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Application of the "Inclined W" Theory in Predicting the Sixth and the Higher Ionization Potentials for the Lanthanide Series*

S. P. SINHA

Eidgenössische Technische Hochschule, Laboratorium für Biochemie, Universitätstrasse 16, CH-8006 Zürich, Switzerland

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The L-dependent linearization of the properties of the lanthanides ("Inclined W" theory) has been used to calculate the sixth through seventeenth ionization potentials (IP) for the whole series. Two simple correlations based on the inclined-W concept, i.e. *(i) the Series Correlation:* $[IP(\Sigma IP) = w_iL + k_i]$ *and (ii) the Successive Correlation:* $[IP = m\Delta L + c]$, *connecting the IP's with L or* ΔL *values of the originating ions at the ground states, have been developed for the calculations of the IP's presented here. It has been assumed that the ground states of all highly ionized lanthanides belong to the* $4f^n$ *configuration. The* IP_3 *to* IP_5 *values have been used to start the initial calculation. The trend of the calculated* IP_6 *through* IP_{17} *values has been discussed and reasons have been given as to why there should be a correlation between the total orbital angular momentum (L) of the lanthanide ions* ($4f^n$) *at the ground states and their ionization potentials.*

Introduction

The energy level structures of the lanthanides in different oxidation states are very complex. A fairly comprehensive analysis of the optical spectra of the neutral (M^0) and singly ionized (M^+) lanthanides is available [1]. This gave reliable limits for the first (IP_1) and the second (IP_2) ionization potentials for the lanthanides. However, the ionization processes

$$M^0 \xrightarrow{IP_1} M^+ \text{ and } M^+ \xrightarrow{IP_2} M^{2+}$$

invariably involve removal of the 6s electrons from the valence shell of the lanthanides. But nearly all doubly (M^{2+}) and triply (M^{3+}) ionized lanthanides possess $4f^n$ ground state configuration with the exceptions of $La^{2+}(5d^1)$, $Gd^{2+}(4f^75d^1)$ and $Lu^{2+}(4f^{14}6s^1)$. Thus, further ionization removes the f-electrons, except for those ions mentioned above. Faktor and Hanks [2] first attempted to calculate the third ionization potentials (IP_3) for the lanthanides using a Born–Haber cycle and the thermodynamic data for the oxides and the arsenides. Sugar and Reader [3] have recently systematized the ionization energies IP_3 and IP_4 of all doubly and triply ionized lanthanides and later Sugar [4] has extended the procedure to calculate the fifth ionization potentials (IP_5) for the quadruply ionized lanthanides. They have expressed [3] the ionization energies as the sum of four parameters

$$IP = SD + \Delta E + \delta + T \qquad (1)$$

SD represents the so called system difference energy ($4f^n - 4f^{n-1}5d$), ΔE the energy interval between $4f^{n-1}5d$ and $4f^{n-1}6s$, δ the electrostatic energy of interaction of a 6s electron with the parent core $4f^{n-1}$, and T is the energy of ionization of the 6s electron after the interaction energy δ is removed.

When a property of the trivalent lanthanides is plotted as a function of their atomic numbers (Z), the plot usually shows a break around gadolinium (Z = 64, $4f^7$) with further irregularities occurring on both sides of gadolinium. Thus, the plot of extraction coefficients *vs.* Z could normally be represented by four segmented convex curves (tetrad plot), having breaks around Nd–Pm, Gd and Ho–Er regions. However, there are considerable variations in the profile of the four segmented tetrad plots, when properties other than the extraction coefficients are plotted against Z [5–8].

Sinha [9] has recently proposed a linearization of the properties (P_i) of the f-elements (lanthanides and actinides) by plotting the observed data as a function of the total orbital angular momentum (L) of the originating ions in the ground state ("Inclined W" theory)

$$P_i = w_iL + k_i \qquad (2)$$

where i is a given tetrad and can assume the values from 1 to 4, w_i and k_i are the slope and the intercept respectively of the least squares straight line in a given tetrad. It has been shown, amongst others, that the

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individual ionization potentials (IP's), as well as the sum of several IP's(ΣIP), exhibit linear variation with the L quantum numbers of the originating ions at the ground state [5]. The variation of IP_3, IP_4 and even IP_5 with the ground state L quantum numbers of M^{2+}, M^{3+} and M^{4+} ions was found to be linear within the four tetrads [10] Furthermore, it was shown [10] that the sum of the five ionization potentials ΣIP_{1-5}, of the process $M^0 \rightarrow M^{5+}$ varies linearly within each tetrad, with the ground state L values of the neutral lanthanides (M^0) From the "Inclined W" plot (Fig 1 of [10]) of the IP_5 values *vs* L(M^{4+}) of the Tm(L = 6), Yb(L = 5) and Lu(L = 3) tetrad, it was possible to predict the IP_5 value for Hf^{4+} (L = 0) from the intercept (k = 68 16 eV) of the least squares line (Eq 2) [10] This value agrees extremely well with that calculated by Sugar [4], *e g* 68 356 eV, using Eq 1 We want to show here an application of the "Inclined W" theory in deriving the sixth and higher IP's using the L-dependent linearization

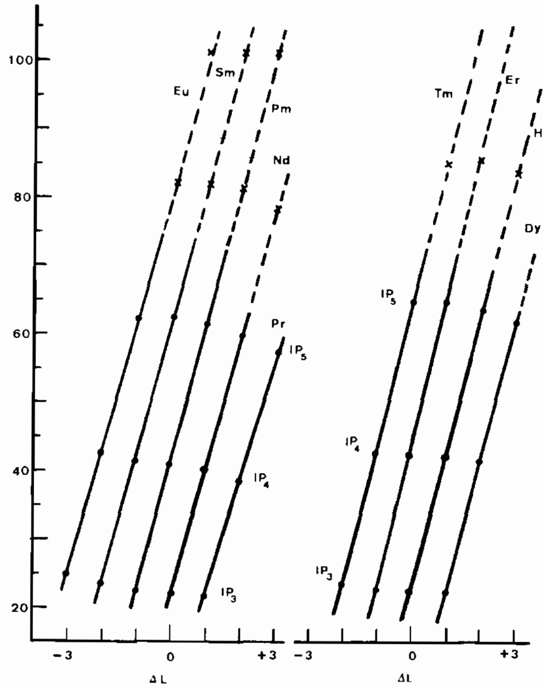

Figure 1 The linear variation of IP_3, IP_4 and IP_5 with ΔL-(L_o − L_t) for Pr, Nd, Pm, Sm, Eu, Dy, Ho, Er and Tm

Method of Calculation

The method of calculation is simple In this systematics, we treat a given ionization energy as a single variable and not as a four component system of Sugar The calculations are based on two observed relationships

1 Series Correlation for a given IP or ΣIP's, the variation within each of the tetrads is linear when these values are plotted against the ground state L quantum numbers of the originating ions

$$IP(\Sigma IP) = w_1L + k_1 \qquad (2a)$$

2 Successive Correlation for a given lanthanide with f^n ground electronic configuration, the successive IP's vary linearly with ΔL, the difference between the L values of the originating (L_o) ion and the terminating (L_t) ion in question

$$IP = m\Delta L + c \qquad (3)$$

For a lanthanide (f^n), the ΔL values could only vary between −3 and +3 as the ionization proceeds and after reaching the highest value (+3) it restarts again at −3, if the ion could still be ionized

For the starting point of our calculations, we have used the three sets of IP's, the IP_3, IP_4 and IP_5, of Sugar [3, 4] and the assumption that the ground states of the highly ionized lanthanides correspond to the $4f^n$ electronic configuration

Calculation of the Sixth Ionization Potentials

First we have plotted the third, fourth and the fifth ionization potentials for Nd, Pm, Sm, Eu, Ho, Er and Tm as a function of ΔL (Fig 1) and using a least squares fit we immediately obtained the sixth and some of the higher ionization potentials for these ions (the parameters m and c of Eq 3 are given in parenthesis)

Nd	IP_6 = 78 71 eV [m = 18 93, c = 21 92]	
Pm	IP_6 = 81 07, IP_7 = 100 76 eV [m = 19 685, c = 41 7]	(4)
Sm	IP_6 = 81 72, IP_7 = 101 33, IP_8 = 120 95 eV [m = 19 615, c = 62 102]	
Eu	IP_6 = 82 06, IP_7 = 101 32, IP_8 = 120 59, IP_9 = 139 85 eV [m = 19 265, c = 82 057]	
Ho	IP_6 = 84 17 eV [m = 20 545, c = 22 538]	
Er	IP_6 = 85 86, IP_7 = 107 04 eV [m = 21 18, c = 43 497]	
Tm	IP_6 = 85 67, IP_7 = 106 54, IP_8 = 127 41 eV [m = 20 87, c = 64 8]	

For Gd and Lu, the use of ΔL *vs* IP's plots could not be made, as only two values (IP_4, IP_5) are available, the ground states of the M^{2+} ions being f^7d^1 and $f^{14}s^1$ respectively For these two ions, as well as for Tb, Dy and Yb, we have used the Series Correlation, and have plotted the required ΣIP's *vs* L to extract the sixth potentials from the intercept values of the least squares lines of the tetrad in question Thus, the least squares line defined as ΣIP_{4-6} = −1 325L + 192 03 for the plot of ΣIP_{4-6} *vs* L(M^{3+}) of the Pm–Gd tetrad gives a value of 83 26 eV (192 03 − 108 77) for IP_6 of Gd Similarly, the following values for other lanthanides are obtained

TABLE I. The Ground Electronic Configurations, the Total Orbital Angular Quantum Numbers (L) and the Successive Ionization Potentials for the Lanthanides (in eV)[a].

Z	M	IP_1	IP_2	IP_3	IP_4	IP_5	IP_6	IP_7	IP_8	IP_9	IP_{10}	IP_{11}	IP_{12}	IP_{13}	IP_{14}	IP_{15}	IP_{16}	IP_{17}
57	La	ds^2[2] 5.577	d^2[3] 11.06	d^1[2] 19.175														
58	Ce	$f^1d^1s^2$[4] 5.47	f^1d^2[5] 10.85	f^2[5] 20.20	f^1[3] 36.76													
59	Pr	f^3s^2[6] 5.42	f^3s^1[6] 10.55	f^3[6] 21.62	f^2[5] 38.98	f^1[3] 57.53												
60	Nd	f^4s^2[6] 5.49	f^4s^1[6] 10.72	f^4[6] 22.14	f^3[6] 40.41	f^2[5] 60.00	f^1[3] 78.71											
61	Pm	f^5s^2[5] 5.55	f^5s^1[5] 10.90	f^5[5] 22.32	f^4[6] 41.09	f^3[6] 61.69	f^2[5] 81.07	f^1[3] 100.76										
62	Sm	f^6s^2[3] 5.63	f^6s^1[3] 11.07	f^6[3] 23.43	f^5[5] 41.37	f^4[6] 62.66	f^3[6] 81.72	f^2[5] 101.33	f^1[3] 120.95									
63	Eu	f^7s^2[0] 5.67	f^7s^1[0] 11.25	f^7[0] 24.70	f^6[3] 42.65	f^5[5] 63.23	f^4[6] 82.06	f^3[6] 101.32	f^2[5] 120.59	f^1[3] 139.85								
64	Gd	$f^7d^1s^2$[2] 6.14	$f^7d^1s^1$[2] 12.1	f^7d^1[2] 20.63	f^7[0] 44.01	f^6[3] 64.76	f^5[5] 83.26	f^4[6] 103.26	f^3[6] 122.89	f^2[5] 142.51	f^1[3] 162.14							
65	Tb	f^9s^2[5] 5.85	f^9s^1[5] 11.52	f^9[5] 21.91	f^8[3] 39.79	f^7[0] 66.46	f^6[3] 85.20	f^5[5] 105.18	f^4[6] 124.34	f^3[6] 143.69	f^2[5] 163.05	f^1[3] 182.41						
66	Dy	$f^{10}s^2$[6] 5.93	$f^{10}s^1$[6] 11.67	f^{10}[6] 22.79	f^9[5] 41.47	f^8[3] 62.08	f^7[0] 88.34	f^6[3] 109.04	f^5[5] 128.09	f^4[6] 148.24	f^3[6] 168.12	f^2[5] 187.99	f^1[3] 207.87					
67	Ho	$f^{11}s^2$[6] 6.02	$f^{11}s^1$[6] 11.80	f^{11}[6] 22.84	f^{10}[6] 42.48	f^9[5] 63.93	f^8[3] 84.17	f^7[0] 114.82	f^6[3] 133.29	f^5[5] 153.97	f^4[6] 173.18	f^3[6] 192.75	f^2[5] 212.33	f^1[3] 231.90				
68	Er	$f^{12}s^2$[5] 6.10	$f^{12}s^1$[5] 11.93	f^{12}[5] 22.74	f^{11}[6] 42.65	f^{10}[6] 65.10	f^9[5] 85.86	f^8[3] 107.04	f^7[0] 142.24	f^6[3] 164.25	f^5[5] 183.31	f^4[6] 204.34	f^3[6] 224.87	f^2[5] 245.41	f^1[3] 265.94			
69	Tm	$f^{13}s^2$[3] 6.18	$f^{13}s^1$[3] 12.05	f^{13}[3] 23.68	f^{12}[5] 42.69	f^{11}[6] 65.42	f^{10}[6] 85.67	f^9[5] 106.54	f^8[3] 127.41	f^7[0] 180.26	f^6[3] 198.5	f^5[5] 220.69	f^4[6] 240.25	f^3[6] 260.46	f^2[5] 280.68	f^1[3] 300.89		
70	Yb	$f^{14}s^2$[0] 6.254	$f^{14}s^1$[0] 12.17	f^{14}[0] 25.03	f^{13}[3] 43.74	f^{12}[5] 65.58	f^{11}[6] 87.15	f^{10}[6] 107.43	f^9[5] 128.25	f^8[3] 149.07	f^7[0] 223.82	f^6[3] 248.63	f^5[5] 268.17	f^4[6] 291.23	f^3[6] 313.40	f^2[5] 335.57	f^1[3] 357.75	
71	Lu	$f^{14}d^1s^2$[2] 5.426	$f^{14}s^2$[0] 13.9	$f^{14}s^1$[0] 20.96	f^{14}[0] 45.19	f^{13}[3] 66.79	f^{12}[5] 87.35	f^{11}[6] 108.60	f^{10}[6] 129.68	f^9[5] 150.76	f^8[3] 171.84	f^7 [0] 292.92	f^6[3] 311.47	f^5[5] 337.05	f^4[6] 357.94	f^3[6] 380.01	f^2[5] 402.07	f^1[3] 424.14

[a] The predicted value of IP_5 for Hf^{4+} from the "Inclined W" plot is 68.16 eV agreeing well with that calculated by Sugar, *e.g.*, 68.356 eV. The predicted IP_6 value for Hf^{5+} is 88.83 eV (present calculation).

The least squares line ($\Sigma IP_{5,6} = -1.235L + 151.66$) for the plot of $\Sigma IP_{5,6}$ *vs.* $L(M^{4+})$ of the Sm–Tb tetrad gives a value of 85.20 eV (151.66 – 66.46) for Tb, and the least squares line ($IP_6 = -1.0357L + 88.34$) for the plot of IP_6 *vs.* $L(M^{5+})$ of the Eu–Dy tetrad generates directly the value of 88.34 eV for Dy. The ΣIP_{3-6} *vs.* $L(M^{2+})$ plot of the Ho–Yb tetrad was used ($\Sigma IP_{3-6} = -1.2336L + 221.5$) to extract the value of IP_6 for Yb, *e.g.* 87.15 eV (221.5 – 134.35). In the case of Lu, the ΣIP_{4-6} *vs.* $L(M^{3+})$ plot of the Er–Lu tetrad is made ($\Sigma IP_{4-6} = -1.0093L + 199.33$) and from the intercept a value of 87.35 eV (199.33 – 111.98) for IP_6 of Lu is obtained. Finally, it was of interest to derive the IP_6 value for $Hf^{5+}(f^{14}) \rightarrow Hf^{6+}(f^{13})$ process by plotting $\Sigma IP_{5,6}$ *vs.* $L(M^{4+})$ for the Tm–Hf tetrad ($\Sigma IP_{5,6} = -0.9721L + 157.19$) which yielded the value of 88.83 eV (157.19 – 68.36) for the said process.

Calculation of the Ionization Potentials Higher than Six

As has already been mentioned, by knowing at least three IP's corresponding to three ΔL values, higher ionization potentials could be predicted using the Successive Correlationship of Eq. 3, until the highest ΔL value (+3) is reached. Thus, the least squares fit of $IP_{3,4,5}$ data generated some of the higher IP's for Pm, Sm, Eu, Er, and Tm (Eq. 4).

For other ions, the use of Eq. 2(a) with either IP *vs.* L or the appropriate ΣIP's *vs.* L resulted in the derivation of the higher IP's. For a given lanthanide, once three IP values corresponding to $\Delta L = -3, -2, -1$, are obtained, the rest of the higher ionization potentials are derived by using Eq. 3. By utilizing these two procedures all ionization potentials for the lanthanide series have been calculated* and the values are presented in Table I.

Discussion

In the plot of the properties of the lanthanides (and/or actinides) as a function of their atomic numbers (Z), no distinction is usually made as to the oxidation states of the ions. Sugar and Reader [3] have plotted the values of IP_3 and IP_4 as a function of the number of the f-electrons (f^n) in Fig. 5 of reference [3]. However, these plots like the Z-dependence plots are nonlinear for both IP's and system difference (SD). According to these authors "the irregular behaviour of these intervals produces the major source of uncertainty in the resulting values for the ionization energies" [3]. Although these plots in themselves are interesting in comparing the general profiles, these are neither suitable for predicting the higher ionization potentials nor for any direct quantitative calculation.

We would also remark here that both Z and n in the abscissa increase by unity as we pass from one lanthanide to another. Hence, nothing new could be achieved if one preferred to use n instead of Z. Furthermore, the external f-electrons do not experience the full nuclear charge (Z). The effective nuclear charge (Z_{eff}) "seen" by the external f-electrons can be obtained by subtracting the screening constant (σ) from the nuclear charge (Z). The atomic screening constant (σ) obtained from the SCF functions by Clementi *et al.* [11] for the neutral lanthanides do not show a constant difference between the adjacent lanthanides. Thus, a Z_{eff} *vs.* Z plot is nonlinear (Fig. 2). Moreover, the screening constants being dependent on the charge of the ions, these would be different for different oxidation states of the ions. At present we do not have any data available for the lanthanides in different stages of oxidation.

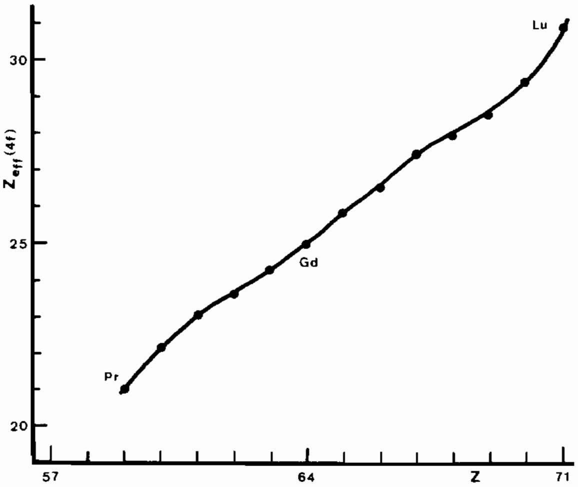

Figure 2. The variation of Z_{eff} with atomic numbers (Z) of the neutral lanthanides.

Contrary to the Z-dependent plots, it has been shown here and elsewhere [5, 9, 10] that the P_i's (here IP's) are linear functions of L and ΔL, and the relationships of Eq. 2(a) and Eq. 3 could be used benificially to calculate the higher ionization potentials for the lanthanide series. The calculated IP's, IP_6 through IP_{15}, for the lanthanides are plotted against the L values of the originating ions at the ground states in Fig. 3. These plots may be compared to the usual Z-dependent plots (not shown) or the n of f^n dependent plots (Fig. 4). The usefulness of the L dependent plots becomes immediately clear.

As a measure of the consistency of the calculated values, we have tabulated the standard deviations of the calculated ionization potentials (IP_6 to IP_{15})

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*A step by step procedure of complete calculation is available from the author upon request.

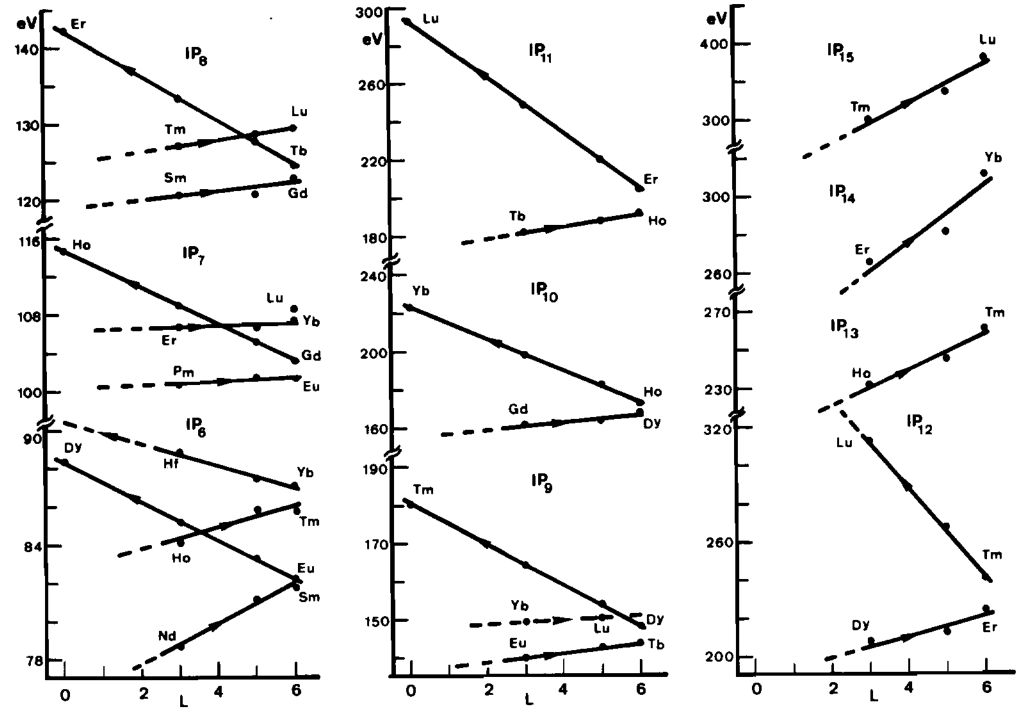


Figure 3. Plots of the ionization potentials, IP_6 through IP_{15}, of the lanthanides against the ground state L values of the originating ions showing linearization.

TABLE II. The "Inclined W" Parameters (w_i, k_i) and their Standard Deviations (SD).

IP_6
Nd–Sm: $w_1 = 1.0286$, $k_1 = 75.7$; Eu–Dy : $w_2 = -1.0357$, $k_2 = 88.34$; Ho–Tm: $w_3 = 0.5493$, $k_3 = 82.67$; Yb–Hf: $w_4 = -0.5857$, $k_4 = 90.51$; SD = 0.20eV

IP_7 (excluding Lu)
Pm–Eu: $w_1 = 0.2007$, $k_1 = 100.2$; Gd–Ho: $w_2 = -1.927$, $k_2 = 114.82$; Tm–Lu: $w_3 = 0.0757$, $k_3 = 106.65$; SD = 0.21eV

IP_8
Sm–Gd: $w_1 = 0.5286$, $k_1 = 119.01$; Tb–Er: $w_2 = -2.9286$, $k_2 = 142.24$; Tm–Lu: $w_3 = 0.7086$, $k_3 = 125.14$; SD = 0.52eV

IP_9 (excluding Yb, Lu)
Eu–Tb: $w_1 = 1.2871$, $k_1 = 136.01$; Dy–Tm: $w_2 = -5.3086$, $k_2 = 180.26$; SD = 0.13eV

IP_{10} (excluding Lu)
Gd–Dy: $w_1 = 1.1774$, $k_1 = 156.16$; Ho–Yb: $w_2 = -8.3193$, $k_2 = 223.82$; SD = 1.15eV

IP_{11}
Tb–Ho: $w_1 = 3.3529$, $k_1 = 172.07$; Er–Lu: $w_2 = -14.65$, $k_2 = 292.92$; SD = 0.67eV

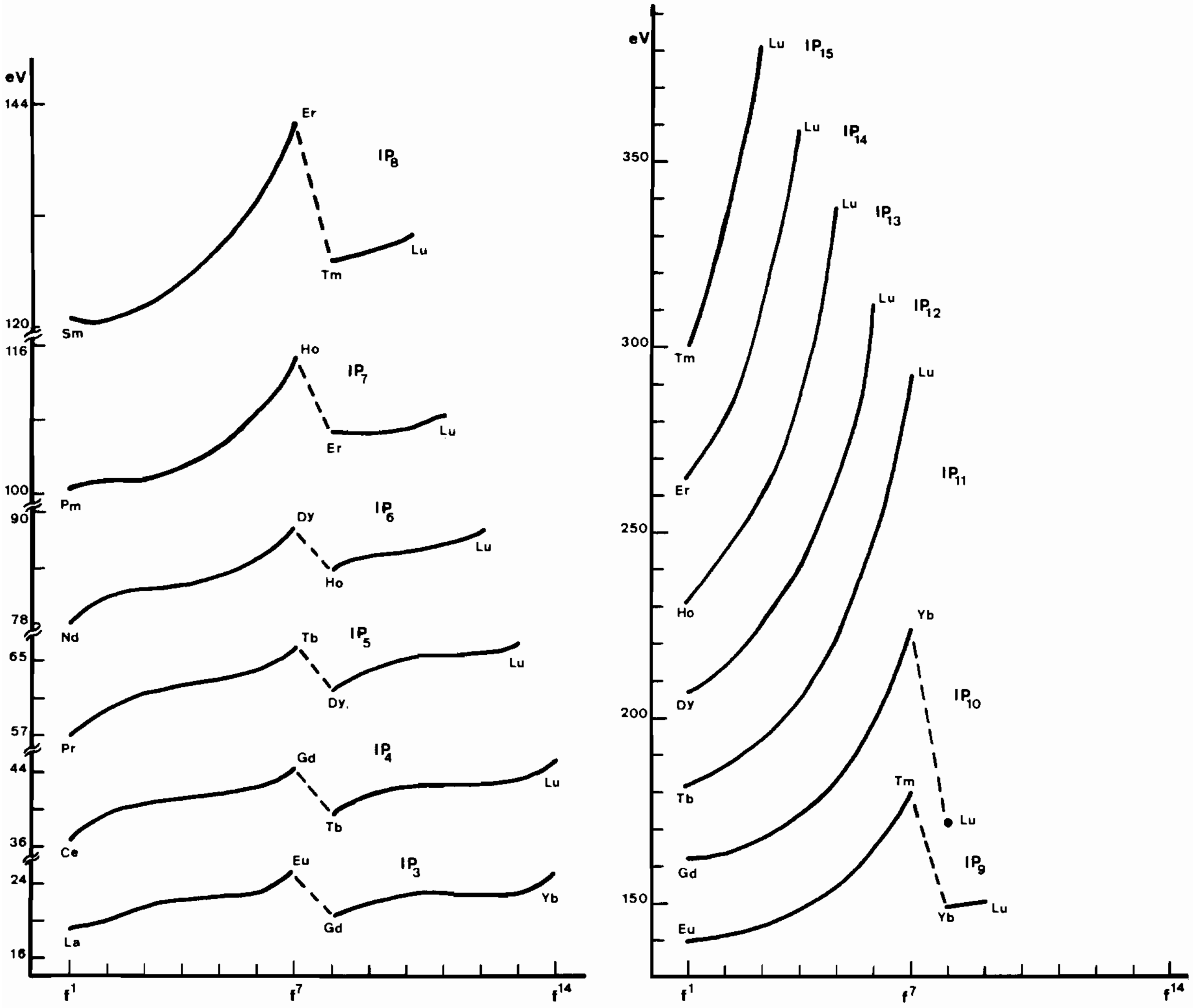
IP_{12}
Dy–Er: $w_1 = 5.1757$, $k_1 = 190.87$; Tm–Lu: $w_2 = -23.441$, $k_2 = 382.69$; SD = 2.86eV

IP_{13} (excluding Yb, Lu)
Ho–Tm: $w_1 = 9.125$, $k_1 = 203.34$; SD = 3.14eV

IP_{14} (excluding Lu)
Er–Yb: $w_1 = 14.613$, $k_1 = 218.48$; SD = 9.58eV

IP_{15}
Tm–Lu: $w_1 = 25.083$, $k_1 = 221.77$; SD = 10.24eV

along with the parameters w_i and k_i of Eq. 2 in Table II. These deviations are indeed very small for IP_6 through IP_9 and are reasonable for IP_{10} and IP_{11}. However, these become larger from IP_{12} onward. Such deviations may be caused due to one or both of the factors mentioned below:



(a) (b)

Figure 4. Plots of the ionization potentials, IP_3 through IP_{15}, of the lanthanides against the number of the f-electrons.

(i) the assumption that the very highly ionized lanthanides possess f^n ground configurations may not be valid, and

(ii) the Eq. 3, which is invariably used to deduce the IP's above IP_{12}, may not be too rigorously followed at this end.

However, from the analysis of the trend for the IP's (IP_6 to IP_9) with those obtained by Sugar for IP_{3-5}, a generous estimate of the uncertainty in the values of IP_{6-9} is between 0.2–0.5 *eV*.

The question is generally asked why there should be such a good correlation of the properties in general and the IP's in particular, with the L quantum numbers of the lanthanide ions at the ground state.

The process of ionization and complex formation usually involve the extranuclear valence electrons experiencing a charge of Z_{eff} and not Z. The valence electrons in an atom or ion in the ground or low excited states could be described by their angular momentum vectors, *l*'s and *s*'s where *l* is the orbital part and *s* is the spin part of the angular momentum vectors. For elements with low or medium atomic numbers (Z) having more than one valence electron, the ground and the low excited states are usually described by the LS coupling of the angular momentum vectors l_1s_1, l_2s_2, ... *etc., i.e.*, the electrostatic interaction parameters:

$$[(l_1l_2)L, (s_1s_2)S]\,J \tag{5}$$

But for elements with high atomic numbers, the magnetic interaction between the spin of each electron and its own orbital motion predominates, giving rise to what is known as jj coupling

$$[(l_1s_1)j_1, (l_2s_2)j_2]\,J \tag{6}$$

For the lanthanide ions, the LS coupling is usually not a good approximation except for the ground multiplets. However, "it is of fundamental importance, because LS coupling states form the basic states for further approximation" [12], and interpretation of the lanthanide spectra, as no restriction is placed on the magnitude of the spin–orbit interaction. Indeed, the LS purity of the ground states of a given configuration of the lanthanide ions is very high (often above 95%).

As the ionization process involves removal of one or more valence electrons from the ground configuratio (here 4f^n to infinity, one would expect a correlation to hold between the ionization energy and the orbital angular quantum number L at the ground state, as is indeed the case, and it has been amply demonstrated here and elsewhere [5, 10].

The complex formation between the trivalent lanthanide ions and ligands usually does not involve the participation of the f-orbitals of the lanthanides [13] and the nephelauxetic effect being very small [13–21], the radial integrals F^k's and G^k's related to the magnitude of $(l_1, l_2....)$ and $(s_1, s_2....)$ aspects of the electrostatic interaction, are only slightly affected from the free ion values. Thus, the ground state eigenfunctions of the lanthanides are nominally perturbed due to complex formation, and justify the use of the ground state L values of the free ions as parameters for eventual correlation of the observed properties of the lanthanide complexes.

Lastly, we would like to comment on the variation of the four parameters of Sugar with the L values of the originating ions at the ground state. No pronounced irregularity was observed within the tetrads when the parameters SD, ΔE, and ΔT for M^{2+} (M III), M^{3+} (M IV) and M^{4+} (M V) ions were plotted against the ground state L values of these ions (Figs. 5, 6), as one would expect from the general behaviour of the "Inclined W" plots [5].

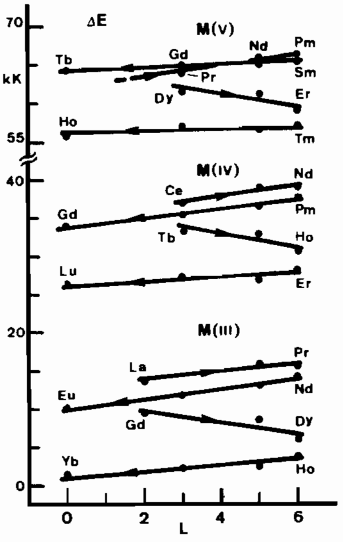


Figure 5. Inclined W plot of ΔE for M^{2+}(M III), M^{3+}(M IV) and M^{4+}(M V) lanthanide ions against the ground state L values of the originating ions.

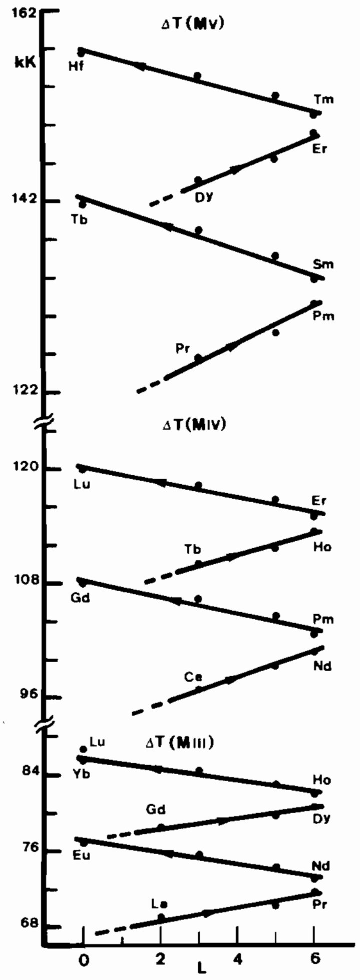


Figure 6. Inclined W plot of ΔT for M^{2+}(M III), M^{3+}(M IV) and M^{4+}(M V) lanthanide ions against the ground state L values of the originating ions.

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