MULTIPLE IONIZATION OF STRONTIUM BY VISIBLE PICOSECOND LASER LIGHT: AN ELECTRON SPECTROSCOPY STUDY

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ABSTRACT

Multiphoton simple and double ionization of strontium was studied using picosecond laser light and electron spectroscopy techniques, under laser intensities ranging from 10^{11} to a few 10^{12} W.cm^{-2}. Simple ionization is shown to leave the ion in either the ground state or one of the lower-lying excited states. Two and three-photon resonances can occur in this process on intermediate states lying either below or above the first ionization limit. Double ionization is shown to be essentially a stepwise process.

INTRODUCTION

Multiphoton ionization of complex atoms, essentially rare gases and alkaline earths has been the source of a few surprising experimental findings these past few years. The most important of these is probably the fact that complex atoms are rather easily multiply ionized. For instance quintuple ionization of xenon at 1064 nm is observed for intensities exceeding the saturation intensity for single ionization by less than one order of magnitude [1]. Also alkaline earths are easily subject to double ionization [2-6] and even triple ionization of Ca has been observed in ref 2. This is particularly surprising in the case of rare gases, the number of photons necessary for such ionization processes being of the order of several hundreds. Of course the question of the physical processes involved in multiple ionization has been addressed by many authors. Some of them proposed some new collective excitation mechanisms [7], but a usual muliphoton excitation is still seriously considered as the probable mechanism. In this framework the question arises wether multiple ionization occurs directly from the ground state of the neutral atom or by steps, in a sequence of simple ionization processes. To answer this question we certainly need a better knowledge of the core excitation mechanisms which can lead to the simultaneous excitation, and ultimately ionization, of two or more electrons. Alkaline earth atoms are well fitted to basic studies of these core excitation mechanisms. They are the simplest atoms presenting "two electron" spectra, both below and above the first ionization limit, the latter causing the well known "autoionization" mechanism. The study of these states under laser excitation is an important field of today's atomic physics, one of the goals beeing the study of "double Rydberg" states and of the so-called "Wannier" states [8-10]. There is also a large interest in theoretical studies of autoionizing states in intense electromagnetic fields [11- 14].

In this paper, we present the results of an electron spectroscopy study of multiphoton ionization of strontium. Electron spectroscopy can bring important informations on the final state of the ionization process, and thus on the possibility of a significant core excitation. Beside the use of electron spectroscopy techniques, these experiments are characterized by the use of Fourier-limited picosecond laser pulses, in the 10^{11} to a few 10^{12} W.cm^{-2} intensity range. After a brief presentation of the exerimental conditions and of the relevant strontium spectroscopy, we present and discuss the main results of these experiments.

EXPERIMENTAL SET UP

Details of our experimental set up can be found elsewhere [15,16]; therefore we limit ourselves here to a brief summary of the main characteristics of our apparatus.

Lasers: Two different lasers have been used in this experiment. First a Nd:Yag laser, whose frequency doubled output consists in 25 ps pulses at a wavelength of 532 nm, with an energy-per-pulse of a few millijoules. It can be directly used in the experiment, yielding after focusing intensities of a few 10^{12} W.cm^{-2}. It can also be used as a pump source for a synchronously-pumped dye laser[17], delivering pulses of the same duration whose wavelength can be tuned throughout the Rhodamine 6G emission band (558-575 nm). In this case the output energy-per-pulse is reduced to about one millijoule, with a maximum intensity in the interaction region of 10^{12} W.cm^{-2}, which is quite enough because this laser is mainly used to study resonnant processes. Both lasers are operated at a 10-Hertz repetition rate.

Electron spectrometer: A 23 centimeter long time-of-flight electron spectrometer was used in this experiment. An electrostatic collection system was used to study very low energy electrons. Electron counting techniques had to be used because of the low collection efficiency of our spectrometer which does not allow the use of analog detection without having to face serious space charge problems. Strontium atoms were supplied by a standard effusive atomic beam with densities estimated to about 10^9 cm^{-3}. A general outline of our experimental set up is shown on figure 1

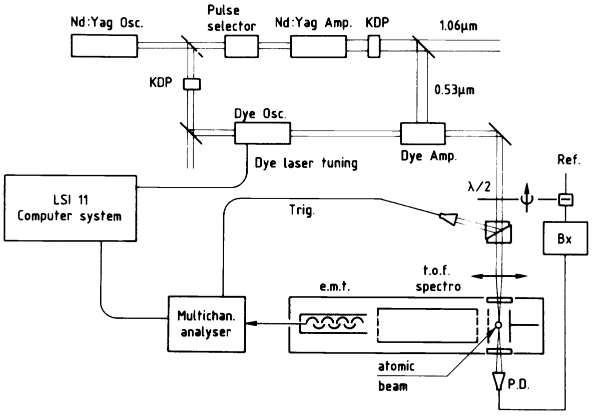


Figure 1: Experimental set-up

THE STRONTIUM ATOMIC SPECTRUM

Figure 2 gives a partial view of the atomic spectra of strontium I and II. Only the states involved in this experiment have been represented. Three photons of either the Nd:Yag or the Dye laser are necessary to ionize the strontium in its ground state. In this case the ion is left in its 5s ground state in a standard multiphoton ionization process labeled #1 on fig .2. Absorption of a fourth photon allows to reach two of the lower lying excited states of the ion, namely the 4d and 5p states in processes labeled #3 and 4, when process #2 is a well known Above Threshold Ionization (ATI) process leaving the ion in its ground state. Several intermediate resonances can be reached in the dye laser tuning range on states (not shown on fig. 2) lying either below (two-photon resonances on states 5p^2 or 5s5d) or above the first ionization limit . The latter case is parent to the well known autoionization process, but it should be said that this is true in the case of process # 1 only. In the case of four-photon ionization processes yielding an excited ion, these resonances have to be regarded as usual three-photon intermediate resonances. Note that the autoionization spectrum of strontium is not as precisely known as that of other alkaline earths, but in the relevant energy range, states as 4d4f and 5p6s have been identified [18,19].

Double ionization can then proceed, in a sequential process, from any of the ion states reached in the first ionization process (channels #5,6 and 7 on fig. 2). These processes can possibly be enhanced by intermediate resonances, and this has been use to identify the second ionization of strontium as sequential [3,5]. Double ionization can also occur directly from the atom ground state, as in channel # 8 of fig. 2. Concerning this point it should be said that, since the dipole approximation is usually considered as valid in the framework of perturbation theory, as applied to multiphoton ionization, one photon absorption can only change the state of one electron. Therefore double ionization is always a sequential process. But it may very well happen that the first electron is ejected with a kinetic energy which does not allow energy conservation with any of the ion real states. Such "virtual" states are very short lived (a few optical cycles) so that the correspondant double ionization process can be seen as direct in the way non resonnant multiphoton processes are generally considered. A more detailed discussion of this point can be found in ref 20

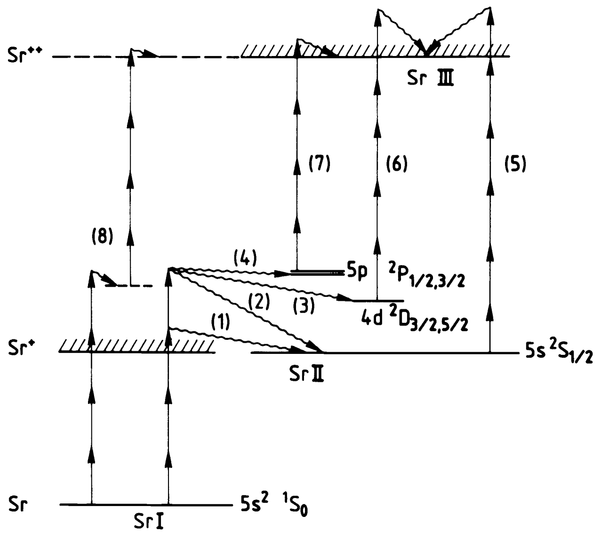


Figure 2: Partial vue of the Sr I and II atomic spectra

EXPERIMENTAL RESULTS

Ionization of Sr at 532 nm: We first study ionization of strontium at 532 nm. Simple and double ionization were observed on the ion signal and their dependences on laser intensity is shown on figure 3 in the usual log-log representation. In the linear part, slopes of 3.3 and 5.4 were respectively measured on the simple and double ionization signals which are, within our experimental uncertainty, equal to the number of photons respectively necessary to ionize the strontium atom and singly charged ion. This, together with the fact that double ionization is detected at intensities above the onset of saturation for simple ionization, is generaly considered a good hint that double ionization is in this case a sequential process. The horizontal axis of fig. 3 is marked off in energy per laser pulse. Conversion to intensities is as usual in the case of tightly focused picosecond pulses rather unprecise, and within a factor of two, 1mJ/pulse corresponds to an intensity of $4x10^{12}$ $W.cm^{-2}$.

Electron spectra were taken at different intensities, and three of them are displayed on fig. 4a,b and c. The spectrum of fig. 4a was taken at 2.8 10^{12} $W.cm^{-2}$, that is for an intensity were simple ionization is almost complete (no neutral atoms are left in the interaction volume). Spectra of fig. 4b and c were taken at intensities of respectively $3x10^{11}$ and $1.2x10^{12}$ $W.cm^{-2}$, and with a 1V acceleration applied to the electrons, in order to detect low energy electrons (energies around 0.1 eV) which can be released in some of the processes discussed above.

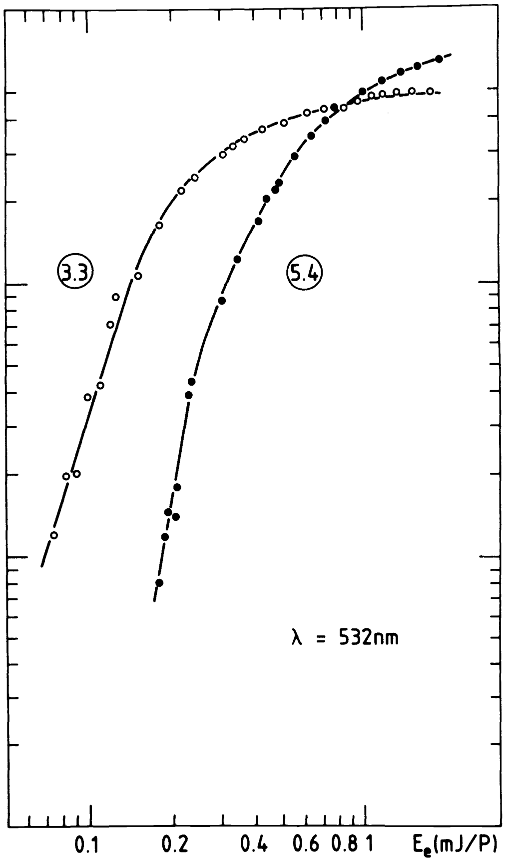


Figure 3: simple and double ionization signals versus the laser intensity

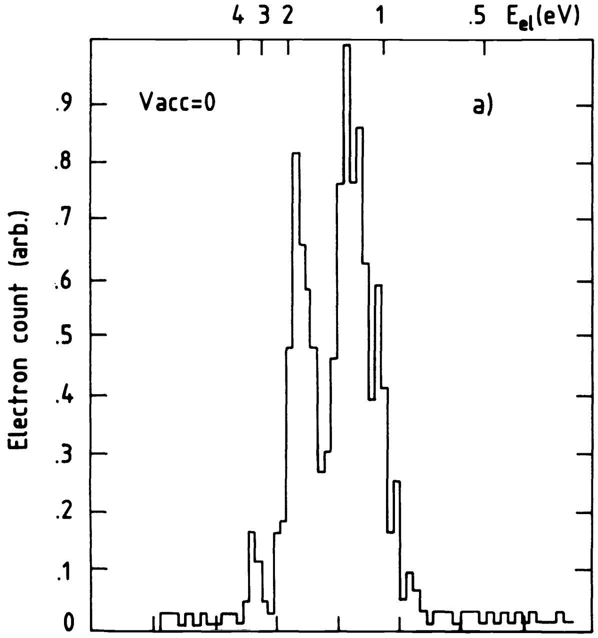


Figure 4a: Electron energy spectrum taken at 532 nm

On fig. 4a, three peaks are clearly displayed at energies of 1.2, 1.8 and 3.1 eV. Two processes can contribute to the peak at 1.2 eV: three photon ionization of neutral Sr (channel #1 on fig. 2) which yields an electron of 1.29 eV, or four photon ionization of the 5p state of SrII (channel #7), which yields an electron of energy 1.23 or 1.35 eV. The intensity dependence of the peak amplitude, however, is similar to that of the simple ionization signal which allows to conclude that this peak is mainly due to simple ionization of channel #1. The second peak, at 1.8 eV, can be unambiguously assigned to the process of channel #3 (four photon ionization of SrI, leaving the ion in the 4d state). The last peak at 3.1 eV is certainly due to an ATI process, most probably following the three photon process of channel #1. Comparison between the last two peaks, which both correspond to a four-photon process, shows that the process which involves a "core excitation" (one of the electrons is excited on the 4d state) is more probable than the other (ATI) where only one electron is concerned.

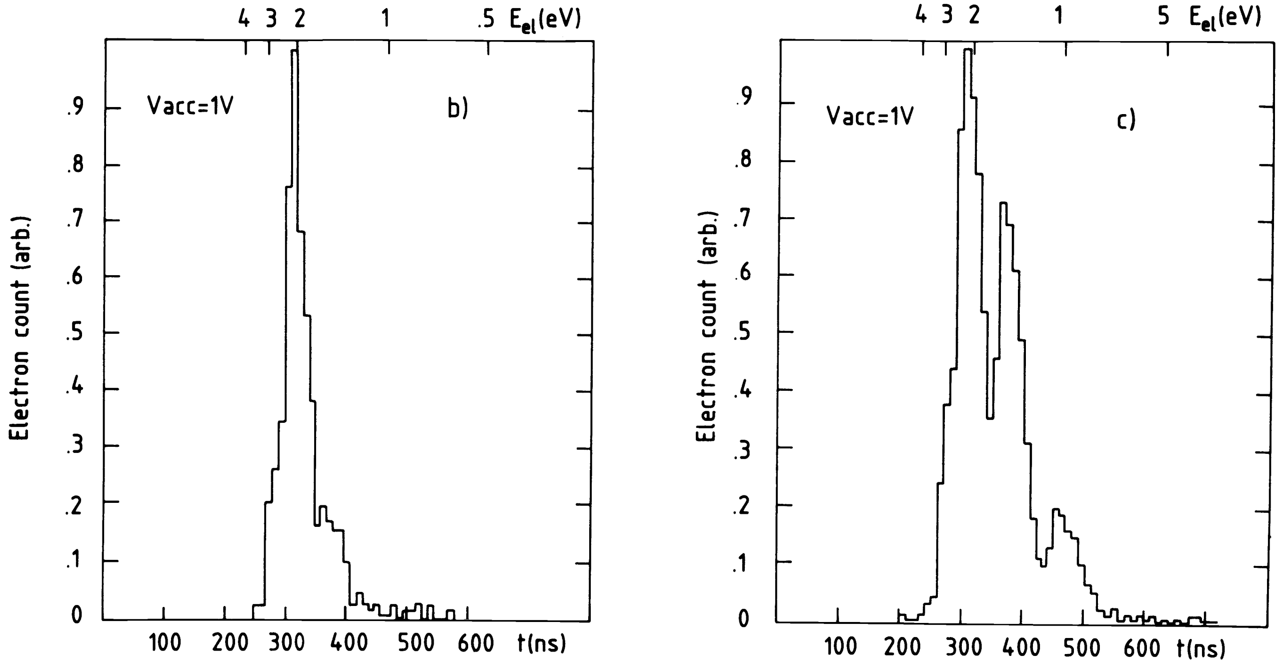


Figure 4: Electron spectra taken at 532 nm. On spectra b) and c) a 1 V acceleration is applied to collect low energy electrons

On the spectrum of fig. 4b, taken at a much lower intensity, only one peak is clearly seen, at an energy of about 2.2 eV. Given the 1V acceleration, this peak is the first peak discussed above. The peak at 1.8 eV has either disappeared or is not separated of the main peak anymore. On the trailing edge of the main peak, a weak feature appears, which is clearly visible on the spectrum of fig. 4c, at an energy of 0.6 eV corresponding to processes of channels #4 (four photon ionization of the atom in the 5p state) and #5 (five photon ionization of the ground state ion). A third peak is also detected at energy 0.1 eV, corresponding to electrons of channel #6 (four photon ionization of the 4d ion). The intensity dependence of these last two peaks show no saturation of the count when simple ionization does, indicating that second ionization brings a dominant contribution to these two peaks, whereas the peak at 1.2 eV saturates as simple ionization does. A general result of this study is that double ionization is almost certainly in this case a stepwise process, involving to a noticeable degree a core excitation in the lower lying states.

Ionization of Sr between 558 and 575 nm: When the dye laser is used, the aspect of the electron spectra can significantly change. This is due first to the change in wavelength, which can change by one unit the order of some of the processes discussed above, but also to the fact that, as discussed below, intermediate resonnances can change the branching ratios between the different processes.

Two spectra obtained with the dye laser are shown on figure 5a and b. The spectrum of fig. 5a was taken at a high laser intensity ($3x10^{12}$ $W.cm^{-2}$), with no acceleration, that of fig 5.b was taken at a low intensity (10^{11} $W.cm^{-2}$) and with a 1V acceleration applied to the electrons. The peaks on these spectra are labeled with channel numbers corresponding to those on fig. 2. All the processes detected at 532 nm are also observed in these conditions. Some of them can be dramatically emphasized by resonnance effects; this is the case of the 0.1 eV peak (acceleration deduced) of fig. 5b which is particulary important at this wavelength (563.5 nm). Assignment of the different peaks is based on (i) energy considerations, (ii) the intensity dependence, (iii) in some cases, the wavelength dependence.

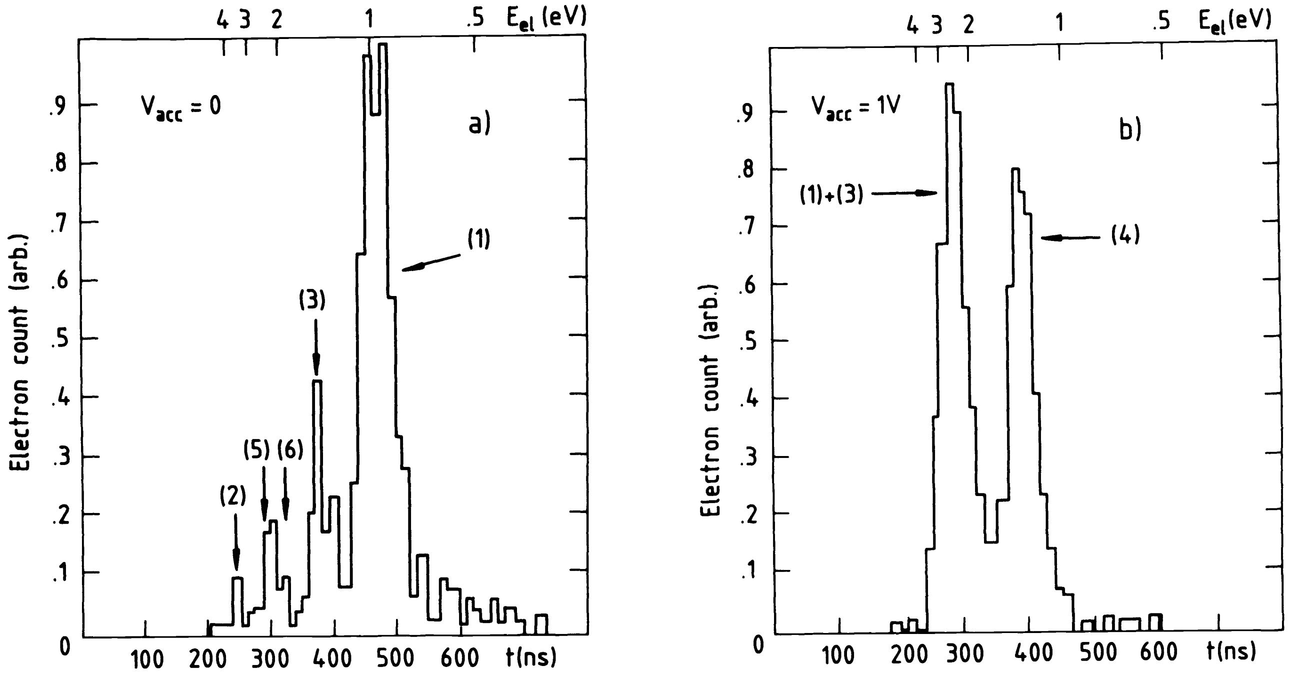


Figure 5: Two electron spectra taken with the dye laser. Peaks are labelled after the corresponding channels of fig. 2

Within the dye laser tuning range, two ionization thresholds can be crossed: that of the four photon ionization of the neutral atom leaving the ion in the $5^2P_{3/2}$ state (at 567.8 nm) or in the $5^2P_{1/2}$ state (at 574.3 nm), and the threshold for five-photon ionization of the ground state ion (at 562 nm). The wavelength dependence of the amplitude of peak 4 of fig. 5b is shown on fig. 6.

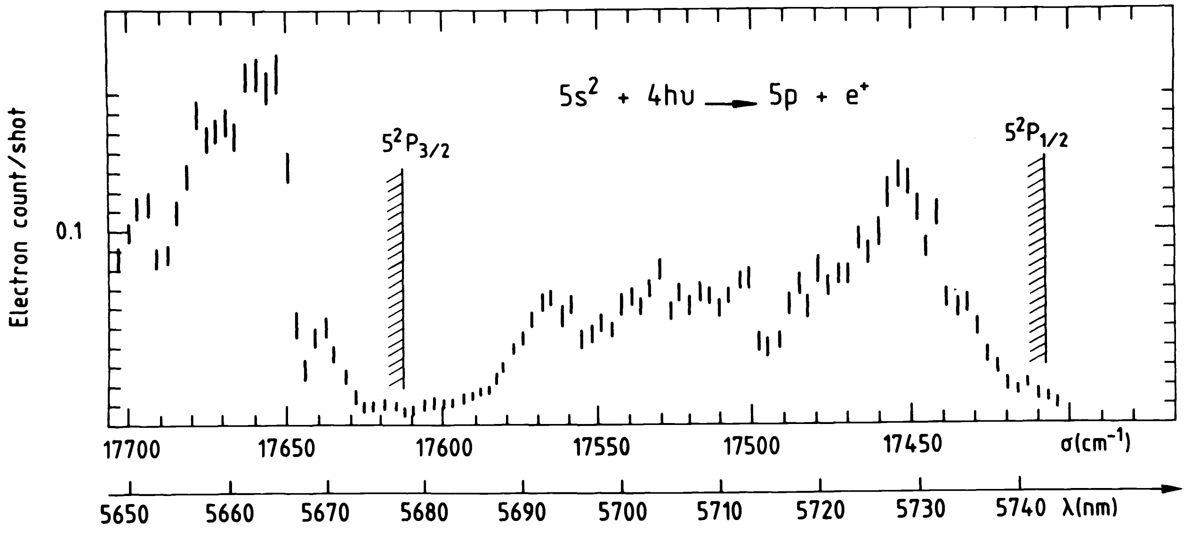


Figure 6: Wavelength dependence of peak 4 of fig. 5b around the $5^2P_{1/2,3/2}$ ionization thresholds

The fine structure of the 5p ion state is too small to be observed on the electron spectrum. In this experiment, the electrons were detected along the laser polarization direction, around which they are preferentially emitted, so that the peak amplitude represents the ionization probability for the corresponding channel. Fig. 6 shows a rapid increase of this probability when the thresholds are crossed for decreasing wavelengths, that is each time a five-photon process becomes a four-photon one. This threshold effect can even be emphazised by observing the electrons at a right angle from the laser polarization[15], because in this configuration, the collection efficiency of the spectrometer drops very rapidly for electron energies above a few hundredths of an electron-volt. This was used to confirm the identification of peak #4.

The peak labeled #5 on fig. 5a represents the six-photon ionization probability for the ground state ion. It could have been anticipated that it would vanish when the five-photon ionization threshold is crossed (at 562 nm). This is not the case, as shown on figure 7 where only smooth variations are observed in the threshold region. As a matter of fact, when the five-photon threshold is crossed, the six-photon peak becomes an ATI peak and, because of the continuity of the wavefunctions for Rydberg states when $n \rightarrow \infty$ and of the continuum states when $k \rightarrow 0$, there is no rapid variation of this cross section at the crossing of the threshold.

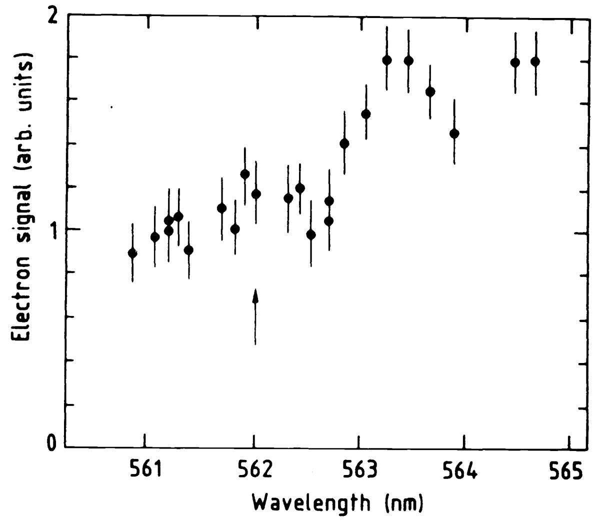
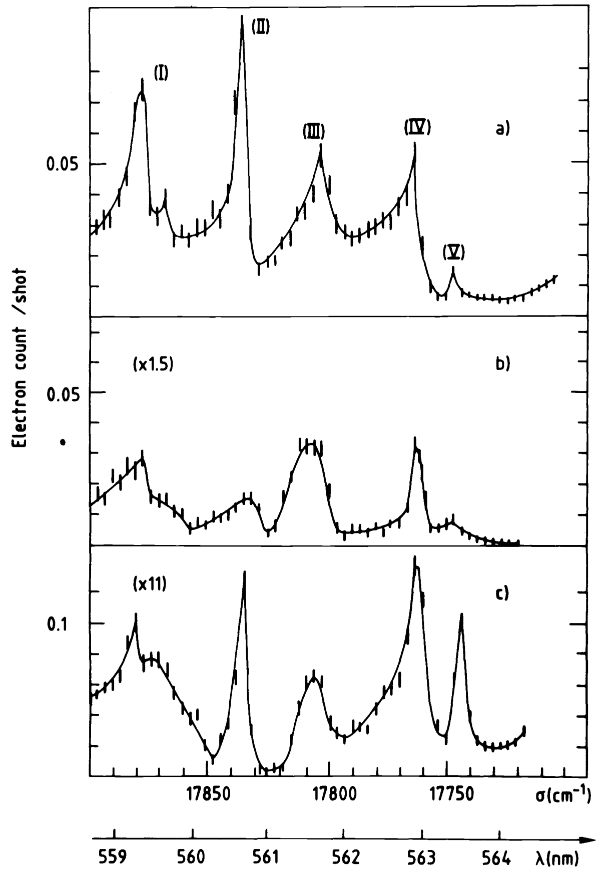


Figure 7: Wavelength dependence of the double ionization peak #5 of fig. 5a



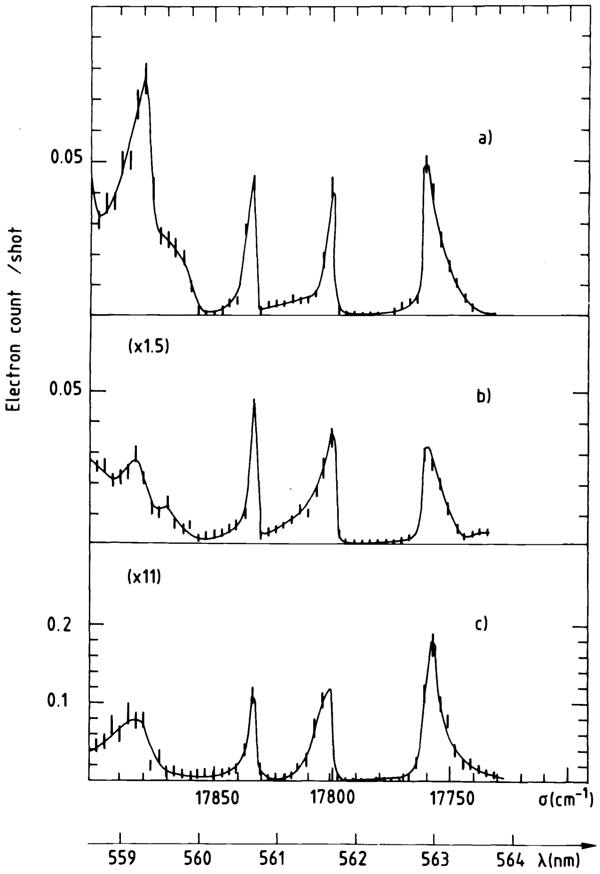


Figure 8 Figure 9

Wavelength dependence of different peaks of fig. 5 - (a) : #1, (b) : #3, (c) : #4 - in the 558 to 565 wavelength range. Fig. 8: linear polarization, fig. 9: circular polarization

In the wavelength range between 559 and 564 nm, a set of intermediate resonances can be reached, which can be detected on the three peaks corresponding to simple ionization (channels 1,3 and 4), as they had been seen using ion detection [3,5,21]. They are shown on figure 8 (for a linearly polarized laser, detection along the laser polarization) and on figure 9 (for a circularly polarized laser). A tentative assignment of these different resonances has been made in refs 3,5 and 21, which is not contradicted by these new results. Additional information can be obtained concerning these resonances from the electron spectra. Since, in a four-photon, three-photon resonant, ionization proces like those of channels #3 or 4, the last photon absorbed is used to eject one of the previously excited electrons it cannot, in the dipole approximation, contribute to core excitation. Therefore a resonance detected on a given electron peak has to have a core corresponding to the final ion state. The fact that most of the resonances displayed on fig. 8 and 9 are observed on all the electron peaks proves that there is a strong configuration mixing between the different autoionizing states involved in this experiment.

Only two resonnances show different behaviors depending on the electron peak considered: the resonnance labeled II on fig. 8a, which is a mixture of a two photon resonance on the $5p^2\ ^3P_0$ state and of a three photon resonance on $4d(^2D_{5/2})\ 4f(3/2)$ autoionizing state, and whose behavior is expected to be complicated, and the resonance labeled V. The latter only appeared as a weak feature in ion detection [3,5,21] as well as in the electron peaks #1 and 3 (core 5s and 4d respectively), when it is a dominant feature in case af peak #4 (core 5p). This seems to indicate that the resonant state has a 5p core, as would a 5p5d state which was sought for in vain in this energy region in spectroscopy experiments [18,19].

Comparison between the results obtained in linear polarization (fig. 8) and in circular polarization (fig. 9) shows only minor differences. Resonance V has disappeared and resonance II is modified, which can be due to the elimination by selection rules of the $5p^2\ ^3P_0$ resonant state (only the three-photon 4d4f resonance is left). Another difference is that all resonances appear to be narrower in circular polarization, which should be explained by the reduction of possible ionization channels caused by the selection rules in circular polarization. All the resonances which remain in circular polarization must then have a J equal to three [21], provided that the ground state is a pure s^2 state.

All the resonances discussed above appear not to be shifted by the laser field. This is not the case of an other set of resonances which can be detected at longer wavelengths, between 568 and 572 nm. They can be observed on electron peaks 1 and 4, and are due to two-photon resonances on states $5p^2\ ^3P_2$ and 5s5d $^3D_2$ at respectively 568.3 and 571.3 nm. They are responsible for the rather ragged feature which can be seen on fig. 6 at the corresponding wavelengths. This is due to the fact that, at the intensities used in fig. 6, the two resonances are already strongly shifted and broadened.

The resonance shifts are best measured on the ion signal and are shown on figure 10. This effect is now well known in high intensity resonant processes, the surprise here comes from the fact that interediate states with almost complete similarity behave in a very different way: shifts of the $5p^2\ ^3P_0$ and 5s5d $^3D_2$ resonances are respectively 60 and 20 times larger than that of the $5p^2\ ^3P_2$ one, when a 5s5d $^1D_2$ resonance observed at longer wavelengths is unshifted within our measurement precision. This problem is still under study, but it seems probable that this is due to a quasi-resonant coupling of the resonant intermediate states with a discrete state embedded in the continuum such as the 5p5d state mentioned above.

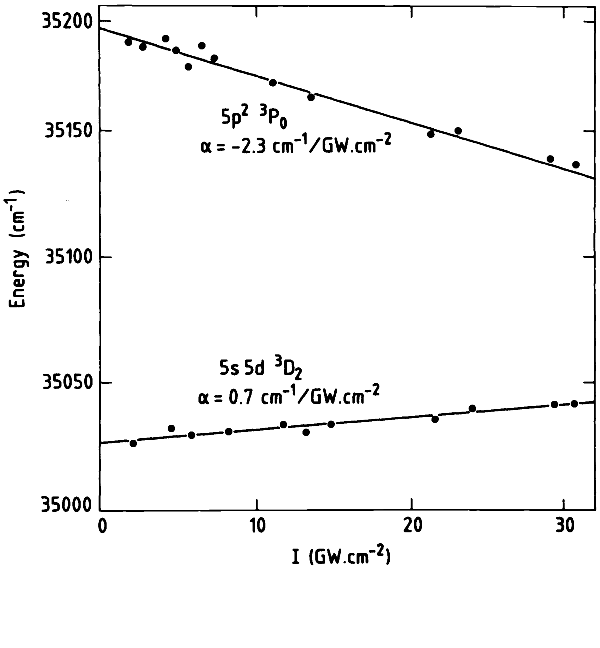


Figure 10: A.C. Stark shift of the 5s5d and $5p^2$ resonances

Information about the degree of core excitation can also be extracted from the data of fig. 8 and 9. Because of the many resonances, it is strongly wavelength dependent. In addition, raw data have to be corrected for the collection efficiency of our apparatus (numbers in parenthesis on fig. 8 and 9). After these corrections it appears that about 10% of the ions can be created in the 4d state and almost 50% in the 5p state, which is an important effect. However these figures must not be taken as too general: they are probably partially due to the quasi resonant character of some of the four-photon channels involved in fig. 8 and a different result would be obtained with the same analysis carried from fig. 4.

CONCLUSION

We have studied simple and double multiphoton of Sr using electron spectroscopy techniques. Simple ionization has been proved to occur not only in the ion ground state, but also in a few low-lying excited ion states, with probabilities larger than that of other processes of the same order, like ATI. Configuration interaction was shown to play a major role in the resonant transitions observed in our experiment. All this makes the problem of multiphoton ionization of alkaline earths considerably more complicated than that of one electron atoms.

Double ionization was shown to be essentially a stepwise process. Two-electrons excited states can play a role in these processes but it merely results in the excitation of a few low-lying ion states. Of course this could be a particular property of alkaline earths and the situation in an atom with no low-lying excited ion states, such as the rare gases, could be different.

Although assigning the observed resonances is not an easy task, no evidence was found of resonances on high-lying two-electron excited states. No evidence was found either of the existence of a direct double ionization process. On the other hand it can be said that, given the reasonable number of photons involved and the fact that one can point to some specific ionization channels, a perturbative approach seems reasonably qualified to treat the problem of double multiphoton ionization of alkaline earths, even if it does not lead to easy calculations.

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