Lowest Energy Vibrational Modes of Nine Naphthalene Derivatives; Experiment and Theory

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Introduction

Polycyclic Aromatic Hydrocarbons: PAHs

- Potential responsible for the unidentified infrared bands (UIBs) specific to C–C and C–H bendings of PAHs ($\rightarrow$ AIBs)
- To date: several propositions of identification but no unambiguous detection in the interstellar medium (ISM)
- Naphthalene: one of the simplest example of a PAH

Numerous experimental and theoretical studies BUT far infrared (FIR) spectra often remain unknown

Introduction

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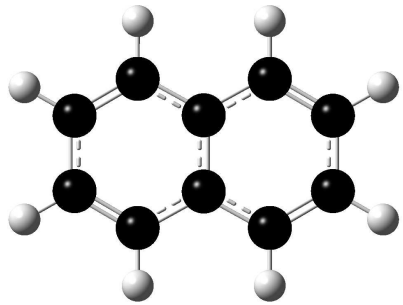
- Naphthalene: one of the simplest example of a PAH

Numerous experimental and theoretical studies BUT far infrared (FIR) spectra often remain unknown

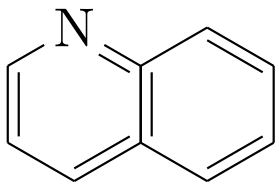
Studied Naphthalene derivatives:

- Isomer of Naphthalene
- PANHs
- Polyphenyl-type molecules

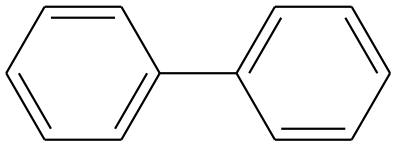


Studied Molecules

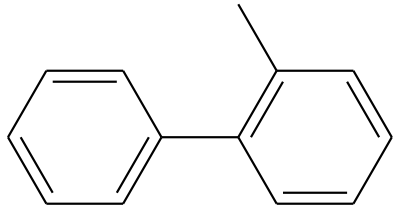
Quinoline
(C_9H_7N)



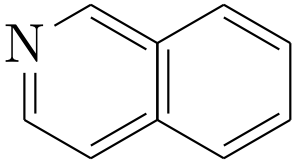
Biphenyl
($C_{12}H_{10}$)



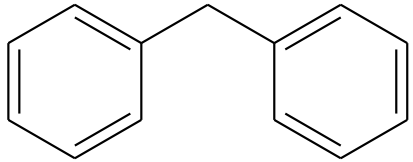
2-phenyltoluene
($C_{13}H_{12}$)



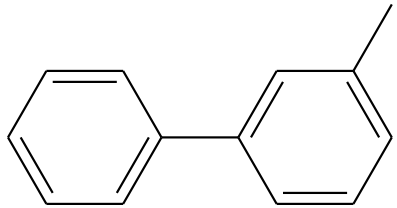
Isoquinoline
(C_9H_7N)



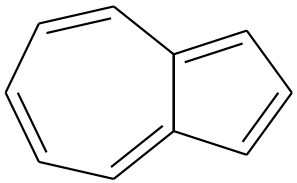
Diphenylmethane
($C_{13}H_{12}$)



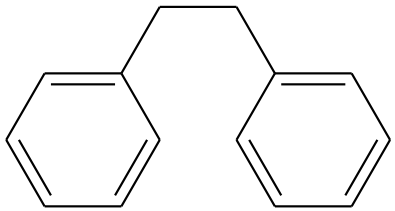
3-phenyltoluene
($C_{13}H_{12}$)



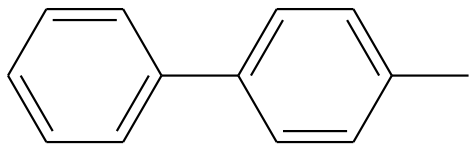
Azulene
($C_{10}H_8$)



Bibenzyl
($C_{14}H_{14}$)



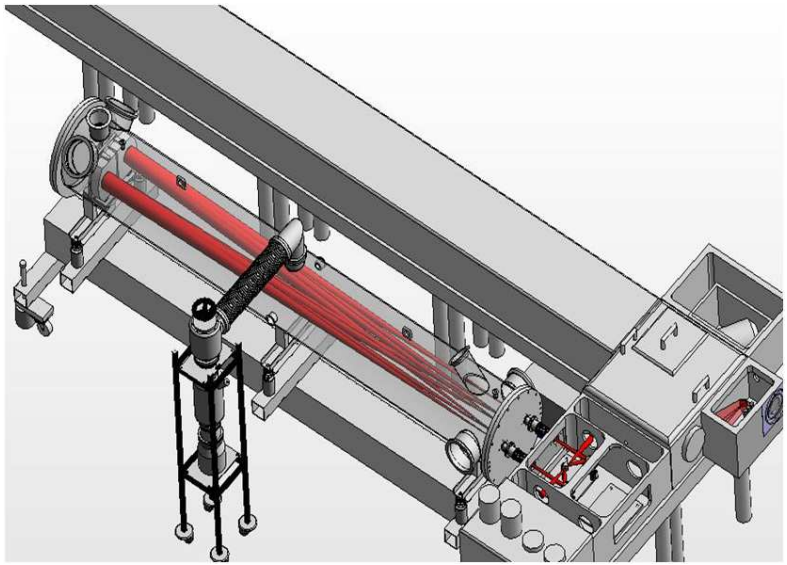
4-phenyltoluene
($C_{13}H_{12}$)



FIR spectroscopy

Gas phase absorption spectra:

Fourier-transform FIR spectroscopy on the AILES beamline at SOLEIL Synchrotron

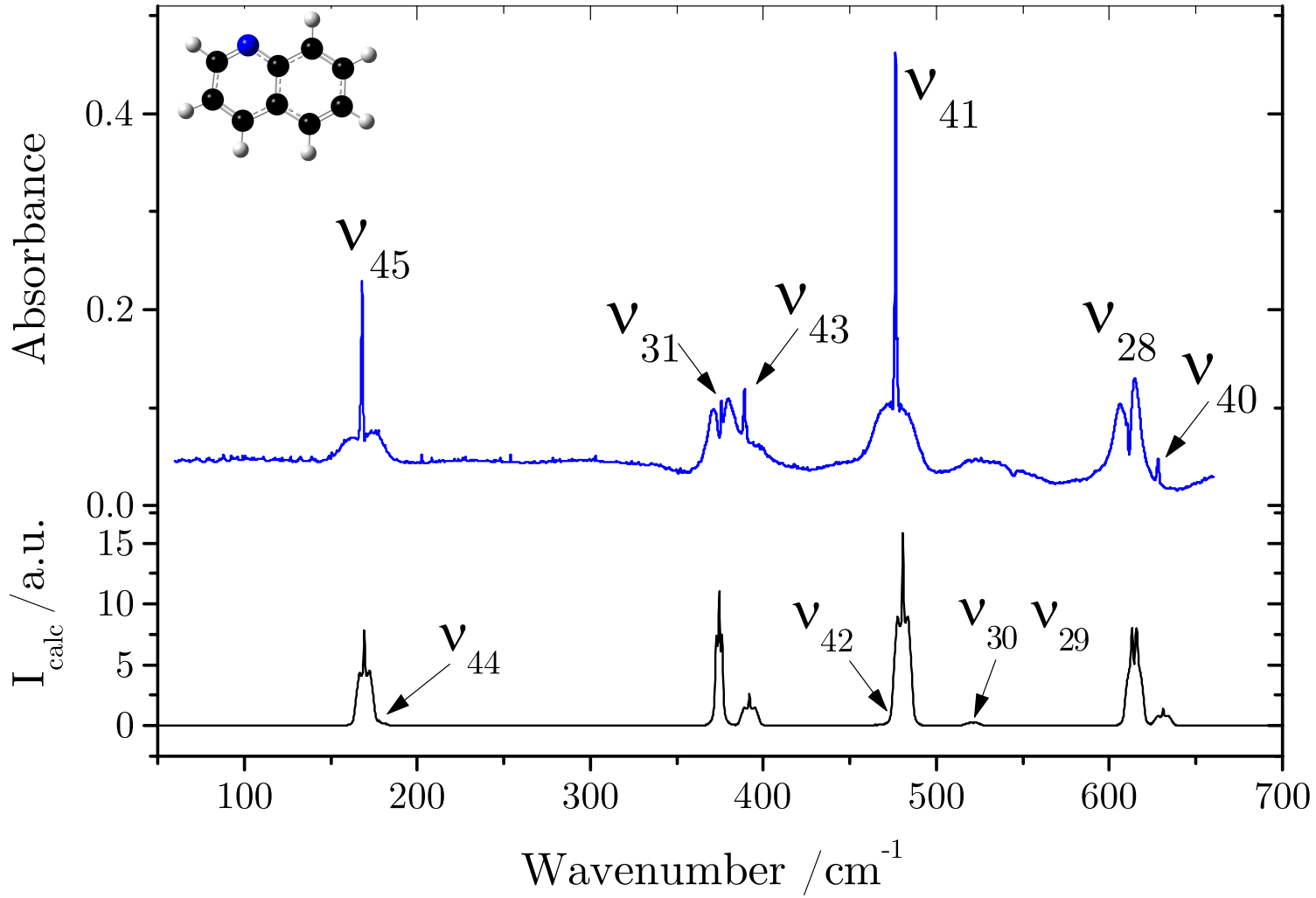


- Globar source
- Optical path length: 150 m
- Room temperature
- $R = 0.5$ cm^{-1}
- Spectral range: 0 – 700 cm^{-1}
- 1000 transmission scans + 1000 reference scans

DFT calculations (Gaussian 09):

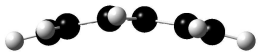
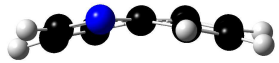
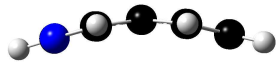
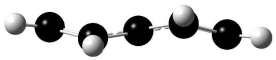
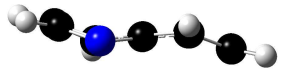
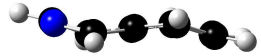
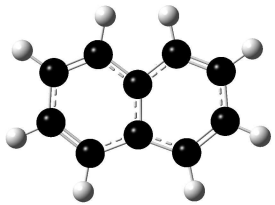
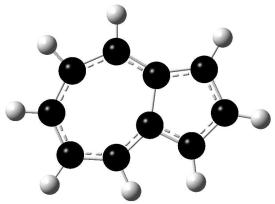
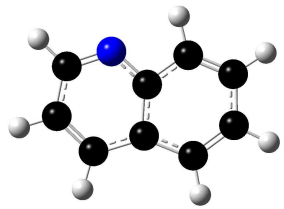
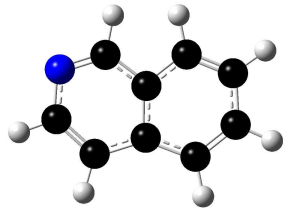
B97-1/6-311G(d,p) (harmonic + anharmonic)

FIR spectrum of quinoline



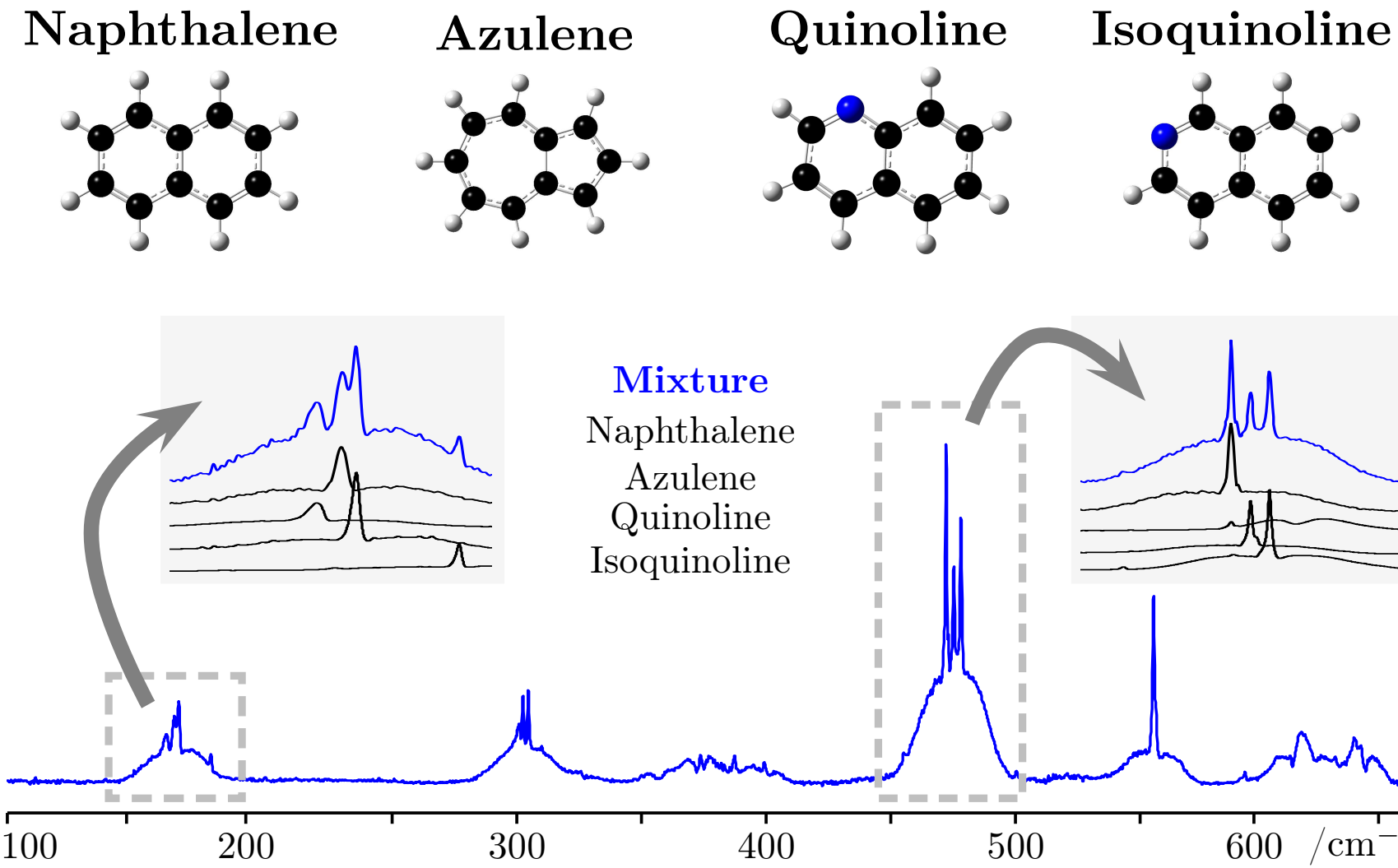
Simulation: anharmonic frequencies + ground state rotational constant (Pgopher)

Evolution of 3 low vibration modes

		Naphthalene	Azulene	Quinoline	Isoquinoline
		Out-of-Plane Vibrations			
Butterfly (♣)					
	ν	166 cm^{-1}	163 cm^{-1}	168 cm^{-1}	166 cm^{-1}
	Δ		-2 %	-1 %	0 %
Chair (♦)					
	ν	*388* cm^{-1}	307 cm^{-1}	392 cm^{-1}	376 cm^{-1}
	Δ		21 %	1 %	-3 %
		In-Plane Vibration			
Scissor (♠)					
	ν	359 cm^{-1}	329 cm^{-1}	374 cm^{-1}	*355* cm^{-1}
	Δ		-8 %	4 %	-1 %

$$\Delta_i = (\tilde{\nu}_i^M - \tilde{\nu}_i^{Napht})/\tilde{\nu}_i^{Napht}$$

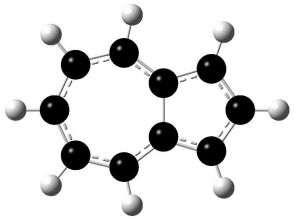
Mixture of Naphthalene derivatives



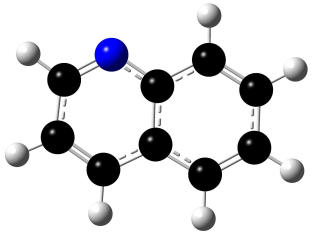
Partial pressures: 11 µbar

First conclusions

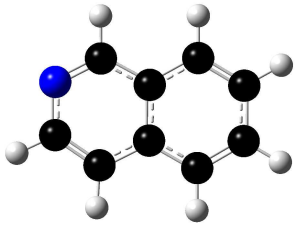
Azulene



Quinoline



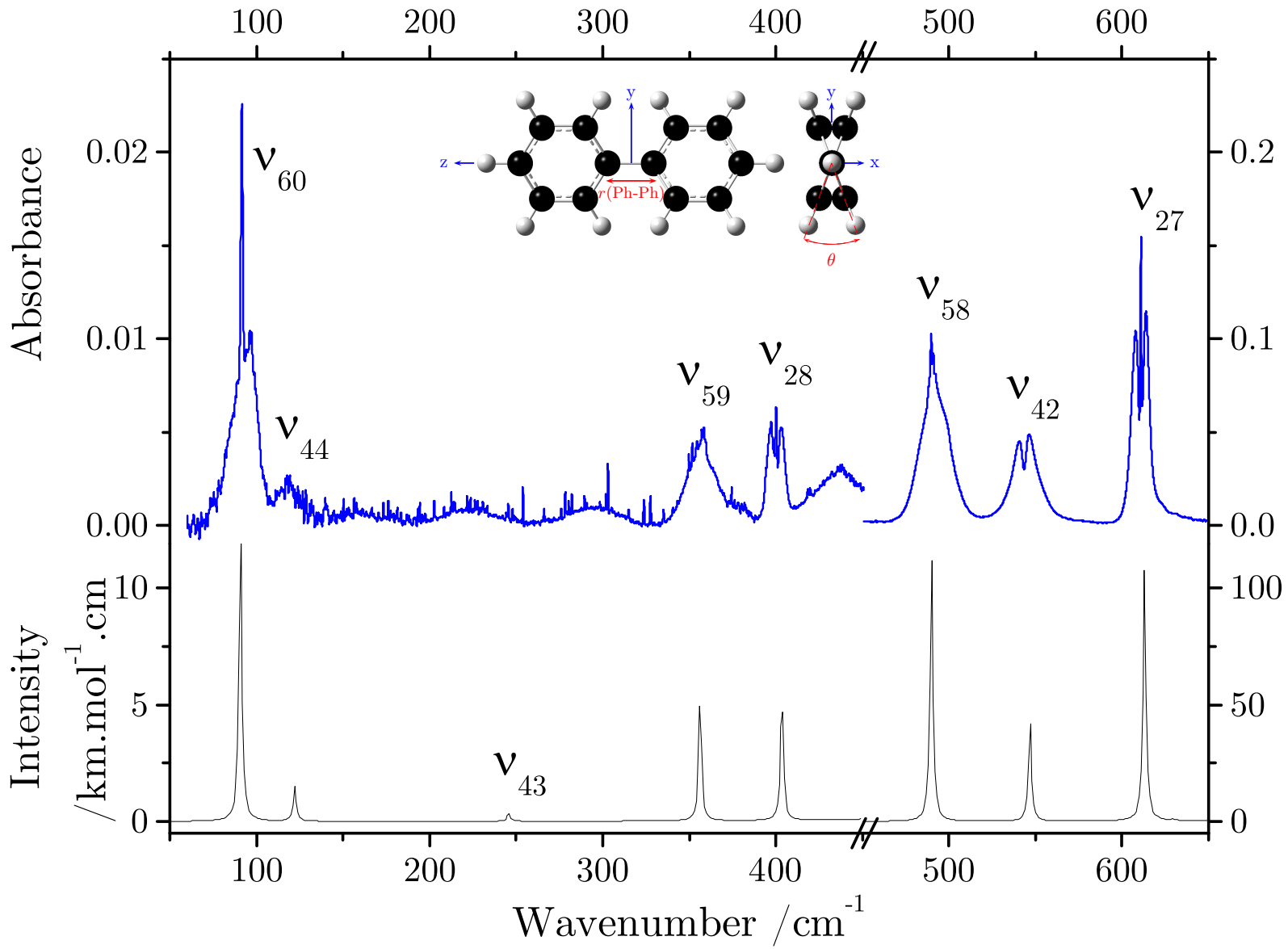
Isoquinoline



- 1^{st} gas phase FIR spectra
- Accurate frequency determination of most active FIR modes
- Identifications using DFT calculations
- Very good agreement between experimental and anharmonic frequencies (≤ 5 %, $\simeq 1$ %)
- Observation of a significant influence of the skeletal structure on the FIR spectra

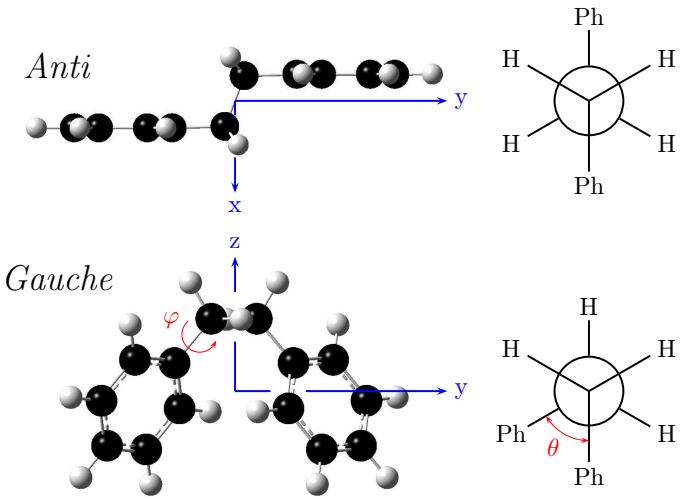
Martin-Drumel *et al.*, *Chem. Phys. Lett.* (2013)

FIR spectrum of biphenyl



Simulation: anharmonic frequencies (GaussView)

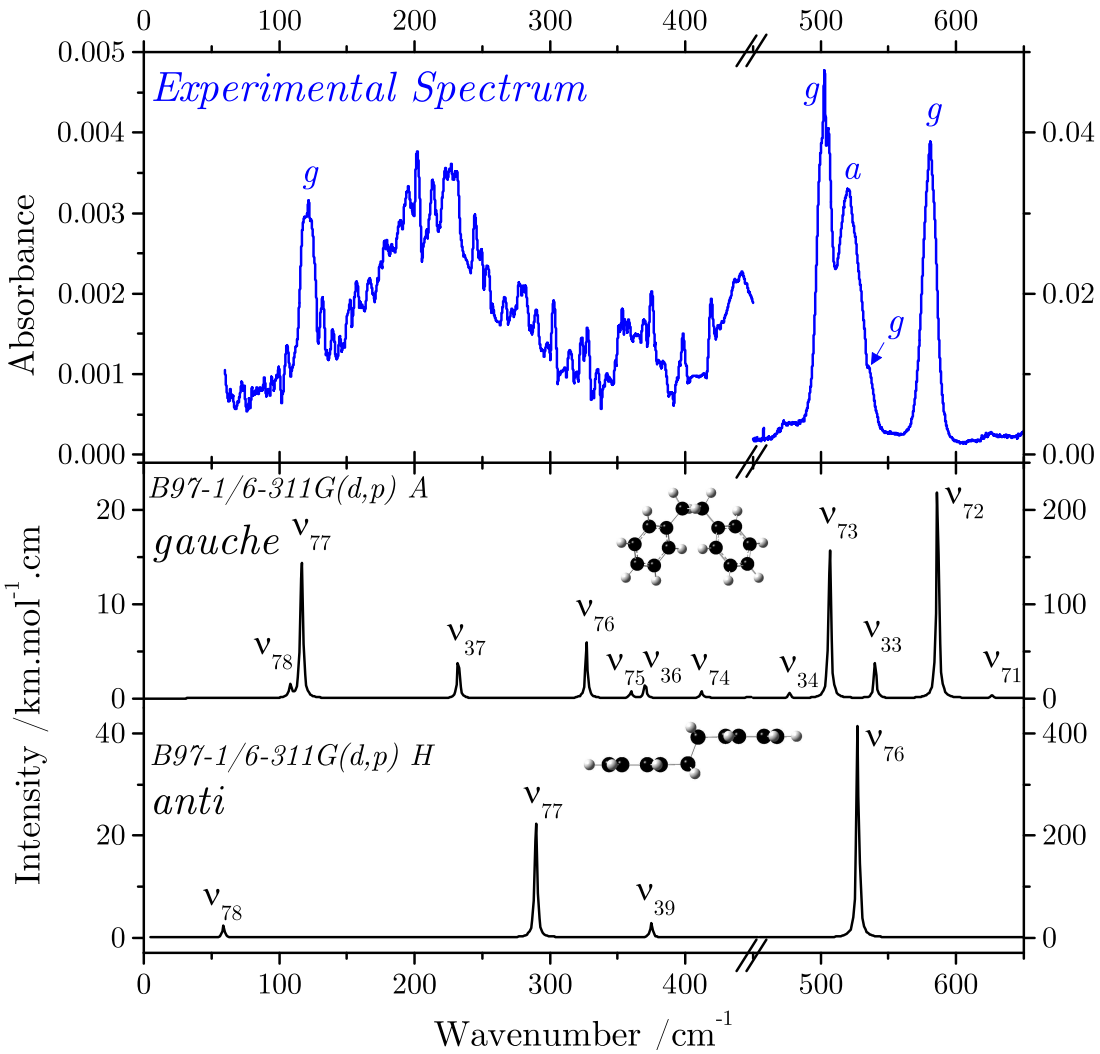
FIR spectrum of Bibenzyl



Shen, *J. Mol. Struct.* (1998):
anti form (*gauche* not excluded)
gas phase, electron diffraction

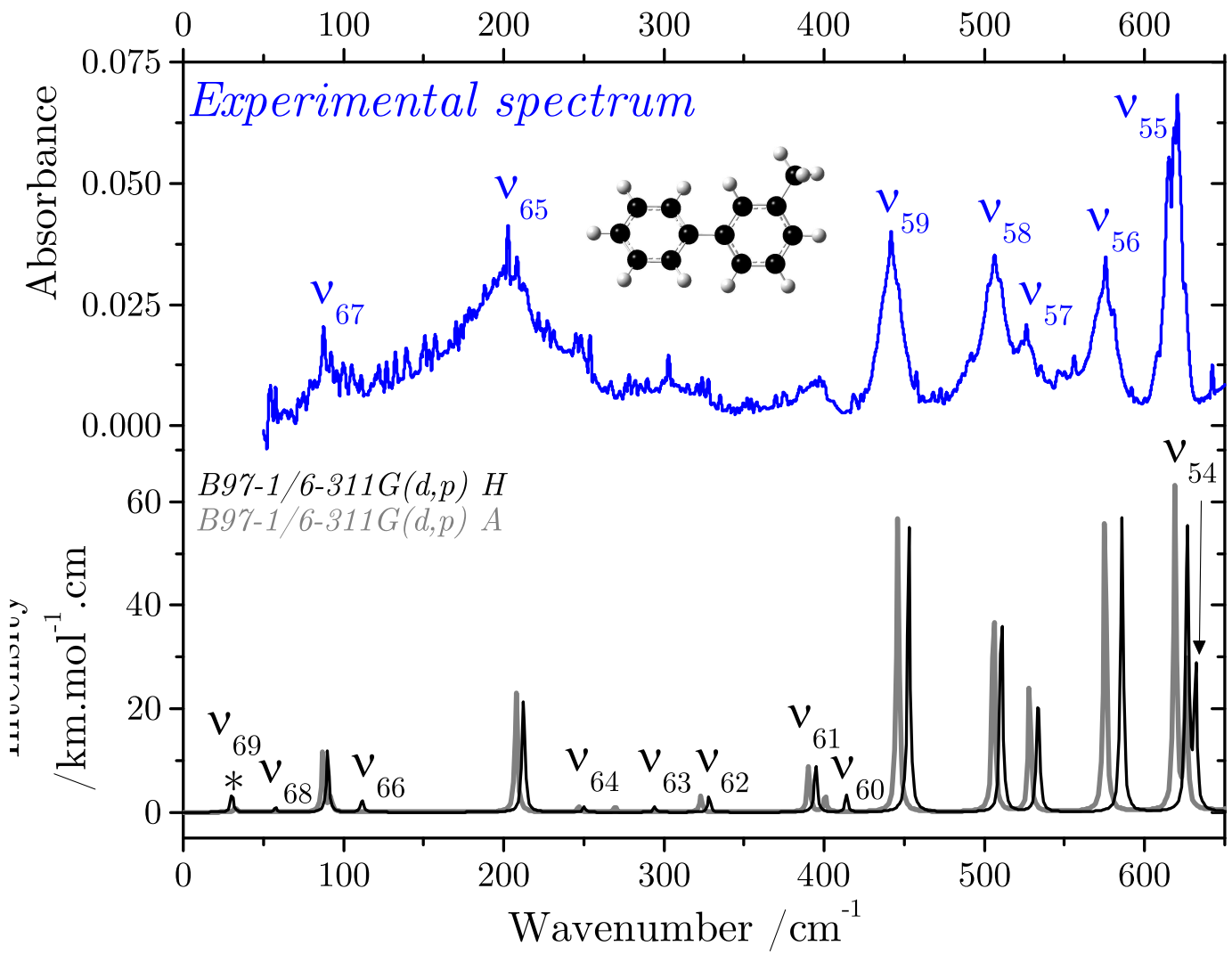
This work:
gauche form (*anti* not excluded)

Estimation of the ratio:
gauche:*anti* = 2:1
(66 % *gauche*, 33 % *anti*)



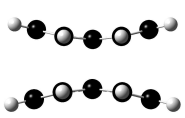
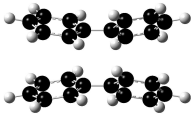
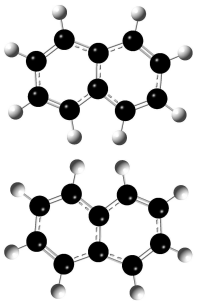
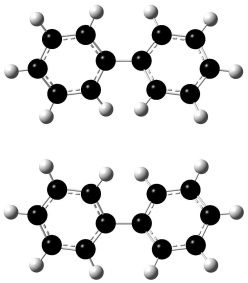
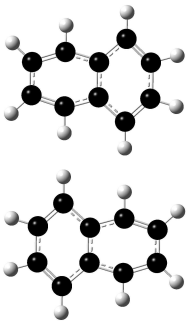
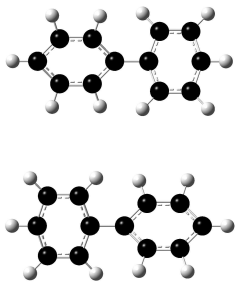
Simulation: anharmonic frequencies (GaussView)

FIR spectrum of 3-phenyltoluene



Simulation: harmonic (black) + anharmonic (gray) frequencies (GaussView)

Evolution of low-frequency vibrational modes

	Naphthalene	Biphenyl
	Butterfly	
		
ν	166 cm^{-1}	92 cm^{-1}
Δ		-45 %
	Cissors	
		
ν	359 cm^{-1}	118 cm^{-1}
Δ		-67 %
	Antisymmetric stretching	
		
ν	620 cm^{-1}	611 cm^{-1}
Δ		-1 %

Butterfly mode:

Biphenyl	94 cm^{-1}
Diphenylmethane	64 cm^{-1}
Bibenzyl *gauche*	47 cm^{-1}
Bibenzyl *anti*	54 cm^{-1}
2-phenyltoluene	43 cm^{-1}
3-phenyltoluene	58 cm^{-1}
4-phenyltoluene	67 cm^{-1}

(Calculated harmonic values)

- C–C bond
  → diminution of the rigidity
  → diminution of the frequencies of the "butterfly" and "cissors" modes
- Great variability of the butterfly mode
- Phenyltoluenes: steric crowding
  → diminution of the rigidity
  → diminution of the frequency of the "butterfly" mode

Conclusions

Diphenyls molecules:

- 1st gas phase FIR spectra of 6 flexible diphenyl molecules
- Observation of most of active FIR modes
- Identifications using DFT calculations
- Very good agreement between experimental and calculated frequencies (≤ 5 %)
- 1st estimation of bibenzyl *gauche*:*anti* ratio

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Prospects:

- Study of the anharmonicity of vibrational modes
- Resolution of rotational structure

Tomorrow: **RF14**, O. Pirali et al.