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Halogen−Halogen Interactions in Halomethanes

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Abstract: We report the study of the electronic structure of $CHFI_2$, $CHBrI_2$, $CHBr_2I$, $CHClI_2$, and $CHCl_2I$ using VUV photoelectron spectroscopy (UPS). The lone pair orbital interactions are discussed on the basis of experimental results and comparisons with other halomethanes.

Halomethanes are small five-atomic molecules which are of considerable interest to chemists, especially because of the role that they play in the atmospheric chemistry (ozone layer and greenhouse effects).[1] The electronic structure of halomethanes is especially interesting, because it allows accurate determination of intramolecular orbital interactions between the geminal halogens. We report in this work the analysis of such interactions based on the careful comparison of electronic structures within the closely related sets of molecules. Although the overall electronic structure of some halomethanes had been extensively investigated in the past[2] the interactions between different geminal halogens have not.

Experimental Section

Synthesis. General. Unless otherwise specified, all the materials were obtained from commercial suppliers and used without further purification. Mass spectra were recorded in electron ionization (EI) mode. FT-IR spectra were recorded as either neat film or KBr salt plate. ^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$ and ^{13}C NMR spectra were obtained at 75 MHz in $CDCl_3$, the ^{19}F NMR spectrum was obtained at 282 MHz in $CDCl_3$, and chemical shifts were referenced internally with trifluoroacetic acid (TFA) (δ 0.00) as the internal standard. Bromodiiodomethane,[3] dibromoiodomethane[3], dichloroiodomethane,[4] and chlorodiiodomethane[4] were prepared as reported previously. The synthesis of diiodofluoromethane was reported previously,[5] but we prepared the compound by the modified procedure described below.

Diiodofluoromethane. Sodium iodide (75 g, 0.5 mol) and dibromofluoromethane[6] (19.2 g, 0.1 mol) were charged into a 250 mL Teflon stopcock flask under nitrogen, and anhydrous acetone (100 mL) was added. After the flask was tightly closed, the mixture was heated to 100−110 °C for 8 days with stirring. After being cooled to room temperature, the products were distilled under high vacuum with a dry ice condenser. The resulting liquid was concentrated under water aspirator at room temperature to remove acetone, and the residue was redistilled under reduced pressure to afford diiodofluoromethane as a brown liquid (7.0 g, 24.5%): bp 62−64 °C/30 mmHg; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, $J_{H-F} = 48.1$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.33 (d, $J_{C-F} = 318.5$ Hz); ^{19}F NMR (282 MHz, $CDCl_3$) (TFA) δ −26.38 (t, $J_{F-C} = 30.5$ Hz, $J_{F-H} = 15.2$ Hz); MS(EI): 285.9 (M^+); HRMS(EI) calcd for CHI_2F 285.8149, found 285.8150; IR-(neat): 1681.6, 1615.0, 1089.6, 1053.9, 1016.6, 623.6 cm^{-1}.

Data for bromodiiodomethane: yield 52.4%; mp 59 °C (lit.[3] 60 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.74 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ −99.58; MS(EI): 345.7 (M^+), 347.6($[M + 2]^+$); HRMS-(EI): calcd for $CHBrI_2$ 345.7349, found 345.7351; IR(KBr): 1113.6, 1064.4, 616.7, 590.6, 573.9 cm^{-1}.

Data for dichloroiodomethane: yield 24.3%; bp 64−67 °C/30 mmHg (lit.[4] bp 26 °C/13 mmHg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.83; MS(EI): 209.9 (M^+); HRMS(EI) calcd for $CHCl_2I$ 209.8499, found 209.8499; IR (neat): 1207.2, 1129.1, 751.8, 702.8 cm^{-1}.

Data for chlorodiiodomethane: yield 20.5%; bp 106−108 °C/30 mmHg [lit.[4] bp 81 °C/13 mmHg]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.19 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ −67.78; MS(EI): 301.7 (M^+); HRMS(EI): calcd for $CHClI_2$ 301.7854, found 301.7849; IR (neat): 1162.7, 1105.2, 1068.7, 720.4 cm^{-1}.

Data for dibromoiodomethane: yield 71.1%; bp 124 °C/30 mmHg [lit.[3] 91 °C/42 mmHg]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.38 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ −43.11; MS(EI): 299.8 ($[M + 2]^+$); HRMS(EI): calcd for $CHBr_2I$ 297.7490, found 297.7489; IR(neat): 639.9, 608.7, 450.3 cm^{-1}.

UPS Measurements. The HeI/HeII photoelectron spectra were recorded on a Perkin-Elmer PS 16/18 spectrometer modified to allow preacceleration of photoelectrons and energy analysis at constant pass energy. Spectra were recorded at room temperature. The HeI spectra were recorded with an electron pass energy of 2 eV, and the resolution of 15 meV as measured on Ar^+ $^2P_{3/2}$ peak. The HeII spectra were measured at 30 eV pass energy and 150 meV resolution in order to generate sufficient signal. The rising background above 20 eV in HeII spectra is due to high pass energy. The spectra were calibrated by adding small amounts of N_2O and CH_3I to the sample flow and assuming the established ionization energies for these molecules.

Calculations. The ab initio calculations were performed with Gaussian 98 program.[7] The calculations were performed with full optimization at CCD level using TZ2P basis sets for carbon, hydrogen, chlorine, and bromine atoms and SDD effective core potential set[8] (which includes relativistic effects) for iodine. Subsequently, ROVGF method was used to calculate ionization energies. This method is not based on Koopmans approximation and is often used for the interpretation of photoelectron spectra.[9]

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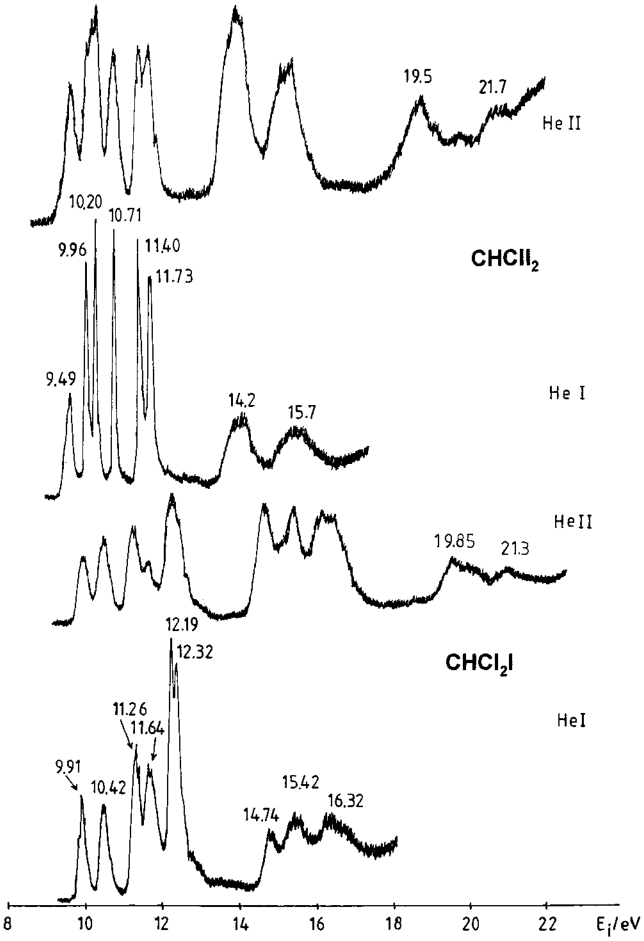

Figure 1. HeI and HeII photoelectron spectra of $CHClI_2$ and $CHCl_2I$.

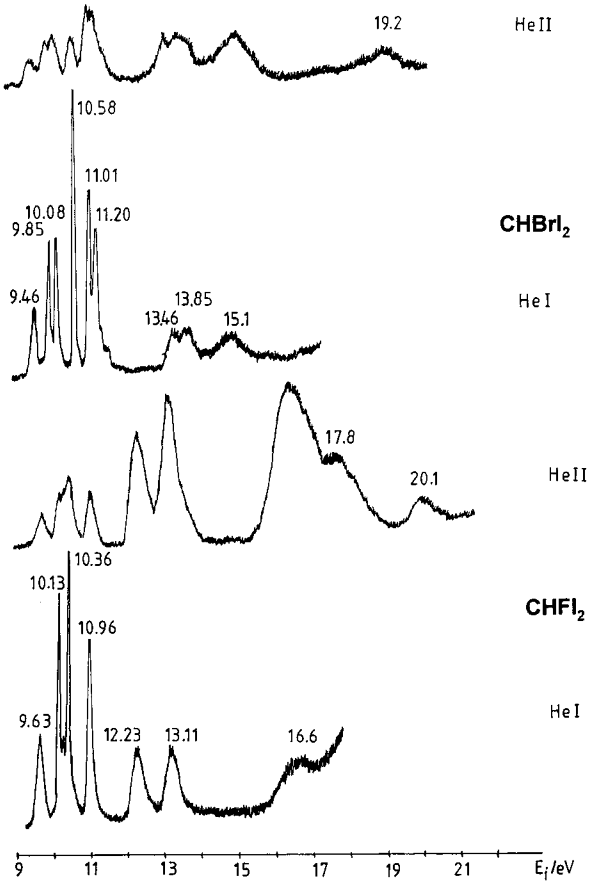

Figure 2. HeI and HeII photoelectron spectra of $CHFI_2$ and $CHBrI_2$.

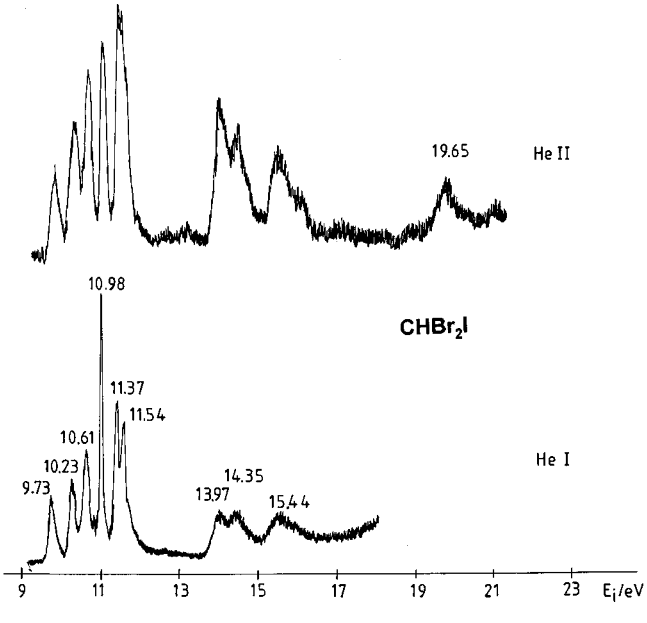

Figure 3. HeI and HeII photoelectron spectra of $CHBr_2I$.

The VUV photoelectron spectra (UPS) of halomethanes studied are shown in Figures 1−3. The unambiguous assignment of all the spectra (Table 1) can be readily obtained by the comparison with spectra of related halomethanes[10−14] as shown in the energy level correlation diagram (Figure 4). All the molecules studied have C_s symmetry. The HeII measurements confirm the nature of orbital ionizations (halogen lone pairs or σ-bonding orbitals) via the well-known variation of relative band intensities upon increasing photon energy. The results of MO calculations also support the proposed assignment (Table 1). The bands in 9−13 eV region exhibit a pronounced decrease in relative intensity on going from the HeI to HeII photon excitation and can be assigned to the halogen lone pair ionizations. The intensity decrease is due to a large decrease in photoionization cross-section for the halogen np orbitals on going from HeI to HeII excitation.[15] The bands in 13−16 eV range correspond to σ-bonding orbital ionizations. These orbitals have some C2p character and thus do not show the same decrease in relative band intensity as the lone pairs. On the other hand, the F2p photoionization cross-section decreases only marginally on going from HeI to HeII. This leads to relative band intensity increase for F2p ionizations as shown by the increased intensity of bands in the 16−17 eV range. The assignment of inner valence ionizations at >19 eV (Table 1) was based on the comparison with the spectra of related halomethanes. However, it is well established that the ionizations in inner valence region cannot always be described on the basis of single electron Koopmans

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Table 1. Vertical Ionization Energies (E_i/eV), Theoretical Ionization Energies (ROVGF/eV) and Band Assignments for Halomethanes[a]

molecule	band	E_i (±0.01 eV)	ROVGF (symm)	assignment
$CHFI_2$	X−C	9.63, 10.13, 10.36, 10.96	9.28(a″), 9.67(a″), 9.78(a′), 10.20(a′)	n_I
	D, E	12.23, 13.11	11.94(a″), 13.10(a′)	σ(CI)
	F, G	16.6, 16.6	16.58(a′), 16.96(a″)	σ(CH/n_F)
	H	17.8		σ(CF)
	I	20.1		C2s/I5s
$CHBrI_2$	X−C	9.46, 9.85, 10.08, 10.58	9.10(a″), 9.46(a″), 9.56(a′), 9.77(a′)	n_I
	D, E	11.01, 11.20	10.42(a″), 10.51(a′)	n_{Br}
	F, G	13.46, 13.85	13.23(a″), 13.45(a′)	σ(CI)
	H	15.1	14.91(a′)	σ(CBr)
	I	19.2		σ(CH)
$CHClI_2$	X−C	9.49, 9.96, 10.20, 10.71	9.22(a″), 9.61(a″), 9.72(a′), 10.00(a′)	n_I
	D, E	11.40, 11.73	11.13(a″), 11.48(a′)	n_{Cl}
	F−H	14.2, 14.2, 15.7	13.88(a″), 14.17(a′), 15.63 (a′)	σ(CI)
	I	19.5		σ(CCl/CH)
	J	21.7		C2s/Cl3s
$CHCl_2I$	X, A	9.91, 10.42	9.77(a″), 9.91(a″)	n_I
	B−E	11.26, 11.64, 12.19, 12.32	11.09(a′), 11.56(a″), 12.14(a′), 12.22(a″)	n_{Cl}
	F−H	14.74, 15.42, 16.32	14.74(a′), 15.42(a″), 16.34(a′)	σ(CI), σ(CCl)
	I, J	19.85, 21.3		C2s/I5s/Cl3s
$CHIBr_2$	X, A	9.73, 10.23	9.42(a″), 9.64(a′)	n_I
	B−E	10.61, 10.98 11.41, 11.54	10.19(a′), 10.21(a″) 10.83(a′), 10.84(a″)	n_{Br}
	F−H	13.97, 14.35, 15.44	13.66(a′), 13.97(a″), 15.30(a′)	σ(CI), σ(CBr)
	I	19.65		σ(CBr/CH)

[a] The ionization energies are accurate to ±0.01 eV in the halogen lone pair region and to ±0.05 eV in the rest of the spectrum.

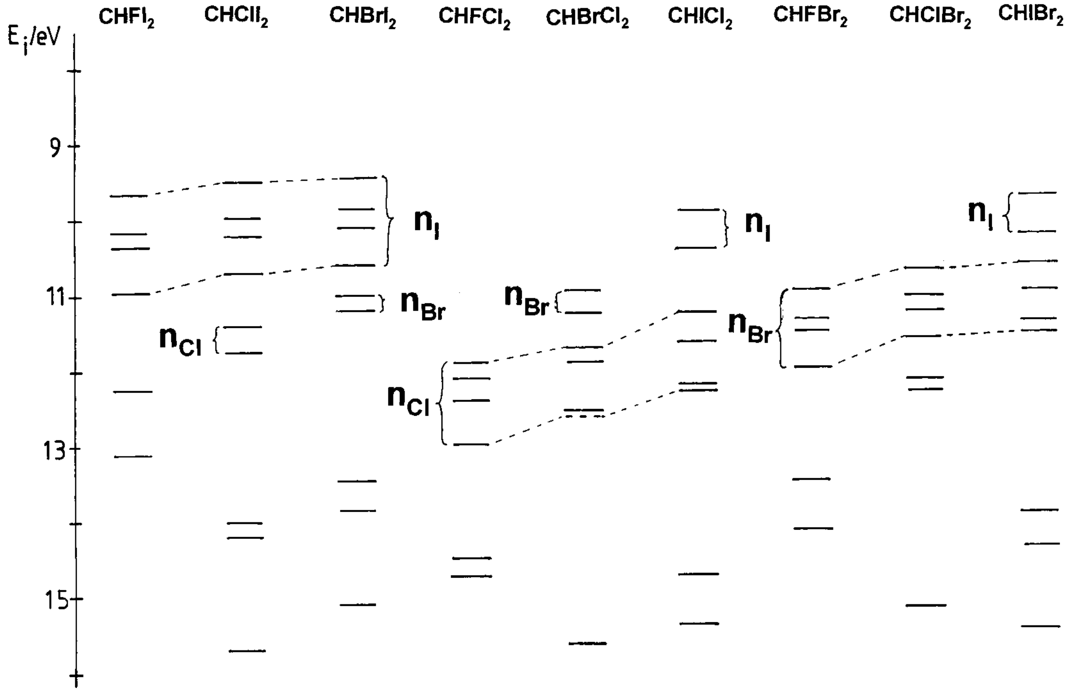

Figure 4. Energy level diagram for halomethanes studied in this and previous[10−14] work.

approximation (i.e. configuration interaction type processes need to be invoked). Bands at 9.73 and 10.23 eV in $CHBr_2I$ show vibrational fine structures of 310 ± 30 cm^{-1}; bands at 9.49 eV in $CHClI_2$ and 9.91 eV in $CHCl_2I$ also show fine structures of 230 and 380 cm^{-1}, respectively. The fine structures can be attributed to C−I and C−Br stretching modes on the basis of comparison with IR spectra of the corresponding methyl halides.[16]

The nonbonding, intramolecular halogen−halogen interactions are of considerable interest, and the use of UPS for interaction analysis has been extensively reviewed.[17] Halomethanes are especially suitable for studying such interactions due to the appearance of a small number of well resolved, unambiguously assignable, halogen lone pair bands which can act as an internal probe for intramolecular interactions.

The interactions considered in previous studies on haloalkanes took place between halogens attached to different carbons, and the mechanism of such interactions is often described as being of through-bond (TB) or through-space (TS) type. The study of UPS of dihaloalkanes, where halogens are separated by two or more CH_2 groups is of TB type.[18] In this work we describe halogen−halogen interactions where both halogens are on the same carbon (i.e. 1,1-*n*,*n*-interactions in Martin and Mayer's notation[17]) and where both TB and TS mechanisms are effective.

The observed splittings in the bromine, chlorine, and iodine lone pair ionizations reflect both the spin−orbit coupling (SOC)

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Table 2. Magnitude of Lone Pair−Lone Pair Intramolecular Interactions (IM/eV) in Halomethanes. The Original PES Data Are from the References Indicated

interaction	molecular pair	IM
F → Cl	$CH_3Cl \rightarrow CH_2FCl$ (refs 10,11)	1.60
Cl → Br	$CH_3Br \rightarrow CH_2BrCl$ (refs 10, 12)	0.43
Cl → I	$CH_3I \rightarrow CH_2ClI$ (refs 10, 13)	0.40
F → I	$CH_2I_2 \rightarrow CHFI_2$ (refs 10, this work)	1.06
Cl → I	$CH_2I_2 \rightarrow CHClI_2$ (refs 10, this work)	0.34
Br → I	$CH_2I_2 \rightarrow CHBrI_2$ (refs 10, this work)	0.23
F → Cl	$CH_2Cl_2 \rightarrow CHFCl_2$ (refs 10, 12)	2.18
Br → Cl	$CH_2Cl_2 \rightarrow CHBrCl_2$ (refs 10, 12)	1.53
I → Cl	$CH_2Cl_2 \rightarrow CHICl_2$ (refs 10, this work)	0.50
F → Br	$CH_2Br_2 \rightarrow CHFBr_2$ (refs 10, 14)	1.78
Cl → Br	$CH_2Br_2 \rightarrow CHClBr_2$ (refs 10, 12)	0.72
I → Br	$CH_2Br_2 \rightarrow CHIBr_2$ (refs 10, this work)	0.58

and the spatial interactions between orbitals localized on different halogens and/or various σ-bonding orbitals (N.B. Cl3p lone pairs have very small relativistic SOC effects <0.1 eV due to chlorine's relatively small atomic number). To circumvent the SOC complication we make comparisons between classes of molecules which have the same number of halogens of one type, while the other halogen type is varied (Table 2). The interaction magnitude (IM) is calculated as the sum of absolute values of energy shifts for halogen lone pairs. For example, when studying $Y \rightarrow X$ influence in the molecular pair $CH_2X_2 \rightarrow CHYX_2$, the IM is equal to the sum of absolute values of energy shifts of the four X_2 lone pairs in $CHYX_2$ vs the energies of the same four lone pairs in CH_2X_2 (Table 2). We have introduced IM descriptors because they can be taken as quantitative measures of halogen−halogen interactions. Classical TS and TB concepts can certainly be used to rationalize these interactions, but they are of qualitative nature, and in any case, TS and TB effects may be difficult to distinguish experimentally.

The data presented in Table 2 reveal the following general trends concerning 1,1-n,n-interactions:

(1) The fluorine atom has the strongest influence on other halogens (IM = 1−2.2 eV). This influence is predominantly of an inductive nature as established previously.[19]

(2) The Cl ↔ I and Br ↔ I interactions are weak (IM = 0.34−0.50 and 0.23−0.58 eV, respectively).

(3) Br ↔ Cl interactions are of moderate strength (IM = 0.43−1.53 eV).

Our experimental results show that X−Y type lone pair interactions involving iodine are the weakest (despite the large size of iodine atom). This can be attributed to the diffuse nature of I5p orbitals. We did not analyze the $CHXF_2$ series (X = Cl, Br, I), because the fluorine lone pairs (having much lower energies than X) interact with single X atom only inductively, not causing changes in X lone pair energy splittings. This effect can be observed, for instance, on going from CH_2X_2 to $CHFX_2$ families in this work.

The halogen lone pairs often represent frontier orbitals in organic reagents and are sources of nucleophilic activity. Our work is related to the modification of nucleophilicity[20] which may occur when an electronegative atom Z (with an unshared electron pair) is adjacent to another nucleophilic atom Y. In our case the two atoms would be the two halogens.

The modification is known as “α-effect” and it had been reported previously.[20] Furthermore, we have analyzed the interactions without recourse to population analysis, which partitions the electron density among atoms. This partitioning is not unique and several alternative descriptions of bonds, bond orders, and partial atomic charges (e.g. Mulliken population analysis, NBO analysis, AIM method, etc.) are in use.

Supporting Information Available: Geometries and computed total energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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