

# Photoelectron Spectra of Bromo- and Iodotrifluoromethane

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Z. Naturforsch. **33a**, 1528–1532 (1978); received October 19, 1977

The HeI and HeII photoelectron spectra of the title compounds have been recorded and analysed on the basis of comparison with chlorotrifluoromethane and methyl halides. Spin-orbit splitting could be observed in the ground state of  $\text{CF}_3\text{I}^+$  where it amounts to 0.73 eV and is unresolved in  $\text{CF}_3\text{Br}^+$ . Vibrational fine structure observed in two band systems  $\tilde{\text{D}}$  and  $\tilde{\text{E}}$  in  $\text{CF}_3\text{Br}^+$ , and  $\tilde{\text{X}}$  and  $\tilde{\text{E}}$  in  $\text{CF}_3\text{I}^+$  is also discussed.

## Introduction

In our investigation of the photoelectron (PE) spectra of chlorofluoromethanes [1] we found a marked variation of the ionization cross-section for the various systems when going from HeI to HeII excitation. The dependence of the photoionization cross-section on the energy of the exciting radiation has been investigated already by Price et al. [2]. They found that on increasing photon energy the ionization cross-section for s electrons rose relative to that for p electrons. Schweig and Thiel [3] examined the problem from the theoretical aspect. Their results predict that the transition probabilities of the 2s electrons of B, C, N, O, and F and the 3s and 3p electrons of Si, P, S, and Cl significantly decrease at higher photoelectron energies e.g. in changing from HeI and HeII excitation. At the same time the ionization cross-sections of the 2p electrons of N, O, and F should remain constant or rise (for carbon 2p a slight decrease is expected). Similarly, Rabalais [4] calculated photoionization cross-sections of p electrons in F, Cl, Br and I. For a change from HeI to HeII excitation their results indicate that the strongest decrease of ionization cross-section is expected for iodine while for bromine and chlorine this decrease is less pronounced. For fluorine, however, a small increase of ionization cross-section on going from HeI to HeII excitation was predicted.

In the chlorofluoromethanes it was found that the most pronounced difference is in the behaviour of fluorine relative to chlorine lone pairs [1]. In order to compare the bromine and iodine lone pair ionizations, we decided to investigate the HeI and HeII spectra of bromo- and iodotrifluoromethane.

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The HeI PE spectrum of  $\text{CF}_3\text{Br}$  has been recorded previously under low resolution by Doucet et al. [5] but only the first two systems have been assigned.  $\text{CF}_3\text{I}$  has not been studied by PE spectroscopy.

## Experimental

The PE spectra were recorded on a Vacuum Generators UV-G3 instrument in the energy range from 11 to 25 eV using HeI and HeII excitation. The details of the instrument were described earlier [6]. For calibration small amounts of xenon and argon were added to the sample.

The resolution in the HeII spectra was better than 50 meV and in the HeI spectra better than 30 meV. The high resolution spectra (Figs. 2, 3, 5 and 6) were recorded at 10 meV resolution. The gases were of commercial origin (Matheson Gas Products, EGA Chemie).

## Results and Discussion

### Bromotrifluoromethane

The HeI and HeII PE spectra of bromotrifluoromethane are shown in Figure 1. The vertical ionization energies ( $\pm 0.05$  eV) are given at the top of the systems. The spectra are very similar to those of  $\text{CF}_3\text{Cl}$  [1] with the first two systems shifted by about 1 eV to lower ionization energy. These are easily identified as the bromine lone pair ionization ( $^2\text{E}$ ) at vertical ionization energy of 12.08 eV and the ionization from the C—Br bonding orbital at 14.28 eV. The first system is much broader than the corresponding system of  $\text{CF}_3\text{Cl}$  which can be interpreted by the unresolved splitting due to spin-orbit coupling (vide infra). The next four systems at 15.86, 16.55, 17.57 and 19.8 eV arise from predominantly fluorine lone pair electrons whose participation in bonding increases with



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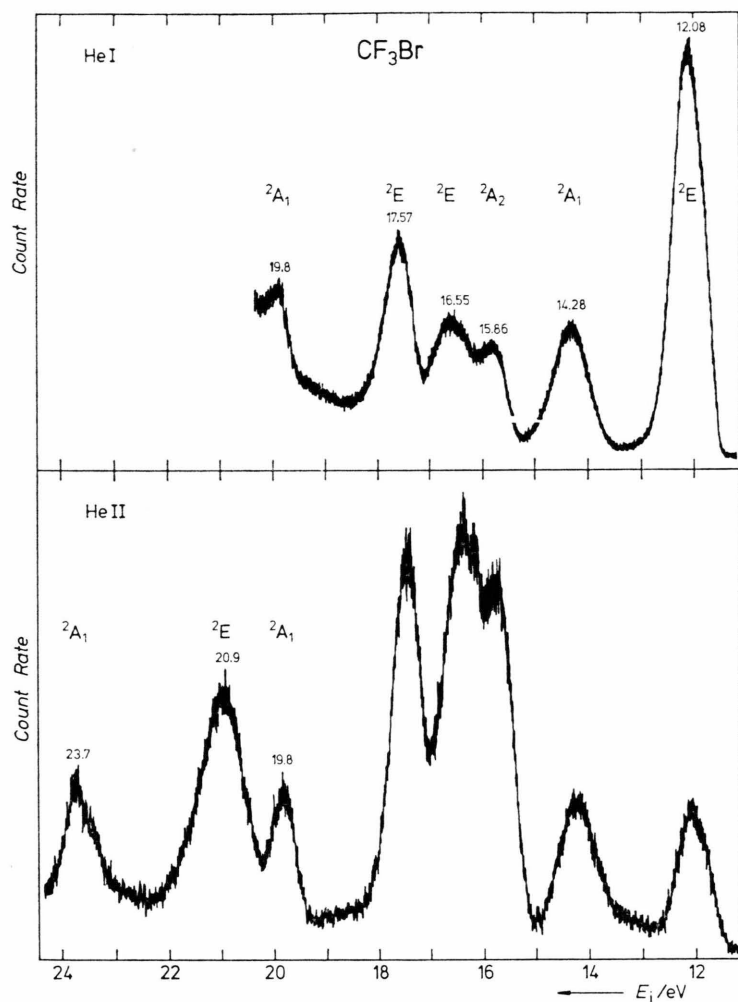


Fig. 1. HeI and HeII PE spectra of bromotrifluoromethane.

increasing ionization energy. Their position and relative intensities match those in  $\text{CF}_3\text{Cl}$  very closely so that the assignment can also be directly transferred. The last two systems at 20.9 and 23.7 eV can only be observed with HeII excitation and can be assigned as  $^2\text{E}$  and  $^2\text{A}_1$ , respectively, just as in the case of  $\text{CF}_3\text{Cl}$ .

Under high resolution two systems show vibrational fine structure. The 17.7 eV  $^2\text{E}$  system is shown in Fig. 2 and reveals two active vibrations of 1080 and 690  $\text{cm}^{-1}$ . As in the case of  $\text{CF}_3\text{Cl}$  [1] and fluoroform [7] these will be the  $\text{CF}_3$  stretching and  $\text{CF}_3$  deformation modes having molecular ground state wave numbers of 1089 and 760  $\text{cm}^{-1}$ , respectively [8]. In the 19.8 eV system (Fig. 3) a progression of 620  $\text{cm}^{-1}$  is observed which we

assign to the  $\text{CF}_3$  deformation vibration — the most likely mode to be excited on ionization of fluorine lone pairs electrons. The weaker bands separated by 360  $\text{cm}^{-1}$  from the main progression can be attributed to the C—Br stretching vibration.

#### *Iodotrifluoromethane*

The HeI and HeII PE spectra of iodotrifluoromethane are shown in Figure 4.

The spectra are very similar to those of  $\text{CF}_3\text{Br}$  (Fig. 1), except that the first system in the  $\text{CF}_3\text{I}$  spectrum caused by ionization of iodine lone pair electrons is split by spin-orbit coupling into two components  $^2\text{E}_{3/2}$  and  $^2\text{E}_{1/2}$  at vertical ionization energies of 10.45 and 11.18 eV, respectively. The next system at 13.25 eV is assigned to the C—I

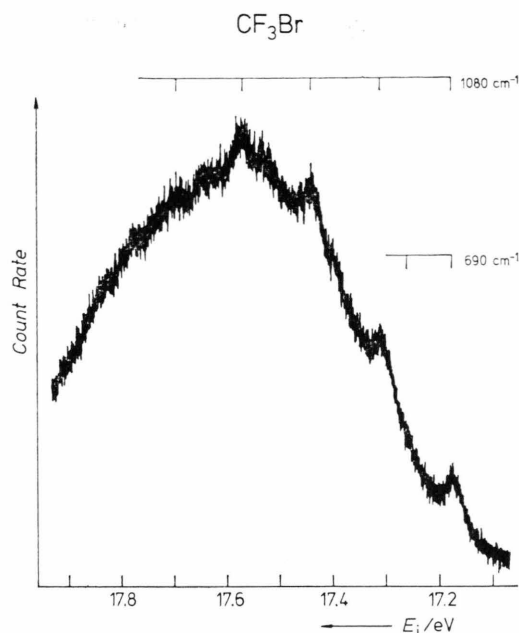


Fig. 2. High resolution PE spectrum of system  $\tilde{D}^2E$  of  $CF_3Br^+$ .

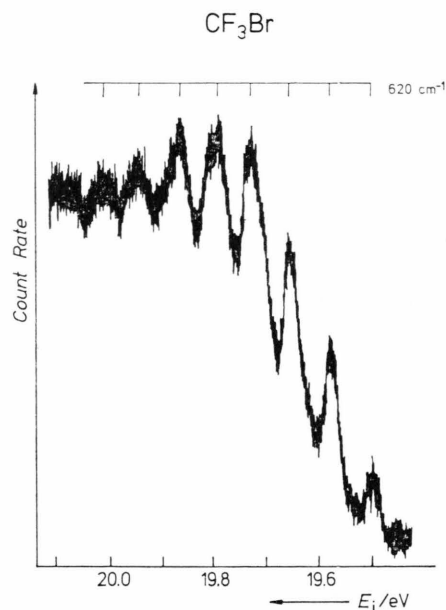


Fig. 3. High resolution PE spectrum of system  $\tilde{E}^2A$ , of  $CF_3Br^+$ .

bonding orbital. It is shifted by about 1 eV toward lower ionization energy relative to the corresponding system in the  $CF_3Br$  spectrum. The systems at higher ionization energies correspond to electrons

in the  $CF_3$  group. The spectra of  $CF_3Cl$ ,  $CF_3Br$ , and  $CF_3I$  are almost identical between 15 and 24 eV and the assignment indicated at the top of the systems in Fig. 4 is therefore straightforward.

Under high resolution there is discrete structure observable in the first two systems corresponding to the two components of the  $^2E$  ground state of the ion. In Fig. 5 the fine structure of the lower ionization energy system is shown. Two vibrations are active: one of 1090  $cm^{-1}$  and one of 240  $cm^{-1}$ . These are the  $CF_3$  and  $CI$  stretching vibrations which have ground state wave numbers of 1080 and 286  $cm^{-1}$ , respectively [8], in the molecule. These vibrations are also active in the  $^2E_{1/2}$  state having approximately the same wavenumbers as in the  $^2E_{3/2}$  state. In the  $^2E$  system at 17.28 eV no fine structure could be resolved but in the  $^2A_1$  system at 19.2 eV similar vibrational structure is observed (Fig. 6) as in the corresponding systems of  $CF_3Cl$  and  $CF_3Br$ . There are three active vibrations of 1090, 600 and 190  $cm^{-1}$  which can be attributed to the three totally symmetric modes  $CF_3$  stretching,  $CF_3$  deformation, and  $CI$  stretching, respectively. The first stronger band in the system is not the  $O-O$  band. There is a weak band separated from it by 470  $cm^{-1}$  which does not correspond to any ground state vibrational wave-number. The adiabatic ionization energy must therefore be less than 18.8 eV.

On comparing the PE spectra of  $CF_3Cl$ ,  $CF_3Br$ , and  $CF_3I$  one is struck by their similarity in the region between 15 and 25 eV which indicates that the electronic structure of the  $CF_3$  group is hardly affected by the substituent. The best defined system in both the HeI and HeII spectra in this region is the system  $\tilde{D}$  at about 17.5 eV. We therefore chose it as a reference against which to measure the intensities of all the other systems. The ratios of these relative intensities in the HeII spectra to those in the HeI spectra are given in Table 1.

Table 1. Relative intensity ratios for PE band systems under HeII and HeI excitation.

Compound	System				
	$\tilde{X}^2E$	$\tilde{A}^2A$	$\tilde{B}^2A_2 + \tilde{C}^2E$	$\tilde{D}^2E$	$\tilde{E}^2A_1$
$CF_3Cl$	0.09	0.45	1.5	1	0.49
$CF_3Br$	0.14	0.50	1.9	1	0.78
$CF_3I$	0.16	0.59	1.8	1	1.0

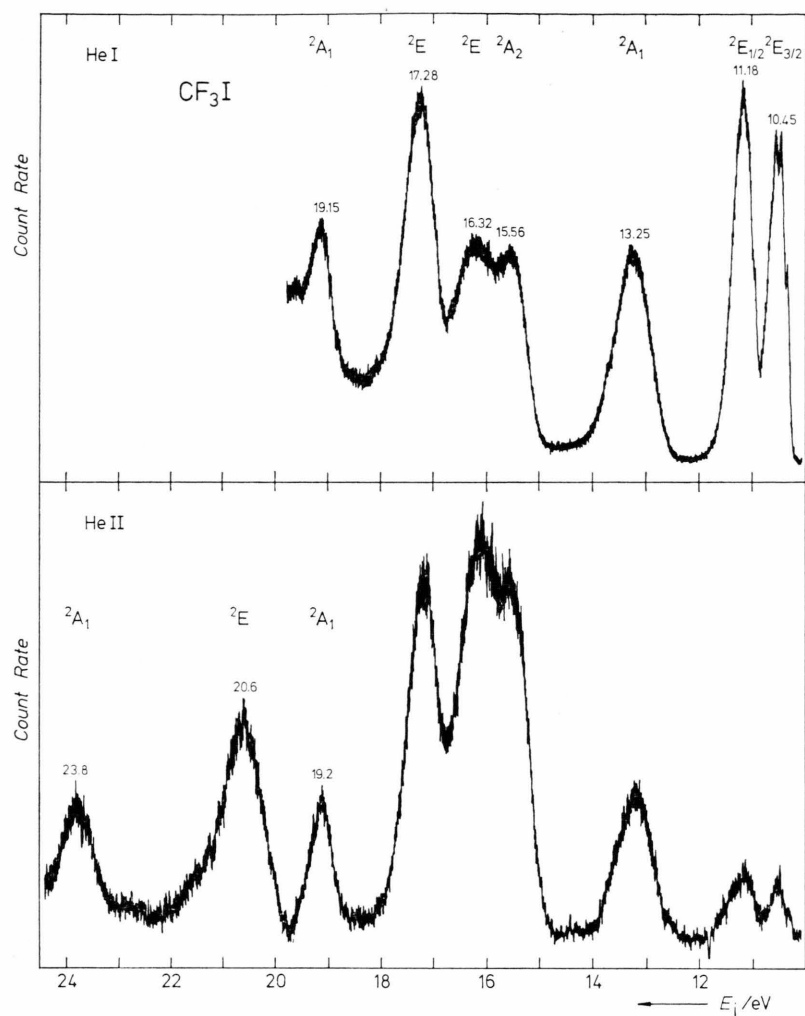
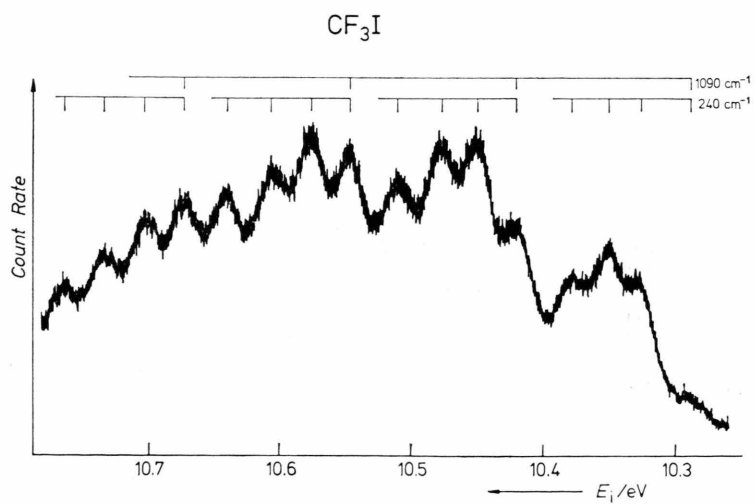


Fig. 4. HeI and HeII PE spectra of iodotrifluoromethane.

Fig. 5. High resolution PE spectrum system  $\tilde{X}^2E_{3/2}$  of  $\text{CF}_3\text{I}^+$ .

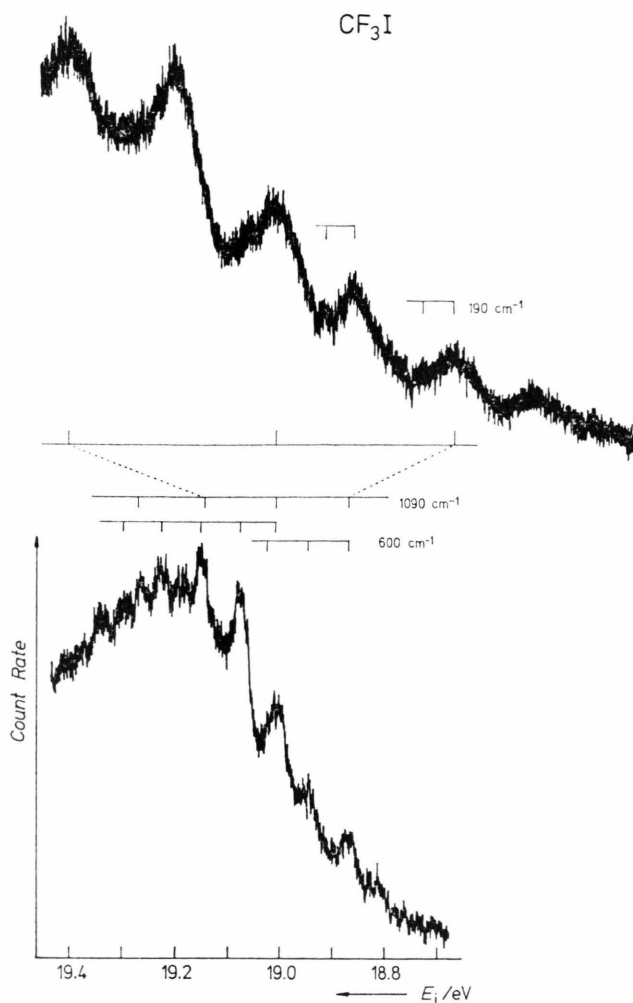


Fig. 6. High resolution PE spectrum of system  $\tilde{E}^2A$ , of  $CF_3I^+$ .

The large decrease in intensity of the halogen lone pair ionization on going from HeI to HeII excitation is clearly seen and most pronounced in the case of

chlorine. This is somewhat unexpected since theoretical considerations predict a stronger decrease for bromine and especially iodine [4]. The relative intensity increase for the fluorine lone pairs (especially systems  $\tilde{B}$  and  $\tilde{C}$ ) relative to the bonding electron ionizations (system  $\tilde{A}$ ) is also obvious and agrees with the calculations [3, 4].

It is interesting to note that the two components of the  $^2E$  ground state of the ion  $CF_3I^+$  are separated by 0.73 eV i.e. by slightly more than in  $CH_3I^+$  where the splitting amounts to 0.62 eV [9]. The spin-orbit splitting, however, is well resolved in  $CH_3Br^+$  (0.32 eV) [9] and not at all in  $CF_3Br^+$ . As already mentioned, when comparing the first systems  $\tilde{X}(^2E)$  of  $CF_3Cl^+$  and  $CF_3Br^+$  under high resolution it is seen that the one corresponding to the ground state of  $CF_3Br^+$  is significantly broader than that of  $CF_3Cl^+$ . Particularly its shape indicate that it must consist of two overlapped components. The fact that they cannot be resolved is not caused by decreased spin-orbit coupling as compared with  $CH_3Br^+$ , but rather by the much stronger bonding character of these systems in halotrifluoromethanes than in the corresponding halomethanes. This is most obviously seen by the long progression in the first system of  $CF_3I^+$  shown in Figure 5. If a similar structure would be present in the two ground state components of  $CF_3Br^+$  they could not be resolved if the splitting were of the order of 0.3 eV.

#### Acknowledgement

This work has been performed on the basis of a German-Yugoslav scientific co-operation program. The financial support by Internationales Büro, Kernforschungsanlage Jülich, and by the Republic Council for Science of Croatia (SIZ II) is gratefully acknowledged.

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