

PE spectra of transients

The electronic structure of free radicals and other transient species is of great importance in chemistry, particularly for an understanding of the rates of chemical reactions. The IE's and ionic excited states of radicals are directly relevant to mass spectrometry and to the study of ionic decomposition.

Usual techniques to produce the species of interest are as follow:

– microwave discharge – atomic H, N, O, F, Cl, Br etc.; $\text{CH}_3\cdot / (\text{CH}_3)_2\text{Hg}$

– pyrolysis

high-temperature pyrolysis

$\text{CH}_3\cdot / \text{CH}_3\text{-N=N-CH}_3$, $\text{C}_2\text{H}_5\cdot / \text{C}_2\text{H}_5\text{-N=N-C}_2\text{H}_5$

CH_2SH (thioformaldehyde) / CH_3SCl (methylsulfenyl chloride)

medium-temperature pyrolysis

$\text{CpCo(CO)} / \text{CpCo(CO)}_2$

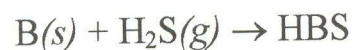
low-temperature “pyrolysis”

$(\text{CH}_3)_3\text{Al}$ (monomer) / $[(\text{CH}_3)_3\text{Al}]_2$

– photolysis



– surface reaction



– atom-molecule reaction



PE spectra of transients

Examples

Atoms: O, and N

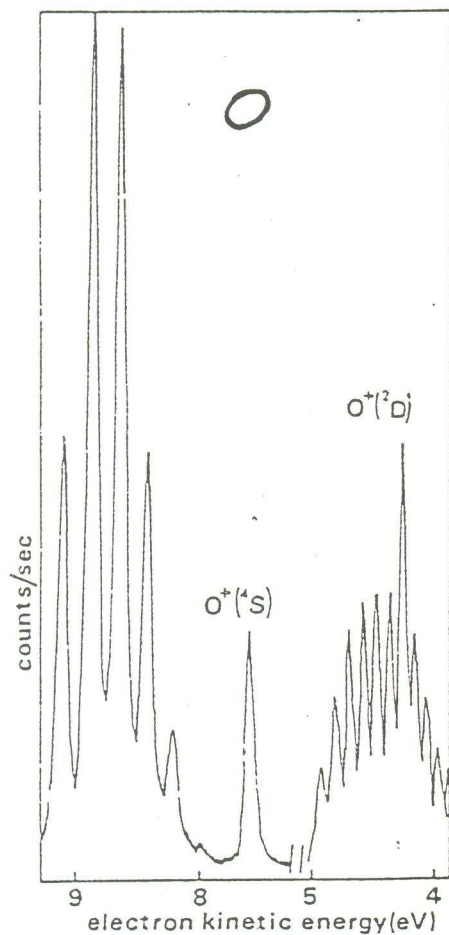


Fig. 2. Photoelectron spectrum of discharged oxygen showing atomic and molecular transitions, obtained with 21.21 eV HeI resonance radiation. Abscissa: Electron kinetic energy (eV). (Note break in scale). Ordinate: Counts/sec.

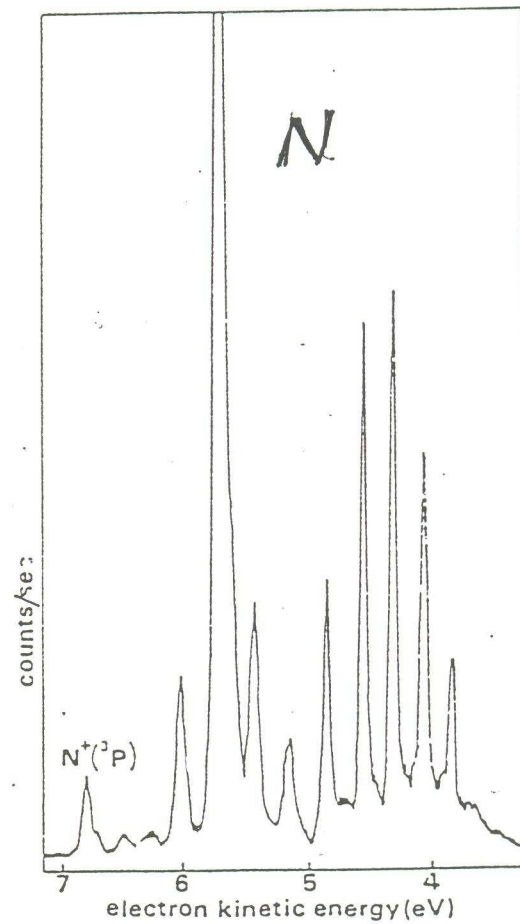
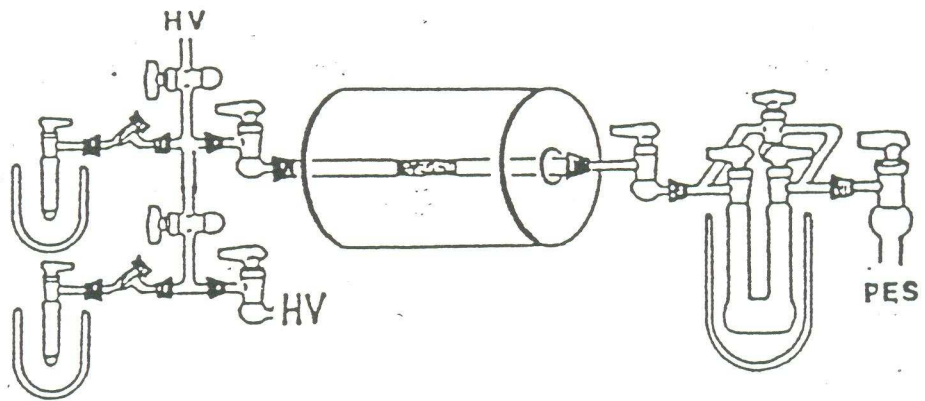
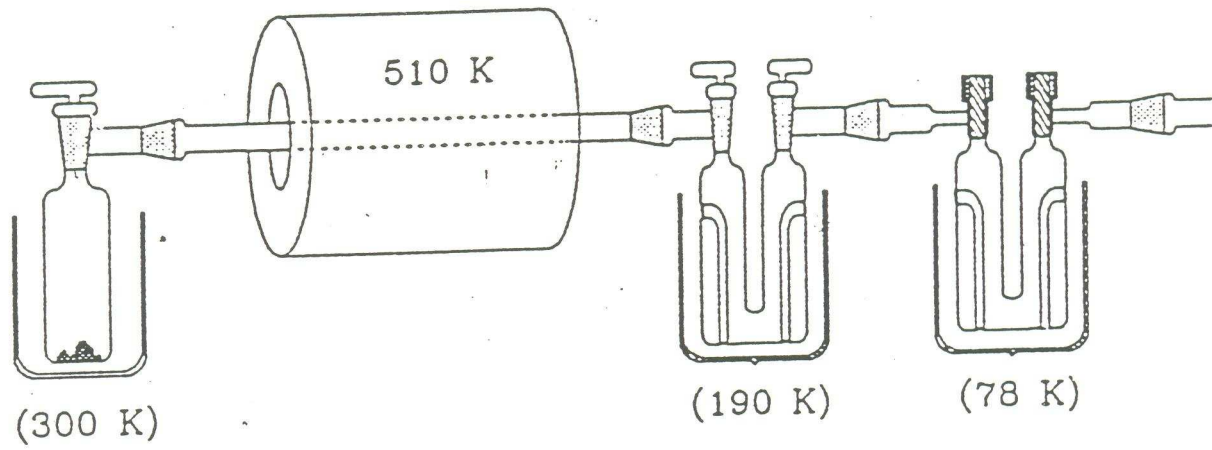
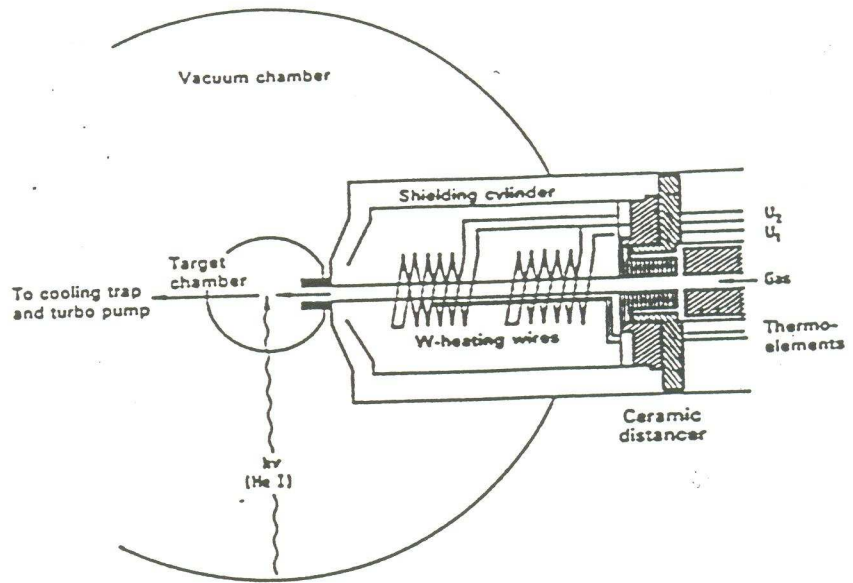


Fig. 3. Photoelectron spectrum of discharged nitrogen showing atomic and molecular transitions, obtained with 21.21 eV HeI resonance radiation. Abscissa: Electron kinetic energy (eV). Ordinate: Counts/sec.

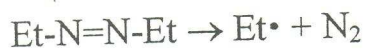
PE spectra of transients

Pyrolyzers



PE spectra of transients

Examples: ethyl-radical



$T = 800\text{-}1400 \text{ K}$

There are practical problems involved, because generally the transient species is a minor component in a mixture of more stable species.

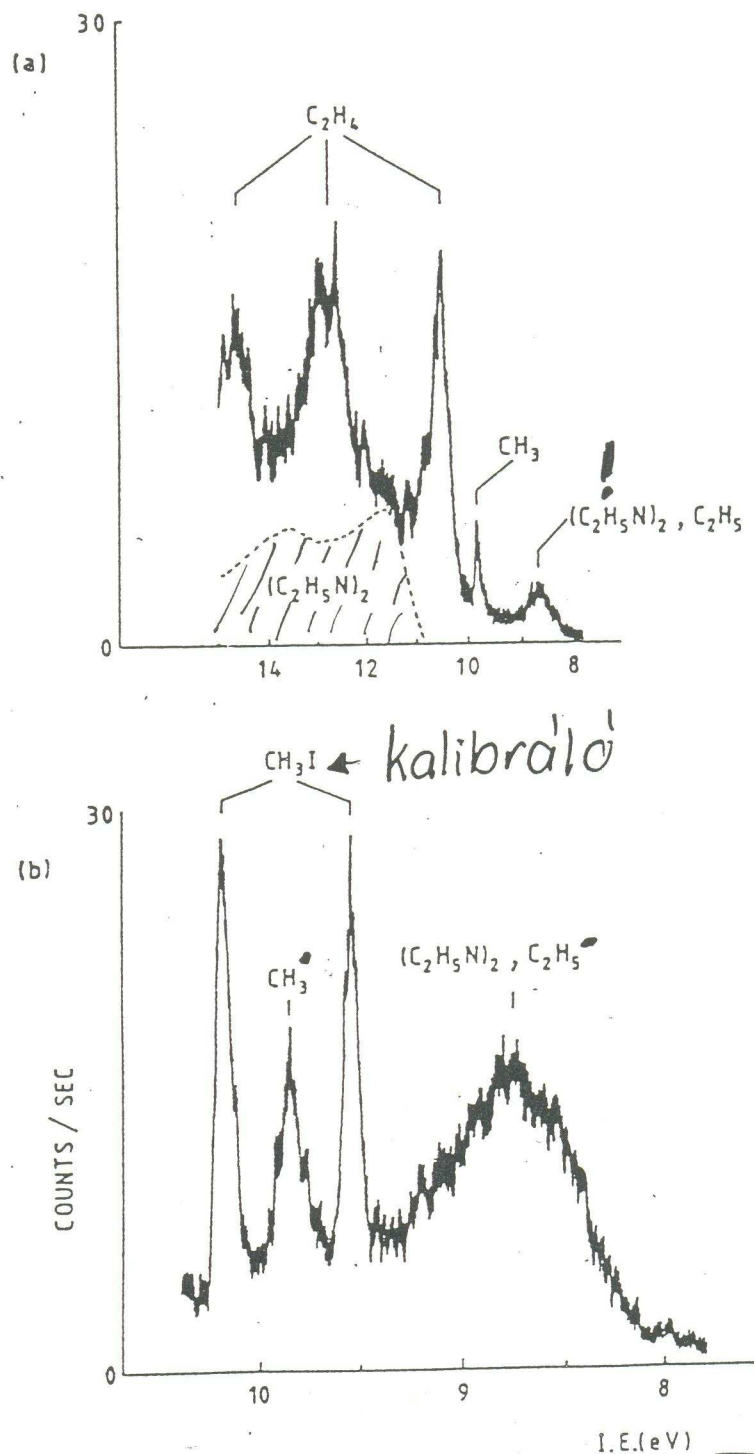
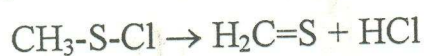


Figure 1. The He I photoelectron spectrum of pyrolyzed azoethane recorded with a single detector spectrometer in (a) the 8.0–15.0-eV and (b) the 8.0–10.5-eV ionization energy regions. Methyl iodide has been added in Figure 1b as a calibrant.

PE spectra of transients

Examples: thioformaldehyde



$p = 13 \text{ Pa}, T = 860 \text{ K}$

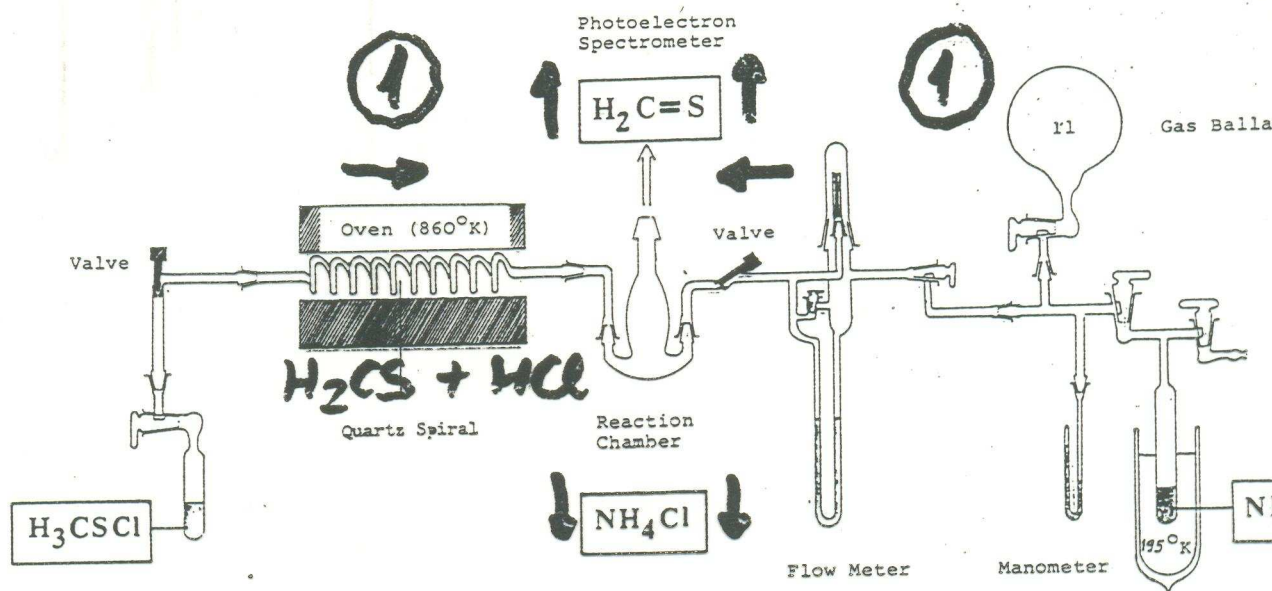


Figure 1. Vacuum-line apparatus for gas-phase synthesis of pure monomeric thioformaldehyde.

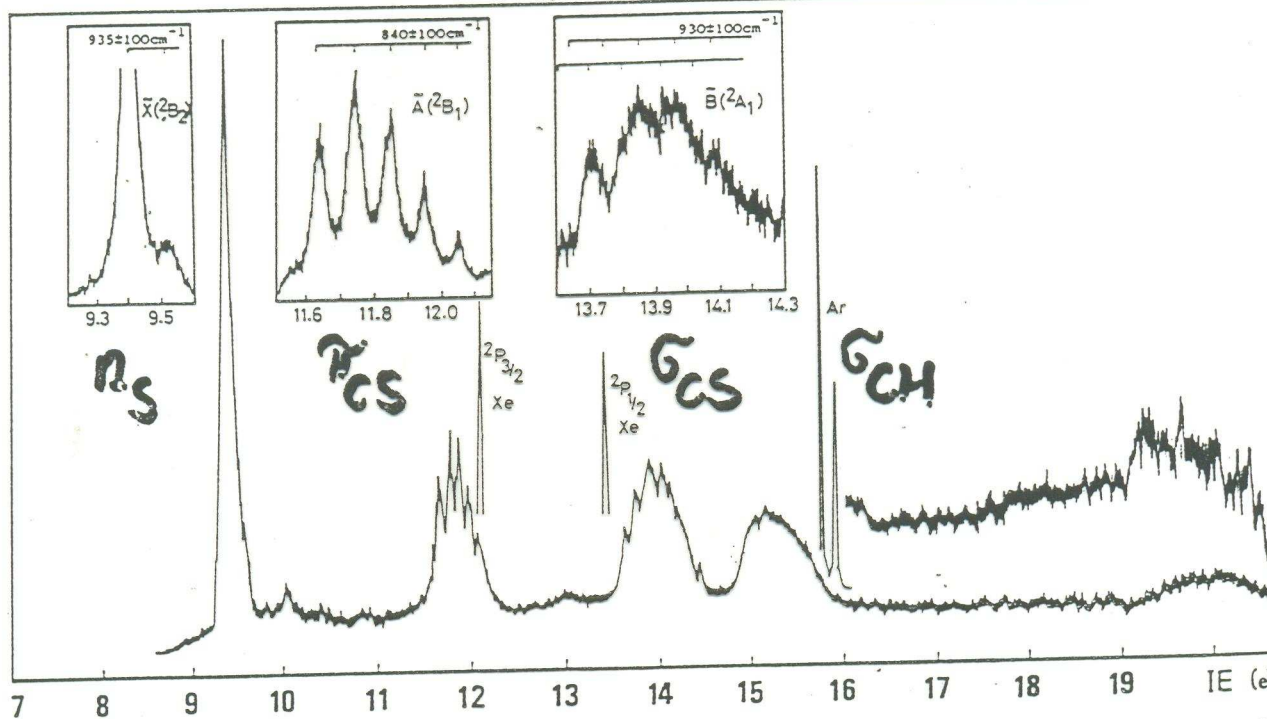
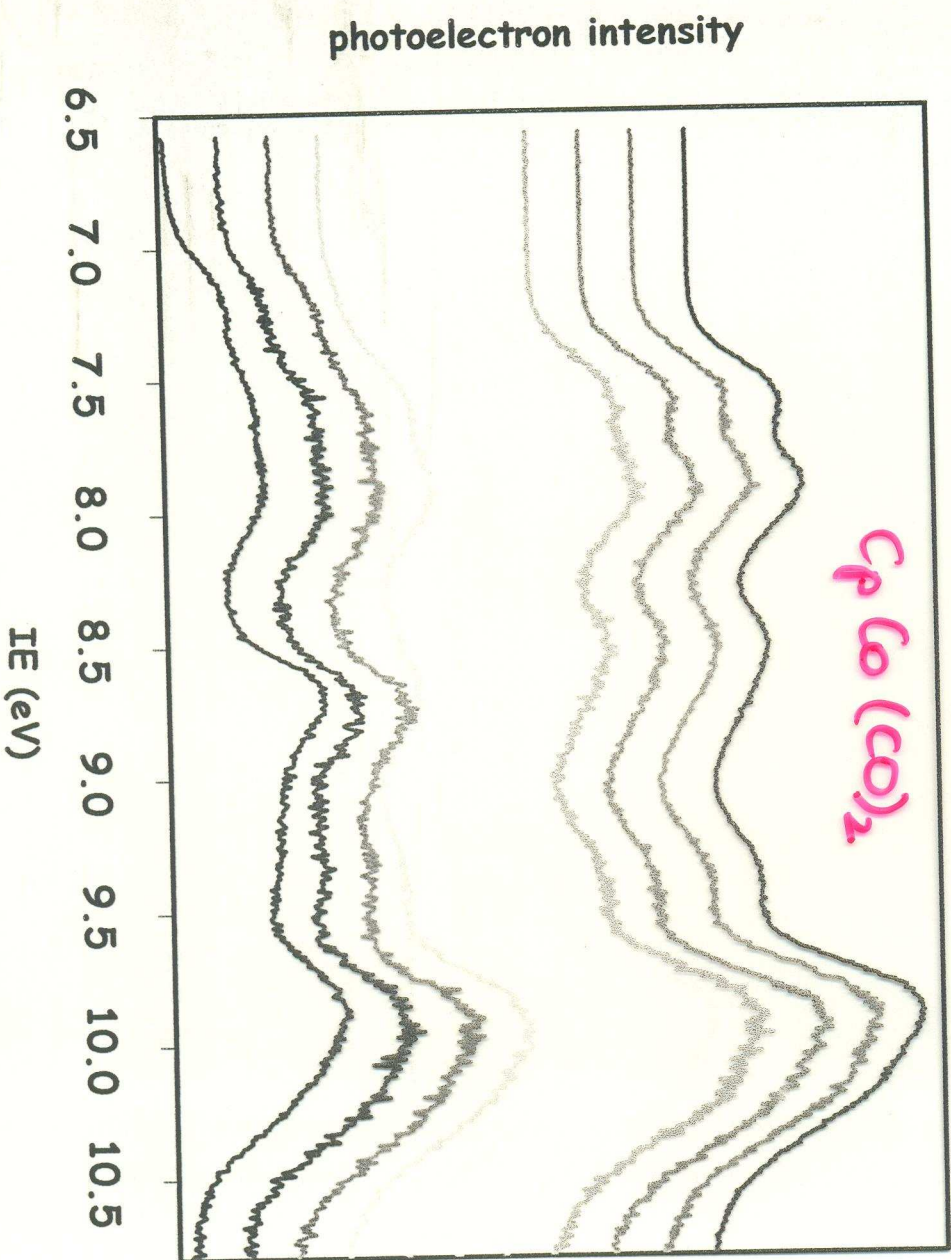


Figure 2. He(I) photoelectron spectrum of thioformaldehyde with expanded records for the $\bar{X}(^2B_2)$, $\bar{A}(^2B_1)$, and $\bar{B}(^2A_1)$ radical cations.

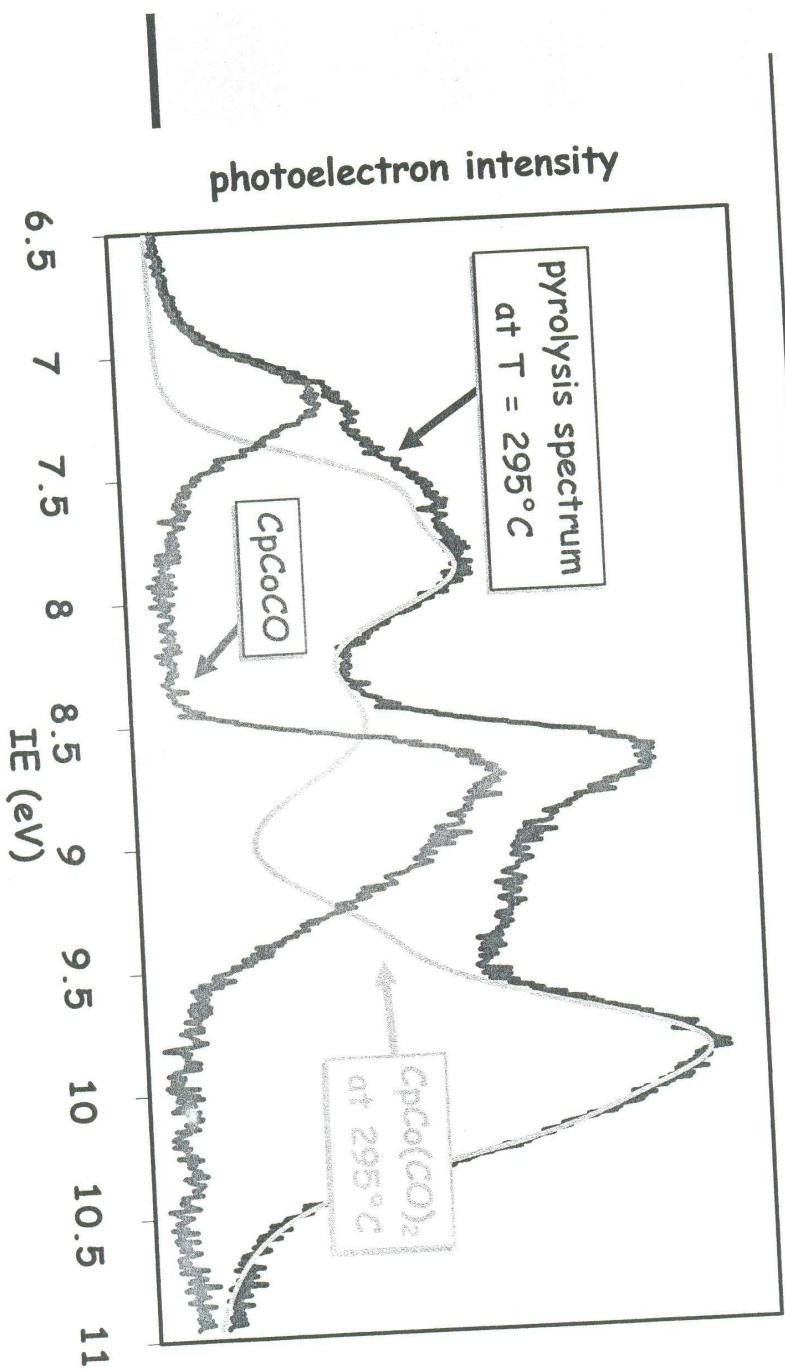
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Pyrolysis PE spectra



25°C
100°C
150°C
200°C
250°C
275°C
300°C

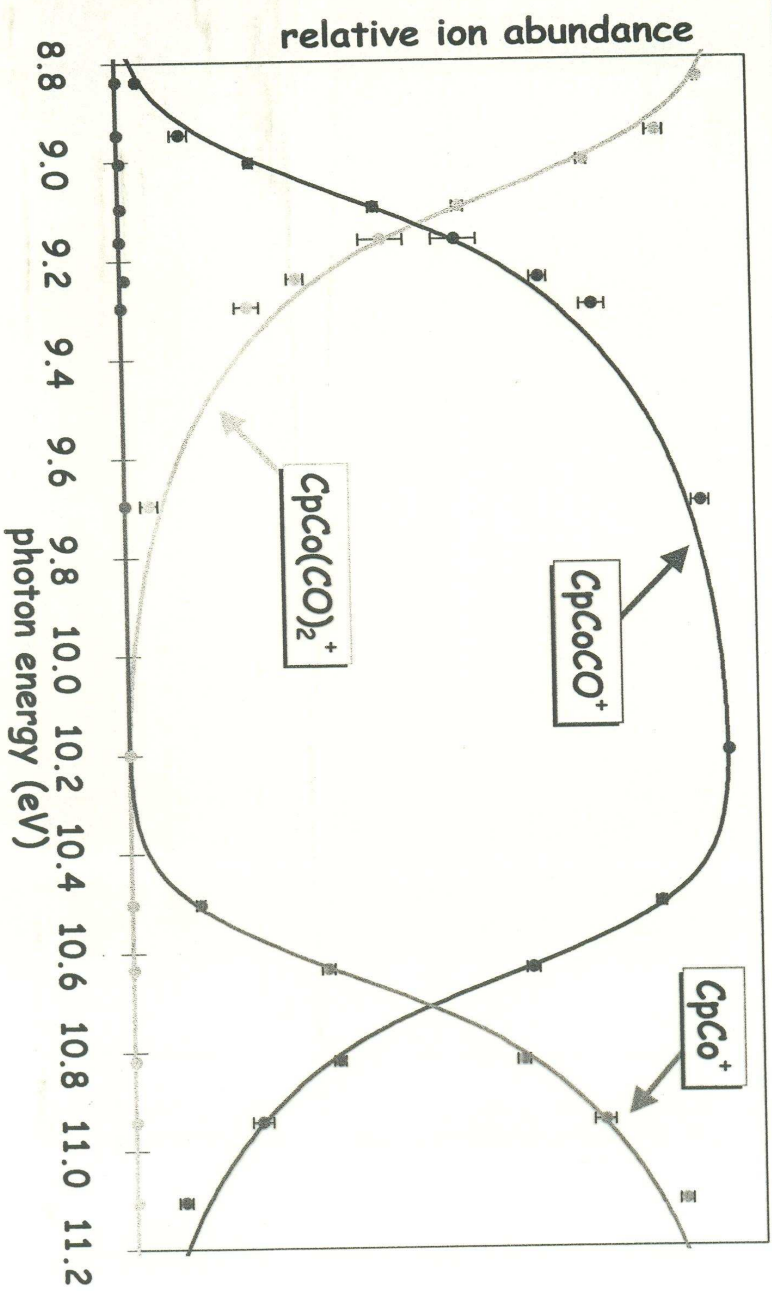
PE spectrum of CpCoCO



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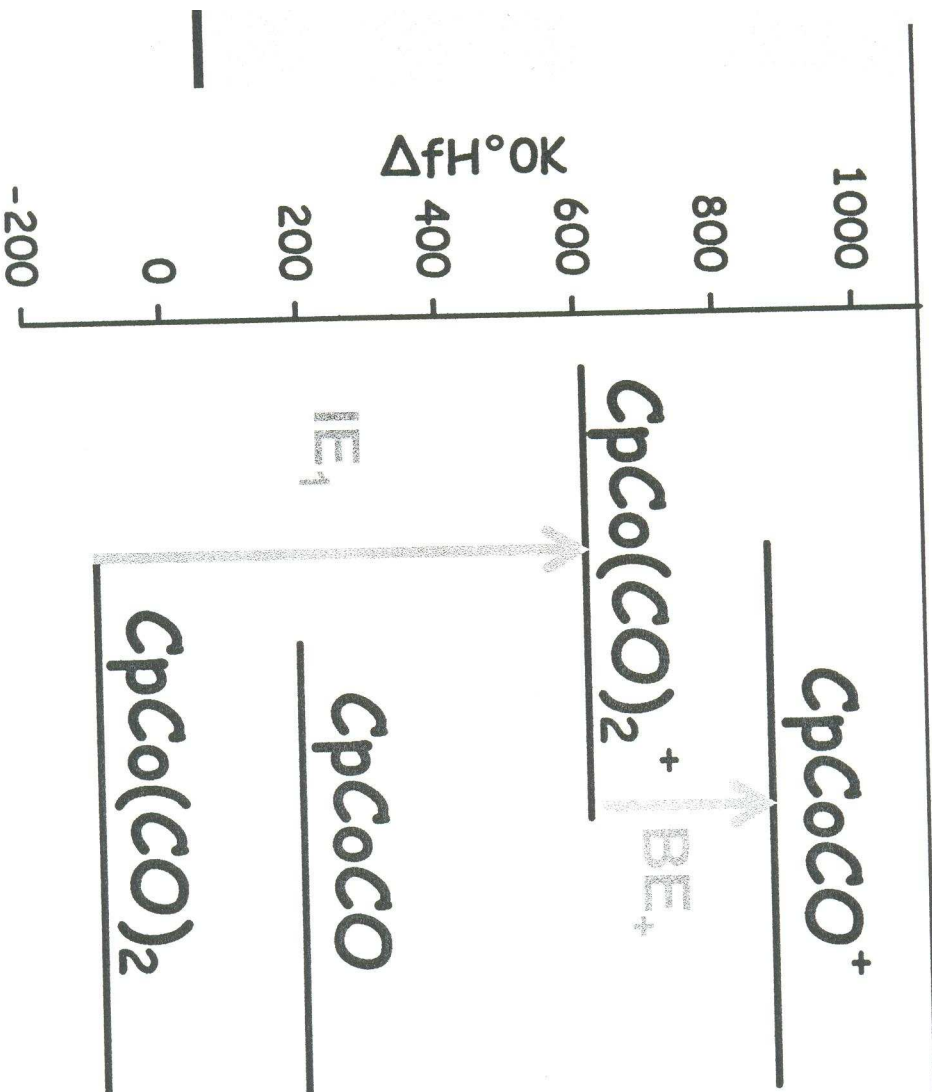
Breakdown curves of $\text{CpCo}(\text{CO})_2$

(Sztáray, B., Szepes, L., Baer, T., *J. Phys. Chem. A* 2003, 107, 9486)



L. Szepes: Structure, Bonding and Energetics of Organometallic Compounds as Studied by UV Photoelectron Spectroscopy and Related Techniques

Obtaining ionic bond energy

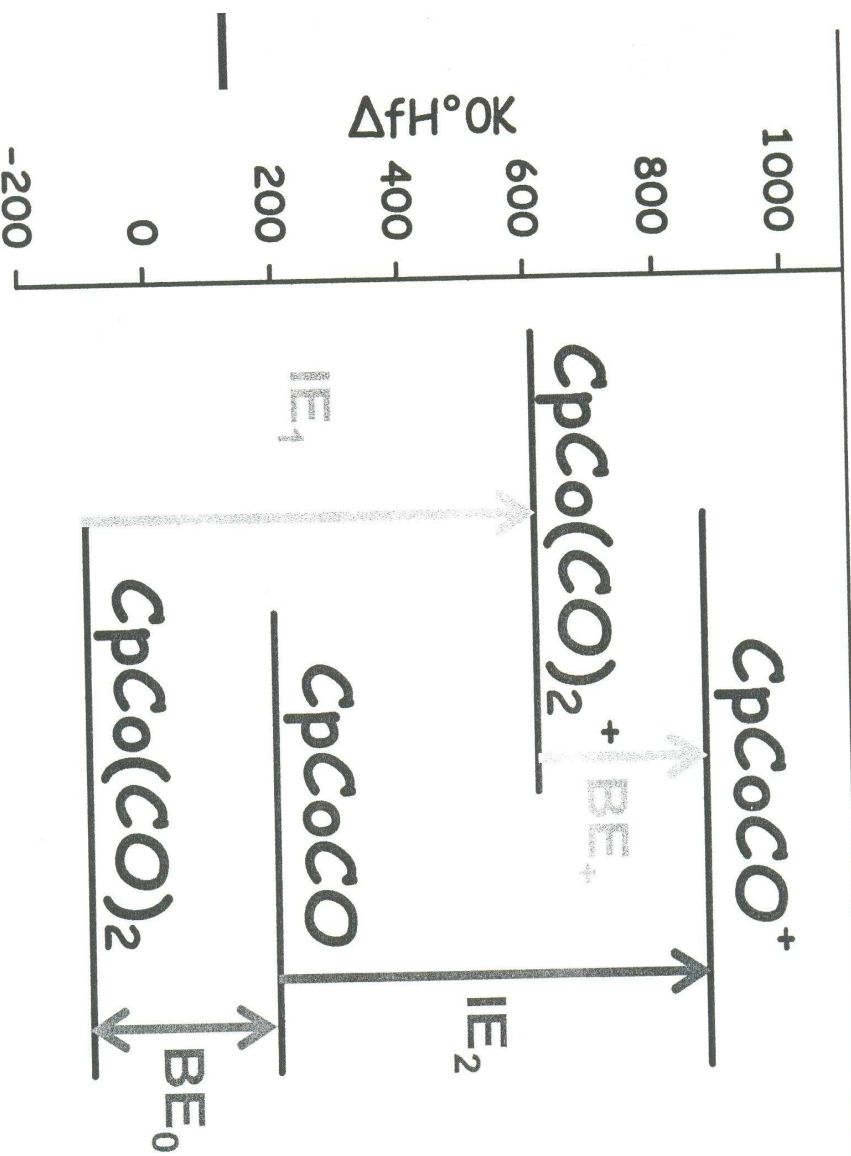


• TPEPICO:

• $I_{\text{E}_1} = 7.35 \text{ eV}$

• $\text{BE}^+ = 1.53 \text{ eV}$

Obtaining neutral bond energy



• TPEPICO:

• $IE_1 = 7.35 eV$

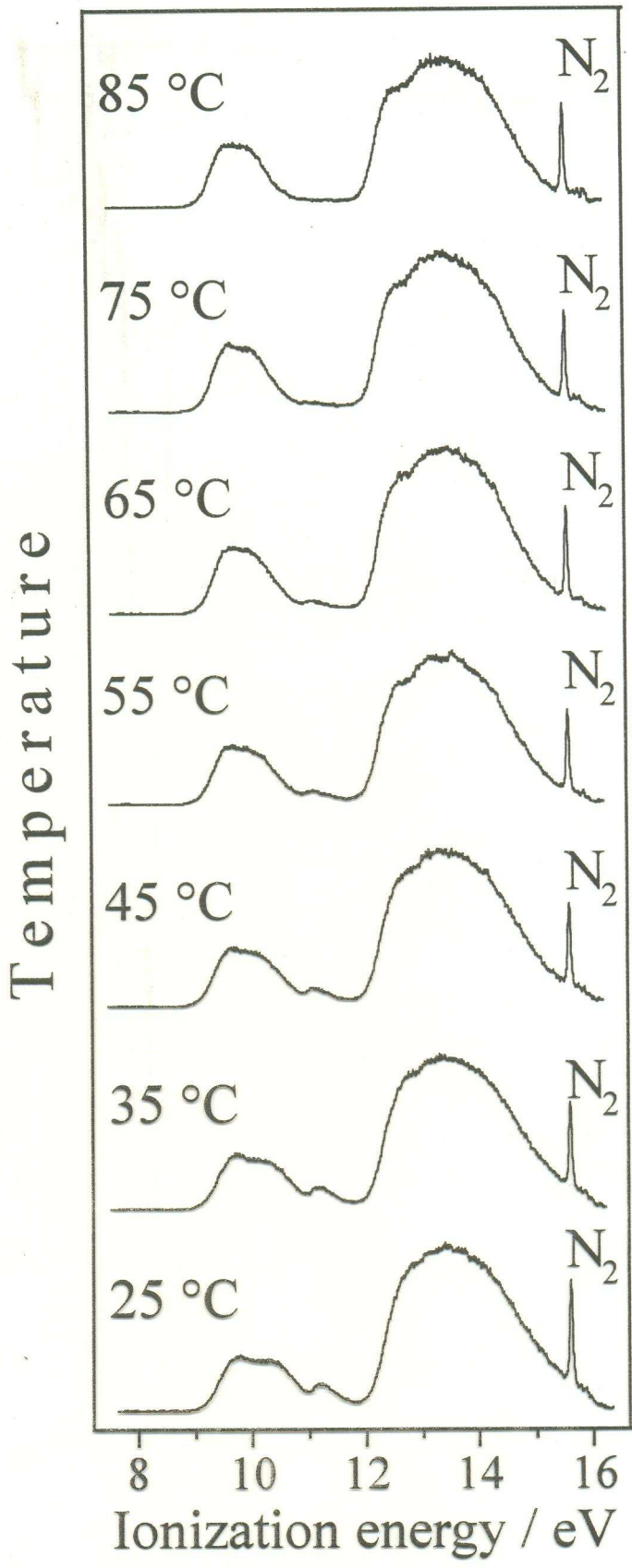
• $BE_+ = 1.53 eV$

• Pyrolysis UPS:

• $IE_2 = 6.97 eV$

• Neutral bond

energy: 1.91 eV



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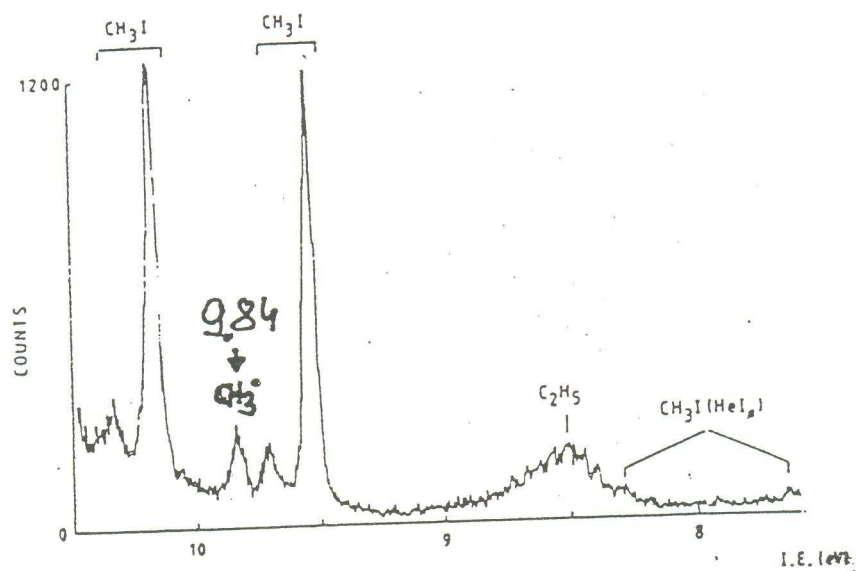
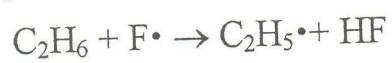
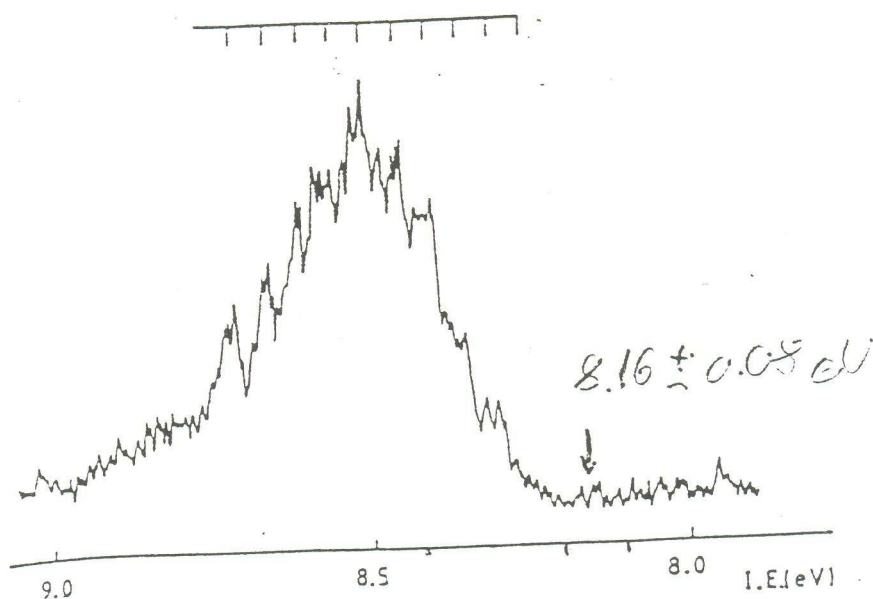


Figure 2. The He I photoelectron spectrum obtained from the reaction $\text{F} + \text{C}_2\text{H}_6$ recorded in the ionization energy range 7.5–10.5 eV with a multichannel detector photoelectron spectrometer. It consists of 250 scans recorded in a total time of 40 s. Methyl iodide was added as a calibrant.

Ethyl Radical



Kezdeti reakciólépések:

