# Electronic Structure of Chiral Halomethanes

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**Synopsis.** The electronic structures of 5 possible chiral halomethanes have been studied using relativistic and nonrelativistic semiempirical MO calculations. Some thermodynamic properties of title molecules and their vibrational modes are also described in the light of calculations performed.

The molecular and electronic structure of several halomethane molecules has been studied in considerable detail by theoretical and spectroscopic methods mainly because of their technological and ecological importance. However for the five chiral asymmetrical molecules belonging to $C_1$ point group very few studies have been reported so far; none describing their electronic structure. One of these molecules (CFClBrI) is often mentioned in organic chemistry textbooks as an example of the asymmetrically substituted carbon atom leading to optical activity. In the continuation of our study of halomethanes we wished to examine the electronic structures of CFClBrI, CHFClBr, CHFBrI, CHClBrI, and CHFClI not only because they are the smallest known chiral molecules but also because they can be regarded as a convenient model of halogen substitution displaying changes in the electronic structure as a consequence of varying atomic number.

The MO methods used in this work include relativistically and nonrelativistically parametrized extended Hückel methods (REX, EHT), the all electron extended Fenske-Hall method (FH) and AM1 method. The first two were chosen because of their ability to (at least approximately) describe the role of relativistic effects introduced by heavier halogens, Fenske-Hall has previously[1] been successfully applied in the interpretation of halomethanes' photoelectron spectra while AM1 method is widely applied in the prediction of molecular geometries and thermodynamic properties of little known systems.

## Method of Calculation

The REX and EHT methods employed in this work were described by Pyykko[2,3] whose program and halogen parametrization were used in the calculation. The all electron FH method utilized the double zeta STO functions compiled by Clementi and Roetti.[4] The AM1 method used the new halogen parameters introduced recently by Dewar and Zoebisch.[5] The molecular geometries when fully optimised in the AM1 calculations differed only slightly (e.g. the bond lengths by $<0.005$ nm) from the idealized input geometry based on the gas-phase electron diffraction study of CHFClBr[6] and C-I bond length obtained from the microwave spectrum of $CH_2ClI$.[7] This observation is in accordance with Jacob's analysis of electron diffraction data which showed very shallow minima in the electron distribution curves for these molecules.[6]

## Results and Discussion

The results obtained in this work are given in Figs. 1 and 2 and Table 1. Figure 1 shows on the example of CFClBrI the kind of results obtained with different MO methods used. There are no available experimental ionization energies for halomethanes studied. The choice of MO method which would best describe their electronic structure has to be made with reference to other halomethanes for which comparisons between experiment and theory can be made. The photoelectron spectra of bromochloromethanes,[8] and fluorochloromethanes,[8] and chloroiodomethane[9] show that ionization energies of iodine, bromine, and chlorine lone pairs are in the ranges 9.6—10.6, 10.8—11.2, and 11.8—12.0 eV, respectively. It is also well established that F 2s ionization energies have value close to 40 eV irrespective of the type of halomethane molecule. Using these criteria as guidelines it can be shown from Fig. 1 that FH method is prefered over AM1 which generally does not predict binding energies well.

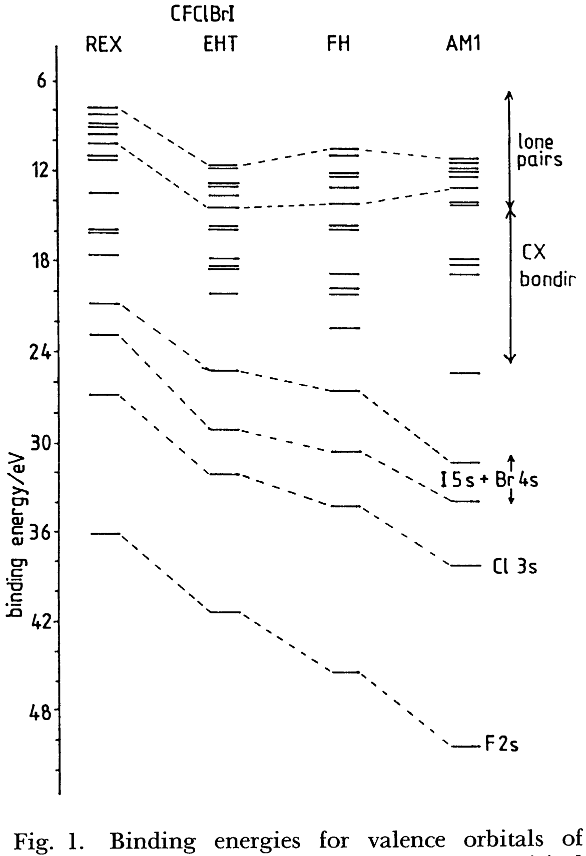

Fig. 1. Binding energies for valence orbitals of CFClBrI obtained by various semiempirical methods.

We have hence concentrated in Fig. 2 on the results of Fenske-Hall calculations.

The orbital character regions are recognizable throughout the series and consist of I, Br, Cl lone pairs, CX bonding orbitals and inner valence shells (Fig. 2). Several general observations concerning the electronic structures presented in Fig. 2 can be made. The molecule with the lowest ionization energy is CHClBrI. From previous experimental studies[1,8,9] and relative electron affinities of halogens it is known that iodine 5p orbital has the smallest binding energy which is reflected in the electronic structure of iodo substituted molecules. The other three iodo substituted methanes contain fluorine whose strong inductive effect increases binding energies of all orbitals. The CX binding energies in CHClBrI are lower than in other members of the series presumably due to the absence of fluorine inductive effect. F 2s and C 1s binding energies do not show significant changes as can be expected of the inner valence levels. I 5s and Br 4s orbitals lost their distinct atomic characters altogether forming linear combinations with each other and other bonding orbitals.

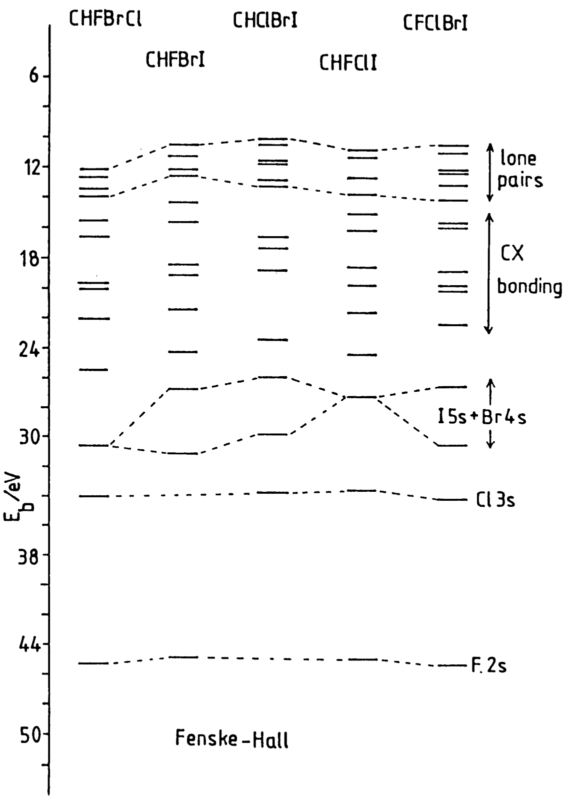

Fig. 2. Binding energies ($E_b$) of chiral halomethanes obtained from extended Fenske-Hall calculations.

It is instructive to consider results of other MO methods used as well. The comparison of REX and EHT results shown in Fig. 1 provides some indication of the importance of relativistic effects. All "relativistic" levels appear to be shifted linearly towards lower binding energies on average by 3—4 eV. The shifts are slightly larger than average for heavy halogen (Br, I) lone-pair orbitals as can be expected. The shifts can be associated with radial contraction of s and p AOs which would cause reduced overlap between orbitals and consequent destabilization of levels. The other two well-known relativistic effects: spin-orbit splitting of degenerate levels and radial expansion of d and f AOs were not observed.[10] Low molecular symmetry precludes the former effect while the latter one cannot be assessed because the REX

Table 1. Thermodynamic Properties (at 298 K), Dipole Moments ($\mu$), and Normal Modes of Vibration for Halomethanes[a]

| Molecule | $\mu$/D | $\Delta H$/kJ mol$^{-1}$ | | $H^\circ$/kJ mol$^{-1}$ | | $S^\circ$/kJ mol$^{-1}$ | | $C_p^\circ$/kJ mol$^{-1}$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | Calcn. | Estd. | Calcn. | Estd. | Calcn. | Estd. | Calcn. | Estd. |
| CFClBrI | 0.86 | −82.80 | −124.93 | 17.8 | — | 0.35 | — | 0.081 | — |
| CHFClBr | 1.30 | −208.07 | −229.83 | 13.64 | 13.84 | 0.305 | 0.304 | 0.062 | 0.063 |
| CHFClI | 1.30 | −156.86 | −168.57 | 13.96 | — | 0.31 | — | 0.062 | — |
| CHFBrI | 1.20 | −99.6 | −120.54 | 14.5 | — | 0.32 | — | 0.064 | — |
| CHClBrI | 0.97 | 32.0 | 58.0 | 15.46 | — | 0.34 | — | 0.069 | — |

| Molecule | Normal modes' frequencies (cm$^{-1}$) | | | | |
|---|---|---|---|---|---|
| CHFBrI | CHFBrCl | CFClBrI | CHClBrI | CHFClI | |
| 3007 | 2993(3025) | | 3028 | 3001 | (CH-stretch) |
| 1412 | 1399(1311) | | 1111 | 1408 | (HCX-bending) |
| 1274 | 1257(1205) | | 1036 | 1269 | (HCX-bending) |
| 1022 | 1071(1079) | 1383 | | 1072 | (CF-stretch) |
| | 801(788) | 825 | 875 | 809 | (CCl-stretch) |
| 722 | 630(664) | 760 | 744 | | (CBr-stretch) |
| 574 | | 513 | 545 | 608 | (CI-stretch) |
| | 464(427) | 357 | | 453 | (FCCl-bending) |
| 388 | 337(315) | 302 | | | (FCBr-bending) |
| 293 | | | | 304 | (FCI-bending) |
| | 225(226) | 250 | 284 | | (BrCCl-bending) |
| | | 165 | 182 | 183 | (ICCl-bending) |
| 127 | | 118 | 128 | | (ICBr-bending) |

a) The frequencies in brackets represent experimental data by Diem and Burow.

parametrization does not include Br 3d and I 4d orbitals. Effects of d shells can at any rate be expected to be small due to their core character.

Comparison with the photoelectron spectra of similar mixed halomethanes[9] indicates that REX relativistic shifts make binding energies too small. The linearity of shifts is somewhat surprising since one can expect the largest shifts for heavy halogen lone pair orbitals. A possible explanation is that REX (like most extended Hückel methods) exaggerates orbital mixing in halomethanes and thus introduces "relativistic" character into all orbitals. The effect can be especially significant in our molecules which lack any symmetry. Mulliken population analysis performed as a part of REX calculation tends to support this conclusion. Thermodynamic functions and normal modes of vibration have also been calculated and are given in Table 1.

Our thermodynamic results can be compared with enthalpies of formation estimated on the basis of bond enthalpies and tabulated by Kudchadker and Kudchadker.[11] Our values appear too large by around 20 $\mathrm{kJ\,mol^{-1}}$ although the detailed discussion must await the report of experimental values for the enthalpies. The ideal gas thermodynamic properties calculated from the partition functions are in good agreement with Kudchadker.

The vibrational frequencies obtained from AM1 calculations agree very well with the only experimental result reported so far for a chiral halomethane.[12]

Calculated enthalpies of formation indicate that the thermodynamic stability of compounds decreases in sequence $\mathrm{CHFClBr} > \mathrm{CHFClI} > \mathrm{CHFBrI} > \mathrm{CFClBrI} > \mathrm{CHClBrI}$. This may account for the fact that bromochlorofluoromethane as the most stable in the group is the only chiral halomethane synthesized so far. The chiral halomethanes probably hydrolyze fast. Study of rates of base hydrolysis conducted by Hine et al.[13] has shown the CHFClBr rate to be much faster than other mixed nonchiral halomethanes.

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