Excitation and ionization dynamics in short-pulse multiphoton ionization

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We present results from a time-dependent two-level-plus-continuum model of multiphoton ionization in order to better understand the short-pulse photoelectron spectrum resulting from multiphoton ionization and the role of intermediate states. Both resonant and nonresonant population transfer to the upper state are found to play an important role in the multiphonon ionization process. The dynamic modeling reveals the potential for broadening and shifting peaks in the photoelectron spectrum. However, we conclude that despite the complex dynamics of the excitation, short-pulse photoelectron spectra can be used to measure ac Stark shifts of both ponderomotively and nonponderomotively shifted states in strong laser fields.

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INTRODUCTION

There is much interest in the interpretation of the sharp peaks in the photoelectron energy spectrum of atoms ionized by short-pulse high-intensity laser fields [1–7]. Surprisingly, it was found that intermediate resonances play a dominant role in this process [1]. The mechanism through which these resonances influence the electron spectrum and wavelength dependence of the process, however, has recently been the subject of some controversy [2–4]. It is the purpose of this paper to present a fairly general time-dependent two-level-plus-continuum model of multiphoton ionization and numerical results from direct integration of the Schrödinger equation in order to facilitate the interpretation of some of the seemingly conflicting experimental results. We conclude that the sharp peaks in the spectrum can be directly correlated with intermediate resonant states even in the case where the intermediate state shifts differently from the continuum in the intense laser field. Thus, the ac Stark shift of nonponderomotively shifted states can be measured.

Short-pulse photoelectron spectroscopy of atoms in strong fields began with the observation that in the short-pulse regime (in which the pulse length of the laser is much shorter than the time taken by an electron to leave the laser focus) the photoelectron spectrum consists of a pattern of sharp peaks with the pattern reproduced at intervals corresponding to the photon energy [1,8,9]. The origin 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. This enhancement was thought to occur through an excitation to the intermediate state when the state is in resonance followed by rapid ionization of the upper state. The original assumption in this model was that the ionization resulting from the interaction with a particular state only occurs at the resonance intensity. This simple picture has been used successfully to theoretically model experimental results, but, like other models, it is fundamentally a static description [5,10].

The resonance enhancement model of mulitphoton ionization leaves out two significant effects. (1) As was pointed out by deBoer and Muller [2], the upper state has a finite lifetime in the presence of the laser field. If the lifetime is too short, the upper-state resonance will be severely broadened and will not show up as a sharp peak in the electron spectrum. If the upper-state lifetime is long, real population can survive past the curve crossing in the upper state and can be ionized later in the laser pulse *at an intensity different from the resonance intensity* [2]. In the latter case, it is critical to consider the time-dependent nature of the problem. In fact, real population has been found, experimentally, to reside in excited states of the atom after interacting with a short-pulse laser showing that the upper-state lifetime can be at least on the order of the pulse duration [2]. (2) The highly nonlinear coupling between states in a multiphoton interaction can produce a strong driven population in the upper state even if the state is not in resonance. At intensities above the resonance intensity, it would appear that the coupling to the excited state would decrease as the state is shifted out of resonance. However, the detuning only

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scales as the square of the field strength if the state is shifted by the second-order ac Stark effect. On the other hand, in the perturbative limit, the multiphoton coupling strength increases as the nth power of the field. So for $n>2$ the coupling increases faster than the detuning, leading to a nonresonant interaction with the single intermediate state which can be greater than the resonant interaction. This is purely a multiphoton effect and will not occur in situations involving single-photon interactions and second-order Stark shifts. This nonresonant population transfer can just as well be ionized, but, again, *the ionization will not take place at the resonance intensity.*

For states with an ac Stark shift equal to the ponderomotive shift, the effect of real population transfer to the excited state changes the time in the pulse at which the ionization occurs but not the energy of the ionized electron [2,3]. This is not true for states with an ac Stark shift different from the ponderomotive energy and one might expect to see the sharp electron peaks associated with these states broaden and shift in the electron energy spectrum as a function of peak laser intensity [3]. Experimentally measured energy shifts of states in strong laser fields are of interest spectroscopically, as they can test calculations of ac Stark shifts.

Nonponderomotively shifted states have been identified in two different experiments [3,11]. In one of these experiments [3], it was observed that the electron peaks associated with the nonponderomotively shifted states did not broaden or shift with the peak laser intensity. One aim of this paper is to understand the behavior of the photoelectron peaks associated with nonponderomotively shifted states.

In order to gain a better understanding of the short-pulse photoelectron spectrum, we have constructed a two-level-plus-continuum model for MPI [12]. The model includes an ac Stark shift of the upper level, a nonlinear coupling between the states, a linear coupling of the upper state to the continuum, and the time dependence of the laser field. The Schrödinger equation is directly integrated in the rotating-wave approximation under various different conditions. We also include a discussion of the effects of volume integration over the focal distribution of intensities present in any real experiment.

The findings of this work are the following: (1) For short upper-state lifetimes the resonant structure of the ionization is severely broadened, (2) the effects of real population transfer and nonresonant excitation are clearly visible in the total ionization yield as a function of peak laser intensity, (3) independent of the upper-state lifetime, there is a sharp peak in the total ionization as a function of peak intensity at the resonance intensity, which explains the success of the resonant enhancement model of MPI, and (4) volume integration over the focal volume tends to enhance the peak in point (3) above, while reducing the importance of delayed ionization of the upper-state population and nonresonant excitation noted in point (2).

TWO-LEVEL MODEL FOR MPI

The full problem of the ionization of an atom in a strong field involves an infinite number of bound levels plus a continuum. While this complete system is very difficult to solve, several excellent approximations can reduce the problem to a two-level system. Many different methods have been used to study resonant MPI by strong fields and we will not reproduce those approaches here. We will simply state the main approximations to justify the actual set of equations used in the present study, which are based on the development of Holt, Raymer, and Reinhardt [12].

The two-level approximation includes the ground state $|g\rangle$ and the excited state $|a\rangle$ of the atom which is near to a multiphoton resonance with the laser field. The main effect of the rest of the nonresonant bound states is in the ac Stark shift of $|a\rangle$ and $|g\rangle$. The continuum can be incorporated into the model through an incoherent decay (ionization) of the excited state. We use the rotating-wave approximation and assume that the n-photon coupling is proportional to the electric field to the nth power resulting in the following equations [12]:

$$i\frac{d}{dt}\psi(t)=H\psi\ , \tag{1}$$

where

$$H(t)=\begin{bmatrix} 0 & \Omega(t) \\ \Omega(t) & \Delta(t)-i\Gamma(t) \end{bmatrix}\ , \tag{2}$$

and

$$\begin{aligned} \psi(t)&=\begin{bmatrix} g(t) \\ a(t) \end{bmatrix}\ , \\ E(t)&=E_0 e^{-t^2/\tau^2}\ , \\ \Omega(t)&=\Omega_n |E(t)|^n\ , \\ \Delta(t)&=\Delta_0+\alpha|E(t)|^2\ , \\ \Gamma(t)&=\Gamma_0|E(t)|^2\ . \end{aligned} \tag{3}$$

E_0 is the peak field, $\tau(2\ln 2)^{1/2}$ is the intensity full width at half maximum (FWHM) in time, Δ_0 is the zero-field detuning, α is the ac Stark shift coefficient, Γ_0 is the ionization cross section of the upper state, and Ω_n is the dipole coupling strength. All quantities are in atomic units. These equations were numerically integrated from $-t_0$ to t_0 with the initial conditions $g(-t_0)=1$ and $a(-t_0)=0$ using the fourth-order adaptive step size Runge-Kutta routine in Mathematica™.

NUMERICAL RESULTS

The first case that we consider in detail is similar to the experiments of Refs. [1] and [2], namely, the MPI of xenon through the $4f$ resonance with 620-nm radiation. The parameters that we hold constant are the following: $n=6$ (six-photon resonance), $\tau=3539$ (100-fsec intensity FWHM), $\Delta_0=-0.0265$ (zero-field detuning of the $4f$ level from six 620-nm photons), $\alpha=46.1$ (assumes that the ac Stark shift equals the ponderomotive shift at 620 nm), $t_0=10\,000$, and $\Omega_n=385\,000$. Ω_n was chosen simply to keep the total ionization through any one level very small, approximately 1%. This small value of Ω_n results

in mostly diabatic behavior at the curve crossing. This is in accordance with the general observation in short-pulse MPI experiments that the contribution of any single photoelectron peak is small compared to the overall ionization [1], although adiabatic effects have been seen to play a very important role in some related experiments [13–16]. Now, only two more parameters need to be specified: Γ_0 and E_0. The results will consist of the dependence of the total amount of ionization as a function of both the peak laser intensity and the final-state ionization cross section, or the upper-state population as a function of time during the laser pulse.

Figure 1 shows a typical example of the population of the upper state as a function of time through the pulse and displays a number of characteristic features. As the intensity in the pulse rises and brings the upper state into resonance (at the arrows in Fig. 1), real population is transferred to the upper state. This real population then experiences rapid Rabi oscillations. These oscillations damp out over the course of the pulse as the real population is ionized. If the upper-state lifetime is long enough, there is a possibility of interference in these oscillations between excitation on the rising and falling edges of the laser pulse [17]. The fact that real population persists through the pulse in Fig. 1 shows that ionization will take place throughout the laser pulse for this value of the upper-state cross section, an effect which cannot be described by static models [2]. In addition to the oscillatory behavior of the real population there is also a slowly varying component to the upper-state population which corresponds to the nonresonant population, as discussed in the introduction. The nonresonant excitation comes from the adiabatic following of the dressed states. When the field decreases the nonresonant part falls off, not because of ionization but because the driving force is gone. However, the nonresonant or driven excitation does represent population which can be ionized. This ionization will also occur throughout the laser pulse.

Figures 2(a) and 2(b) show the total fraction of atoms ionized by the laser pulse for two values of Γ_0, 3.0, and 0.3, and illustrate the effects discussed above in a somewhat different way. For the conditions indicated above,

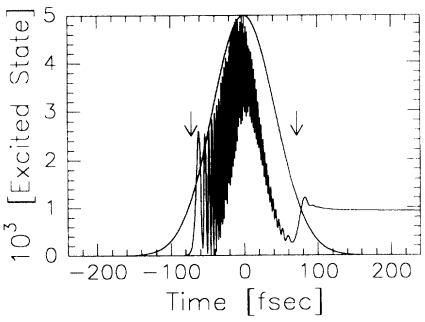

FIG. 1. Squared amplitude of the upper-state population during the laser pulse at a peak intensity of 8.4×10^{13} W/cm^2. $\Gamma_0=0.3$ corresponding to a lifetime of 140 fsec at the resonance intensity. The smooth line is the laser intensity pulse shape. The state is shifted through resonance at ±72.0 fsec, indicated by the arrows, at an intensity of 2×10^{13} W/cm^2.

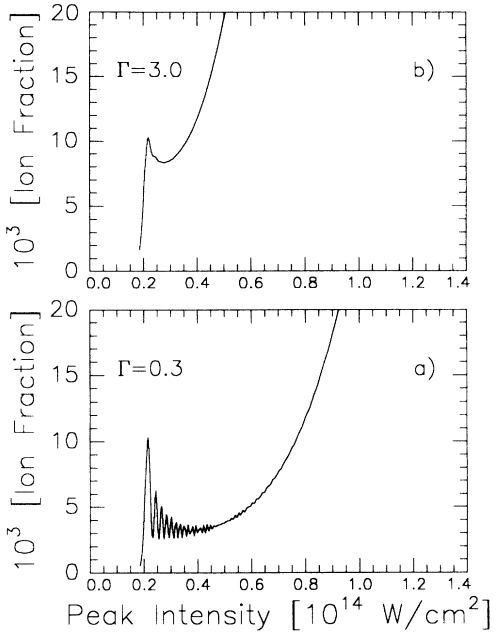

FIG. 2. Total fraction ionized as a function of peak laser intensity. The resonance intensity is at 2×10^{13} W/cm^2.

the intensity required to bring the upper state into resonance with the laser is 2×10^{13} W/cm^2. At this resonance intensity, the upper-state lifetimes for Γ_0 equal to 3.0 and 0.3 are 14 and 140 psec, respectively. In Figs. 2(a) and 2(b), the ionization has a local maximum when the peak laser intensity is equal to the resonance intensity. This maximum results from the long interaction time between the upper and lower states when the upper state is shifted into resonance just at the peak of the laser pulse. At higher intensities the ionization starts to increase nonlinearly. This is due to the nonresonant excitation of the upper state. The oscillations in the ionized fraction in Fig. 2(a) are a manifestation of the interferences in the Rabi oscillations of the real population excited on the rising and falling edges of the pulse. The oscillations are not present at the higher intensities because the ionization is dominated by the nonresonant excitation. Figure 2(b) shows that for short upper-state lifetimes there is only a very small peak in the ion yield as a function of peak intensity and much of the structure in Fig. 2(a) is washed out.

The second example we used is based on the experiment in Ref. [3]: MPI of argon with 308-nm radiation through a three-photon resonance with the 4s state, where the 4s state experiences a nonponderomotive shift. The parameters are as follows: $n=3$ (three-photon resonance), $\tau=3539$, $\Delta_0=0.009\,13$ (zero-field detuning of the 4s level from three 308-nm photons), $\alpha=16.94$ (ponderomotive shift at 308 nm times an ac Stark shift coefficient of 1.47), $t_0=10\,000$, and $\Omega_n=5.73$. Figure 3 shows the results for a relatively small upper-state cross section of $\Gamma_0=0.03$ corresponding to a lifetime at the resonance intensity of 1.5 psec. Again, there is a maximum at the resonance intensity and a rising ionization fraction at higher intensities. However, under these conditions, the in-

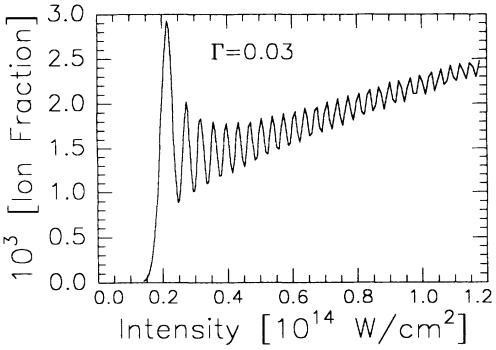

FIG. 3. Ion fraction vs peak laser intensity. The resonance intensity is at 1.9×10^{13} W/cm^2 The slight shift of the peak in ionization from the resonance intensity is on the order of the bandwidth of the pulse.

crease in the ionization is linear (when averaged over the oscillations) [2]. This was predicted by deBoer and Muller [2] and results from the ionization of real population. The increase in the ionization is linear for the following reason: when the excited state is brought into resonance in the temporal wings of the pulse, the amount of real population transferred to the upper state is relatively insensitive to the peak intensity (for a Gaussian pulse). However, at higher intensities there is more total flux available to single-photon ionize the upper state. Since the total flux is linearly proportional to peak intensity the increase in ionization is approximately linear. Figure 4 shows the upper-state population as a function of time through the pulse at an intensity of 1.3×10^{14} W/cm^2. Population is transferred to the upper state at the resonance intensity and then undergoes the Rabi oscillations. The oscillations damp out much more slowly in this case since the upper-state cross section is much smaller. However, there is almost no effect due to the nonresonant population because of the lower order of the dipole coupling. The interferences between the real population excited on the rising and falling edges of the pulse are also apparent in Figs. 3 and 4.

Although the effects of resonant population transfer and nonresonant excitation of the upper state are apparent in Figs. 1–4, it is clear that, except for very large

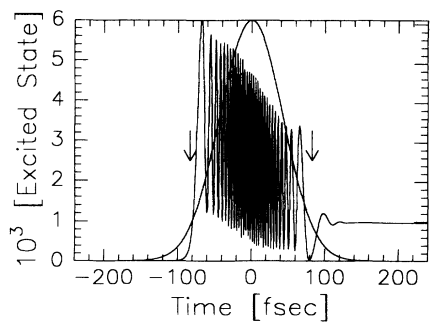

FIG. 4. Squared amplitude of the upper-state population as a function of time during the laser pulse at an intensity of 1.3×10^{14} W/cm^2. The state is shifted through resonance at ±82.8 fsec, indicated by the arrows.

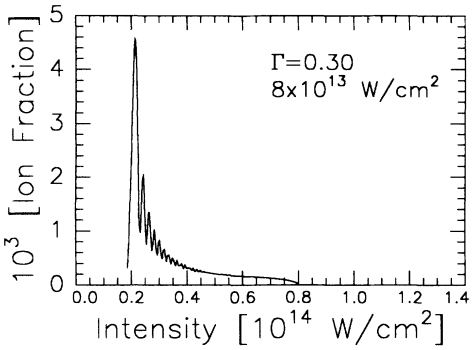

FIG. 5. Graph from Fig. 1(a) with volume factor at an intensity of 8×10^{13} W/cm^2.

Γ_0, the ionization peaks when the resonance occurs at the peak of the laser pulse. Furthermore, this peak is greatly enhanced by the effects of volume integration. If a laser beam with a spatial Gaussian mode is focused to an absolute peak intensity of I_0, then the volume which experiences a peak intensity greater than some intensity I is given by [18]

$$V(I,I_0)=\pi z_0\omega_0^2\left\{\frac{4}{3}\left[\frac{I_0-I}{I}\right]^{1/2}+\frac{2}{9}\left[\frac{I_0-I}{I}\right]^{3/2}-\frac{4}{3}\tan^{-1}\left[\frac{I_0-I}{I}\right]^{1/2}\right\}, \quad (4)$$

where z_0 is the confocal parameter and ω_0 is the waist of the beam. The absolute peak intensity means the maximum intensity anywhere in space *and* time. The local peak intensity is the maximum intensity in time at a given spatial coordinate. The question here is how does the volume averaging affect a result like Fig. 3: the total ionized fraction of atoms plotted as a function of peak intensity. If an experiment is performed with an absolute peak intensity of, say, $I_0=8\times10^{13}$ W/cm^2, the volume exposed to this intensity is zero [$V(I_0,I_0)=0$]. However, there will be volumes finite in size which see a local peak intensity I lower than I_0. The ionization at I must be weighted by a factor $dV(I,I_0)/dI$ where the derivative is with respect to I, not I_0. Now, from Eq. (4),

$$\frac{d}{dI}V(I,I_0)=\frac{\pi z_0\omega_0^2}{3}\frac{2I+I_0}{I^2}\left[\frac{I_0-I}{I}\right]^{1/2}. \quad (5)$$

Figure 5 shows the same graphs as Fig. 1(a) with the spatial weighting factor included with $I_0=8\times10^{13}$ W/cm^2. The volume factor is heavily weighted to the lower intensity. Thus, if an experiment is performed with an absolute intensity of 8×10^{13} W/cm^2 nearly all of the ionization signals will come from the spatial volume which sees a local peak intensity equal to the resonance intensity *independent of the ionization cross section of the upper state.*

DISCUSSION

Given the results above, it is not surprising that the original interpretation of the short-pulse electron spec-

trum, simply assuming a resonant enhancement of the ionization rate at the resonance intensity, worked so well in explaining the spectrum. Indeed, the electrons within a given peak in the energy spectrum are predominantly created at one intensity—the resonance intensity. However, it is critical that the pulse be smoothly varying in time and space: in time, so as to have a long interaction time at the peak of the pulse at a relatively constant intensity, and in space, so as to have a broad distribution of peak intensities. If, for instance, the pulse shape in time were triangular and the beam was focused to a flat top intensity distribution, it would not be true that the electrons would all be produced at the resonance intensity. In this sense, Ref. [2] was correct to point out that it cannot be taken for granted that the electrons are all ionized at the resonance intensity (for small Γ_0). However, for a laser pulse that is Gaussian in space and time, the assumption that all electrons are created at the resonance intensity is very good.

Finally, the combined effects of the long interaction time at the peak of the pulse and the volume averaging explains why the nonponderomotively shifted states identified in Ref. [3] did not broaden and shift with peak intensity. The energy of an electron ionized from a nonponderomotively shifted state will depend on the intensity at which the ionization occurred. The observation of narrow peaks associated with nonponderomotively shifted states implied that all of the ionization occurred at one intensity—the resonance intensity. This could have been explained by a short upper-state lifetime, but it is now clear that the electrons will always be dominated by the resonance intensity, independent of the upper-state lifetime.

CONCLUSIONS

The photoelectron spectrum has been seen to be characterized by sharp energy peaks reflecting the laser intensity which shifts the intermediate states into resonance. This is true even when intermediate states are shifting relative to the continuum. This verifies the value of the multiphoton ionization spectrum as a tool for studying the effect of strong laser fields on atomic energy levels even in the high-intensity nonperturbative limit.

We have shown that short-pulse electron-energy peaks are dominated by ionization at the resonance intensity independent of the upper-state ionization cross section because of two effects: the long interaction time at the peak of the pulse and volume averaging. This was previously shown for the case of very short upper-state lifetimes, but is here generalized to include long upper-state lifetimes.

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