Deep Terms in the Isoelectronic Sequence V I to Cu VII

P. GERALD KRUGER, *Department of Physics, University of Illinois*
AND
HELEN T. GILROY, *Department of Physics, Cornell University*

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By the use of constant second differences in the radiated frequencies from terms involving an electron transition to the ground state, it has been possible to identify the $3d^5\ {}^6S_{5/2}$ and $3d^4\ 4p\ {}^6P^\circ$ terms of this sequence. Ionization potentials cannot be computed because of the lack of completeness in the data on the first three members of the sequence.

THE spectra of this sequence have been studied previously by Helen T. Gilroy.[1] At that time certain lines in the Mn III, Fe IV and Co V spectra were classified as the $3d^5\ {}^6S_{5/2} - 3d^4\ 4p\ {}^6P^\circ_{7/2,\ 5/2,\ 3/2}$ transitions. It now appears that these classifications are wrong and that the ${}^6S_{5/2}$ term lies somewhat deeper than was previously reported.

The data, reported in this paper, on Mn III and Fe IV were obtained from spectrograms taken at Cornell University with a one and one-half meter normal incidence vacuum spectrograph; on Cr II, with a Rowland mounting grating. The wave-lengths for Cr II agree with those previously reported by Russell,[2] C. E. Moore[3] and others. For Co V, Ni VI and Cu VII the lines have been photographed with a twenty-one foot grazing incidence vacuum spectrograph at the University of Illinois.[4] A hot spark previously described[5] was used as the light source. Pure metals of Co, Ni and Cu were used as electrodes and the length of exposure varied from one to two hours.

In all members of this sequence except V I the deepest term is $3d^5\ {}^6S_{5/2}$ which combines strongly with $3d^4\ 4p\ {}^6P^\circ$ to give three very strong and characteristic lines which can be followed down the sequence readily. These lines were recognized as part of an isoelectronic sequence, on the spectrograms of Co, Ni and Cu because they appeared with other characteristic groups of lines on all these spectrograms, in such a way that the group arrangement on one spectrogram (Co) was exactly reproduced on another spectrogram (Ni) at shorter wave-lengths. The three strongest lines, forming what appeared to be a triplet, were picked out and plotted on a graph like that in Fig. 1. The graph was then extrapolated to Fe and the corresponding three lines found within 500 cm^{-1} of the predicted wave-length. A further extrapolation to Mn and Cr showed that the corresponding three lines in Cr were the $3d^5\ {}^6S_{5/2} - 3d^4\ 4p\ {}^6P^\circ$ of Cr II as classified by Russell.[2] This fixed the identity of the other lines of the sequence, as being the corresponding transitions in the more highly ionized ions. An extrapolation to V I predicts the corresponding radiation to be approximately 3000 cm^{-1}. Thus it is quite understandable that it has not been observed.

Table I gives the radiated frequencies of these lines and the first and second differences. The second differences of this table are compared with the second differences in other sequences involving similar electron configurations, in Table II.

The classified lines are given in Table III. Since these radiations are caused by transitions to the ground state, the values of ν in cm^{-1} in

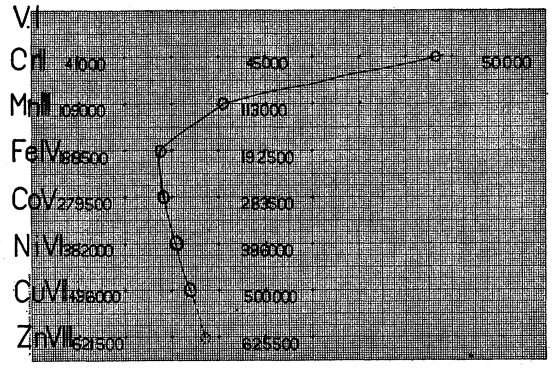

FIG. 1. Radiated frequencies, cm^{-1}, $3d^5\ {}^6S_{5/2} - 3d^4\ 4p\ {}^6P^\circ_{7/2}$

[1] Gilroy, Phys. Rev. **38**, 2217 (1931).
[2] Russell, Astrophys. J. **66**, 184 (1927).
[3] Moore, *Term Designations for Excitation Potentials*, Princeton University Observatory Publication (1934).
[4] Kruger, Rev. Sci. Inst. **4**, 128 (1933).
[5] Kruger and Shoupp, Phys. Rev. **46**, 124 (1934).

TABLE I. *Radiated frequencies (cm^{-1}) with first and second differences.*

ELEMENTS OF THE SEQUENCE	$3d^5\,{}^6S_{5/2}-3d^4\,4p\,{}^6P^\circ_{7/2}$	FIRST DIFFERENCE	SECOND DIFFERENCE
V I	(3,000)		
		(45,500)	
Cr II	48,633		(18,000)
		63,425	
Mn III	112,058		14,747
		78,172	
Fe IV	190,230		12,873
		91,045	
Co V	281,275		11,781
		102,826	
Ni VI	384,101		11,416
		114,242	
Cu VII	498,343		(11,500)
		(125,740)	
Zn VIII	(624,080)		

TABLE II. *Comparison of second differences.*

FIRST MEMBER OF THE ISOELECTRONIC SEQUENCE	ELECTRON CONFIGURATIONS	APPROXIMATE VALUE OF SECOND DIFFERENCE
Ne I	$2p^6-3p^5 3s$	30,000 cm^{-1}
Cl I	$3p^5-3p^4 4s$	11,000 cm^{-1}
A I	$3p^6-3p^5 4s$	11,000 cm^{-1}
K I	$3d\ -4p$	11,000 cm^{-1}
V I	$3d^5-3d^4 4p$	3,500 cm^{-1} [1]
		(new) 11,500 cm^{-1}
Ni I	$3d^{10}-3d^9 4p$	11,000 cm^{-1}
Pd I	$4d^{10}-4d^9 5p$	7,100 cm^{-1}

TABLE III. *Observed lines from transition to the deepest term in ions of the isoelectronic sequence V I to Cu VII.*

ELEMENTS OF THE SEQUENCE	INT.	λ (vac.)	$\nu(cm^{-1})$	COMBINATIONS $3d^5\,{}^6S_{5/2}-3d^4\,4p\,{}^6P^\circ$
V I		(33,330 A)	(3,000)	${}^6S_{5/2}-{}^6P^\circ_{7/2}$
		(34,610 A)	(2,889)	${}^6S_{5/2}-{}^6P^\circ_{5/2}$
		(35,600 A)	(2,809)	${}^6S_{5/2}-{}^6P^\circ_{3/2}$
Cr II	90	2,056.22	48,633	${}^6S_{5/2}-{}^6P^\circ_{7/2}$
	80	2,062.20	48,492	${}^6S_{5/2}-{}^6P^\circ_{5/2}$
	70	2,066.12	48,400	${}^6S_{5/2}-{}^6P^\circ_{3/2}$
Mn III	45	892.39	112,058	${}^6S_{5/2}-{}^6P^\circ_{7/2}$
	35	893.75	111,888	${}^6S_{5/2}-{}^6P^\circ_{5/2}$
	25	894.65	111,775	${}^6S_{5/2}-{}^6P^\circ_{3/2}$
Fe IV	100	525.68	190,230	${}^6S_{5/2}-{}^6P^\circ_{7/2}$
	75	526.28	190,013	${}^6S_{5/2}-{}^6P^\circ_{5/2}$
	60	526.60	189,897	${}^6S_{5/2}-{}^6P^\circ_{3/2}$
Co V	20	355.523	281,275	${}^6S_{5/2}-{}^6P^\circ_{7/2}$
	18	355.876	280,996	${}^6S_{5/2}-{}^6P^\circ_{5/2}$
	12	356.060	280,851	${}^6S_{5/2}-{}^6P^\circ_{3/2}$
Ni VI	400	260.348	384,101	${}^6S_{5/2}-{}^6P^\circ_{7/2}$
	300	260.591	383,743	${}^6S_{5/2}-{}^6P^\circ_{5/2}$
	250	260.713	383,564	${}^6S_{5/2}-{}^6P^\circ_{3/2}$
Cu VII	200	200.665	498,343	${}^6S_{5/2}-{}^6P^\circ_{7/2}$
	150	200.851	497,881	${}^6S_{5/2}-{}^6P^\circ_{5/2}$
	100	200.948	497,640	${}^6S_{5/2}-{}^6P^\circ_{3/2}$

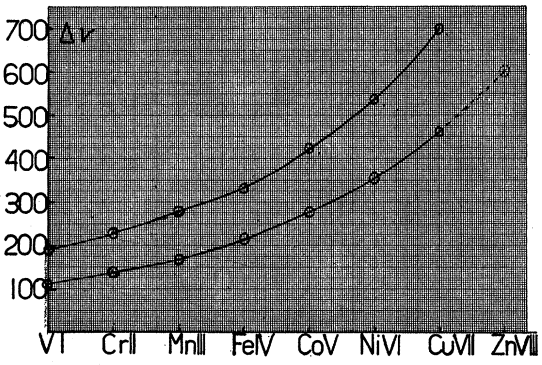

FIG. 2. $3d^4\,4p\,{}^6P^\circ_{7/2,\ 5/2,\ 3/2}$ term separations in cm^{-1}.

TABLE IV. *Splitting of ${}^6P^\circ$ terms for various ions of the seauence.*

	V I	Cr II	Mn III	Fe IV	Co V	Ni VI	Cu VII	Zn VIII
$\Delta\nu\ {}^6P^\circ_{7/2,\ 5/2}$	111	141	170	217	279	358	462	(600)
$\Delta\nu\ {}^6P^\circ_{5/2,\ 3/2}$	80	92	113	116	145	180	241	(320)
$\Delta\nu\ {}^6P^\circ_{7/2,\ 3/2}$	191	233	283	333	424	538	703	(920)

column four are also the respective term values of the ${}^6P^\circ_{7/2,\ 5/2,\ 3/2}$ terms, when the ${}^6S_{5/2}$ is taken as zero. In the spectrum of Mn a group of lines near 50,000 cm^{-1}, reciprocal wave-length, appears to be the $3d^4 4s\ {}^6D-3d^4 4p\ {}^6P^\circ$ multiplet. Since this multiplet has not been located in the higher members of the sequence, the wave-lengths are not included in this report.

Since the data for Cr II and Mn III are so incomplete, it is not possible to extrapolate accurately the $(\nu/R)^{\frac{1}{2}}$ graph and obtain ionization potentials for the ions of this sequence. This may be done as soon as higher series members have been obtained in Mn III and its ionization potential well established.

Table IV and Fig. 2 show the increase in the splitting of the ${}^6P^\circ$ terms for the ions of this sequence. The smoothness of the curves gives added support to their correctness.

The study of these spectra, for the identification of other multiplets from the electron configurations $3d^5$, $3d^4\,4s$ and $3d^4\,4p$ in this sequence, is being continued.

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