

# *Valence photoelectron spectroscopy*

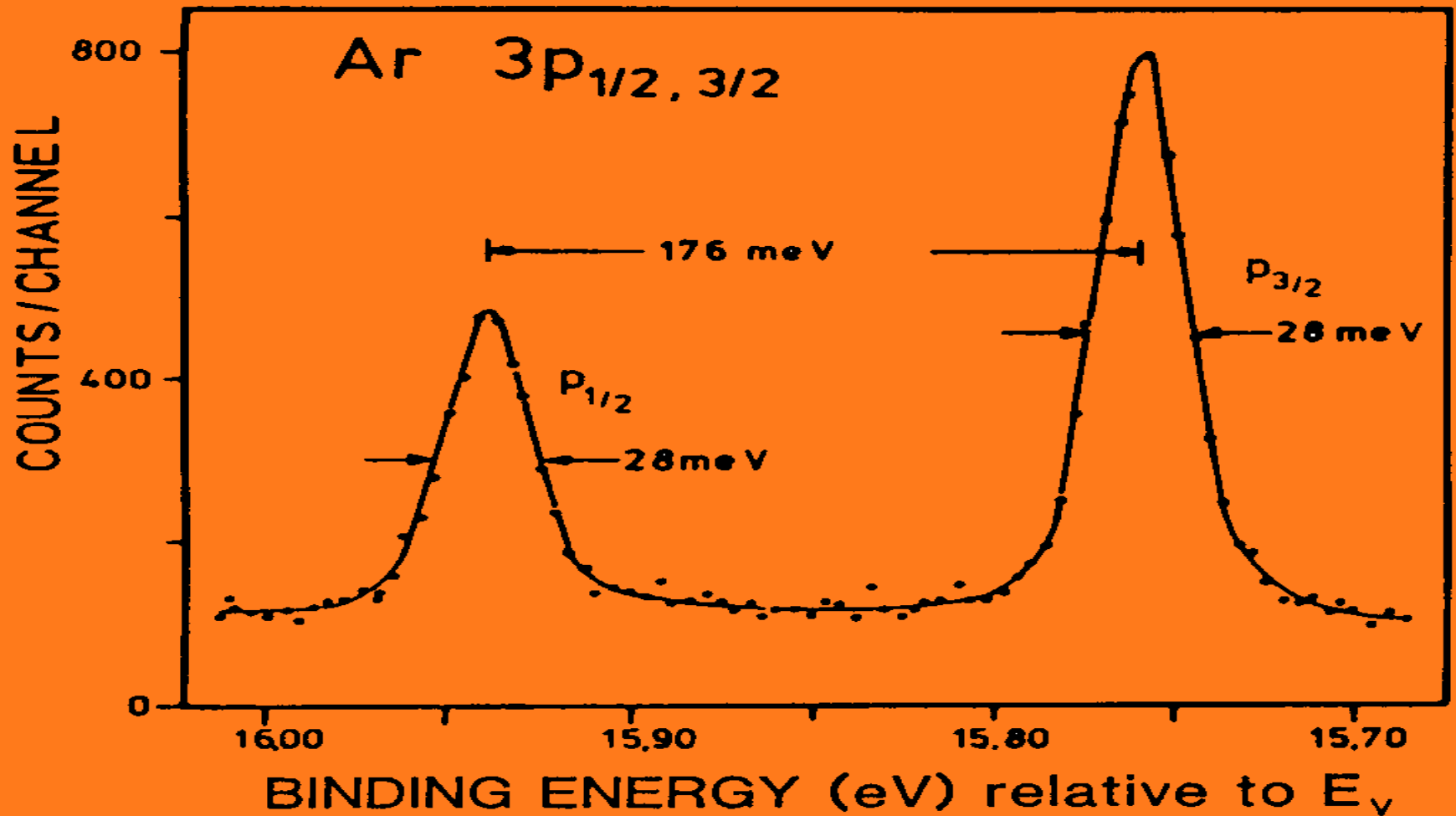
**Atoms**

**Molecules**

**Adsorbed molecules**

**Insulating solids**

# *Atoms*



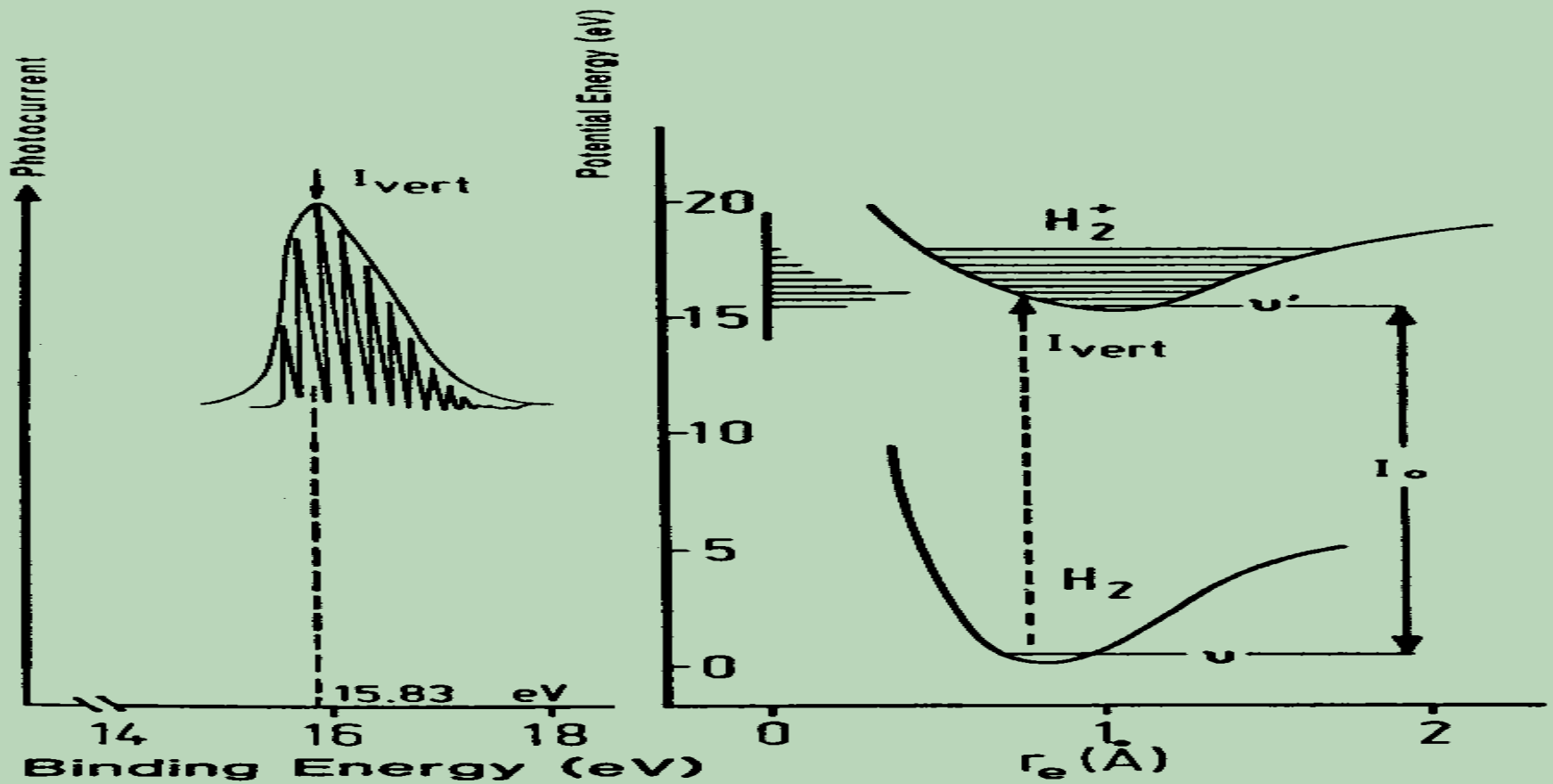
**UPS spectrum of gaseous argon (from S. Hüfner).**



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

**Occupation numbers of  
emitting orbitals**

*Diatomic  
molecules*



UPS of  $H_2$  and the PECs of  $H_2$   
and  $H_2^+$  (from S. Hüfner).

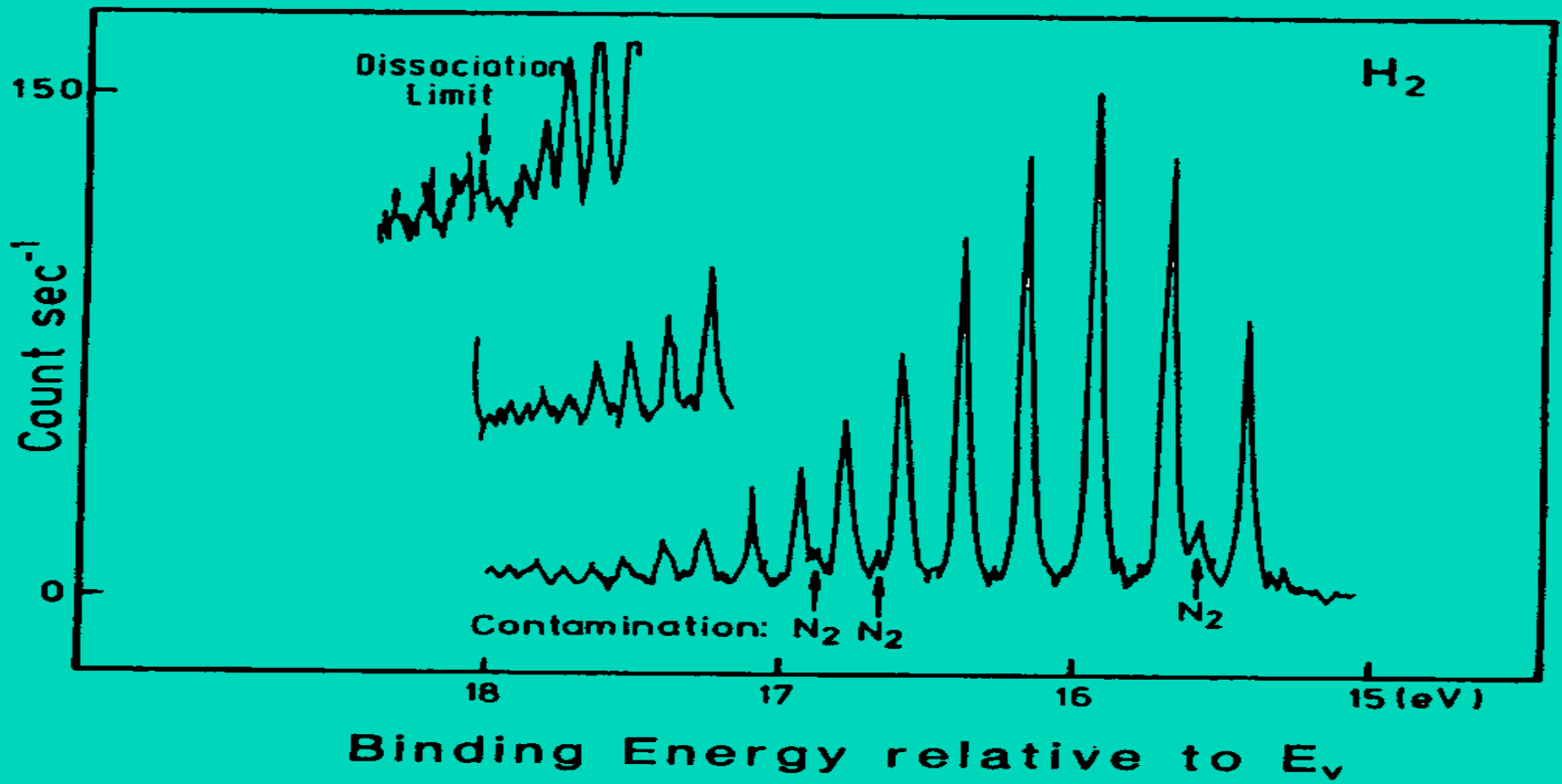
# *Born-Oppenheimer Approximation*

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

**Franck-Condon Factor**

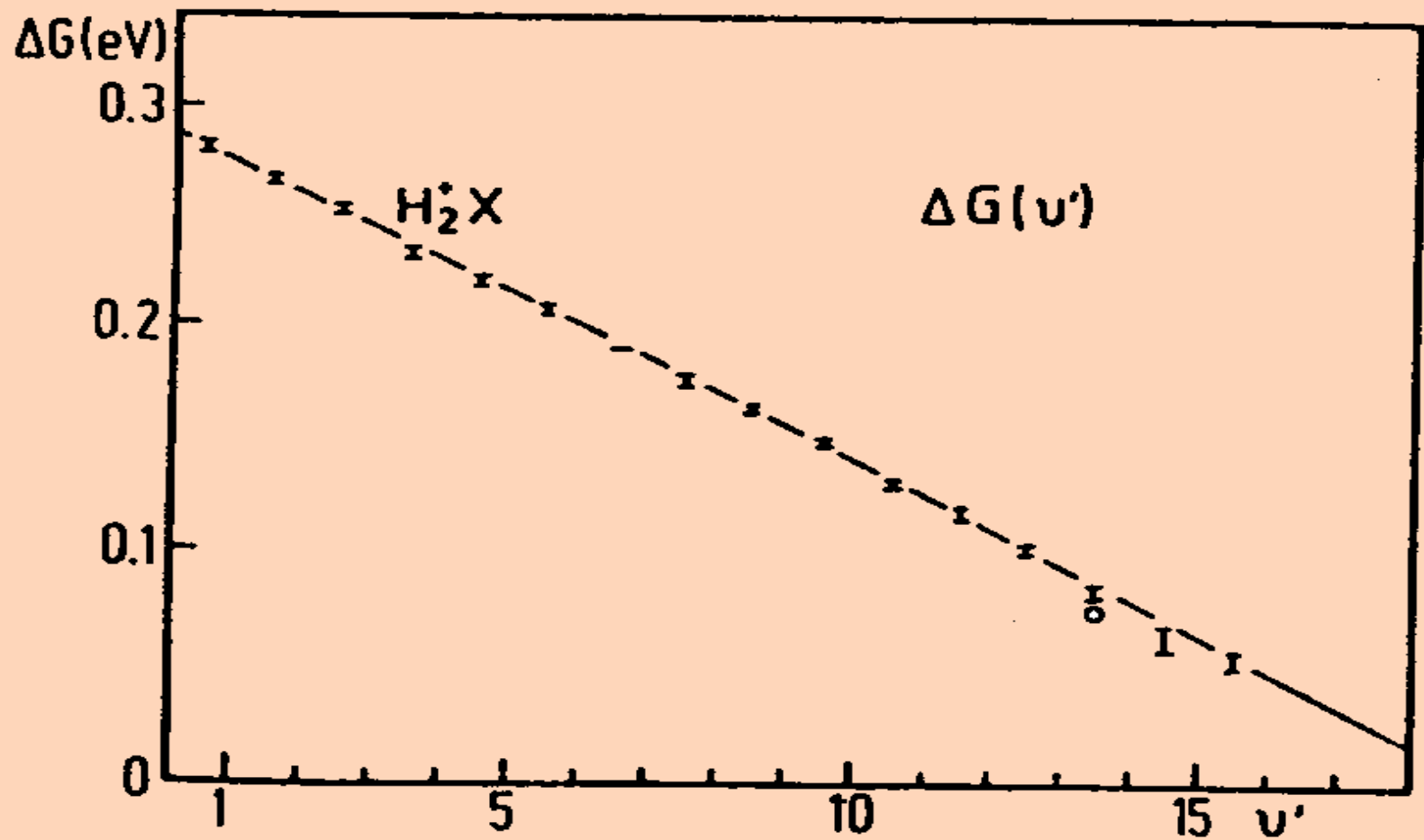
**Vibrational structure of the ion**

**Parameters of the ionic  
potential surfaces**

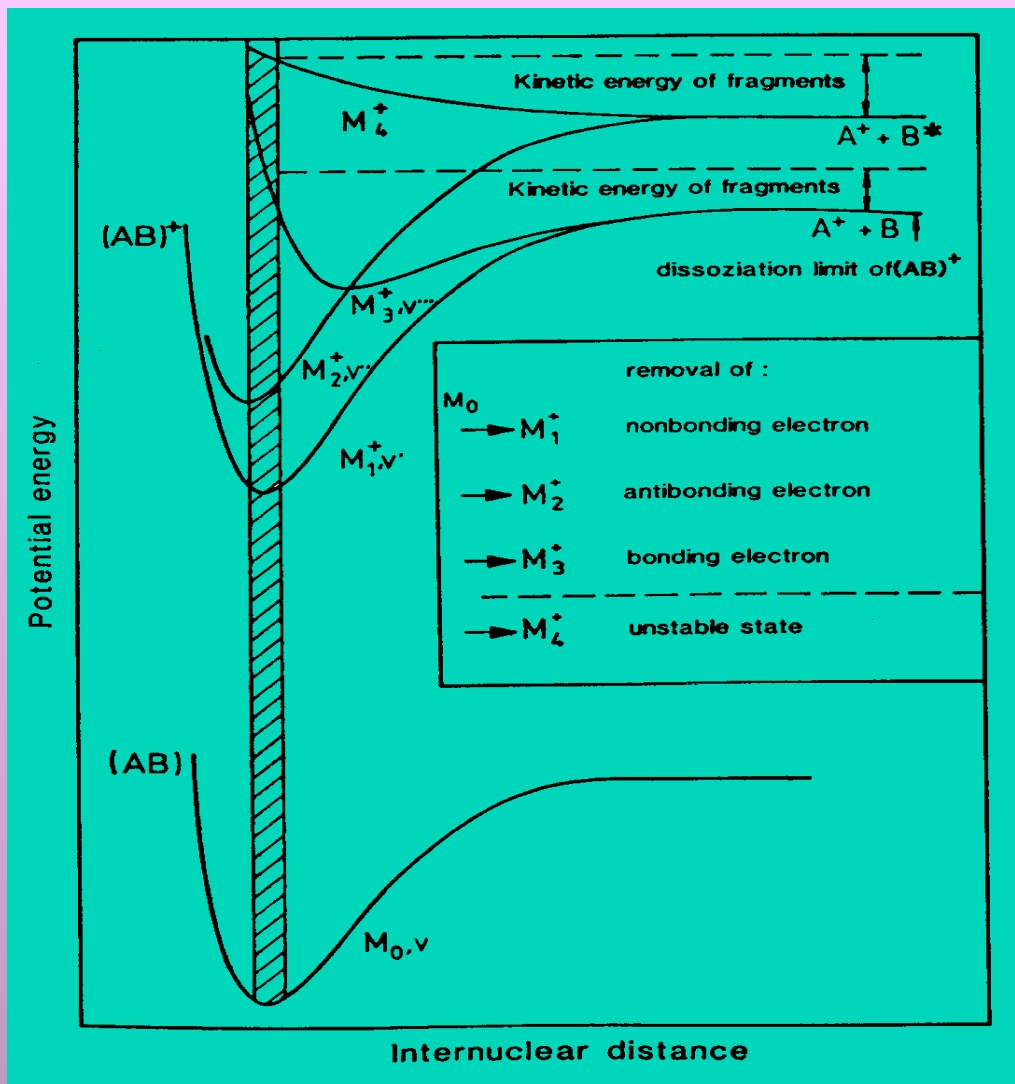


**Vibrational structure of  $H_2$  in  
UPS (from S. Hüfner).**

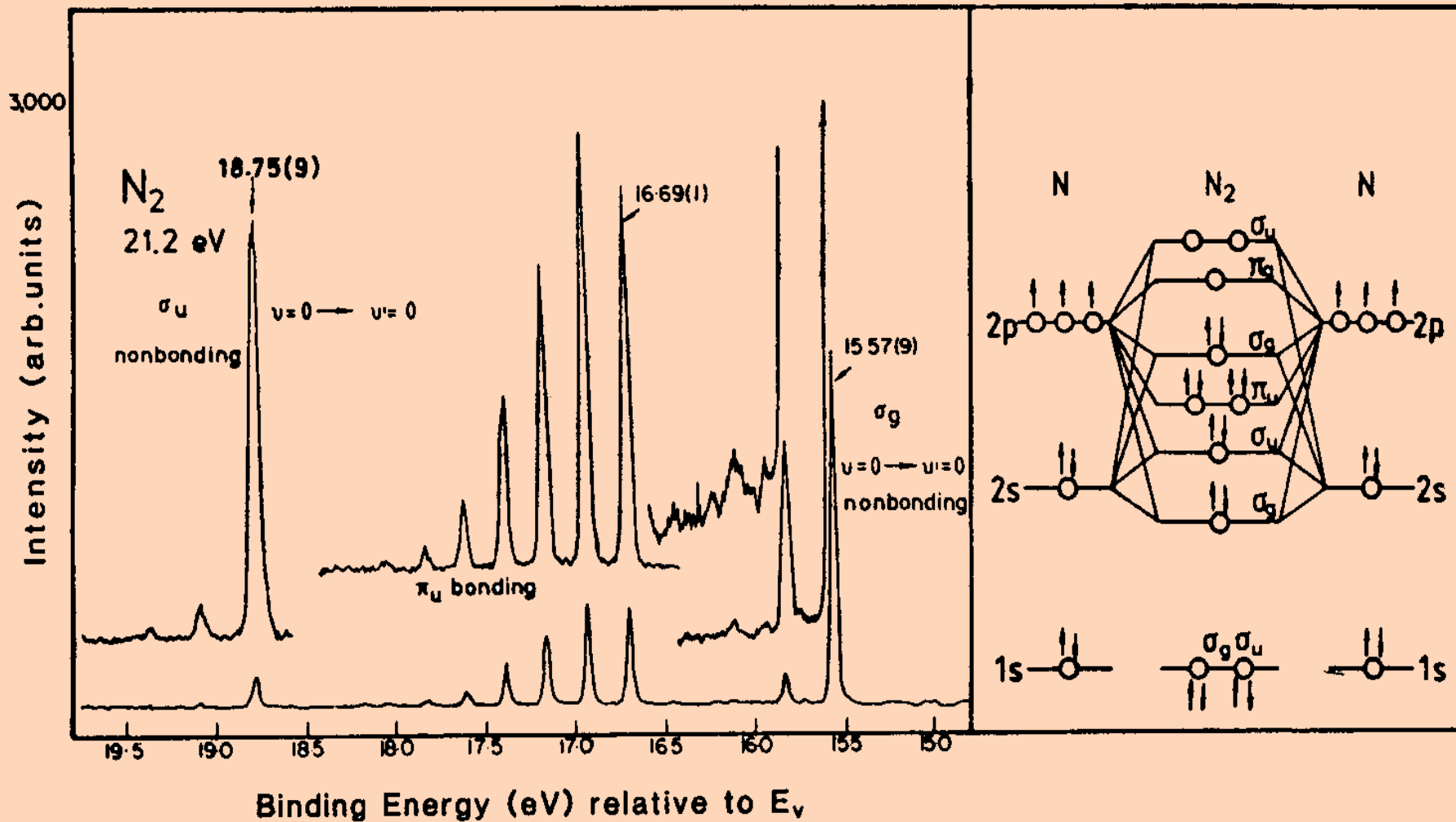




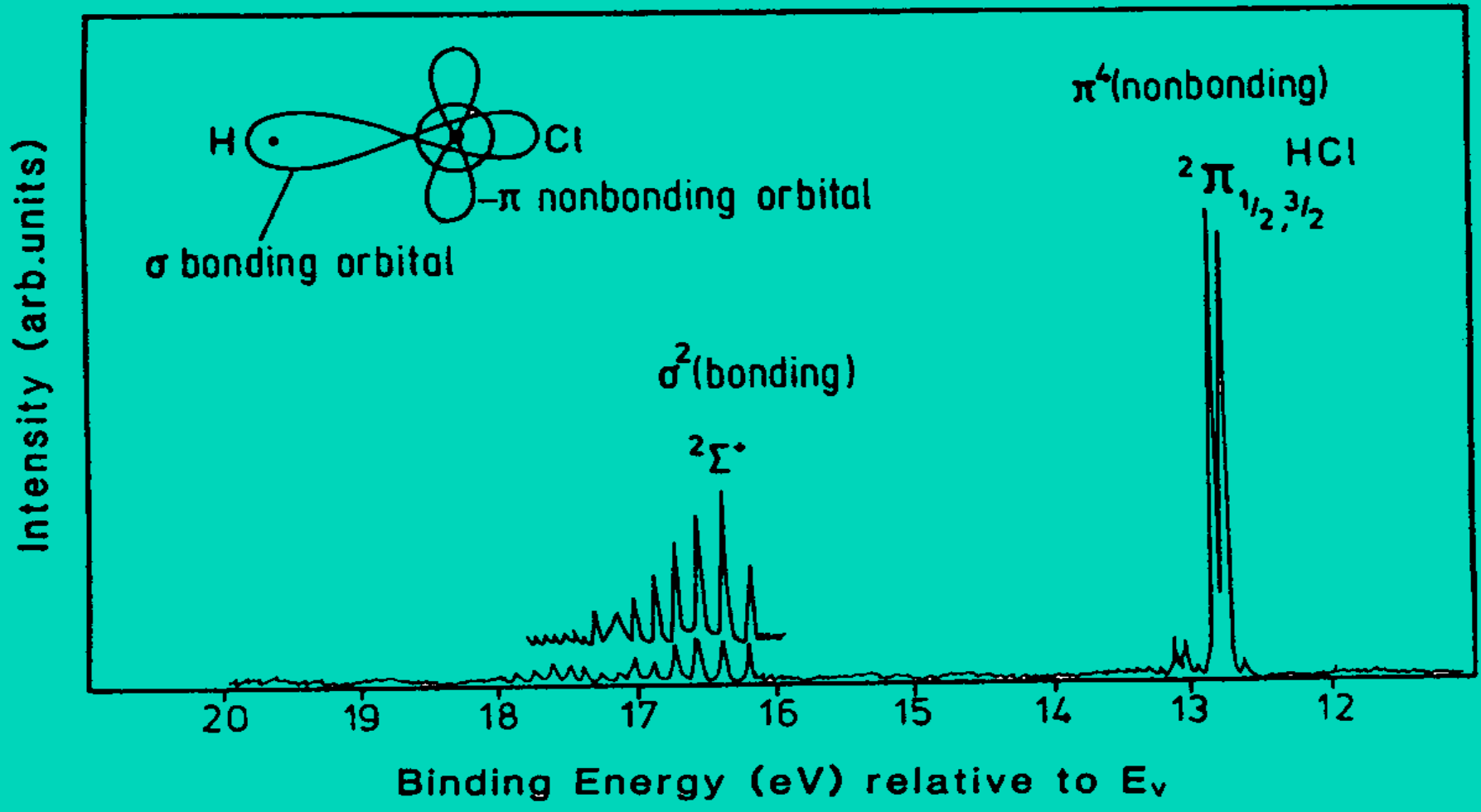
**Plot of  $\Delta G$  as a function of  $\nu'$   
in  $H_2^+$  (from S. Hüfner).**



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



**UPS spectrum of  $N_2$**   
**(from S. Hüfner).**



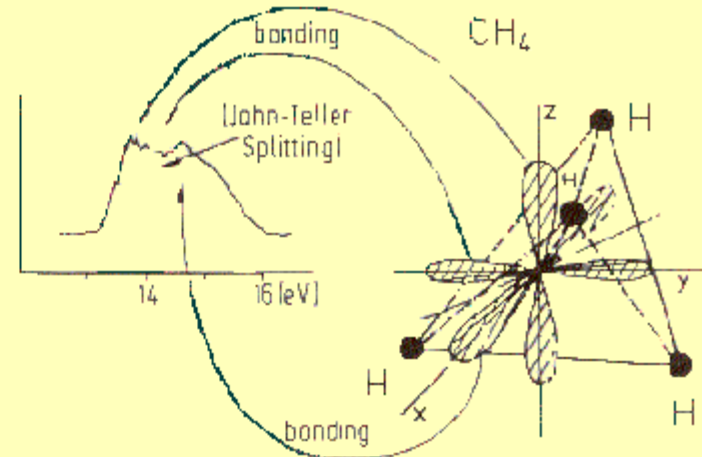
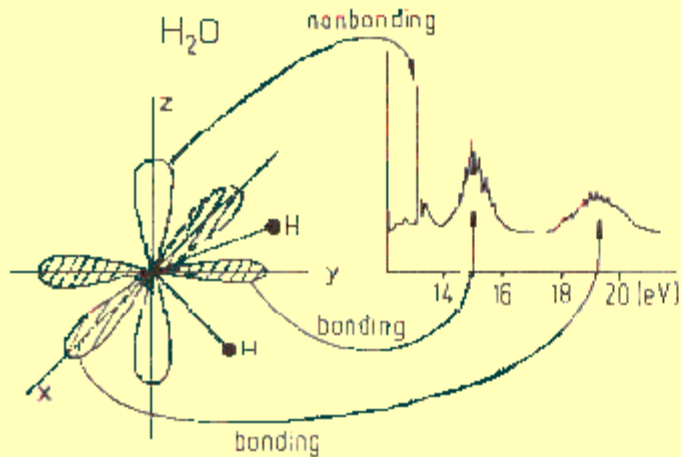
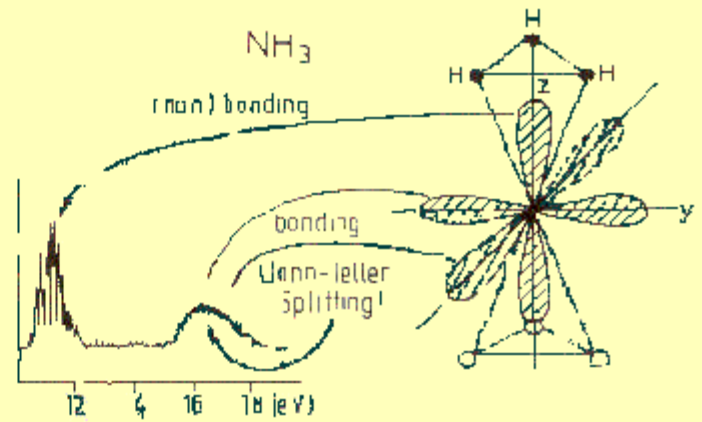
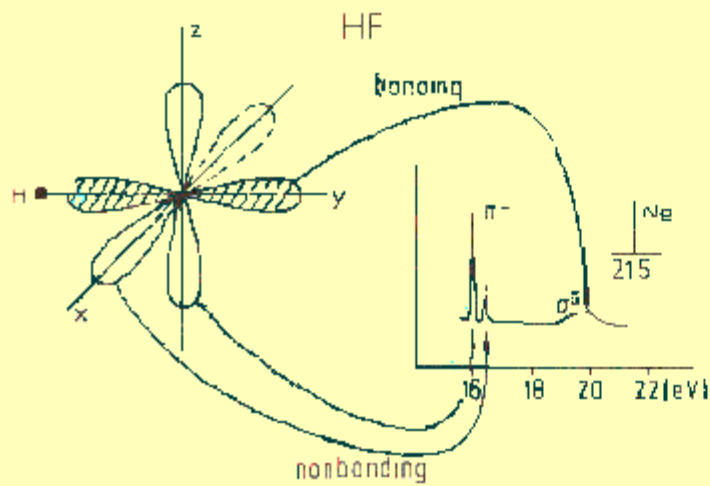
**UPS spectrum of HCl**  
**(from S. Hüfner).**

# *Polyatomic molecules*

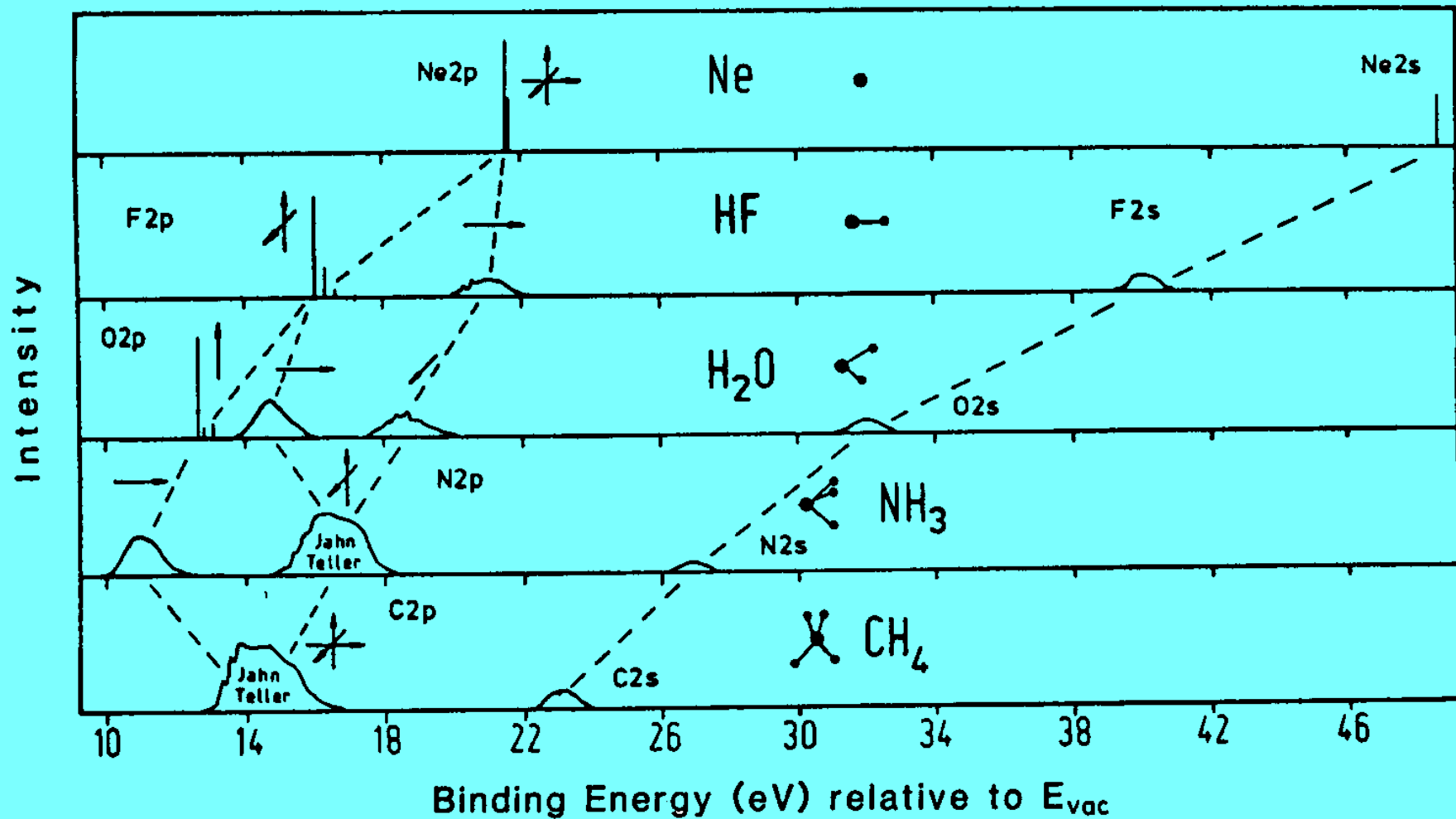
**Koopmans' approximation**

**Jahn-Teller distortion**

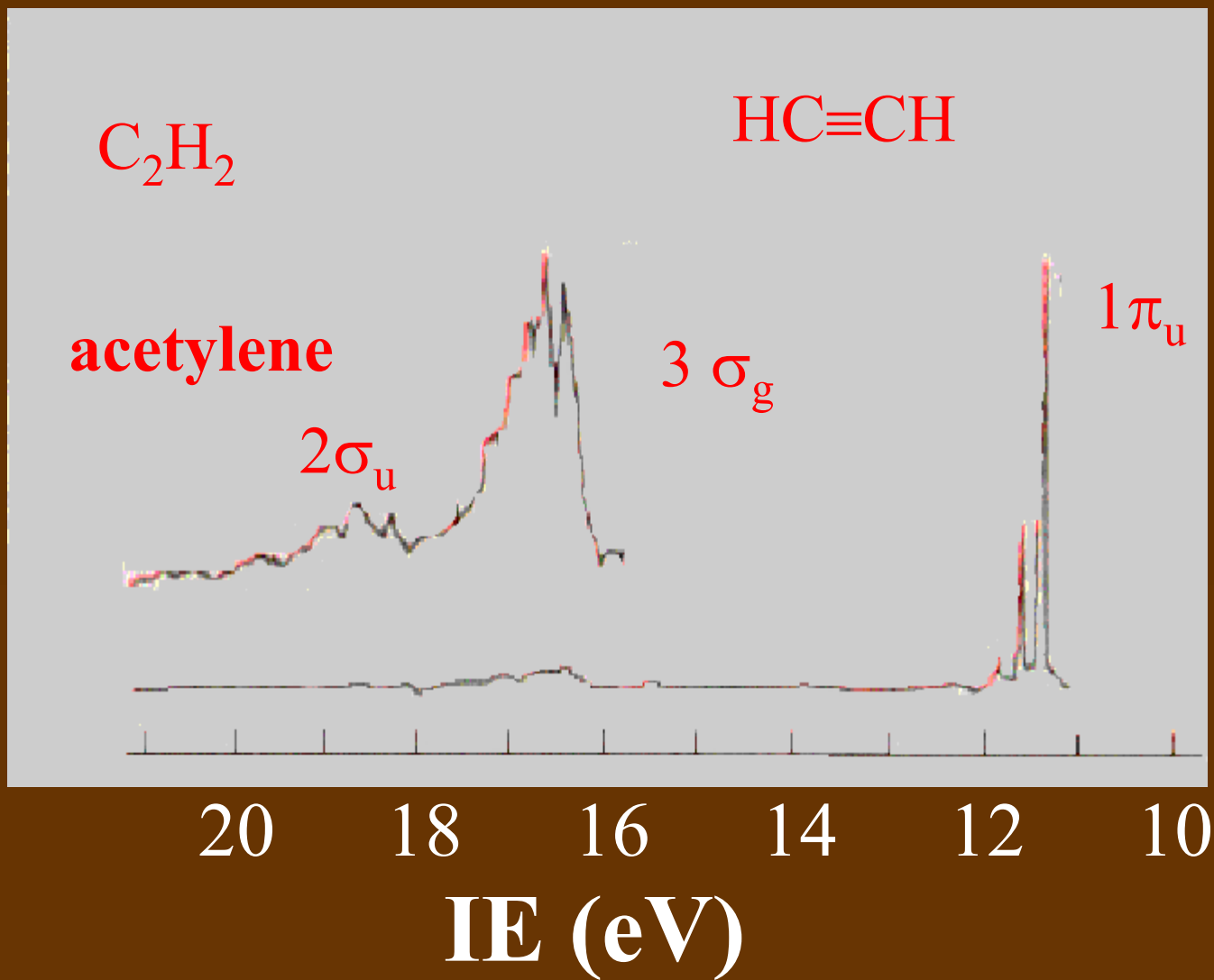
**Renner-Teller splitting**



**UPS of HF, H<sub>2</sub>O, NH<sub>3</sub> and CH<sub>4</sub>  
(from S. Hüfner).**

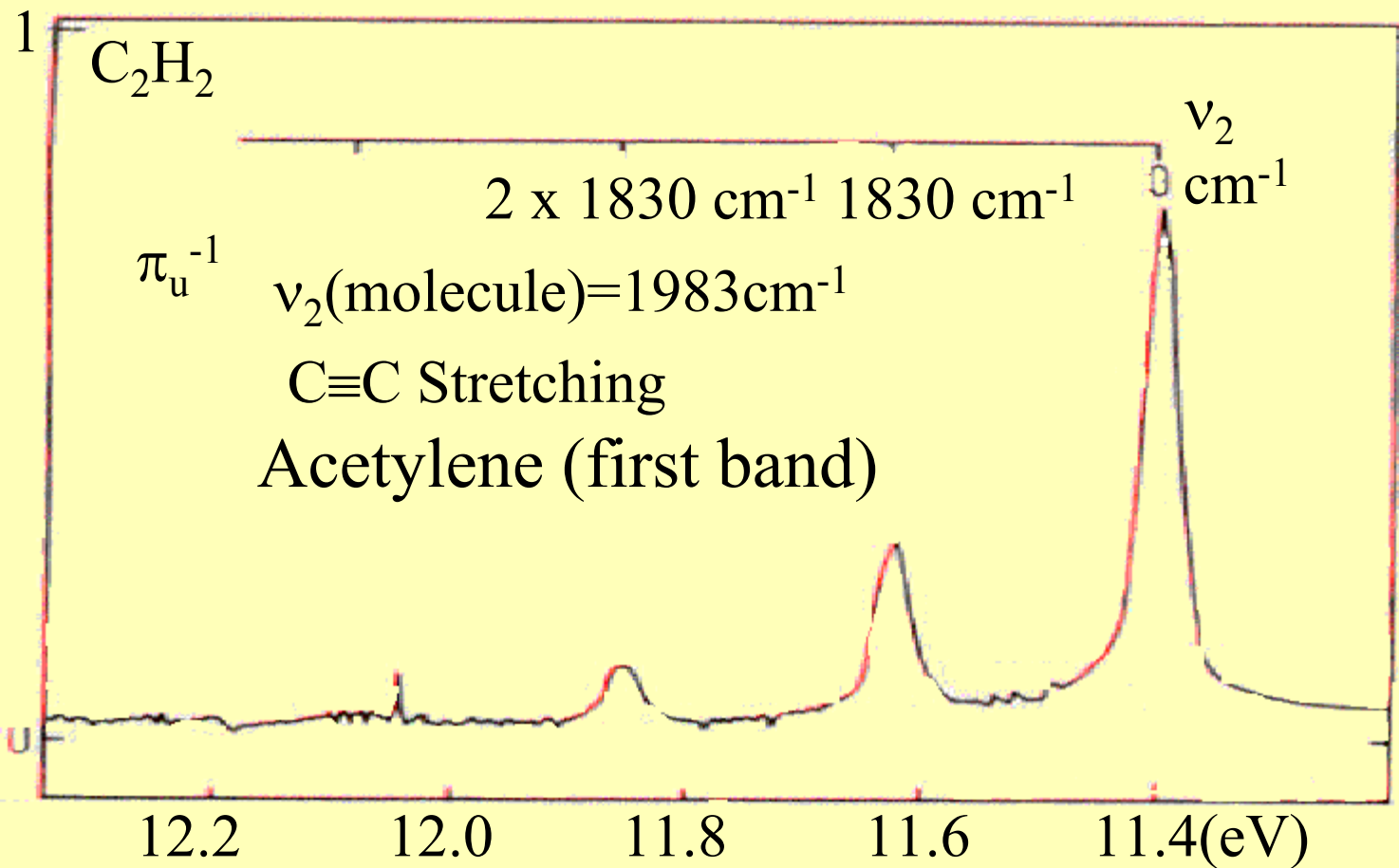


**UPS spectra of Ne and its isoelectronic hydrides (from S. Hüfner).**

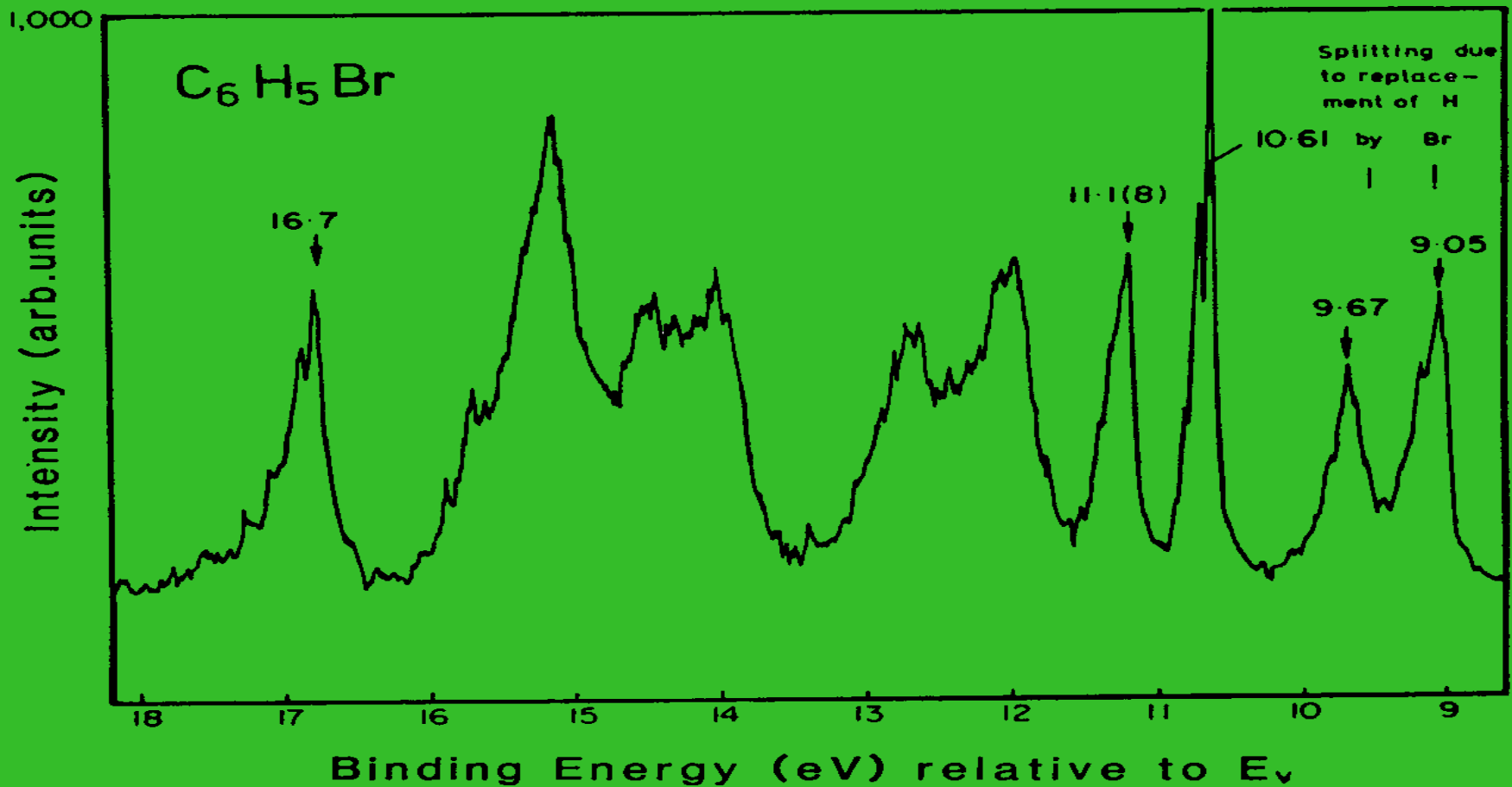


UPS of acetylene (from S. Hüfner).

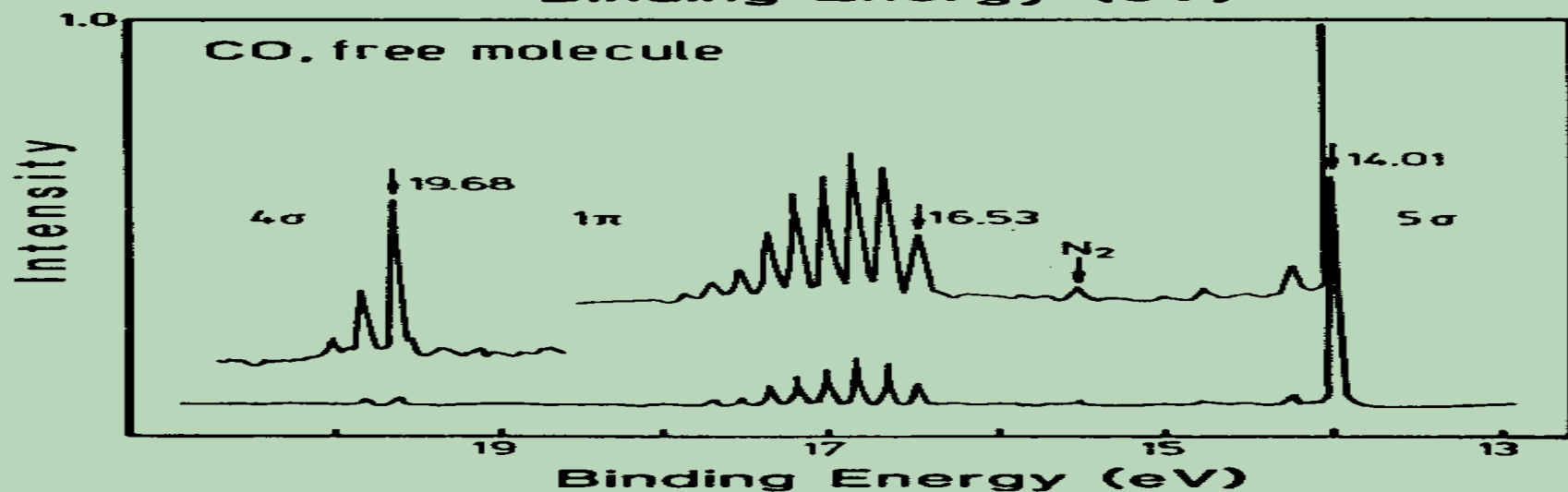
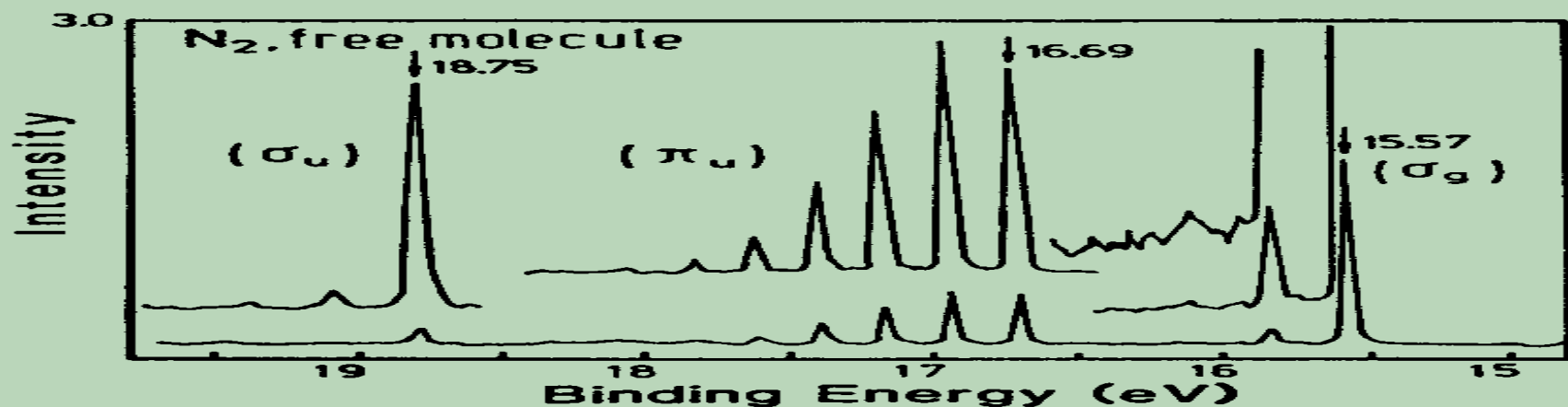




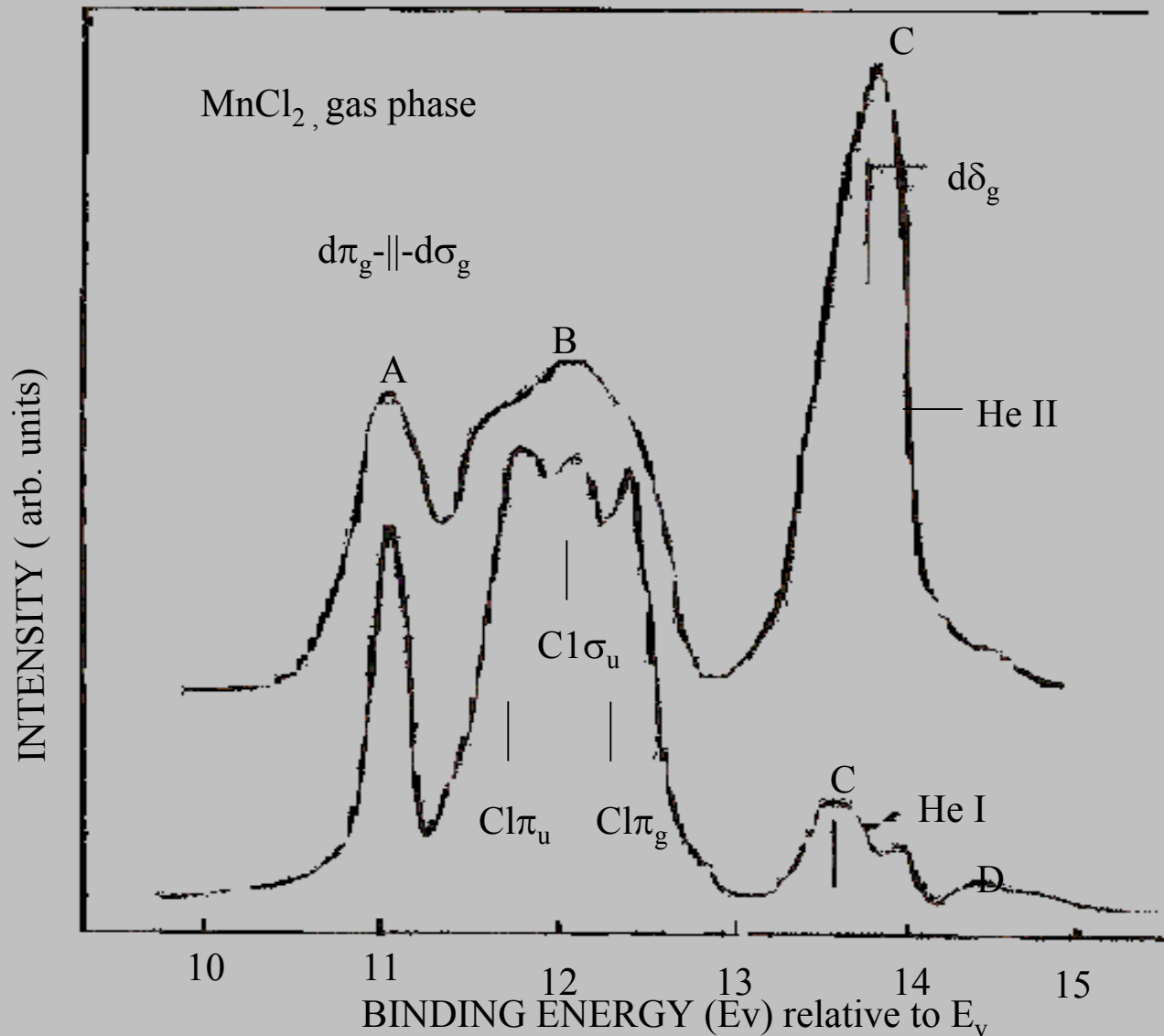
**Vibrational structure in the UPS of acetylene (from S. Hüfner).**



**UPS spectrum of  $C_6H_5Br$**   
**(from S. Hüfner).**



UPS spectra of the isoelectronic N<sub>2</sub> and CO ( from S. Hüfner).



**UPS of MnCl<sub>2</sub> (from S.Hüfner).**

# *Guidelines for interpretation*

**Calculations**

**Vibrational structure**

**Isoelectronic molecules**

**Chemical trends**

**Substitutions**

**Systematics**

**Photon energy variation**

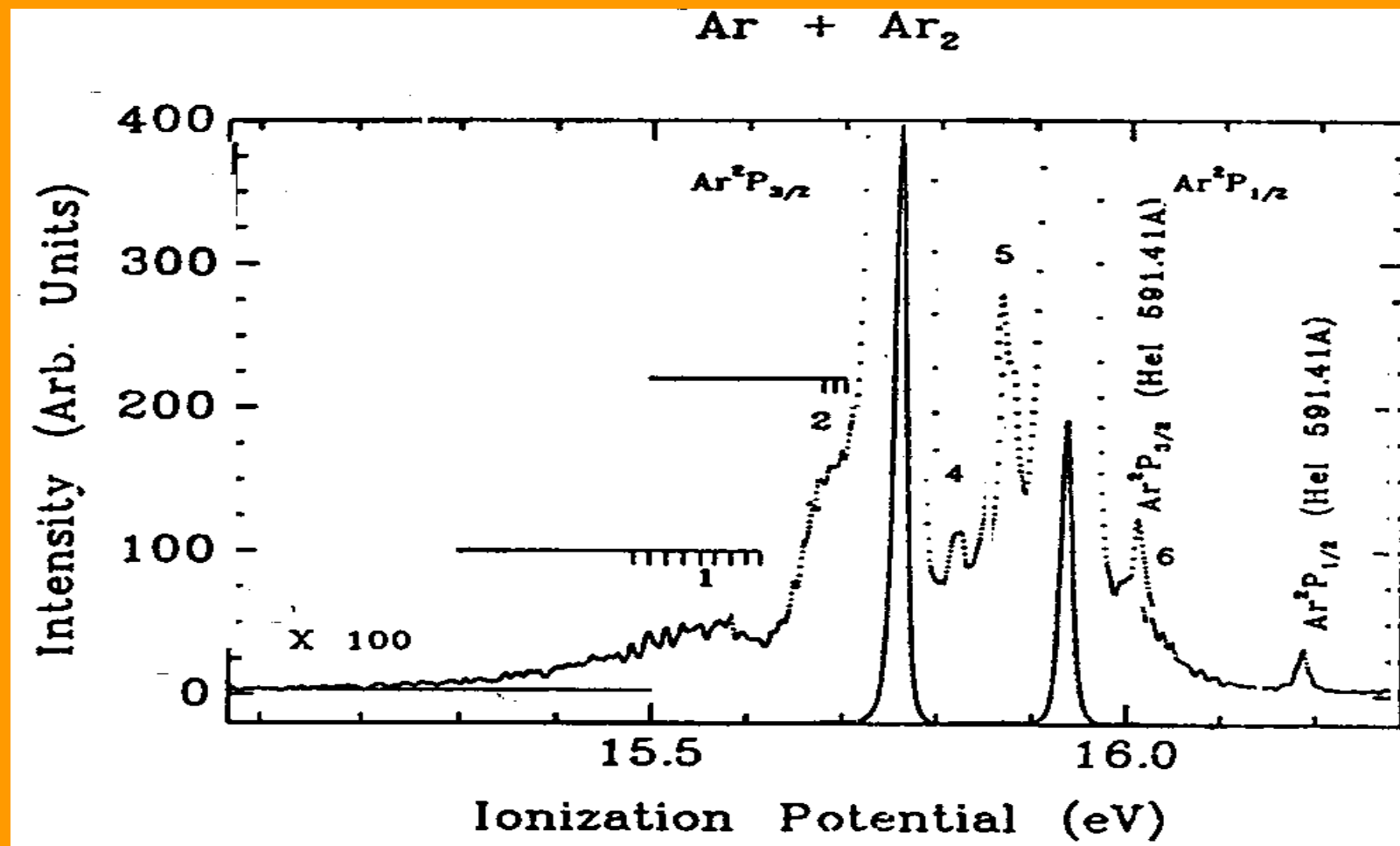
# *Recent studies*

**Transient species**

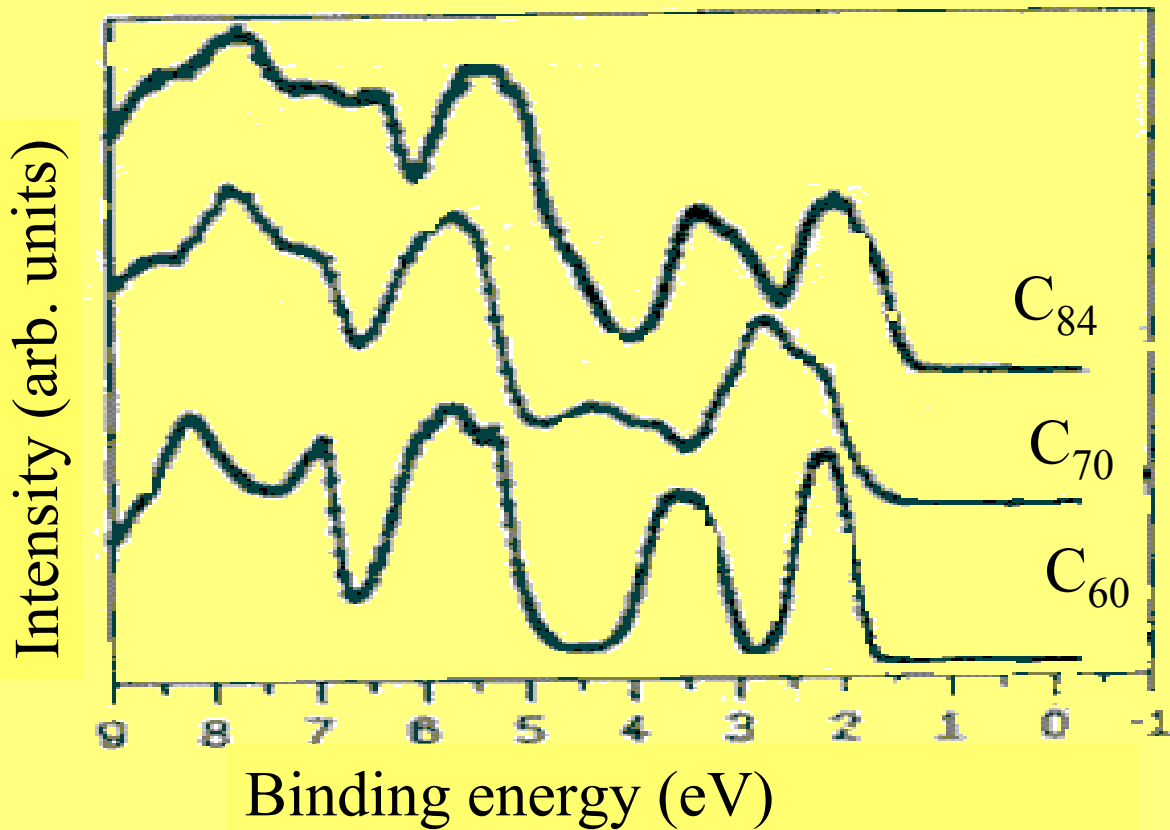
**High temperature species**

**van der Waals molecules**

**Fullerenes**



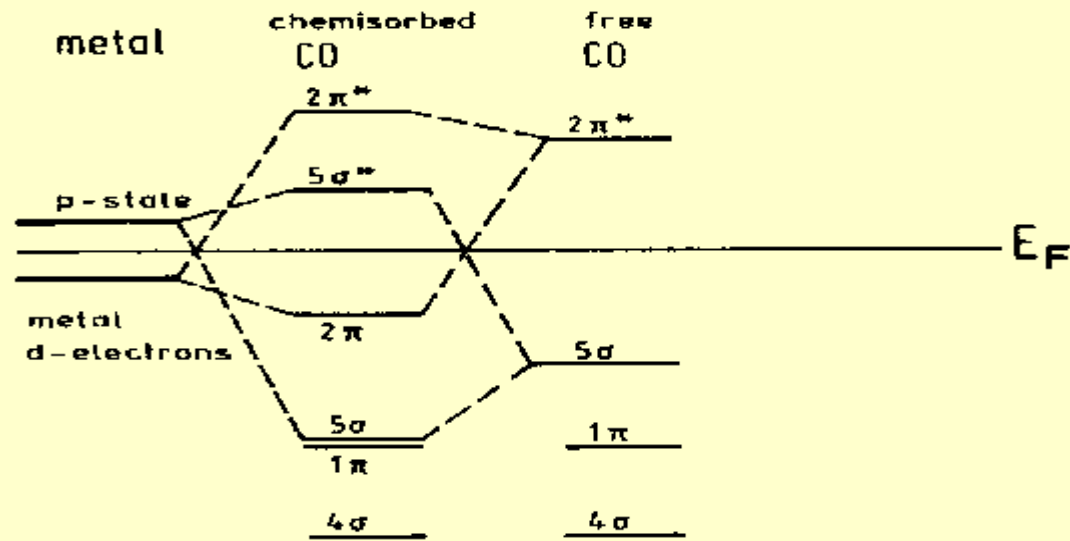
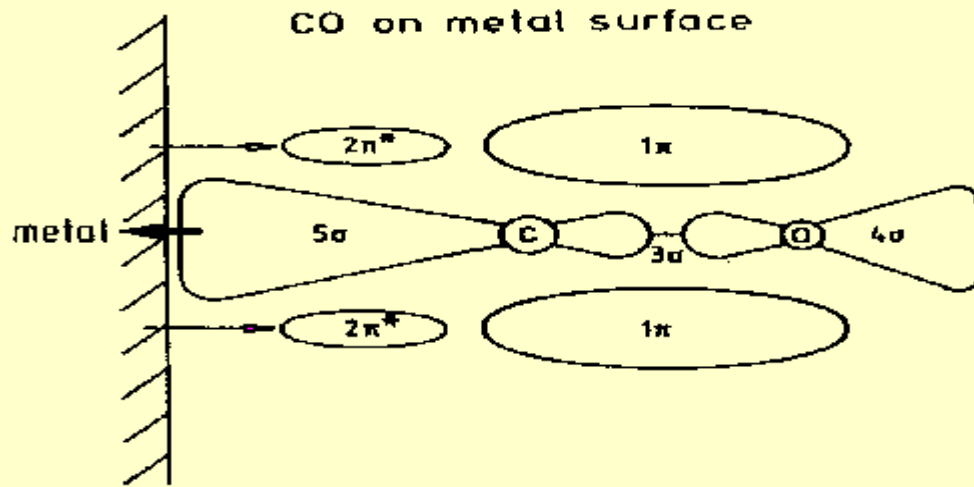
**UPS of a mixture of Ar<sub>2</sub> and Ar (from  
T. Pradeep, et. al. J. Chem. Phys. 98  
(1993) 5269.**



**UPS of C<sub>60</sub>, C<sub>70</sub> and C<sub>84</sub> (from M. S. Dresselhaus et. al., *Science of Fullerenes and Carbon Nanotubes*, Academic Press, New York, 1996).**



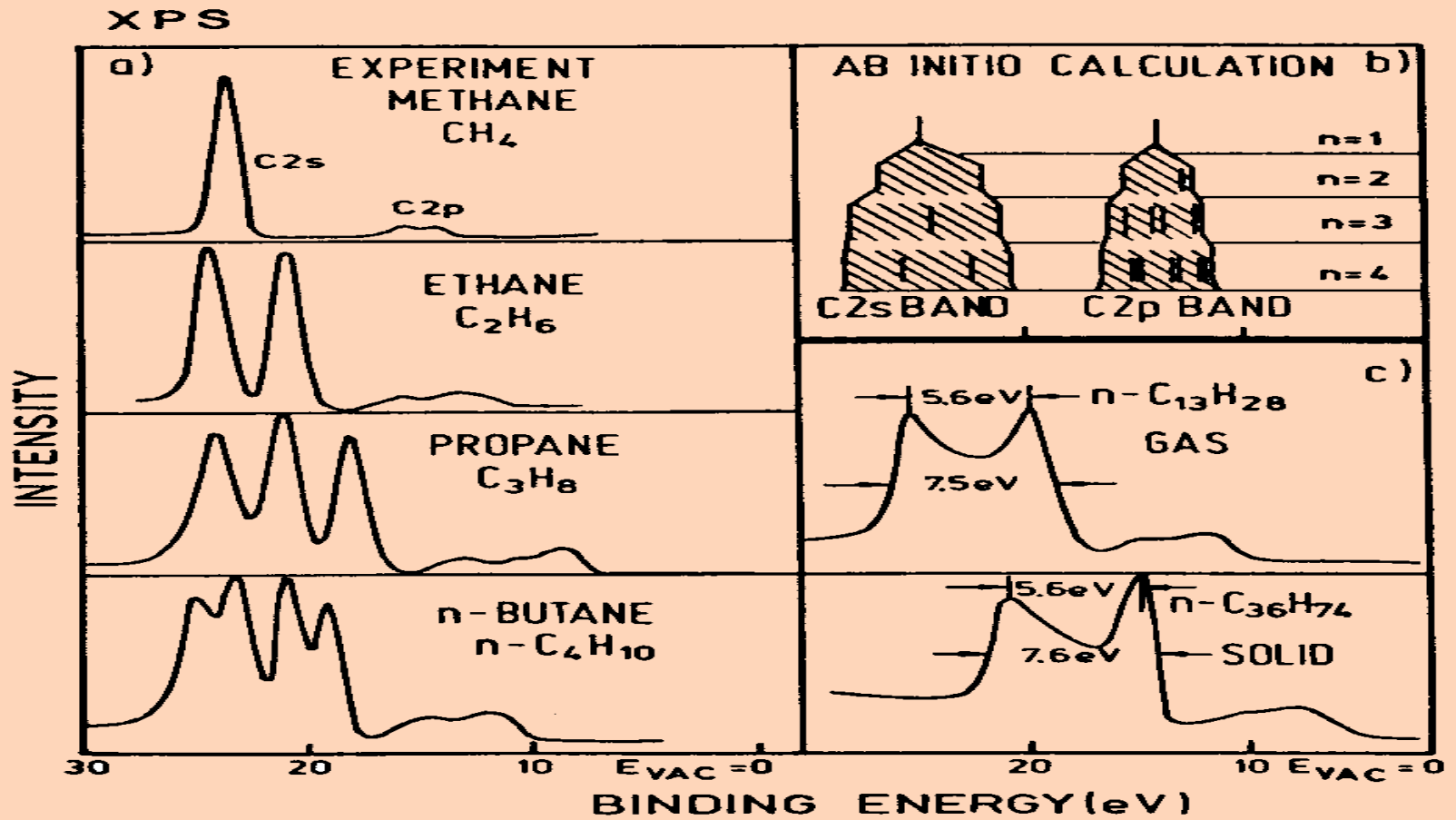
*Adsorbed  
molecules*



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

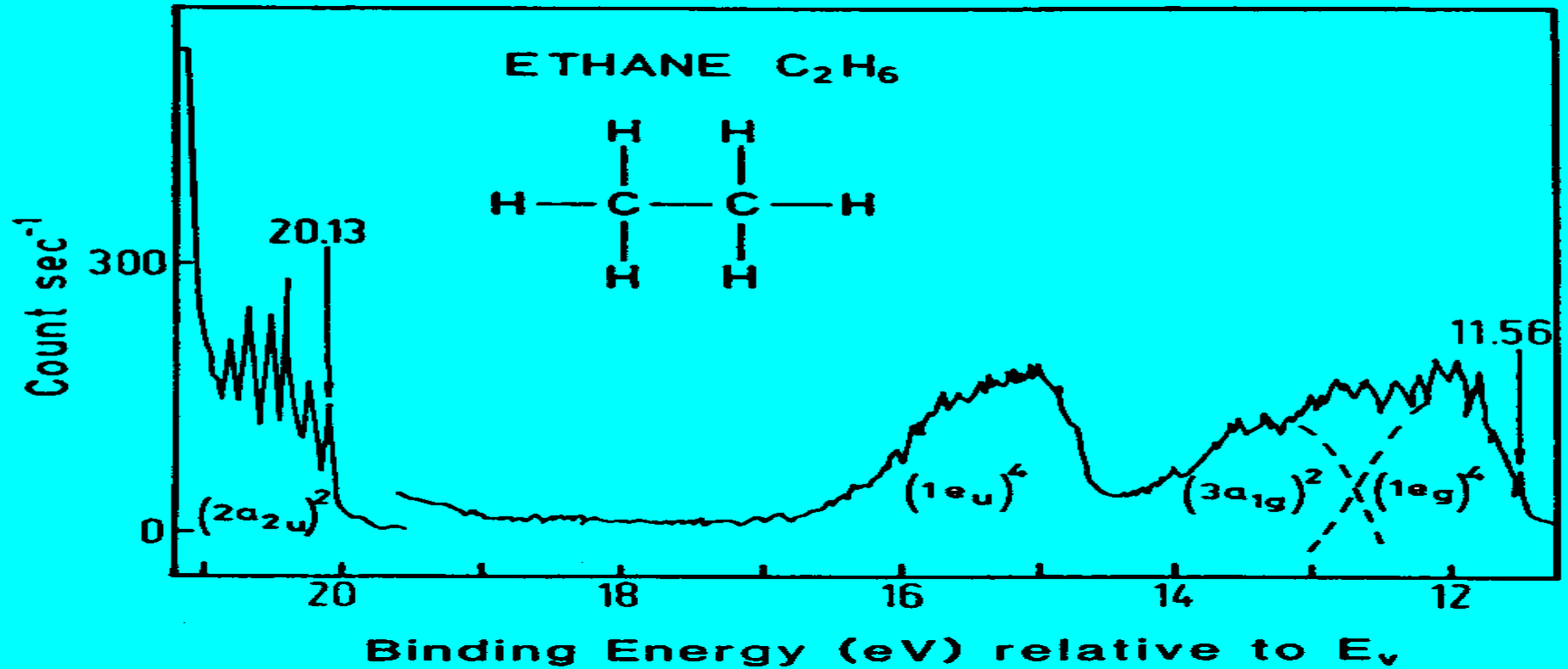
*Insulating  
solids*

**Evolution of band structure**

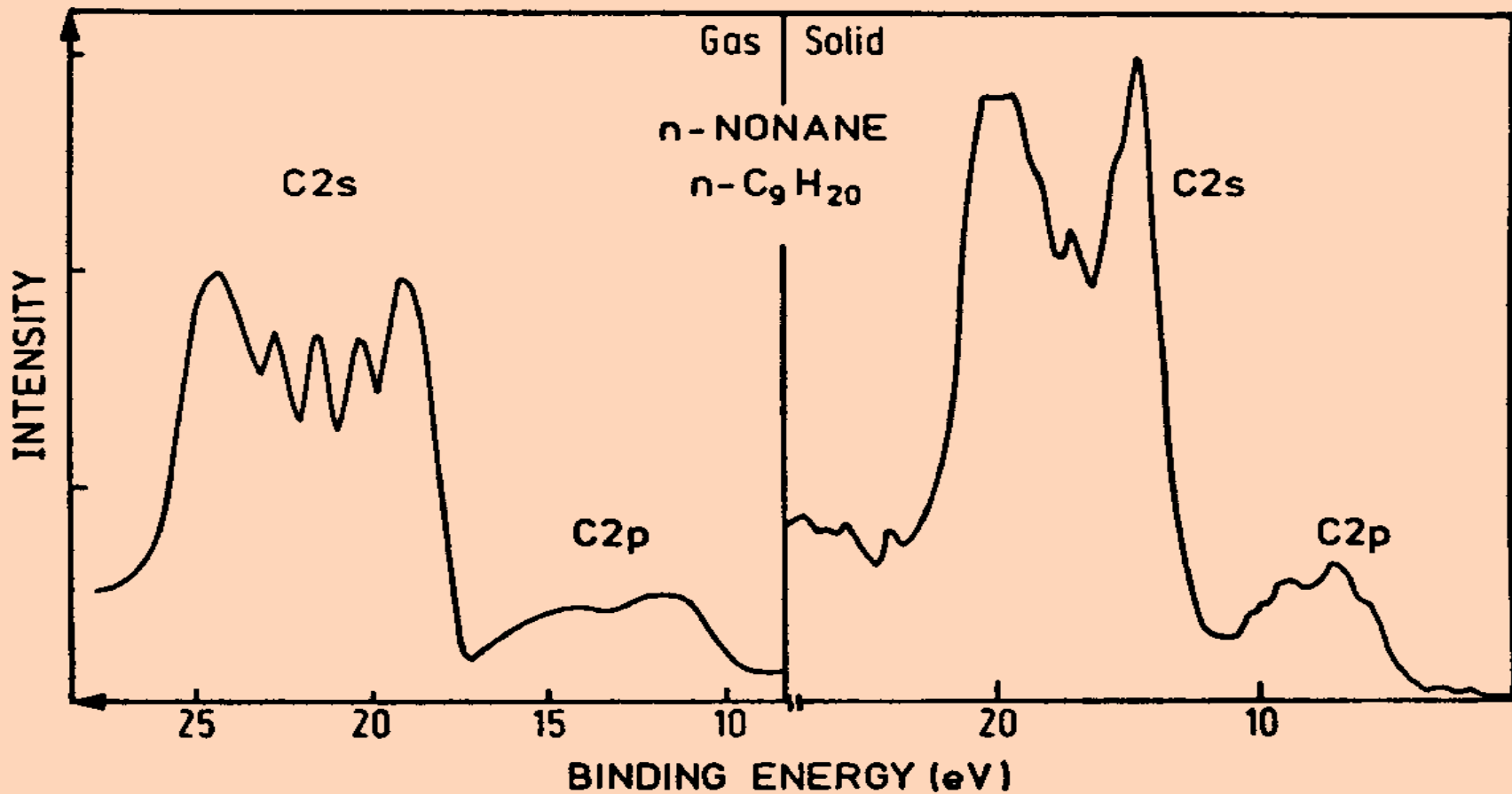


**EDCs of a number of linear polymers (from S. Hüfner).**

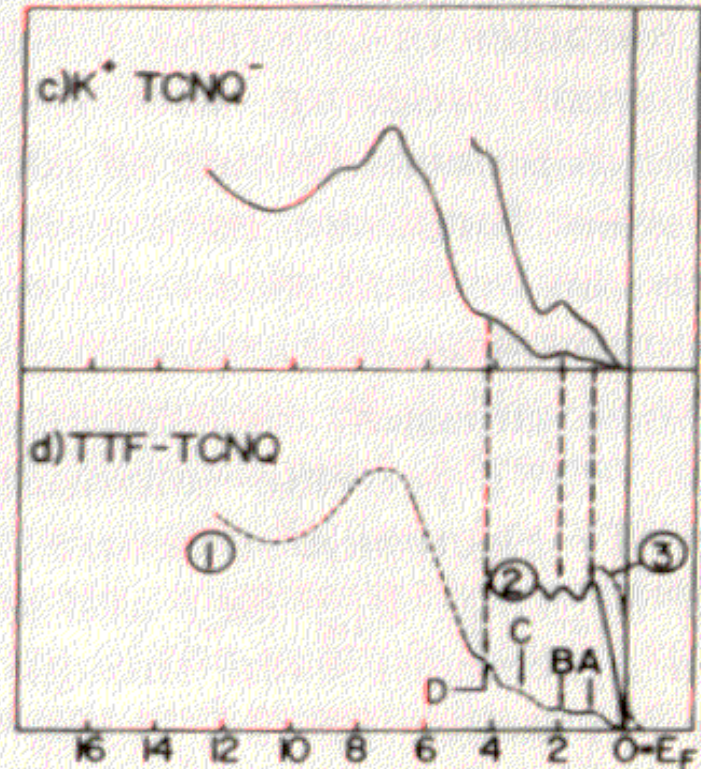
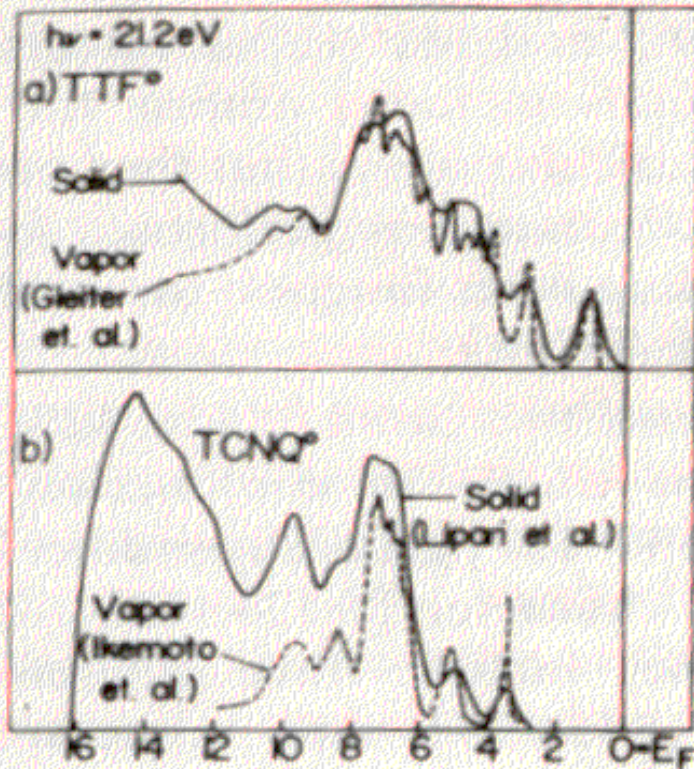
UPS



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



**PES spectra of  $\text{C}_9\text{H}_{20}$**   
**(from S. Hüfner).**

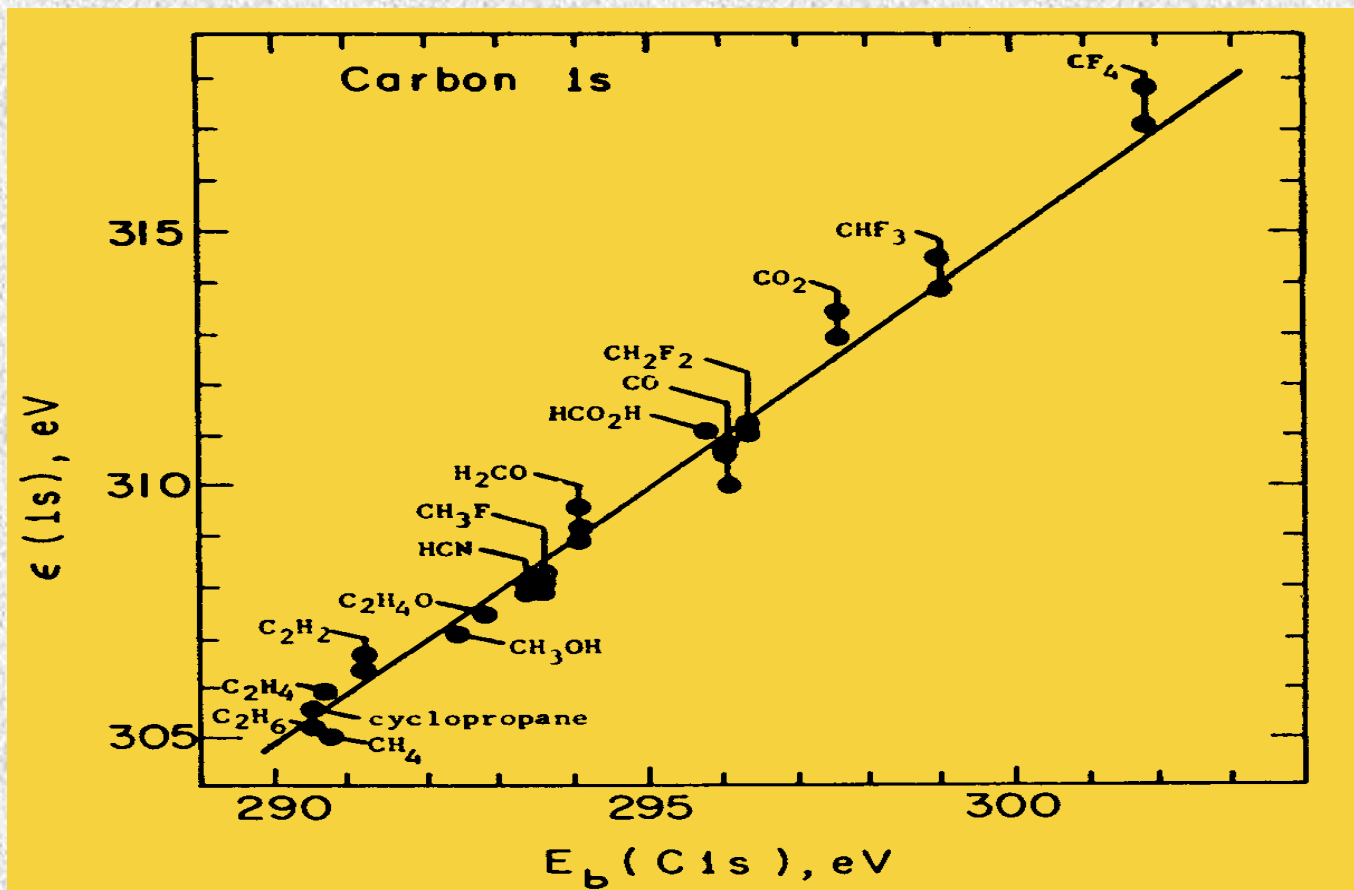


UPS of TTF(g), TCNQ(g), K<sup>+</sup>TCNQ<sup>-</sup> and TTF.TCNQ (from W. D. Grobman et al. Phys. Rev. Lett., 32 (1974) 534.

# *Complications*

**Relaxation and correlation**





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