LBL-15924 c.2
Preprint

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY

AUG 10 1983

LIBRARY AND
DOCUMENTS SECTION

Materials & Molecular Research Division

Submitted to the Journal of the Optical Society of America

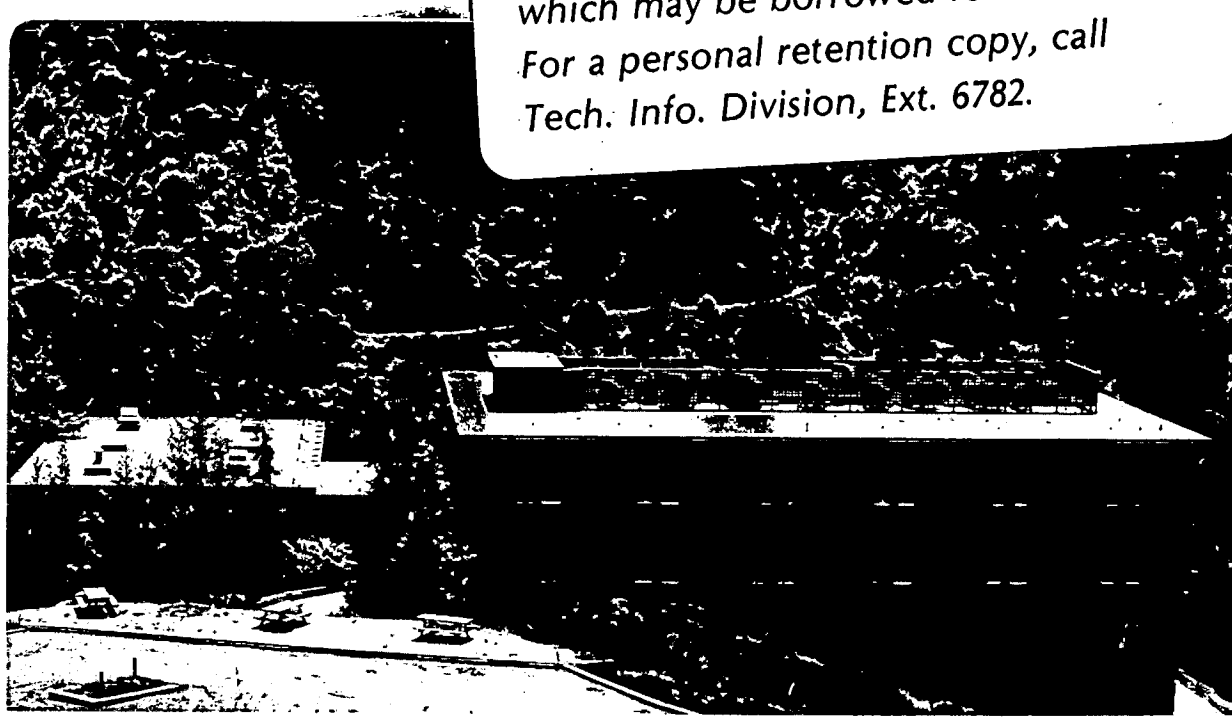
THE $^1S_0$ LEVEL AND A PARAMETRIC ANALYSIS IN THE $5f^2$ CONFIGURATION OF U V

C.H.H. Van Deurzen, K. Rajnak, and J.G. Conway

July 1983

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.



LBL-15924 c.2

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-15924

The $^1S_0$ Level and a Parametric Analysis in the $5f^2$ Configuration of U V

C. H. H. Van Deurzen
British Columbia Institute of Technology
3700 Willingdon Avenue
Burnaby, V5G 3H2, British Columbia, Canada

K. Rajnak*
John G. Conway
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

The $^1S_0$ level of the $5f^2$ configuration of U V has been found at 43613.58 ± 0.1 cm^{-1}. A parametric fit of the 13 levels of the $5f^2$ configuration gives an rms deviation of 9.8 cm^{-1} with F^2 = 51938 ± 39, F^4 = 42708 ± 100, F^6 = 27748 ± 68, α = 35.5 ± 0.4, β = −664 ± 25, γ = 744 ± 26, ζ = 1968 ± 2, P^2 = 573 ± 66, P^4 = 524 ± 144 and P^6 = 1173 ± 321, all in cm^{-1}. An additional calculation using the recently defined (B. R. Judd, Jørgen E. Hansen and A. J. J. Raassen, J. Phys. B 15, 1457 (1982)) α', β' and γ' parameters was carried out.

*Permanent address: Kalamazoo College, Kalamazoo, Michigan 49007

The spectrum of four times ionized uranium has been analyzed by Wyart, Kaufman, and Sugar (WKS).[1] For the $5f^2$ configuration they found twelve of the thirteen possible levels. The position of the missing $^1S_0$ level is determined by the value of the configuration interaction parameter γ.[2] WKS set $\gamma = 0$ which placed the calculated $^1S_0$ at 45812 cm^{-1}. A recent calculation by Goldschmidt[3] including γ and spin-dependent interactions placed it at 45154 cm^{-1}. γ is known to be ~ 1000 cm^{-1} for trivalent actinides in crystals.[4] Fixing it at this value and performing a least squares fit of the other parameters of WKS predicts the $^1S_0$ at 43480 cm^{-1}. These predictions all place the transitions to the $^1S_0$ from the 5f6d levels in the wavelength range between 2000 and 7000 Å which we have investigated.

The spectra were produced in a sliding spark discharge in vacuum at 250 and 1000 amperes peak current. They were recorded photographically on a 3.4 m Ebert spectrograph in air above 2489 Å (8th to 22nd order, dispersion 0.5 Å/mm) and on a 3.4 m normal incidence vacuum spectrograph below 2489 Å (1st order, dispersion 2.77 Å/mm). Fewer than seven characteristic lines due to U V were observed in the regions examined. Three of these lines can be interpreted as transitions from the $^3D_1$, $^3P_1$ and $^1P_1$ levels of 5f6d to the $^1S_0$ level of $5f^2$ as shown in Table I. Therefore, we place the $^1S_0$ at 43613.58 ± 0.1 cm^{-1}.

To analyze the energy levels of the, now complete, $5f^2$ configuration, we have added to the Hamiltonian of WKS the terms

$$H' = \gamma\, G(R_7) + \sum_{k=2,4,6} p_k P^k + \sum_{k=0,2,4} m_k M^k \,.$$

The magnetic, M^k, and electrostatic spin-orbit, P^k, parameters have been defined by Judd, Crosswhite and Crosswhite.[5] The Q^k of Ref. 3 and the P^k are equivalent with

$$\frac{P^k}{Q^k} = \frac{6}{(\ell \| C^k \| \ell)^2} \,.$$

Evaluating the reduced matrix elements we find that $Q^2 = Q^4 = Q^6$ used by Goldschmidt correspond to $P^4 = 1.467\ P^2$, $P^6 = 1.144\ P^2$ with $P^2 = 3.214\ Q^2$. Fixing these P^k ratios and the HF M^k's of Goldschmidt and fitting the other parameters gives (without the $^1S_0$) $P^2 = 381 \pm 68\ \mathrm{cm}^{-1}$, which corresponds to $Q^2 = 118 \pm 21\ \mathrm{cm}^{-1}$, $\sigma = 11.6\ \mathrm{cm}^{-1}$. This can be compared to $Q^2 = 116 \pm 27$ and $\sigma = 14.7\ \mathrm{cm}^{-1}$ for the equivalent calculation (variation 4) of Goldschmidt.

In our notation Goldschmidt's γ is one-twelfth of our β and her β is equivalent to our γ. Since these parameters are not orthogonal to the F^k's, the change from β to γ requires an adjustment in the F^k values.[6] In particular our F^6 is ~ 1900 cm^{-1} lower than that of Ref. 3.

Since it is not possible to vary all of these additional parameters simultaneously, we have fixed the M^k's at the values obtained from an HFR calculation using the code of Cowan and Griffin[7] and also at the HF values given by Goldschmidt.[3] The

latter, slightly larger, values result in rms deviations ~ 0.7 cm^{-1} smaller. Since the two sets of M^k values have the same ratios we tried fixing these and allowing only M^0 to vary. The resultant $M^0 = 1.2 \pm 0.6$ is better determined than the value obtained by Goldschmidt,[3] but the rms deviation was 1.5 cm^{-1} larger.

The results are summarized in Table II. There are no significant changes in the other parameters when the ratios of the P^k's are changed. We initially fixed $P^4/P^2 = .75$ and $P^6/P^2 = .50$ as has been done for the rare earths and trivalent actinides.[4] But taking $P^2 = P^4 = P^6$ decreased σ by 5 cm^{-1} and allowing all P^k's to vary independently lead to a further decrease.

If we look at the sum of the (O-C) spread, defined by Goldschmidt[3] as the difference between the absolute values of the maximal and minimal deviations between observed and calculated levels for an LS multiplet, we also find a significant improvement when all of the P^k's are allowed to vary.

The ratio $P^6/P^2 \sim 2$ which results from calculation 3 is contrary to that which resulted from the parametric potential calculation of Goldschmidt;[3] evaluation of the P^k's for other quadruply ionized actinides is necessary to determine if this large ratio is a general result.

The observed and calculated energy levels and (O-C) spreads for calculations 2 and 3 are given in Table III along with the Landé g-values and eigenvectors from calculation 3. The eigenvectors differ from those of WKS only in the third decimal place.

Judd, Hansen and Raassen[6] have recently defined alternate parameters α', β' and γ' whose matrix elements are orthogonal to those of the Coulomb interaction. Consequently the values of the F^k parameters should be unchanged by the addition or exclusion of α', β' or γ', which is not the case with the current parameterization scheme. The new parameters make possible more meaningful comparisons between calculations using different numbers of parameters. α', β', and γ' are related to α, β, and γ by[8]

$$\alpha' = \frac{4}{5}\alpha$$

$$\beta' = -4\alpha - \beta/6$$

$$\gamma' = \frac{8\alpha}{5} + \frac{\beta}{15} + \frac{2\gamma}{25} .$$

The results of a fit using these parameters are shown as calculation 4 of Table II. The resultant α', β', γ' are related to α, β, and γ by the above relationship and σ is unchanged as expected. The F^k values are somewhat different than those of calculation 3 and should provide a better basis for extrapolation to other ions.

Table I. Transitions to the $^1S_0$

Observed Line	fd Level	$^1S_0$
4090.411 Å	$^3D_1$	
24440.52 cm^{-1}	68053.98 cm^{-1}	43613.46 cm^{-1}
3211.75 Å	$^3P_1$	
31126.7 cm^{-1}	74740.33 cm^{-1}	43613.63 cm^{-1}
2206.789 Å	$^1P_1$	
45300.58 cm^{-1}	88914.24 cm^{-1}	43613.66 cm^{-1}
	Avg.	43613.58 ± 0.1 cm^{-1}

Table II. Parameter Values[a] (cm^{-1}) for U V $5f^2$

	Calc 1	Calc 2	Calc 3	Calc 4
E_{avg}	12649 ± 11	12649 ± 8	12648 ± 3	12648 ± 3
F^2	51894 ± 61	51909 ± 44	51938 ± 39	51294 ± 35
F^4	42721 ± 231	42721 ± 168	42708 ± 100	42414 ± 108
F^6	27673 ± 120	27710 ± 87	27748 ± 68	29907 ± 66
α	35.6 ± .7	35.6 ± 0.5	35.5 ± 0.4	–
β	–662 ± 40	–669 ± 29	–664 ± 25	–
γ	763 ± 37	763 ± 27	744 ± 26	–
α'	–	–	–	28.4 ± 0.3
β'	–	–	–	–31 ± 3
γ'	–	–	–	72 ± 2
ζ	1970 ± 3	1969 ± 2	1968 ± 2	1968 ± 2
P^2	484 ± 61	495 ± 44	573 ± 66	574 ± 66
P^4	b	c	524 ± 144	524 ± 144
P^6	b	c	1173 ± 321	1174 ± 320
σ	18.0	12.9	9.8	9.8
(O–C) spread				
LS multiplets	81	68	32	33

[a]In all cases $M^0 = 0.987$, $M^2 = 0.550$, $M^4 = 0.384$ cm^{-1}, the HF values of ref. 3.

[b]$P^4 = 0.75\ P^2$, $P^6 = 0.50\ P^2$.

[c]$P^2 = P^4 = P^6$.

Table III. Energy Levels (cm^{-1}) of U V $5f^2$

		Calc. 2		Calc. 3			
Level	E_{obs}	$E_{obs}-E_{calc}$	(O-C) (multiplet)	$E_{obs}-E_{calc}$	(O-C) (multiplet)	g_J	Eigenvector
$^3H_4$	0.0	8.8	17 (^3H)	6.9	16 (^3H)	0.823	$-.9450\,^3H - .3139\,^1G + .0918\,^3F$
$^3F_2$	4160.6	3.5	12 (^3F)	-2.5	9 (^3F)	0.715	$-.9291\,^3F - .3599\,^1D + .0847\,^3P$
$^3H_5$	6136.9	-8.3		-8.6		1.033	$1.0000\,^3H$
$^3F_3$	8983.5	-1.1		3.0		1.084	$1.0000\,^3F$
$^3F_4$	9433.8	-8.3		-5.5		1.108	$.7045\,^3F - .6502\,^1D + .2845\,^3H$
$^3H_6$	11513.6	1.0		3.0		1.158	$.9727\,^3H - .2320\,^1I$
$^1D_2$	16455.3	-7.5	8 (^1D)	0.9	1 (^1D)	1.129	$-.7417\,^1D + .5782\,^3P + .3400\,^3F$
$^1G_4$	16655.7	5.5	6 (^1G)	3.5	4 (^1G)	1.119	$.7038\,^3F + .6918\,^1G - .1615\,^3H$
$^3P_0$	17128.2	8.1	24 (^3P)	0.9	2 (^3P)	-	$.9670\,^3P + .2548\,^1S$
$^3P_1$	19818.6	-12.5		-0.7		1.501	$1.0000\,^3P$
$^1I_6$	22276.1	-0.1	0 (^1I)	-0.2	0 (^1I)	1.009	$.9727\,^1I + .2320\,^3H$
$^3P_2$	24652.9	11.4		-0.5		1.323	$.8115\,^3P + .5660\,^1D - .1453\,^3F$
$^1S_0$	43613.6	-0.6	1 (^1S)	-0.1	0 (^1S)	-	$.9670\,^1S - .2548\,^3P$

Acknowledgements

We wish to thank Hannah Crosswhite for the M^k and P^k matrix elements and V. Kaufman and B. R. Judd for helpful discussions. K. R. would like to thank Norman Edelstein for his hospitality at LBL.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

References

1. J. F. Wyart, V. Kaufman, and J. Sugar, "Analysis of the Spectrum of Four Times-Ionized Uranium (UV)." Physica Scripta 22, 389-396 (1980).

2. K. Rajnak and B. G. Wybourne, "Configuration Interaction Effects in ℓ^N Configurations," Phys. Rev. 132, 280-290 (1963).

3. Zipora B. Goldschmidt, "Spin-dependent Interactions in U V $5f^2$, Phys. Rev. A 27, 740-753 (1983).

4. H. M. Crosswhite, H. Crosswhite, W. T. Carnall, and A. P. Paszek, "Spectrum Analysis of U^{3+}: $LaCl_3$," J. Chem. Phys. 72, 5103-5117 (1980).

5. B. R. Judd, H. M. Crosswhite, and Hannah Crosswhite, "Intra-Atomic Magnetic Interactions for f Electrons," Phys. Rev. 169, 130-138 (1968).

6. B. R. Judd, Jørgen E. Hansen, and A. J. J. Raassen, "Parametric Fits in the Atomic d Shell," J. Phys. B 15, 1457-1472 (1982).

7. R. D. Cowan and D. C. Griffin, "Approximate Relativistic Corrections to Atomic Radial Wave Functions," J. Opt. Soc. Am. 66, 1010-1014 (1976).

8. B. R. Judd, private communication, 1983.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720