Resonant Multiphoton Ionization of Krypton by Intense uv Laser Radiation

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Low-pressure Kr and Xe gas has been irradiated by a high-intensity (3×10^{12}–10^{14} W cm^{-2}), short-pulse (1.3 ps), tunable uv laser beam. Enhancement of the Kr^+ yield by 2 orders of magnitude by three-photon–resonant four-photon ionization is observed at intensities 1 to 2 orders of magnitude above previous results. The $4p \rightarrow 5d\,[\frac{1}{2}]_1$ and $4p \rightarrow 4d\,[\frac{3}{2}]_1$ three-photon Kr resonance profiles are measured as functions of peak laser intensity and are well fitted by a simple model incorporating line shifts and widths scaling linearly with laser intensity.

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New laser technology has renewed interest in high-intensity multiphoton ionization.[1-3] For wavelengths > 250 nm, three or more photons per atom are needed to ionize the valence electrons of rare-gas atoms. The high order of these multiphoton processes requires laser irradiances above 10^{10} W cm^{-2} to ionize a substantial fraction of the atoms within a typical laser pulse length $\lesssim 10$ ns. An important question in such laser-atom interactions is the behavior of the atomic states when the laser field E_L approaches the Coulomb field E_C on the outer electrons, where the ratio $E_L/E_C \approx [I/(7\times10^{16}$ W cm$^{-2})]^{1/2}$. A direct experimental approach to the problem is to examine the influence of individual atomic resonances on multiphoton ionization as a function of laser intensity and frequency. Specifically, the electric field of the laser has been shown both theoretically[4,5] and experimentally[6-8] to shift the electronic levels and, hence, resonances of an atom, an effect commonly known as the ac Stark shift. In addition, lifetime broadening of the resonances occurs because of rapid photoionization of the electron out of the excited states.

Published experimental resonance profiles for Xe up to a maximum intensity of 3×10^{11} W cm^{-2} are well fitted by perturbation theory and show up to 15-meV line shifts.[6] Resonance profiles obtained in Xe at 3×10^{12} W cm^{-2} show reportedly smaller widths than expected by perturbation theory.[9] At even higher intensities, only tentative evidence of resonance structure in Kr and Xe has been reported at irradiances of[10] 10^{13} and[11] 3×10^{13} W cm^{-2}, respectively.

In this Letter, we present detailed three-photon–resonance profiles for Kr, obtained via four-photon ionization in the intensity range 3×10^{12}–10^{14} W cm^{-2} and exhibiting up to 0.3-eV shifts. A partial KR level diagram for the present three-photon energy range is shown in Fig. 1.

The experiment consisted of the measurement of the number of singly charged Kr and Xe ions produced under collisionless conditions as a function of laser frequency and intensity. The output of a dye-laser system operating at 2.5 Hz and described in detail elsewhere[2] is frequency doubled in a 1-cm potassium dihydrogen phosphate (KDP) crystal to give a 0.5-mJ, 1.3-ps, transform-limited 0.1-nm-bandwidth beam tunable between 285 and 310 nm. The linearly polarized uv beam is separated from the remaining fundamental by a prism and focused by an $f/15$ optic in a mixture of Kr and Xe gas at 10^{-6}–10^{-5} Torr pressure. The ions produced on each shot are extracted by a 5000-V/cm applied field, sorted according to mass and charge by a time-of-flight spectrometer, and detected by direct impact on a microchannel plate. In addition, the laser energy is recorded on each shot with use of a calibrated vacuum photodiode monitoring a uv reflection from the prism. The ion and photodiode signals are sent to gated integrators and the former binned by computer according to laser energy. At each laser wavelength investigated, beam alignment is

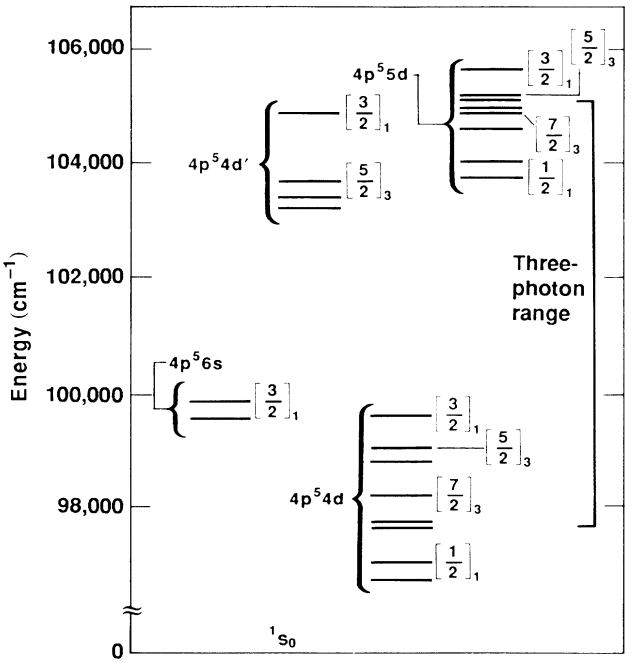

FIG. 1. Partial Kr energy-level diagram showing states reached by three laser photons. Only the three-photon allowed $J=1$ and $J=3$ states are labeled.

readjusted, the photodiode signal calibrated, and 300 to 1000 shots are recorded as the laser intensity is slowly varied with a pair of rotatable Glan-Thompson polarizers. The laser wavelength is known to within 0.05 nm by use of a calibrated grating spectrometer. The uv pulse length is measured by a multishot cross-correlation technique using the difference frequency from noncollinear mixing of the uv beam with the remaining fundamental beam in a KDP crystal. The intensity distribution at the focus is determined from a series of pinhole throughput measurements.

For all intensities investigated, the Xe^+ signal exhibited no resonance behavior above experimental fluctuations in the range 285–310 nm, although a systematic decrease in signal was detected above 293 nm. In contrast, at much lower intensity, 3×10^{10} W cm^{-2}, three-photon autoionizing resonances between the $P_{3/2}$ and $P_{1/2}$ fine-structure ionization thresholds of Xe at 280–290 nm were observed previously.[12] However, extrapolating from these published results to our intensity conditions, we would expect such resonances to be merged with the three-photon nonresonant ionization signal to the $P_{3/2}$ Xe^+ core state. The present lack of resonance structure in the production of Xe^+ made it possible to use the Xe^+ signal as a means of measuring the laser intensity on each shot. By the examination of the production of Xe^+ and Kr^+ simultaneously, the intensity at which the Kr^+ is produced can then be determined on each shot.

Kr spectra with clear resonant structure are shown in Fig. 2 for increasing peak laser intensity. Each datum point corresponds to a twenty- to sixty-shot average. The vertical lines denote resonance positions[13] in the limit of zero intensity. The observed resonances, all shifted to shorter wavelengths, are taken to be $4p\rightarrow4d$ and $4p\rightarrow5d$ $\Delta J=1$ and 3 allowed three-photon transitions (see Fig. 1), identified in the caption of Fig. 2 with the $j_c l$ coupling notation.[13,14] The dashed vertical lines denote the positions of the $4p$-$6s$ (Ref. 14) and two $4p$-$4d'$ three-photon transitions, which we assume are so broadened and shifted that they do not contribute significantly to the sharp resonance features seen. As expected, the resonances broaden and shift further as the intensity is increased, until the ionization process saturates,[15] as is the case for the prominent $4p$-$4d$ $[\frac{3}{2}]_1$ resonance at $\simeq2\times10^{13}$ W cm^{-2}.

The $4p$- $5d$ $[\frac{1}{2}]_1$ Kr resonance examined in greater detail is shown in Fig. 3 for increasing peak laser intensity. The asymmetric profile is typical of realistic laser pulses with spatially and temporally varying intensity.

The resonance profile can be modeled by an effective two-level atom with the assumption of a rate-limiting three-photon excitation step followed by rapid one-photon ionization from the excited state. The ionization rate $W(\omega,I)$ as a function of laser detuning from a three-photon resonance, if we assume a resonance shift

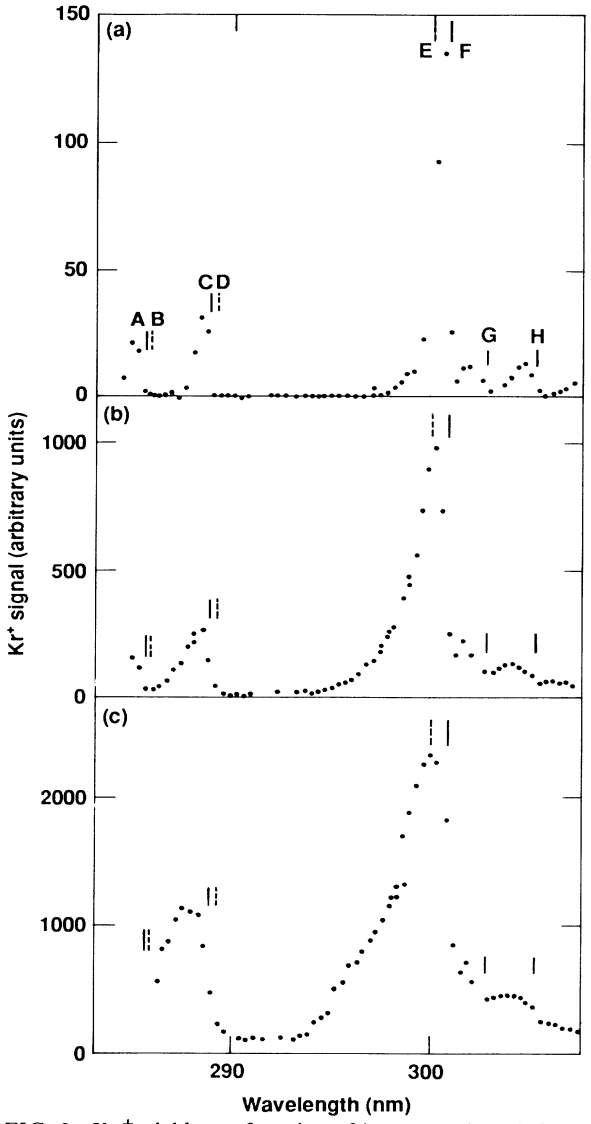

FIG. 2. Kr^+ yield as a function of laser wavelength for various peak laser intensities I_0: (a) $I_0=0.6\times10^{13}$ W cm^{-2}; (b) $I_0=1.4\times10^{13}$ W cm^{-2}; (c) $I_0=2.9\times10^{13}$ W cm^{-2}. Vertical lines mark unshifted resonance positions of A, $4p\rightarrow5d$ $[\frac{7}{2}]_3$; B, $4p\rightarrow4d'$ $[\frac{3}{2}]_1$; C, $4p\rightarrow5d$ $[\frac{1}{2}]_1$; D, $4p\rightarrow4d'$ $[\frac{5}{2}]_3$; E, $4p\rightarrow6s$ $[\frac{3}{2}]_1$; F, $4p\rightarrow4d$ $[\frac{3}{2}]_1$; G, $4p\rightarrow4d$ $[\frac{5}{2}]_3$; H, $4p\rightarrow4d$ $[\frac{7}{2}]_3$.

proportional to intensity with a width dominated by lifetime broadening of the excited state, is given by[5]

$$W(\omega,I)=\frac{\Omega^2}{2}\,\frac{\delta I}{(3\omega-\omega_0-\alpha I)^2+\delta^2 I^2}, \qquad (1)$$

where Ω is the three-photon Rabi rate $\propto I^{3/2}$, αI is the ac Stark shift of the resonance, δI is the HWHM of the lifetime broadening of the excited state, ω_0 is the unshifted resonance frequency, and ω is the laser frequency. In the limit of large detuning, the nonresonant four-

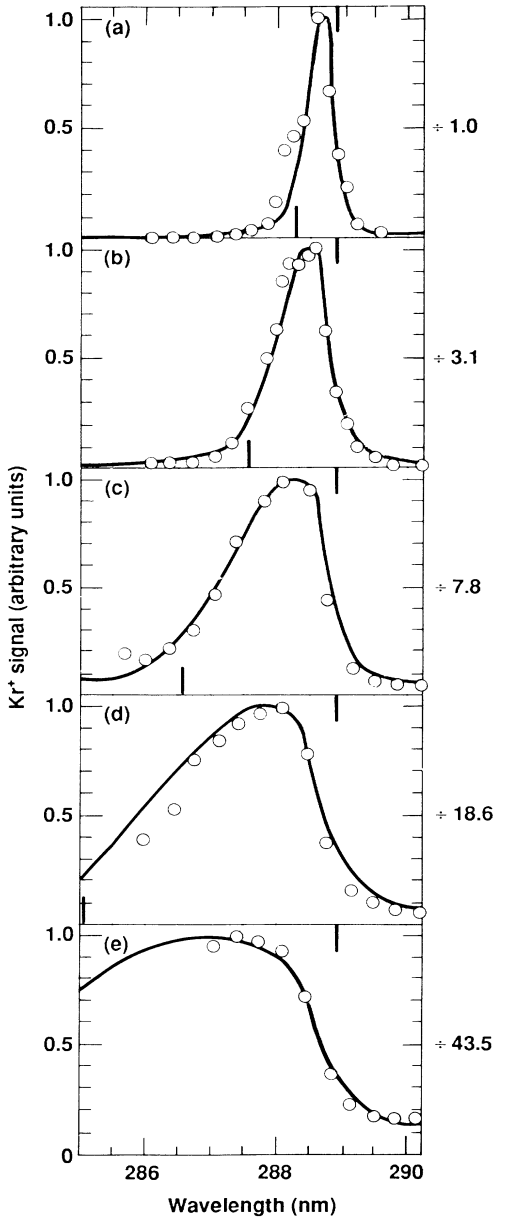

FIG. 3. Kr $4p \rightarrow 5d\,[\frac{1}{2}]_1$ three-photon resonance profiles for various peak intensities I_0: (a) $I_0=0.74\times10^{13}$ W cm^{-2}; (b) $I_0=1.5\times10^{13}$ W cm^{-2}; (c) $I_0=2.7\times10^{13}$ W cm^{-2}; (d) $I_0=4.5\times10^{13}$ W cm^{-2}; (e) $I_0=7.8\times10^{13}$ W cm^{-2}. Top vertical lines mark unshifted resonance positions and solid curves are theoretical fits described in text. Bottom vertical lines mark calculated shifted resonance positions at peak laser intensity I_0.

photon ionization rate, proportional to I^4, is recovered from Eq. (1). The parameters Ω, α, and δ are taken to be independent of frequency over a given resonance profile, a good approximation even for Figs. 2(c) and 3(e). In addition, the laser bandwidth and the Doppler and radiative lifetime broadening of the excited state could be neglected, even for Fig. 2(a).

The total number of ions produced at a given laser wavelength is obtained by the integration of the rate $W(\omega,I)$ over the spatiotemporal intensity distribution at the laser focus. In the present experiment, this distribution was found to be well modeled by

$$I=\frac{I_0\,\mathrm{sech}^2(1.76t/\tau)}{1+A\lambda^2z^2/\pi^2r_0^4}\exp\left[-\frac{2r^2}{r_0^2(1+A\lambda^2z^2/\pi^2r_0^4)}\right], \tag{2}$$

where τ is 1.3 ps, the temporal FWHM of the laser pulse, A is 20, an experimentally determined constant accounting for a divergence- rather than diffraction-limited focus, z is the distance along the laser axis, r_0 is 12.5 μm, the $1/e^2$ beam radius at $z=0$, and I_0 is the peak laser intensity at $r=z=t=0$.

The solid curves in Fig. 3 represent best fits to the data, normalized to the peak height, but with α and δ kept constant for all fits. The values deduced for α and δ are 3.9 and 1.4 meV/(TW cm^{-2}), respectively, yielding a photoionization cross section from the $5d\,[\frac{1}{2}]_1$ state, σ_{5d}, of 3×10^{-18} cm^2 at $\lambda=289$ nm. Hence, the $5d$ excited state is depopulated within 2 to 20 fs at 10^{13}–10^{14} W cm^{-2}, implying a saturated photoionization process for a 1.3-ps pulse and justifying the use of Eq. (1). The fitting error in the ratio δ/α which reflects possible departures from a Gaussian spatial profile and $\mathrm{sech}^2 t$ temporal profile is small, $\pm25\%$, because the calculated resonance shape is fairly insensitive to the exact focal-intensity distribution chosen and fairly sensitive to the ratio α/δ. There is, however, a possible factor-of-3 systematic error in δ and α due to uncertainties in the focal volume and laser temporal history.

The $4p$-$4d\,[\frac{3}{2}]_1$ three-photon resonance was also well fitted by Eq. (1), yielding $\alpha=8.0$ meV/(TW cm^{-2}) and $\delta=4.0$ meV/(TW cm^{-2}) and, hence, $\sigma_{4d}=8\times10^{-18}$ cm^2 at $\simeq300$ nm. We note that the ratio of the measured photoionization cross sections from the $4d$ and $5d$ states, 2.7, is in agreement with the calculated value, 3, from a simple quantum-defect approximation.[16]

It is interesting to note that while all resonances in Fig. 3 are "blue" shifted, ac-Stark-shift calculations which are difficult to perform for excited states lead, in general, to both "blue" and "red" shifts. Hence, an additional stronger "blue" shift may be present, perhaps due to coupling between the continuum and upper resonance state.[17] On the basis of fine structure observed in the photoelectron spectra of short-pulse multiphoton ionization of Xe, Freeman[11] suggests that highly excited states are shifted to higher energy by nearly the value of the ponderomotive potential,[18] that is, the quiver energy of a free electron in the laser electric field. Indeed, the present shifts of the $4p$-$5d\,[\frac{1}{2}]_1$ and $4p$-$4d\,[\frac{3}{2}]_1$ transitions are 0.46 and 0.95 of this ponderomotive shift, respectively. However, a detailed comparison of the shifts and broadening of several resonances as well as resonant

photoelectron energy spectra, to be presented later, are clearly needed to decouple ac Stark shifts of ground and excited states.

In summary, the present experiment extended to $\simeq 10^{14}$ W cm^{-2} the intensity range to for which resonance enhancement of ion yields has been observed. The resonance profiles recorded for over a decade change in laser intensity were well modeled by a simple single-rate analysis, even when the laser electric field reached 3% of the atomic field strength.

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