Observation of Large Populations in Excited States after Short-Pulse Multiphoton Ionization

M. P. de Boer and H. G. Muller
FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands
(Received 22 January 1992)

Atoms subjected to an intense subpicosecond laser pulse (10^{13} W/cm^2, 100 fs) survive in excited states, as is shown by probing with a second laser. Electron spectroscopy with this 5-ns probe pulse enables identification of the resonant intermediate states as well as an unusually reliable energy calibration of the short-pulse electron spectrum. Only after incorporating population of intermediate levels is the mechanism for short-pulse multiphoton ionization consistent with the new data.

PACS numbers: 32.80.Rm

Advanced laser techniques are now making it possible to study atoms in super-intense light fields. Unfortunately a laser focus necessarily contains a range of intensities, which often complicates the experimental confirmation of the exotic effects predicted theoretically. Thus data which can shed light on the intensity at which an event takes place are of paramount importance.

A major breakthrough was an article by Freeman *et al.* [1], who measured narrow electron energy peaks while studying multiphoton ionization (MPI) with short pulses. ac Stark shifts of the excited states were comparable to the photon energy and each transition to an intermediate state was ac Stark shifted into resonance with a harmonic of the light field at one specific intensity. Acceleration of electrons by ponderomotive forces in the focal fringes, which previously cancelled such Stark shifts, was prevented by using subpicosecond pulses. Different resonances showed up as distinguishable peaks, typically 100 meV wide, in the electron spectrum. Following their discovery, these narrow peaks have been discussed in a variety of articles and for a selection of atoms. A topical review has recently appeared [2].

In this Letter we present the results of new experiments which are inconsistent with the generally accepted explanation of these peaks. We offer an alternative explanation, consistent with our measurements and with previous results. Our interpretation has large consequences for understanding already measured spectra, for studying the feasibility of future experiments, and for comparisons between theory and experiment.

Before discussing our experiment we will first describe two possible mechanisms for forming the narrow peaks seen in short-pulse MPI. Both mechanisms are largely based on ac Stark shifts of the ionization potential and of the excited states that occur at high intensities. Usually, shifts of the ground states of the atom and the ion can be neglected and the ionization threshold shifts upward, with an intensity-dependent ponderomotive energy

$$U_p(I) = e^2 I / 2 m_e \omega^2 \varepsilon_0 c . \quad (1)$$

At an intensity of 10^{13} W/cm^2 and for 620-nm light, this corresponds to a shift of 0.4 eV. This ponderomotive energy is equal to the additional kinetic energy, averaged over one optical cycle, of an electron quivering in a light field. Like the ionization threshold, but in contrast to the ground state, an excited state will shift in a light field. For high-lying states in which the electron is loosely bound this ac Stark shift will closely follow the threshold shift.

The generally accepted scenario to explain them is as follows [1–3]. A state shifts into resonance at one specific value of the ac Stark shift and thereby at one intensity [see Fig. 1(a)]. This selects the *excitation* intensity. It is then assumed that ionization out of the excited state always occurs before the intensity has drastically changed. This assumption is needed to extend the intensity selection to the *ionization* step, and implies that hardly any population remains in the excited states after the intense pulse.

Our alternative explanation for the narrow peaks [see Fig. 1(b)] treats resonant multiphoton ionization as an essentially two-step process. First a state is ac Stark shifted into resonance and populated. Subsequently, a fraction of the excited atoms is ionized. Ionization takes place at all intensities after excitation. The energy of all

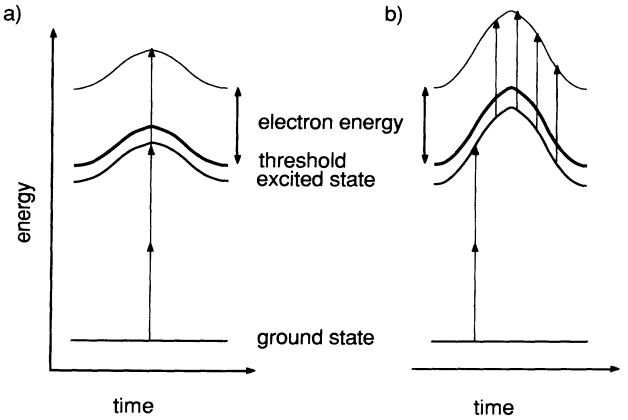

FIG. 1. The intensity-dependent shifts of an excited state and the ionization threshold as a pulse progresses. (a) The previously accepted mechanism for short-pulse MPI. Atoms are only ionized at an intensity where the excited state is resonant with the light field. (b) Our mechanism shows how ionization at a range of intensities, which we experimentally find to be the case, still leads to electrons being emitted at the same kinetic energy.

electrons ionized out of the same state is independent of the ionizing intensity because the intermediate state shifts along with the ionization threshold. This mechanism is similar to that described by Federov [4], except that our experimental intensity is not sufficiently large to produce enough mixing of the resonant Rydberg states to cause stabilization.

The width of a peak in the electron spectrum imposes a lower limit on the duration of its creation through the uncertainty relation. In the generally accepted scenario the entire width is due to this effect [3]. Most of the ionization must result from those parts of the focus where the resonant intensity is reached at the peak of the pulse, because the time of resonance on the leading or trailing edges of the pulse is too short to allow the narrow peaks. In our scenario ionization is going on during the entire pulse after excitation. If the shift of the resonant state is sufficiently close to that of the threshold, shifts will contribute little to the width of the peaks.

In order to discriminate between the two possible explanations we measure the excited-state population after the subpicosecond ("pump") laser pulse. On the nanosecond time scale of our experiment the excited states are stable against spontaneous decay. To probe the excited-state atoms, we use a second laser ("probe") pulse of a different color to photoionize all atoms left in excited states after the pump pulse. Saturating the one-photon transition, which depends on the fluence of the probe pulse, is necessary for a quantitative measurement. We therefore use a nanosecond probe pulse, enabling us to have a large fluence even at a relatively low intensity ($\approx 10^{11}$ W/cm^2).

Our experimental setup generates the pump pulses in a colliding-pulse mode-locked dye laser (CPM), amplified at 10 Hz in four Bethune-type dye cells. This system, that has been described elsewhere [5], delivers 620-nm, 100-μJ, 100-fs pulses. An injection-seeded Nd:YAG (yttrium aluminum garnet) laser pumps the amplifier stages. After frequency doubling, it delivers 5-ns, 532-nm pulses with a smooth temporal profile. Part of the light from the Nd:YAG laser is split off and used as a probe pulse. The pump and probe pulses are synchronized to better than 1 ns.

For our experiment we make use of a magnetic-bottle electron spectrometer [6] to attain 2π-sr solid angle in time-of-flight detection. To enhance resolution in a selected energy interval the electrons can be retarded before entering the flight tube. The spectrometer has a background pressure of ~ 0.5 μPa. During the experiments the interaction region was homogeneously filled with ~ 1 mPa of xenon. The pump and probe pulses are both linearly polarized along the spectrometer axis. We focus the pump pulse with a 200-mm achromatic lens into the spectrometer. The focusing of the probe pulses is much less tight than that of the pump pulses, so that the intensity of the probe pulses is virtually constant throughout the focus of the pump pulses. Observing the electron spectrum allows the overlap of the two foci to be optimized.

The spectrometer was calibrated with photoelectrons from xenon ionized by the 532-nm, 5-ns bandwidth-limited pulse. The energy of these electrons is sharply defined because the long pulse duration guarantees that Stark shifts of the ionization potential are cancelled by ponderomotive effects [1,7]. The energy of the peaks due to the subpicosecond light is reliably determined by generating these peaks simultaneously with the calibration peaks from an overlapping focus. This excludes systematic errors due to contact potentials.

The four different traces of Fig. 2 show the main results of our measurements. Traces (a) and (b) are similar to the spectra measured by Freeman *et al.* [1]. They are due to ionization of xenon with only the pump pulse present. Trace (b) was measured with a higher retarding voltage on the flight tube than trace (a). This improves the resolution at high electron energies but blocks low-energy electrons.

The new measurement is seen in trace (c) of Fig. 2. Both the pump and probe pulses are now present. Two new peaks, labeled $5f$ and $6f$, are readily seen. Trace (d) shows the difference between traces (b) and (c), and reveals a third new peak, labeled $4f$. The signal-to-noise ratio of the spectra is such that even with the loss of precision due to the subtraction this $4f$ peak is highly significant, as can be judged from the cancellation of the

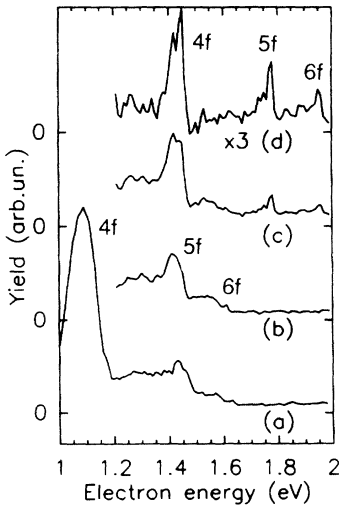

FIG. 2. The electron spectrum of xenon ionized by 100-fs, 620-nm pump pulses and measured at two different retarding voltages is shown in traces (a) and (b). Trace (c) is the electron spectrum with both pump and probe laser on. Trace (d) is the difference between traces (b) and (c) magnified 3 times. It is due to atoms excited to the $4f$, $5f$, and $6f$ states by the pump laser and subsequently ionized by the probe laser. These intermediate states also contribute the structure in traces (a) and (b), allowing its assignment.

pump-induced signal on its low-energy side. The new peaks, henceforth to be referred to as combination peaks, are due to the combined effect of both lasers since the intensity of the probe beam is too low to ionize ground-state xenon. They correspond to six-photon excitation by the pump pulse and subsequent ionization with one probe photon.

Assigning the combination peaks is assisted by angular momentum selection rules which only allow p, f, and h states to be reached with six photons from the $(5p)^6$ ground state of xenon. The h states are, however, very unlikely to occur. In addition, the intensity of the probe pulse is so low that ac Stark shifts and ponderomotive energies are negligible. Peaks should occur at electron energies exactly equal to the photon energy minus the binding energy of these states according to Moore's tables [8]. The combination peaks at 1.46, 1.78, and 1.95 eV thus correspond to ionization of the $4f$, $5f$, and $6f$ states, respectively.

We assign the structure in traces (a) and (b) of Fig. 2 to the same three f states but now ionized by one pump laser photon. In our scenario any ac Stark shift between the moment of excitation and the time of ionization is almost completely cancelled because the ionization threshold shifts just like the excited states. We therefore expect each peak in traces (a) and (b) to be approximately $\hbar\omega_{\text{probe}} - \hbar\omega_{\text{pump}} = 0.33$ eV lower in energy than the peak in trace (d) corresponding to the same resonance. From Fig. 2 we see that this is indeed the case. The correspondence between the peaks in traces (a) and (b), on the one hand, and the peaks of trace (d) was also checked in a different way. When the intensity of the red pulses was lowered so that a certain excited state cannot be shifted enough to become resonant, both peaks corresponding to this state disappeared at the same time.

We will now discuss our effort to make the results more quantitative. For photoionization via the three f states, the yield due to one green photon is seen in trace (d) of Fig. 2 and the yield due to one red photon is seen in trace (a). For one f state, the ratio of these two yields is insensitive to many experimental parameters such as the pressure, angular dependences of the ionization, and the detection efficiency of the microchannel plates.

Amplified spontaneous emission (ASE), which surrounds the intense red pulse in a ns-long, low-intensity pedestal, accounted for 20% of the energy in the red beam when measuring Fig. 2. If the green fluence is low, ASE might compete with it for the one-photon transition. We minimized this effect by ensuring correct timing of the pulses and by using a green fluence that was about 2 orders of magnitude larger than that due to ASE.

The ratio of the photoionization yield due to one green photon and one red photon was calculated by dividing the corresponding peak areas in Fig. 2. Two peak areas to be divided were measured with equal time of flights, to help avoid systematic errors owing to a possibly flight-time-dependent collection efficiency. This entailed measuring the peaks at different retarding voltages.

The measured ratios were 11%, 25%, and 56% for the $4f$, $5f$, and $6f$ states, respectively. According to Eq. (1) these states will be resonantly excited at intensities of 20, 11, and 7 TW/cm^2, respectively. The $4f$ state, needing the largest ac Stark shift to become resonant, will be predominantly excited in those parts of the focus where the red peak intensity is highest. A high peak intensity implies a high fluence and hence the $4f$ state should be the most likely to ionize during the red pulse, just as observed.

In our presented spectra, a signal due to p states is conspicuously absent. The peak intensity at which Fig. 2 was measured was not high enough to observe a signal due to the $7p$ resonance but was high enough for higher p states to be shifted into resonance. These higher p states are not discernible in our spectra but we cannot rule out that they do play a role. Their ionization cross section, an order of magnitude larger than for the f states, could explain their absence in the combination spectra. Either an ac Stark shift very different from the threshold or a short interaction time due to rapid ionization could cause their absence as narrow peaks in the pump-only spectrum.

We carried out additional experiments to see if the combination peaks behaved as expected. First, we confirmed that the combination peaks occur by ionization of excited states that remain after the red pulse. In the spectra shown, the center of the long probe pulse is delayed 2.5 ns with respect to the pump pulse. Delaying the probe pulse an additional 10 ns did not significantly decrease the combination peaks. Second, to confirm that we had sufficient fluence to ionize all the excited-state population with the probe pulse, we measured the size of the $5f$ combination peak as a function of the probe fluence. At very low fluences the yield is expected to increase linearly, but a plateau will rapidly set in once saturation has occurred. Assuming diffraction-limited focusing, we find this saturation fluence to be 3 J/cm^2. This value is in reasonable agreement with a saturation fluence of 1.39 J/cm^2 calculated on the basis of a hydrogenic model for the $5f$ state.

The calculated cross section can also be compared with the amount of population which is observed to survive the pump pulse. The calculated $5f$ cross section, 5.0×10^{-19} cm^2 for 2-eV photons, is also in accordance with the observed amount of population which survives the pump pulse. Therefore there is no experimental evidence that strong-field stabilization, as predicted to occur under more extreme circumstances by some theories [4,9,10], has played an important role.

Our experimental finding of population in excited states is not in accordance with the generally accepted mechanism for short-pulse MPI. In addition, we have shown that the assumption we need in our scenario, that the excited states shift along with the threshold, is indeed

fulfilled in our experiment.

The finding of population trapped in resonances after an intense pulse, although unexpected and not incorporated into the general theory, has been predicted theoretically [4,11,12]. Most articles, however, disregard population of excited states. Feldmann [13] has shown remarkable agreement between calculations by Dörr, Potvliege, and Shakeshaft [14] and the experimental data of Rottke *et al.* [15]. As far as we can see the calculations disregard population in the excited states after the pulse, and we wonder if the agreement is not rather fortuitous.

An important consequence of a slower ionization rate than is generally assumed is that a different spatial yield than generally assumed will result. McIlrath *et al.* [3] stated that the ionization yield will originate mainly from regions in the focus where the intensity needed to shift a certain state into resonance is reached at the peak of the pulse: There the interaction time is longer and the yield is quadratically higher. However, this is only true for the excitation yield. A case in point is a state which shifts into resonance at an intensity much lower than the peak intensity in the focus. Every atom at the moment of excitation experiences the same intensity. At positions where an atom is excited at the peak of the pulse, the fluence following excitation is too low to efficiently ionize it. At places where an atom is excited on the leading edge of the pulse, however, the high fluence during the rest of the pulse effectively ionizes the excited-state population. The ionization yield then arises mainly from those parts of the focus where the intensity at the peak of the pulse is much higher than the resonant intensity.

In conclusion, we have found that a substantial fraction of atoms excited by an intense, 100-fs pulse is not ionized. Our results show that an atom is ionized at a range of intensities following excitation. The sharp electron energy spectrum, found in short-pulse MPI, should be explained by taking into account the shift of the excited state as the intensity varies. The ionization lifetime of the excited state is of the same order of magnitude as the pulse duration and should be incorporated into theories relating to MPI.

We acknowledge stimulating discussions with P. H. Bucksbaum and also thank N. J. van Druten, A. Lagendijk, and B. Broers for carefully reading the manuscript. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for the Fundamental Research on Matter) and was made possible by the financial support of the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Research) and the European Community through Grant No. SCI-0103C.

[1] R. R. Freeman, P. H. Bucksbaum, H. Milchberg, S. Darack, D. Schumacher, and M. E. Geusic, Phys. Rev. Lett. **59**, 1092 (1987).

[2] R. R. Freeman and P. H. Bucksbaum, J. Phys. B **24**, 325 (1991).

[3] T. J. McIlrath, R. R. Freeman, W. E. Cooke, and L. D. van Woerkom, Phys. Rev. A **40**, 2770 (1989).

[4] M. V. Federov, in *Multiphoton Processes*, edited by G. Mainfray and P. Agostini (CEA, Saclay, France, 1991), p. 89.

[5] L. D. Noordam, W. Joosen, B. Broers, A. ten Wolde, A. Lagendijk, H. B. van Linden van den Heuvell, and H. G. Muller, Opt. Commun. **85**, 331 (1991).

[6] P. Kruit and F. H. Read, J. Phys. E **16**, 313 (1983).

[7] H. G. Muller, A. Tip, and M. J. van der Wiel, J. Phys. B **16**, L679 (1983).

[8] C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular No. 467 (U.S. GPO, Washington, DC, 1958), Vol. III.

[9] M. Pont and R. Shakeshaft, Phys. Rev. A **44**, R4110 (1991).

[10] R. J. Vos and M. Gavrila, Phys. Rev. Lett. **68**, 170 (1992).

[11] B. Sundaram and L. Armstrong, J. Opt. Soc. Am. B **7**, 414 (1990).

[12] K. C. Kulander, K. J. Schafer, and J. L. Krause, Phys. Rev. Lett. **66**, 2601 (1991).

[13] D. Feldmann, Comments At. Mol. Phys. **24**, 311 (1990).

[14] M. Dörr, R. M. Potvliege, and R. Shakeshaft, Phys. Rev. A **41**, 558 (1990).

[15] H. Rottke, B. Wolff, M. Brickwedde, D. Feldmann, and K. H. Welge, Phys. Rev. Lett. **64**, 404 (1990).