Proton diffusion in a benchmark entangled hydrogen bonding network

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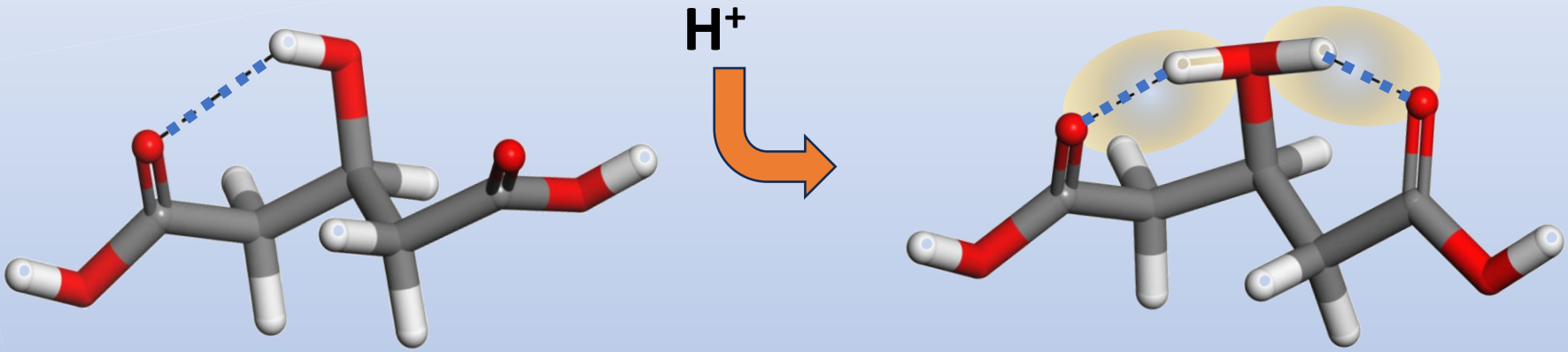
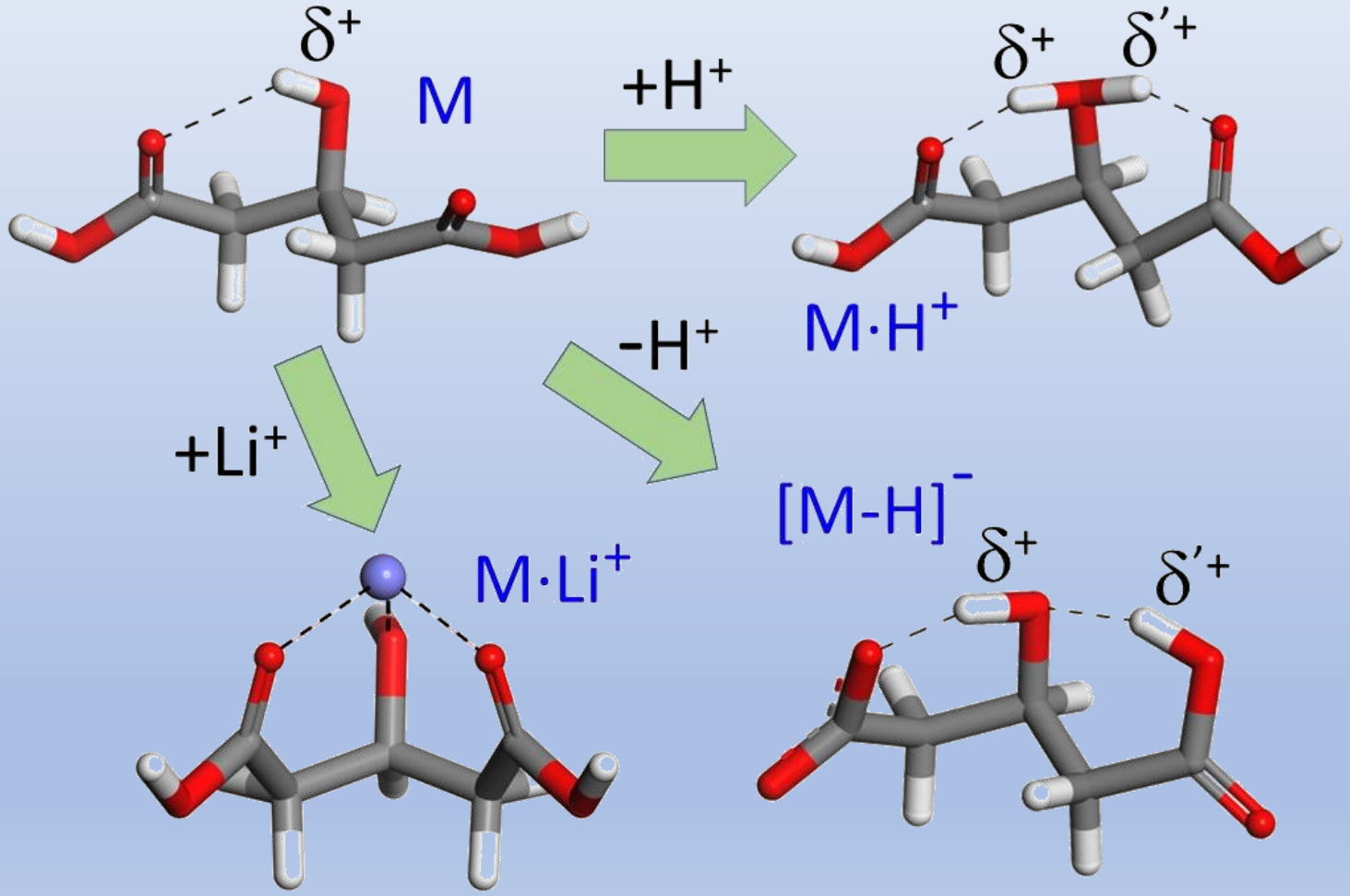
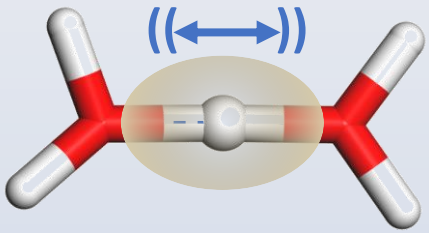
Entangled proton delocalization in 3-hydroxy glutaric acid



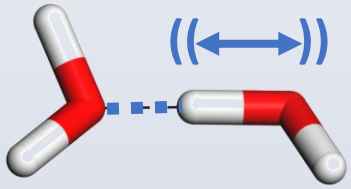
Entangled proton delocalization in 3-hydroxy glutaric acid



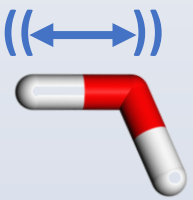
Vibrational signatures of proton bonding



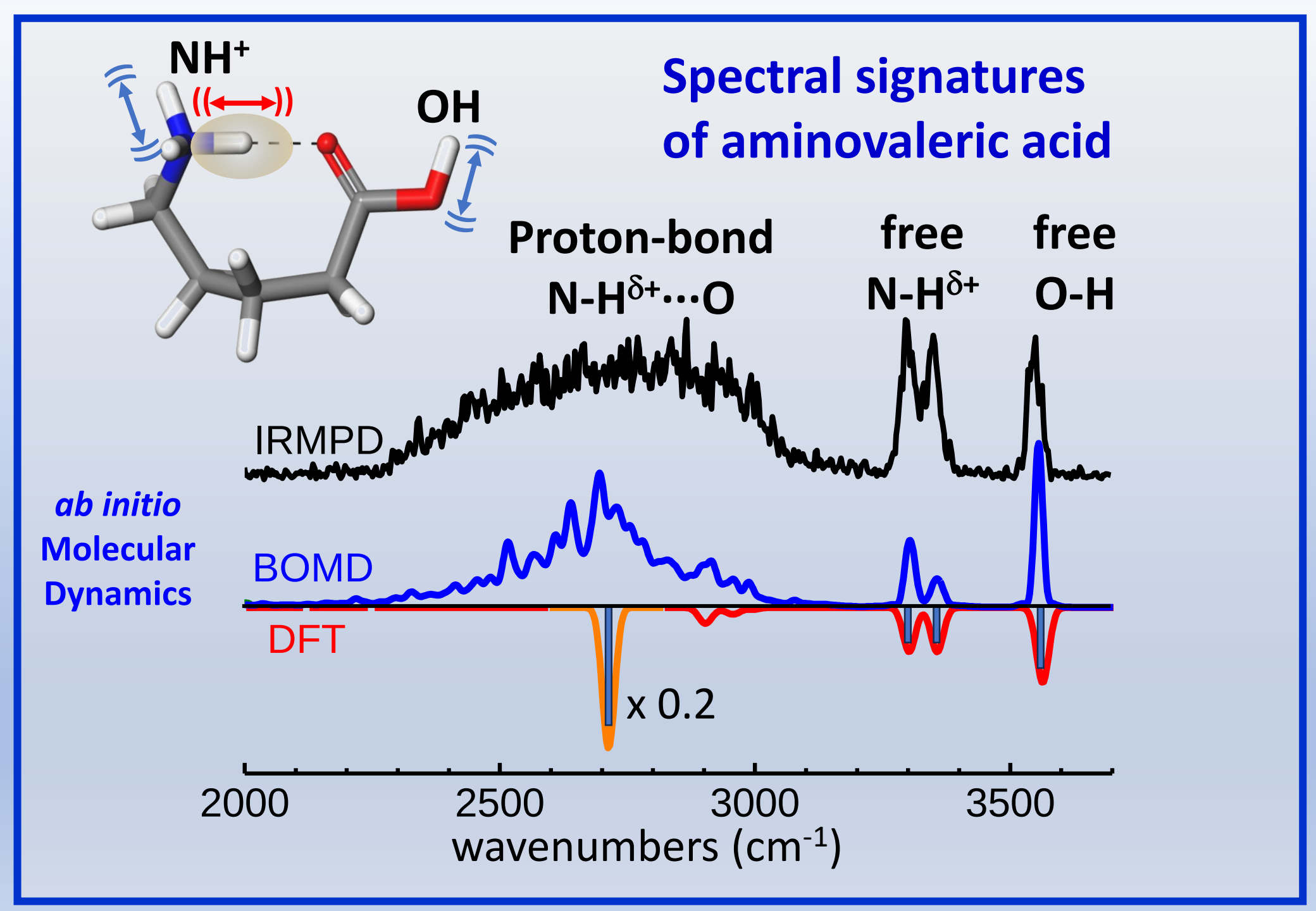
Loose
proton-bond
$O\text{-}H^{+}\cdots O$



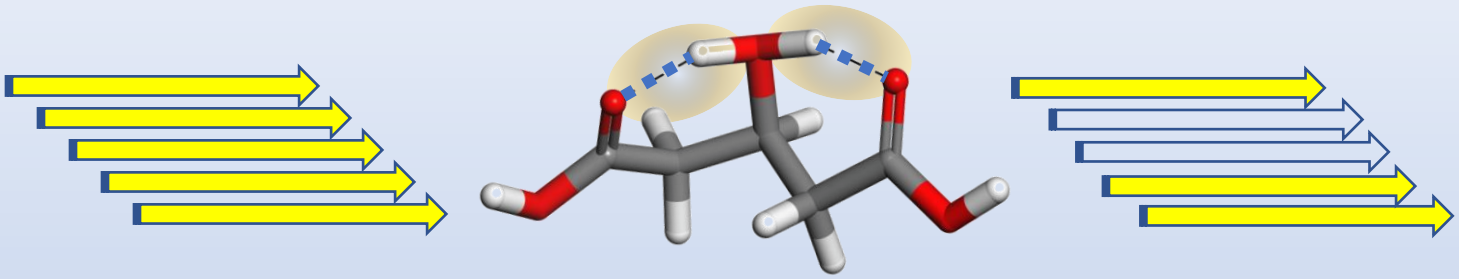
H-bond
O-H···O



free
O-H


NH+
OH
Spectral signatures
of aminovaleric acid
Proton-bond
N-Hδ+···O
free
N-Hδ+
free
O-H
IRMPD
ab initio
Molecular
Dynamics
BOMD
DFT
x 0.2
2000
2500
3000
3500
wavenumbers (cm-1)

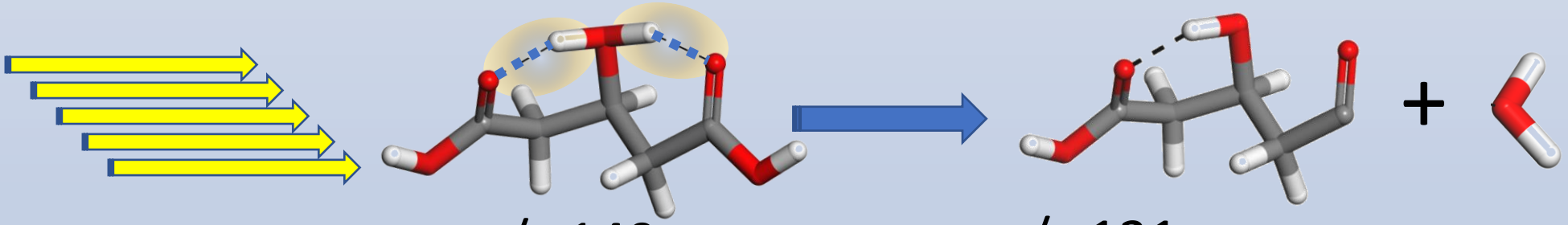
“conventional” spectroscopy, based on “what molecules do to light”



light detected

requires > 10^8 cm^{-3}

“action” spectroscopy, based on “what light does to molecules”

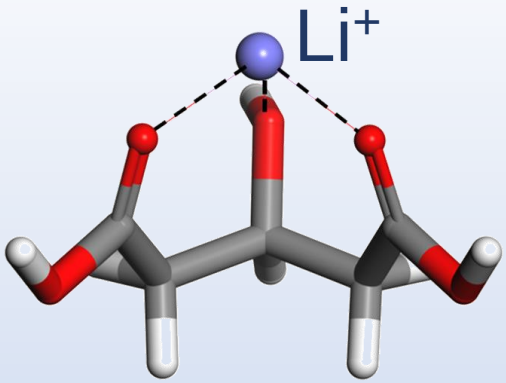


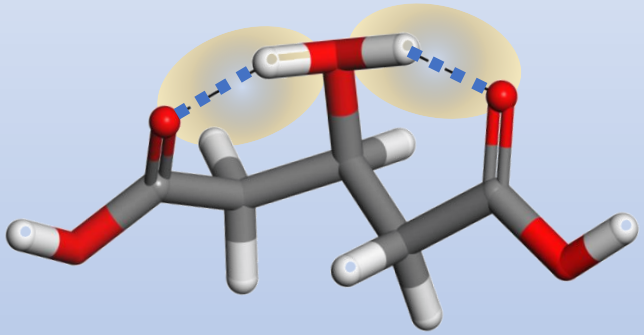
m/z 149

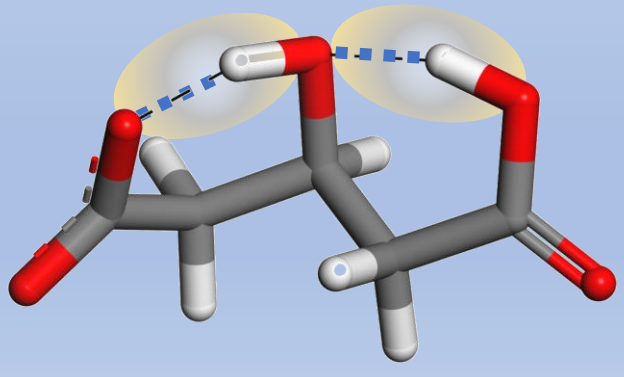
m/z 131

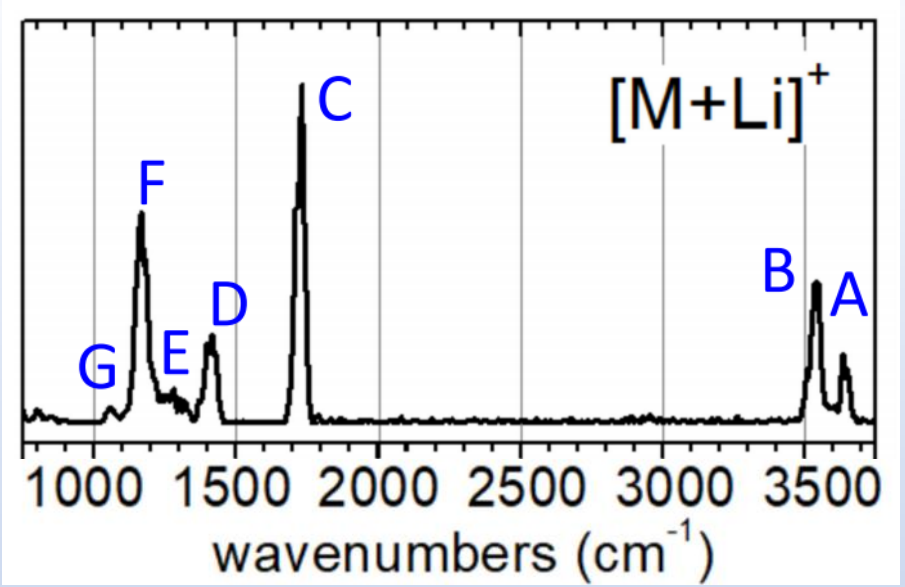
works with ~10^3 cm^{-3}

product ions detected

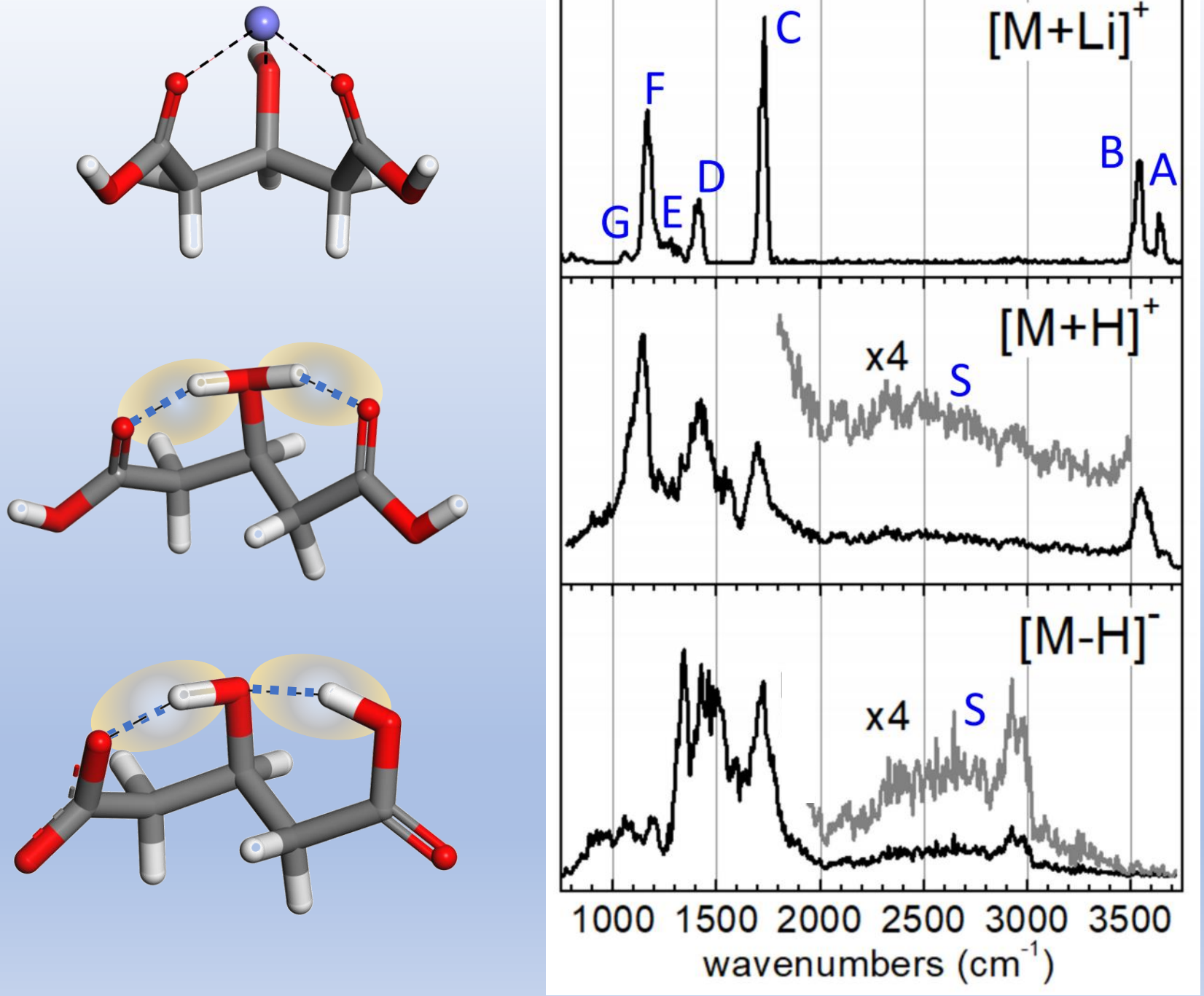




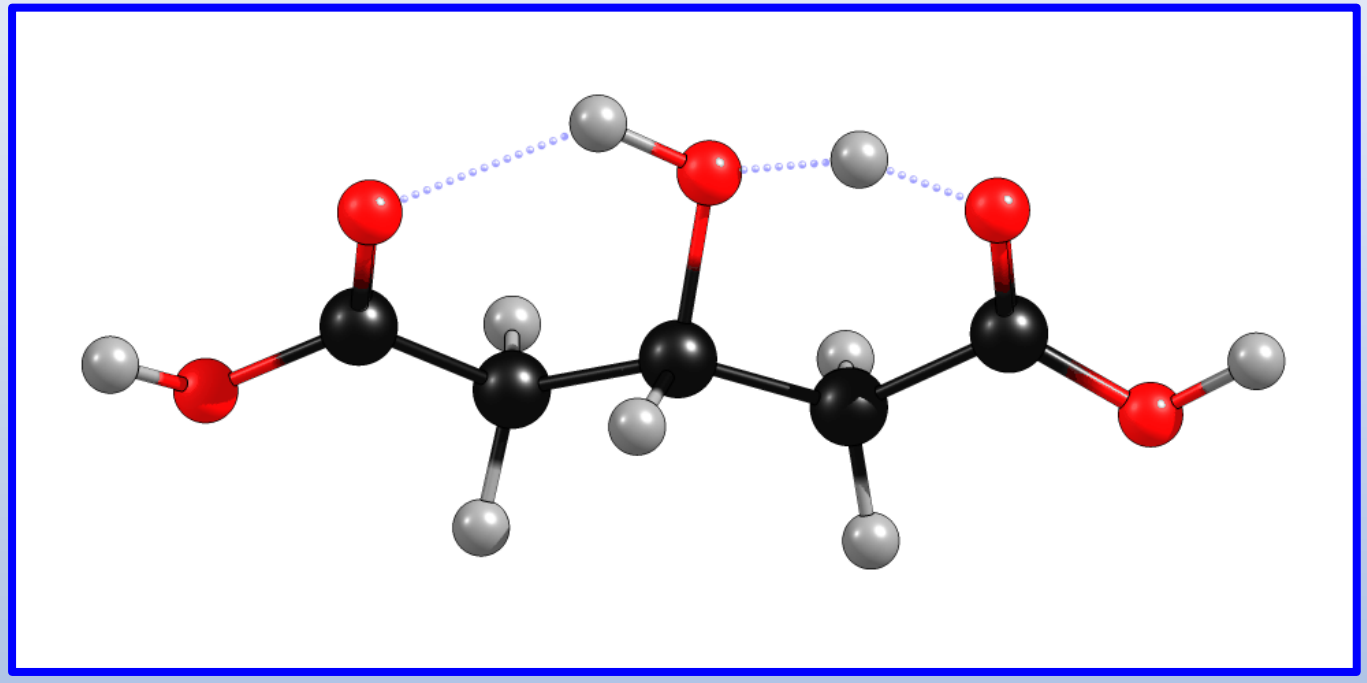


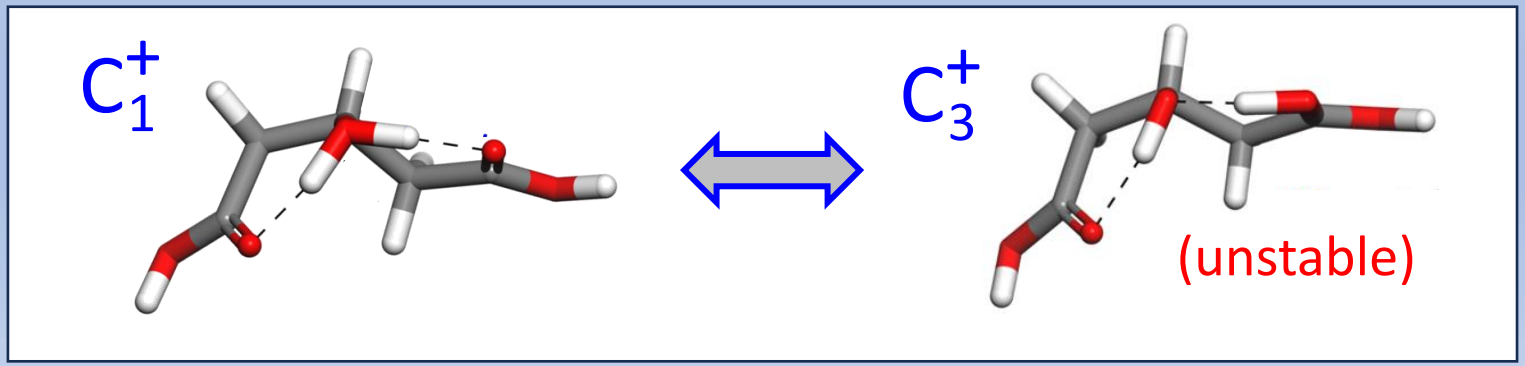


A: O-H stretching (hydroxy group)
B: O-H stretching (carboxylic group)
C: C=O stretching
D: CH_2 scissoring
E: C-C stretching, mixed with CH/CH_2 wagging
F: C-OH stretching and bending (carboxylic group)
G: C-O (hydroxy) and C-C stretching

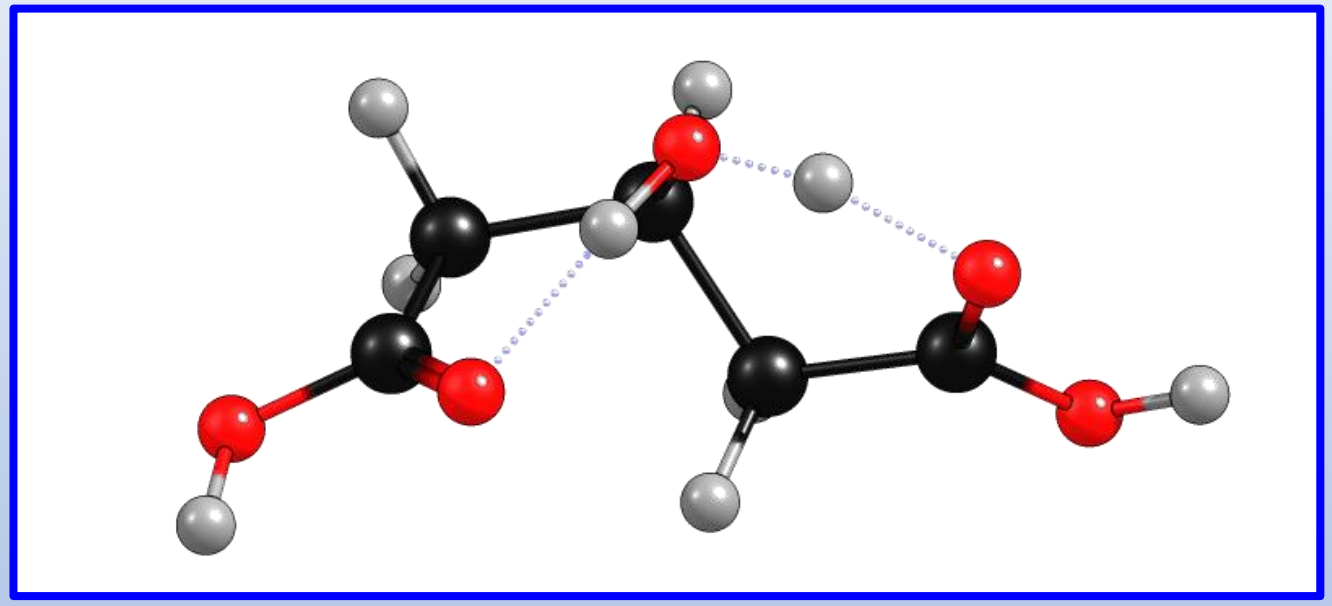

[M+Li]+
C
F
B
A
G
E
D
[M+H]+
x4
S
[M-H]-
x4
S
1000 1500 2000 2500 3000 3500
wavenumbers (cm-1)

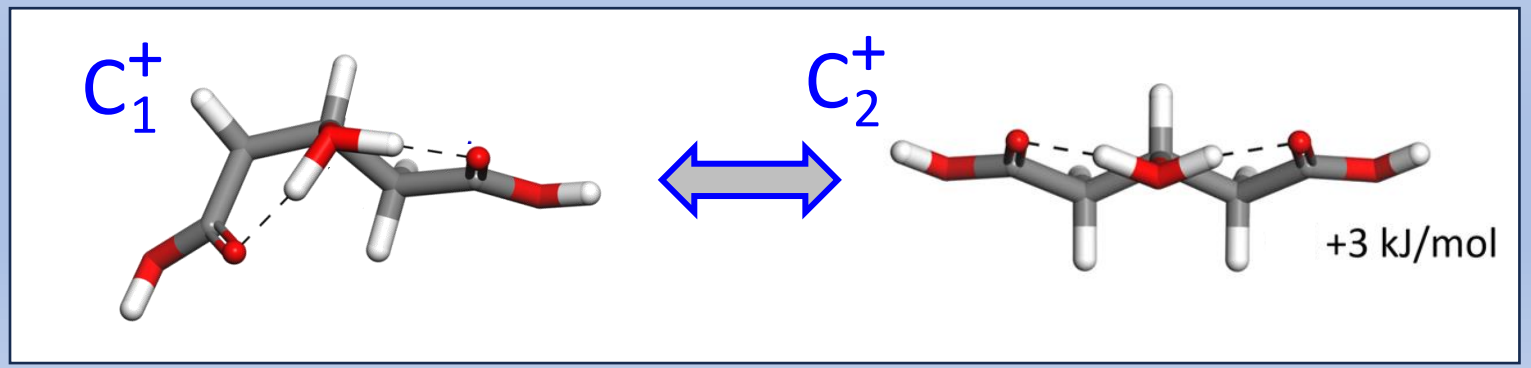
Motion I: **proton difussion along H-bonds**

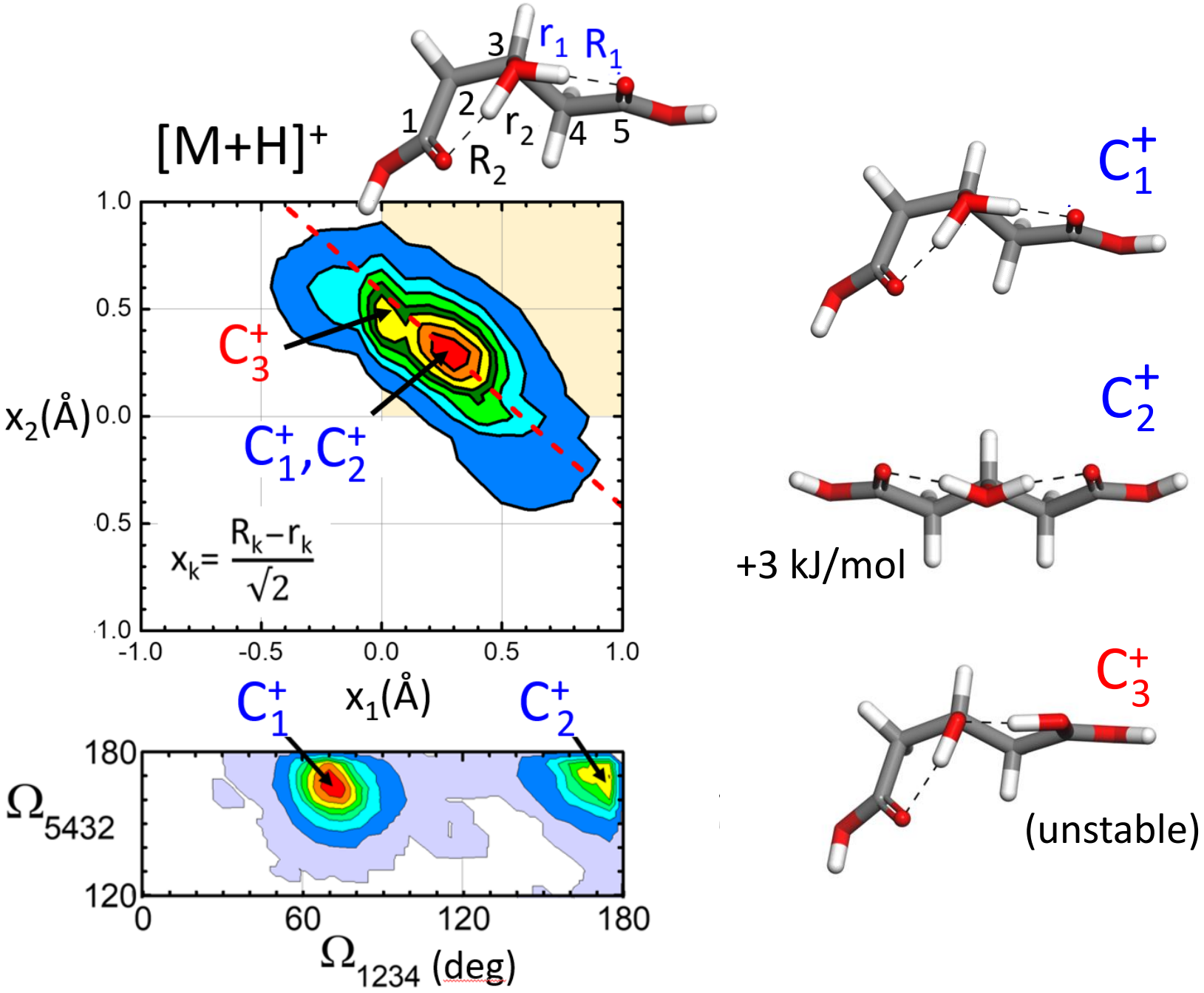


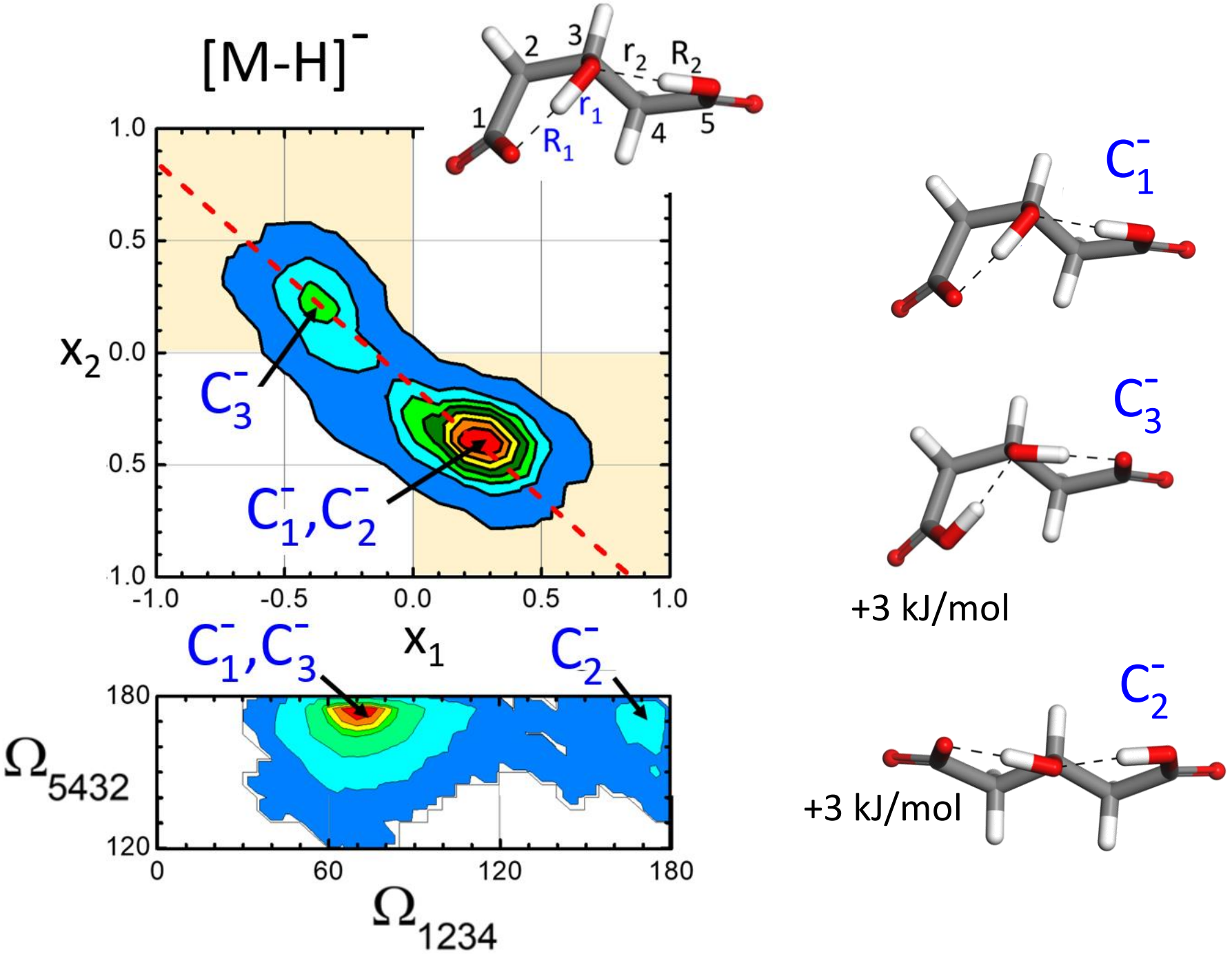


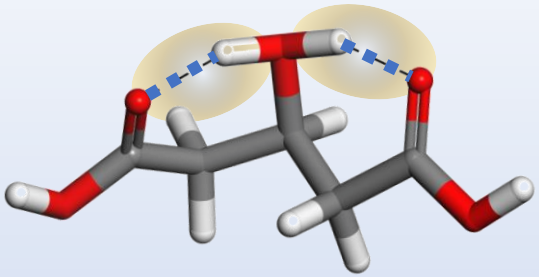
Motion II: **backbone stretching/bending**



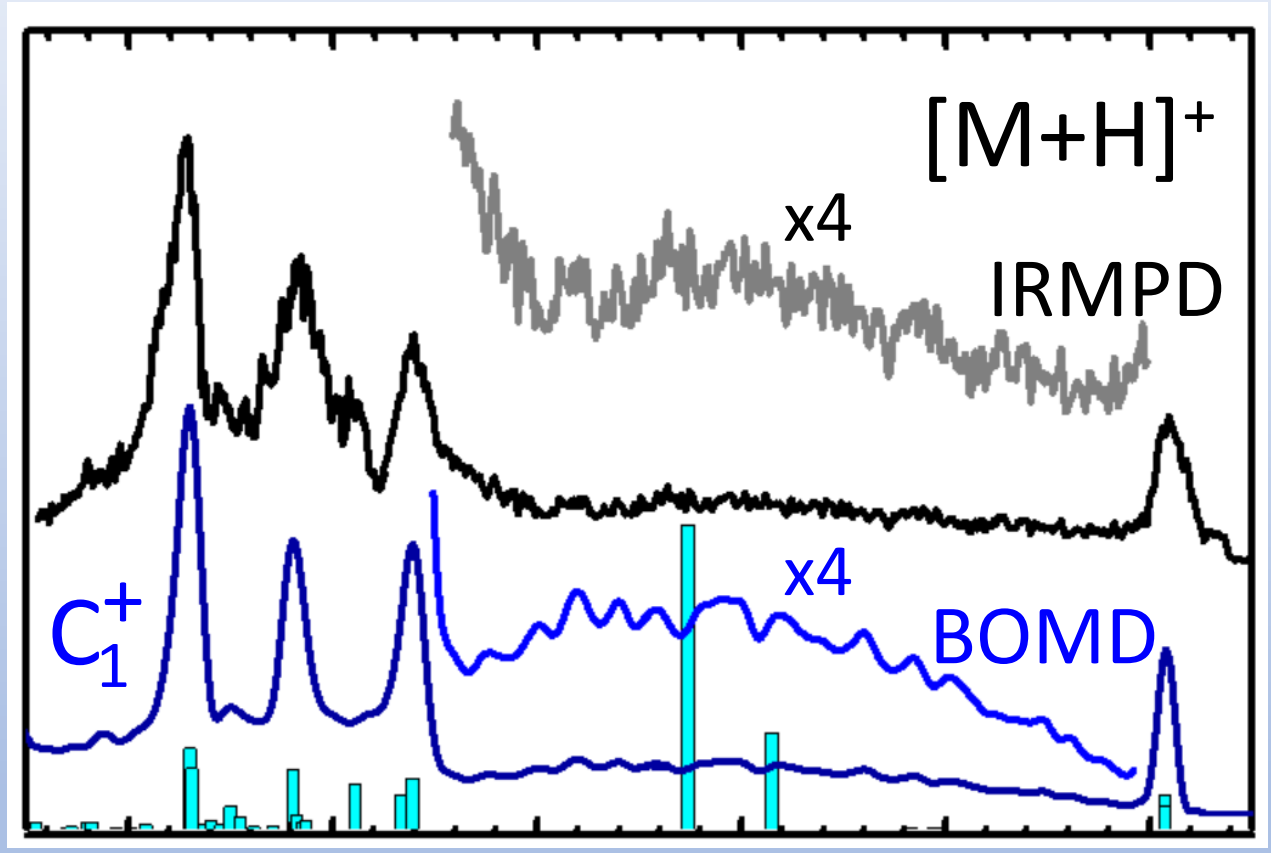


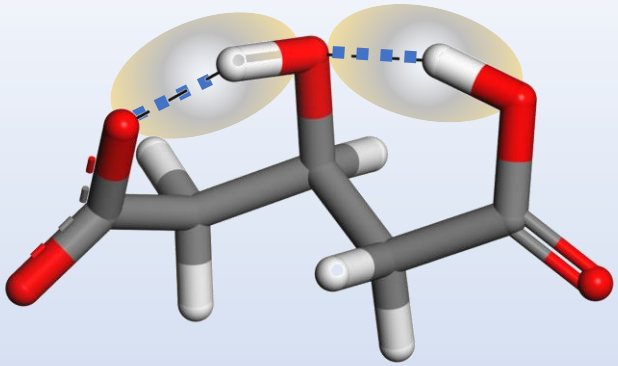

[M+H]+
1
2
3
4
5
r1
R1
r2
R2
C1+
C2+
+3 kJ/mol
C3+
(unstable)
x2(Å)
x1(Å)
C3+
C1+,C2+
xk= (Rk−rk)/√2
1.0
0.5
0.0
0.5
1.0
-1.0
-0.5
0.0
0.5
1.0
C1+
C2+
Ω5432
Ω1234 (deg)
180
120
0
60
120
180


[M-H]⁻
1
2
3
4
5
r2
R2
r1
R1
1.0
0.5
0.0
0.5
1.0
x2
C3⁻
C1⁻,C2⁻
-1.0
-0.5
0.0
0.5
1.0
x1
C1⁻,C3⁻
C2⁻
180
120
0
60
120
180
Ω5432
Ω1234
C1⁻
C3⁻
+3 kJ/mol
C2⁻
+3 kJ/mol

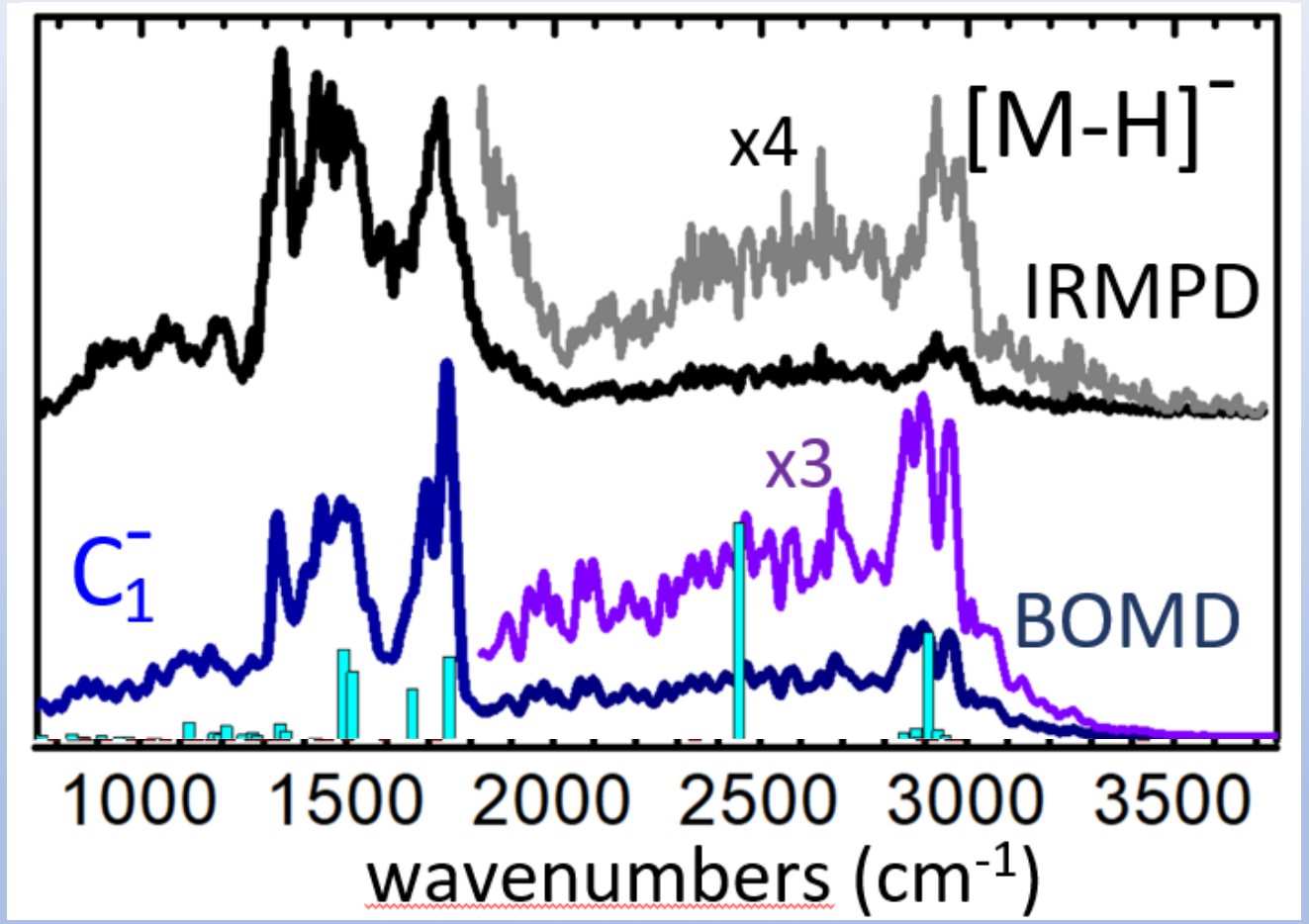


Comparison theory vs experiment

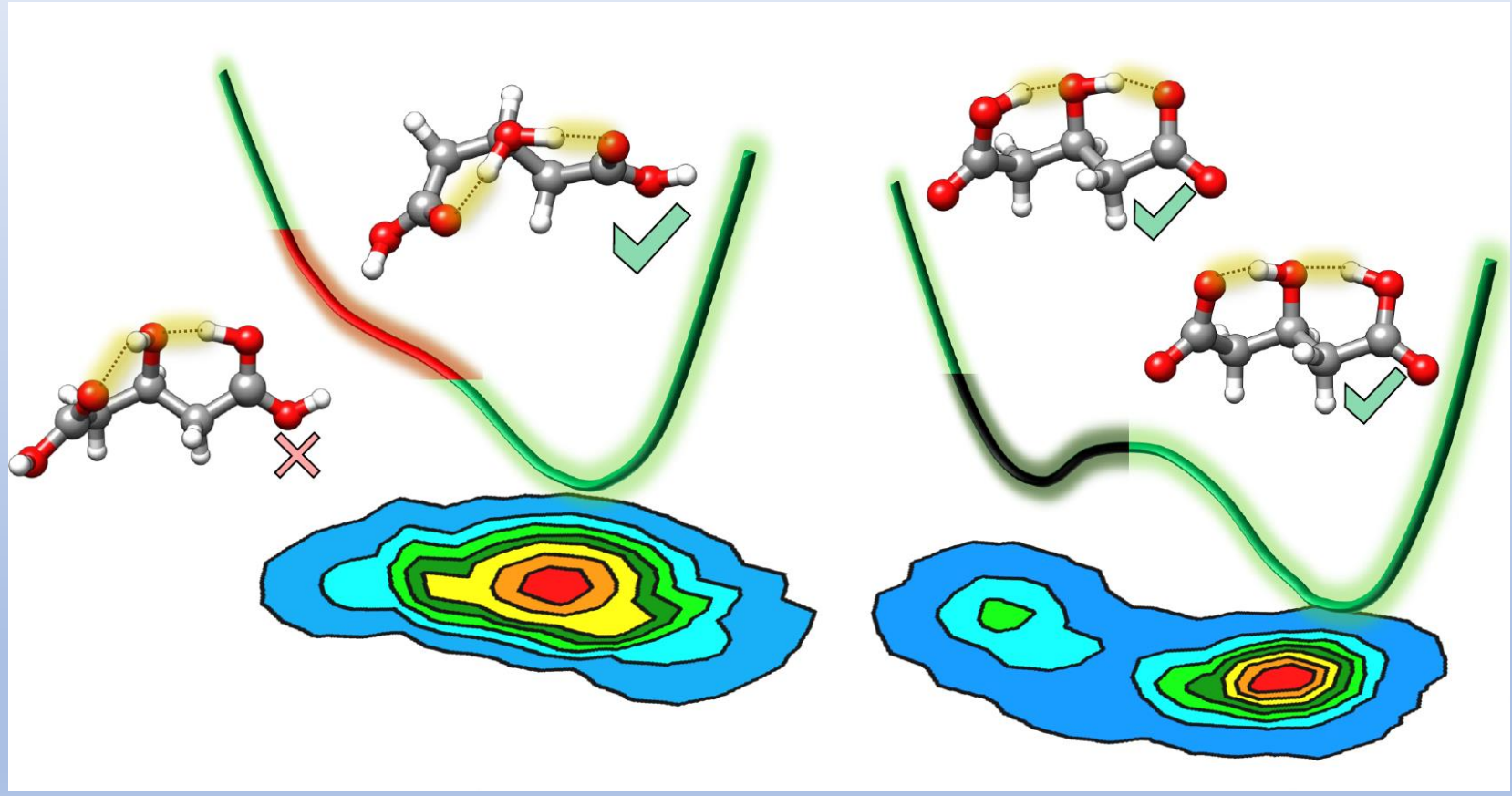




Comparison theory vs experiment



Conclusion: simple molecular ions provide nice benchmarks to study entangled proton dynamics



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FELIX
Free Electron Lasers for Infrared eXperiments
Radboud University

Francisco Gámez

Juan Ramón Avilés-Moreno

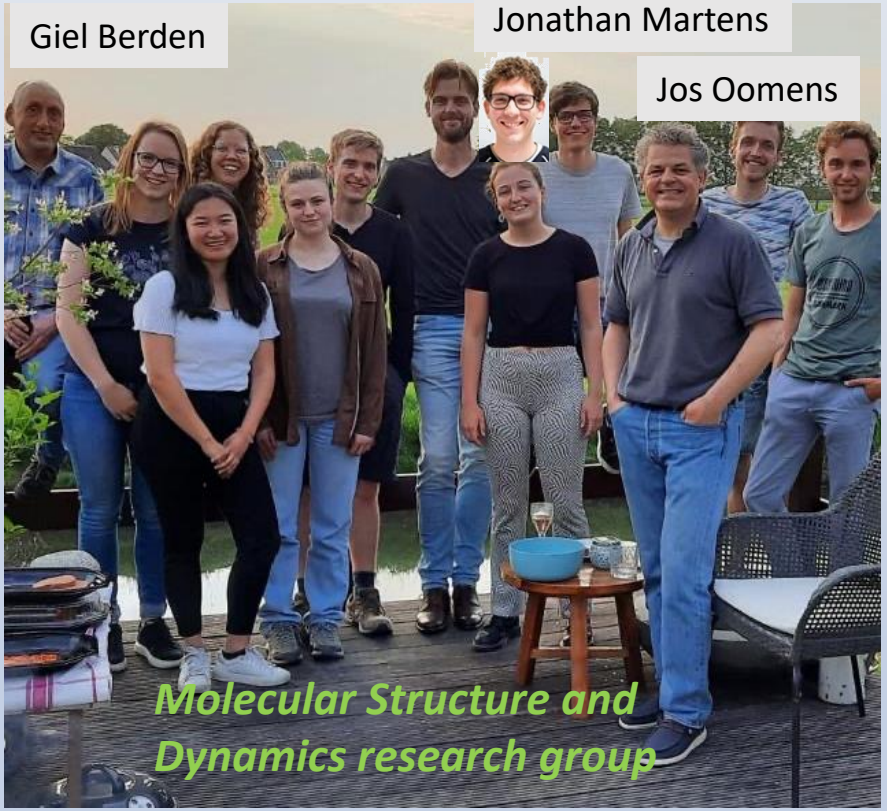
Universidad Complutense Madrid

UAM
Universidad Autónoma de Madrid

Giel Berden

Jonathan Martens

Jos Oomens



…and thank you for your kind attention

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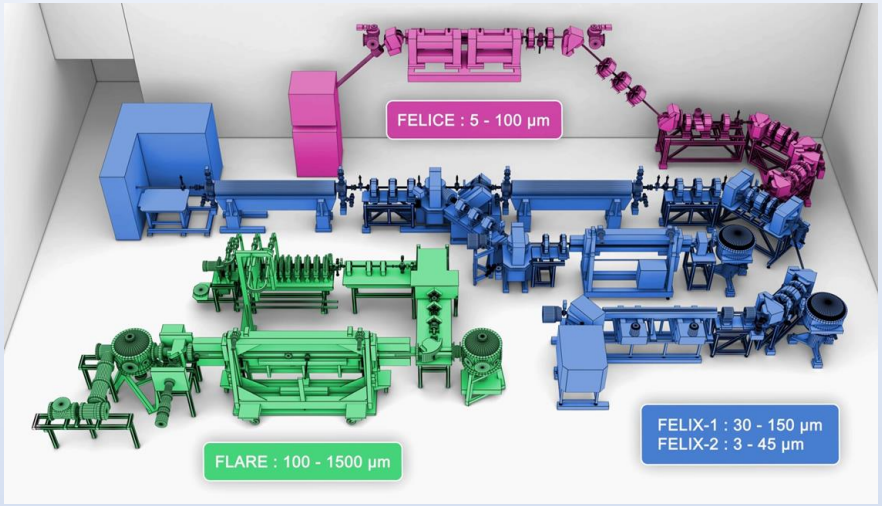
FELIX
Free Electron Lasers for Infrared eXperiments
Radboud University

Biomolecular Mass Spectrometry Lab



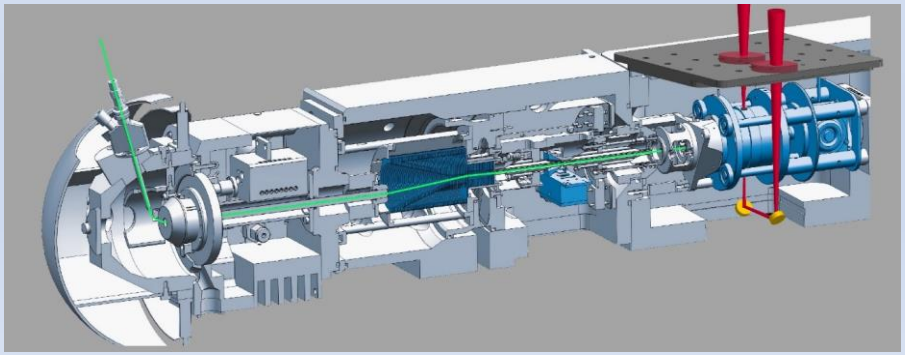
Ion trapping experiments

- Complex formation with ESI, APCI, MALDI sources
- Relative stabilities, dissociation channels, etc

Computations:

- Born-Oppenheimer Molecular Dynamics (BOMD)
- DFT and MP2 “static” computations

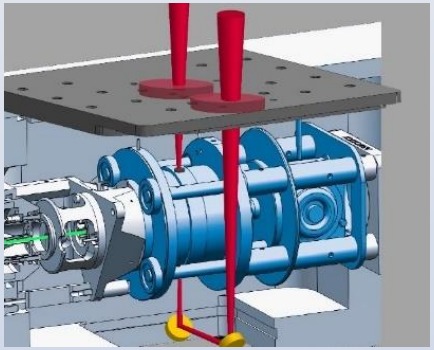
IRMPD spectroscopy of trapped ions

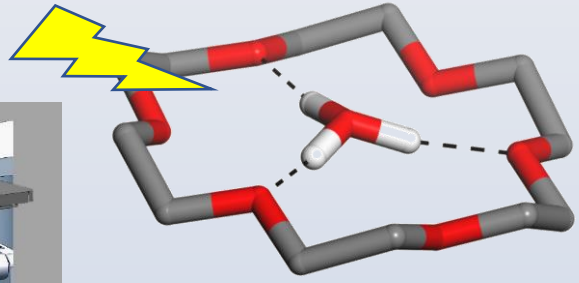


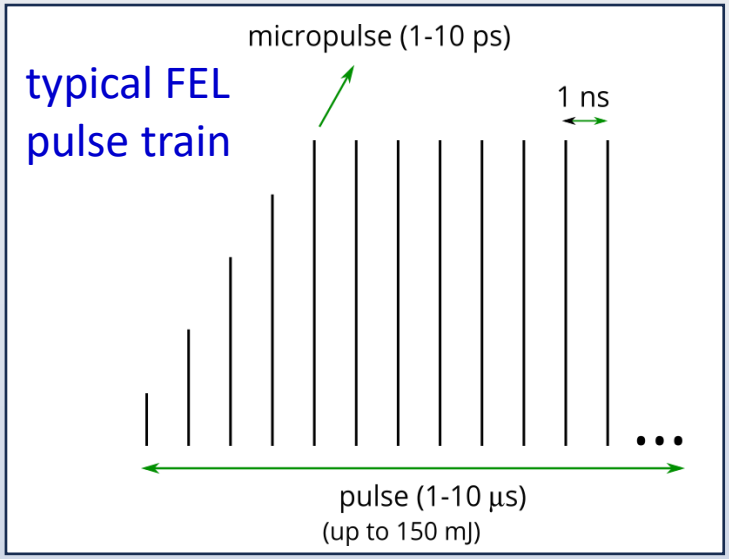
Resonant IR multiple-photon dissociation (IRMPD)

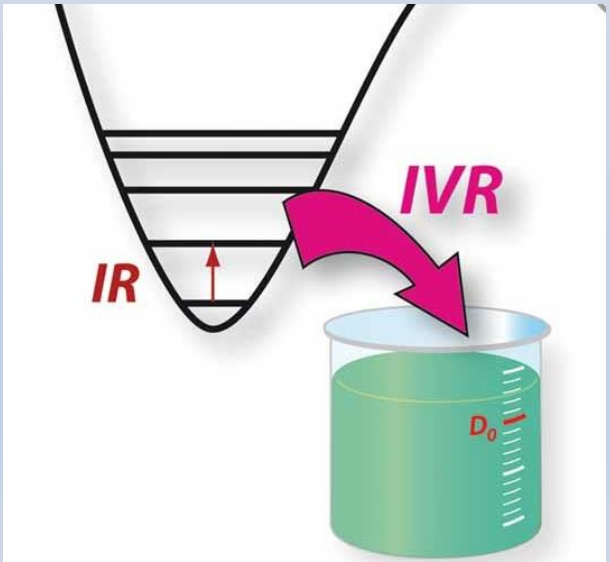
IR-FEL

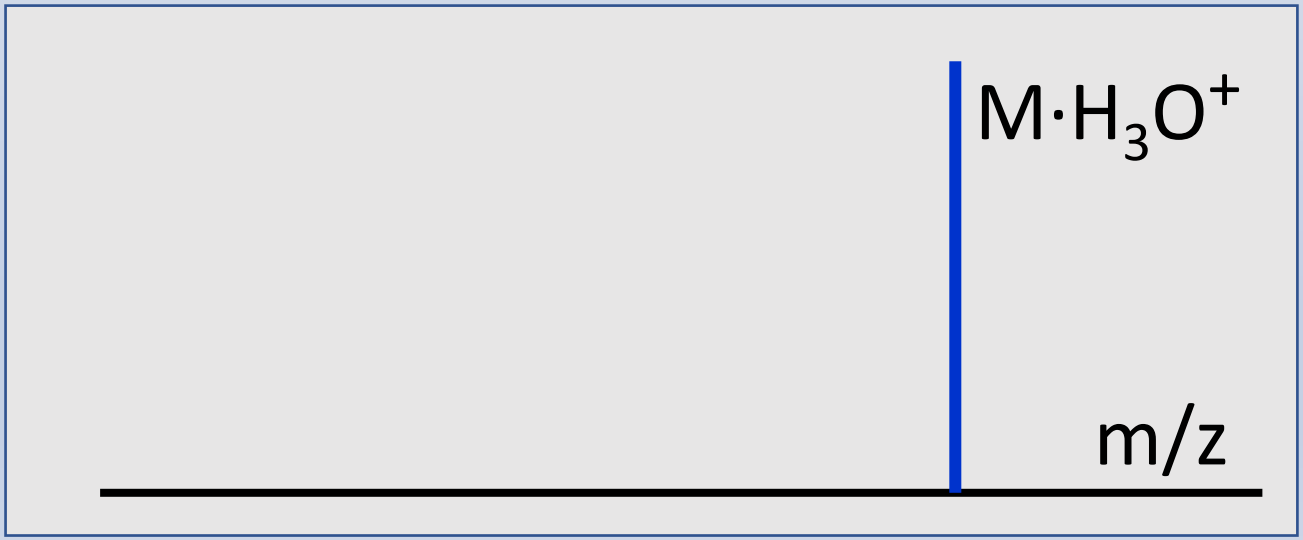
500-3800 cm^{-1}





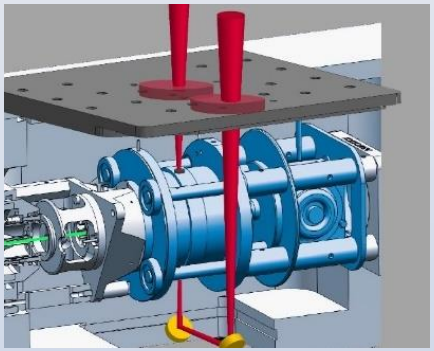


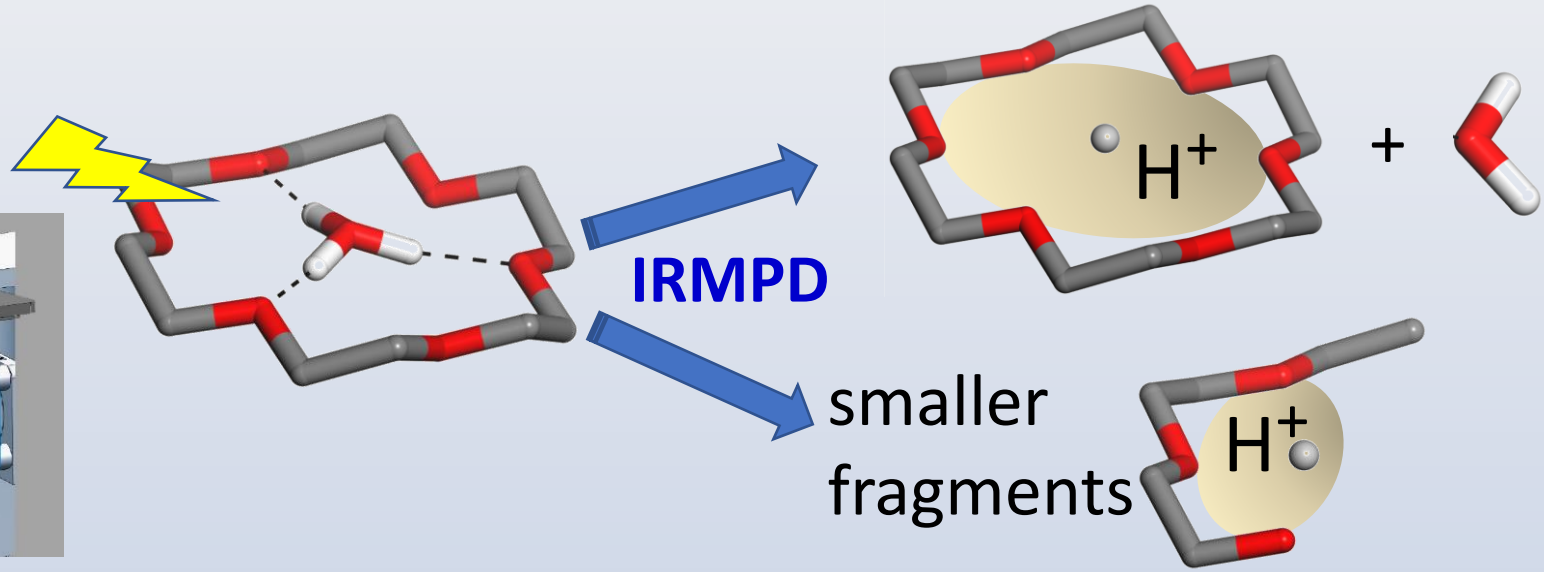


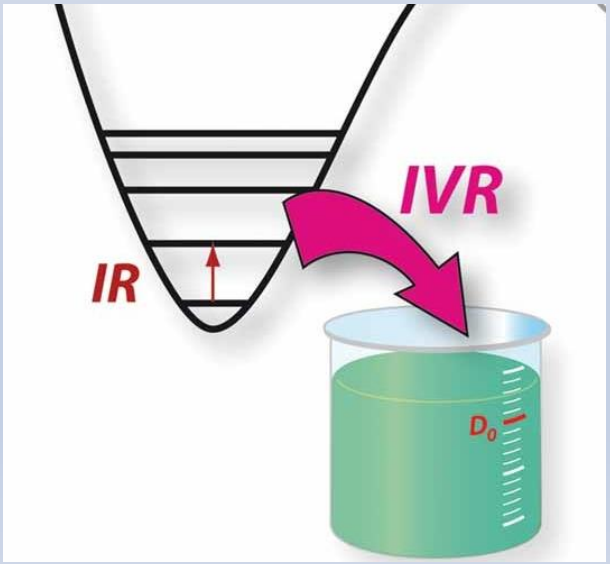


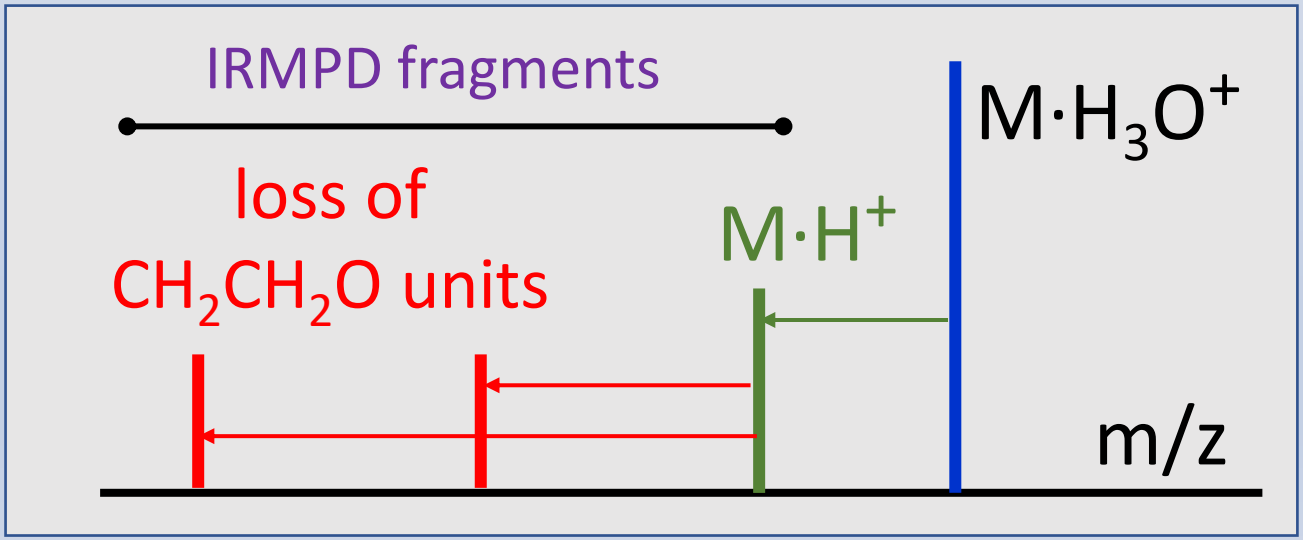
Resonant IR multiple-photon dissociation (IRMPD)

FELIX IR





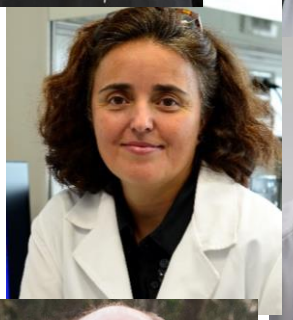


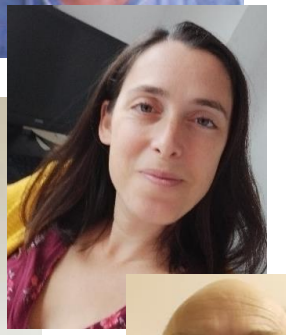




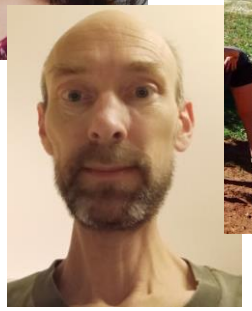










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