Resonantly Enhanced Multiphoton Ionization and Third-Harmonic Generation in Xenon Gas

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Resonantly enhanced multiphoton ionization signals through the $6s[3/2]J=1$ state of Xe rapidly disappear at pressures above 0.30 Torr; concurrently, intense, vacuum-ultraviolet third-harmonic radiation is detected in the forward direction. Laser excitation spectra of the vacuum ultraviolet light exhibit increasing blue shifts and bandwidths with increasing pressure. The observed competition between ionization and third-harmonic generation is discussed in terms of a model involving fast collective emission.

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Gas-phase multiphoton excitation and ionization processes have been extensively studied in recent years. Xenon gas has been a convenient system for studying these nonlinear phenomena. Recently, Aron and Johnson[1] reported the first resonantly enhanced multiphoton ionization (MPI) spectra of xenon and observed a number of atomic resonances at pressures ranging from 1 to 100 Torr. They noted, however, the complete absence of any ionization signal when tuning through the $6s[3/2]J=1$ three-photon-allowed intermediate state. In a recent publication[2] we reported that at pressures below about 0.30 Torr, MPI through the $6s$ state dominated the spectrum. We also reported the first resonantly enhanced multiphoton photoelectron spectrum through the $6s$ and other intermediate states. In the work described here, it is shown that the strong $6s$ ionization signal disappears at pressures greater than 0.30 Torr, accompanied by the production of intense third-harmonic radiation in the forward direction relative to the pump laser. The third-harmonic emission is characterized by its laser excitation spectrum which exhibits large shifts and linewidths relative to the low-pressure results. The disappearance of the ionization signal and the characteristics of the vacuum ultraviolet (VUV) emission have been attributed by two of us to a collective emission and the theoretical model will be described elsewhere.[3] The present work represents the first experimental study of this multiphoton collective processes.

Kung[4] has observed nonlinear mixing in xenon; however, his emphasis was on off-resonant processes and no collective phenomena were implicated.

The experimental apparatus, shown in Fig. 1, consists of a six-way cross (Varian) connected to an ion pump (Perkin-Elmer) and capable of background pressures of 10^{-8} Torr. The beam of a N_2 laser (Molectron UV-24) pumped dye laser (Molectron DL400) is focused by a 3.8-cm lens to a spot (≤ 20 μm), giving a power density on the order of 5×10^9 W/cm^2. Photoelectrons resulting from the MPI process are monitored with a flat-plate collector biased at +100 to +300 V. Amplification occurs by an electron avalanche in the xenon sample gas. Emitted VUV radiation passes through a MgF_2 window and a broadband VUV-transmitting dielectric filter (Acton) into a differentially pumped chamber filled with xenon or other counter gas at 1–5 Torr. This light impinges on a tantalum foil and ejected photoelectrons are collected with another biased, flat-plate detector. The filter is used to block the laser light from hitting the tantalum foil and producing background counts; however, the VUV signal was apparent without the filter. The VUV detector could be placed in either a 180° or 90° geometry relative to the pump laser beam. Signals, originating from either electrons or VUV photons, were detected with a charge-sensitive preamplifier and displayed on an oscilloscope. Multiple shots were averaged in a boxcar integrator

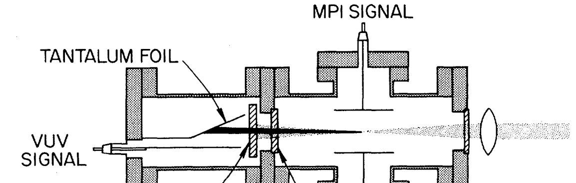

FIG. 1. Schematic diagram of the apparatus used to measure the MPI spectra and the emitted third-harmonic VUV radiation. The VUV detector can also be positioned at 90° with respect to the pump laser.

(Princeton Applied Research) and recorded on an x-y plotter. In other experiments, a $\frac{3}{4}$-m McPherson monochromator was used to disperse the VUV emission in the forward direction. The spectral resolution in first order was 5 Å.

Figure 2 shows the MPI spectrum in the region of the $6s[3/2]J=1$ and the $4f[3/2]J=1$ intermediate resonances as a function of pressure. The former is a three-photon resonant, five-photon ionization process, and the latter a four-photon resonant, five-photon ionization process. At low pressure, the $6s$ peak [full width at half maximum (FWHM) $\cong 0.5$ Å] dominates the spectrum; however, it is rapidly decreased in intensity relative to the $4f$ signal as the pressure increases. Because of the changing amplification factor with pressure in a proportional counter, only relative intensities can be reliably obtained. Actually, the MPI signal through the $4f$ resonance may contain a contribution from associative ionization which would be pressure dependent. Consequently, the $6s$ signal may not be disappearing as rapidly as the figure indicates. At low pressure, power-dependent ac Stark shifts and broadening are observed. The laser power dependence of the $6s$ MPI signal was approximately fifth order. As the $6s$ MPI signal disappears, its excitation spectrum broadens and shifts to the blue. At pressures around 0.3 Torr the resonantly enhanced MPI signal via the $6s$ intermediate can no longer be observed.

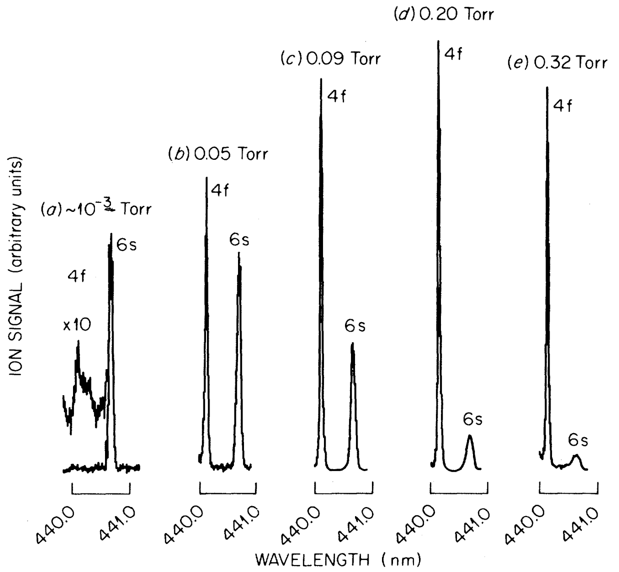

FIG. 2. A portion of the MPI spectrum of xenon showing the $6s$ and $4f$ resonances in the pressure region where the $6s$ ion signal disappears. The first trace was recorded in a low-pressure mass-spectrometer apparatus (Ref. 2) where the xenon is introduced as a beam through a collimated hole array. The pressure in the beam is unknown but is probably between 5×10^{-4} and 5×10^{-3} Torr. Traces (b) through (d) were recorded in the static pressure cell of Fig. 1.

The dependence of the emitted third-harmonic photons at a 0° geometry relative to the pump beam as a function of laser excitation wavelength is shown in Fig. 3 at a series of pressures from 0.20 to 300 Torr. Use of a VUV monochromator and solar-blind photomultiplier confirm that the emission occurs at one-third the wavelength of the pump laser. In the low-pressure regime (0.1–1 Torr) the shifts and width (FWHM) are approximately linear with pressure. The third-harmonic excitation spectrum shifts to the blue and broadens according to

$$\Delta_S = 1.6P + 0.20$$

$$\Delta_W = 2.5P + 0.46,$$

where Δ_S and Δ_W are the shift and width in angstroms when P is in Torr. The shift is measured relative to the low-pressure (10^{-4} Torr) result where the level is only shifted and broadened by the ac Stark effect. The third-harmonic intensity measured at the maximum of the excitation spectrum, while approximately linear with pressure below 0.2 Torr, saturates rapidly and levels off by about 0.75 Torr. The total integrated intensity of the third-harmonic emission increases slightly greater than linearly with pressure ($P^{1.2}$) in the range 0.1–1 Torr. At a given pressure, the third-harmonic radiation intensity is approxi-

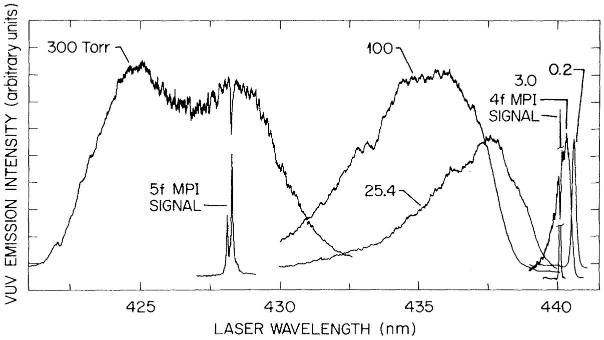

FIG. 3. Excitation spectra of the third-harmonic VUV emission at pressures of 0.2, 3.0, 25.4, 100, and 300 Torr. For the 3.0- and 300-Torr pressures, the MPI spectra are also shown. Note the "dips" in VUV emission at wavelengths corresponding to resonantly enhanced MPI.

mately third order in laser power. No VUV light could be detected at the 90° geometry, although Faisal, Wallenstein, and Zacharias[5] have observed right-angle fluorescence following three-photon excitation of xenon at pressures of a few millitorrs. They attributed the disappearance of the emission at pressures above 8 mTorr to radiation trapping and collisional ionization with background gases. However, the collective-emission model[3] predicts that the third-harmonic emission would also quench the right-angle fluorescence in this pressure range.

Clearly, the abrupt loss of the MPI signal from the 6s resonance can be coupled with production of intense, forward directed, third-harmonic radiation which rapidly depletes the 6s state before ionization can occur. It is also certain that collisional quenching effects are not important at such low pressures as an unreasonably large cross section ($\sim 10^8$ Å^2) would be required. The absence of excimer emission at 172 nm in the monochromator experiments precludes any mechanism based upon xenon dimers. The very large shifts and bandwidths of the excitation spectra at low pressure indicate that the third-harmonic production imposes large perturbations on the 6s state. Existing third-harmonic generation theories appear to be insufficient as they do not address level populations and, hence, could not predict the disappearance of the 6s ion signal. Payne and Garrett[3] have attributed these results to resonantly enhanced third-harmonic generation following a coherent, collective excitation of an ensemble of xenon atoms. A quantitative theoretical description and more detailed comparison with the experiment will be presented elsewhere.[3] Qualitatively, coherent excitation of a group of xenon atoms results in a collection of coupled dipoles, producing a "giant dipole." Spontaneous emission to the ground state with an enhanced oscillator strength then rapidly ($<10^{-9}$ s) depletes the 6s level with resultant uncertainty broadening of the state. Phase matching requirements in propagation through the focal region leads to the large pressure-dependent shifts.[3] This greatly reduced lifetime for the 6s intermediate state is responsible for the very effective quenching of the five-photon ionization signal at higher pressures. The observed pressure dependence of the ionization signal and the saturation of the third-harmonic intensity are also predicted by the theory of collective emission.[3]

Another interesting facet of this study is shown in Fig. 3. When the pressure is adjusted such that the 6s level is broadened and shifted to a position overlapping an allowed four-photon resonance a dip is observed in the photon excitation spectrum. As shown for two examples in Fig. 3, the dips coincide exactly with the $4f[3/2]\,J=2$ and $5f[3/2]\,J=2$ resonances in the MPI signal shown superimposed. Several other examples have been observed in other regions of the excitation spectrum. In these cases, the ionization cross section apparently increases such that ionization is competitive with the collective emission. This explanation is consistent with the pressure-dependent four-photon resonances observed by Aron and Johnson.[1]

Ongoing experiments are designed to further characterize this novel phenomenon and will be reported elsewhere. For example, similar VUV emission is observed near the 6s' resonance in xenon; in this region ionization and third-harmonic generation take place concurrently. Excitation profiles for both processes are shifted and broadened identically. Similar studies of krypton and argon have been completed (the latter gas requires use of a neodymium-doped yttrium aluminum garnet–pumped dye laser whose output is then doubled to provide the necessary wavelength). In both gases the resonantly enhanced MPI is observed at low pressures (<1 Torr) via the 5s and 4s intermediate states, respectively. This ion signal is no longer observed above 2 Torr in either case. For krypton, third-harmonic photons are observed; however, for argon the VUV emission at 106 nm could not be observed because of $\mathrm{LiF_2}$ window absorption and lack of a bandpass filter to eliminate the pump light.

Finally, the unique properties, particularly the narrow bandwidth and tunability of this VUV radiation, should make it an attractive light source for other spectroscopic studies. Such experiments are currently being planned.

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