Alkalilike Spectra in the Promethium Isoelectronic Sequence

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Highly ionized members of the Pm sequence should produce strong resonance lines in the uv spectra of hot plasmas contaminated by heavy elements. These ions for $Z \geq 74$ have an alkali structure with ground configuration $4f^{14}5s$. Hartree-Fock calculations show that in W XIV through U XXXII the dominant resonance lines are the $5s$-$5p$ doublets in the range $\lambda = 100$–400 Å. Approximate predictions are given for the doublet wavelengths, line strengths, and mean lives.

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This Letter presents the first theoretical investigation of the promethium isoelectronic sequence and predicts that hot plasmas contaminated with heavy elements should exhibit strong alkalilike resonance lines in the range $\lambda = 100$–400 Å because of highly ionized members of this sequence.

Isoelectronic sequences which are alkalilike for very high stages of ionization have recently come under urgent study as a result of their importance for radiative energy loss and diagnostics in controlled nuclear devices containing heavy metal contaminants.[1] There are five such sequences, corresponding to ions isoelectronic to H, Li, Na, Cu, and Pm. Although the H, Li, Na, and Cu sequences have been studied in much detail, this Letter presents the first investigation of the spectra of the Pm isoelectronic sequence, and reports theoretical wavelengths and transition probabilities for the $5s\,^2S$–$5p\,^2P$ transitions in W XIV, Ir XVII, Au XIX, Pb XXII, and U XXXII. In all these spectra this resonance transition, analogous to the sodium D doublet, should be easily excited and produce characteristic bright lines in the ultraviolet (100–400 Å).

Alkalilike spectra, which are characterized by very strong ^2S-^2P resonance transitions, occur when the ground state of an atom or ion consists of a single s electron outside of a core composed of closed shells or subshells. In neutral and few times ionized atoms this situation occurs for the group-IA alkali metals and group-IB "coinage" metals. Here the energy ordering can, as a result of core penetration, place an ns configuration below configurations of lower n and higher l; however, for higher stages of ionization penetration is reduced and the energy ordering approaches that of hydrogen. Thus in the high-ionization limit, only a configuration with a filled-shell core will retain the ns ground state and alkali character, corresponding to isoelectronic sequences with a number of electrons N given by $N = 1 + n_0(n_0+1)(2n_0+1)/3$, where $n_0 = 0$, 1, 2, 3, and 4. The promethium sequence of ions corresponds to $n_0 = 4$ and $N = 61$; for high Z, all orbitals with $n \leq 4$ are filled, leaving a single electron to move among the $n \geq 5$ orbitals.

The calculations presented here were performed by means of the numerical Hartree-Fock program MCHF 77 developed by Froese Fischer,[2] with use of the nonrelativistic single-configuration model. Clearly this method ignores many processes which could be important in these complex atoms, but it does give a reasonably reliable (although not precise) estimate of the wavelengths which

must be searched for experimentally. Further, it provides a well-defined prediction to be tested against spectroscopic data and more sophisticated calculations, when these become available. We have also calculated, using the Pauli approximation, the leading relativistic corrections to the wavelengths of the $5s$-$5p$ lines. Finally, in order to provide a further estimate of the reliability of our predictions, we have performed the same calculations for the $4s$-$4p$ transitions in the Cu sequence where comparison with other results is possible.

The lowest configuration for neutral Pm is quite unlike an alkali, being $4f^5 5s^2 5p^6 6s^2$. However, as the nuclear charge is increased the $4f$ orbital energy is gradually reduced, crossing the $6s$, $5p$, and $5s$ energies until W XIV is reached, in which Hartree-Fock calculations predict the lowest configuration to be $4f^{14}5s$. Figure 1 shows an isoelectronic plot of the relative Hartree-Fock energies of the lowest configurations in the Pm sequence for ions with core charge $\zeta = 14$–32. In this figure is plotted E/ζ^2 vs $1/\zeta$, where E is the average excitation energy of the indicated configurations above the ground configuration $4f^{14}5s$. Clearly the lowest-lying levels of U XXXII will be alkalilike: The first excited states are in the $4f^{14}5p$ and $4f^{14}5d$ configurations and are well separated in energy, and also in orbital radius, from the $4f^{13}5s^2$ and $4f^{13}5s5p$ configurations. At the other end of the figure W XIV seems less clear since the $4f^{14}5p$ is well above the $4f^{13}5s^2$ and comparable with the $4f^{13}5s5p$. (There is one unpublished calculation[3] for W XIV which predicted that the $5s$ configuration still lies slightly above the $5s^2$ and $5s^2 5p$ for this degree of ionization.) Nevertheless there are reasons to believe that the $5s$-$5p$ doublet in W XIV can still be considered alkalilike to a reasonable approximation: First, neither the $4f^{13}5s^2$ nor the $4f^{13}5s5p$ contains a ^2P term; these configurations are thus hindered in interacting with the $4f^{14}5p$ and in being excited from the $4f^{14}5s$. Second, the Hartree-Fock orbitals are well separated spatially—the $n=4$ orbitals are all concentrated around $r = 0.5$ a.u., while the $5s$ and $5p$ wave functions are largest for $r \geq 1$ a.u. Table I shows the expectation values $\langle r \rangle_{nl}$ for the Hartree-Fock orbitals in W XIV; the other ions considered here all show the same pattern in which the orbitals are clearly separated according to principal quantum number.

We therefore take as a reasonable first approximation the Hartree-Fock energies and wave functions for the $5s\ ^2S$ and $5p\ ^2P$ levels in the Pm sequence ions W XIV through U XXXII. Relativistic corrections for these high-Z systems are substantial. To estimate these effects, perturbation calculations were made to order[4] (αZ) and higher-order corrections were included by a semiempirical method. First, the expectation values for each of the three terms in the Pauli Hamiltonian (Darwin, relativistic mass, and spin-orbit) were calculated for each orbital and the results were summed. For these high-Z elements it was only necessary to compute the electron-nucleus form of these interactions since the electron-electron form grows much more slowly with increasing Z. Next, the differences between the Dirac and Pauli energies were estimated from a screened hydrogenlike Sommerfeld expansion.[4] The effective charge was obtained by equating the Pauli energy of the active electron with the Z^4 term in the Sommerfeld expansion and used to compute the higher-order terms. The relativistic corrections to the ^2S-^2P intervals were estimated by considering

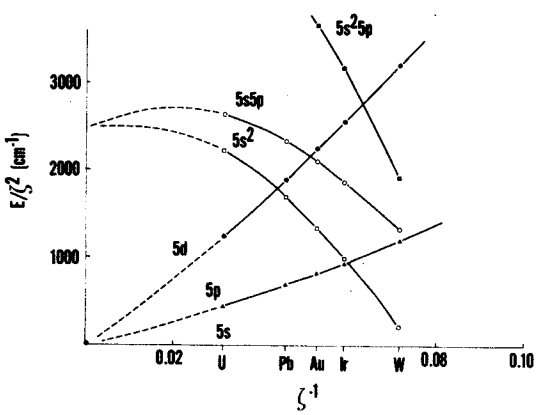

FIG. 1. Configuration energies in the promethium isoelectronic sequence. E/ζ^2 is plotted against $1/\zeta$, where $\zeta = Z - 60$ is the core charge and E is the average energy of the configuration above the ground-state configuration $4f^{14}5s$. These energies are the results of single-configuration Hartree-Fock calculations with no relativistic corrections. Triangles, $4f^{14}5p$; filled circles, $4f^{14}5d$; open squares, $4f^{13}5s^2$; open circles, $4f^{13}5s5p$; filled squares, $4f^{12}5s^2 5p$.

TABLE I. $\langle r \rangle_{nl}$ in W XIV (a.u.).

	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$
$l=0$	0.02	0.09	0.22	0.49	1.05
$l=1$		0.07	0.21	0.50	1.11
$l=2$			0.18	0.51	
$l=3$				0.55	

TABLE II. Energy differences (in 10^3 cm^{-1}).

Element Z		Er 68	W 74	Ir 77	Pt 78	Au 79	Pb 82	U 92
Cu $4P_{1/2}$-$4P_{3/2}$								
this work	Pauli	457	693		892		1132	
	higher order	55	104		156		228	
	total	512	797		1048		1360	
Ref. 6			816		1079		1406	
Ref. 7		522						
Ref. 8		517	806		1060		1376	
Cu $4S_{1/2}$-$4P_{1/2}$								
this work	NRHF	601	687		745		802	
	Pauli	57	78		92		112	
	higher order	5	8		12		16	
	total	663	773		849		930	
Ref. 5			777					
Ref. 6			798		882		969	
Ref. 7		671						
Pm $5P_{1/2}$-$5P_{3/2}$								
this work	Pauli		90.4	125.3		152.7	200.7	431.1
	higher order		6.3	10.2		13.9	21.2	69.9
	total		96.7	135.5		166.6	221.9	501.0
Pm $5S_{1/2}$-$5P_{1/2}$								
this work	NRHF		235.1	272.1		296.7	333.8	457.2
	Pauli		27.3	33.4		36.9	42.8	71.5
	higher order		1.7	2.3		2.9	3.9	9.4
	total		264.1	307.8		336.5	380.5	538.1

separately the $^2P_{1/2}$-$^2P_{3/2}$ fine structure separations and the corrections to the $^2S_{1/2}$-$^2P_{1/2}$ interval.

To test the accuracy of predictions in the Pm sequence similar calculations were performed for the homologous Cu sequence for the same range of atomic numbers ($Z > 60$), and compared with relativistic calculations,[5,6] measurements,[7] and semiempirical extrapolations[8] which are available for some ions in this sequence. A breakdown of our calculations and a comparison with other results for the Cu sequence is given in Table II, and indicates agreement to within (1–4)% (although our calculations are systematically on the low side of other results). For a similar range of Z values ($68 \leq Z \leq 82$) we would expect the uncertainties for the Pm sequence to be no greater than this, since there the effective screening is larger. A breakdown of our calculations for the Pm sequence is also given in Table II, which (on the basis of the comparison for the Cu sequence with Refs. 5–8) we assume to be accurate to within about 4%.

Table III gives the predicted $5s$-$5p$ wavelengths λ, line strengths S, and mean lives τ for select-

TABLE III. $5s\,^2S$–$5p\,^2P$ lines in Pm sequence.

Z	Spectrum	Line	λ (Å)	τ (ps)	S (a.u.)
74	W XIV	1/2-1/2	379	80	1.16
		1/2-3/2	277	31	
77	Ir XVII	1/2-1/2	325	63	0.96
		1/2-3/2	226	20	
79	Au XIX	1/2-1/2	297	56	0.86
		1/2-3/2	199	16	
82	Pb XXII	1/2-1/2	263	47	0.73
		1/2-3/2	166	11	
92	U XXXII	1/2-1/2	186	31	0.47
		1/2-3/2	96	4	

ed ions in the Pm sequence. The dipole transition matrix elements were computed directly from the Hartree-Fock 5*s* and 5*p* wave functions with use of a frozen core: No corrections for relativity or core polarization (an inert-gas core tends to be rigid to dipole distortions) were made in the line-strength calculations. The leading relativistic corrections to the energy levels were made as discussed above and these effects have been included in the predicted wavelengths and mean lives.

These systems should be amenable to study by beam-foil excitation methods. In the grazing incidence spectral region techniques have been developed[9] which permit a beam segment as short as 80 μm to be spatially resolved, which should permit lifetime measurements down to the 10-psec range with the beam velocities required to produce these states.[10] Beams of sufficient energy to produce these ionizations have already been produced[11] for studies in the $\lambda = 30-80$ Å region.

In conclusion we suggest that the spectra of the ions in the upper half of the promethium sequence will be approximately alkalilike, will be of interest in plasma diagnostics, and will be fruitful objects of further research, both experimental and theoretical.

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