Empirical Relation of Delta Function Strength for Transition Elements

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A modified empirical relation for computing delta-function strengths for transition elements has been proposed and applied to a number of polyatomic molecules. The validity of this relation has been tested by comparing experimental and calculated values of bond and molecular polarizabilities, and bond polarizability derivatives. It has been found that they are in close agreement compared on the results published hitherto.

Introduction

The empirical expression for delta-function strengths formulated by Lippincott and Dayhoff [1] gives reasonable results of bond and molecular polarizabilities, and bond polarizability derivatives for polyatomic molecules possessing light and non-transition elements, but fails for molecules containing transition elements. We here suggest a modified empirical expression for delta function strengths which is also suited for polyatomic molecules containing transition elements.

Modified Empirical Expression for Delta-Function Strength

The empirical expressions of Lippincott and Dayhoff [1] for the delta-function strengths A and A^* of an atom in a diatomic molecule and an atom in a polyatomic molecule are, respectively,

$$A = [\chi / (2.6\, n - 1.7\, p - 0.8\, D + 3.0\, F)]^{\frac{1}{2}} \quad (1)$$

and

$$A^* = A\, [1 - 0.20/(n-1)]^{\frac{1}{2}}, \quad (2)$$

where χ is the electronegativity of the atom on Pauing scale, n the principal quantum number, $p = 1$ for atoms with p-electrons in the valence shell and $p = 0$ for atoms with no p-electrons in the valence shell, D the total number of completed p- and d- shells in an atom and F the total number of completed f-shells in an atom.

Our modified empirical relation takes into account the effective principal quantum number n' instead of n, and it contains a constant multiplier whose magnitude depends on the atomic number z. The modified form of (1) is

$$A = [q\, \chi / (2.6\, n' - 1.7\, p - 0.8\, D + 3.0\, F)]^{\frac{1}{2}}, \quad (3)$$

where $q = [1 - 0.2/(n-1)]$, 0.75, 0.60 and 0.80 for atoms with $1 \leqq Z \leqq 20$, $21 \leqq Z \leqq 38$, $39 \leqq Z \leqq 57$, and $72 \leqq Z \leqq 86$, respectively.

To test relation (3), we have used analytical expressions for the bond and molecular polarizabilities and bond polarizability derivatives due to Lippincott and Stutman [2] and Lippincott and Nagarajan [3]. The analytical expression for the average molecular polarizability, α_M, of a polyatomic system with polarity corection is given by [2]

$$\alpha_M = \frac{1}{3} \left[\sum_i \sigma_i\, \alpha_{\| b_i} + \sum_j f_j\, \alpha_j + n_{df}\, \frac{\sum \chi_j^2\, \alpha_j}{\sum \chi_j^2} \right] \quad (4)$$

where $\alpha_{\| b_i}$, f_j, α_j, n_{df} and χ_j stand for bond parallel component of the polarizability, fraction of the valence electrons in the jth atom not involved in the bonding, atomic bolarizability of the jth atom, residual atomic polarizability degrees of freedom and electronegativity of the jth atom on Pauling scale, respectively. The derivative $(\partial \bar{\alpha} / \partial R)$ is given by [3]

$$\frac{\partial \bar{\alpha}}{\partial R} = \frac{1}{3} \left(\frac{\sigma}{a_0} \right) A_{12}\, N\, R^3 \quad (5)$$

where R, N and a_0 are the internuclear distance, bond order and first Bohr radius, respectively. σ is the Pauling covlent character. A_{12} is the root-mean-

Table 1. Delta-function strength in atomic units of some elements for bonds of polyatomic systems.

Atom	A	Atom	A	Atom	A	Atom	A
H	1.000	K	0.307	Rb	0.288	Cs	0.261
He	–	Ca	0.344	Sr	0.322	Ba	0.297
Li	0.394	Sc	0.348	Y	0.329	La	0.328
Be	0.481	Ti	0.374	Zr	0.341	Hf	0.337
B	0.687	V	0.386	Nb	0.365	Ta	0.362
C	0.757	Cr	0.387	Mo	0.385	W	0.386
N	0.829	Mn	0.385	Tc	0.397	Re	0.408
O	0.895	Fe	0.410	Ru	0.428	Os	0.439
F	0.953	Co	0.410	Rh	0.428	Ir	0.440
Ne	–	Ni	0.410	Pd	0.454	Pt	0.460
Na	0.340	Cu	0.444	Ag	0.422	Au	0.480
Mg	0.393	Zn	0.408	Cd	0.399	Hg	0.427
Al	0.506	Ga	0.466	In	0.465	Tl	0.466
Si	0.553	Ge	0.494	Sn	0.479	Pb	0.466
P	0.598	As	0.521	Sb	0.492	Bi	0.479
S	0.653	Se	0.571	Te	0.517	Po	0.491
Cl	0.715	Br	0.616	I	0.565	At	0.515
Ar	–	Kr	–	Xe	–	Rn	–

Table 2. Experimental and calculated polarizabilities in 10^{-25} cm^3 for some molecules $^+$.

Molecule	$\Sigma \sigma_i \alpha_{\|b_i}$	$\Sigma f_j \alpha_j$	$\Sigma 2 \alpha_{\perp i}$	α_M Cal. (PW)	Exptl.	Cal.*
$TiCl_4$	130.14	55.75	153.53	113.14	141.00	104.14
SiH_4	74.41	—	73.03	49.48	43.39	41.04
SiF_4	24.43	23.55	57.58	35.18	33.01	28.53
$SiCl_4$	138.37	55.75	124.66	106.26	111.72	100.00
$SiBr_4$	187.18	86.83	183.63	152.55	156.14	136.16
GeH_4	75.44	—	88.18	54.54	49.66	45.71
GeF_4	30.16	16.80	65.99	37.65	36.42	32.21
$GeCl_4$	145.02	55.75	138.51	113.09	121.23	106.32
$SnCl_4$	219.34	55.75	135.48	136.86	137.08	131.18
$SnBr_4$	287.57	86.50	195.29	189.78	189.07	172.22
SnI_4	461.22	116.00	252.83	276.69	277.81	253.76
$SbCl_5$	288.74	69.68	149.86	169.42	156.78	176.92
BaF_2^{*+}	16.63	11.78	73.67	34.03	38.51	33.81
$BaCl_2^{*+}$	90.77	27.87	131.26	83.30	79.81	84.72
ZrO_2^{**}	17.60	11.05	112.09	46.92	49.92	50.58
$ZnCl_2^{*+}$	28.54	27.87	150.68	69.03	67.36	60.86
$HgCl_2$	108.39	27.87	157.25	97.83	90.67	101.08
$HgBr_2$	135.75	44.45	211.59	130.59	125.96	115.96
HgI_2	193.33	56.29	254.79	168.13	164.74	170.61
SeH_2	34.78	21.19	80.71	45.56	45.73	38.43

$^+$ Exptl. and Cal.* from ref. [2].
$^{*+}$ Exptl. and Cal.* from ref. [4].
** Exptl. and Cal.* from ref. [5].
PW: Present Work.

Table 3. Experimental and calculated bond polarizability derivatives in Å^2 for some molecules.

Molecule	$\partial\bar{a}/\partial R$ Cal. (PW)	Exptl.	Ref. ^{a}	Cal. ^{b}
CH_4	0.68	1.07	[6]	—
CF_4	1.24 *	1.14	[6]	—
CCl_4	2.37	2.04, 2.38	[7, 11]	1.99
CBr_4	3.07	3.23	[7]	2.76
SiH_4	1.48	1.38	[6]	—
SiF_4	1.19 *	1.11	[6]	—
$SiCl_4$	2.24	2.12, 2.68	[10, 11]	2.03
$SiBr_4$	2.85	2.98	[7]	2.75
SiI_4	4.47	4.11	[7]	4.43
GeH_4	1.54	1.50	[6]	—
GeF_4	1.41 *	1.40	[6]	—
$GeCl_4$	2.35	2.65	[7]	2.44
$GeBr_4$	3.25	3.65	[7]	3.56
GiI_4	4.60	5.22	[7]	5.09
SnH_4	2.10	1.72	[6]	—
$SnCl_4$	3.13	3.06, 3.49	[7, 10]	3.19
$SnBr_4$	3.87	4.34, 3.68	[7, 10]	4.18
SnI_4	5.33	6.68, 6.75	[7, 10]	3.86
$TiCl_4$	1.90	3.74	[7]	1.88
$TiBr_4$	2.42	4.85	[7]	2.59
TiI_4	3.52	8±2	[7]	3.87
$ZrCl_4$	2.05	—	—	—
OsO_4	2.77	2.55	[8]	—
BCl_3	1.90	1.89	[12]	—
BBr_3	2.36	2.57	[12]	—
$HgCl_2$	3.09	2.44	[9]	—
$HgBr_2$	3.69	3.67	[9]	—
HgI_2	4.91	5.33	[9]	—

PW: Present Work; ^{a} Ref. for exptl. data; ^{b} From Ref [7].
* Values without polarity correction.

square delta function strength for heteronuclear bond determined by the relation $A_{12} = \sqrt{A_1 A_2}$, where A_1 and A_2 are the delta function strengths of the atoms 1 and 2 constituting the bond.

Results and Discussion

Delta-function strengths as calculated from (3) are collected in Table 1. These values have been used to calculate the mean molecular polarizabilities (collected in Table 2) and bond polarizability derivatives (collected in Table 3) with the help of (4) and (5), respectively. The value of bond order N involved in the calculation of bond polarizability derivatives has been taken equal to the number of electron pairs involved in bonding. Experimental and calculated values of mean molecular polarizabilities [2, 4, 5] and bond polarizability derivatives [6 – 12] reported by other workers are also listed in Tables 2 and 3 and show that our values are closerto the experimental ones than those from the literature.

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