Verification of the Dominant Role of Resonant Enhancement in Short-Pulse Multiphoton Ionization

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We report experimental results which imply that observed peaks in the short-pulse photoelectron spectrum of atoms in high fields result only from a resonant enhancement of the multiphoton ionization rate at the peak of the laser pulse, rather than a two-step process of real population transfer and subsequent single-photon ionization. These results consist of the first identification, in a high intensity ($>10^{13}$ W/cm^2) short-pulse photoelectron spectrum, of low-lying states of argon with an ac Stark shift significantly different from the ponderomotive energy.

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Over the past few years, the interpretation of the photoelectron spectra of atoms in strong fields has been marked by several major shifts [1]. One of the most important observations was that in the short-pulse regime (in which the pulse length of the laser is much less than the time it takes an electron to leave the laser focus) the photoelectrons experience no ponderomotive acceleration from the laser field subsequent to ionization and, thus, the spectrum measured at the detector faithfully reproduces the spectrum of emitted electrons in the laser focus [2]. As is well known, the short-pulse spectrum consists of many narrow electron peaks, with the pattern reproduced in energy at intervals corresponding to the photon energy. The original explanation for the observed spectrum suggested that the peaks simply correspond to an enhancement of the multiphoton ionization (MPI) rate brought about by the shifting of excited states into resonance with the laser field by the ac Stark shift [2,3]. More recently [4], it has been suggested that the photoelectron peaks actually result from a two-step process: As intermediate states are brought into resonance with the laser by the ac Stark shift a real population is transferred to the excited state. Subsequently, those excited states ionize by single-photon absorption later in the laser pulse. Unfortunately, these two possibilities predict identical electron spectra for states whose ac Stark shift is equal to the ponderomotive energy. While they predict different results for states with a nonponderomotive ac Stark shift, no such states have yet been identified in actual spectra. Our new result is the identification of such nonponderomotively shifted states in argon irradiated by short-pulse high-intensity 308-nm laser light. This observation requires that the electron peaks in the photoelectron spectrum must result only from a resonant enhancement of the photoionization process.

Since we will be considering states with nonponderomotive shifts, we must rederive the equations governing short-pulse MPI for arbitrary ac Stark shifts. The energy of an ionized electron is simply given by the generalized photoelectric formula [1]:

$$E_{\text{elec}} = nh\nu - I_p(0) - U_p(I) , \tag{1}$$

where n is the number of absorbed photons, $h\nu$ is the photon energy, $I_p(0)$ is the ionization potential at zero field, and $U_p(I)$ is the ponderomotive energy, which is a function of the laser intensity. (We have neglected the difference in the ground-state Stark shifts of the neutral atom and the ion.) In the laser field the ionization potential is increased by an amount equal to the ponderomotive energy, $I_p(I) = I_p(0) + U_p(I)$, which is incorporated into Eq. (1). The ponderomotive energy is given by $U_p = e^2E^2/4m\omega^2$, where E is the electric field strength, e and m the charge and mass of an electron, and ω the frequency of the radiation, and, thus, U_p is simply proportional to the laser intensity. The electron energy in Eq. (1) is the energy associated with the drift motion of the electron in the laser focus. In the short-pulse regime, the electron does not move significantly before the laser pulse has vanished. Thus, the electron does not experience any ponderomotive acceleration on the way to the detector and Eq. (1) represents the measured photoelectron energy. For a peak laser intensity, I_0, Eq. (1) gives the range of possible energies of the emitted electrons: $[nh\nu - I_p(0)] - U_p(I_0)$ to $nh\nu - I_p(0)$. However, it does not predict the exact spectrum of the photoelectrons.

We now consider the implications of Eq. (1) for the two competing models of MPI. It is well known that the photoelectron energy spectrum consists mainly of a series of sharp peaks. It was first postulated that these peaks result from a resonant enhancement of the MPI brought about by the ac Stark effect shifting states in and out of resonance with the laser field. Up to second order in perturbation theory [5], the ac Stark shift of each level relative to the ground state is simply proportional to the laser intensity, and, thus, to the ponderomotive energy aU_p. The resonance condition is given by

$$E(0) + aU_p = n'h\nu , \tag{2}$$

where $E(0)$ is the zero-field energy of an intermediate state and n' the number of photons required to reach the intermediate state from the ground state. We are neglecting the ac Stark shift of the ground state. It is also useful to write down the binding energy of an excited state in the presence of the laser field:

$$E_b(I) = E_b(0) - (\alpha - 1)U_p , \quad (3)$$

where $E_b(0)$ is the binding energy at zero field. Since the resonance condition [Eq. (2)] is fulfilled at only one laser intensity, photoelectrons will be emitted with a single energy

$$E_{\text{elec}} = nh\nu - I_p(0) - [n'h\nu - E(0)]/\alpha \quad (4)$$

if the ionization is due solely to resonant enhancement. This also implies, as has been noted previously [6], that the spatial distribution of the ionization will consist of shells of constant intensity at which a particular excited state has been brought into resonance.

Despite the success of the above model in explaining all of the observed phenomena, another origin for the sharp peaks has been proposed recently [4]: In this alternate model, MPI is considered to be a two-step process. When an intermediate state is brought into resonance the most important effect is a real transfer of population from the ground state to the excited state, rather than an enhancement in the MPI rate. The second step then consists of single or multiphoton ionization out of the excited state. The key feature of this model is that the excited-state population is ionized not only while that state is in resonance, but it survives into the laser pulse and can be ionized at different laser intensities and different times throughout the laser pulse. The electron energy, in this case, is given by $E_{\text{elec}} = mh\nu - E_b(I)$ for the absorption of m photons. Using Eq. (3) this becomes

$$E_{\text{elec}} = mh\nu - E_b(0) + (\alpha - 1)U_p . \quad (5)$$

In contrast to Eq. (4), the electron energy in Eq. (5) does depend, in general, on the laser intensity through U_p. Since in the two-step model ionization occurs over a range of times and, hence, values of U_p, Eq. (5) implies that the photoelectrons will be emitted with a range of energies. However, if $\alpha = 1$, this intensity dependence cancels out and, again, the electron energy will be independent of intensity. Thus, for states whose ac Stark shift is equal to the ponderomotive energy, the two models predict the same sharp electron energy spectrum. Conversely, for nonponderomotively shifted states, the two models predict significantly different spectra.

To distinguish sensitively between these two models, a clean simple spectrum, with electron energy peaks which can be unambiguously assigned to states with a nonponderomotive ac Stark shift, is required. Such spectra are shown, for the first time, in Fig. 1. These data were taken with a laser and spectrometer described previously [7,8]. Briefly, a 120-fsec 616-nm CPM laser is amplified

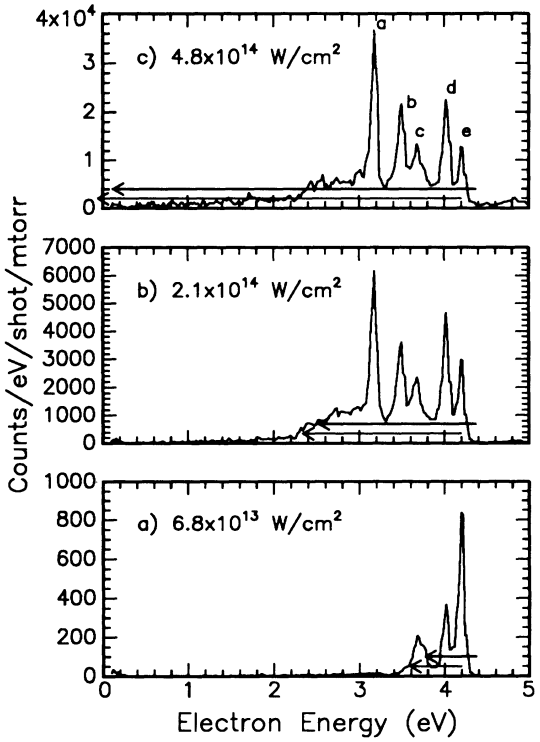

FIG. 1. Electron energy spectra of argon. The arrows show the magnitude of the peak ponderomotive energy and, thus, delimit the range of possible electron energies. The upper arrow is for ionization to the $^2P_{3/2}$ limit, the lower arrow for the $^2P_{1/2}$ limit [see Eq. (1) and Ref. [7]].

and doubled to 308 nm. This laser pulse is then reamplified in an XeCl excimer to a single-pulse energy of 1 mJ. The laser pulse is then focused onto the center of a parabolic electron mirror [9] and the electron energies are measured with a time-of-flight spectrometer. The use of uv radiation [7] greatly simplifies the analysis of the data, compared to longer wavelengths, since far fewer states can be brought into resonance due to the lower order of the MPI process and the smaller magnitude of the ponderomotive energy. Indeed, a comparison of Figs. 1(b) and 1(c) shows that the ionization is saturated, yet only five peaks are present. Figure 2 shows a simplified energy-level diagram of argon [10]. Since the photon energy is 4.03 eV, there will never be one- or two-photon resonances from the ground state. Four photons end in the continuum and will first come into resonance with the high-lying Rydberg levels, as these levels are shifted up by the ponderomotive energy. Such Rydberg series of resonances are the most prominent feature of most short-pulse electron spectra [1]. For a four-photon resonance, the allowed series are np and nf. We can assign peaks a, b, and c in Fig. 1 to the $4f$, $5f$, and $6f$ Rydberg levels as it is known that the f Rydberg series has an ac Stark shift equal to the ponderomotive energy [2,3].

Peaks d and e in Fig. 1 do not fall in this series and

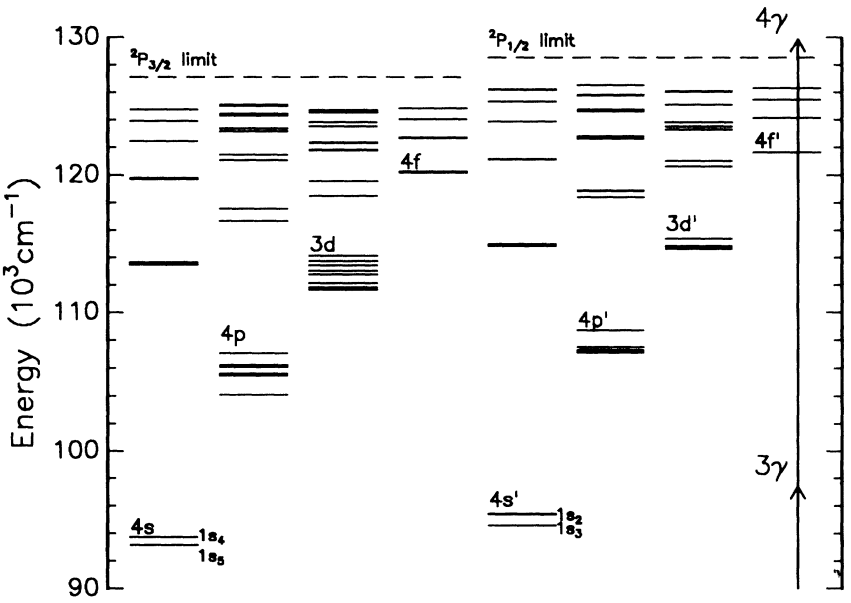

FIG. 2. Energy-level diagram of argon from Ref. [10]. The arrows show where three and four uv photons fall in the diagram, at zero field.

cannot result from a four-photon resonance. This leaves only a three-photon resonance. Three photons can only couple to the *ns* or *nd* series, and from Fig. 2 it is immediately clear that the only candidates for an intermediate resonance are the $4s$ and $4s'$ states. This can be further restricted by the three-photon selection rule for linearly polarized light ($\Delta J = \pm 1$ or ± 3) to the states with $J=1$ [11]. Using the notation in the tables of Moore [10], these are the $1s_2$ and $1s_4$ levels. Since the $4s$ and $4s'$ states do not have pure $^2P_{3/2}$ or $^2P_{1/2}$ cores, we must consider ionization from both levels to either the $^2P_{3/2}$ or $^2P_{1/2}$ ionization limit.

Assuming an ac Stark shift equal to the ponderomotive energy ($\alpha=1$) does not correctly predict the energies of the peaks in the data. Second-order perturbation theory [5] for the two states gives $\alpha(1s_2)=1.48$ and $\alpha(1s_4)=1.28$. Now using Eq. (4) with these ac Stark shift coefficients, the $1s_2$ state would produce two peaks at 4.20 and 4.02 eV corresponding to the $^2P_{3/2}$ and $^2P_{1/2}$ limits, respectively. Similarly, the $1s_4$ state produces peaks at 4.01 and 3.84 eV. Looking at Fig. 1, these results are in excellent agreement with the data. However, it should be noted that these peaks actually result from a three-photon resonant five-photon ionization process, unlike the more typical n-photon resonant $(n+1)$-photon ionization. In the case of the 4.20-eV peak the three-photon resonant four-photon ionization process is also allowed. This would produce a peak at 0.17 eV which is well below the low-energy cutoff of the electron spectrometer. Thus, we have identified the intermediate states responsible for the two peaks, *d* and *e*, in Fig. 1. Furthermore, we have verified that these states have an ac Stark shift significantly different from the ponderomotive energy. We have not attempted to explain the relative intensities of the four ionization pathways specified above, as would be necessary to understand the apparent absence of the 3.84-eV peak. However, it has been noted that MPI in the rare gases tends to favor ionization to the $^2P_{3/2}$ limit by more than what would be expected from a statistical argument (a factor of 2) [8]. This would select the 4.20- and 4.01-eV peaks and may simply be the dominant ionization pathway in this experiment.

The data in Fig. 1 were taken over a factor of 7 in peak intensity. In this range of intensity the position and width of the nonponderomotive peaks did not change at all within the accuracy of the measurement (10 meV). This entirely consistent with the resonant enhancement picture of MPI. If, on the other hand, a real population transfer had occurred, followed by ionization out of the excited state later in the laser pulse, the peaks would be broadened on the low-energy side of the peak by an amount up to the difference in the ac Stark shift and the ponderomotive energy at the peak laser intensity. In Fig. 1(b) the peak ponderomotive energy is 1.90 eV, and for the $1s_2$ state, this would lead to a possible broadening of 0.48×1.90 eV $=0.91$ eV. This is clearly inconsistent with the data. Thus, the only possible conclusion is that the electron peaks must result from a resonant enhancement of the MPI rate.

The widths of the electron energy peaks are consistent with the resonant model of multiphoton ionization [6]. The question arises as to whether a particular state is in resonance with the laser long enough to produce a narrow electron energy peak. If we assume that the time a level is in resonance with the laser is determined by the relatively large bandwidth of the laser, it is a simple matter to calculate the time in resonance as a function of peak intensity. Figure 3 displays this resonance time for a typ-

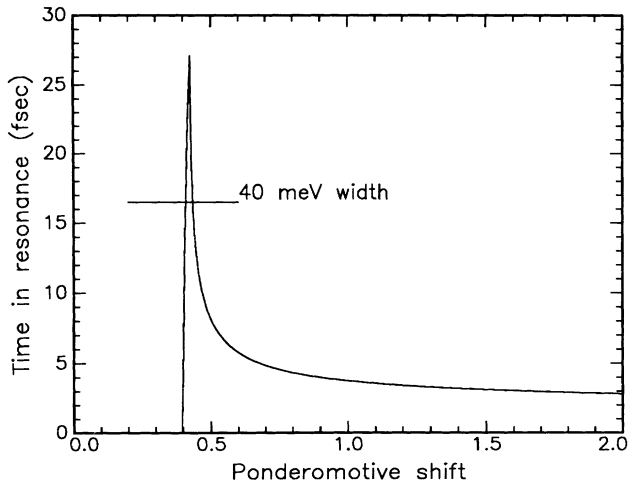

FIG. 3. Time in resonance vs peak intensity for a state with an energy of 15.6 eV.

ical Rydberg state in a 150-fsec laser pulse. From the measured width of the electron peak we can determine the minimum time required to produce a sharp peak from the uncertainty principle ($\Delta E \Delta t = \hbar$). The measured width of the peaks is 80 meV. However, the spectrometer resolution at 4 eV is no better than 40 meV. Assuming an upper bound on the real width of 40 meV we find that $\Delta t_{\min} = 16.5$ fsec. From Fig. 3 it is clear that the resonance must occur near the peak of the pulse. (Of course, due to the spatial gradients in the laser focus, there is always a volume where the peak laser intensity exactly matches the intensity required for resonance.) Resonantly enhanced ionization can still occur on the rising and falling edges of the laser pulse. However, this would symmetrically broaden the lines, and there is no indication of this in Fig. 1. The continuum in Figs. 1(b) and 1(c) in the 2.5–3-eV range is most likely due to nonresonant ionization at higher intensities.

One final point needs to be considered. It has recently been observed that after being exposed to short-pulse high-intensity radiation substantial population is left in excited states [4]. Based on the intensity dependence of the excited-state population it was concluded that the only states populated were those which had been brought into resonance with the laser field. Furthermore, the excited states with population were the same as those contributing to the short-pulse electron spectrum. It was from this observation that a two-step model of resonant excitation and subsequent ionization was proposed. While the two-step model can now be ruled out, the observation of excited-state population remains to be explained. It has been recently shown, under fairly general assumptions, that if an excited state has a large single-photon ionization cross section it will not give sharp photoelectron spectral peaks [12]. Conversely, it is those states with small photoionization cross sections that provide the resonant enhancement in the short-pulse spectrum. We, thus, propose the following scenario: When a state is shifted into resonance at the peak of the laser pulse it provides the resonant enhancement necessary to produce a sharp peak in the electron spectrum. There will also be a real population transfer. However, since the single-photon ionization rate out of this excited state will be small and the state is populated at the peak of the pulse, the real population will survive intact after the laser pulse is gone. This explains why it is seen [4] that precisely those states with an excited-state population after the laser pulse are the ones responsible for the short-pulse electron spectrum.

We conclude that (1) photoelectron peaks result from a resonant enhancement of the MPI from the ground state through intermediate states, (2) ionization from the temporal wings of the pulse is small with the main contribution coming from the peak of the pulse, and (3) real population transfer appears to occur when the resonant enhancement takes place although the contribution to the ionization from the excited states must be small.

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