

# Extended Fenske-Hall LCAO MO Calculations for Mixed Methylene Dihalides

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The electronic structure of mixed methylene dihalides  $\text{CH}_2\text{XY}$  ( $X, Y = \text{F, Cl, Br, I}$ ) has been studied using extended Fenske-Hall LCAO MO method. The comparison with available photoelectron spectra confirms previous assignments of all bands with binding energies  $< 100$  eV. The electronic structure changes occurring upon varying the halogen substituents are discussed.

## 1. Introduction

The halomethanes constitute an interesting class of compounds for several reasons. They have important technological applications (refrigeration, propellants) and are presently considered to be significant air pollutants. Also, they represent a prototype of halogen substituted molecules. The electronic structure of some halomethanes has been investigated previously by experimental and theoretical methods. However the electronic structure of halomethane molecules with low symmetry ( $C_s$  and  $C_1$  point groups) remains to be studied in any detail. In this work we have chosen to study methylene dihalides ( $\text{CH}_2\text{XY}$ ) mainly for two reasons. Firstly, the good quality photoelectron spectra of  $\text{CH}_2\text{FCl}$ ,  $\text{CH}_2\text{BrCl}$  and  $\text{CH}_2\text{ClI}$  reported some time ago and assigned through purely empirical considerations [1, 2] allow a comparison to be made with the calculated electronic structure. Secondly, we wished to test the applicability of extended Fenske-Hall (EFH) LCAO MO method in molecules of low symmetry containing several heavy atoms. This method has so far been mainly used to study the electronic structure of inorganic metal complexes. The EFH method has previously been employed in the calculation of inner-shell binding energies of fluoromethanes with some success [3].

basis sets. Calculations with two different kinds of basis sets were performed for six methylene dihalides. The basis sets adopted in the calculation were of double zeta and Hartree-Fock quality [4]. The EFH method does not involve any adjustable or empirical parameters, so the resulting eigenvalues and eigenvectors will be sensitive to the choice of basis functions and molecular geometry only. In the present work, experimentally determined molecular geometries were used where ever possible [5–9]. In case of  $\text{CH}_2\text{FI}$ , for which no experimental data exist, the molecular structure adopted was derived by assuming the  $\text{CH}_2\text{ClI}$  geometry [5] and the CF bond length taken from data on  $\text{CH}_2\text{FBr}$  [6]. The molecular coordinate system was defined in such a way that the  $yz$  plane was the plane of symmetry ( $C_s$  point group).

It is worth mentioning that the calculations are non relativistic and electronic structure correlations are based on Koopmans' approximation. The inclusion of relativistic effects will possibly induce some energy shifts in predominantly iodine lone pair type molecular orbitals. Fully relativistic MO calculations on molecules with several heavy atoms and low molecular symmetry are rare at present due to the necessity of introducing very large basis sets and the lack of symmetry simplifications which help in the evaluation of matrices and electron integrals.

## 2. Method of Calculation

The EFH method used in this work was an all electron method employing good quality extended

## 3. Results and Discussion

The eigenvalues obtained from the calculations for six  $\text{CH}_2\text{XY}$  molecules using HF STO basis sets are presented in Table 1. The differences in eigenvalues and eigenvectors obtained when using double zeta

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Table 1. Binding energies (eV) for CH<sub>2</sub>XY<sup>a, b</sup>.

Mole- cule	Orbital sym- metry	Calc. energy	AO character	Exp. energy	
CH <sub>2</sub> FCl	a''	11.9	0.92 Cl 3p	11.9	
	a'	12.09	0.92 Cl 3p	12.3	
	a'	13.97	0.65 F 2p+0.22 Cl 3p	14.35	
	a''	14.57	0.88 F 2p	14.6	
	a'	17.82	0.24 F 2p+0.41 Cl 3p +0.13 C 2p	16.85	
	a'	19.39	0.63 F 2p+0.13 C 2p	18.0	
	a''	22.54	0.45 C 2p+0.42 H 1s	19.5	
	a'	25.62	0.21 C 2s+0.19 C 2p+0.36 H 1s		
	a'	32.02	0.15 C 2s+0.1 C 2p+0.64 Cl 3s		
	a'	42.7	0.78 F 2s+0.11 C 2s		
	CH <sub>2</sub> FBr	a''	10.83	0.95 Br 4p	
		a'	10.99	0.95 Br 4p	
		a'	13.36	0.54 F 2p+0.31 Br 4p	
		a''	14.44	0.88 F 2p	
a'		17.25	0.37 F 2p+0.31 Br 4p+0.12 C 2p		
a'		19.22	0.66 F 2p+0.13 C 2p		
a''		22.16	0.45 C 2p+0.42 H 1s		
a'		25.0	0.16 C 2s+0.19 C 2p +0.32 H 1s+0.21 Br 4s		
a'		29.86	0.2 C 2s+0.56 Br 4s		
a'		42.6	0.1 C 2s+0.79 F 2s		
CH <sub>2</sub> FI	a''	9.56	0.98 I 5p		
	a'	9.70	0.98 I 5p		
	a'	12.38	0.41 I 5p+0.42 F 2p		
	a''	14.11	0.88 F 2p		
	a'	16.27	0.49 F 2p+0.16 I 5s+0.19 I 5p		
	a'	18.87	0.7 F 2p+0.11 C 2p		
	a''	21.91	0.46 C 2p+0.42 H 1s		
	a'	22.88	0.52 I 5s+0.18 C 2p		
	a'	27.34	0.36 C 2s+0.28 H 1s+0.17 I 5s		
	a'	42.3	0.1 C 2s+0.8 F 2s		
CH <sub>2</sub> ClBr	a'	10.77	0.67 Br 4p+0.27 Cl 3p	10.77	
	a''	11.36	0.94 Br 4p	11.06	
	a''	12.27	0.93 Cl 3p	11.81	
	a'	12.30	0.59 Cl 3p+0.27 Br 4p	11.81	
	a'	16.44	0.18 Cl 3p+0.41 Br 4p +0.22 C 2p	14.64	
	a'	17.6	0.43 Cl 3p+0.11 Br 4p +0.19 C 2p	15.39	
	a''	22.24	0.48 C 2p+0.46 H 1s	16.34	
	a'	25.14	0.17 Br 4s+0.32 H 1s +0.21 C 2p+0.15 C 2s	21.3	
	a'	29.2	0.26 Cl 3s+0.5 Br 4s +0.16 C 2p	23.5	
	a'	33.1	0.45 Cl 3s+0.11 Br 4s +0.3 C 2s	26.6	
CH <sub>2</sub> ClI	a'	9.76	0.83 I 5p+0.13 Cl 3p	9.76	
	a''	10.11	0.98 I 5p	10.35	
	a'	11.52	0.27 I 5p+0.65 Cl 3p	11.34	
	a''	11.94	0.95 Cl 3p	11.57	
	a'	15.2	0.41 I 5p+0.13 I 5s +0.16 Cl 3p+0.17 C 2p	13.87	
	a'	16.96	0.56 Cl 3p+0.16 C 2p	15.14	
	a''	21.68	0.46 H 1s+0.49 C 2p	16.22	
	a'	23.01	0.54 I 5s+0.19 C 2p	20.4	
	a'	26.63	0.23 Cl 3s+0.17 I 5s +0.2 C 2s	22.3	
	a'	32.27	0.27 C 2s+0.56 Cl 3s	26.6	
	65.2	I 4d			

Table 1. (continued).

Mole- cule	Orbital sym- metry	Calc. energy	AO character	Exp. energy
CH <sub>2</sub> BrI	a'	9.38	0.68 I 5p+0.26 Br 4p	
	a''	10.01	0.98 I 5p	
	a'	10.94	0.27 I 5p+0.59 Br 4p	
	a''	11.0	0.97 Br 4p	
	a'	14.71	0.43 I 5p+0.22 C 2p	
	a'	16.12	0.48 Br 4p+0.19 C 2p	
	a''	21.28	0.49 C 2p+0.46 H 1s	
	a'	22.70	0.53 I 5s+0.18 C 2p	
	a'	25.83	0.35 Br 4s+0.17 I 5s+0.12 C 2s	
	a'	30.54	0.44 Br 4s+0.35 C 2s	
		65.0	I 4d	
		86.9	Br 3d	

<sup>a</sup> The EFH eigenvalues are linearly shifted so that HOMO binding energy equals the measured ionization energy.

<sup>b</sup> Only AO characters > 10% are included in the Table.

basis sets instead are negligible (<0.5 eV in binding energy and <1% in atomic orbital character). It seems adequate therefore to use double zeta sets and achieve savings in computer time if necessary. The experimental binding energies deduced from photoelectron spectra are also included in Table 1.

The comparison of experimental with calculated binding energies (via Koopmans' approximation) shows the latter ones to be consistently too large. The overestimation, while quite small for halogen lone pair ionizations, gradually becomes larger reaching discrepancies of around 10 eV for inner shell d orbitals of bromine and iodine. Similar discrepancies were observed by Zwanziger and Reinhold [3] in fluoromethanes.

The assignment of molecular orbitals derived from the present calculations is in excellent agreement with the one obtained empirically from photoelectron spectra of CH<sub>2</sub>FCl, CH<sub>2</sub>BrCl and CH<sub>2</sub>CII [1, 2]. The assignment proposed in this work for the three remaining dihalides whose spectra have not yet been reported thus seems fairly reliable.

It is informative to comment on several aspects of photoelectron spectra reported by Doucet et al. [1] and Novak et al. [2].

The photoelectron spectrum of CH<sub>2</sub>FCl reported by Doucet et al. has been interpreted in a qualitative way only, without description of MO symmetries or characters. The first two bands in the spectrum (with lowest ionization energies) have been assigned to chlorine lone pair ionization, which is confirmed by

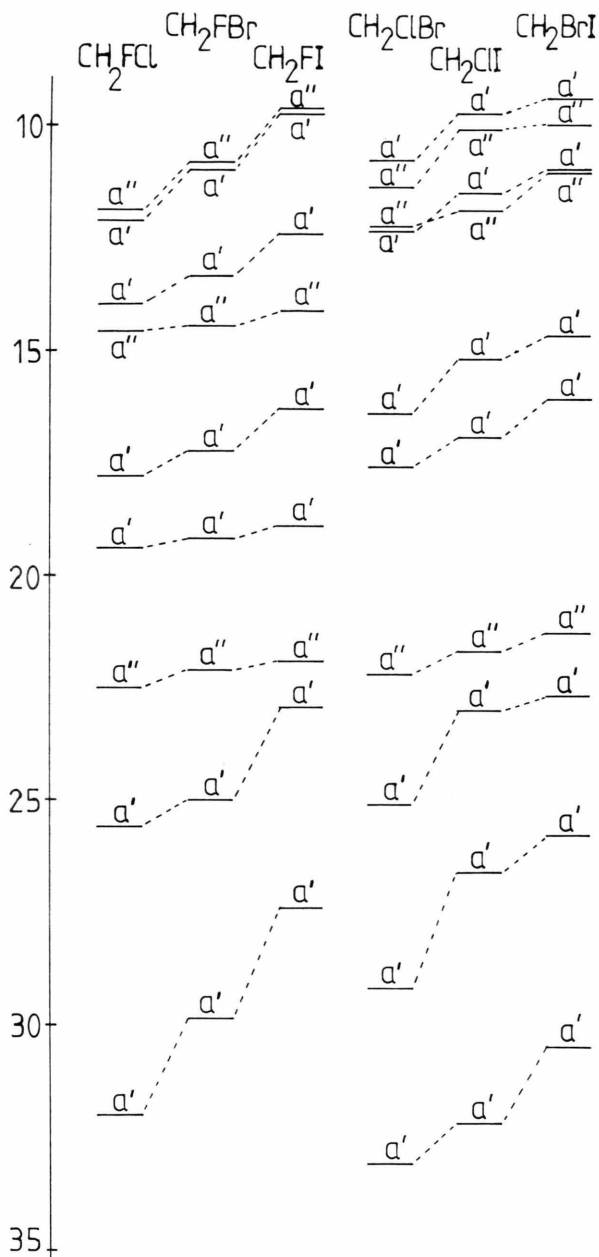


Fig. 1. Correlation diagram for the occupied MOs deduced from EFH calculations via Koopmans' approximation.

our calculation. The next group of bands at around 14 eV and 16–19 eV was described as corresponding to CCl, CH and CF bonding orbital ionization. Our calculations suggest a more complex picture. The 14 eV band should be associated with the orbitals of

predominantly F2p and Cl3p character (Table 1). Similar orbital character pertains to bands at 16.85 and 18.0 eV, which can be described as CCl and CF bonding orbitals, while the last band at 19.5 eV corresponds to predominantly CH bonding orbital. The orbitals with higher binding energies appear to be of strongly mixed character with the exception of the highest which possesses predominantly F2s composition.

It should be born in mind that the Koopmans' approximation breaks down at high binding energies (> 20 eV) with many-body effects causing the appearance of satellite bands and general redistribution of photoelectron intensities. Consequently the electronic structure calculated for this energy region must be regarded as of qualitative value only.

Our interpretation of bonding characteristics of  $\text{CH}_2\text{FCl}$  appears in good agreement with results reported by Li et al. [10] for their MS X $\alpha$  calculations on  $\text{CH}_2\text{F}_2$  and  $\text{CH}_2\text{Cl}_2$ .

The photoelectron spectra of  $\text{CH}_2\text{BrCl}$  and  $\text{CH}_2\text{ClI}$  have been assigned by Novak et al. [2], and their empirically derived assignments fully agree with ours. A slightly different interpretation of bands in the 20–27 eV region is worth commenting upon. The 3 bands in this region correspond to ionization from orbitals with strongly mixed I5s, Br4s, Cl3s and C2s character as revealed by our calculations (Table 1). It should be emphasized that these orbitals cannot be described in terms of single I5s, Br4s or Cl3s character due to heavy mixing taking place in the region.

The suggestion made by Novak et al. regarding the shape of the photoionization asymmetry parameter  $\beta$  for lone pair ionization can now be reexamined in the light of the present calculations. The difference in  $\beta$  curves between  $\text{CH}_2\text{BrCl}$  and  $\text{CH}_2\text{ClI}$  should indeed be attributed to the different shapes of constituent  $\beta$  curves for Br and I lone pairs and not to the extent of halogen mixing. Table 1 shows that the mixing, while considerable in both dihalides, is actually slightly higher in  $\text{CH}_2\text{BrCl}$ . On the basis of mixing considerations alone we would expect stronger  $\beta$  oscillations for  $\text{CH}_2\text{BrCl}$  than for  $\text{CH}_2\text{ClI}$ , which is not observed experimentally. The present results appear to support our original argument about the importance of individual curve shapes in determining the final  $\beta$  variation.

Figure 1 shows the general trends in eigenvalues for six dihalides. As expected, the introduction of a less electronegative halogen into the molecule inductively

shifts the energy levels towards lower ionization energies. The inner shell Br 3d and I 4d binding energies seem to be unaffected by substituent changes as can be expected from orbitals with predominantly atomic character. The most manifest shifts occur for orbitals with significant heavy atom s character possibly due to their spherically symmetrical shape, which permits overlap and interaction with several other bonding orbitals in the molecule ("through-bond" interaction). In conclusion, we believe that the EFH method provides a useful and convenient method to study small molecules with several heavy atoms and of low symmetry provided large enough basis sets and carefully

selected molecular geometries are adopted in the calculation. The results described in this work will hopefully stimulate further study of low symmetry halomethanes.

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