Calculation of Photoelectron Spectra of Group IV Tetrachlorides and Carbon Tetrahalides by SCF-X_α-SW Method

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Photoelectron spectra and one-electron eigenfunctions of group IV tetra-chlorides, ACl_4, where A = C, Si, Ge, Sn and carbon tetrahalides, CB_4, where B = F, Cl, Br, I, have been calculated by SCF-X_α-SW method. Excellent agreement is obtained with the observed photoelectron spectra. The radius reduction factors of atomic sphere F_r were adjusted instead of changing individual atomic radii. The comparison of photoelectron spectra and one-electron eigenfunctions for molecules ACl_4 for different central atoms A and halogen atoms B is discussed.

Key words: Photoelectron spectra – Group IV tetrachlorides – Carbon tetrahalides SCF-X_α-SW method – Transition state – Ionization energy – Electronic structure.

1. Introduction

The SCF-X_α-SW method has been applied to a number of subjects in chemistry and solid state physics recently [1–6]. The method has been proved quite successful in the interpretation of photoelectron spectra of a wide range of compounds because of Slater's concept of "transition state" [7]. One-electron eigenvalues of the SCF-X_α-SW equation differ from their Hartree–Fock counterparts by not obeying Koopman's theorem. They are derivatives of the total

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energy with respect to occupation number, that is

$$\varepsilon(X_\alpha)_i = \frac{\partial\langle E_{X_\alpha}\rangle}{\partial n_i}.$$

If the total energy is approximated by a quadratic function of the orbital occupation number the ionization potential of electron i may be calculated as the one-electron eigenvalue in a "transition state" model with half an electron in the orbital. We have

$$I_i \equiv \langle E_{X_\alpha}(n_i = 0)\rangle - \langle E_{X_\alpha}(n_i = 1)\rangle \simeq -\varepsilon(X_\alpha)_i(n_i = \tfrac{1}{2})$$

since $\varepsilon_i(n_i)$ is obtained from a separate self-consistent calculation at each n_i such an approach accounts for the effects of orbital relaxation while the semiempirical method and the Hartree–Fock method do not.

The high resolution photoelectron spectra of various kinds of compounds have been reported [8, 9]. The photoelectron spectra of group IV tetrahalides have been available [10, 11]. The first ionization potentials of carbon, silicon and germanium tetrahalides were calculated by using CNDO method [12]. Barber [13] and Connelly [14] calculated the photoelectron spectra of CF_4 with SCF-X_α-SW method.

In this paper we present the results of SCF-X_α-SW transition state calculations on molecules ACl_4 (A = C, Si, Ge, Sn) and CB_4 (B = F, Cl, Br, I). Excellent agreement was obtained with the available observed photoelectron spectra.

The calculated result can be significantly improved with adjusting the radius reduction factor F_r instead of individual radii of atomic spheres. The relationship between the photoelectron spectra of molecules ACl_4 and CB_4 for different central atoms A and halogen atoms B is discussed.

2. Method of Calculation

The geometric parameters of the seven molecules are taken from Sutton's work [15]. The partial wave expansions were truncated at $L = 4$ for the outer sphere,

Table 1. The values of R_s (in a_0)

Molecule	$F_r = 0.88$			$F_r = 0.85$			$F_r = 0.82$		
	Rout	R_A	R_B	Rout	R_A	R_B	Rout	R_A	R_B
CCl_4	5.75	1.73	2.41	5.67	1.67	2.33	5.59	1.61	2.25
$SiCl_4$	6.32	2.21	2.52	6.23	2.13	2.43	6.15	2.06	2.35
$GeCl_4$	6.44	2.29	2.51	6.35	2.21	2.42	6.27	2.13	2.34
$SnCl_4$	6.94	2.63	2.59	6.85	2.54	2.50	6.76	2.45	2.41
CF_4	4.18	1.50	1.69	4.13	1.45	1.63	4.07	1.40	1.57
CBr_4	6.34	1.81	2.67	6.25	1.75	2.58	6.16	1.69	2.49
CI_4				6.90	1.80	2.90			

$L = 1$ for the others. The radii of the regions around each nucleus were chosen from Norman's value [16]. Then multiplied by a radius reduction factor F_r. The outer sphere origins and radii were chosen to make the outer sphere tangent to the four outlying halogen spheres. The values of radii R_s were listed in Table 1 and three sets of F_r values were set. The exchange scaling parameters α for each atomic sphere have been taken from Schwarz's atomic calculations [17]. The values α in the intersphere and outersphere regions have been chosen as the weighted average according to the number of valence electrons of the various atoms. The computer program of the SCF-X_α-SW method was prepared by Prof. M. Karplus and Dr. M. Cook of Harvard University and kindly made available to us by Dr. M. Cook. Each iteration of the calculation required about 10 s on an IBM 370/158 computer.

3. Results and Discussions

Three sets of the calculated values which correspond to three F_r values (088, 085, 082) for molecules CCl_4, $SiCl_4$, $GeCl_4$, $SnCl_4$, CF_4, CBr_4, one set for molecule CI_4 ($F_r = 0.85$), available observed results and CNDO results are listed in Tables 2–8. We also present the best assignments of the experimental values from photoelectron spectra. The eigenfunctions in Tables 2–8 correspond to $F_r = 0.85$. The charges of interspheres regions are slightly increased with reducing

Table 2. CCl_4 ionization potentials and wavefunctions

Orbitals	Transition state (ev)			CNDO (ev) [12]	Expt. (ev) [9]	Wavefunction
	0.88	0.85	0.82			
$1t_1$	11.56	11.97	12.26	12.43	11.69	$0.86Cl(p) + 0.12Q_i$
$3t_2$	12.11	12.54	12.83		12.62	$0.02C(p) + 0.80Cl(p) + 0.15Q_i$
$1e$	12.74	13.14	13.40		13.44	$0.81Cl(p) + 0.15Q_i$
$2t_2$	16.28	16.55	16.68		16.58	$0.26C(p) + 0.66Cl(0.07s + 0.93p) + 0.06Q_i$
$2a_1$	19.89	20.24	20.47		20.00	$0.25C(s) + 0.69Cl(0.48s + 0.52p) + 0.04Q_i$
$1t_2$	25.06	25.41	25.67			$0.07C(p) + 0.88Cl(s) + 0.04Q_i$
$1a_1$	28.54	28.68	28.71			$0.30C(s) + 0.68Cl(0.84s + 0.16p) + 0.01Q_i$

Table 3. $SiCl_4$ ionization potentials and wavefunctions

Orbitals	Transition state (ev)			CNDO (ev) [12]	Expt. (ev) [10]	Wavefunctions
	0.88	0.85	0.82			
$1t_1$	11.69	12.16	12.50	12.92	12.03	$0.86Cl(p) + 0.12Q_i$
$3t_2$	11.95	12.41	12.74		12.85	$0.01Si(p) + 0.84Cl(p) + 0.13Q_i$
$1e$	12.33	12.87	13.11		13.35	$0.83Cl(p) + 0.15Q_i$
$2t_2$	14.77	15.00	15.11		15.05	$0.20Si(p) + 0.73Cl(p) + 0.05Q_i$
$2a_1$	18.07	18.32	18.62		17.98	$0.31Si(s) + 0.65Cl(0.27s + 0.73p) + 0.02Q_i$
$1t_2$	24.69	24.99	25.28			$0.05Si(p) + 0.92Cl(s) + 0.03Q_i$
$1a_1$	26.17	26.45	26.63			$0.19Si(s) + 0.80Cl(0.94s + 0.06p) + 0.01Q_i$

Table 4. $GeCl_4$ ionization potentials and wavefunctions

Orbitals	Transition state (ev)			CNDO (ev) [12]	Expt. (ev) [10]	Wavefunctions
	0.88	0.85	0.82			
$1t_1$	11.78	12.16	12.45	13.84	12.12	$0.86Cl(p)+0.12Q_i$
$3t_2$	12.00	12.37	12.64		12.60	$0.01Ge(p)+0.84Cl(p)+0.13Q_i$
$1e$	12.29	12.67	12.93		13.08	$0.82Cl(p)+0.15Q_i$
$2t_2$	14.50	14.69	14.78		14.07	$0.19Ge(p)+0.72Cl(p)+0.07Q_i$
$2a_1$	18.42	18.61	18.76		18.00	$0.36Ge(s)+0.59Cl(0.31s+0.69p)+0.03Q_i$
$1t_2$	24.53	24.75	24.96			$0.04Ge(p)+0.92Cl(s)+0.04Q_i$
$1a_1$	26.01	26.25	26.38			$0.19Ge(s)+0.78Cl(s)+0.03Q_i$

Table 5. $SnCl_4$ ionization potentials and wavefunctions

Orbitals	Transition state (ev)			Expt. (ev)[10]	Wavefunctions
	0.88	0.85	0.82		
$1t_1$	11.68	12.00	12.25	12.10	$0.87Cl(p)+0.12Q_i$
$3t_2$	11.80	12.11	12.35	12.38	$0.85Cl(p)+0.13Q_i$
$1e$	11.98	12.29	12.53	12.71	$0.85Cl(p)+0.14Q_i$
$2t_2$	13.63	13.74	13.77	14.00	$0.17Sn(p)+0.74Cl(p)+0.07Q_i$
$2a_1$	16.91	17.09	17.15	17.00	$0.41Sn(s)+0.53Cl(0.18s+0.82p)+0.05Q_i$
$1t_2$	24.08	24.37	24.61		$0.03Sn(p)+0.93Cl(s)+0.04Q_i$
$1a_1$	24.75	24.98	25.16		$0.10Sn(s)+0.86Cl(s)+0.03Q_i$

Table 6. CF_4 ionization potentials and wavefunctions

Orbitals	Transition state (ev)			Expt. (ev) [8]	CNDO (ev) [12]	X_α (ev) [13]	Wavefunction
	0.88	0.85	0.82				
$1t_1$	15.61	16.23	16.70	16.10	17.61	15.34	$0.90F(p)+0.09Q_i$
$3t_2$	16.17	16.81	17.27	17.04		16.26	$0.01C(p)+0.86F(p)+0.10Q_i$
$1e$	16.85	17.49	17.92	18.05		16.80	$0.85F(p)+0.11Q_i$
$2t_2$	21.24	21.92	21.92	22.02		20.07	$0.21C(p)+0.70F(0.05s+0.95p)$ $+0.07Q_i$
$1t_2$	36.17	38.68	37.03	40.03		35.07	$0.06C(p)+0.88F(s)+0.05Q_i$
$1a_1$	39.23	39.53	39.70	43.08		37.62	$0.16C(s)+0.79F(0.94s+0.06p)$ $+0.05Q_i$

F_r values. The calculated and experimental values of five high lying energy bands for molecules CCl_4, $SiCl_4$, $GeCl_4$, $SnCl_4$ were shown in Figs. 1–4.

It is clear that the calculated values are in excellent agreement with the experimental values and better than the available CNDO results with F_r values being adjusted carefully. The Figs. 1–4 show that much of the variability in the transition state energies can be represented as an approximate rigid shift of the entire energy scale without ordering crossing. The ordering of the three highest energy bands is not changed even though they are very closed. The transition state

Table 7. CBr_4 ionization potentials and wavefunctions

Orbitals	Transition state (ev) 0.88	0.85	0.82	CNDO (ev) [12]	Expt. (ev) [10]	Wavefunction
$1t_1$	10.34	10.69	10.98	10.84	10.40	$0.85Br(p) + 0.13Q_i$
$3t_2$	10.88	11.21	11.51		11.05	$0.03C(p) + 0.80Br(p) + 0.16Q_i$
$1e$	11.45	11.88	12.15		12.06	$0.81Br(p) + 0.16Q_i$
$2t_2$	14.74	14.94	15.06		15.04	$0.29C(p) + 0.62Br(0.06s + 0.94p) + 0.06Q_i$
$2a_1$	18.94	19.24	19.34		19.48	$0.29C(s) + 0.65Br(0.53s + 0.47p) + 0.05Q_i$
$1t_2$	23.32	23.60	23.80			$0.05C(p) + 0.90Br(s) + 0.04Q_i$
$1a_1$	26.10	26.22	26.25			$0.30C(s) + 0.68Br(0.86s + 0.14p) + 0.01Q_i$

Table 8. CI_4 ionization potentials and wavefunctions

Orbital	Transition state (ev)	CNDO (ev) [12]	Wavefunctions
$1t_1$	9.43	7.46	$0.82I(p) + 0.16Q_i$
$3t_2$	9.89		$0.04C(p) + 0.74I(p) + 0.19Q_i$
$1e$	10.43		$0.80I(p) + 0.19Q_i$
$2t_2$	13.50		$0.29C(p) + 0.60I(0.09s + 0.91p) + 0.08Q_i$
$2a_1$	16.98		$0.20C(s) + 0.70I(0.69s + 0.31p) + 0.08Q_i$
$1t_2$	19.84		$0.07C(p) + 0.86I(s) + 0.06Q_i$
$1a_1$	23.88		$0.42C(s) + 0.55I(0.74s + 0.26p) + 0.02Q_i$
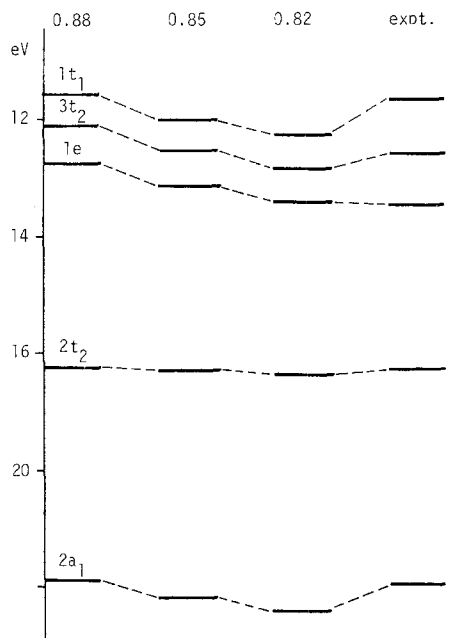
Fig. 1. CCl_4 ionization potentials
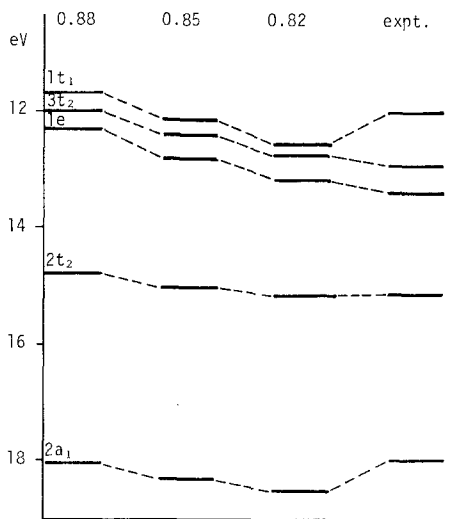
Fig. 2. SiCl$_4$ ionization potentials
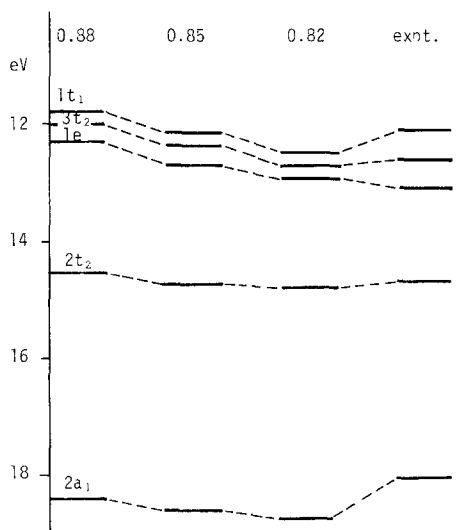
Fig. 3. GeCl$_4$ ionization potentials

energies of benzene and some planar heterocyclic compounds were reported by Case, Cook and Karplus [6] and some energy band crossings occur for these planar molecules.

We define a quantity:

$$\sigma = \left[\sum_{i=1}^{N} (\varepsilon_{cal}^{i} - \varepsilon_{expt}^{i})/N \right]^{1/2}$$

where ε_{cal}^{i} and ε_{expt}^{i} represent the calculated and experimental values of ionization potentials of ith state respectively and N the number of the states.
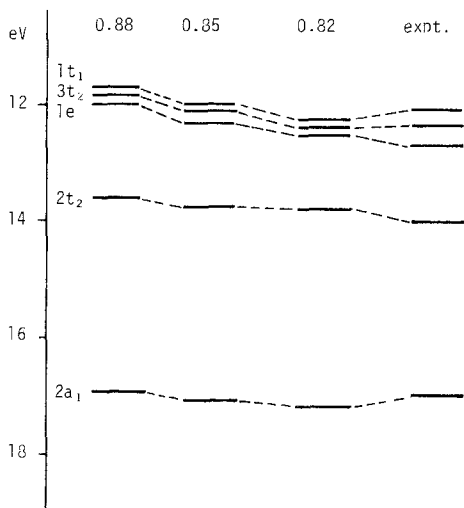
Fig. 4. $SnCl_4$ ionization potentials

Table 9. The values of root mean square difference σ (ev)

Molecule	$F_r = 0.88$	$F_r = 0.85$	$F_r = 0.82$
CCl_4	0.42	0.22	0.35
$SiCl_4$	0.64	0.33	0.38
$GeCl_4$	0.51	0.35	0.38
$SnCl_4$	0.49	0.26	0.16
CF_4	1.11	0.60	0.41
CBr_4	0.40	0.21	0.34

The quantities measure the errors between the calculated and experimental values and are listed in Table 9 for different F_r. Different energy levels move down by different amounts as the F_r values decrease. The three highest ones move down most. This is not surprising since the wave functions of the three states are largely the $3p$ orbitals of chlorine atoms and having considerable intersphere charge. They all have 12–15% of their charge in the intersphere region as compared to 1–7% for the other orbitals. This makes them more sensitive to F_r values than the others since smaller atomic spheres contain less electronic charge to shield the intersphere region from the nuclear potential, the intersphere potential is lowered as the sphere size is decreased. For instance the constant potential V_{int} in the intersphere region for molecule $SnCl_4$ are -5.3 ev ($F_r = 0.88$), -6.01 ev ($F_r = 0.85$), -6.6 ev ($F_r = 0.82$) respectively. The energy shift from larger F_r to smaller F_r parallels the shift in V_{int}.

3.1. The Photoelectron Spectra of Molecules ACl_4 (A = C, Si, Ge, Sn)

A comparison of ionization energy data for the group IV tetrachlorides is plotted in Fig. 5. The solid lines and crosses represent the experimental values and
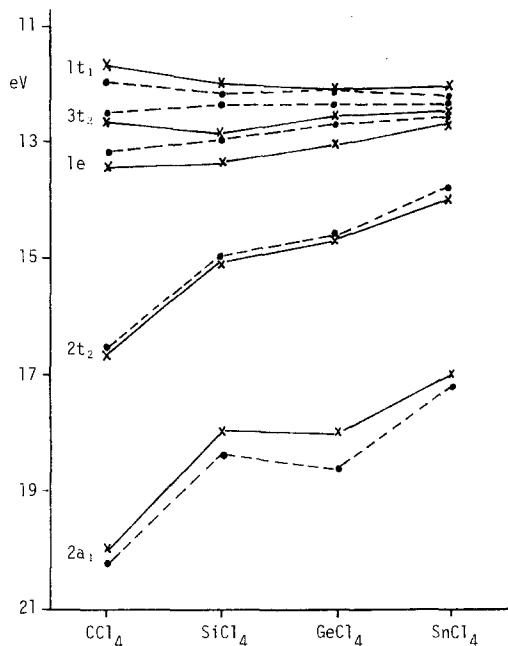
Fig. 5. A comparison of calculated and experimental ionization data for the group IVB tetrachlorides

dotted lines and circles represent the calculated values corresponding to the best F_r values. The three high energy bands are the least sensitive to variation of central atoms A and closer together with increasing atomic number of the group IV atoms than the other bands. The effect may be ascribed simply to the predominantly chlorine character of the molecular orbitals and diminishing interactions between the chlorine atoms as the size of the central atom increases.

The bands $2t_2$ and $2a_1$ are rather sensitive to the nature of the central atoms. This is to be expected because they are largely the bonding orbitals between chlorine central atoms. The bonding orbitals $2t_2$ have p character of the central atoms and the bonding orbitals $2a_1$ have s character of the central atoms. The irregular form of the plot for $2a_1$ bands (Fig. 5) is similar to that of the average ionization energy plot for the s valence electrons of the neutral atoms. As matter of fact the energy level $4s$ of Ge atom is lower than energy level $3s$ of Si atom.

Tables 2–5 show that bands $1t_2$ and $1a$, are getting closer with increasing atomic number of the group IV atoms. We are not surprised if it is noted that they have 88% and 68% of their charge in 2s orbitals of chlorine atoms for CCl_4 and 93% and 80% for $SnCl_4$ respectively.

3.2. The Photoelectron Spectra of Molecules CB_4 ($B = F$, Cl, Br, I)

The calculated and experimental results for the four molecules are listed in Tables 2, 6, 7, 8. Barber [13] et al. have calculated the ionization potentials of molecule CF_4 by SCF-X_α-SW method and their results are also listed in Table 6. Our results are in better agreement with the experimental results than their's
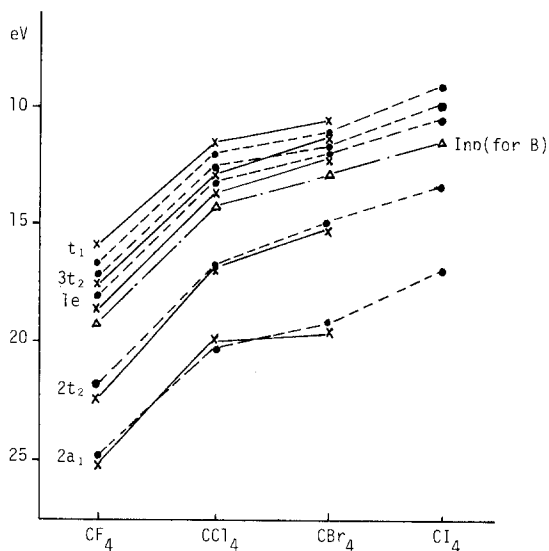
Fig. 6. A comparison of calculated and experimental ionization data for the carbon tetrahalides

due to adjusting the reduction factor F_r. Only one F_r value was chosen for molecule CI_4 because its experimental data are not available.

The comparison of calculated and experimental ionization data for the carbon tetrahalides is graphed in Fig. 6. The changes in energy of the three high lying energy bands parallel the changes in the averaged ionization potentials for the p valence electrons of the halogen atoms.

As mentioned above the bands $2t_2$ are the bonding orbitals between $2p$ orbitals of carbon atom and p valence orbitals of halogen atoms. The change in their ionization potentials with increasing the atomic number of the halogen atom should reflect the change in corresponding bonding energies. The relationship between the bonding energies and ionization potentials of the orbitals $2t_2$ of molecules CCl_4, CBr_4, CI_4 was plotted in Fig. 7. The bonding energy values were taken from Cottrell [18] and Glockler [19]. The value of the ionization
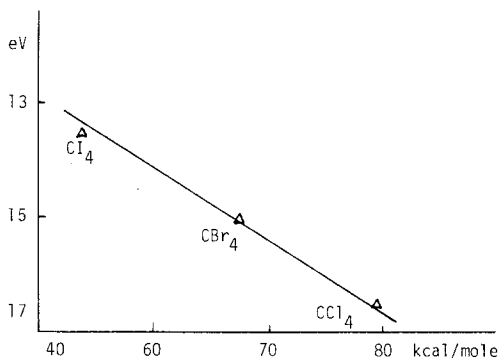

Fig. 7. The relationship between bond energies and ionization potentials of orbital $2t_2$ of CCl_4, CBr_4 and CI_4

potential for CI_4 is the calculated one in Table 7. The others are the experimental ones. The good linearity of the plot shows that the calculated result of band $2t_2$ for molecule CI_4 should be in good agreement with the experimental one.

In contrast to molecules ACl_4, the orbitals $1a_1$ and $1t_2$ of molecules CB_4 are getting slightly apart from each other with increasing the atomic number of halogen atom B. Since the energy level $2s$ of carbon atom is closer to the valence s shells of heavier halogen than those of lighter halogen atoms, $1a_2$ orbital of molecule CI_4 has 42% of their charge in carbon 2s orbital much more than 10% for molecule CF_4 (Tables 6, 8). But orbitals $1t_2$ keep their $2p$ constituent of carbon atom nearly constant (5%–7%).

4. Conclusions

The present SCF-X_α-SW calculations of ionization potentials for molecules ACl_4 and CB_4 lead to excellent agreement with the experimental photoelectron spectra by adjusting the radius reduction factors F_r carefully instead of changing individual atomic radii. The results of the present work are also significantly better in quantitative agreement with experimental data than the results of CNDO method and Barber's previous calculation. Some of other group IV halides have already been calculated by us, for example, CH_nX_{4-n} [20], and very good results have been obtained.

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