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Photoionization of laser-excited Cesium atoms above the 4d ionization threshold.

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Abstract:

The photoionization of ground state and 6p laser-excited Cesium atoms was studied above their 4d ionization threshold. The 4d photoelectron spectrum of 6p laser-excited atoms shows a stronger excitation of satellites upon ionization than its ground state counterpart. The relative intensities of satellite and main photolines show a slow variation with the incoming photon energy for both the ground state and the 6p laser-excited states. An assignment of the excited state spectra, supported by recently published ground state photoionization spectra and calculations, is given and a preliminary analysis of the 4d Auger spectrum of laser-excited atoms is also presented.

Keywords: core ionization, atomic spectroscopy, two-color experiments; laser and synchrotron radiation;

PACS: 82.53.Hn; 42.62.Fi; 32.30.-r; 32.80.Dz;

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1. Introduction:

Inner shell photoemission spectroscopy is an ideal tool to investigate the electronic structure of atoms and to test theoretical methods. The possibility to examine how certain parameters or couplings change with the size of the atom and atomic number allows detailed comparison with theory. From the experimental point of view gas phase studies are often complicated by the fact that atoms different from rare gases need to be prepared in situ. Alkali metals, being easy to evaporate, are a relatively convenient target for studies and were investigated over the years. The series from Lithium to Cesium has been studied extensively [1,2,3] using inner-shell spectroscopy techniques. Alkali metals are however very reactive, thus the target densities have to be kept relatively low in order to avoid contamination of the experimental setup. High resolution studies were started only in the last 15 years or so with the advent of third generation light sources which provide a sufficiently high flux to offset the low target concentration [4, 5, 6, 7]. Theoretically alkali metals are appealing, because of their hydrogen-like electronic structure with only one electron in an s-orbital outside a noble gas closed shell configuration. In addition, for the heavier atoms relativistic effects become very important, and the change of coupling from LS to jj [8] can be investigated moving from one atom to the next.

Two color experiments add a further degree of control, as the target can be prepared in a well-defined quantum state by the absorption of the first photon, and then studied using the second. This type of investigation can give very detailed insights into the electronic structure and ionization dynamics, as, depending on the characteristics of the two light sources, very high experimental energy resolution, time resolution, or population of specific sublevels (by polarization control) can be achieved. Thus the application of laser-synchrotron pump-probe techniques is an

important tool in the study of the electronic structure [9]. Alkali atoms are also a particularly convenient target for such experiments. All of them have very strong resonance lines, which are located in the tuning range of commercial lasers, so that a substantial fraction of the ground state population can be transferred into an excited state. The coupling of lasers and synchrotrons to investigate alkali atoms was started already in the eighties at second generation light sources [10]. Those pioneering studies were very important to show the potential of such experiments. With the development of third generation light sources the available photon flux and resolution have improved, but the main experimental difficulties – low target density and the risk of contamination due to a highly reactive sample – have remained unchanged [3, 4, 5, 9]. Investigations of laser-excited atoms using high resolution have been essential to unravel the complexity of the satellite structure in the np valence ionization of Rubidium [11] and Cesium [12]. The selective excitation gave access to final states which are otherwise only populated via shake-up processes, significantly simplifying the spectra. Thus theoretical predictions could be tested in detail. Also, the excitation of the outermost ns electron leaves the atom in a state with an electron less tightly bound. The study of photoelectron and shake-up spectra, in comparison to their ground state counterparts, permits the evaluation of electron correlation and relativistic effects in theoretical models [2].

Here we describe experiments carried out using a tunable mode-locked Ti:Sapphire oscillator and synchrotron light pulses in the EUV range applied, to the 4d ionization of Cesium.

The spectrum of Cesium in the vicinity of the 4d ionization threshold is very complex. Below threshold the spectrum is dominated by several sharp features assigned to excitations of 4d electrons to empty np orbitals, although it has been

shown that a single configuration approach is not sufficient for a correct description of the spectrum [13,14,15]. Above threshold Cesium exhibits a giant resonance due to transitions into the ϵf continuum, where the cross section increases to ~ 35 Mb [16]. The spectrum of ground state atoms has been studied by absorption [13], ionization [14, 15], photoelectron [4,17] and Auger [18,19] spectroscopy with always increasing resolution, and has also been the subject of theoretical investigations [4].

There are fewer reports on laser-excited Cesium atoms, but Schulz et al [12] have studied 6p excited atoms near the 5p ionization threshold. More recently, the absorption spectrum below the 4d ionization threshold has been investigated both experimentally and theoretically [20]. Here we present results on the 4d ionization of 6p excited Cesium atoms recorded at various photon energies above the ionization threshold. The 4d photoelectron spectrum is discussed, and a preliminary analysis of a part of the Auger spectrum is presented.

2. Experimental:

The experiments were performed at a branch line of the Gas Phase beamline at the storage ring Elettra (Trieste, Italy). The general layout and performance of the beamline [21] and the laser setup [22] have been described previously, and so only the changes to the apparatus relevant for the present experiment will be briefly given here.

The photoelectron spectra were recorded using a commercial hemispherical photoelectron analyzer (VG). The analyzer was placed at the magic angle (55°) with respect to the synchrotron light polarization vector, in the plane defined by the polarization and the propagation direction of the light. The analyzer was used in constant pass energy mode with the resolution set to ~ 100 meV to record the

photoelectron spectra, and to ~ 200 meV to record the Auger spectra. Cesium was introduced into the ionization region using a resistively heated, anti-inductively wound oven, perpendicular to the plane defined by the light beam and the analyzer. The temperature was kept at $\sim 90^\circ\text{C}$ throughout the experiment, monitored using a thermocouple. The ionization region was surrounded by a liquid nitrogen cooled copper shield in order to minimize the contamination of the chamber and analyzer by Cesium vapor. Nevertheless small shifts in the kinetic energy scale of the analyzer due to Cesium coating were observed. To minimize the effects of this shift on the analyzer resolution multiple spectra were recorded and then, if necessary, the spectra were aligned on strong features due to ionization of ground state Cesium atoms, and summed. The overall spectral resolution of the experiment including the contribution of the beamline monochromator was determined to be ~ 120 meV. The transmission of the analyzer in the kinetic energy range of interest was determined by recording the Auger spectrum of Xenon [23]. The spectra of Cesium were recorded several times during the experiment. The changes in analyzer transmission were small and limited to the lowest kinetic energies used in the experiment (< 15 eV). Spectra of laser-excited atoms were obtained by subtraction, after alignment on the strongest line of ground state photoionization. The effect of the subtraction is seen in the spectra, where strong ground state features cause small oscillations in the baseline.

While the procedure outlined above proved accurate enough for the analysis of the strong XPS spectra, the analysis of the Auger spectra, in which the intensity is distributed over many transitions, was affected much more by the small shifts in the kinetic energy scale. Therefore for this part of the experiment a chopper with a modulation frequency of ~ 3 kHz was inserted into the laser beam. In this way the laser-on/laser-off spectra were recorded almost simultaneously making the subtraction

procedure more reliable. The signal-to-noise (S/N) ratio was enhanced by using zero-order light coming from the undulator, with the undulator gaps set to center the emission at 145 eV and the higher harmonics of the undulator efficiently cut by the beamline optics. The photon energy resolution corresponds to the width of the undulator emission (~ 8 eV) and so photoelectron features are washed out, while Auger peaks are not affected by photon bandwidth.

A commercial mode-locked Ti:Sapphire oscillator (Tsunami, Spectra Physics) was used to excite Cesium atoms in the interaction region. The laser beam was set counter-propagating to the synchrotron radiation. Typically ~ 1 W of tunable radiation was measured at the entrance window of the chamber. During the experiment it was tuned to the D_1 and D_2 ($6s\ ^2S_{1/2} \rightarrow 6p\ ^2P_{1/2,3/2}$) absorption lines of the Cesium atom at 894 nm and 852 nm, respectively [24]. As both lines are very narrow, a reference cell (glass cuvette) was used to monitor the stability of the laser wavelength by measuring the absorption of the metal vapor.

The polarization of the laser was adjusted using $1/2$ and $1/4$ waveplates. In the experiments the laser was used mode-locked and running at a frequency ~ 83 MHz, but not synchronized to the ring frequency [22], as the lifetime of Cesium excited states is long (>30 ns [24]) compared to the period of the laser. The mode-locked laser was operated in the picosecond configuration with a pulse width of ~ 12 ps which was monitored continuously. The picosecond pulse configuration gives high power densities, so the beam was used unfocused at an estimated power density in the interaction region of ~ 30 kW/cm². From the spectra we estimate that we saturate the transitions. The unfocussed beam approximately matches the site of the effusive beam of Cesium atoms from the furnace (~ 2 mm diameter), with the synchrotron beam size ~ 5 times smaller. Thus variations in the spatial overlap of the two beams are

negligible. The signals in the photoelectron spectrum turned out to be strong enough to fine-tune the laser wavelength directly, thus possible differences in the lineshape due to the different Doppler widths in the reference cell and experimental chamber, or saturation effects were not a cause of instabilities. Assuming the same cross-sections for the 4d ionization of the ground state and the laser excited states we estimate that more than 30% of the atoms in the interaction region are excited – indicating saturation of the transition.

3. Results and Discussion:

The Cesium photoelectron spectrum at the 4d edge has been reported [4, 17] and is relatively simple when compared to the spectrum below threshold or to other thresholds of the same atom. This is somewhat surprising, as the 4d region is characterized by the strong 4f absorption above threshold, and in other atoms like barium for example, leads to many satellite features showing the importance of electron correlation [25]. The recent high resolution investigation by Fritzsche et al [4] has shown that also in Cesium shake-up and conjugate shake-up states are populated upon ionization, but their relative intensity is low. In the former process the dipole ionization of a core electron is accompanied by the monopole excitation of a valence electron while in the conjugate shake-up the monopole ionization of a core electron is accompanied by the dipole excitation of a valence electron to an unoccupied atomic orbital. Here we examine first the 4d ionization spectrum recorded with resolution similar to the recently published data, and then compare it with the spectra of laser excited atoms. The ionization of laser-excited Cesium generates some of the same final states observed in the ionization of ground state Cesium, so a comparison allows an assignment of the spectral features.

3.1 Ground state atoms, 4d photoelectron spectrum:

The spectra were recorded at nine photon energies between 105 eV and 145 eV. They are dominated by two strong lines due to the ionization of the two spin-orbit components of the 4d orbital. As different photon energies were used overlapping Auger peaks can be distinguished from the photoelectron spectrum. The experimental resolution was similar to that used in the recent study [4], so no new features in the spectrum were observed in our experiments. Therefore we adopt the published assignment, and only discuss the differences observed between the spectra recorded at various photon energies. Care was taken in identifying the Auger peaks, which were accounted for in the analysis. The spectrum taken at 145 eV photon energy is shown in figure 1. It was analyzed as follows: the final state energies given by Fritzsche et al [4] were used as starting parameters of the fit, and the strongest transition (to the $4d^{-1}_{5/2}6s$ final state) was used to calibrate the binding energy scale. The change in line shape and the possible shift due to post-collision-interaction [26] was neglected in the analysis. This is justified by the long lifetime of the state and the high photon energy, 30-60 eV above threshold. The experimental resolution was treated as a free parameter (giving a Gaussian of ~ 120 meV FWHM). The lifetime width was fitted for the strongest lines in the spectrum, and then set equal for all peaks in the spectrum, at ~ 100 meV. With these values all peaks identified in the spectrum agree within 5 meV with the binding energy values given in reference [4]. There are, however some differences in the relative intensities, which can be attributed to the different photon energies used. Also, within our S/N (signal/noise) ratio the $8s_{1/2}$ and $7d_{3/2,5/2}$ (following the notation of reference [4]) final states are too weak to be observed, either for the $4d^{-1}_{5/2}$ group transitions or their $4d^{-1}_{3/2}$ counterparts. This difference is

particularly clear for the $4d^{-1}_{3/2}8s_{1/2}$ state, which lies in a region free from overlapping Auger bands.

In order to examine the dependence of the ratio between the $4d^{-1}_{3/2}$ and $4d^{-1}_{5/2}$ main lines we have recorded the XPS spectra for various photon energies in the range 105 eV ... 145 eV (step 5 eV). The results are summarized in Figure 2, together with the ratios of some satellite lines and data obtained from the spectra of laser-excited atoms. For the main lines the ratio at the photon energy of 105 eV is ~ 0.69 , and a monotonic increase to ~ 0.82 at the highest energy is observed. The latter value is in good agreement with the value of ~ 0.8 given by Fritzsche et al. [4] at 142.5 eV. Older results by Prescher et al [27] show a similar dependence on photon energy, but are systematically higher. This discrepancy may be due to the lower resolution used in that experiment, which made the evaluation of intensity of overlapping features more difficult.

The smaller values near threshold, which are closer to the statistically expected $2/3$ ratio, might be ‘accidental’ in view of the fact that the partial ionization cross section depends on the shape resonance near threshold [4,28]. The results by Prescher et al. [27] show strong variations of the main line intensity ratio when approaching the ionization limits. Some insight can be obtained from a comparison with the 4d ionization of Xenon which has been studied in great detail both experimentally and theoretically [28]. At a similar energy above threshold the main line ratio in Xenon is well predicted by Relativistic Random Phase Approximation (RRPA) theory and very similar to what we observed for Cesium. It approaches the statistical ratio at ~ 200 eV above the ionization edge. The observed similarity – although our experiments cover only a limited photon energy range – indicates that the 4d core electron ionization is only weakly influenced by the presence of valence

electrons. Notably, also the main features of the 3d ionization cross section of Rubidium [4] are similar to the 3d ionization of Krypton [29].

There is a clear difference in the 7s/6s shake-up to main line ratio, which – at the photon energy of 105 eV – we determine to be ~ 0.085 (± 0.03) (for $4d^{-1}_{5/2}$) and ~ 0.076 (± 0.03) (for $4d^{-1}_{3/2}$), respectively. The corresponding values derived by Fritzsche et al [4] for ionization at 142.5 eV are ~ 0.12 for both, in good agreement with our spectra recorded at 145 eV photon energy. The monopole shake-up intensity increases slowly in the range of experimental photon energies, while the $4d^{-1}_{3/2}7s:4d^{-1}_{5/2}7s$ ratio follows that of the main photolines. This observation reinforces the hypothesis that the shape resonance affects the monopole shake-up lines and the 4d main lines similarly [4], and core-valence interaction is small.

The conjugate shake-up probabilities can be determined for the 6p and 5d lines. Both show a small decrease with respect to the main lines with rising photon energy (see figure 2). The results are in good agreement with the published single photon energy data at 142.5 eV [4]. The trends with photon energy are similar to the ones observed in Rubidium [4], but there Multi-Configuration-Dirac-Fock (MCDF) calculations only qualitatively reproduce the experimental data, especially at lower photon energies. At 142.5 eV the calculated values [4] for Cesium are in good agreement with experiments, but energy dependent calculations are required to test the theoretical description of valence-excited core-hole states.

3.2 Laser-excited atoms, 4d photoelectron spectra:

We have recorded spectra exciting the D₁ and D₂ transitions of Cesium with linearly (parallel and perpendicular to the synchrotron light polarization vector) and circularly polarized light. Synchrotron photon energies of 105 eV and 145 eV were

used, as for ground state Cesium. The spectra shown (figure 1) have been recorded using linearly polarized laser radiation, perpendicular to the synchrotron light polarization vector. Using other polarizations did not lead to any difference in the relative intensities of peaks – within our signal-to-noise ratio. For D_1 ($6s\ ^2S_{1/2} \rightarrow 6p\ ^2P_{1/2}$) excitation, we observed a reduction of signal by approximately a factor of two when exciting it with circularly polarized light. This is an additional indication that the transition is saturated, as the m_j selection rules for circularly polarized light limit the signal. The polarization dependence of the photoelectron spectrum was checked also at a laser power reduced by a factor of 4, and no differences in the relative peak intensities were observed.

The spectrum of ground state Cesium atoms has been subtracted after rescaling the intensity of the $4d^{-1}_{5/2}6s$ peaks in the two spectra, and the binding energy adjusted for the laser excitation energy in each trace. Thus the features correspond directly to binding energies of core-excited states. Key features can be assigned by comparison with the ground state spectrum and published calculations. The assignment follows the calculations by Fritzsche et al [4], so the dominant peaks in the spectrum correspond to the $4d^{-1}6p$ states. As in the ground state spectrum, and also in the case of Rubidium [30] and Potassium [31] the fine-structure of the main photolines is not resolved. If the outermost $6p$ electron conserves its angular momentum in the D_1 excited spectrum mainly the $6p_{1/2}$ states are accessed, while the D_2 excitation will lead to $6p_{3/2}$ states. Thus the spin-orbit splitting in the core-excited state can be measured directly. Within the experimental resolution we see the same $4d$ splitting for both $6p$ states (2.27 eV and 2.28 eV for D_2 and D_1 excitation, respectively), indicating that core-valence interaction is not very strong. The $6p$ spin-

orbit splitting determined for the two main lines is also very similar (0.21 eV for $4d^1_{3/2}$ and 0.22 eV for $4d^1_{5/2}$).

Both the D_1 and D_2 excited spectra exhibit similar features. Shake-up (7p, 6d) and also very weak shake-down (6s, 5d) transitions can be identified. The selective preparation of the state by the laser permits the identification of spin-orbit components of states which cannot be distinguished in the ground state spectrum. So, for the 7p shake-up state we observe a clear separation of the 3/2 and 1/2 components of $\sim 74 (\pm 10)$ meV, indicating a preference for the conservation of angular momentum of the valence electron upon shake-up. The 4d spin-orbit splitting of the $4d^1 7p$ states is determined to be 2.27 eV, confirming that the core-valence interaction is weak. The splitting between the two components of the 7p orbital was not observed in previous studies. In the ionization of laser-excited atoms the 7p states are populated via the monopole shake-up process from selectively excited atoms, leading to higher intensities and more selectivity in the population of the final states.

While the S/N ratio of the spectra does not permit an accurate evaluation of the spin-orbit splitting of the other states, a small difference is observed for the 6d shake-up transition. Fritzsche et al [4] have determined the spin-orbit splitting of the $4d^1 5d$ states to be ~ 100 meV, while the corresponding value for the 4d orbital of these states is 2.2 eV. The corresponding values for the neutral atom are ~ 69 meV for 6p, ~ 22 meV for 7p and ~ 12 meV for 5d [32]. This comparison indicates that while the 4d spin-orbit splitting is little affected by the outer electron, the 6p and 7p splitting are increased by a factor of ~ 3 for the core-ionized states. For states with the occupied 5d orbital the increase is much larger, indicating mixing between the 4d and 5d orbitals. We note that Hartree-Fock calculations [33] predict that also other configurations (e.g. the 4f states) are located in this energy range.

When compared to the spectra of the ground state Cesium atom, the spectra of laser excited atoms show significantly more excitation to shake-up states. For example in the spectra recorded at 145 eV photon energy the intensity of the 7p final states amounts to ~28% of the main photoelectron line. This is in general agreement with theoretical predictions [2]. At 105 eV photon energy the amount of excitation is less (~18%), but still significantly higher than in the ground state spectra. A similar effect has been observed for other alkali atoms and also investigated theoretically [2]. For example in Rubidium 4p [11] and Cesium 5p [12] ionization different fine-structure components were accessed selectively and identified in the laser-excited atom spectra. In the case of the 4d ionization of Cesium (similar to the 3d ionization of Rubidium [30]) all the different final states are located within the lifetime-width of the nd hole, so a direct identification of the fine structure components is impossible. In Lithium [34] the shake-up probabilities have been examined in a systematic way by following higher excitations and their energy dependence. The increased shake-up probability in the core ionization of excited states has been attributed to an improved overlap between the initial state and final state wave-functions [34]. Unexpectedly, in the case of Lithium, the increased shake-up probability was similar for conjugate shake-ups, despite the fact that a different mechanism leads to their formation. An examination of the intensities of conjugate shake-up final states in the spectra of 6p laser excited states (final state configurations $4d^{-1}6d$, $4d^{-1}7s$) of Cesium does not show a similar enhancement. It has to be kept in mind, however, that here we examine spectra of a single excited state, so a more systematic investigation of higher excited states (e.g. 7p and 8p, lying in the wavelength range of commercial lasers) – both theoretical and experimental – is necessary to provide definite answers.

3.3 Auger spectra:

The 4d Auger spectrum of ground state Cesium atoms has been studied with varying resolution over many years [18,19]. The most recent high resolution study [19] concentrated on secondary Auger processes, and showed a spectrum in the kinetic energy range up to 40 eV recorded at photon energy of 140 eV. We have recorded Auger spectra for ground state and laser excited Cesium atoms at a photon energy of 145 eV. The ground state Cesium atom 4d Auger spectrum agrees well with previously published data [19] and is shown in figure 3. The D_1 and D_2 excited Auger spectra of Cesium are shown in the panels (a) and (b) of figure 4.

We briefly discuss the main features of the Auger spectra, concentrating on the similarities between the ground state and laser-excited data. A detailed assignment of the spectra requires calculations, but the main features can be interpreted by comparison with published data on ground state Cesium, resonant Auger spectra of Xenon [35] and ground and laser-excited state Auger spectra of Rubidium [30]. The binding energies of many states of the Cs^{2+} ion– final states of the Auger decay – in the energy range of interest were reported in a recent high-resolution optical study [36]. The $Cs^{2+} 5p^4 6s$ configuration generates 8 distinct states which have all been observed. Using the energies reported in reference [36], together with the $4d^{-1}_{5/2,3/2} 6s$ binding energies, all strong features in the part of the Auger spectrum shown in figure 3 can be matched exactly. Several peaks in the spectrum overlap, so their relative intensity is uncertain. The spectrum is dominated by the decay to states of the $5p^4(^1S)6s$ and $5p^4(^1D)6s$ configurations, while $5p^4(^3P)6s$ states are weaker. Spectra from the $4d^{-1}_{5/2}$ and $4d^{-1}_{3/2}$ core-hole ion states can be identified by their spin-orbit separation. The assignment agrees with previously published results, and is indicated in the figure. In order to show the various contributions the spectrum has been fitted

including the dominant decays. Only the main line ($4d_{3/2}^{-1}6s$ and $4d_{5/2}^{-1}6s$ to states of $5p^46s$ configuration) and the most intense shake-up ($4d_{3/2}^{-1}7s$ and $4d_{5/2}^{-1}7s$ to states of $5p^47s$ configuration) decays were considered. In the fit the energies of all final states were kept fixed, with the relative intensities and a single common width treated as adjustable parameters. The uncertainties are mainly caused by the overlap of various final states. The results are included in the graph (figure 3). While still not all structures are accounted for, the main features in the spectrum are well reproduced. Based on the results of the fit also the two main-line components' contributions can be separated, and the final states leading configurations identified. Similar to Xenon [35] the main line decay shows a different relative population distribution of the final states, with the $4d_{3/2}^{-1}$ hole decay to states of (1S) $6s$ configuration being stronger than for its $4d_{5/2}^{-1}$ counterpart.

While the Auger spectra of ground state Cesium are dominated by the decay of the $4d^{-1}6s$ states, in the case of laser-excited atoms the decaying states are mainly of the $4d^{-1}6p$ configuration. However, due to the higher shake-up intensities in the $4d$ ionization of laser-excited atoms, also decays from other core-ionized states can contribute significantly. The ground state Cesium Auger spectra resemble closely the resonant Auger spectra of $4d \rightarrow 6p$ excited Xe [19, 35]. For the laser-excited atoms, an even closer correspondence can be expected, as the configurations involved are identical. An important difference, however, results from the excitation process. The resonant excitation in Xenon is governed by dipole selection rules and this limits the number of populated fine-structure components to $J=1$ states. In the $4d$ ionization of Cesium more states can be populated and have comparable intensity [30].

The most intense lines in the spectrum are in the kinetic energy range 30 - 40 eV, where the most intense features of the ground state spectrum also appear. This

energy range corresponds to final states of $5p^46p$ configuration [19, 36]. This single configuration leads to 21 states, which have been identified in the resonant Auger spectrum of Xe. We calculate the positions of the 82 lines in the spectra using tabulated energies from the recent high resolution experiment [36] and the binding energies of the core hole states measured in the XPS of laser-excited atoms.

Figures 4 (a) and (b) show the part of the Auger spectra in the kinetic energy range 31 eV – 42 eV recorded at 145 eV photon energy, following D_1 and D_2 excitation of Cesium. The S/N ratio of the D_1 excited spectrum is lower due to the lower excitation cross-section. As for ground state Cesium and Xenon [35], the most intense lines correspond to states of the $(^1S)6p$ and $(^1D)6p$ configurations, but due to the large number of transitions many lines overlap even within a single configuration. Spectra from the $4d^{-1}_{5/2}$ and $4d^{-1}_{3/2}$ core-hole ion states can be identified by their spin-orbit separation. Without an intensity calculation a complete assignment of the spectra is impossible, but a general description can be obtained based on the energies of the final states. The three strong peaks marked by arrows correspond to the decay of the $4d^{-1}_{3/2}$ core hole to $(^1S)6p$ states, and of the $4d^{-1}_{5/2}$ core hole decay to $(^1S)6p$ and $(^1D)6p$ [$J=3/2$]. The weaker structure centered at ~ 36.5 eV is due to $4d^{-1}_{5/2}$ core hole transitions to different $(^3P)6p$ states, which continue in the higher kinetic energy range and overlap the structures due to $(^1D)6p$ final states in the $4d^{-1}_{3/2}$ core hole decay. A similar pattern is of $(^3P)6p$ states repeated in the spectrum due to the decay of the $4d^{-1}_{3/2}$ core hole. The D_2 excited spectrum (figure 4 (b)) shows a similar pattern, but there are some differences in the details. The feature indicated by the arrow is due to the decay to $J=5/2;3/2$ components of the $5p^4(^1D)6p$ states. Also the intensity distribution of the $5p^4(^3P)6p$ states centered at ~ 36.5 eV kinetic energy (marked in the graph) changes noticeably. Similar differences have been observed in the spectrum of laser-

excited Rubidium published recently [30]. In the resonant Auger spectra of Xenon [35] and Auger spectra of laser-excited Rubidium [30] states of shake-up configurations appear in the range of the $np^4(n+1)p$ final states. Similar complications of the spectrum can be expected in laser-excited Cesium, where already the 4d photoelectron spectra show considerable excitation of satellites. The recent high resolution study of the Cs^{2+} ion indicates that many states of $5p^4nl$ configuration are located in the same energy range.

Despite their high complexity the Auger spectra of laser-excited atoms permit the identification of leading configurations in the final states. The kinetic energy ranges corresponding to states built on the 1S , 1D and 3P cores have been marked in the figures. Detailed theoretical studies and high S/N experimental spectra are needed to further refine the assignment.

Conclusions:

We have described results obtained using a pump-probe setup available at the Gas Phase beamline at the storage ring Elettra (Trieste). The combination of a high resolution spectrometer and selective excitation allows a detailed study of the electronic structure of core ionized states of Cesium. The spectra were assigned by comparison with core level spectra of ground state Cesium atoms, and the photoionization dynamics were examined. The results for ground state Cesium are in good agreement with recent studies. Although the electronic structure of Cesium at first appears to be simple because it consists of a closed shell and a single valence electron, in practice it is very complex, due to correlation and relativistic effects. The 4d core hole photoelectron spectra are however simpler than the 5p spectra. The 4d spin-orbit splitting is not significantly affected by the valence electron, but correlation

is evident because the 6p and 7p splitting is affected by the angular momentum of the core hole, either 5/2 or 3/2. A noticeable increase of the relative intensity of the shake-up features has been observed for excited atoms. The main features in the Auger spectra of laser-excited atoms were interpreted using the recently published [36] energies of the Cs²⁺ ion. In spite of the complexity many Auger features can be assigned, although some intensities are not yet explained.

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Figures:

Figure 1 (color online). Comparison of ground state (bottom trace, black), D_1 (middle trace, red) and D_2 (top trace, blue) excited Cs 4d photoelectron spectra recorded at 145 eV photon energy. The ground state ionization contribution has been subtracted from the excited state spectra. The figure (bottom panel) also includes an expanded view of the Cesium atom ground state spectrum.

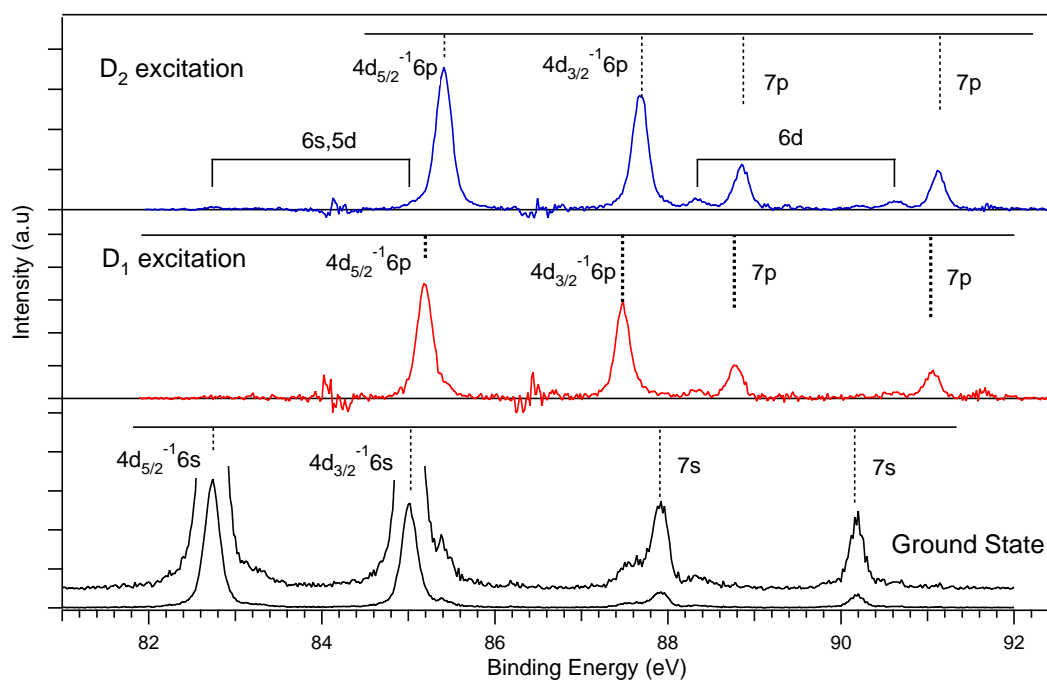


Figure 2. (color online) Intensity ratios between main lines (circles) and main and satellite lines obtained from the analysis of ground state (open symbols) and excited state (solid symbols, photon energies 105 eV and 145 eV) photoelectron spectra. Data for both D_1 and D_2 excitation are shown, and are almost identical for the main line intensity ratio. (*) indicates the corresponding values calculated from the data shown in reference [4]. Note the break and scale change in the vertical axes.

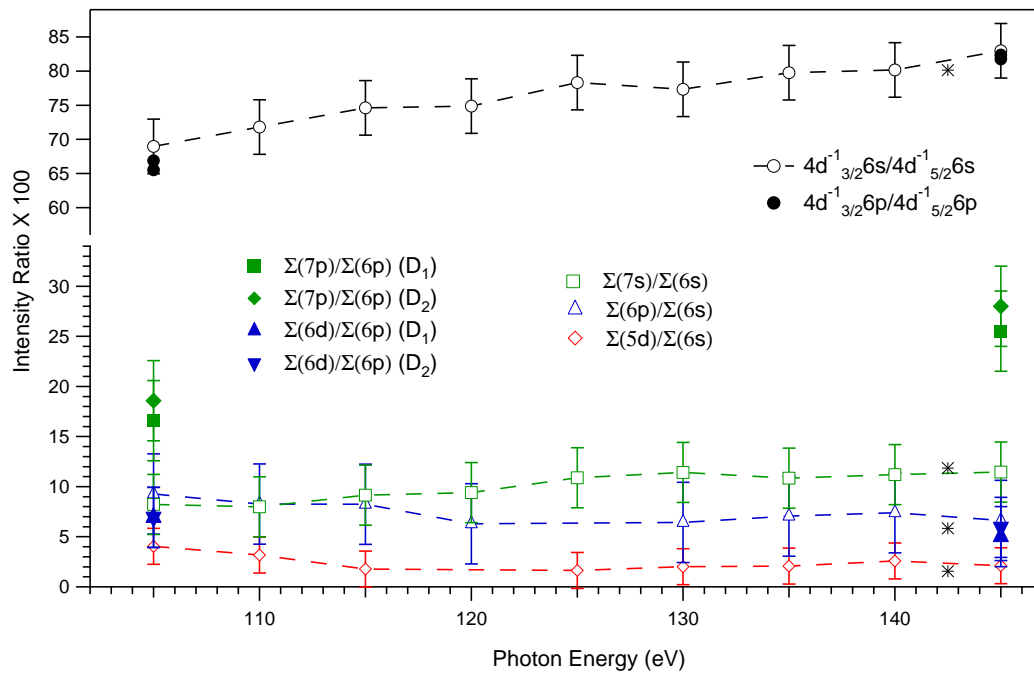


Figure 3. (color online) Part of the Auger spectrum of ground state Cesium recorded at 145 eV. The comb in the top of the figure indicates the energies of the Cs^{2+} final states from reference [36]. The contribution of states of $5p^47s$, as obtained from the fit of the spectrum, is indicated by the dashed line. States of different parentage of the $5p^46s$ configuration are indicated by different shading (^1S – dark gray, ^1D – gray and ^3P light gray). The intensities are results of a fit to the experimental data (see text for details).

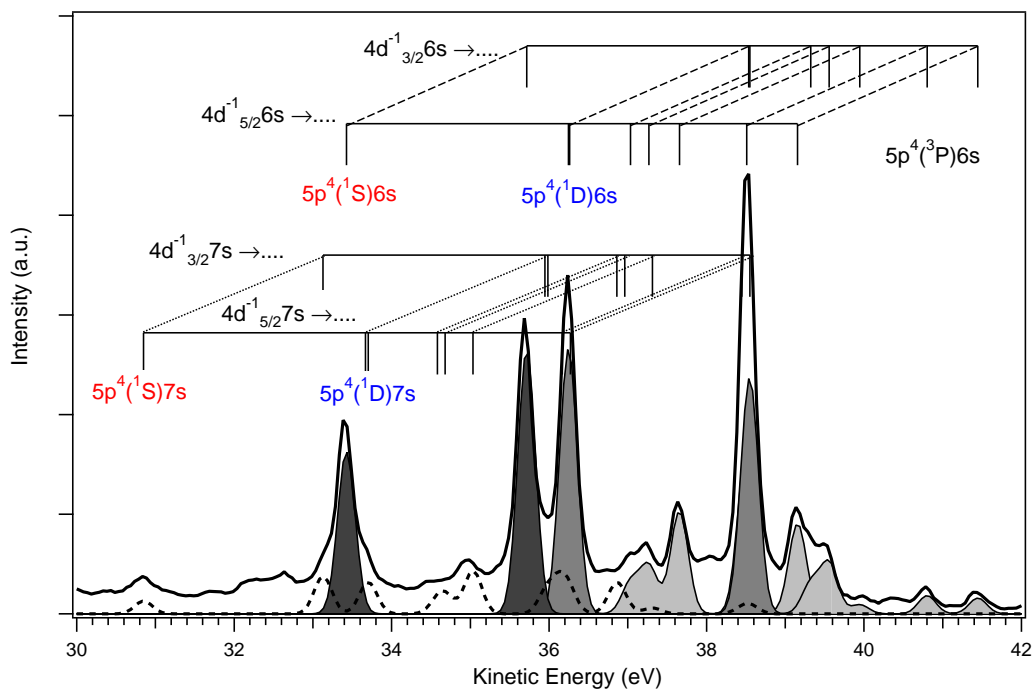
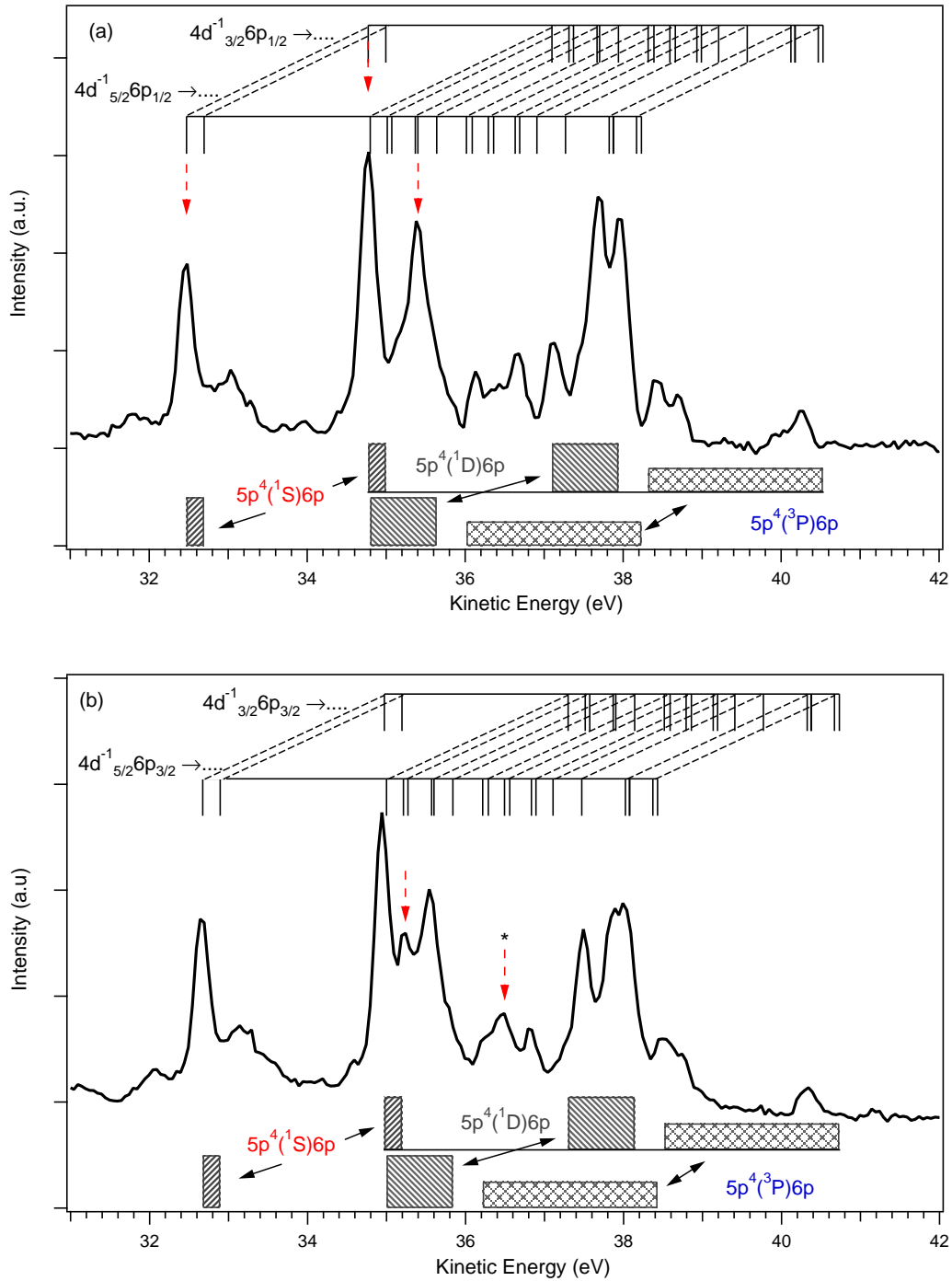


Figure 4. (color online) Part of the Auger spectra of excited atoms recorded at 145 eV: D_1 ($6p_{1/2}$) (a) and D_2 ($6p_{3/2}$) (b) excitation. The contribution of ground state atoms has been subtracted. The comb in the top of each figure indicates the energies of the Cs^{2+} final states from reference [36]. Regions of the spectrum with final states of different parentage are indicated by rectangles.



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