Linear Relations of Effective Nuclear Charges and Force Constants with Electronegativities of Diatomic Hydrides

S. Noorizadeh* and Z. Ramezani†

Chemistry Department, College of Sciences, Chamran University, Ahvaz, 61357-43151, Iran
Fax: (98)(611)3337009;   E-mail: noorizadeh_s@cua.ac.ir

It is shown that for more than forty diatomic hydrides, HX, a linear relation between the force constant and the χ/R_0 ratio is $K = 321.869501\chi/R_0 - 84.291988$, in which χ is the Pauling electronegativity of X atom composing the hydride. Satisfactory correlation coefficient is obtained for this line (0.985843). A new empirical relation is also found between effective nuclear charge (Z_{eff}) and electronegativity of the X atom in these molecules, *i.e.*, $ZZ_{eff} = 0.688688\chi n^3 + 13.780372$, where n is the row's number of X atom in the periodic table. It shows that as Badger's rule, ZZ_{eff} has something to do with the third power of principal quantum number (n). A good correlation is achieved (0.960157).

Key Words: Linear relations, Effective nuclear charges, Force constants, Electronegativities, Hydrides.

INTRODUCTION

During the past few years many attempts had been made to find accurate relations among the molecular properties[1-4]. These relations have a wide range of theoretical applications such as the construction of potential energy functions, simplifying the molecular calculations, predicting a property from the others and so on. All the relations are at best an attempt to find a considerable amount of data with the smallest possible number of arbitrary constants.

A large number of empirical expressions have been proposed, which relate the force constant or vibrational frequency to the internuclear distance, dissociation energy of the bond, electronegativities of constituent atoms and the other molecular properties of a diatomic molecule. Perhaps the first of these relations was proposed by Kratzer[5] for the hydrogen halides but Badger's rule[6, 7] can also be used:

$$K(R_0 - d_{ij})^3 = C \tag{1}$$

where K, R_0 and C are the force constant, internuclear distance and a constant, respectively. d_{ij} is a parameter which is fixed for given rows in the periodic table. Badger[6, 7] also observed that in the case of diatomic molecules the equilibrium

---

†School of Pharmacy, Jundi Shapour Medicine University, Ahvaz, Iran.

bond length could be expressed as a function of two parameters, which are the second derivative of potential with respect to the internuclear distance at the equilibrium position (force constant) and the position of atoms composing the molecules in the periodic system. It is obvious from this rule that force constants are related to the third power of the periodic number or, in other words, principal quantum number. The present authors also observe such dependency in our relations later. Freeman and March[8], by using this fact, have introduced an empirical relation between inverse covalent bond length and force constant of a diatomic molecule as $K = A \exp (s/R_c)$, in which "s" depends on the period in the periodic table, but is approximately constant throughout a period.

Some other rules have been proposed, but some of these rules cannot be used for fitting the various excited states of a given molecule (in spite of the Badger's rule). The constants of these rules could be expressed as a function of the atomic numbers of the atoms composing the molecule.

Schomaker and Stevenson[9] have suggested the relation:

$$R_0 = r_A + r_B - 9\Delta\chi$$

where $\Delta\chi$ is the difference in electronegativity between atoms A and B. r_A and r_B are the covalent radii of atoms A and B, respectively. Walls[10] has discussed deficiencies in this equation and Pauling[11] has suggested modifications to improve the accuracy.

Sutherland[12] pointed out that if a general type of potential function is adopted for a series of diatomic molecules, then some relationship between the force constant and the internuclear distance follows automatically. Linnett[13], Wu and Yang[14] and Lippencott[15] had used different potential functions and deduced other formulas. Steele and coworkers[16] collect some of these relations for different potential functions. An attempt was made by Guggenheimer[17] to explain these relationships by quantum mechanical methods. But in this theory, nuclear repulsion term, which has a great contribution to the force constant, was not included and, therefore, it was not successful for a wide range of molecules. A relation had also been found between bond length and bond energy for homopolar bonds[18].

Ghosh *et al.*[19] have proposed an electronegativity-based approach to covalent binding in homonuclear diatomic molecules in terms of the accumulation of electron density of the bond center during molecule formation.

Another important molecular parameter is effective nuclear charge. Slater[20] proposed a set of simple rules for the computation of the effective nuclear charge experienced by an electron in an atom. In neutral molecules this parameter can be interpreted in two ways[21]: the amount of unshielded positive charge on each nucleus and the number of electrons in each atom which are actively bonding.

The object of this study is to introduce new relations among some molecular properties. We draw a plot of K *vs.* χ/R_0 for 46 diatomic hydrides to show there is a good linear relation between these parameters. It was also shown that there is a good linearity between $Z Z_{eff}$ and χn^3 for these hydrides, where n is the period's number in which X is placed.

RESULTS AND DISCUSSION

The present studies will be restricted to diatomic molecules in the gas phase, mainly hydrides. This choice is based on the facts that:

(1) All bonds can be considered as single bonds,

(2) These molecules do not have lone pair and hence its effect of bond weakening,

(3) Data is available for more than forty hydride molecules,

(4) We can compare only similar bonds with a constant atom or group in their structures, and HX molecules have all of these conditions.

This study consists of two major parts, which are as follows:

(a) Relation between force constant and electronegativity

The excess bond stabilization depends on the differences in the electronegativities of the bonded atoms and since the force constant is a measure of the strength of a bond, therefore we expect to have a relation between force constants and electronegativities. Pearson[22] claimed that for diatomic molecules KR_0 has a linear relation with respect to the electronegativity. KR_0 and χ have the same dimension (dimension of force), and both of them are a measure of the force exerted on the valence shell electrons by shielded nucleus[23].

Some properties of selected hydrides are presented in Table-1. Although there are different electronegativity scales[24], we use Pauling electronegativities.[25] From this table it is obvious that the relative spread in KR_0 and χ/R_0 is smaller than that in K and χ, respectively. This has motivated us to assume a form $K = f(1/R_0)$. Since both of K and χ/R_0 have the same dimension, therefore they must have nearly the same characteristics. The most interesting result that is shown in Fig. 1 illustrates a good linearity between K and χ/R_0. The best straight line in this figure was obtained by the least-squares method, which has the following form:

$$K = 321.869501\chi/R_0 - 84.291988 \qquad (2)$$

The entire least square processes are done in the software "Curve Expert 3.1". The correlation coefficient is 0.985815, which is an acceptable regression for 46 points and better than Pearson's plot (0.9489). Small and big deviations are found for the transition metals and the hydrides of group 2 respectively, which can be interpreted by the promotion energies of these elements[22, 26, 27]. Hybridization affects electronegativity because of the lower energy and hence greater electron-attracting power of s-orbitals. These orbitals have greater "s" character being more electronegative.

Because of the abnormal potential energy and low dissociation energy (9 kcal/mol) of HgH^{28}, it presents some difficulties in this study and the biggest deviation is seen for this hydride, but it is included in the comparison. Eliminating this point improves linearity (0.987078).

(b) Relation between effective nuclear charge and electronegativity

A periodic behaviour is seen for the electronegativity of elements in different rows from Table-1. Since the force constant is affected by the nuclear repulsion term, which is directly proportional to the nuclear charges of atoms (Z), we expect to have a relation between electronegativities and nuclear charges; but there is no such relation between Z and χ, because in this case the χ for heavier elements becomes infinite. It is better to examine effective nuclear charge (Z_{eff}) instead of the nuclear charge itself. Effective nuclear charges are obtained from the following equation for a homonuclear diatomic molecule:

TABLE-1

PROPERTIES OF SELECTED DIATOMIC HYDRIDES
(ALL DATA FROM REF. 30, EXCEPT WHERE INDICATED)

Mol.	K^a	Z_{eff}^b	χ^c	R_0^f	Mol.	K^a	Z_{eff}^b	χ^c	R_0^f
LiH	145.625	1.80	0.98	1.60	CoH	309.911	3.40	1.76	1.54^d
BeH	324.627	2.35	1.57	1.34	NiH	333.108	3.25	1.86	1.48^d
BH	436.585	2.45	2.04	1.23	CuH	315.068	2.96	1.74	1.46
CH	651.786	2.76	2.55	1.12	ZnH	215.625	2.65	1.60	1.60
NH	848.077	2.86	3.04	1.04	RbH	73.840	2.96	0.82	2.37
OH	1112.371	3.06	3.44	0.97	SrH	121.861	3.65	0.95	2.15
FH	1378.261	3.23	3.98	0.92	InH	182.065	3.41	1.78	1.84
NaH	111.640	2.27	0.93	1.89	SnH	235.393	4.00	1.96	1.78
MgH	181.503	2.83	1.31	1.73	IH	447.205	5.63	2.66	1.61
AlH	230.303	3.12	1.61	1.65	RhH	344.805^e	3.79	2.28	1.54^e
SiH	340.789	3.61	1.90	1.52	PdH	345.752	3.73	2.20	1.53
PH	461.972	3.97	2.39	1.42	AgH	259.876	3.33	1.93	1.62
SH	604.478	4.38	2.58	1.34	CdH	150.000	2.55	1.69	1.78
ClH	730.469	4.61	3.16	1.28	CsH	67.068	3.11	0.79	2.49
KH	79.203	2.70	0.82	2.26	BaH	114.350	3.82	0.89	2.23
CaH	139.500	3.36	1.00	2.00	TeH	162.567	3.20	1.62	1.87
GaH	215.663	2.97	1.81	1.66	PbH	206.522	3.87	1.87	1.84
GeH	280.503	3.40	2.01	1.59	BiH	225.414	4.01	2.02	1.81
AsH	382.353	4.12	2.81	1.53	PtH	443.421	4.69	2.28	1.52
SeH	480.405	4.67	2.55	1.48	AuH	448.421	4.74	2.54	1.52
BrH	589.362	4.99	2.96	1.41	HH	828.378	1.01	2.20	0.74
CrH	215.663	2.97	1.45	1.66^d	HgH	121.469	2.04	1.76	1.77
MnH	199.422	3.11	1.55	1.73^d					
FeH	233.129	3.04	1.70	1.63^d					

^{a}Force constant (in kcal mole^{-1} Å^{-2}), ^{b}Effective nuclear charge on x,
^{c}Pauling electronegativity, ^{d}Ref. [31], ^{e}Ref. [32], ^{f}in Å.

$$KR_0 = \frac{Z_{eff\,X}^2}{R_0^2}$$

where K and R_0 for these molecules are achieved from Ref. 29.

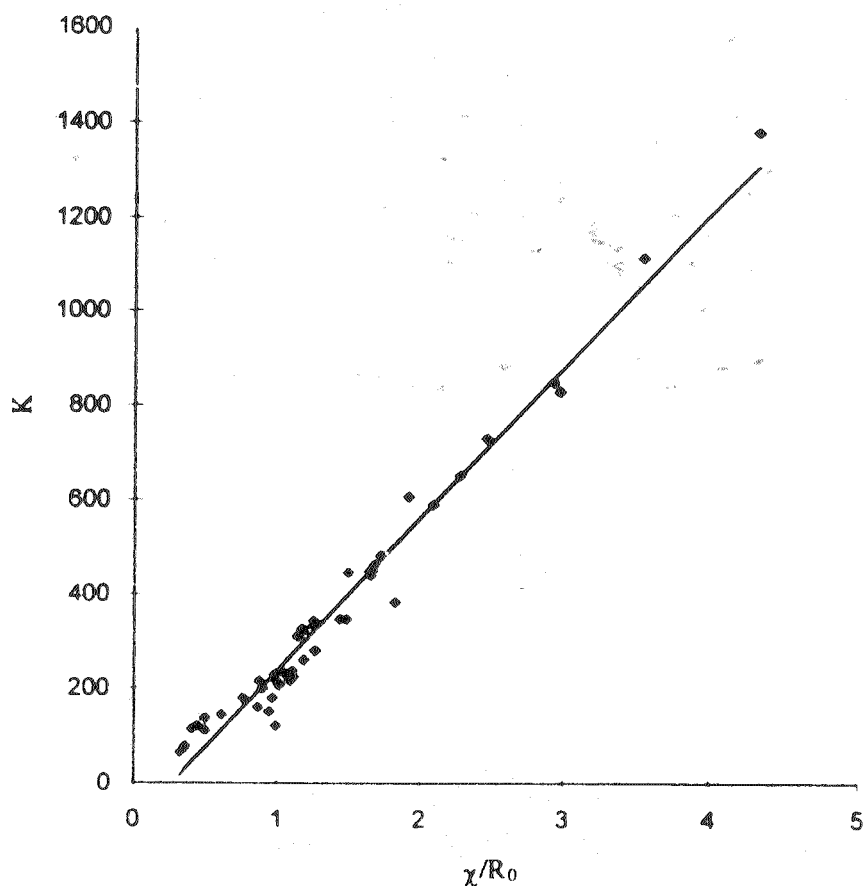Fig. 1. Plot of K vs. χ/R_0 ratio for selected hydrides. The regression line is also shown.

As is shown in Fig. 2, the plot of ZZ_{eff} vs. χ consists of a series of lines and each line belongs to the elements of a given row in the periodic table. In this plot, each line better is formed by the elements of a row having quite a different slope from the lines which are obtained from the elements of the other rows and different lines correspond to the elements of a given row of X atom. If we replace χ with χn^p (n is the period's number of the X element and p is an integer), by increasing the power of n, the lines slowly converge to each other. Interestingly, a better convergence and the best linearity is achieved for $p = 3$ (correlation coefficient equal to 0.96017) with the following form, which is shown in Fig. 3:

$$ZZ_{eff} = 0.688688\chi n^3 + 13.780372 \tag{3}$$

It is interesting to note that ZZ_{eff} is related to the third power of the row's number (n).

Such as the previous section, the highest deviation is observed for H_2 and HgH molecules. By eliminating these molecules from the graph, linearity is improved (correlation coefficient becomes 0.974365).
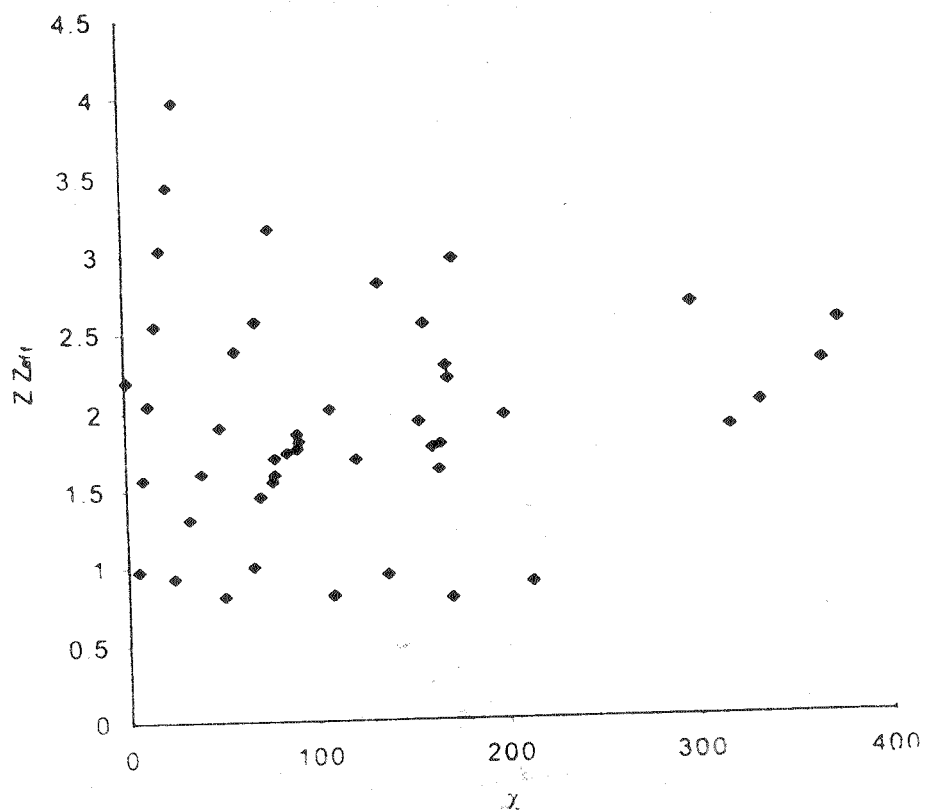
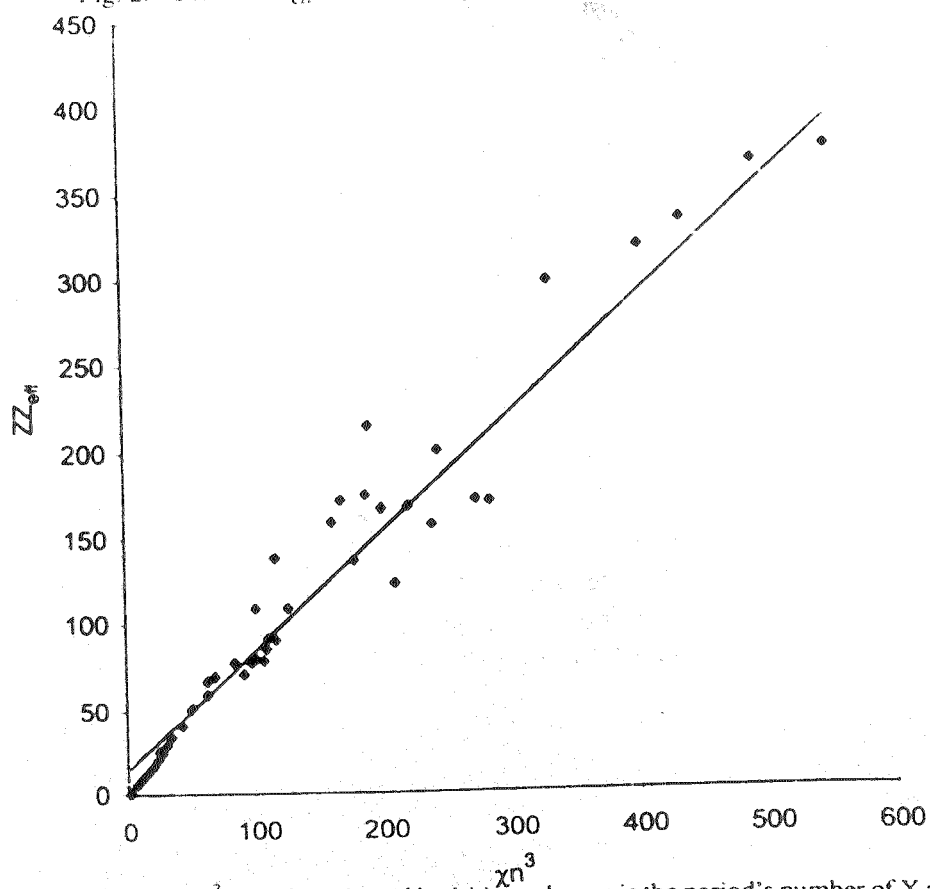Fig. 2.   Plot of ZZ_{eff} *vs.* electronegativity for selected hydrides

Fig. 3.   Plot of ZZ_{eff} *vs.* χn^3 ratio for selected hydrides, where n is the period's number of X atom. The regression line is also shown

Conclusion

In the present work it was shown that there is a linear relation between force constant and the χ/R_0 ratio for diatomic hydrides. Greater deviation is seen for HgH hydride, which can be interpreted by its low dissociation energy and abnormal potential energy function. It was also concluded that there is a linear dependency for ZZ_{eff} and of these molecules. These dependencies can be examined for different force constants of polyatomic molecules too. Since there is some relation between electronegativities and molecular hardness, it seems that there must be some other relation among hardness and such properties.

REFERENCES

1. W. Grochala, A.C. Albrecht and R. Hoffmann, *J. Phys. Chem. A*, **104**, 2195 (2000).
2. P.W. Ayers and R.G. Parr, *J. Phys. Chem. A*, **104**, 2211 (2000).
3. P. Politzer, M.E. Grice and J.S. Murray, *J. Mol. Struct. (Theochem.)*, **549**, 69 (2001).
4. P. Bultinck and R. Carbó-Dorca, *Chem. Phys. Lett.*, **364**, 357 (2002).
5. A. Kratzer, *Z. Physik*, **3**, 289 (1920).
6. R.M. Badger, *J. Chem. Phys.*, **2**, 128 (1934).
7. ————, *J. Chem. Phys.*, **3**, 710 (1935).
8. G.R. Freeman and N.H. March, *J. Mol. Struct.*, **333**, 261 (1995).
9. V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 37 (1941).
10. A.F. Walls, *J. Chem. Soc.*, **55**, 261 (1949).
11. L. Pauling, The Nature of the Chemical Bond, 3rd Edn., Cornell University Press, Ithaca, N.Y., p. 228 (1960).
12. G.B.B.M. Sutherland, *J. Chem. Phys.*, **8**, 161 (1940).
13. J.W. Linnett, *Trans. Faraday Soc.*, **36**, 1123 (1940); **38**, 1 (1941).
14. C.K. Wu and C.-T. Yang, *J. Phys. Chem.*, **48**, 295 (1944).
15. E.R. Lippencott, *J. Chem. Phys.*, **21**, 2070 (1953).
16. D. Steele, E.R. Lippencott and J.T. Vanderslice, *Rev. Mod. Phys.*, **34**, 239 (1962).
17. K.M. Guggenheimer, *Proc. Phys. Soc.*, **63**, 456 (1946).
18. J.E. Huheey and R.S. Evans, *J. Inorg. Nucl. Chem.*, **32**, 383 (1970).
19. T.K. Ghanty and S.K. Ghosh, *J. Phys. Chem.*, **95**, 6512 (1991).
20. J.C. Slater, *Phys. Rev.*, **36**, 57 (1930).
21. R.G. Pearson, *J. Am. Chem. Soc.*, **99**, 4869 (1977).
22. ————, *J. Mol. Struct.*, **300**, 519 (1993).
23. A.L. Allred and E.G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958).
24. R.G. Pearson, *Acc. Chem. Res.*, **23**, 1 (1990).
25. L. Pauling, *J. Am. Chem. Soc.*, **54**, 3570 (1932).
26. P.E. Cade and W.M. Huo, *J. Chem. Phys.*, **47**, 614 (1967).
27. ————, *J. Chem. Phys.*, **47**, 649 (1967).
28. W.C. Stwalley, *J. Chem. Phys.*, **63**, 3063 (1975).
29. R.G. Parr and R.G. Pearson, *J. Am. Chem. Soc.*, **105**, 1503 (1983).
30. K.P. Huber and G. Herzberg, Constants of Diatomic Molecules, van Nostrand Reinhold, New York, 1979.
31. A.E.S. Miller, C.S. Feigerle and W.C. Lineberger, *J. Chem. Phys.*, **87**, 1549 (1987).
32. K. Balasubramian and D.W. Liao, *J. Chem. Phys.*, **88**, 317 (1988).