

# SPECTROSCOPIC CONSTANTS OF MOLECULES. VI, DEPENDENCE OF FORCE CONSTANT ON ELECTRONEGATIVITY

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**ABSTRACT.** For diatoms formed out of elements belonging to the same sub-group of the periodic table, it has been shown that

$$\log k_e = g \log x_A x_B + h$$

where  $g$  and  $h$  are constants and  $x_A$  and  $x_B$  are the electronegativities.

A relation between the force constants of diatoms  $AA$  and  $AH$  has also been suggested

$$k_e(AH) = p k_e(AA) + q$$

where  $p$  and  $q$  are constants for each group.

## I N T R O D U C T I O N

The concept of "electronegativity" introduced by Pauling (1932, 1944) has proved to be very useful in the understanding of the chemical bond. Electronegativity ( $x$ ) is a measure of the power of an atom to attract electrons to itself. It has achieved an astonishing success "in correlating a vast field of chemical knowledge and experience"

Pauling's original values of electronegativities have been revised and extended by him and others, and various comparisons have been made between electronegativities computed on basis of Pauling's assumptions and those computed in other ways. Recently the subject has been exhaustively reviewed by Pritchard and Skinner (1955). Gordy and Thomas (1956) have compared electronegativity values derived by different methods and have suggested the "best" values.

A number of attempts have been made to investigate the dependence of molecular properties *e.g.* dipole moment, force constant, ionic character etc. on electronegativity.

Gordy (1946a, b) has found that for bonds of similar nature

$$k_e = \alpha N \left[ \frac{x_A x_B}{r_e^2} \right]^{3/4} + b \quad \dots \quad (1)$$

where

$k_e$  — force constant

$r_e$  — internuclear distance

$N$  — bond order

$\alpha, b$  — constants

An interesting feature of eq. (1) is the fact that  $x_A$  and  $x_B$  are involved as product  $x_A x_B$  rather than as a difference. Exceptions to Gordy's relation have been found by several workers (Cottrell and Sutton, 1947)

Recently, Williams (1956) has proposed that for elements of groups IV to VII

$$x_A = .761(z_A/r_A)^7 \quad \dots (2)$$

where  $z$  is the number of valence electrons in the atom and  $r_A$  is its covalent radius. Combining eq. (2) with Gordy's eq. (1) he derives

$$k_e = \alpha(z_A z_B)^{.625}/r_e^{2.625} + \beta \quad \dots (3)$$

From this, Williams puts forward the view that force constant is primarily a function of number of valence electrons, rather than that of electronegativities.

#### NEW RELATIONS

In diatomic molecules formed out of elements  $A$  and  $B$ , both belonging to the same sub-group of the periodic table, the valence forces are very similar. In view of this it was conjectured that the  $k_e$  of such molecules may show simple relationship with the electronegativities of the constituent atoms.

It has been found that for such molecules  $\log k_e$  is linear with  $\log x_A x_B$ . The relationship can be represented as

$$\log k_e = g \log x_A x_B \quad (1)$$

where  $g$  and  $h$  are constants for each molecular group.

Pritchard and Skinner (1955) and Gordy and Thomas (1956) have suggested the "best" values of electronegativities. While for most of the elements the two scales agree, for IVb group elements there are serious differences. A compromised set of values selected with the guiding principle that electronegativity should decrease regularly as one passes downwards in any subgroup of the periodic table (Pajans, 1928; Walsh, 1951) is given in Table I and has been used in the present paper.

TABLE I

1a	4b	6b	7b
Li .95	C 2.5	O 3.5	F 3.9
Na .9	Si 1.9	S 2.6	Cl 3.0
K .80	Ge 1.8	Se 2.4	Br 2.8
Rb .78	Sn 1.7	Te 2.1	I 2.5
Cs .75	Pb 1.6		

The applicability of equation (4) has been illustrated for 1a-1a, 6b-6b and 7b-7b groups in figures 1, 2 and 3 respectively. The values of the constants

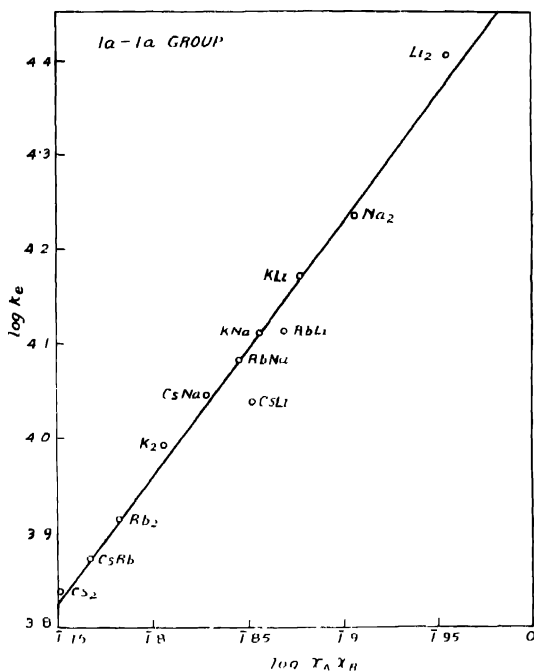


Fig. 1.

$g$  and  $h$  are recorded in Table II. Numerical results have been tabulated in Table III. All force constants are in Des. ( $10^5$  dynes/cm.). Uncertain values are in parentheses.

The applicability of relation (4) for such molecules in which the two atoms belong to two different groups was examined but the results are not very encouraging. Figure 4 shows  $\log k_e$  against  $\log x_A x_B$  for 4b-6b group. Force constant data were taken from Varshni and Majumdar (1955).

TABLE II

Group	$g$	$h$
1a-1a	2.684	4.498
6b-6b	1.59	4.357
7b-7b	1.55	4.004

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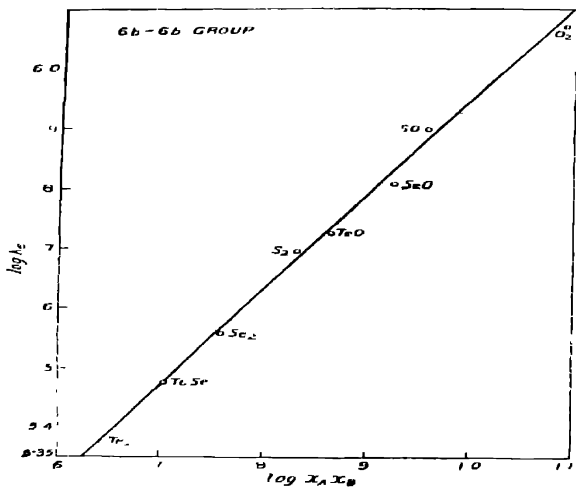


FIG. 2

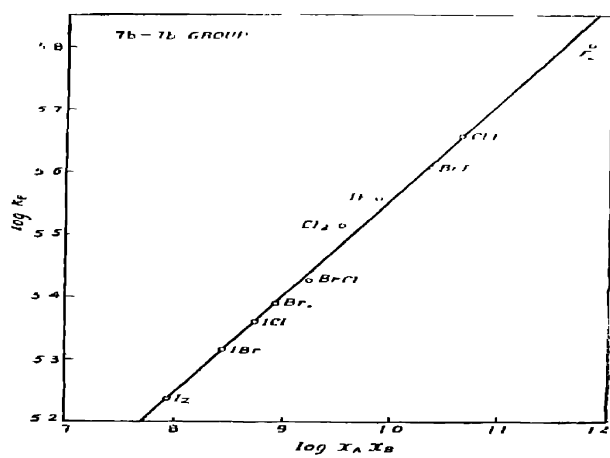


Fig. 3

TABLE III

Group	Diatom	$k_t$ obs.	$k_r$ calc.	% error
1a-1b	LiLi	2552	2389	- 6.39
	NaNa	1717	1803	+ 5.00
	KK	0985	0950	- 3.55
	RbRb	.08205	.0820	+ 1.03
	CsCs	.06902	.0672	- 2.64
	KLi	(.1487)	.1507	+ 1.34
	RbLi	(.1294)	.1408	+ 8.81
	CsLi	(.1094)	.1267	+ 15.81
	KNa	.1296	.1303	+ .54
	RbNa	.1213	.1218	+ .41
	CsNa	(.1109)	.1096	- 1.17
CsRb	.0748	.0747	- .13	
6b-6b	OO	11.76	12.22	+ 3.91
	SS	1.959	1.75	- 4.21
	SeSe	3.613	3.682	+ 1.91
	TeTe	2.368	2.401	+ 1.41
	SO	7.93	7.62	- 3.91
	SeO	6.446	6.707	+ 4.05
	TeO	5.304	5.425	+ 2.28
	TeSe	3.002 S <sub>1</sub>	2.977	- .83
7b-7b	FF	6.336 eV <sub>q</sub>	6.869	(+ 8.41)
	ClCl	3.279	3.044	- 7.17
	BrBr	2.457	2.459	+ .08
	II	1.721	1.73	+ .52
	ClF	4.562	4.573	+ .24
	BrF	1.071	1.11	+ .95
	IF	3.621 D <sub>1</sub>	3.446	- 4.83
	BrCl	(2.675)	2.736	+ 2.28
	ICl	2.296	2.295	- .04
	IBr	2.064	2.063	- .05
	See notes below Table V			Average

Walsh (1951) noticing that the variation of force constants of diatomic hydrides is very similar to Pauling's electronegativities, has suggested that the force constant of a diatomic hydride  $AH$  may be considered to be a measure of the electronegativity of the corresponding atom  $A$ . This suggests the possibility of a connection between  $k_o(AA)$  and  $k_r(AH)$ . It was found that in this case  $k_r(AA)$  is linear with  $k_o(AH)$ . Thus

$$k_r(AH) = p k_o(AA) + q \quad (5)$$

Figures 5 and 6 depict the relation graphically. The numerical values of  $\rho$  and  $\gamma$  for different groups are given in Table IV. Observed and calculated values of  $k_e(AH)$  have been compared in Table V.

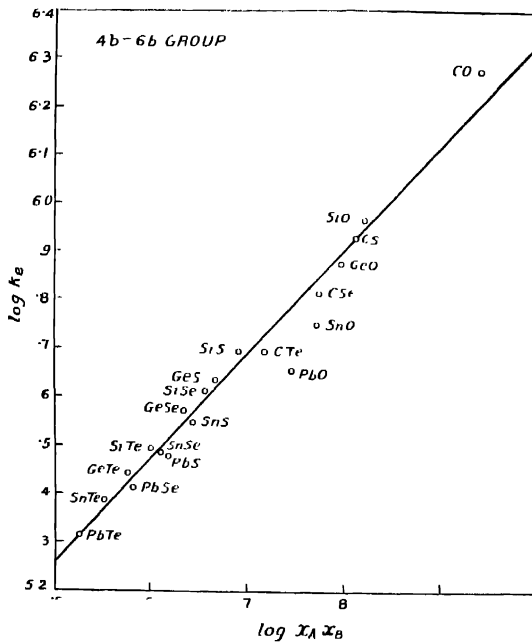


FIG. 4.

TABLE IV

Group	$\rho$	$\gamma$
1a-H	2.952	.273
6b-H	.5602	1.206
7b-H	1.405	.065

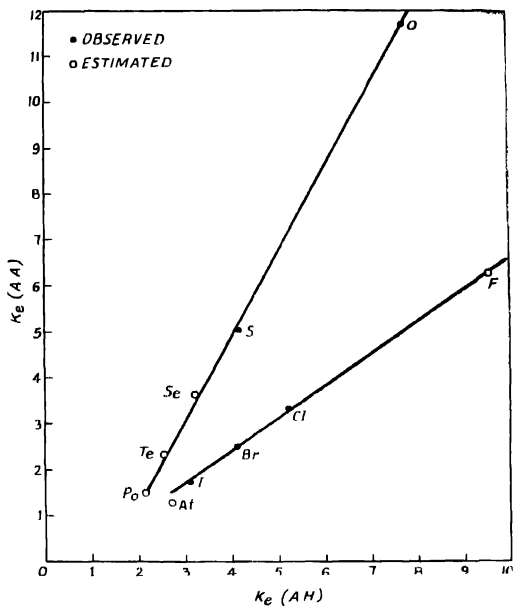


Fig. 5

TABLE V

Group	Diatom A.A.	$k_e(A.A)$ obs.	Diatom A.H.	$k_e(A.H)$ obs.	$k_e(A.H)$ calc.
1a	LiLi	2552	LiH	1.026	1.026
	NaNa	1717	NaH	781	.780
	KK	.0985	KH	561.4	.564
	RbRb	0820	RbH	514.8	.5150
	CsCs	.0690	CsH	.467	.477
	FrFr	.0595 eC <sub>1</sub>	FrH		.449
6b	OO	11.76	OH	7.792	7.794
	SS	4.959	SH	4.193 L <sub>2</sub>	3.984
	SoSo	3.613	SeH	3.18 eS <sub>3</sub>	3.23
	ToTo	2.368	ToH	2.53 eS <sub>3</sub>	2.533
	PoPo	1.51 eC <sub>1</sub>	PoH	2.1 eS <sub>3</sub>	2.052
7b	FF	6.336 eV <sub>1</sub>	FH	9.655	9.567
	ClCl	3.279	ClH	5.157	5.272
	BrBr	2.457	BrH	4.117	4.117
	I	1.721	IH	3.142	3.083
	AtAt	1.213 eC <sub>1</sub>	AtH	2.7 eS <sub>3</sub>	2.37

Notes on Tables III and V. Except for the follow ing, other data have been taken from Herzberg (1951)

e—estimated value, C<sub>1</sub>—Clark (1937), D<sub>1</sub>—Durio (1951), L<sub>2</sub>—Lench (1954), S<sub>3</sub>—Sheline (1950). Force Constant of AtH has been freshly estimated, S<sub>4</sub>—Sharma, private communication, V<sub>3</sub>—Majumdar and Varshni (1954).

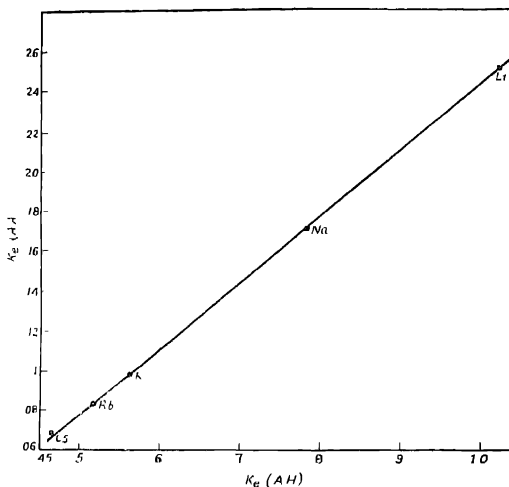


Fig. 6.

## DISCUSSION

*First relation .*

Equation (4) (Figures 1 to 3, Table III). Making due allowance for the uncertainties in the electronegativity values, the relationship is well followed. However, in case of  $\text{CsLi}$  the calculated value is much higher than the observed value. It may be pointed out that the observed value is uncertain and that other methods also predict a higher value of  $\omega_r$  for this diatom (Varshni, 1955). It is not unlikely that further investigations on this molecule may lead to a higher observed value. In figure 3, for  $\text{PF}$ , the estimated value of  $k_e$  (Majumdar and Varshni 1954) which is higher than the reported value has been plotted. The position of  $\text{PF}$  in the figure supports the estimated value.

*Second relation*

Equation (5) (Figures 5 and 6, Table V). The linearity is well obeyed.

Line for 7b group further supports the estimated value of  $k_e$  ( $\text{PF}$ ) (Majumdar and Varshni 1954).

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