

Multiphoton Double Ionization via Field-Independent Resonant Excitation

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The double ionization of xenon in the multiphoton regime has been studied at two wavelengths (0.77 and 0.79 μm) using an electron-ion coincidence technique and an intensity binned ion ratio method. Sharp resonant structures in the electron energy distribution correlated with the doubly charged ion, as well as a wavelength dependence of the $\text{Xe}^{2+}/\text{Xe}^+$ ratio provides new insights. A mechanism involving the shelving of population in Rydberg states followed by excitation of a core electron is proposed.

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The three-body interaction of an atomic core and two electrons under the influence of an intense laser field is still not completely understood. Although theories using a single active electron (SAE) approximation have successfully modeled the intensity-dependent single ionization rates of inert gas atoms over several orders of magnitude [1], extension to the measured yield of higher charge ($Z \geq 2$) states has failed. A signature of this breakdown is an enhancement in the total production rate of doubly charged ions over SAE predictions and has been well documented beginning with xenon [2] and culminating in a precise measurement in helium [1]. Enhanced double or nonsequential (NS) ionization has been observed in most rare gases [3].

In the high intensity limit, or tunneling regime, progress has been made in understanding double ionization based on a quasiclassical rescattering model [4,5]. In this model, a single electron that has tunneled through the distorted Coulomb potential is driven back to the core by the oscillating laser field, undergoing elastic or inelastic scattering. For double ionization to occur the returning electron must have gained enough field energy to liberate a second electron via inelastic ($e, 2e$) scattering. A number of experiments [6–8] have been performed in this limit and have yielded electron energy distributions that are consistent with the rescattering ($e, 2e$) process. A many-body S -matrix quantum theory of double ionization [9] showed that the inclusion of configurations which include rescattering is necessary to reproduce quantitatively the observed enhancement in total rate, electron momenta, and energy distributions.

In the low intensity or multiphoton limit the interpretation of NS ionization is less clear although well documented experimentally [10]. In this regime, the rescattering mechanism is inappropriate since the primary electron cannot gain enough field energy to free another one and the intensity is too weak to initiate tunnel ionization. The expectation based on the single electron theory of Keldysh [11] is that the dynamics will evolve

between these two limits. In fact, studies have demonstrated this change in dynamics in single ionization [12]. Recently, this transition was examined in double ionization by using electron-ion coincidence techniques [13]. A clear transformation was observed in the electron distributions which closely correlated to the evolution first discussed by Keldysh. The study of Chaloupka *et al.* [13] reinforced the high intensity rescattering limit, but it did not establish a clear mechanism in the low intensity limit.

In this Letter we aim at elucidating the behavior of xenon exposed to femtosecond, red light pulses in the multiphoton regime. The single and double ionization is studied at two wavelengths using total rate measurements and an electron-ion coincidence technique. Two striking observations characterize this case: (i) the double ionization rate displays an enhancement at low intensity that is wavelength dependent (see Fig. 1) and (ii) similar structures appear in the photoelectron energy distribution correlated with singly charged and doubly charged ions. These structures are identified as the well-known Rydberg (Freeman) resonances [14] and therefore put strong constraints on the possible double ionization mechanism. A field-independent resonant excitation (FIRE) model

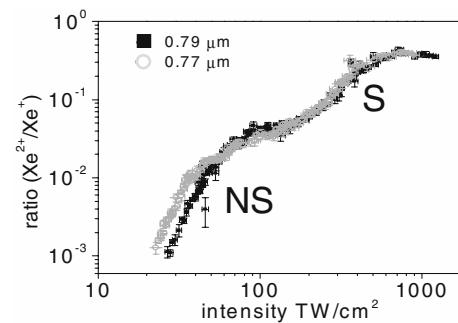


FIG. 1. The ratio of double-to-single ionization as a function of intensity for xenon at 0.77 μm (open circles) and 0.79 μm (solid squares). Horizontal and vertical error bars are the intensity and statistical uncertainty, respectively.

based on dynamical resonant core excitation is proposed to help explain these observations.

The current experiment is performed in the low intensity limit where inelastic ($e, 2e$) rescattering is energetically forbidden. In this limit, a few different proposals have been advanced to explain the enhanced NS rate. Walker *et al.* [15] speculated, based on multiphoton arguments, on the existence of a doubly excited state at an energy halfway between the neutral ground state and the $2e$ threshold to explain the NS rate for xenon at short wavelength (0.5 μm). Charalambidis *et al.* [16] proposed a core-excited state as a likely candidate and calculated scaled generalized cross sections for the following scenario. In the first step, one valence p electron is excited to a Rydberg state ($10s$) by a 5-photon absorption. In a second step an inner-shell $5s$ electron is excited producing a doubly excited state from which 1-photon absorption frees one electron, leaving the ion in the excited core-hole state $5s5p^6$. Double ionization is subsequently achieved by a 5-photon transition, freeing one p electron while another fills the s hole. Thus, double ionization in this case is a resonant higher-order sequential process. Although this scenario was never actually tested, it was supported *a contrario* by an experiment in which such a resonance was forbidden by selection rules and in which indeed no NS enhancement was observed. The current experiment differs from this earlier study [15] because the longer wavelength and shorter pulse duration result in large ac-Stark shifts of the excited states (as large as a 2–3 photon shift for some states); also the high-resolution coincidence measurement provides the first details of the energy distributions of the two electrons. A recent experiment, performed under similar laser conditions to the current one, proposed a mixed multiphoton-rescattering scenario [17] based on the appearance of low-energy electrons at the same intensity at which the NS yield was enhanced. Multiple rescattering, required to provide enough energy to at least excite the ion, was invoked to explain the double ionization, but it did not explain the NS enhancement itself.

The electron-ion coincidence technique used here has been described in detail elsewhere [8]. The 100 fs, 0.78 μm (tunable) output of a Ti:S laser was used to acquire ion-correlated electron energy spectra resulting in a 4:1 ratio of true to false coincidences. In order to obtain a precise double-to-single ion yield ratio, the laser intensity was monitored by imaging the interaction region onto a nonlinear crystal and the unsaturated frequency-doubled light was measured with a photodiode. The ratio value was binned accordingly, reducing the effective shot-to-shot laser intensity fluctuation to less than 1%.

Figure 1 shows the ratio ($\text{Xe}^{2+}/\text{Xe}^+$) for the total production rate of the doubly and singly charged ions as a function of intensity at two wavelengths, 0.77 μm (open circles) and 0.79 μm (solid squares). The curves have the following general interpretation, at low intensity

(labeled NS) production of Xe^{2+} ion increases until the neutral ground state is depleted (saturation). In the current experiment saturation occurs at 80 TW/cm²; beyond this intensity the ratio is constant. Finally in the high intensity region the ratio curve again increases since the Xe^{2+} starts to form by direct ionization of the Xe^+ ground state (sequential ionization labeled S in Fig. 1) and eventually this process saturates near 1 PW/cm².

The direct measurement of the ratio rather than independent rates reduces the systematic error since both ions are collected in the same laser shot. The absolute intensities for each curve were independently calibrated using the helium electron energy spectrum [1]. This calibration, coupled with the intensity binning technique, allows a precise measure of the ratio curves at the two wavelengths. The 0.77 μm curve shows a distinct enhancement in NS ionization at low intensities as compared with the 0.79 μm data and a published curve [3] at 0.80 μm with similar pulse characteristics. As the saturation intensity is approached the difference decreases; in the sequential regime both curves become superimposed. The data in Fig. 1 clearly establish the existence of a wavelength dependence in the NS enhancement.

Figure 2 shows the electron energy spectra correlated to single (gray shaded) and double (black line) ionization at 0.77 μm at a fixed intensity. Prominent Rydberg structure is apparent in both distributions. This is the second key result of this work. Similar Rydberg peaks are also observed in the single and double ionization distributions at 0.79 μm except that the peaks are shifted to lower energies consistent with the change in photon energy. The Rydberg structure in short-pulse, intense field single ionization was first observed and explained by Freeman *et al.* [14]. In a laser pulse, the Xe^+ ionization thresholds shift ponderomotively [18] causing a net increase in the binding energy as the intensity increases (the shift of the tightly bound neutral ground state is negligible). Similarly, a quasifree Rydberg state also experiences an ac-Stark shift which is approximately ponderomotive. The lower portion of Fig. 3 illustrates the time evolution

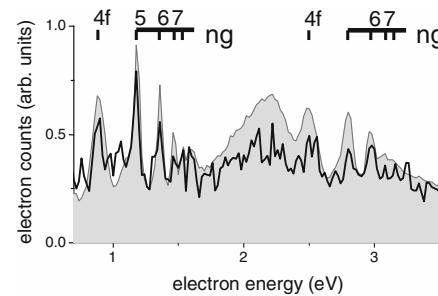


FIG. 2. The low-energy portion of the electron energy spectra correlated to single (shaded area) and double (black line) ionization for xenon interacting with 80 TW/cm², 0.77 μm pulse. The complete spectrum extends out to 30 eV [13]. The Rydberg state assignments in the single ionization spectrum are shown and are repetitive with the photon energy.

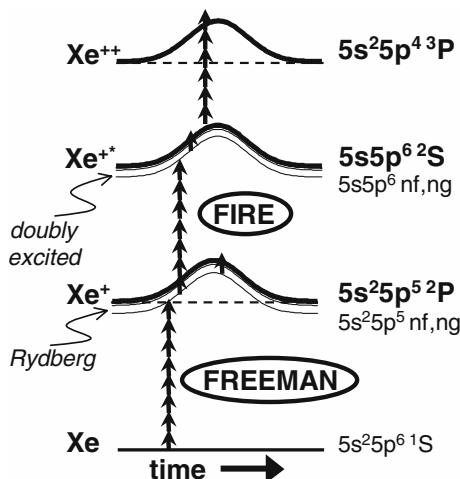


FIG. 3. Illustration of the FIRE and Freeman dynamics for xenon energy levels as a function of intensity.

of the xenon levels in an intense, low-frequency laser pulse. As a function of time (intensity), Rydberg levels transiently shift through resonance enhancing the rate at discrete electron energies. As long as U_p is large enough, Rydberg levels will shift into resonance for any wavelength. In this experiment, xenon single ionization exhibits strong *f*- and *g*-Rydberg states as detailed by Hansch *et al.* [19].

Chaloupka *et al.* [13] showed that in Xe the mean electron energies for single and double ionization are identical. The existence of Rydberg structure in the NS spectra reinforces the absence of rescattering since the energy partitioning in the ($e, 2e$) or any other inelastic process would wipe out any structure. The narrow (10–20 meV) peaks indicate that the lifetime of these states is approximately the pulse length. In fact, all gauges of this interaction, including the Keldysh parameter, corroborate the ionization as being multiphoton.

We propose a FIRE scenario to explain the Rydberg structure in the NS photoelectron distribution and the enhanced NS ionization rate at 0.77 μm . Referring to Fig. 3, following the excitation of the first electron, another seven photons can couple the core transition via doubly excited state configurations $5s5p^6nf$ or ng . The field-free $5s^25p^5 \rightarrow 5s5p^6$ transition frequency is resonant with seven 0.77 μm photons. The key point of FIRE is that the Rydberg levels $5s^25p^5nf, ng$ and the doubly excited states $5s5p^6nf, ng$ undergo a similar ac-Stark shift since only the outer Rydberg electron energy is affected significantly by the field-induced quiver motion. Hence, to first order, the energy difference between the two resonant states is constant throughout the temporal evolution of the laser pulse and consequently wavelength dependent. Once population is transferred from the single to the doubly excited configurations, the absorption of one more photon can free the Rydberg electron above the $5s5p^6{}^2S$ threshold, producing an excited state ($\text{Xe}^+{}^*$). The photoelectron spectrum reflects this process by ex-

hibiting peaks similar in energy to those in single ionization since this core excitation should not affect the Rydberg state binding energies. The double ionization threshold is then reached in a process that returns one *p* electron to the *s* hole while liberating another, producing a ground state $5s^25p^4{}^3P$ Xe^{2+} ion. The photoelectron signature of that last step (second electron) is not clearly identified in the current experiment. The reason could be that either this is also a resonant Rydberg process with energies that more or less coincide with those of the first step or it is a nonresonant process that produces a broad photoelectron distribution due to the ponderomotive dependence of the ionization potential. The double ionized photoelectron spectrum does show some evidence for the latter process since the fidelity of the Rydberg peaks is reduced as compared to the single ionization spectrum.

The FIRE scenario is reminiscent of the well-known isolated core excitation (ICE) that was used to extensively explore the spectroscopy of doubly excited states in alkaline-earth atoms [20]. In this scheme, a weak laser pulse first resonantly excites a Rydberg electron while a second laser is used to excite a resonant core transition. Essentially ICE promotes two electrons independently by producing a Rydberg state that behaves as an inactive spectator as the core (inner) electron is excited. In the strong field multiphoton regime, the low-frequency laser field naturally transfers population to Rydberg states due to the dynamics illustrated in Fig. 3. Thus, Rydberg population is shelved and the possibility exists for driving a core transition, similar to the ICE mechanism, but in this case between ponderomotively shifted levels that have zero differential shift. Excitation of Rydberg (Freeman) states is intensity dependent since the energy gap between the ground and Rydberg states is changing but is basically frequency independent. However in FIRE, the change in the core state configuration imposes a frequency dependence on the NS ionization rate which is reflected in the enhanced rates near the core frequency.

If the excited Rydberg electron were truly a spectator during the core excitation, we would not expect an enhancement in NS ionization, particularly one that saturates when the neutral atom population becomes depleted. The double ionization mechanism then would simply be that for sequential ionization through the core resonance. We propose that in FIRE unlike ICE, the Rydberg electron is far from being only a spectator, and its presence is the crucial factor in enhancing the double ionization rate. First it creates a vacancy in the $5p$ shell allowing the core transition, $5s^25p^5 \rightarrow 5s5p^6$, and, second, it increases the core transition rate well above that for the ion. The dense Rydberg series of doubly excited states converging to the first excited state of the ion, $5s5p^6{}^2S$, allows the double excitation involving the core transition to remain quasi-resonant for a range of wavelengths. The high density of Rydberg states accessible to the outer electron coupled to the substantial quiver energy, $U_p \gg |E_{nl} - E_{n'l'}|$, available, maintains the resonance condition. Moreover, since

the core changes from a 2P to a 2S configuration, its shape and parity alter during this excitation, and hence the outer electron cannot be completely insensitive to this transition. Thus it will either remain in the same orbital or be transferred into one of the other available states with roughly the same energy. Conversely the bare core transition, $5s^25p^5 \rightarrow 5s5p^6$, in the ion would be resonant only at a particular wavelength. Thus, during the pulse, the total rate of this resonance step in the ion can be expected to be lower than that for the corresponding double excitation (FIRE) step in the neutral. The enhancement is even more pronounced when the entire focal volume is included, and, as observed, disappears as the neutral atoms are depleted. Consequently, by shelving Rydberg population and allowing dynamics that can change its state during the core excitation to facilitate energy conservation, FIRE can account for the key observations: (i) Rydberg structure in the electron energy distributions and (ii) the wavelength dependence in the enhanced double ionization. At $0.79 \mu\text{m}$, where the double ionization yield is partially suppressed, the structure in the double ionization electron energy spectrum is altered but not eliminated. This may be a result of a partial overlap of the laser bandwidth with the $0.77 \mu\text{m}$, 7-photon resonance, enabling FIRE even at a nonresonant center wavelength, or it may indicate that other unidentified processes are at work that do not depend strongly on wavelength. An experiment using a more tunable laser could provide additional insight.

FIRE is a general multiphoton double ionization mechanism and should be valid for all high- Z inert gas atoms. At low intensity where the ac-Stark shift of Rydberg states is small, the resonant scheme of Charalambidis *et al.* [16] is active. As the magnitude of the ac-Stark shift approaches the photon energy at higher intensity, the FIRE process of double ionization becomes dynamic. The natural shelving of population in Rydberg states acts as a gateway for driving the core transition. At higher intensities as the ac-Stark shift approaches many photons in energy, the wavelength sensitivity of the FIRE process may diminish since the core level differential shift may no longer be negligible. Furthermore, the rescattering channel will open and contribute to the NS rate. Consequently, the evolution of double ionization is a continuous function of intensity in a manner consistent with the Keldysh theory [11] for single ionization.

In a recent 1D two-electron calculation, Panfili and Liu [21] observed resonantly enhanced double ionization in the total rate that depends on intensity and wavelength. Their calculations show a similar behavior to the data shown in Fig. 1, but the relevance of their results is unclear; no predictions of the electron spectra were made.

In conclusion, the wavelength dependence of the total rate and the structures in the electronion coincidence

spectra provide new insights on the process of double ionization of xenon in the multiphoton regime. The findings considerably restrict the possible routes to the double ionization threshold, especially in presence of large ac-Stark shifts. The proposed FIRE scenario is consistent with the features observed in the experiment. It builds upon previously discussed models involving higher-order processes and provides a general mechanism for the so-called nonsequential double ionization of high- Z inert gases. Theoretical FIRE excitation rates do not exist, except as scaled multiphoton cross sections [16] and remain a challenge for theory. Refined measurements would also help in the identification of the second electron spectrum.

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