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Electronic Structure of Chiral Halomethanes

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We report the study of the electronic structures of CHBrFI and CHClFI using HeI/HeII photoelectron spectroscopy. The orbital interactions are discussed on the basis of high-level quantum chemical calculations and empirical arguments.

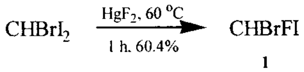
Introduction

Chiral halomethanes are the smallest stable chiral molecules,[1] and one of them (CHBrClF) has been the subject of several investigations dealing with the important physical and chemical aspects of chirality. The physical aspect comprises energy difference between enantiomers which can be expected on the basis of parity violating weak interactions. However, no energy difference was observed in a high-resolution vibrational spectroscopic[2] study of CHBrClF although experimental sensitivity was 3 orders of magnitude higher than the size of the expected enantiomeric effect. The chemical aspect comprises enantiomer separation, measurement of optical rotation, and the determination of molecule's absolute configuration.[3,4] Recently, a further important aspect of chirality emerged when "chiral photoionization" was observed.[5] To interpret asymmetry in photoelectron distributions from chiral molecules (induced by circularly polarized VUV light) the previous knowledge of electronic structure of such molecules is, of course, essential.[5] Besides the chirality aspect, the electronic structure of chiral halomethanes allows the accurate determination of intramolecular orbital interactions between geminal halogens. Out of the five possible chiral halomethanes (enantiomeric pairs), two (CHBrClF and CHBrClI) have been studied by UV photoelectron spectroscopy.[6,7] We report in this work the improved synthetic procedure for the preparation and the electronic structure analysis of CHBrFI and CHClFI. The remaining chiral halomethane (CBrClFI) is the subject of our current research program.

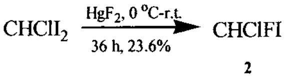
Experimental Section

Synthesis. The reported methods for the preparation of CHBrFI and CHClFI involve the classical Hunsdiecker reactions of silver bromofluoroacetate with silver chlorofluoroacetate under demanding conditions, such as high temperature, anhydrous environment, etc.[8] Since the use of pure, dry silver salts is often difficult due to their thermal instability, we have tried to find more convenient and milder methods for the preparation of CHBrFI and CHClFI by starting from $CHBrI_2$ and $CHClI_2$, respectively.[9,10] $CHBrI_2$ reacts with mercuric fluoride at 60 °C to give high purity CHBrFI in a good yield (Scheme 1). More conveniently, $CHClI_2$ can even react with mercuric fluoride at room temperature to afford CHClFI in a reasonably good yield and of high purity (Scheme 2).

SCHEME 1



SCHEME 2



Preparation of Bromofluoroiodomethane (1). $CHBrI_2$ (8.7 g, 25 mmol) and mercuric fluoride (3.0 g, 12.5 mmol) were charged into a 50 mL stopcock, round-bottomed flask under nitrogen. The mixture was continuously stirred and slowly heated to 60 °C for 1 h. After cooling, the products were removed under high vacuum with a dry ice condenser to give the light-sensitive liquid, which was redistilled under water-aspirator to afford **1** (3.61 g, 60.4%) as the light-sensitive liquid. bp 36−38 °C/30 mmHg (Lit.[1] bp 50 °C/50 mmHg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, $J_{H-F} = 49.1$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.55 (d, $J_{C-F} = 316.1$ Hz); ^{19}F NMR (282 MHz, $CDCl_3$) (TFA) δ −15.60 (d, $J_{F-H} = 53.3$ Hz); EIMS 239.8 (M^+); EIHRMS: *m/z* calcd for CHBrFI: 237.8289; found: 237.8287; IR (neat): 908.6, 735.3, 673.2 cm^{-1}.

Preparation of Chlorofluoroiodomethane (2). The fresh chlorodiiodomethane (25.4 g, 84 mmol) was charged into a 250 mL stopcock, round-bottomed flask under nitrogen. With stirring, mercuric fluoride (10.0 g, 42 mmol) was added in small portions at 0 °C under nitrogen. After addition, the resulting mixture was allowed to warm to room temperature and stirred for 36 h. The products were removed under high vacuum with dry ice condenser to give a light-sensitive liquid, which was redistilled under nitrogen to afford **2** as a light-sensitive liquid (3.85 g, 23.6%). bp 74−76 °C (Lit.[1] bp 35 °C/150 mmHg), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, $J_{H-F} = 50.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.04 (d, $J_{C-F} = 306.2$ Hz); ^{19}F NMR (282 MHz, $CDCl_3$) (TFA) δ −11.04 (d, $J_{F-H} = 53.3$ Hz); EIMS 193.8 (M^+); EIHRMS: *m/z* calcd for CHClFI: 193.8794; found: 193.8798; IR (neat): 908.5, 735.0, 651.0 cm^{-1}.

Spectral Measurements. The HeI/HeII photoelectron spectra were recorded on the Perkin-Elmer PS 16/18 spectrometer at

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TABLE 1: Experimental Ionization Energies (E_i/eV), Theoretical Ionization Energies (ROVGF/eV), Band Assignments, and Vibrational Frequencies (ν/cm^{-1}) for CHBrFI and CHClFI

band	E_i (±0.01 eV)	ROVGF	assignment	$\nu \pm 80$ cm^{-1}
		CHBrFI		
X, A	9.86, 10.49	9.82, 10.01	n_I	420 (C−Br str; X band)
B, C	11.02, 11.55	10.80, 11.27	n_{Br}	1090 (C−F str; B band)
D	12.83	12.73	σ(CH/CI)	
E	13.66	13.77	σ(CH/CBr)	
F, G	16.8, 16.8	16.95, 17.27	n_F, n_F	
H	18.0		σ(CF)	
I	20.6		C2s	
J	22.0		I5s	
		CHClFI		
X, A	10.06, 10.64	9.94, 10.05	n_I	410 (C−Br str.), 140 (C−I str.)
B, C	11.62, 12.41	11.30, 12.11	n_{Cl}	
D	13.46	13.30	σ(CH/CI)	
E	14.18	14.33	σ(CH/CBr)	
F	17.0	17.18	n_F	
G	18.2	17.48	σ(CF)	
H	20.5		C2s	
I	22.1		I5s	

room temperature. The HeI spectra were recorded with the 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 40 eV pass energy and 300 meV resolution in order to generate sufficient signal. The rising background above 20 eV in HeII spectra is due to high pass energy.

Calculations. The ab initio calculations were performed with Gaussian 98 set of programs.[11] The calculations were performed with full optimization at the CCD level using 6-311+G(3df,-3pd) basis sets for carbon, hydrogen, chlorine, and bromine atoms and SDD effective core potential set[13] for iodine (which includes relativistic effects). Subsequently, the ROVGF method[14] was used to obtain the ionization energies.

Results and Discussion

The photoelectron spectra of CHBrFI and CHClFI are shown in Figures 1 and 2. The unambiguous assignment of both spectra (Table 1) can be readily obtained by comparison with the reported spectra of CHBrClF[6] and CHBrClI[7] (Figure 3). 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 first four bands (X−C) show a pronounced decrease in their relative intensity on going from the HeI to HeII photon excitation. This is due to a large decrease of photoionization cross-section for Br4p and I5p orbitals on going from HeI to HeII excitation.[15] On the other hand, the F 2p photoionization cross-section decreases only marginally upon change from HeI to HeII. This leads to the relative band intensity increase for F2p ionization as is shown by the increased intensity of 16.8 eV band. The assignment of inner valence ionizations at >20 eV (Table 1) was based on the comparison with the spectrum of CH_2ClI.[16] However, it is well established that the ionizations in the inner valence region cannot always be described on the

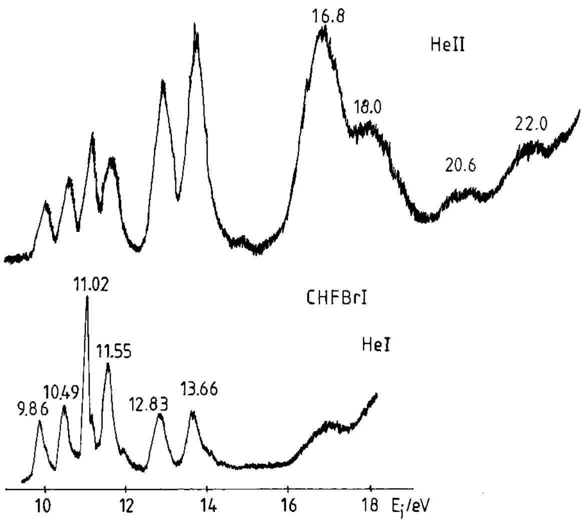

Figure 1. HeI and HeII photoelectron spectra of CHBrFI.

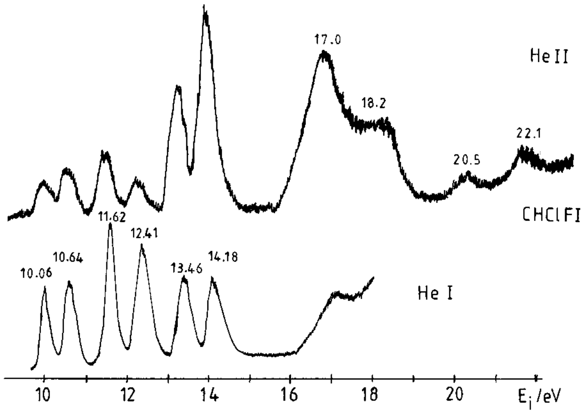

Figure 2. HeI and HeII photoelectron spectra of CHClFI.

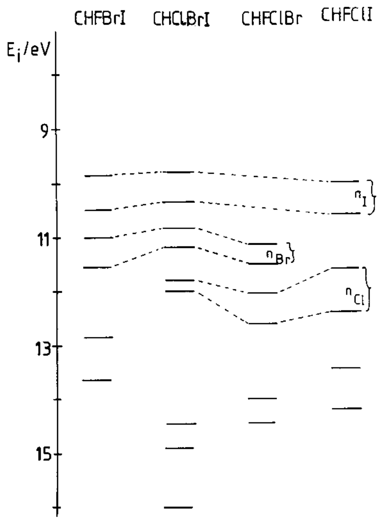

Figure 3. Energy level diagram for chiral halomethanes studied in previous works[6,7] and this work.

TABLE 2: Lone Pair Ionization Energy Splitting (ΔE_i/EV) in Halomethanes[a,b]

molecule	ΔE_i (Br)	ΔE_i (Cl)	ΔE_i (I)
CH_3Br[21]	0.32		
CH_3I[21]			0.62
CF_2BrCl[18]	0.30		
CH_2BrCl[19]	0.36		
$CHBrCl_2$[19]	0.30		
$CBrCl_3$[19]	0.31		
CF_3I[17]			0.73
CH_2ClI[16]		0.23	0.59
CHBrFI	0.53		0.63
CHBrClI[7]	0.35	0.22	0.55
CHBrClF[6]	0.33	0.55	
CHClFI		0.79	0.58

[a] Only the splittings >0.2 eV are listed. [b] The UPSdata are from references given as superscripts.

basis of Koopmans approximation (i.e., configuration interaction type processes need to be invoked). We must thus add that these ionizations have mixed C2s and halogen np character. The expanded scans of some bands (not shown in Figure 1) revealed vibrational progressions which were assigned by comparison with other halomethanes[16−19] (Table 1).

In the molecules with no symmetry, all intramolecular interactions become possible and the separations between lone pair energies provide a measure of such interactions. Furthermore, in halomethanes the small number of well resolved, halogen lone pair bands makes these molecules suitable for fine probing of intramolecular interactions.

The observed splitting in the bromine, chlorine, and iodine lone pair ionizations (Table 2) reflects both the spin−orbit coupling (SOC) and spatial interactions between orbitals localized on different halogens and/or various σ-bonding orbitals (N. B. Cl3p lone pairs have a very small relativistic SOC effects <0.1 eV due to its relatively small atomic number). SOC description strictly applies only to molecules with high symmetries. In an attempt to unravel different contributions to the measured splitting we have used the ROVGF method which does not include the relativistic SOC effect, but only spatial interactions. The difference between the calculated and measured splitting can then be used to gauge the relative contribution of each effect. Tables 1 and 2 and Figure 3 suggest that for I5p orbitals the SOC effect predominates, while for Cl3p only the spatial interactions are important. For Br4p both effects are important as can be seen, for example, from distinctly different bromine lone pair splittings in CHBrFI vs CHBrClF (Table 2).

The spatial orbital interactions are often described in terms of inductive and resonance effects. The electrostatic field nature of inductive effect causes equal shifts in lone pair orbital energies of both lone pair components (without changing the measured splitting), while the resonance effect influences the two components differently (and leads to measurable change in the splitting). A similar approach was outlined previously for dihaloalkanes $X(CH_2)_nX$ ($X = Br, I, n= 1-5$), but the presence of two identical halogens (Br or I) gives rise to four lone pairs bands.[20] The existence of four bands complicates the analysis and prevents the direct use of measured spin−orbit coupling as the probe for intramolecular interactions. We use experimental lone pair splitting for methyl bromide and methyl iodide as references and search for discrepancies from these values in other halomethanes as evidence of intramolecular halogen−halogen interactions. Two halomethanes exhibit unusually large/small splittings in Br4p and I5p: CF_3I exhibits an increase in I5p, while CHBrFI shows an increased splitting for Br4p. To understand these observations one must recall that halogen lone pair energy can be affected by resonance type interactions with other halogen lone pairs and with bonding σ-orbitals (whose energies are lower than Br, Cl, or I lone pairs).

In CF_3I, the increased splitting implies a destabilizing interaction with σ-orbitals since the F2p energies are considerably lower than I5p and thus make F2p−I5p interaction unlikely.

In CHBrFI the increased splitting of Br4p suggests the existence of strong I5p−Br interactions. The interactions with σ(CX) orbitals are less prominent, because if this were not the case one would expect an overall reduction in the Br4p splitting. Also, the broadening of Br4p component at higher ionization energy provides further evidence of strong Br4p−I5p interactions. The broad, symmetrical bandwidth usually indicates more bonding character and hence more delocalized nature of the corresponding ionized orbital and this can be rationalized through orbital mixing/interaction. This argument is based on the Franck−Condon principle. Br4p band at higher ionization energy is broader and has a symmetrical profile. I5p−Br4p interactions would also lead to a decrease in I5p splitting. The fact that none is observed suggests the predominance of relativistic effects (see above).

In CHClFI a very pronounced splitting of Cl3p ionizations is observed (Figure 3); the strongest in all halomethanes (Table 2). The existence of this splitting, both gives further evidence for and can be rationalized by the "CHF effect" described previously.[6]

Conclusion

Chiral halomethanes are good case studies for detailed analysis of various intramolecular interactions. Their photoelectron spectra contain a small number of well resolved, unambiguously assigned bands which can act as an internal probe for such interactions. The interactions can thus be analyzed without recourse to various theoretical models of population analysis, which are often subject to ambiguous descriptions of bonds, bond orders, and partial atomic charges (e.g., Mulliken population analysis, NBO analysis, AIM method, etc.)

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