The L-MM Auger spectra of Na and Mg†

E. J. McGuire

Sandia Laboratories, Albuquerque, New Mexico 87115

(Received 28 April 1976)

Calculations, including spin-orbit interaction, were performed for the $(2p)^5$ $(3s)(nl)$ Auger spectra of Na and Mg, and compared with recent measurements. For these elements it was found that spin-orbit interaction cannot be neglected, that the statistical hypothesis for the population of terms involving inner-shell vacancies arising in ion-atom collisions is poor in relating terms of different configurations, and erratic for terms in a single configuration, and that, while some terms are calculated to have an Auger yield significantly less than unity, the available experimental data lack sufficient resolution to address this question. In comparing calculations and experiment for the Auger spectra resulting from protons incident on Na, agreement was found only by postulating a $(2s)^1(2p)^6(4s)^1$ configuration at 79.0 eV and a $(2s)^2(2p)^4(3s)^2\,{}^1S$ term at 81.1 eV above the ground state in Na.

I. INTRODUCTION

Until recently, most of the theoretical and experimental work on high-resolution Auger spectroscopy dealt with transitions involving filled shells.[1,2] Recently, there have appeared high-resolution measurements on Na vapor including effects due to partially filled outer shells.[3] An extensive literature exists on valence Auger spectra from solid surfaces but the poor energy resolution obscures much spectroscopic detail.[4] There are extensive Auger spectra from ion-atom collision experiments, but the complexity of the overlapping spectra from different ions has prevented detailed analysis.[5] Recently, too, there have appeared calculations on the Auger transition rates[6] and fluorescence yields[7,8] for ions with partially filled shells. The most striking effects occur for ions with a less than half-filled outer shell. However, these calculations[6-8] were done in LS coupling and the importance of spin-orbit perturbations was not examined. In addition, in Ref. 7, a statistical hypothesis was used to assign weights to terms arising from different configurations of comparable energy. These weighted terms were used to determine a fluorescence yield. In this paper, both the effect of spin-orbit perturbations on the calculations and the validity of the statistical hypothesis, in two simple cases, are examined.

A further motivation for this study is the possibility that elements with two outer electrons and a single vacancy in an otherwise filled shell can lead to a soft x-ray laser.[9] Two outer electrons are required because the lower laser level is then a closed shell with one outer electron. By ionizing the remaining electron one can quench the lower-level population. The price paid in this system is that the upper laser level can Auger decay. Thus it is important to consider possible upper levels

in which the Auger decay rate is smaller than or comparable to the radiative decay rate. In this regard the alkali earth elements are interesting. For example, in Mg^+ the $(2p)^5(3s)^1(3p)^1$ configuration leads to the terms ${}^4D$, ${}^4P$, ${}^4S$, ${}^2D$, ${}^2P$, ${}^2S$. In LS coupling, in lowest order, the quartet terms neither radiatively nor Auger decay. All the doublets can radiatively decay to the $(2p)^6(3p)^2P$ term, but, in lowest order, only the ${}^2D$ and ${}^2S$ terms Auger decay. This occurs because the selection rule in the Auger transition leads to a continuum electron with angular momentum $l=0$ or $l=2$. Since the residual ion is a $(2p)^6\,{}^1S$ term, the final state in the Auger process is ${}^2S$ or ${}^2D$. Since in LS coupling, both total L and total S are conserved in Auger decay, the ${}^2P$ term cannot Auger decay. Then, in this context, departures from LS coupling, specifically spin-orbit interaction, and its effect on the Auger decay rate become important. A comparison will be made of $(2p)^5(3s)(nl)$ Auger spectrum with recent measurements of Ziem et al.[10] on Na and Pegg et al.[11] on Na and Mg. Ideally, one would like experimental confirmation that for some terms of the $(2p)^5(3s)(3p)$ configuration the Auger yield is less than unity. We will see that this is not possible with the available data. In Sec. II the expressions used in calculating the energy levels, Auger and radiative transition rates, and the initial term populations are listed. In Sec. III the calculated spectra are compared with experiment. The configurations included are $(2p)^5(3s)^2$, $(2p)^5(3s)(3p)$, and $(2p)^5(3s)(4s)$.

II. CALCULATIONS

Following Slater,[12] angular momentum are added for $(2p)^5(3s)(nl)$ via $[(2p)^5(nl)LS^1](3s)LS$. For the $(2p)^5(3s)(3p)$ configuration the nondiagonal matrix elements between $({}^3L,{}^2L)$ and $({}^1L,{}^2L)$ have a domi-

TABLE I. Comparison of calculated electrostatic integrals (first entry) with those of Ref. 15 (second entry) for Mg.

nl	$n'l'$	$F^0(nl, n'l')$	$F^2(nl, n'l')$	$G^1(nl, n'l')$
$2p$	$2p$	2.829	1.286	
		2.696	1.224	
$2p$	$3s$	0.793		0.0431
		0.745		0.0326
$3s$	$3s$	0.589		
		0.557		

nant effect on the energy levels of the terms. For $(2p)^5(3s)(4s)$ the nondiagonal matrix elements and spin-orbit interaction have comparable effect. The accuracy of the calculation of the nondiagonal matrix elements will determine the relative energy of the various peaks in the Auger spectrum. Since

the electrostatic matrix elements for excited configurations are not available, the relevant ones were calculated using one-electron orbitals found by approximating the central potential of Herman and Skillman[13] with a series of straight lines.[14] For comparison purposes electrostatic integrals for filled levels in neutral Mg were also calculated. The results are compared in Table I with values from Mann's Hartree-Fock calculations.[15] Mann's calculations are the second entry, and it is clear that the electrostatic matrix elements were consistently overestimated.

For the spin-orbit interaction between three electrons where

$$H_I = \sum_{i=1}^{3} \xi(r_i)[J_i^2 - L_i^2 - S_i^2],\qquad (1)$$

it was determined that

$$\langle l_1 l_2 L'_{12} S'_{12} l_3 L'_{123} S'_{123} J'_{123} M_{J'_{123}} | H_I | l_1 l_2 L_{12} S_{12} l_3 L_{123} S_{123} J_{123} M_{J_{123}} \rangle = \delta_{J_{123}, J'_{123}} \delta_{M_{J_{123}}, M_{J'_{123}}} (I_1 + I_2),\qquad (2a)$$

where

$$I_1 = -\delta_{L_{12}L'_{12}}\delta_{S_{12}S'_{12}}\delta_{L_{123}L'_{123}}\delta_{S_{123}S'_{123}} \sum_{i=1}^{3} \overline{\xi}_i[l_i(l_i + 1) + \tfrac{3}{4}],\qquad (2b)$$

$$I_2 = \sum_{J_{12}, j_1, j_2, j_3} (2j_1 + 1)(2j_2 + 1)(2j_3 + 1)(2J_{12} + 1)\left(\sum_{i=1}^{3} \overline{\xi}_i j_i(j_i + 1)\right)$$

$$\times [(2L_{123} + 1)(2S_{123} + 1)(2L'_{123} + 1)(2S'_{123} + 1)(2L_{12} + 1)(2S_{12} + 1)(2L'_{12} + 1)(2S'_{12} + 1)]^{1/2}$$

$$\times \begin{Bmatrix} J_{123} & j_3 & J_{12} \\ L_{123} & l_3 & L_{12} \\ S_{123} & \tfrac{1}{2} & S_{12} \end{Bmatrix} \begin{Bmatrix} J_{123} & j_3 & J_{12} \\ L'_{123} & l_3 & L'_{12} \\ S'_{123} & \tfrac{1}{2} & S'_{12} \end{Bmatrix} \begin{Bmatrix} J_{12} & j_1 & j_2 \\ L_{12} & l_1 & l_2 \\ S_{12} & \tfrac{1}{2} & \tfrac{1}{2} \end{Bmatrix} \begin{Bmatrix} J_{12} & j_1 & j_2 \\ L'_{12} & l_1 & l_2 \\ S'_{12} & \tfrac{1}{2} & \tfrac{1}{2} \end{Bmatrix},\qquad (2c)$$

with

$$\overline{\xi}_i = \int_0^{\infty} \xi(r) |\Psi_i(r)|^2 r^2\, dr .\qquad (2d)$$

This expression was then evaluated for $l_1 = l_2 = 1$, $l_3 = 0$ and $l_1 = 1$, $l_2 = l_3 = 0$, to find the spin-orbit interaction matrix elements. The resulting $N \times N$ matrix was then diagonalized (including the nondiagonal matrix element) to determine eigenvalues and mixing coefficients. As a result we have the eigenvectors

$$\Psi_{i,J} = \sum_{L'S',LS} C_i(L'S', LS, J)\Psi(L'S', LSJM_J),\qquad (3)$$

where for $(2p)^5(3s)(3p)$ i ranges from 1 to 6 for $J = \tfrac{1}{2}$, 1 to 7 for $J = \tfrac{3}{2}$, and 1 to 4 for $J = \tfrac{5}{2}$. For $(2p)^5(3s)(4s)$, $i = 1, 2, 3$ for both $J = \tfrac{1}{2}$ and $J = \tfrac{3}{2}$.[16] The eigenvalues for Na and Mg are listed in Tables II and III, respectively. The unprimed,

single primed, and double primed letters in Tables II and III are associated with levels whose J value is $\tfrac{1}{2}$, $\tfrac{3}{2}$, and $\tfrac{5}{2}$, respectively. Each level has been assigned to a dominant parent, though in several instances the mixing is so severe that the assignment has little significance.

With this notation the Auger transition rate in atomic units for an (i, J) term of the $(2p)^5(3p)(3s)$ configuration is

$$W_{i,J} = 2\pi \left[\frac{3}{2} \left| C_i(^1S, {}^2S, J) \left(\frac{D(1, 0)}{3} - 2E(0, 0)\right) \right.\right.$$

$$\left. - C_i(^3S, {}^2S, J)\frac{D(1, 0)}{\sqrt{3}} \right|^2$$

$$+ \frac{3}{5} \left| C_i(^1D, {}^2D, J)\left(\frac{D(1, 2)}{3} - \frac{2}{5}E(2, 2)\right) \right.$$

$$\left.\left. - C_i(^3D, {}^2D, J)\frac{D(1, 2)}{\sqrt{3}} \right|^2 \right].\qquad (4a)$$

From the above it is clear that Auger decay of

TABLE II. Relative energy, Auger and radiative transition rates and yields [a is the Auger yield and $\omega(3s - 2p)$ is the $3s - 2p$ fluorescence yield], and initial populations for terms in the $Na(2p)^5(3s)(3p)$ and $(2p)^5(3s)4s$ configurations.

Configuration	Level	Relative energy (eV)	Principal constituent	A_a (nsec^{-1})	$A_R(3s - 2p)$ (nsec^{-1})	$A_R(3p - 3s)$ (nsec^{-1})	a	$w(3s - 2p)$	Rel. pop. (BA)
$(2p)^5(3p)(3s)$	a	1.671	$^3S, {}^2S_{1/2}$	1700	0.850	0.098	1		21.2
	a'	1.557	$^3P, {}^2P_{3/2}$	2.46	0.88	0.137	0.71	0.25	0
	b'	1.478	$^3P, {}^2D_{3/2}$	140	0.87	0.143	1		1.2
	b	1.474	$^3P, {}^2P_{1/2}$	1150	0.865	0.089	1		15.3
	a''	1.469	$^3D, {}^2D_{5/2}$	115	0.870	0.108	1		2.5
	c	0.074	$^1S, {}^2S_{1/2}$	8550	0.029	0.36	1		42.0
	c'	−0.235	$^1D, {}^2D_{3/2}$	96.5	0.0065	0.252	1		3.3
	d	−0.274	$^1P, {}^2P_{1/2}$	105	0.0094	0.26	1		0.3
	d'	−0.389	$^1P, {}^2P_{3/2}$	62.4	0.0024	0.229	1		1.9
	b''	−0.403	$^1D, {}^2D_{5/2}$	116	0.0024	0.194	1		3.6
	e	−0.413	$^4P_{1/2}$	725	0.0047	0.051	1		3.5
	e'	−0.433	$^4P_{3/2}$	0.180	0.0039	0.100	0.63	0.013	0.03
	f	−0.501	$^4D_{1/2}$	242	0.0041	0.027	1		1.3
	c''	−0.562	$^4P_{5/2}$	74	0.0018	0.131	1		3.4
	f'	−0.650	$^4D_{3/2}$	5.15	0.0033	0.033	1		0.2
	d''	−0.660	$^4D_{5/2}$	4.3	5.5×10^{-4}	79×10^{-4}	1		0.3
	$^4D_{7/2}$	−0.713	$^4D_{7/2}$	0	0	0	...	...	0
	g'	−0.803	$^4S_{3/2}$	0.0253	5.3×10^{-4}	13×10^{-4}	0.93	0.020	0
$(2p)^5(4s)(3s)$	a	0.457	$^3P, {}^2P_{1/2}$	86.4	0.61		1		0.04
	a'	0.365	$^3P, {}^2P_{3/2}$	63.5	0.79		1		5.90
	b	0.124	$^1P, {}^2P_{1/2}$	0.27	0.11		0.71		6.10
	b'	−0.007	$^1P, {}^2P_{3/2}$	27.0	0.042		1		8.20
	c	−0.070	$^3P, {}^4P_{1/2}$	3.26	0.16		1		4.53
	c'	−0.187	$^3P, {}^4P_{3/2}$	0.014	0.050		0.22		6.33
	$^4P_{5/2}$	−0.288	$^3P, {}^4P_{5/2}$						

terms with $J = \frac{1}{2}$, $(\frac{3}{2}, \frac{5}{2})$ involve only the matrix elements $D(1,0)$ and $E(0,0)$ $[D(1,2)$ and $E(2,2)]$. For an (i,J) term of the $(2p)^5(4s)(3s)$ configuration the Auger transition rate is

$$W_{i,J} = \frac{2\pi}{18}|C_i({}^1P, {}^2P, J)[D(1,1) - 2E(1,1)]$$
$$- \sqrt{3}\,C_i({}^3P, {}^2P, J)D(1,1)|^2 . \qquad (4b)$$

In Eqs. (4a) and (4b),

$$D(K, l_2) = \int_0^\infty \int_0^\infty \Psi_{2p}(r_1)\Psi_{el_2}(r_2)\left(\frac{r_<^K}{r_>^{K+1}}\right)$$
$$\times \Psi_{3s}(r_1)\Psi_{nl}(r_2)\,dr_1\,dr_2, \qquad (4c)$$

and $E(K, l_2)$ is $D(K, l_2)$ with $3s$ and nl interchanged. Radiative decay of an (i,J) term of the $(2p)^5(3p)(3s)$ configuration is possible to either $(2p)^6(3p)^2P$ or $(2p)^5(3s)^2\,{}^2P$. For the former the transition rate is, per nanosecond,

$$A_{i,J}(3s - 2p) = 1.34(\Delta E_{Ry})^2 f_{nl,n'l'} \sum_L \left|\sum_{S'} C_i(LS', {}^2L, J)(-1)^{S'}(2S' + 1)^{1/2}\right|^2 , \qquad (5a)$$

while for the second (resonance) transition it is

$$A_{i,J}((3s)(3p) \to 3s^2) = 1.34(\Delta E_{Ry})^2 f_{nl,n'l'} \sum_L \left|\sum_{S'} C_i(LS', {}^2L, J)(2S' + 1)^{1/2}\right|^2 . \qquad (5b)$$

For an (i,J) term of $(2p)^5(4s)(3s)$ the radiative transition rate to $(2p)^6(4s)^2S$ is, per nanosecond,

$$A_{i,J} = 1.34(\Delta E_{Ry})^2 f_{nl,n'l'} \left|\sum_{S'} C_i(S'P, {}^2P, J)(-1)^{S'}(2S' + 1)^{1/2}\right|^2 . \qquad (5c)$$

TABLE III. Relative energy, Auger and radiative transition rates, and yields [a is the Auger yield and $\omega(3s - 2p)$ is the $3s - 2p$ fluorescence yield], for terms in the $\text{Mg}(2p)^5(3s)(3p)$ and $(2p)^5(3s)(4s)$ configurations.

Configuration	Level	Relative energy (eV)	Principal component	$A_{\text{Aug}}(\text{nsec}^{-1})$	$A_{3s-2p}(\text{nsec}^{-1})$	$A_{3p-3s}(\text{nsec}^{-1})$	a	w_{3s-2p}
$(2p)^5(3p)(3s)$	a	3.863	$^1S, ^2S_{1/2}$	12 700	2.93	0.034	1	
	a'	3.155	$^3P, ^2P_{3/2}$	4.30	3.62	0.037	0.540	0.455
	b	3.130	$^3P, ^2P_{1/2}$	752	3.62	0.38	1	0.005
	b'	2.968	$^3D, ^2D_{3/2}$	150	3.63	0.41	0.975	0.0236
	a''	2.937	$^3D, ^2D_{5/2}$	105	3.68	0.32	0.964	0.0338
	c	0.655	$^3S, ^2S_{1/2}$	22 400	0.80	1.17	1	
	c'	−0.386	$^1D, ^2D_{3/2}$	441	0.045	0.74	1	
	d	−0.423	$^1P, ^2P_{1/2}$	299	0.040	0.78	1	
	d'	−0.620	$^1P, ^2P_{3/2}$	260	0.0034	0.82	1	
	b''	−0.697	$^1D, ^2D_{5/2}$	672	2.3×10^{-5}	0.77	1	
	e	−0.824	$^4P_{1/2}$	562	0.008	0.023	1	
	e'	−0.853	$^4P_{3/2}$	66.3	0.013	0.038	1	
	c''	−1.041	$^4P_{5/2}$	85.0	0.010	0.091	1	
	f	−1.115	$^4D_{1/2}$	15.1	0.011	0.016	1	0.0007
	f'	−1.241	$^4D_{3/2}$	11.0	0.011	0.030	1	0.001
	d''	−1.385	$^4D_{5/2}$	11.2	0.0045	0.011	1	
	$^4D_{7/2}$	−1.522	$^4D_{7/2}$		0	0		
	g'	−1.959	$^4S_{3/2}$	0.0206	1.3×10^{-4}	0.0051	0.799	0.005
$(2p)^5(4s)(3s)$	a	0.944	$^3P, ^2P_{1/2}$	145	2.36		1	
	a'	0.623	$^3P, ^2P_{3/2}$	26.0	3.46		0.88	
	b	0.175	$^1P, ^2P_{1/2}$	61.5	0.90		1	
	b'	0.075	$^1P, ^2P_{3/2}$	180	0.007		1	
	c	−0.187	$^3P, ^4P_{1/2}$	37.4	0.44		1	
	c'	−0.385	$^3P, ^4P_{3/2}$	13.5	0.226		1	
	$^4P_{5/2}$	−0.572	$^3P, ^4P_{5/2}$					

The quantities ΔE_{Ry} and $f_{nl,n'l'}$ are the energy difference in the radiative transition in rydberg and the one-electron oscillator strength.

One other formal expression is necessary for comparison with experiment, the cross section for proton excitation at 300 keV in the Born approximation. This is required in comparing the calculations with the measurements of Ziem et al.[10] On the other hand Pegg et al.[11] use incident Na and Mg projectiles on a gaseous target. For this experiment we assume the (i,J) levels are statistically populated, i.e., proportional to $(2J+1)$. In the Born approximation the cross section for excitation of the (i,J) term of the $(2p)^5(3s)(3p)$ configuration is given by

$$\sigma_{i,J} = (2J + 1)[3\sigma_0 C_i(^1S, ^2S, J)^2$$

$$+ \tfrac{6}{5}\sigma_2 C_i(^1D, ^2D, J)^2], \qquad (6a)$$

where σ_t is the cross section arising from the matrix element

$$\int_0^\infty \Psi_{2p}(r)\Psi_{3p}(r)j_t(kr)r^2\,dr . \qquad (6b)$$

For excitation of (i,J) terms of the $(2p)^5(4s)(3s)$ configuration the cross section is given by

$$\sigma_{i,J} = \sigma_{\text{TOT}} \frac{(2J+1)}{6} C_i(^1P, ^2P, J)^2 . \qquad (6c)$$

In the calculation of the radiative transition rate no attempt was made to use the observed energy differences. That is, the energy difference in the $3s$-$2p$ and $3p$-$3s$ transition in Na were taken as 33 and 4 eV, respectively, while for Mg they were 48 and 7 eV, respectively. For the $3s$-$2p$ and $3p$-$3s$ oscillator strengths in Na, 0.0276 and 0.920 were calculated, respectively, and for Mg, 0.0555 and

TABLE IV. Comparison of the variation of Auger matrix with Auger electron energy for the $(2p)^5(3s)(3p) \rightarrow (2p)^6$ Auger transition. The matrix elements are in units of 10^{-2} inverse Bohr radii.

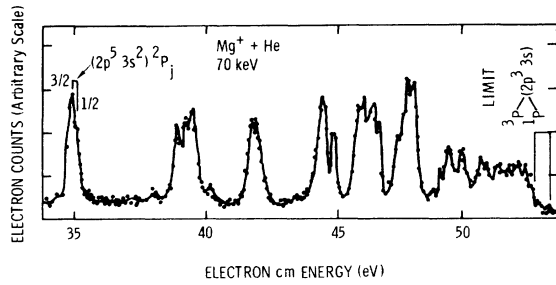| Element	$E_a(\text{eV})$	$E(0,0)$	$D(1,0)$	$D(1,2)$	$E(2,2)$
Na	23	0.283	0.156	−0.107	−0.282
	28	0.226	0.155	−0.085	−0.190
	30	0.221	0.154	−0.0793	−0.159
	33	0.214	0.153	−0.073	−0.121
Mg	35	0.634	0.401	−0.305	−0.574
	40	0.622	0.424	−0.218	−0.456
	45	0.613	0.443	−0.154	−0.358

FIG. 1. Measured Auger spectra from Ref. 11 for a Mg beam incident on a gaseous target.

0.841, respectively.

For Na in the Born approximation $\sigma_0 = 8.45 \times 10^{-19}$ cm^2 and $\sigma_2 = 1.66 \times 10^{-19}$ cm^2. In addition for Na I calculate the excitation cross section for $(2p)^6(3s) \rightarrow (2p)^5(3s)(nl)$ to be 9.5, 10.1, 1.3, 3.2, 3.1, and 0.07×10^{-19} cm^2 for $nl = 3s$, $3p$, $3d$, $4s$, $4p$, and $4d$, respectively. These cross sections provide a means of identifying terms in the Auger spectrum via relative intensities. The relevant Auger matrix elements for $(2p)^5(3s)(3p) \rightarrow (2p)^6$ are shown in Table IV. They are seen not to vary significantly with continuum electron energy. With this information one can calculate the additional entries in Tables II and III. From these tables the pervasive nature of Auger decay is apparent. With few exceptions all the terms decay with close to unity Auger yield.

III. COMPARISON WITH EXPERIMENT

In Fig. 1 is shown the $(2p)^5(3s)(nl)$ Auger spectra measured by Pegg et al. arising from a Mg ion beam incident on a gaseous target. In Fig. 2 we show the $(2p)^5(3s)^2$, $(2p)^5(3s)(3p)$, and $(2p)^5(3s)(4s)$ Auger spectra calculated with the data in Table III,

using a rectangular detector response 0.11 eV wide, and neglecting Doppler effects. In calculating Fig. 2 it was assumed that the initial term population was $2J + 1$, independent of configuration. The energy scale for the $(2p)^5(3s)(nl)$ Auger spectrum was established by locating peak (c) at 40.2 eV. On comparing Figs. 1 and 2 it is clear that there is rough general agreement for the $(2p)^5(3s)(3p)$ spectrum, i.e., four peaks in the 38–39-eV range, small peaks (a) and (c), and a multiple-peaked structure at 42–43 eV. (The calculated energy splitting is too large.) In addition the peak intensity at 42–43 eV is comparable to that at 38 eV. This good agreement confirms two points; (i) most of the terms in the $(2p)^5(3s)(3p)$ configuration decay with Auger yield near unity, indicating the importance of spin-orbit interaction; and (ii) within the $(2p)^5(3s)(3p)$ configuration the term intensities are consistent with a statistical population. The structure of the peak at 42 eV in Fig. 1 indicates that the Auger yield for term (a') is higher than 0.54 as calculated, a calculated value that we hoped would be confirmed. However, the lack of experimental confirmation may be due to either lack of experimental resolution, or to the calculated position of (b') relative to a' and b. Comparing the size of the L_{23}-M_1M_1 peaks relative to the $(2p)^5(3s)(3p)$ peaks in Figs. 1 and 2 established the point that (iii) the statistical hypothesis does not appear applicable between different configurations. Finally the $(2p)^5(3s)(4s)$ Auger spectrum does not appear clearly in Fig. 1. This is likely due to the overlapping $(2p)^5(3s)(3d)$ spectrum.

The $(2p)^5(3s)(nl)$ spectra of Na measured by Pegg et al. is shown in Fig. 3. The calculated spectrum is shown in Fig. 4. The energy scale was established by locating the peak a'' at 29.7 eV. Then the calculated spectrum indicates many peaks between 27.4 and 28 eV, the peak (c) at 28.3
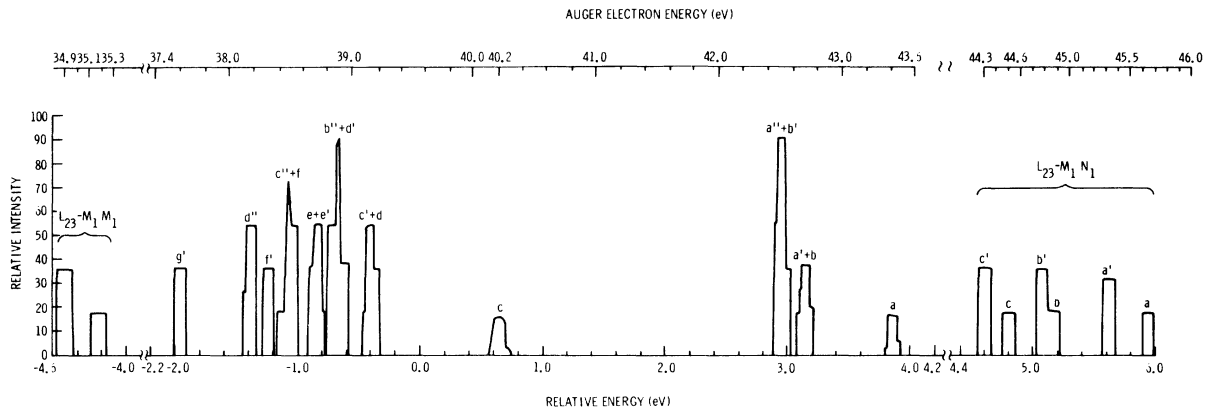

FIG. 2. Calculated $(2p)^5(3s)^2$, $(2p)^5(3s)(3p)$, and $(2p)^5(3s)(4s)$ Auger spectra of Mg assuming all terms are populated with weight $2J + 1$. The lower scale is relative energy, while the upper scale is absolute energy.
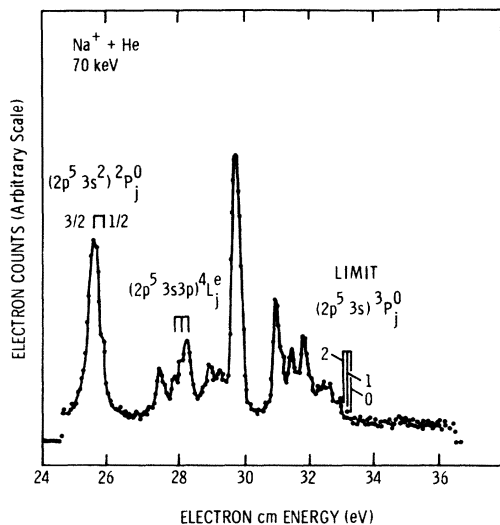
FIG. 3. Measured Auger spectra from Ref. 11 for a Na beam incident on a gaseous target.

eV, no structure between 28.3 and 29.6 eV, and structure between 29.6 and 30 eV. The $(2p)^5(3s)(3p)$ Auger spectrum in Fig. 2 is similar in intensity distribution to that in Fig. 4. However, Figs. 1 and 3 are drastically different. In Fig. 1 the high-energy peak in the $(2p)^5(3s)(3p)$ spectrum is comparable in intensity to the low-energy peak. In Fig. 3 the high-energy peak is a least a factor of 3 larger. Since the calculations in Fig. 2 are similar to those in Fig. 4 and the measurements in Fig. 1, the results in Fig. 3 appear anomalous. Two possible explanations are (a) breakdown of the statistical population hypothesis among terms of the $(2p)^5(3s)(3p)$ configuration; and (b) the large peak at 29.7 eV in Fig. 3 does not arise from the $(2p)^5(3s)(3p)$ Auger decay. If the calculated

$(2p)^5(3s)(4s)$ Auger spectrum is associated with the observed structure between 31 and 32 eV, then Fig. 4 indicates that the $(2p)^5(3s)(4s)$ intensities, with statistical populations, have the expected magnitude compared with the large peak at 29.7 eV. Further, if the large peak at 29.7 eV were discarded as irrelevant then the L_{23}-M_1M_1 intensity is at least twice that of the low-energy portion of the $(2p)^5(3s)(3p)$ spectrum. This is inconsistent with both the interconfiguration statistical hypothesis and the observations in Fig. 1. The tentative conclusion is that the peak in Fig. 3 at 29.7 eV arises from the $(2p)^5(3s)(3p)$ Auger spectrum, and that the low-energy portion of this spectrum is significantly depleted relative to the statistical population hypothesis.

Proton excitation of terms of the $(2p)^5(3s)(nl)$ configuration should permit more quantitative discussion of the resulting Auger spectra. In Sec. II it was indicated that in the Born approximation proton excitation is selective in term excitation. However 300-keV protons can excite and ionize the $(2s)$ shell of Na, e.g., excitation to $(2s)^1(2p)^6(3s)(nl)$ configurations. Configuration interaction effects can also occur, e.g., "shakeup" in ionization producing $(2s)^1(2p)^6(4s)$ as well as $(2s)^1(2p)^6(3s)$ configurations. If configuration interaction is important there is no reason to expect it to be limited to shakeup configurations, e.g., one might produce the $(2s)^1(2p)^4(^1S)(3s)^2$ ^1S term. Some of these processes are readily calculated. My calculations indicate that for 300-keV protons incident on Na, the cross sections for excitation to $(2s)^1(2p)^6(3s)^2$, $(2s)^1(2p)^6(3s)(3p)$, and $(2s)^1(2p)^6(3s)(4s)$ are 12.0, 3.3, and 5.5×10^{-20} cm^2, respectively. For comparison, the calculated cross sections for $(2p)^5(3s)^2$, $(2p)^5(3s)(3p)$, and $(2p)^5(3s)(4s)$ excitations are 95, 101, and 32×10^{-20} cm^2, respectively.
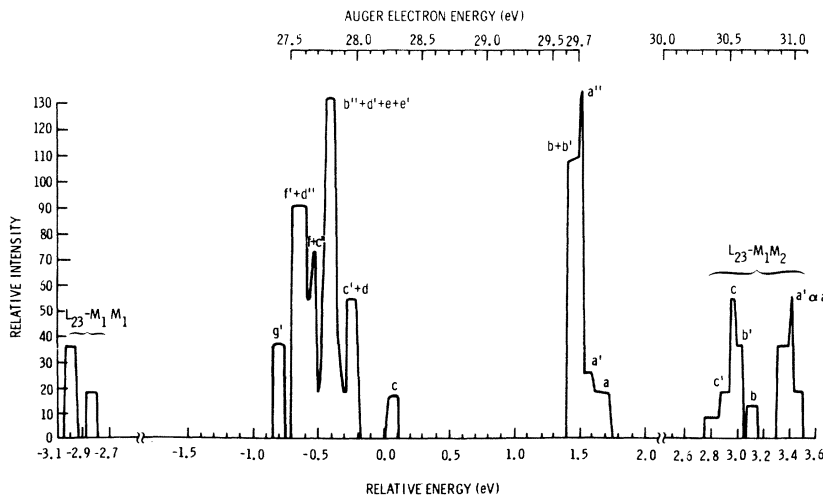

FIG. 4. Calculated $(2p)^5(3s)^2$, $(2p)^5(3s)(3p)$, and $(2p)^5(3s)(4s)$ Auger spectra of Na assuming all terms are populated with weight $2J + 1$. The lower scale is relative energy, while the upper scale is absolute energy.
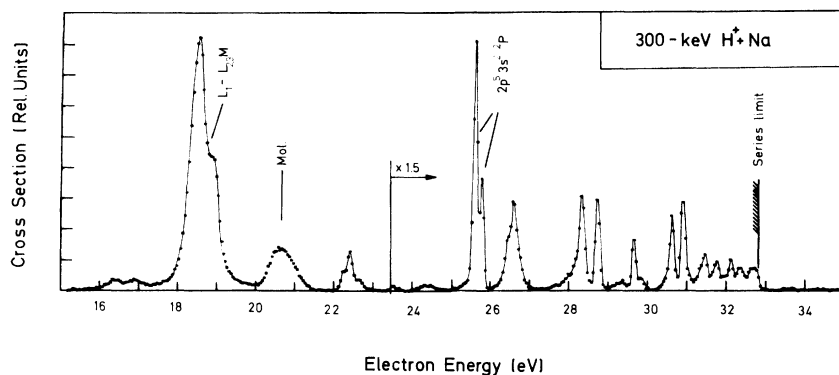
FIG. 5. Measured Auger spectra from Ref. 10 resulting from 300-keV protons incident on Na vapor.

The calculated cross section for ionization of the (2s) electron is 800×10^{-20} cm^2. Wolff et al.[17] have observed photoabsorption in Na at 66.6 eV. They identify this as the $(2s)^2(2p)^6(3s)$
→ $(2s)^1(2p)^6(3s)^3S(3p)^2P$ transition. If the $(2s)^1(2p)^6(3s)^3S(3p)^2P$ decays via an Auger transition to the $(2s)^2(2p)^5(3s)$ configuration (^3P at 38.0 eV, ^1P at 38.4 eV)[18] one would expect to see Auger electrons at 28.6 and 28.2 eV, respectively. When the $(2s)^1(2p)^6(3s)^2 \, ^2S$ configuration is excited one expects an Auger electron at a somewhat lower energy.

With this in mind the measurements of Ziem et al.[10] on the Na Auger spectra, following excitation by 300-keV protons, are shown in Fig. 5. The calculated $(2p)^5(3s)^2$, $(2p)^5(3s)(3p)$, and $(2p)^5(3s)(4s)$ spectra are shown in Fig. 6. The energy scale was established in Fig. 4. In comparing Figs. 5 and 6 one sees that the peak labeled (c) in Fig. 6 corresponds to the peak at 28.3 eV in Fig. 5, while that labeled (b) corresponds to the peak at 29.7 eV. The calculated peak labeled (a) is larger than the measured peak at 29.9 eV in Fig. 5. The relative intensities of peaks (b) and (c) compared to L_{23}-M_1M_1 in Fig. 6 agree with

those in Fig. 5. On the other hand, the calculated intensities of the peaks at 30.5 and 31.0 eV $[(2p)^5(3s)(4s)]$ are smaller than those measured by a factor of 3. An additional check on the Born approximation can be made by comparing the intensity of the Auger peaks corresponding to L_1-$L_{23}M_1$ and L_{23}-M_1M_1 transitions. For the former the (2s) ionization cross section is 800×10^{-20} cm^2 and the linewidth is about 0.5 eV.[3] Thus one expects a relative peak intensity of ≈1600. For the latter the $(2p)^5(3s)^2$ excitation cross section is 95×10^{-20} cm^2 and the instrumental resolution is 0.11 eV. Thus one expects a relative peak intensity of ≈900. To within a factor of 2 this is observed in Fig. 5.

The striking differences between Figs. 5 and 6 are the peaks at 26.6 and 28.7 eV in Fig. 5. Based on energetics alone, it was shown that these peaks could correspond to $(2s)^1(2p)^6(3s)^2 - (2s)^2(2p)^5(3s)$ and $(2s)^1(2p)^6(3s)(3p) - (2s)^2(2p)^5(3p)$ Auger transitions. However, the maximum excitation cross section, in the Born approximation is 12×10^{-20} cm^2. With a linewidth of 0.5 eV, the relative peak intensity is at most 25. This is barely above the noise level in Fig. 5. Alternatively the peaks at 26.6 and 27.8 eV could arise from "shakeup," i.e.,
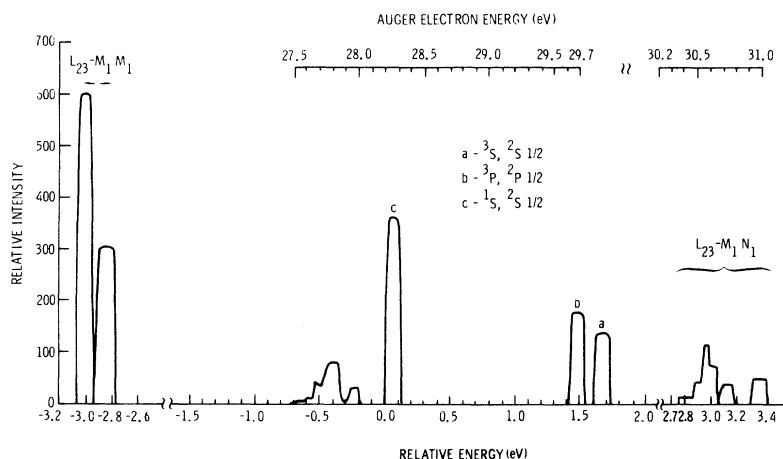

FIG. 6. Calculated $(2p)^5(3s)^2$, $(2p)^5(3s)(3p)$, and $(2p)^5(3s)(4s)$ Auger spectra of Na with initial term populations determined from the Born approximation. The lower scale is relative energy, while the upper scale is absolute energy.

$(2s)^1(2p)^6(4s)$ and $(2s)^1(2p)^6(5s)$ initial configurations. This appears unlikely as both peaks have comparable intensities. A rough estimate of the energy position of such shakeup peaks can be obtained by using the $3s$-$4s$ and $3s$-$5s$ energy differences in Na^+,[18] i.e., 8.6 and 11.5 eV. Since the L_1-$L_{23}M_1$ Auger peak is at 18.5 eV, the shakeup peaks would be at 27.1 and 30.0 eV. This indicates that the peak at 26.6 eV could arise from Auger decay of the $(2s)^1(2p)^6(4s)^1S, ^3S$ terms, but that it is unlikely that the peak at 28.7 eV arises from $(2s)^1(2p)^6(5s)$.

By elimination this leads to the hypothesis[19] that the additional peak at 28.7 eV arises from the $(2s)^2(2p)^4 {}^1S(3s)^2 {}^1S - (2s)^2(2p)^5$ Auger transition. It is hypothesized that the initial level is populated via configuration interaction with the $(2s)^1(2p)^6(3s)^1S$ term. Since the L_1-$L_{23}M_1$ Auger peak is at 18.5 eV and the $(2s)^2(2p)^5 {}^2P$ term is 52.4 eV above the Na ground state, the $(2s)^1(2p)^6(3s)^1S$ term is at 70.9 eV. The difficulty is to accurately estimate the energy of the $(2s)^2(2p)^4(3s)^2 {}^1S$ term. Since $(2s)^2(2p)^6$ is at 5.1 eV, and the energy difference between $(2s)^2(2p)^6$-$(2s)^2(2p)^5(3s)$ is about 33 eV,[18] one expects the $(2s)^2(2p)^4(3s)^2 {}^1S$ term to be at an energy greater than 71.1 eV. An upper bound is found by observing that the $(2s)^2(2p)^4(3s)$ configuration is at 97.9 eV.[18] By ionizing a $(3s)$ electron from $(2s)^2(2p)^4(3s)^2$ one obtains $(2s)^2(2p)^4(3s)$. The ionization energy is at least 14.3 eV, the energy required to ionize a $3s$ electron from $(2s)^2(2p)^5(3s)$. Thus an upper limit is 83.6 eV. This upper bound would lead to an Auger peak at 31.2 eV. Our hypothesis is that it occurs at 28.7 eV, which locates the $(2s)^2(2p)^4({}^1S)(3s)^2 {}^1S$ at 81.1 eV. Some additional evidence for this identification is the relatively narrow width and unstructured appearance of the Auger peak at 28.7 eV.

If one accepts the identification of the Na Auger peaks at 26.6 and 28.7 eV, additional evidence appears on the validity of the interconfiguration statistical population hypothesis. That is, the peak at 26.6 eV does not appear in Fig. 3. The conclusion is that in the experiment of Pegg $et\ al.$, a negligible number of $(2s)$ vacancies are produced.

IV. CONCLUSIONS

The aims of this study were to examine the effect of spin-orbit coupling on Auger transition rates and Auger yields, to examine the statistical hypothesis with regard to term populations in ion-atom collisions, and to examine the possibility that experimental Auger spectra can be used to verify calculations of less than unity Auger yields for selected terms. The approach is to compare calculations and experiment. The conclusions reached are that spin-orbit coupling is important, that the statistical hypothesis is poor in predicting interconfigurational populations, and erratic in predicting term populations within a configuration, and that in the case of Mg the experimental data provide no support for a less than unity Auger yield in a case where calculations so indicated. Qualifying these conclusions, it must be emphasized that they were reached for singly ionized Mg and neutral Na. The neglect of spin-orbit interaction and the use of the statistical population hypothesis may well be valid at higher stages of ionization. In addition the difference between an Auger yield of 0.90 and 0.99 may make no measurable difference in an Auger spectrum, while the difference between a 0.10 and 0.01 fluorescence yield can be extremely important in studying possible x-ray laser transitions. In hope of establishing more quantitative conclusions the Auger spectra resulting from protons incident on Na was compared with calculations. It was found that a complete description of the large Auger peaks in the spectrum led to the hypothesis that the $(2s)^1(2p)^6(4s)$ configuration is at 79.0 eV and the $(2s)^2(2p)^4(3s)^2 {}^1S$ term is at 81.1 eV and that they both have a substantial configuration interaction with $(2s)^1(2p)^6(3s)^1S, ^3S$ term at 70.9 eV.

ACKNOWLEDGMENTS

†Work supported by the Energy Research and Development Administration.

[1] E. H. S. Burhop and W. N. Asaad, Adv. At. Mol. Phys. 8, 163 (1972).

[2] E. J. McGuire, $Atomic\ Inner$-$Shell\ Processes$, (Academic, New York, 1975), Vol. I.

[3] H. Hillig, B. Cleff, W. Mehlhorn, and W. Schmitz, Z. Phys. 268, 225 (1974).

[4] C. C. Chang, $Characterization\ of\ Solid\ Surfaces$ (Plenum, New York, 1974).

[5] G. N. Ogurtsov, Rev. Mod. Phys. 44, 1 (1972).

[6] E. J. McGuire, Phys. Rev. A 10, 32 (1974).

[7] M. H. Chen and B. Crasemann, Phys. Rev. A 10, 2232 (1974).

[8] C. P. Bhalla, Phys. Rev. A 12, 122 (1975).

[9] E. J. McGuire and M. Duguay, Appl. Opt. (to be published).

[10] P. Ziem, G. Wüstefeld, and N. Stolterfoht, presented at International Conference on Inner Shell Ionization Phenomena, Freiburg, April, 1975. (unpublished).

[11] D. Pegg, H. Haselton, R. Thoe, P. Griffin, M. Brown,

and I. Sellin, Phys. Rev. A 12, 1330 (1975).

[12]J. C. Slater *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960).

[13]F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

[14]E. J. McGuire, Phys. Rev. 175, 20 (1968).

[15]J. B. Mann, "Atomic Structure Calculations. I. Hartree-Fock Energy Results for the Elements Hydrogen to Lawrencium," Los Alamos Scientific Laboratory Report No. LASL-3690, 1967 (unpublished).

[16]The mixing coefficients are available from the author.

[17]H. W. Wolff, K. Radler, B. Sonntag, and R. Haensel, Z. Phys. 257, 353 (1972).

[18]C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stds. (U. S.) Circ. No. 467 (U. S. GPO, Washington, D. C., 1957).

[19]This was initially suggested to N. Stolterfoht by E. Breukmann of Professor Mehlhorn's group at Freiburg.