An Electronegativity Scale based upon Geometry Changes on Ionization

By **Peter H. Blustin** * and **William T. Raynes**,* Department of Chemistry, The University, Sheffield S3 7HF

An electronegativity scale has been derived from the geometries of first- and second-row diatomic hydrides and their positive ions. In general, the electronegativities thus obtained are closely similar to Mulliken, Pauling, and Allred–Rochow values. However, in principle, the new scale appears to have a major advantage over the other three in that electronegativity values may be determined from accurately measurable spectroscopic data or, failing this, from high-quality *ab initio* calculations.

IN a recent publication [1] it was shown that simple rules could account for the direction of the change in bond length following the ionization of heteronuclear diatomic molecules. The model assumed that qualitative differences in electronegativity could be used for this purpose. The present Note describes results which suggest that the *magnitude* of the change in bond length is proportional to the electronegativity differences and that an electronegativity scale might therefore be derived from usually well characterized spectroscopic data on diatomic hydrides.

Except for Group 1 elements, all diatomic hydrides AH include one or more electrons localized in a non-bonding orbital nb_A. Removal of such electrons can lead to one of the ionization processes (1) and (2).[1] The sign of the change in bond length follows from changes in Coulombic attraction in the molecules before and after ionization.

$$\text{Type I: } A^{+}H^{-} - e^{-}(nb_A) \longrightarrow A^{2+}H^{-}; \quad \Delta r \text{ is negative} \qquad (1)$$

$$\text{Type II: } A^{-}H^{+} - e^{-}(nb_A) \longrightarrow A^{0}H^{+}; \quad \Delta r \text{ is positive} \qquad (2)$$

The rules seem to be of quite general application, regardless of how ionic or covalent the bond may be and how much redistribution of charge may occur following ionization. To derive an electronegativity scale, it is assumed that the relative change in bond length, $s = \Delta r_{AH}/r_{AH}$, is directly proportional to the eletronegativity difference [equation (3)]. To obtain representative values for electronegativities in the Geometry Ionization (GI) scale, we assume $x_H = 2.10$ and $x_F = 4.00$ (similar to Pauling's values [2,3]). Using data for HF,[4] we have $\Delta r_{HF} = +0.0843$ Å, $r_{HF} = 0.9168$ Å, and $s = +0.091\,95$. A value for k of 20.66 is then obtained. Using the expression (4), GI electronegativities of several first- and second-row elements, together with Br and Zn, have been calculated and are listed in the Table. Pauling, Mulliken, and Allred–Rochow electronegativities [2,3] have been included for purposes of comparison. All ions and parent molecules are in their respective ground states.

$$x_A - x_H = ks \qquad (3)$$

$$x_A = 2.10 + 20.66s \qquad (4)$$

The first point to be made is that, because the GI scale is closely similar to the other electronegativity scales (nearest to Allred–Rochow), geometry changes on ionization *are* proportional to electronegativity differences.[1]

Electronegativity scales

		Electronegativities			
Element	$\Delta r_e/r_e$ [a]	GI	Pauling	Mulliken	Allred–Rochow
Be	−0.0226	1.63	1.57	1.46	1.47
B	−0.0230,[b,c] −0.0039 [d]	1.62,[c] 2.02 [d]	2.04	2.01	2.01
C	+0.0098	2.30	2.55	2.63	2.50
N	+0.0326	2.77	3.04	2.33	3.07
O	+0.0611	3.36	3.44	3.17	3.50
F	+0.0920	(4.00)	3.98	3.91	4.10
Mg	−0.0450	1.17	1.31	1.32	1.23
Al	−0.0279	1.52	1.61	1.81	1.47
Si	−0.0105	1.88	1.90	2.44	1.74
P	+0.0021 [b]	2.14	2.19	1.81	2.06
S	+0.0141	2.39	2.58	2.41	2.44
Cl	+0.0315	2.75	3.16	3.00	2.83
Br	+0.0240	2.60	2.96	2.76	2.74
Zn	−0.0501 [c]	1.07	1.65	1.49	1.66

[a] Calculated from data given in ref. 4. [b] r_0 Values taken. [c] Data for BH^+ and ZnH^+ are now 40 years old (see text). [d] Using *ab initio* values.[5]

The major difference between the new scale and the others is that the more strongly electron-attracting elements have slightly lower x_{GI} values. It is especially gratifying that in the GI scale there is a larger electronegativity difference between fluorine and the other elements than is obtained by the other methods. This parallels the extreme chemical reactivity of the element.[2]

The values for B and Zn are rather lower than other estimates, although it should be mentioned that the data on BH^+ and ZnH^+ are more than 40 years old.[4] Fortunately, however, in the case of boron, Δr_{BH} may also be obtained from Cade and Huo's high-quality *ab initio* calculations,[5] giving an excellent value for x_B (see Table). In principle, this means that *ab initio* calculations of a similar quality may be used to determine Δr_{AH}, if no reliable value is known experimentally.

It is of particular interest that the chemical concept of electronegativity should be related to accurately measurable (or precisely calculable) spectroscopic data.[6] This is the major advantage of the GI scale. A disadvantage at present is that, apart from the first two rows of the Periodic Table, little is known about the geometries of AH^+ molecules. It is hoped that this Note may prompt further studies in this direction.

[0/1695 *Received, 6th November*, 1980]

REFERENCES

[1] P. H. Blustin, *Chem. Phys. Lett.*, 1977, **46**, 386.

[2] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Wiley, New York, 1966.

[3] G. J. Moody and J. D. R. Thomas, 'Dipole Moments in Inorganic Chemistry,' Arnold, London, 1971.

[4] K. P. Huber and G. Herzberg, 'Molecular Spectra and Structure, vol. IV. Constants of Diatomic Molecules,' Van Nostrand–Reinhold, New York, 1979.

[5] P. E. Cade and W. M. Huo, *J. Chem. Phys.*, 1967, **47**, 614; quoted in W. G. Richards, T. E. H. Walker, and R. K. Hinkley, 'A Bibliography of *ab initio* Molecular Wave Functions,' Oxford University Press, London, 1971.

[6] See also, N. K. Ray, L. Samuels, and R. G. Parr, *J. Chem. Phys.*, 1979, **70**, 3680; P. Politzer and H. Weinstein, *ibid.*, 1979, **71**, 4218.