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Linear Relationship between First Ionization Potential (IP) of Element and ι(iota) Value. Removal of Periodicity

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The plot of square root of IP against ι value exhibited two straight lines depending on the type of the outer shell being s- or p-valence orbital. The stretching frequencies of H-X and H_nX species also showed a linear correlation with ι after correction using the reduced mass.

We previously proposed a new scale based on electronegativity, namely, inductive substituent parameter, ι(iota in Gk),[1] defined by Eq. 1,

$$\iota_{atom} = (Z_{eff} + 1) / n_{eff} \quad (1)$$

where Z_{eff} and n_{eff} denote effective nuclear charge and effective principal quantum number by the Slater's rule,[2] respectively.

The ι values for groups (ι_{group})[3b] can be calculated from group electronegativity (χ_X).[3a] The periodical dependency in C_α-SCS of CH_3X or C_{ipso}-SCS of C_6H_5X against χ_X[4] was removed using the ι_{group} value.[1,3b]

It is well known that the first ionization potentials (IP) of elements exhibit a periodicity with respect to the atomic numbers.[5] According to Slater,[6] IP can be approximated very simply in terms of Z_{eff}^2 / n_{eff}^2. Thus it is expected that square root of IP might be roughly correlated with ι_{atom}.

As shown in Fig. 1(a), the plot of square root of IP[7] against ι_{atom} exhibited two straight lines depending on the type of the outer shell being s- or p-valence orbital, the well known periodicity was first removed dramatically, but some sort of s-valence electron transition elements scattered considerably from the corresponding line.

Recently, Mullay[8] modified the Slater's original rule in order to maximize the fit between Z_{eff}^2 / n_{eff}^2 and IP values of alkali metals and halogens. Therefore, screening constants (s) in the Slater's rule were corrected for s-valence electron elements of higher periods as follows: 1) For the 4th period s(3s and 3p) = 0.80 was used instead of 0.85, 2) for the 5th period s(4s and 4p) = 0.78 was used instead of 0.85 and for $^{39}Y - ^{45}Rh$ the Z_{eff} values were calculated using number of 4d electrons less by one instead of that of 5s electrons, 3) for the 6th period s(5s and 5p) = 0.79 was used instead of 0.85, for $^{57}La - ^{70}Yb$ s(4f) = 0.95 instead of 1.0, and for $^{71}Lu - ^{80}Hg$ s(5d) = 0.70 instead of 0.85, and 4) for the 7th period (n_{eff} was assumed to be 4.3) s(6s and 6p) = 0.77 was used instead of 0.85, s(5f) = 0.93 instead of 1.00, and s(6d) = 0.70 instead of 0.85.

Table 1. The ζ, $Z_{eff(mod)}$, and $\zeta_{(corr)}$ Values of the Whole Element

Period (n_{eff})	Atom	ζ	Z_{eff} (mod) [a]	ζ (corr) [a]	outer shell
I (1)	1. H	2.00			s
	2. He	2.70			s
II (2)	3. Li	1.15			s
	4. Be	1.48			s
	5. B	1.80			p
	6. C	2.13			p
	7. N	2.45			p
	8. O	2.78			p
	9. F	3.10			p
	10. Ne	3.43			p
III (3)	11. Na	1.07			s
	12. Mg	1.28			s
	13. Al	1.50			p
	14. Si	1.72			p
	15. P	1.93			p
	16. S	2.15			p
	17. Cl	2.37			p
	18. Ar	2.58			p
IV (3.7)	19. K	0.86	2.60	0.97	s
	20. Ca	1.04	3.25	1.15	s
	21. Sc	1.08	3.40	1.19	s
	22. Ti	1.12	3.55	1.23	s
	23. V	1.16	3.70	1.27	s
	24. Cr	1.07	3.35	1.18	s
	25. Mn	1.24	4.00	1.35	s
	26. Fe	1.28	4.15	1.39	s
	27. Co	1.32	4.30	1.43	s
	28. Ni	1.36	4.45	1.47	s
	29. Cu	1.27	4.10	1.38	s
	30. Zn	1.45	4.75	1.55	s
	31. Ga	1.62			p
	32. Ge	1.80			p
	33. As	1.97			p
	34. Se	2.15			p
	35. Br	2.32			p
	36. Kr	2.50			p
V (4)	37. Rb	0.80	2.76	0.94	s
	38. Sr	0.96	3.41	1.10	s
	39. Y	1.00	4.06	1.27	s
	40. Zr	1.04	4.21	1.30	s
	41. Nb	0.95	3.86	1.22	s
	42. Mo	0.99	4.01	1.25	s
	43. Tc	1.03	4.16	1.29	s
	44. Ru	1.06	4.31	1.33	s
	45. Rh	1.10	4.46	1.37	s
	46. Pd [b]	1.14	4.61	1.40	s
	47. Ag	1.18	4.26	1.32	s
	48. Cd	1.34	4.91	1.48	s
	49. In	1.50			p
	50. Sn	1.66			p
V (4)	51. Sb	1.83			p
	52. Te	1.99			p
	53. I	2.15			p
	54. Xe	2.31			p
VI (4.2)	55. Cs	0.76	2.68	0.88	s
	56. Ba	0.92	3.33	1.03	s
	57. La	0.95	3.63	1.10	s
	58. Ce	0.95	3.68	1.11	s
	59. Pr	0.92	3.48	1.07	s
	60. Nd	0.92	3.53	1.08	s
	61. Pm	0.92	3.58	1.09	s
	62. Sm	0.92	3.63	1.10	s
	63. Eu	0.92	3.68	1.11	s
	64. Gd	0.95	3.98	1.19	s
	65. Tb	0.92	3.78	1.14	s
	66. Dy	0.92	3.83	1.15	s
	67. Ho	0.92	3.88	1.16	s
	68. Er	0.92	3.93	1.17	s
	69. Tm	0.92	3.98	1.19	s
	70. Yb	0.92	4.03	1.20	s
	71. Lu	0.95	3.63	1.10	s
	72. Hf	0.99	3.93	1.17	s
	73. Ta	1.02	4.23	1.25	s
	74. W	1.06	4.53	1.32	s
	75. Re	1.10	4.83	1.39	s
	76. Os	1.13	5.13	1.46	s
	77. Ir	1.17	5.43	1.53	s
	78. Pt	1.08	5.38	1.52	s
	79. Au	1.12	5.68	1.59	s
	80. Hg	1.27	6.33	1.75	s
	81. Tl	1.43			p
	82. Pb	1.58			p
	83. Bi	1.74			p
	84. Po	1.89			p
	85. At	2.05			p
	86. Rn	2.20			p
VII (4.3) [c]	87. Fr	0.74	2.84	0.89	s
	88. Ra	0.90	3.49	1.04	s
	89. Ac	0.93	3.79	1.11	s
	90. Th	0.97	4.09	1.18	s
	91. Pa	0.93	3.93	1.15	s
	92. U	0.93	4.00	1.16	s
	93. Np	0.93	4.07	1.18	s
	94. Pu	0.90	3.91	1.14	s
	95. Am	0.90	3.98	1.16	s
	96. Cm	0.93	4.28	1.23	s
	97. Bk	0.90	4.12	1.19	s
	98. Cf	0.90	4.19	1.21	s
	99. Es	0.90	4.26	1.22	s
	100. Fm	0.90	4.33	1.24	s
	101. Md	0.90	4.40	1.26	s
	102. No	0.90	4.47	1.27	s

a) See text. b) Calculated as $[Kr]4d^{9}5s^{1}$ instead of $[Kr]4d^{10}$ c) Assumed.

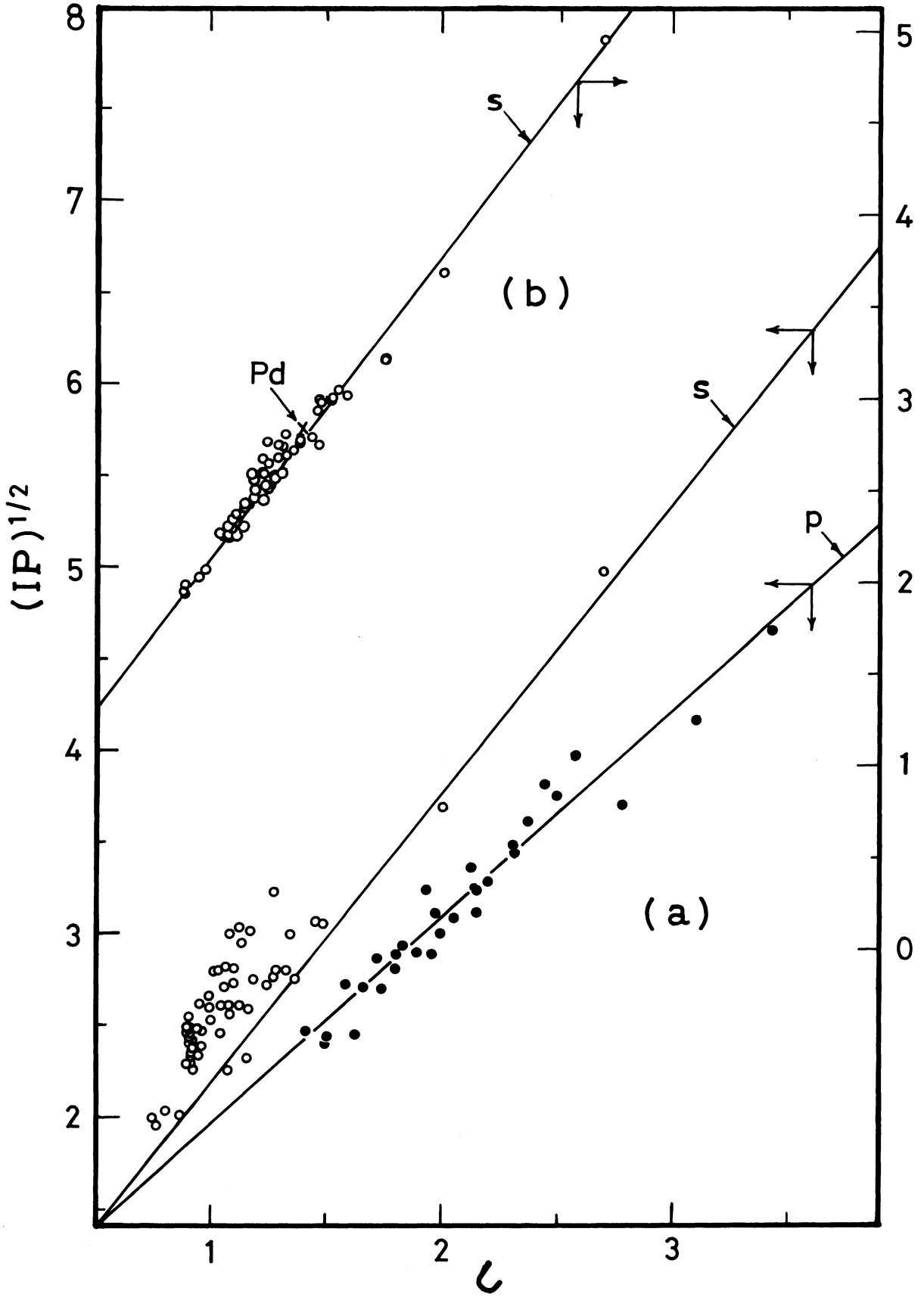

Fig. 1. Plot of $(IP)^{1/2}$ against ι.

The $Z_{eff(mod)}$ and $\iota_{(corr)}$ values thus obtained are shown in Table 1 together with the original ι values, and the plot for s-valence electron atoms using the corrected ι values is shown in Fig. 1(b), indicating a remarkable improvement of the linearity. Thus the following correlations were obtained.

For s-valence electron elements (using $\iota_{(corr)}$ values),

$$(IP)^{1/2} = 1.57 \cdot \iota + 0.63 \quad (eV^{1/2}) \quad (n = 71,\ r = 0.986,\ SD = 0.14)$$

For p-valence electron elements,

$$(IP)^{1/2} = 1.12 \cdot \iota + 0.85 \quad (eV^{1/2}) \quad (n = 30,\ r = 0.974,\ SD = 0.12)$$

Although Pd is a d-valence electron element ($[Kr]4d^{10}$), if one regards it as s-electron element ($[Kr]4d^{9}5s^{1}$), it was found that the point is placed very close to the line as shown by cross mark in Fig. 1(b).

The ι values were applied to the stretching frequencies ($\tilde{\nu}_{H-X}$ / cm^{-1}) of H-X species (partly contain H_n–X species)[9] as follows:

$$\tilde{\nu}_{H-X}(M_R)^{1/2} = 1338.5 \cdot \iota - 316.0 \quad (n = 38,\ r = 0.960,\ SD = 224.3)$$

where M_R represents the corresponding reduced mass.

Such removal of periodicity in some correlations might be very useful to discuss and predict quantitatively reactivities in the compounds of the whole element, especially transition metal complexes.

The detail and other application of the ι values will be described in full paper.

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