

Gas Phase IR spectroscopy:

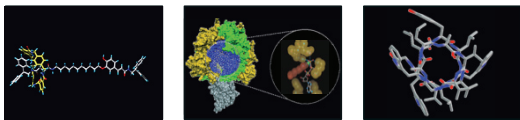
towards large biomolecules
&
far-IR wavelengths

Anouk M. Rijs

Winterschool Han-sur-Lesse 2012, 10-14 December 2012

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Probing directed molecular motion by gas phase IR spectroscopy



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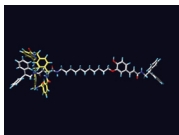
Directed motion: (bio) molecular motors

Linear motor: kinesin
cargo transport



*protein based
complicated - efficient
unidirectional
energy: ATP (chemical)
conversion of ATP into mechanical motion*

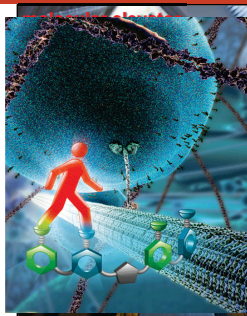
Linear motor: rotaxane



*synthetic, designed
2 component interlocked structure
equilibrium
energy / trigger: controlled
light, solvent, pH, charge state*

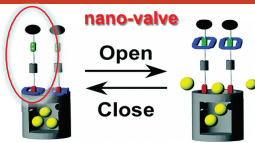
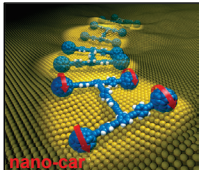
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Molecular motors Rotaxanes !!



nano-valve

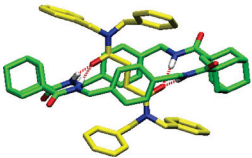
Open ↔ Close

nano-car

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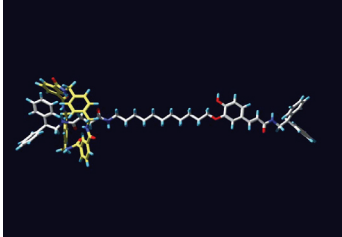
What are rotaxanes ?



- macrocycle
- thread
- bulky stoppers
- Hydrogen bonds

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Rotaxanes as artificial motors



- macrocycle
- thread
- bulky stoppers
- Hydrogen bonds
- Binding stations**

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Approach

to understand **function** = study **structure**
 to obtain full **control** over molecular motion

↓

- Intrinsic properties
- Hydrogen bond interactions

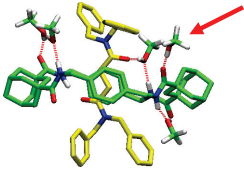
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Gas Phase IR spectroscopy

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Characterization of Rotaxanes

- Gas phase spectroscopy
 - intrinsic conformational properties
 - controllable addition of the environment



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Characterization of Rotaxanes

- Gas
 - perties environm
- IR-UV ion dip spectroscopy / IR-MPD
 - provides detailed structural information
 - direct view on hydrogen bond interactions (shift in IR frequency)

Neutral molecular beam

Charged FTICR

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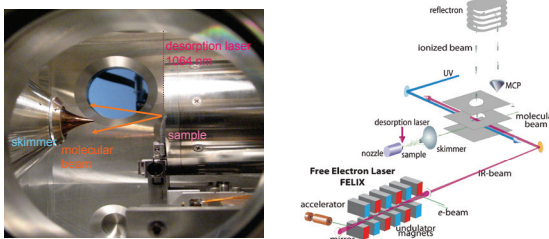
Experimental Method: Molecular Beam

laser desorption: Creation gaseous molecules

Molecular Beam: Cooling neutral molecules

Spectroscopic Techniques: IR / UV excitation

Mass selective Detection



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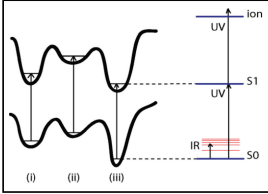
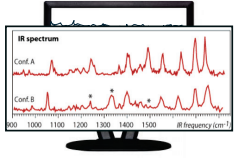
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Aim

Can we characterize & control intra-molecular interactions in rotaxanes ???

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Gas phase experiments on rotaxanes

Characterization of isolated rotaxanes

Direct view of structure and binding interactions in a rotaxane by IR spectroscopy

Rijs et al. J.Am.Chem.Soc. 131, 2428 (2009)

fingerprint NH bend C=O stretch

macrocycle thread rotaxane

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fingerprint NH bend C=O stretch

macrocycle thread rotaxane

C=O stretch H-bonded

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Releasing a molecular brake

Start of molecular motion by discrete microsolvation

Rijs et al. Angew. Chem. Int. Ed. 49, 3896 (2010)

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The beginning of molecular motion...

= the release of the molecular brake!

Communications

Controlled Hydrogen-Bond Breaking in a Rotaxane by Discrete Solvation

David M. Ruiz, Nadja Khatib, Martina N. Baum, Jan Oomens, Jeffrey S. Homan, David J. Leigh, Francesco Zerbetto, and Wynne J. Braud

Angewandte Chemie International Edition

Rijs et al. Angew. Chem. Int. Ed. 49, 3896 (2010)

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Microsolvation of rotaxanes by methanol

neutral rotaxanes

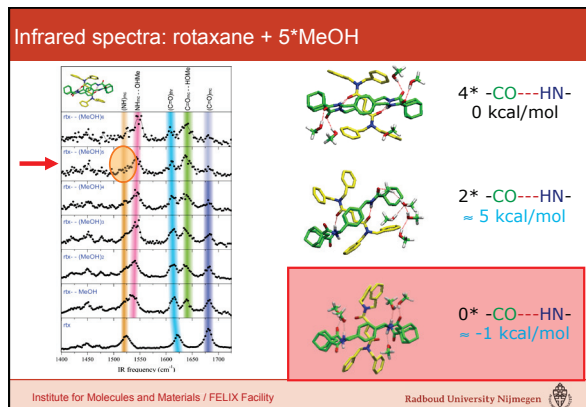
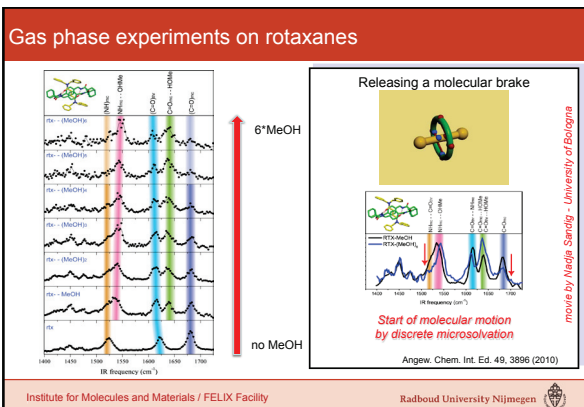
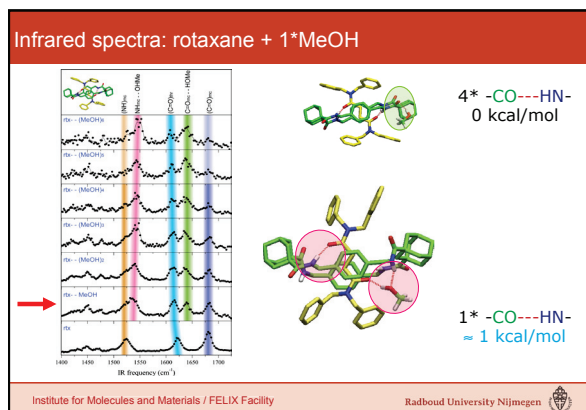
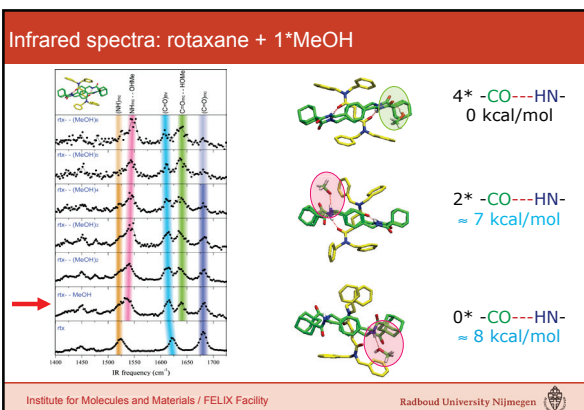
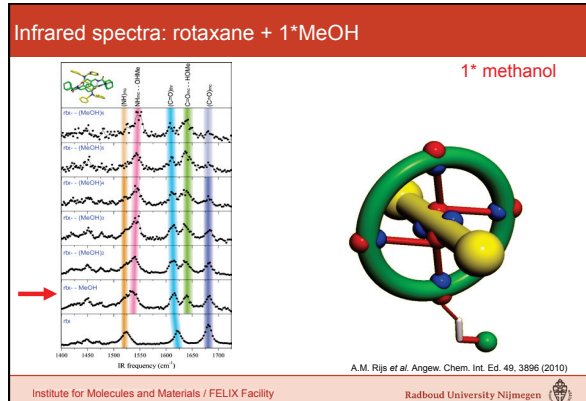
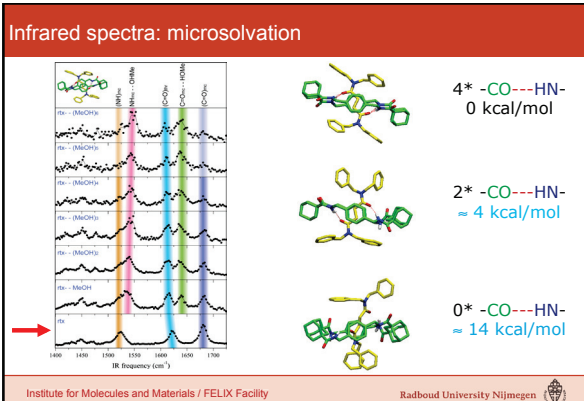
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Infrared spectra: microsolvation

no methanol

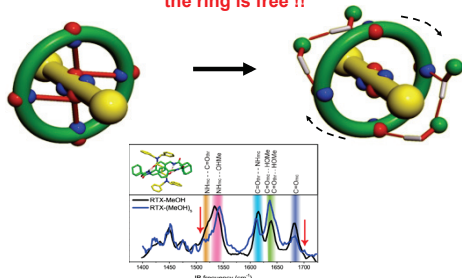
A.M. Rijs et al. Angew. Chem. Int. Ed. 49, 3896 (2010)

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Releasing a molecular brake

all intra-molecular hydrogen bonds are broken...
the ring is free !!



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Aim-2

Can we increase the rotaxane with an extra station?

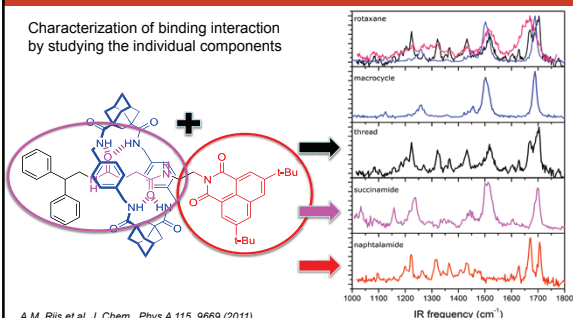
Can we measure the position of the macrocycle?

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Characterization of two-station rotaxane

Characterization of binding interaction
by studying the individual components

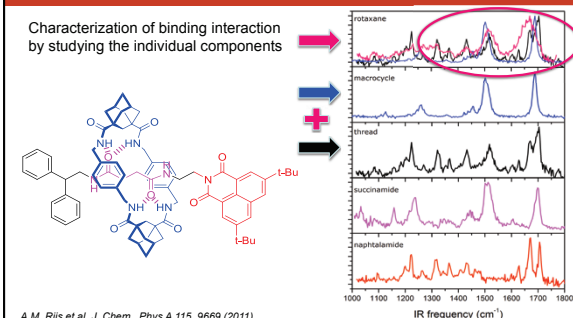
A.M. Rijs et al. *J. Chem. Phys. A* 115, 9669 (2011)

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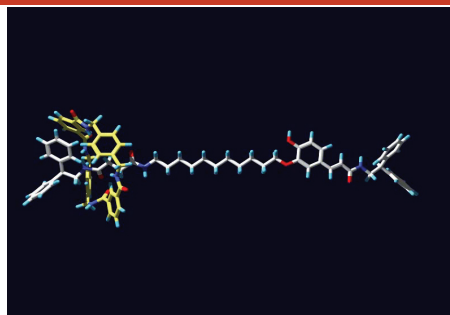
Aim-3

Can we induce molecular motion in a rotaxane ?

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Motion in isolated molecular motors



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Other spectroscopic techniques: Ions

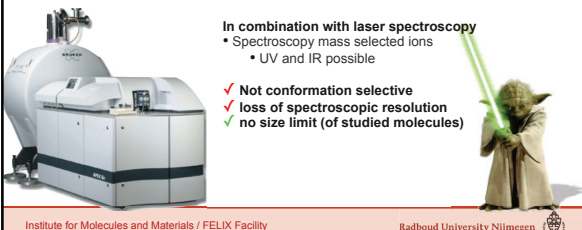
Mass Spectrometry

- ions
- room temperature
- analytical tool (identification)
- gas phase chemistry
- mass selective

In combination with laser spectroscopy

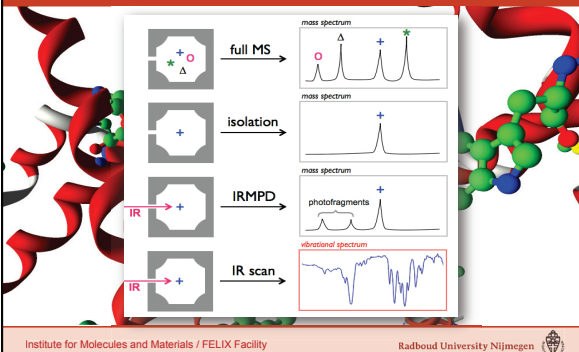
- Spectroscopy mass selected ions
 - UV and IR possible

✓ Not conformation selective
 ✓ loss of spectroscopic resolution
 ✓ no size limit (of studied molecules)



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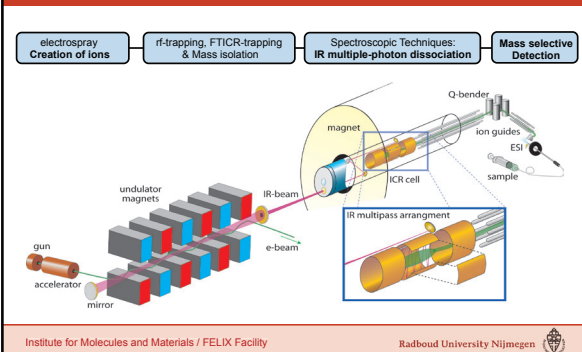
Ion Spectroscopy



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Experimental Method: FTICR

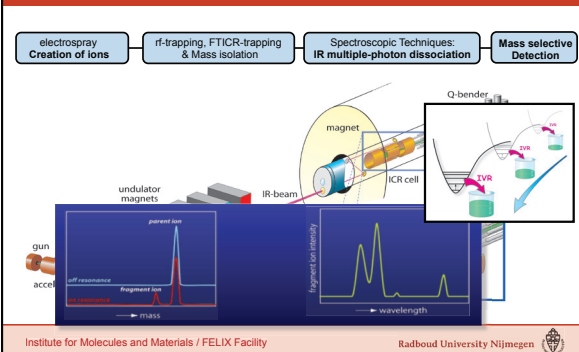
electrospray Creation of ions → rf-trapping, FTICR-trapping & Mass isolation → Spectroscopic Techniques: IR multiple-photon dissociation → Mass selective Detection



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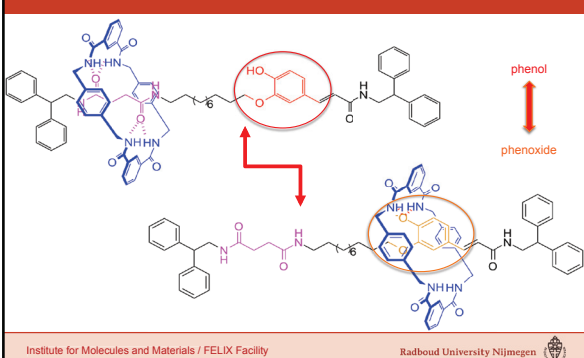
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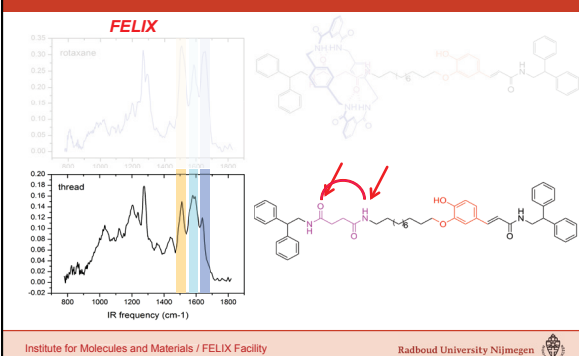
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Motion in isolated molecular motors



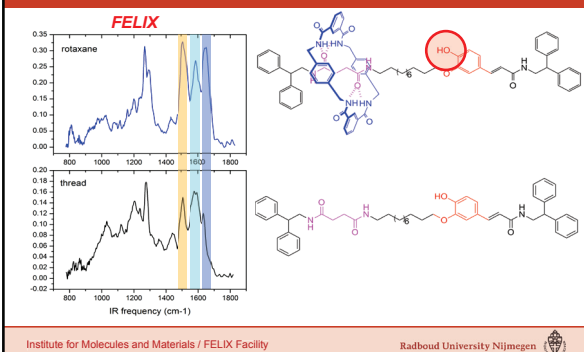
Protonated Rotaxane

FELIX

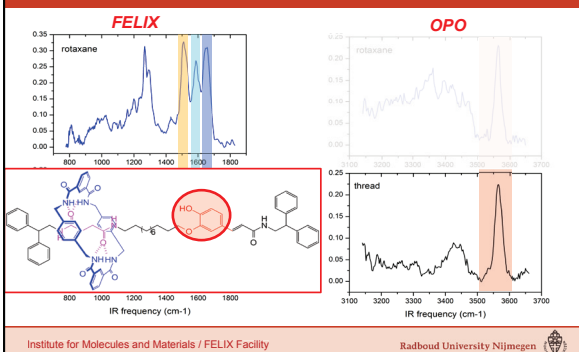


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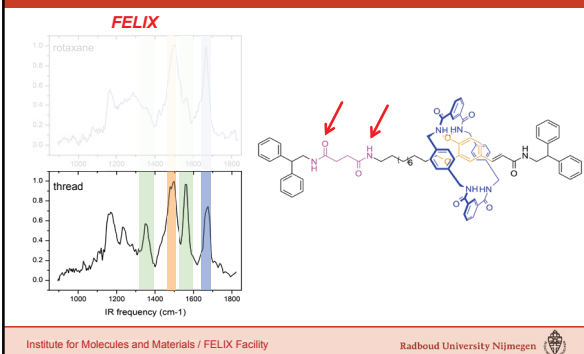
Where is the macrocycle?



The "home" position

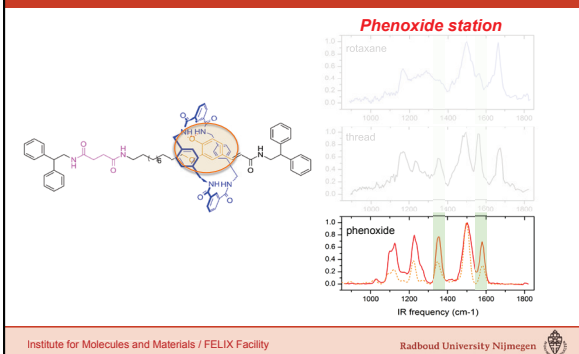


Deprotonated Rotaxane



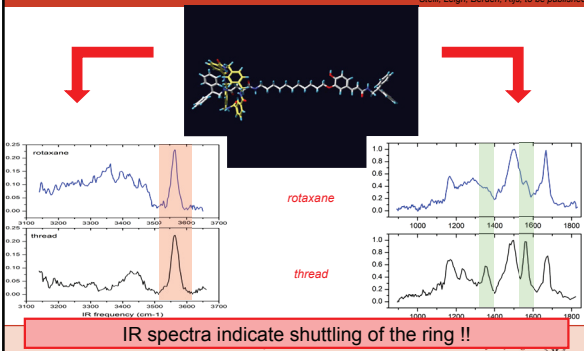
Shuttling?

Yes !!



Shuttling !!

Stell, Leigh, Berden, Rijk, to be published

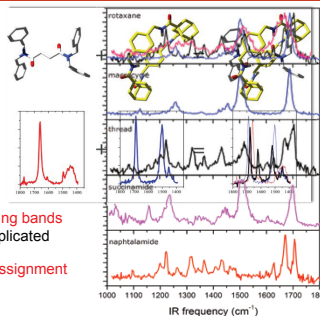


Dark clouds in the sky?

How large can we go while maintaining spectral resolution ??

Problem in IR spectroscopy for large molecules

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



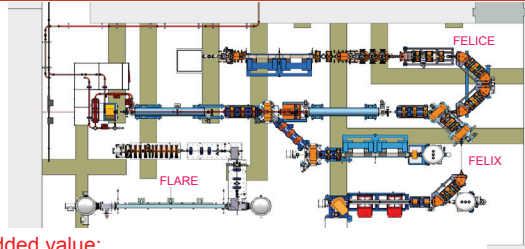
Larger molecular systems = overlapping bands
 → structural assignment complicated

Extend range to far-IR for structural assignment

- Extra probe
- Backbone vibrations

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FELIX facility Nijmegen



Added value:

- Spectral range: 3 - 1500 μm
- Simultaneous operation FLARE / FELIX / FELICE
- mid-IR/far-IR double-resonance experiments

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IR action Spectroscopy @ Nijmegen

IR action spectroscopy

FELIX

Amide I (C=O bend)
Amide II (NH stretch)
fingerprint

mid-IR
1800 cm^{-1} to 1000 cm^{-1}


local modes

FLARE

backbone modes
hydrogen bond vibrations
large amplitude motions

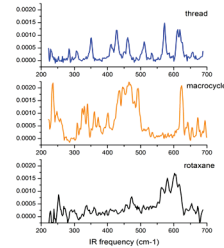
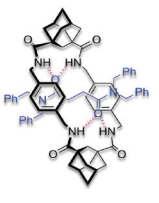
far-IR
100 cm^{-1} to 1 cm^{-1}

global modes



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Far-IR spectroscopy on rotaxanes

Far-IR spectroscopy:

- Using the far-IR as a diagnostic tool.... many highly-resolved bands
- Improve theoretical methods for better understanding
- Direct probing of hydrogen bonds

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Summary


- Gas-phase spectroscopy not limited to small and medium sized molecular systems
- Characterization of **interactions**
IR spectroscopy provides direct view on structure and interactions
- Juggle with interactions to induce **movement**
 - breaking of hydrogen bonds: free macrocycle
 - first steps towards moving of macrocycle

	Neutral rotaxanes	Charged rotaxanes
method	molecular beam + TOF-MS IR ion-dip spectroscopy	FTICR IR multiple photon dissociation
activation	microsolvation	changing electric charge
IR probe	NH bend/ CO stretch	Phenoxide modes

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Acknowledgements

MolDyn & Team FELIX - FOM Rijnhuizen
 FLARE team – Radboud University Nijmegen



Rotaxanes

Jeff Steill (Sandia National labs)
 Giel Berden (Rijnhuizen)
 Wybren Jan Buma (UvA)
 Nadja Sandig & Francesco Zerbetto (Bologna)
 Group of David Leigh (Edinburgh)



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