RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 47, NUMBER 1 JANUARY 1993

High-angular-momentum states as population traps in multiphoton ionization

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(Received 23 July 1992)

Resonant and nonresonant multiphoton ionization of xenon is studied using short, circularly polarized light pulses (100 fs, 597 nm, 22 TW/cm^2). A pump-probe measurement shows that, although bound states are substantially populated, they do not enhance the ionization signal. The bound states do not ionize because their high angular momentum repels the wave functions from the nucleus. Ionization does occur through intermediate states in the continuum, in spite of a large energy mismatch, because these states have more energy and therefore suffer less from the centrifugal barrier.

PACS number(s): 32.80.Rm

Recently several situations have been discovered in which an atom subjected to intense electromagnetic radiation is unexpectedly resistant to photoionization [1–3]. This "stabilization" occurs because, under the influence of the radiation, the atom is brought into a state where the electron stays far away from the nucleus. Such a state cannot readily be ionized because energy and momentum conservation make it difficult for the quasi-free electron to absorb photons.

The stabilized state can be permanent, caused by a deformation of the electron-nucleus interaction due to the field-driven quiver motion of the electron [1]. It can also be transient, a wave packet of excited states, which cancel each other's ionization by destructive interference [2,3]. In this Rapid Communication we present experimental evidence of yet another type of stable state, for the case of circularly polarized light, namely Rydberg states with large angular momentum [4]. As such these states have little to do with intense-field stabilization [1–3]. Their relevance is that they show how ionization can be precluded; i.e., by moving the electron far away from the nucleus. A further connection is that such states can withstand the high intensities needed to reach the stabilization regime.

To properly introduce our experiment we shall first discuss high-intensity effects. Due to the quiver motion imposed by the oscillating electric field, loosely bound states as well as the ionization threshold experience an upward energy shift. At 600 nm this shift is 33 meV per TW/cm^2 of light intensity. The excitation yield to Rydberg states is enhanced as they successively shift into resonance during the laser pulse. Subsequent photoionization out of the Rydberg states gives rise to narrow peaks in the electron spectrum [5].

An important step in unravelling the resonant from the nonresonant contribution to intense-field multiphoton ionization (MPI) was made using circularly polarized light [6]. The accessible resonances are limited by selection rules that in the case of circular polarization only allow $\Delta m = 1$ transitions. Starting from the ground state of xenon, $(5p)^6$, the lowest bound state accessible by a six-photon transition is the circular state, reached by promoting a $5p$ ($m = -1$) electron to the $6h$ ($m = 5$) orbital. At a wavelength of 620 nm, the intensity where such high-lying states are shifted into resonance via the ac Stark effect is too low to drive the six-photon transitions. Indeed, in the experiment [6] no resonant structure was observed and all the ionization consisted of nonresonant ionization. In the experiments described in the following, we show that by choosing an appropriate wavelength, six-photon excitation to nh Rydberg states does occur. However, the states act as population traps and still do not contribute to the photoionization.

Our experimental setup encompasses an amplified femtosecond laser system utilizing continuum generation in water to allow the wavelength to be varied. The resulting pump laser pulses (597 nm, 100 fs, 22 TW/cm^2, up to 100 μJ) are approximately transform limited. The main difference with a previous description of this system [7] is the use of an interference filter to select the wavelength after continuum generation. A Soleil-Babinet compensator is used to circularly polarize the light.

A second laser beam (532 nm, 5 ns, 0.6 TW/cm^2, 10 mJ) can be used to probe the population that survives the pump laser pulse in excited states. The probe pulse relies on a large fluence (intensity times pulse duration equal to 3 kJ/cm^2) to ionize all the population in excited states. Only one photon is needed to ionize the excited states, so that the intensity can be low and no xenon in the ground state is ionized by the probe.

For our experiment we make use of a magnetic-bottle electron spectrometer [8]. For its energy calibration we refer to a previous description [9]. When the polarization is changed from linear to circular, the electrons are preferentially emitted in a plane perpendicular to the light beam instead of along the spectrometer axis. Our magnetic-bottle spectrometer collects 2π sr solid angle so that the spectra are not affected by such differences in angular distribution. The spectrometer has a background pressure of ~ 0.5 μPa. During the experiments it was homogeneously filled with ~ 1 mPa of xenon. In the spectrometer the pump and probe focus diameters are 10 and 20 μm, respectively.

The experimental data are shown in Figs. 1 and 2 for linearly and circularly polarized light, respectively. Similar conditions prevailed when these spectra were collected. We will first discuss the results for linearly polarized light. Figure 1(a) shows the electron spectrum using just

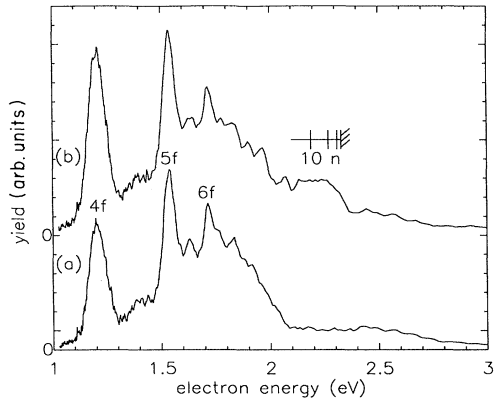

FIG. 1. (a) Electron spectrum of xenon ionized by *linearly* polarized, 100-fs, 597-nm pump pulses. Large resonant contributions to the (6+1) photoionization have been labeled $4f$, $5f$, and $6f$. (b) Electron spectrum with both pump and probe lasers on. Population in high Rydberg states survives the intense pump pulse. Subsequent ionization of these states by the probe laser causes the bump at 2.2 eV.

the pump beam. The $4f$, $5f$, and $6f$ resonances can be clearly distinguished. Higher in the Rydberg series the individual resonances are more closely spaced and can no longer be individually resolved.

Adding the probe laser results in the similar spectrum of Fig. 1(b). The only addition is a bump corresponding to electrons emitted with an energy of about 2.2 eV. These electrons survive the pump pulse in high Rydberg states ($n \geq 10$) and are subsequently ionized by the probe laser ($h\nu = 2.33$ eV). The classical round-trip time of these states, $\tau_n = 2\pi n^3$ in atomic units, exceeds the pulse duration so that in fact a radial wave packet is launched that does not return to the core during the pulse [10]. For these states, or a wave packet of these states, most of the wave function is far from the nucleus. The probability to be ionized by the pump pulse is small: the calculated saturation fluence of the $10f$ state, 5.3 J/cm^2, is higher than the pump fluence. The probe pulse in contrast has sufficient fluence to ionize all the Rydberg states. The photoelectron distribution should vary as the product of density of states, which increases as n^3, and the excitation probability, which decreases as n^{-3}. The observed distribution in Fig. 1(b) is indeed approximately constant. In contrast to an earlier experiment [9], no population survives in states with $n < 10$, because the larger intensities needed to shift these states into resonance at the current wavelength, lead to too short lifetimes.

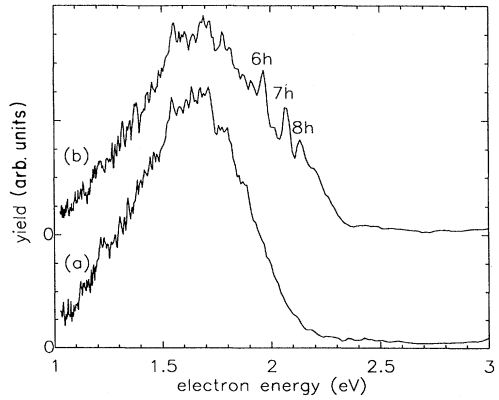

FIG. 2. (a) Electron spectrum of xenon ionized by *circularly* polarized, 100-fs, 597-nm pump pulses. Selection rules only allow ionization via h states. No sharp peak indicating resonance enhancement is seen, although a nonresonant signal is present where the resonance is expected. (b) Electron spectrum with both the pump and the probe lasers on. The $6h$, $7h$, and $8h$ states that are populated by the pump laser can now be ionized by the much larger fluence of the probe laser.

Figure 2(a) was measured using just the circularly polarized pump pulses. The signal in Fig. 2(a) is much too broad to be due to ionization via the $6h$ state. The $6h$ state is expected to shift more like the threshold than the $6f$ state does, and it should ionize less rapidly. We cannot therefore conceive a mechanism that would predict the $6h$ signal to be broader than the $6f$ signal [shown in Fig. 1(a)].

To determine whether we were populating the $6h$ state we used the probe laser to measure Fig. 2(b). The spectrum now contains three additional peaks corresponding to ionization of the $6h$, $7h$, and $8h$ states by the probe pulse. The energies are 1.95, 2.05, and 2.12 eV, respectively. Figure 2(b) therefore proves that the intensity, which shifts the $6h$ state into resonance at this wavelength, is sufficient to appreciably populate the state.

The broad electron signal in Fig. 2(a) shows that the resonant intensity is sufficient to cause seven-photon ionization. However, we have argued that the broad electron signal is not due to resonant ionization via the $6h$ state. Apparently the $6h$ state behaves as a population trap: although it can be resonantly excited it is not readily ionized. This is plausible from the saturation fluences. The calculated saturation fluence of the $6h$ state, 66 J/cm^2, is much higher than the fluence of the pump laser, 2.2 J/cm^2. This shows that population excited to the $6h$ state will be trapped. That we can see the influence of the bound states in Fig. 2(b) is due to the high fluence of the probe laser, 3 kJ/cm^2, much higher than the $6h$ saturation fluence. Population in the $6h$ state will survive up to an intensity of 660 TW/cm^2 during a 100-fs pulse, an intensity at which the ground state of xenon will be completely depleted. The saturation fluences are based on one-photon cross sections. This is justified because our arguments are only qualitative and so the small fraction of two- and more-photon ionization can be discounted.

Apparently the broad electron signal is not caused by ionization via *bound* states. As a result of selection rules, any ionization will proceed via intermediate h states at the six-photon level. We can only conclude that the ionization proceeds via h states lying in the *continuum* with a large energy mismatch.

To show that this scenario is realistic we performed lowest-order perturbation theory (LOPT) on hydrogen, which serves as a model. Such a model does not automatically incorporate ac Stark shifts, finite bandwidth of the laser pulse, or lifetime broadening of the excited state. These effects prevent the yield from becoming arbitrarily large when a harmonic of the laser frequency is

degenerate with a bound state. In the model the rate-limiting effects are incorporated as a small imaginary contribution to the photon energy, which results in a minimum detuning from the nearest bound state. The measured autocorrelation width (full width at half maximum) of our pump pulses was 133 fs. The leading (trailing) part of a hyperbolic secant pulse can then be modeled as $E(t)=E_0\exp[i(\omega\pm i/\tau)t]$, with an inverse pulse turn-on time, $\tau=46$ fs. At the six-photon level this imaginary part of the photon energy corresponds to an energy detuning of 87 meV. In our model we use an equally large real detuning.

The perturbed radial wave function Ψ_f after absorbing a photon from state Ψ_i is in LOPT

$$|\Psi_f\rangle \propto (E_i+h\nu-H)^{-1}r|\Psi_i\rangle \ , \tag{1}$$

where H is the atomic Hamiltonian. The angular part and the part dependent on the electric field strength have been factored out, because they do not depend on whether the ionization is resonant or nonresonant. The resolvent operator, $(E_i+h\nu-H)^{-1}$, can also be written as

$$(E_i+h\nu-H)^{-1}=\sum_k (E-E_k)^{-1}|\Psi_k\rangle\langle\Psi_k| \ , \tag{2}$$

where $\sum_k$ is a summation over the applicable bound states and an integration over the continuum states. We can then write

$$I_{\text{rate}}^{1/2} \propto \sum_k (E-E_k)^{-1}\langle\Psi_f|r|\Psi_k\rangle\langle\Psi_k|r|\Psi_i\rangle \ , \tag{3}$$

and in this way isolate the contribution of each bound state to the total ionization yield.

We are interested in h states as resonances. A difference between model and experiment is that in xenon six photons are used to reach an $m=5$ state from an $m=-1$ ground state, whereas in the hydrogenic model we start with $m=0$, so h states are reached with five photons. Therefore, in the model we use the fourth-order perturbed wave function for Ψ_i.

In Fig. 3 the relevant wave functions are shown. The bound-state contribution to the wave function after absorption of five photons is significant, which shows that it should be possible to excite these bound states. The part of the wave function that will effectively ionize is the part near the nucleus, but the bound states are effectively kept out of this region by the centrifugal barrier. The continuum states have higher energy than the bound states and therefore their wave function does approach the nucleus. The centrifugal barrier has similarly been invoked by Bucksbaum *et al.* [11] to explain their results on above-threshold ionization.

The various contributions to the total matrix elements are given in Table I. The model confirms the experimental observation that the largest contribution to the ionization, for circularly polarized light, is via the free states rather than via the bound states. In the linearly polarized case the centrifugal barrier is less high ($l=3$) and therefore the repulsion is not so effective in reducing the contribution of the bound states. A complication is now that both $\Delta l=+1$ and $\Delta l=-1$ transitions are possible

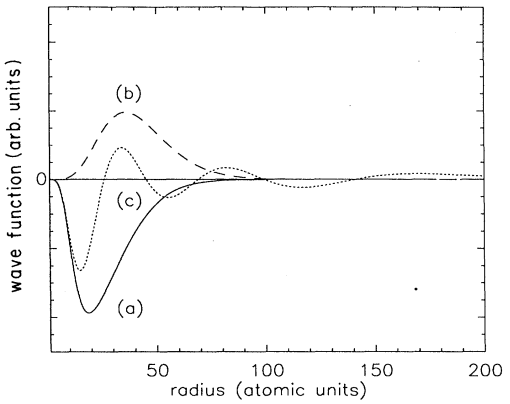

FIG. 3. Model calculation of multiphoton ionization with circularly polarized light: (a) radial wave function after absorption of five photons, i.e., fifth-order perturbed wave function. (b) The $6h$ state as an example of a bound-state wave function. (c) Continuum contribution to trace (a). Note that only the continuum contribution penetrates the region near the core where ionization is possible.

so that to reach the f state with five photons many different paths are possible. We have chosen to tabulate the path with the largest contribution in Table I, but the other paths behave similarly.

Our model neglects ac Stark shifts. The quiver motion

TABLE I. (a) Circular polarization: calculated radial contributions of different states to the total ionization matrix element. The contribution is the product of the radial excitation and ionization matrix elements divided by the energy detuning of the resonance, all in atomic units. (b) Linear polarization: calculated radial contributions of different states to the total ionization matrix element.

(a) Circular polarization

h state	Excitation (units of 10^3)	Ionization	Detuning (units of 10^{-3})	Contribution (units of 10^6)
6	77	0.068	−3.1	−1.7
7	79	0.084	−6.8	−0.9
8	72	0.088	−9.2	−0.7
9	64	0.085	−10.8	−0.5
10	57	0.081	−12.0	−0.4
11–∞				−1.7
free				−363
total				−369

(b) Linear polarization

f state	Excitation (units of 10^3)	Ionization	Detuning (units of 10^{-3})	Contribution (units of 10^6)
4	2780	0.76	14.3	147
5	1570	0.83	3.0	432
6	1040	0.78	−3.1	−260
7	754	0.70	−6.8	−78
8	583	0.62	−9.1	−39
9	470	0.55	−10.8	−24
10	390	0.49	−12.0	−16
11–∞				−71
free				−723
total				−632

of the electrons in the field is not incorporated in lowest-order perturbation theory, because it is a higher-order correction. For the calculation of the overlap integrals, this is not very important because the electrons, bound as well as free, always quiver in phase. The ac Stark shifts, plus the fact that in hydrogen five instead of six photons are needed to reach h states, are compensated for by using a different photon frequency in the model (472 instead of 597 nm).

Note that our data using just the pump pulses is in agreement with previous measurements [6] at these and similar wavelengths. Therefore we have focused on explaining the new data using the probe pulses.

In conclusion, we have observed certain excited states to be appreciably populated, due to six-photon absorption, without contributing to the seven-photon ionization occurring simultaneously. These excited states are a dead-end to the ionization pathway, because they are very hard to ionize due to severe repulsion by the centrifugal barrier. They even survive intensities at which the ground state is completely depleted. In agreement with a model calculation, the observed ionization signal is explained as proceeding through continuum states whose large energy mismatch is more than compensated by their ability to penetrate the centrifugal barrier.

This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter) and was made possible by financial support of the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Research) and the European Community through Grant No. SCI-0103-C.

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