Bond and Molecular Polarizabilities in some Polyatomic Molecules

G. Nagarajan

Department of Chemistry, University of Maryland, College Park, Maryland, U.S.A.

(Z. Naturforschg. **21 a**, 238—243 [1966]; received 11 June 1965)

The delta-function potential model and its application to the calculations of bond region as well as nonbond region electron contributions to the parallel component and bond perpendicular component are briefly surveyed. The Lewis–Langmuir octet rule modified by Linnett as a double-quartet of electrons is employed. The calculations of bond and molecular polarizabilities have been made by the Lippincott–Stutman method for 109 molecules having six, seven, eight, ten, twelve and thirteen as the residual atomic polarizability degrees of freedom. The available experimental values of the molecular polarizabilities are in good agreement with the calculated ones.

One of the fundamental electrical properties of a molecular system is the molecular polarizability which cannot be directly measured but can only be deduced from dielectric constant and index of refraction through the well-known relations such as Clausius–Mossotti equation, Langevin–Debye equation and Lorentz–Lorentz equation. However, an average molecular polarizability may be obtained by averaging the three dicretional diagonal components of the polarizability tensor i. e.,

$$\text{if } \alpha = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix},$$

then $\alpha_M = (1/3)\,(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$.

Several investigators in recent years have computed in many ways, on the basis of quantum mechanical models, the atomic and molecular molarizabilities for many molecules and ions in order to test how far the polarizability could be a useful criterion for testing the accuracy of wave functions adopted. The most recent one is the delta-function potential model initiated by Frost[1] and modified by Lippincott[2] which yields very encouraging values of D_e, ω_e, $\omega_e x_e$ and r_e for many diatomics and bonds of polyatomic molecules according to the investigations of Lippincott and Dayhoff[3]. The model assumes that at each nucleus there exists a potential which is infinite and that everywhere else the potential is zero. The integral of the potential over all space is however finite and equal to a parameter called the "delta-function strength" or "reduced electronegativity". At each nucleus, then, a delta-function wave function is generated representing the probability amplitude of the electron for this isolated nucleus. These delta-function atomic orbitals are then linearly combined to form molecular orbitals with the restriction that only two atoms may interact at a time and only if bonds are believed to exist between the atoms. The major advantage of a delta-function model lies in its one-dimensional nature. Lippincott and Stutman[4] recently applied this semi-empirical model in generating component polarizabilities in order to compute the molecular or average polarizabilities with the expression $\alpha_M = (1/3)\,(\alpha_1 + \alpha_2 + \alpha_3)$ where α_1, α_2 and α_3 refer to the three principal polarizability components. It is the aim of the present investigation to evaluate the polarizabilities (bond and molecular) of some polyatomic molecules with varying residual atomic polarizability degrees of freedom by the Lippincott–Stutman method[4] employing such delta-function model of chemical binding.

Parallel Component of the Polarizability

According to the method developed by Lippincott and Stutman[4], the molecular polarizability is composed mainly of bond parallel components obtainable from the molecular delta-function model and bond perpendicular components obtainable from the atomic delta-function polarizabilities. The contribution to the parallel component of the polarizability by the bond region electrons is calculated using a linear combination of atomic delta-function wave

---

[1] A. A. Frost, J. Chem. Phys. **22**, 1613 [1954]; **23**, 985 [1955]; **25**, 1150 [1956].

[2] E. R. Lippincott, J. Chem. Phys. **23**, 603 [1955]; **26**, 1678 [1957].

[3] E. R. Lippincott and M. O. Dayhoff, Spectrochim. Acta **16**, 807 [1960].

[4] E. R. Lippincott and J. M. Stutman, J. Phys. Chem. **68**, 2926 [1964].

functions representing the two nuclei involved in the bond i. e., the expectation value of the electronic position squared $\langle x^2\rangle$ along the bond axis is calculated and the analytical expression for the parallel component of the polarizability is given as

$$\alpha_{\parallel b} = 4\, n\, A_{12}\, (1/a_0)\, (\langle x^2\rangle)^2$$

where n is the bond order, A_{12} the root mean-square delta-function strength of the two nuclei, a_0 the radius of the first BOHR orbit of atomic hydrogen and $\langle x^2\rangle$ the mean-square position of a bonding electron and is expressed as

$$\langle x^2\rangle = (R^2/4) + (1/2\, c R_{12}^2)\ .$$

Here R is the internuclear distance at the equilibrium configuration. This clearly demonstrates an explicit dependence of $\langle x^2\rangle$ on R^2 or alternatively indicates that $\alpha_{\parallel b}$ is proportional to R^4. It is to be noted that GOSS [5] and CLARK [6] developed a linear empirical relationship between the mean polarizability and R^3 while DENBIGH [7] found a linear empirical relationship between the parallel component and R^3 for different bond types. However, the dependence of the parallel component of the polarizability on the fourth power of the internuclear distance derived by LIPPINCOTT and STUTMAN [4] is quite useful and approximates to an unusually simple form for the contribution by the bond region electrons to the parallel component of the polarizability. The influence of nonbond region electrons is not accounted for in the above expression.

In the case that the bond is of the heteronuclear type, a polarity correction is introduced using PAULING's scale of electronegativities [8] to determine the percent covalent character believed to exist. Then the expression for the parallel component of the polarizability by introducing the polarity correction is given as $\alpha_{\parallel p} = \alpha'_{\parallel b}\, \sigma$ where

$$\sigma = \exp[-(1/4)\,(X_1 - X_2)^2]\,.$$

Here X_1 and X_2 are the PAULING's electronegativities of the two atoms involved in bonding.

Contribution by the Nonbond Region Electrons

The contribution by the nonbond region electrons to the parallel component of the polarizability $\alpha_{\parallel n}$ is calculated from the remaining electrons in the valence shell of each atom not involved in bonding and the atomic polarizability of the concerned atom. The basis for such calculation is the LEWIS–LANGMUIR octet rule [9, 10] modified by LINNETT [11] as a double-quartet of electrons. As an example, the electronic configuration of O_2 molecule in the ground state is represented by

$$\begin{array}{cccccccc} & \bullet & & \times & & & & \bullet \\ \times & \bullet & \mathrm{O} & \times & \bullet & \mathrm{O} & \times & \bullet \\ & \bullet & & \times & & & & \bullet \end{array}$$

where the "dots" represent the electrons with spin quantum number of $+1/2$ and the "crosses" the electrons with spin quantum number of $-1/2$ or vice versa. The above configuration is the most stable one to represent the ground state of O_2 molecule, not the conventional double bond. One may refer to LINNETT [11] for a detailed discussion on this regard. Since each oxygen atom in its ground electronic state has four electrons which are not involved in bonding, the contribution by the nonbond region electrons to the parallel component of the polarizability is written as $\alpha_{\parallel n} = (4/3)\,\alpha_0$ where α_0 is the atomic polarizability of the oxygen atom. This may analytically be expressed as $\Sigma\, \alpha_{\parallel n} = \Sigma\, f_j\, \alpha_j$ where f_j is the fraction of the electrons in the jth atom not involved in bonding and α_j the atomic polarizability of the jth atom obtainable from the delta-function strength A_j.

In the case of a diatomic molecule, the total parallel component of the polarizability is given as

$$\alpha_{\parallel} = \alpha_{\parallel p} + f_1\, \alpha_1 + f_2\, \alpha_2$$

where f_1, f_2, α_1 and α_2 refer to the fraction of electrons not involved in bonding and the atomic polarizabilities of atom 1 and atom 2, respectively. In the case of a polyatomic molecule, the bond angular considerations must be employed to calculate these components. However, since most of the experimental data involve the use of either the LANGEVIN–DEBYE or LORENTZ–LORENTZ equation which assumes spherical local fields and yields isotropic (average) polarizabilities, it is well adopted here to calculate the average values over the three components as described in the introduction of this text.

---

[5] F. R. GOSS, Proc. Leeds Phil. Lit. Soc. Sci. Sect. **3**, 23 [1936].

[6] C. H. D. CLARK, Proc. Leeds Phil. Lit. Soc. Sci. Sect. **3**, 208 [1936].

[7] K. G. DENBIGH, Trans. Faraday Soc. **36**, 936 [1940].

[8] L. PAULING, The Nature of the Chemical Bond, Cornell University Press, Ithaca, New York 1960.

[9] G. N. LEWIS, J. Am. Chem. Soc. **38**, 762 [1916].

[10] I. LANGMUIR, J. Am. Chem. Soc. **38**, 2221 [1916].

[11] J. W. LINNETT, J. Am. Chem. Soc. **83**, 2643 [1961].

Perpendicular Component of the Polarizability

The perpendicular component of a diatomic molecule is, according to the method of Lippincott and Stutman [4], simply the sum of the two atomic polarizabilities. In a polar bond it would take on more of the character of the more electronegative element where more charge is located. The analytical expression for the perpendicular component of the polarizability is given as $\alpha_{\perp} = 2\,\alpha_A$ for a nonpolar A_2 molecule and in the case of an $A-B$ molecule

$$\alpha\perp = 2\,(X_A{}^2\,\alpha_A + X_B{}^2\,\alpha_B)/(X_A{}^2 + X_B{}^2)$$

where X refers to the electronegativity of the atom on Pauling's scale. This gives a greater contribution to the bond perpendicular component for the atom which has in its vicinity a large charge distribution. Extending this princple to a polyatomic molecule, the analytical expression for the sum of all the perpendicular components is, according to Lippincott and Stutman [4], given as follows:

$$\Sigma\, 2\,\alpha\perp = n_{\mathrm{df}}\;(\Sigma\, X_j^2\,\alpha_j)/(\Sigma\, X_j^2)$$

where n_{df} is the number of residual atomic polarizability degrees of freedom. n_{df} is directly obtained from a consideration of the symmetry of the molecular system and the assumption that every isolated atom is allowed to posses three degrees of polarizability freedom and every bond which is formed between two atoms removes two of these degrees of freedom with the exception that 1) if two bonds are formed from the same atom (carbon in carbon dioxide) and exist in a linear configuration, then only three atomic degrees of freedom are lost, and 2) if three bonds are formed from the same atom (sulphur in sulphur trioxide) and exist in a plane, then only five atomic degrees of freedom are lost. One may refer to Lippincott and Stutman [4] for a detailed discussion on this regard.

Results

The molecular structural data used for such calculations were taken from Sutton [12] and the electron diffraction and microwave studies. The Lewis–Langmuir octet rule [9, 10] modified by Linnett [11] has been adopted here as a double-quartet of electrons rather than as four pairs for all the molecules having the elements in and beyond the fourth group of the periodic table. The molecules for which the bond and molecular polarizibilities have been calculated here from the delta-function potential model are classified according to their respective numbers of residual atomic polarizability degrees of freedom and the calculated values in 10^{-25} cm^3 are given in Tables

Molecules	$\Sigma\,\alpha_{\parallel p}$	$\Sigma\, 2\,\alpha_{\perp}$	$\Sigma\,\alpha_{\parallel n}$	α_M (calcd)	α_M (obsd)
AsH_3	61.096	73.268	13.208	49.191	
AsF_3	34.809	42.379	25.808	34.332	
$AsCl_3$	183.591	98.098	48.899	110.196	112.933[a]
$AsBr_3$	211.673	128.329	63.121	134.375	
AsI_3	320.930	181.801	89.631	197.454	
SbH_3	89.515	90.467	19.456	66.479	
SbF_3	58.184	47.757	32.056	45.999	
$SbCl_3$	192.286	107.877	55.147	118.437	
$SbBr_3$	257.075	139.797	69.367	155.413	
SbI_3	352.945	196.648	95.879	215.157	
$BiCl_3$	214.310	159.610	84.391	152.770	
$BiBr_3$	266.914	198.166	98.611	187.897	
SOF_2	41.039	39.969	20.387	33.798	
$SOCl_2$	129.286	71.689	35.781	78.919	83.214[b]
$SOBr_2$	173.022	86.124	45.261	101.469	
H_2O_2	28.296	35.520	7.893	23.903	
O_2F_2	63.793	32.054	16.294	37.380	
H_2S_2	85.703	78.719	24.267	62.896	
S_2F_2 (trans)	72.604	51.816	32.667	52.604	
S_2F_2 (pyramidal)	68.472	51.816	32.667	50.985	

[a] U. Grassi and L. Pucciante, Nuovo Cimento **14**, 461 [1937].

[b] I. E. Coop and L. E. Sutton, Trans. Faraday Soc. **35**, 505 [1939].

Table 1. Observed and calculated polarizabilities in 10^{-25} cm^3 for molecules with six residual atomic polarizability degrees of freedom.

---

[12] L. E. Sutton, Tables of Interatomic Distances and Configuration in Molecules and Ions, The Chemical Society, Special Publication No. 11, London 1958.

Molecules	$\Sigma\alpha_{\|\mathrm{p}}$	$\Sigma 2\alpha_{\perp}$	$\Sigma\alpha_{\|\mathrm{n}}$	α_{M} (calcd)	α_{M} (obsd)
SiH_3F	62.616	54.658	4.200	40.491	
SiH_3Cl	93.980	82.464	11.897	62.780	
SiH_3Br	110.501	94.247	16.636	73.795	
SiH_3I	141.015	111.187	25.473	92.558	
SiF_3H	37.652	45.046	12.599	31.766	
$SiCl_3H$	127.001	100.541	35.690	87.744	
$SiBr_3H$	166.445	130.128	49.909	115.494	
SiF_3Cl	53.819	53.096	24.496	43.804	
SiF_3Br	73.779	57.368	29.236	53.461	
$SiCl_3Br$	167.182	114.659	52.326	111.389	
SiH_2F_2	50.439	48.588	8.400	35.809	
SiH_2Cl_2	107.989	92.883	23.793	74.888	
SiH_2Br_2	155.008	114.406	33.273	100.895	
SiF_2Br_2	111.477	76.703	41.672	76.618	
GeH_3F	69.248	60.665	4.200	44.704	
GeH_3Cl	104.236	90.122	11.897	68.752	66.967[a]
GeH_3Br	120.680	102.271	16.636	79.862	
GeH_3I	158.050	119.772	25.473	101.098	
$GeHCl_3$	146.919	106.170	35.690	96.260	
GeF_3Cl	64.498	56.334	24.496	48.443	

[a] C. P. Smyth, A. J. Grossman, and S. R. Ginsbury, J. Am. Chem. Soc. **62**, 192 [1940].

Table 2. Observed and calculated polarizabilities in 10^{-25} cm^3 for molecules with seven residual atomic polarizability degrees of freedom.

Molecules	$\Sigma\alpha_{\|\mathrm{p}}$	$\Sigma 2\alpha_{\perp}$	$\Sigma\alpha_{\|\mathrm{n}}$	α_{M} (calcd)	α_{M} (obsd)
Al_2Cl_6	284.490	126.609	63.451	158.183	
Al_2Br_6	381.483	169.089	88.731	213.101	
Al_2I_6	693.111	245.869	135.863	358.281	
Ga_2Cl_6	342.156	140.464	63.451	182.024	
Ga_2Br_6	429.275	184.288	88.731	234.098	
Ga_2I_6	628.210	263.353	135.863	342.475	
In_2Cl_6	507.132	161.155	63.451	243.913	
In_2Br_6	632.232	207.158	88.731	309.374	
In_2I_6	923.268	290.058	135.863	449.729	
HCOOH	38.353	52.237	7.894	32.828	33.682[a]
C_2H_5N	87.431	58.720	2.972	49.708	
CCl_4S	188.676	111.267	59.822	119.922	
PF_5	47.603	47.045	20.999	38.549	36.455[b]
PCl_5	257.667	118.030	59.483	145.060	
PF_3Cl_2	122.979	66.971	36.394	75.448	
$SbCl_5$	312.544	131.692	59.486	167.907	156.758[b]
$SiCl_3SH$	191.449	119.595	47.825	119.623	
NFO_3	69.607	47.006	18.013	44.875	

[a] C. T. Zahn, Phys. Rev. **37**, 1516 [1931].

[b] S. S. Batsanov, Refractometry and Chemical Structure, Translated by P. P. Sutton from Russian to English, Consultants Bureau, New York 1961.

Table 3. Observed and calculated polarizabilities in 10^{-25} cm^3 for molecules with eight residual atomic polarizability degrees of freedom.

from 1 to 6. The available experimental values of dielectric constants and refractive indices were used to obtain the molecular polarizabilities through the well-known Langevin–Debye and Lorentz–Lorentz equations and thus the obtained values in 10^{-25} cm^3 are also given in Tables from 1 to 6. The electronic structures adopted here for the aluminium, gallium, and indium halides (see Table 3) are in accordance with the suggestion of Fajans[13]. Whether the H_2O_2, O_2F_2, H_2S_2 and S_2F_2 molecules (see Table 1) possess a *cis* or *trans* configuration, the molecular polarizability values are not changed as the number of residual atomic polarizability degrees of freedom remains the same. Recently, two kinds of structures, namely, *trans* and *pyramidal,* were proposed for the

---

[13] K. Fajans, Z. Elektrochem. **34**, 502 [1928].

Molecules	$\Sigma\alpha_{\|p}$	$\Sigma 2\alpha_{\perp}$	$\Sigma\alpha_{\|n}$	α_M(calcd)	α_M(obsd)
Si_2H_6	186.676	106.334	0	97.670	93.992[a]
Si_2Cl_6	312.544	155.943	71.383	179.956	
SiF_3CH_3	74.856	66.665	12.600	51.376	
$SiCl_3CH_3$	180.441	122.892	35.691	113.008	
$SiBr_3CH_3$	202.930	149.823	49.911	134.221	
SiH_3CH_3	110.976	87.545	0	66.160	
SiH_2FCH_3	98.587	77.171	4.200	59.986	
$SiHF_2CH_3$	84.922	70.889	8.400	54.737	
Ge_2H_6	203.219	123.253	0	108.824	
GeH_3CH_3	119.069	95.256	0	71.441	
SnH_3CH_3	164.682	107.945	0	90.876	
$SnCl_3CH_3$	252.190	137.671	35.691	141.851	
$SnBr_3CH_3$	299.185	165.715	49.911	171.604	
SnI_3CH_3	422.050	209.065	76.423	235.846	
$B(OH)_3$	31.892	64.876	11.841	36.203	40.656[b]
CH_3N_3	66.969	73.162	8.916	49.682	
CH_3COH	63.555	70.582	3.947	46.028	45.966[c]
CH_3COF	63.864	65.115	8.147	45.709	
CH_3COCl	91.107	84.719	15.844	63.890	66.571[c]
CH_3COBr	104.117	92.812	20.584	72.504	

[a] E. C. Hurdis and C. P. Smyth, J. Am. Chem. Soc. **65**, 89 [1943].
[b] as ref. [b] of Table 3.
[c] C. T. Zahn, Phys. Z. **33**, 686 [1932].

Table 4. Observed and calculated polarizabilities in 10^{-25} cm^3 for molecules with ten residual atomic polarizability degrees of freedom.

Molecules	$\Sigma\alpha_{\|p}$	$\Sigma 2\alpha_{\perp}$	$\Sigma\alpha_{\|n}$	α_M(calcd)	α_M(obsd)
$P(CN)_3$	171.882	116.835	18.384	102.367	
$P_3Cl_6N_3$	358.800	160.877	77.327	199.001	
CF_3SF_5	135.046	68.505	33.600	79.050	
C_3H_3N	82.273	96.213	2.972	60.486	61.816[a]
$C_3H_3N_3$	132.641	94.060	8.916	78.539	
$(CH_3)_2NH$	76.640	85.210	2.972	54.941	59.835[b]
$C_2H_2O_4$	87.720	79.274	15.787	60.927	
$1:1\text{-}C_2H_4ClNO_2$	133.515	93.091	21.764	82.790	86.780[c]
CH_3COCN	97.341	90.420	6.919	64.893	
C_3H_6	86.796	90.250	0	59.015	60.231[d]
C_3F_6	92.916	56.698	25.200	58.271	
C_3H_5Cl	117.972	105.742	11.897	78.537	80.836[e]
C_3H_5Br	130.430	114.988	16.637	87.352	
C_3H_5I	151.983	127.533	25.474	101.663	
$1:3\text{-}C_3H_4Cl_2$	149.148	118.620	23.794	97.187	100.649[f]
C_2H_5N	96.874	91.754	2.972	63.867	

[a] as ref. [a] of Table 4.
[b] R. Sanger, O. Steiger, and K. Gachter, Helv. Phys. Acta **5**, 200 [1932].
[c] E. C. Hurdis and C. P. Smyth, J. Am. Chem. Soc. **64**, 2829 [1942].
[d] H. E. Watson, G. P. Kane, and K. L. Ramaswamy, Proc. Roy. Soc. London A **156**, 130, 144 [1936].
[e] N. B. Hannay and C. P. Smyth, J. Am. Chem. Soc. **68**, 1005 [1946].
[f] R. A. Oriani and C. P. Smyth, J. Chem. Phys. **17**, 1174 [1949].

Table 5. Observed and calculated polarizabilities in 10^{-25} cm^3 for molecules with twelve residual atomic polarizability degrees of freedom.

S_2F_2 molecule by Kuczkowski[14] from his microwave studies. However, the molecular polarizability values are not much altered as the contribution by the nonbond region electrons and the sum of all the perpendicular components remain the same for both configurations.

It is seen from the good agreement between the observed and calculated values of the molecular polarizabilities that the present investigation further testifies in addition to the previous study[4] that the delta-function potential model is more satisfactory than any other model so far developed. Thus the model gives explicit expressions for the parallel and

---

[14] R. L. Kuczkowski, J. Am. Chem. Soc. **86**, 3617 [1964].

Molecules	$\Sigma\alpha_{\parallel p}$	$\Sigma 2\alpha_{\perp}$	$\Sigma\alpha_{\parallel n}$	α_M(calcd)	α_M(obsd)
$(CH_3)_2AlCl$	154.058	127.377	11.897	97.777	
$(CH_3)_2AlBr$	167.024	137.613	16.637	107.091	
$(CH_3)_2AsCl$	184.490	134.076	25.105	114.557	
$(CH_3)_2AsBr$	202.261	144.113	29.845	125.406	
$(CH_3)_2AsI$	230.798	157.738	38.682	142.406	
$(CH_3)_2SnCl_2$	273.437	150.953	23.794	149.395	
$(CH_3)_2SnBr_2$	308.013	169.246	33.274	170.178	
$(CH_3)_2SnI_2$	386.047	195.044	50.949	210.680	
$(CH_3)_2SiF_2$	125.288	93.296	8.400	75.661	
$(CH_3)_2SiCl_2$	180.147	135.084	23.794	113.008	
$(CH_3)_2SiBr_2$	217.927	152.742	33.274	134.648	
$(CH_3)_2SiH_2$	158.665	109.035	0	89.233	
$(CH_3)_2SiClF$	152.718	112.014	16.097	93.610	
$(CH_3)_2CO$	97.901	93.334	3.947	65.061	64.193[a]
C_3H_4O	89.657	96.304	3.947	63.303	63.797[b]

[a] as ref. [c] of Table 4.

[b] N. B. Hannay and C. P. Smyth, J. Am. Chem. Soc. **68**, 1357 [1946]

Table 6. Observed and calculated polarizabilities in 10^{-25} cm^3 for molecules with thirteen residual atomic polarizability degrees of freedom.

perpendicular components and the mean polarizabilities. All these are in accordance with the investigations of Denbigh [7] in which the molar refraction of a molecule is assumed to be the sum of the refractions of all the bonds in the molecule and similarly, the molecular polarizability is assumed to be the sum of the bond polarizabilities. The polarizability contributions from the bond region electrons and those from nonbond region electrons are clearly distinguished. The sum of all the perpendicular components in a molecule is a linear combination of atomic polarizabilities and is independent of the internuclear distances. Hence the perpendicular component will always be transferable from one molecular system to another having similar chemical bonds irrespective of the accuracy of the internuclear distances in both systems involved, but such a transfer would be well possible in the case of parallel component only when the internuclear distances in the two systems are nearly identical. Hence, very reliable values of the bond as well as molecular polarizabilities would be obtained only when the internuclear distances were very accurately determined.