Fluorescence studies of multiphoton ionization of Ca and Sr: Emission from highly excited ionic states

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Multiphoton ionization of Ca and Sr was studied at a wavelength of 532 nm with optical pulses of 12-ns and 35-ps duration. Excess photon absorption followed by autoionizing decay leads to populations of excited states of singly charged ions that can be observed via their spontaneous emission. Relative measurements were performed on fluorescence from $Ca^+(4p)$, $Ca^+(5s)$, and $Ca^+(4d)$, and from $Sr^+(5p)$ and $Sr^+(6s)$. The contribution of the highly excited states was found to be favored under short-pulse (35-ps) irradiation.

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I. INTRODUCTION

Multiphoton ionization (MPI) of alkaline-earth-metal atoms has attracted considerable interest in the past decade. Investigations were first stimulated by the early reports of a direct two-electron ionization mechanism [1]. Subsequently, a number of studies with ns and ps duration optical pulses have indicated that double ionization is primarily a two-step process (see, e.g., Refs. [2–6]). In a single case, L'Huillier *et al.*[7] observed evidence for a direct mechanism through the slope of the Xe^{+2} production curve in MPI of Xe. These results were strongly dependent on the pulse length, with the single-step mechanism being enhanced with the shortest (5 ps) optical pulses. However, experiments based on detection of a direct signature of one-step two-electron MPI based on electron-energy measurements have not been successful. Nevertheless, between the two extreme cases of direct double ionization and two-step double ionization via the ground state of the singly charged ion, a number of two-step channels are possible via excited ionic states. An example is the recent observation by Hou *et al.* [8] of direct transitions to highly excited two-electron states in magnesium through electron-spectroscopic techniques. Such data provide a quantitative measure of the relative significance of high-order multiphoton absorption in the neutral atom in double-ionization processes. In an analogous experiment, we observed, via fluorescence detection, transitions to highly excited states in Ca and Sr for an irradiation wavelength of 532 nm and optical pulses of 12-ns and 35-ps duration.

The "all-optical" approach to the study of MPI phenomena is an extension of earlier work with a nanosecond dye laser and a strontium target [9,10]. This technique has been shown to be sensitive to the detection of weak channels and is particularly useful as a complementary approach to electron spectroscopy for low electron energies (≤ 100 meV) or where, within experimental resolution, the electron energies for different channels overlap. In the present case, improvements in the experimental setup as well as the extension to picosecond duration pulses greatly facilitated the observation of signals from highly excited ionic states. The relevant channels and energy levels in Ca and Sr are shown in Fig. 1. In the calcium case, direct four-photon absorption populating $Ca^+(4p)$ and six-photon absorption leading to population of $Ca^+(5s)$ and $Ca^+(4d)$ were analyzed. In the strontium case, the four-photon absorption signal associated with $Sr^+(5p)$ was compared with the $Sr^+(6s)$ five-photon signal. We monitored the strong electric-dipole emissions from the above states that have lifetimes $\sim 5-15$ ns. Since information on multiphoton absorption leading to population of low-lying ionic states is often available, the data obtained here can be placed on a quantitative basis by normalization to other works.

II. EXPERIMENTAL TECHNIQUE

The experimental setup is similar to that described earlier [9,10]. The frequency-doubled output from a Q-switched or mode-locked Nd:YAG laser was employed at a repetition rate of 10 Hz. The Q-switched laser yielded pulses of 12-ns duration and up to 300 mJ in energy at 532 nm. The mode-locked laser is based on a combination of acousto-optic mode locking and passive mode locking via a saturable absorber dye. Subsequent electro-optic pulse selection, double-pass amplification, and frequency doubling yielded pulses of 35-ps duration, and up to 12 mJ of energy. The laser intensity was adjusted by means of a combination of a half-wave plate and a Glan-Thompson polarizer. The laser-beam intensity in the focal place was determined by measuring the amount of energy transmitted through small apertures. Only linearly polarized light was used in this work. In spectroscopic studies, a ns-pulse-duration dye laser was pumped by the third harmonic of a Q-switched Nd:YAG laser. The laser beams were focused with a 35-cm focal-length lens into an oven where an atomic vapor was maintained at low density (~ 1 mTorr). Argon-buffer gas was utilized (≤ 100 mTorr) to prevent coating of the windows, but no signals were observed due to MPI of Ar.

The spontaneous emission from excited Ca^+ or Sr^+ ions was collected at 90° to the laser beam and analyzed with a 0.3-m monochromator, typically with slits of width 200 μm, which was also equipped with an EMI 9635 QB photomultiplier. The time-dependent analog signals were analyzed by a gated integrator and a boxcar averager.

Numerous careful tests were performed to characterize the dependence of the signals on both argon-buffer and alkaline-earth-metal atomic density. No dependence on Ar density was observed over the range of ~10–500 mTorr. Fluorescence signals were linear in alkaline-earth-metal atomic density from 20 μTorr up to ~100 mTorr, indicating that collisional effects are negligible on the time scale of ionic fluorescence. A density-squared dependence was observed for higher vapor pressures, with the onset of nonlinearity occurring first for the higher-lying states. A combination of color-glass filters was utilized to minimize effects from scattered laser light. In addition, calibrated neutral-density filters were employed to ensure a linear photomultiplier response.

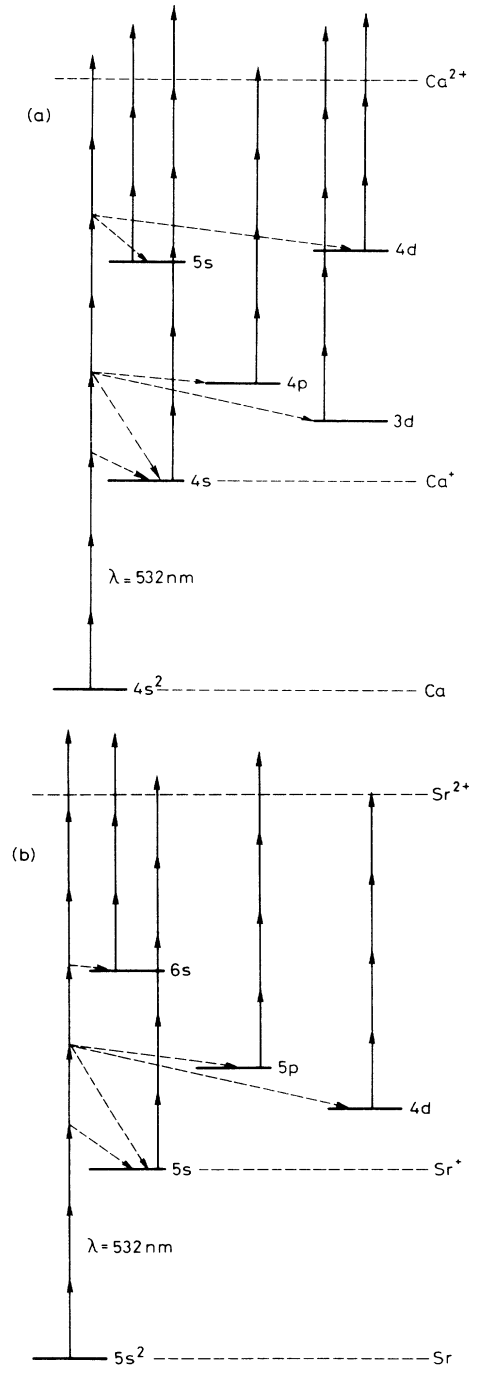

FIG. 1. Simplified energy-level diagrams and relevant MPI channels for neutral and singly ionized (a) Ca and (b) Sr.

III. RESULTS

A. Ca

Using a narrow-band (~0.08 cm^{-1}) resolution dye laser of ~10-ns pulse duration, the signal from $Ca^+(4p)$ was studied as a function of wavelength in the vicinity of the frequency-doubled Nd:YAG laser wavelength. Multiphoton ionization at 532 nm and leading to $Ca^+(4p)$ was determined to be nonresonant provided that intensity-induced level shifts and broadening effects are not dominant. Similarly, no resonant enhancement at this wavelength was found to occur for the highly excited states. (A detailed description of the spectroscopic studies in the wavelengths ranges of 490–540 nm and 555–590 nm can be found in Ref [11].) We subsequently conducted extensive measurements at 532 nm where a comparison of results for ns- and ps-optical-pulse irradiation could be made. The results are shown in Fig. 2, where the fluorescence intensity is plotted as a function of laser-pulse energy. The maximum intensity is $\sim 2\times 10^{11}$ W/cm^2 and $\sim 1\times 10^{12}$ W/cm^2 for the Q-switched and mode-locked cases, respectively. In cases where light emission could be studied down to sufficiently lower pulse energies [for both $Ca^+(4p)$ and $Sr^+(5p)$], the I^4 laser-intensity dependence expected from a perturbative treatment was observed. As seen from Fig. 2, a deviation from the I^n dependence (nth-order process) occurs at the highest intensities. This saturation of the fluorescence signal is caused by depletion of the neutral target atoms due to three-photon ionization. Results are shown for $Ca^+(4p)$, $Ca^+(5p)$, and a single point from $Ca^+(4d)$. The emission wavelengths are for $Ca^+(4p)$ (393.5 and 397.0 nm), $Ca^+(5s)$ (370.7 and 373.8 nm) , and $Ca^+(4d)$ (316.0, 318.2, and 318.0 nm), where the wavelengths are those found in vacuum. The correction for the combined wavelength-dependent efficiency of the photomultiplier tube and diffraction grating was negligible. The signals represent a sum over the fine-structure contributions, e.g., $J=\frac{1}{2}$ and $J=\frac{3}{2}$ in the case of $Ca^+(4p)$, although the separate contributions can be readily determined with the present experimental approach. In the region of saturation and for the highest pulse energies, the $Ca^+(4p)$ to $Ca^+(5s)$ fluorescence ratio is ~960 for Q-switched pulses and ~56 for mode-locked pulses.

B. Sr

Dye-laser scans indicated that MPI at a wavelength of 532 nm, and which populates $Sr^+(5p)$ and $Sr^+(6s)$, is

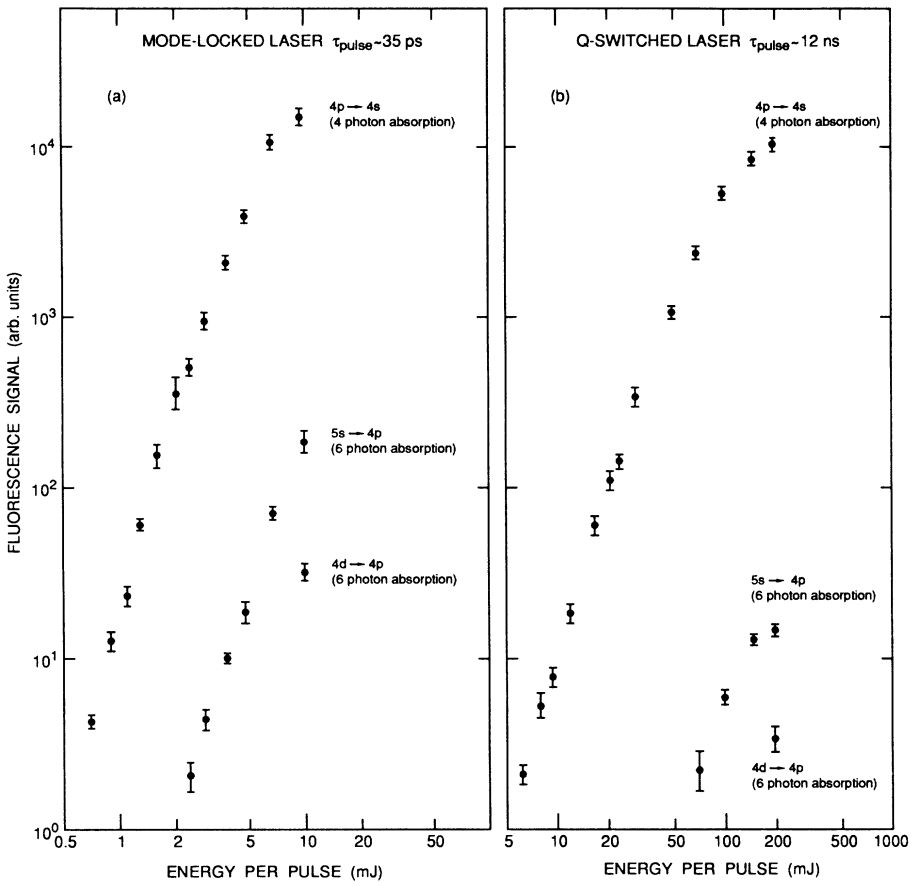

FIG. 2. State-specific MPI fluorescence signals for irradiation of a Ca target with (a) 35-ps-long and (b) 12-ns-long optical pulses. Note that only a single point at the highest irradiation intensity has been measured in the case of $Ca^+(4d)$.

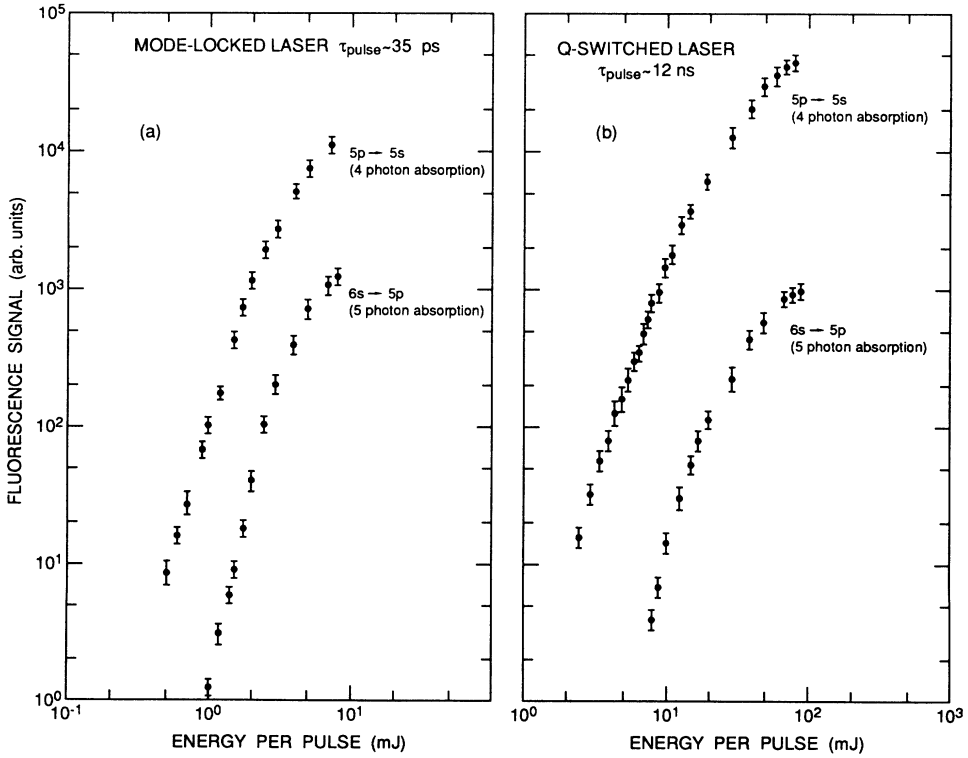

FIG. 3. State-specific fluorescence signals for irradiation of a Sr target with (a) 35-ps and (b) 12-ns optical pulses.

nonresonant. (The reader is referred to Kompitsas *et al.* [12] for a discussion of the autoionizing spectrum of Sr up to the $4d$ threshold.) The fluorescence wavelengths that were monitored, 407.7 and 421.5 for $Sr^+(5p)$ and 416.3 and 430.7 for $Sr^+(6s)$ are, as in the case of Ca, sufficiently close that corrections for wavelength-dependent detection efficiency were negligible. The fluorescence results are shown in Fig. 3 for the short- and long-pulse-irradiation cases. The correspondence of pulse energy with peak intensity is the same as in the calcium work. As in the case of Ca, the 35-ps-long pulses favor the population of the highly excited states. The $Sr^+(5p)$ to $Sr^+(6s)$ fluorescence ratio is in the saturation region ~ 47 for the Q-switched pulses and ~ 9 for the mode-locked pulses. Finally, it should be noted that the observation of more than one emission wavelength per state in both the Ca and Sr experiments provides a double check on the integrity of the signals. In addition, for both targets, very weak fluorescence signals were observed from a few other states [e.g., $Sr^+(6p) \rightarrow Sr^+(5d)$], but we have not attempted to quantify these results in the present work.

C. Computer simulation

In order to provide a first semiquantitative comparison with experimental results, a computer model of the atom-laser field interaction was developed. The model, which is analogous to that described by L'Huillier *et al.*[7] employed the energy levels from Fig. 1 in a set of coupled differential equations. The spatial and temporal properties of the laser pulse were approximated by Gaussian functions. The MPI cross sections were incorporated, but no account was taken of the ac Stark shifts of atomic and ionic states. Unfortunately, not all cross sections for the channels indicated in Fig. 1 were available. We decided to test the model only in the Sr case where considerable earlier experimental and theoretical work has been performed. (See the summary of Lambropoulos *et al.* [13].) The cross sections for four-photon pumping of $Sr^+(5p)$ and $Sr^+(4d)$, respectively, were taken as 2.3×10^{-109} $cm^8 s^3$ and 6.8×10^{-110} $cm^8 s^3$ from Ref. [13], while the corresponding value for five-photon pumping of $Sr^+(6s)$ was estimated to be 7×10^{-140} $cm^{10} s^4$. Extrapolation of a calculation by Crance and Aymar [14] yielded a value of 1×10^{-110} $cm^8 s^3$ for the channel $Sr^+(5p) \rightarrow Sr^{2+}$. Finally, the process $Sr^+(6s) \rightarrow Sr^{2+}$ was estimated to have a cross section 1×10^{-79} $cm^6 s^2$. In the case of the Q-switched (multimode) laser, the quantum-statistical factor $n!$, where n is the order of the process, was introduced into the individual transition probabilities [15]. This assumes that the Q-switched output approximated chaotic light.

On the basis of these values, we predict that in the saturation region, the $Sr^+(5p)$ to $Sr^+(6s)$ fluorescence ratio would be a factor of 30 for the ns pulses and a factor of 15 for the ps pulses. This should be compared with the experimental values of 47 and 9, respectively. The corresponding calculated ratios for four- to five-photon *absorptions* would be 45 and 7 for the ns and ps cases, respectively. Although the difference in fluorescence ratios for ns and ps irradiations is approximately a factor of 5 experimentally and only a factor of 2 from this computer model, the prediction is quite acceptable in light of the relatively large uncertainties that are involved. This simulation simply demonstrates that the data are consistent with reasonable assumptions for the various transition probabilities, and no attempt was made to adjust the initial cross-section estimates to fit the data.

IV. DISCUSSION

A. Comparison with results of other studies

The relative emission data for excited ionic states can be placed on an absolute scale through comparison with experimental works where the fractional contribution of $Ca^+(4p)$ and $Sr^+(5p)$ are determined separately. For example, in the Sr case, Lambropoulos *et al.* [13] concluded that for 20-ps pulses and an intensity of $\sim 10^{12}$ W/cm^2 at a wavelength of 532 nm, $\sim 7\%$ of the population is transferred to $Sr^+(5p)$. Assuming that the same fraction applies to the present 35-ps pulse situation and that the depletion to the Sr^{2+} limit is not much greater for $Sr^+(6s)$ population than for $Sr^+(5p)$, the maximum fluorescence signals from $Sr^+(6s)$ correspond to $\sim 0.7\%$ of the entire ionization. The computer model of Sec. III C was seen to support semiquantitatively the Sr data. The propensity for short optical pulses to favor the population of highly excited states is also expected on simple physical grounds based on minimizing depletion saturation during the rise time of the pulse [16]. However, contrary to the ps case, the 12-ns laser pulses are comparable to or longer than the fluorescence lifetimes, meaning that ions emit spontaneous radiation during the pulse. Though the computer model accounts for this fact, as well as the multimode structure of the ns-pulse laser (*but* only by assuming chaotic light), a long pulse more suitable for comparison would have been of ~ 1-ns duration and derived from a monomode oscillator.

The present results on the role of excited ionic states are in qualitative agreement with other results on alkaline-earth-metal atoms. Much recent experimental effort has been directed to the Mg case, where a larger number of photons is required for ionization than in the Sr or Ca cases. Hou *et al.* [8] have studied MPI in Mg, using picosecond pulses and $\lambda \sim 586$ nm. The role of highly excited states was elucidated through electron spectroscopy. Strong evidence was obtained for the absorption of nine photons to populate $Mg^+(4p)$ and possibly ten-photon absorption, leading to population of $Mg^+(5p)$. Their uncertainty in peak identification arises due to the overlapping electron energies from four different channels. Processes of higher order than in the present study have been observed in Mg, partly due to enhancement of the $3p^2\,{}^1S$ doubly excited state which lies above the $Mg^+(3s)$ threshold. The signals from high-lying states, although a smaller fraction of the total ionization, contributed in Mg at the level of several percent. The increased significance of high-order absorption processes in Mg as compared with Ca and Sr is also expected, due to the much higher saturation intensity of magnesium.

Other recent studies using electron spectroscopic techniques to investigate the role of excited ionic states have been conducted in a long-pulse regime. Kim *et al.* [17] observed above-threshold ionization effects leading to a population of excited Mg^+ states with 10-ns pulse irradiation at 532 nm. At this wavelength, the lowest-order ionization occurs through the absorption of four photons. The MPI populating $Mg^+(3p)$, which requires a minimum of six-photon absorption, contributed at a level of several percent to the total electron yield. A tentative identification was also made of signals at the 1–2 % level from $Mg^+(3d)$ and $Mg^+(4s)$. Di Mauro *et al.* [18] investigated the multiphoton ionization of Ca, using ~10-ns pulses at 532 nm and 1.06 μm. Evidence was obtained for four-photon absorption at 532 nm that populated $Ca^+(4p)$. Although the efficiency of the electron spectrometer was rather uncertain for energies < 100 meV, it appears that this channel represents ~1–2 % of the entire electron production. This fraction would likely be much enhanced in the picosecond-pulse case, but no electron-spectroscopic data are yet available for short-pulse irradiation of calcium.

B. Stark-shift effects and comparison with electron-spectroscopic techniques

A number of accurate cross sections are required before detailed quantitative conclusions are possible in the present work. In particular, the cross sections for pumping to the doubly charged ion limit [e.g., associated with $Ca^+(5s)+3\hbar\omega \rightarrow Ca^{2+}$] are difficult to calculate accurately due to transient resonance effects involving Rydberg states of the singly charged ions. Such Stark effects can also play a role in populating states of lower excitation. For example, the energy of $Sr^+(5s)+3\hbar\omega$ is detuned from the $J=\frac{3}{2}$ level of $Sr^+(6p)$ by only ~320 cm^{-1}. Another example is that of four-photon excitation from the $J=\frac{3}{2}$ level of $Ca^+(3d)$, which is almost exactly resonant with $Ca^+(8g)$. However, a multistep cascade through states, which are readily pumped to the Ca^{2+} limit, would be required to influence the observed fluorescence signals. To examine the role of transient resonances, we recorded the fluorescence signals with a fast digital oscilloscope. Cascade contributions from higher-lying states with longer lifetimes would be expected to extend the temporal duration of fluorescence decay. No significant change was observed in the temporal behavior over the full range of laser intensities. Hence, we conclude that under the present experimental conditions, ac-Stark-shifted mechanisms make at most a minor contribution to the population of excited ionic states. A different situation would be encountered with shorter optical pulses and higher laser intensities. This was illustrated by Freeman *et al.* [19] with subpicosecond pulses and intensities $> 10^{13}$ W/cm^2. Thus, an extension of the present work to the fs-duration regime offers interesting perspectives for the investigation of transient resonances.

There are obvious limitations to the optical studies in the investigation of high-order two-step double ionization. One is the ionization of the highly excited Ca^+ and Sr^+ states in the strong laser field. It is difficult for this reason to extend the work to even higher levels where the A coefficients also decrease. Nevertheless, the light-emission studies are quite complementary to detailed electron-spectroscopic work. For laser pulses < 1 ns in duration, the spontaneous emission reveals the population remaining in the states after the pulse, while the electron spectra are measurements of the total population transferred via a specific state. In addition, as many channels become comparable in importance in fs-pulse experiments, additional difficulties arise in the interpretation of electron-energy spectra due to overlapping electron-peak energies. In contrast, even optical studies with a monochromator represent high-resolution measurements and, as noted above, more than one emission line per state can often be utilized.

V. SUMMARY AND CONCLUSIONS

A study has been performed on the direct production of highly excited states of Ca^+ and Sr^+ in MPI of the neutral atoms by monitoring the spontaneous emission from these states. The channels associated with the high-lying states represent a small but non-negligible (~ a few percent) fraction of the total ionization for 35-ps optical irradiation at a wavelength of 532 nm. This conclusion is in qualitative agreement with results obtained in other works that employed electron-spectroscopic techniques. Indirect-population mechanisms, through transient resonant effects induced on excited states in the strong laser field, were found to play at most a minor role for intensities $\leq 10^{12}$ W/cm^2. A comparison of results for Q-switched (12 ns) and mode-locked (35 ps) optical pulses showed that the picosecond-long irradiation more effectively populates the highly excited states.

The population remaining in excited states of atoms and ions after irradiation with a strong laser pulse is part of the overall strong-field process and can be conveniently studied by the attendant spontaneous decay. Such an approach may even be relevant in the search for experimental evidence for stabilization effects at very high laser intensity [20]. In the future, experiments are planned that extend the present studies to wavelength-tunable setups and much shorter pulse lengths in the range of ~100 fs–1 ps, with an intensity range of $\sim 10^{11}$–10^{14} W/cm^2.

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