes may be expected from the introduction of a second-laser field. We wish to make $\Delta k < 0$ at the detuning $\delta_1 < 0$. This will occur for a small $\delta_2 < 0$ for some nonzero $|\Omega_{12}|^2$. Thus, the phase matching can be adjusted with laser two to allow third-harmonic generation in a normally forbidden region.

Note that the ac Stark effect on the nonlinear susceptibility, introduced by resonantly coupling $|1\rangle$ and $|2\rangle$ is equivalent to saying that the $\chi^{(5)}$ $(-3\omega_1;\omega_1,\omega_1,\omega_1,\omega_2,-\omega_2)$ and higher-order susceptibilities must be considered along with that of $\chi^{(3)}$ $(-3\omega_1;\omega_1,\omega_1,\omega_1)$. In fact, the strong coupling of levels $|1\rangle$ and $|2\rangle$ by the laser allows the susceptibility $\chi^{(3)}$ to be written in a modified form due to the resonant coupling:

$$\chi(-3\omega_1)=\frac{\chi_0^{(3)}(-3\omega_1;\omega_1,\omega_1,\omega_1)}{1-|\Omega_{12}|^2/[\delta_1(\delta_2+i\Gamma_2)]}\ , \tag{2}$$

where $\chi_0^{(3)}$ is the nonlinear susceptibility in the absence of the second-laser field.

In the presence of the strong laser field near four-photon resonance the total TH intensity is controlled by the magnitude of Δk, $\chi(-3\omega_1)$ and by losses due to two-photon absorption of the generated photons (one TH plus one-laser photon). In good agreement with the experimental findings, the theory predicts that red-side TH production is weak for small detunings from the three-photon resonance (three orders of magnitude smaller than that at optimum phase matching on the blue side). Further to the red, the output grows larger and can reach several percent of the $3\omega_1$ signal at optimum phase matching on the blue side. On the other hand, the TH related signals are comparable in magnitude on the two sides at equivalent detunings. Finally, the theory predicts the general trends of TH *and* ionization dips and peaks on the negative dispersive (blue) side.

Note, for example, near the maximum third-harmonic production at optimal phase matching, on the negatively dispersive side of resonance, all modifications of the phase matching through Eq. (1) will result in less-than-optimal phase matching and, thus, decreased third-harmonic production in the vicinity of the resonance. Since ionization follows third-harmonic intensity, there can be a dip in ionization of xenon atoms at the resonance. Note that laser two influences the ionization in two ways: (1) it enhances ionization by providing a two-photon $(\omega_{TH}+\omega_2)$ resonant step in the ionization pathway, and (2) it affects the actual production of third-harmonic photons involved in the dominant ionization mechanism. Thus, for example, in the case in which laser two is spoiling the phase matching, tending to decrease ion yield, it is also opening the resonant pathway to increased ionization. Thus, a sort of competition is involved in ionization. Indeed, it is precisely this competition which gives rise to a dip at a high laser-two power density, but only a peak at conditions of more gentle focusing or lower power.

In summary, we have demonstrated directly that the introduction of a seccnd, strong, resonant field can induce third-harmonic generation in normally positively dispersive regions. Furthermore, by changing the frequency of the inducing laser, *tunable* vuv can be produced. Consequently, by an appropriate choice of the second frequency, coherent vuv light can be generated at virtually any required wavelength, independent of the nominal phase-matching conditions in the absence of the second field. In addition, in negatively dispersive media, the resonant coupling can dramatically alter both the TH and ion yield.

Research sponsored by the Office of Health and Environmental Research, U.S. Department of Energy under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. One of us (P.R.B.) would like to thank the Chemical Physics Section, Health and Safety Research Division, of the Oak Ridge National Laboratory and Oak Ridge Associated Universities for support through the Laboratory Graduate Participant Program. One of us (J.C.M.) acknowledges use of NATO International Collaboration Grant No. 79/82 during the course of this work.

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