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Multiphoton Ca^{2+} production occurring before the onset of Ca^{+} saturation: Is it a fingerprint of direct double ionization?

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Abstract.

Singly and doubly charged Ca ions have been produced by multiphoton excitation of Ca vapor with 5 ns, low intensity ($\leq 3\times10^{11}$ W/cm^2) dye-laser pulses in the 675 - 685 nm wavelength range, including the four-photon $4s^2\ ^1S_0 \rightarrow 4p^2\ ^1S_0$ excitation. The intensity and wavelength dependence of the ion yields was recorded as well as the fluorescence emission from excited states of the Ca ion in an effort to identify the excitation pathways leading to single and double ionization. Unambiguous evidence for the absorption of at least two photons above the first ionization threshold was recorded, in agreement with earlier results for Mg and Sr obtained under similar conditions. However, certain characteristics of the process differ significantly from those earlier results, despite the apparent similarity in both the atomic structure and the excitation scheme. The most striking and unexpected finding is that for a certain wavelength the Ca^{2+} yield is observable well before the saturation intensity of Ca^{+} and, moreover, it grows with intensity and saturates in parallel with the Ca^{+} yield. Possible mechanisms behind this outcome are discussed in detail as well as their implications for the multiphoton multiple ionization of complex atoms. Our tentative conclusion is that the occurrence of doubly charged ion production before the singly charged ion saturation should not be considered as "synonymous" to direct (or non-sequential) multiphoton double ionization.

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1. Introduction

The multiphoton single and double ionization of alkaline earth atoms (Mg, Ca, Sr and Ba) is a process of fundamental interest for the field of laser-atom interactions because it can provide crucial details on the role of electron correlation in the process of multiphoton multiple electron ejection from complex atoms. The dense spectrum of autoionizing (AI) states above the first ionization threshold and all the way up to the double ionization threshold is a common feature of all alkaline earth atoms that is critically determined by correlation effects of the two optically-active outer electrons. Early work on single and double ionization of those atoms [1-6] with ns, moderate peak intensity ($\leq 10^{12}$ W/cm^2) laser pulses, revealed that the number of photons absorbed above the first ionization limit depends upon the nonlinearity of the process. For example, if the minimum number of photons required for single ionization was three or less, the number of photons absorbed above-threshold was rarely found to be more than one. On the other hand, high excitation/ionization nonlinearities lead to resonant or near-resonant ladder excitation schemes formed within the dense AI spectrum. The latter's role, however, was not very thoroughly investigated (in most cases due to the lack of tunability). More recently, studies on Mg [7] and Sr [8] re-examined the effect by intentionally connecting the ground state $ms^2\ ^1S_0$ (m = 3, 4 and 5 for Mg, Ca and Sr respectively) to the highly correlated doubly excited states $mp^2\ ^1S_0$, located just above the first ionization threshold, via four photons. In those experiments, it was unambiguously established that at least two (Mg and Sr) and possibly up to four (Sr) photons are absorbed in the structured continuum above the first ionization threshold. Subsequently, fast AI decay populates the ground state of the ion as well as a number of excited ionic states from which efficient double ionization occurs by further multiphoton absorption within the same laser pulse. These results on double ionization were in agreement with the body of existing fragmented experimental evidence [1-6,9-11] and offered a clearer and more systematic account of the details of excitation/ionization pathways. Despite the apparent similarities of the spectra of Mg and Sr and although common general features of the process were identified in both systems, certain non-trivial differences also emerged, obviously related to the specific structure of each atom. In view of this, we presently extend our study to the Ca atom, for the purpose of acquiring further insight into the particulars of the underlying mechanism. In the past, multiphoton excitation of Ca atoms with ns laser pulses at infra-red (1064 nm) and visible (532nm) wavelengths has provided evidence for excess photon absorption above the first ionization threshold [11], in accordance to other studies based on detection of fluorescence from excited Ca^+ states [12]. Recent results on double ionization of Ca by shaped femtosecond intense laser pulses [13] have hinted to the possible enhancing contribution of AI states to the process, but the evidence was partly inconclusive. In the present study, laser pulses of ~5 ns duration, intensity up to 3×10^{11} W/cm^2 and wavelength in the range 675 – 685 nm were employed, in accordance with excitation conditions in our earlier experiments with Mg and Sr. Recording Ca^+ and Ca^{2+} ion yields as a function of wavelength and intensity, as well as fluorescence emission from excited ionic states, we were able to confirm unambiguously the absorption of at least two photons above the first ionization threshold as well as AI-induced population of certain excited ionic states. The double ionization of Ca was confirmed to

occur by further multiphoton excitation within the ion for an extended range of wavelengths within the window scanned, as expected from our earlier findings. A signature of this sequential process, easily discernible from the intensity dependence of the ion yields at specific wavelengths, is that the onset of double ion production occurs at intensities higher than the saturation intensity of the singly charged ion. However, we have also identified a wavelength (~ 678.5 nm) for which the Ca^{2+} yield is significant and clearly observable well before Ca^{+} starts to saturate. In fact, the two ionic signals start to saturate at comparable intensities. In the context of our experimental conditions this is an extremely rare [2] and unexpected feature. With sub-ns pulses, the simultaneous occurrence and saturation of the singly and doubly charged ionic signals was always considered as a signature of direct or non-sequential double ionization [14-17], the two terms being used, almost indiscriminately, to describe a process in which the doubly charged ion is formed without any intermediate single ion production. However, this process has been mostly recorded for systems quite different from the alkaline earths (mostly heavy rare gases and He, whose structure is quite different from that of the alkaline earths, despite being the prototypical two-electron system) excited by short, intense infrared laser pulses. Under such conditions, double ionization is commonly attributed to a tunneling and rescattering mechanism [18]. Another criterion, often employed under such conditions, is the value of the Keldysh parameter, $\gamma = (\mathrm{IP}/2U_p)^{1/2}$, where IP is the ionization threshold and U_p the ponderomotive potential [16]. For $\gamma \leq 1$ the tunneling and rescattering mechanism is considered dominant, while for $\gamma >> 1$ the multiphoton mechanism prevails. Under our experimental conditions, the latter is the case, as explained below. Therefore, it is clear that from every point of view the conditions of the present experiment are vastly different from the ones described above and a tunneling and rescattering mechanism cannot be evoked to interpret the observed behavior. In the following paragraphs, after analyzing the available data as thoroughly as possible, we offer a tentative interpretation of this surprising finding, while awaiting further insight from future experiments.

2. Experimental procedure

The experimental setup and procedure has been previously described in detail [7,8] so here their presentation will be brief. Multiphoton ionization experiments are performed in an atomic beam apparatus whilst the fluorescence studies in a vapor cell. In both experiments the light source is a Nd:YAG pumped dye laser delivering linearly polarized pulses of ~5 ns duration and ~0.1 cm^{-1} linewidth at a repetition rate of 10 Hz. The laser system operates within the 675 - 685 nm wavelength range. The optogalvanic signal of an Ar-filled commercial hollow cathode lamp, into which a small part of the dye laser beam is directed, is used as an absolute wavelength calibration standard. The laser beam pulse energy (with amplified spontaneous emission (ASE) content less than 1.5%) is controlled by a variable attenuator without any spatial misalignment and measured by a digital joule-meter. Its maximum value is ~20 mJ. The latter corresponds to a maximum power density of $I \sim 3\times10^{11}$ W/cm^2 (under the assumption of a diffraction limited Gaussian beam profile) when the beam is focused by an $f \approx 10$ cm focal length lens.

Either the atomic beam chamber or the vapor cell is pumped by a 250 lt/min turbo molecular pump and a rotary pump system resulting to a background pressure of ~10^{-6} mbar. In the atomic beam experiment Ca vapor is produced in an electrically heated stainless steel oven at the top of the chamber. The oven temperature is ~700 ^{o}C resulting in an atomic density of ~10^{8} atoms/cm^{3} at the interaction point. The laser-atom interaction takes place within two circular stainless steel plates. One of the plates is grounded while a positive voltage is applied to the other for creating a ~70 Volts/cm static electric field. The produced singly- and doubly-charged Calcium ions are pushed by the field into a direction perpendicular to both the atomic and laser beams. The ions pass through the grounded plate via a ~2 mm hole and towards a 30 cm long time-of-flight (TOF) tube where they are discriminated according to their mass-to-charge ratio and detected by a dual micro-channel plate detector (MCP). The TOF system resolves the most abundant $^{40,42,44}Ca^{+}$ and $^{40,42,44}Ca^{2+}$ isotopes (see figure 1). The MCP signal is monitored by a digital oscilloscope, processed by a boxcar integrator and fed to a chart recorder and a personal computer.

For the fluorescence experiments the laser beam is focused into a quartz T-shaped tube where Ca undergoes continuous evaporation. Coating of the quartz windows with Ca is prevented by the use of a metallic mesh rolled around its main body and by the presence of 3 - 7 Torr He buffer gas (slightly higher than the Ca vapor pressure). An $f\approx$11 cm focusing lens is mounted inside the tube. The metal vapor fluorescent light is collected at 90^{o} with respect to the laser beam direction and analyzed by a monochromator - photomultiplier tube (PMT) system, sensitive within the 200 nm - 550 nm range. The PMT signal is processed by the same recording/storage system employed for the ions.

3. Excitation and ionization pathways

The partial – in scale – energy level diagram of figure 2 depicts the most relevant atomic and ionic levels involved in the present study. The aforementioned wavelength range is chosen so as to include the four-photon excitation of ground ($4s^2\ ^1S_0$) state Ca atoms to the $4p^2\ ^1S_0$ doubly excited state [19,20] above the first ionization potential. Owing to the dipole selection rules and the given initial state, four-photon absorption by linearly polarized light allows excitation of even parity states with total angular momentum J=0, 2 and 4. According to available spectroscopic data [19, 21], two $[3d6d]_{J=2,4}$ and two $[3d5g]_{J=2,4}$ neighboring states may also be excited by four-photon absorption, the relevant wavelengths lying between 679 nm and 682 nm. Within the third photon energy range only the bound doubly excited $3d4p\ ^1P_1$ state may be reached, expected at ~682.7 nm [22]. On the contrary, at the fifth photon level (where excitation to odd parity states with J=1, 3 and 5 is dipole-allowed) several members of the $4pns\ ^{1,3}P_1$ (n=11-15), $4pnd\ ^1P_1$ (n=10-14) and $[4pnd]_{J=3}$ autoionizing series [23] may be excited. All these states possess fairly large autoionization widths (tenths or even hundreds of cm^{-1}), particularly the 4pnd ones. There are no spectroscopic data for J=5^{o} levels. No resonances are expected around the sixth photon range, while the doubly excited state spectrum corresponding to the seventh- or higher-photon ranges is largely unknown. However, dense doubly excited 4fnl and 6fnl Rydberg series are expected around the eighth and ninth photon respectively,

since the corresponding Ca^+ 4f and 6f ionization thresholds lie within the corresponding wavelength range. Additionally, above the ninth photon energy range there exist the 8s and 7d thresholds with respect to which the relevant effective quantum numbers are ν ~6 – ~11 and ν ~7 – ~20, respectively. Therefore, the energy level structure around the ninth photon should be even denser and more complicated. Hence, the ladder system formed by 3d4p $^1P_1$ (third photon), $4p^2\ ^1S_0$ (fourth photon) and $[4pnl]_{J=1}^{o}$ with l=s,d and n~11 (fifth photon), as well as other unknown states lying even higher in energy could facilitate absorption of a number of photons larger than that expected on the basis of long-pulse/low-intensity multiphoton ionization studies (as implied also by our recent experiment in Sr [8]). Consequently, under the assumption of sequential double ionization, a number of excited ionic states would acquire population. Apart from Ca^+ 4s ground state, our experimental findings prove (directly or indirectly) the formation of 3d and 4p Ca^+ ions. For the presently available laser intensities, we expect a fairly weak Ca^+ 4s ground state contribution to the double ionization yield, since the latter would stem from either a seven-photon non-resonant or a 6+1-photon resonant ionization process though the 8d Ca^+ level. Both of these two processes should have very low cross sections. Therefore the largest, by far, contributions to sequential Ca^{2+} production must originate from 3d and 4p states. Six-photon ionization of the former level may proceed either non-resonantly or through the (possibly AC-Stark shifted) 5d and 7f ionic excited states (four- and five-photon resonance respectively). As for the Ca^{2+} yield stemming from the 4p states, it is of non-resonant character (five-photon ionization), even by taking into account possible AC-Stark or ponderomotive shifts of excited ionic states in the proximity of each absorbed photon.

For the purpose of comparison between the required number of photons necessary for Ca^{2+} production by the sequential pathways (a)-(c) and the direct one ($Ca \rightarrow Ca^{2+}$), the latter (d) is also included in figure 2. It is evident that, assuming that both Ca^+ and Ca^{2+} yields are unsaturated, Ca^{2+} production requires absorption of ten photons for the direct path and eleven photons for all sequential paths. The distinction between these two high orders of nonlinearity is not always easy as it is usually masked by experimental uncertainties. On the other hand, it is customarily expected that Ca^+ yield will saturate at intensities much lower than those corresponding to Ca^{2+} production due to the lower order of nonlinearity. Consequently, Ca^{2+} production through the direct process or other highly nonlinear mechanisms mimicking it, could possibly be assessed more reliably by simply observing if Ca^+ yield is saturated (or not) upon the appearance of Ca^{2+} signal.

4. Results and discussion

4.1 Laser wavelength dependence of Ca^+, Ca^{2+} and fluorescence yields

Typical Ca^+, Ca^{2+} and $4p_{3/2} \rightarrow 4s_{1/2}$ ionic fluorescence spectra are given in figure 3 for linearly polarized light and the maximum available laser intensity. Below we discuss separately the wavelength dependence of each yield.

4.1.1 Ca^+ yield. The highest laser intensity spectrum of Ca^+ (figure 3(a)) is dominated by three broad resonances structured over a considerable non-resonant background. Two of the resonances, at ~682.4 nm and ~683 nm respectively, are blended. The latter is assigned to the $4s^2\ ^1S_0 \text{—}4\omega\rightarrow 4p^2\ ^1S_0$ transition since its location and width practically coincide, within experimental uncertainties, to the spectroscopically determined values for the $4p^2\ ^1S_0$ doubly excited state [19,20]. The line is therefore found unshifted both for high as well as low intensities. This fact implies the occurrence of a stabilizing effect, whereby AC-Stark shift contributions from one-photon resonant states below ($3d4p\ ^1P_1$) and above ($[4pnl]_{J=1^o}$) the $4p^2\ ^1S_0$ one, lead to a nearly-zero dynamic dipole polarizability. A similar situation was encountered also in Sr [8]. On the contrary, the maximum of the line at ~682.4 nm (attributed to three-photon resonant, four-photon ionization of ground state Ca through the $3d4p\ ^1P_1$ intermediate state [22]), is found to be blue-shifted by ~0.35 nm with respect to its unperturbed location (~23 cm^{-1} in total excitation energy). This is to be expected since the $3d4p\ ^1P_1$ state has important AC-Stark shift contributions stemming solely from higher lying levels ($4p^2\ ^1S_0$). However, the shift is found to be intensity-independent down to the lowest intensity values allowed by the detection efficiency of our TOF system. In order to explain the above observation, it is first noted that the line is evidently quite asymmetric. It is well-known that under the employed laser intensities and tight focusing conditions such asymmetric profiles stem from the combination of two phenomena: (i) The AC-Stark shift, on one hand and (ii) The collection of ions produced over the entire laser-atom interaction volume on the other. Ions produced at different distances from the focal point sense different laser intensities and therefore undergo different shifts. The latter effect leads to asymmetric profiles and washes-out any shift intensity-dependence after spatiotemporal integration over the interaction volume. By recording the Ca^+ spectrum with the same pulse energy but under smoother focusing conditions (f~25 cm - not shown here) the line is found much more symmetric and slightly shifted towards its unperturbed location, since in that case the range across the focus over which the intensity suffices to produce Ca^+ is greatly reduced. However, under such conditions no Ca^{2+} was detected.

The weaker line at ~677.1 nm can not be assigned to any three- or four-photon excited level. Moreover, the fact that the line appears also in the fluorescence spectrum as well as the intensity dependence of the line's maximum (both discussed in more detail below) point towards a five photon resonance. Among the known relevant $[4p_jnl]_{J=1,3}$ (n~12-14, l=s,d) levels [23], the $4p14s\ ^1P_1$ one lies closest to the line maximum (within -40 cm^{-1}). All of the above states however are quite broad, particularly the 4pnd ones. This fact, in conjunction with the strong blue tail of the three-photon resonance ($3d4p\ ^1P_1$), may explain why it is the only five-photon excited state observed, while there are several other candidates within the same spectra range.

4.1.2 Ca^{2+} yield. The doubly charged ion spectrum consists of two broad resonant-like features and a non-zero background (figure 3(b)). The weaker and broader resonance (~683 nm) is evidently correlated to three-and four-photon excited atomic states ($3d4p\ ^1P_1$, $4p^2\ ^1S_0$) while for the strongest one (~678.5 nm) there is no straightforward connection to any atomic (singly or doubly excited) level. Within the studied wavelength range there are two groups of transitions connecting the $3d_j$ ionic

levels with the $5d_j$ (four photons) and $7f_j$ (five photons) ones before the ions ionize further to produce Ca^{+2}. The unperturbed locations of these transitions are marked in figure 3(b). It can be seen that they do not match well the maxima of the broad resonances. In order to clarify the role of AC-Stark shift to the disagreement, the relevant dynamic dipole polarizabilities of the above states were calculated by the Dalgarno-Lewis method and the numerical technique developed in [24]. The fine-structure splitting is ignored and the computation is restricted to an azimuthal quantum number m=0. The parametric Ca^+ potential curves given in [25] (see equation 3.26 therein) were used as input for the calculation. The computed dynamic polarizabilities are found to vary smoothly with photon energy so here we provide their frequency-averaged values which are: $\bar{a}_{3d} \approx -73$ atomic units (au), $\bar{a}_{5d} \approx +310$ au and $\bar{a}_{7f} \approx -247$ au. Using the value 3.5095×10^{16} W/cm^2 as an atomic unit of light intensity, these values result to $\approx -2.64\times10^{-11}$ nm/(W/cm^2) and $\approx +1.03\times10^{-11}$ nm/(W/cm^2) for the $3d_j \rightarrow 5d_{j'}$ and $3d_j \rightarrow 7f_{j'}$ transitions, respectively. Hence, by taking into account the AC-Stark shifts the agreement between expected and experimental Ca^{2+} maxima in figure 3(b) *worsens* (for both transitions). Therefore, there is no clear assignment for the strong feature around 678.5 nm. On the other hand, its shape, as recorded for different laser intensities (inset of figure 3(b)), implies that it may be composed from several resonances. Indeed, the weak bump at ~674.4 nm and the strongest feature at ~678.5 nm survive at low intensity, while another apparent maximum at ~679.3 nm is emerging for higher intensity values. Note that by computing the dipole polarizabilities of a number of other ionic states we have ruled-out the possibility that any of these levels come into resonance during the laser pulse.

4.1.3 Ca^+ radiative decay. The only ionic radiative decay lines detected, by widely scanning the monochromator's wavelength for several fixed laser photon energies, correspond to two resolved Ca^+ $4p_{3/2,1/2} \rightarrow 4s_{1/2}$ transitions at 393.4 nm and 396.8 nm respectively. All the data were acquired after ensuring that for our Ca-cell operating conditions the PMT signal varied linearly with Ca density. These experimental findings verify the absorption of six photons from Ca ground state (two of them above the first ionization threshold) and confirm the trend observed earlier in Mg [7] and Sr [8], under similar excitation conditions. It is anticipated that Ca^+ $3d_j$ states are also populated by five-photon ionization and/or by the unobserved ionic $4p_{3/2,1/2} \rightarrow 3d_j$ radiative decay. On the other hand, the data do not provide evidence for absorption of more than six photons by the Ca atom, in accordance to Mg experiment but in contrast to Sr data. Therefore, if other ionic states (lying higher than the $4p_j$ ones) are indeed populated, subsequently to, for example, autoionization of doubly excited Ca, these states should be further ionized to Ca^{2+} quite efficiently (saturated $Ca^+ \rightarrow Ca^{2+}$ step). As for the fluorescence's laser wavelength dependence, let us first note that it is identical for the $4p_{1/2} \rightarrow 4s_{1/2}$ and $4p_{3/2} \rightarrow 4s_{1/2}$ components, so only the latter is given in figure 3(c). It is remarkable that there is a small non-resonant background even at laser intensities somewhat lower than the maximum ones employed in the photoionization experiment. Moreover, there is a clear spectral fingerprint of the resonances corresponding to the 3d4p $^1P_1$ and $4p^2$ $^1S_0$ states. A comparison with Ca^+ spectra reveals more symmetric fluorescence line profiles as well as the absence of any long blue tail for the 3d4p $^1P_1$ resonance, presumably because six-photon absorption occurs only near the la-

ser beam focus whereas the (lower nonlinearity) ionization signal is produced over a wider interaction volume. Thus, fluorescence detection experiences spatiotemporal laser-atom effects of much lesser importance. Finally, the spectrum shows two additional broad lines that should be attributed to five-photon excitation of doubly excited 4p*nl* states having appreciable autoionization widths. The first at ~677.1 nm is also observed in Ca^+ spectrum while the other at ~679.5 nm is probably masked under the aforementioned blue tail. Both resonances are located below the $4p_{1/2}$ limit (by ~650 cm^{-1} and ~900 cm^{-1} respectively) and they show-up in the fluorescence spectra due to the absorption of an additional (sixth-) photon leading to the population of both $4p_{3/2,1/2}$ states. The ~679.5 nm line is found to be somewhat shifted with respect to the strongest resonance of the Ca^{2+} spectrum.

4.2 Orders of nonlinearity for singly and doubly charged ion production

Signal *vs* laser intensity (*S vs I*) curves for Ca^+ and Ca^{2+} were recorded for the laser wavelengths labeled as A-E in figure 3(b). The apparently unsaturated parts of those curves were fitted to the power-law form $S \propto I^K$ and the orders of nonlinearity (K_+ and K_{2+} for singly and doubly charged ions, respectively) extracted from the fits are assembled in table I. Two examples of signal *vs* laser intensity curves are given in figure 4 for 683.7 nm (E) and 678.5 nm (B). The former lies on the red side of the $4p^2\ ^1S_0$ resonance and was chosen for reducing any influence stemming from a possible red tail of the 3d4p $^1P_1$ three-photon excitation. Nevertheless, for point (E) as for the $4p^2\ ^1S_0$-maximum (D) the Ca^+ order of non-linearity is $K_+ \approx 4$ - a result to be expected for a four-photon excitation/ionization process. In fact, most of the fitted K_+ values are found to be ≈4. There are two exceptions corresponding to 682.3 nm (3d4p $^1P_1$-maximum, C) and 677.1 nm (maximum of weaker broad line, A). For the latter wavelength, due to the absence of three- or four-photon resonances, the order of nonlinearity $K_+ \sim 5$ clearly implies a five-photon resonance, in accordance to the appearance of this line in the fluorescence spectrum. The $K_+ > 4$ value for wavelength C can be explained by the presence of the 3d4p $^1P_1$ intermediate level. It is well known that in the vicinity of a resonance the observed order of nonlinearity may be found to be higher as well as lower than the true number of photons absorbed by the atom, since in this case this quantity only expresses atomic level shifts [26].

Let us now discuss the fitted K_{2+} values. From table I it may be noted that they all fall in the range 7-10 except the one corresponding to 677.1 nm, which exhibits the very low value of $K_{2+} \sim 4$. Taking into account that for that wavelength Ca^{2+} appears when Ca^+ is already saturated, the low K_{2+} value simply reflects the occurrence of ionic 3d→5d transitions shifted into resonance by the laser field. Among the other wavelengths, particularly interesting are the B and D ones which show high $K_{2+} \sim 10$ nonlinearities. However, even more important is the fact that of all the data of table I, it is only for B that the Ca^{2+} signal appears *well below* the onset of Ca^+ saturation. The relevant graph is shown in figure 4(b) and corresponds to the maximum of the main Ca^{2+} lobe - see figure 3(b). In fact, this graph shows practically simultaneous saturation of both Ca^+ and Ca^{2+} signals which are, additionally, of comparable magnitude. It is interesting to note that, as mentioned earlier, there are

no ionic resonances at that wavelength (since the nearest 3d→5d one is shifted *away* from the observed maximum). As for the atomic spectrum, it may be postulated that there exist five-photon resonances (particularly the $[4p13s]_{J=1}$ one - see figures 3(a),(b) - which however does not appear in the fluorescence spectrum) as well as others lying above the sixth photon from the ground state. These resonances may not be exact and therefore it is expected that excitation takes place under (either atomic or ionic) *near*-resonant conditions.

4.3 Synthesis

Having presented our data, we now proceed to their discussion and comparison to the findings from our previous studies on Mg [7] and Sr [8]. In all three experiments the atomic ground state is connected to $mp^2\ ^1S_0$ doubly excited states via four photons. These states are strongly one-photon coupled with bound (below) and autoionizing (above) atomic levels. In Mg this strong coupling results to a large nonperturbative shift of the resonance, apparently because there is just a single state at the fifth-photon level. On the contrary, for Ca and Sr the existence of a large number of five-photon excited autoionizing Rydberg states leads to an overall nullification of the dynamic dipole polarizability and mp^2 resonances experience small (Sr) or zero (Ca) shifts. Nevertheless, the multitude of near-resonant levels establishes in all cases favorable conditions for absorption of two photons within the continuum. In fact, the (fluorescence) data of Sr support the absorption of at least two more photons before the production of singly charged ions.

It is also interesting to compare the signal *vs* laser intensity plots concerning the doubly charged ions. The Mg^{2+} yield appeared above the onset of Mg^+ saturation (in fact theory predicted it was itself saturated). The same holds for Sr apart of the location of the $5p^2\ ^1S_0$ resonance where the (weak) Sr^{2+} signal appeared *slightly* below the onset of Sr^+ saturation and it was accompanied by a weakly evident but reproducible inflection point ("knee" structure, see [8] and references therein). A more interesting behavior emerges in the Ca experiment. By recording signal *vs* intensity curves for a number of wavelengths, quite different behaviors are unveiled. In all but one cases, the, by now, trivial observation emerges that Ca^{2+} appears well above the saturation intensity of Ca^+. There is however a specific photon energy, which cannot be correlated to known doubly excited atomic states (or even ionic states) and at which Ca^{2+} appears *well before* the occurrence of Ca^+ saturation. Moreover, at that photon energy Ca^{2+} and Ca^+ yields are comparable in magnitude, although the nonlinearity of the process is quite high (K_{2+}~10). Surprisingly, this high order of nonlinearity is compatible with the direct double ionization process. On the other hand, at that photon energy the Ca^{2+} spectrum suggests the presence of at least one resonance which, additionally, disappears with circular laser polarization (not shown here). Evidently, doubly excited intermediate states, located necessarily above the fourth-photon level are involved in the process. Nevertheless, by taking into account the long laser pulse duration and its low intensity it is difficult to adopt a direct double ionization scenario. The latter is furthermore not supported by the fluorescence experiment since it did not reveal the presence of population into ionic states lying higher that the $4p_j$ ones. Of course, this fact may be attributed to the low maximum available laser intensity (~3×10^{11} W/cm^2); the lowest

employed in our experiments with alkaline-earths so far. It is probable that fluorescence signals were just too low as compared to our detection efficiency. There exist however other possible, sequential in nature, double ionization scenarios that could mimic the direct process and involve double Rydberg states. Assume, for example, that an atomic resonance is reached at, say, the eighth or ninth photon from the ground state and that the transition is (presumably) unsaturated. One possibility is, of course, that by an additional photon the atom will be doubly-ionized [27]. Alternatively (and far more probably), autoionization may produce highly excited Ca^+ ions. The latter may subsequently be ionized by one or two photons. The measured order of nonlinearity will simply reflect the excitation process since the one- or two-photon ionization step within the ion is expected to be saturated. Additionally, no highly excited Ca^+ ions will survive over such a process while its identification by fluorescence detection is quite improbable because ionization will dominate over their radiative decay for the laser intensities considered here. Mechanisms resembling the above scenario have already been observed in Alkaline Earth atoms, albeit within a different, multi-color stepwise excitation scheme [27,28]. There is however another alternative explanation to the above observation. Note, for example, that at wavelength D an order of nonlinearity of ~10 is also recorded while Ca^{2+} appears above the saturation intensity of Ca^+. Hence, it is possible that the detection efficiency of our TOF system is in the case of wavelength B simply enough for Ca^{2+} to be observable below Ca^+ saturation, while this is not so for the other wavelengths at which the signal is weaker. Even so, this quite different behavior implies different underlying mechanisms. Clarifying this point and the exact role of near-resonant doubly excited states (by, for example, an electron energy analysis experiment) is thus of great interest. Nonetheless, the results of the present study raise another issue of, perhaps, even greater importance. Specifically, it renders the so far considered as a well established criterion on the emergence of direct or non-sequential double ionization of questionable significance and value. Since in the present experiment the multiphoton laser-atom interaction picture applies (as implied by the Keldysh parameter [16] value of ~15>>1) the discussion at present should be restricted to that picture only and no appeal to tunneling or over the barrier ionization mechanisms can be reasonably made.

5. Conclusion

We have presented the results of an experimental study on single and double multiphoton ionization of Calcium with laser pulses of ns duration, low intensity ($\leq 3\times10^{11}$ W/cm^2) and a photon energy range that included the four-photon $4s^2\ ^1S_0 \rightarrow 4p^2\ ^1S_0$ transition. The study was based on detection of Ca^+ and Ca^{2+} in an atomic beam apparatus as well as detection of fluorescence stemming from the $4p_{1/2,3/2} \rightarrow 4s_{1/2}$ radiative decay of excited Ca^+ in a vapour cell experiment. Observation of the particular fluorescence transition constitutes a direct proof of absorption of two photons above the first ionization threshold. This fact signifies that laser-atom interaction is critically mediated by the presence of (autoionizing and bound) doubly excited states forming resonant or near-resonant excitation ladders. For the present experiment, for which the multiphoton picture applies, the process relies on the existence of dense AI structure whose properties are determined by intra-atomic electron corre-

lation effects. It, therefore, differs qualitatively from the mechanisms involved when short and intense infrared laser pulses are employed to irradiate rare gases. In that latter case, for which the tunnelling and recollision mechanism is considered valid, the dominance of electron correlation is not critical for observing multiple photon absorption within the continuum and eventually double electron ejection.

Our present findings are in agreement with the trend observed also in Mg [7] and Sr [8] in the vicinity of the corresponding four-photon transitions. Nevertheless, an additional, interesting and rare feature was revealed by the orders-of-nonlinearity for Ca^+ and Ca^{2+} production. For all-but-one wavelengths the onset of Ca^{2+} detection occurred at power densities higher than Ca^+'s saturation intensity. For a specific wavelength however, Ca^{2+} yield was found comparable in magnitude to that of Ca^+, it showed a resonant maximum, exhibited an order-of-nonlinearity compatible with a direct double ionization scenario and, finally, the onset of its detection occurred well before Ca^+'s saturation intensity. Moreover, the two yields saturated at the same laser intensity. The latter observations were considered in the past as a strong indication of direct double ionization because they imply that singly and doubly charged ions pump out of the same population of neutral atoms [14]. Our dynamic polarizability calculations are also supportive towards such a scenario as they show that the observed resonant structure could not be attributed to any AC Stark-shifted ionic multiphoton transition. On the other hand, the absorption of more than two photons in the continuum is not supported by the fluorescence experiment, contrary to observations in Sr [8] and in accordance to a very low direct double ionization probability expected under our conditions. Therefore, the double ionization mechanism around that specific Ca^{2+} resonance remains unclear at present, the only certainty being its coexistence with well understood and unambiguously interpreted, sequential double ionization pathways within the examined laser wavelength range.

Evidently, more helpful for clarifying the above or similar situations would be an electron energy analysis experiment or the employment of presently available experimental techniques of multi-coincidence nature, such as COLTRIMS and related ones [29]. The latter may under specific circumstances unambiguously unveil the exact double or multiple ionization mechanisms. The technique however has been mostly applied to noble gasses [29], lacking dense manifolds of doubly excited states just above the first ionization limit. Additionally, these studies are not been customarily carried out within the multiphoton regime. It is for the above reasons that in numerous recent multiphoton multiple ionization studies, performed with short and intense EUV pulses, the findings are still discussed in terms of the observed orders of nonlinearity (see, for example, [30]). Consequently, one of the major conclusions of the present work is that doubly charged ion detection before singly charged ion saturation should no longer be considered as an unambiguous indicator of direct double ionization, particularly under the presence of intermediate resonances. It is anticipated that this remark could hold for a variety of laser wavelength, peak intensity and pulse duration values. Also, it will be worth examining its pertinence under conditions such that the tunnelling and rescattering mechanism prevails.

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Figure Captions.

Figure 1. Typical TOF mass spectrum recorded for the indicated laser wavelength and intensity. Note that at this wavelength the singly and doubly charged Ca ions are of comparable magnitude. The Ca^{+} peak is somewhat broader, as compared to the Ca^{2+} one, due to weak space charge effects.

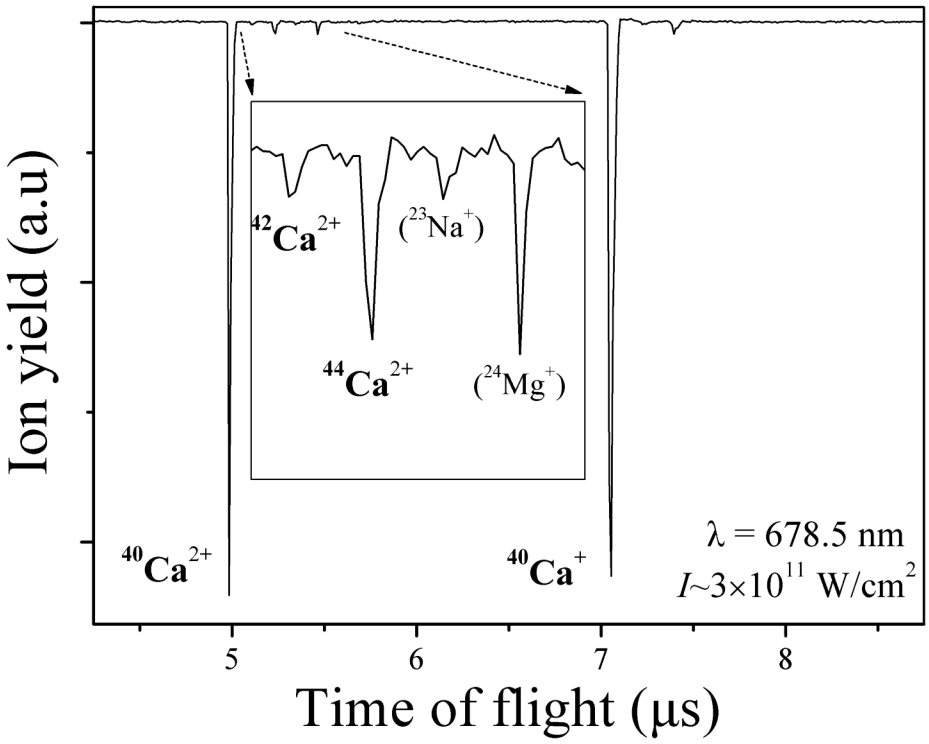

Figure 2. Partial – in scale – energy level diagram depicting the most relevant Ca and Ca^+ levels involved in the present study. Pathways (a)-(c) refer to sequential double ionization while pathway (d) to the direct one. For the latter, a few thresholds in the vicinity of the eighth and ninth photon have been drawn. Also noted is the observed ionic $4p_{1/2,3/2} \rightarrow 4s_{1/2}$ radiative decay.

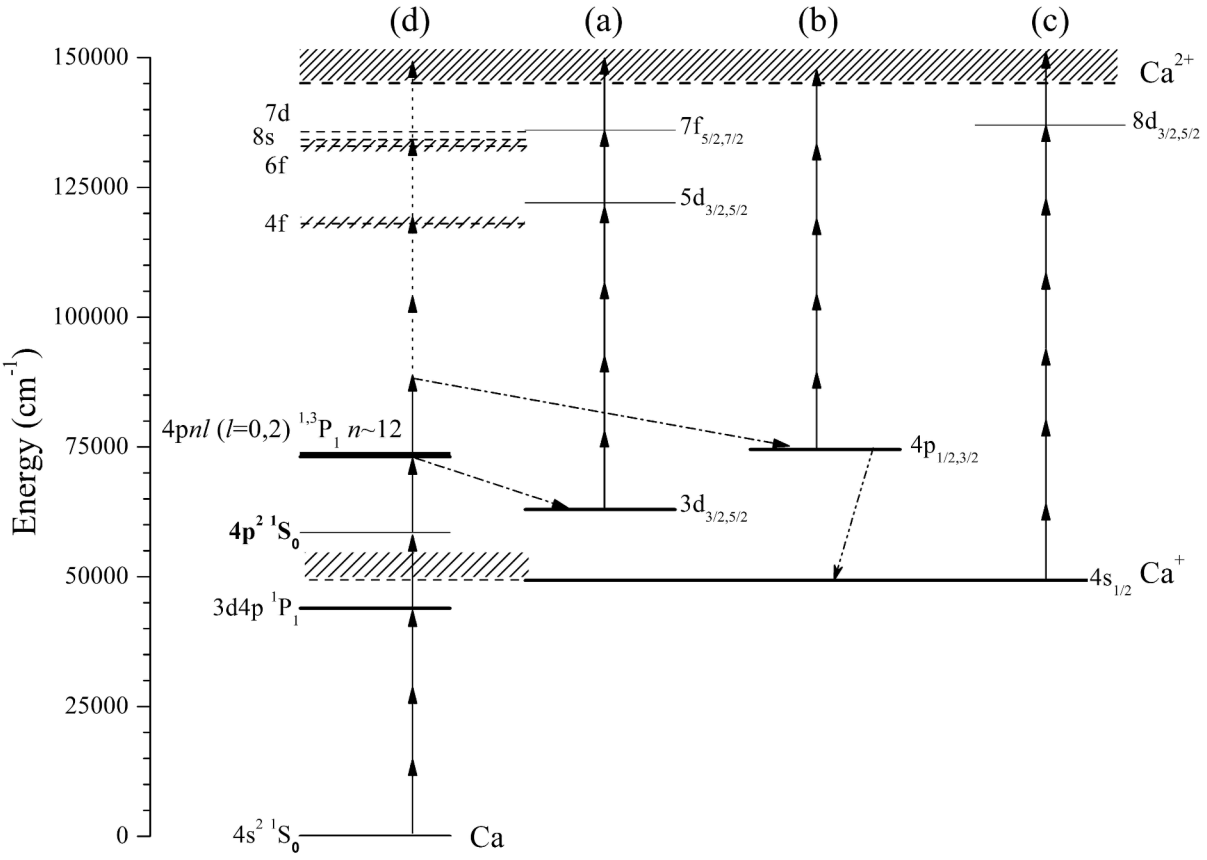

Figure 3. (a) Ca^+ (b) Ca^{2+} ionization yields (recorded with laser intensity I~3×10^{11} W/cm^2) and (c) Ca^+, $4p_{3/2}\rightarrow4s_{1/2}$ fluorescence (~2×10^{11} W/cm^2) as a function of laser wavelength. In (a) and (b) the locations of most relevant, unperturbed, atomic and ionic states and resonance transitions are noted. In (b) the inset shows the spectrum around the strong ~678.5 nm resonance recorded with I~(0.9, 1.4, 1.7 and 2)$\times10^{11}$ W/cm^2 (higher I values correspond to higher Ca^{+2} signals) while letters A-E mark the wavelengths at which the signal *vs* laser intensity curves were recorded. In (c) the profile of the dye laser output is shown by the dashed line.

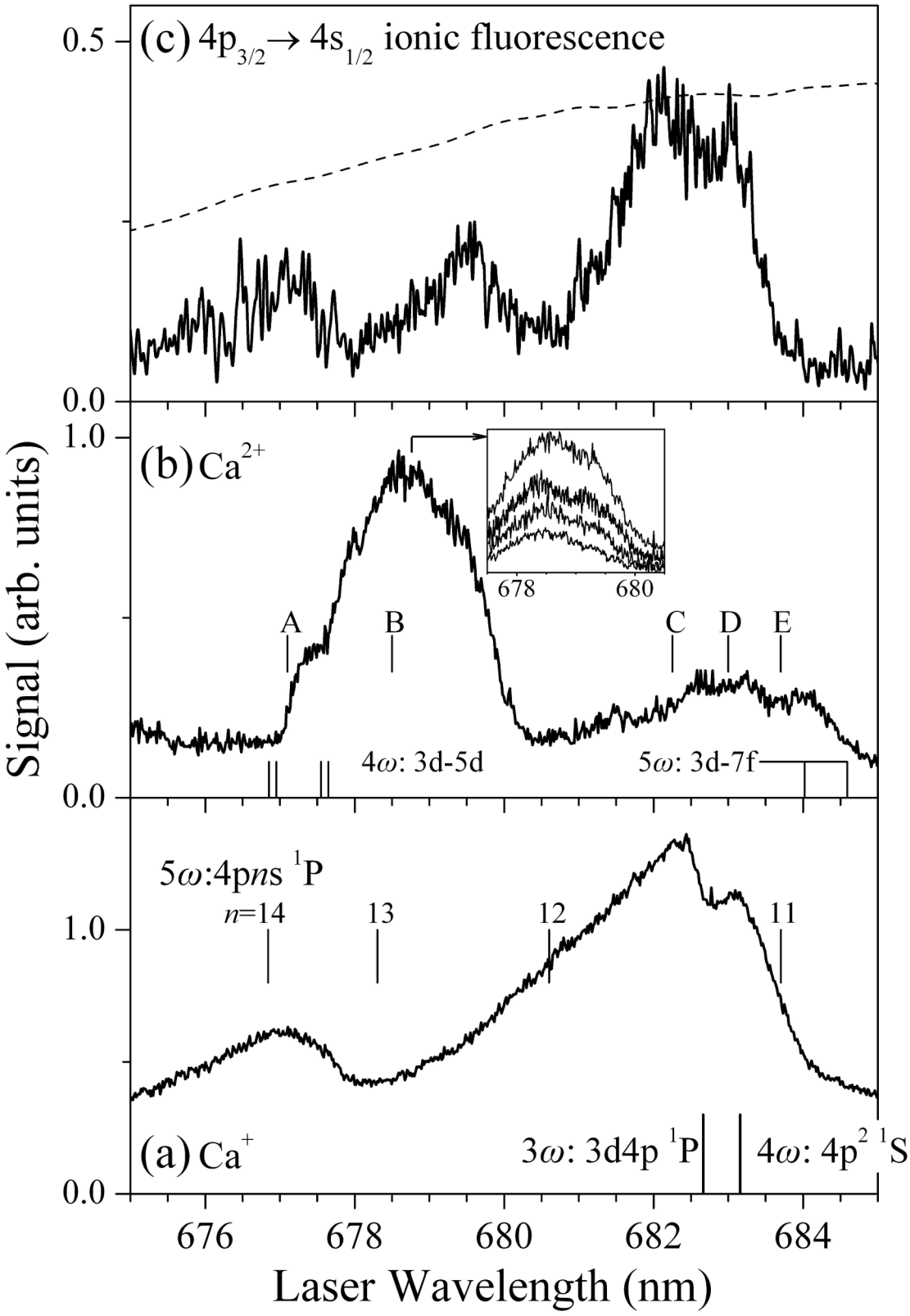

Figure 4. Log-Log plots of signal *vs* intensity for Ca^+ and Ca^{2+} for two indicated laser wavelengths. Most of the (not fitted) saturated parts of the plots are not parallel to the intensity axis but continue to increase with a lower slope. This well-known phenomenon is due to the increase of the focal volume with increasing intensity (see [7] and references therein). The data points denote the ionic signals integrated over the TOF peak profiles. Due to the fact that the width of Ca^+ signal is larger than that of Ca^{2+}, its integrated doubly charged ion signal for 678.5 nm appears to be lower although the peak heights are comparable (see figure 1). In (b) the vertical dashed line separates saturated and unsaturated parts of both ionic signals.

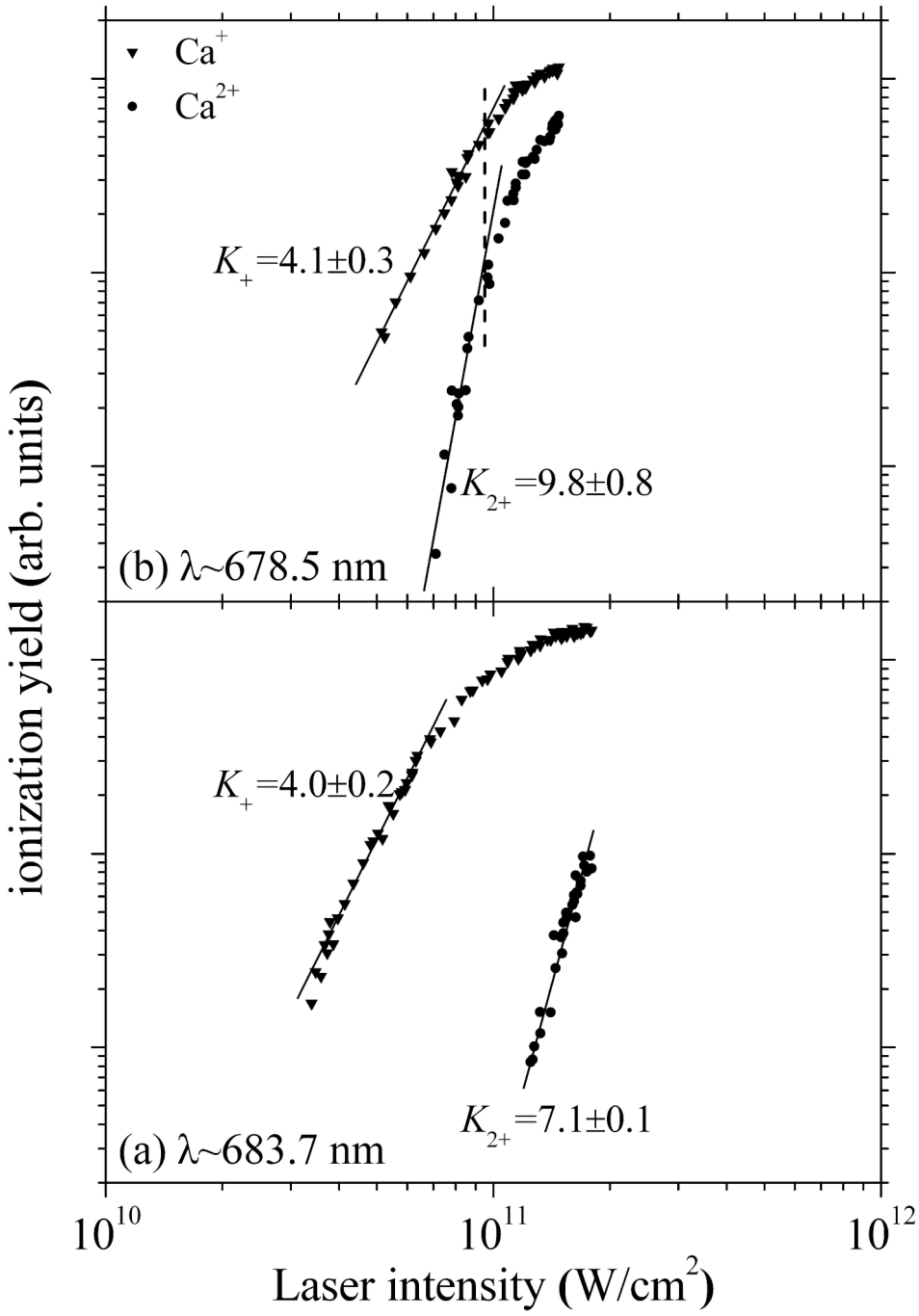

Table Captions.

Table 1. The orders of nonlinearity for Ca^{+} (K_{+}) and Ca^{2+} (K_{2+}) extracted by fitting the linear parts of signal *vs* intensity log-log plots to a power-law form I^{K} and for the indicated wavelengths. The labels are also shown in figure 3(b).

Label	λ (nm)	K_{+}	K_{2+}
A	677.1	4.7±0.5	4.3±0.2
B	678.5	4.1±0.3	9.8±0.8
C	682.3	6.7±0.7	8.3±0.8
D	683.0	4.2±0.2	9.5±0.7
E	683.7	4.0±0.2	7.1±0.1