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Experimental and theoretical shake-up studies.
The rare gases

D. J. Bristow, J. S. Tse, and G. M. Bancroft*
Department of Chemistry and Centre for Chemical Physics, University of Western Ontario,
London, Canada

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The x-ray photoelectron shake-up spectra on the Ar *2p* and Kr *3d* core levels have been obtained to high statistics. The shake-up energies and intensities on the Ne 1*s*, Ar 2*p*, Kr 3*d*, and Xe 3*d* levels have been calculated using Hartree-Fock-Slater $X\alpha$ calculations. These calculations generally show good agreement with experiment and confirm the assignments. The shake-up energies are in good agreement with the optical-transition energies for the equivalent core alkali-metal ions. The relaxation energies from shake-up have been calculated from the experimental spectra, and are shown to be much smaller than the relaxation energies from shake-off.

I. INTRODUCTION

There have been several experimental and theoretical studies of the shake-up structure on the core-level rare-gas photoelectron spectra.[1–4] Well-resolved shake-up spectra have been published for He,[2] Ne,[3] and Xe,[3] but the statistics on the Ar and Kr spectra[4] were not sufficient to enable a full interpretation. The assignments have generally been made using theoretical shake-up energies. For example, the Ne assignments were made with the shake-up energies calculated from multiconfigurational Hartree-Fock calculations,[3] and Carlson *et al.*[4] assigned the major shake-up peak in the Kr and Ar spectra using nonrelativistic Hartree-Fock calculations. More recently, Ne shake-up energies have been calculated using the SCF-$X\alpha$ method.[5] Intensity calculations have only very recently been performed on the rare-gas shake-up by Loubriel on He using the $X\alpha$ method,[6] and Talman *et al.*[7] on Ne, Ar, Kr, and Xe using an optimized potential model.

Interest in rare-gas shake-up energies and intensities in our laboratory stems from the development of the atomic model[8] for approximating molecular shake-up energies. The basic premise involved in this method is that the Rydberg levels of rare-gas fluorides are essentially atomic in character. Thus, by obtaining accurate atomic shake-up energies and intensities, one has a valuable tool for analyzing the more complex molecular spectra of the Xe and Kr fluorides.[8,9] In the present study, we have obtained the Ar 2*p* and Kr 3*d* shake-up spectra to high statistics. Using the $X\alpha$ method, we have calculated both shake-up energies and intensities which are in good agreement with the observed values.

II. EXPERIMENTAL

The shake-up spectra interpreted in this work were obtained on a McPherson ESCA-36 photoelectron spectrometer using a Mg x-ray source. The research grade Ar and Kr gases were bled into a sample chamber at a sufficiently low pressure to minimize inelastic scattering effects. The spectra were fit by a least-squares program written by Coatsworth[10] and modified to constrain spin-orbit doublets by Gupta. Each peak is fitted to an analytical function which is a sum of Gauss-Lorenz shape functions.

III. RESULTS

A. Ar and Kr shake-up spectra

The Ar and Kr shake-up spectra obtained appear in Figs. 1 and 2, respectively. In order to fit the shake-up peaks, and minimize subjectivity, the following procedure was employed. Initially, the main photolines were fit with no constraints in order to obtain a spin-orbit splitting value and the re-

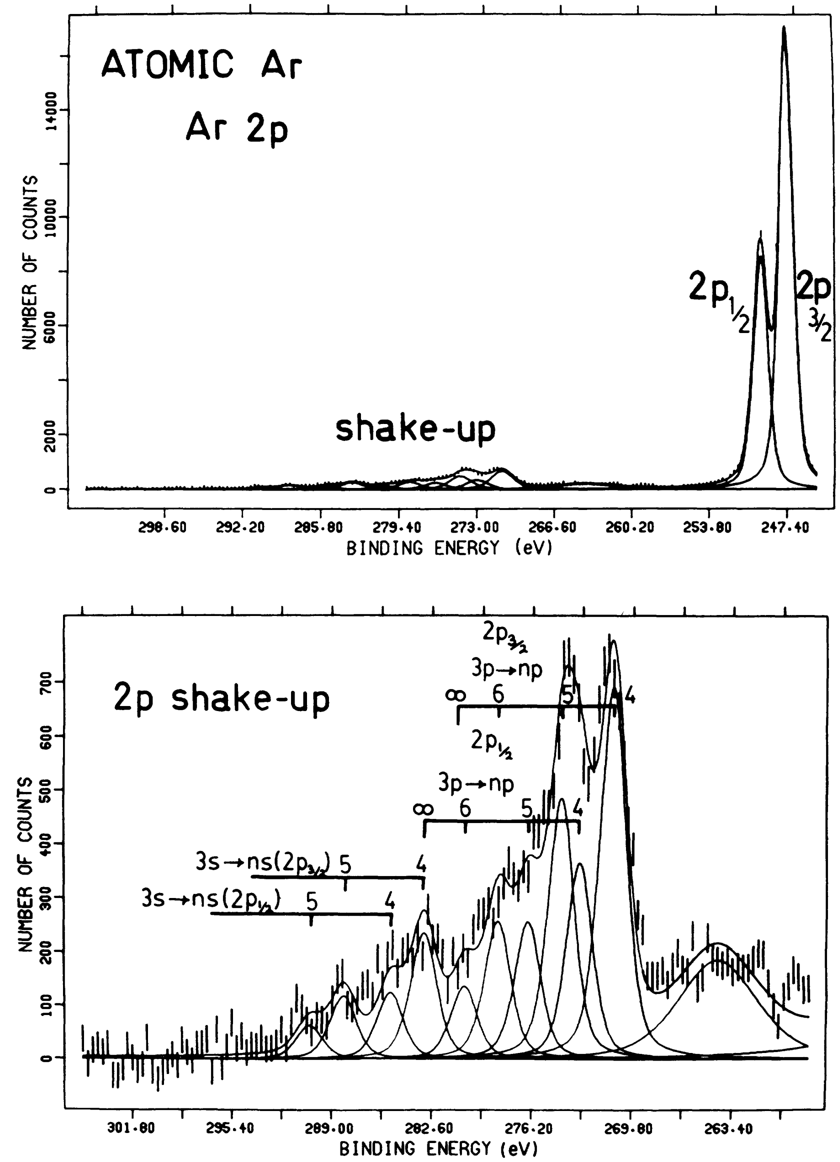

FIG. 1. The Ar 2*p* shake-up spectrum: top, the full Ar 2*p* binding energy region; bottom, a blowup of the shake-up region.

lative intensities of the two lines. The shake-up peaks were then fitted as spin-orbit doublets, with the spin-orbit splitting and intensity ratio constrained to the values obtained for the main lines, but with no restrictions on their energies. As can be seen in the spectra, the total fitted curves provide an excellent representation of the data. A broad peak about 15 eV from the main photoline has been fitted in both spectra. Peaks at a similar energy have been observed previously in the Xe 4*d* shake-up spectrum,[3] and assigned to inelastic scattering rather than shake-up.

B. Calculations

Hartree-Fock-Slater-$X\alpha$ calculations have been performed on Ne, Ar, Kr, and Xe in order to obtain both shake-up energies and intensities. Both shake-up energies employing Slater's "transition state" concept,[11] as well as upper and lower spin energies have been calculated. The coupling procedure used for the upper- and lower-state calculations is described by Tse.[5]

Shake-up intensity calculations have been carried out following the method of Loubriel,[6] in which

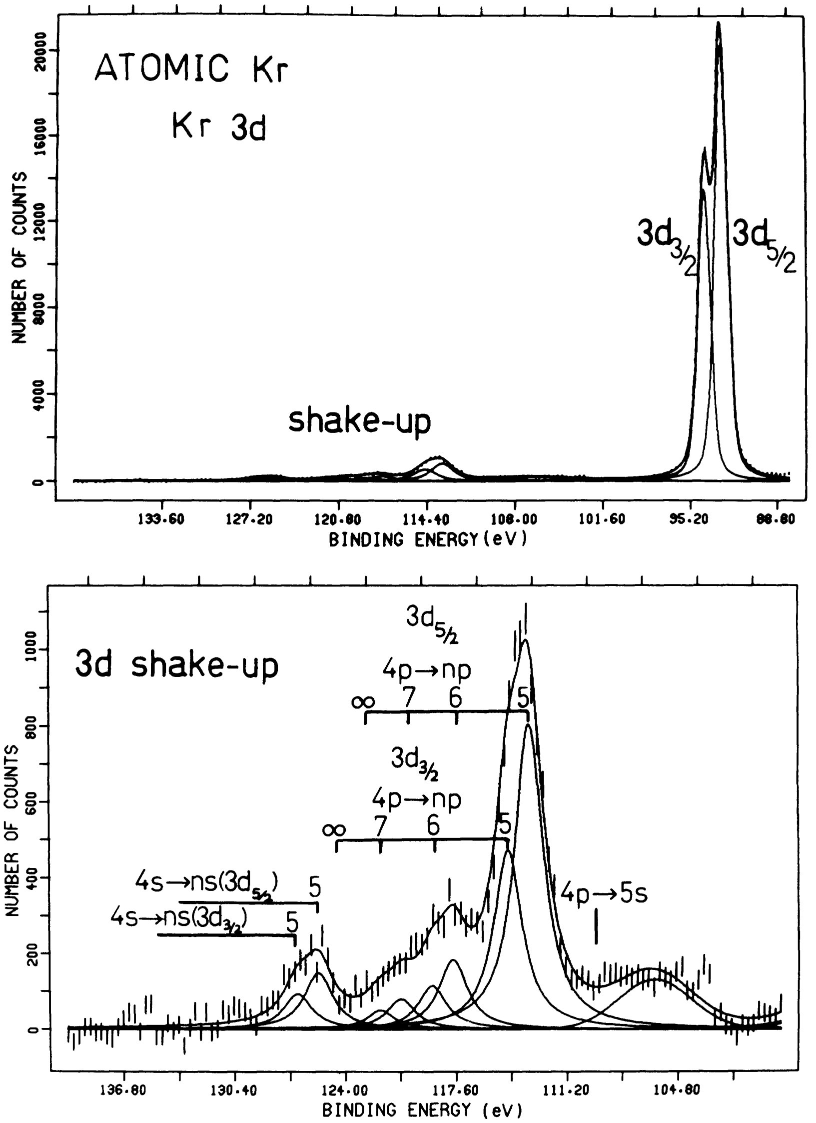

FIG. 2. The Kr 3*d* shake-up spectrum: top, the full Kr 3*d* binding energy region; bottom, a blowup of the shake-up region.

TABLE I. Comparison of experimental and theoretical shake-up energies (eV) and intensities (relative to the main photoline) for the Ne 1*s* spectrum ($\alpha = 0.730\ 81$).

		Experimental[a]				Theoretical		
Transition	ΔE (Upper)	ΔE (lower)	Intensity	ΔE (SCF)[b]	ΔE (upper)[b]	ΔE (lower)[b]	Intensity[c]	Intensity[d]
$2p \to 3p$	40.76	37.35	6.30	39.05	40.92	37.00	5.07	11.77
$2p \to 4p$	46.44	42.34	2.98	44.12	46.30	42.15	2.18	1.50
$2p \to 5p$	48.47	44.08	0.59	46.10	48.65	44.18	0.54	0.47
$2p \to 6p$		45.10	0.5	47.07	49.95	45.19	0.15	0.21
$2p \to 2np$	51.7	47.4		47.34	49.96	45.43		
$2s \to 73s$	65.9	59.8	1.06	57.32	60.14	54.60		0.99

[a] Reference 3.

[b] Reference 5.

[c] Reference 12.

[d] This work.

TABLE II. Comparison of experimental and theoretical shake-up energies (eV) and intensities for the Ar $2p$, Kr $3d$, and Xe $3d$ spectra.

Atom		Experimental			Theoretical			
(α)	Transition	ΔE	Int. %		ΔE (SCF)	ΔE (upper)	ΔE (lower)	Int. %
Ar	$3p \rightarrow 4p$	23.5	6.0		23.12	23.12	22.30	10.91
(0.721 77)	$3p \rightarrow 5p$	26.8	4.2		26.97	27.10	26.22	1.34
	$3p \rightarrow 6p$	30.9±3	2.3		28.58	28.77	27.86	0.40
	$3p \rightarrow np$	~32			29.49	29.68	28.77	
	$3s \rightarrow 4s$	35.7	2.1		35.60	35.59	34.72	1.12
	$3s \rightarrow 5s$	40.8	1.0		41.26	41.34	40.39	0.17
Kr	$4p \rightarrow 5p$	20.5	8.1		19.26	19.04	18.65	9.20
(0.705 74)	$4p \rightarrow 6p$	24.8±3	2.4		22.71	22.58	22.16	1.11
	$4p \rightarrow 7p$	27.8±3	1.2		24.17	24.10	23.67	0.32
	$4p \rightarrow np$	~29			26.63	26.58	26.14	
	$4s \rightarrow 5s$	32.6	1.9		31.46	31.30	30.77	0.87
Xe	$5p_{3/2} \rightarrow 6p_{3/2}$	16.47[a]	3.8[a]	6.4	16.06	15.71	15.60	9.74
(0.699 84)	$5p_{1/2} \rightarrow 6p_{1/2}$	17.72	2.6					
	$5p_{3/2} \rightarrow 7p_{3/2}$	19.44	1.4					
	$5p_{1/2} \rightarrow 7p_{1/2}$	21.0			19.13	18.87	18.73	1.14
	$5p_{3/2} \rightarrow 8p_{3/2}$	21.5	1.5					
	$5p \rightarrow np$	25.1						
	$5s_{1/2} \rightarrow 6s_{1/2}$	26.96	1.2		25.29	24.96	24.82	1.12

[a] Reference 3.

overlaps O_n of the wave functions of the neutral Φ_n and excited states of the ion Φ_{ex} are calculated:

$$O_n = \langle \Phi_n \mid \Phi_{\text{ex}} \rangle \ . \tag{1}$$

The squares of these overlaps are then compared with the observed intensities. Nonorthogonality of the excited-state wave functions has been estimated by subtracting the calculated intensity generated by overlap of the core-hole state and the excited state from the square of Eq. (1). The results of these calculations are listed in Tables I and II.

Electron correlation is known to be important in this type of multielectron process.[12] Our previous experience with the $X\alpha$ method, which did not explicitly include electron correlation, provided good agreement with respect to excitation energies, especially for neon gas.[5] Intensity calculations using the above-mentioned procedure for polyatomic molecules yielded qualitative agreement with experiment.[9] Based on this experience and the relatively low resolution of these spectra, it is our intention to simply correlate the experimental findings with the results obtained from the "one-electron" sudden approximation.

IV. DISCUSSION

Our calculated shake-up energies in Tables I and II are in very good agreement with the experimental values. Generally, where the shake-up peaks can be fit uniquely, the agreement is better than 1.0 eV. As shown previously for the Ne shake-up energies,[5] the $X\alpha$ calculated energies compare very favorably with those calculated using multiconfiguration Hartree-Fock (MCHF) methods.[3] The major advantage of the $X\alpha$ method over the MCHF methods is that one saves considerable computing time and labor. The calculated intensities are in qualitative agreement with the observed values, and agree very well with those calculated previously using an optimized potential model.[7]

Included in Table I are the results of previous work on the shake-up intensities in neon gas.[12] The calculation was performed with both initial- and final-state configuration interaction. The agreement with experiment is considerably better than the present work. However, the qualitative trend is certainly well reproduced via the $X\alpha$ method and the direct application of the sudden approximation.

Resolution of the spectra was not sufficient to observe the relatively small splittings between the upper and lower states in the Ar and Kr spectra. As for the $X\alpha$ shake-up spectra,[3] this effect broadens each peak. Another cause of broadening or splitting comes from the spin-orbit splitting of the valence and Rydberg levels in the core-hole state. A combination of large core Xe $3d$ spin-

TABLE III. Comparison of transition energies in the rare-gas hole state and the equivalent cores alkali ion (in eV).

Rare gas (alkali metal)	Transition	ΔE (exp.) rare gas	ΔE (opt.) alkali metal
Ne	$2p \rightarrow 3p$ (upper)	40.76[a]	38.29
(NaII)	$2p \rightarrow 3p$ (lower)	37.35[a]	36.36
	$2p \rightarrow np$	47.4[a]	47.3
Ar	$3p \rightarrow 4p$	23.5	23.53
(KII)	$3p \rightarrow np$	~32	31.81
Kr	$4p \rightarrow 5p$	20.5	19.99
(RbII)	$4p \rightarrow np$	~29	27.5
Xe	$5p_{3/2} \rightarrow 6p_{3/2}$	16.47[a]	16.51
(CsII)	$5p_{1/2} \rightarrow 6p_{1/2}$	17.72[a]	17.92
	$5p_{3/2} \rightarrow 7p_{3/2}$	19.94[a]	19.56
	$5p_{1/2} \rightarrow 7p_{1/2}$	21.0[a]	20.8
	$5p \rightarrow np$	25.1[a]	25.1

[a] From Ref. 3.

orbit splitting (12.6 eV) and Xe $5p$ spin-orbit splitting (1.41 eV) made resolution of this effect possible in the previously observed Xe $3d$ shake-up spectrum.[3] However, as shown below, for the Ar and Kr shake-up spectra, only a broadening would be expected.

To estimate the valence level spin-orbit splittings for Ar and Kr, the equivalent cores formalism is utilized. In this procedure, the removal of a core electron is taken as essentially equivalent to the addition of a proton to the nucleus. Thus, the core equivalent of Ar* (core ionized Ar) is K^+, and that of Kr* is Rb^+. The appropriate K II (K^+) optical data[13] predicts a spin-orbit splitting of 0.62 eV for the $3p$ orbital in core ionized Ar, and 0.79 eV for the $4p$ orbital in core ionized Kr. Both of these splittings are too small to be resolved, and lead to broadening of the shake-up peaks.

The equivalent cores treatment can also be used to compare shake-up and shake-off energies in the rare gases to optical-transition energies in the corresponding core equivalent alkali-metal ions. The rare-gas shake-up and shake-off energies appear in Table III, along with the available optical data from Moore.[13] The excellent agreement with the alkali-metal data implies, as is expected,[14,15] that the core-hole states effectively screen one unit of positive charge from the valence electrons.

Finally, an analysis of the spectral weight function of the core-hole spectra enables us to calculate the relaxation shift due to shake-up. Other theoretical work on the rare-gas atoms[16] presents theoretical relaxation shifts due to a combination of both shake-up and shake-off. The equation used to calculate the relaxation shift is[17–18]

$$I_R - I_0 = \sum_{i=1}^{\infty} |\langle \psi_i | \psi_R \rangle|^2 (I_i - I_0)\,, \tag{2}$$

where I_R represents Koopman's ionization energy, I_0 the relaxed ionization energy, $|\psi_i|\psi_R\rangle|^2$ the probability of shake-up or shake-off, and $I_i - I_0$

TABLE IV. Relaxation contributions (in eV) to the rare-gas core level binding energies from shakeup and shakeoff.

Atom	Core hole	ΔE_R (shake-off)[a] + (shake-up)	ΔE_R (Shake-up)[b]	ΔE_R (Shake-off)
Ne	$1s$	15.9	4.41	11.5
Ar	$2p_{3/2}$	9.9	3.81	6.1
Kr	$3d_{5/2}$	7.7	2.83	4.9
Xe	$3d_{5/2}$	12.6	1.81	10.8

[a] Reference 15.
[b] This work.

the shake-up or shake-off energy. We have calculated the right-hand side of this equation for the experimental shake-up results and combine these with the total shake-up plus shake-off results[16] in Table IV.

It is clear in all cases here, that for the core levels studied, relaxation due to shake-off is much more significant than that for shake-up.[3,4] For Ne, Ar, and Kr, shake-up relaxation is from 40 to 60% of shake-off while in the case of Xe, it is only about 17%. These results point out very clearly the importance of both shake-up and shake-off in the shifts of photoelectron peaks and the need to consider these factors carefully when drawing conclusions about binding energy shifts.

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[*] To whom correspondence should be addressed.

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