MULTIPHOTON IONIZATION IN INTENSE ULTRAVIOLET LASER FIELDS*

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ABSTRACT

The mechanism of collision-free multiphoton ionization of rare gases irradiated with ultraviolet radiation at an intensity of up to $\sim 10^{16}$ W/cm² at 248 nm and a pulse length of ~ 0.5 ps and $\sim 10^{15}$ W/cm² at 193 nm and ~ 5 ps, respectively, has been studied by observing the electron energy spectra and ion charge state threshold intensities. The formation of multiply charged ions by a sequential process of ionization has been directly detected in the electron energy spectra in the form of a characteristic pattern of interwoven above threshold ionization (ATI) ladder line series. The threshold intensities for ion production have been compared with the Keldysh model and were found to be in good agreement for light ions (Ne) and consistently lower for heavier ions (Xe), scaling with the atomic number. These measurements, together with estimates of the ion population dynamics during the rise of the laser pulse can be reasonably understood on the basis of a single electron picture.

INTRODUCTION

A question of principal significance, especially in the context of coherent short wavelength generation, concerns the identification of the dominant laser-atom coupling mechanism under collision-free irradiation with an intense laser pulse.¹⁻⁶ Specifically, what are the important physical parameters governing the atomic response to the radiation field, and is the interaction adequately described by a single electron picture or one involving ordered many-electron motions?

The hypothesis has been advanced⁷ that multiply excited states representing the coherent motion of outer-shell electrons may be an important agent for the population of inner-shell excited states and the subsequent reradiation of energy in the soft x-ray range. In order to study the conditions necessary for this desired atomic response to occur and the influence of possible loss mechanisms, ion charge state distributions and electron energy spectra produced by irradiation of rare gas atoms with ultraviolet radiation with different pulse lengths, wavelengths, and intensities have been investigated.

EXPERIMENTAL

For these measurements, two ultraviolet laser systems were available. One was a recently developed KrF* (248 nm) laser system⁸ which produces pulses having a maximal energy of ~ 23 mJ

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with a pulse duration of ~ 0.5 ns. The second source used was an ArF* (193 nm) laser system⁹ capable of producing a ~ 5 ps pulse with a maximal energy of ~ 40 mJ. The focussing systems used in these studies produced a maximum intensity of 10^{16} W/cm² at 248 nm and of 10^{15} W/cm² at 193 nm, respectively, in the experimental volume. The focussing lens was not corrected for spherical aberration and had, therefore, a focal diameter⁵ of ~ 20 μ m which limited the achievable laser intensity, but made the experiments relatively insensitive to the detailed spatial properties of the laser beam. The apparatus used for the measurement of the ion states¹⁰ and the electron spectra have been described previously. Both are time-of-flight type spectrometers; for the electron measurements a magnetic mirror collimates the electrons while the ions are extracted by a static electric field.

Rare Gas Electron Energy Spectra With 193 nm Irradiation

Fig. 1 illustrates typical electron time-of-flight spectra produced at a peak laser intensity of $\sim 5 \times 10^{14}$ W/cm² at 193 nm for helium and at an intensity of $\sim 2 \times 10^{13}$ W/cm² for xenon. Also shown are the relevant energy level diagrams with the multi-photon transitions and the electron emission lines indicated. Similar recordings have been obtained for neon, argon, and krypton and their specific features have been discussed in Ref. 5.

In addition to the generally prominent lowest order ionization lines, corresponding in the two examples to the absorption of four photons by helium and two photons by xenon, processes which leave the singly charged ions in their respective ground states, several above threshold ionization (ATI) lines spaced by the photon energy (6.41 eV) are present. In xenon, the resolved line at ~ 5.7 eV indicates that the first ion is preferably produced in its lowest excited $ns^2 np^5 2p_{1/2}$ state after absorption of three 193 nm photons.

The intensity of the observed ATI-lines drops more rapidly in a monotone manner with increasing order in the ultraviolet as compared to corresponding results obtained at visible and infrared wavelengths, in accordance with calculations performed by several authors.¹¹⁻¹⁴

For the range of radiative intensities studied ($\leq 10^{15}$ W/cm²), the distributions on the ATI-lines seem to be unaffected in all species examined by highly excited configurations of the neutral atoms above the ionization threshold or by excited ionic configurations, which represent possible competing decay channels, when energetically open. Furthermore, if the intensities of the ATI-lines are interpreted as a measure of the photon absorption rate for high order processes, the probability for sufficient energy transfer in order to allow direct double ionization or excitation is fairly low, and therefore, cannot account for the observed relative ion-charge state abundance.^{5,10} On the other hand, evidence for the sequential removal of outer-shell electrons is readily observed in these spectra in the form of additional sharp electron lines. For helium, the prominent ATI-

Fig. 1a,b: Electron time-of-flight spectra for He and Xe irradiated with a 193 nm, 5 ps laser pulse. The line identification is given in the schematic energy level diagrams showing the relevant energy level, multiphoton transitions, and electron emission lines. Excited neutral or ionic configurations are indicated by the boxes below the ionization limits.

ladder from the first ionization step to the He^+ ground state after absorption of four or more photons, is accompanied by a much weaker ATI-ladder originating from the sequential removal of the second electron after absorption of 9, 10, or 11 photons. Similar results have been obtained for argon and krypton, for which the presence of weak additional line groups confirms the formation of the second charge state in ground and low-lying ground configuration states by a sequential process.⁵ In the case of xenon

Fig. 2: High resolution Xe-electron energy spectrum at full laser intensity of 10^{15} W/cm^2 at 193 nm. The line identifications with their respective above-threshold ladder series are shown on top of the spectrum. The letter labeling refers to specific sequential processes listed in Table I. The associated number indicates the number of photons absorbed.

Table I: Multi-photon ionization channels for the production of Xe ions by a sequential mechanism. Some of these channels have been identified with observed line series in Fig. 2.

a	Xe	$5s^2 5p^6 1s_0 + 2\gamma, 3\gamma, 4\gamma, 5\gamma \rightarrow \text{Xe}^{1+} 5s^2 5p^5 52p_0 + e^-$	g	$\text{Xe}^{1+} 5s^2 5p^5 52p_{1/2} + 4\gamma, 5\gamma, 6\gamma, 7\gamma \rightarrow \text{Xe}^{2+} 5s^2 5p^4 43p_2 + e^-$
b		$3\gamma, 4\gamma, 5\gamma \rightarrow 2p_{3/2}^{1/2} + e^-$	h	$4\gamma, 5\gamma, 6\gamma, 7\gamma \rightarrow 3p_1 + e^-$
c	$\text{Xe}^{1+} 5s^2 5p^5 52p_{3/2} + 4\gamma, 5\gamma, 6\gamma, 7\gamma \rightarrow \text{Xe}^{2+} 5s^2 5p^4 43p_2 + e^-$		i	$4\gamma, 5\gamma, 6\gamma, 7\gamma \rightarrow 3p_0 + e^-$
d	$4\gamma, 5\gamma, 6\gamma, 7\gamma \rightarrow 3p_1 + e^-$		j	$4\gamma, 5\gamma, 6\gamma, 7\gamma \rightarrow 3d_2 + e^-$
e	$4\gamma, 5\gamma, 6\gamma, 7\gamma \rightarrow 3p_0 + e^-$		k	$\text{Xe}^{2+} 5s^2 5p^4 43p_2 + 6\gamma, 7\gamma, 8\gamma \rightarrow \text{Xe}^{3+} 5s^2 5p^3 34s_0 + e^-$
f	$4\gamma, 5\gamma, 6\gamma, 7\gamma \rightarrow 1d_2 + e^-$		l	$6\gamma, 7\gamma, 8\gamma \rightarrow 2d_{3/2} + e^-$
			m	$6\gamma, 7\gamma, 8\gamma \rightarrow 2d_{5/2} + e^-$
			n	$6\gamma, 7\gamma, 8\gamma \rightarrow 2p_{3/2} + e^-$
			o	$6\gamma, 7\gamma, 8\gamma \rightarrow 2p_{1/2} + e^-$
			p	$\text{Xe}^{2+} 5s^2 5p^4 43d_2 + 5\gamma, 6\gamma, 7\gamma \rightarrow \text{Xe}^{3+} 5s^2 5p^3 34s_{3/2} + e^-$

(Fig. 1b), the line at about 4.5 eV indicates the formation of the $\text{Xe}^{2+} \text{ } ^3\text{P}_2$ ground state after four photon absorption from the $\text{Xe}^+ \text{ } ^2\text{P}_{3/2}$ ionic ground level.

At the full 193 nm laser intensity of $\sim 10^{15} \text{ W/cm}^2$, the xenon electron energy spectrum develops a complex line structure as shown in Fig. 2, in which the time-of-flight spectrum has been converted to a linear energy scale. As shown in the figure, the lines which are manifest in the measured spectrum closely match a pattern of overlapping ATI-ladder series with each series associated with the population of a respective ionic state. Some of the processes which are believed to be significant are listed in Table I. The accidental near coincidence of several line energies makes it difficult to isolate certain individual ladder contributions, especially those for processes leading to Xe^{3+} and higher charge states. The sequential process can account for the first and second ionic charge state abundances observed for argon, krypton and xenon¹⁰ within the experimental uncertainty, a finding indicated by a comparison of the integrated intensities of the corresponding lines. In helium, about 2 - 3% of all electrons originate from the stepwise He^{2+} production; however, the relative He^{2+} ion abundance has not been unambiguously determined in ion time-of-flight measurements due to interference from impurities.

Another salient feature of the electron spectra is the relative suppression of low energy lines,⁵ an observation which has been made in many experiments at longer wavelengths.¹⁵⁻¹⁷ The lowest order lines in xenon at 0.7 eV and in helium at $\sim 1 \text{ eV}$, as well as low energy lines from the production of higher charged ions (Xe^{2+} and He^{2+}), appear relatively suppressed at full laser intensity, a phenomenon that is attributed to the influence of the ponderomotive potential.

ELECTRON SPECTRA OBTAINED WITH 248 nm IRRADIATION

On a subpicosecond time scale it is expected that the non-linear coupling with intense radiation may be significantly modified.^{18,19} As an example, the electron time-of-flight spectra from argon irradiated with a 248 nm, $\sim 500 \text{ fs}$ laser pulse at different laser peak intensities are shown in Fig. 3. At laser intensities too low for the production of higher charge states (e.g. $\sim 10^{14} \text{ W/cm}^2$), the principal ATI-ladders leading to the production of Ar^+ in the $^2\text{P}_{1/2}$ and $^2\text{P}_{3/2}$ ground multiplet states (which are resolved in the spectra at higher resolution) are readily observed up to the fourth ATI order. At higher laser intensities, new line features appear at about 3.5 eV and 4.5 eV energy together with corresponding higher order features, which can be related to the formation of higher charge states (see below). However, in contrast to the results with the 193 nm $\sim 5 \text{ ps}$ pulse, the ATI-ladders associated with the higher ion charge states seem to be shifted in energy up to a value of about 1.5 eV, a finding which is confirmed in comparable spectra from helium, neon, and xenon at 248 nm. Again, similar to observations at 193 nm, the low energy and shifted five photon line for Ne at 2 eV and

the three photon absorption line for krypton at 0.97 eV are suppressed relative to the next higher order lines. Another general feature of all electron spectra at 248 nm is the appearance of relatively high energy electrons with energies up to a maximum of about 200 eV for xenon and ~ 120 eV for argon. These were observed in the laser intensity range spanning from 10^{15} W/cm² to 10^{16} W/cm².

Fig. 3: Photoelectron time-of-flight spectra for Ar produced at different peak intensities in a 248 nm ~ 500 fs laser pulse.

IONIZATION THRESHOLD INTENSITIES AT 248 nm

The ion time-of-flight technique has been used to measure the threshold laser intensities for all charge states of the rare gases which appear below 10^{16} W/cm². The experimental values are plotted in Fig. 4 as functions of the ionization energies for

each charge state. They are compared to calculated threshold laser intensities for a transition probability of about 10^{-3} , which corresponds to the detection limit of the apparatus, using Keldysh's formula²⁰ (including coulomb correction) in the tunneling approximation ($\gamma \ll 1$) and the Keldysh-Raizer formula²¹ in multiphoton approximation ($\gamma \gg 1$). The observed thresholds for neon, which range from $\sim 8 \times 10^{13} \text{ W/cm}^2$ (Ne^+) to $\sim 7 \times 10^{15} \text{ W/cm}^2$ (Ne^{4+}), agree remarkably well with the calculations, whereas they are consistently lower for the heavier ions, apparently scaling with the atomic number or the complexity of the atom, a possible hint to collective effects. The shapes of the threshold curves, however, are generally preserved at intensities above $\sim 10^{14} \text{ W/cm}^2$ and, extrapolating this trend, charge states up to Xe^{23+} may be well observable in the near future with the use of subpicosecond sources capable of focussed intensities of $\sim 10^{18} \text{ W/cm}^2$. This would follow unless the ionization probability decreases again for ultrahigh laser intensities.²²

DISCUSSION

The appearance of high energy ($> 100 \text{ eV}$) electrons together with a general upshift of the average electron energies in the intensity regime above 10^{15} W/cm^2 with subpicosecond 248 nm irradiation is believed to originate from the high charge state production at high field intensities. In this situation it is expected that the lower charged ions are greatly depleted in the high intensity part of the focal volume. The higher observed charge states may preferably be produced by a laser pulse with a short risetime, when a certain charge species is carried to a higher field intensity, before its population is depleted by a low order process, and thereby possibly enhancing the coherent transition probability for higher order. In addition, above 10^{15} W/cm^2 , the ponderomotive potential becomes significant (Fig. 4) by increasing the effective ionization threshold energy and forcing the electrons to absorb more photons, probably by an inverse Bremsstrahlung mechanism when oscillating in the vicinity of the parent ion. Such a two-step ionization mechanism is suggested by experiments at infrared wavelengths,²³⁻²⁵ where high order processes and ponderomotive potential effects appear at much lower intensities compared to the ultraviolet regime.

Interestingly, in ion yield measurements at $1.06 \mu\text{m}$ with helium, the order of nonlinearity measured at $\sim 5 \times 10^{14} \text{ W/cm}^2$ for the He^+ production was 21, closely matching the minimum number (22) of photons needed to overcome the low field ionization threshold. However, the quiver barrier at this intensity should have shifted the effective ionization threshold to about 75 eV, energetically allowing a complete ionization only after absorption of more than 50 additional photons or, alternatively, trapping the lower energetic electrons until the field intensity has dropped sufficiently. Indeed, energetic electrons (80 eV) have been detected²⁵ under these conditions together with a dramatic upshift of the average electron energy after the laser intensity is

Fig. 4: Threshold laser intensity for ion charge state production with a 248 nm 500 fs laser pulse. A transition probability of $T \approx 10^{-3}$ has been assumed for the calculation (detection limit).

Fig. 5: Xe ion population dynamics in the high intensity region of a gaussian beam. FWHM = 500 fs $I_0 = 10^{16}$ W/cm².

increased beyond the saturation intensity, a feature similar to effects seen in our electron spectra above 10^{15} W/cm². This trapping of the electrons close to the parent ion by the ponderomotive potential could become essential to enhance the recombination and collisional energy transfer rate to inner core electrons, provided that damping processes like continuum-continuum transitions are sufficiently suppressed.

In order to investigate the influence of the pulse risetime on the interaction process, a simple estimate of the ion charge state population dynamics has been carried out for xenon using the measured threshold intensities to calibrate the onset of each ionization step. In these calculations it has been assumed that the pulse has a gaussian temporal profile and that lowest order perturbation theory is valid, or equivalently, that the rates scale as I^N . Fig. 5 shows the temporal beam profile with the experimental ionization threshold intensities and the populations of the different charge states during the rise of the laser pulse. The subsequent removal of the outer 5p and 5s shells and the final liberation of the 4d electron are apparent. As seen in Fig. (5), the shell structure is reflected in the distribution of the ionization threshold intensities.

In the lowest and highest intensity range, the charge states are well separated from each other and only for the ionization of the last 5p-electrons (e.g. the formation of Xe⁴⁺, Xe⁵⁺, Xe⁶⁺ ions) there may be a chance for a significant contribution by a direct multiple ionization process. However, at these laser intensities, the cross-sections for the necessary photon absorption rate may be still too low (compare to the minimum order of each ion production drawn at the right vertical scale in Fig. 5).

CONCLUSION

Experimental processes involving multiple ionization of rare gas atoms have been examined at both 193 nm and 248 nm. For the former, intensities up to $\sim 10^{15}$ W/cm² have been used in ~ 5 ps pulses while, for the latter, intensities up to $\sim 10^{16}$ W/cm² in ~ 500 fs pulses were utilized. On the basis of the observations of ion charge state distributions and electron energy spectra, the dominance of the sequential ionization process is evident. This finding is predicated on the (1) observation of sharp electron lines in the energy spectra and their partial identification with certain interwoven ATI-ladders, (2) estimates of the ion population dynamics in the high field region of the laser pulse based on measured ionization threshold intensities, (3) rapid decrease of ATI-ladder line intensities with increasing order, especially for lower charge states, and (4) the absence of influence of doubly excited states or excited ionic configurations on the ATI-ladder line intensities. These results indicate, for the experimental regime studied, that the atomic behavior can be reasonably understood within the framework of a single electron picture. Finally, we note, however, that certain other important characteristics of the interaction, such as the energy transfer rate,

have been seen to change sharply with the use of subpicosecond radiation as discussed in other work appearing in this volume.¹⁸

The intensity thresholds for ion production exhibit shell effects and are in good agreement with calculations based on the Keldysh model for neon. The heavier atoms, however, deviate in a consistent manner with increasing atomic number and exhibit ionization at intensities less than that represented by the Keldysh picture.

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