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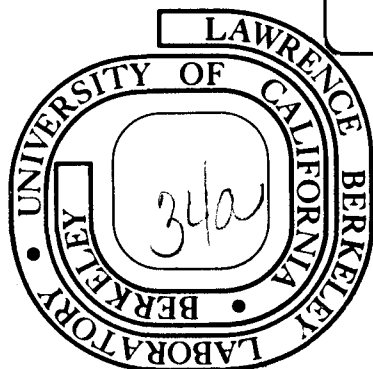
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MOLECULAR PHOTOELECTRON SPECTROSCOPY AT 132.3 eV.
METHANE, THE FLUORINATED METHANES AND HYDROGEN FLUORIDE

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ABSTRACT: Molecular photoemission spectra of the valence orbitals of HF, CH₄, CH₃F, CH₂F₂, CHF₃, and CF₄ were taken using the 132.3 eV Mg ζ line of yttrium. Dramatic decreases of relative intensity were observed, in comparison to higher-energy photoemission spectra, for molecular orbitals with substantial atomic 2s character, thereby facilitating orbital assignments.

W. C. Price et al.¹⁾ have emphasized the importance of the variation with photon energy of photoemission cross section ratios as a diagnostic device for establishing the atomic orbital (AO) composition of molecular orbitals (MO's). They compared cross section ratios obtained by ultra-violet photoemission spectroscopy (UPS) with those from x-ray photoemission (XPS, or ESCA) for a number of molecules. It is also advantageous for a variety of reasons to vary the photon energy substantially (i.e., by an order of magnitude) within the context of an XPS experiment. To this end Wuilleumier and Krause used the $Y_{M\zeta}$ line^{2,3)} (132.3 eV), and a number of other x-ray sources, to study the photoionization of neon gas.⁴⁾ Inspired by their work we have constructed an yttrium source and utilized it to study the XPS-MO spectra of HF, CH₄ and the fluorinated methanes. These spectra are reported and contrasted with the $MgK\alpha_{1,2}$ (1253.6 eV) spectra reported earlier.⁵⁾

Design and operation details of the $Y_{M\zeta}$ line source will be given elsewhere. Briefly, the x-ray tube possesses the main features of the one built by Krause: a) an anode maintained at a positive potential and a filament near ground, and b) a window capable of transmitting $Y_{M\zeta}$ x-rays. Formvar films of $\sim 20 \mu\text{gms}/\text{cm}^2$ thickness were used because they formed a better seal than polystyrene (used by Krause) in our particular experimental arrangement. Krause reported a FWHM of 0.6 eV for Ne 2p.³⁾ We were unable to maintain maximum resolution in most cases, probably due to anode contamination. However, the CF₄ spectrum discussed below should illustrate the resolution capabilities of the new source.

All gases were purchased commercially and studied in the Berkeley Iron-Free Spectrometer⁶⁾ at pressures of ca. 10^{-1} torr. A right-angle

geometry was used between the unpolarized x-ray beam and the analyzed electrons. No correction was made for the possible change in detector efficiency (Bendix Channeltron) with electron kinetic energy. However, such a correction must be small, as there was no noticeable drop in background counts with decreasing kinetic energy.

Lorentzian lines were nonlinear-least-squares fitted to the experimental data. A point by point correction was made for the change in spectrometer transmission with electron kinetic energy. All area ratios reported below were computed after subtracting the contributions due to the x-ray satellites accompanying the main ($M_{V}N_{III}$) exciting line.³⁾

The essential features of the cross section ratios studied here depend on a single physical factor. The photoemission transition probability is proportional to the square of a one-electron momentum matrix element,

$$T.P. \propto |\langle \chi_f(j) | \vec{p}_j | \phi_i(j) \rangle|^2 \quad (1)$$

Here $\phi_i(j)$, $\chi_f(j)$, and \vec{p}_j denote, respectively, the initial bound state, final continuum state, and momentum operator for electron j . The matrix element corresponds very roughly to a Fourier transform of $\phi_i(j)$. It tends, therefore, to be largest when the curvature of $\phi_i(j)$ is such as to yield large Fourier components at the deBroglie wavelength of the outgoing electron continuum state χ . For second-row elements the inner radial nodes of the atomic 2s functions have curvatures that match the wavelength of valence electrons ejected by high-energy ($\sim 10^3$ eV) photons, but not by those of low energies ($\sim 10^2$ eV). (The wavelength of electrons

with these two kinetic energies are 0.39 Å and 1.2 Å respectively.) On the other hand, 2p functions have no nodes and their size matches the low energy electrons better. Thus $\sigma(2s)/\sigma(2p)$ would be expected to decrease dramatically from excitation by $MgK\alpha_{12}$ to $Y\text{M}\zeta$; and as a result of such a change these XPS-MO spectra should reflect atomic orbital composition of each MO.

Inspection of Fig. 1, which compares the $Y\text{M}\zeta$ and $MgK\alpha_{12}$ spectra of CH_4 and HF, shows clearly that these expectations are fulfilled. The intensity ratio $I(2a_1)/I(1t_2)$ in CH_4 drops by a factor of ~ 22 from Mg to Y energies, confirming the C2s character of the a_1 orbital and the C2p character of the t_2 orbital.

Three Lorentzians were used to give a good overall fit of the experimental points corresponding to the $1t_2$ peak on the assumption that this state is fully Jahn-Teller split. This is consistent with the UPS spectrum.¹⁰⁾ However, the area ratios and separations of these peaks cannot both be uniquely determined.

The changes in peak intensities in HF are equally dramatic, and the spectrum is cleaner. We need consider only the fluorine atomic orbitals. The 1π orbital is made up entirely of p functions, with no s admixture, by symmetry. Using the 1π peak as a reference, we note that the 2σ peak intensity drops significantly in going from the magnesium to the yttrium spectrum. This confirms the s character of the 2σ orbital. It sets a very low limit on the atomic $2p\sigma$ contribution. The $3\sigma/1\pi$ intensity ratio also drops, indicating some $2s\sigma$ character, but the decrease is much less dramatic, showing that this orbital is mainly $2p\sigma$ in nature.

The major result of this research is the dramatic variation in photoelectric cross section ratios with photon energy, both in the above molecules and in the fluorinated methane, discussed below. These variations are in every case in good qualitative agreement with expectations based on previous molecular orbital symmetry assignments, and they confirm those assignments. A rigorous interpretation of the photoemission cross section ratios would require a sophisticated calculation that accounted for the properly orthogonalized final-state continuum function of the photoelectron. Rabalais, et al.⁷⁾ have made such a calculation for methane, finding that the $2a_1/1t_2$ intensity ratio decreases from 20:1 at $MgK\alpha$ energies to 1:7.5 at $YM\zeta$ energies, in qualitative agreement with our values of 8:1 and 1:2.7, respectively. Unfortunately such calculations are not available for the other molecules studied here. In the discussion below the spectra are tentatively interpreted according to an approximate model given by Gelius.⁸⁾

According to this model, the photoelectric cross section at high photon energies for electrons in molecular orbital i is related to the atomic-orbital cross sections as follows:

$$\sigma_i(MO) \cong \sum_j P_{ij} \sigma_j(AO) \quad (2)$$

Here P_{ij} is the electron population in AO ϕ_j , for molecular orbital i . We have used this relation, the wavefunctions of Snyder and Basch,⁹⁾ and experimental area ratio ($2a_1/1t_2$ of CH_4 and $2\sigma/1\pi$ of HF) to calculate the atomic cross-section ratio $\sigma(C2p)/\sigma(C2s)$ and $\sigma(F2p)/\sigma(F2s)$ at yttrium $M\zeta$ energies. The $3a_1$ and $4a_1$ levels of CH_3F were used to compute

$\sigma(\text{F}2s)_Y/\sigma(\text{C}2s)_Y$. The results are shown in Table I. Three types of electronic populations were employed: gross, net, and overlap (gross minus net). The photoelectric cross section of hydrogen 1s was taken as zero throughout these calculations. This is reasonable since the calculated differential photoelectric cross section of the hydrogen 1s orbital is an order of magnitude smaller than that of the MO's of CH_4 .⁷⁾ Furthermore, we have tried unsuccessfully to detect the $\text{YM}\zeta$ photoemission spectrum of H_2 .

With the three ratios in Table I we were able to use the wavefunction of Snyder and Basch⁹⁾ to make a very rough analysis of the relative intensities of the fluoromethane levels. The results are compared with experiment in Table II. In the same Table we also list the binding energies of the MO's in each molecule. The binding energies obtained in earlier work using $\text{MgK}\alpha$ x-rays are also listed for comparison. Energy differences are known more accurately than are absolute energies. We have therefore used one orbital as a reference in each molecule and normalized to that orbital. The agreement between peak energy spacings in the $\text{MgK}\alpha$ and $\text{YM}\zeta$ spectra is excellent.

For methane, Eq. (2) has no predictive value in our analysis, because the $2a_1/1t_2$ intensity ratio was used to deduce $\sigma(\text{C}2p)/\sigma(\text{C}2s)$. The same is true for the $2\sigma/1\pi$ intensity ratio in HF. The 3σ intensity is predicted quite well, however, especially if gross populations are used.

The $\text{MgK}\alpha$ and $\text{YM}\zeta$ XPS-MO spectra of CH_3F and CH_2F_2 are shown in Fig. 2. In fitting the $\text{YM}\zeta$ $3a_1$ peak of CH_3F we have deliberately excluded the structure to the right of the peak. This is probably due to satellite peaks from the outer levels and therefore should not be added to the area

of $3a_1$. For CH_2F_2 , the interference of this structure with the $3a_1$ and $2b_1$ levels was so bad that these two peaks had to be deconvoluted by hand, yielding only rough estimates of their intensities.

The experimentally derived intensity ratios of CH_3F agree reasonably well with predictions based on either gross or net populations. The large decrease in the $3a_1$ peak's relative intensity and a similar but somewhat less pronounced effect in the $4a_1$ peak, in going from the $\text{MgK}\alpha$ to the $\text{YM}\zeta$ spectrum, is characteristic of the F2s and C2s atomic orbitals, respectively. Although particularly clear in CH_3F , it is also very apparent in the other fluorine derivatives.

The improved energy resolution in the $\text{YM}\zeta$ spectrum makes it even clearer than before⁵) that the peak at lowest binding energy arises from a single final state (the 2e orbital) while the next peak has two components (the $5a_1$ and 1e orbitals). On fitting this compound peak with two components we found good agreement between the 1e - $5a_1$ spacings as derived from the $\text{MgK}\alpha$ and the $\text{YM}\zeta$ spectra (0.7 eV in both cases). The lower binding-energy component was more intense in each spectrum, and the 1e peak was predicted to be more intense in each case. Thus on the basis of intensities the lower-energy component of the second peak appears to belong to the 1e state.

In CH_2F_2 the $3a_1$ and $2b_1$ (fluorine 2s) states yield a low broad peak as expected. The $4a_1$ (carbon 2s) state is also identified by its loss of relative intensity in the $\text{YM}\zeta$ spectrum. The 19-eV peak gains in intensity relative to these three, but loses relative to those at 13 and 15 eV. This is strong evidence for mixed 2s and 2p character, thus strongly supporting the previous assignment of the $1b_2$, $5a_1$, and $3b_1$ states

to this peak. The $YM\zeta$ data yield no new information on the order of these three states without the peak: in fact the $MgK\alpha$ spectrum was better in this respect, because only two component peaks were required to fit this peak in the $YM\zeta$ spectrum. (The complete deconvolution of the $MgK\alpha$ spectrum of CH_2F_2 is shown in Fig. 3 of reference 5.)

The high relative intensities of the 13- and 15-eV peaks in the $YM\zeta$ spectrum confirm their 2p character, in agreement with the previous assignments.⁵⁾ The $2b_2$ peak at 13 eV is well resolved. The 15-eV peak has a slightly rounded but symmetrical appearance, indicating that the $1a_2$, $4b_1$, and $6a_1$ states lie close in energy.

The CHF_3 and CF_4 spectra are shown in Fig. 3. Their general appearance is similar to that of CH_2F_2 : tightly-bound compound F(2s) peaks near 40 eV, the $4a_1$ (C2s) peak near 25 eV, and two more peaks, of which the one near 22 eV has strongly mixed 2s and 2p character. The CF_4 spectrum has been thoroughly discussed before, and we note only that the $YM\zeta$ spectrum (see inset) shows a resolution of the $1e$, $4t_2$, and $1t_1$ peaks that rivals the results obtained by Siegbahn et al.¹¹⁾ with monochromatic $AlK\alpha$ x-rays.

The CHF_3 spectrum illustrates the power of using $YM\zeta$ radiation. The peak at 21 eV is asymmetric toward high binding energy. Since the $3e$ component peak is predicted to have at least twice the intensity of the $5a_1$ peak, the former appears to have the lower binding energy. The spectral area between 14 and 18 eV requires at least four peaks for a fit: its detailed shape further requires that the peak intensities increase monotonically with binding energy, with the exception that the two most tightly bound peaks can have similar intensities. The fit shown in Fig. 3 was based on the known UPS (vertical) energy separations¹⁰⁾ among the three least tightly bound components. The derived intensities agree

fairly well with predicted values, confirming the listed level ordering.

In summary, the spectra presented here confirm the anticipated changes in relative intensities that were expected to accompany this large reduction in photon energy. Intensity ratio predictions based on the simple atomic orbital population model show generally good qualitative agreement with experiment. These results give no basis for choice among gross or net populations. The $YM\zeta$ line appears to possess real diagnostic value for molecular photoelectron spectroscopy.

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TABLE I. Derived relative atomic photoelectric cross sections at 132.3 eV photon energy.

Ratio, R	R (gross) ^a	R (net) ^a	R (overlap) ^a
$\sigma(\text{C}2\text{p})/\sigma(\text{C}2\text{s})^{\text{b}}$	1.16	1.13	1.20
$\sigma(\text{F}2\text{p})/\sigma(\text{F}2\text{s})^{\text{c}}$	1.38	1.22	1.82
$\sigma(\text{F}2\text{s})/\sigma(\text{C}2\text{s})^{\text{d}}$	3.82	3.67	6.81

^aPopulations were calculated from the wavefunctions of ref. 9.

^bFrom relative areas of $2a_1$ and $1t_2$ levels of methane.

^cFrom relative areas of 2σ and 1π levels of hydrogen fluoride.

^dFrom relative areas of $3a_1$ and $4a_1$ levels of methyl fluoride.

Table II. Relative molecular orbital binding energies and intensity ratios for HF, CH₄ and the fluorinated methanes.

Molecule	MO	E _B (MgKα) ^a	E _B (YMζ) ^a	I (MgKα) ^b exp	I (YMζ) exp	I _G ^c (YMζ)	I _N ^c (YMζ)	
HF	→ 2σ	39.65(2)	39.65(4) ⁱ	1.	1.	1.	1.	
	3σ	19.89(7)	20.14(5)	.19(3)	1.18(4)	1.16	1.08	
	1π	16.12(4)	16.47(4)	.24(2)	2.93(2)	2.94	2.94	
CH ₄ ^d	→ 2a ₁	23.05(2)	23.05(3) ⁱ	1.	1.	1.	1.	
	1t ₂	14.2 (2)	14.5 (1)	.12(2)	2.69(8)	2.69	2.69	
CH ₃ F	→ 3a ₁	38.41(3)	38.41 ^e	1.	1.	1.	1.	
	4a ₁	23.48(3)	23.48(6) ⁱ	.23(1)	.4 (1)	.40	.39	
	5a ₁	17.56(9)	17.55(8)	.08(2)	.9 (1)	1.00	1.00	
	1e ¹	16.85(7)	16.88(8)	.11(2)	1.2 (1)	1.93	1.78	
	2e	13.31(4)	13.35(6)	.13(1)	1.52(4)	1.30	1.56	
CH ₂ F ₂	→ 3a ₁	40.13(7)	40.13 ^e	3.18(5)	~1.3	1.55	1.50	
	2b ₁	38.20(7)	38.20 ^e	3.57(6)	~1.5	1.63	1.72	
	4a ₁	23.86(3)	23.86(3) ⁱ	1.	1.	1.	1.	
	1b ₂	19.76(7)	--	.14(1) ^g	--	1.41	1.25	
	5a ₁	19.07(3)	19.31(3)	.28(1)	1.13(4)	1.73	1.61	
	3b ₁	18.51(4)	18.71(3)	.28(1)	1.81(4)	1.93	1.91	
	1a ₂	15.61(2)	15.60(5) ^f	.32(1)	2.5 (1)	2.33	2.47	
	4b ₁	15.20(2)	15.19(5) ^f	.32(1)	1.3 (2)	2.29	2.55	
	6a ₁	14.91(2)	14.90(5) ^f	.25(1)	1.1 (2)	1.74	1.98	
	2b ₂	13.17(2)	13.16(4)	.18(1)	1.02(6)	1.12	1.45	
	CHF ₃	→ 3a ₁	42.03(9)	42.03 ^e	1.	1.	1.	1.
2e ¹		39.15(4)	39.15 ^e	2.38(2)	2.17(7)	2.12	2.41	
4a ₁		24.38(3)	24.38(3) ⁱ	.43(1)	.52(9)	.89	.97	
5a ₁		20.89(3)	20.89(3)	.14(1)	.78(7)	1.02	1.00	
3e ¹		20.25(3)	20.39(3)	.21(1)	1.41(7)	2.52	2.66	
4e		17.03(4)	17.08(3)	.21	2.35(8)	3.02	3.42	
5e		15.99(4)	16.00(4) ^h	.21	2.3 (1)	2.98	3.59	
1a ₂		15.29(4)	15.30(4)	.12	1.8 (1)	1.53	1.89	
6a ₁		14.67(4)	14.60(4)	.071	.6 (2)	.92	1.28	
CF ₄	→ 3a ₁	43.81(10)	43.81 ^e	1.	1.	1.	1.	
	2t ₂	40.30(4)	40.30 ^e	3.45(3)	2.06(7)	3.16	3.73	
	4a ₁	25.11(2)	25.11(2) ⁱ	.55(1)	.61(6)	1.14	1.30	
	3t ₂	22.14(2)	22.21(3)	.59(1)	2.46(6)	3.69	4.09	
	1c	18.43(4)	18.55(3)	.28(1)	2.09(7)	3.07	3.53	
	4t ₂	17.41(4)	17.48(3)	.38(1)	3.32(7)	4.42	5.49	
	1t ₁	16.23(3)	16.28(3)	.41(1)	3.66(6)	4.61	5.96	

continued . . .

Table II (continued)

^a E_B is MO binding energy in electron volts. $E_B(\text{MgK}\alpha)$ were obtained from reference 5.

^bFrom reference 5.

^c $I_G(YM\tau)$ is the calculated relative intensity using the atomic cross section ratios in Table I and gross populations, I_N using net populations.

^d $\text{AlK}\alpha$ x-rays were used instead of $\text{MgK}\alpha$.

^eSeparation from $4a_1$ level obtained from $\text{MgK}\alpha$ results of reference 5.

^fSeparations from reference 5.

^gArea ratios calculated from the Gelius model using CNDO populations.

^hSeparations obtained from the UPS results of reference 10.

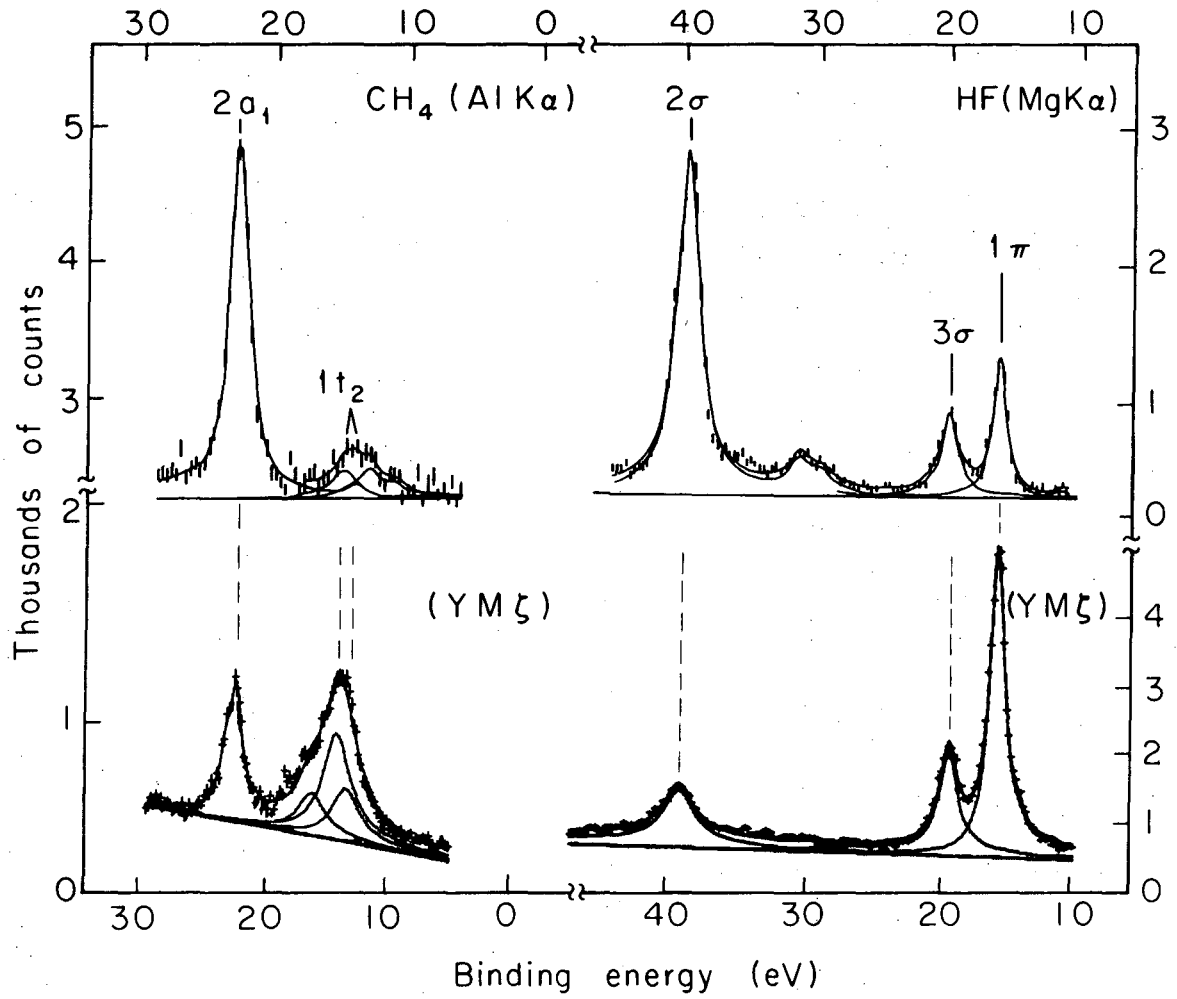
ⁱReference value obtained from the XPS results of reference 5. Arrows indicate reference level.

FIGURE CAPTIONS

Fig. 1. High-energy photoemission spectra (top) and $YM\zeta$ spectra (bottom) of CH_4 and HF valence orbitals. Counts were obtained at ~ 0.3 eV (with $MgK\alpha$) and ~ 0.2 eV (with $YM\zeta$) kinetic energy increments.

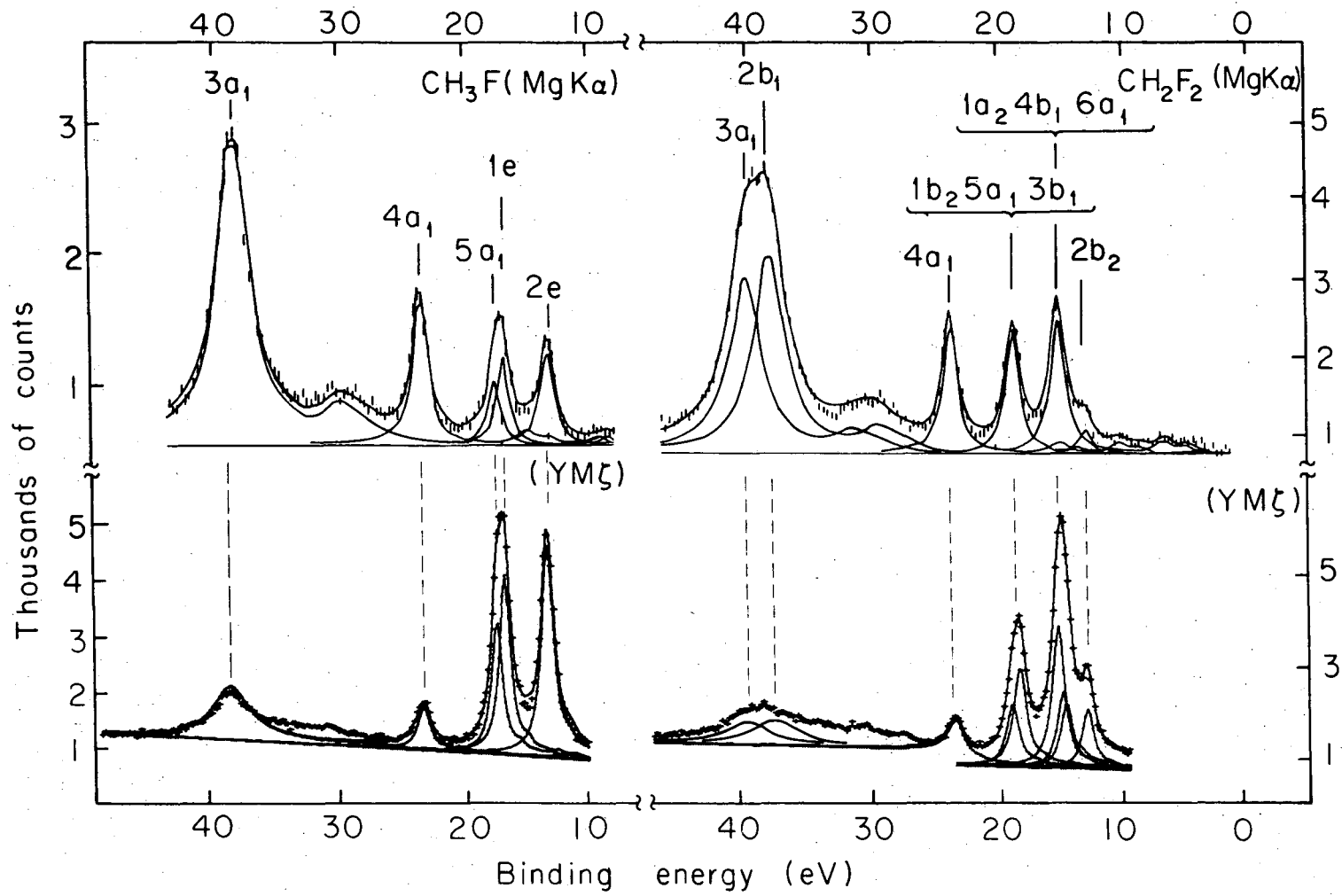
Fig. 2. $MgK\alpha$ (1253.6 eV) and $YM\zeta$ (132.3 eV) photoemission spectra of CHF_3 and CF_4 valence orbitals. Counts were obtained at ~ 0.3 eV (with $MgK\alpha$) and ~ 0.2 eV (with $YM\zeta$) kinetic energy increments.

Fig. 3. $MgK\alpha$ (1253.6 eV) and $YM\zeta$ (132.3 eV) photoemission spectra of CHF_3 and CF_4 valence orbitals. Inset shows the outer three MO's of CF_4 measured at high resolution. Counts were obtained at ~ 0.3 eV (with $MgK\alpha$) and ~ 0.2 eV (with $YM\zeta$) kinetic energy increments.



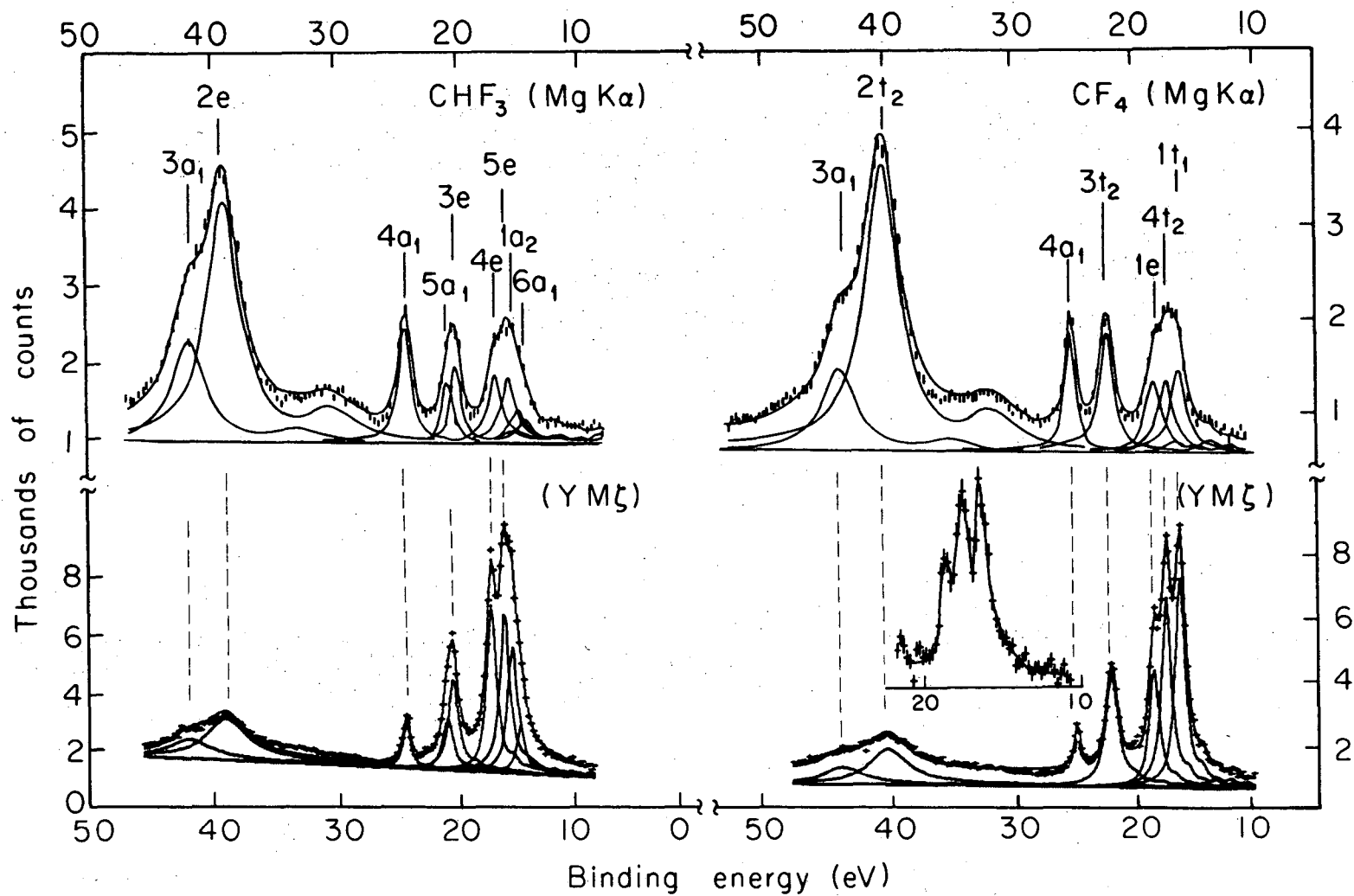
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Fig. 1



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Fig. 2



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Fig. 3

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