

Fig. 43. Energy level diagrams illustrating the alternative modes of decay of a core hole state. (From Ref. 10.)

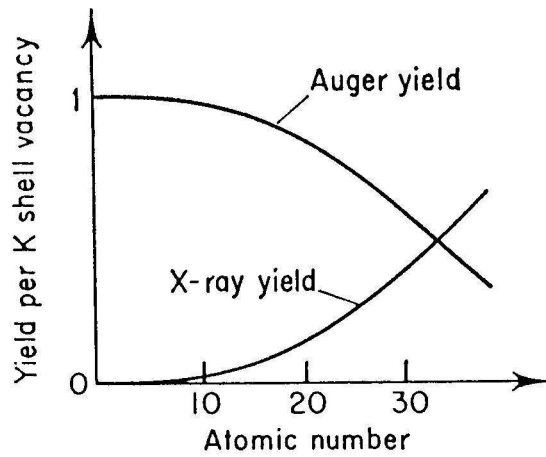
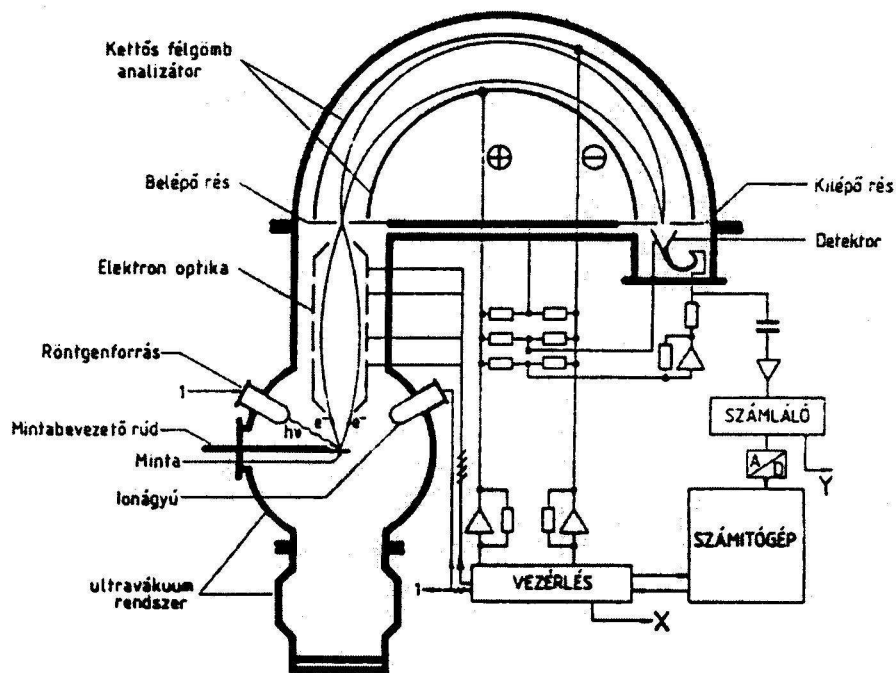


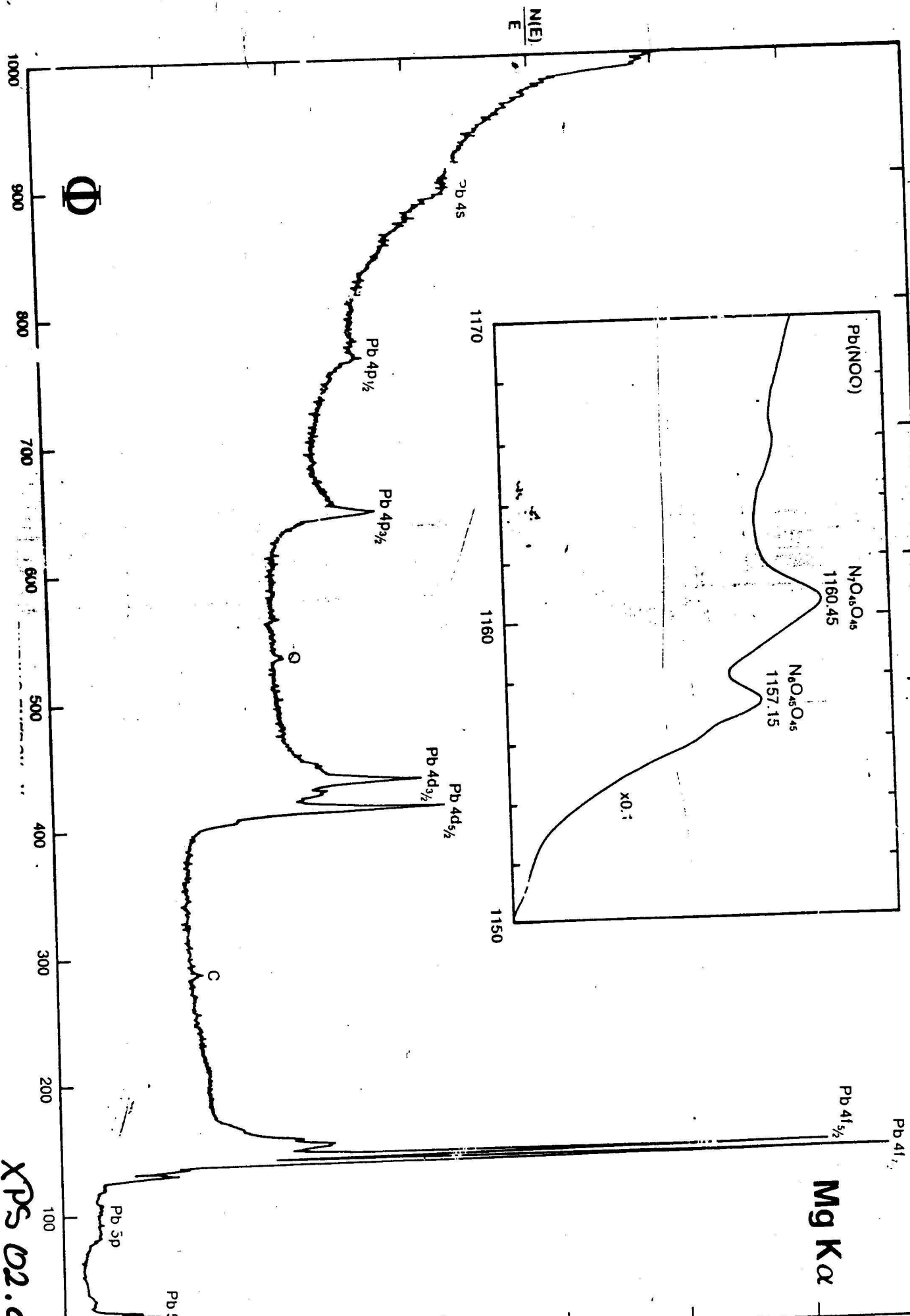
Fig. 44. The relative probabilities of X-ray emission and Auger electron emission for the decay of K (1s) holes in the lighter elements.

### 3. A SPEKTROMÉTER

Egy korszerű, harmadik generációs, számítógéppel vezérelt, nagy energiafelbontású, kettős-félgömb alakú elektrosztatikus analizátorral ellátott, ultranagy vákuumban működő ESCA spektrométer felépítésének vázlatát és vezérlésének sémáját mutatja be a 3. ábra.



3. ábra XPS spektrométer főbb szerkezeti elemeinek és vezérlésének sémája



HK 10

60 min Ar<sup>+</sup>

$\times 10^3$

Intensity (Counts)

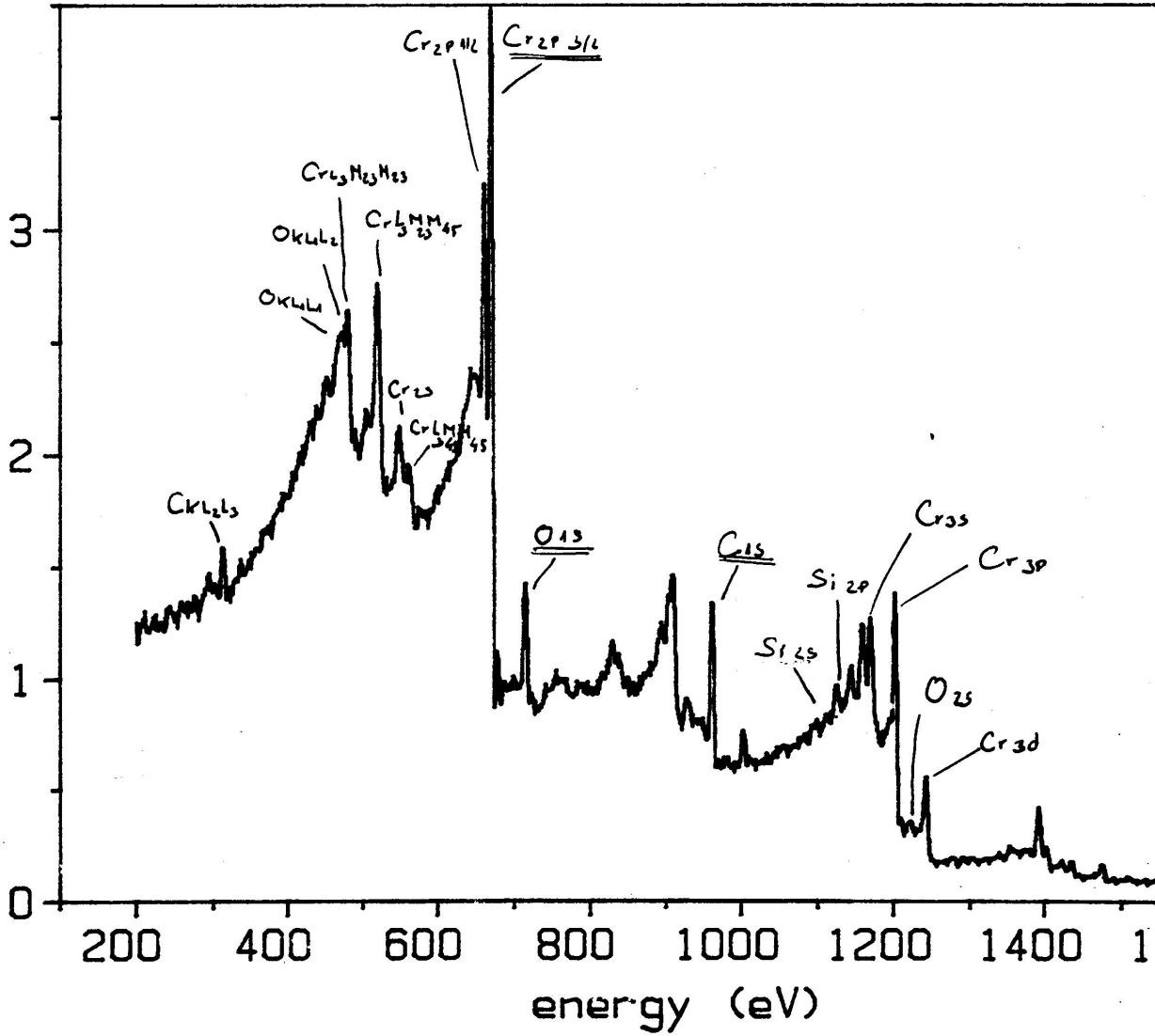


Figure 6 and Table 1.

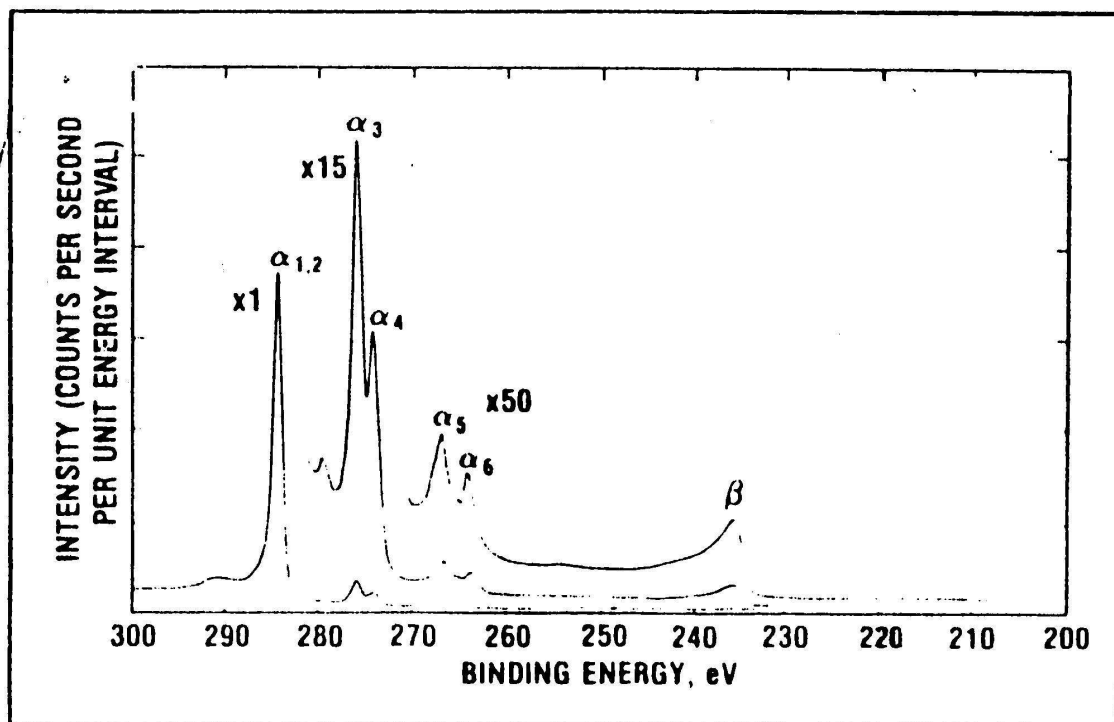


Figure 6. Mg x-ray satellites (C1s graphite spectrum).

Table 1 — X-ray satellite energies and intensities

		$\alpha_{1,2}$	$\alpha_3$	$\alpha_4$	$\alpha_5$	$\alpha_6$	$\beta$
Mg	displacement, eV	0	8.4	10.2	17.5	20.0	48.5
	relative height	100	8.0	2.1	0.55	0.45	0.5
Al	displacement, eV	0	8.8	11.8	20.1	23.4	69.7
	relative height	100	6.4	3.2	0.4	0.3	0.55

v. **Shake-Up Lines.** Not all photoelectric processes are simple ones, leading to the formation of ions in the ground state. Rather often, there is a finite probability that the ion will be left in an excited state, a few electron volts above the ground state. In this event, the kinetic energy of the emitted photoelectron is reduced, with the difference corresponding to the energy difference between the ground state and the excited state. This results in the formation of a satellite peak a few electron volts lower in kinetic energy (higher in binding energy) than the main peak. As an example, the characteristic shake-up line for carbon in unsaturated compounds, a shake-up process involving the energy of the  $\pi \rightarrow \pi^*$  transition, is shown in Figure 7.

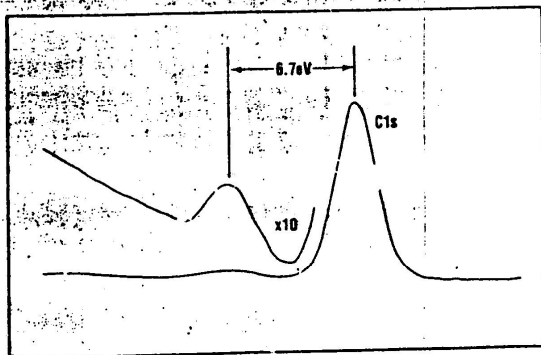


Figure 7. The  $\pi$ -bond shake-up satellite for the C1s line in polystyrene.

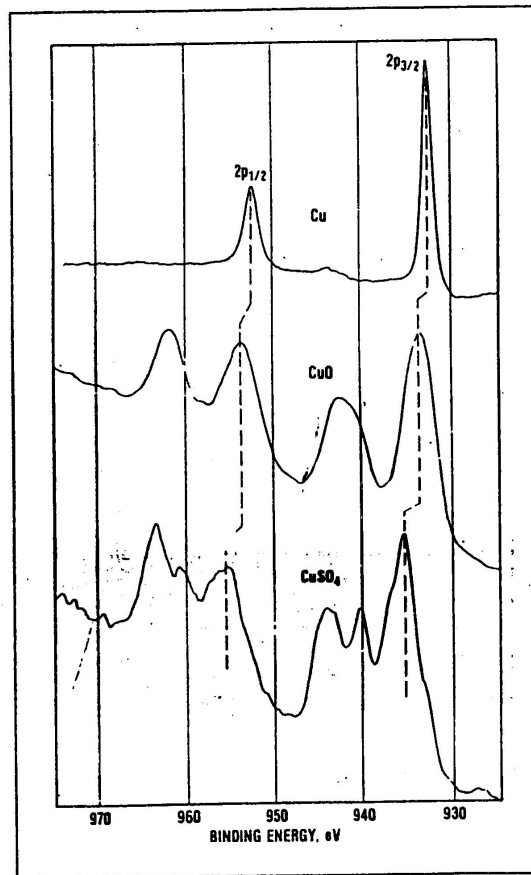
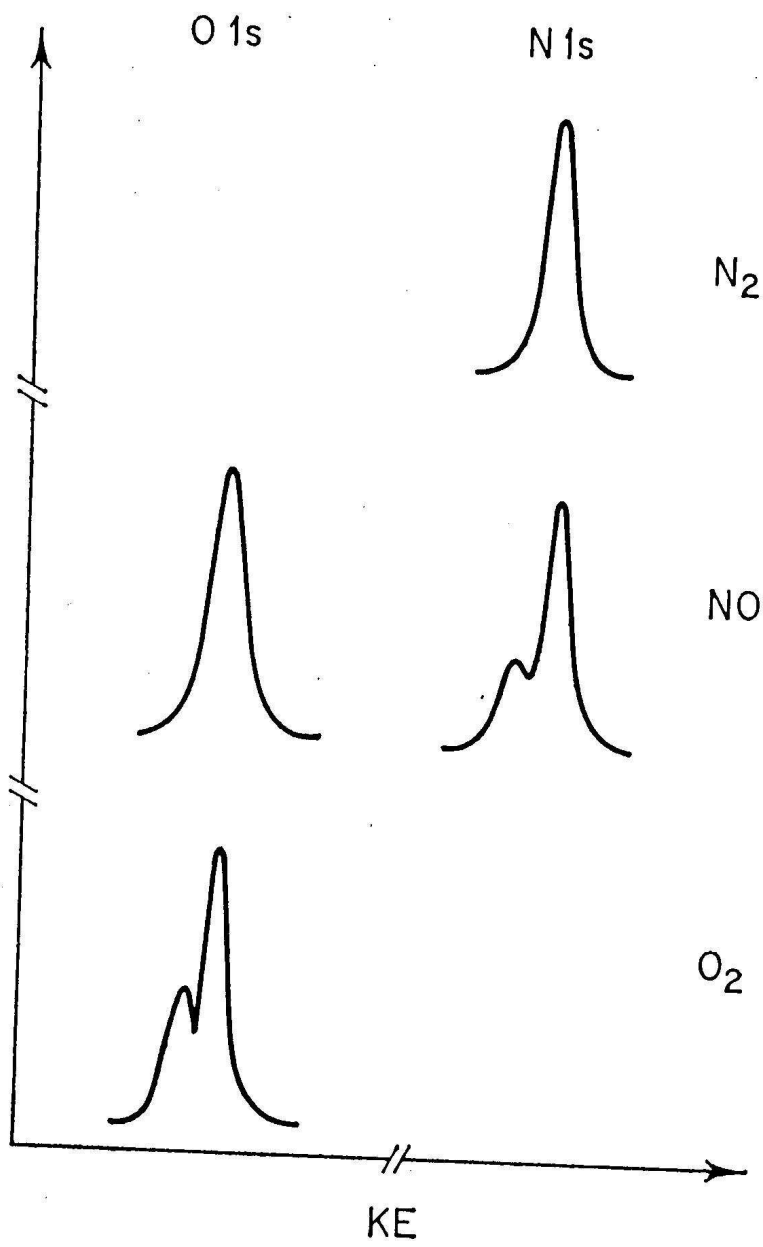


Figure 8. Examples of shake-up lines observed with the copper 2p spectrum.



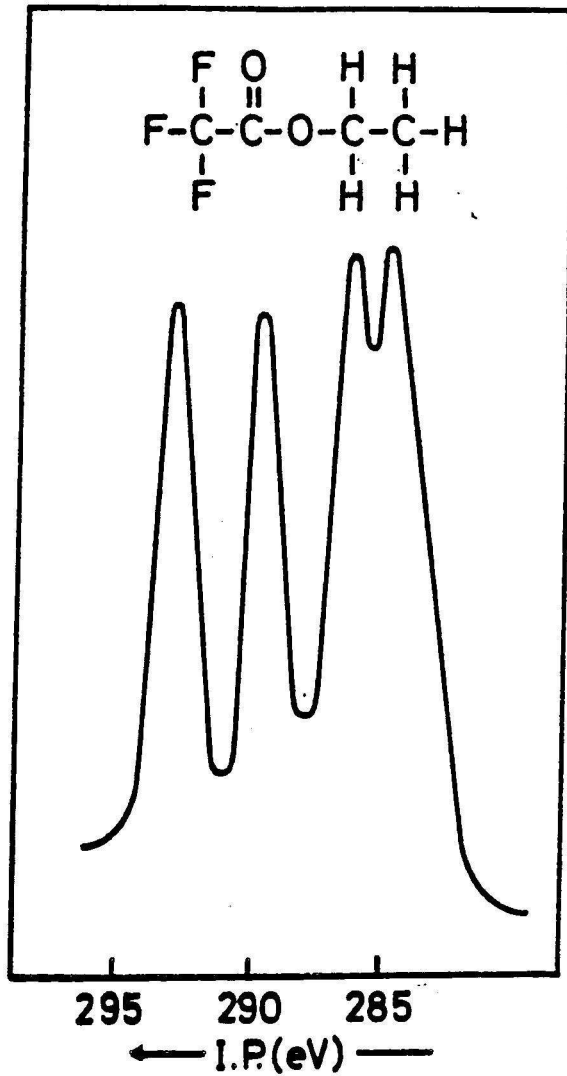


FIG. 5.1. C 1s part of the X-ray photoelectron spectrum of ethyltrifluoro acetate.<sup>(1)</sup>



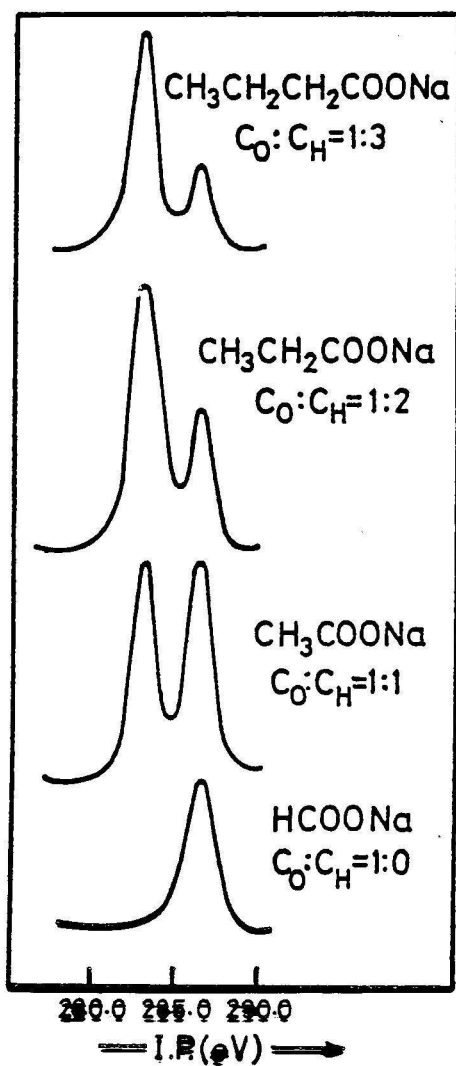


FIG. 5.2. C 1s part of the X-ray photoelectron spectrum of the sodium salts of some aliphatic carboxylic acids.<sup>(1)</sup>

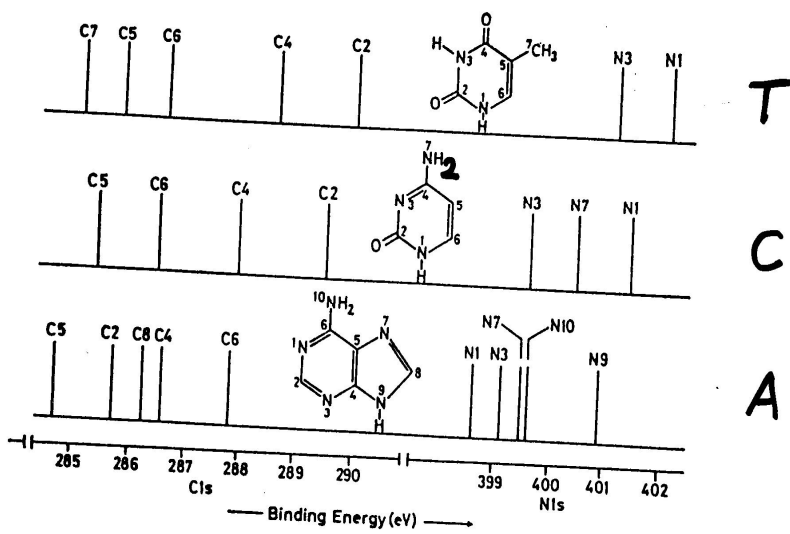
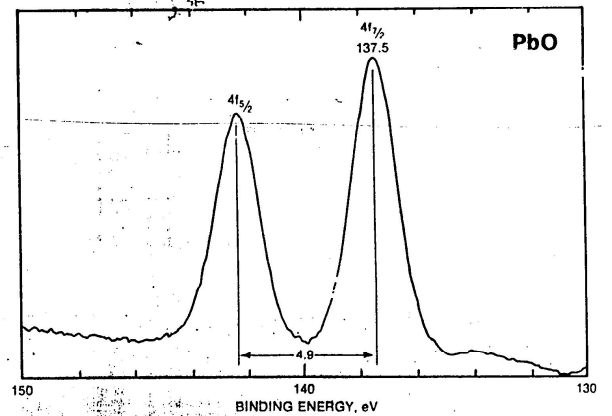
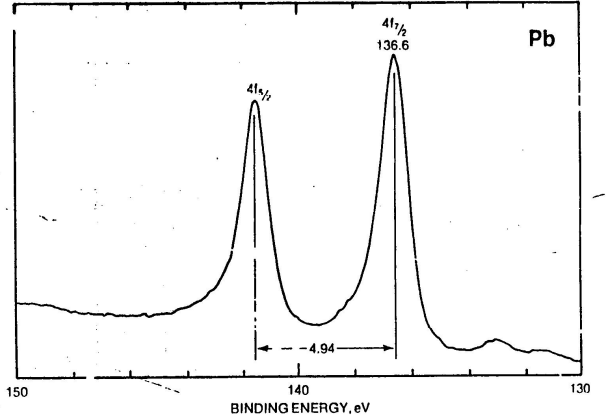


FIG. 5.3. Schematic representation of the different C 1s and N 1s binding energies for the nucleic acid bases, adenine, thymine and cytosine.

XPS 09

COMPOUND	$4f_{7/2}$ BINDING ENERGY, eV					REF.
	135		140		145	
Pb						Φ
Pb						LKM
Pb						BM
Pb						MWM
Pb						SFS
Pb						KOW
PbTe						SFS
PbSe						SFS
PbS						SFS
PbS						MV
Ph <sub>2</sub> Pb						MV
PbI <sub>2</sub>						MV
PbO						KOW
PbO						Φ
PbO						MV
PbO						TT
Pb <sub>2</sub> O <sub>3</sub>						MV
Pb <sub>3</sub> O <sub>4</sub>						KOW
PbO <sub>2</sub>						KOW
PbO <sub>2</sub>						MV
Ph <sub>2</sub> PbCl						MV
Ph <sub>2</sub> PbCl <sub>2</sub>						MV
PbF <sub>2</sub>						MV



**TABLE 6**

Nitrogen 1s chemical shifts (ionization energies relative to N<sub>2</sub>) for some gaseous compounds

Compound	N 1s chemical shift/eV
ONF <sub>3</sub>	7.1
NF <sub>3</sub>	4.3
NO <sub>2</sub>	3.0
<u>N</u> NO <sup>a</sup>	2.6
<u>N</u> <sub>2</sub> F <sub>4</sub>	2.4
ONCl	1.5
NO	0.8
N <sub>2</sub>	0
<u>N</u> NO <sup>a</sup>	-1.3
<u>H</u> CN	-3.1
N <sub>2</sub> H <sub>4</sub>	-3.8
NH <sub>3</sub>	-4.3
MeNH <sub>2</sub>	-4.8
Me <sub>2</sub> NH	-5.0
Me <sub>3</sub> N	-5.2

<sup>a</sup> The underlining of N in NNO indicates the nitrogen atom that is ionized.

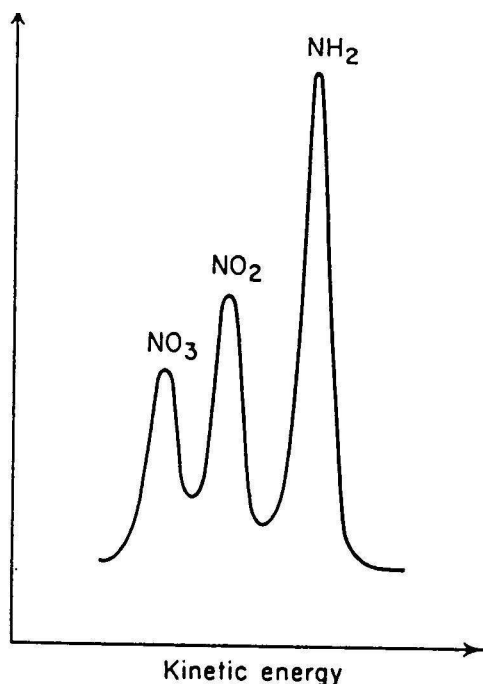


Fig. 51. The nitrogen 1s signals in the X-PE spectrum of *trans*  $(\text{Co}(\text{en})_2(\text{NO}_2)_2\text{NO}_3)$ . (From D. N. Hendrikson, J. M. Hollander and W. L. Jolly, *Inorg. Chem.* 8, 2642 (1969).)

$[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+\text{NO}_3^-$  (Fig. 51), and includes also compounds of the *metallic* elements in which more than one oxidation state is present (so called 'mixed-valency' compounds).<sup>67</sup> Familiar examples of the latter are oxides such as  $\text{Fe}_3\text{O}_4$  (which is an Fe(II)–Fe(III) compound, 'FeO·Fe<sub>2</sub>O<sub>3</sub>'),  $\text{Pb}_3\text{O}_4$  (a Pb(II)–Pb(IV) compound, '2PbO·PbO<sub>2</sub>') and  $\text{KCr}_3\text{O}_8$  (a Cr(III)–Cr(VI) compound). Part of the XPE spectrum of  $\text{KCr}_3\text{O}_8$  is reproduced in Fig. 52: it shows two, quite distinct chromium 3p signals with an intensity ratio close to 2:1.<sup>68</sup> This confirms the formulation of the material as a Cr(III)–Cr(VI) compound—( $\text{K}^+$ ,  $\text{Cr}^{3+}$ ) ~~( $\text{CrO}_4^{2-}$ )<sub>2</sub>~~, to be precise.

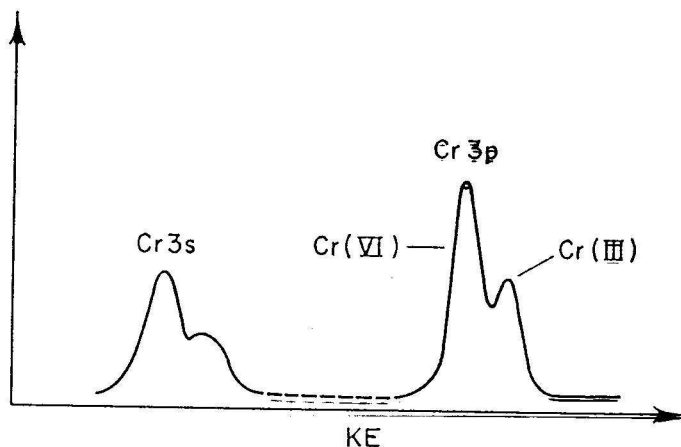


Fig. 52. Chromium 3p and 3s structure in the X-PE spectrum of  $\text{KCr}_3\text{O}_8$ . (From Ref. 68.)

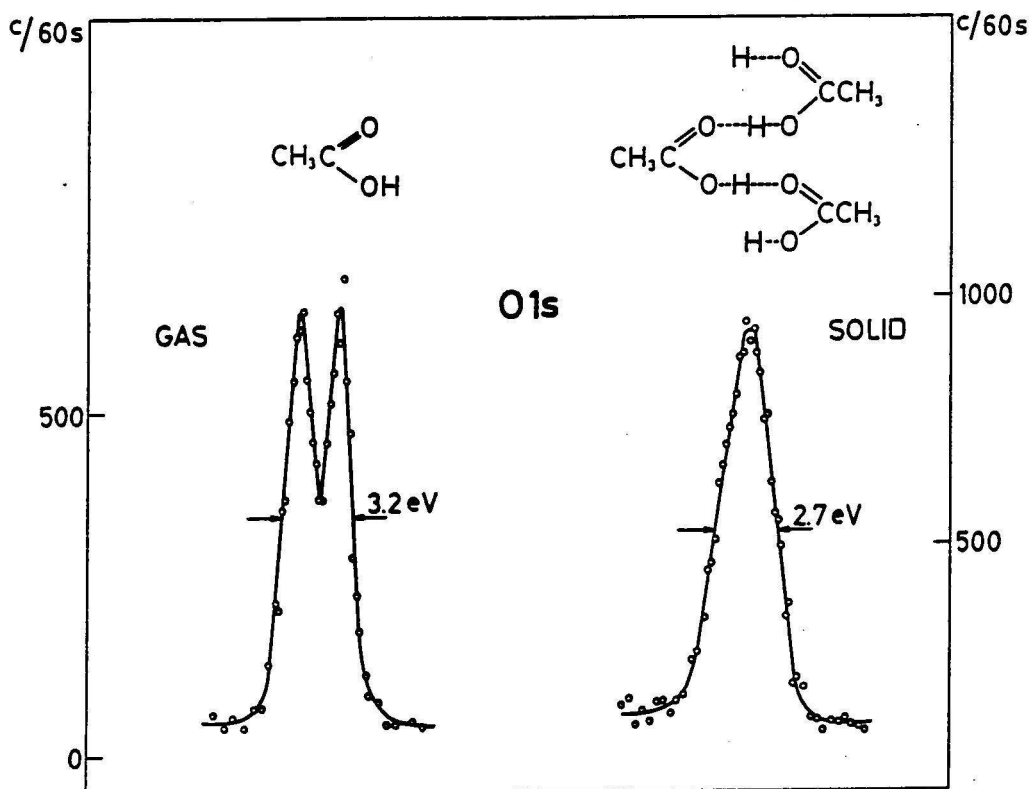
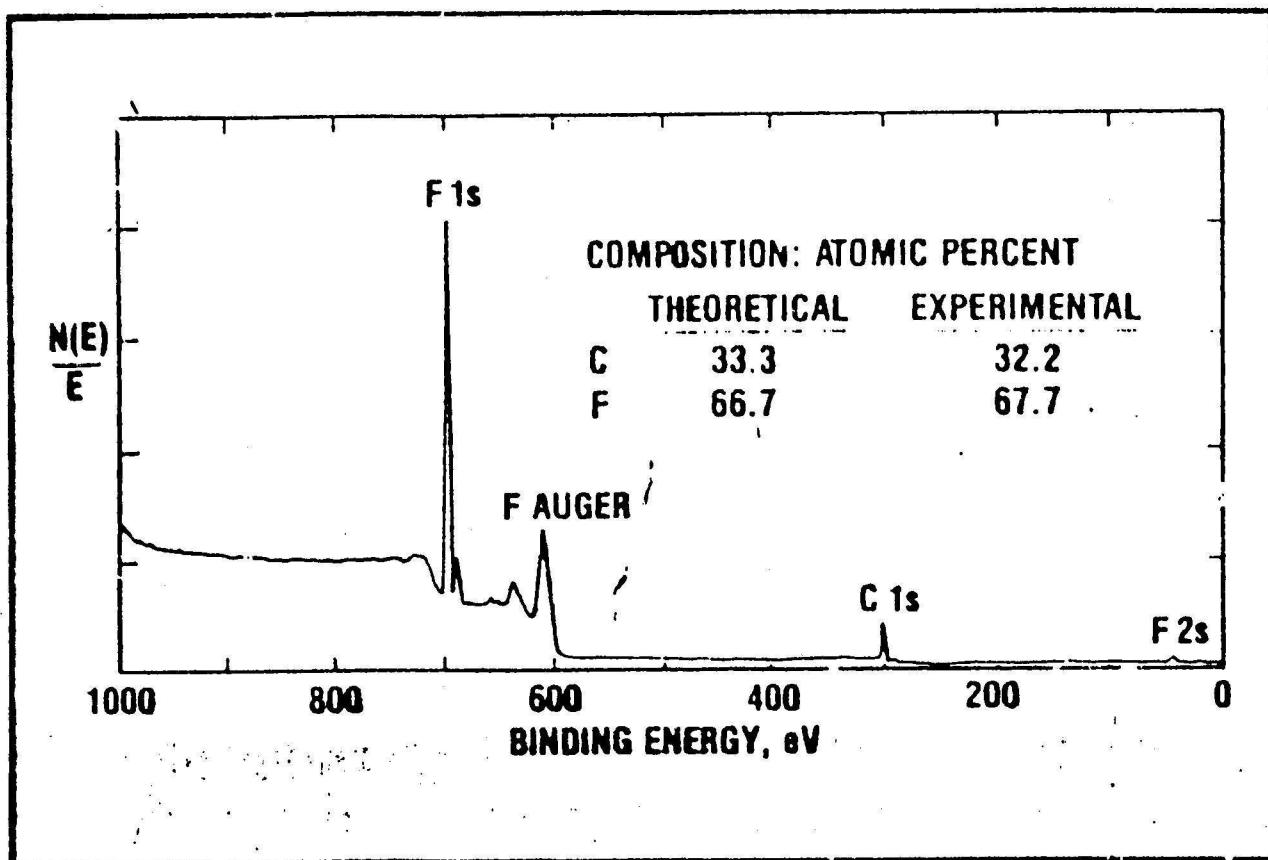


Fig. 5.4.17. The oxygen 1s lines from acetic acid in the gaseous phase at a pressure of 0.1 torr and in the solid phase. Upon solidification the sample polymerizes by formation of hydrogen bonds, the charges of the two oxygen atoms in the molecule tend to become equalized and the two lines observed in the ESCA spectrum of the gas merge into one broad line in the solid.



**Figure 14. Quantitative analysis of polytetrafluoroethylene (by peak area of F1s and C1s).**