# $L_1$-$L_{2,3}M$ Coster-Kronig transitions in argon

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The $L_1$-$L_{2,3}M$ Coster-Kronig spectrum of argon has been measured by using photon excitation. The intensity ratio of $0.30 \pm 0.02$ between the $L_1$-$L_{2,3}M_1$ main lines and the $L_1$-$L_{2,3}M_{2,3}$ lines is extracted from experiment. The experimental results for the ratio and partial decay rates are compared with present and previous theoretical estimates. [S1050-2947(99)03405-8]

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## I. INTRODUCTION

The only published $L_1$-$L_{2,3}M$ Coster-Kronig (CK) spectrum of argon was measured by Mehlhorn [1] thirty years ago but the transition energies and intensity distributions are still not known very reliably. The electron beam excited spectrum [1] consists of two broad low intensity groups in the kinetic energy range below 50 eV and a huge background which increases strongly towards lower kinetic energies. The first group of peaks originates from the $L_1$-$L_{2,3}M_1$ CK transitions and the second one from the $L_1$-$L_{2,3}M_{2,3}$ CK transitions. The inherent widths of Coster-Kronig lines are very large which also make the analysis of the spectrum difficult. In this work the $L_1$-$L_{2,3}M$ Coster-Kronig spectrum of argon has been measured by using photon excitation. The groups are now much better resolved from the background than before. This allows us to carry out a more reliable analysis of the spectrum, especially of the intensity ratio between the $L_1$-$L_{2,3}M_1$ and $L_1$-$L_{2,3}M_{2,3}$ groups.

Coster-Kronig transitions are typically more sensitive to the methods of calculations than normal Auger transitions. This is related to low kinetic energies of CK transitions and to the heavy overlap of the wave functions needed to calculate the decay rates. Transition energies are affected by both the spin-orbit and electrostatic interactions in the final state. Changes in kinetic energies and in the potential, where the wave functions are generated, may easily affect the decay rates, as demonstrated by Dyall and Larkins [2]. Low kinetic energy transitions are also sensitive to such effects as the exchange between the continuum electron and the bound electrons [3] and the mixing of final-state channels [4]. Coster-Kronig transitions thus offer a sensitive case to test the validity of various calculation methods in reproducing the experiment.

## II. EXPERIMENTAL

The measurements were performed at the Gas Phase Photoemission beamline at the Elettra light source, Trieste, Italy [5]. An undulator source (U12.5) with a 12.5 mm period provides high-intensity synchrotron radiation in the photon energy range from around 20 to well above 900 eV. The light is dispersed by a variable-angle spherical grating monochromator, equipped with five interchangeable gratings, with fixed entrance and exit slits, and prefocussing and postfocussing optics [6].

The $L_1$-$L_{2,3}M$ CK spectrum of argon was measured using a VSW hemispherical electron analyzer with mean radius of 50 mm mounted at the magic angle of 54.7° with respect to the electric vector of the incoming radiation. The analyzer was operated at 25 eV pass energy to give an energy resolution of about 350 meV. Argon was introduced into the experimental chamber through a needle mounted on an $xyz$ translator, and the working pressure was of $5.7 \times 10^{-5}$ mbar in the experimental chamber. Data were acquired at a photon energy of 401.9 eV and resolution of 100 meV using grating 4 (1200 l/mm, radius = 32 000 mm) and slits of 50 (entrance) and 100 (exit) microns. The kinetic energy scale of the spectrum was calibrated to the kinetic energy of the $L_1$-$L_{2,3}M_{2,3}(^1S_0)$ line given by Mehlhorn [1]. The spectrum has been normalized to both the photon flux and the spectrometer transmission. The incident photon flux was monitored by a photodiode (IRD Ltd. type AXUV-100) located at the exit of the experimental chamber. To determine the spectrometer's transmission at kinetic energies of interest, the $1s$ photoelectron line of He was measured at different photon energies and compared to the published photoionization cross section [7].

## III. RESULTS AND DISCUSSION

### A. Calculations

There are several calculations for the intensity ratio of the $L_1$-$L_{2,3}M_1$ and $L_1$-$L_{2,3}M_{2,3}$ manifolds and for their individual transitions [1–4]. Intermediate coupling (IC) was used by Mehlhorn [1], and configuration interaction in the final state (FISCI) was introduced by Dyall and Larkins [2]. The roles of exchange interaction, relaxation, and channel mixing were studied by Karim *et al.* [3,4]. We also repeated the calculations for the kinetic energies and intensities of the $L_1$-$L_{2,3}M$ transitions by using the nonrelativistic Cowan pro-

 

gram [8]. The single channel calculations of the $L_1$-$L_{2,3}M_1$ transitions were made using two basis sets in the final state, first including the $2p^5 3s^1$ and $2p^5 3p^4 3d^1$ configurations and second, in addition to them, also the $2p^5 3p^4 4d^1$ configuration. Continuum wave functions were generated in the field of the final ion which was different for the main and satellite states. The results with both basis sets were nearly the same, which is related to the fact that the mixing is the strongest between the $2p^5 3s^1$ and $2p^5 3p^4 3d^1$ configurations and the $2p^5 3p^4 4d^1$ plays only a minor role. Due to the FISCI the total $L_1$-$L_{2,3}M_1$ decay rate is divided by 60:40 between the main and satellite lines. The ratio is in good agreement with previous calculations [2].

Calculations for the $L_1$-$L_{2,3}M_{2,3}$ transitions were also carried out by using our relativistic MCDF code [9]. The relativistic partial decay rates of the $L_1$-$L_{2,3}M_{2,3}$ transitions were found to agree well with the nonrelativistic results. Also the total decay rate was almost the same in both calculations. MCDF calculations predicted slightly broader energy splittings for the $L_1$-$L_{2,3}M_{2,3}$ transitions than the HF calculations. This is most probably related to the fact that the Cowan code uses a scaling of Coulomb integrals in order to compensate for the missing electron correlation. We thus conclude that besides the correlation also the relativistic effects are fairly well accounted for in the Cowan code.

Our calculated total linewidth for $L_1$, $\Gamma_{L_1}$, is 2.33 eV. The contributions of 0.45, 0.67, and 1.21 eV to the total rate arising from the correlation satellite, $L_{2,3}M_1$ and $L_{2,3}M_{2,3}$ final states, respectively, deviate somewhat from previous predictions. In previous calculations the total linewidths ranged from 2.34 to 3.11 eV [2,4] which are somewhat larger than our value.

### B. Experimental results

The analysis of the CK spectrum is quite complicated even when the spectrum is excited by photons and the background is lower than in the electron-excited spectrum. There are large discrepancies between experimentally determined linewidths for $\Gamma_{L_1}$: $2.25 \pm 0.15$ eV was obtained from x-ray emission spectroscopy and $2.25 \pm 0.05$ eV from photoelectron spectroscopy (PES) [10], whereas $1.84 \pm 0.2$ eV was extracted from Auger electron spectroscopy [1]. We assume the PES result, since this method is the most straightforward. The inherent widths of the $L_1$-$L_{2,3}M$ lines are also broadened by the lifetimes of the final states, which we estimate to be 0.11 eV (or about the same as the natural widths of the $2p^{-1}$ states [11]). The Lorentzian contribution to the CK lines thus amounts $\sim 2.36$ eV. In comparison, the Gaussian broadening due to the electron spectrometer is much smaller (0.35 eV) and does not appreciably affect the line shape. A Lorentzian therefore remains a good approximation to the line profile. In the analysis we have fixed its width to 2.40 eV. The shape of the background was then estimated so that the flanks of the CK groups and the region between between them were well reproduced by the Lorentzians of this width.

In order to gain information also about the relative intensities of the transitions within the CK groups, a least-squares fit was carried out for the spectrum. The fit program, however, failed to find a trustworthy solution for the $L_1$-$L_{2,3}M_{2,3}$ group, when the energies and intensities of these lines were allowed to change freely. This was probably because there are many unresolvable lines within a short energy range. The splittings of these lines were then fixed relative to the $^1S_0$ term using the semiempirically determined results of Mehlhorn [1]. Some nearby peaks were combined and their positions were set at weighted averages using the energies of Mehlhorn and intensities calculated with the Cowan code [8]. The fit of the spectrum so obtained is shown in Fig. 1. Energies and partial decay rates obtained from the fit are given in Table I. Errors were defined as the maximum deviation from the average value, when the linear background was set at different levels.

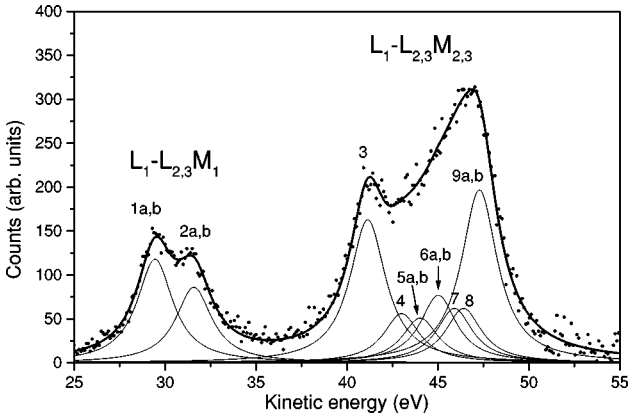


FIG. 1. $L_1$-$L_{2,3}M$ Coster-Kronig spectrum of Ar. Experimental data after normalization to light intensity and background subtraction are shown with dots. The thick solid curve shows the total fit, while thinner curves display individual components.

The overall intensity distribution agrees generally quite well with the results of Mehlhorn [1], considering the large widths of the peaks. The $L_1$-$L_{2,3}M_{2,3}(^1D_2)$ transition, however, appears distinctly smaller in our spectrum. The reason for this is not clear but it could be due to overlapping satellite transitions in the CK spectrum of Mehlhorn that was excited with 4-keV electrons. The $L_1$-$L_{2,3}M_1$ transition energies are found to be 0.7–1.1 eV higher than in the previous experiment [1], which is clearly outside the experimental uncertainty. The relative intensities of these lines are similar in both experiments.

Despite obvious difficulties in the background subtraction for the electron-excited CK spectrum, the $L_1$-$L_{2,3}M_1$ to $L_1$-$L_{2,3}M_{2,3}$ branching ratio of 0.26 originally given by Mehlhorn [1] agrees rather well with our result of $0.30 \pm 0.02$. In fact, his later determination of 0.37 [12] using the same measurement differs slightly more from the present result.

### C. Comparison between experiment and theory

The theoretical and observed kinetic energies and intensities are compared with each other in Table I. The calculations reproduce fairly well the spread of the energies of the $L_1$-$L_{2,3}M$ transitions. The calculated positions of the $L_1$-$L_{2,3}M_1$ satellite lines, which are at least as intense as the $L_1$-$L_{2,3}M_1(^3P_0)$ line, are more than 5 eV below the main lines which agrees fairly well with the experimental energy separation of about 6 eV (correlation satellites are not shown

TABLE I. Intensities and kinetic energies of the Ar $L_1$-$L_{2,3}M$ Coster-Kronig transitions relative to the $L_1$-$L_{2,3}M_{2,3}(^1S_0)$ line.

| Line | Transition | Intensity Calc. [a] | Intensity Expt. [b] | Intensity Expt. | Kinetic energy (eV) Calc. [a] | Kinetic energy (eV) Expt. |
|---|---|---|---|---|---|---|
| 1*a* | $L_1$-$L_{2,3}M_1(^1P_1)$ | 167[c] | 76 | 71±5 | −11.01 | −11.70±0.10 |
| 1*b* | $L_1$-$L_{2,3}M_1(^3P_0)$ | 1[c] | | | −10.51 | |
| 2*a* | $L_1$-$L_{2,3}M_1(^3P_1)$ | 117[c] | 57 | 52±4 | −8.97 | −9.57±0.15 |
| 2*b* | $L_1$-$L_{2,3}M_1(^3P_2)$ | 3[c] | | | −8.39 | |
| 3 | $L_1$-$L_{2,3}M_{2,3}(^1S_0)$ | 100 | 100 | 100±4 | (42.54) | (41.14)±0.15 |
| 4 | $L_1$-$L_{2,3}M_{2,3}(^1D_2)$ | 60 | 70 | 35±5 | 2.08 | 1.86 |
| 5*a* | $L_1$-$L_{2,3}M_{2,3}(^3P_1)$ | 14 | 9 | 31±10 | 3.00 | 2.89 |
| 5*b* | $L_1$-$L_{2,3}M_{2,3}(^3P_0)$ | 13 | 16 | | 3.49 | |
| 6*a* | $L_1$-$L_{2,3}M_{2,3}(^3D_1)$ | 48 | 45 | 47±9 | 4.31 | 3.88 |
| 6*b* | $L_1$-$L_{2,3}M_{2,3}(^3P_2)$ | 12 | 15 | | 4.36 | |
| 7 | $L_1$-$L_{2,3}M_{2,3}(^3S_1)$ | 61 | 41 | 38±5 | 5.28 | 4.77 |
| 8 | $L_1$-$L_{2,3}M_{2,3}(^3D_2)$ | 81 | 79 | 38±10 | 5.76 | 5.27 |
| 9*a* | $L_1$-$L_{2,3}M_{2,3}(^3D_3)$ | 124 | 122 | 120±10 | 6.62 | 6.14 |
| 9*b* | $L_1$-$L_{2,3}M_{2,3}(^1P_1)$ | 10 | 8 | | 6.91 | |

[a]HFR calculation.

[b]Experimental results by Mehlhorn [1].

[c]Multiconfiguration calculations with the $2p^5 3s^1$ and $2p^5 3s^2 3p^4 3d^1$ configurations.

in Fig. 1). Theory slightly underestimates the energy difference between the $L_1$-$L_{2,3}M_1$ and $L_1$-$L_{2,3}M_{2,3}$ groups.

Our calculated $L_1$-$L_{2,3}M_1$ (main lines) to $L_1$-$L_{2,3}M_{2,3}$ intensity ratio of 0.55 does not agree well with our experimental value of 0.30±0.02. The effect of channel mixing was shown by Karim *et al.* [4] to result in a transfer of intensity from the $L_1$-$L_{2,3}M_1$ channel to the $L_1$-$L_{2,3}M_{2,3}$ channel; it diminished the $L_1$-$L_{2,3}M_1$ to $L_1$-$L_{2,3}M_{2,3}$ intensity ratio by ~23% (see Table II). The channel mixing was omitted in our calculations. If the effect is as strong as estimated in Ref. [4], our calculated branching ratio would decrease to close to 0.40. This value is still quite far from the experimental result. The CI value of Dyall *et al.* [2], if corrected for channel mixing, would give a branching ratio in better agreement with experiment.

Our calculations in estimating the total transition rate agree well with the CI calculations of Dyall *et al.* [2] but both predictions slightly overestimate the lifetime width as compared with experiment. If CI is omitted in the calculations, the total rate is overestimated even more. Note that the $L_1$-$MM$ Auger transitions have been neglected in all theoretical total rates that are denoted in Table II. According to Mehlhorn [1], the experimental intensity ratio between the $L_1$-$MM$ and $L_1$-$L_{2,3}M_{2,3}$ transitions is about 0.07, hence the Auger channels are not particularly significant.

## IV. CONCLUSION

The Ar $L_1$-$L_{2,3}M$ Coster-Kronig spectrum was measured with synchrotron radiation which allowed us to obtain a much lower background than in the electron excited experiment [1]. The extracted $L_1$-$L_{2,3}M_1$ to $L_1$-$L_{2,3}M_{2,3}$ branching ratio of 0.30±0.02 differs only slightly from the earlier experimental determination, but substantially from the theoretical branching ratio of 0.55 obtained from MCHF calculations. The neglect of channel mixing does not fully explain the discrepancy. The calculations predict a lifetime width of 2.33 eV for the $2s^{-1}$ state, in good agreement with the result of 2.25±0.05 eV reported in the literature from x-ray photoelectron spectroscopy [10]. The contributions of 0.45, 0.67, and 1.21 eV to the total rate were computed to arise from the correlation satellite, $L_1$-$L_{2,3}M_1$ and $L_1$-$L_{2,3}M_{2,3}$ final states, respectively.

TABLE II. The ratio of the Ar $L_1$-$L_{2,3}M_1$ and $L_1$-$L_{2,3}M_{2,3}$ transitions, and the total $L_1$-$L_{2,3}M$ transition rate.

| | This work | | | Mehlhorn | | Dyall *et al.* [2] | | | Karim *et al.* [4] | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Calc. | Calc. | Expt. | Expt. [1] | Expt. [12] | HF [a] | CI [b] | NHF [c] | Calc. [a] | Calc. [d] |
| $L_1$-$L_{2,3}M_1$ / $L_1$-$L_{2,3}M_{2,3}$ | 0.55 | ~0.4 [f] | 0.30±0.02 | 0.26 | 0.37 | 0.56 | 0.40 | 0.51 | 0.62 | 0.48 |
| Total $L_1$-$L_{2,3}M$ rate (eV) | 2.33 | | | | | 2.84 | 2.34 | 3.01 | 2.93 | 3.11 |
| Total $L_1$ decay rate (eV) | | | 2.25±0.05 [e] | 1.84±0.2 | | | | | | |

[a]Nonrelativistic single-configuration Hartree-Fock calculation.

[b]Nonrelativistic multiconfiguration Hartree-Fock calculation.

[c]Non-orthogonal Hartree-Fock approximation.

[d]Nonrelativistic single-configuration Hartree-Fock calculation corrected for channel coupling.

[e]From photoelectron spectroscopy, Ref. [10].

[f]Approximately corrected for channel coupling.

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