

Valence photoelectron spectroscopy

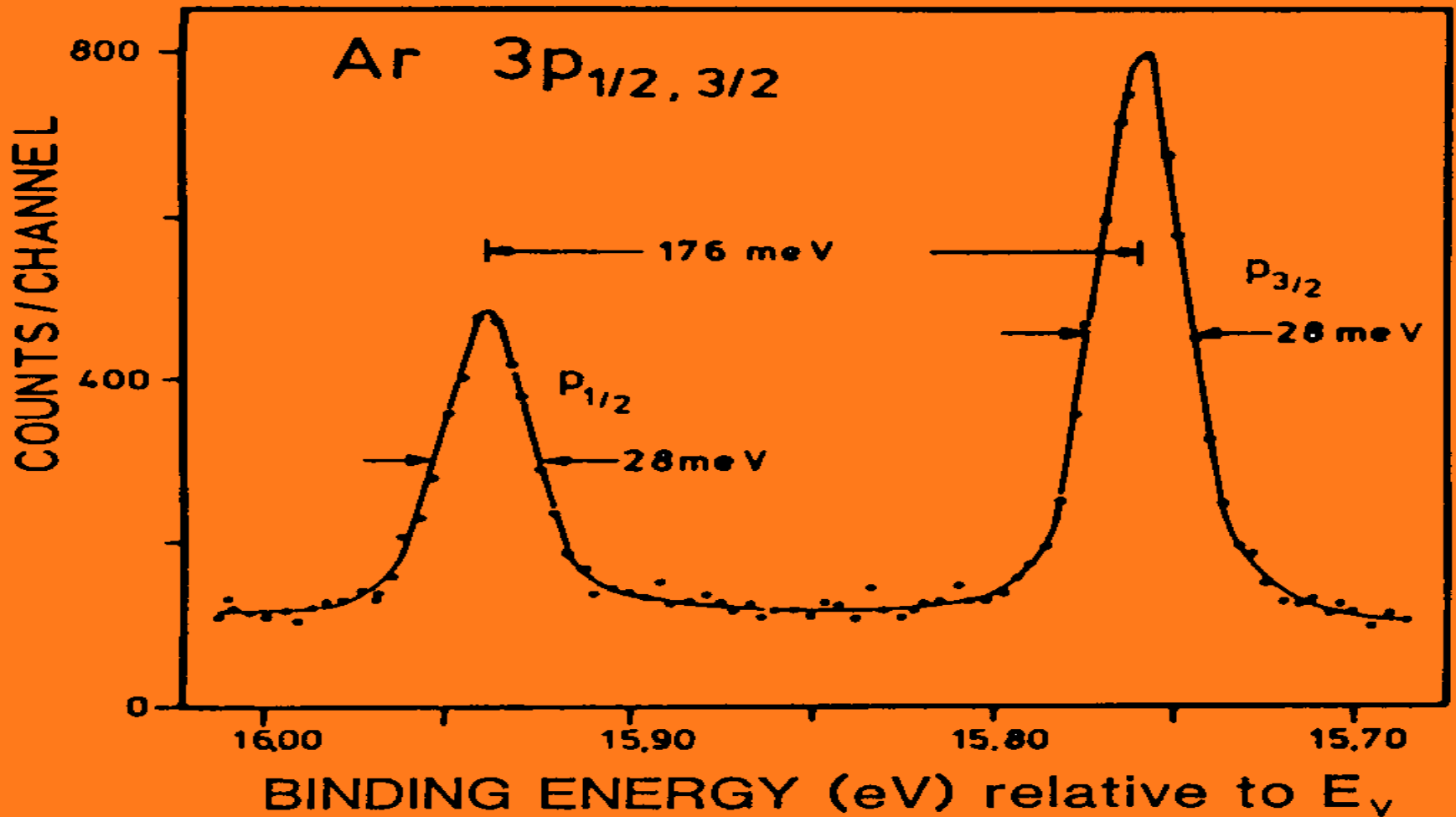
Atoms

Molecules

Adsorbed molecules

Insulating solids

Atoms



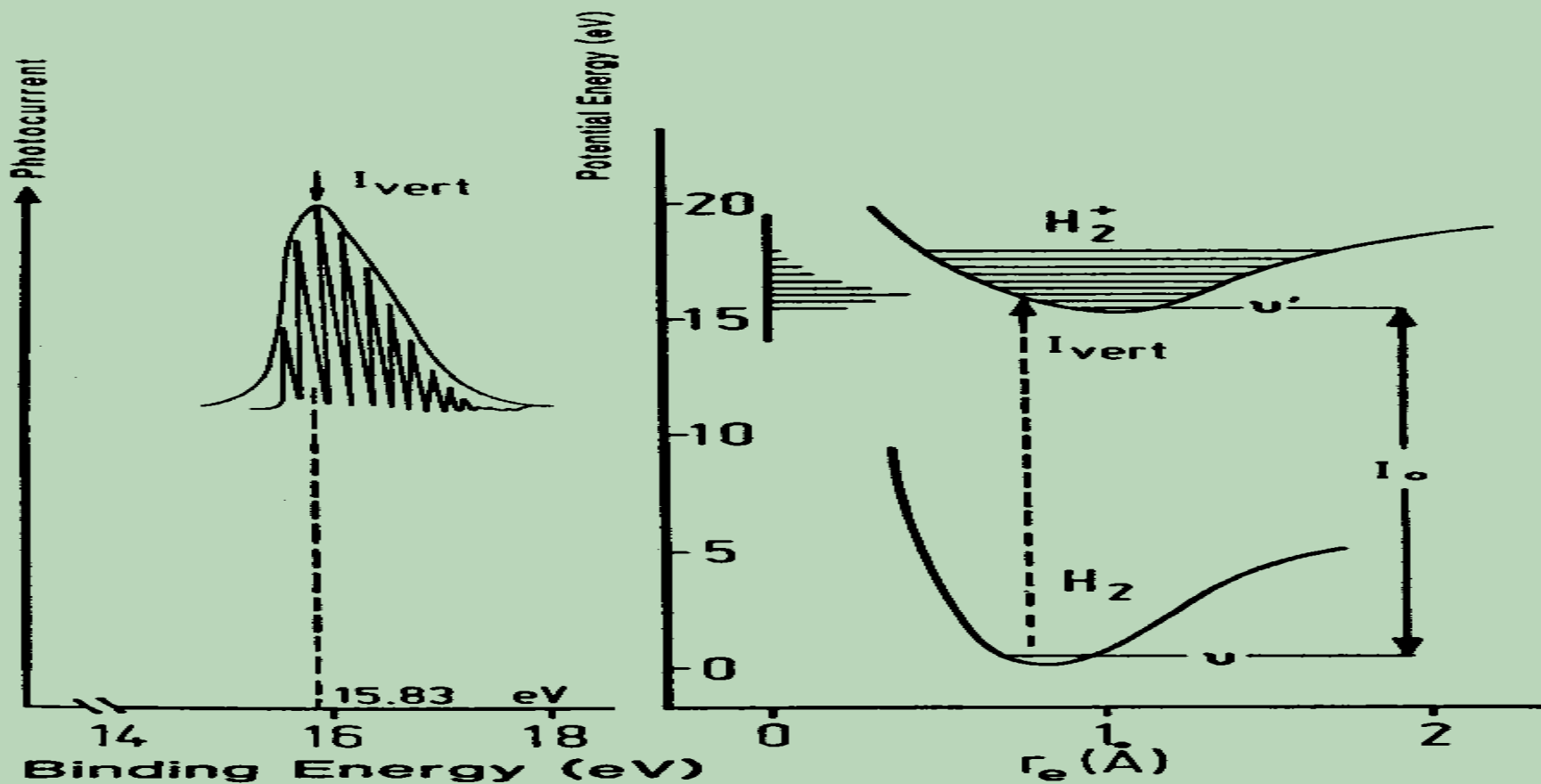
UPS spectrum of gaseous argon (from S. Hüfner).



$$\begin{aligned} \text{Intensity ratio} &= (2J_2 + 1) / (2J_1 + 1) \\ &= 4/2 \\ &= 2 \end{aligned}$$

**Occupation numbers of
emitting orbitals**

*Diatomic
molecules*



UPS of H₂ and the PECs of H₂
and H₂⁺ (from S. Hüfner).

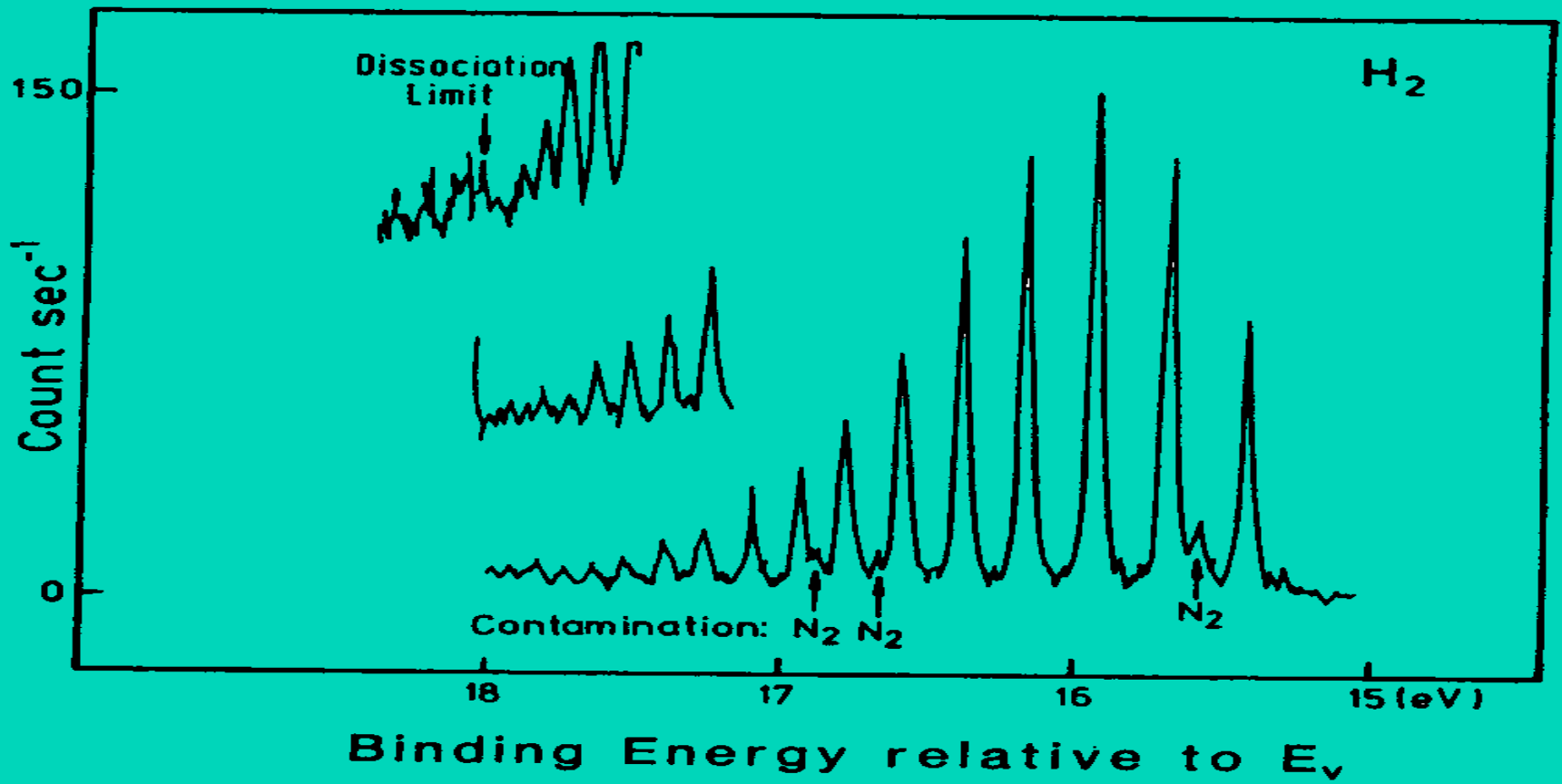
Born-Oppenheimer Approximation

$$I = |\mathbf{M}_e|^2 + \left| \int \psi_v \psi_v^* d\tau \right|^2$$

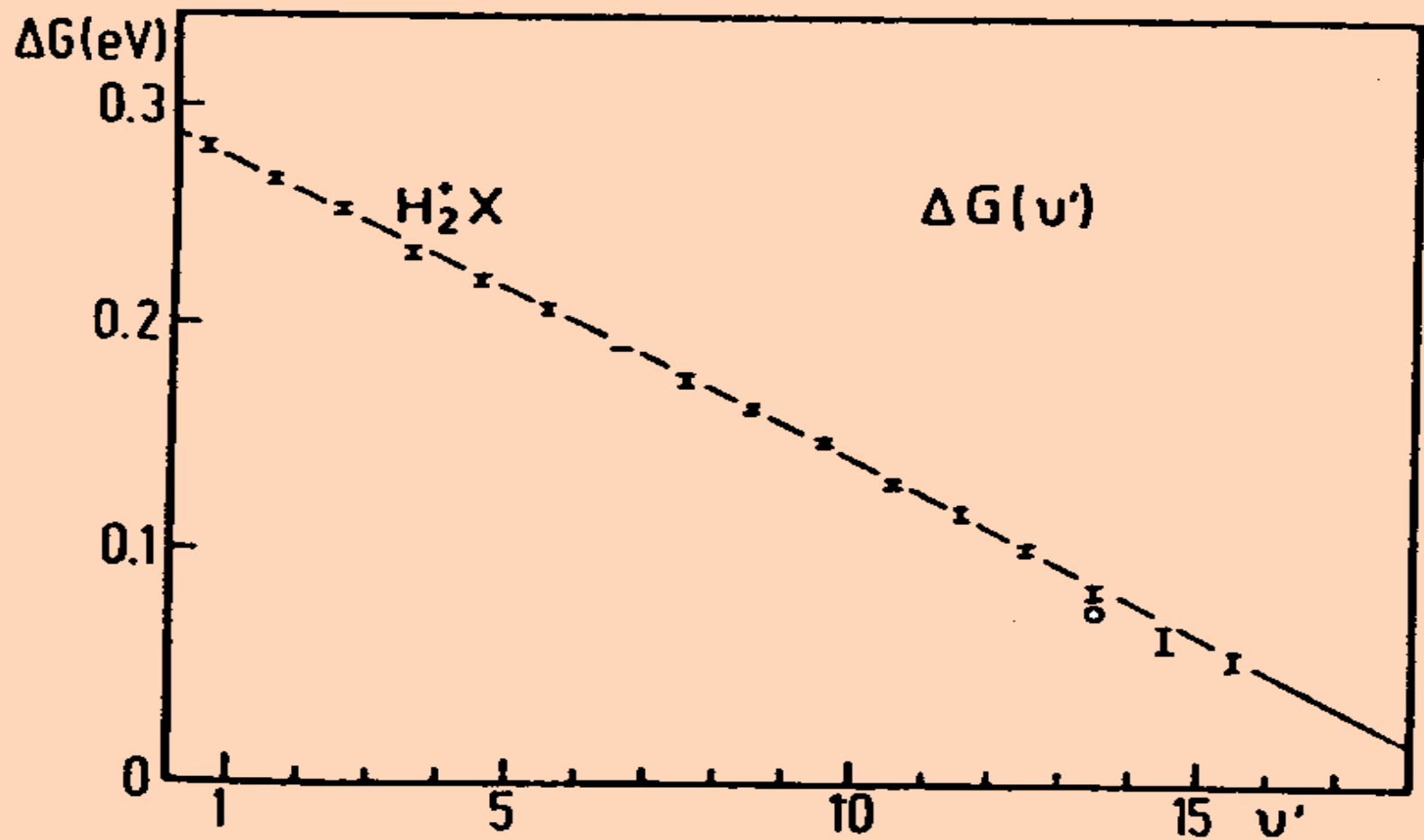
Franck-Condon Factor

Vibrational structure of the ion

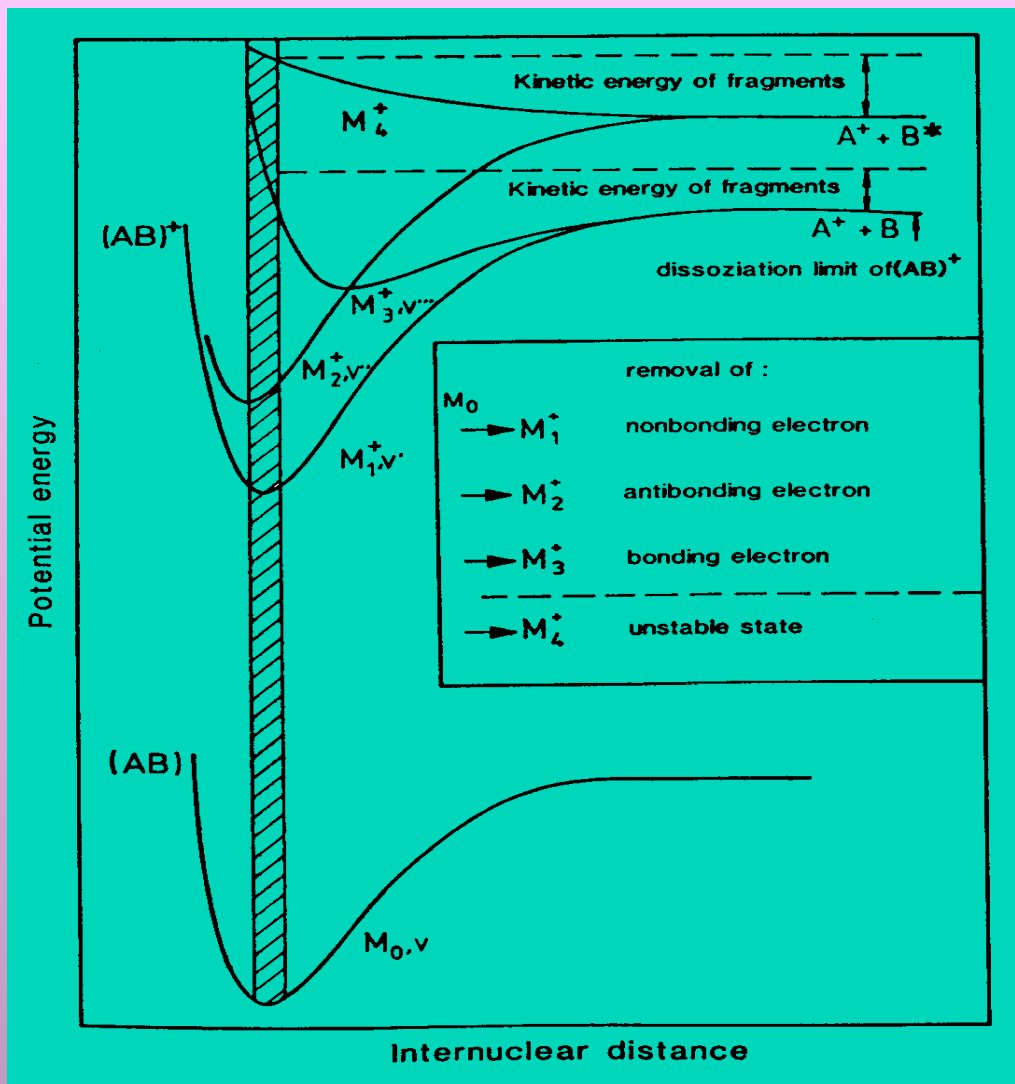
**Parameters of the ionic
potential surfaces**



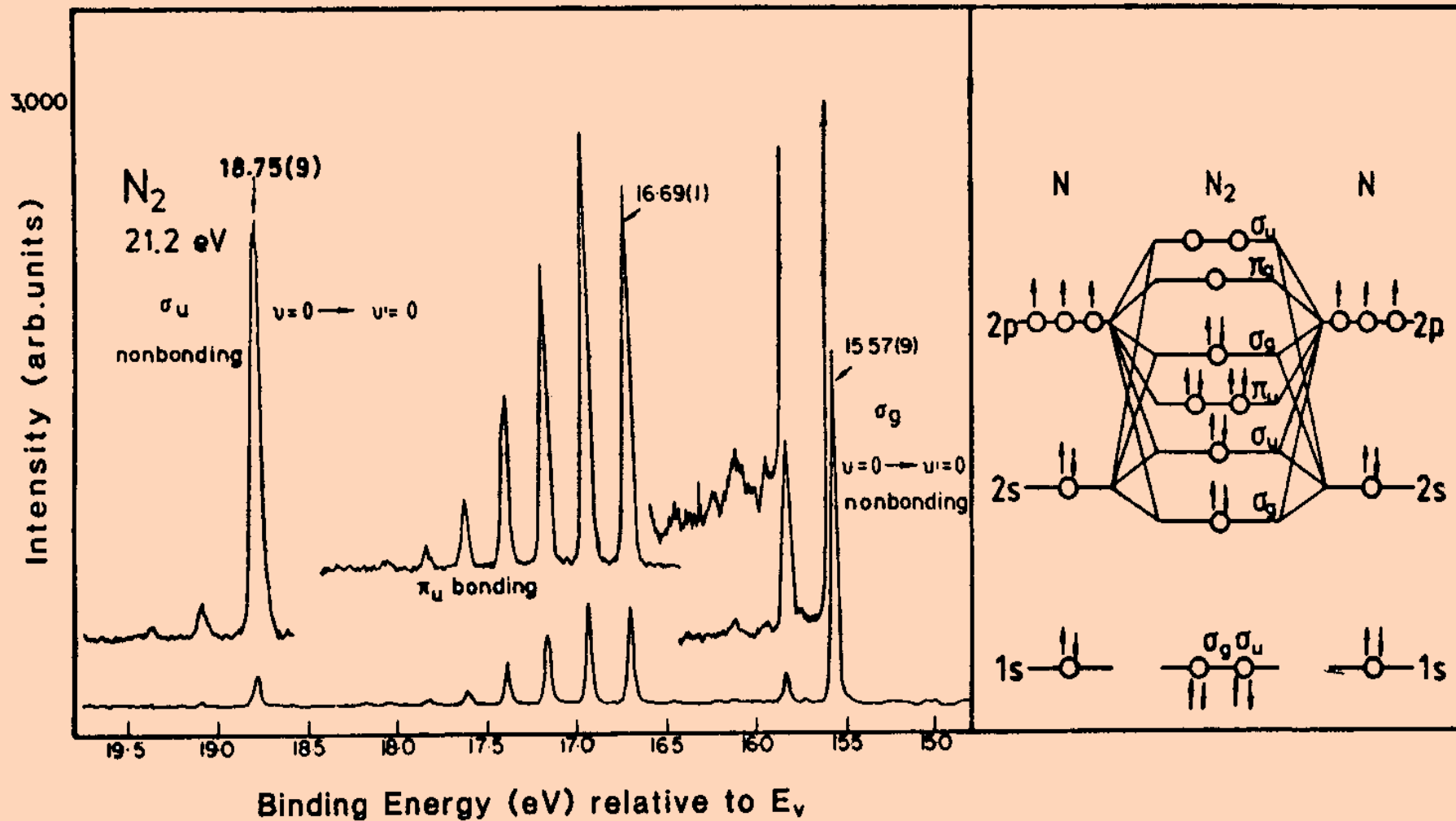
**Vibrational structure of H_2 in
UPS (from S. Hüfner).**



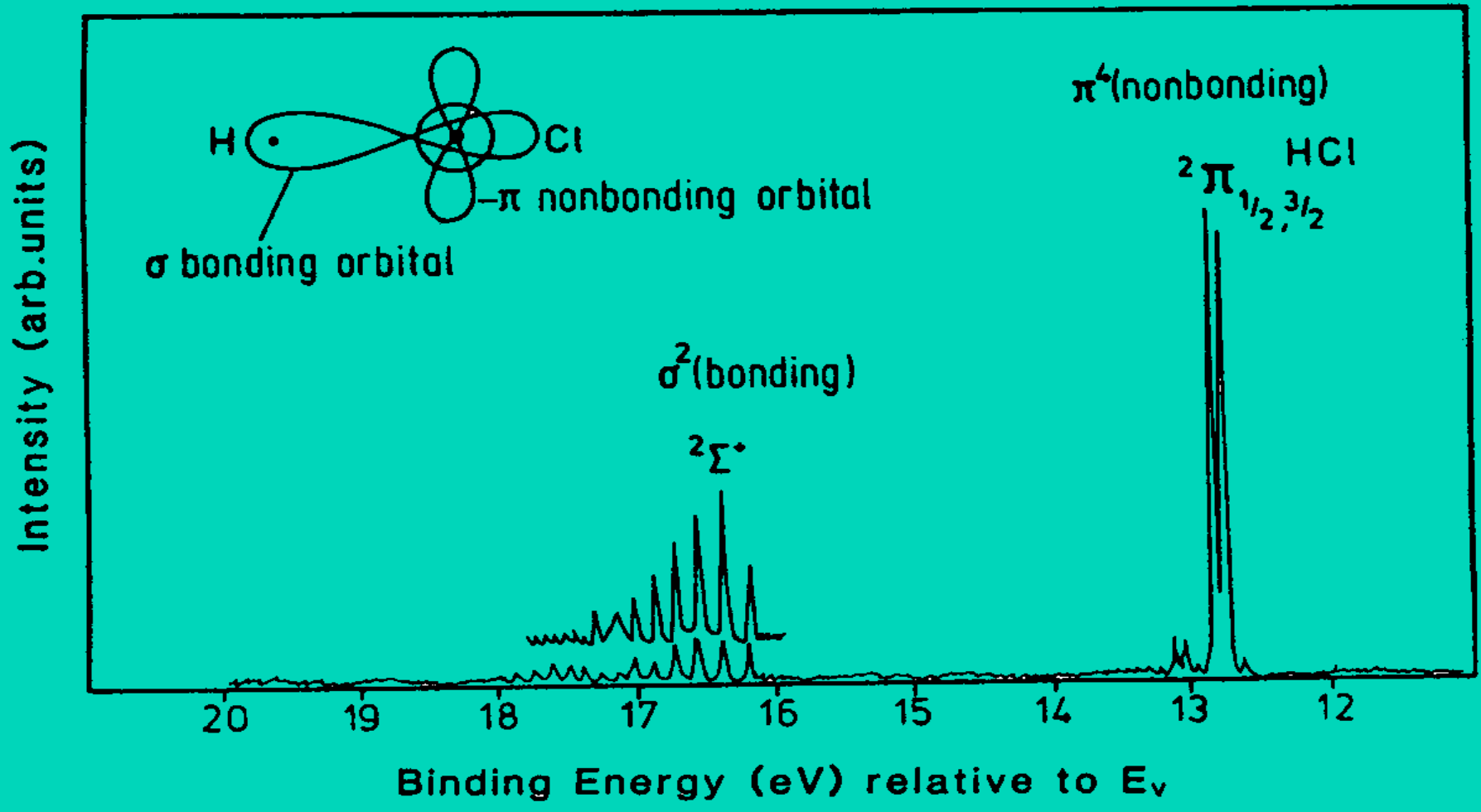
**Plot of ΔG as a function of v'
in H_2^+ (from S. Hüfner).**



PECs for AB in the ground and excited states (from S. Hüfner).



UPS spectrum of N_2
(from S. Hüfner).



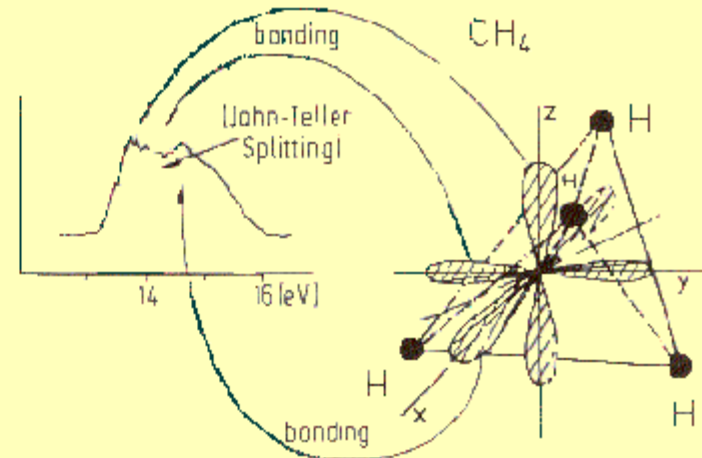
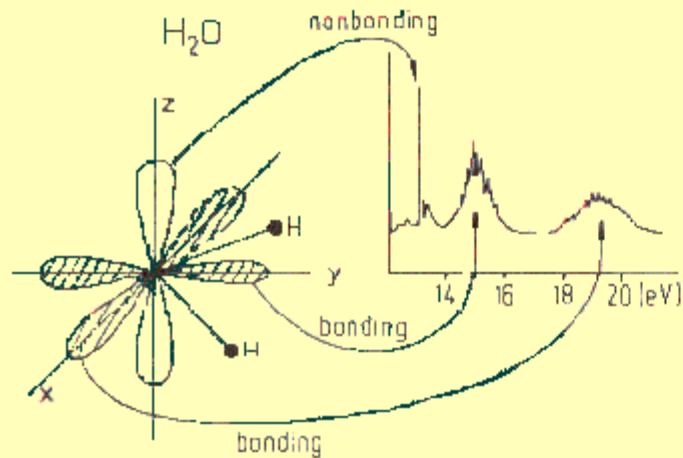
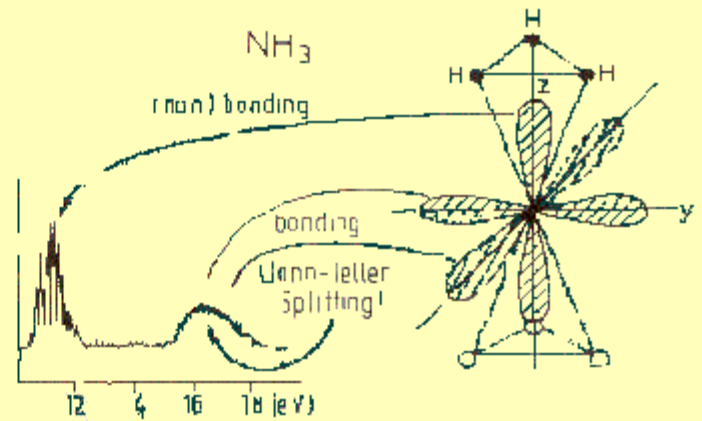
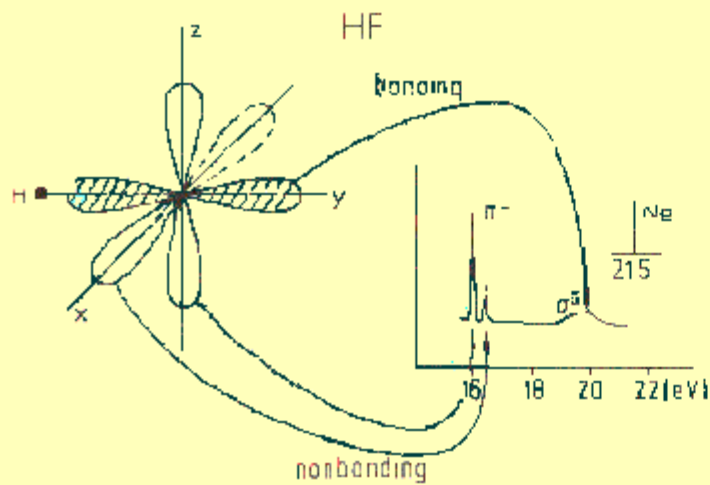
UPS spectrum of HCl
(from S. Hüfner).

Polyatomic molecules

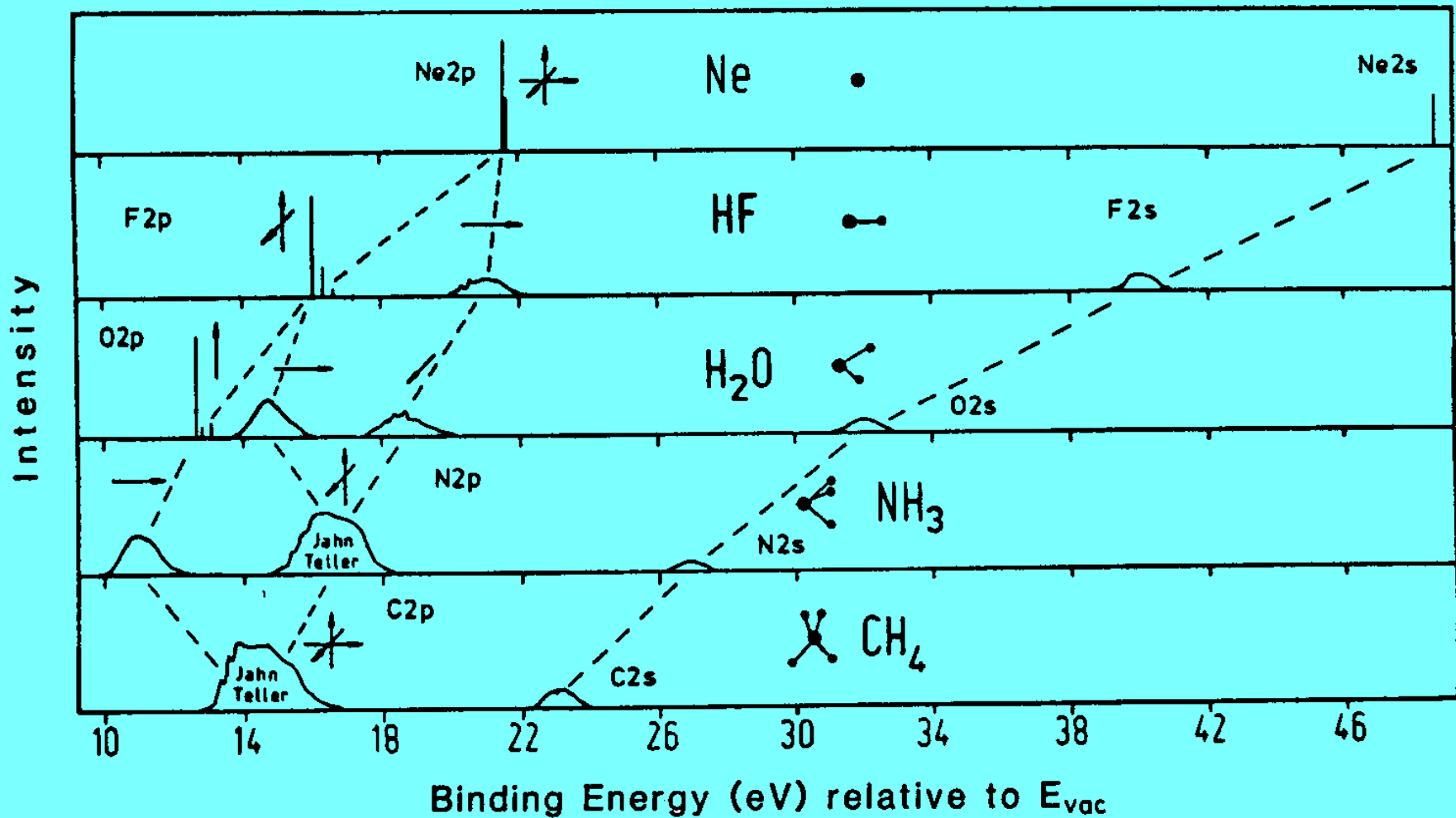
Koopmans' approximation

Jahn-Teller distortion

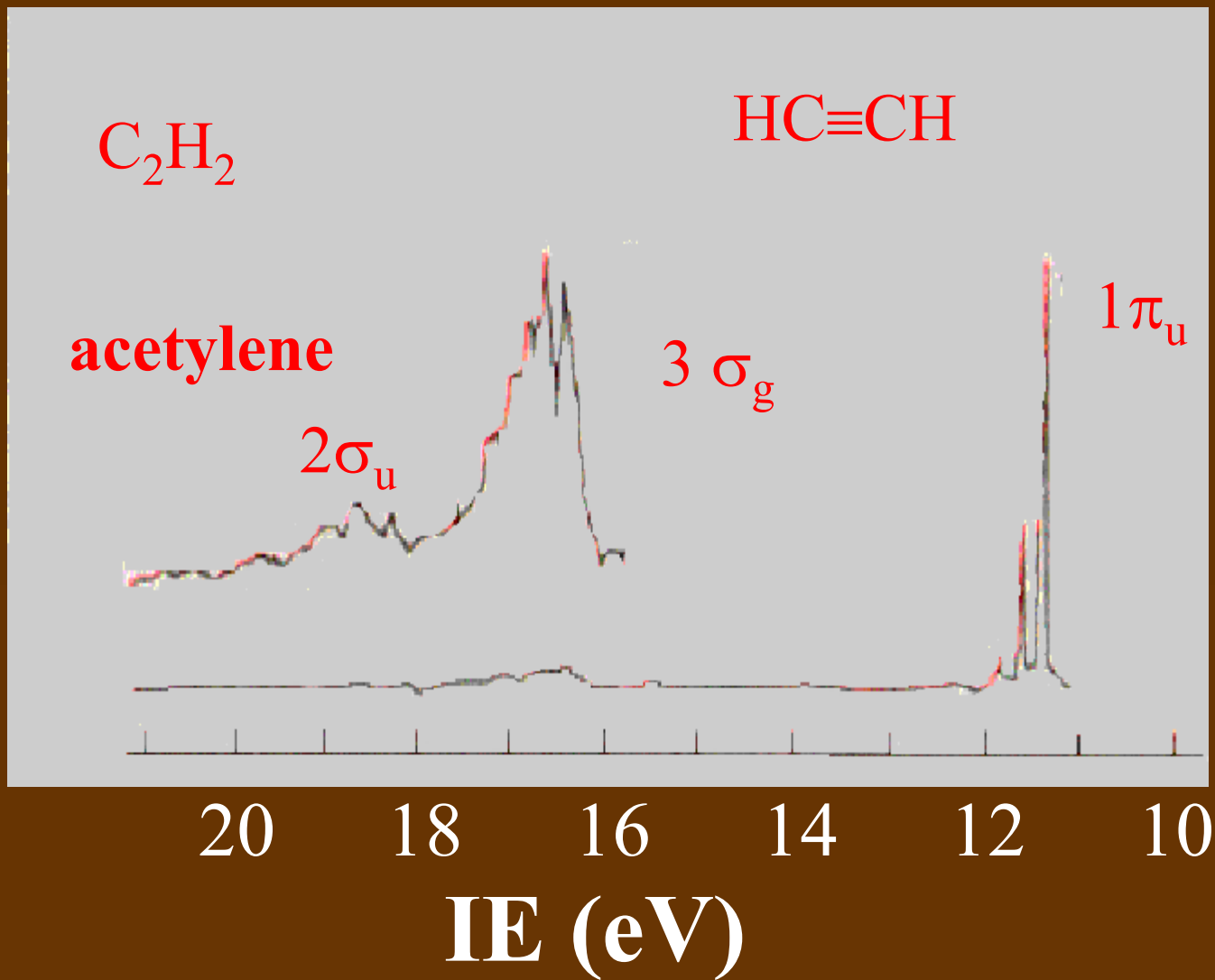
Renner-Teller splitting



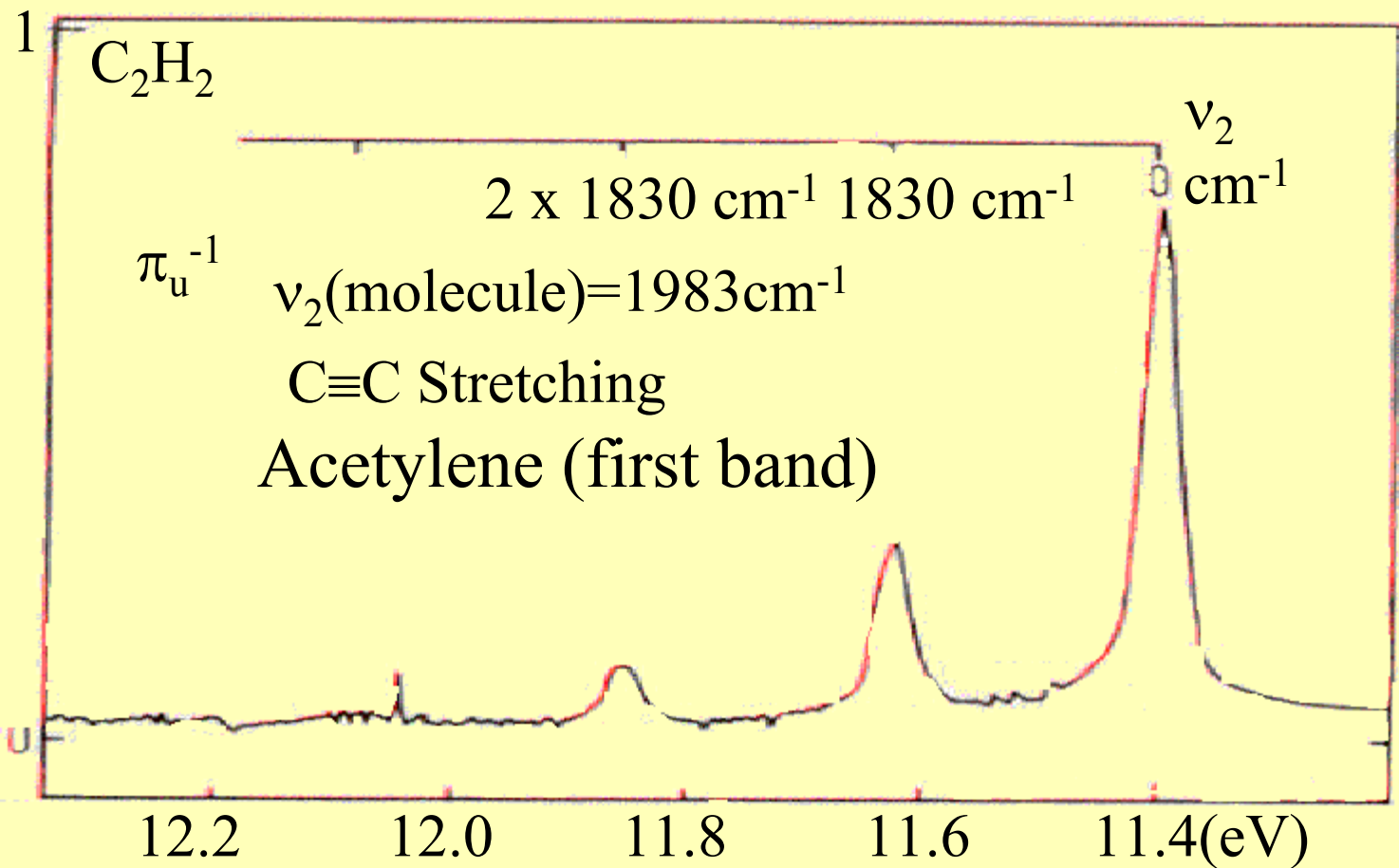
UPS of HF, H₂O, NH₃ and CH₄
(from S. Hüfner).



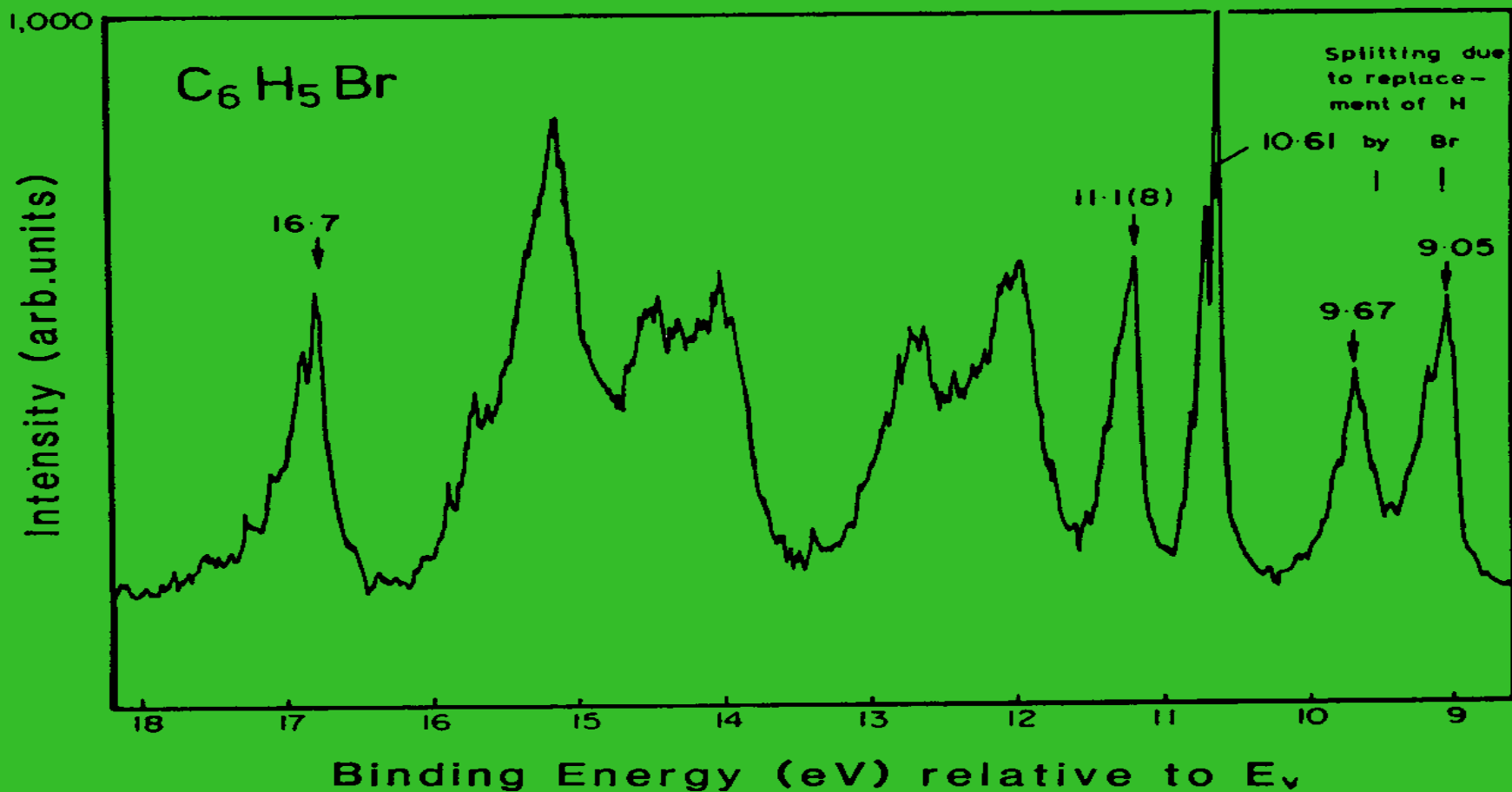
UPS spectra of Ne and its isoelectronic hydrides (from S. Hüfner).



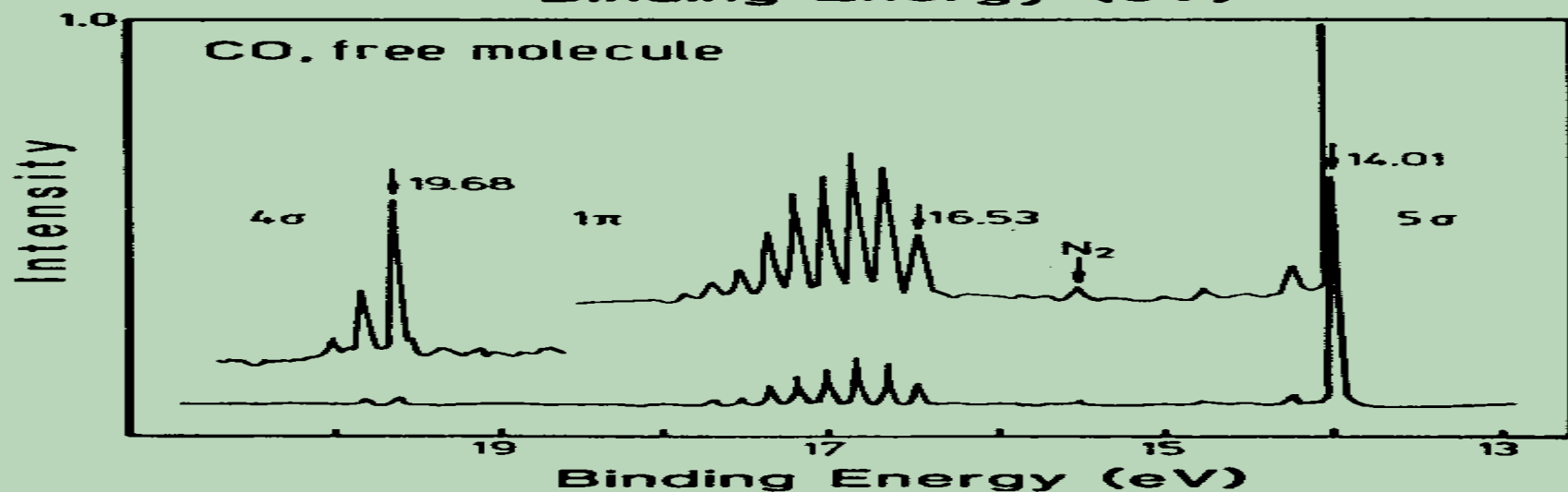
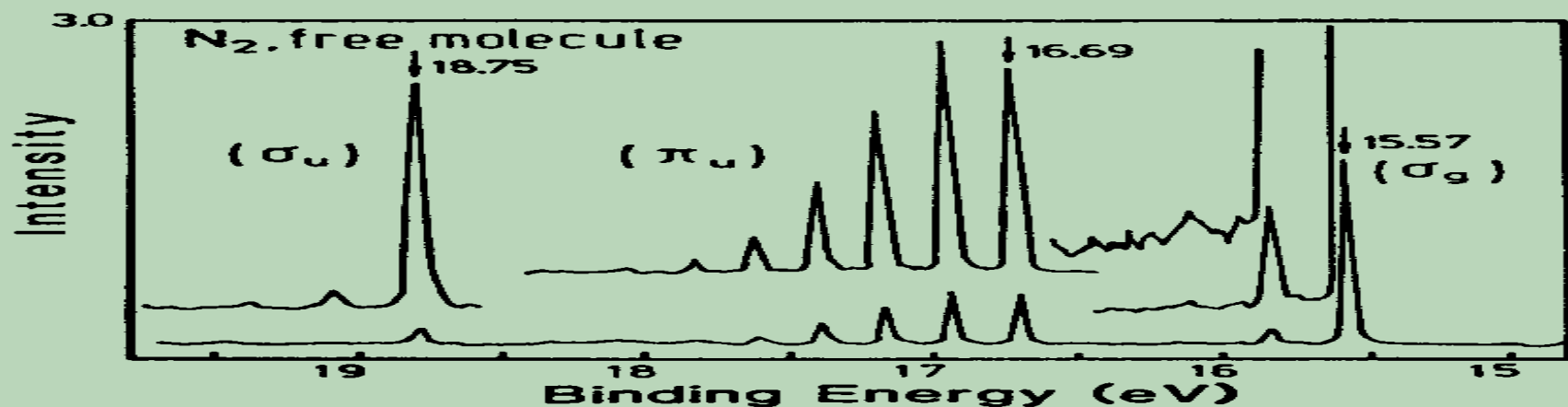
UPS of acetylene (from S. Hüfner).



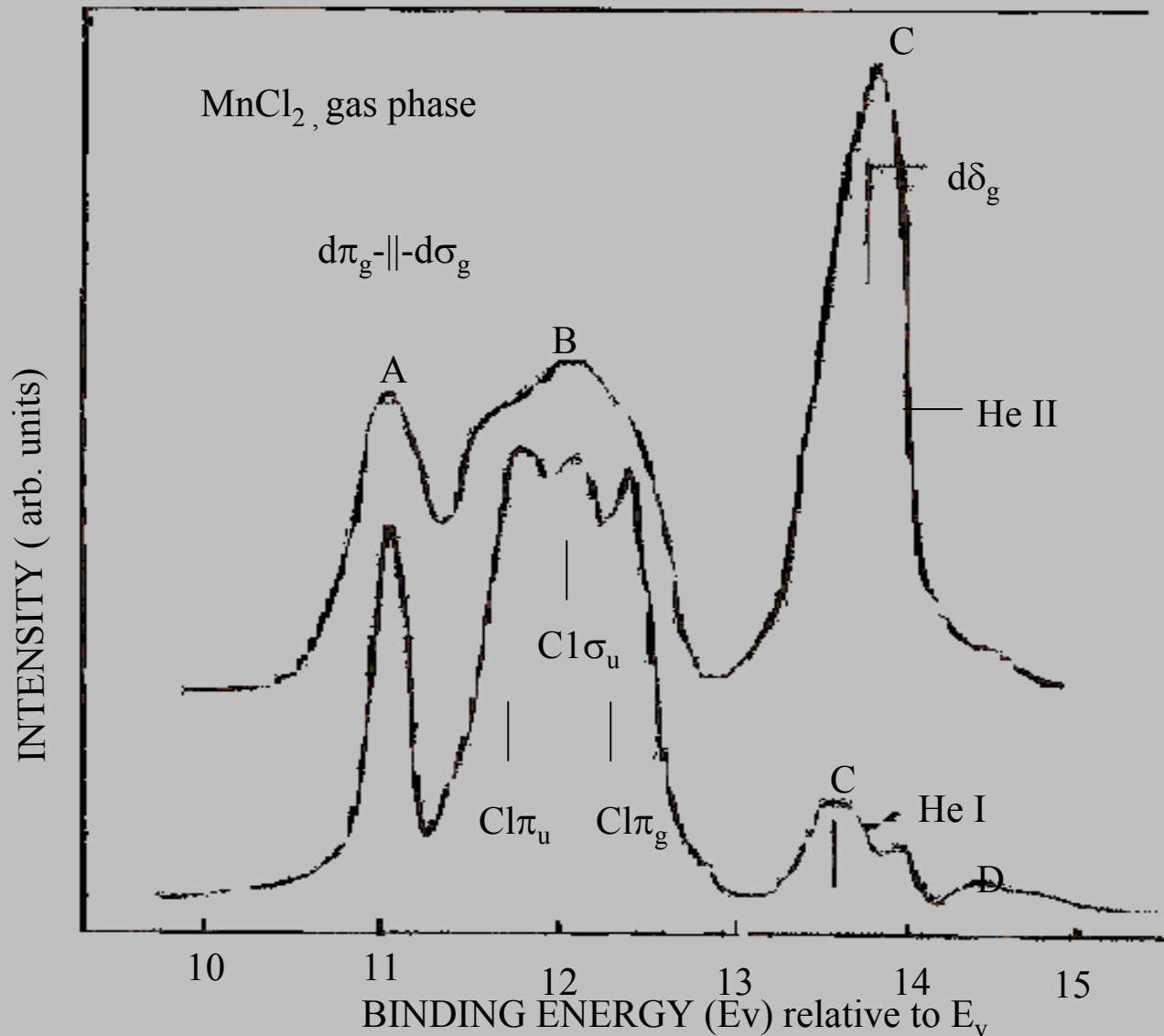
Vibrational structure in the UPS of acetylene (from S. Hüfner).



UPS spectrum of C_6H_5Br
(from S. Hüfner).



UPS spectra of the isoelectronic N₂ and CO (from S. Hüfner).



UPS of MnCl₂ (from S.Hüfner).

Guidelines for interpretation

Calculations

Vibrational structure

Isoelectronic molecules

Chemical trends

Substitutions

Systematics

Photon energy variation

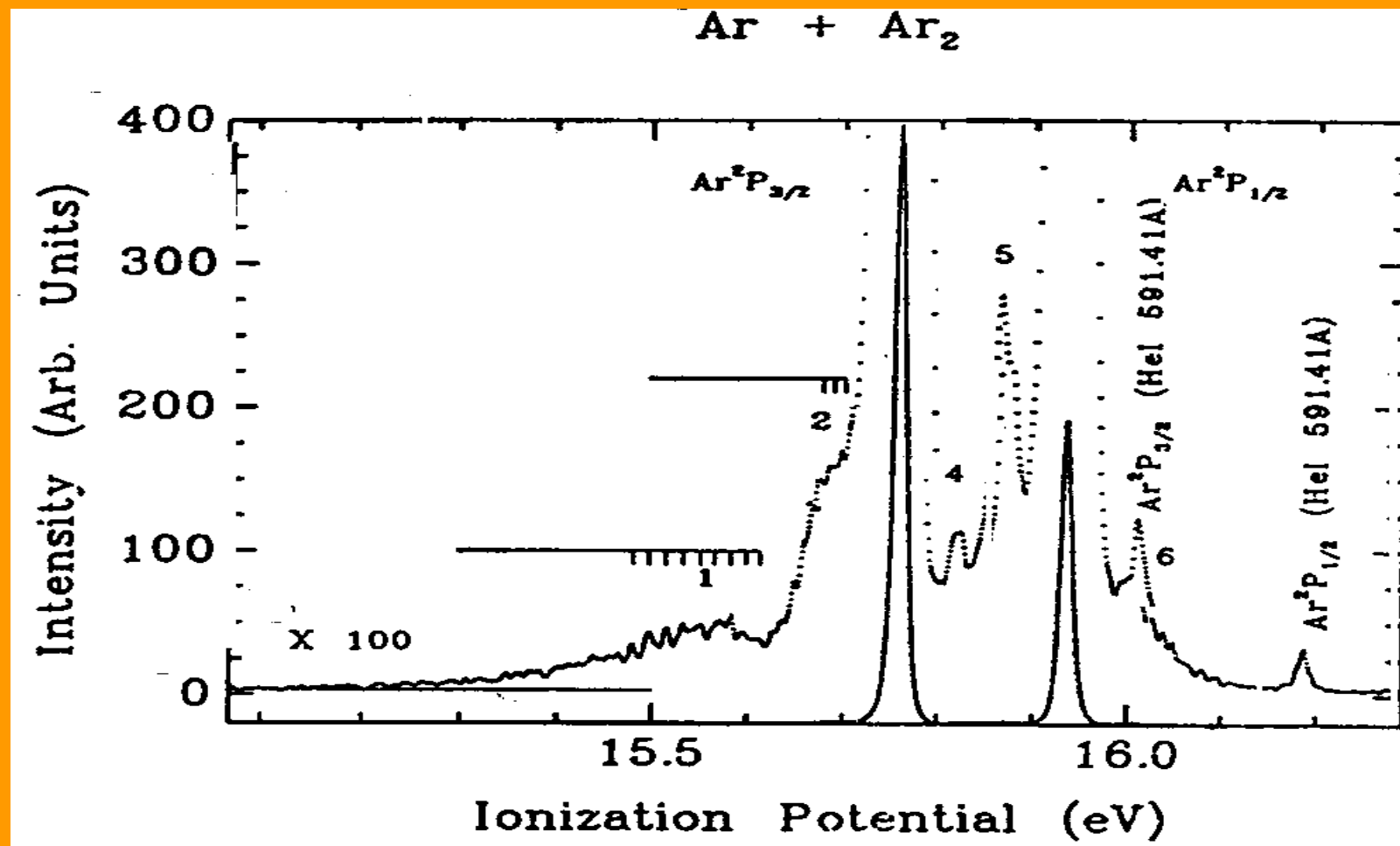
Recent studies

Transient species

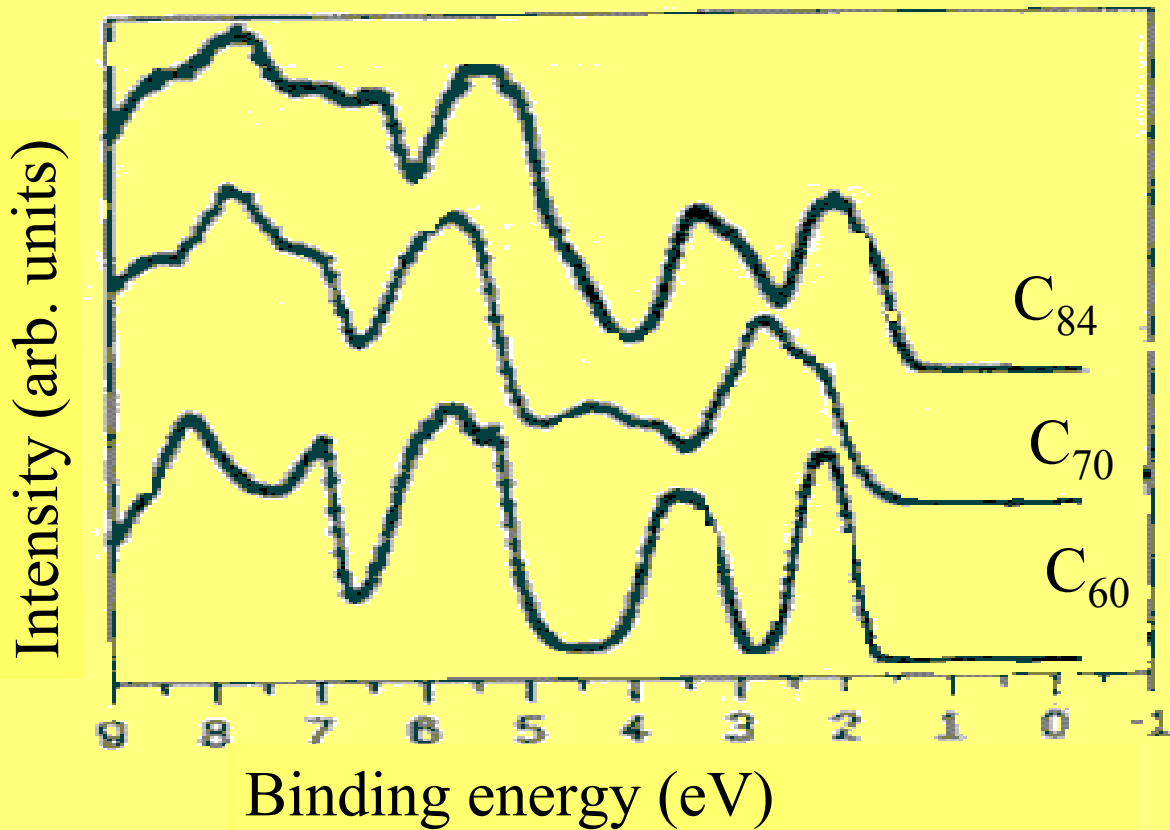
High temperature species

van der Waals molecules

Fullerenes

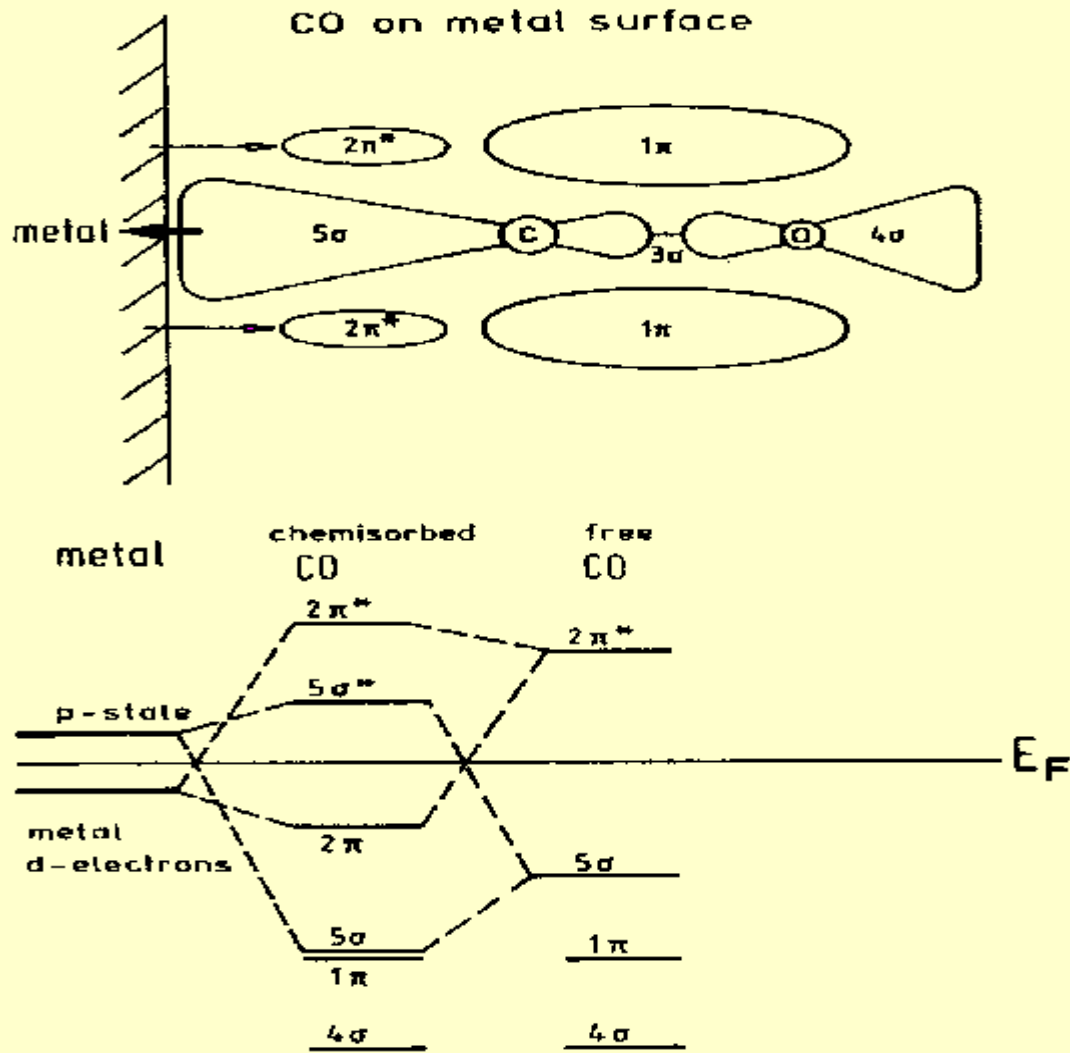


**UPS of a mixture of Ar₂ and Ar (from
T. Pradeep, et. al. J. Chem. Phys. 98
(1993) 5269.**



UPS of C₆₀, C₇₀ and C₈₄ (from M. S. Dresselhaus et. al., *Science of Fullerenes and Carbon Nanotubes*, Academic Press, New York, 1996).

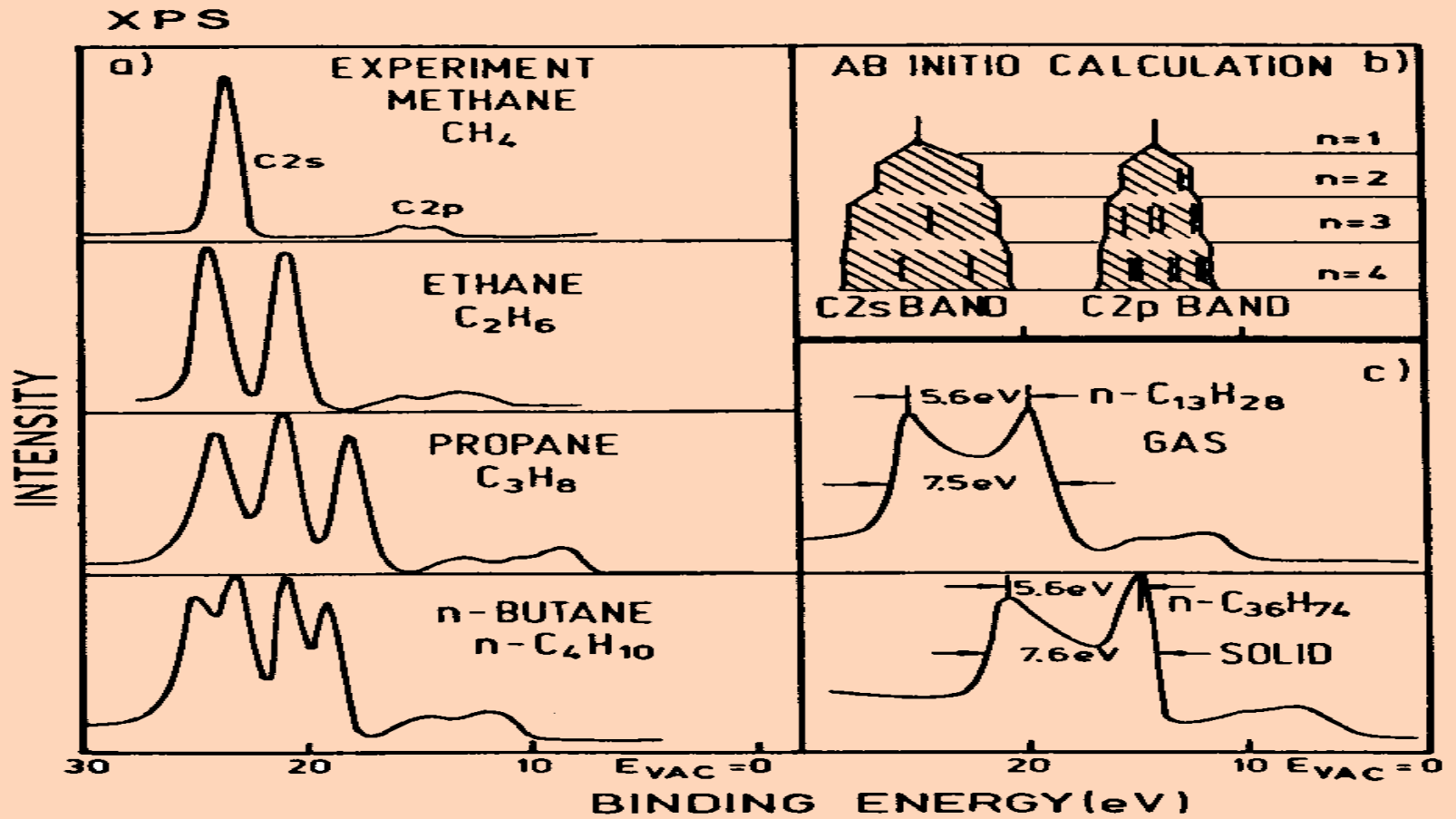
*Adsorbed
molecules*



Bonding of a CO molecule to a metal surface (from S. Hüfner)

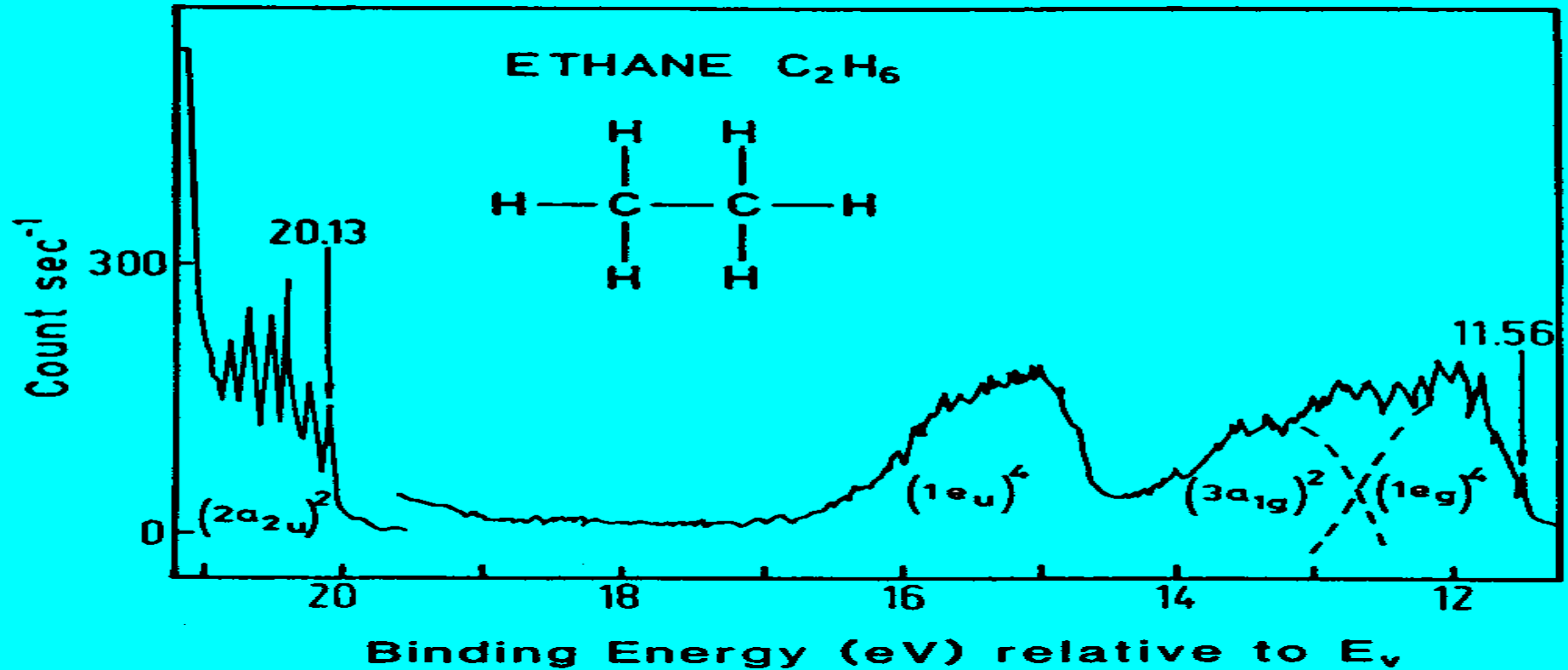
*Insulating
solids*

Evolution of band structure

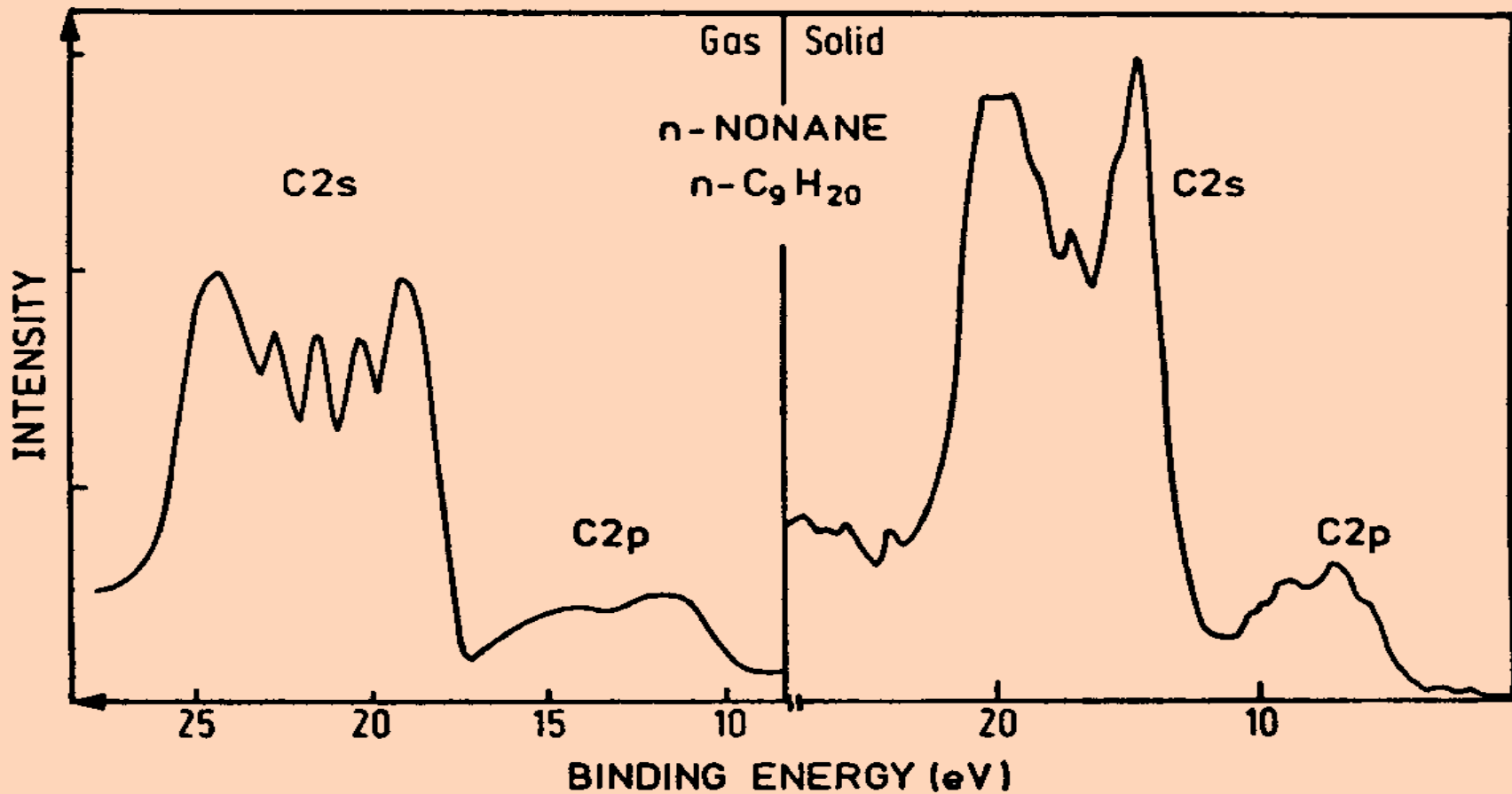


EDCs of a number of linear polymers (from S. Hüfner).

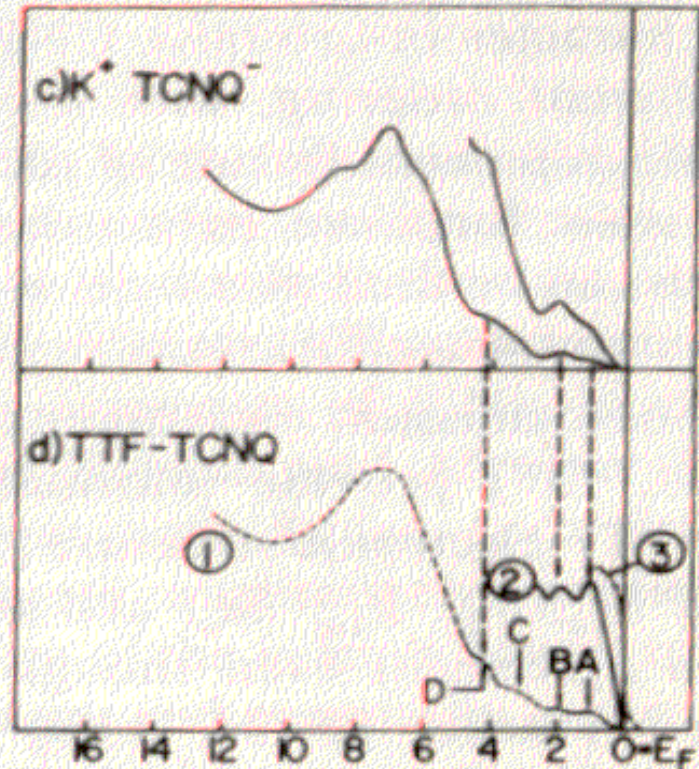
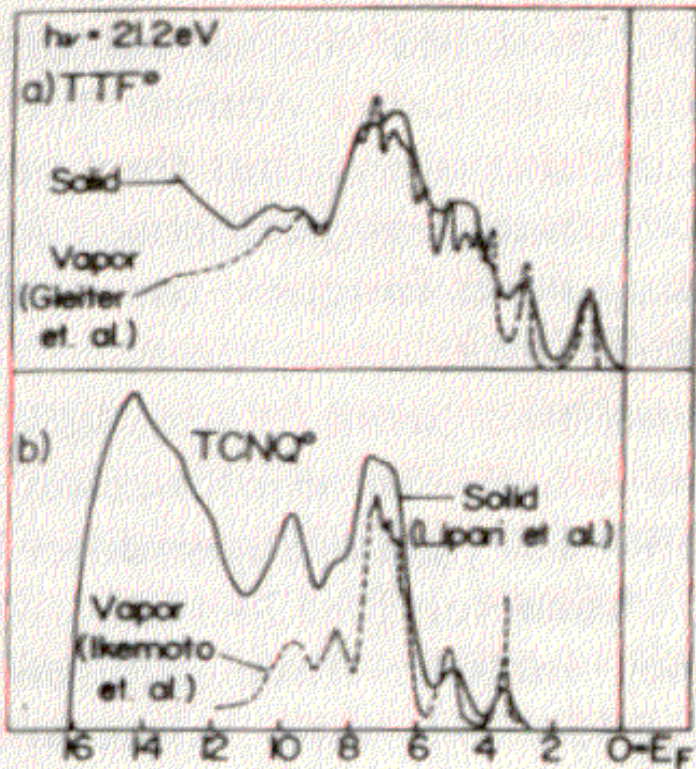
UPS



UPS of C_2H_6 showing 2p-derived orbitals (from S. Hüfner).



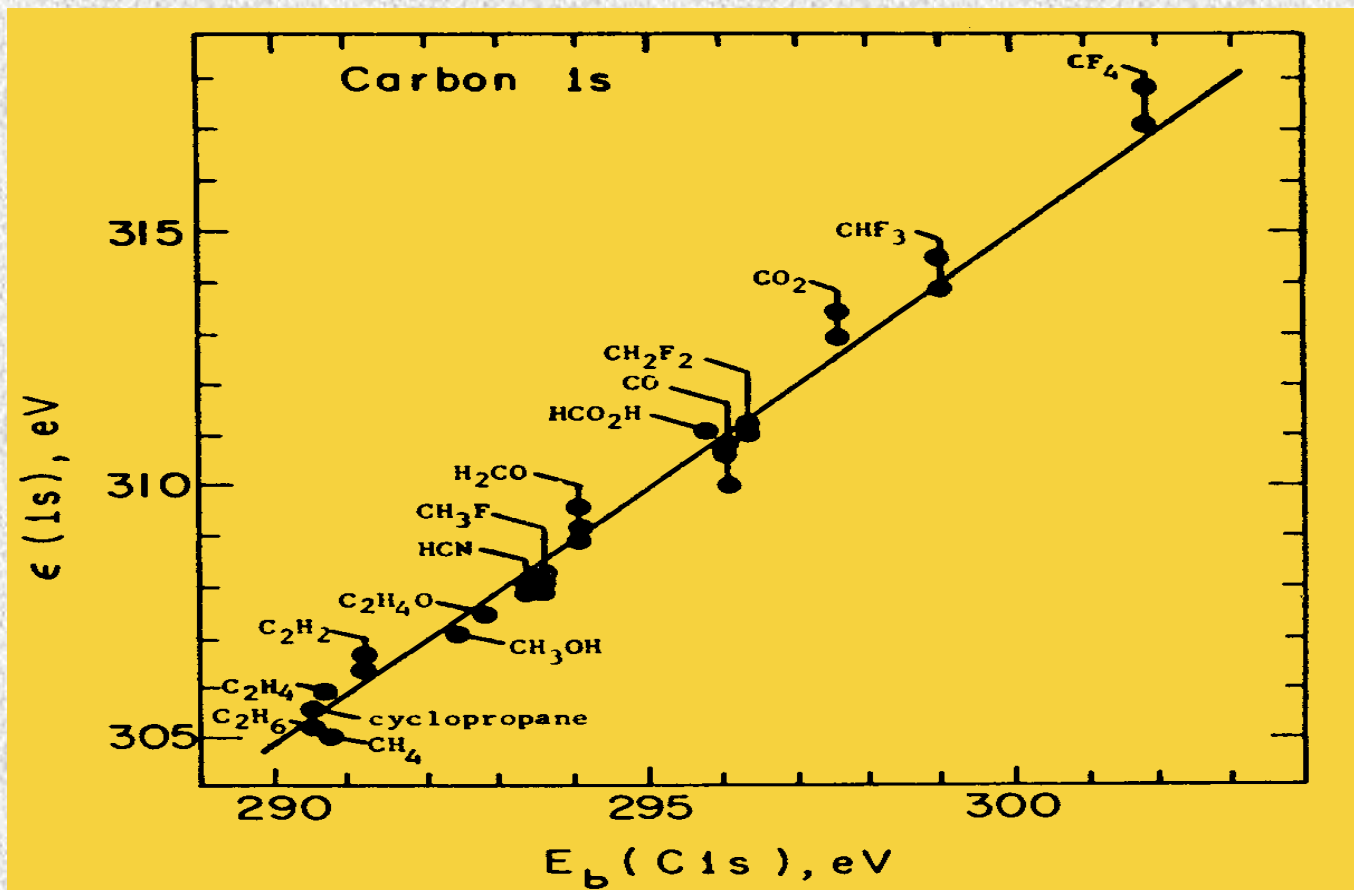
PES spectra of C_9H_{20}
(from S. Hüfner).



UPS of TTF(g), TCNQ(g), K⁺TCNQ⁻ and TTF.TCNQ (from W. D. Grobman et al. Phys. Rev. Lett., 32 (1974) 534.

Complications

Relaxation and correlation



Calculated C1s BEs vs. experimental BEs (from D.A. Shirley, *Adv. Chem. Phys.*, 23, 85, 1973).