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L-Shell Auger and Coster-Kronig Electron Spectra*

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Individual-term electron transition rates for initial L-shell holes are presented in j-j coupling. Comparison with experimental-term intensities are made for platinum, tellurium, uranium, argon, and krypton. For the latter two elements agreement is poor. Comparison with experiment indicates some prominent peaks in the uranium L_2 Coster-Kronig spectrum are improperly identified.

I. INTRODUCTION

In a previous paper[1] we used computed L-shell Auger, Coster-Kronig, and radiative total transition rates to compute Coster-Kronig and fluorescence yields. In examining the K-shell Auger electron spectrum[2] we found good agreement between calculation and experiment, but there were discrepancies at low, intermediate, and high Z. However, it is known that at low Z, configuration interaction[3] can reduce the discrepancies; while, at high Z a proper relativistic treatment,[4,5] and at intermediate Z use of intermediate coupling,[6] can reduce the discrepancies appearing between calculation and experiment. Generally, the K Auger spectrum is composed of readily resolved lines. The L Auger and Coster-Kronig spectra, more often than not, are composed of overlappling lines or even overlapping spectra. The procedures used by Albridge and collaborators[7-9] to resolve the spectrum result in a consistent assignment of spectral intensities but their procedures are probably not optimum. In Sec. II we present the computed transition rates for the stronger lines in j-j coupling, and in Sec. III we compare the calculations with measurements on platinum,[7] tellurium,[8] uranium,[9] argon,[10,11] and krypton.[12] We will use the term "reasonable agreement" for spectra where calculated strong lines are measured as strong, and weak lines are measured as weak with, for the most part, better than 25% agreement between intensities for strong lines. For argon we do not find reasonable agreement between measurements and computed intensities in j-j coupling, primarily because pure j-j coupling is not applicable.[13] But the analysis of experimental data starts with energy levels which are of the j-j type. For instance, the electron spectroscopy-for-chemical-analysis (ESCA)[14] tabulation presents ionization thresholds in j-j coupling.

The procedures used to compute the transition rates are described elsewhere.[1,2] Briefly, we obtain the Herman and Skillman[15] potential for the atom with a single inner-shell hole. We approximate the central potential with a series of seven straight lines, and with this approximation determine one-electron eigenvalues and discrete and continuum orbitals. For Auger transitions we use the one-electron eigenvalues to determine the continuum-electron energy. For Coster-Kronig transitions, we use the ESCA[14] ionization thresholds in place of the one-electron eigenvalues. This is an *ad hoc* procedure; however, the continuum-electron energies determined from the ESCA tabulation are closer to the measured continuum energies; and the Coster-Kronig rates are sensitive to the energy of the continuum electron.

II. ABSOLUTE TRANSITION RATES

In Table I we list the computed Coster-Kronig transition rates for $18 \leq Z \leq 90$. In addition we include the total transition rates A_i^T (all rates are in 10^{-4} a.u.; 1 a.u. $= 2.42 \times 10^{-17}$ sec). The total transition rate is the sum of the Auger, Coster-Kronig, and radiative rates. If N_1, N_2, and N_3 are the number of holes in the L_1, L_2, and L_3 shells, respectively, the intensity of a line α is given by $I(\alpha) = N_i A_i(\alpha)/A_i^T$ and the intensity of line α relative to line β is $I(\alpha)/I(\beta) = N_i A_i(\alpha) A_j^T / N_j A_j(\beta) A_i^T$.

TABLE I. Computed Coster-Kronig L-shell transition rates and total transition rates in 10^{-4}/a.u. (1 a.u. $=2.42\times10^{-17}$ sec).

Term \ Z	18	22	26	30	36	40	47	54	60	67	74	79	83	90
$L_1L_2M_1$	163	151	189	223										
M_2	67	74.8	97.6	118										
M_3	76	68.5	110	150										
M_4		47.4	159	250	257	150								
M_5		82.6	273	424	426	231								
N_1						39.0	46.6	58.5	68.0	71.5				
N_2						23.1	30.4	48.0	65.4	56.5	61.3	53.5		
N_3						34.4	48.8	80.6	109	92.9	105	99.8		
N_4						2.6	16.7	20.9	20.8	25.9	30.3	26.5	47.6	27.4
N_5						4.7	31.1	36.6	36.3	42.3	44.7	39.7	78.8	50.5
$N_{6,7}$									41.1	68.3	225	216	285	345
O_1						4.9	1.8	9.6	11.1	10.5	11.8	14.7	13.7	18.4
O_2								5.9	7.2	6.9	8.4	9.7	11.7	14.5
O_3								9.9	12.1	11.3	14.3	17.7	21.3	26.0
O_4											1.0	3.1	4.0	6.9
O_5											1.7	5.0	7.1	12.4
$L_1L_3M_1$	326	332	358	395										
M_2	76	60.9	92.9	115	159									
M_3	190	202	271	314	403									
M_4		108	370	594	705	783	1005				1197	1277	1165	1411
M_5		150	517	833	993	1100	1397				1603	1695	1544	1828
N_1						60.6	74.4	77.8	95.6	108	67.2	58.0	62.4	44.4
N_2						10.5	27.4	30.7	29.2	27.3	22.6	19.8	19.4	16.7
N_3						35.9	68.7	77.7	76.6	77.5	65.7	56.1	59.0	53.4
N_4						8.3	64.2	84.1	114	124	158	152	167	186
$L_1L_3N_5$						11.2	85.0	110	145	158	198	189	210	234
$N_{6,7}$									51.0	155	356	270	377	439
O_1						7.7	1.5	13.3	8.9	11.9	10.9	10.6	7.4	14.1
O_2								5.5	4.9	3.6	3.9	3.8	4.2	5.0
O_3								14.0	12.7	10.0	11.3	10.5	12.8	15.7
O_4											6.0	18.0	24.6	38.1
O_5											7.4	22.2	30.4	47.7

TABLE I. (*continued*)

Term \ Z	18	22	26	30	36	40	47	54	60	67	74	79	83	90
$L_2L_3M_5$														117
N_1					8.2	10.1	11.1	12.1	12.5	10.3	10.3	9.6	11.0	11.6
N_2					22.7	43.6	40.7	61.5	57.6	63.7	60.1	88.7	61.0	61.7
N_3					9.8	12.0	16.2	22.7	22.7	25.7	25.4	40.9	28.0	28.4
N_4						8.6	56.3	83.7	77.6	91.4	109	113	103	111
N_5						3.3	20.3	29.7	26.9	29.5	34.2	35.4	30.5	30.3
$N_{6,7}$									2.6	7.0	11.8	11.5	13.1	14.8
O_1						1.3	0.4	2.1	1.9	1.7	1.8	2.0	2.1	2.4
O_2								7.7	8.6	13.6	5.9	8.2	10.0	13.3
O_3								3.1	3.7	5.6	2.7	4.6	5.3	6.2
O_4											3.6	11.1	13.9	21.0
O_5											1.2	3.4	4.2	5.7
Total L_1 transition rate		1428	2810	3670	3520	3071	3333	1506	1784	2181	2719	5872	6833	7531
Total L_2 transition rate		88.6	158	287	454	671	950	1283	1528	1827	2179	2523	2881	4162
Total L_3 transition rate		88.5	154	295	408	542	781	990	1258	1440	1715	1910	2045	2560

In Tables II–IV we list the transition rates for L_iMM transitions and for all other transitions whose intensity is greater than 1% of A_i^T.[16]

III. COMPARISON WITH EXPERIMENT

Our transition rates are for a selection of elements in the Periodic Table. We compare our results with experiments on elements for which we have not computed the transition rate. Comparison is made with nearby elements for which we have done the computations. This is justified because the rates do not, in general, vary rapidly from element to element, providing the strong transitions arise from the same completely filled shells in the different elements. In addition, we do not use the absolute rates, but the rates normalized so that the summed calculated and experimental rates for groups of terms are equal. The rates, so normalized, are less sensitive to variation with Z, again providing the strong transitions from completely filled shells are common to the elements, and providing the normalization is done with the same group of terms.

In Table V we compare the measurements of Toburen and Albridge on platinum[7] and Casey and Albridge on tellurium.[8] In analyzing the Pt spectrum we used the computed Auger spectrum for $Z=79$. The low-energy Auger spectrum for Pt is dominated by terms arising from an L_3 hole ($L_3M_1M_2-L_3M_3M_5$). We normalized the computed total intensity for this group of lines to the experimental group total intensity, and used the experimental ratios $N_1:N_2:N_3=0.84:0.56:1.09$ to complete the calculation. Comparison indicates reasonable agreement. The results for Te are normalized so that the computed total intensity for $Z=54$ equals the total measured intensity. Agreement seems poor. However, the published[8] spectrum indicates four large peaks, one of which is due to the β-decay electron from ^{125}I. Under the heading configuration for Te we list the computed dominant term. Groups 4 and 5, 7 and 8, and 10 and 11 correspond to the other three large peaks. When these are taken in combination the computed values differ from experiment by 20, 15, and 28%, respectively. One striking discrepancy is the $L_2M_{4,5}N_{4,5}$ to $L_3M_{4,5}N_{4,5}$ intensity ratio. This is approximately given by $N_2A_3^T/N_3A_2^T=0.43$. The calculated ratio for group 18 relative to group 13 is 0.465 while the measured ratio is 1.88. Comparison indicates the discrepancy lies in group 13, and group 13 sits in the wing of the β-decay electron peak. Zender, Pou, and Albridge[9] measured the Coster-Kronig and Auger electron spectra of Ur following β decay of ^{233}Pa. They isolate many terms of the L_3 Auger spectrum and of the L_1 Coster-Kronig spectrum, but they find the L_2 Coster-Kronig spectrum overlapping the M-shell

TABLE II. Computed Auger L_1-shell transition rates in 10^{-4}/a.u. (1 a.u. = 2.42×10^{-17} sec).

Term \ Z	18	22	26	30	36	40	47	54	60	67	74	79	83	90
$L_1M_1M_1$	7.4	9.1	9.4	8.9	10.0	11.7	13.9	15.7	17.2	15.4	17.8	18.7	14.7	16.3
M_2	14.2	17.6	17.8	17.3	21.1	23.6	28.1	32.7	36.5	31.9	37.3	37.9	39.3	42.3
M_3	28.4	35.2	35.6	34.6	42.2	47.2	56.2	65.4	73.1	63.8	74.6	75.8	78.6	84.6
M_4		3.4	13.2	23.4	30.0	36.2	43.2	54.3	60.8	58.0	67.8	73.1	71.8	74.0
M_5		5.2	19.8	35.0	45.1	54.4	64.8	81.4	91.2	87.0	101	110	108	111
M_2M_2	0.3	0.4	0.3	0.3	0.3	0.3	0.3	0.1	0.2	0.2	0.2	0.1	0.1	0.1
M_3	0.1	0.3	0.6	0.5	1.1	1.7	2.2	3.2	3.2	3.5	4.1	5.3	4.3	5.0
M_4		0.05	0.2	0.3	0.4	0.6	0.7	1.1	1.2	1.2	1.5	2.1	1.9	2.0
M_5		0.8	3.45	4.91	8.54	12.4	15.3	22.8	22.4	22.5	26.2	30.7	30.5	32.5
M_3M_3	0.7	0.9	0.9	0.9	1.1	1.4	1.6	1.9	2.0	2.1	2.4	2.8	2.3	2.7
M_4		1.0	4.2	6.0	10.4	15.1	18.6	27.7	27.3	27.4	31.9	37.4	37.2	39.5
M_5		0.7	3.1	4.6	7.6	10.9	13.5	20.3	20.2	20.3	23.8	28.4	28.0	29.7
M_4M_4		0.01	0.2	0.7	1.4	1.9	2.3	3.3	3.9	4.1	4.5	5.0	4.3	4.5
M_5		0.5	12.0	37.6	65.0	78.9	92.4	124	142	146	159	171	150	158
M_5M_5		0.2	3.3	10.5	18.3	22.6	26.6	36.0	41.4	42.6	46.6	50.3	44.0	46.1
M_1N_3					4.6	5.6	9.3	13.5	16.1	15.3	17.7	16.1	18.6	21.4
M_1N_4						0.7	5.5	7.9	10.3	11.1	12.9	12.9	15.2	17.2
M_1N_5						1.0	8.1	11.9	15.5	16.6	19.5	19.5	22.7	25.9
M_3N_1		3.0	2.7	2.3	4.0	5.6	6.9	9.6	11.8	10.8	12.1	11.6	12.3	13.8
M_4N_5						2.3	8.3	13.2	16.5	18.7	19.9	18.9	20.7	22.6
$M_4N_{6,7}$									2.0	4.5	7.9	8.3	10.5	14.8
M_5N_1		0.4	1.4	2.2	4.2	6.5	7.5	13.2	13.8	14.4	15.4	15.8	18.8	17.6
M_5N_4						2.3	8.3	13.2	16.5	18.7	19.9	18.4	20.7	22.6
M_5N_5						1.4	5.0	8.5	10.2	11.6	12.6	12.1	13.1	14.6
$M_5N_{6,7}$									2.9	6.8	11.9	12.4	15.8	22.2

TABLE III. Computed Auger L_2-shell transition rates in 10^{-4}/a.u. (1 a.u. = 2.42×10^{-17} sec).

Term \ Z	18	22	26	30	36	40	47	54	60	67	74	79	83	90
$L_2M_1M_1$	0.8	0.9	0.9	0.9	1.4	1.0	1.2	1.2	1.4	1.1	1.4	1.3	1.3	1.4
M_2	11.9	15.2	14.8	13.9	16.0	17.7	23.1	25.4	28.4	25.8	29.8	29.0	21.4	24.0
M_3	0.9	1.2	1.4	1.3	1.6	1.9	2.5	2.8	3.2	2.9	3.4	3.6	3.4	3.7
M_4		0.3	0.6	1.2	0.7	0.6	0.6	0.8	0.8	1.0	1.2	1.7	1.3	1.5
M_5		0.3	1.2	1.9	2.6	3.4	4.0	5.0	5.3	5.5	6.2	6.9	6.2	6.9
M_2M_2	10.1	13.2	12.8	12.4	15.8	18.7	22.2	24.6	29.4	26.4	30.2	28.6	28.6	30.6
M_3	36.7	46.9	45.8	44.2	55.9	66.2	78.8	87.6	104	93.2	107	101	101	108
M_4		3.1	11.4	20.2	27.4	33.2	39.4	47.5	55.3	54.9	61.4	64.4	59.8	61.9
M_5		6.2	22.4	39.7	52.1	61.5	73.4	89.4	104	101	113	116	110	113
M_3M_3	1.0	1.3	1.4	1.3	1.6	1.9	2.1	2.4	2.8	2.5	2.8	2.7	2.8	3.0
M_4		3.5	14.6	26.7	37.6	46.4	53.6	61.0	73.6	77.3	83.9	93.1	80.0	86.4
M_5		0.6	2.2	3.8	5.2	6.2	7.1	8.4	9.9	10.0	10.9	11.8	10.7	11.1
M_4M_4		0.3	6.4	19.5	31.1	42.3	48.2	55.2	65.7	72.7	75.2	80.0	68.3	73.6
M_5		1.4	29.6	89.6	141	192	218	249	293	325	336	354	304	330
M_5M_5		0.07	1.4	4.3	6.8	9.1	10.4	11.9	14.1	15.4	16.0	16.7	14.8	15.7
M_2N_3					6.1	8.1	13.0	18.3	21.9	21.9	24.4	20.8	23.4	26.5
M_2N_4						0.6	4.6	7.7	9.4	10.2	11.7	11.3	12.7	14.6
M_2N_5						1.14	8.7	14.5	17.6	19.1	22.0	20.7	23.6	27.0
M_3N_2					4.7	10.2	9.6	13.5	15.5	15.0	16.4	13.5	16.1	17.9
M_3N_4						0.8	5.5	8.5	10.5	11.9	13.1	13.4	14.1	16.5
M_4N_3					4.0	9.0	8.3	12.3	13.8	14.9	15.5	13.6	15.0	16.2
M_4N_4						1.4	12.1	15.1	19.3	22.6	23.8	24.3	24.9	28.9
M_4N_5						3.3	30.6	36.9	46.9	55.0	57.1	59.5	60.7	70.9
$M_4N_{6,7}$									2.5	8.4	20.3	19.6	24.3	34.2
M_5N_2					3.7	7.6	8.7	11.9	14.7	16.8	17.8	18.2	17.3	20.3
M_5N_4						2.8	24.3	28.0	34.3	40.8	42.7	41.9	44.2	50.0
M_4O_5											2.3	6.9	8.6	14.9
N_4N_5						0.03	2.2	4.3	5.8	7.2	8.3	7.4	9.1	10.3

TABLE IV. Computed Auger L_3-shell transition rates in 10^{-4}/a.u. (1 a.u. = 2.42×10^{-17} sec).

Term \ Z	18	22	26	30	36	40	47	54	60	67	74	79	83	90
$L_3M_1M_1$	0.8	0.9	0.9	0.9	1.4	1.0	1.2	1.2	1.4	1.1	1.4	1.5	1.3	1.4
M_2	0.5	0.6	0.7	0.6	0.8	0.9	1.2	1.4	1.6	1.5	1.7	1.8	1.7	1.8
M_3	12.4	15.7	15.4	14.5	16.8	18.6	24.3	26.7	30.0	27.2	31.5	30.7	23.1	25.8
M_4		0.2	0.8	1.3	1.7	2.1	2.5	3.1	3.3	3.4	3.8	4.3	3.8	4.3
M_5		0.4	1.0	1.9	1.7	1.9	2.2	2.7	2.8	3.1	3.5	4.3	3.6	4.2
M_2M_2	0.2	0.2	0.3	0.2	0.3	0.4	0.4	0.5	0.6	0.6	0.6	0.6	0.6	0.6
M_3	19.1	24.3	23.8	22.9	28.9	34.2	40.7	45.2	53.6	48.0	55.0	52.0	52.3	55.8
M_4		0.2	0.8	1.4	2.1	2.8	3.2	3.7	4.4	4.7	5.1	5.8	5.0	5.3
M_5		1.8	7.4	13.5	18.8	23.0	26.6	30.3	36.5	38.2	41.4	45.8	39.5	42.6
M_3M_3	28.7	36.8	35.9	34.7	44.0	52.2	62.1	68.9	82.0	73.6	84.2	79.7	79.9	85.3
M_4		4.5	16.6	29.3	38.7	45.8	54.4	65.8	76.6	75.1	84.0	86.5	81.2	83.7
M_5		6.7	25.6	45.8	62.2	75.2	88.9	106	124	125	138	146	134	140
M_4M_4		0.05	1.1	3.2	5.2	7.1	8.1	9.3	11.1	12.2	12.7	13.6	11.6	12.4
M_5		1.0	21.6	65.3	103	139	159	181	213	236	244	257	221	239
M_5M_5		0.7	14.8	44.9	71.0	96.7	110	126	149	165	170	180	154	167
M_3N_2					3.1	4.2	6.7	9.4	11.2	11.2	12.5	10.7	12.0	13.5
M_3N_3					8.5	14.6	17.9	25.1	29.7	29.3	32.4	27.3	31.3	35.2
M_3N_4						0.8	6.3	10.4	12.6	13.7	15.7	14.9	16.9	19.3
M_3N_5						1.3	10.1	16.6	20.3	22.3	25.4	24.6	27.4	31.6
M_4N_5						2.1	18.1	21.3	26.2	31.1	32.5	32.2	33.9	38.4
M_5N_3					5.3	11.4	11.8	16.9	19.9	22.1	23.2	22.2	22.7	25.7
M_5N_4						2.3	21.3	25.8	32.7	38.4	40.0	41.3	42.4	49.2
M_5N_5						3.1	27.8	33.5	42.3	49.8	52.2	53.1	54.7	63.3
$M_5N_{6,7}$									2.4	8.3	20.0	19.3	23.9	33.6

TABLE V. Comparison of the calculated and experimental L-shell electron spectra for Pt (Ref. 7) and Te (Ref. 8). The calculated values are normalized as described in the text.

Platinum configuration	Intensity Meas	Intensity Calc		Tellurium configuration	Intensity Meas	Intensity Calc
$L_3M_1M_2$	1.5	0.3				
M_2M_2	1.0	0.1				
M_1M_3	4.1	5.1				
M_2M_3	12.0	8.7				
$M_1M_{4,5}$	2.3	1.5				
M_3M_3	17.1	13.3				
M_2M_4	0.7	1.0				
M_2M_5	3.7	7.6				
$L_2\,M_1M_1$	1.0	0.1				
$L_3M_3M_4$	14.9	14.4				
M_3M_5	18.9	24.3				
$L_2M_1M_2$	2.2	1.9				
$L_3M_4M_4+L_2M_2M_2$	13.0	4.2				
$L_3M_4M_5+L_1M_1M_1$	34.6	43.6				
$L_2M_1M_3+L_3M_5M_5$	18.4	30.2				
$L_1M_1M_2$	1.0	1.6				
$L_2M_2M_3+L_3\,M_1N_1$	7.8	6.6				
7*a*	2.8	1.3				
$L_1M_1M_3$	1.9	3.2				
$L_2M_3M_3+L_3M_2M_2$	2.7	0.2				
$L_3M_1\,N_{4,5}+L_2\,M_2M_4$	4.0	4.4				
$L_3M_2N_3$	1.0	1.2				
$L_2M_2M_5$	6.0	7.5				
$L_1M_2M_3$	2.0	0.2				
8*b*	1.1	2.4				
$L_1M_1M_4$	4.9	3.0				
$L_2M_3M_4$	7.7	6.0				
$L_1M_3M_3$	5.1	0.1				
$L_2M_4M_4+L_3M_5N_2$	5.9	7.0				
10*c*	15.2	25.9				
$L_3M_4N_{4,5}+L_1M_3M_5$	6.4	7.3				
$L_3M_5N_{4,5}$	11.3	15.7				
$L_1M_4M_5$	6.9	7.1				
$L_1M_5M_5$	1.4	2.1				
$(L_3N_3+L_2M_{4,5})N_{4,5}$	5.8	9.4				
			(1)	$L_3M_2M_3$	1281	925
			(2)	$\cdot\cdot L_3M_3M_3\,\cdot\cdot$	928	1635
			(3)	$L_3M_1M_{4,5}$	235	118
			(4)	$L_2M_2M_2+L_3M_2M_{4,5}$	2480	354
			(5)	$\cdot\cdot L_3M_3M_{4,5}\,\cdot\cdot$	3380	4395
			(6)	$\cdot\cdot L_1M_1M_2\,\cdot\cdot$	150	225
			(7)	$\cdot\cdot L_2M_2M_{4,5}\,\cdot\cdot$	6600	1743
			(8)	$\cdot\cdot L_3M_{4,5}M_5\,\cdot\cdot$	3460	6832
			(9)	$\cdot\cdot L_1M_1M_{4,5}\,\cdot\cdot$	322	739
			(10)	$\cdot\cdot L_2M_4M_{4,5}\,\cdot\cdot$	2370	3850
			(11)	$L_1M_2M_{4,5}$	735	127
			(13)	$L_3M_{4,5}N_{4,5}$	320	1703
			(14)	$\cdot\cdot L_1M_4M_{4,5}\,\cdot\cdot$	900	760
			(15)	$\cdot\cdot L_1M_5M_5\,\cdot\cdot$	470	220
			(16)	$L_1M_1N_{2,3}$	92	108
			(17)	$\cdot\cdot L_1M_1N_{4,5}\,\cdot\cdot$	343	141
			(18)	$\cdot\cdot L_2M_{4,5}N_{4,5}\,\cdot\cdot$	600	792

Auger spectrum. We normalized our computed values for the groups $L_1L_3M_4 - L_1L_3O_{4,5}$ and $L_3M_1M_3 - L_3M_1N_1$ by equating the group total intensity for $Z = 90$ to the measured-group total intensity. The results are shown in Table VI, and are in reasonable quantitative agreement with the measurements. The normalization so obtained was used to compute L_1 and L_3 intensities for the terms numbered 1 to 23 (see Ref. 9 for the identification of the unlabeled terms). We also show in Table VI the L_2 Coster-Kronig terms, the group $L_2L_3N_1 - L_2L_3O_{4,5}$, and the calculated values with the group normalization as above. We argue that the measured L_2 Coster-Kronig values are misidentified and the values in parentheses are the correct ones. The modified experimental values are then in reasonable agreement with the calculations. However, if we accept the L_2 normalization as obtained from the L_2 Coster-Kronig group, then the L_2 Auger terms (21 and 22) $L_2M_4M_4 + L_2M_4M_5$ have a computed intensity of 356 while the measured intensity is 11.5. Using the argument that the transition rate for $L_3M_4M_5 + L_3M_5M_5$ is approximately equal to the rate for $L_2M_4M_4 + L_2M_4M_5$ and the expression for converting the transition rate to an observed intensity, the above L_2 normalization would lead to $N_2/N_3 = 15.6$. This is unreasonable. We argue that while the separation of the experimental L_2 Coster-Kronig spectrum from the M Auger spectrum may be relatively correct (i.e., within the L_2 Coster-Kronig group), the subtraction of the M Auger spectrum is not reliable enough to compare the L_2 Coster-Kronig spectrum with the L_2 Auger spectrum. We normalize the L_2 Auger spectrum so that the measured and computed intensities for $L_2M_4M_4 + L_2M_4M_5$ are equal. This leads to $N_2/N_3 = 0.50$, a more reasonable value. If we accept this latter normalization, accept the L_2 Coster-Kronig experimental

TABLE VI. Comparison of the calculated and experimental L-shell electron spectra for Ur (Ref. 9). The calculated values are normalized as described in the text.

Term	Meas	Calc	Group	Meas	Calc
$L_1L_3M_4$	73	66	1	3.6	1.8
$L_1L_3M_5$	103	85	2	2.5	2.9
$L_1L_3N_4$	11	8.7	3+4	5.1	4.0
$L_1L_3N_5$		10.9	5	4.0	1.4
$L_1L_3N_{6,7}$	6.7	20.5	7	3.4	7.5
$L_1L_3O_{2,3}$	1.3	1.0	8	2.5	2.1
$L_1L_3O_{4,5}$	1.6	4.0	9	5.1	1.7
$L_3M_1M_3$	3.3	2.3	11+12	2.0	6.4
$L_3M_2M_3$	4.1	4.9	13	1.4	1.1
$L_3M_2M_5$	2.3	3.8	14	3.0	5.0
$L_3M_3M_3$	8.0	7.5	15	1.8	7.6
$L_3M_3M_4$	9.2	7.4	16	5.2	0.7
$L_3M_3M_5$	9.9	12.4	17	1.6	4.1
$L_3M_4M_4$	1.9	1.1	18	14	13.6
$L_3M_4M_5$	22	21	20	2.8	3.0
$L_3M_5M_5$	13	15	21	2.0	2.1
$L_3M_1N_1$	1.7	0.77	22	9.5	9.4
$L_2L_3N_1$	46	10.3	23	5.5	8.2
$L_2L_3N_2$	35 (46)	55	Remainder	27	24.3
$L_2L_3N_3$	101 (35)	25			
$L_2L_3N_4$	45 (101)	99			
$L_2L_3N_5$	(45)	27			
$L_2L_3N_{6,7}$	8	13			
$L_2L_3O_2$	12	12			
$L_2L_3O_{4,5}$	4.7	24			

intensities, and reject the computed L_2 Coster-Kronig yields, we find a Coster-Kronig rate 8850 $\times 10^{-4}$ a.u. and $f_{2,3} \approx 0.6$, an unreasonable value. Thus, we argue that the correction made for the M Auger yield was not sufficient.

With the latter L_2 normalization the terms 1–23

TABLE VII. Comparison of the calculated and experimental L-shell electron spectra for Ar (Refs. 10 and 11). The calculated values are normalized as described in the text. Expt* are values calculated using experimental continuum energies.

Term	Model	ESCA	Expt*	Ref. 16	Expt
$L_1L_{23}M_1$	70.2	122	95.6	114	26.3
$L_1L_{23}M_{2,3}(^1S)$	17.6	30.4	23.8	17.8	22.9
(^3S)	13.3	20.2	17.0	11.5	10.4
(^1D)	16.3	9.5	12.8	15.2	15.2
$(^3D_1)$	10.5	8.0	9.3	11.1	10.4
$(^3D_2)$	17.6	13.3	15.4	18.5	17.1
$(^3D_3)$	24.6	18.6	21.6	25.9	24.1
$\Gamma(L_1L_{23}M_1)$ eV	1.64	1.33	1.45	1.37	0.38
$\Gamma(L_1L_{23}M_{23})$ eV	2.34	1.09	1.53	1.35	1.46
$L_1M_1M_1(^1S)$	0.31			0.47	0.42
$M_1M_{2,3}(^1P)$	0.83			0.82	0.83
$M_1M_{2,3}(^3P)$	1.00			1.00	1.00
$M_{2,3}M_{2,3}(^1S)$	0.04			0.04	0.08
$M_{2,3}M_{2,3}(^1D)$	0.01			0.01	0.01
$L_2M_1M_1(^1S)$	1.6			1.9	7.2
$M_1M_{2,3}(^1P)$	14.2			16.8	8.0
$M_1M_{2,3}(^3P)$	12.7			16.8	11.1
$M_{2,3}M_{2,3}(^1S)$	11.2			9.3	12.2
$M_{2,3}M_{2,3}(^1D)$	40.8			49.3	46.0
$M_{2,3}M_{2,3}(^3P)$	48.1			41.4	41.8

were computed and are shown in Table VI. We supplemented the identifications of Zender, Pou, and Albridge by adding the intensity for $L_2\ M_1M_2$ to that for $L_3M_1N_1$, adding $L_2M_2M_2$ to group 1, and adding $L_1M_1M_2$ and $L_2M_1M_3$ to group 2. The ratios 1.5 : 0.52 : 1.00 were deduced for $N_1 : N_2 : N_3$.

Pure j-j coupling is inappropriate for the analysis of the Coster-Kronig and Auger spectra of argon. Asaad and Mehlhorn[13] have treated Ar in a mixed coupling scheme and we use the results of their analysis. Mehlhorn[10] has measured the L_1 Coster-Kronig spectrum of Ar and compared his results with calculations of Rubenstein.[17] There is a significant discrepancy and Mehlhorn suggests the reason lies in use of the incorrect L_1 binding energy by Rubenstein. Rubenstein used 287 eV, while the measured value is 327 eV. We use 355 eV so that Rubenstein's value and ours bracket the experimental value. In addition, we have chosen three values for the continuum-electron energy, one directly from our approximation to the central potential of Herman and Skillman,[15] the second using ESCA[14] values, and the third using the experimental electron energies. In Table VII we show our three calculations for the Ar L_1 Coster-Kronig term intensities, Rubenstein's calculations, and the measurements. The results are normalized so that the total $L_1L_{23}M_{23}$ intensity equals 100. In addition we show the total transition rate converted to eV by $\Gamma = \hbar A_T$. The $L_1L_{23}M_1$ transition rate, however computed, disagrees with experiment. The results are energy sensitive but primarily via the $L_1L_{23}M_{23}$ transitions. In our calculations best agreement with relative term intensities occurs for the model calculation and worst agreement for the ESCA calculation. However, for the total half-width best agreement occurs for the ESCA calculation and worst for the model calculation. In addition in Table VII we show Rubenstein's and our calculations and the measurements of Mehlhorn[10] and Mehlhorn and Stalherm[11] on L-shell Auger relative intensities.

Finally, Krause[12] has examined the LMM spectrum of krypton. One reason given for the study was that the $2p3p3d/2p3d3d$ transition rate ratio given by Rubenstein's[16] calculation was too low to be consistent with data on charge distributions resulting from the removal of a L electron. Rubenstein's results, our results, and the experimental values are shown in Table VIII, normalized to a total intensity of 100. The striking feature is the large discrepancy between both calculations and experiment and the even larger discrepancy between the two calculations. A comparison of our radial matrix elements for these transitions with Rubenstein's shows little agreement.

TABLE VIII. Calculated and experimental relative intensities for L_3MM configurations in Kr.

Transition	Ref. 16	Relative intensity Model	Expt
$2p3d3d$	72.5	47.8	61.7
$2p3p3d$	9.7	32.5	25.9
$2p3p3p$	17.8	19.6	12.3

IV. CONCLUSIONS

We have presented tables of Auger and Coster-Kronig transition rates for initial L-shell vacancies. The tables are for j-j coupling and should be useful when j-j coupling applies, or when j-j coupling does not apply and experimental electron-energy resolution is such that individual term intensities cannot be resolved but individual configuration intensities can. Comparison of the calculated intensities with experiment for the heavier elements indicates reasonable agreement, considering the inherent difficulty in resolving the experimental spectra. The discrepancy found in the indentification of peaks in the uranium L_2 Coster-Kronig spectrum indicates how the computed transition intensities supplement energetics in identifying peaks in the spectra. For the L_1 Coster-Kronig spectrum in Ar, there is a striking discrepancy for which we have no explanation, though we can rule out the hypothesis that it arises merely from the use of incorrect energies in one-electron orbitals. For the discrepancy between our computed $(3p)^2/(3d)^2$ and $(3p3d)/(3d)^2$ intensity ratios and experiment for decay of an L_3 hole in krypton we argue that the situation is similar to that for the $(2s)^2/(2p)^2$ and $(2s2p)/(2p)^2$ intensity ratios for K-shell decay in the elements Fl-Al[18] (where the K-shell ionization energy is comparable to the L_3 ionization energy in Kr). For the K-shell situation, configuration interaction can improve the situation but not resolve the discrepancy.

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Low-Energy Level Structure of Neutral Cerium (Ce I)

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The low portion of an extensive level structure derived from analysis of the optical spectrum is reported. Positions, J values, and g_J factors are given for 98 levels, including all 91 levels expected below 10 000 cm^{-1}. A previous report on this analysis showed the ground level to be $4f5d6s^2\ {}^1G_4^\circ$ and gave the lowest levels of $4f5d^26s$. Comparison of the observed odd-parity levels with calculations by Goldschmidt and Salomon shows that all 86 of the odd levels tabulated here belong to these configurations. All but seven of these odd levels are assigned LS names, although the calculations show that many of them have low LS purities, and a few have strong mixtures of the two configurations. The much simpler system of even levels below 10 000 cm^{-1} includes only the six levels of $4f^26s^2\ {}^3H$ and ${}^3F$, beginning with ${}^3H_4$ at 4762.718 cm^{-1} above the ground-state level. The table of even levels also includes $4f^26s^2\ {}^1G_4$ and the lowest two levels of each of the lowest two terms of $4f^25d6s$, ${}^5I_{4,5}$, and ${}^5K_{5,6}$.

INTRODUCTION

One reason for special interest in the outer structure of the cerium atom is the rapid increase in the binding energy of the $4f$ electron through the sequence Ba–Pr ($Z = 56$–59). Well before any analysis of the arc spectrum of Ce existed, its complexity supported the deduction that at $Z = 58$ the $4f$ binding energy was about equal to that for $5d$ and $6s$. The ground configuration of La I ($Z = 57$) is $5d6s^2$, and $5d^26s$ is also very low. Thus after the discovery[1] in 1953 that $4f^36s^2$ was the ground-state configuration of Pr I ($Z = 59$), each of the configurations $4f^26s^2$, $4f5d6s^2$, and $4f5d^26s$ remained a reasonable possibility as lowest in Ce I. Racah's finding[2] that the $4f5d^2$, $4f5d6s$ configurations[3] extended lowest in Ce II made the Ce I $4f^26s^2$ possibility remote. An atomic-beam resonance measurement of three Ce I g_J factors differing by several percent from any expected LS-coupling values gave further evidence that the normal configuration had at least one $5d$ electron.[4]

In 1963 an analysis of the Ce I spectrum[5] gave energies, g_J values, LS designations, and configuration assignments for nine levels of $4f5d6s^2$ and for five levels of $4f5d^26s$. These were the lowest levels of the lowest two configurations, and the ground level was shown to be $4f5d6s^2\ {}^1G_4^\circ$. By 1967 the analysis had been greatly extended.[6] All levels were known to well above 10 000 cm^{-1}, including those of the three lowest $4f^26s^2$ terms. A theoretical interpretation of the low odd levels had also been accomplished.[7,8] Although only a small portion of the extended analysis can be given here, this report includes what are for several purposes the most important and interesting results.

OBSERVATIONS

The cerium-line list contains some 25 000 wavelengths.[9] These data and a description of the observations will eventually be published elsewhere. The most accurate wavelengths have been obtained in the region 3800–7100 Å from spectrograms taken in the eighth through the fifteenth orders of a plane-grating spectrograph.[10] An electrodeless lamp was the source. The probable wave-number error for averages from these plates is less than 0.01 cm^{-1}. The infrared spectrum has been observed out to 2.42 μm by Verges,[11] and was important in confirming the low even Ce I levels.

Extensions of the previously described Zeeman data[5] were obtained from infrared observations[12] to 9106 Å at a field of 24 000 G, and from observations in the visible region by Vander Sluis[13] with a