Thresholds of the $K+L$ double photoexcitation in argon

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The argon photoabsorption cross section has been measured absolutely in the energy range around 3500 eV. Resonant $K+L$ double photoexcitations and shake-up threshold jumps with an inner-shell $1s^12p^5$ double-hole configuration have been found. The observed energy positions agree quite well with those determined by relativistic self-consistent field calculations. Former determinations of the $K+L$ shake-up threshold jump height have been confirmed.

Multielectron effects are present in the photoabsorption spectra above the K edge of atoms. Rare gases are especially suitable for investigations of these small contributions because their spectra do not exhibit an extended x-ray-absorption fine structure (EXAFS) as atoms in molecules or solids [1]. In photoabsorption spectra the thresholds of neon $K+L$ excitation and argon $K+M$ excitation are well known [2–5]. $K+L$ excitation was also observed above the K edge of atoms in compounds. The gas-phase photoabsorption spectrum of silicon in molecules shows resonant double excitation into antibonding molecular orbitals [6]. Only small additional edges appear above the K edge of solid silicon and heavy $3d$ transition metals [7–10]. The evidences for $K+L$ double excitation reported for the metal foils have been called into doubt [11]. Here we present the threshold spectrum of $K+L$ double photoexcitation of argon in the gas phase leading to the inner-shell configuration $1s^22p^5$.

For the experimental realization and the understanding of the $K+L$ threshold photoexcitation spectrum presented later on, three introductory considerations are helpful: (i) a short discussion of the known facts about the x-ray emission satellites due to $K+L$ inner-shell holes, (ii) a relativistic self-consistent-field (SCF) calculation to find the absolute energies of the $K+L$ double-ionization edges, of selected single-ionization edges and of a few discrete two-electron resonances, and (iii) an estimation of the magnitude of the effect by a result of shake theory.

This threshold study is closely related to the experimental and theoretical studies of the x-ray emission $K\alpha$ and $K\beta$ satellites due to $K+L$ inner-shell vacancies. The $K\alpha$ satellites in $3d$ transition-metal atoms occur between 10 and 40 eV above the diagram emission lines and form a spectrum that consists of overlapping contributions from different initial states of the $K+L$ double hole [12–15]. Heavy-ion collisions, however, produce a $K\alpha$ satellite spectrum due to multiple L vacancies, which can be much stronger than the diagram lines [16]. The weak $K\beta$ satellites due to $K+L$ double excitation in argon have been investigated only theoretically [17]. In calcium, $K\beta$ satellites due to multiple L vacancies were found experimentally by heavy-ion collisions [16]. If the photoabsorption threshold of the double excitation is known excitation-energy-dependent satellite spectra can be measured. This has been done only for the case of argon $K+M$ double photoexcitation [3,18].

For the calculation of the argon $K+L$ double-excitation energies, the relativistic multiconfiguration Dirac-Fock (MCDF) code of Grant and co-workers, including the "Breit energy analysis" program package, was used [19,20]. The relativistic calculation, the consideration of finite nuclear size, and the QED corrections are necessary for the determination of absolute binding energies of inner shells. To calculate absolute threshold energies relaxation also had to be taken into account. Therefore transition and ionization energies were determined as differences from the atomic level energies of the ground state and the excited or ionized configurations. Energy differences, but not transition probabilities, can be calculated in this way [17]. Since for argon the correlation corrections to the K- and L-shell binding energies are about 2 eV, only "nonrelativistically defined single-configuration" calculations were performed [21]. The "extended-average-level" method was applied to the open-shell cases [19]. As a test for the procedure the energy of the well-known $1s^2\rightarrow 1s^14p^1$ Rydberg transition and the K-edge energy of argon were calculated. The calculated values of 3202.3 and 3204.9 eV are only 1.3 eV lower than the experimental results of 3203.54 and 3206.26 eV [22]. This difference is in full agreement with the correlation correction to the argon K-shell binding energy [21].

The inner-shell configuration $1s^12p^5$ in the final state leads to four double-ionization (shake-off) thresholds which are grouped in a lower-lying inverted triplet $^3\mathbf{P}_{2,1,0}$ (calculated energies: 3509.2, 3511.0, 3512.3 eV) and a singlet $^1\mathbf{P}_1$ (3521.1 eV). This splitting shows that the LS notation is applicable. If Rydberg orbitals, e.g., $4p$, are occupied in the final state more levels occur. As an example for single-ionization edges (shake-up) all levels of the configuration $1s^12p^54p^1$ were calculated. The 18 ionic levels are grouped according to the four $K+L$ double-hole levels since all further splittings caused by inner-outer-shell exchange interaction and outer-shell spin-orbit coupling are less than 0.3 eV. These substructures cannot be resolved because the experimental broadening and the K-hole width together amount to about 1 eV. Therefore Table I only contains the corresponding mean ionization energies and the four $K+L$ double-ionization edges. They are separated by about 8 eV. The single-

TABLE I. Calculated energies in eV of the shakeoff and some shakeup thresholds in the argon $K+L$ double-photoexcitation spectrum. They are arranged according to the multiplet states of the inner-shell configuration $1s^12p^5$. Mean values are given in the case of further splittings for the final ionic configuration $1s^12p^54p^1$.

Ionic configuration	Multiplet states of the inner-shell configuration $1s^12p^5$			
	$^3\mathbf{P}_2$	$^3\mathbf{P}_1$	$^3\mathbf{P}_0$	$^1\mathbf{P}_1$
$1s^12p^5$	3509.2	3511.0	3512.3	3521.1
$1s^12p^54p^1$	3500.9	3502.6	3503.6	3512.8

ionization edge belonging to the $^1\mathbf{P}_1$ inner-shell state coincides with the double-ionization edge of the $^3\mathbf{P}_0$ inner-shell state. As a first approximation to resonant double excitations the atomic levels with total angular momentum $J=1$ of the configuration $1s^12p^54p^2$ were also calculated. Since, in addition to the previous ionic case, the multiplet splitting of the $4p^2$ electrons is of the same order of magnitude as the $K+L$ double-hole spin-orbit coupling it is suitable to label the final states for resonant double excitation as $(^{2S+1}\mathbf{L}_J, ^{2S+1}\mathrm{L})_J$. Boldface letters indicate the $K+L$ hole states and plain letters the $4p^2$ multiplets. This notation again implies mean values for outer-shell spin-orbit coupling and inner-outer-shell exchange interaction. Table II shows the mean energies of the dipole-allowed resonant $K+L$ transitions from the $^1S_0$ ground state to the states with $J=1$ of the configuration $1s^12p^54p^2$ arranged according to the notation given above. They are located about 2–3 eV below the corresponding single-ionization edges.

Up to now nothing has been said about the mechanism that is responsible for the double photoexcitation and the magnitude of the effect. Multielectron processes are caused by electron correlation and relaxation in the atom [23,24]. However, it is beyond the scope of this paper to discuss, for the argon $K+L$ two-electron excitations, to what amount final- or initial-state effects contribute to the experimental threshold spectrum presented below. Frequently these multielectron processes are referred to as shake-off or shake-up. But the calculation of shake effects in the sudden approximation is not applicable for threshold studies because the assumption of quick ionization does not hold [25,26]. However, the experimental and theoretical investigation of the energy dependence of Auger and photoelectron satellite intensities due to argon $K+M$ double holes indicates what may be expected for the present case [27,28]. First, the cross section for shake-off (double ionization) drops to zero near threshold. Second, the cross section for shake-up (single ionization accompanied by excitation) remains essentially constant from close to threshold up to several hundred eV above. Both these facts allow us to compare the experimental threshold jump with the shake-up cross section for higher excitation energies though it has been calculated in the sudden approximation [29]. The contribution of argon $K+L$ shake-up to the total photoionization cross section that leads to the ionic configurations $1s^12p^5nl^1$ has been calculated to be about 0.27% in the sudden approximation [29]. This number gives a hint how carefully the photoabsorption experiment has to be carried out.

The experimental photoionization cross section was recorded with a standard x-ray-absorption experiment. The Bonn 2.5-GeV electron synchrotron served as the light source [30]. The end energy was 2 GeV and the beam current about 20 mA. The double-crystal monochromator at the windowless beamline SYLI-2 was equipped with a pair of InSb(111) crystals [31]. The monochromatic photon flux was 10^9/s and the transmission width about 0.8 eV. The monochromator was calibrated with the well-known energy of the argon $1s\rightarrow 4p$ Rydberg transition at 3203.54 eV [22]. Two parallel-plate ionization chambers, 10 and 40 cm long, which were separated from the monochromator by a single 12.5-μm Kapton foil were directly connected and filled with 96 mbar argon. This corresponds to about two absorption lengths in the first chamber. This double-ion chamber arrangement allows us to measure absolute photoabsorption cross sections of gases directly [32]. The linear attenuation coefficient α of the gas filling is derived from the chamber currents I_1 and I_2 and the effective length of the first chamber L_1 by

$$\alpha=(1/L_1)\ln(I_1/I_2+1)\ .$$

This relation holds if the length L_2 of the second

TABLE II. Calculated energies in eV of resonant argon $K+L$ double excitations to the final states of the configuration $1s^12p^54p^2$ ordered by the quantum numbers in LS coupling of the open inner shells $1s^12p^5$ and by the multiplets of the open outer shell $4p^2$: $(^{2S+1}\mathbf{L}_J, ^{2S+1}L)_{J=1}$. Only final states with the total angular momentum $J=1$ are taken into account.

Multiplets of $4p^2$	Multiplet states of the inner-shell configuration $1s^12p^5$			
	$^3\mathbf{P}_2$	$^3\mathbf{P}_1$	$^3\mathbf{P}_0$	$^1\mathbf{P}_1$
^3P	3497.1	3598.8	3500.1	3508.9
^1D	3497.6	3599.4		3509.5
^1S		3500.2		3510.4

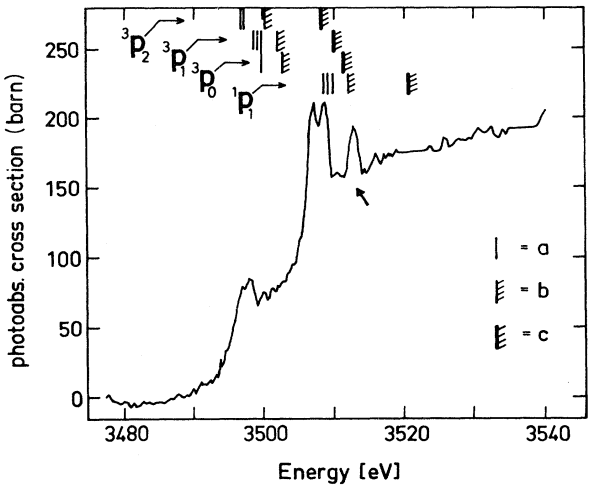

FIG. 1. The argon $K+L$ double-photoexcitation spectrum leading to the inner-shell configuration $1s^12p^5$. The zero of the absolute cross section corresponds to 77 000 b/atom. (a) Resonant double excitations of Table II; (b) single-ionization thresholds (shake-up); and (c) double-ionization thresholds (shake-off) of Table I. See text for the marked peak.

chamber is much longer than the length L_1 of the first chamber and the pressure has a value so that $\exp(-\alpha L_2)\approx 0$. From α and the pressure of the filling the absolute cross section is derived. Several scans were performed, but only three scans were selected because of the synchrotron current stability. The monochromator step width was about 0.33 eV and the integration time per point was 4 s. The total time to achieve the spectrum of Fig. 1 was 2 h. With special care the time constants of the two electrometer amplifiers were matched to the same value in order to suppress intensity fluctuations of the synchrotron light. In this way a signal-to-noise ratio of better than 10^4 was achieved, which is necessary to observe the expected 0.3% effect in the total cross section. The electrometer output was voltage-to-frequency converted and integrated by counters in a microcomputer which also positioned the monochromator. Since the double-ion chamber was not an optimized arrangement [32] the main source of error is the unknown effective length of the first chamber. Hence the accuracy of the cross-section measurement including the error of the pressure determination is estimated to about 10%.

Figure 1 shows the experimental threshold spectrum of the argon $K+L$ double photoexcitations. The $K+L$ edges could be extracted from the total cross section by fitting a Victoreen function to the total photoionization cross section that precedes the additional structures at lower energies. The zero of the cross-section axis corresponds to 77 000 b. All structures except that marked by an arrow could be reproduced in different beam times. The intensity of the marked peak depends on the adjustment of the monochromator and the double-ion chamber. Its origin is still not clear. The calculated energies of the resonances and of the ionization edges are also indicated in the figure. They are ordered in lines according to the four triplet and singlet inner-shell double-hole states.

The spectrum exhibits resonances and single-ionization edges at the triplet and at the singlet thresholds. The agreement of the energy positions with the theoretical predictions is fairly good. The resonances and the edges with an inner-shell state belonging to the triplet are less pronounced compared to those with the singlet inner-shell state. The single-ionization (shake-up) thresholds produce two jumps in the cross section. They are separated by about 8 eV in accordance with the calculation. The components of the inner-shell triplet cannot be resolved. Above the shake-up threshold with a singlet inner-shell state the total jump amounts to $\sigma\approx 180$ b, which corresponds to 0.24% of the total cross section. This result is close to the theoretical value 0.27% for shake-up in the sudden approximation mentioned above [29]. Thus the magnitude of $K+L$ threshold jumps for $3d$ transition metals which have been investigated before is confirmed also [8–10]. At the isolated lying singlet double-ionization threshold (3521.1 eV) no additional edge occurs in the photoabsorption spectrum. This reflects the fact that shake-off cross sections start with zero at threshold [27].

In conclusion, for argon $K+L$ photoexcitation, which leads to the $1s^12p^5$ inner-shell configuration, we find full agreement between experiment and theoretical considerations on the level of the present paper. Further calculations of the magnitude of the $K+L$ thresholds and of the transition probabilities and the final-state character for the discrete $K+L$ double excitations would be useful. This would be especially helpful for a better understanding of the two well-resolved resonances at the singlet edge. Based on the results of the present paper in principle it should be possible to carry out excitation-energy-dependent emission satellite spectroscopy [3,18]. This could be a further approach to untangle the complicated $K\alpha$ and $K\beta$ satellite spectra due to $K+L$ double holes [12,13,16].

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