

chiral molecule (R,L)
& chiral solvent (r,l)
R-r R-l L-r L-l

Questions

chiral recognition

potential energy surface
binding energy, stability, reactivity
geometry & binding site
isomers
electronic structure (excitation, ionisation)
functional groups
solvation

Tools

cluster sources

electron impact & discharge
laser desorption
electrospray

IR & UV-vis spectroscopy (ns)

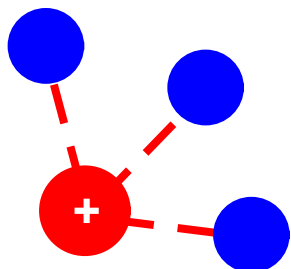
photodissociation
photoionisation
electron detachment
double resonance (isomers)

tandem mass spectrometry

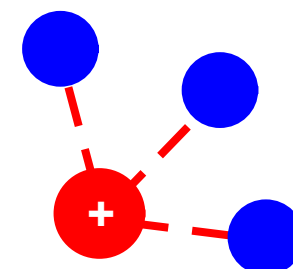
multipoles (quadrupole, octopole, 22-pole)
ReTOF
composition, stability & reactivity

quantum chemistry

ab initio (HF, MP2, CASPT2, ri-CC2, ...)
density functional theory (DFT, TD-DFT)

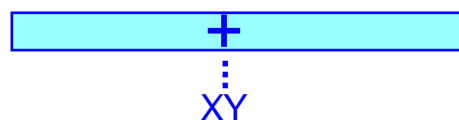


Ion-Ligand Interactions



interfaces

adsorption & catalysis



supramolecular systems

polymers & colloids



solvation

hydration & electrolytes



bio-sciences

molecular recognition



plasma & combustion

formation of soot



planetary atmospheres

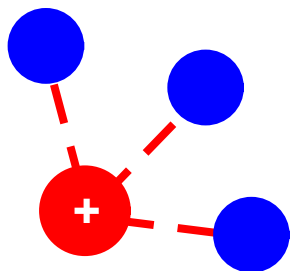
ionosphere



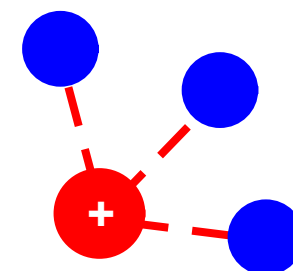
chemical reactions

mechanisms

ion-molecule reactions ($\text{S}_{\text{N}}2$, $\text{S}_{\text{E}}\text{Ar}$, ...)



Ion-Ligand Interactions



Quantum Chemistry
potential energy surface

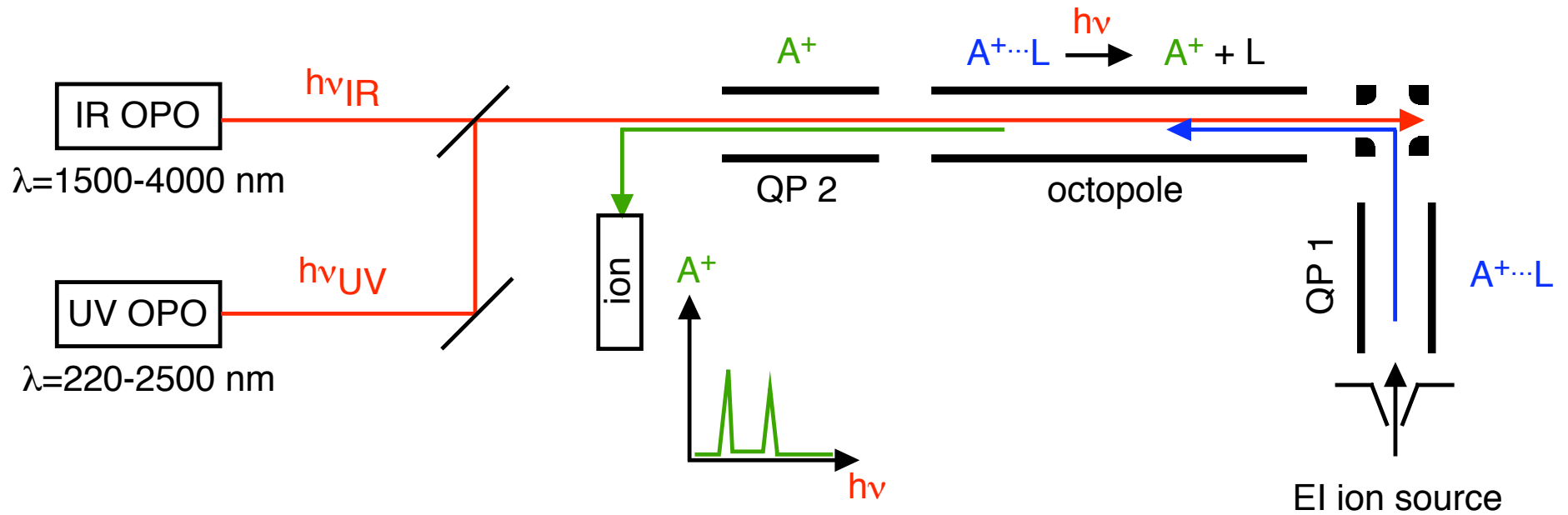
Tools for Potential

Mass Spectrometry
sensitivity & selectivity

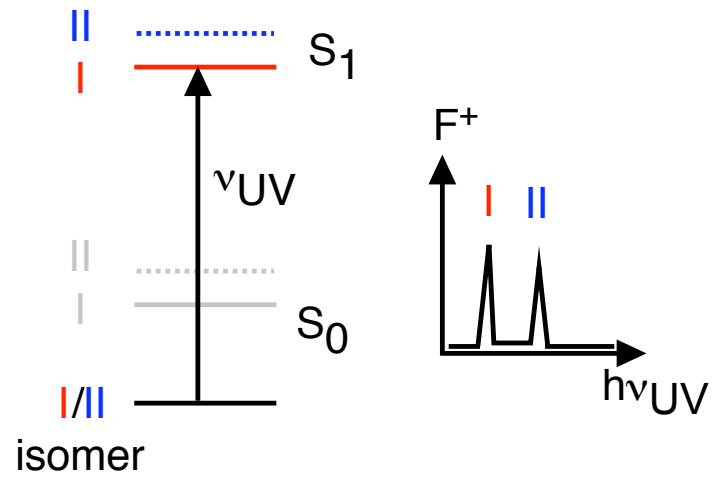
Spectroscopy

structure & dynamics & reactivity

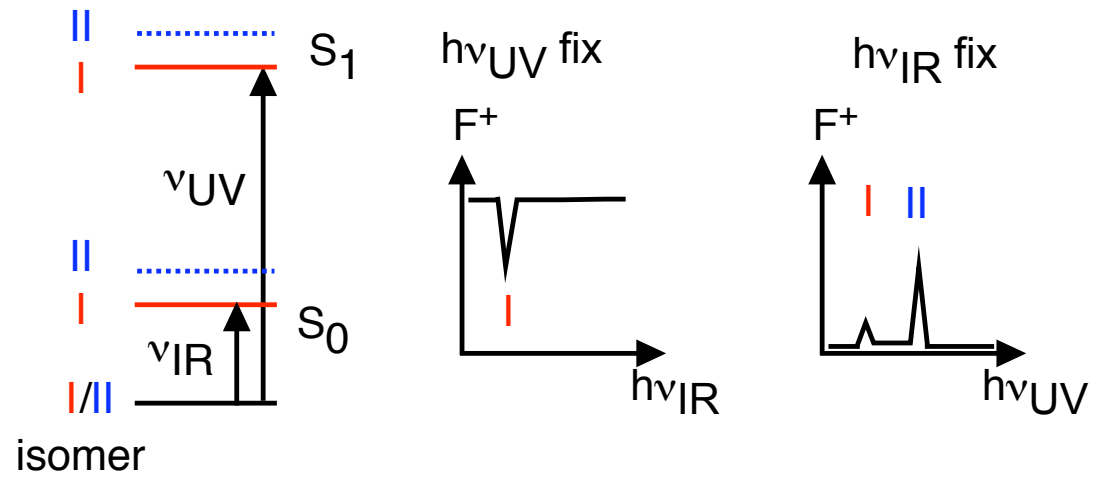
photodissociation in QQQ tandem mass spectrometer



UVPD

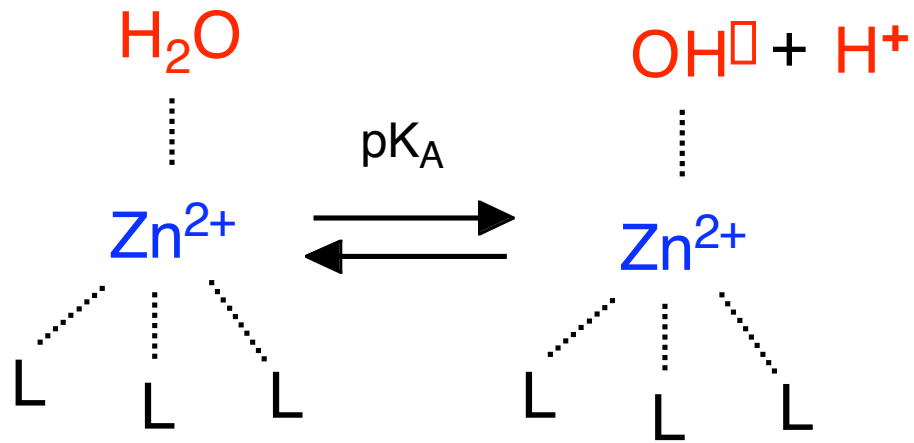


IR-UV und UV-IR double resonance

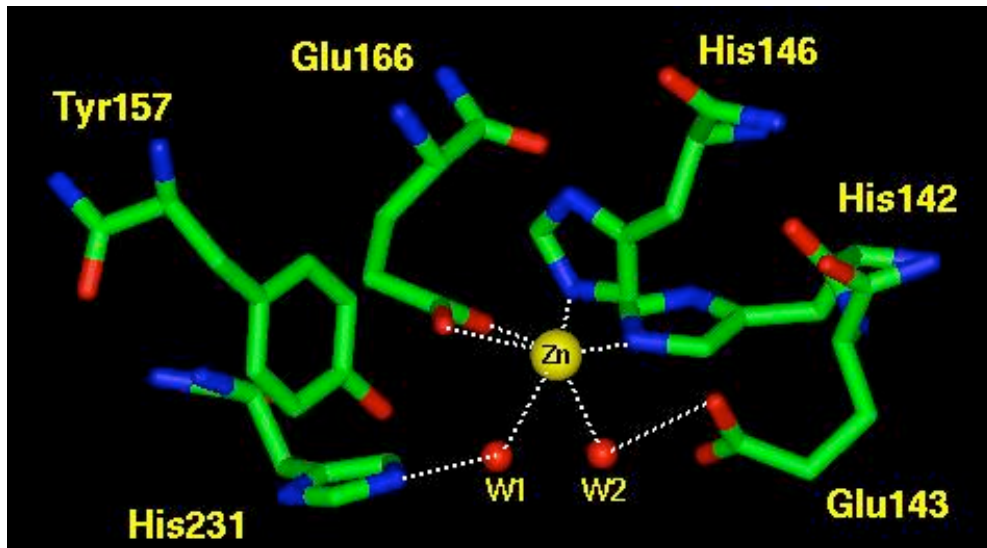


Metal-Catalysis in Biology

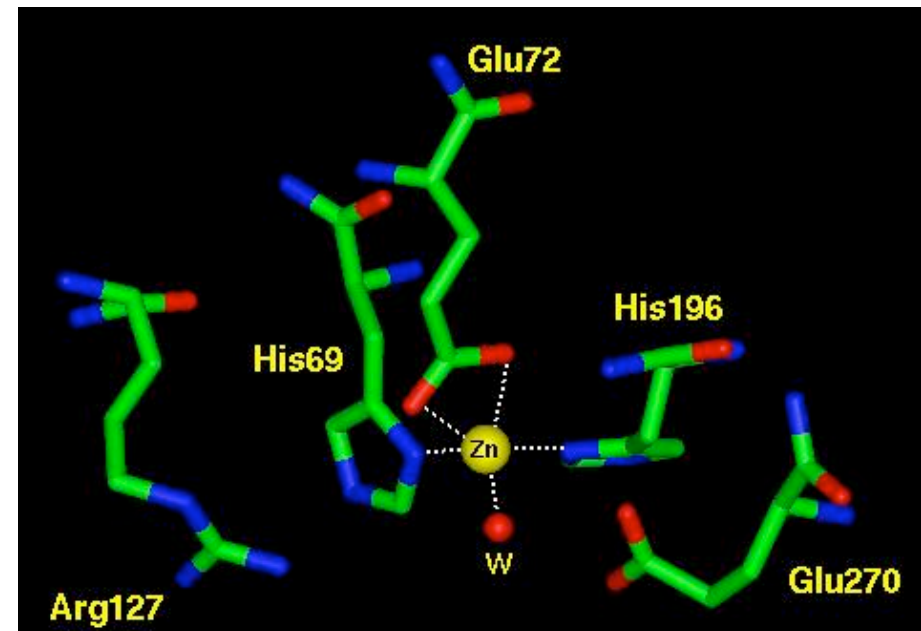
Protonation and Deprotonation



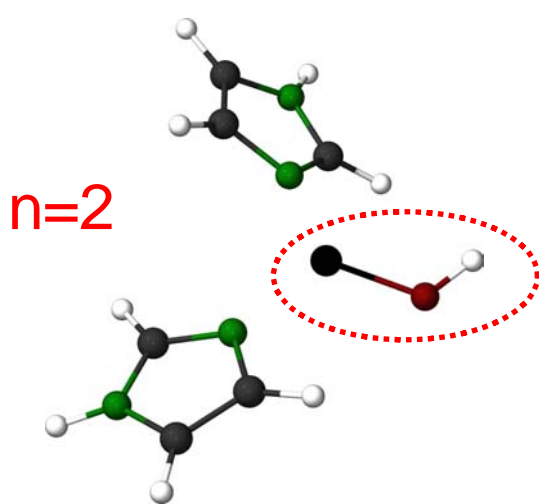
(L = Imidazol, Histidine, ...)



active center in enzyme **Termolysin**

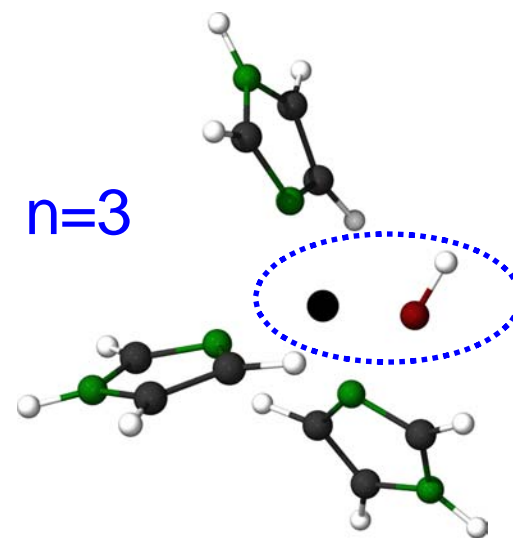


active center in enzyme **Carboxypeptidase A**

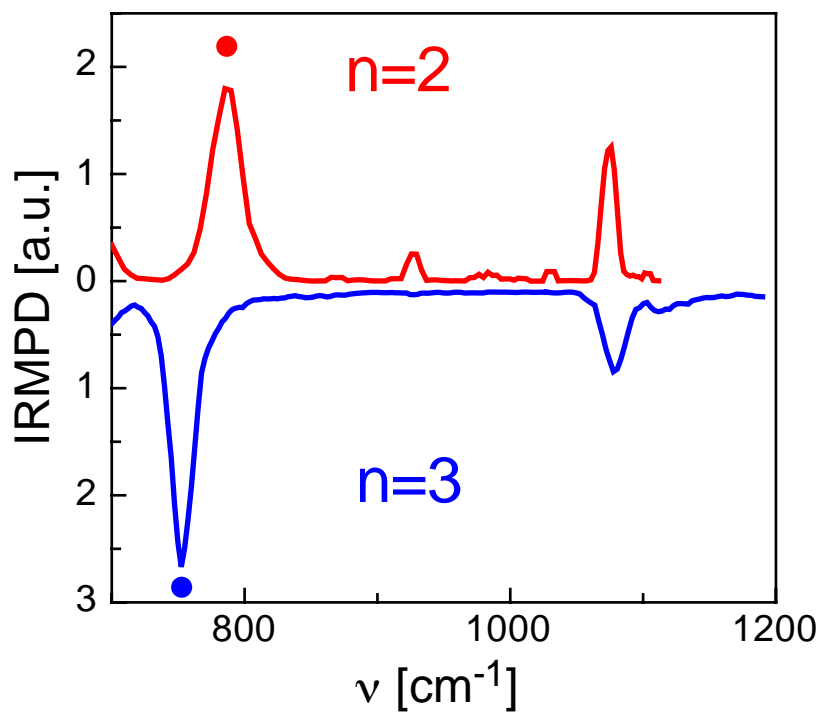


Zn-O-H strongly cluster size dependent

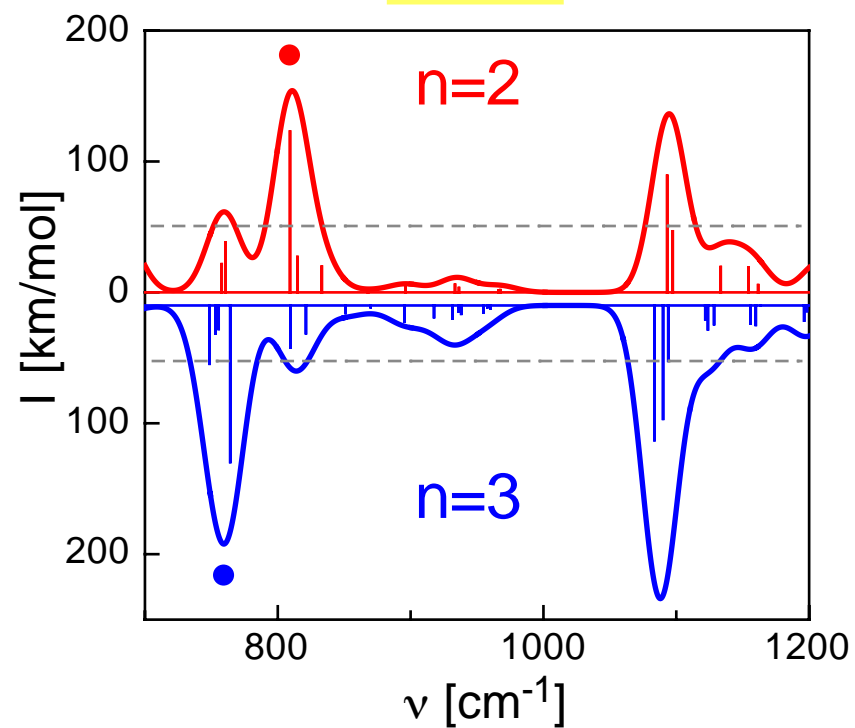
● β_{Zn-O-H}



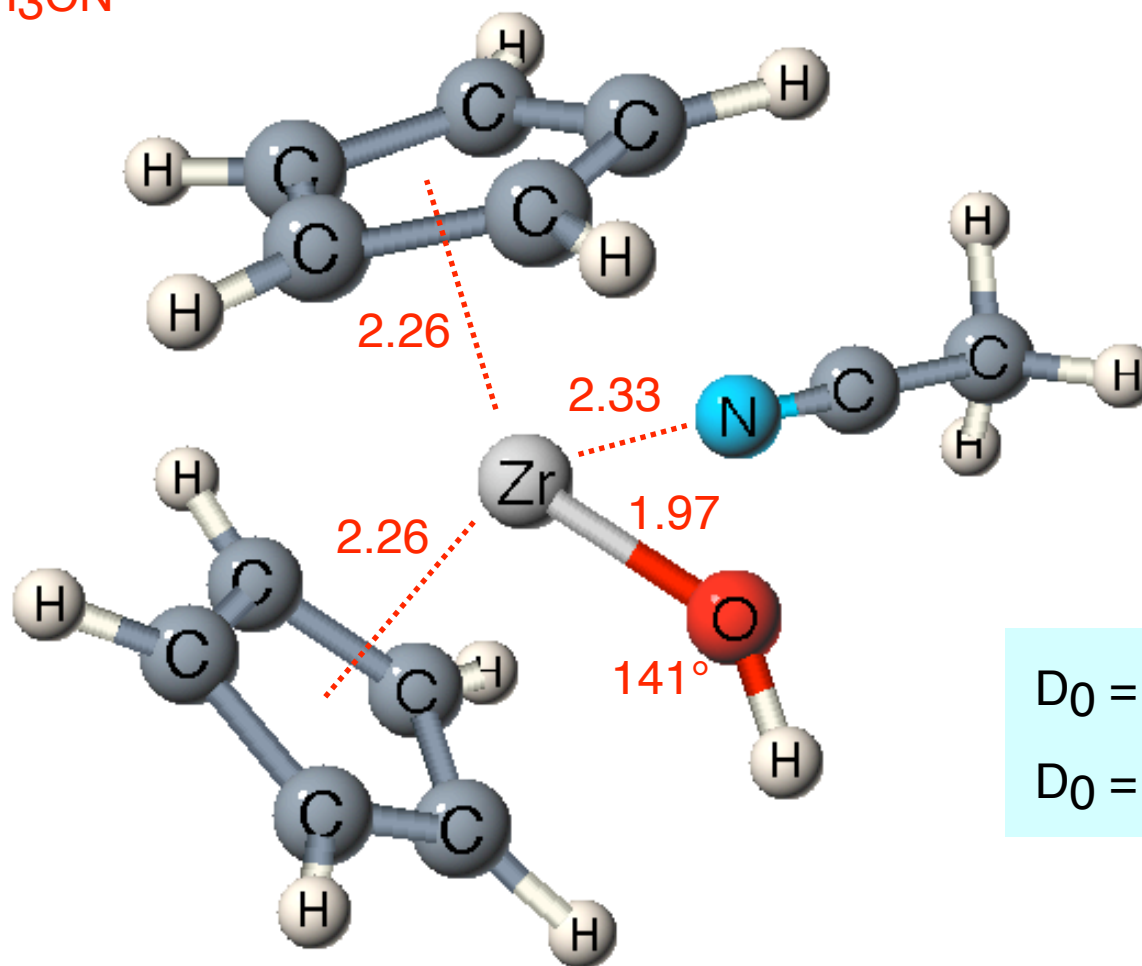
experiment



DFT



Quantum Chemical Results



$D_0 = 417 \text{ kJ/mol (Zr-O)}$

$D_0 = 149 \text{ kJ/mol (Zr-N)}$

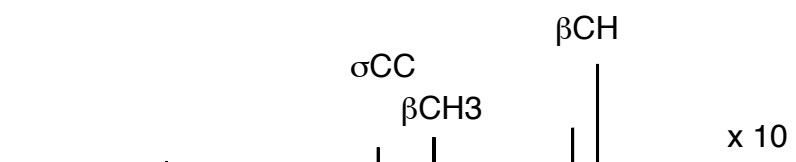
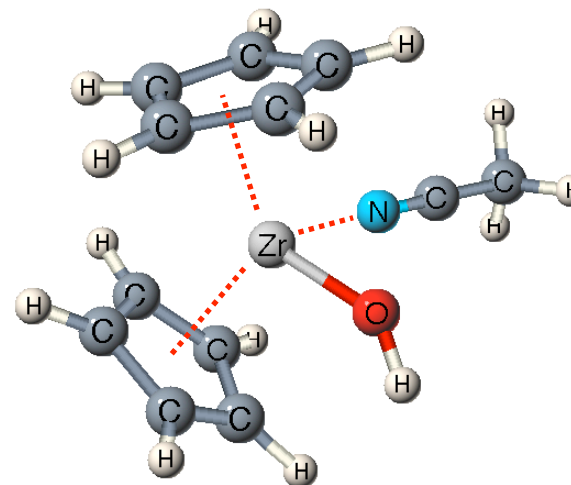
tetrahedral-like geometry

B3LYP/6-311G* (+ Stuttgart ECP)

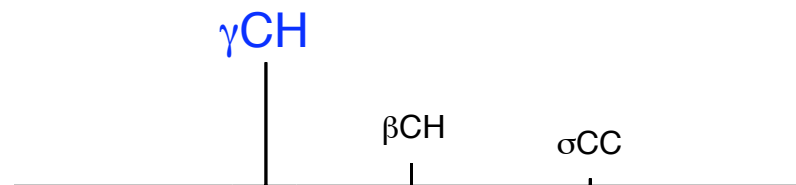
Quantum Chemical Results

closed shell cation

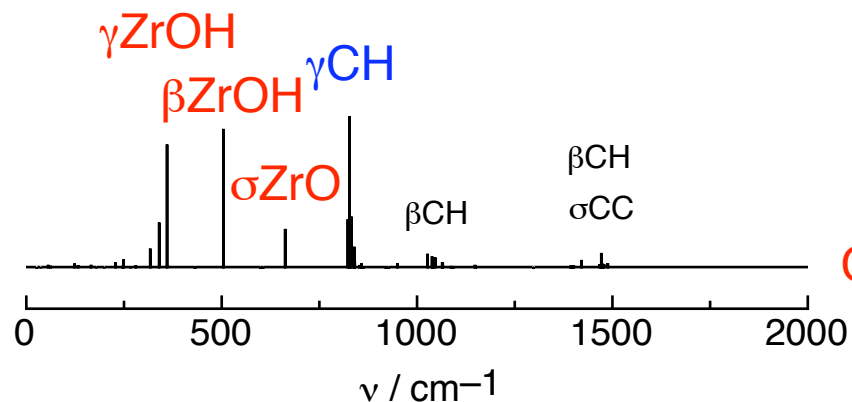
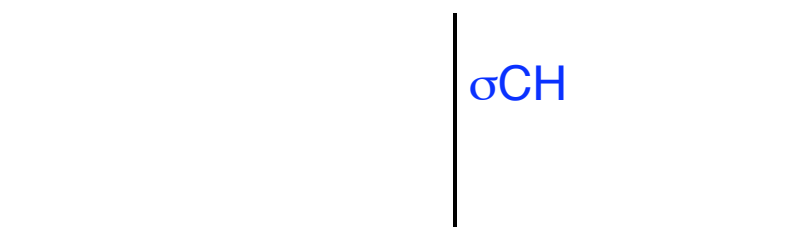
Zr⁴⁺ (+1.62 e) C₅H₅⁻ (-0.19 e)
 OH⁻ (-0.44 e) CH₃CN (+0.20 e)



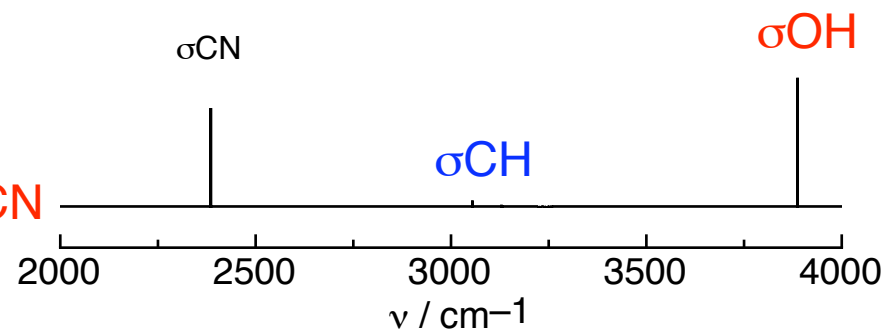
OH⁻
 CH₃CN



Cp⁻ = C₅H₅⁻

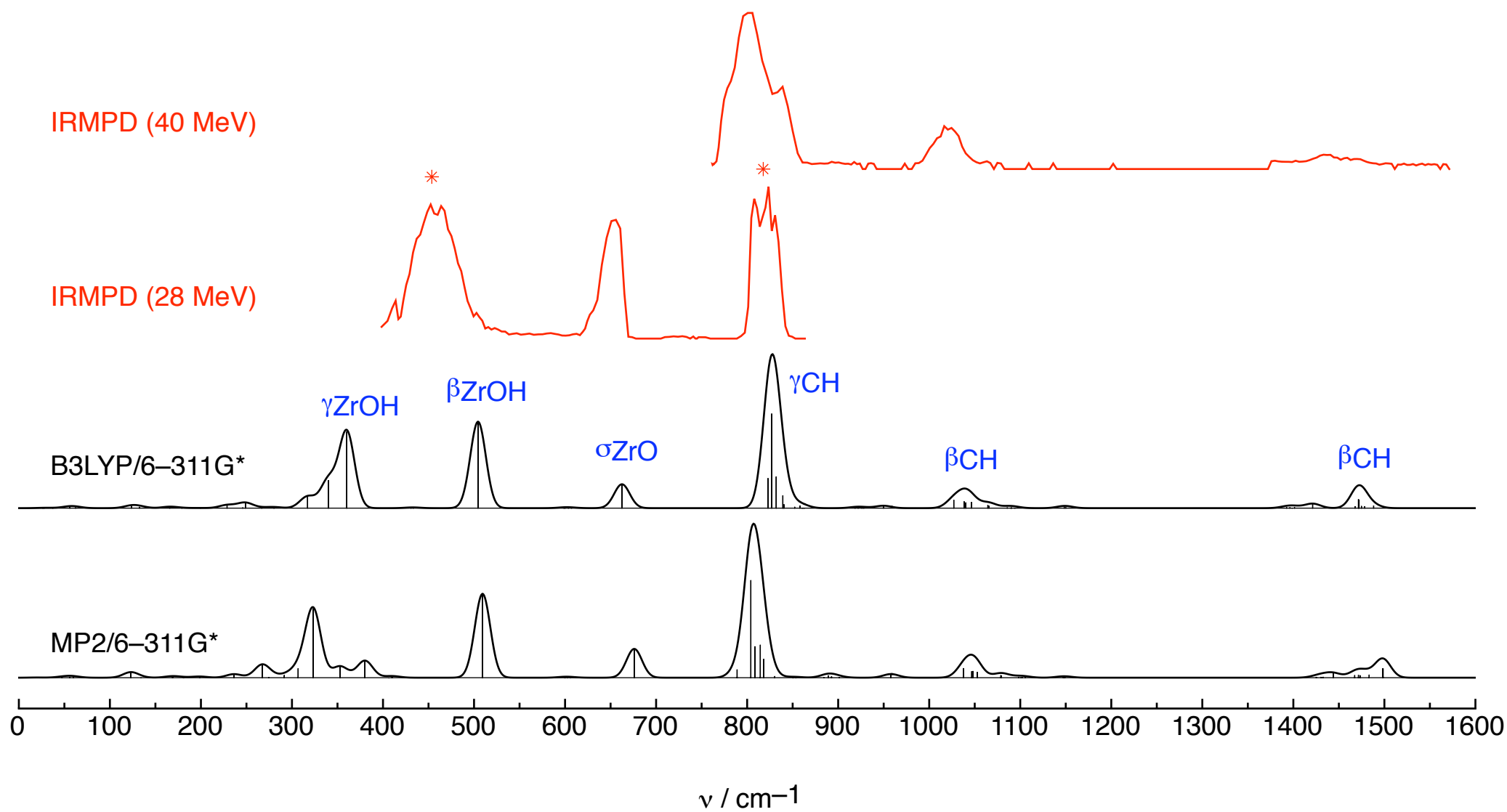


Cp₂Zr(OH)CH₃CN



B3LYP/6-311G* (+ Stuttgart ECP)

Comparison IRMPD vs calculated IR spectra

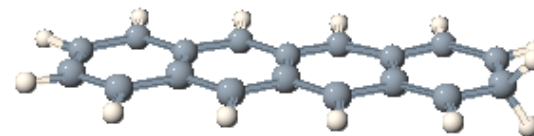
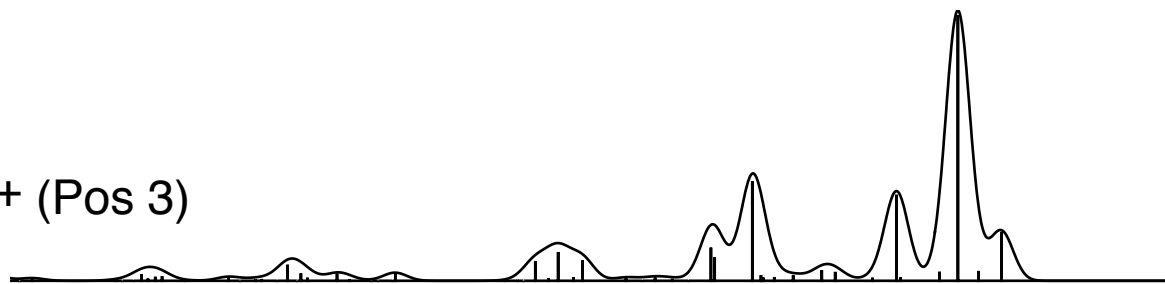


TetraceneH⁺ IR Spectrum

B3LYP/6-31G^{**}

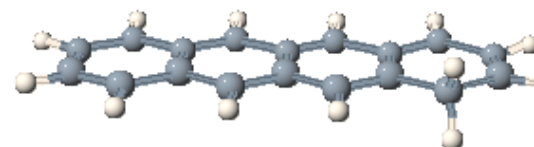
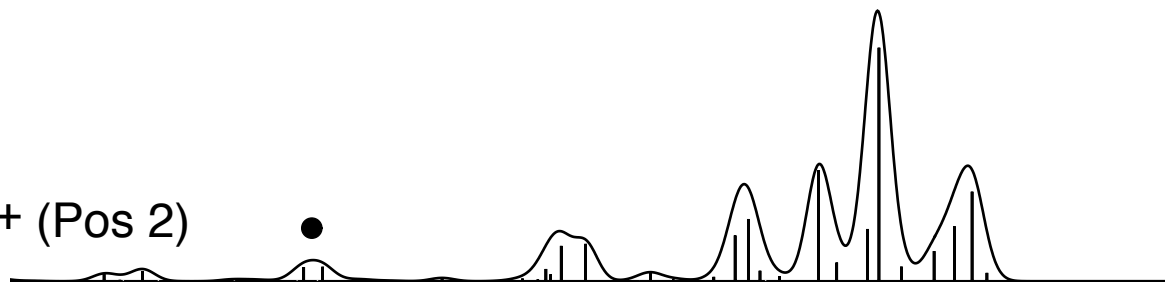
(x 0.96, convolution 30 cm⁻¹)

TetH⁺ (Pos 3)



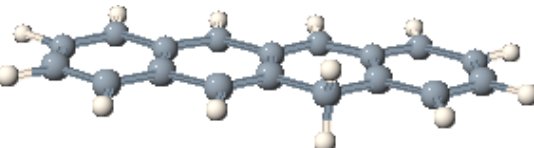
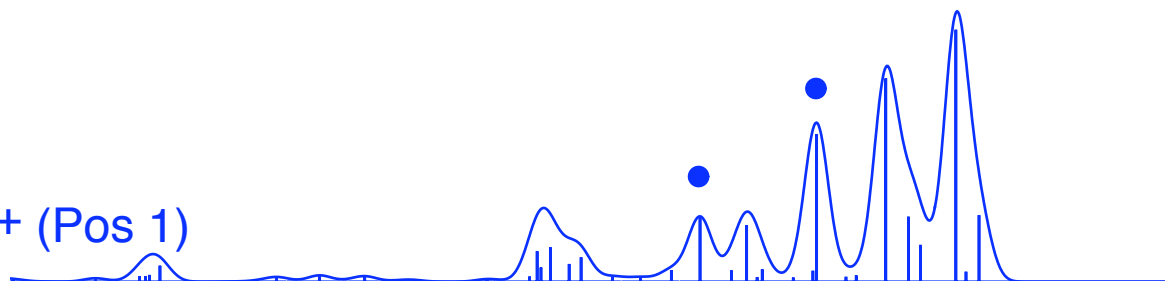
5242 cm⁻¹

TetH⁺ (Pos 2)



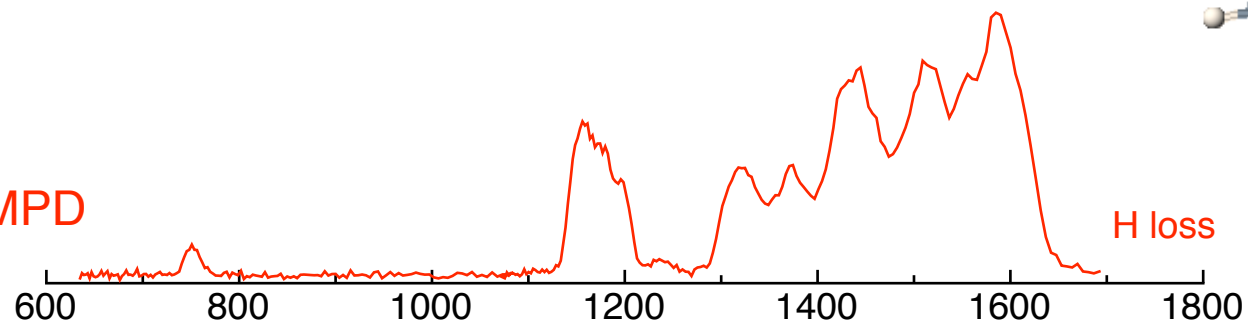
4186 cm⁻¹

TetH⁺ (Pos 1)



0 cm⁻¹

IRMPD



H loss

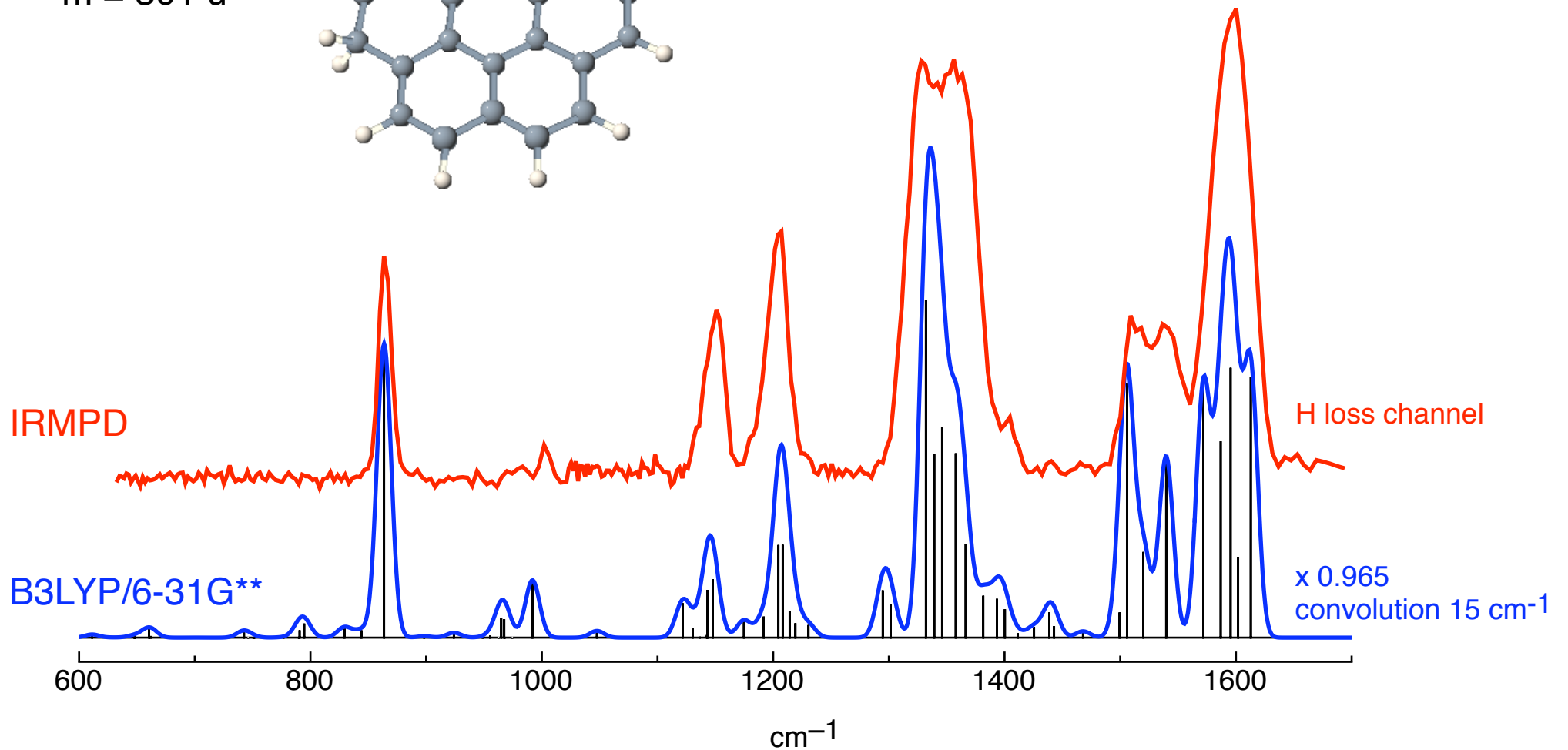
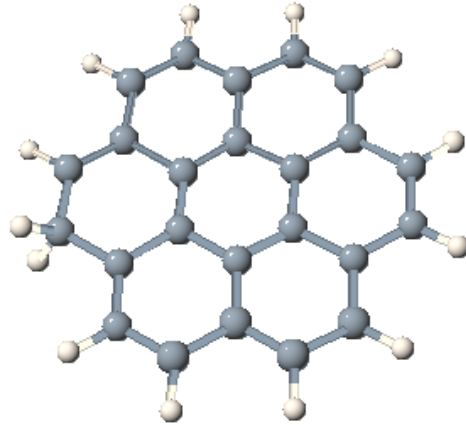
cm⁻¹

Knorke, Langer, Oomens, Dopfer (FELIX 2008)

CoroneneH⁺ IR Spectrum

(C₂₄H₁₂)H⁺

m = 301 u



bisher keine Vorarbeiten zu chiralen Clustern

Aber:

Sehr wenig (!) spektroskopische Daten zu chiralen Clustern in Literatur

Noch weniger Daten zu geladenen Systemen

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& chiral solvent (r,l)
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electron impact & discharge
laser desorption
electrospray

IR & UV-vis spectroscopy (ns)

photodissociation
photoionisation
electron detachment
double resonance (isomers)

tandem mass spectrometry

multipoles (quadrupole, octopole, 22-pole)
ReTOF
composition, stability & reactivity

quantum chemistry

ab initio (HF, MP2, CASPT2, ri-CC2, ...)
density functional theory (DFT, TD-DFT)