Gas Phase IR spectroscopy:

towards large biomolecules
&
far-IR wavelengths

Anouk M. Rijs

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Layout

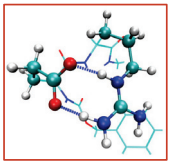
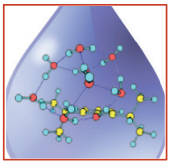
Introduction
- Why, o why?
- What & how?

Experimental methods
- Cooling methods
  - Why cooling
  - Supersonic expansions
  - Collisional cooling
- Molecule production --> larger & larger
  - heating
  - Laser desorption
  - Molecular beams & laser desorption

Spectroscopic Techniques
- History
- Use of lasers
- Experimental approach
  - UV, IR spectroscopy
- Free electron lasers
- Other methods:
  - IR-UV, UV-UV
  - Combination with VUV sources

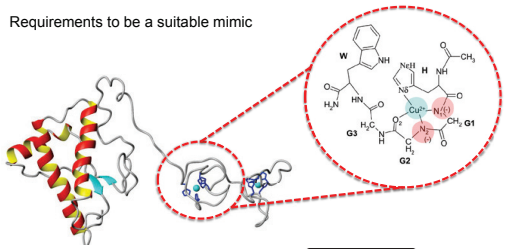
Applications
- **Biomolecules**
  - **Local environment**
  - **Biological environment**
  - **Larger and larger….**
- Molecular motors: functioning of rotaxanes

Biological environment interactions probed by Gas Phase IR Spectroscopy

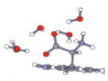
Biomolecular mimics

Requirements to be a suitable mimic



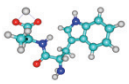
AA-sequence

Biological environment (in the gas phase)



Micro-solvation
Blom *et al.*; JPC-A **2007**, 111, 7309

Peptide design
A.M. Rijs *et al.*
Angew. Chem. Int. Ed. 49, 2332 (2010)

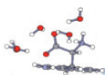


Metal Complex

Effects of biological and local environment on neutral peptides

Microsolvation ⇨ water molecules
peptide design ⇨ Neigboring residues
Metal chelation ⇨ metal complexes

Looking for a zwitterion! (in the gas phase)



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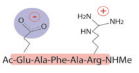

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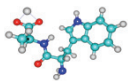
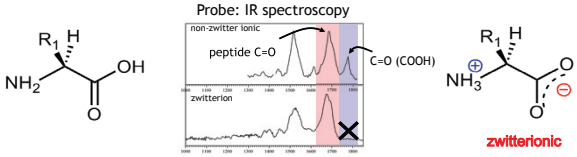


Metal Complex

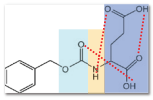
Probe: IR spectroscopy



zwitterionic

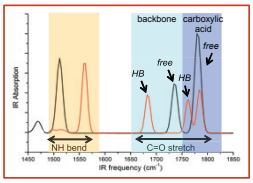
What does an IR spectrum tell you: H-bonding!

IR spectroscopy direct view on the hydrogen bond network present in your molecule



Amide I - C=O stretch: 1700-1800 cm^{-1}

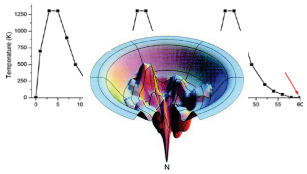
Amide II – NH bend: 1500 cm^{-1}



Conformational Search – calculated IR spectra

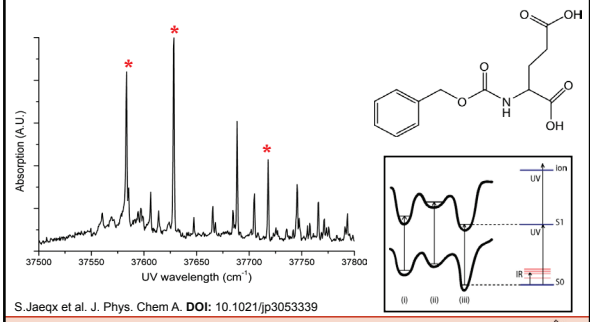
- Measure **experimental** IR absorption spectrum
- Calculate **theoretical** IR spectra of different low energy conformations

- Simulated annealing
  - Max T: 1300 K
  - Simulation time: 10 – 20 ns
  - # structures: 500 – 1000



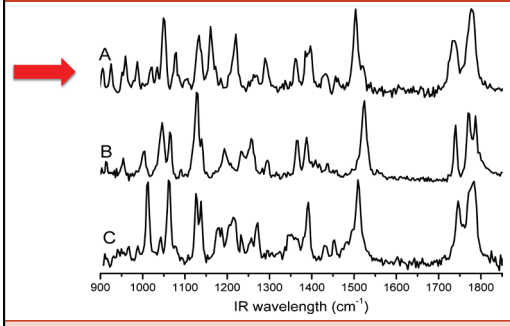
~50 structures optimized on B3LYP/6-31G** level
~25 structures optimized and frequency calculation on B3LYP/6-311+G** level

REMPI Z-Glu-OH

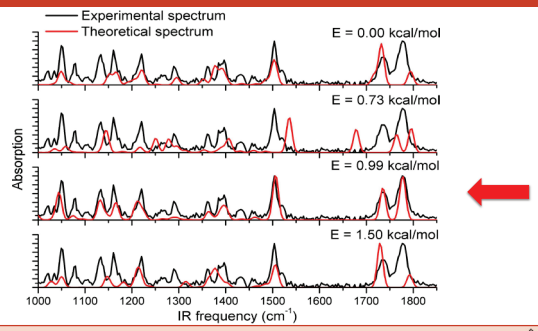


S.Jaeqx et al. J. Phys. Chem A. **DOI:** 10.1021/jp3053339

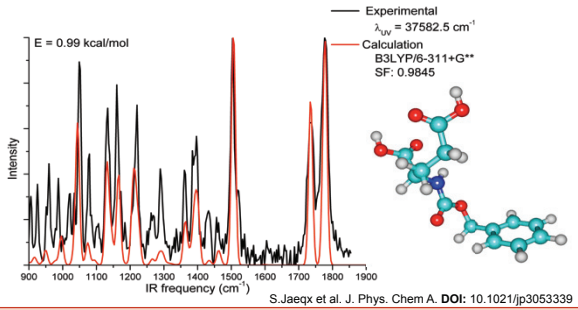
IR-UV ion dip spectra Z-Glu-OH



Structural assignment Z-Glu-OH



Results - Structure assignment Z-Glu-OH



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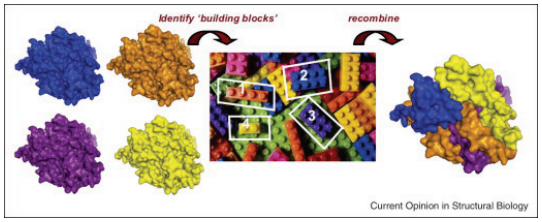
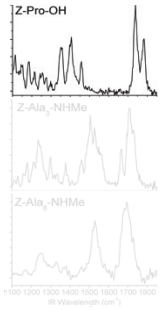
Larger & larger: including more parts



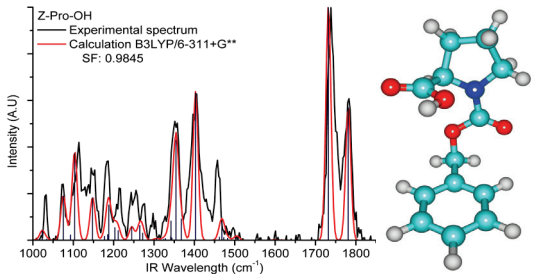
Far-IR the solution to maintain high-resolution

Problem in IR spectroscopy

- structural assignment:
  - Amide A: NH stretch
  - Amide I: C=O stretch
  - Amide II: NH in plane bend



Small peptides: no problem



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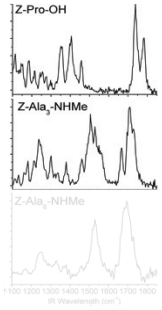
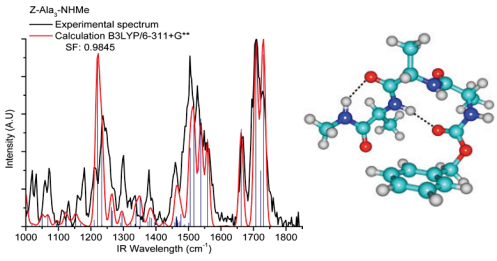
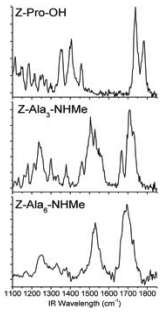


Medium-sized: still ok

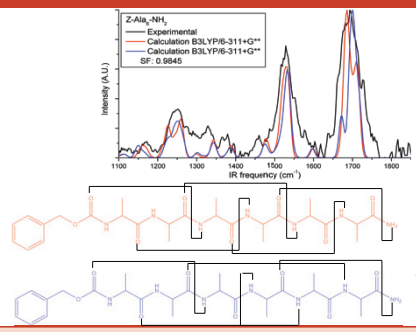


Problem in IR spectroscopy

- structural assignment:
  - Amide A: NH stretch
  - Amide I: C=O stretch
  - Amide II: NH in plane bend
- Larger molecules = overlapping peaks:
  - Structural assignment complicated



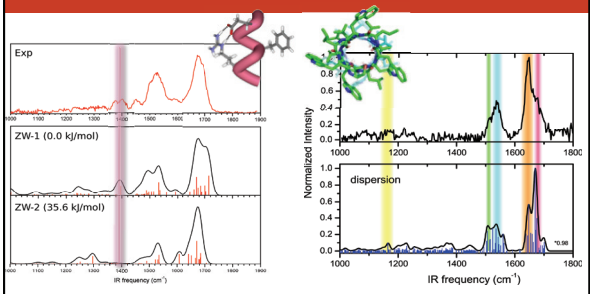
Larger peptides… challenging!



5 x C10 Interaction

3 x C10 + 2 x C13 Interaction

IR spectroscopy: the "Felix" region

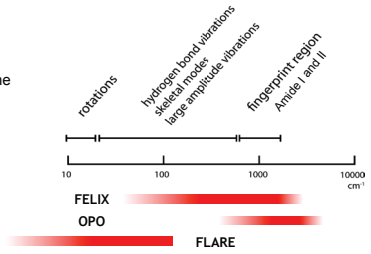


A.M. Rijs *et al.*, Angew. Chem. Int. Ed. 49, 2332 (2010)

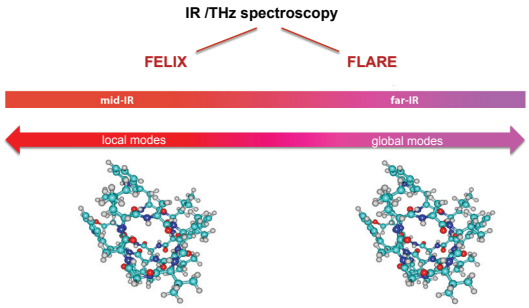
A.M. Rijs, and M.S de Vries et al., ChemPhysChem **12**, *1816 (2011)*

far-IR spectroscopy

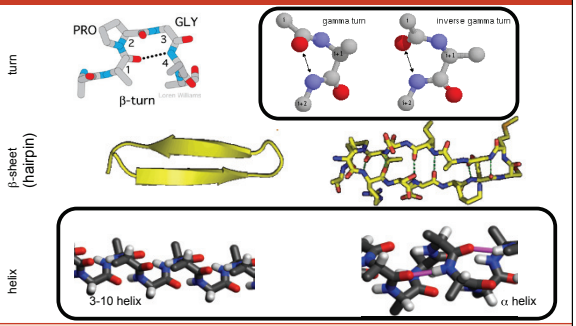
- Extend range to far-Infrared for structural assignment
  - Extra probe
  - Backbone vibrations
- Requirements:
  - Resolved peaks in the far-Infrared
  - Calculations for the far-Infrared



Why is the IR / terahertz region interesting?



Model systems of specific secondary structures



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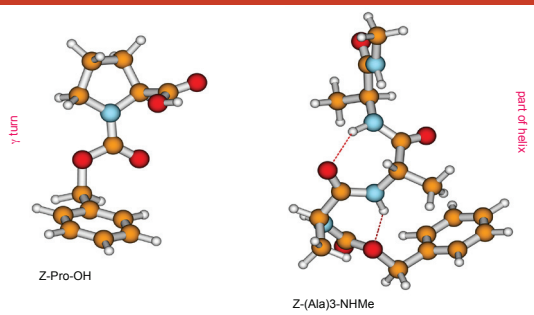


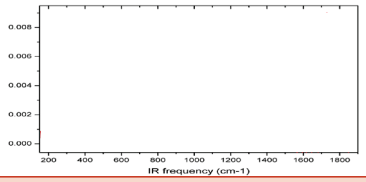
Approach

Strategy:

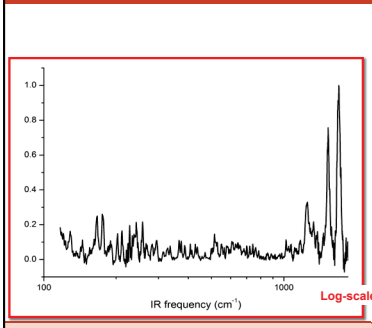
- Confirm the expected secondary structure
  - * amide I & II region + fingerprint
  - * DFT calculations

FAR-IR difficulties
Calculations have to be adapted
Ion-dip signal strength decreases
First time structural identification

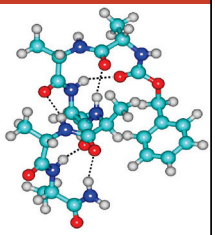
- Explore the far-IR wavelength region for diagnostic bands



Far-IR spectroscopy on Z-Ala$_6$-NH$_2$



Log-scale !!!!!



Z-Ala$_6$-NH$_2$
3$_{10}$-helix

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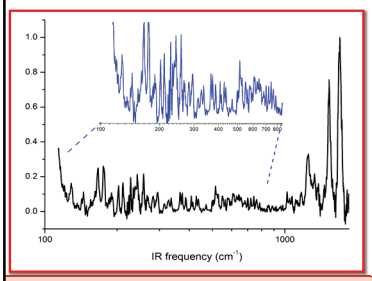
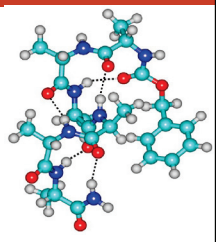




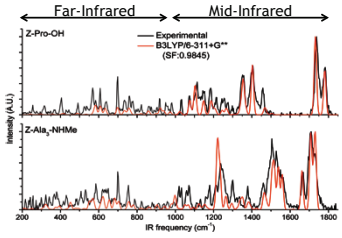
Z-Ala$_6$-NH$_2$
3$_{10}$-helix

Analysis of Z-Ala$_3$-NHMe

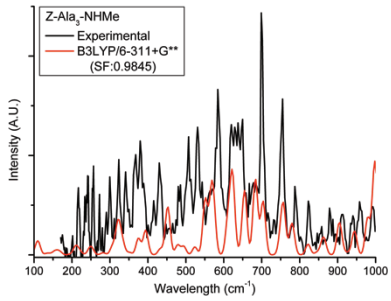
mid-IR for structural assignment

Peaks are resolved far-Infrared

Calculations not in desired agreement

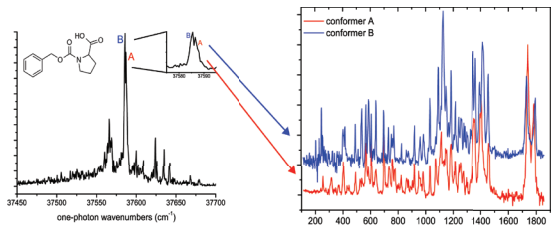


How does the calculations hold in the far-IR??



Start simple → Z-Pro-OH

Z-Pro-OH: step 1 & 2

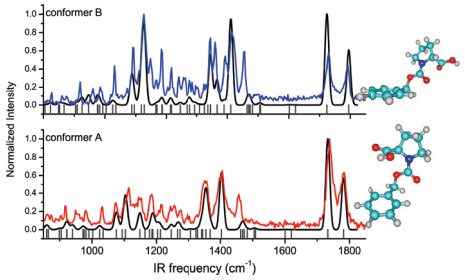


UV spectrum to locate origins of present conformers

Expand IR spectrum to far-IR

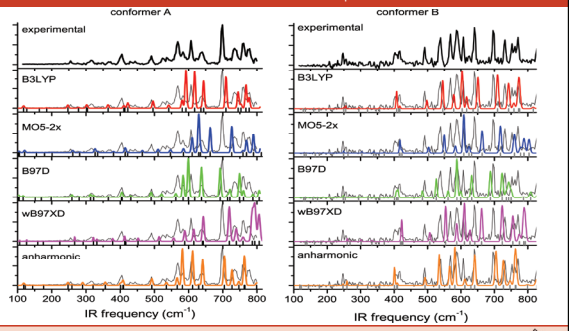
Z-Pro-OH: step 3

Assign structures using the known mid-IR region

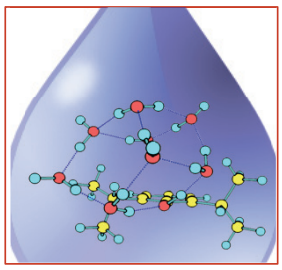


Z-Pro-OH far-IR: step 4

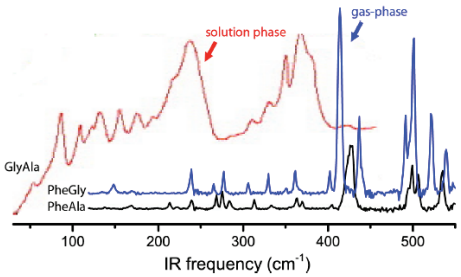
Explore the current theoretical methods



Water-clusters – far IR

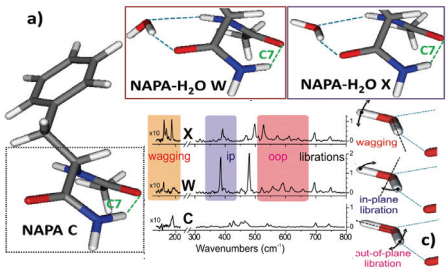


Gas phase vs solution phase



NAPA – Water: probing water motions

J.Phys.Chem.Lett. 2012, 3 , 3307



Prof. Michel Mons - CEA Saclay

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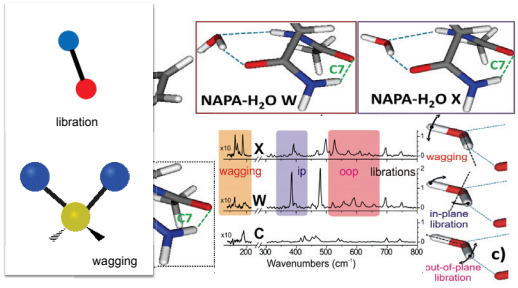

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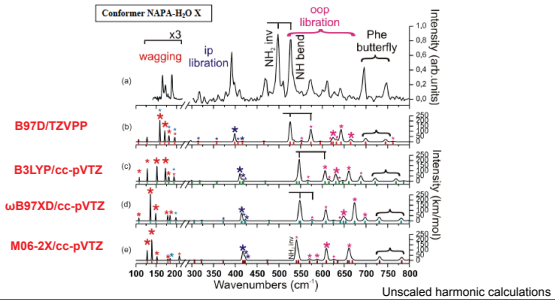
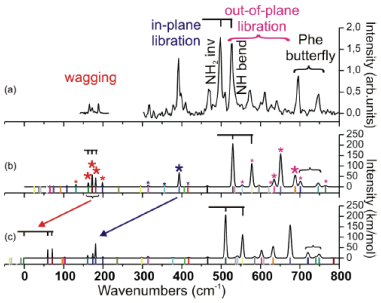
NAPA – Water: calculations / functionals

J.Phys.Chem.Lett. 2012, 3 , 3307



Unscaled harmonic calculations

NAPA – Water: calculations → anharmonicity



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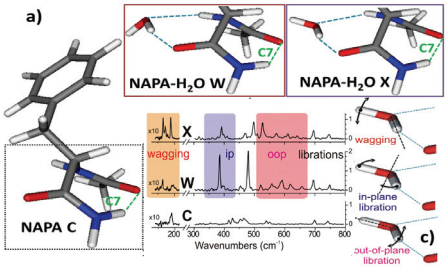

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Acknowledgements

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Dennis Löwik (Nijmegen)
Sander Jaeqx (Rijnhuizen)

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FOM Rijnhuizen
MolDyn & Team FELIX