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PHOTOIONIZATION CROSS-SECTIONS OF GROUND AND EXCITED VALENCE LEVELS OF ACTINIDES

by

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The photoionization cross-sections of ground and excited atomic states of actinide atoms were calculated by the Dirac-Fock-Slater method for two excitation energies of X-ray radiation (1253.6 eV and 1486.6 eV). These data are required for calculations of intensities of X-ray photoelectron spectra of actinide compound valence bands and interpretation of experimental spectra.

Key words: photoionization, actinide compounds, electron structure

INTRODUCTION

The high resolution X-ray photoelectron spectroscopy makes it possible to investigate the outer valence orbitals with binding energies 0-~13 eV and the inner valence orbitals with binding energies ~13-~50 eV of actinide compounds (An) [1]. The theoretical electronic structure of compounds and photoionization cross-sections are required for identification of the fine structure of these spectra. The structure of these spectra is very complicated and their identification requires theoretical calculations of the electronic structure and photoionization cross-sections. The electronic structure of actinide compounds has been calculated with the non-relativistic X_α-scattering wave method (X_α-SWM) and the X_α-discrete variation method (X_α-DVM) [2-5]. Results of the calculations are only in qualitative agreement with the experimental data [1]. The same approximations have been used for the calculation of the electronic structure of actinide compounds [3, 5]. The X_α-DVM method enables the calculations for a large number of atoms in a cluster [5]. Modification of these methods by taking the relativistic correction into account improved the agreement with the experimental data [6].

Nowadays the relativistic self-consistent field discrete variation method (SCF RDVM) is used for these calculations [2, 4, 6-9]. The calculations use the MO LCAO (molecular orbitals as linear combinations of atomic orbitals) approximation and yield the AO contributions in cluster MO. It should be noted that these calculations showed that the occupied An6s,6p,5f,6d,7s and the vacant 7p orbitals contribute to the ground molecular state. The contribution of the vacant AO to the actinide compounds MO may be quite significant. In order to compare the theoretical results with experimental intensities of photoelectron spectra, the atomic photoionization cross-sections of ground and excited states are required.

For example, Th does not have the Th5f electrons, but according to the calculations, the Th5f electrons are present in the valence band of Th compounds and since the Th5f photoionization cross-section is quite large, these electrons should be taken into account in calculating the photoelectron spectrum [10]. Thus, the existing atomic ground state photoionization cross-sections [11, 12] should be supplemented by photoionization cross-sections for excited states.

CALCULATION METHODS

For high photon energies in the approximation of independent atomic centers, a photoionization cross-section of molecular orbital γ may be written as [13]

$$\sigma_\gamma (h\nu) \quad _j \rho_{\gamma, j} \sigma_j (h\nu) \tag{1}$$

The electron densities in eq. (1) may be approximated as

$$\rho_{\gamma,j} \quad \alpha_{\gamma,j}^2 \tag{2}$$

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where the values $\alpha_{\gamma, j}$ are coefficients of decomposition of MO Ψ_γ in the LCAO form

$$\psi_\gamma = \sum_j \alpha_{\gamma, j} \varphi_j \qquad (3)$$

where φ_j is the atomic orbital.

In some cases one can attribute a part of the overlap population to the values $\rho_{\gamma, j}$ [14]. To describe the shape of the whole spectrum, the experimental line positions should be also used.

In the present work, the Dirac-Fock-Slater method was used to calculate the electron wave functions of ground (excited) and continuum states, and all multipoles in the decomposition of the electron-photon interaction were taken into account. The continuum wave function was calculated in the same field as the wave function of the initial bonded state. It has been shown in [15] that photoionization cross-sections obtained with different techniques for the vacancy after photoionization differ no more than by 10%. The results of calculations are presented in the table. Photoionization cross-sections are normalized to a completely filled *j*-shell. For example, in order to obtain the photoionization cross-section of the Pa 5f $^2_{5/2}$ shell, one must divide the value in the table by 6 (the value of $2j + 1$) and multiply by 2 (actual number of electrons). The ground atomic configurations are also presented in the table. When photoionization cross-sections of excited states were calculated, one electron from the occupied shell was moved to the excited state and this configuration was calculated self-consistently. In particular, the An5f electrons were interchanged with the An6d electrons and also the An7s electrons were interchanged with the An7p electrons. It should be noted that a photoionization cross-section depends on the actual configuration, but since the cross-sections of excited states for X-ray lines MgK$_\alpha$ ($h\nu = 1253.6$ eV) and AlK$_\alpha$ ($h\nu = 1486.6$ eV) are relatively small, the contributions of these orbitals to MO are also small. The above-mentioned uncertainty of the cross-sections', calculations is not significant for the calculations of total spectral distribution.

RESULTS AND DISCUSSION

The photoionization cross-sections obtained in the present work (see table) are necessary for calculations of peak intensities of X-ray photoelectron spectra for the actinide compound valence levels in the binding energy range from 0 eV to 50 eV. The data are needed for the processing of X-ray photoelectron spectra of the valence electrons of UF$_4$ [7], γ-UO$_3$ [8], UO$_2$F$_2$ [9], UO$_2$ [16], and ThF$_4$ [17].

In the MO LCAO approximation the contribution of each orbital to the MO is equal to the squared decomposition coefficient. As a result the theoretical density of the filled and vacant electronic states of an actinide compound can be determined. However, comparison of theoretical populations with the experimental intensities of XPS spectrum requires photoionization cross-sections. This comparison provides a conclusion on the correctness of the theoretical calculations. However, for the most part of actinides *e. g.* An5f$_{7/2}$ and An7p photoionization cross-sections of 5f and 7p orbitals were absent, and photoionization cross-sections for Md, No, and Lr did not exist *et all*. As a result a complete comparison of the theory with the experiment was not possible. The results of the present work eliminate this gap.

We consider as an example the calculations of the electronic structure for ThF$_4$ in cluster approximation (ThF$_8^{4-}$ of symmetry group C$_2$). The calculations of electronic structure were carried out with the SCF RDVM [17, 18]. According to the calculations of the $19\gamma_{3,4}$, the molecular orbital consists mainly of the atomic F2p (95%), and of a small part of the Th5f (5%) orbitals [17]. Theoretical photoionization cross-sections of the F2p$_{1/2}$ and the F2p$_{3/2}$ per one electron for AlK$_\alpha$ radiation are practically the same and are equal to 0.13 kilobarns [12]. Making use of the Th 5f photoionization cross-section ($19\gamma_{3,4}$ MO consists of 1% of the Th5f$_{5/2}$, σ_j (Th5f$_{5/2}$) = 256.4 kilobarns and 4% of the Th5f$_{7/2}$, σ_j (Th5f$_{7/2}$) = 326.3 kilobarns (see table), we determined that the contribution of the Th5f orbitals to the intensity of this line is 51%. Also the SCF RDVM calculations yield the total contribution of the Th7p electrons to the valence band to be equal to 0.27 electrons. It is significant that the photoionization cross-sections of the Th5f,7p electrons which do not belong to the pure atomic ground state are unavailable in the literature.

We will also note that according to the calculation data in the Dirac-Fock-Slater approximation, the total ground state energies E_{tot} = –875764.9845 eV for Bk5f^{9}7s^2 and E_{tot} = –875765.2248 eV for Bk5f^8 6d^{1}7s^2 are close, what makes possible the existence of the Bk5f^8 6d^{1}7s^2 electronic configuration also, see the table.

CONCLUSIONS

Photoionization cross-sections of ground and exited states of actinide atoms were calculated for photon energies 1253.6 eV and 1486.6 eV. The calculations were carried out on the basis of relativistic self-consistent field wave functions by the Dirac-Fock-Slater method. These data are required for calculations of intensities of X-ray photoelectron spectra of actinide compound valence bands and interpretation of experimental spectra.

ACKNOWLEDGEMENT

Table 1. Photoionization cross-sectionσ_j (in kilobarns) per completely filled ($2j + 1$)-shells of actinides (An) for the X-ray excitation energy ($h\nu$) of MgKα (1253.6 eV) and AlK$_\alpha$ (1486.6 eV)

$n1_j$	Ac 6d^{1}7s^2		Th 6d^{2}7s^2		Pa 5f^{2}6d^{1}7s^2		U 5f^{3}6d^{1}7s^2		Np 5f^{4}6d^{1}7s^2	
$h\nu$	Mg	Al	Mg	Al	Mg	Al	Mg	Al	Mg	Al
eV	1253.6	1486.6	1253.6	1486.6	1253.6	1486.6	1253.6	1486.6	1253.6	1486.6
7p$_{3/2}$	0.3952	0.3019	0.4551	0.3476	0.4028	0.3079	0.4039	0.3088	0.4045	0.3095
7p$_{1/2}$	0.1504	0.1212	0.1743	0.1405	0.1497	0.1211	0.1478	0.1197	0.1452	0.1178
7s	0.3068	0.2345	0.3521	0.2691	0.3179	0.2434	0.3205	0.2457	0.3218	0.2470
5f$_{7/2}$	22.32	14.43	31.45	20.45	37.03	24.19	41.94	27.53	46.91	30.88
5f$_{5/2}$	18.23	11.86	25.13	16.43	32.07	21.49	33.47	22.10	37.21	24.69
6d$_{5/2}$	3.897	2.957	5.878	4.467	4.263	3.246	4.366	3.332	4.431	3.388
6d$_{3/2}$	2.776	2.136	4.092	3.155	3.057	2.363	3.142	2.435	3.202	2.487
6p$_{3/2}$	5.803	4.439	6.492	4.965	6.406	4.903	6.662	5.102	6.896	5.284
6p$_{1/2}$	2.018	1.631	2.193	1.775	2.144	1.739	2.185	1.777	2.216	1.806
6s	2.641	2.025	2.849	2.186	2.850	2.190	2.937	2.259	3.014	2.321
5d$_{5/2}$	52.44	40.03	56.05	42.87	58.36	44.76	61.21	47.05	63.98	49.31
5d$_{3/2}$	35.45	27.48	37.74	29.33	39.25	30.59	41.05	32.09	42.80	33.56
5p$_{3/2}$	34.48	26.64	36.17	27.96	37.54	29.04	39.03	30.23	40.51	31.40
5p$_{1/2}$	10.64	8.795	10.81	8.962	10.89	9.061	10.96	9.150	10.99	9.211
5s	11.95	9.335	12.26	9.591	12.50	9.802	12.74	10.01	12.96	10.21
4f$_{7/2}$	484.6	304.0	517.8	326.3	551.6	349.1	586.6	372.9	622.6	397.6
4f$_{5/2}$	378.9	238.9	404.7	256.4	431.0	274.3	458.1	293.0	486.0	312.3

$n1_j$	Pu 5f^{6}7s^2		Am 5f^{7}7s^2		Cm 5f^{7}6d^{1}7s^2		Bk 5f^{9}7s^2		Cf 5f^{10}7s^2	
$h\nu$	Mg	Al	Mg	Al	Mg	Al	Mg	Al	Mg	Al
eV	1253.6	1486.6	1253.6	1486.6	1253.6	1486.6	1253.6	1486.6	1253.6	1486.6
7p$_{3/2}$	0.3391	0.2597	0.3380	0.2591	0.4026	0.3087	0.3338	0.2562	0.3310	0.2543
7p$_{1/2}$	0.1170	0.09524	0.1140	0.09302	0.1356	0.1108	0.1073	0.0870	0.1037	0.08527
7s	0.2772	0.2132	0.2768	0.2130	0.3222	0.2482	0.2744	0.2116	0.2726	0.2105
5f$_{7/2}$	47.79	31.675	52.63	35.05	61.48	41.14	62.73	42.18	67.81	45.82
5f$_{5/2}$	38.27	25.53	42.27	28.33	48.98	33.00	50.315	34.07	54.36	37.00
6d$_{5/2}$	4.466	3.422	4.477	3.437	4.477	3.446	4.456	3.438	4.418	3.417
6d$_{3/2}$	3.241	2.524	3.263	2.548	3.279	2.562	3.281	2.577	3.270	2.576
6p$_{3/2}$	6.710	5.147	6.906	5.301	7.506	5.765	7.255	5.580	7.409	5.704
6p$_{1/2}$	2.139	1.748	2.154	1.765	2.254	1.850	2.161	1.778	2.154	1.776
6s	2.990	2.3074	3.054	2.359	3.201	2.475	3.161	2.449	3.206	2.487
5d$_{5/2}$	66.19	51.14	68.88	53.37	72.00	55.92	74.11	57.73	76.64	59.87
5d$_{3/2}$	44.20	34.77	45.87	36.20	47.76	37.81	49.05	38.98	50.57	40.32
5p$_{3/2}$	41.83	32.46	43.26	33.61	44.80	34.85	46.07	35.89	47.43	37.00
5p$_{1/2}$	10.97	9.228	10.93	9.233	10.88	9.222	10.6E	9.159	10.64	9.080
5s	13.14	10.37	13.32	10.54	13.49	10.69	13.60	10.81	13.72	10.93
4f$_{7/2}$	659.3	423.0	697.1	449.3	735.9	476.6	775.2	504.3	815.3	533.0
4f$_{5/2}$	514.4	332.2	543.6	352.8	573.5	374.0	603.6	395.7	634.3	418.1

$n1_j$	Es 5f^{11}		Fm 5f^{12}7s^2		Md 5f^{13}7s^2		No 5f^{14}7s^2		Lr 5f^{14}6d^{1}7s^2	
$h\nu$	Mg	Al	Mg	Al	Mg	Al	Mg	Al	Mg	Al
eV	1253.6	1486.6	1253.6	1486.6	1253.6	1486.6	1253.6	1486.6	1253.6	1486.6
7p$_{3/2}$	0.332	0.256	0.3284	0.2543	0.3208	0.2473	0.3170	0.2448	0.387	0.2988
7p$_{1/2}$	0.100	0.0823	0.0965	0.0796	0.0929	0.0767	0.0893	0.0738	0.109	0.0904
7s	0.271	0.209	0.2685	0.2077	0.2661	0.2061	0.2635	0.2045	0.314	0.2438
5f$_{7/2}$	72.90	49.51	78.01	53.25	83.12	57.03	88.24	60.85	97.53	67.59
5f$_{5/2}$	58.43	39.98	62.52	43.00	66.61	46.06	70.71	49.15	77.68	54.29
6d$_{5/2}$	4.362	3.382	4.292	3.335	4.206	3.277	4.109	3.209	4.000	3.132
6d$_{3/2}$	3.247	2.566	3.214	2.547	3.170	2.520	3.118	2.486	3.057	2.445
6p$_{3/2}$	7.551	5.820	7.683	5.928	7.802	6.028	7.912	6.120	8.526	6.602
6p$_{1/2}$	2.140	1.769	2.122	1.757	2.099	1.740	2.072	1.720	2.127	1.763
6s	3.246	2.522	3.281	2.553	3.313	2.581	3.342	2.606	3.461	2.701
5d$_{5/2}$	79.11	61.89	82.52	64.06	83.87	66.10	86.16	68.11	88.91	70.48
5d$_{3/2}$	52.02	41.63	53.42	42.91	54.76	44.15	56.03	45.35	57.53	46.73
5p$_{3/2}$	48.77	38.11	50.07	39.18	51.34	40.24	52.58	41.28	53.93	42.40
5p$_{1/2}$	10.48	8.974	10.31	8.845	10.11	8.693	9.914	8.522	9.724	8.347
5s	13.82	11.03	13.90	11.12	13.97	11.20	14.03	11.27	14.12	11.34
4f$_{7/2}$	586.0	562.4	897.3	592.6	939.5	623.4	982.4	654.8	1027.	687.4
4f$_{5/2}$	665.5	441.0	697.0	464.4	729.2	488.3	761.7	512.6	795.2	537.8

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**Виктор Г. ЈАРЖЕМСКИ, Антон Ј. ТЕТЕРИН,
Јури А. ТЕТЕРИН, Малвина Б. ТРЖАСКОВСКАЈА**

ЕФЕКТИВНИ ПРЕСЕЦИ ФОТОЈОНИЗАЦИЈЕ ОСНОВНИХ И ПОБУЂЕНИХ СТАЊА ВАЛЕНТНИХ НИВОА АКТИНИДА

Ефективни пресеци фотојонизације основних и побуђених атомских стања израчунати су коришћењем Дирак-Фок-Слејтерове методе за две енергије ексцитације Х-зрачења (1253.6 eV и 1486.6 eV). Ови подаци су потребни за прорачуне интензитета фотоелектричних спектара валентних зона Х-зрачења у једињењима актинида и интерпретацију експерименталних спектара.

Кључне речи: фотојонизација, једињења актинида, електронска структура