

Ground Levels and Ionization Potentials for Lanthanide and Actinide Atoms and Ions

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Values of the first four ionization potentials of the lanthanides ($Z=57-71$) and of Hf have been compiled. All except the value for neutral Hf are based on spectroscopic data. The spectroscopic designations of the ground levels of the neutral through triply ionized atoms ($Z=57-72$) are also tabulated. A similar compilation for the actinides ($Z=89-103$) lists Sugar's recent values for the first ionization potentials through No ($Z=102$). Accurate spectroscopic ionization potentials have been determined for only two of the actinide ions (Ac^+ and Th^{3+}). The ground-level designations for the neutral through triply ionized actinides are given where they are known or can be predicted with near certainty. A selection of references to the most complete and most recent work on the analyses of the optical spectra of the neutral through triply ionized lanthanide and actinide elements is included.

Key words: Actinide elements; atomic data; atomic ground levels; ionization energies; ionization potentials; lanthanide elements.

1. Introduction

Recent progress on the analyses of lanthanide and actinide optical spectra has allowed a large increase in the number of spectroscopically determined ionization potentials for these elements. Some of these values were derived directly from spectroscopic series, but most were obtained by more indirect methods that nevertheless rely on known energy-level data or on predictions based on certain regularities in these data. The main purpose of this paper is to give a compilation of the most accurate available values of the ionization potentials (tables 1 and 2). We have also tabulated the spectroscopic designations of the ground levels of the neutral through triply ionized species, and given a selection of references from the most complete and most recent work on the analyses. The data in table 1 (except for Hf) represents a small part of an ongoing compilation of the energy levels of the rare earth atoms and ions [1].¹

C. E. Moore's 1970 compilation of ionization potentials and ionization limits is notable for its coverage of the entire periodic table, including all ionization stages for which data were available [2]. However, at the time of its publication, I.P. values based on spectroscopic data were unavailable for most of the doubly and triply ionized lanthanide species, and only three or four such values had been obtained for the actinide elements in any ionization stage. About fifty of the I.P. values listed here are new or improved values compared to the compilation of four years ago.

2. Explanation of References to Analyses of Spectra

The references following each table comprise a

broader bibliography than would be required for substantiation of the ground levels and ionization potentials. This is indicated by the heading "Analysis" in the keys to the references (instead of "Ground level"). The references under this heading for each atom or ion were chosen mainly as sources for most of the known levels and their designations. We have also given a number of recent references that supplement previous bibliographies [3,4], including some references to abstracts that describe major ongoing work on the analyses. If the optical spectrum has been analyzed, the references are thus a selection from the most complete and most recent work on the analysis. Some of the choices are unavoidably arbitrary.

The references for analyses of the spectra of ions in solutions or crystals are especially incomplete. Such a reference is cited only if it gives a significant number of low energy levels (of the f^N ground configuration) that have not been determined from the free-ion spectrum. To aid in the identification of such spectra, we note that references 20, 32, 37, 42, 52, and 62 for table 1, and references 9, 11, 15, 17, 20, 22, 24, 26, 27, and 29 for table 2 are all to papers on the spectra of ions in solution or in crystals. Such references are thus given for all the triply ionized lanthanides except La, Ce, Pr, and Lu. The only free-ion spectra of doubly or triply ionized actinides that have been analyzed are Ac III, Th III, and Th IV.

3. Ground Levels

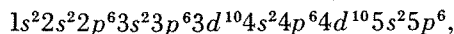
The designation under this heading is the electron configuration and term (with subscript J value) to which the ground level has been assigned. A more exact characterization of the level is given by its eigenvector, obtained by diagonalization of the energy matrix for the appropriate configuration or configurations. The single-term designation can represent only the leading component of such an eigenvector. Ideally, the eigenvector should be expressed in the coupling scheme(s) most appropriate to the known levels of the

¹ Numbers in brackets indicate references in section 5.

ground configuration (configuration group).² We have tried to list the designations on this basis, but many of the configurations have been calculated only in *LS* coupling. In cases of significant doubt, the *LS* designation is given. For simplicity, parent terms are omitted from the designations except in cases of *J₁j* coupling (see below). (The complete designation of the ground level of Gd II, for example, is $4f^7(^8S^o)5d(^2D^o)6s^2 10D^o_{5/2}$ [5]).

3.1. Lanthanide Atoms (Table 1)

All the indicated configurations include implicitly the Xe-like configuration



which is the complete configuration for the La IV ground level. The Hf species have the additional $4f^{14}$ filled subshell. The designations of the ground levels of Tb II, Pm III, and Dy III are not in real doubt, but are shown in braces because the indicated levels have not yet been experimentally established as lowest.

The low levels of several of the singly ionized lanthanide atoms are grouped in pairs, clearly indicating a *J₁j* coupling scheme for the corresponding $4f^N 6s$ ground configurations. In this scheme, *J₁* is the total angular-momentum quantum number of the $4f^N$ core electrons and *j* represents the (spin) angular-momentum of the *s* electron [6]. The ground level, to a good approximation, thus belongs to a (*J₁, 1/2*) pair term. The *J* value (*J* = *J₁ ± 1/2*) for such a ground level in table 1 appears as a subscript to the term symbol.

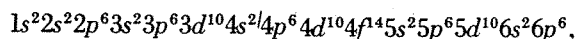
The designations vary widely in the completeness of their characterizations of the corresponding levels.³ The term designation of the Gd II ground level, for example, accounts for 100 percent (to the nearest 1%) of the composition of the calculated eigenvector, and the corresponding percentage for the Eu I ground-level designation is 98 percent. The ground levels of neutral and singly ionized cerium, on the other hand, are two of those least completely described by their designations. The $4f^5 d^2 ^4H^o_{7/2}$ component accounts for only 48 percent of the calculated eigenvector composition of the Ce II ground level, which may be the lowest leading percentage represented by any designation in table 1. The $4f^5 d 6s^2 ^1G^o_4$ component is 55 percent of the composition of the Ce I ground level [7].

3.2. Actinide Atoms (Table 2)

The electron configurations shown are in addition to the Rn-like configuration

² This is usually, but not necessarily, the scheme in which the ground level itself has the highest eigenvector purity. It appears best to designate the ground level in accordance with the known structure of the configuration to which it belongs. Thus the ground level of Th III is designated $^3H^o_4$ in table 2 because of the overall appropriateness of *LS* coupling for the $5f 6d$ configuration; the calculated purity of the ground level alone is 99 percent ($5f_{5/2} 6d_{3/2}$) in *jj* coupling, and only 76 percent $^3H^o_4$ in *LS* coupling [see ref. in table 2].

³ Sources for quantitative results quoted without references in the remainder of this paper are the references following the tables.



except for Ac IV, for which this is the complete ground configuration. Some practically certain ground-level designations that have not been experimentally established are given in braces. Brewer [8] and Vander Sluis and Nugent [9] have given estimates of the energies of the lowest levels of a number of configurations in the neutral through triply ionized actinide atoms.

The low levels of those neutral actinide atomic ground configurations that include a *6d* electron are best described in a *J₁j*-coupling scheme [10] made obvious by the notations in table 2. The ground levels of Cf II and Es II have *J₁j* designations analogous to those described above for lanthanide ions.

Although the ground level of Th II has usually been designated either $6d^2 7s ^4F_{3/2}$ or $6d 7s^2 ^2D_{3/2}$, Minsky's calculation [11] indicates that neither name is appropriate. The two largest eigenvector percentages for the level are 43 percent $6d^2 7s ^4F_{3/2}$ and 27 percent $6d 7s^2 ^2D_{3/2}$, as compared with the equivalent quantities for a level 1859 cm^{-1} higher, which are 52 percent $6d^2 7s ^4F_{3/2}$ and 36 percent $6d 7s^2 ^2D_{3/2}$. The designation $6d 7s^2 ^2D_{3/2}$ is thus not suitable as a name for any Th II level, and $6d^2 7s ^4F_{3/2}$ is more appropriate for the excited level. The group of three strongly interacting Th II configurations $6d 7s^2$, $6d^2 7s$, and $6d^3$ are indicated in table 2 by a conventional notation, $(6d + 7s)^3$; Th II has no "ground configuration," only this ground configuration group or complex. Similar strong interactions among the low configurations in a number of other cases (Ce II, for example) are not apparent from tables 1 and 2 only because the ground level itself is less affected than in Th II.

Litzén has very recently shown that the $5f 6d ^3H^o_4$ level of Th III lies 63 cm^{-1} below the $6d^2 ^3F_2$ level previously considered more likely to be lowest [ref. 5 in table 2]. The latter (metastable) level is apparently the lowest level of opposite parity to the ground level in any atomic species whose structure has so far been analyzed.

The actinide ground configurations containing a $5f^N$ electron group have level structures less well described by *LS* coupling than the corresponding lanthanide configurations. This tendency away from *LS* coupling arises from the relatively larger spin-orbit interaction (compared to the electrostatic interactions) for the *5f* electrons. Thus the purity of the $5f^6 ^7F_0$ designation of the Am IV ground level is only 47 percent, as compared with a purity of 94 percent for the $4f^6 ^7F_0$ ground level of Eu IV [12]. Wybourne has suggested that some of the $5f^N$ configurations in the actinides may be better described in *jj* coupling than in *LS* coupling [13], but no systematic investigation of this point appears to have been carried out.

Crystal spectra of higher than triply ionized actinide species have been observed; as expected, in all known cases the higher members of each isoelectronic se-

quence have the same ground-level designation as the triply ionized member of the sequence.

4. Ionization Potentials

The values listed are the principal ionization potentials. The most accurately determined values in table 1 were obtained by fitting spectroscopic series of three or more members to series formulae [14]. Such series are known in only a few lanthanide spectra and no actinide spectra, however; most of the I.P. values for the lanthanides were obtained by a method involving the interpolation of series properties [refs. 3, 14, 8, and 5 in table 1]. Sugar has also applied this method to obtain the ionization potentials of the neutral actinide elements given in table 2 [ref. 2 in table 2].

The estimated uncertainty in the last digit of each I.P. value is given in parentheses following the value. The confidence levels of the quoted uncertainties were not given for some of the original I.P. determinations, but we believe most can safely be taken as standard-deviation errors (~70% confidence level). Specifically, the "uncertainties" given with the I.P. values in refs. 3, 5, 8, and 14 of table 1 and in ref. 2 of table 2 are at least this large. Values with no listed uncertainties are discussed after the appropriate references in the tables.

All ionization energies originally obtained in units of cm^{-1} have been converted to electron-volts with a divisor of $8065.479 \text{ cm}^{-1}/\text{eV}$ [15]. The standard-deviation uncertainty in this divisor ($0.021 \text{ cm}^{-1}/\text{eV}$) contributes significantly to the I.P. error only for Yb I and Tm I; the stated uncertainty for each of these values before conversion was $\pm 0.1 \text{ cm}^{-1}$.

The most accurate value of the I.P. for Hf I appears to be a recent determination by the electron-impact method [ref. 68 in table 1], and the value listed for Eu I is based mainly on a measurement by a photoionization technique [ref. 28 in table 1]. Although all the other values in the tables are from spectroscopic series or interpolation of series properties, it deserves mention that consistent values have been obtained by other methods in a number of cases. In particular, the accuracy of the third ionization potentials of the lanthanides obtained by Faktor and Hanks [16] from the Born-Haber cycle appears to have been limited mainly by the errors in the values used for the first two ionization potentials of these elements.

The second and higher ionization potentials for the actinide elements are not tabulated, since sufficient data to obtain reliable values are available only for the two ions noted below.

Note Added in Proof

K. L. Vander Sluis and L. J. Nugent have recently obtained new values for some of the third and fourth ionization energies of the lanthanides using theoretically-based expressions with parameters deter-

mined by fitting accepted values along the lanthanide series [J. Chem. Phys. **60**, 1927 (1974)]. Their new values and the values in table 1 are generally in satisfactory agreement.

4.1. Ac II and Th IV

The ionization potential of Ac II can be obtained by taking the $7s^2$ and $7s8s$ configurations as a two-member series having an accurately known value for the difference (Δn^*) between the quantum defects of the two members [17]. The corresponding difference in the isoelectronic spectrum Ra I is $\Delta n^* = 1.053$, and for the somewhat less analogous Ra II $7s$ and $8s$ terms, $\Delta n^* = 1.063$. An assumed value of $\Delta n^* = 1.055 \pm 0.006$ for Ac II gives an I.P. of $11.75 \pm 0.03 \text{ V}$ ($94800 \pm 250 \text{ cm}^{-1}$).⁴

Klinkenberg and Lang [18] have obtained the ionization potential of Th IV from the $7s$ and $8s$ terms. Their value for the limit relative to the $5f^2 F_{5/2}^\circ$ ground level ($231\,900 \text{ cm}^{-1}$) corresponds to a value of $n^*(8s) - n^*(7s) = 1.054$. This value is consistent to within 0.01 not only with the homologous case of Ce IV noted by them, but also with the value of 1.063 obtained from the isoelectronic spectrum Ra II. The above limit is equivalent to $28.75 \pm 0.12 \text{ V}$ for the Th IV I.P., where the error corresponds to an error of ± 0.01 for Δn^* .

5. References for Text

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⁴ This value differs from the value obtained by Meggers et al. [17] partly because they used the Ac II $7s8s^1S$ term as the upper series member (instead of the $7s8s$ configuration barycenter), and partly because of a numerical error. Their value for the limit, 97300 cm^{-1} , gives $n^*(7s8s^1S) - n^*(7s^2^1S) = 1.037$, instead of the stated value 1.055.

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6. Tables and References for Individual Species

TABLE I. Ground levels and ionization potentials for the neutral through triply ionized lanthanide atoms (and Hf). The designations of the ground levels of Tb II, Pm III, and Dy III are enclosed in braces because the indicated levels have not yet been experimentally established as lowest.

Z	Element	Neutral, I		Singly ionized, II		Doubly ionized, III		Triply ionized, IV	
		Ground level	I.P. ^a (volts)	Ground level	I.P. ^a (volts)	Ground level	I.P. ^a (volts)	Ground level	I.P. ^a (volts)
57	La	$5d6s^2 2D_{3/2}$	5.5770(6)	$5d^2 3F_2$	11.060(10)	$5d 2D_{3/2}$	19.1774(6)	$5p^6 1S_0$	49.95(6)
58	Ce	$4f5d6s^2 1G_4$	5.466(20)	$4f5d^2 4H_{7/2}$	10.85(8)	$4f^2 3H_4$	20.198(3)	$4f 2F_{5/2}$	36.758(5)
59	Pr	$4f^3 6s^2 4I_{9/2}$	5.422(20)	$4f^3 (4I_{9/2})6s (9/2, 1/2)_4$	10.55(8)	$4f^3 4I_{9/2}$	21.624(3)	$4f^2 3H_4$	38.98(2)
60	Nd	$4f^4 6s^2 5I_4$	5.489(20)	$4f^4 (5I_4)6s (4, 1/2)_{7/2}$	10.73(8)	$4f^4 5I_4$	22.1(3)	$4f^3 4I_{9/2}$	40.41(20)
61	Pm	$4f^5 6s^2 6H_{5/2}$	5.554(20)	$4f^5 6s 7H_2$	10.90(8)	$\{4f^5 6H_{5/2}\}$	22.3(4)	$4f^4 5I_4$	41.1(3)
62	Sm	$4f^6 6s^2 7F_0$	5.631(20)	$4f^6 6s 8F_{1/2}$	11.07(8)	$4f^6 7F_0$	23.4(3)	$4f^5 6H_{5/2}$	41.4(4)
63	Eu	$4f^7 6s^2 8S_{7/2}$	5.666(7)	$4f^7 6s 9S_4$	11.241(6)	$4f^7 8S_{7/2}$	24.92(10)	$4f^6 7F_0$	42.6(3)
64	Gd	$4f^7 5d6s^2 9D_2$	6.141(20)	$4f^7 5d6s 10D_{5/2}$	12.09(8)	$4f^7 5d 9D_2$	20.63(10)	$4f^7 8S_{7/2}$	44.0(3)
65	Tb	$4f^8 6s^2 6H_{15/2}$	5.852(20)	$\{4f^8 6s 7H_8\}$	11.52(8)	$4f^8 6H_{15/2}$	21.91(10)	$4f^8 7F_6$	39.79(20)
66	Dy	$4f^{10} 6s^2 5I_8$	5.927(8)	$4f^{10} (5I_8)6s (8, 1/2)_{17/2}$	11.67(8)	$\{4f^{10} 5I_8\}$	22.8(3)	$4f^9 6H_{15/2}$	41.47(20)
67	Ho	$4f^{11} 6s^2 4I_{15/2}$	6.018(20)	$4f^{11} (4I_{15/2})6s (15/2, 1/2)_8$	11.80(8)	$4f^{11} 4I_{15/2}$	22.84(10)	$4f^{10} 5I_8$	42.5(3)
68	Er	$4f^{12} 6s^2 3H_6$	6.101(20)	$4f^{12} (3H_6)6s (6, 1/2)_{13/2}$	11.93(8)	$4f^{12} 3H_6$	22.74(10)	$4f^{11} 4I_{15/2}$	42.65(20)
69	Tm	$4f^{13} 6s^2 2F_{7/2}$	6.18436(6)	$4f^{13} (2F_{7/2})6s (7/2, 1/2)_4$	12.05(8)	$4f^{13} 2F_{7/2}$	23.68(10)	$4f^{12} 3H_6$	42.69(20)
70	Yb	$4f^{14} 6s^2 1S_0$	6.25394(2)	$4f^{14} 6s 2S_{1/2}$	12.184(6)	$4f^{14} 1S_0$	25.03(2)	$4f^{13} 2F_{7/2}$	43.74(20)
71	Lu	$4f^{14} 5d6s^2 2D_{3/2}$	5.42589(2)	$4f^{14} 6s^2 1S_0$	13.9(4)	$4f^{14} 6s 2S_{1/2}$	20.9596(10)	$4f^{14} 1S_0$	45.19(2)
72	Hf	$5d^2 6s^2 3F_2$	6.65(10)	$5d6s^2 2D_{3/2}$	14.9	$5d^2 3F_2$	23.3	$5d 2D_{3/2}$	33.33(2)

^a The number in parentheses is the estimated standard-deviation error in the last digit of the quoted value.

Key for references to table 1

Z	Element	Neutral, I		Singly ionized, II		Doubly ionized, III		Triply ionized, IV	
		Analysis	I.P.	Analysis	I.P.	Analysis	I.P.	Analysis	I.P.
57	La	1	2	1	3	4	5	6	6
58	Ce	7	8	9	3	10	5	11	5
59	Pr	12, 13	14	15	3	16	5	17	5
60	Nd	18	14	18	3	19	5	20, 21	5
61	Pm	22	14	23	3	24	5	20	5
62	Sm	25	14	25	3	26	5	20	5
63	Eu	27	28	29	30	31, 31a	31a	32	5
64	Gd	33, 34	8	33, 35	5	36	5	37, 38	5
65	Tb	39	14	40	3	41	5	42	5
66	Dy	43, 44	44	43, 44	3	24	5	20	5
67	Ho	45, 46	14	47	3	48	5	20	5
68	Er	49	14	50	3	51	5	20, 52, 53	5
69	Tm	54	55	55	3	56	5	20	5
70	Yb	57, 58	58	59, 60	60	61	5	62	5
71	Lu	63, 64	64	65	3	66	66	67	67
72	Hf	1	68	1, 69	70	71, 72	71	71	5

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TABLE 2. Ground levels (where known) for the neutral through triply ionized actinide atoms; ionization potentials for the neutral actinide atoms. A level that has not been experimentally established as lowest is listed (designation enclosed in braces) only if it is practically certain to be the ground level.

Z Element	Neutral, I		Singly ionized, II	Doubly ionized, III	Triply ionized, IV
	Ground Level	I.P. ^a (volts)	Ground level	Ground level	Ground level
89 Ac	$6d7s^2 2D_{3/2}$	5.17(12)	$7s^2 1S_0$	$7s 2S_{1/2}$	$\{6p^6 1S_0\}$
90 Th	$6d^27s^2 3F_2$	6.08(12)	$(6d + 7s)^3 J=3/2$	$5f6d 3H^{\circ}_4$	$5f 2F^{\circ}_{5/2}$
91 Pa	$5f^2(3H_4)6d7s^2 (4, 3/2)_{11/2}$	5.89(12)	$5f^27s^2 3H_4$		$\{5f^2 3H_4\}$
92 U	$5f^3(4I^{\circ}_{9/2})6d7s^2 (9/2, 3/2)^{\circ}_6$	6.05(7)	$5f^37s^2 4I^{\circ}_{9/2}$		$5f^3 4I^{\circ}_{9/2}$
93 Np	$5f^4(5I_4)6d7s^2 (4, 3/2)_{11/2}$	6.19(12) ^b			$5f^4 5I_4$
94 Pu	$5f^67s^2 7F_0$	6.06(3)	$5f^67s 8F_{1/2}$		$5f^5 6H^{\circ}_{5/2}$
95 Am	$5f^77s^2 8S^{\circ}_{7/2}$	5.993(10)	$5f^77s 9S^{\circ}_4$	$5f^7 8S^{\circ}_{7/2}$	$5f^6 7F_0$
96 Cm	$5f^7(8S^{\circ}_{7/2})6d7s^2 (7/2, 3/2)^{\circ}_2$	6.02(3)	$5f^77s^2 8S^{\circ}_{7/2}$		$5f^7 8S^{\circ}_{7/2}$
97 Bk	$5f^97s^2 6H^{\circ}_{15/2}$	6.23(3)	$5f^97s 7H^{\circ}_8$		$5f^8 7F_6$
98 Cf	$5f^{10}7s^2 5I_8$	6.30(3)	$5f^{10}(5I_8)7s (8, 1/2)_{17/2}$		$5f^9 6H^{\circ}_{15/2}$
99 Es	$5f^{11}7s^2 4I^{\circ}_{15/2}$	6.42(3)	$5f^{11}(4I^{\circ}_{15/2})7s (15/2, 1/2)^{\circ}_8$	$5f^{11} 4I^{\circ}_{15/2}$	$\{5f^{10} 5I_8\}$
100 Fm	$5f^{12}7s^2 3H_6$	6.50(7) ^c			$\{5f^{11} 4I^{\circ}_{15/2}\}$
101 Md	$\{5f^{13}7s^2 2F^{\circ}_{7/2}\}$	6.58(7) ^d			$\{5f^{12} 3H_6\}$
102 No	$\{5f^{14}7s^2 1S_0\}$	6.65(7) ^e	$\{5f^{14}7s 2S_{1/2}\}$	$\{5f^{14} 1S_0\}$	$\{5f^{13} 2F^{\circ}_{7/2}\}$
103 Lr					$\{5f^{14} 1S_0\}$

^a The number in parentheses is the estimated standard-deviation error in the last digit of the quoted value. Some values have additional uncertainties that are not included; see footnotes as indicated.

^b This value is based on an assumption that the ground level of Np II belongs to the $5f^46d7s$ configuration. Since the lowest level of the $5f^57s$ configuration was taken as lying only $130 \pm 800 \text{ cm}^{-1}$ higher, the derived I.P. value would not be significantly altered by assuming $5f^57s$ to be lowest. However, it is also possible that the ground level belongs mainly to the $5f^47s^2$ configuration, in which case the quoted I.P. value would be an upper limit.

^c This value is based on an assumption that the ground configuration of Fm II is $5f^{12}7s$. If another configuration is lower, the value is an upper limit.

^d This value is based on an assumption of the ground configuration shown for Md I, and on the ground configuration $5f^{13}7s$ for Md II. The error estimate does not include other possibilities.

^e This value is based on an assumption that the ground configurations of No I and No II are as shown.

Key for references to table 2

Z	Element	Neutral, I		Singly ionized, II	Doubly ionized, III	Triply ionized, IV
		Analysis	I.P.	Analysis	Analysis	Analysis
89	Ac	1	2	1	1	
90	Th	3	2	4	5	6
91	Pa	7	2	8		9
92	U	10	2	10		11
93	Np	12	2			11
94	Pu	13	2	14		11, 15
95	Am	16	2	16	17	11
96	Cm	18	2	19		11, 20
97	Bk	21	2	21		22
98	Cf	23	2	23		15, 24
99	Es	25	2	25	26	27
100	Fm	28	2			29
101	Md		2			
102	No		2			

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