Nephelauxetic Effect and Pauling Electronegativity

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Summary Polarizing cations, *e.g.* S^{6+}, H^+, P^{5+}, reduce the nephelauxetic properties of the oxide ligand, its Jørgensen *h*-function depending quantitatively upon the oxidation number of these cations, their stoicheiometric proportion and their Pauling electronegativity.

The nephelauxetic parameter β can be expressed in terms of two numbers h and k (parameters of the ligands and central ion respectively) by equation (1).[1] The h parameter thus

$$\beta = 1 - hk \qquad (1)$$

expresses the contribution the ligands make in bringing about outer orbital expansion of the central ion. Equation (1) applies in the case not only of *d–d* spectra, but also of *s–p* spectra of $d^{10}s^2$ ions (*e.g.* Tl^+, Pb^{2+}, Bi^{3+}), β then being the ratio of the ${}^1S_0 \rightarrow {}^3P_1$ frequency of the complexed $d^{10}s^2$ ion to the (corrected) frequency of the free ion.[2]

Spectral shifts for these *s–p* transitions are much greater than for *d–d*, and it is possible to observe how h for a particular ligand is affected when the ligand is subjected to the effects of polarizing cations outside the co-ordination sphere. The ${}^1S_0 \rightarrow {}^3P_1$ transition of the $d^{10}s^2$ ion, to which the ligand is co-ordinated, is always blue-shifted, indicating that h decreases as the ligand becomes polarized. For oxide, this effect has been expressed in terms of the optical basicity, Λ,[2] which is the ratio $h'/h_{O^{2-}}$ where h' and $h_{O^{2-}}$ are the values of h for oxide in its polarized and unpolarized forms respectively. The media for which Λ has been obtained are oxide systems where polarization effects are brought about by 'cations' such as S^{6+}, H^+, P^{5+}, B^{3+}, *etc.* (*e.g.* 100% sulphuric acid and phosphate and borate glasses).

We report our observation that there is a relationship between the reduction in the value of h for oxide and the

Values of γ and electronegativities of some elements

Element	λ	Calculated electro-negativity[a]	Pauling electro-negativity[b]
Sulphur	3·1	2·5(7)	2·6
Phosphorus	2·6	2·2(0)	2·1
Hydrogen	2·5	2·1(3)	2·1
Boron	2·3	1·9(8)	2·0
Silicon	2·0	1·7(5)	1·8
Aluminium	1·7	1·5(3)	1·5
Calcium	1·0	1·0(0)	1·0
Sodium	1·0	1·0(0)	0·9

[a] Obtained from equation (3). [b] Taken from ref. 3.

Pauling electronegativity of the polarizing cations. The effect that the cations A, B $\cdots$ have on h is expected to depend upon (i) their nature (expressed here by a parameter, γ_A, $\gamma_B \cdots$), (ii) their oxidation number, z_A, $z_B \cdots$, and (iii) their ratio with respect to the total number of oxide ions, r_A, $r_B \cdots$ From experimentally determined Λ_{PbII} values,[2] the relationship in equation (2) is found to hold with the γ-values linearly related to Pauling

$$\frac{h'}{h_{O^{2-}}} = \frac{z_A r_A}{2\gamma_A} + \frac{z_B r_B}{2\gamma_B} + \cdots \qquad (2)$$

electronegativities, x, by equation (3) (see Table). Similar

$$x = 0{\cdot}25 + 0{\cdot}75\gamma \qquad (3)$$

results are obtained using values based on Tl^+ and Bi^{3+}.

The Table indicates that the covalency of the oxide–central ($d^{10}s^2$) ion bond, as measured by the nephelauxetic effect, depends upon the properties of the oxide ligand as modified by its environment through electronegativity effects. Indeed it seems possible that measurements of the nephelauxetic effect may provide an independent route to electronegativity values.

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[1] C. K. Jørgensen, 'Absorption Spectra and Chemical Bonding in Complexes', Pergamon, London and New York, 1962, p. 138.

[2] J. A. Duffy and M. D. Ingram, *J. Amer. Chem. Soc.*, 1971, **93**, 6448.

[3] L. Pauling, 'The Nature of the Chemical Bond', 3rd edn., Cornell University Press, 1960, p. 93.