Ar 3s satellite spectrum studied by asymmetric (e, 2e) experiments

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The Ar 3s satellite spectrum has been studied by means of asymmetric (e,2e) experiments at 1-keV incident energy and in three different kinematical conditions. The intensities of the main satellite lines relative to the intensity of the 3s main line (29.3 eV) have been determined. The three chosen kinematical conditions allow for studying the dependence of the relative intensity on the momentum transfer in a region which is intermediate between the binary and dipolar regimes. The discrepancy between the relative intensity of the transition to the $3d\,^2S$ ion state measured by (e,2e) and high-energy photoionization experiments is confirmed. Sizeable contributions from transitions not belonging to the ^2S manifold and a kinematical dependence of the peaks centered at 36.5 and 41.3 eV have been observed.

I. INTRODUCTION

The ionization spectra of inner valence shells in atoms and molecules display a rich satellite structure due to strong electron correlations. The Ar 3s ionization spectrum is a prototype for such behavior and it has been extensively investigated by both photoionization[1–10] and binary (e,2e) experiments.[11–15]

Photoionization experiments have been performed from threshold[9–10] up to 1487-eV incident energy.[1,7] The results of the high-energy experiments[1,7] have shown that both initial- and final-state correlations contribute to determining the features observed in the spectra.[16–21] At lower incident energy[3–6] it has been recognized that initial-state correlations as well as interchannel and continuum-continuum coupling play a non-negligible role. As a consequence, the relative intensities of the satellite peaks, at threshold, have been shown to be strongly dependent on the photon energy.[9,10]

The Ar 3s satellite structure has also been investigated by (e,2e) spectroscopy,[11–15] which is an electron-induced ionization experiment where both the final unbound electrons are detected in coincidence and the kinematics of the process is fully determined. These Ar investigations have been performed at incident energies between 300 and 1500 eV and always in symmetric kinematics.[11–14] These kinematical conditions involve collisions characterized by large momentum transfer, $\mathbf{K}=\mathbf{K}_0-\mathbf{K}_a$, and small-ion recoil momentum, $\mathbf{q}=\mathbf{K}_0-(\mathbf{K}_a+\mathbf{K}_b)$, where $\mathbf{K}_0$, $\mathbf{K}_a$, and $\mathbf{K}_b$ are the momenta of the incident, scattered, and ejected electrons, respectively. The recent asymmetric (e,2e) investigation of the Ar 3s satellites[15] has shown that both symmetric and asymmetric experiments are a suitable tool for a spectroscopic investigation of the target, whenever they can be interpreted within the impulse approximation (IA) model. Similarities and differences between photoionization and impulsive (e,2e) experiments have been reviewed in several papers.[22–24] Namely, the quite-different portions of the electron wave functions sampled by the two spectroscopies[22] and the uncertainties introduced by the background subtraction in x-ray photoemission spectroscopy (XPS) experiments[24] were extensively discussed. Here it is only to be that in the high-energy limit both (e,2e) and XPS are expected to yield satellite spectra in which the energies and the relative intensities of the different transitions are identical provided that the initial-state correlations are negligible. In the case of Xe, the 5s satellite spectrum displayed a fair agreement between XPS (Ref. 25) and the (e,2e),[13] even though it is noted that the accurate (e,2e) investigation by Cook *et al.*[16] has shown significant disagreement with some of the XPS results.[25] Conversely the relative intensities of the strongest lines in the argon 3s spectrum are different in XPS (Refs. 1 and 7) and (e,2e) (Refs. 11–15) experiments.

Amusia and Kheifets[27] attempted to explain this discrepancy by many-electron correlations in the initial state of the atom, which are shown to be sizable in photoionization, and negligible for impulsive (e,2e) experiments. Even though their results are in reasonable agreement with the Ar experimental data, it remains to be verified if this mechanism can account for the Xe case as well.

Brion and co-workers[4,5] have tried to connect the (e,2e) and photoionization results measuring the relative intensities of several satellite lines in the Ar 3s spectrum as a function of the photon energy in the range 60–170 eV. They concluded that much of the controversy is ascribable to the very different energy resolutions used in the various experiments.[5]

In the present work the Ar 3s satellite spectrum has been studied by asymmetric (e,2e) experiments. The asymmetric kinematics allow for studying ionizing collisions in a variety of kinematics ranging from the Bethe ridge[28] (binary regime) to the optical limit (dipolar regime $K \rightarrow 0$). In these experiments the kinetic energies of the free electrons are kept constant. Therefore they are particularly suited for studying the dependence, if any, of the relative intensity of the different transitions on the momentum transfer K and/or the ion recoil momentum q. In the present experiments the scattered and ejected electron energy, E_a and E_b, respectively, were kept fixed, while the incident electron energy was varied in order to scan the transition energy range 27–47.5 eV. The $(e,2e)$ energy separation spectra have been measured at three different values of the momentum transfer, namely, $K=1.3$, 2.15, and 3 a.u. Recent papers[29,30,15] have shown that asymmetric $(e,2e)$ experiments can be interpreted within the IA framework provided the kinematics met the Bethe ridge conditions. The experiment at the largest K value fully complies with this condition, while the other two kinematics are intermediate between the impulsive and dipolar regimes.

This work is meant to investigate the satellite structure in a regime which is intermediate between the dipolar regime, widely investigated by photoionization experiments, and the binary one, extensively studied by symmetric $(e,2e)$ experiments. To the purpose it has been chosen an ejected electron energy of 120 eV which is lower than the photoelectron kinetic energy of the XPS experiments, and approaches the values used in recent photoemission experiments.[4–6]

II. EXPERIMENT

The experimental setup and the procedures adopted in measuring the triple differential cross sections have been presented in previous papers[30,31] and here only the details relevant to the present work will be discussed. The coincidence spectrometer is a crossed-beam apparatus. A well-collimated beam of monochromatic electrons crosses an effusive gaseous beam. Two electron hemispherical analyzers rotate independently around the scattering center and detect pairs of electrons coincident in time and selected in energy and scattering angle. The acceptance solid angles and the energy resolutions for both analyzers were $\Delta\Omega_a=\Delta\Omega_b=3\times10^{-4}$ sr and $\Delta E_a=\Delta E_b=1.2$ eV, respectively. The overall energy resolution in the coincidence energy-separation spectrum has been determined by measuring the transitions to the He $1s^{-1}$ and Ar $3p^{-1}$ ionic states and it was found to be $\Delta E=1.7$ eV, full width at half maximum (FWHM).

In each measurement both the scattered- and ejected-electron angles were kept fixed. The energies E_a and E_b were set at 880 and 120 eV, respectively, while the incident energy scanned the range 1027–1047.5 eV. The measurements have been performed at three different values of the scattering angle θ_a, namely, 8°, 14°, and 20°, which correspond to K values of 1.3, 2.15, and 3 a.u., respectively. The values of the ejected-electron angle, θ_b, have been chosen in order to have $\hat{K}_b \| \hat{K}$. This condition selects the minimum achievable q in the three different kinematics, namely, 0.00, 0.83, and 1.63 a.u. at $K=3.00$, 2.15, and 1.30 a.u., respectively.

The experimental spectra are reported in Fig. 1. The main line relative to the ion configuration $3s3p^6\ ^2S$ at 29.3 eV as well as the satellite spectrum from 35 eV up and above the Ar^{2+} ionization threshold are clearly present in all the measured spectra. In previous symmetric $(e,2e)$ (Refs. 11–14 and 23) experiments it was found that the main contribution to the 3s satellite spectrum comes from five dominant transitions to the ^2S manifold of Ar II. According to these results five independent peaks, labeled a, b, c, d, and e in Table I, have been fitted to the energy separation spectra measured by this work. Intensities and energy positions of the peaks were free-fitting parameters. The line shape was assumed identical to the model function that was independently fitted to the $3s^23p^5\ ^2P$ line, not shown in Fig. 1. The same transition was used to calibrate the energy-separation scale. The solid lines in Fig. 1 are obtained from a χ^2 fit to the data, while the dashed lines are the individual contributions to the fit. The best-fitting parameters, determined by this procedure, are collected in Table I.

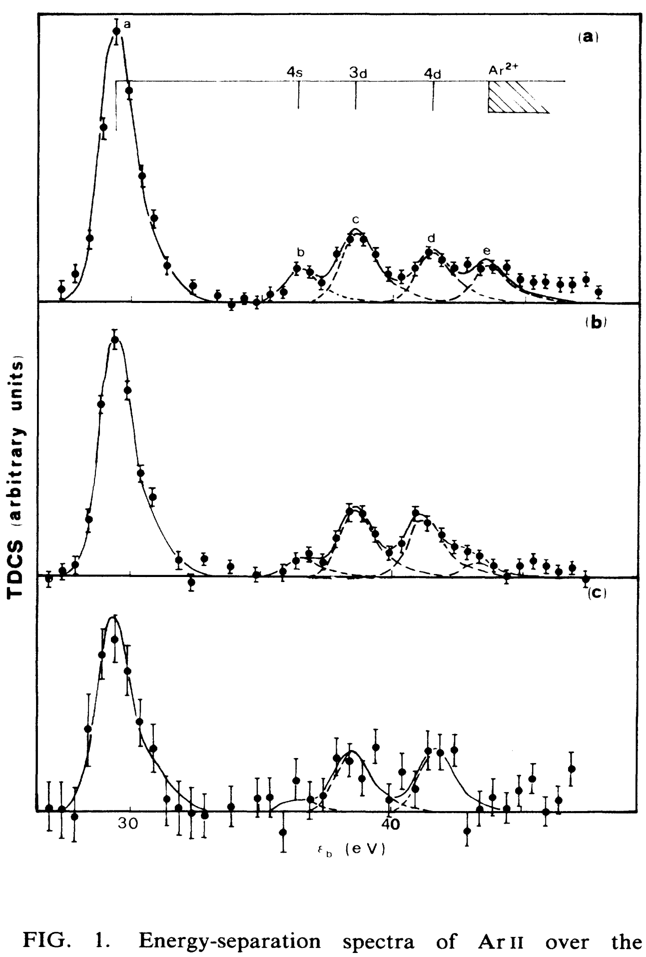

FIG. 1. Energy-separation spectra of Ar II over the 27.0–47.5-eV region at (a) $\theta_a=20°$ and $K=3.0$ a.u.; (b) $\theta_a=14°$ and $K=2.15$ a.u.; (c) $\theta_a=8°$ and $K=1.3$ a.u. The solid curves show the best fit to the data with peaks at 29.3, 36.5, 38.5, and 43.4 eV. The dashed curves are the individual contributions to the best fit.

TABLE I. Relative intensities and energy positions of the five deconvoluted contributions to the Ar II spectrum as derived from relative $(e,2e)$ cross sections. The kinematical conditions are $E_0=1027.0-1047.5$ eV, $E_a=880$ eV, and $E_b=120$ eV. The columns headed binary $(e,2e)$ give the assignment and the energy position of the dominant satellite structures as determined by previous $(e,2e)$ symmetric experiment (Ref.23).

Binary $(e,2e)$		Present work				
				Relative intensity		
				$\theta_a=20°$	$\theta_a=14°$	$\theta_a=8°$
^2S manifold		Peak		$q=0.0$ a.u.	$q=0.8$ a.u.	$q=1.6$ a.u.
transitions	ε (eV)	label	ε (eV)	$K=3.0$ a.u.	$K=2.1$ a.u.	$K=1.3$ a.u.
$3s3p^6$	29.3	*a*	29.3±0.1	100.0±1.8	100.0±6.0	100.0±17.0
$3s^23p^44s$	36.7	*b*	36.5±0.2	12.1±2.5	8.3±6.5	11.0±15.0
$3s^23p^43d$	38.6	*c*	38.5±0.2	27.0±2.6	28.1±7.1	30.0±15.0
$3s^23p^44d$	41.2	*d*	41.3±0.2	20.4±2.5	26.6±8.2	35.0±16.0
$3s^23p^45d$	42.7					
	43.4	*e*	43.4±0.2	8.1±1.4	8.0±7.2	
$Ar^{2+}+e$			43.5−47.5	15.9±4.8	8.0±7.0	

III. RESULTS AND DISCUSSIONS

The energy positions of the individual peaks $a-e$ measured by these experiment are in good agreement with the dominant configurations of the ^2S manifold as found by all the previous $(e,2e)$ works.[11–14] As far as the relative intensities are concerned, the results of the experiments on the Bethe ridge [$K=3$ a.u., $\theta_a=20°$, Fig. 1(a)] can be directly compared with the symmetric $(e,2e)$ data. In fact a previous investigation[15] has shown that the angular distributions of the transition to the $3s^{-1}$ and $3p^{-1}$ ion states, measured upon kinematics identical to those of the present work, are satisfactorily described by an IA model. Therefore the $(e,2e)$ cross section is directly related to the probability of populating the different final ionic states of the target. A general agreement is therefore found among all the $(e,2e)$ experiments performed under impulsive conditions, irrespective of the kinematics symmetry. The energy-separation spectrum of Fig. 1(a) can be also compared with the photoionization data at high incident energy, where the sudden approximation is expected to be valid. The present results confirm the discrepancy existing between the relative intensities as determined by $(e,2e)$ and XPS. This is clearly shown in Fig. 2 where the same Ar 3*s* satellite spectrum reported in Fig. 1(a) is compared with the XPS data by Svensson *et al.*[7] and, for sake of completeness, with the photoionization results by Kossmann *et al.*[6] at $h\nu=120$ eV. The curves labeled (*a*) and (*b*) in Fig. 2 are obtained by convoluting with the response function of the $(e,2e)$ spec-

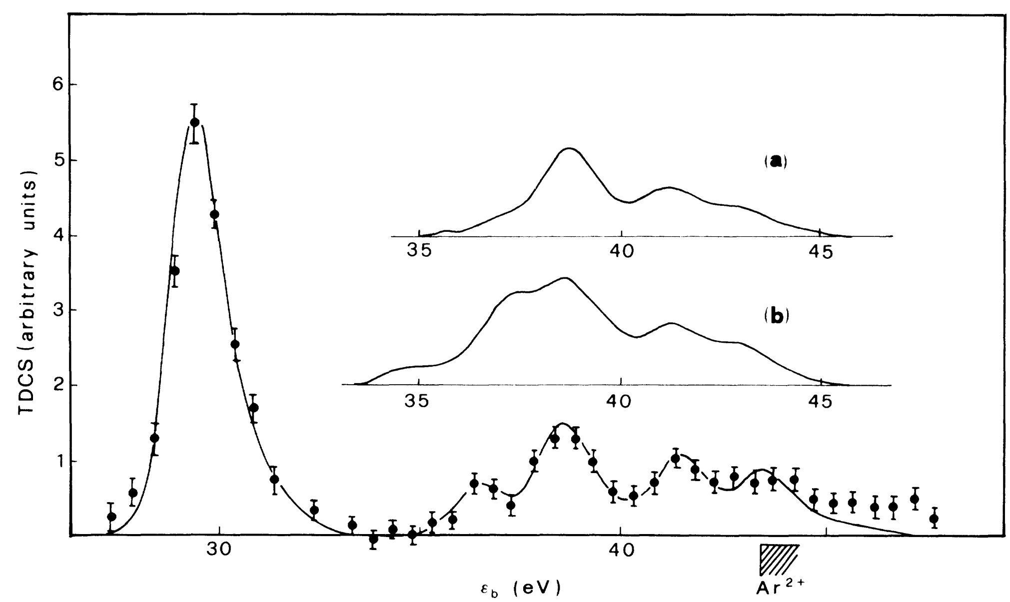

FIG. 2. $(e,2e)$ energy-separation spectrum of Ar II over the 27.0–47.5-eV region. The kinematical conditions are $E_a=880$ eV, $E_b=120$ eV, $\theta_a=20°$ ($K=3.0$ a.u.), and $\theta_b=68°$. The results of the photoionization experiments at (a) 1487 eV (Ref. 7) and (b) 120 eV, convoluted with the response function of the $(e,2e)$ spectrometer, are reported over the $(e,2e)$ spectrum.

trometer all the relative satellite intensities determined by Svensson *et al.*[7] [curve (a)] and Kosmann *et al.*[6] [curve (b)]. The largest differences among the three spectra are observed in the neighborhood of transitions which do not belong to the ^2S manifold, i.e., approximately 35 and 40 eV. The XPS spectrum is largely dominated by the transitions of the ^2S manifold [the sum of the contributions from transitions to ionic states with ^2P symmetry amounts only to 12% of the total intensity in the energy range 34.5–47.5 eV (Ref. 7)], while at 120 eV transitions to ionic states not belonging to the ^2S manifold remarkably contribute to the total intensity.[6] The $(e,2e)$ spectrum appears to be an intermediate case between the high- and low-energy limits. The experimental spectra shown in Figs. 1(b) and 1(c) have been measured at $K=2.15$ and 1.3 a.u. Only the intensity of the peak centered at 38.5 eV does not appear to be dependent on the kinematics. This is better seen in Fig. 3, where the relative intensities of the deconvoluted individual contributions to the energy separation spectrum at 36.5, 38.5, and 41.3 eV (see Table I) are plotted versus q and K [Figs. 3(a) and 3(b) respectively]. The previous $(e,2e)$ results[13,14,23] obtained upon symmetric kinematics and incident energies ($E_0 \geq$ 1000 eV) are also reported in the figure. In the case of the peaks at 36.5 and 38.5 eV all the $(e,2e)$ results agree within the experimental uncertainties. It is to be noted that the present results are in good agreement with the distorted-wave impulse approximation (DWIA) predictions by McCarthy,[32] also reported in the figure. A least-squares fit to a straight line of the experimental data, shown in Fig. 3, does not allow for establishing any dependence of the peak intensity on the q value. Indeed, for the two peaks at lower energies the best fitted lines are horizontal within the uncertainties of the fitting parameters (Table II), while no acceptable fit is obtained for the peak d. Conversely the relative intensities of the peaks at 36.5 and 41.3 eV, show a monotonic dependence versus K, as shown by Fig. 3(b). A high-resolution photon-induced fluorescence work[8] has pointed out that the $4d\ ^2S$ line is separated by 100 meV from the $5d\ ^2D, ^2P$ satellite lines, the three of them being indistinguishable with the present energy resolution. For photon energies between threshold and 125 eV the $5d\,^2D, ^2P$ lines contribute with about 25% $\pm$5% (Ref. 8) to the total apparent intensity of the $4d\ ^2S$ line. The $5d\ ^2D, ^2P$ configurations are characterized by a (^1S) core [while the configurations of the ^2S manifold refer to a (^1D) core] and are not due to final-state correlations. The excitation probability of such final ionic states in $(e,2e)$ experiments might be dependent on the kinematical conditions (E_0, K). Therefore a non-negligible contribution of the $5d\ ^2D, ^2P$ transitions to the measured intensity of the peak at 41.3 eV might explain the observed behavior of the peak intensity versus K. This hypothesis is consistent with the finding that at small K the DWIA prediction for the transition to the $4d\ ^2S$ ion state underestimates the relative intensity of the peak. Conversely at larger K the peak intensity has been shown to converge to the DWIA prediction.[23] Photoionization experiments[7,8] have also shown that in the energy region 36.0–37.5-eV transitions belonging to the ^2P and ^2D manifolds dominate over the ^2S ones, which can be as small as 6% of the total intensity in this energy interval. Therefore also the relative intensity of the peak centered at 36.5 eV can be expected to monotonically decrease with K. The results of Fig. 3 show that the $(e,2e)$ intensities do not converge to the XPS values in the limit of large q. This is an opposite finding, at least within the range of q explored, with respect to the theoretical predictions by Amusia and Kheifets.[27] If the initial-state correlations were responsible for the kinematical dependence of the intensity of the peak at 41.3 eV, the relative intensity measured by the different $(e,2e)$ experiments should have defined an unique trend versus q. This is not found by the experiments. The relative intensity of the peak dominated by the transition to the $3d\ ^2S$ is consistently larger than the XPS result. Such a difference cannot be explained by the poor resolution of the $(e,2e)$ experiments (never better than 1.5 eV full width at half maximum, which does not allow the resolution of all the transitions ($3d\ ^2D$, $3d\ ^2S$, $4p\ ^2P$) (Refs. 6–8) in the energy range 38.0–39.5 eV. In fact the total $(e,2e)$ intensity of the unresolved transitions in this region is larger than the one obtained by convoluting the XPS intensities with the $(e,2e)$ energy response function [shown by the arrow in Fig. 3(b)]. Finally it is to be noted that the $(e,2e)$ spectrum at $K=3$ a.u. shows a contribution above the double-ionization threshold larger than the XPS one. The intensity in this region decreases faster than the intensity of the satellite lines of the ^2S manifold (see Table

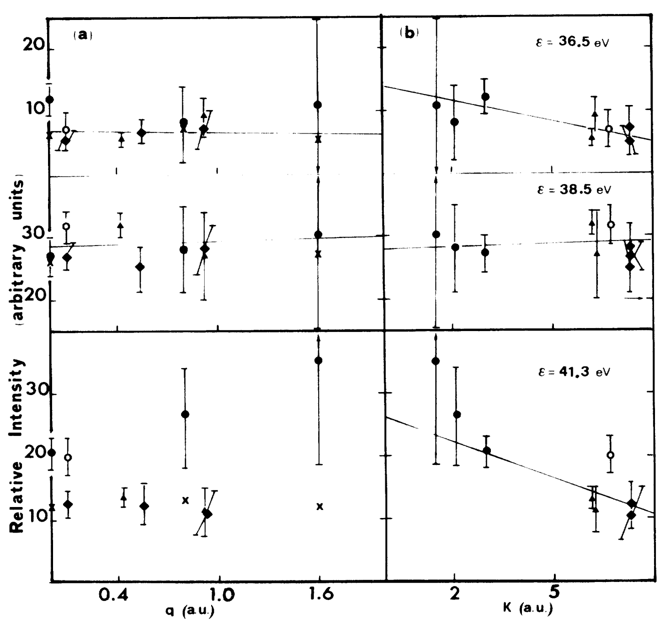

FIG. 3. Relative intensity of the three main features of the satellite spectrum plotted vs (a) q and (b) K. The intensity of the transition to the $3s^{-1}$ Ar^+ state at 29.3 eV has been assumed to be 100. Experimental data: ●, this work; ○, Ref. 13; ▲, Ref. 14; ♦, Ref. 23; ×, theoretical predictions by McCarthy (Ref. 32). The arrows to the right of the vertical axis show the XPS value (Ref. 7). The straight lines are least-squares fits to the $(e,2e)$ data.

TABLE II. The most probable estimates for the parameters of the trial function $ax+b$ ($x=q$ or K) fitted to the data in Fig. 3. The quoted uncertainties are one standard deviation and $\bar{\chi}^2$ is the reduced χ^2 function value.

	ε (eV)					
	36.5		38.5		41.3	
	Fig. 3(a)	Fig. 3(b)	Fig. 3(a)	Fig. 3(b)	Fig. 3(a)	Fig. 3(b)
a	-0.4 ± 2.9	-1.1 ± 0.6	0.8 ± 3.5	0.1 ± 0.6		-1.9 ± 0.6
b	7.3 ± 1.4	13.9 ± 3.8	28.8 ± 1.5	28.2 ± 4.0		26.2 ± 4.0
$\bar{\chi}^2$	0.87	0.40	0.79	0.79		0.98

I). This is a different finding with respect to the previous symmetric $(e,2e)$ experiments where the transition intensity above the Ar III threshold was found to be independent from incident energy and recoil momentum.[23]

IV. CONCLUSIONS

An investigation of the Ar $3s$ satellite structures by asymmetric $(e,2e)$ experiments has been presented. This represents the first attempt to study the dependence of the satellite intensity on the momentum transfer in the collision.

The relative intensity of the peak at 38.5 eV, which is the only one to be largely dominated by a transition of the ^2S manifold is found to be independent on the ionization kinematics. The discrepancy between its value measured by the $(e,2e)$ and XPS experiments, already observed in previous works, is confirmed. The intensity of the peaks centered at 36.5 and 41.3 eV, previously assigned by symmetric $(e,2e)$ experiments to transitions of the ^2S manifold, show a dependence on K. This is explained with a sizeable contribution from transitions belonging to the ^2D and ^2P manifolds, whose intensity could be dependent on the dynamics of the ionizing collision. A recent investigation by McCarthy *et al.*[33], which was made available to us after submission of this paper, clearly detects contributions from transitions belonging to the ^2P and ^2D manifolds in the $(e,2e)$ energy-separation spectrum of the Ar $3s$ satellites. It also gives evidence of a dependence on the recoil momentum q for the relative intensity of these satellite structures. This new investigation samples the angular distributions of the satellites with a fine grid in q and good accuracy, but always in symmetric conditions, i.e., at large momentum transfer ($4\leq K\leq 8$ a.u.). In our study, on the other hand, the investigation of the relative intensity has been performed in asymmetric kinematics and with a much lower momentum transfer, $K\geq 1.3$ a.u. It is therefore plausible that both of the effects, the dependence of the relative satellite intensity upon q and K, are present. $(e,2e)$ experiments with energy resolution comparable to the XPS measurements would establish on firmer grounds the aforementioned dynamical effects.

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