Vol. 80 (1991) *ACTA PHYSICA POLONICA A* No 4

QUANTUM MECHANICAL STUDIES OF BOND AND MOLECULAR POLARIZABILITIES OF GAS-PHASE METAL HALIDES

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(Received July 5, 1991; in final version September 11, 1991)

The bond and molecular polarizabilities are studied for the gas-phase metal halides using delta-function potential model of chemical binding on the basis of quantum mechanical approach. The applicability of the model is demonstrated. The contribution of the polarity corrections for the metal halides is thoroughly investigated and it has been found that it plays a significant role for fluorides. Our polarizability calculations resolve the discrepancy about the conformation of the barium dichloride and mercury dichloride and favour the nonlinear structure. Due to lack of experimental results for most of halides of transition metals, the decision whether to incorporate polarity corrections or not remains uncertain at this stage: we must await measurements of more experimental values before we reach any final conclusion. The ionic bond orders have been used for the first time to investigate polarizabilities of monomers and dimers of alkali halides. The results for dimers reveal that polarity contribution is essential for the lithium halides dimers and not for other dimers. The computed results will be asset for the interpretation of experimental measurements.

PACS numbers: 31.10.+z, 31.90.+s

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1. Introduction

Theoretical studies of the weak interactions between static external or internal fields of the electrons of an atom or molecule can increase our understanding of the electronic structure of a system and aid in the interpretation of experimental measurements. In this regard the delta-function potential model has played an important role in investigating a number of properties related to molecule [1–5]. Lippincott and Stutman [6] extended this model to compute bond and molecular polarizabilities for a variety of molecules. The model has been successfully applied to simple polyatomic molecules having non-polar and polar bonds by Lippincott et al. [7], Nagarajan [8, 9], Sanyal et al. [10] and Pandey et al. [11, 12]. Beran and Kevan [13] have used it to calculate molecular polarizabilities of fluorocarbons, substituted fluorocarbons, ether, esters, ketones and aldehydes as well as a few halogen substituted alkanes and alkyl benzenes. A systematic study of bond and molecular polarizabilities for substituted hydrocarbons with ring and chain structures has been underkarten by Puranchandra and Rammurthy [14], Sanyal et al. [15] and Kumar et al. [16]. Till now a very limited attempt has been made to study the bond and molecular polarizabilities for alkali halides [17, 18] possessing ionic bonds and transition metal halides [6].

On account of renaissance in instrumental and theoretical techniques such as spectroscopic methods, electron diffraction, molecular beam deflection, quantum chemical calculations, and combination techniques in past few years more accurate and reliable data on the geometry of the variety of molecules have been accumulated in the literature. Recently, Hargittai [19] has compiled the structural data of gas-phase metal halides, therefore, in the light of current information about the equilibrium geometries of halides, it was thought timely and worthwhile to study the bond and molecular polarizabilities for the gas-phase metal halides using delta-function potential model of chemical binding on quantum mechanical basis with a view to test the applicability of the model for the halides under present investigation on the one hand and present results for the interpretation of experimental measurements, whenever available in the near future, on the other hand.

2. Polarizability calculations

The general expression in cartesian coordinates for molecular polarizability is written as:

$$\alpha = \frac{\frac{2}{3}\sum_{i\neq 0}(\mu_x)_i^2 + (\mu_y)_i^2 + (\mu_z)_i^2}{E_i - E_0}, \tag{1}$$

where

$$\mu_{xi} = \left(\Psi_i^* | \sum_j e x_j | \Psi_0\right), \tag{2}$$

e is the electronic charge, Ψ_0 is the ground-state delta-function wave function, and E represents the energy. Equation 2 poses difficulty in evaluation, in general,

except for diatomic molecules where fairly accurate wave functions lead to comparable results with experiments [17, 20]. In order to compute the polarizabilities for general types of molecules, Lippincott and Stutman [6] used the semiempirical delta-function model of chemical binding [2, 5]. In this model the colombic potentials in Schrödinger equation of molecular system is replaced by the delta-function potentials. The molecular wave functions are constructed from the linear combinations of atomic delta-function wave function. Using variational procedure [21] first introduced by Hylleraas [22] and Hasse [23] the xx–component of the polarizability can be written in the form:

$$\alpha_{xx} = \frac{4nA}{a_0}\left[\overline{(x_1 - \overline{x})^2} - (n-1)\overline{(x_1 - \overline{x})(x_2 - \overline{x})}\right]^2, \tag{3}$$

where x_1 refers to the coordinate of any one of the n equivalence classes of electrons, $\overline{x}$ refers to the average coordinate of any one of these electrons, A is the delta-function strength or reduced electronegativity of the nucleus [5] and a_0 is the radius of the first Bohr orbit of hydrogen atom. Since the model does not allow any interaction between coordinates, $(x_1 - \overline{x})(x_2 - \overline{x}) = 0$. Further, with mean delta-function strengths it predicts $\overline{x} = 0$, so Eq. (3) takes the form:

$$\alpha_{xx} = \frac{4nA}{a_0}\overline{[x_1^2]}^2 \tag{4}$$

or equivalently

$$\alpha_{xx} = \frac{4nA}{a_0}\sum_i \overline{[x_i^2]}^2. \tag{5}$$

Molecular polarizability is contributing to the parallel and perpendicular components of the constituent bond polarizabilities. The bond parallel component is taken to be the sum of the bonding electron contribution and the contribution from the valence shell non-bonding electrons in each atom of the bond. The bonding electron contribution is calculated by using a linear combination of atomic delta-function wave functions representing the nuclei involved in the bond; i.e. the expectation value of the electron position squared $\overline{x}^2$ along the bond axis is calculated and this in turn is used to obtain the bond parallel component of the polarizability $\alpha_{\|b}$ from the equation:

$$\alpha_{\|b} = 4nA_{12}\frac{\overline{[x^2]}^2}{a_0}, \tag{6}$$

where

$$\overline{x}^2 = \frac{R^2}{4} + \frac{1}{2C_{12}^2}; \quad A_{12} = (A_1A_2)^{1/2}, \tag{7}$$

n is the bond order, R is the internuclear distance at the equilibrium position, and

$$C_{12} = (n_1N_2N_1N_2)^{1/4}(A_1A_2)^{1/2}. \tag{8}$$

Here n_i and $N_i (i = 1, 2)$ are the principal quantum number and number of electrons making contributions to the binding, respectively. In case the bond is of

heteronuclear type, the bond parallel component of the polarizability must be corrected to account for the charge density introduced by the electronegativity difference of the bonding atoms. Here, the charge density in the bond region should then be related to the percent covalent character σ believed to exist in the form:

$$\sigma = \exp\left[-\frac{(X_1 - X_2)^2}{4}\right], \tag{9}$$

where X_1 and X_2 are the electronegativities of the atoms 1 and 2, respectively, on the Pauling's scale [24]. Taking into account the polarity correction, the bond parallel component of the polarizability is given by

$$\alpha_{\|p} = \sigma\alpha_{\|b}. \tag{10}$$

The contribution of the non-bond-region electron to the parallel component of the polarizability α is calculated from the fraction of electrons in the valence shell of the given atom not involved in bonding and its atomic polarizability. Lewis–Langmuir octet rule [25, 26] modified by Linnett [27] as a double-quartet of electrons is followed for such calculations. The general expression for the contribution of the non-bond region electrons to the parallel component of the polarizability $\alpha_{\|n}$ is written as:

$$\alpha_{\|n} = \sum_j f_j \alpha_j. \tag{11}$$

Here f_j is the fraction of the valence electrons in the jth atom not participating in the bonding and α_j is the atomic polarizability of the jth atom. Following an empirical approach Lippincott and Stutman [6] obtained a general expression for the evaluation of the perpendicular component of the bond polarizability which is expressed as:

$$\sum 2\alpha_{\perp j} = \frac{3N - 2n_b}{N} \sum_j \alpha_j, \tag{12}$$

where N is the number of atoms and n_b is the number of bonds in a molecule. A polarity correction is also applied to the perpendicular bond polarizabilities. The modified expression for the sum of perpendicular components of the bond polarizability is written as:

$$\sum 2\alpha_{\perp j} = n_{\mathrm{df}} \sum_j \frac{X_j^2 \alpha_j}{X_j^2}, \tag{13}$$

where $n_{\mathrm{df}} = 3N - 2n_b$, the residual atomic polarizability degrees of freedom. This is obtained by taking into account the symmetry and geometry of the molecules.

The average molecular polarizability α_M without polarity correction can be expressed as:

$$\alpha_M = \frac{1}{3}\left[\sum_i \alpha_i + \sum_j f_j \alpha_j + \frac{3N - 2n_b}{N} \sum_j \alpha_j\right] \tag{14}$$

and with polarity correction:

$$\alpha_M = \frac{1}{3}\left[\sum_i \alpha_i + \sum_j f_j \alpha_j + \frac{n_{df} \sum_j X_j^2 \alpha_j}{\sum_j X_j^2}\right]. \tag{15}$$

The summation subscript i refers to bonds and j refers to atoms. Equations (14) and (15) are used in the present study to compute average molecular polarizability.

3. Results and discussion

The required data for the present computation are the bond lengths, electronegativities on the Pauling's scale [24], delta-function strengths tabulated by Lippincott and Stutman [6], the values of parameter "c", and the atomic polarizabilities. The bond lengths for most of the halides under present study are taken from the compilation of Hargittai [19] and from literature [28–39] for other halides. The Lewis–Langmuir octet rule [25, 26] modified by Linnett [27] has been followed in accounting for the non-bond contribution in polarizability calculations. In determining the residual atomic polarizability degrees of freedom for the halides, the method suggested by Lippincott and Stutman [6] has been considered. The delta-function strength of an atom in bond of polyatomic halides is calculated using the empirical relation:

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

given by Lippincott and Dayhoff [5], where A is the delta-function strength of an atom in the bond of a diatomic halide, n is the principal quantum number of the atom, and A^* is the delta-function strength of an atom in the bond of a polyatomic halide.

The halides, for which the bond parallel components, the contribution of non-bond-region electrons, the bond perpendicular components and the average molecular polarizabilities have been calculated from the delta-function potential model following quantum mechanical approach, are categorized according to their residual atomic polarizability degrees of freedom n_{df}. The results are presented in Tables I to V. The available experimental polarizabilities [32, 33] which are determined by measurements of dielectric constant, refractive indices, dipole moments and molar refraction through the well-known Clausius–Mossotti, Langevin–Debye and Lorentz–Lorenz equations are included in Tables I to V.

3.1. Group 13 and alkali monohalides

Monohalides of group 13 metals have only single bonds with a double-quartet of electrons around a respective halogen atom. The alkali monohalides have ionic bonds, therefore, in order to account for this effect in our calculations, we have used the ionic bond order [34]. The ionic bond orders [34] were determined from the data presented by DeWijn [35] for alkali monohalides. The computed polarizabilities are summarized in Table I. No experimental values of molecular

TABLE I

Calculated polarizabilities in 10^{-25} cm^3 for group 13 metal and alkali monohalides for four residual atomic polarizability degrees of freedom.

Halides	$\sum\alpha_{\parallel p_i}$	$\sum\alpha_{\parallel n}$	$\sum 2\alpha_{\perp i}$	α_M(calc)	α_M(exp)
AlF	5.350	30.320	36.505	24.058	
AlCl	34.176	38.017	75.760	49.318	
AlBr	48.839	42.757	95.274	62.290	
AlI	83.224	51.594	128.896	87.905	
GaF	7.550	41.766	47.986	32.434	
GaCl	39.717	49.463	93.104	60.762	
GaBr	54.407	54.203	114.012	74.208	
GaI	87.772	63.041	149.832	100.215	
InF	12.554	56.646	64.745	44.648	
InCl	56.863	64.343	118.512	79.906	
InBr	74.506	69.083	141.484	95.024	
InI	113.561	77.920	180.791	124.091	
TlF	15.061	118.319	131.606	88.329	
TlCl	61.261	126.061	222.073	136.450	
TlBr	77.836	130.756	255.162	154.584	
TlI	113.354	139.593	312.065	188.337	
LiF	23.118	4.200	34.901	20.740	108.00 [17]
LiCl	19.915	11.897	77.940	36.584	34.60 [18]
LiBr	40.061	16.637	100.500	52.400	
LiI	49.623	25.474	104.065	59.721	
NaF	44.366	4.200	43.488	30.685	
NaCl	72.065	11.897	93.488	59.150	
NaBr	66.467	16.637	118.629	67.244	
NaI	77.425	25.474	164.369	89.089	
KF	62.581	4.200	52.066	39.616	
KCl	106.093	11.897	109.176	75.955	
KBr	117.116	16.637	136.967	90.240	
KI	145.940	25.474	188.067	119.827	
RbF	72.289	4.200	57.675	44.721	
RbCl	123.331	11.897	118.859	84.696	
RbBr	155.786	16.637	147.974	106.800	
RbI	201.684	25.474	201.614	142.924	
CsF	76.062	4.200	61.471	47.244	
CsCl	134.612	11.897	126.421	90.977	
CsBr	174.973	16.637	157.113	115.910	
CsI	225.524	25.474	214.103	155.034	

polarizabilities for the monohalides of group 13 and 1 metals are reported in the literature, but the quantum mechanical results of the polarizability for the monomers of lithium fluoride and lithium chloride exist in literature [17, 18]. The calculated

average molecular polarizability for lithium chloride is in good agreement with the value reported by Bounds et al. [18] but the agreement is not good in the case of lithium fluoride (see Table I) with the value reported by Kolker and Karplus [17]. Since the magnitude of average molecular polarizability for lithium fluoride should not be greater than the corresponding magnitude for lithium chloride, therefore, the comparison of the two calculated values does not seem justified.

The justification of the use of ionic bond orders in case of alkali monohalides cannot be presented at this stage on account of non-availability of experimental results. However, we have tried to present logical (reasonable) evidence in favour of our approach to utilize ionic bond orders in the computation of polarizabilities for the dimers of the alkali halides possessing ionic bonds in further discussion.

3.2. Group 2, 14 and 16 dihalides

The polarizabilities for some dihalides of groups 2, 14 and 16 possessing bent geometries and six residual atomic polarizability degrees of freedom are collected in Table II. The dihalides have only single bonds with a double-quartet of

TABLE II

Calculated and experimental polarizabilities in 10^{-25} cm^3 for groups 2, 14 and 16 dihalides of five residual atomic polarizability degrees of freedom.

Halides	$\sum \alpha_{\parallel p_i}$	$\sum \alpha_{\parallel n}$	$\sum 2\alpha_{\perp i}$	α_M(calc)	α_M(exp)
$SrCl_2$	78.751	23.794	113.753	72.173	
$BaCl_2$	84.878	23.794	119.344	76.005	79.806 [33]
BaI_2	200.286	50.949	214.362	155.200	
SiF_2	13.504	23.340	35.983	24.276	
$SiCl_2$	80.648	38.734	81.603	67.000	
$SiBr_2$	111.519	48.214	106.015	88.583	
GeF_2	18.273	27.640	39.937	28.617	
$GeCl_2$	93.296	43.034	88.163	74.831	
$GeBr_2$	125.523	52.514	113.378	97.138	
$SnCl_2$	117.630	50.074	98.902	88.869	
$SnBr_2$	159.417	59.554	125.434	114.802	
SnI_2	234.650	77.229	172.108	161.330	
PbF_2	28.269	76.445	84.809	63.174	
$PbCl_2$	119.030	91.839	162.611	124.494	99.46 [33]
$PbBr_2$	156.197	101.319	196.956	151.491	
PbI_2	231.904	118.994	258.079	203.000	
$SeCl_2$	123.609	40.621	83.170	82.466	
$TeCl_2$	140.393	49.141	93.152	94.229	

electrons around the halogen atoms. As seen from the table, the calculated values of average molecular polarizabilities with polarity corrections for the dichlorides of barium and lead are in reasonable agreement with the experimental values. The

variation in shape of alkaline earth (group 2) dihalides are reported in literature [19]. Nagarajan [9] computed the average molecular polarizability $\alpha_M = 84.717 \times 10^{-25}\text{cm}^3$ for barium dichloride on the basis of linear structure. As seen from Table II, we have computed this value $\alpha_M = 76.005 \times 10^{-25}\text{cm}^3$ for it, considering a bent configuration. A comparison of these values with the experimental value $\alpha_M = 79.806 \times 10^{-25}\text{cm}^3$ for barium dichloride shows that our value is more close to experimental value than the value reported by Nagarajan [9]. Therefore, it is concluded on the basis of our polarizability calculation that the barium dichloride posseses the bent structure. This is further supported by the ionic model in which the bent geometry is favoured by large, more polarizable metal ions and small, more electronegative halide ions [36].

3.3. Group 2, 12 and first row transition metal dihalides and group 15 trihalides

Table III includes the results of polarizability calculations for some linear dihalides of groups 2, 12 and first row transition metals and pyramidal trihalides of group 15 elements possessing six residual atomic polarizability degrees of freedom. The dihalides and trihalides have single bonds with a double-quartet of electrons around the halogen atoms. A number of features are evident on examination of results presented in Table III. From the analysis of the available experimental values through refractometric method [33] and the computed results with the polarity correction, it is evident that these are in good agreement. In view of the availability of some new experimental results, we have further computed the polarizabilities without polarity corrections for mercury dichloride and mercury diiodide which are included in Table III. It is remarkable to note the new value for mercury dihalide compares very well with the value calculated without the polarity correction, but it is not so in the case of mercury diiodide. In order to resolve this discrepancy we considered the bent geometry of mercury dichloride and mercury diiodide and again computed the polarizabilities with and without polarity corrections and included the results in Table III. An analysis of these results shows that now the values are more comparable than the previous values with the experimental data for mercury dichloride while in the case of mercury diiodide the comparison becomes poor. It is, therefore, concluded that our results favour the bent structure to mercury dichloride in contrast to linear structure to mercury diiodide. The structural problems are also reported in literature. Spectroscopic results [37–40] have been analysed in terms of the bent structure for several dihalides of mercury on the one hand and indication of linearity for mercury dihalides has also been noticed from molecular beam deflection studies [41] on the other hand. Only one experimental value exists for zinc dichloride and we found no experimental values for the dihalides of first row transition metals, therefore, it is not possible to decide at this stage whether polarity corrections are needed or not in the calculations of molecular polarizabilities for the dihalides of first row transition metals. We, therefore, have calculated the polarizabilities with and without polarity corrections for this group of dihalides and the results are included in Table III. Except for the trifluorides of group 15 elements, where polarity corrections seem essential, we

TABLE III

Calculated and experimental polarizabilities in 10^{-25} cm^3 for groups 2, 12 and first row transition metal dihalides and group 15 trihalides or six residual atomic polarizability degrees of freedom.

Halides		$\sum \alpha_{\parallel p_i}$	$\sum \alpha_{\parallel n}$	$\sum 2\alpha_{\perp i}$	α_M(calc)	α_M(exp)
MgF_2		8.437	8.400	49.760	22.200	18.426 [33]
$MgCl_2$		52.806	23.794	114.311	63.636	53.851 [33]
$CaCl_2$		65.456	23.794	127.768	72.400	
$CaBr_2$		90.000	33.274	165.147	96.140	
CaI_2		151.475	50.949	233.893	145.440	
SrI_2		189.200	50.949	246.187	162.112	
ZnF_2		13.797	8.400	56.689	26.295	
$ZnCl_2$		60.106	23.794	122.440	68.779	67.363 [33]
$ZnBr_2$		82.354	33.274	155.946	90.525	
ZnI_2		130.205	50.949	215.629	132.269	
$CdBr_2$		119.511	33.274	165.511	106.100	
$HgCl_2$	l	95.315	23.794	175.884	98.320	90.670 [33]
	b	95.315	23.794	146.536	88.550	
	l′	129.000	23.794	267.980	140.250	
	b′	129.000	23.794	223.317	125.370	116.000 [32]
HgI_2	l	176.690	50.949	281.188	169.609	164.740 [33]
	b	176.690	50.949	234.323	153.987	
	l′	193.330	50.949	331.340	191.873	191.000 [32]
	b′	193.330	50.949	276.116	173.465	
VCl_2		83.574	69.748	130.130	94.484	
		136.419	69.748	208.700	138.289	
CrF_2		14.720	59.455	61.262	45.146	
		62.131	59.455	172.780	98.122	
$CrCl_2$		72.426	74.849	130.130	92.468	
		118.223	74.849	208.700	133.924	
MnF_2		13.469	68.443	60.602	47.505	
		64.259	68.443	187.720	106.807	
$MnCl_2$		68.898	83.837	130.067	94.267	
		120.920	83.837	223.640	142.800	
$MnBr_2$		94.005	93.317	165.137	117.486	
		143.430	93.317	245.760	160.836	
FeF_2		17.644	72.837	74.092	54.860	
		59.169	72.837	191.432	107.813	
$FeCl_2$		77.754	88.231	149.211	105.065	
		111.447	88.231	227.352	142.343	
$FeBr_2$		106.555	97.711	184.794	129.687	
		136.819	97.711	249.472	161.334	
PF_3		26.519	22.068	38.876	29.154	
PCl_3		134.239	45.159	91.527	90.310	103.030 [33]
		164.371	45.159	97.965	102.498	128.000 [32]

TABLE III (cont.)

Halides	$\sum \alpha_{\parallel p_i}$	$\sum \alpha_{\parallel n}$	$\sum 2\alpha_{\perp i}$	α_M(calc)	α_M(exp)
PBr_3	187.243	59.379	120.496	122.372	
	211.644	59.379	122.850	131.291	
PI_3	324.070	85.891	171.408	193.790	
	337.296	85.891	169.245	197.477	
AsF_3	32.851	25.808	42.378	33.679	
$AsCl_3$	153.986	48.899	98.098	100.325	
	197.722	48.899	112.000	119.540	149.000 [32]
$AsBr_3$	207.968	63.119	128.329	133.139	
	244.053	63.119	136.875	148.016	
AsI_3	320.376	89.631	181.801	197.269	
	341.039	89.631	183.270	204.647	
SbF_3	55.152	32.056	47.757	45.000	
$SbCl_3$	185.276	55.147	107.876	116.100	
	250.723	55.147	135.420	147.097	
$SbBr_3$	245.044	69.367	139.796	151.403	
	300.047	69.367	160.305	176.573	
SbI_3	375.113	95.579	196.648	222.447	
	410.439	95.579	206.700	237.573	
$BiCl_3$	185.929	84.391	159.610	143.310	
	251.606	84.391	245.085	193.694	
$BiBr_3$	262.470	98.611	198.166	186.416	
	321.385	98.611	269.970	230.000	

l — linear structure with polarity corrections
b — bent structure with polarity corrections
l′ — linear structure without polarity corrections
b′ — bent structure without polarity corrections

have computed the polarizabilities for the remaining trihalides of this group with and without polarity corrections and results are included in Table III. It is interesting to contrast the polarizabilities calculated with and without polarity corrections.

From the survey of the computed results it has been found that there is an indication that the values calculated without polarity corrections are relatively more comparable to the values calculated with polarity corrections. It is true that the difference between the values calculated with and without polarity corrections increases in trihalides of this group keeping the ligand constant with the decrease of electronegativity of the central atom, but the difference decreases keeping the central atom constant with the decrease of the electronegativity of the halogen atom. However, the polarity-corrected values for the trihalides of group 15 elements show poorer agreement with the available experimental values than do the polarizabilities calculated without polarity corrections. Thus the decision to make use of the polarity correction or not to calculate molecular polarizabilities is rather a delicate one which cannot be decided on the ground of chemical arguments alone. We conclude that for trihalides of group 15 elements except for trifluorides, the

value calculated without polarity corrections can give comparable results with the experimental values.

3.4. Group 13 and first row transition metal trihalides and group 14 transition metal tetrahalides

The results calculated with and without polarity corrections for the halides possessing seven residual atomic polarizability degrees of freedom are tabulated

TABLE IV

Calculated and experimental polarizabilities in 10^{-25} cm^3 for group 13 and first row transition metal trihalides and group 14 and transition metal tetrahalides of seven residual atomic polarizability degrees of freedom.

Halides	$\sum\alpha_{\parallel p_i}$	$\sum\alpha_{\parallel n}$	$\sum 2\alpha_{\perp i}$	α_M(calc)	α_M(exp)
BCl_3	73.229	35.691	96.889	68.603	80.05 [33]
	94.028	35.691	96.635	75.451	93.80 [32]
AlF_3	15.250	12.600	45.044	24.044	
	72.752	12.600	94.290	59.881	
$AlCl_3$	91.219	35.691	110.783	79.231	89.435 [33]
	160.096	35.691	141.435	112.407	
$AlBr_3$	137.920	49.911	147.953	111.928	124.464 [33]
	210.433	49.911	170.467	143.604	
AlI_3	266.845	76.423	215.135	186.134	199.079 [33]
	342.636	76.423	224.595	214.551	
GaF_3	20.267	12.600	52.535	28.467	
	85.540	12.600	124.337	74.159	
GaI_3	219.060	76.423	230.434	175.305	
	265.229	76.423	254.642	198.765	
InI_3	145.348	76.423	253.804	158.524	
	255.852	76.423	293.702	208.659	
ScF_3	16.487	12.600	58.031	29.040	
	102.012	12.600	208.740	107.784	
VF_3	20.353	43.236	59.709	41.100	
	85.906	43.236	159.757	96.300	
CrF_3	19.421	50.895	59.709	43.342	
	81.971	50.895	159.757	97.541	
FeF_3	26.089	66.297	70.160	54.182	
	87.490	66.297	176.078	109.955	
SiF_4	24.650	16.800	42.526	28.059	33.010 [33]
	82.664	16.800	69.272	56.245	54.500 [32]
$SiCl_4$	140.917	47.590	106.408	98.304	111.72 [33]
	201.980	47.590	119.560	123.042	
$SiBr_4$	186.594	66.548	142.733	131.958	156.140 [33]
	239.592	66.548	150.528	152.223	

TABLE IV – (cont.)

Halides	$\sum \alpha_{\parallel p_i}$	$\sum \alpha_{\parallel n}$	$\sum 2\alpha_{\perp i}$	α_M(calc)	α_M(exp)
SiI_4	331.931	101.897	208.169	214.000	
	375.188	101.897	208.264	228.450	
GeF_4	31.648	16.800	45.626	31.358	36.460 [33]
	106.130	16.800	81.312	68.081	
$GeCl_4$	162.967	47.590	111.378	107.312	121.230 [33]
	233.584	47.590	131.600	137.599	151.000 [32]
$GeBr_4$	224.458	66.548	148.370	146.460	
	288.209	66.548	162.568	172.449	
GeI_4	359.239	101.897	215.075	225.404	
	406.056	101.897	220.304	242.752	
$SnCl_4$	210.375	47.590	119.516	125.827	137.700 [33]
	301.537	47.590	151.312	166.813	180.000 [32]
$SnBr_4$	284.041	66.548	157.600	169.396	189.070 [33]
	364.715	66.548	182.280	204.514	220.000 [32]
SnI_4	425.336	101.897	226.383	251.205	277.810 [33]
	480.764	101.897	240.016	274.226	323.000 [32]
TiF_4	24.023	16.800	53.119	31.314	
$TiCl_4$	130.684	47.590	126.058	101.444	141.000 [33]
	229.358	47.590	195.412	157.453	164.000 [32]
$TiBr_4$	187.275	66.548	166.166	140.000	
	285.739	66.548	226.380	192.889	
TiI_4	299.864	101.897	239.448	213.736	
	385.034	101.897	284.116	257.015	
ZrF_4	27.751	16.800	56.086	33.546	
	150.395	16.800	180.936	116.044	
$ZrCl_4$	153.068	47.590	131.771	110.810	
	290.290	47.590	231.122	189.701	
$ZrBr_4$	206.434	66.548	173.024	148.669	
	336.966	66.548	262.192	221.902	
ZrI_4	356.607	101.897	248.711	235.738	
	439.272	101.897	319.928	287.032	
HfF_4	22.371	16.800	70.373	36.481	
	138.418	16.800	313.950	156.389	
$HfCl_4$	125.166	47.590	157.038	109.931	
	257.789	47.590	364.238	223.205	
$HfBr_4$	169.831	66.548	202.175	146.185	
	298.063	66.548	395.206	253.272	
HfI_4	278.787	101.897	285.897	222.086	
	399.594	101.897	452.942	318.144	
VCl_4	100.544	62.907	126.303	107.756	
	218.826	62.907	184.954	155.562	
VBr_4	181.068	81.867	166.078	143.000	
	259.530	81.867	215.922	185.773	

in Table IV. It includes the planar trihalides of group 13 elements as monomers, planar trifluorides of first row transition metals, tetrahalides of group 14 and transition metals. Trihalides and tetrahalides have single bond with a double-quartet of electrons around the halogen atoms. A close examination of the results (Table IV) for the trihalides of group 13 elements shows that though the two sets of calculated values are comparable with the available experimental values in the case of trihalides of aluminium but the values calculated with polarity corrections are relatively more close to the experimental values calculated without polarity corrections. In contrast to this the value calculated without polarity corrections for boron trichloride is more close to the experimental value. It is, therefore, concluded that in case of trihalides of aluminium the introduction of polarity corrections in polarizability calculations seems useful. Due to lack of experimental values for the trifluorides of first row transition metals, the decision whether to incorporate polarity corrections or not remains uncertain, however our results on fluorides and the results reported by others [6, 13] are in favour of inclusion of polarity corrections for calculating polarizability for fluorides by employing delta-function potential model. A survey of the results for tetrahalides of the group 15 shows that for tetrafluorides the polarity corrections are necessary to obtain satisfactory agreement with the experimental values. For tetrachlorides in general both sets of values are in reasonable agreement with the experimental values while the polarizabilities calculated with no polarity corrections for the tetrabromides and tetraiodides are in reasonable agreement with the experimental values. Only one experimental value exists for the polarizability for titanium tetrachloride and we found no experimental data for other tetrahalides of transition metals. It is seen from Table IV that the available experimental value for titanium tetrachloride is in reasonable agreement with the value calculated without polarity corrections. At present it is not possible to decide about the incorporation of polarity corrections in the polarizability calculations with the model employed here, however, we must await the measurements of more experimental values before we reach to any final conclusion. For tetrafluorides the polarity correction is advised as discussed above.

3.5. Group 15 and 5 pentahalides, dimers of group 13 tetrahalides and alkali halides

Table V includes the results of calculations for the monomeric pentahalides of groups 15, 5 and 6 elements, dimers group 13, trihalides and alkali halide dimers possessing eight residual atomic polarizability degrees of freedom.

3.5.1. Monomers

The monomeric pentahalides of the group 15 and group 5 have regular trigonal bibyramidal configuration [19] and pentafluoride of chromium (group 6) has a lower C_{2v} symmetry than the more symmetric D_{3h} structure due to dynamic Jahn–Teller effect [42]. On the basis of the structure of pentahalides there is the double-quartet of electrons around the peripheral halogen atoms while ten electrons surround the central arsenic, antimony, vanadium, niobium and tantalum atoms. The group 6 transition metals also have pentahalides in the present case

e.g. chromium pentafluoride where the electronic configuration is d^1 and it is degenerate with the one electron occupying e'' orbital in a considered D_{3h} symmetry structure. Though the pentahalides partly obey Lewis–Langmuir octet rule [25, 26] and Linnett model [27], the agreement between the experimental and calculated values (Table V) of the average molecular polarizability is good for antimony pentachloride. Since the experimental and calculated values with polarity corrections are in good agreement, we have only included the polarizabilities calculated by incorporating polarity corrections for all pentahalides.

TABLE V

Calculated and experimental polarizabilities in 10^{-25} cm^3 for group 15 and 5 pentahalides and dimers of group 13 trihalides and alkali halides of eight-residual atomic polarizability degrees of freedom.

Halides	$\sum\alpha_{\parallel p_i}$	$\sum\alpha_{\parallel n}$	$\sum 2\alpha_{\perp i}$	α_M(calc)	α_M(exp)
AsF_5	50.883	21.000	64.358	45.413	
$SbCl_5$	292.300	59.485	131.691	161.159	156.758 [33]
VF_5	31.301	21.000	56.981	36.427	
$NbCl_5$	211.759	59.485	143.732	138.325	
$TaCl_5$	180.387	59.485	168.522	136.131	
$TaBr_5$	247.083	83.185	218.404	182.891	
CrF_5	30.634	33.760	56.984	40.459	
Al_2F_6	43.700	22.400	51.479	39.193	
Al_2Cl_6	292.105	63.451	126.609	160.722	158.183 [9]*
Al_2Br_6	412.659	88.731	169.578	223.656	
Al_2I_6	678.324	135.863	245.868	353.352	
Ga_2Cl_6	321.604	63.451	140.464	175.173	182.024 [9]*
Ga_2Br_6	443.863	88.731	184.288	238.961	
Ga_2I_6	630.674	135.353	263.353	343.297	
Fe_2Cl_6	362.058	170.827	172.785	235.223	
$AlFeCl_6$	325.847	117.149	150.079	197.692	
Tl_2F_2	87.676	8.400	263.211	119.762	
$(LiF)_2$	139.582	8.400	69.802	72.595	70.000 [32]
$(LiCl)_2$	203.458	23.794	155.880	127.711	130.000 [32]
$(LiBr)_2$	218.626	33.274	201.000	151.000	190.000 [32]
$(LiI)_2$	251.267	50.949	282.130	194.782	230.000 [32]
$(NaCl)_2$	328.825	23.794	285.440	212.686	230.000 [32]
$(NaBr)_2$	362.248	33.274	296.500	230.674	270.000 [32]
$(KCl)_2$	635.764	23.794	459.620	373.059	320.000 [32]
$(KBr)_2$	772.079	33.274	470.680	425.344	420.000 [32]
$(RbCl)_2$	666.659	23.794	532.540	407.664	430.000 [32]
$(RbBr)_2$	845.264	33.274	543.600	474.050	480.000 [32]
$(CsCl)_2$	624.104	23.794	742.100	463.333	420.000 [32]
$(CsBr)_2$	986.748	33.274	753.160	591.061	540.000 [32]

* calculated value

3.5.2. Dimers

There are two types of dimers structure. One is the dimeric group 13 halides and iron trichloride and another is the alkali halide dimers. Both types of dimers have eight residual atomic polarizability degrees of freedom. According to spectroscopic studies [43, 44] the dimers of the group 13 trihalides belong to D_{2h} point group, this implies a planar four-membered ring. The ground state electronic configuration for the trihalide dimer satisfies the Linnett model [27]. The electron diffraction studies on iron trichloride and thallous fluoride dimers [45, 46] are in favour of a planar rhombic structure and also possess the D_{2h} point group and four-memebered ring but for the thallous fluoride dimer other structural models are presented in literature [19]. The polarizabilities calculated including polarity corrections are listed in Table V. Due to non-availability of experimental data for the first type of dimers, we have compared our results with those reported by Nagarajan [9] which are included in Table V. It is evident that our values for the dimers of the trichlorides of aluminium and gallium are in good agreement with the values reported by Nagarajan [9]. It seems, therefore, important to use the polarity correction in the calculations of polarizabilities using delta-function potential model for the type of dimers of group 13 trihalides as in the case of monohalides of this group (Table I), however, to arrive at a definite conclusion about the configuration of thallous fluoride dimers with the aid of computed data we must wait till experimental measurements are made. Alkali halides dimers possess a planar rhombic structure with D_{2h} symmetry [47–49] containing four-membered ring similar to the dimers discussed above. The dimers have ionic bond, therefore, to take into account this effect in our calculation a similar procedure has been followed as discussed for the monomers. Since the measurements of molecular polarizabilities of the alkali halide dimers using molecular beam deflection technique [50] are now available in the literature [32], therefore, it is possible at this stage to examine the justification of the approach followed in computing the polarizabilities for molecules possessing ionic bonds and to take decision of whether to incorporate polarity corrections or not for the alkali halide dimers. First we computed the polarizabilities for all alkali halides dimers under present study taking into account the polarity correction. On comparing the computed results with the experimental results it was found that except for the dimers of lithium halides in other alkali halide dimers the computed results were too low, therefore, we recalculated the polarizabilities without polarity corrections for the last dimers. The results are included in Table V. Examination of the results displayed in this table shows that the calculated values are in good agreement except the lithium bromide dimer where the error is about 21%. On the basis of reasonable agreement between computed and experimental values, in general, we conclude that the use of ionic bond orders for alkali halides and its dimers is justified and the polarity correction is essential for the lithium halide dimers while for other alkali halide dimers the calculation without polarity corrections give reasonable results.

4. Conclusion

To conclude, we will emphasize the following point. After all, the delta-function potential model extended by Lippincott and Stutman for computing molecular polarizabilities gives reasonable good results for gas-phase metal halides. The polarity corrections are necessary for fluorides but in the case of halides for which no experimental data exist at present we must await for measurements of experimental values for them to decide whether to include polarity corrections or not in such calculations. For alkali halides possessing ionic bonds the ionic bond order can be used successfully to compute molecular polarizabilities under present approach. For transition metal halides there is an indication to exclude the polarity correction in such calculations, but a firm confirmation requires more experimental results. The application of this method to complex metal halides is in progress.

5. Acknowledgements

One of the authors (ANP) is grateful to the Third World Academy of Sciences (ICTP), Trieste, Italy for awarding him the research grant. He is thanful to the authorities of Meerut College, Meerut, India for granting him study leave. He is obliged to Prof. G. De Alti, Director of the department, for providing him the necessary facilities and cordial atmosphere. He is also indebted to Swedish Agency for Research Cooperation (SEREC) for sponsoring his current Associateship visit to the ICTP Trieste.

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