

A p_e spektrumok értelmezése

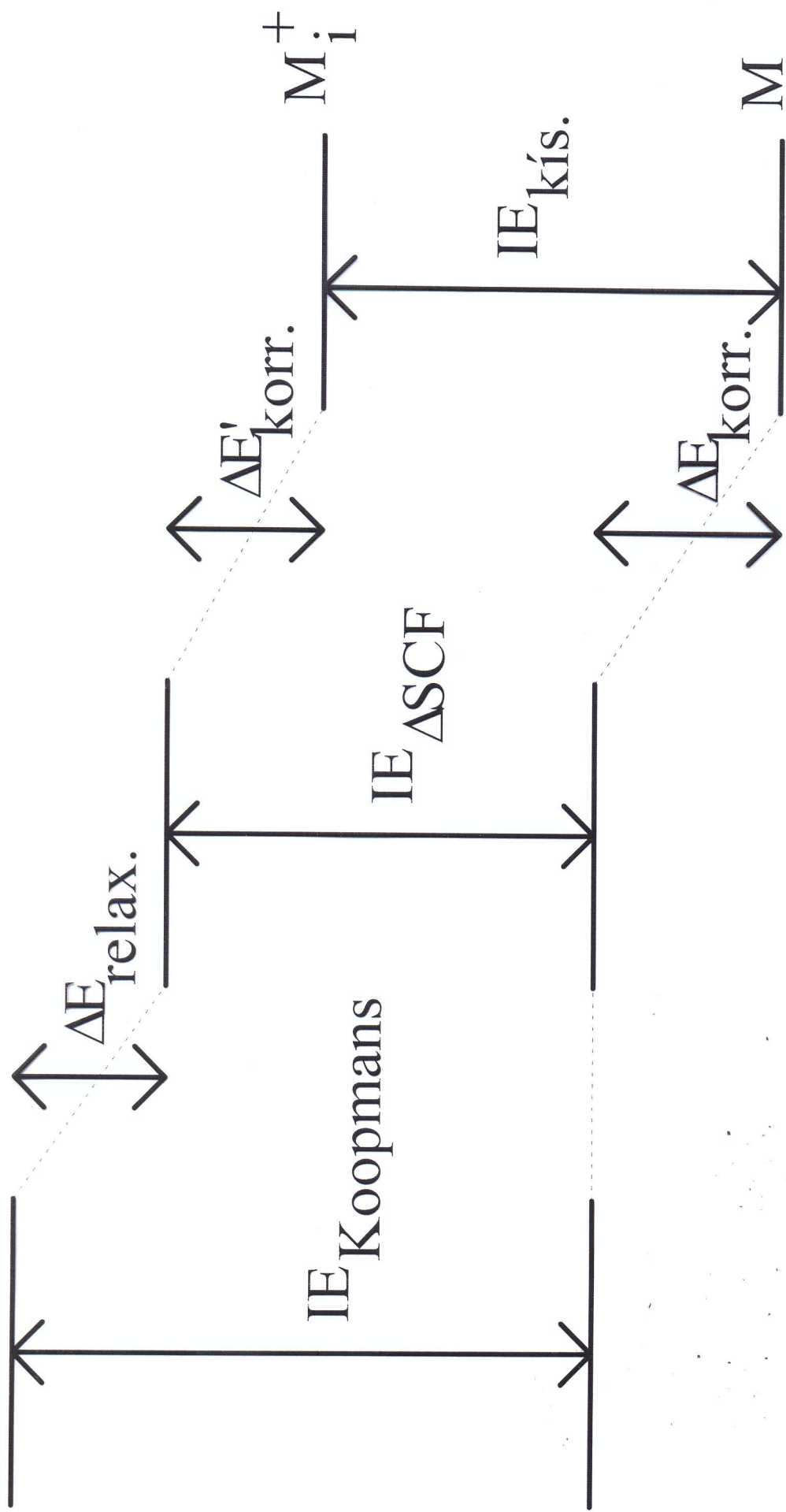
Koopmans elv

A) Elméleti megközelítés

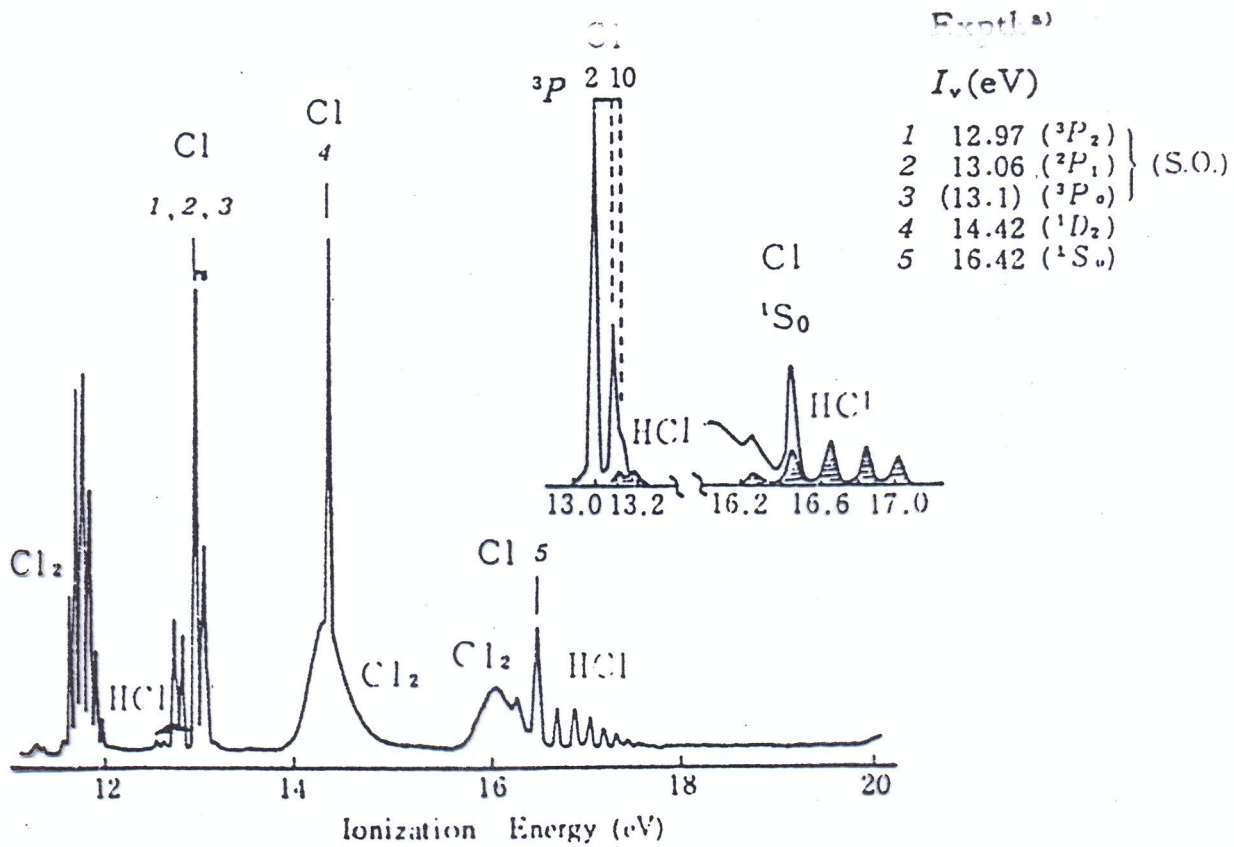
Kvantumkémiai számítások

B) Kísérleti megközelítés

- spektrumok finomszerkezete**
- sávintenzitások**
- perfluoro hatás**
- korreláció hasonló vegyületek spektrumával**
- elektronegativitással kapcsolatos „trendek”**
- sávalakok**
- molekulák Rydberg spektruma**
- egyszerű, kvalitatív MO modellek**
- szubsztituens additív hatások**
- fotoelektronok szögeloszlása**



A pályarelazáció és az elektronkorreláció figyelmen kívül hagyása által okozott hibák



a) Kimura *et al.* (134a). See also other work : Leeuw *et al.* (150b).

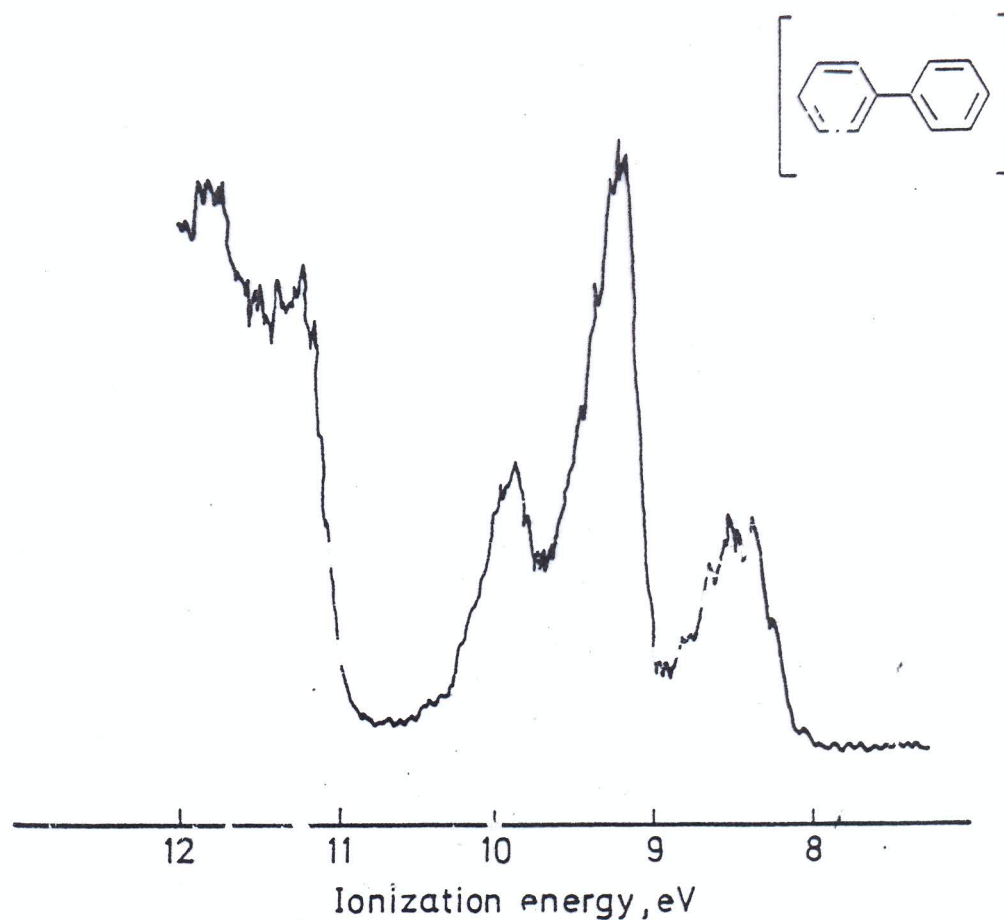
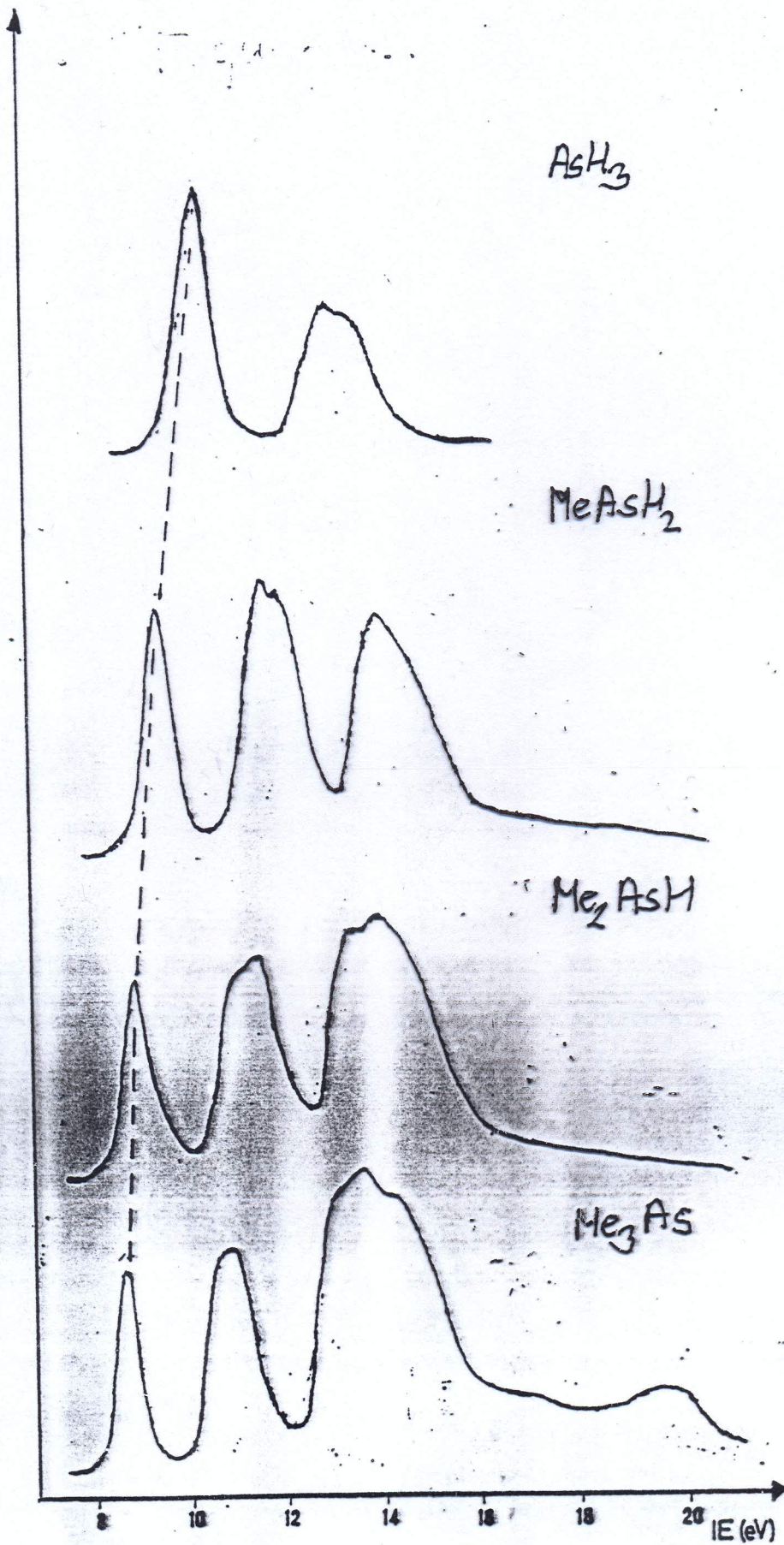
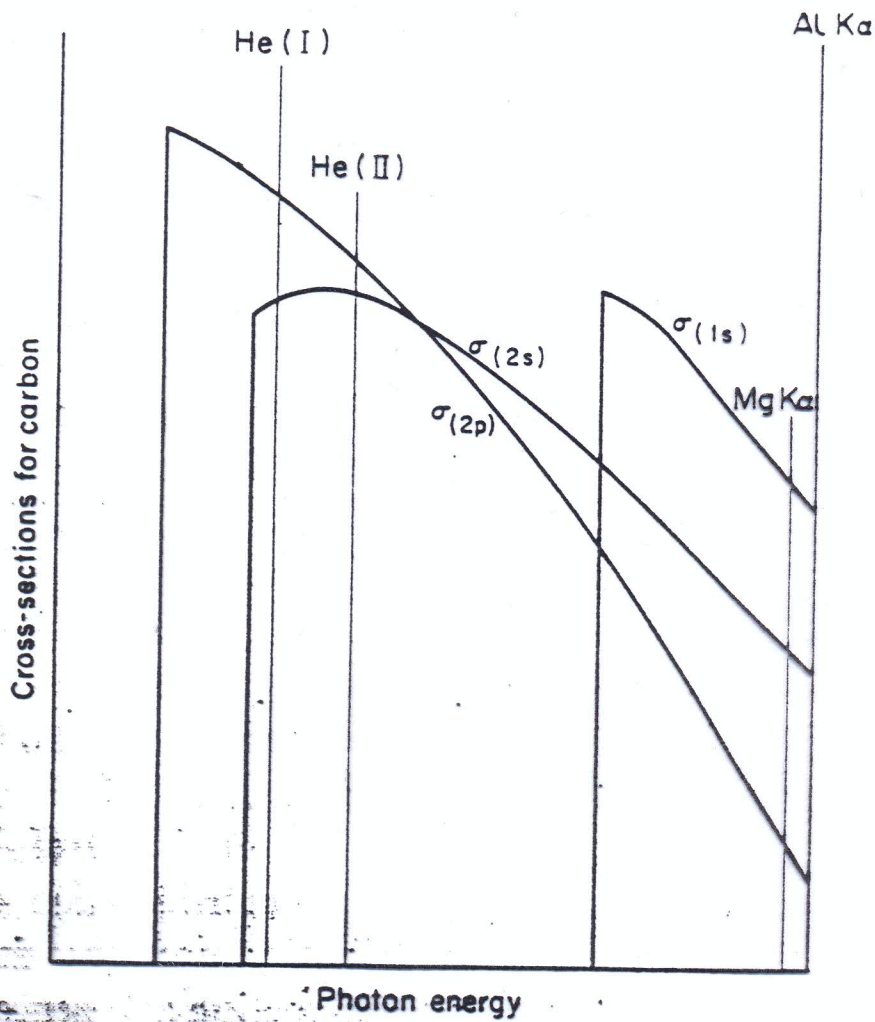


Figure 1.7. Partial photoelectron spectrum of biphenyl, showing the π electron ionization region

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Theoretical variation of cross-section for photoionization as a function of energy for sub-shells of carbon.

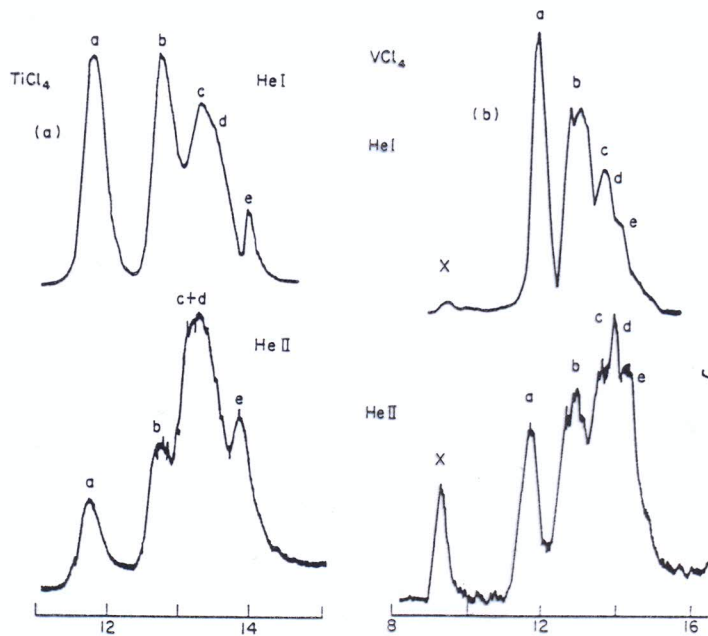


Fig. 33. Ultraviolet-photoelectron spectra of TiCl_4 and VCl_4 (gases). (From Refs 56, 57.)

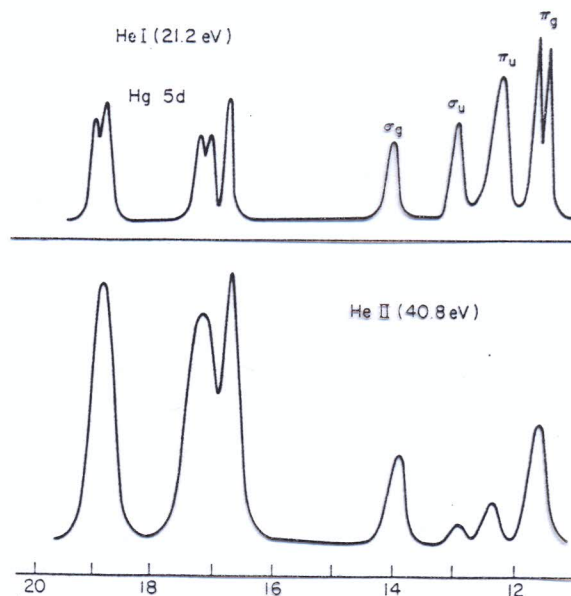
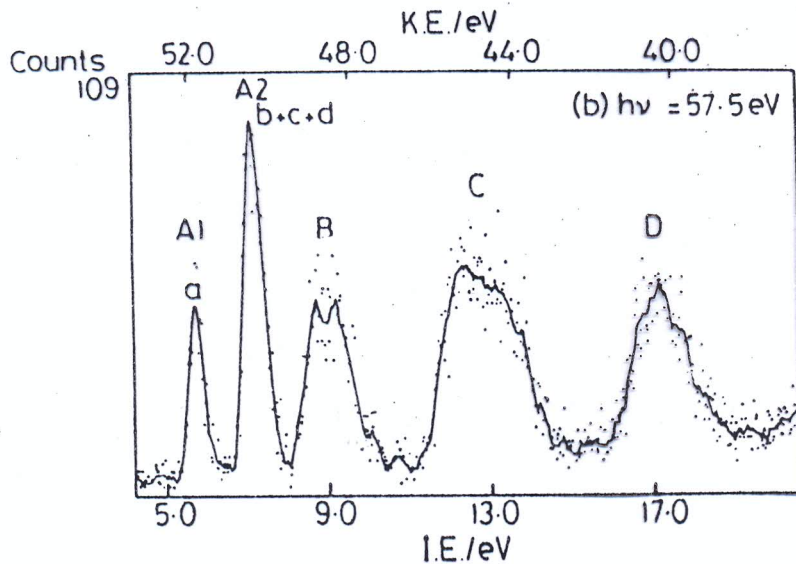
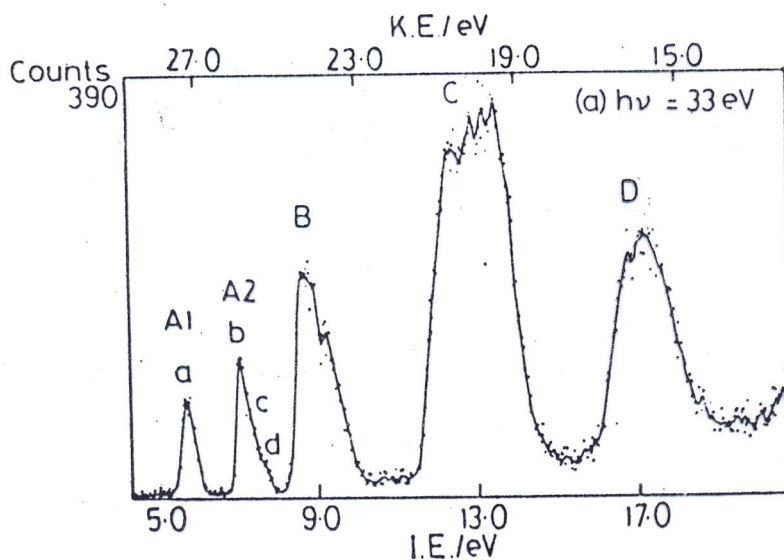
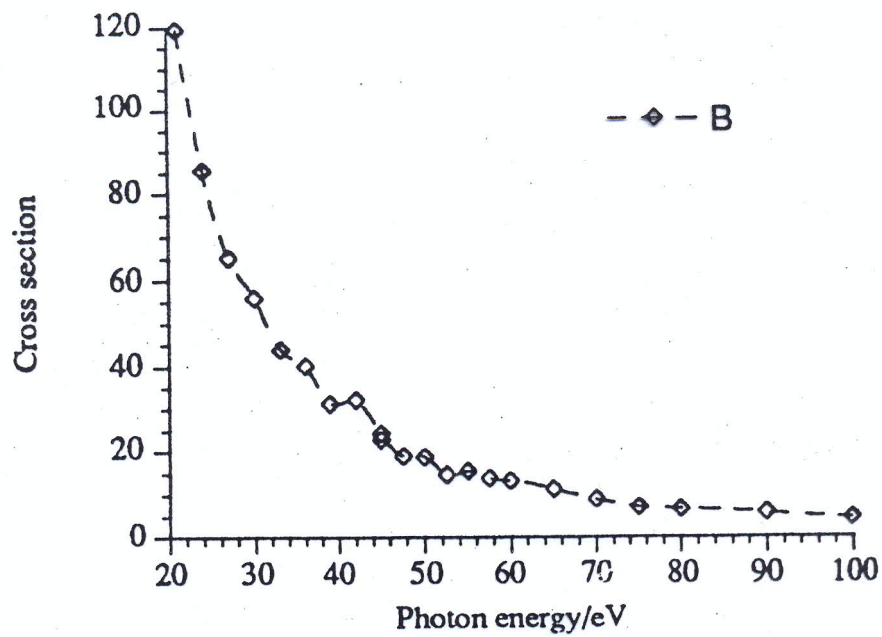
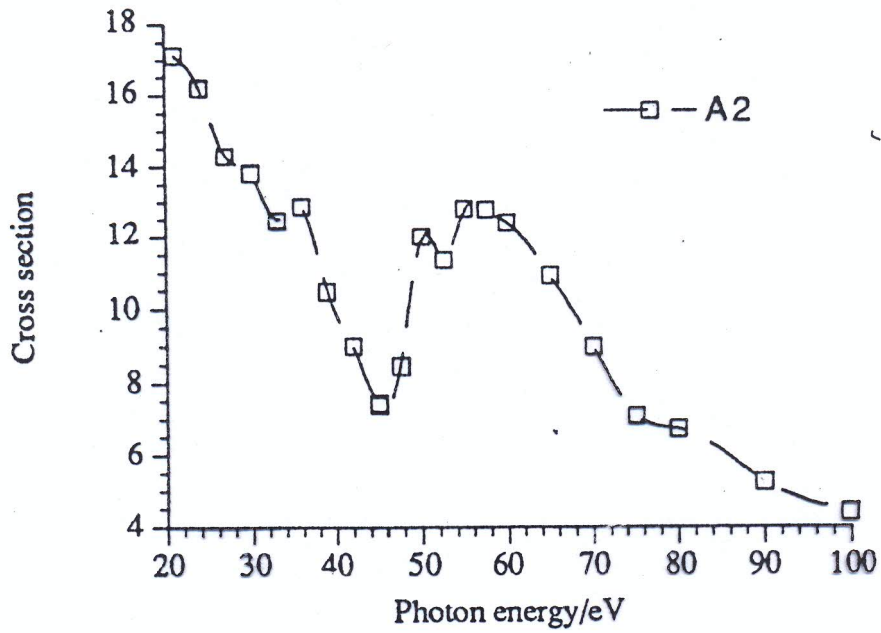
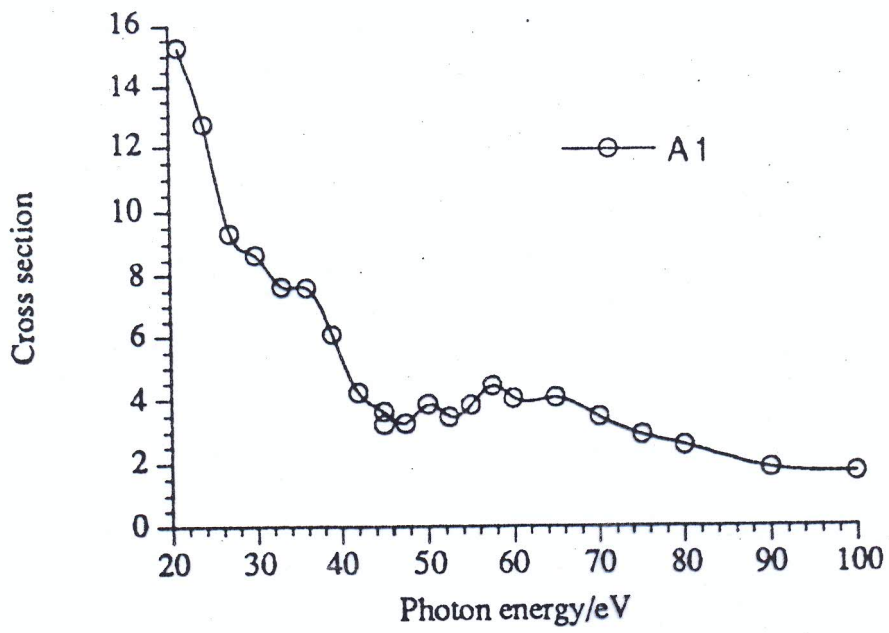


Fig. 34. Ultraviolet-photoelectron spectra of HgCl_2 (gas). (From Ref. 56.)



PE spectra of $\text{Cr}(\eta\text{-C}_5\text{H}_5)_2$ with photon energies of 33 and 57.5 eV.



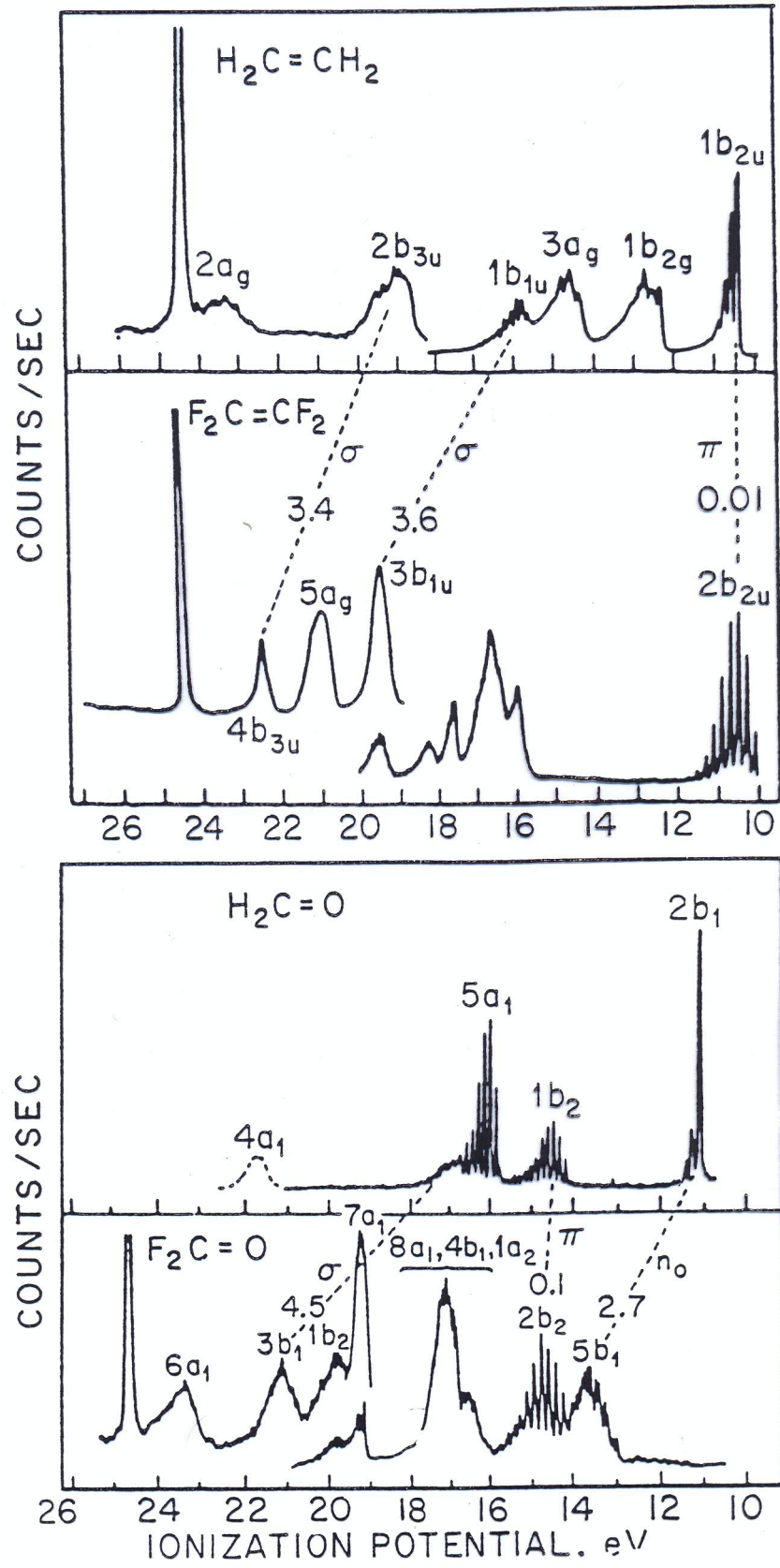
RPPICS of bands A1, A2 and B of $\text{Cr}(\eta\text{-C}_5\text{H}_5)_2$.

Perfluoro effektus

ha sik molekulaban H-t F-ra cserelunk

- σ MO 2-3 eV-tal stabilizalodik

- π MO 0-0.5 eV-tal - " -



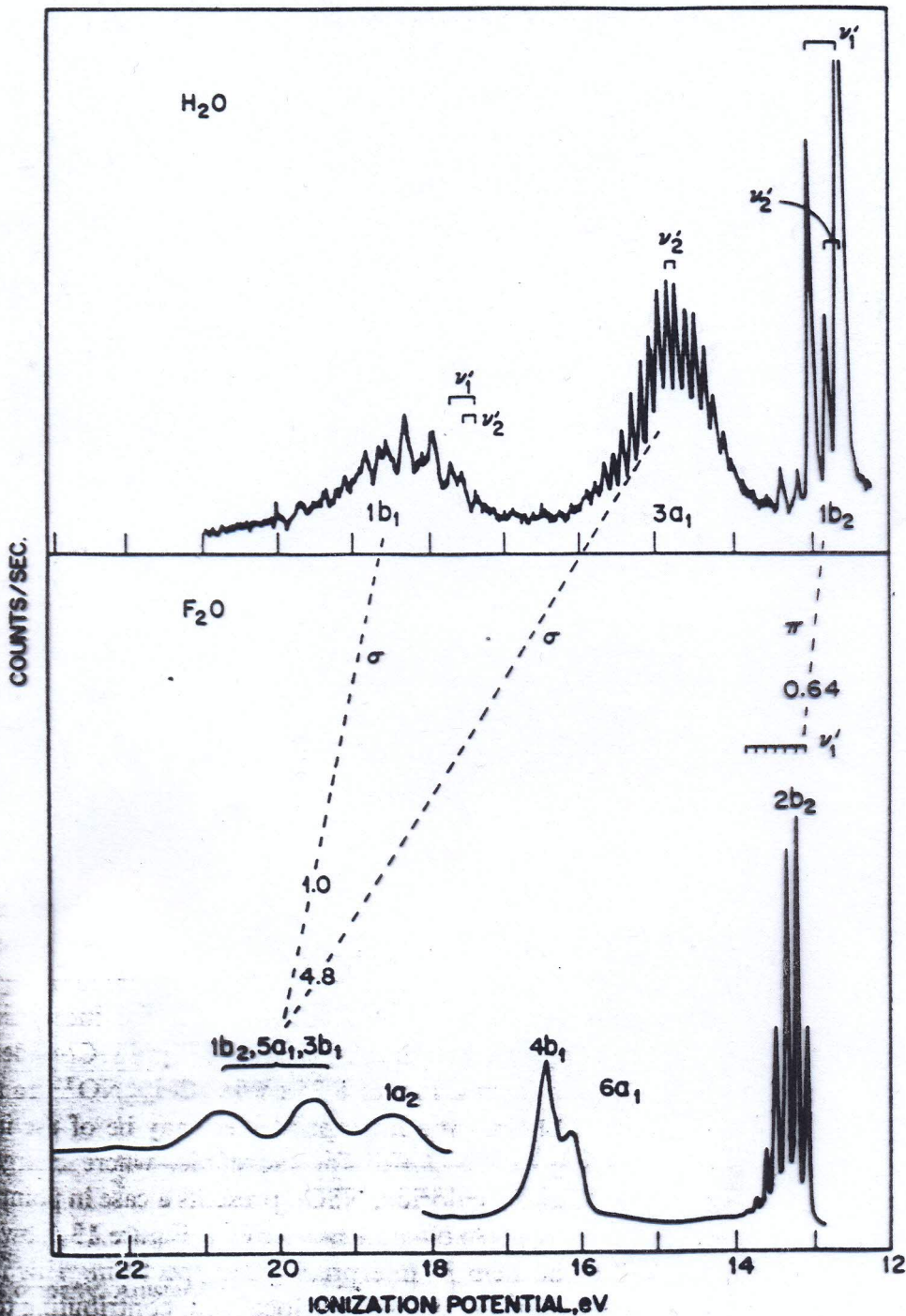


Fig. 12. The photoelectron spectra of water and oxygen difluoride. In the latter, the spectrum above 18 eV was determined using He II excitation. Reproduced from Brundle *et al. J. Amer. Chem. Soc.* 94, 1451. Copyright 1972 by the American Chemical Society. Reprinted with permission of the copyright owner.

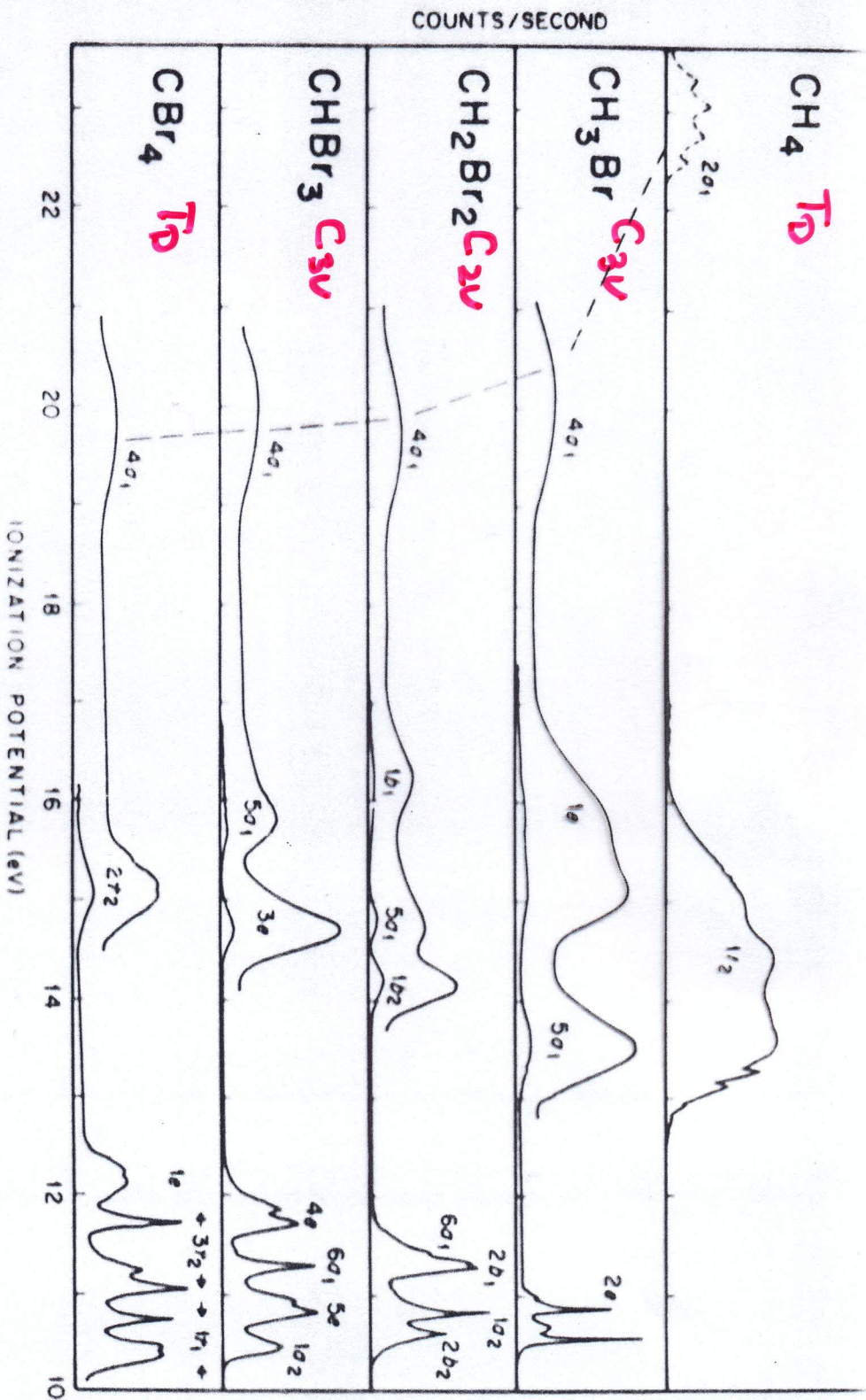
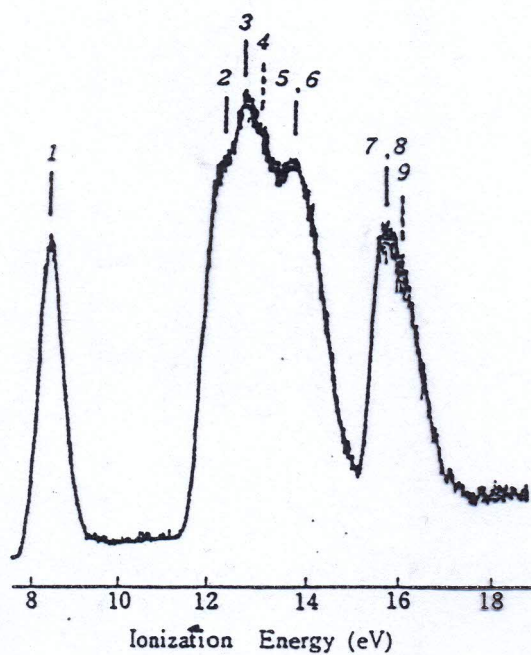
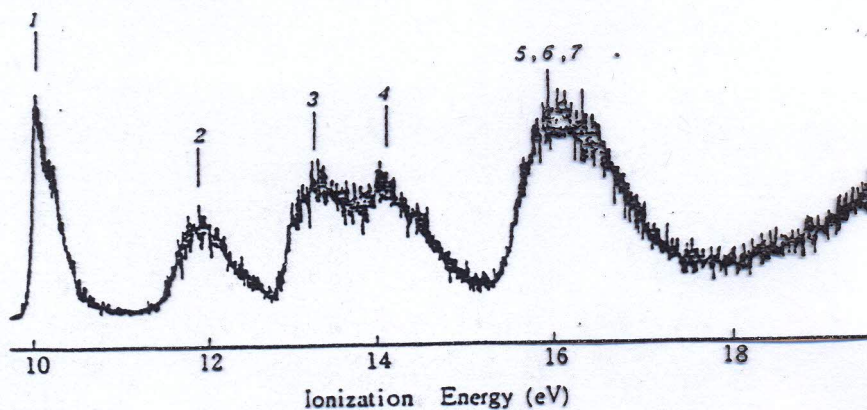


Fig. 10.36. Spectra of the bromomethane series. Reproduced with permission from Ref. 43.

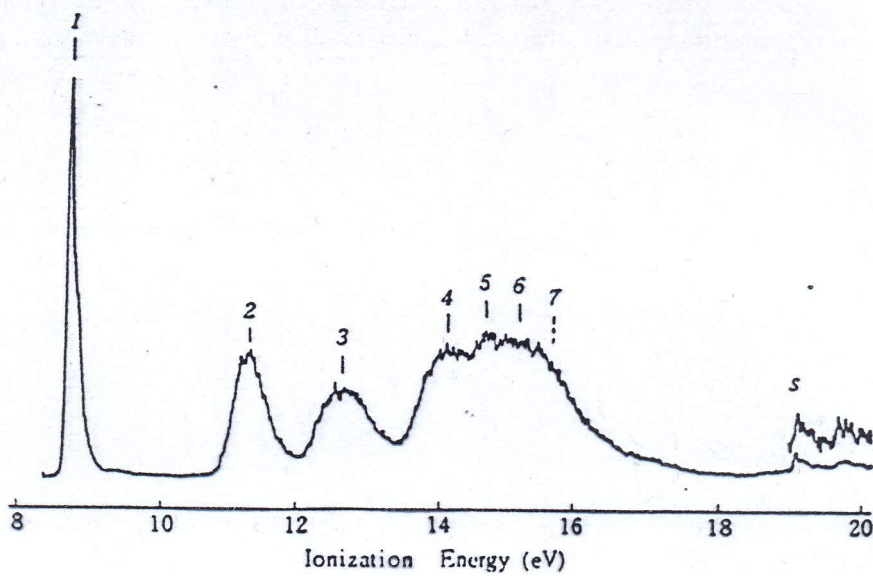
(113) $(\text{CH}_3)_3\text{N}$ Trimethylamine

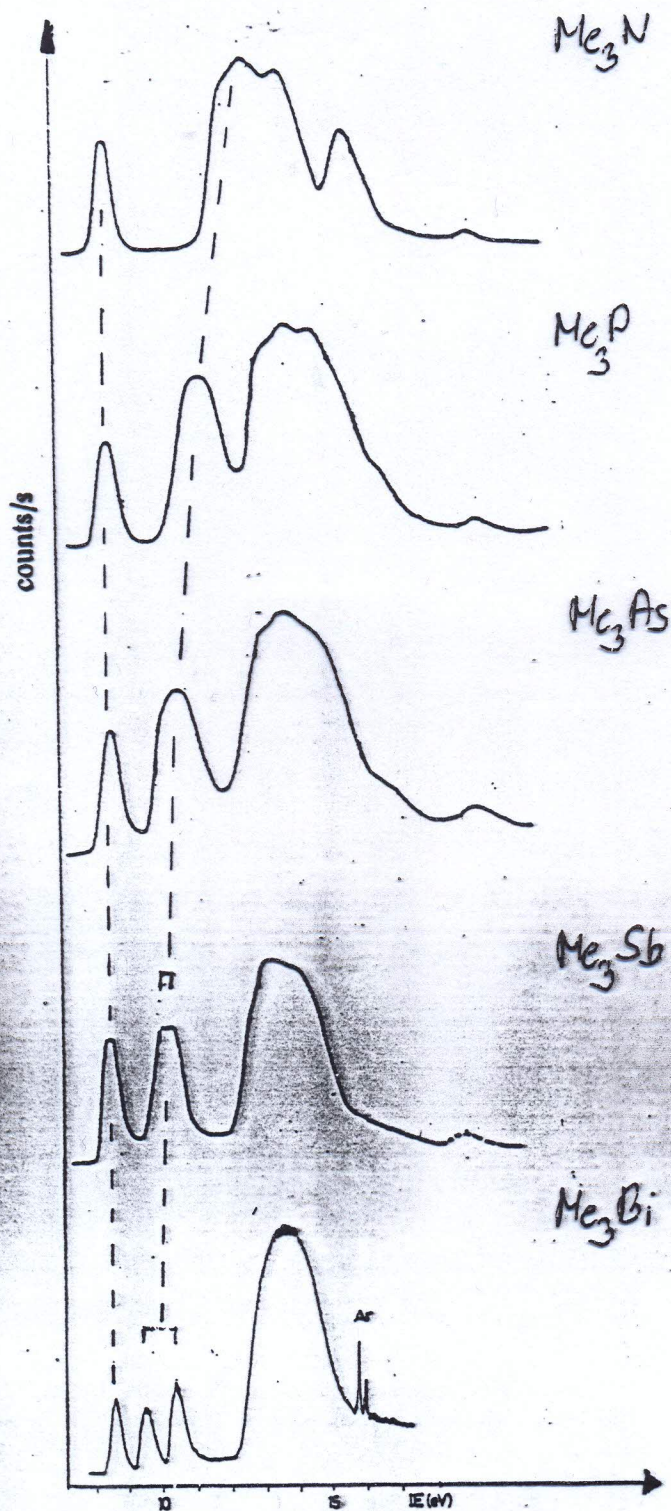


(114) $(\text{CH}_3)_2\text{O}$ Dimethyl Ether

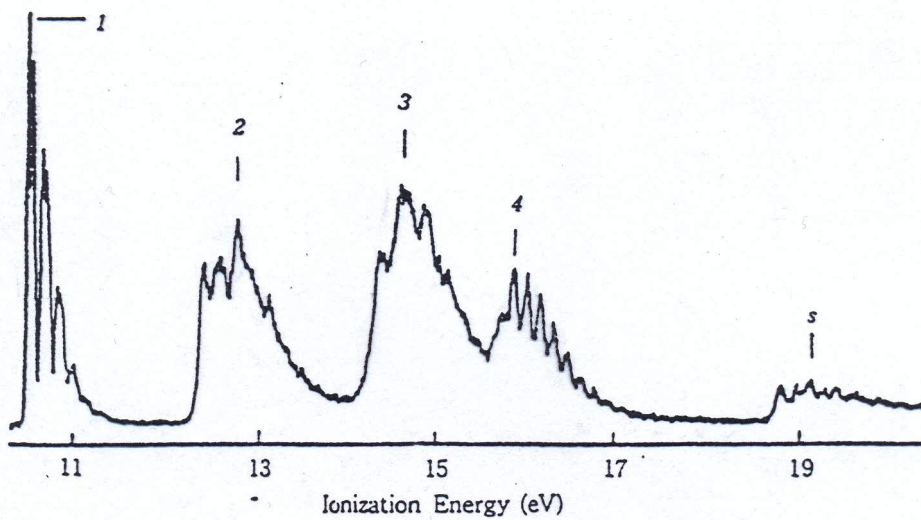


(117) $(\text{CH}_3)_2\text{S}$ Dimethyl Sulfide

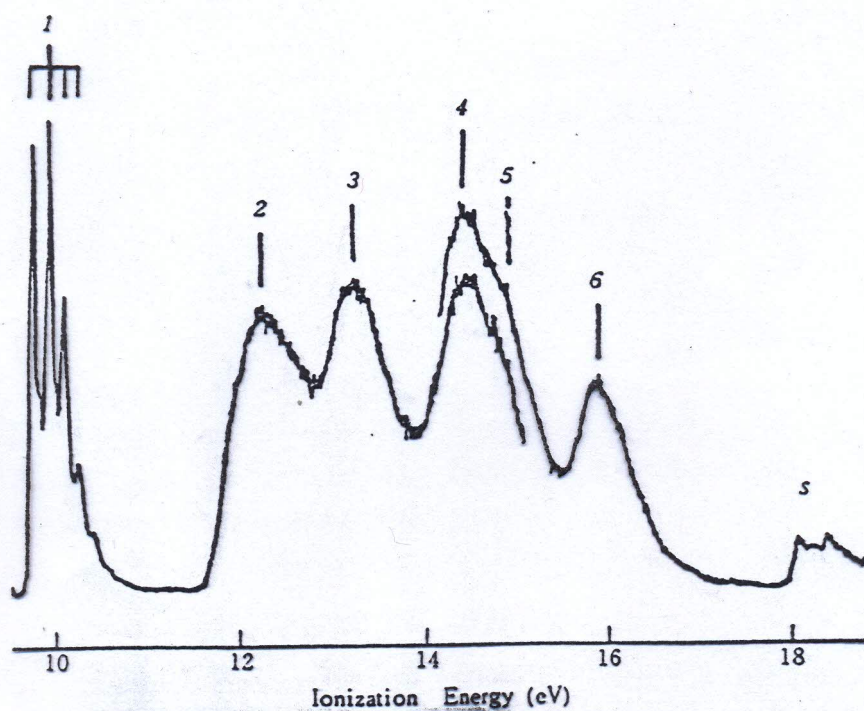




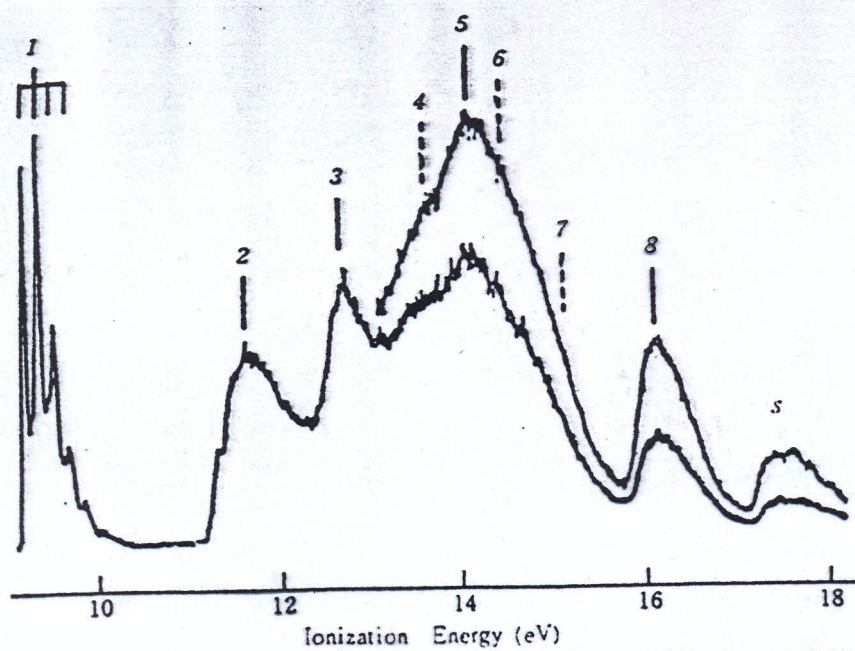
(39) $\text{CH}_2=\text{CH}_2$ Ethylene



(40) $\text{CH}_3\text{CH}=\text{CH}_2$ Propene

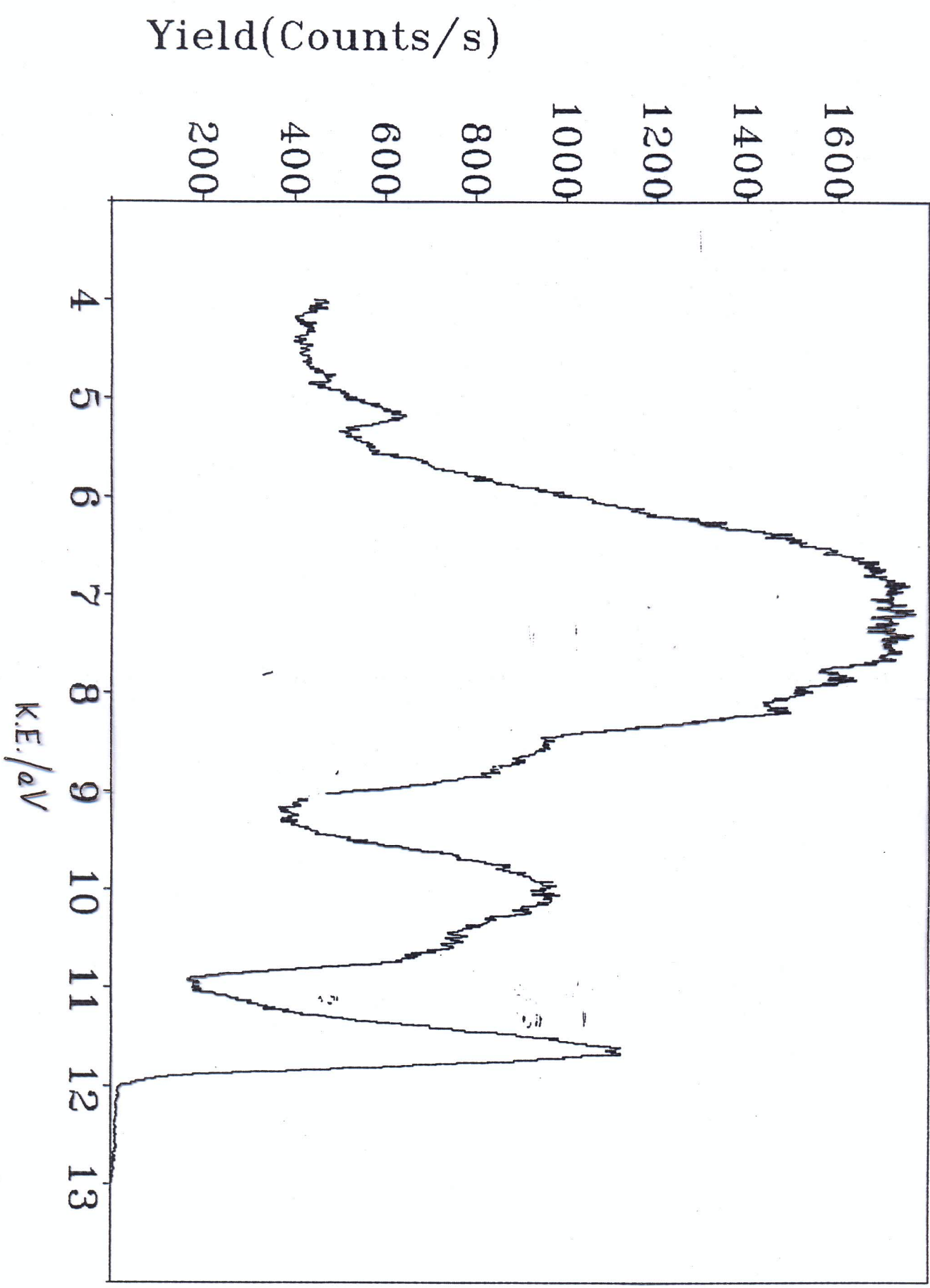


(41) *cis* $\text{CH}_3\text{CH}=\text{CHCH}_3$ *cis*-Butene



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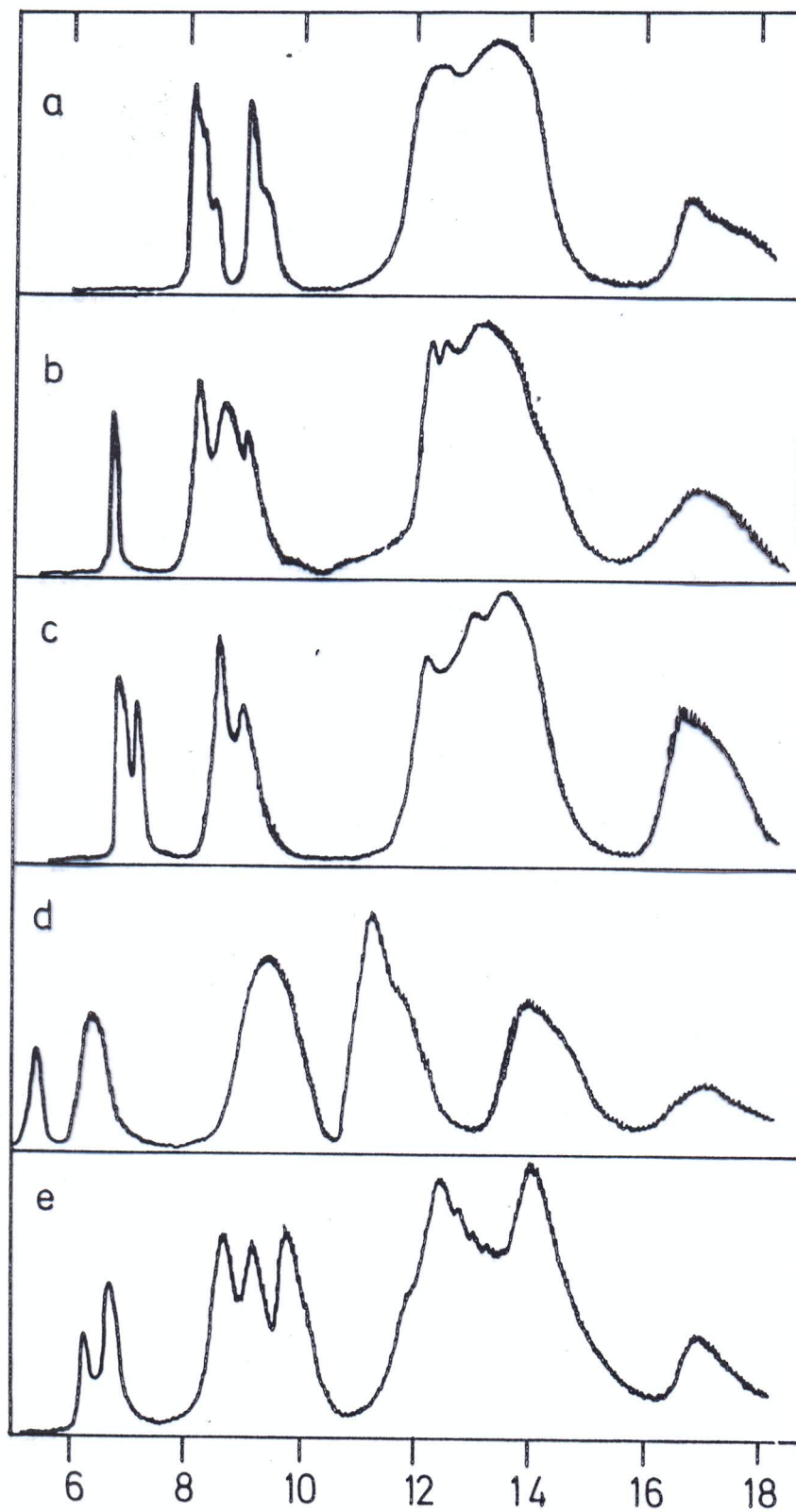


Fig. 6. He(I) P.E. spectra of sandwich complexes: (a) Mgcp_2 (49); (b) Vcp_2 (52); (c) Fecp_2 (49); (d) Crbz_2 (16, 57); (e) Mn(cp)(bz) (57)

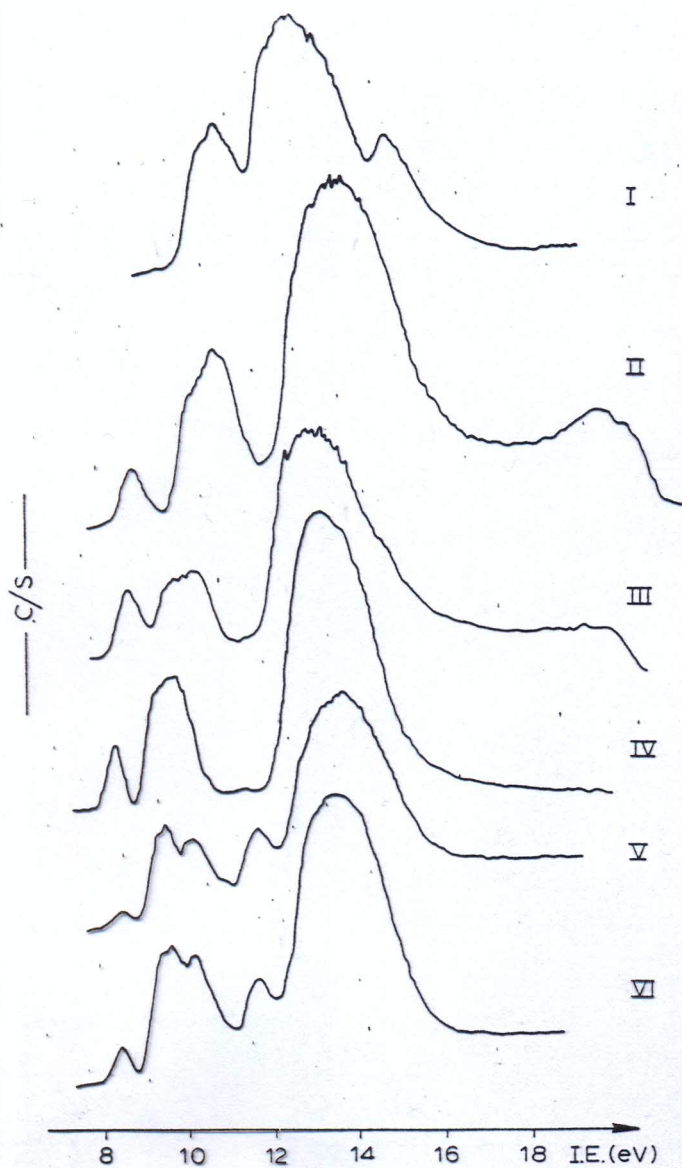


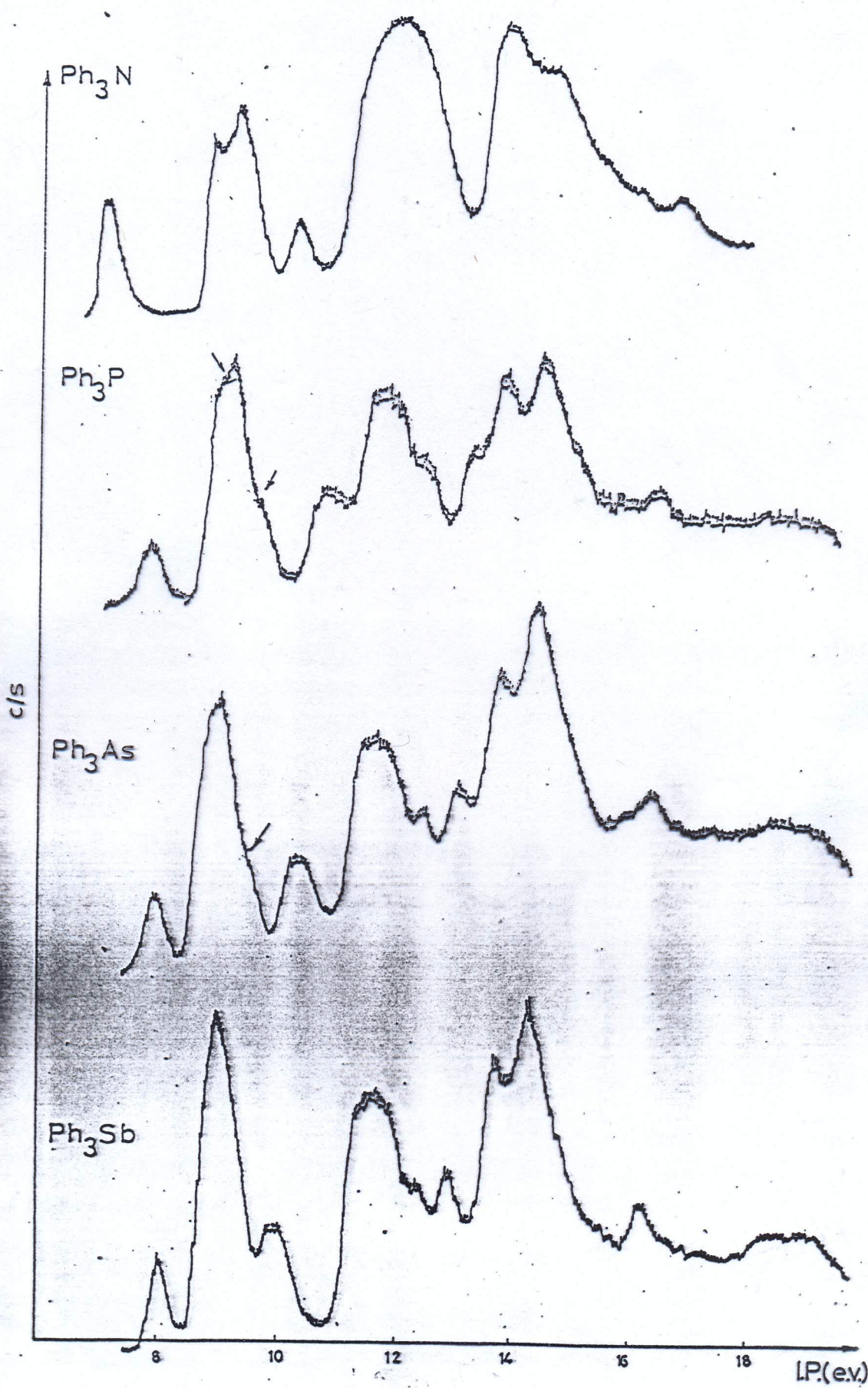
Fig. 1. He(I) photoelectron spectra of $\text{Me}_3\text{M}-\text{M}'\text{Me}_3$ derivatives. I-IV: $\text{M} = \text{M}' = \text{C}, \text{Si}, \text{Ge}$ and Sn ; V: $\text{M} = \text{Sn}, \text{M}' = \text{Si}$; VI: $\text{M} = \text{Sn}, \text{M}' = \text{Ge}$.

TABLE I

ORBITAL STRUCTURE, EXPERIMENTAL AND THEORETICAL IONIZATION ENERGIES (eV) FOR $\text{Me}_3\text{C}-\text{CMe}_3$ (UPPER ROW) AND $\text{Me}_3\text{Si}-\text{SiMe}_3$ (LOWER ROW) ^a

Species	Character	Composition (%)			Energy (eV)	
		$\text{C}_c(\text{Si}_c)$	C_p	H	Exp	CNDO/2
$4a_{1g}$	X-X	48.8	20.6	30.6	10.3	13.6
		65.7	27.0	7.3	8.7	10.8
$4e_g$	X- C_p	26.2	50.6	23.2	{ 10.7 11.0	13.9
		(C_p -H)	8.9	58.3	32.8	{ 10.2 10.7
$4e_g$	C_p -H	19.2	43.5	37.3		16.1
		12.4	59.0	28.6	{ 10.2 10.7	13.45

^a $\text{C}_c(\text{Si}_c)$ and C_p denote central and peripheral atoms, respectively.



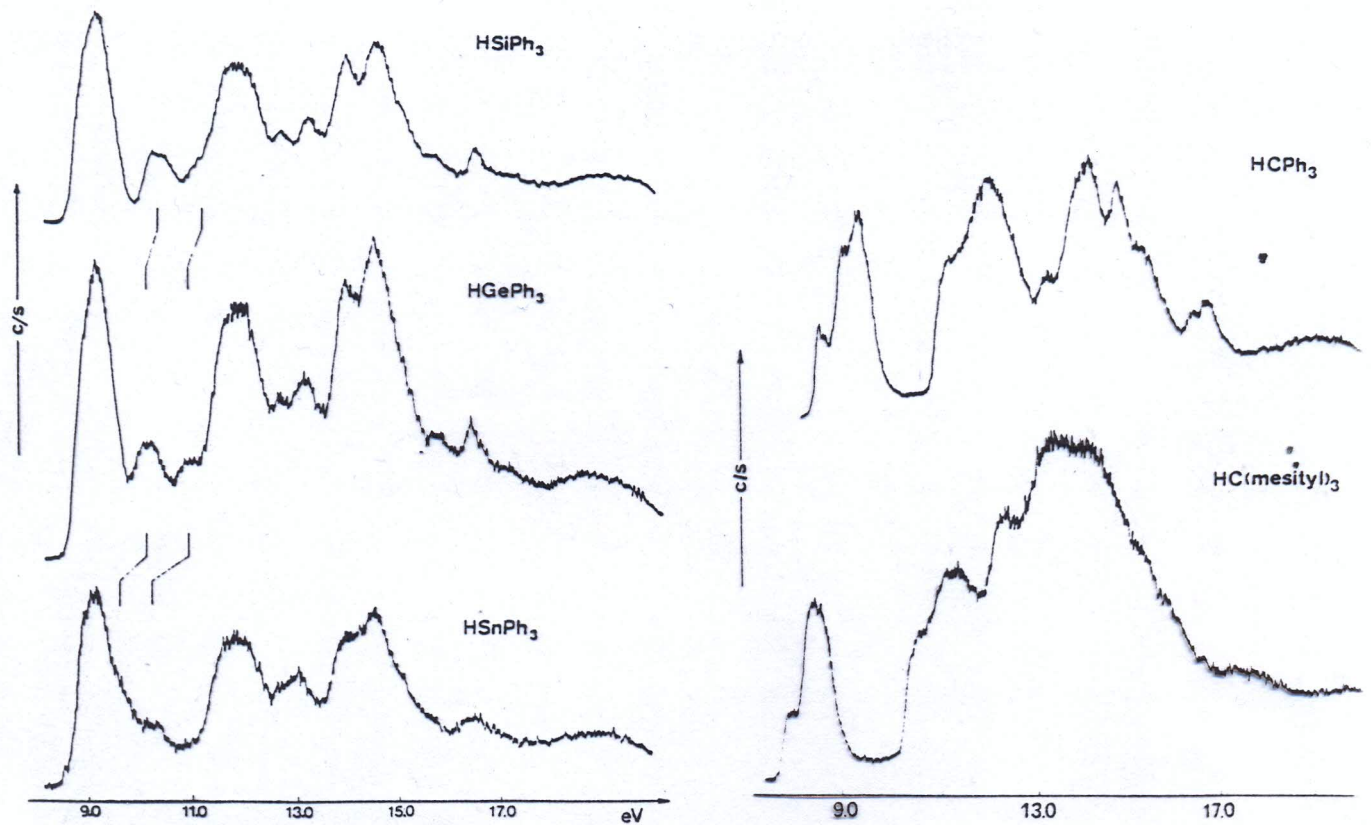
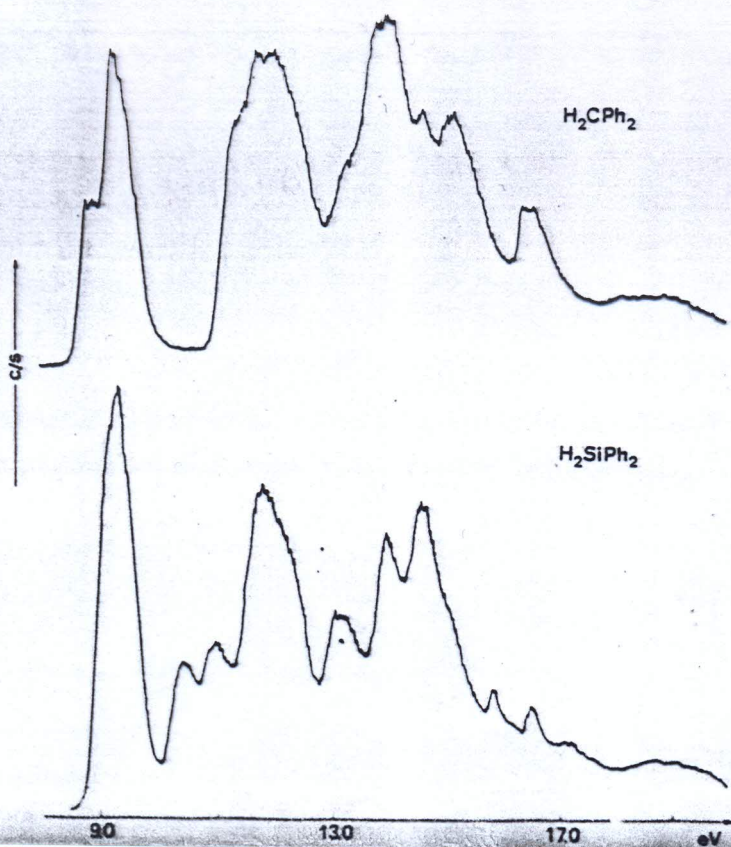


Fig. 1. Photoelectron He(I) spectra of HXPh_3 ($\text{X} = \text{Si}, \text{Ge}$ and Sn).

Fig. 2. Photoelectron He(I) spectra of HCPPh_3 and HC(mesityl)_3 .



6.4 Angular Distribution

Angular distribution studies are potentially one of the most useful methods for the orbital assignment of bands in a UP spectrum. In such studies the photoelectron intensity or relative intensity is measured as a function of the angle between the incident radiation beam and the detector (Fig. 17). The type of information obtained is as shown in Fig. 18.

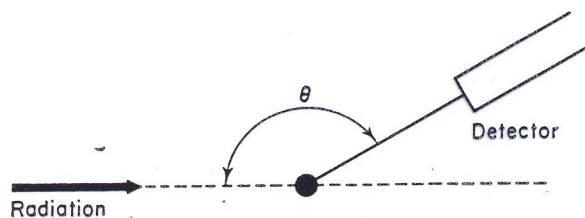


Fig. 17. Study of the angular distribution of photoelectrons.

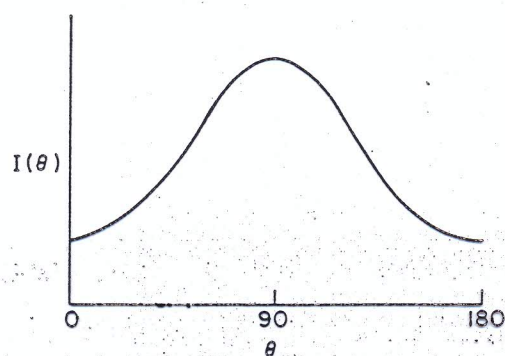


Fig. 18. Example of information obtained from angular distribution studies. Plot of intensity versus θ .

For gaseous atoms and molecules, and for unpolarized radiation the following equation is applicable:

$$I(\theta) \propto 1 + \frac{\beta}{2} \left(\frac{3}{2} \sin^2 \theta - 1 \right)$$

β is termed the asymmetry parameter and is characteristic of the angular distribution. β can range from -1 to $+2$. A positive value indicates that the photoelectrons are ejected preferentially at right angles to the incident photon. In the case of a negative value the photoelectrons are preferentially ejected in forward and backward directions. If the distribution of the emitted photoelectrons is isotropic then $\beta = 0$.

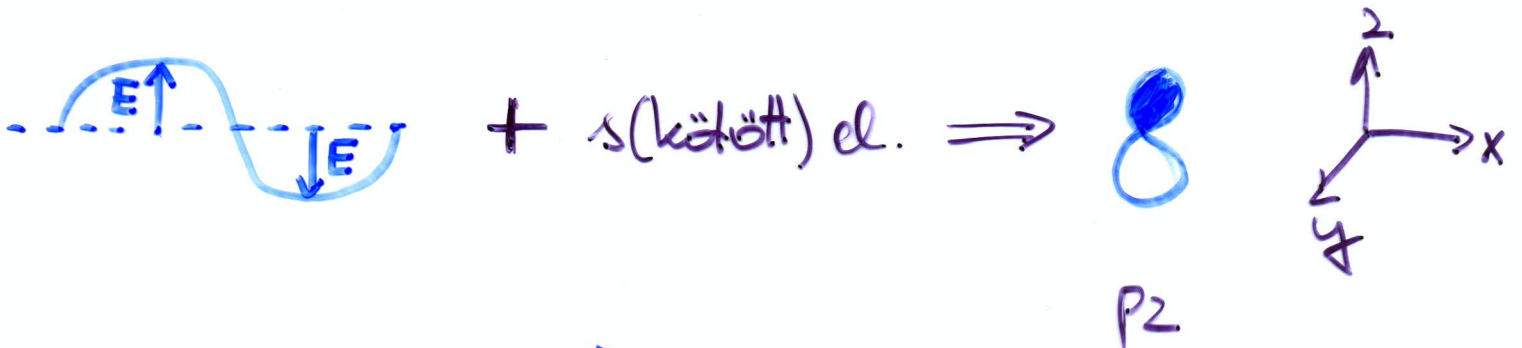
The value of β is dependent upon both the energy of the electron and the nature of the orbital from which it originated. For an orbital having a spherical distribution of charge with angular momentum (l) equal to zero the value of β will be $+2$. In this case the angular distribution can be calculated using the equation above.

Ionizáció, egy-elektron átmenet.

Kiválasztási szabály: $\Delta l = \pm 1$

$s \Rightarrow p$; $p \Rightarrow s$, vagy d elektron

Síkpoláros fény + s (kötött) el. \Rightarrow p (szabad) el.



A szögeloszlást \vec{E} irányához viszonyítjuk

ψ_{p_2} szögtől függő része $\sim \cos \Theta$

$|\psi_{p_2}|^2$ tart. valószínűség $\sim \cos^2 \Theta$

$$I(\Theta) \sim \frac{3}{4\pi} \cos^2 \Theta$$

Általános kifejezés

$$I(\Theta) = \frac{\sigma_0}{4\pi} \left[1 + \frac{\beta}{2} (3 \cos^2 \Theta - 1) \right]$$

Nem polarizált fény esetén

$$I(\alpha) = \frac{\sigma_0}{4\pi} \left[1 + \frac{\beta}{2} \left(\frac{3}{2} \sin^2 \alpha - 1 \right) \right]$$

Interpretation of PE spectra

Koopmans' theorem

- Quantumchemical calculations
- Spectral fine structure
- Band intensities
- Angular distribution of photoelectrons
- Perfluoro effect
- Correlation with a series of related compounds
- Electronegativity trends
- Band shapes
- Orbital interactions
- Rydberg spectra
- Substituent additivity effects

Spectral interpretation (cont)

Band shapes

Even though fine structure is not resolved, it is sometimes possible to obtain qualitative information from band shapes. For example, nonbonding orbitals produce sharp bands with identical adiabatic and vertical IE's, whereas strongly bonding orbitals are expected to produce a more rounded spectral band and may lead to very broad band if dissociation occurs.

Continuous bands

- short ion lifetime

$$\Delta E \Delta \tau \leq h/2\pi$$

$$\Delta E \Rightarrow \text{eV} \quad \Delta \tau \Rightarrow \text{sec}$$

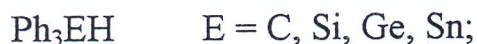
$$\Delta E \Delta \tau = 10^{-15} \text{ eV s } (h/2\pi)$$

If $\Delta E = 10 \text{ meV} = 10^{-2} \text{ eV}$

then $\Delta \tau = 10^{-13} \text{ s} \Rightarrow$ direct dissociation

Orbital interactions

Symmetry restrictions allow only certain orbitals to interact in symmetrical molecules. Such "through-space" interactions, as between the π orbitals of benzene and ethylene and their substituents, or "through-bond" interactions often serve to distinguish specific spectral bands when a composite molecule is compared to its separate subunits.



Spectral interpretation (cont)

Rydberg spectra

Molecular Rydberg states are generated by exciting a valence electron to an orbital that is large and diffuse \Rightarrow Rydberg orbital

The energy of this type of transition is given as

$$E_n = IE_i - R/(n - \delta)^2$$

where IE_i is the valence electron ionization energy, R is the Rydberg constant, n is the principal quantum number of the AO that dominates the constitution of the Rydberg orbital, and δ is the quantum defect (the penetration of the Rydberg electron to the interior of the molecule).

At high n values the series converges to the IE_i .

Substituent additivity effects

Shifts in the energies of certain orbitals caused by addition of specific substituents onto a molecule can provide unique means of identifying a certain orbital within a series of similar molecules.

E.g.: $IE (P_{1p})$ of $R_nPX_{(3-n)}$ series.

Analysis of vibrational structure

In general:

- the selection rules are based on the Franck-Condon principle.
- if there is little change in the potential energy surface on ionization, the only strong transitions are those in which the vibrational quantum number remains the same (0-0).
- if there is a change in the shape of the potential energy surface on ionization so that the equilibrium positions of the nuclei are different, the vibrational mode that corresponds most closely to the change in nuclear positions are most strongly excited.

For molecules with some elements of symmetry there are more exact selection rules:

- excitation of symmetric vibrational modes is allowed with any number of quanta; $\Delta v = 0, \pm 1, \pm 2, \dots$
- antisymmetric vibrational modes can be excited on ionization only in units of two quanta; $\Delta v = 0, \pm 2, \pm 4, \dots$

Explanation

If the overlap integral is to be non-zero, the product of the vibrational wavefunctions ($\chi_{v''}, \chi_{v'}$) must be fully symmetric, that is the direct product of the representations to which $\chi_{v''}$ and $\chi_{v'}$ belong must be the totally symmetric representation in the point group of the molecule and ion. It can only do so for combinations of vibrational species of identical symmetry.

Analysis of vibrational structure

In ionization from the vibrationless ground state of the molecule ($v'' = 0$), which is always totally symmetric, only totally symmetric vibrational levels can be reached.

$\chi_{v'}$ for symmetric vibrational modes are fully symmetric.

$\chi_{v'}$ for antisymmetric vibrational modes are antisymmetric for odd and symmetric for even vibrational quantum numbers.

Example

Vibrational wavefunctions

$v'' = 0$ (ground state)

$$\chi_0(Q) \sim \exp[-1/2 \gamma Q^2]$$

$v' = 1$ (ion)

$$\chi_1(Q) \sim \exp[-1/2 \gamma Q^2] Q$$

$v' = 2$ (ion)

$$\chi_2(Q) \sim \exp[-1/2 \gamma Q^2] (a + Q^2)$$

$Q \Rightarrow$ an internal co-ordinate.

H_2O / C_{2v}

$Q_1 = r_1 + r_2 \Rightarrow$ symmetric stretching (a_1)

$Q_2 = r_1 - r_2 \Rightarrow$ antisymmetric stretching (b_2)

$Q_1 \Rightarrow A_1$ for any value of v' ($\Delta v' = 0, \pm 1, \pm 2, \dots$)

$Q_2 \Rightarrow B_2$ antisymmetric for $v' = 1$, and

symmetric for $v' = 2$ ($Q^2 \Rightarrow Q_2 \times Q_2 \Rightarrow A_1$; $\Delta v' = 0, \pm 2, \pm 4, \dots$)

4. The C_{nv} Groups

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		$x^2 - y^2$
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

C_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$		
A_1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	R_z	
E_1	2	$2 \cos 72^\circ$	$2 \cos 144^\circ$	0	$(x, y)(R_x, R_y)$	(xz, yz)
E_2	2	$2 \cos 144^\circ$	$2 \cos 72^\circ$	0		$(x^2 - y^2, xy)$

C_{6v}	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$		
A_1	1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	1	-1	-1	R_z	
B_1	1	-1	1	-1	1	-1		
B_2	1	-1	1	-1	-1	1		
E_1	2	1	-1	-2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)
E_2	2	-1	-1	2	0	0		$(x^2 - y^2, xy)$

The Jahn-Teller effect

- The J-T theorem states that a molecule in a degenerate electronic state is unstable toward distortions that lower the molecular symmetry, thereby removing the electronic degeneracy. E.g. $V(\text{CO})_6$
- In UPS: removal of one electron from a degenerate orbital of a nonlinear molecule \Rightarrow distortion to lower symmetry \Rightarrow stabilization.
- The distortion is brought about by excitation of degenerate vibrational modes of the undistorted molecule \Rightarrow J-T active vibrations (degenerate vibrational modes of the undistorted molecule - tabulated).
- The excitation of these vibrations causes a change in electronic energy; the total energy can no longer be separated into electronic and vibrational parts \Rightarrow coupling of vibrational and electronic motion.
- *Static J-T effect* – changes in the effective pot. en. surfaces \Rightarrow UPS ???
- *Dynamic J-T effect* – complications of the vibrational structure (splitting of the vibrational levels – not easily observed in UPS)
- *J-T stabilization energy*: $\Delta E = h \nu D$ where D is a dimensionless parameter (the reduction in energy on going from the symmetrical nuclear configuration to the new equilibrium positions).
- The presence of progressions that show excitation of J-T modes is the most sensitive indication of the J-T effects in pe spectra.
- Example: J-T effect in methane.

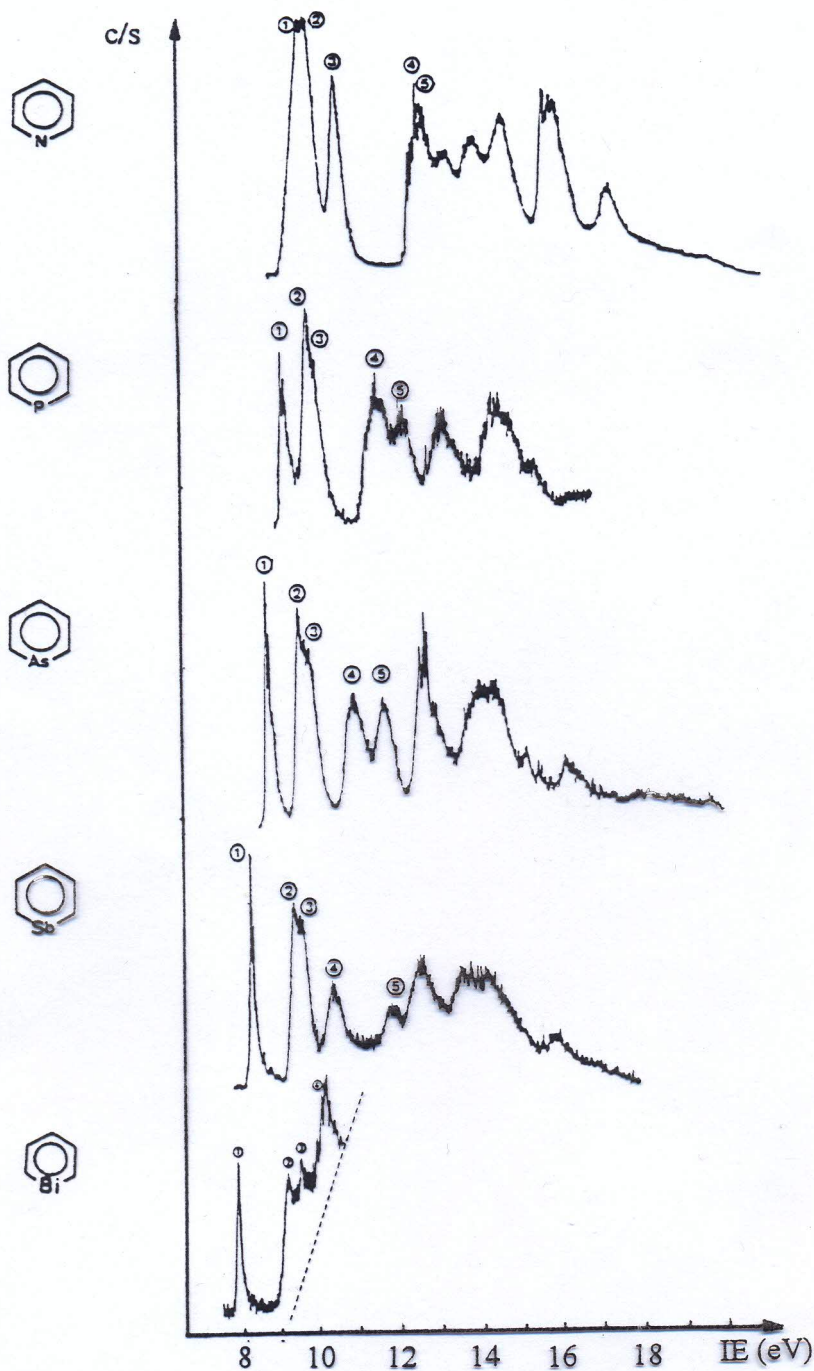


FIGURE 21. HeI PE spectra of C_5H_5E ($E=N, P, As, Sb$ and Bi)^{85,86}

TABLE 8. Vertical ionization energies (in eV) and assignment of bands in the PE spectra of the C_5H_5E molecules. The relative sequence of bracketed pair of orbitals is uncertain (see text)⁸⁶

Band No.	C_5H_5N	C_5H_5P	C_5H_5As	C_5H_5Sb	C_5H_5Bi
1.	$\{ 9.7(a_2, \pi) \}$	9.2(b_1, π)	8.8(b_1, π)	8.3(b_1, π)	7.9(b_1, π)
2.	$\{ 9.8(a_1, n) \}$	$\{ 9.8(a_2, \pi) \}$	$\{ 9.6(a_2, \pi) \}$	$\{ 9.4(a_2, \pi) \}$	$\{ 9.2(a_2, \pi) \}$
3.	10.5(b_1, π)	$\{ 10.0(a_1, n) \}$	$\{ 9.9(a_1, n) \}$	$\{ 9.6(a_1, n) \}$	$\{ 9.6(a_1, n) \}$
4.	12.5(b_2, σ)	11.5(b_2, σ)	11.0(b_2, σ)	10.4(b_2, σ)	10.2(b_2, σ)
5.	12.6(b_1, π)	12.1(b_1, π)	11.8(b_1, π)	11.7(b_1, π)	

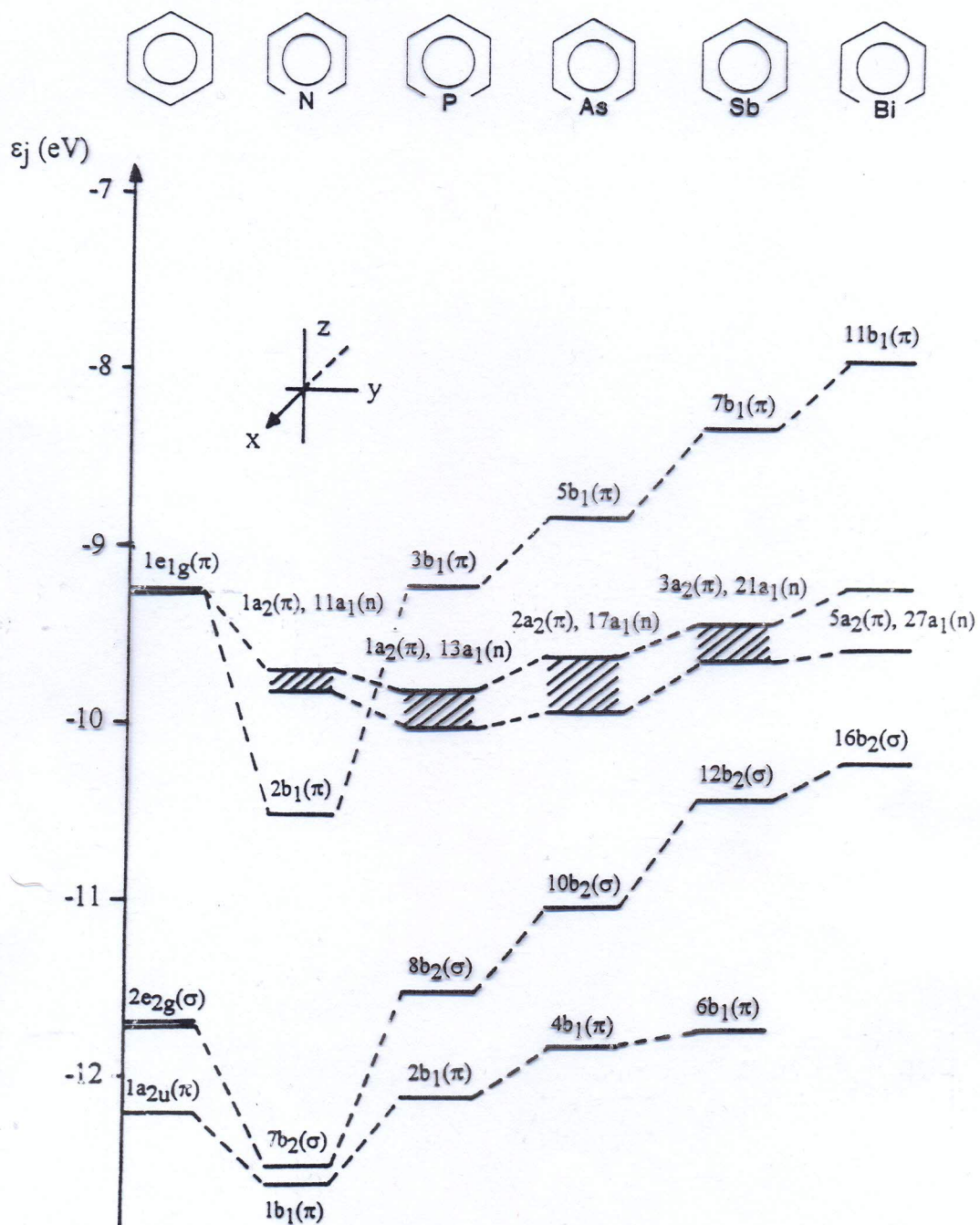
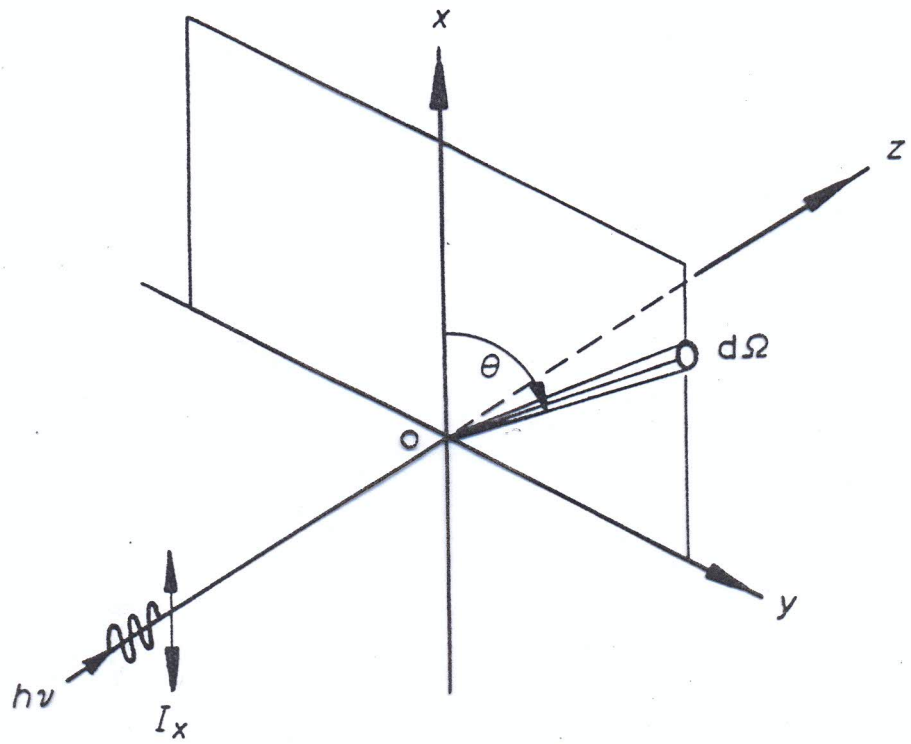
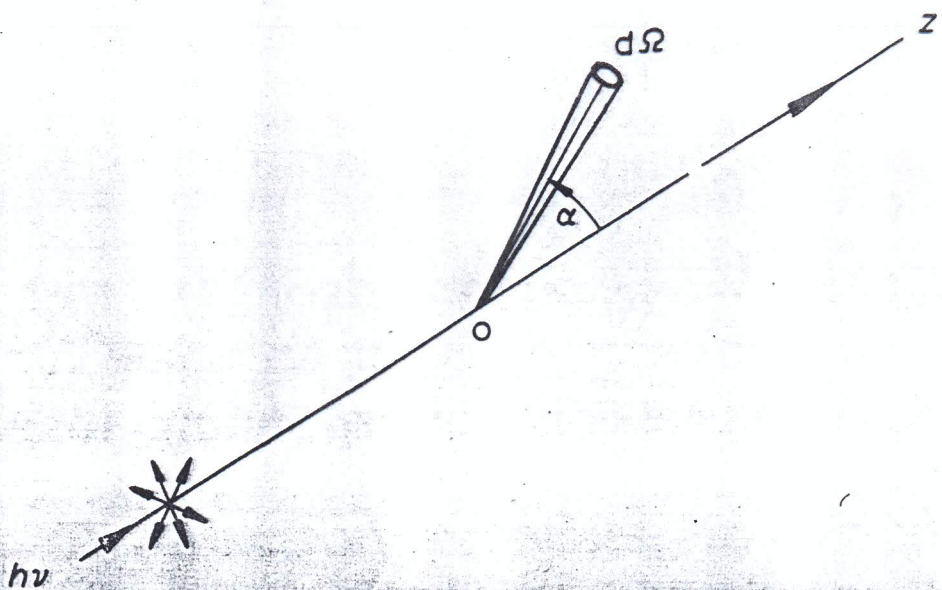


FIGURE 22. Orbital correlation diagram for C_6H_6 and C_5H_5E ($E = N, P, As, Sb$ and Bi). Reprinted from Reference 86, Copyright (1976), with permission from Pergamon Press Ltd, Headengton Hill Hall, Oxford OX3 OBW, UK



$$(a) \quad N(\theta) = N \frac{d\Omega}{4\pi} \left[1 + \frac{\beta}{2} (3 \cos^2 \theta - 1) \right]$$



$$(b) \quad N(\alpha) = N \frac{d\Omega}{4\pi} \left[1 - \frac{\beta}{4} (3 \cos^2 \alpha - 1) \right]$$