Semiempirical study of bond and molecular polarizabilities of polyatomic molecules

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The delta-function potential model of chemical binding has been employed to compute the bond and molecular polarizabilities for seventy one molecules having five to nineteen residual atomic polarizability degrees of freedom. The experimental values of molecular polarizabilities are in good agreement with those calculated on the basis of delta-function potential model. The transferability of bond parallel component has been examined. The evaluated results will be helpful in the study of ionic-reaction, electron ionization cross section and Raman intensities.

1. INTRODUCTION

Molecular polarizabilities (Otvos & Stevenson 1956, Franklin *et al.* 1957, Beran & Kevan 1969) have played a very important role in the studies of kinetic aspects of positive ion chemistry, ion-molecule reaction cross sections, cross sections, electron ionization cross sections and Raman intensities. On account of immense utility of such data, the study of bond and molecular

polarizabilities has attracted considerable attention in recent years (Beran & Kevan 1969, Sanyal *et al.* 1972, 1973, Nagarajan 1973, Sharma *et al.* 1974). Theoretical and in few cases the experimental values of polarizabilities exist for mostly hydrocarbons and their halogen derivatives, but for most other molecular types comprehensive data are lacking. In particular, the data on silicon and germanium compounds are limited. Recent interest in the ionic reaction (King & Elleman 1968) and electron ionization cross sections (Beran and Kevan 1969) has created a need for polarizability data on different compounds. We have, therefore, evaluated bond and molecular polarizabilities for different types of compounds especially for silicon and germanium.

2. POLARIZABILITY EVALUATION

Among the different semiempirical methods used for the calculation of polarizabilities, the calculation of bond and molecular polarizabilities using deltafunction potential model of chemical binding, proposed by Lippincott & Stutman (1964) has gained wide popularity now-a-days. In this model the Coulombic potentials are replaced by delta-function potentials in the Schroedinger equation of a molecular system. The linear combinations of atomic delta-function wave functions are used to obtain molecular wave functions.

Molecular polarizability is composed of bond parallel and perpendicular components. The bond parallel component is obtained from the contribution of two sources, namely, the bond region electrons and non-bond region electrons. The contribution by the bond region electrons is calculated by using a linear combination of atomic delta-function wave functions representing the two nuclei involved in the bond. This is the expectation values of the electronic position squared $<x^2>$ along the bond axis and used to compute the bond parallel component of the polarizability $\alpha_{\parallel b}$ from the expression

$$\alpha_{\parallel b} = \frac{4n\ A_{ij}}{a_0}\ (<x^2>)^2 , \tag{1}$$

where n is the bond order A_{ij} is the root mean-square delta-function strength of the nuclei i, and j, involved in the bond ij, and a_0 is the Bohr radius. The expectation value $<x^2>$ is evaluated from relation,

$$<x^2> = \frac{R^2}{4} + \frac{1}{2C_{ij}^2} ,$$ where R is the internuclear distance at the

equilibrium configuration and $C_{R\ ij}$ is the root mean-square value of $C_{R_{ij}}$ and $C_{R_{ij}}$ which are known from principal quantum number and column number in the periodic table. For a heteronuclear bond, a polarity correction is introduced using the Pauling's scale of electronegativities (Pauling 1960) to determine the percent covalent character; accordingly the expression with polarity correction is given as $\alpha_{iij} = \alpha_{iib}$ σ where $\sigma = \exp\ [-(\frac{1}{4})$ $(X_i - X_j)^2]$. Here X_i and X_j are the electronegativities of the atoms i, and j, respectively on the Pauling's scale.

The contribution of the non-bonded region electrons to the bond parallel component of the polarizability α_{in} is calculated from the fraction of remaining electrons not involved in the bonding and the atomic polarizability of the atom concerned. This is analytically expressed as $\Sigma\ \alpha_{iin} = \Sigma\ f_i\ \alpha$ where f_i is the fraction of electrons in the ith atom not involved in bonding and α_i the atomic polarizability of the atom obtainable from the delta-function strength A_i

The sum of the bond perpendicular components of the bond polarizability is obtained by an empirical approach made by Lippincott & Stutman (1964), which is given by the expression

$$\Sigma\ 2\alpha_{\perp i}\ =\ (3N\ -\ 2n_b)\ \frac{\Sigma\ X_i^2\ \alpha_i}{\Sigma\ X_i^2} \tag{2}$$

Here, N is the number of atoms in the molecule, n_b the number of bonds in the molecule, X_i the electronegativity of the ith atom on Pauling's scale (1960), and α_i the atomic polarizability of the i th atom. The term $(3N-2n_b)$ gives the number of remaining (residual) atomic polarizability degrees of freedom, denoted by n_{df}. This is obtained from the knowledge of the symmetry of geometry of the molecular system.

Now the analytical expression for the average or mean molecular polarizability for a polyatomic molecule with polarity correction is given by

$$\alpha_M = \frac{1}{3}\ \Sigma_i\ \sigma_i\ \alpha_{iibi} + \Sigma\ f_i\ \alpha_i + n_{df}\ \frac{\Sigma\ X_i^2\ \alpha_i}{\Sigma\ X_i^2} \tag{3}$$

Eq. (3) has been applied to many polyatomic molecules by using atomic polarizabilities, parallel bond polarizabilities, Pauling's electronegativities and

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delta-functon strength A values, tabulated by Nagarajan (1973) together with
the experimental bond length in the molecules which have been currently
reported in literature, Sutton 1958, Kennard *et al*. 1970, *Durig et al*. 1968,
1969, 1970, 1971, 1972, 1973, 1974, Carney *et al*. 1961, Rankin and Robertson
1975, Sverdlov & Razbegaeva 1974.

3. RESULTS AND DISCUSSION

The molecules under present study have been classified according to their
respective number of residual atomic polarizability degrees of freedom ranging
from five to nineteen. The individual values of bond parallel component
($\Sigma\ \alpha_{\parallel p}$) contribution from non-bonded region electrons, bond perpendicular
component and mean molecular polarizability for each molecule are collected
in table 1. In the last column of the table 1 the experimental values of
mean molecular polarizability have been included for a few molecule for
which the data are available in literature Smyth & McAlpine 1934, Landot
& Bornstein 1950, Le Fevre and Le Fevre 1954, Lippincott & Stutman 1964,
Rao *et al*. 1967. It is apparent from the table 1 that the calculated values
are in good agreement with the experimental ones. This shows the sound-
ness of the method followed here.

The bond perpendicular component is a linear combination of atomic
polarizabilities and independent of internuclear distance and hence may be
transferred from one molecular system to another for the same pair of atoms.
The bond parallel component depends on internuclear distance and, therefore.
it is not readily transferable from one molecular system to another. However,
in cases where the internuclear distances are nearly identical, it is transfer-
able. In order to examine the transferability of bond parallel component
among different molecules, we have collected the values of bond parallel
component for individual bond in table 2 and are compared with experi-
mental values reported in literature Rao *et al*. 1967, Lippincott & Stutman
1964, Rendell *et al*. 1975. It is seen from table 2 that the values are well
comparable and, therefore, the bond parallel component is transferable in
these molecules. The small changes in values of bond parallel components
from one molecular system to another may be on account of slight difference
in bond lengths. Thus, the present study leads us to conclude that the delta-
function potential model is very useful for the evaluation of bond and mole-
cular polarizabilities. The results of this investigation will be helpful in
the study of ionic reaction, electron ionization cross sections, and Raman
intensities, particularly, for the compouds involving silicon and germanium.

Table 1. Calculated values of molecular polarizabilities in 10^{-25} cm^3 for molecules of different atomic polarizability degrees of freedom

Molecule	n_{d}	$\Sigma\,\alpha_{IIp}$	$\Sigma\,\alpha_{IIn}$	$\Sigma\,^2\alpha_{\perp}$	α_M (cal.)	α_M (expt.)
SH_2	5	25.512	14.233	61 596	33 781	36.4*
O_3	5	46.759	16.680	41 450	34.930	
Se H_2	5	35.910	16.827	67.763	40 166	45 73*
S Cl_2	5	101.342	42.108	87 859	77 103	
CO_2	6	23.260	11.053	56.337	30 217	26.5††
COS	6	52.477	19.760	77.726	49 988	
CS_2	6	78.821	28.467	112.800	73 362	87 4††
COSe	6	68.234	22.353	82.248	57 612	
CSTe	6	118.627	39.580	137 219	98 475	
Cl_2CO	6	74.212	33.401	76 026	61 213	65.778**
S_2Cl_2	6	153.960	56.341	110 076	106 792	
BCl_3	7	75.036	41.811	116 358	77 735	80.05*
CH_4	7	27.755	0	55 687	27.814	26.0††
CBr_4	7	182 784	88 903	167 283	145.323	
CI_4	7	267.477	101.897	185 612	184.995	
$CHCl_3$	7	103.381	41.811	102 370	82 521	82 30*
GeH_2Cl_2	7	131 176	27 874	112.584	90 543	
GeH_2Br_2	7	163.085	44 451	150.702	119 413	
GeH_2I_2	7	227.262	50.948	160 261	146 157	
$C_2Cl_2O_2$	8	110.095	38.927	92 005	80 342	
$C_2Br_2O_2$	8	121.031	55.505	118.593	98 376	
$ClCH_2CN$	8	143.236	13.937	64.862	74.012	
$BrCH_2CN$	8	152.158	22.226	89 663	88 016	
ICH_2CN	8	181 618	25.208	109.630	105 485	
CH_3AsF_2	9	72 464	11.777	83.684	55 975	
CH_3AsCl_2	9	142.478	27.874	127 733	99 362	
CH_3AsBr_2	9	196.303	44 451	161 441	134.065	
CH_3AsI_2	9	297.745	55.417	166.974	171.712	
B_2F_4	10	45 144	23.554	82 255	50 318	
B_2Cl_4	10	127.415	55.748	167.709	116.957	
P_2F_4	10	115.771	45 794	94.050	85 205	
C_2H_4	10	38.971	0	91.466	43 479	42.60*
C_2F_6	10	65.712	35.331	76.568	59.204	46†
C_2Cl_6	10	214 081	83.623	157 788	151 830	155 5*†
C_2Br_6	10	284 993	133.354	233.624	217.324	
Si_2F_6	10	122.233	35.331	83 249	80 271	
$CSiCl_6$	10	244.978	83.623	167.030	165.210	
CH_3SiH_2Cl	10	134.613	13.937	113.298	87.283	
CH_3SiHCl_2	10	151 578	27.874	128.860	102.771	

Table 1 (*Contd.*)

Molecule	n_{dl}	$\Sigma 2\alpha_{llp}$	$\Sigma \alpha_{lln}$	$\Sigma \alpha_l$	α_M (cal.)	α_M (expt.)
CH_2ClSiH_3	10	142.920	13.937	113.298	90.052	
$CHCl_2SiH_3$	10	168.019	27.874	128.862	108.252	
CH_3GeH_3	10	119.686	0	105.937	75.540	
CH_3GeCl_3	10	192.852	41.814	149.143	127.936	
CH_3GeBr_3	10	240.716	66.667	197.317	168.239	
H_3PBH_3	10	167.175	0	101.956	89.710	
Cl_3PBH_3	10	236.941	41.811	147.249	142.001	
CH_3CHCl_2	10	103.461	27.874	117.989	83.108	
CH_2CHBF_2	10	90.705	20.008	88.400	63.627	
CH_2CHGeH_3	11	143.128	0	121.591	88.240	
$CH_2CHGeCl_3$	11	218.018	41.811	162.566	140.800	
$CH_2CHGeBr_3$	11	265.883	66.667	209.149	180.569	
$CH_3CH_2SiH_3$	13	147.818	0	133.017	93.612	
$CH_3CH_2SiCl_3$	13	176.378	41.811	168.066	128.752	
$CH_3CH_2SiBr_3$	13	211.461	66.677	263.179	183.772	
$(CH_3)_2O_3$	13	87.464	16.580	108.614	70.886	
$(CH_3)_2GeH_2$	13	158.860	0	148.109	202.323	
$CH_3CH_2GeH_3$	13	151.940	0	144.666	98.868	
$CH_3CH_2GeCl_3$	13	226.830	41.811	176.446	148.362	
$CH_3CH_2GeBr_3$	13	274.694	66.667	222.471	187.947	
$(CH_3)_3CH$	16	131.286	0	139.756	90.347	
$(CH_3)_3C$ Cl	16	159.737	13.937	157.156	110.277	98.0*†
$(CH_3)_3CBr$	16	171.472	22.226	172.233	121.977	111.0*†
$(CH_3)_3SiH$	16	186.720	0	148.829	121.850	
$(CH_3)_3SiF$	16	170.165	5.888	143.887	106.647	
$(CH_3)_3SiCl$	16	205.097	13.937	166.382	128.472	
$(CH_3)_3GeH$	16	197.784	0	158.841	118.875	
$(CH_3)_3GeCl$	16	216.350	13.937	175.836	135.374	
$(CH_3)_3GeBr$	16	232.305	22.225	192.375	148.968	
$(CH_3)_3GeI$	16	264.393	50.948	192.237	169.193	
$(C_2H_3)_3B$	18	202.430	0	182.903	128.444	
$(CH_3)_3PBH_3$	19	282.855	0	182.464	155.106	

** Smyth & McAlkine (1934)
† Landolt & Bornstein (1950)
* Lippincott & Stutman (1964)
†† Rao *et al.* (1967)
*† LeFevre & LeFevre (1954)

Table 2. Bond parallel components of palarizability (in 10^{-25} cm^3) for Individual bonds

Bond	(Cal.)	(exp)
C-C	19.8	18 8
C-H	6.8	7 9
C-F	7.2	7.1
C-Cl	33.3	36 7
C-Cl ($C_2Cl_2O_2$)	28.0	25 8 ($C_2H_2I_2$)
C-Br	45.1	50 4
C-Br ($C_2Br_2O_2$)	36.9	37.2 ($C_2H_2Br_2$)
C-I	66.8	57 9 ($C_2H_2Cl_2$)
C=O	18 2	19 9
C=Se	56.6	—
C=Te	78.0	—
Si-H	19.5	10 8
Si-C	36.2	—
Si-Si	82.4	—
Si-F	6.9	8 2
Si-Cl	37 1	37 2
B-B	29 4	—
B-Cl	24.4	—
P-P	78.0	—
P.F	9.4	—
S-H	12 7	—
S-Cl	52.9	—
S-S	43 7	—
Se-H	17.9	—

*Rao *et al.* (1967) ; †Lippincott and Stutman (1964) ; **Rendell *et al.* (1915)

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