

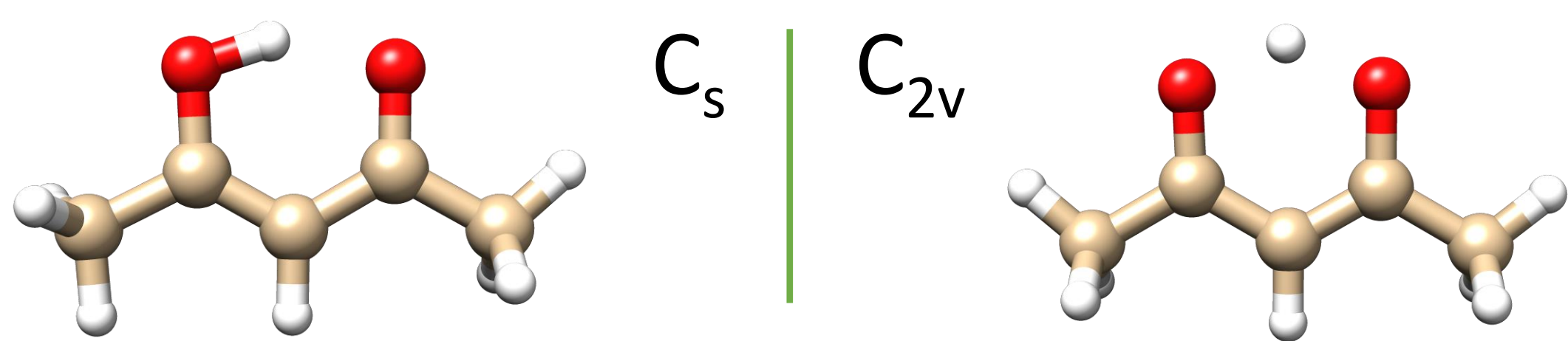


# Proton in a double-well potential: acetylaceton derivatives by microwave and core level spectroscopy

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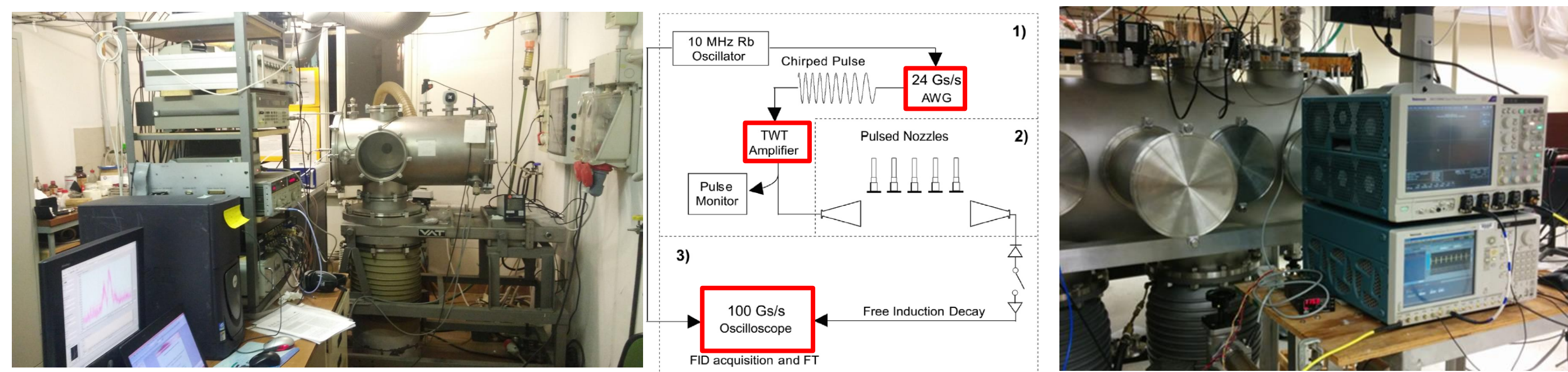
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## Prototype system: Acetylaceton\*



Computational modeling of molecules always requires some approximations, and nuclear motion is commonly described by molecular dynamics with the assumptions of the Born–Oppenheimer approximation and classical behavior. This is at the cost of neglecting the quantum mechanical nature of HB, particularly nuclear quantum effects, which we show may be of crucial importance. The molecular systems chosen here allow us to examine this aspect and to give a full description of quantum effects in intramolecular HB.

## Microwave spectroscopy Methods



### Molecular Beam Fourier Transform Microwave Spectroscopy (MB-FTMW) in Bologna

Range: 6-18 GHz; Sweep rate: 0.2 GHz per day; Sensitivity:  $10^{-11}$ - $10^{-12}$ ; Resolution: few kHz  
Accuracy of frequency measurements < 0.003 MHz.

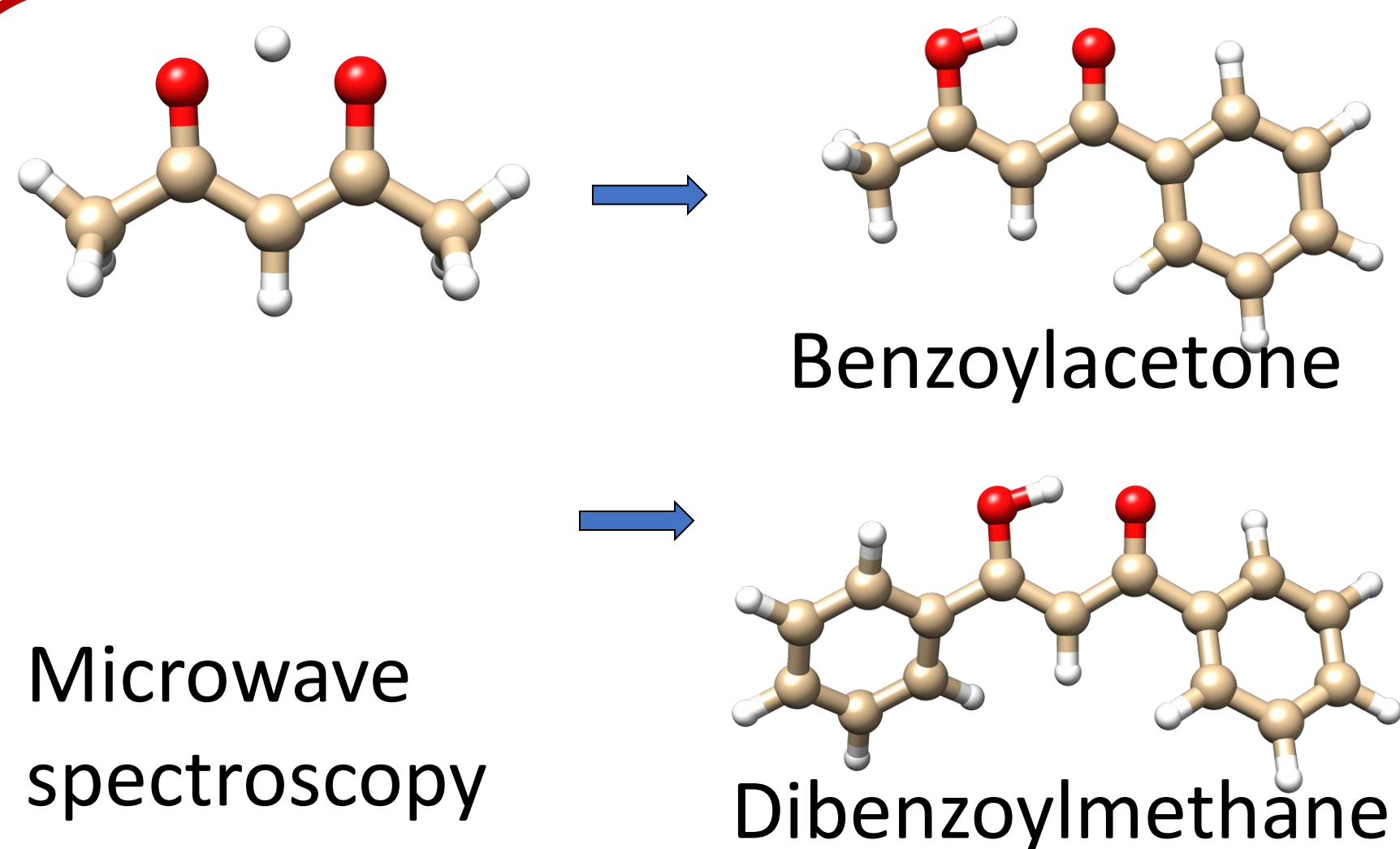
### CPFTMW in University of Virginia (Prof. B.H. Pate Lab)

Spectra measured using broadband chirped pulse excitation to measure 6 GHz of instantaneous bandwidth. Typical spectrum at >1000:1 S/N (99.9% diastereomer purity) in ~12 hours

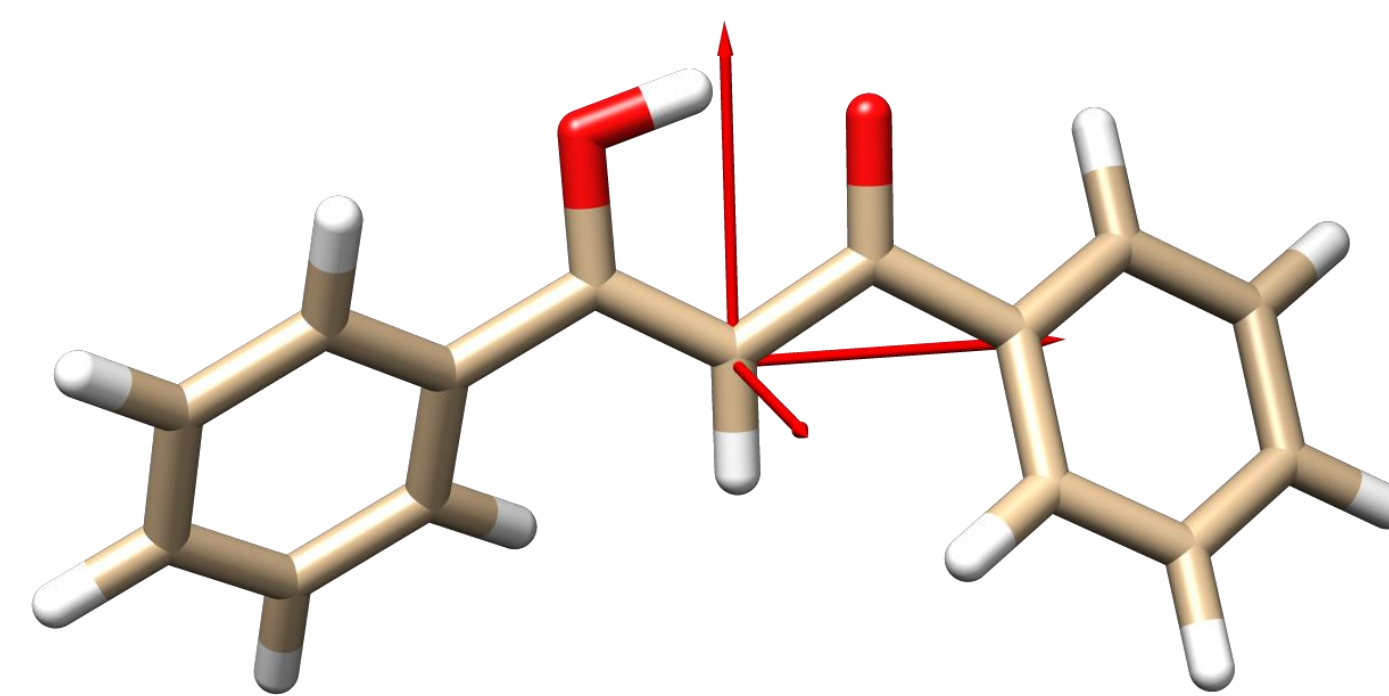
### Theoretical calculations

Quantum mechanical calculations were performed to predict the relative energies of plausible conformations and the molecular properties relevant to the interpretation of the rotational spectra. The Gaussian16 package of programs was used.

## Acetylaceton derivatives

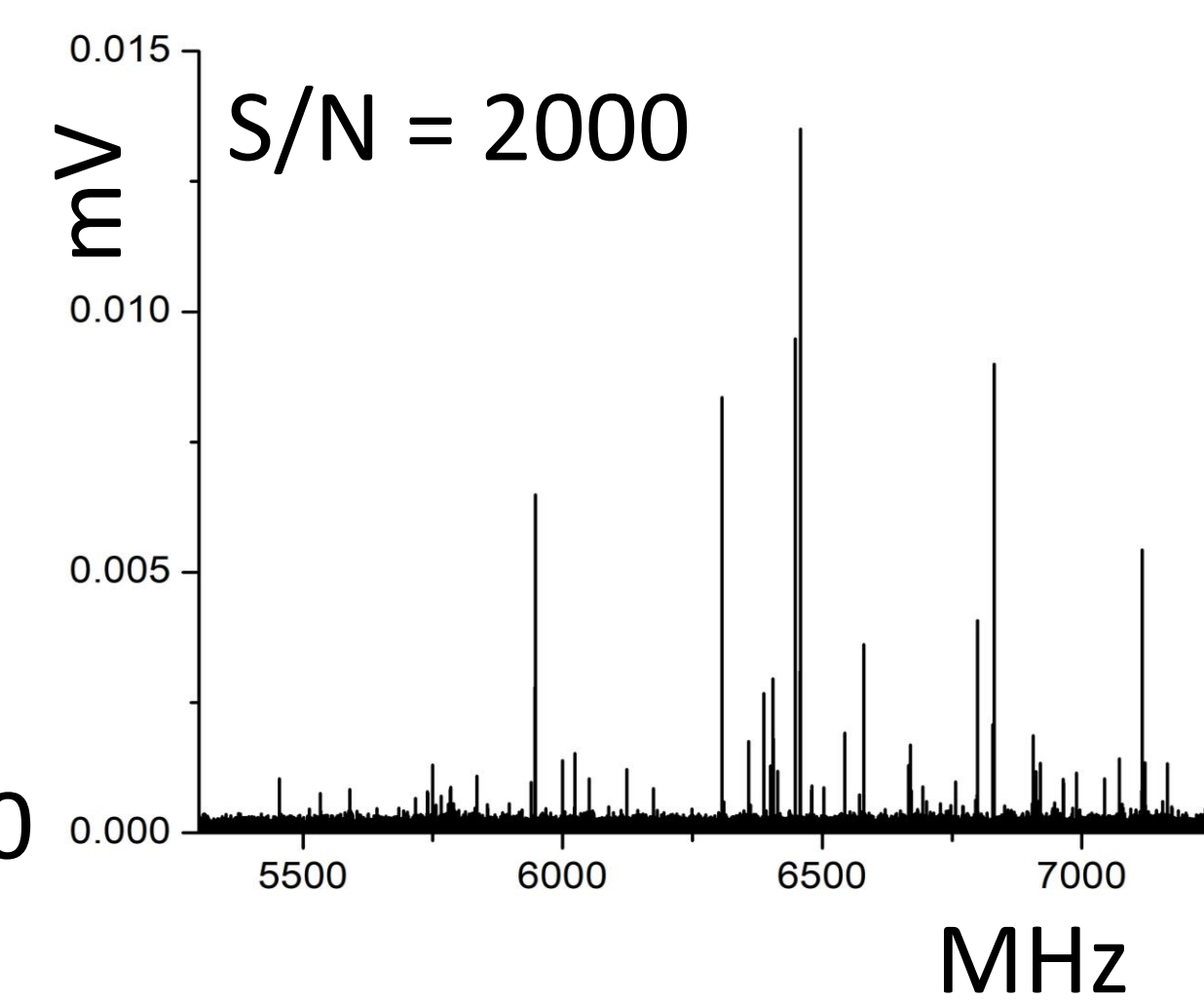


Microwave spectroscopy



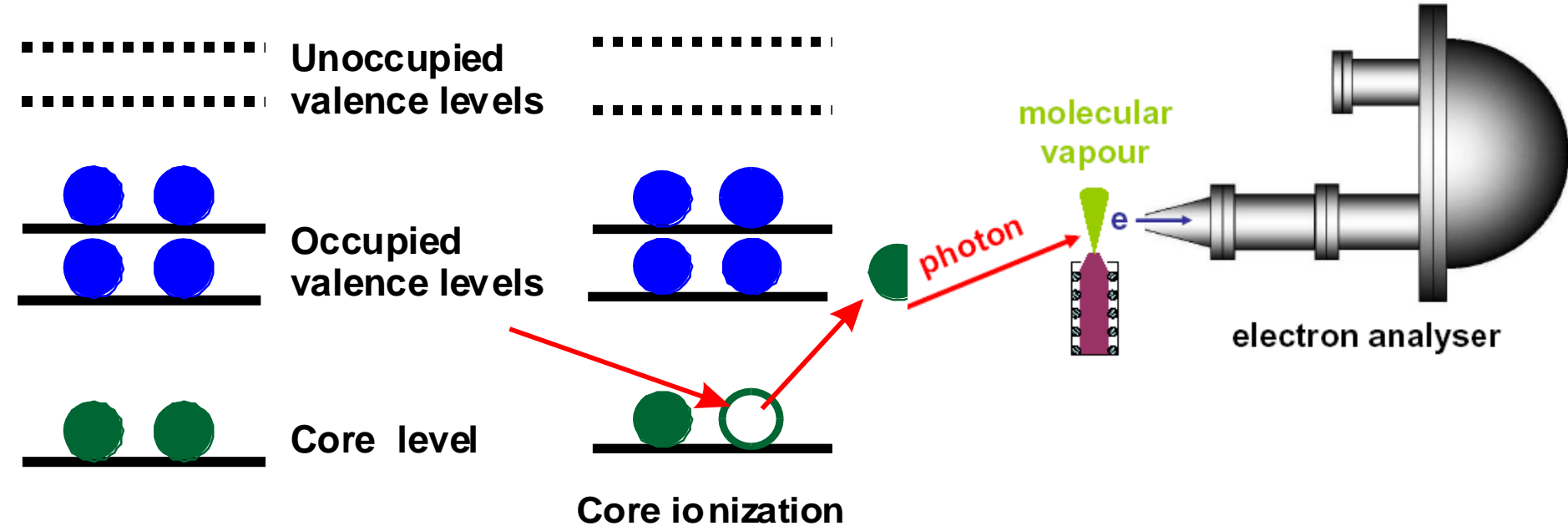
$C_{2v}$ :  
 $\mu_b$  strong and  $\mu_a = \mu_c = 0$   
7 pairs of equivalent  $^{13}C$

$C_s$ :  
 $\mu_b \gg \mu_a$  and  $\mu_c = 0$   
15 different  $^{13}C$

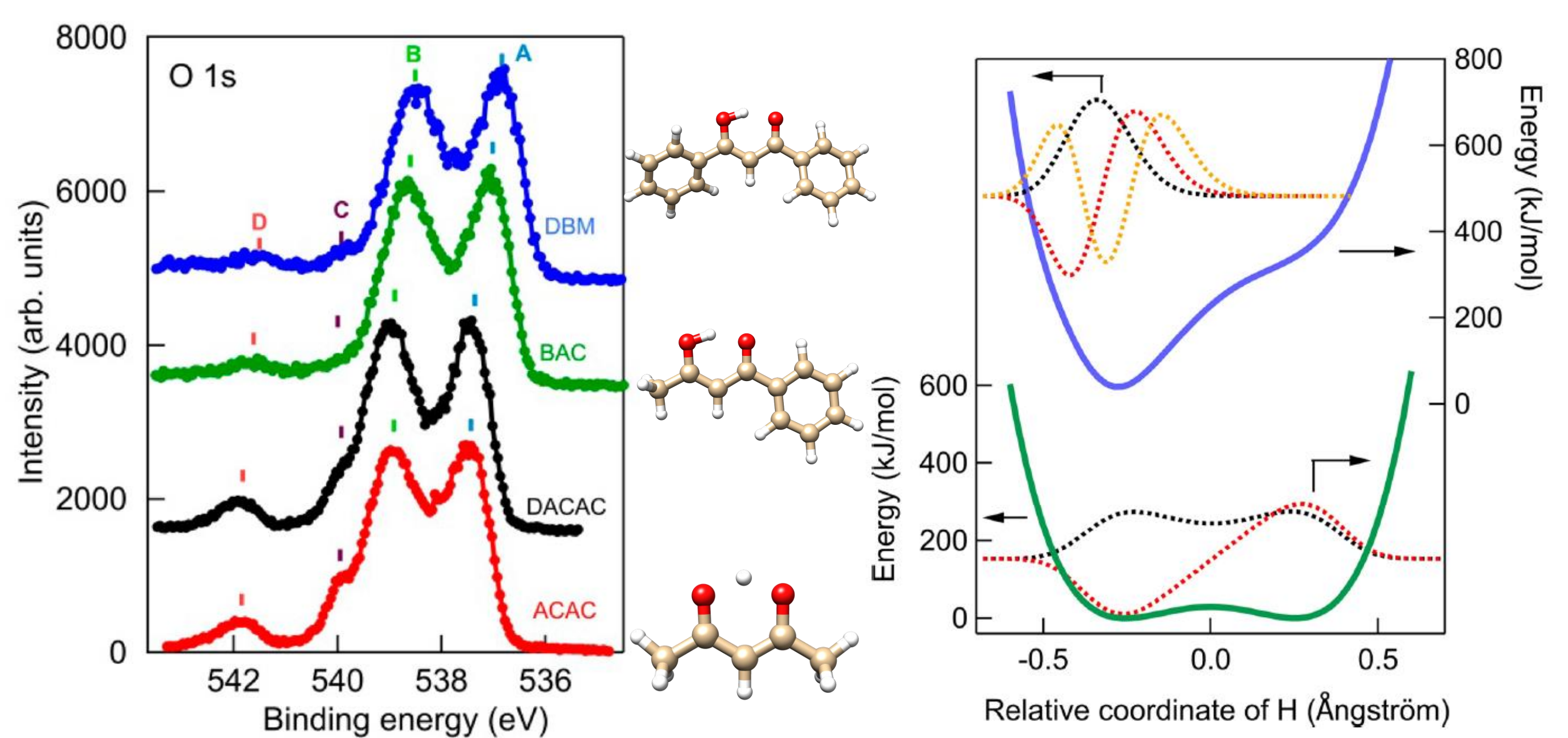


## XPS

Photoelectric effect:  $h\nu = E_B + E_K$



- Advantages:
- chemical shifts;
  - the peak intensities (areas) directly reflect population;
  - thermal equilibrium;

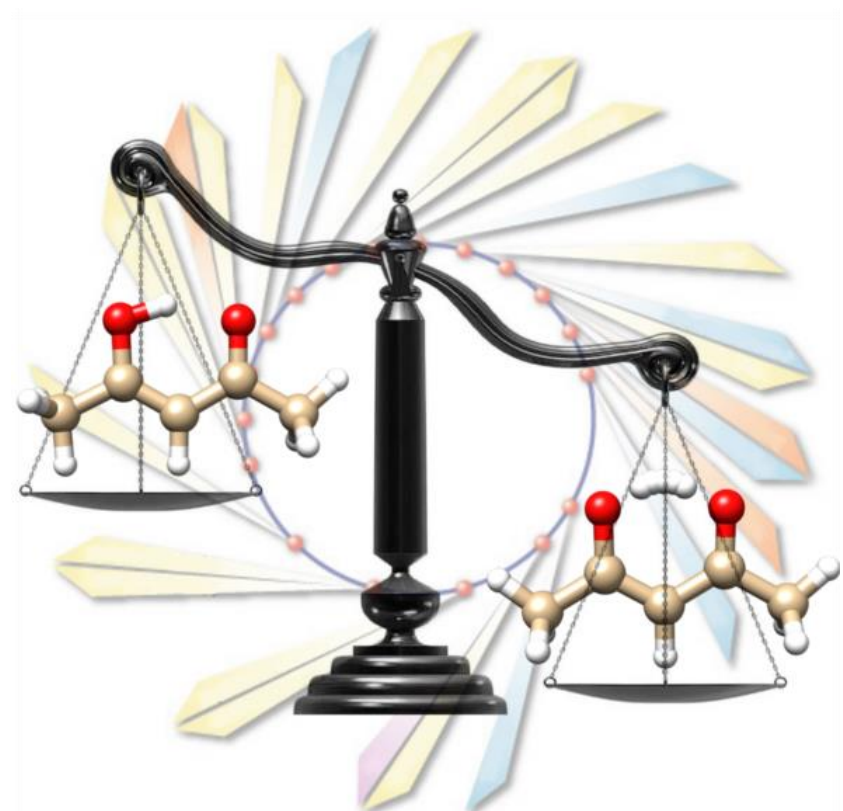


Two distinct O1s core hole peaks are observed, previously assigned to two chemical states of oxygen. We provide an alternative assignment of the double-peak structure of O1s spectra by taking full account of the extended nature of the wave function associated with the nuclear motion of the proton, the shape of the ground and final state potentials in which the proton is located.

## Conclusions

Our theoretical calculations suggest that an unusual FC distribution derived from the strongly asymmetric structure of the final state potential, coupled with the delocalization of the proton in the ground state, gives an equally good description for ACAC and a better one for BAC and DBM spectra.

\*V. Feyer et al. *J. Phys. Chem. Lett.* 2018, 9, 521-526



Elettra Sincrotrone Trieste

