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M-Shell Auger and Coster-Kronig Electron Spectra*

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Individual-term electron-transition rates for M-shell holes are presented in j-j coupling. As the only available experimental data are best described in the mixed-coupling scheme, further calculations are performed in the mixed-coupling scheme and compared with measured term intensities in Kr and Xe. Agreement is reasonable except for the ($4s$, $4p$) ($^1P_1$) transition in Kr. A tentative identification is made of the $M_{4,5}N_1N_1$ doublet in Kr and a hypothesis is advanced on the origin of the remaining doublet.

I. INTRODUCTION

In an earlier paper,[1] computed Auger, Coster-Kronig, and radiative transition rates were used to determine Auger, Coster-Kronig, and fluorescence yields for the M subshells in atoms. These are gross atomic parameters in that each term in the various ratios is a sum over many individual transitions. In this paper, calculations are presented on individual electron term transition rates. Calculations for L-shell yields[2] and term transition intensities have previously been presented.[3] Thus there are available calculations on intensities and widths of Auger and Coster-Kronig transitions for all the shells of Be through Kr and for the K, L, and M shells of the heavier elements. It must be emphasized that the calculations apply to the first step in the inner-shell hole decay, i.e., to the primary spectrum excluding satellites. However, expressions for the transition rates in a multiholed ion are indispensible in computing final-charge-state populations following inner-shell ionization, and we plan to calculate such expressions in the near future. The M-subshell electron intensities exhibit a wide range of satellite spectra. Consider that electron ionization of the M_5 shell leads to the primary Auger decay spectrum. There is a small probability that double ionization can occur leading to an M_5 hole and another outer-shell hole. The Auger transitions are slightly shifted in energy and some in intensity but the satellite spectrum is weak because the double ionization cross section is small. This is the classic (e.g., K-shell x-ray) satellite spectrum. However, the incident electron has a substantial probability of creating an M_3 hole. This can decay by an M_5X Coster-Kronig transition leading to a satellite spectrum similar to but much stronger than that in the M_5X double ionization. However, when super Coster-Kronig transitions are allowed the M_3 hole can decay by an M_5, M_5 transition leading to a satellite spectrum arising from a doubly ionized M_5 shell. This will be significantly shifted in energy.

As in the paper on M-subshell yields, we have a situation where there are few experimental data with which to compare the calculations. The only data are the $M_{4,5}NN$ spectrum of Kr and the $M_{4,5}N_{4,5}N_{4,5}$ spectrum of Xe. However, the data indicate that these cases belong to the mixed-coupling scheme. In Sec. III we will compare calculations in the mixed-coupling scheme with these term intensities. The necessary expressions are found in the preceding paper[4] and the results are presented in Table IX. The bulk of the calculations (Tables I–VIII) are done in j-j coupling. The expressions used have been published elsewhere.[5] The j-j coupling scheme applies, in general, to those transitions involving final-state configurations where the spin-orbit interaction splitting is stronger than the electrostatic splitting. It should therefore apply to the strong Auger transitions in the heavier elements and to all the Coster-Kronig transitions. In many cases (e.g., Auger surface spectroscopy[6]) where the resolution of an electron spectrometer is not sufficient to resolve individual terms, one will measure intensities of final-state configurations. These can be compared with the calculations by summing over the individual-term intensities.

II. ABSOLUTE TRANSITION RATES

In Tables I–VIII we list a selection of the absolute transition rates in j-j coupling for $22 \leq Z \leq 90$. All rates are in 10^{-4}/a.u. (1 a.u. $= 2.42 \times 10^{-17}$ sec). In addition, we include the total transition rate which is the sum of all Auger, Coster-Kronig, and radiative rates. The tables contain a selection, i.e., only those individual rates which are at least 1% of the total for some element listed in the table. We do not list the Auger rates for $Z = 63$, 70, 76, and 83 as we did not do the calculations for these elements, merely interpolating between elements for which we did the calculations. Complete tables of matrix elements and transition rates in j-j coupling are available from the author.[7]

III. COMPARISON WITH EXPERIMENT

The Uppsala group[8] has measured the $M_{4,5}NN$

TABLE I. M_1-subshell individual-term and total transition rates for $22 \leq Z \leq 47$.

Transition \ Z	22	23	24	25	26	27	28	29	30	32	36	40	44	47
$M_1M_2M_4$	64.3	89.2	130	137	164	176	193	190	158	89.9				
M_5	233	313	413	457	547	573	622	518	367	139				
M_3M_4	292	393	521	576	689	723	785	659	472	185				
M_5	302	411	564	611	732	775	846	755	578	273				
M_4M_4	0.07	0.21	0.74	0.79	0.91	1.47	1.97	3.63	6.82	6.90	16.8	38.2		
M_5	3.34	9.74	28.0	29.0	45.0	58.6	74.9	109	91.1	76.6	34.8	18.9		
M_5M_5	0.92	2.75	8.11	8.42	12.6	16.8	14.7	32.7	32.6	28.7	31.8	62.0		
M_2N_1	85.4	84.7	36.7	86.9	80.0	78.3	81.3	37.5	89.8	121	127	162	176	199
N_2										26.2	145	136	154	214
N_3										66.6	337	316	329	475
N_4												14.9	91.1	136
N_5												17.6	128	183
M_3N_1	171	169	73.4	174	160	157	163	75.0	180	241	255	308	305	314
N_2										66.6	337	263	258	350
N_3										119	626	490	500	658
N_4												14.1	96.3	112
N_5												25.4	155	188
O_1												33.1	15.2	12
M_5N_1	24.1	37.7	24.7	60.4	66.7	74.5	82.9	45.8	118	137	157	163	236	197
N_3										7.66	29.1	41.4	46.5	45
N_4												3.53	22.1	32
N_5												6.48	35.5	54
Total	1197	1541	1816	2183	2546	2685	2923	2456	2176	1693	2556	2389	2912	3549

Auger electron spectrum of Kr and Xe. Mehlhorn[9] has measured the $M_{4,5}NN$ Auger spectrum of Kr with poorer resolution. Calculations indicate that for Kr the linewidths are about 0.09 eV and for Xe 0.7 eV. The Uppsala group[10] indicate that in Kr the $M_{4,5}NN$ lines have half-widths as small as

TABLE II. M_1-subshell individual-term and total transition rates for $50 \leq Z \leq 90$.

Transition \ Z	50	54	57	60	63	67	70	73	76	79	83	86	90
$M_1M_2N_2$	201												
N_3	422												
N_4	231	300	197	257	315	310	304						
N_5	357	453	273	376	485	493	476						
$N_{6,7}$				288	545	816	1131	1183	946	814	523	545	
M_3N_1	297												
N_2	335	396	397	394	408	348	340	368	364	304			
N_3	646	732	714	725	700	591	609	601	605	555	410	396	341
N_4	223	213	128	146	148	180	160	150	109	113	126	146	113
N_5	340	337	222	246	239	286	262	237	196	206	217	246	225
$N_{6,7}$				595	983	1971	2494	2455	2989	3198	4200	3334	4824
M_4N_1	134	155	146	141	145	138	138	133	137	132	126	139	113
N_4	35.2	39.3	46.1	77.0	47.8	52.3	51.1	53.6	57.0	57.3	62.4	55.5	56.2
N_5	50.5	55.9	65.7	126	71.4	82.8	79.4	82.8	88.7	92.1	102	91.2	97.5
$N_{6,7}$				28.8	55.9	81.8	103	126	144	155	149	143	154
M_5N_1	201	233	225	203	209	203	204	191	198	192	189	193	157
N_3	45.4	47.6	47.4	46.0	45.0	46.0	45.1	45.4	47.5	45.3	52.3	58.1	74.9
N_4	50.5	55.9	63.7	111	69.6	80.8	76.4	150	130	145	95.2	83.1	86.0
N_5	78.1	86.9	98.9	159	103	115	110	201	181	192	132	115	115
$N_{6,7}$				42.2	79.2	125	223.4	180	206	221	223	207	223
M_2O_1	24.7	38.0	46.8	51.2	42.4	44.7	45.9	48.2	51.8	59.2	53.0	72.3	134
O_2	6.5	33.6	47.4	46.8	63.1	39.9	43.4	46.4	52.4	58.1	58.1	80.9	85.8
O_3	13.4	68.7	99.5	96.9	135	81.8	89.4	96.2	109	120	119	165	170
O_5			3.56					13.5	27.3	56.3	64.7	102	100
M_3O_1	38.5	59.1	71.6	52.7	51.0	46.5	46.0	45.6	46.0	46.4	47.3	60.2	66.4
M_3O_2	4.9	55.3	67.4	53.4	49.1	40.1	40.6	41.9	43.6	44.0	48.5	52.8	35.0
O_3	9.9	108	108	105	97.1	80.2	81.3	84.4	87.8	89.5	98.7	109	75.0
N_1N_4	34.2	30.8		36.4		41.9		40.0		42.9		59.0	61.9
N_5	51.4	46.1		54.5		62.9		60.0		64.4		88.5	92.8
$N_{6,7}$				14.9		61.8		66.4		90.8		99.5	76.8
$N_5N_{6,7}$				5.65		27.9		30.7		43.0		54.0	59.4
$N_{6,7}N_{6,7}$				1.30		19.4		51.4		106		59.5	68.2
Total	4004	3758	3432	4750	5516	6741	7679	7119	7513	7715	8018	7456	8370

TABLE III. M_2-subshell individual-term and total transition rates for $22 \leq Z \leq 47$.

Term \ Z	22	23	24	25	26	27	28	29	30	32	36	40	44	47
$M_2M_3N_4$												5.04	19.0	27.8
M_3N_5												12.2	48.3	69.1
M_3O_1												11.6	5.00	4.04
$M_2M_4M_4$	9.09	26.0	74.0	81.6	118	162	216	303	271	282	140			
M_4M_5	46.6	133	381	415	601	802	1086	1540	1342	1352	524			
M_5M_5	1.41	4.03	10.9	12.4	17.7	24.4	33.0	44.0	38.4	41.0	23.1			
M_4N_1	17.8	26.7	17.4	44.5	47.0	52.9	57.8	32.3	70.6	84.6	108	118	139	153
M_4N_2										33.4	154	149	157	197
M_4N_3										51.9	337	230	230	350
M_4N_4												6.19	29.3	41.3
M_4N_5												5.83	29.0	37.8
M_4O_1												19.2	7.52	6.80
M_5N_1	3.12	4.62	3.20	7.70	8.58	9.45	10.2	5.82	12.7	16.5	21.8	24.4	30.1	36.3
N_2										55.1	167	218	236	267
N_3										5.98	29.0	27.6	26.7	33.3
N_4												2.29	3.42	9.22
N_5												1.54	6.37	8.80
O_1												2.44	1.20	1.11
N_1N_2										2.12	5.01	10.8	11.5	12.6
N_2N_2										0.10	3.41	8.02	9.31	10.1
N_3										0.36	12.3	27.2	31.5	34.1
N_4												3.40	14.3	21.5
N_5												5.85	24.7	36.9
Total	78.1	194	487	561	792	1051	1403	1925	1734	1926	1528	895	1074	1379

0.10 eV., in agreement with the calculations. In an appendix the Uppsala group present relative intensities for the Kr and Xe *MNN* spectra as bar graphs. They indicate that the mixed-coupling scheme is appropriate (i.e., there is too much structure in the measurements for *j*-*j* coupling to be appropriate but there is the exact number of peaks expected in the mixed-coupling scheme). Thus we have recomputed the term intensities in the mixed-coupling scheme using the results of the preceding paper. In Table IX we compare the Xe $M_{4,5}N_{4,5}N_{4,5}$ measurements with the calculations, where we have normalized the sum of each set of intensities to unity. The line numbers are taken from Ref. 8. For the most part the calculations and measurements are in qualitative agreement. However, there are striking differences. For the sum of $^3F_{2,3,4}$ we calculate the same relative intensity 0.375 in both the M_4 and M_5 spectrum. For the M_4 spectrum the measured total is 0.150 and for the M_5 spectrum 0.434, a factor of 3 difference. For the combined $^1D_2+{}^1G_4$ just the reverse occurs; for the M_4 spectrum the measured relative intensity is 0.425, for the M_5 spectrum it is 0.238, while in both cases the calculation leads to 0.378. Several possible explanations can be hypothesized: satellite effects, break down of the assumed-coupling scheme, dependence of the matrix elements on continuum-electron energy, etc. However, we have examined the Kr term intensities as a function of continuum electron energy and find little variation in the relative intensities of the strong terms.

For the Kr $M_{4,5}NN$ spectrum the experimental situation is more complex. As indicated in the subshell-yield calculations, super Coster-Kronig transitions are allowed in Kr. However, the observed $M_{4,5}$ decay spectrum indicates that such multi-ionized 3*d* shells do not decay by Auger transitions. In Table IX we compare the calculations with the measurements in Ref. 8. As is clear from Table IX the $(4s,\ 4p)(^1P_1)$ line, the strongest line in both the calculation and experiment, is calculated to hav twice the intensity of the measurement. This has been pointed out by Mehlhorn.[11] Hypotheses which could be used to explain this discrepancy have been mentioned in the discussion of Xe. We have also compared the calculations and experiment with the $(4s,\ 4p)(^1P_1)$ line omitted. This is shown in the last two columns of Table IX. Here the agreement is good, the strong terms agree to 20% and the weak ones to a factor of 2. In both Mehlhorn's measurements[9] and those of the Uppsala group,[10] two doublets are seen at approximately 24.5 and 32 eV, called A_1, A_2 and B_1, B_2, respectively. Mehlhorn identifies the B_1, B_2 doublet as the $M_{4,5}N_1N_1$ Auger transition. The Uppsala group tentatively conclude that the A_1, A_2 doublet is the $M_{4,5}N_1N_1$ Auger transition. Their argument is based on energies. In both cases the identification of the second doublet is left open. In an effort to resolve this situation we have estimated the intensities of the four components of the two doublets in Ref. 10, scaled the intensities to those of the bar graph in Ref. 8, and normalized the measurements and the calculation to the starred entries of Table IX. For the $M_4N_1N_1$ and $M_5N_1N_1$ relative intensities the calculated values are 0.264 and 0.201, respectively; for the doublet A_1, A_2 they are 0.143 and 0.152, respectively; and for the doublet B_1, B_2 they are 0.284 and 0.301, respectively. While the calculated M_5 relative intensity lies between those obtained from the doublets the M_4 relative intensity is in excellent agreement with that obtained from the doublet B_1, B_2. Thus, based on intensities, we would agree with

TABLE IV. M_2-subshell individual-term and total transition rates for $50 \le Z \le 90$.

Term \ Z	50	54	57	60	63	67	70	73	76	79	83	86	90
$M_2M_3N_4$	34.1					35.5	37.2	37.7	36.1	35.2	33.8	33.4	51.0
N_5	88.6					93.6	95.1	103	92.9	92.6	97.5	85.5	129
$N_{6,7}$				78.6	134	230	324	310	364	424	370	452	376
O_1	13.0	16.8	18.4	18.2	16.1	13.5	13.8	13.2	14.9	14.4	10.3	12.1	13.5
O_2	3.97	16.4	20.0	16.9	16.3	13.6	14.0	14.5	14.4	15.3	12.0	15.6	12.3
O_3	5.18	21.0	27.8	24.4	21.2	17.6	18.0	19.1	18.7	18.3	14.6	19.7	14.9
O_4			0.46					1.01	2.54	5.17	6.32	9.44	19.1
O_5			5.85					2.46	5.72	11.1	12.7	17.1	32.1
M_4N_1	149	188	199	198	208	190	206	206	214	198	184		
N_2	180	224	235	226	298	224	229	216	228	225	187	192	193
N_3	283	407	440	426	561	405	423	405	431	422	323	319	288
N_4	79.3	77.4	78.6	73.6	78.4	89.4	93.7	86.3	91.1	95.5	119	81.5	145
N_5	88.2	81.7	81.2	78.2	85.2	101	106	97.9	101	107	133	87.0	159
$N_{6,7}$				454	752	1450	1798	1858	2296	2443	2503	2254	2569
O_1	25.7	31.5	34.6	32.8	28.7	28.0	28.3	29.2	30.6	30.9	32.0	33.5	40.4
O_2	5.90	25.8	35.5	30.4	27.2	23.4	24.4	26.5	28.8	29.6	27.6	35.9	29.5
O_3	10.5	49.5	74.5	63.0	55.0	45.0	46.2	51.1	55.4	56.3	48.8	65.7	42.6
O_4			0.92					2.37	11.8	21.3	15.0	19.5	34.7
O_5			1.02					2.74	13.9	25.3	16.8	21.3	39.4
M_5N_1	39.3	45.1	41.5	41.3	45.9	43.7	44.9	44.3	42.4	43.5	41.2	44.2	39.4
N_2	246	277	429	275	278	293	273	240	239	235	226	243	225
N_3	28.2	34.8	60.4	37.3	37.2	36.3	35.2	31.3	32.9	33.4	28.2	30.2	32.6
$N_{6,7}$				11.7	19.6	38.7	50.0	99.7	126	144	84.2	70.8	105
O_2	6.7	27.7	34.2	28.5	26.1	23.1	24.9	26.0	28.4	29.2	28.6	36.3	31.4
N_2N_3	39.1	45.7		40.1		45.6		41.6		44.6		64.8	38.9
N_4	28.2	31.6		37.1		42.4		39.7		42.9		60.7	68.6
N_5	48.9	54.4		63.6		73.3		68.8		74.0		106	121
$N_{6,7}$				15.6		63.4		67.1		92.1		96.9	77.7
$N_3N_{6,7}$				6.02		24.1		27.0		38.8		41.5	49.7
$N_{6,7}N_{6,7}$				2.05		30.1		46.6		83.7		86.6	115
Total	1361	1783	2124	2467	3089	3839	4342	4431	5145	5439	5370	5125	5711

TABLE V. M_3-subshell individual-term and total transition rates for $22 \leq Z \leq 90$.

Term \ Z	22	23	24	25	26	27	28	29	30	32	36	40	44	47
$M_3M_4M_4$	1.36	3.90	11.1	12.4	17.8	25.4	33.2	46.7	43.4	46.8	29.2			
M_4M_5	33.4	95.2	272	297	430	572	777	1098	953	959	364			
M_5M_5	22.3	63.7	182	200	288	391	525	743	655	670	294			
M_4N_1	3.66	5.43	3.65	9.05	9.84	11.0	11.9	6.72	14.7	18.4	23.9	29.4	36.6	43.0
N_2										3.93	23.6	19.3	22.1	30.5
N_3										40.5	143	167	192	222
N_4												1.96	8.96	13.2
N_5												1.66	4.52	8.44
O_1												3.88	1.64	1.51
M_5N_1	17.3	25.9	16.9	43.1	45.8	51.4	56.2	31.4	68.6	82.7	106	126	156	185
N_2										26.1	164	113	128	197
N_3										75.8	362	326	380	499
N_4												3.48	20.3	27.2
N_5												9.55	46.4	69.1
O_1												20.8	8.10	7.50
N_1N_3										2.23	5.69	11.7	12.6	13.9
N_2N_3										0.19	6.37	13.8	16.0	17.3
N_3N_3										0.29	9.62	21.8	25.3	27.4
N_4												4.00	16.9	25.2
N_5												5.70	23.7	35.6
Total	78.1	194	487	561	792	1051	1403	1925	1734	1926	1523	884	1098	1430

Mehlhorn's identification of the doublet B_1, B_2 as the $M_{4,5}N_1N_1$ Auger transition. The question of the origin of the doublet A_1, A_2 remains. In Ref. 10 the discussion of energetics is continued to cases where there is an N-shell hole in addition to an $M_{4,5}$ hole. The energies are such that $(4s, 4p)$ transitions are in the 27–28 eV range and $(4p)^2$ transitions are in the 44–48 eV range. Associating the (A_1, A_2) doublet with the former and the weak structure seen in the 43–47 eV range with the latter would account for much of the residual structure in the measurements. Then the doublet A_1, A_2 has nothing to do with the $M_{4,5}N_1N_1$ transition. We have not, however, performed the intensity calculations.

IV. CONCLUSIONS

We have presented extensive tables of M-shell Auger and Coster-Kronig transition rates in j-j coupling. The j-j coupling results should prove

TABLE VI. M_3-subshell individual-term and total transition rates for $50 \leq Z \leq 90$.

Term \ Z	50	54	57	60	63	67	70	73	76	79	83	86	90
$M_3M_4N_1$	46.8	57.2											
N_2	26.6	36.6	42.3	42.9	44.6	38.4	42.9						
N_3	202	236	255	250	249	230	246						
N_4	20.3	29.4	30.7	29.2	32.7	38.0	39.1	43.1	41.1	47.3	48.7		
N_5	12.2	17.7	16.4	17.1	21.0	29.1	30.9	38.7	31.5	38.4	52.6		
$N_{6,7}$				53.5	87.1	168	206	197	241	247	203	221	357
M_5N_1	176	222											
N_2	162	223	271	284	278	275	310	282					
N_3	440	555	644	659	643	633	693	647					
N_4	63.8	81.9	78.3	81.3	97.7	134	140	161	129	142	190	234	
N_5	123	162	169	160	186	233	244	268	232	248	298	356	
$N_{6,7}$				431	710	1394	1725	1688	2068	2069	2211	2380	3041
O_1	31.4	37.4	43.1	39.9	37.6	39.0	41.3	42.8	44.0	50.0	51.6	64.3	80.3
O_2	5.85	30.4	44.9	40.0	36.1	31.6	34.1	39.6	44.3	48.1	44.7	64.7	54.1
O_3	14.6	77.5	97.4	86.9	78.6	69.5	74.8	85.0	94.7	101	95.2	135	120
O_4			0.80					3.27	6.48	13.8	20.7	36.1	37.8
O_5			1.60					5.52	11.7	23.9	33.0	54.6	69.1
N_3N_3	31.4	36.7		34.3		36.7		33.4		35.9		52.5	31.8
N_4	33.4	37.2		43.3		50.0		46.9		50.4		71.9	82.0
N_5	46.6	52.2		60.9		69.6		65.4		70.5		100	115
$N_{6,7}$				18.6		75.4		80.6		112		118	103
$N_5N_{6,7}$				2.09		12.6		17.4		16.7		34.3	32.6
$N_{6,7}N_{6,7}$				2.05		30.1		46.6		83.7		86.6	115
Total	1498	2021	1996	2514	2881	3748	4285	3977.0	3445.0	3452	3964	4381	4861

TABLE VII. M_4-subshell individual-term and total transition rates for $32 \leq Z \leq 90$.

Term \ Z	60	63	67	70	73	76	79	83	86	90
$M_4M_5N_{6,7}$	136	242								
O_3		6.70	5.17	6.08	6.64	7.62	8.59			
O_4					7.85	19.6	32.6	31.2	61.0	63.9
O_5					1.23	3.08	5.69	5.17	9.60	11.0
Total	513	686	891	1144	1199	1542	1034	1061	1123	1187

Term \ Z	32	36	40	44	47	50	54
$M_4N_1N_1$	9.00	2.22	0.51	0.02	0.06	0.04	0.01
N_2	3.49	8.35	2.88	1.36	1.51	1.16	1.25
N_3	4.14	10.83	3.70	1.32	1.67	0.71	0.88
N_4			3.80	10.4	20.7	17.6	20.5
N_5			0.75	1.71	3.29	2.26	2.96
N_2N_2	0.23	2.65	0.04	0.34	0.18	0.65	0.56
N_3	0.53	6.62	2.57	3.00	3.29	3.96	4.25
N_4			2.61	9.93	15.8	17.3	17.8
N_5			0.30	1.11	1.72	2.03	2.16
N_3N_3	0.16	2.34	1.24	1.12	1.40	1.38	1.55
N_4			6.23	23.7	37.8	41.4	43.0
N_5			0.33	1.06	1.74	1.78	2.02
N_4N_4			0.35	8.45	19.8	27.1	36.8
N_4N_5			0.82	19.6	45.8	61.5	86.3
N_5N_5			0.13	2.94	6.59	7.85	13.5
N_4O_1						2.52	4.70
N_4O_2						0.57	3.10
N_4O_3						1.34	7.24
Total	17.6	33.0	27.1	86.9	162	192	252

Transition \ Z	60	67	73	79	86	90
$M_4N_1N_4$	23.8	32.3	21.6	22.7	18.3	23.2
$N_{6,7}$	2.59	7.11	9.06	12.1	8.47	8.90
N_2N_3	6.71	4.46	5.08	5.36	3.60	4.88
N_4	20.9	27.7	20.0	21.7	18.7	23.7
N_3N_4	50.6	66.2	48.4	52.4	44.9	57.2
$N_{6,7}$	3.23	7.47	9.20	12.0	8.2	16.0
N_4N_4	41.0	45.0	41.7	44.6	43.3	58.3
N_5	93.6	102	95.1	101	98.4	131
$N_{6,7}$	24.7	83.7	102	144	121	81.5
N_5N_5	12.5	13.7	12.6	12.9	12.5	15.4
$N_{6,7}$	11.4	41.3	50.4	83.7	73.0	61.8
$N_{6,7}N_{6,7}$	8.25	62.5	163	317	308	343
N_3O_4			0.45	4.02	5.68	14.3
N_4O_1	4.31	3.36	3.75	4.66	5.39	9.09
O_2	3.48	2.83	0.64	4.28	7.83	10.2
O_3	8.12	6.59	1.85	9.98	17.8	23.3
O_4			1.88	8.69	16.5	30.1
O_5			2.37	11.3	20.8	38.0
N_5O_4			1.86	8.14	15.2	27.0
$N_{6,7}O_4$			1.97	11.5	15.8	19.2
O_5			1.20	8.42	11.9	17.3

TABLE VIII. M_5-subshell individual-term and total transition rates for $32 \leq Z \leq 90$.

Transition \ Z	32	36	40	44	47
$M_5N_1N_1$	9.00	2.22	0.51	0.02	0.06
N_2	1.91	5.09	1.74	0.58	0.76
N_3	5.72	14.1	4.85	2.10	2.42
N_4			0.50	1.14	2.20
N_5			4.05	11.0	21.8
N_2N_3	0.29	3.96	2.48	2.50	2.98
N_5			3.24	12.3	19.7
N_3N_3	0.60	7.15	1.35	1.96	1.90
N_4			0.34	1.23	1.96
N_5			5.81	22.0	35.1
N_4N_4			0.05	1.29	2.87
N_4N_5			0.60	14.4	33.5
N_5N_5			0.54	15.3	35.7
Total	17.6	33.0	27.1	87.0	162

Transition \ Z	50	54	60	67	73	79	86	90
$M_5N_1N_5$	18.4	21.5	25.2	33.6	22.5	23.6	18.8	24.0
$N_{6,7}$			2.59	7.11	9.06	12.1	8.5	8.9
N_2N_3	3.10	3.46	5.78	3.51	3.96	4.06	2.70	3.67
N_5	21.6	22.4	26.4	34.4	25.2	27.4	23.4	29.9
N_3N_3	2.86	2.88	4.25	3.22	3.68	4.06	2.84	3.88
N_4	2.24	2.42	2.89	3.58	2.76	3.14	2.77	3.74
N_5	38.4	39.8	46.7	61.4	44.7	48.6	41.7	53.1
$N_{6,7}$			4.04	8.17	10.2	13.0	9.00	10.6
N_4N_4	3.42	5.90	5.42	5.96	5.46	5.61	5.41	7.00
N_5	44.6	63.7	68.1	74.1	69.2	73.3	71.3	94.6
$N_{6,7}$			7.46	27.4	33.6	55.8	48.6	41.2
N_5N_5	48.2	66.9	73.3	79.4	74.4	79.3	77.1	103
$N_{6,7}$			28.5	97.4	119	172	145	102
$N_{6,7}N_{6,7}$			8.25	62.5	163	317	308	343
N_3O_5					0.40	3.71	5.19	13.3
N_4O_5					1.36	5.97	10.8	19.0
N_5O_1	2.58	4.82	4.41	3.43	3.84	4.76	5.49	9.22
O_2	0.69	3.74	4.19	3.40	1.03	5.16	9.13	12.0
O_3	1.25	6.76	7.58	6.17	1.70	9.37	16.8	22.0
O_4					1.70	8.09	14.6	26.3
O_5					3.33	15.3	28.7	52.2
$N_{6,7}O_4$					0.80	5.61	7.92	11.5
O_5					2.34	14.3	19.8	25.0
Total	252	270	368	509	664	980	1036	1078

TABLE IX. Comparison of normalized relative intensities for Xe$M_{4,5}N_{4,5}N_{4,5}$ and Kr$M_{4,5}NN$ Auger transitions. The starred values in the last two columns refer to normalization neglecting the $(4s, 4p)$ $(^1P_1)$ term.

Xe$M_{4,5}N_{4,5}N_{4,5}$ Line No.	Term	Rel. Int. Ref. 8	Rel. Int. Calc	Config.	Kr$M_{4,5}NN$ Line No.	Term	Rel. Int. Ref. 8	Rel. Int. Calc	Rel.* Int. Ref. 8	Rel.* Int. Calc
13 M_5	$^1S_0$	0.035	0.036	$4s, 4p$	23 M_5	$^1P_1$	0.328	0.606		
14	$^1D_2, ^1G_4$	0.238	0.378		28	$^3P_0$	0.035	0.012	0.053	0.035
15	$^3P_{0,1}$	0.154	0.075		29	$^3P_1$	0.088	0.034	0.132	0.086
16	$^3P_2$	0.140	0.137		30	$^3P_2$	0.062	0.030	0.092	0.077
17	$^3F_{2,3}$	0.224	0.137	$(4P)^2$	43	$^1S_0$	0.195	0.124	0.289	0.314
18	$^3F_4$	0.210	0.238		47	$^1D_2$	0.292	0.193	0.435	0.489
Line No.										
19 M_4	$^1S_0$	0.103	0.036	$4s, 4p$	26 M_4	$^1P_1$	0.356	0.668		
20	$^1D_2, ^1G_4$	0.425	0.378		31	$^3P_0$	0.007	0.009	0.011	0.027
21	$^3P_{0,1}$	0.167	0.124		32	$^3P_1$	0.029	0.016	0.044	0.046
22	$^3P_2$	0.155	0.088		33	$^3P_2$	0.158	0.069	0.242	0.204
23	$^3F_{2,3}$	0.138	0.330	$(4P)^2$	46	$^1S_0$	0.288	0.137	0.440	0.401
24	$^3F_4$	0.012	0.046		51	$^3P_{0,1}$	0.115	0.064	0.176	0.187
					52	$^3P_2$	0.058	0.046	0.088	0.134

useful in studies of the Coster-Kronig decay of M_1 and $M_{2,3}$ holes. However, at the present time, there are no experimental data known to the author on these low-energy transitions other than the poorly resolved data of Auger surface studies. For the $M_{4,5}$ Auger spectra the only data available are for Kr and Xe, where purely j-j coupling is not applicable. Comparison with the available data indicates reasonable agreement except for the $(4s,\ 4p)(^1P_1)$ term in Kr.

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[1]E. J. McGuire, second preceding paper, Phys. Rev. A 5, 1043 (1972).
[2]E. J. McGuire, Phys. Rev. A 3, 587 (1971).
[3]E. J. McGuire, Phys. Rev. A 3, 1801 (1971).
[4]S. N. El Ibyari, W. N. Asaad, and E. J. McGuire, first preceding paper, Phys. Rev. A 5, 1048 (1972).
[5]E. J. McGuire, Nucl. Phys. A172, 127 (1971).
[6]C. C. Chang, Surface Sci. 25, 53 (1971).
[7]E. J. McGuire, Sandia Research Report No. SC-RR-710835 (unpublished).
[8]K. Siegbahn *et al.*, *ESCA Applied to Free Molecules* Elsevier, New York, 1969).
[9]W. Mehlhorn, Z. Physik 187, 21 (1965).
[10]K. Siegbahn *et al.*, *ESCA Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy* (Almquist and Wiksells Boktryckeri AB, Uppsala, Sweden, 1967).
[11]W. Mehlhorn, in Proceedings of the Conference on the Physics of Electronic and Atomic Collisions, Amsterdam, 1971 (unpublished).

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Stark Effect in Alkali-Metal Ground-State Hyperfine Structure*

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An atomic-beam magnetic-resonance apparatus with separated oscillatory fields has been used to measure the decrease in the ground-state hyperfine energy separation of Cs^{133}, Rb^{87}, Rb^{85}, K^{39}, Na^{23}, and Li^7 because of the presence of a uniform, static, electric field. The hfs frequency shift due to this quadratic Stark effect is designated by $\delta f = -k\times 10^{-6}E^2$ Hz/(V/cm)^2. If the ratio $\delta f(X^A)/\delta f(Cs^{133})$ is denoted by κ_{X^A}, then the results are $\kappa_{Rb^{87}}=0.546(5)$; $\kappa_{Rb^{85}}=0.243(1)$, $\kappa_{K^{39}}=0.0315(6)$, $\kappa_{Na^{23}}=0.0552(12)$, and $\kappa_{Li^7}=0.0270(8)$. Existing theories of the alkali-metal Stark effect are discussed, and none is found to give satisfactory agreement with these experimental ratios.

INTRODUCTION

When an alkali-metal atom is placed in a static electric field, it sustains a decrease in its ground-state hyperfine-energy separation $h\Delta\nu$. The shift in the frequency of the $0 \longrightarrow 0$ hfs transition $(I+\frac{1}{2}, 0) \longrightarrow (I-\frac{1}{2}, 0)$ is given by

$$\delta f = -k\times 10^{-6}E^2\ \text{Hz}/(\text{V/cm})^2$$

so that the frequency shift is $-k$ Hz in a field of 1 kV/cm. This quadratic Stark effect[1] (QSE) has been measured by the atomic-beam magnetic-resonance technique in cesium[2] and potassium[3] and in the hydrogen maser.[4] Except for cesium,[5] discrepancies still exist between theory[6,7] and experiment. The excellent agreement in the case of cesium suggests the possibility of using that atom as a reference to which other Stark shifts may be compared. Such comparisons are free from the experimental uncertainites in the electric field plate spacing and in the so called filling factor associated with the separated oscillatory field method. This paper describes measurements performed on the $0 \longrightarrow 0$ transition in Rb^{87}, Rb^{85}, K^{39}, Na^{23} (which have been reported previously[8]) and on Li^7.
No existing theory suffices to explain these shifts *quantitatively*.

THEORETICAL CONSIDERATIONS

Sandars[7] has shown that the frequency shift of the $0 \longrightarrow 0$ transition in the ground-state hfs of an alkali-metal atom in a uniform, static electric field can be written

$$\delta f = (-1/2Ih)[(2I+1)\alpha_{10} - \alpha_{12}]E^2,$$

where I is the nuclear spin in units of $\hbar$. The dominant contribution to δf comes from the (scalar) polarizability α_{10} which results from the hfs contact interaction

$$H_{10} = \frac{16\pi}{3}\,\frac{\mu_B\mu_I}{I}\,(\vec{I}\cdot\vec{s})\delta(\vec{r})$$

acting on a $^2S_{1/2}$ state that is perturbed by an electric field. ($\vec{s}$ is the electron spin angular momentum, μ_B the Bohr magneton, and μ_I the nuclear