Inorganica Chimica Acta, 22 (1977) L5–L6

Even the Fifth Ionization Potentials of the Lanthanides follow the "Inclined W" Theory

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Received January 25, 1977

Recently Sugar [1] has derived the fifth ionization potentials (IP_5) for the lanthanide series. These data along with the previously published [2] third (IP_3) and fourth (IP_4) ionization potentials and the experimentally determined [3] first (IP_1) and second (IP_2) ionization potentials provide interesting sets of properties for the lanthanide series to test the validity of the "Inclined W" theory [4].

In 1975 I have proposed [4] plotting the properties (P_i) of the f-ions *vs.* the free ion orbital angular quantum numbers (L) at the ground state. Such plots show linear variation of P_i within each of the four tetrads, often exhibiting the profile of an inclined W. Recently, a wide variety of properties for the lanthanides and the actinides in different oxidation states have been examined [5] confirming the general validity of the "Inclined W" theory ($P_i = w_i L + k_i$, where w_i is the slope and k_i is the intercept of the least square straight line for a given tetrad (i), having i = 1–4). In Ref. 5, I have examined among others, the L(originating ion) dependence plots of IP_1, IP_2 and IP_3 for the lanthanides as calculated and quoted by Faktor and Hanks [6] and the validity of linearization within each of the four tetrads was proved. Here, I wish to show that the data of Sugar and his coworkers [1, 2] on IP_3, IP_4 and IP_5 for the lanthanide series vary linearly within each tetrad and follow the Inclined W theory extremely well.

The plots of IP_3, IP_4 and IP_5 *vs.* the free ion ground state L quantum numbers are shown in Fig. 1 (a–c). The straight lines within each tetrad are drawn as least square lines having the following values of the parameters.

For IP_3: First tetrad (La–Pr) $w_1 = 0.5491$, $k_1 = 17.9535$; Second tetrad (Nd–Eu) $w_2 = -0.4445$, $k_2 = 24.7034$; Third tetrad (Gd–Dy) $w_3 = 0.5138$, $k_3 = 19.55$; Fourth tetrad (Ho–Yb) $w_4 = -0.3921$, $k_4 = 24.945$.

For IP_4: First tetrad (La–Nd) $w_1 = 1.2021$, $k_1 = 33.106$; Second tetrad (Pm–Gd) $w_2 = -0.5038$, $k_2 = 44.0434$; Third tetrad (Tb–Ho) $w_3 = 0.8886$, $k_3 = 37.10$; Fourth tetrad (Er–Lu) $w_4 = -0.4464$, $k_4 = 45.13$.

For IP_5: First tetrad (Pr–Pm) $w_1 = 1.365$, $k_1 = 53.37$; Second tetrad (Sm–Tb) $w_2 = -0.6426$, $k_2 = 66.527$; Third tetrad (Dy–Er) $w_3 = 0.995$, $k_3 = 59.06$; Fourth tetrad (Tm–Lu) $w_4 = -0.4779$, $k_4 = 68.16$.

The inclined W parameters for the experimental data [3] are as follows. For IP_1: First tetrad (La–Pr) $w_1 = -0.0393$, $k_1 = 5.646$; Second tetrad (Nd–Eu) $w_2 = -0.0291$, $k_2 = 5.6867$; Third tetrad (Gd–Dy) $w_3 = -0.06$, $k_3 = 6.23$; Fourth tetrad (Ho–Yb) $w_4 = -0.0371$, $k_4 = 6.2683$.

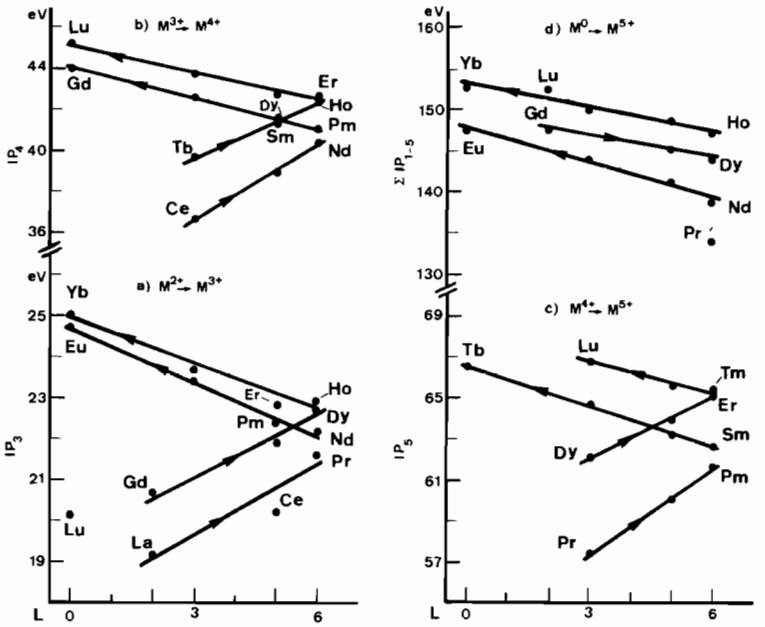

Fig. 1. Plots of the ionization potentials against the orbital angular quantum numbers (L) of the originating lanthanide ions; (a) third ionization potentials [2] (IP_3) *vs.* L of M^{2+} ions, (b) fourth ionization potentials [2] (IP_4) *vs.* L of M^{3+} ions, (c) fifth ionization potentials [1] (IP_5) *vs.* L of M^{4+} ions, and (d) sum of the five ionization potentials [1–3] (ΣIP_{1-5}) *vs.* L of the neutral lanthanide atoms [3].

For IP_2: First tetrad (La–Pr) $w_1 = -0.1607$, $k_1 = 11.57$; Second tetrad (Nd–Eu) $w_2 = -0.0838$, $k_2 = 11.2783$; Third tetrad (Gd–Dy) $w_3 = -0.1273$, $k_3 = 12.315$; Fourth tetrad (Ho–Yb) $w_4 = -0.05833$, $k_4 = 12.1917$.

The average deviations from the least square line are never higher than 0.1 eV, except for the first tetrad of IP_3, where it is around 0.3 eV.

We have earlier shown [5] that the sum of the ionization potentials (*e.g.* ΣIP_{1-3}) could be plotted against the L-values of the neutral lanthanides ($M^{\circ}(MI)$). This also results in an inclined W plot. Here, I have plotted the sum of all five ionization potentials (ΣIP_{1-5}) for the process $M^{\circ} \rightarrow M^{5+}$, against the L quantum numbers of the neutral atoms (Fig. 1d) and I have observed the linearity within

$$\begin{array}{ccccc} & & M^{5+}(MVI) & \xleftarrow{IP_5} & M^{4+}(MV) \xleftarrow{IP_4} M^{3+}(MIV) \\ & & \uparrow & & \uparrow \\ \Sigma IP_{1-5} & & & & IP_3 \\ & & \downarrow & & \downarrow \\ & & M^{\circ}(MI) & \xrightarrow{IP_1} & M^{+}(MII) \xrightarrow{IP_2} M^{2+}(MIII) \end{array}$$

the second through fourth tetrad. In this case, only one point (*i.e.* Pr) is available for the first tetrad. The least square inclined W parameters are as follows. For IP_{1-5}: Second tetrad (Nd–Eu) $w_2 = -1.3860$, $k_2 = 147.8434$; Third tetrad (Gd–Dy) $w_3 = -0.8738$, $k_3 = 149.49$; Fourth tetrad (Ho–Yb) $w_4 = -0.9174$, $k_4 = 152.8067$.

We are at present examining the plots of the system difference [7] (SD) energies *vs.* the L quantum numbers of the originating lanthanide ions, in an attempt to systematize the inclined W concept. The main advantage of this concept is the linearization within each of the four tetrads, which enables us to predict the property of a missing member with greater accuracy than that is usually possible in a non-linear plot of a given property *vs.* the atomic numbers of the lanthanides or the actinides.

References

1 J. Sugar, *J. Opt. Soc. Am., 65,* 1366 (1975).
2 J. Sugar and J. Reader, *J. Chem. Phys., 59,* 2083 (1973).
3 C. E. Moore, "Ionization Potentials and Ionization Limits Derived from the Analyses of Optical Spectra", *Natl. Bur. Std. (U.S.) Circ. NSRDS-NBS* 34, Sept. 1970.
4 S. P. Sinha, *Helv. Chim. Acta, 58,* 1978 (1975).
5 S. P. Sinha, "Struct. Bonding", Springer-Verlag, Berlin, Heidelberg, New York (1976), vol. 30, pp. 1–64.
6 M. M. Faktor and R. Hanks, *J. Inorg. Nucl. Chem., 31,* 1649 (1969).
7 W. C. Martin, *J. Opt. Soc. Am., 61,* 1682 (1971).