Efficient, yet accurate prediction of spectra with GPAW

Michael Walter

Albert-Ludwigs-Universität Freiburg

UNI FREIBURG

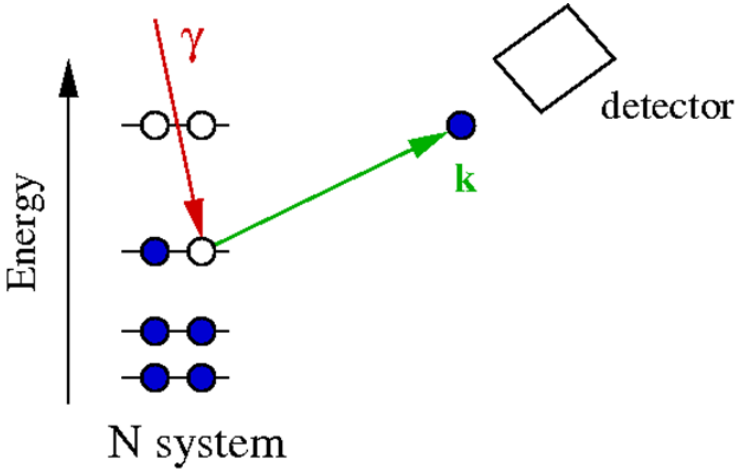
Fraunhofer IWM

Outline

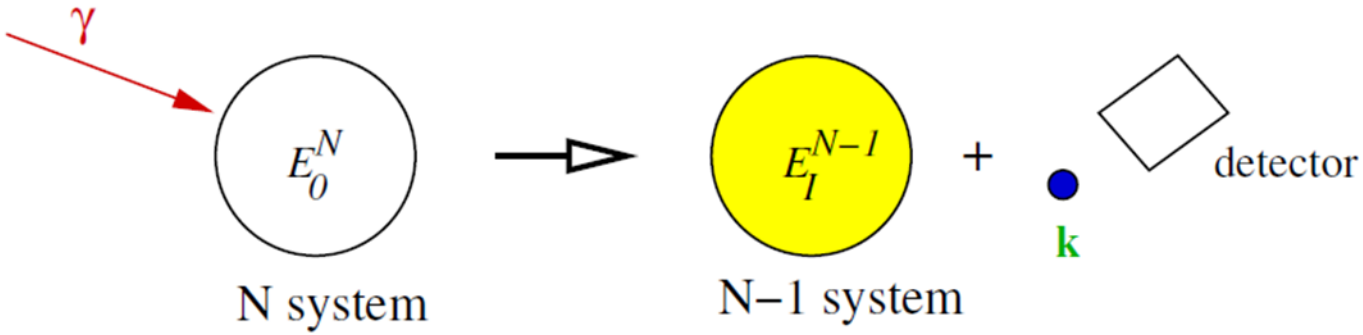
- Photoelectron spectra
  - Kohn-Sham vs many body
  - Valence PES
  - XPS molecules => empirical shift
  - Application to clusters
  - Solids
- Raman spectra (work in progress)
  - Theory
  - Non-resonant
  - Resonant
- Polarizable Continuum Model (PCM)
- Conclusions

Photoelectron spectra

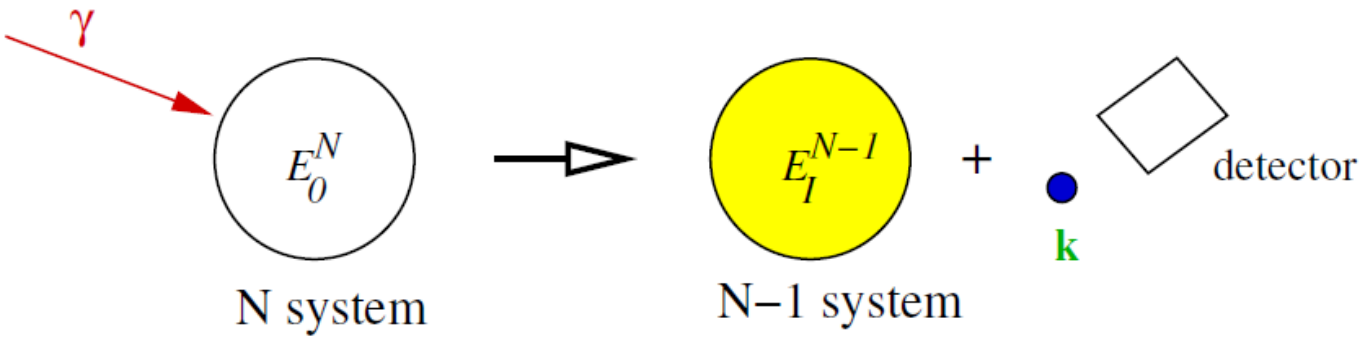
Single particle viewpoint



Many particle viewpoint



Many particle viewpoint

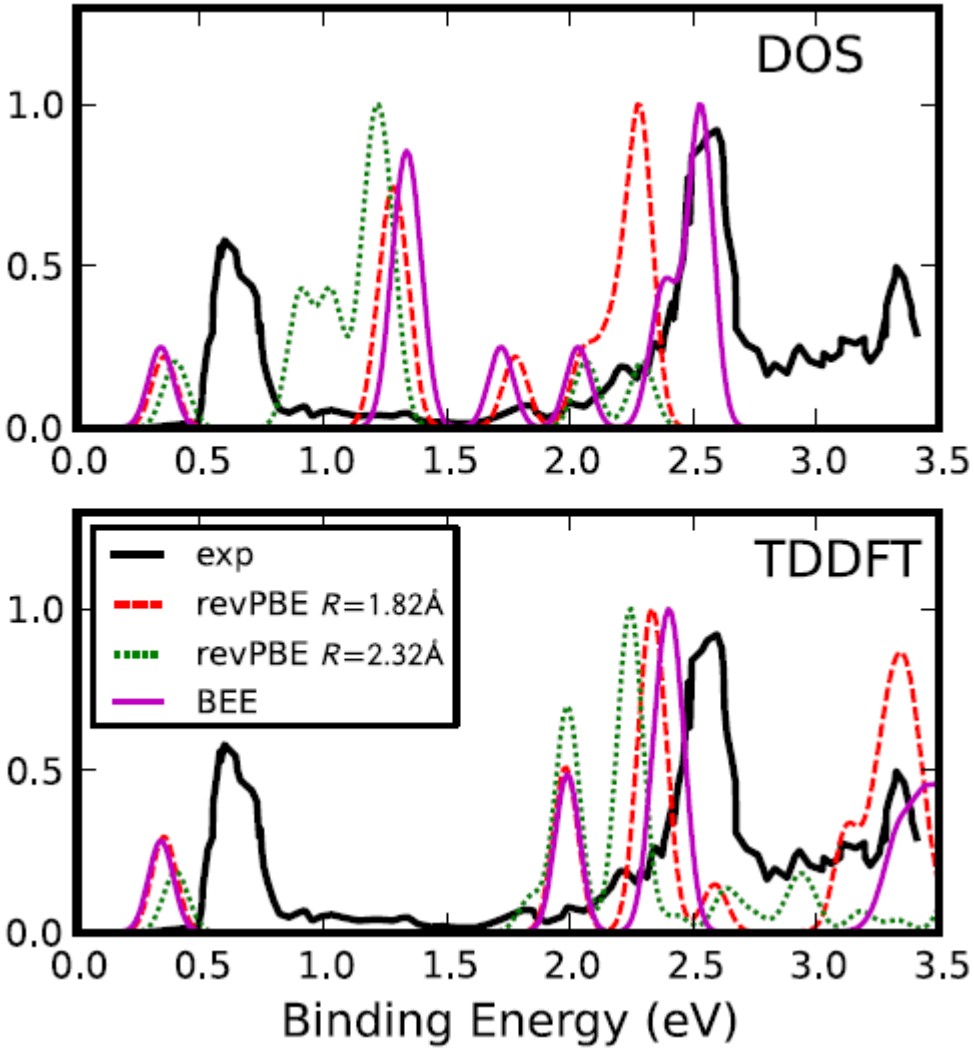


$$E_B = E^{N-1} - E_0^N$$

Valence: E^{N-1} from TDDFT

Walter and Häkkinen *NJP* **10** (2008) 043018

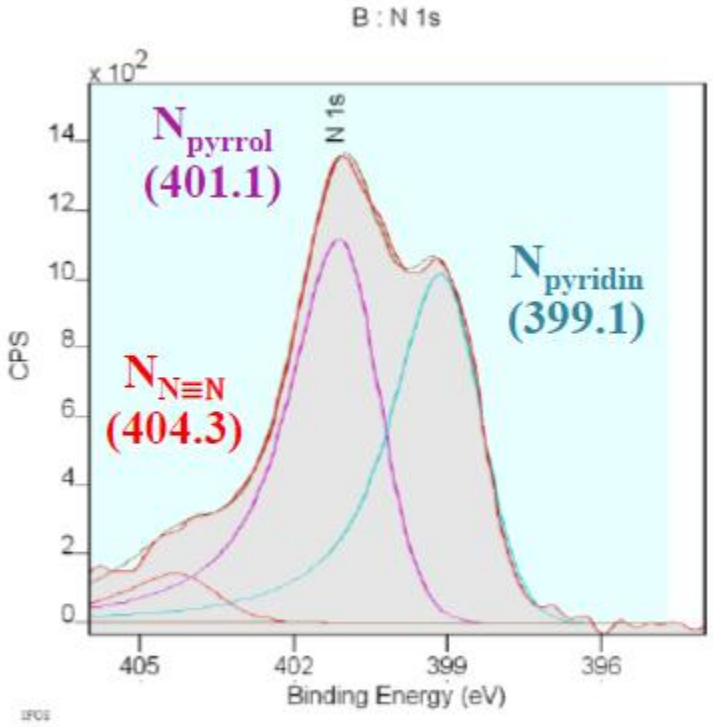
Valence photoelectron spectra: Cr_2^-

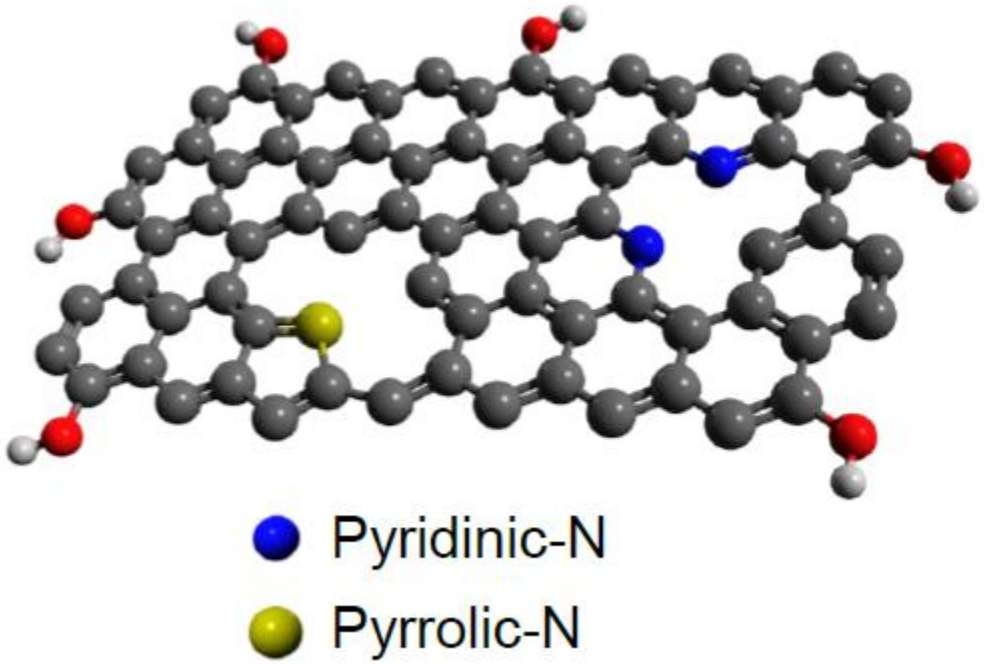


Implementation:
Henrik H. Kristoffersen

Würdemann et al.
JCP **142** (2015) 124316

Ubiquitous X-ray investigations



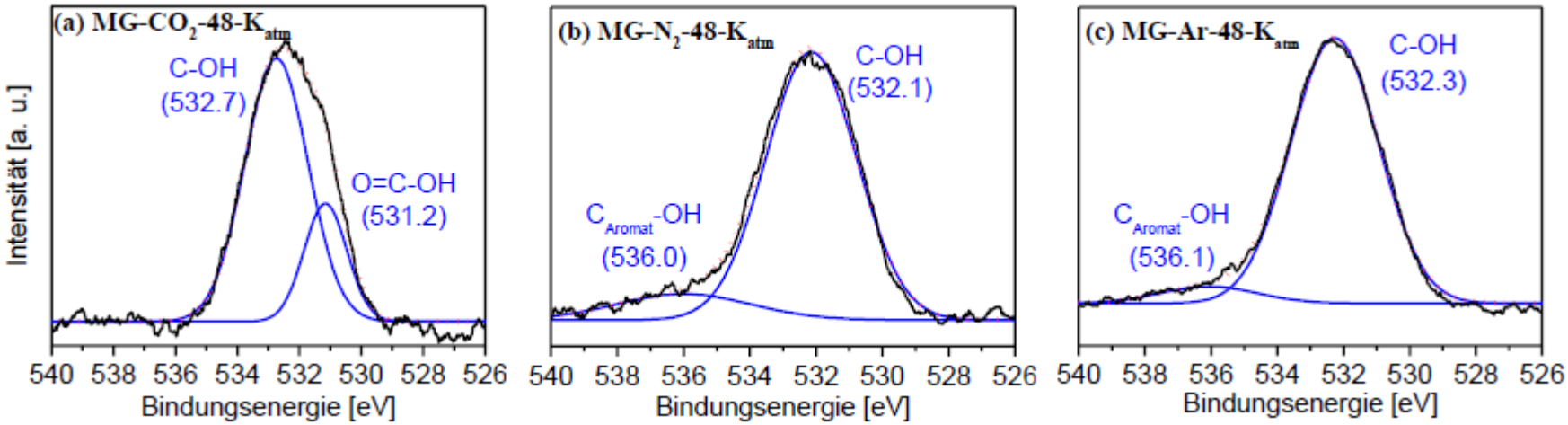


Dissertation Fabian Beckert (2014) University of Freiburg

Assignment not always clear

Grinded graphite under

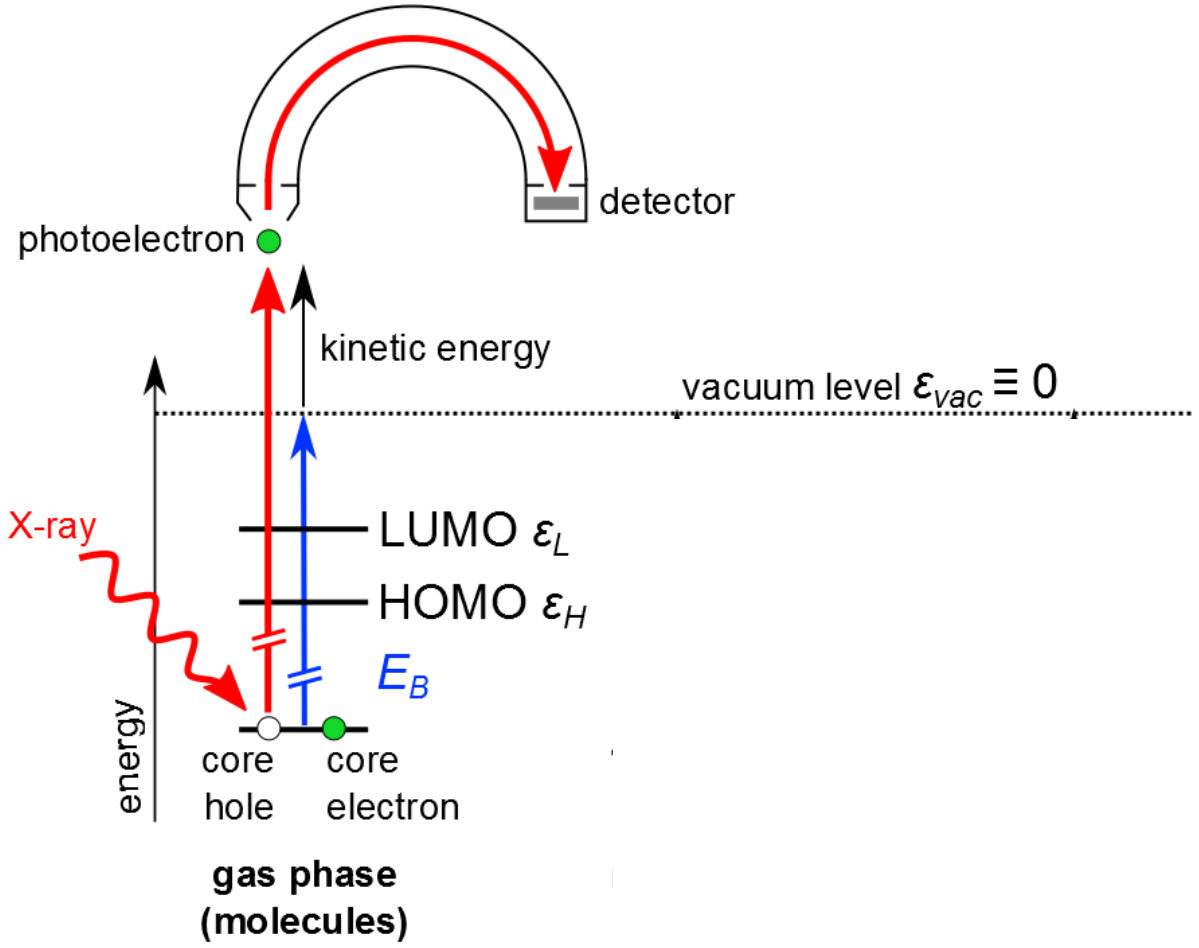
CO_2 N_2 Ar



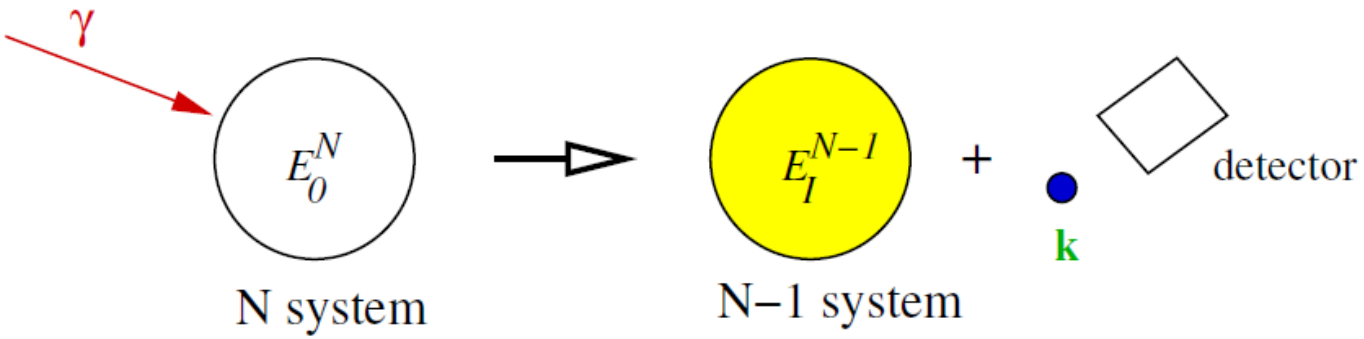
532.7 eV **532.1 eV** **532.3 eV**

Dissertation Fabian Beckert (2014) University of Freiburg

Energy considerations: molecules



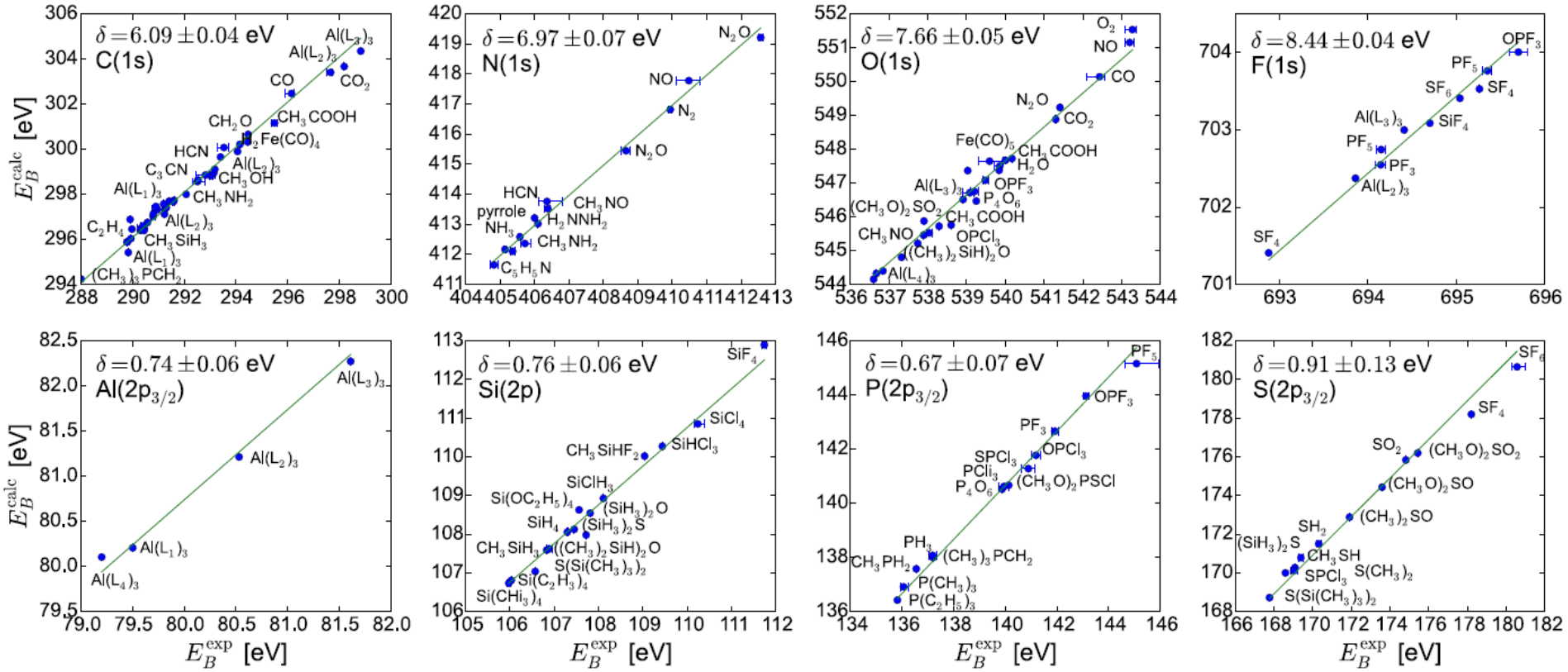
Many particle viewpoint



$$E_B = E^{N-1} - E_0^N$$

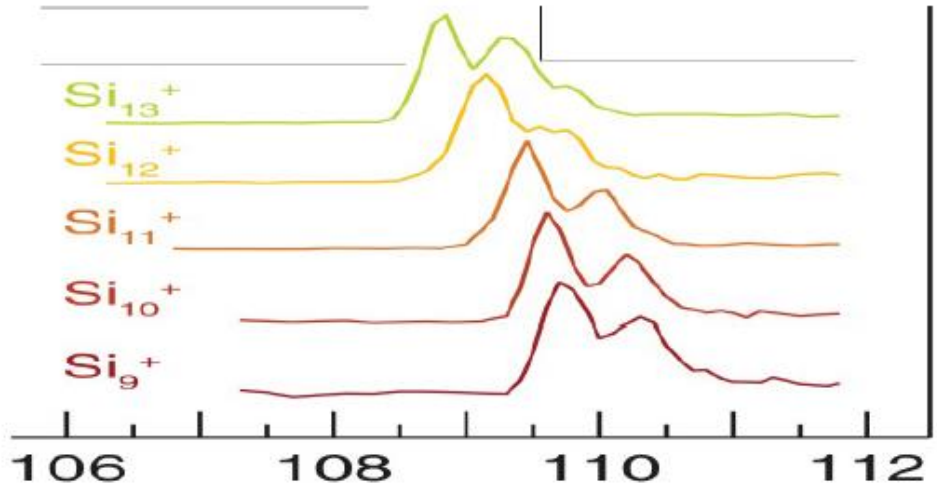
Core: $E^{N-1} \approx E[n - n_{\mathrm{ch}}]$

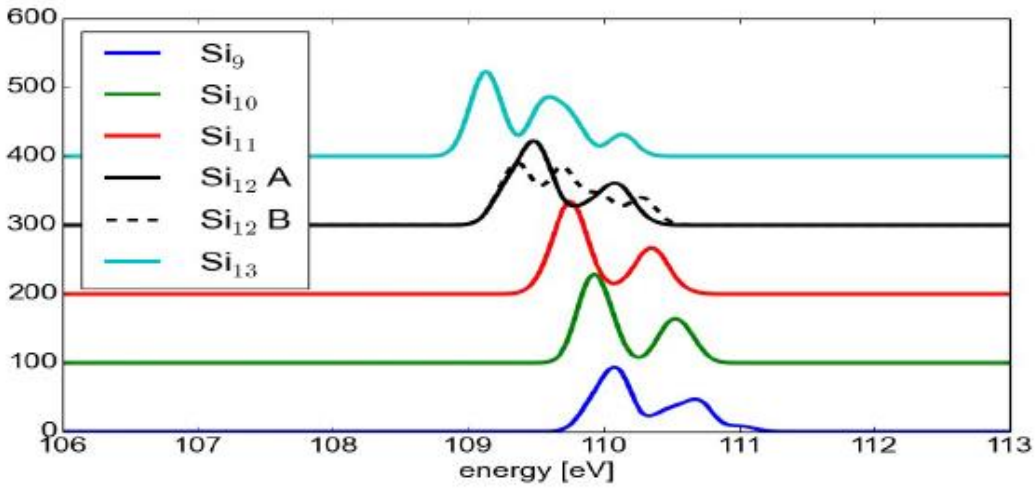
Molecular XPS spectra



=> empirical shift δ(corehole state, xc)

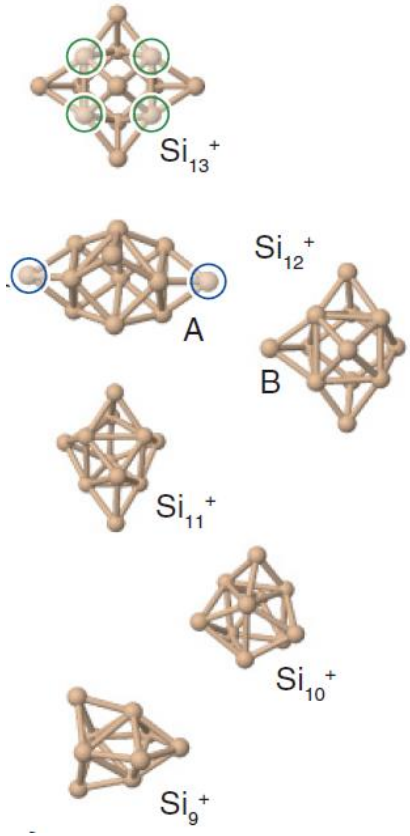
Cationic Si clusters in gas-phase



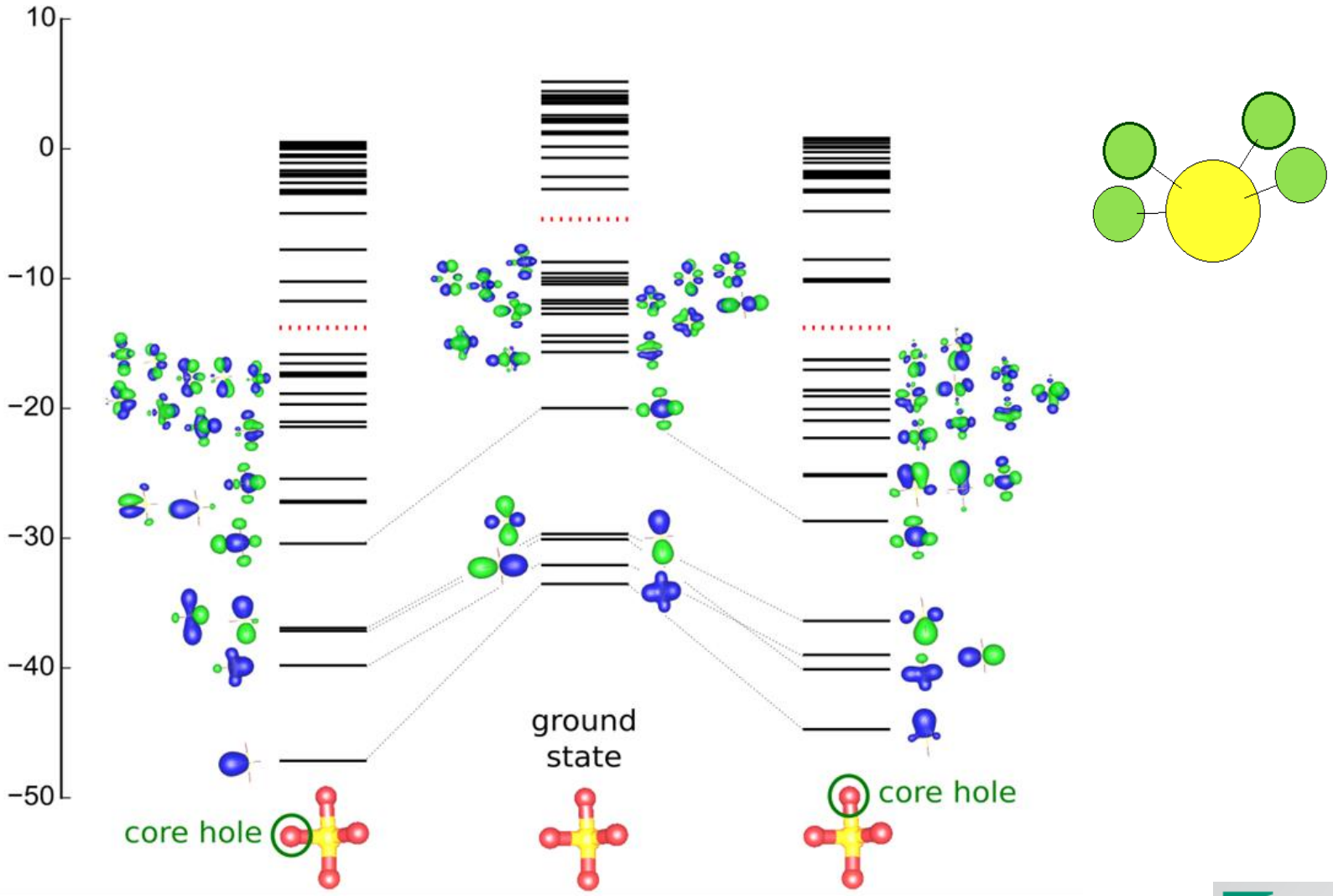


Experiment

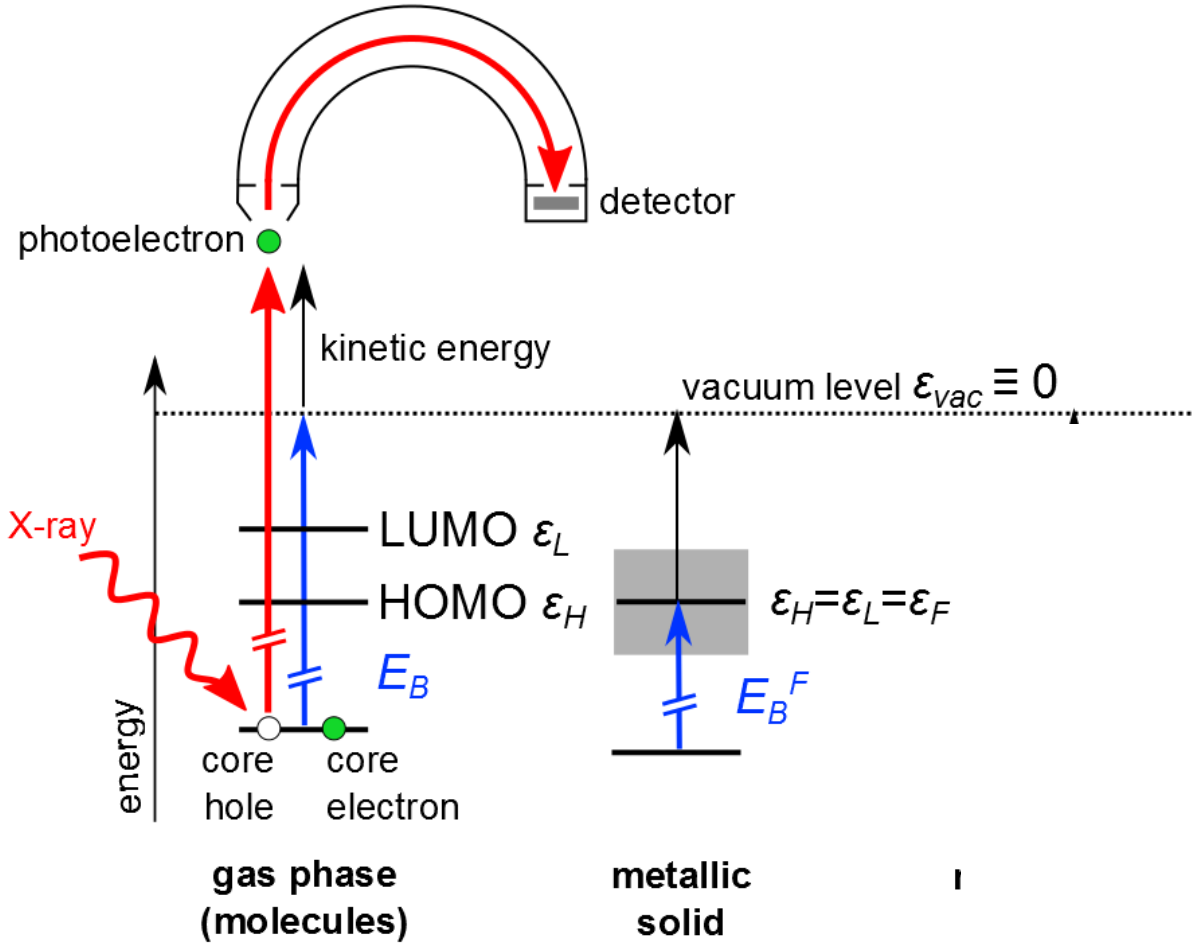
Vogel et al PRB 85



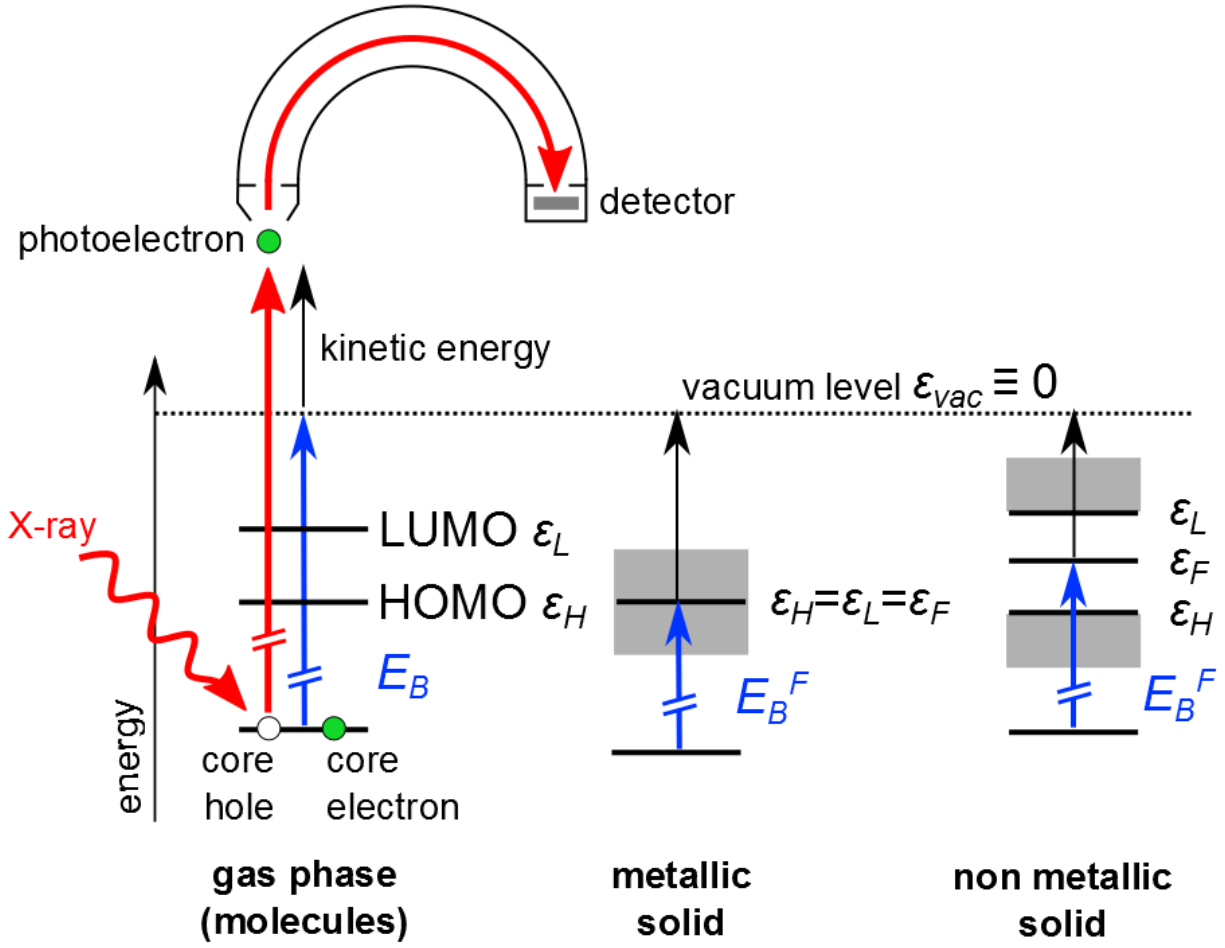
Effect on the valence: SF_4



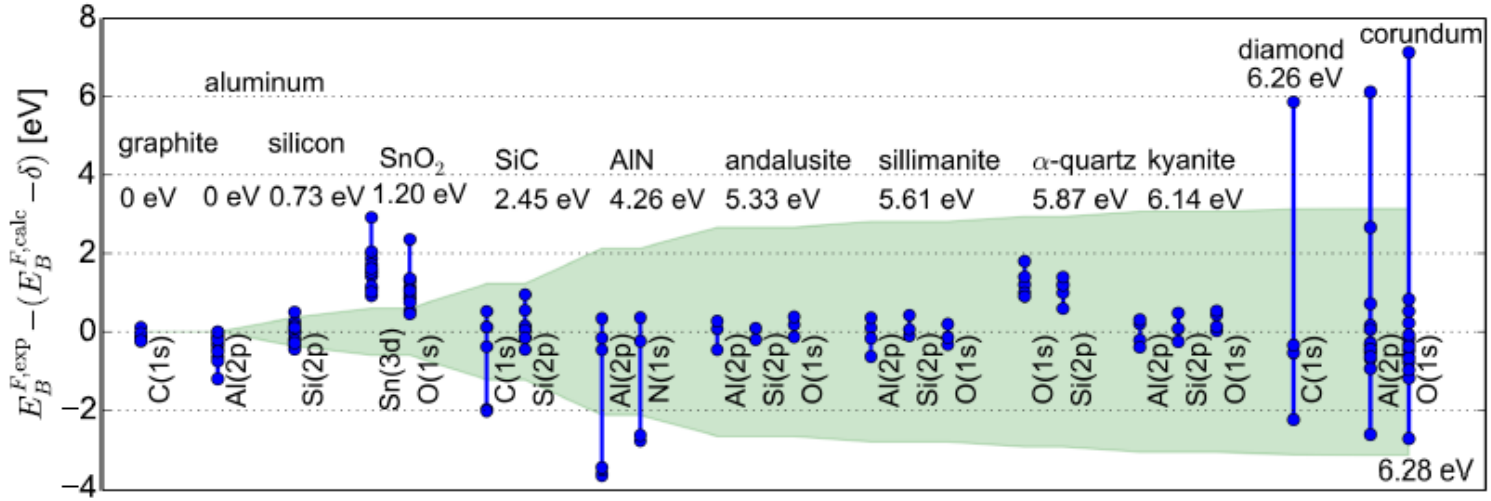
Energy considerations: metals



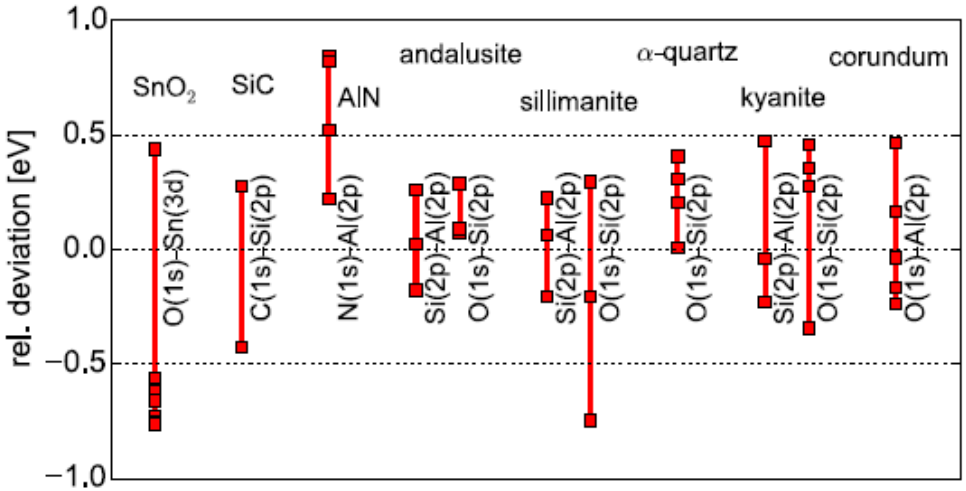
Energy considerations: non-metals



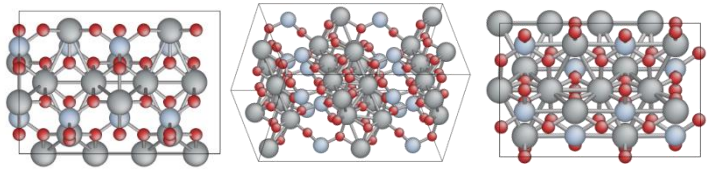
Absolute XPS of solids



$$\varepsilon_F = \frac{\varepsilon_H + \varepsilon_L}{2}$$



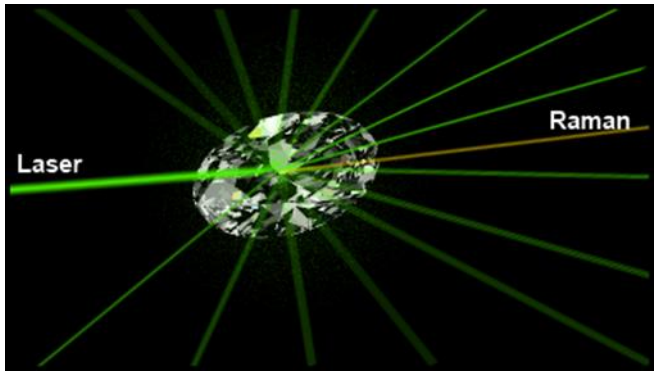
Al_2SiO_5

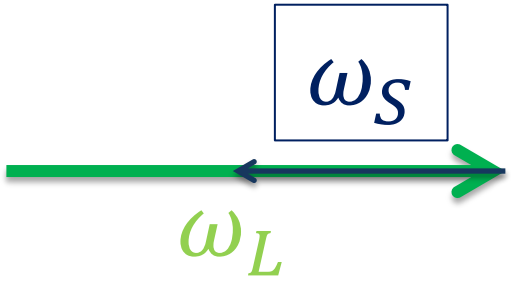


andalusite kyanite silimanite

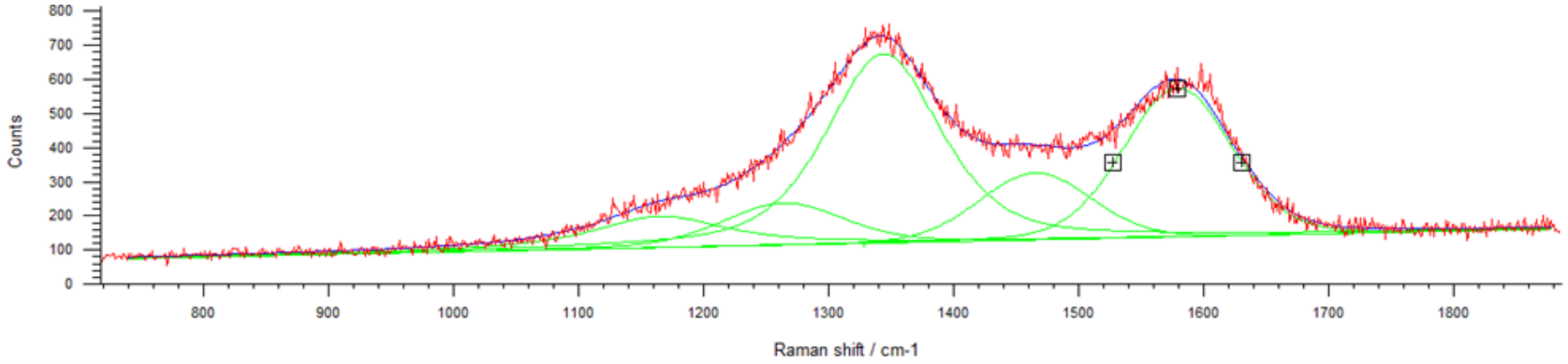
Walter, Moseler and Pastewka
http://arxiv.org/abs/1511.06610

Raman spectra





Vibrational excitation: $\omega_v = \omega_L - \omega_S$



2nd order process

Count rate

$$I \sim \omega^4 |V_{FI}|^2$$

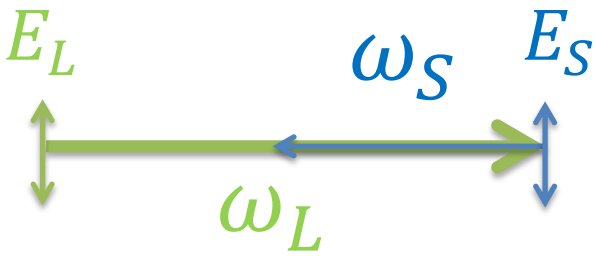
Matrix element (Kramers, Heisenberg, Dirac)

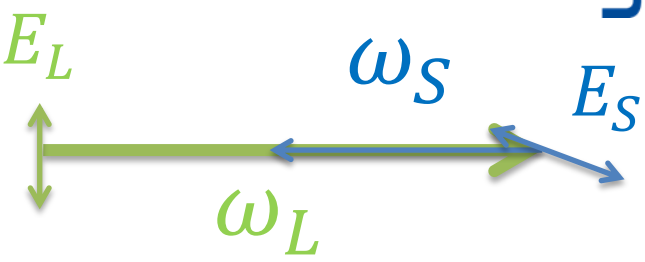
$$V_{FI} = \sum_{K \neq I} \left(\frac{< F|\boldsymbol{u}_S \cdot \boldsymbol{D}|K >< K|\boldsymbol{u}_L \cdot \boldsymbol{D}|I >}{E_I + \omega_L - E_K} + \frac{< F|\boldsymbol{u}_L \cdot \boldsymbol{D}|K >< K|\boldsymbol{u}_S \cdot \boldsymbol{D}|I >}{E_I - E_K - \omega_S} \right)$$

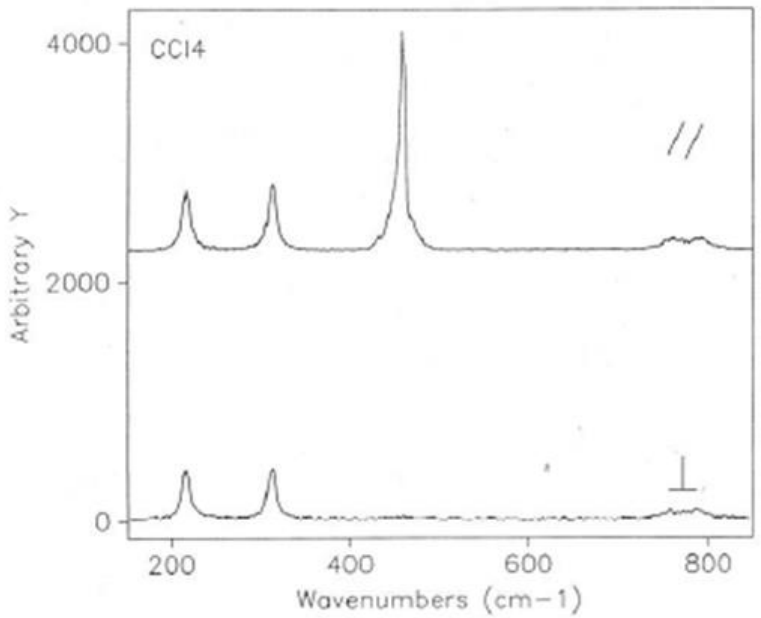
Separation of electronic and nuclear terms

$$\langle I|\boldsymbol{u} \cdot \boldsymbol{D}|K\rangle = \langle 0,0|f_u^e(\boldsymbol{R})|e,k\rangle$$

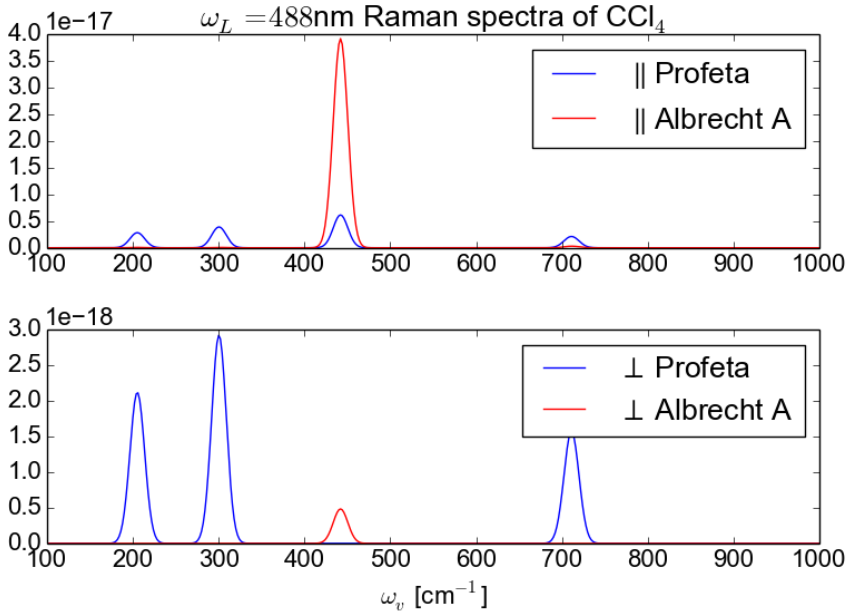
Non-resonant Raman spectra: CCl_4



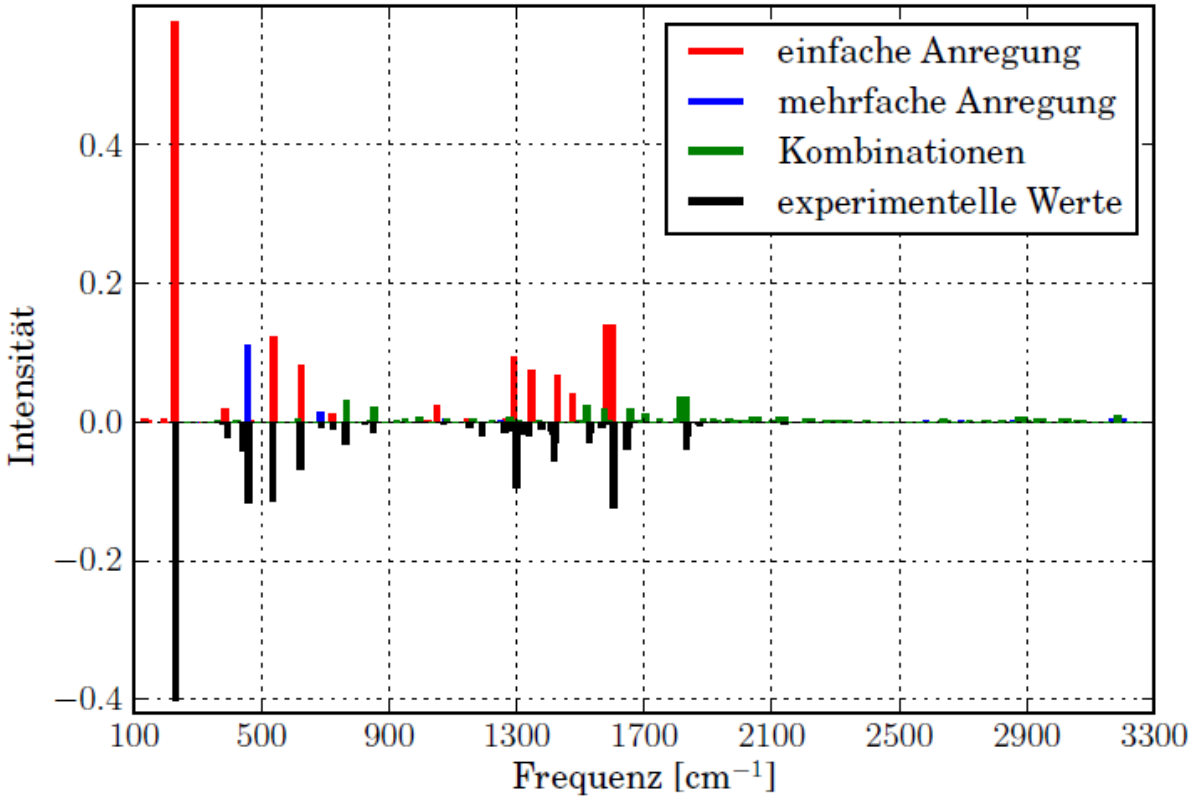


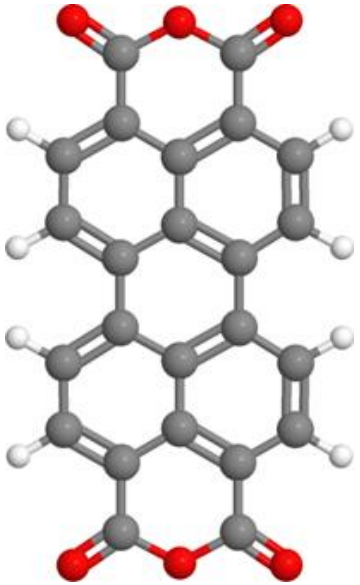


J Chem. Edu. **69**, 803 (1992)



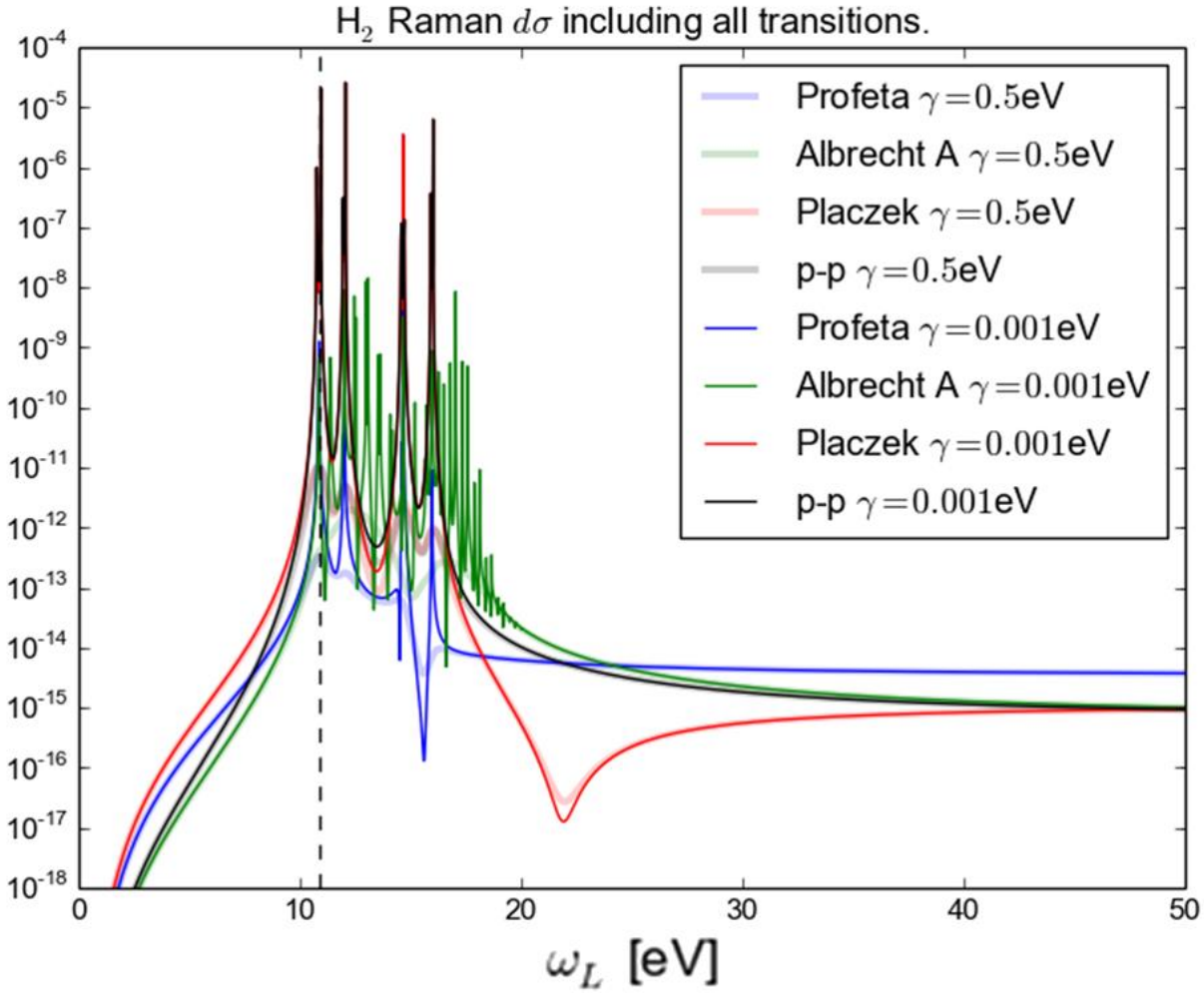
On resonance with single excitation



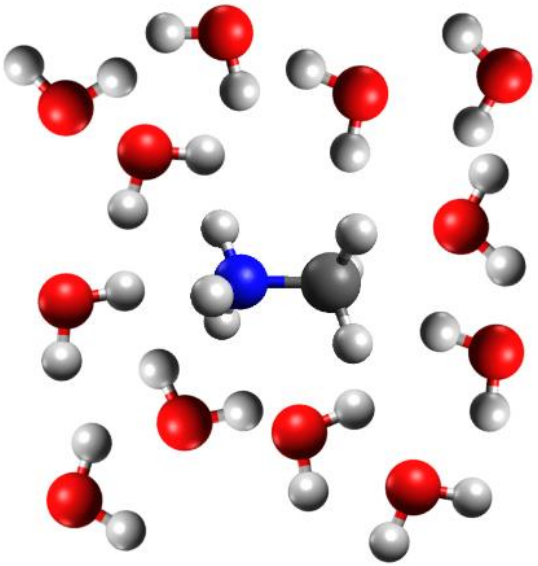


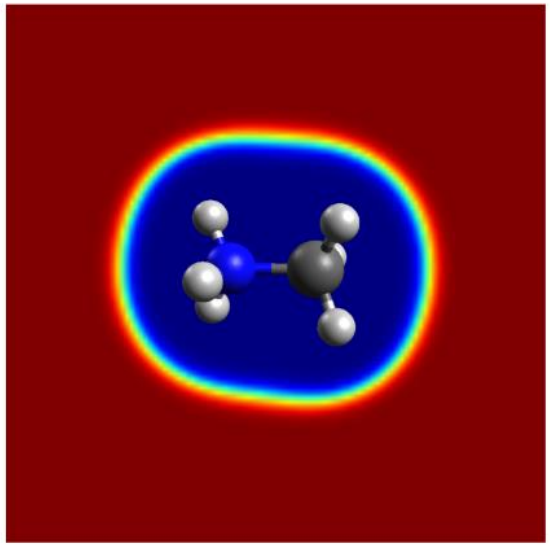
R. v. Waldenfels, experiment: Wewer and Stinkemeier *JCP* (2004)

(Resonant) Raman spectra: H_2



Polarizable contiuum (PCM)

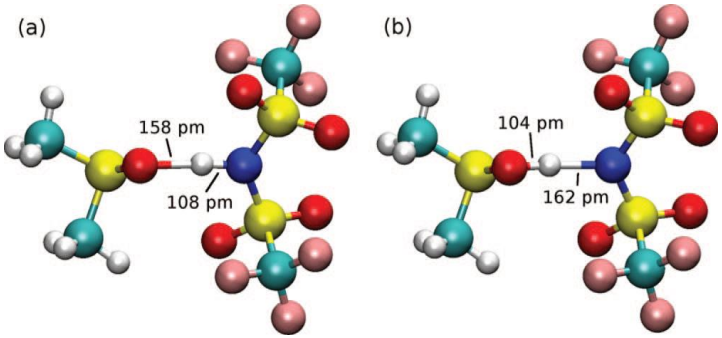


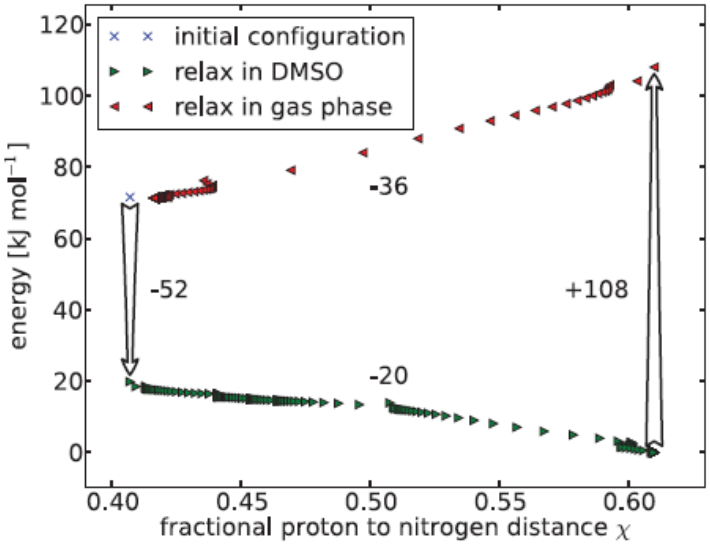


A. Held and M. W. *J. Chem. Phys.* **141**, 174108 (2014)

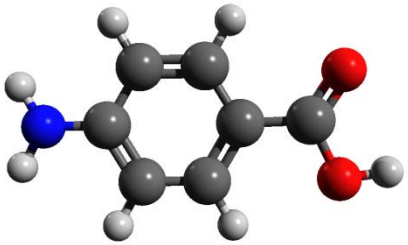
PCM examples

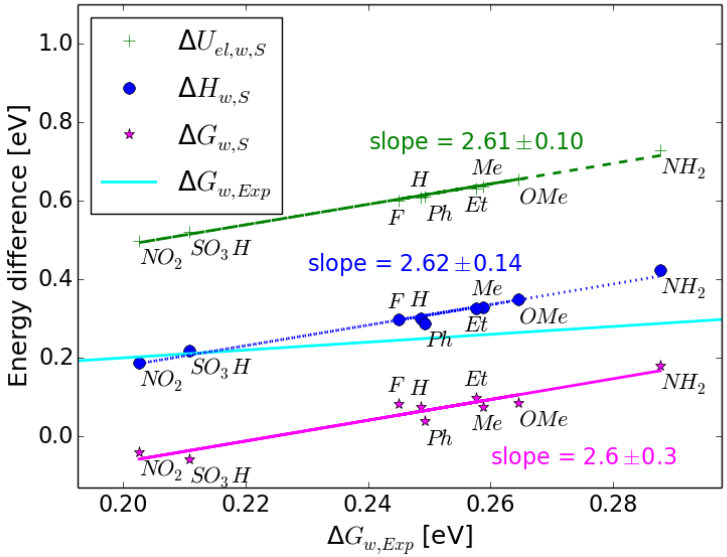
Proton transfer





De-protonation





Conclusions and status

XPS:

- Photoelectron BE = excitation of the ion
- Excellent XPS correlation with experiment
- Empirical shift δ(corehole state, xc)
- Solids: insufficient defininition of Fermi level
- Solids: relative XPS energies very accurate

Non-resonant Raman works, single resonance is there, mixed case is a challenge

Thanks to

Reyhaneh Ghassemizadeh
charge transfer

Oliver Stauffert
Triplets,
van der Waals

Thomas Reichenbach
catalysis

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Hannu Häkkinen

DTU
JJ Mortensen
Ask Larsen

Freiburg Uni/IWM
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Oliver Brügner