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Settling a long-standing question on strong-field double ionization

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Through a theoretical analysis combined with new experimental data, obtained through a technique that allows observation of ionization originating from a constant, sharply limited ion extraction volume, we show that double multiphoton ionization of Xe and Kr in the wavelength range 527 to 531 nm does not involve an observable direct two-electron channel but does involve an inner subshell ($5s$ for Xe and $4s$ for Kr) excited state which can leave the ion in an excited state. This explains the unusual laser power dependence that had been attributed to a direct two-electron channel.

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The 1983 paper by L'Huillier *et al.* [1] on multiple ionization of Xe and Kr has remained until today the only indication, albeit indirect, of the possibility of direct (nonsequential) double-electron ejection. Recently, however, Walker *et al.* [2] have reexamined the question through the study of photoelectron energy spectra (normal as well as coincidence) with the conclusion that no compelling evidence for direct two-electron ejection could be found under conditions similar to those of Ref. [1]. These authors went on to speculate on a possible alternative scenario explaining the unusual laser power dependence of double ions yield in the absence of a direct channel. It is the purpose of this paper to make that scenario specific and quantitative, and to provide in addition separate experimental proof of the validity of the explanation.

We should clarify one important issue before going on with the argument. The processes under consideration are completely distinct from the type of nonsequential two-electron ejection in He at very high intensity and long wavelength (beyond the tunneling regime) which have been discussed in Refs. [2] and [3]. The intensities and wavelengths of interest here are such that double (and in fact higher multiplicity) ionization can be readily observed, but the processes (whether sequential or direct) are assumed to be describable in terms of lowest nonvanishing order of perturbation theory. That is the context in both Refs. [1] and [2]. The possibility of double or multiple direct electron ejection is of course indirectly connected with the by now ten-year-old [3–6] question on the possibility of coherent excitation of two or more electrons under strong pulses, but before tunneling sets in.

The wavelengths employed in the experiments of Refs. [1] and [2], $\lambda = 531$ and 527 nm, respectively, are such that the neutral atom ionizes through six-photon absorption, while the subsequent ionization of the ground state ion occurs by ten-photon absorption. If this sequence of two processes were the only mechanism producing Xe^{2+}, the curve representing its dependence on laser power in a log-log plot should exhibit a monotonic rise with eventual saturation, without an inflection point (or "knee" as referred to in Ref. [2]). Since the knee was observed in both Refs. [1] and [2], an additional mechanism (channel) leading to Xe^{2+} must be present. L'Huillier *et al.* [1] postulated the existence of a direct 15-photon two-electron ejection, while Walker *et al.* [2] have suggested that the presence of a doubly excited autoionizing state, whose ionization leaves the ion in an excited state from which a second electron could be ejected, in a sequential fashion, would be equally effective in producing the knee. At that point, the matter is inconclusive, as neither of the two mechanisms can be either ruled out or firmly established.

To examine the question quantitatively, we describe below a set of rate equations [4] governing the production of ionic species. Let N_0 be the number of neutral atoms, N_1 the singly ionized species in its ground state [Xe^+ ($5s^2 5p^5$)], and N_2 the doubly ionized species in its ground state [Xe^{2+} ($5s^2 5p^4$)]. Let N_1^* be an ionic excited state resulting from an autoionizing state, to be specified later on. We define the reduced quantities n_q by $n_q(t) = N_q(t)/N_0(t) (q = 1,2)$, with $n_1^* = N_1^*/N_0$. Under the assumption that the intensities are such that not much triple ionization is produced, we have the number conservation relation $n_0(t) + n_1(t) + n_1^*(t) + n_2(t) = 1$, which enables us to eliminate one differential equation. The remaining equations thus read

$$dn_1(t)/dt = n_0(t)\sigma_6^{(0)}F^6 - n_1(t)\sigma_{10}^{(1)}F^{10}, \tag{1a}$$

$$dn_1^*(t)/dt = n_0(t)\sigma_{11}^{(0)}F^{11} - n_1^*(t)\sigma_5^{(1)}F^5, \tag{1b}$$

$$dn_2(t)/dt = n_1(t)\sigma_{10}^{(1)}F^{10} + n_1^*(t)\sigma_5^{(1)}F^5 + n_0(t)\sigma_{15}^{(0)}F^{15}, \tag{1c}$$

where $F = F(t)$ is the photon flux whose time dependence is determined by the pulse shape and $\sigma_j^{(i)}$ the multiphoton ionization generalized cross sections, with the subscript indicating the order of the process and the superscript denoting the neutral species or the ion, respectively. Thus, for example, $\sigma_6^{(0)}$ refers to six-photon ionization of the neutral species, while $\sigma_5^{(1)}$ refers to five-photon ionization of the (excited-

state) ion, etc. The initial conditions are $n_0(0)=1$ and $n_1(0)=n_1^*(0)=n_2(0)=0$. If substantial triple or higher ionization is produced, we need to enlarge the number of equations in a straightforward manner, as has been shown in Ref. [4]. This, however, does not affect the question of the knee since the shape of the curves for ions beyond Xe^{2+} is monotonic.

Equations (1a) and (1c) without the term involving n_1^* correspond to those employed by L'Huillier *et al.* [1] who used the cross sections as parameters in fitting their data, extracting thereby values for these cross sections and in particular for $\sigma_{15}^{(0)}$ representing 15-photon direct two-photon ejection. The scenario proposed by Walker *et al.* [2] requires all three equations, (1a)–(1c), without the term corresponding to the direct two-electron process. To go beyond speculation and to quantify that scenario, we need to specify the autoionizing state and to solve the equations with reasonable values for the cross sections.

Note that the energy $\hbar\omega$ of the photons employed in Ref. [2] is such that $5\hbar\omega$ brings a $5p$ electron to near resonance with the excited state $5p^5(^2P^0_{1/2})10s$. The absorption of another five photons can bring the atom to the vicinity of the doubly excited states $5p^4 10s6s\ ^4P$ and $5p^4 10s5d\ ^4D$ or the inner-subshell excited state $5s5p^6 10s\ ^2S$. Although the first two may be expected to be somewhat closer to ten-photon resonance from the ground atomic state, their quartet symmetry diminishes their contribution significantly eliminating them from further consideration. The absorption of an eleventh photon is energetically sufficient to produce decay above the ionic ground state, leaving the ion in the excited state $5s5p^6$. What we have described in steps above is to be understood as an 11-photon ionization process (with five-photon and ten-photon near resonances) leaving the ion in an excited state. It takes another five photons to eject one electron from the excited ion, producing a ground-state Xe^{2+}. This then provides the second channel for double ionization, which is also sequential but not through the ground state of the ion. The question is whether the presence of this channel, instead of the direct two-electron ejection, can be shown to produce a knee similar to that observed in Refs. [1] and [2].

For a quantitative assessment of the question we need reasonable values for the multiphoton generalized cross sections entering Eqs. (1a)–(1c). A method for obtaining such values through scaling was published [4] a few years ago and has been found to produce numbers in reasonable agreement with experiment whenever comparison has been possible. The scaling takes into account the size of the atom (or ion) and its ionization potential, both of which must be calculated in each case, if not known. Thus one can obtain cross sections for ions as well as atoms using the respective quantities for hydrogen as a starting point. The details of the method can be found in Ref. [4] and the scaling factors for Xe and its ions in Ref. [6]. Here we simply list the values (Fig. 1) obtained in this fashion and employed in our calculations. Assuming a Gaussian temporal and spatial pulse shape, we solve the differential equations, (1a)–(1c), and integrate over the spatial shape of the pulse, with an appropriate cutoff to account for the finite extent of the atomic volume.

A typical result, in which cross sections obtained directly from scaling have been used, is shown in Fig. 1. The knee is present (curve *a* of Fig. 1) as in Fig. 1 of Ref. [2] occurring

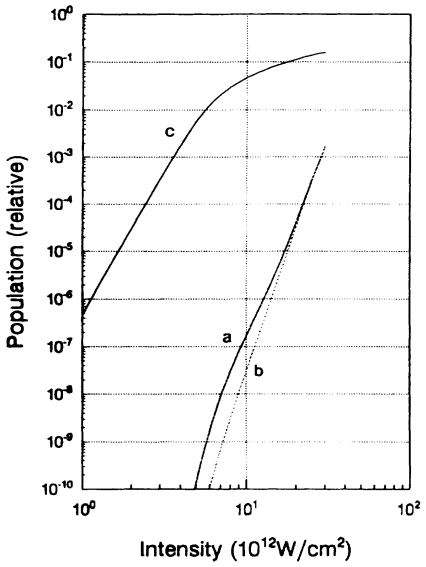

FIG. 1. Theoretical results for the laser intensity dependence of Xe^+ (curve *c*) and Xe^{2+} (curves *a* and *b*) for a 30-ps pulse at 531 nm integrated over a Gaussian volume. Curve *a* includes the effect of the autoionizing state while curve *b* does not. The values of generalized cross sections employed are: $\sigma_6^{(0)}=3\times10^{-177}$, $\sigma_5^{(1)}=3\times10^{-150}$, $\sigma_{10}^{(1)}=6\times10^{-310}$, $\sigma_{11}^{(0)}=1\times10^{-335}$ in units of $\text{cm}^{2N}\,\text{s}^{(N-1)}$ for an N photon process.

to within less than a factor of 2 at the same intensity. It is remarkable that this result has been obtained with independent theoretical cross sections, without any attempt to match anything to any information contained in the experimental data. Given that the method of scaling is not expected to provide values for σ_j better than semiquantitative, it would have been reasonable to attempt some adjustments, but we shall postpone that to a longer paper. We have, however, ascertained that the presence of the knee is not very sensitive to the values of the cross section. The ratio of the signal of Xe^+ to that of Xe^{2+} at and above 10^{13} W/cm^2, on the other hand, is fairly sensitive to the value of $\sigma_5^{(1)}$ which can be used to extract that and other cross sections from the experimental data, provided absolute calibration for Xe^+ and Xe^{2+} is given. That, however, would carry us beyond the main scope of this paper. The reader should keep in mind that a change of a five-photon cross section by a factor of 10 (which sounds large) is equivalent to a change of a single-photon cross section by a factor of $10^{1/5}=1.58$.

Having established the specific process that is sufficient to produce the knee we proceed now to the second part of our argument that demonstrates the necessity of this process. We consider single and double ionization of Xe by photons of energy $\hbar\omega=5$ eV ($\lambda=248$ nm). Now, Xe goes into Xe^+ by three-photon absorption. The experiment to be described below has been performed with a short pulse (500 fs). If the direct two-electron channel were responsible for the knee at the experiments with the longer wavelength, it should be enhanced at shorter wavelength and pulse duration. The reason is that at shorter wavelength, the number of sequential channels competing with the direct two-electron channel is decreased [4,5]. If on the other hand the channel through the doubly excited state were responsible for the knee, it should

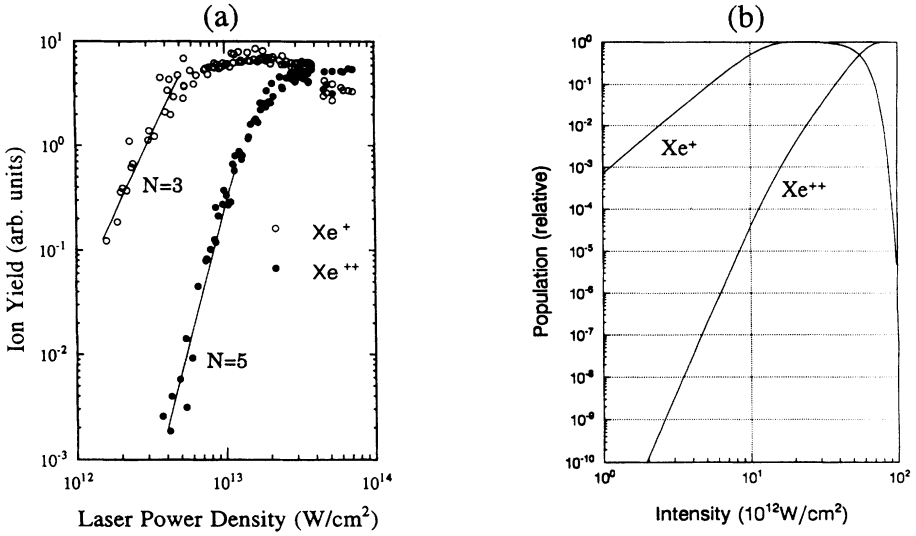

FIG. 2. (a) Measured laser power density dependence of the Xe^+ and Xe^{2+} ion yields at 248 nm and 500-fs pulse duration. The Xe^{2+} ion yield does not show any deviation from the I^5 dependence on the laser power density I before saturation, which is compatible with the five-photon ionization of the Xe^+ ground state. For power densities higher than the saturation power density the ion yield does not follow the $I^{3/2}$ dependence because of the confinement of the ion extraction volume of the mass spectrometer. (b) Theoretical results for the laser intensity dependence of Xe^+ and Xe^{2+} for a 500-fs pulse at 248 nm. The values of generalized cross sections employed are: $\sigma_3^{(0)}=5\times10^{-82}$, $\sigma_5^{(1)}=8\times10^{-148}$, $\sigma_7^{(0)}=1\times10^{-212}$ in units of cm^{2N} $s^{(N-1)}$ for an N photon process.

be absent at this wavelength, because there is no combination of states in the atom and the ion that can lead to a doubly near-resonant process leaving the ion in an excited state. Thus the only possibilities are the sequential process through the ground state of the ion with or without the additional presence of a direct two-electron ejection.

The experimental part of the present work is based on the unique combination of two state-of-the-art systems, namely, a femtosecond KrF laser system and a four-grid reflectron time-of-flight mass spectrometer (TOF). In our experiment, we have measured the ion yield of Xe as a function of laser intensity, as well as the photoelectron spectrum.

The rare gas has been ionized through multiphoton absorption from the focused KrF laser pulses of 500 fs duration, as measured by the autocorrelation method. The pulses at 248 nm have been delivered at a 4-Hz repetition rate from a hybrid dye-excimer laser system [7], providing a 10-mJ energy output with an instantaneous amplified spontaneous emission to pulse contrast ratio $<10^{-6}$ at the focus.

Ion yields have been measured with the TOF mass spectrometer equipped with a four-grid electrostatic ion reflector [8]. The 0.2×2 mm^2 entrance aperture of the flight tube of the spectrometer combined with the four-grid reflectron allow for a confinement of the ion extraction volume of the apparatus. Within this confined volume, absolute saturation of the multiphoton ionization may occur. In the present experiments, absolute saturation of the Xe^+ and Xe^{2+} yields has been achieved, as discussed below. The power density at the focus has been determined from the beam waist, which is estimated (a) via imaging of the focus, (b) from the measured ponderomotive shift of the ionization threshold in photoelectron spectra, as well as (c) by measuring the ion yield as a function of the laser focus position in the confined volume cross section of the TOF perpendicular to the propagation axis. The waist can then be estimated from the shape of the edges appearing in the yield as the beam is crossing the confined volume borders. Photoelectron kinetic energy spectra have been measured with a 20-cm photoelectron TOF spectrometer operating at a background pressure of 10^{-9} mbar.

Upon interaction with the laser pulse, multiply ionized Xe up to charge state 7 has been observed. The Xe^+ and Xe^{2+} yields versus power density are depicted in Fig. 2(a). The data shown are not corrected for the different efficiency of the spectrometer for the two charge states, as this is not relevant to the purpose of the present investigation. Absolute saturation of both single and double ionization can be clearly seen. For laser intensities higher than the saturation intensities of both charge states, the ion yield does not follow the well-known (for non-space-limiting geometries) $I^{3/2}$ dependence [9]. It stabilizes to a steady value when absolute saturation is reached and for Xe^+ it even decreases with further increasing power density to the benefit of the Xe^{2+} yield, as it should (see also Ref. [4]). The overall behavior of the curves does not show any evidence of deviation from the lowest-order perturbation theory. No "knee" structure has been observed in the slope of the Xe^{2+} yield that would indicate the existence of a second double-ionization channel other than the one through the ground state of Xe^+, in contrast to the observations in the previous experiments at 531 nm [1] and 527 nm [2]. This is entirely compatible with theoretical expectations since the photon energy (5 eV) is too large to allow intermediate resonances of the proper parity. A theoretical simulation using *ab initio* cross sections is shown in Fig. 2(b). Note the remarkable agreement between theory and experiment for the saturation intensities. It should be pointed out here that the pulse duration of the present experiment is about two orders of magnitude smaller than the pulse duration for which the "knee" structure has been observed in the previous experiments. As discussed above, the present pulse duration is expected to favor the possible direct double-ionization channel. This in turn would enhance double ionization, so as to become observable at power densities lower than the single-ionization saturation intensity. This was indeed the case in previous studies [10] where the channel requiring a short pulse duration in order to compete with the conventional one (sequential through the ground state of the ion) led to double ionization before saturation of single ionization occurred. Doubly ionized atoms though appear here at intensities for which saturation of the single

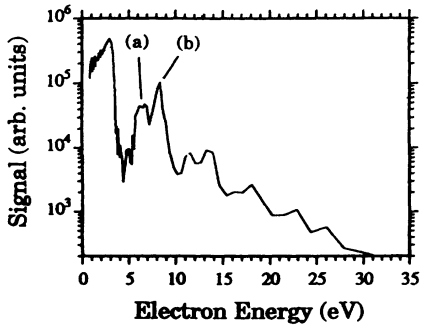

FIG. 3. Photoelectron energy spectra of Xe at 248 nm and 500-fs pulse duration. The laser power density at the focus is $\sim 10^{14}$ W/cm^2. The observed series of partially resolved double peaks [(a), (b)] are ATI peaks in the two continua that correspond to the two fine-structure levels of the Xe^+ ground state. No other peaks are observable in the spectrum.

ionization is reached. A least-squares fit to the Xe^{2+} curve gives, within the experimental error, a slope of 5, which is also consistent with the five-photon ionization of the ground state of Xe^+.

Finally, Fig. 3 depicts a photoelectron energy spectrum obtained at 10^{-6} mbar of Xe for a laser power density of the order of 10^{14} W/cm^2 at the focus. The spectrum consists of series of above-threshold ionization (ATI) double peaks (not resolved for all the ATI peaks) corresponding to transitions from the atomic ground state to the two fine-structure levels $(5p^5)^2P_{1/2,3/2}$ of the ionic ground state. Within the rather low limits of the resolution and sensitivity of the present photoelectron energy measurements, the spectrum shown, as well as other spectra taken at lower power densities or pressure, show no evidence for other resonance channels involving excited atomic states, which might also be blended with the double peak structure observed. We should point out here that the resolution and sensitivity limitations originate from the low repetition rate of the laser system combined with its uv radiation (strong background signal), which do not allow space-charge-free and electron-ion or electron-electron coincidence measurements. It is worth noting that the measured slope of 3 for the Xe^+ curve in Fig. 2(a) indicates also that no dynamical atomic resonances are occurring. One such resonance might have been expected from the $6p[1/2]_0$ atomic state which lies 525.7 cm^{-1} below the two-photon absorption from the ground state.

We note in closing that repetition of the same experiment in Kr has given very similar results, i.e., absence of the "knee" structure and the slopes 3 and 5 for the Kr^+ and Kr^{2+} ion yields versus laser intensity in log-log plots, as expected from the three-photon ionization of neutral Kr and the five-photon ionization of Kr^+. This further confirms our interpretation since it is also compatible with theoretical expectations on the basis of the atomic structure of Kr and Kr^+. In contrast, a slight "knee" can be discerned in the data on Kr by L'Huillier *et al.* [1] at the wavelength 532 nm, although they had chosen not to present a quantitative fit. It is perhaps worth noting here that the cross section of the direct process in Xe obtained through the fit in Ref. [1] was larger by several orders of magnitude than scaling would suggest.

Although this paper proves the absence of observable direct double ionization under the conditions of studies that have spanned ten years, it is not meant to imply that correlated double or multiple electron emission may not be significant under different conditions (e.g., much shorter pulses at longer wavelengths and higher intensity). That remains to be seen.

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