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IONIZATION POTENTIALS OF TRIFLUOROMETHYL AND METHYL HALIDES BY PHOTOELECTRON SPECTROSCOPY AND CALCULATIONS BY EXTENDED HÜCKEL AND CNDO/2 METHODS

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Ionization potentials and electron affinities of trifluoromethyl and methyl halides calculated by EHMO and CNDO/2 were compared with the observed values obtained from photoelectron spectroscopy. The former calculation provides a good agreement for the occupied orbitals, while the latter explains nearly the entire system.

Introduction

It is accepted generally that photoelectron spectra (PES) are not only useful for obtaining ionization potentials of melecules but serve for verification of the calculations according to the molecular orbital method.[1] In the present paper, the ionization potentials of trifluoromethyl and methyl halides were obtained by photoelectron spectroscopy. The orbital energies including the lowest vacant orbitals and their characters were interpreted by use of Extended Hückel (EHMO) and CNDO/2 calculations.[2,3]

A number of PES are already available for methyl halides and some of them were interpreted by molecular orbital calculations.[4-8] However, no attempt has been made to provide a consistent interpretation of a series of compounds comprising different kinds of halogen atoms by the same method of calculation. Particularly, no PES of trifluoromethyl halides have been provided yet.

Experimental and Calculation

The PES of all kinds of methyl halides and those of trifluoromethyl halides except iodide were obtained by a JASCO PE-1 photoelectron spectrometer using He I (584A) as a light source and xenon as an internal reference. The electronic structure of these compounds were calculated by EHMO and CNDO/2 using Slater's orbitals. In the former calculation the n* value for bromine was approximated to 4, and in the latter, calculations of bromide and iodide were not practicable.

Results

The PES obtained are shown in Fig. 1. Trifluoromethyl chloride and bromide give five peaks each. In either case the first peak is attributable, from its

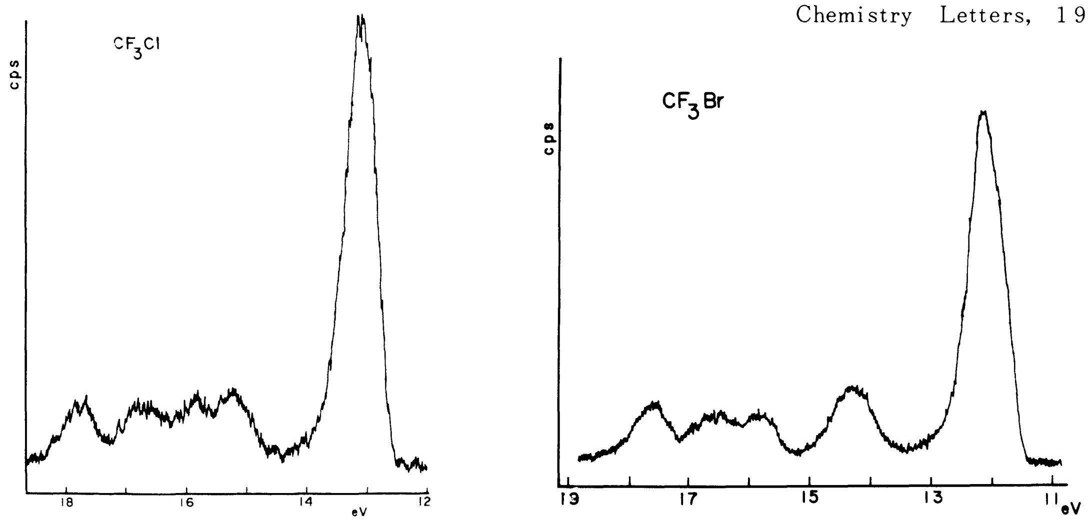

Fig. 1 Photoelectron spectra of trifluoromethyl halides.

shape and size, to the lone pair electron of chlorine and bromine, and the second peak to the C-X bond according to the method proposed by Kimura et al.9) The remaining three peaks seem to correspond to those exhibited by carbon tetrafluoride. In these spectra, neither the spin-orbit splitting as reported in methyl halides, nor any vibrational structure was observed. The PES of other halides are not presented since they differ only little from those given in previous works.4-8)

In Table 1 are shown the ionization potentials of halides from the PES and the corresponding values calculated by EHMO and CNDO/2 along with dominant atomic orbital bond populations (EHMO) and overlap populations (CNDO/2). The ionization potentials of methyl halides and carbon tetrafluoride obtained from the PES in this work are also shown to compare with the calculated in Table 1. They nearly coincide with those of previous experiments.4-8)

Discussion

(1) Occupied orbitals. In the EHMO schem, the observed first ionization potentials of methyl halides are about 0.9 times the calculated highest occupied orbitals (HO), but the other ionization potentials are in good agreement with the calculated values. For trifluoromethyl halides the agreement in the first ionization potentials is improved, but a slight scattering is observed in the others. Generally, however, the two series of the compounds exhibit a good agreement between the calculated and the observed ionization potentials. As for the nature of the orbital, the HOs of all halides are attributed from the populations to the lone pair electron of the heterogeneous halogen atom except methyl fluoride. The HOs of trifluoromethyl halides are highly populated being compatible with those of methyl halides. The second ionization potentials are all assigned to the C-X

Table 1 Observed and calculated molecular orbitals of trifluoromethyl and methyl halides and their localizabilities.

		EHMO					CNDO/2				
Compound	Ionization potential (obs.) eV	Molecular orbital (calc'd) eV			Localizability, Atomic orbital bond population ***		Molecular orbital (calc'd) eV			Localizability, Overlap population*	
CF_4		4.82	e	LV	C-F	-0.2513	5.18	a_1	LV	C-F	-0.0799
										F	0.0835
	16.26	-17.82	t_1	HO	F	0.2207	-20.19	t_1	HO	F	0.3075
	17.57	-17.88	t_1		F	0.2543	-22.27	t_1		F	0.2500
	18.61	-18.25	e		F	0.2473	-23.30	e		F	0.2500
		-18.79	t_2		F	0.1620	-29.19	t_2		F	0.1581
CF_3Cl		3.19	a_1	LV	C-Cl	-0.4600	1.87	a_1	LV	C-Cl	-0.2540
	13.10	-13.36	e	HO	Cl	0.9072	-16.23	e	HO	Cl	0.8654
	15.20	-14.70	a_1		C-Cl	0.0840	-16.56	a_1		C-Cl	0.0982
	15.82	-17.84	e		F	0.3331	-20.57	e		F	0.3037
	16.69	-17.87	a_2		F	0.3390	-22.11	a_2		F	0.3332
	17.73	-18.13	e		F	0.1024	-22.74	e		F	0.0787
		-18.32	a_1		F	0.0193	-25.23	a_1		C-Cl	-0.0298
CF_3Br		3.19	a_1		C-Br	-0.4149					
	12.10	-12.09	e		Br	0.7329					
	14.33	-14.11	a_1		C-Br	0.0979					
	15.84	-17.83	e		F	0.3216					
	16.54	-17.87	a_2		F	0.3390					
	17.60	-17.89	a_1		C-Br	-0.0047					
					F	0.0025					
		-18.13	e		F	0.1077					
CH_3F							9.04	a_1		C-F	-0.2267
							7.91	e		C-H	-0.0454
		- 0.05	a_1	LV	C-F	-0.3921	6.81	a_1	LV	C-H	-0.1410
	13.05	-14.54	e	HO	F	0.0964	-17.57	e	HO	F	0.4826
					C-H	0.0944				C-H	0.0724
	17.40	-18.15	a_1		C-F	0.0401	-21.29	a_1		C-F	0.0801
		-18.29	e		F	0.9099	-24.12	e		F	0.5072
CH_3Cl		0.83	a_1	LV	C-Cl	-0.5385	4.00	a_1	LV	C-Cl	-0.2628
	11.33	-12.74	e	HO	Cl	0.8589	-14.25	e	HO	Cl	0.8979
	14.46	-14.42	a_1		C-Cl	0.0902	-16.64	a_1		C-Cl	0.1216
	15.36	-15.32	e		C-H	0.0776	-21.39	e		C-H	-0.1275
		-21.05	a_1		C-H	0.0450	-27.21	a_1		C-Cl	0.1231
CH_3Br		2.29	a_1	LV	C-Br	-0.5873					
	10.53	-11.55	e	HO	Br	0.9735					
	10.86										
	13.45	-13.54	a_1		C-Br	0.0999					
	15.38	-15.18	e		C-H	0.0835					
		-19.86	a_1		C-H	0.0345					
CH_3I		- 1.49	a_1	LV	C-I	-0.4707					
	9.51	-10.59	e	HO	I	0.9934					
	10.12										
	12.50	-12.67	a_1		C-I	0.0824					
	14.55	-15.04	e		C-H	0.0934					
		-17.47	a_1		C-I	0.0301					

* The populations are given for one bond in a molecule and for one component of a degenerate set.

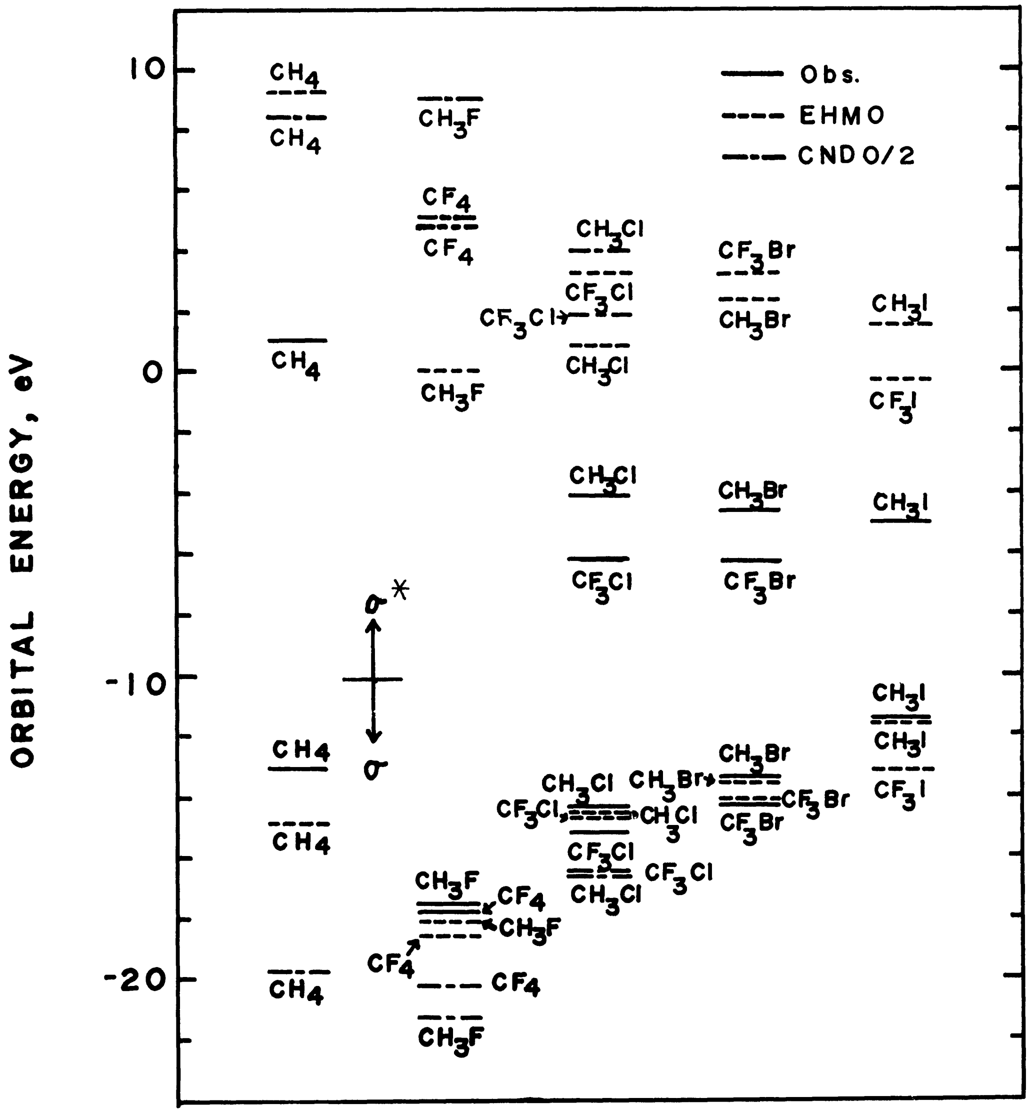

Fig. 2 Observed and calculated molecular orbitals of σ(C-X) and σ*(C-X).[13]

bond except carbon tetrafluoride. They explain the experimental results very well.

With respect to methyl fluoride, the HO is the orbital that the C-H bond and the lone pair electron of fluorine are equally mixed. The peak of first ionization potential of this compound has a vibrational structure of 1129 cm^{-1}, which is smaller than any of the vibrations due to the C-H bond in the ground state, whereas the vibrational frequencies for the other methyl halides are not very different from those in their ground states. This supports the results of EHMO.

The above interpretations agree with those obtained previously for methyl halides and the experimental results obtained here for trifluoromethyl halides. It is also verified by a comparison of the observed and the calculated populations that the remaining three spectra of trifluoromethyl chloride and bromide are due to the lone pair electrons of the fluorine atoms.

The symmetry of the occupied orbitals of each molecule is also shown in Table 1. It gives proper results for methyl and trifluoromethyl halides. But for carbon tetrafluoride, the order of the present work, $2t_1 > 1t_1 > 1e > 3t_2 > 4a_1$, differs from that of Frost et al.,[10] $4t_2 > 1t_1$, or those of Brundle et al.[4] and Potts et al.,[6] $1t_1 > 4t_2$, in the first position, where t_2 is slightly included in our t_1.

On the other hand, the results calculated by CNDO/2 give orbital values 3 to 4 eV higher than the observed. They are no doubt higher than those obtained from EHMO or those given by Brundle et al.,[4,8] but the same interpretation is given for the order of the occupied orbitals and their characters obtained except the HO of methyl fluoride. At the HO of this compound, the lone pair of fluorine atom is dominant in the CNDO/2 schem in contrast to the results of EHMO. It is considered from PES that the interpretation by EHMO is more correct as described avove. The symmetry of the orbitals is the same with that of EHMO.

(2) Lowest vacant orbitals. The most remarkable difference between two calculation methods is found in the lowest vacant orbital (LV) of methyl fluoride, as shown in Table 1. The LV in EHMO is -0.05 eV and C-F anti-bonding is dominant, while that in CNDO/2 is 6.81 eV and consists of the C-H anti-bonding. The orbital that the C-F anti-bonding becomes dominant is the second level above the LV. The symmetry of LV of carbon tetrafluoride given by EHMO differs from that in CNDO/2. The LV represents the electron affinity of a molecule.

The observed values of electron affinities of halides are very few, but there are some data on the $n - \sigma^*$ transition given by vacuum ultra-violet spectra. By use of the UV data and the PES in the present experiment, it is possible to obtain the experimental LV values.[11,12] The experimental values of σ^*(C-X) thus obtained and values of σ(C-X) from the PES are shown in Fig. 2 along with the corresponding orbitals calculated by EHMO and CNDO/2. It can be seen from Fig. 2 that the ionization potentials of σ(C-X) of trifluoromethyl and methyl halides decrease in the order of F, Cl, Br and I, and conversely, the electron affinities, σ^*(C-X) increase in the same order. As discussed above, the σ(C-X) agree fairly well with the values calculated, but at the LVs there are discrepancies of 5 to 9 eV in EHMO and about 8 eV in CNDO/2 from the observed values. This indicates that the absolute values obtained by these calculation methods are not sufficiently correct for the vacant levels.

Although the observed LV values of methyl fluoride is lacking, it is clear that EHMO provides only irregular results, while CNDO/2 gives a trend which is quite similar to that of the observed. The latter tendency is also in good agreement with those observed for relative electron affinities provided by various other experimental methods.[14,15]

Conclusion

In conclusion EHMO gives correct knowledge for the occupied orbitals of trifluoromethyl and methyl halides, but not fully for the vacant orbitals, while CNDO/2 better explains all the system except the HO of methyl fluoride.

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