TOWARDS THE DETECTION OF EXPLOSIVE TAGGANTS: MICROWAVE AND MILLIMETER-WAVE GAS PHASE SPECTROSCOPIES OF 3-NITROTOLUENE

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Outline

- Context
- Internal rotation motion
- Measurements and data analysis
  - Jet-FTMW spectroscopy (2-20 GHz)
  - Room temperature millimeter-wave spectroscopy (70-220GHz)
- Conclusion and prospects

Context

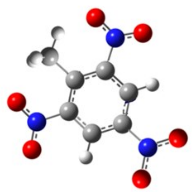
A. Cuisset

G. Mouret

- Nitrotoluene compounds are focused in my PhD project :

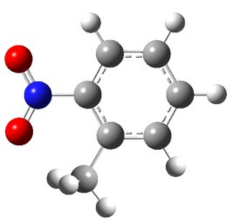
Military interest + Industrial compound

Taggants of explosives (TNT)

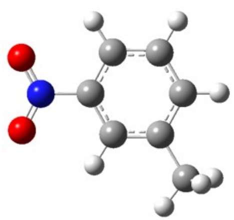


Widely used in dyestuffs, pesticides, rubber and in the pharmaceutical industry.

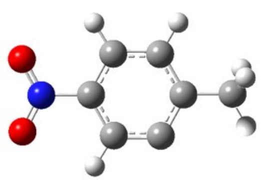
- **The detection, quantification and monitoring** of explosives and their taggants requires methods with **high selectivity and sensitivity**.
- First **gas phase high resolution THz** measurements of **explosives taggants** at **room temperature**



2-Nitrotoluene



3-Nitrotoluene

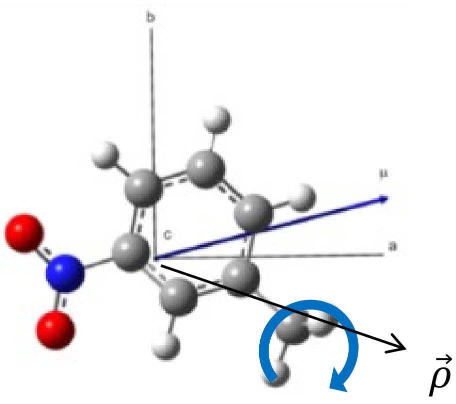


4-Nitrotoluene

Species	P_{vap} (293 K) /mbar	/Pa
TNT	6.10^{-6}	0.0006
2,4-DNT	5.10^{-4}	0.05
2,6-DNT	$2.5.10^{-4}$	0.025
2-NT	**0.127**	**12.7**
3-NT	**0.086**	**8.6**
4-NT	**0.038**	**3.8**

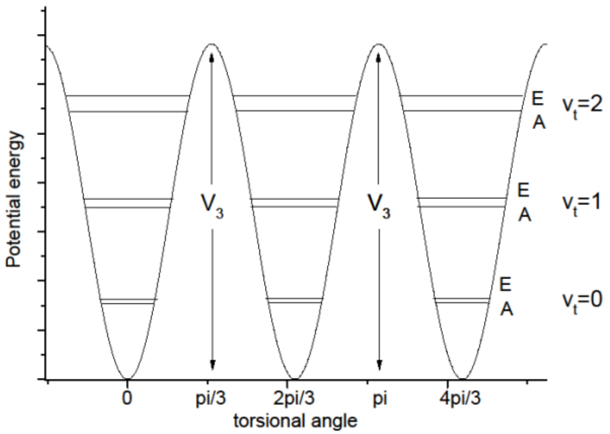
Internal rotation motion

- **Spectroscopic properties of 3-Nitrotoluene (3-NT)**
  - Asymetric rotor (K=−0,7), a-type (μ_a = 5D) and b-type (μ_b = 1D) transitions
  - **Hyperfine structure** I(N)=1
  - **Internal rotation coupling with the methyl group**



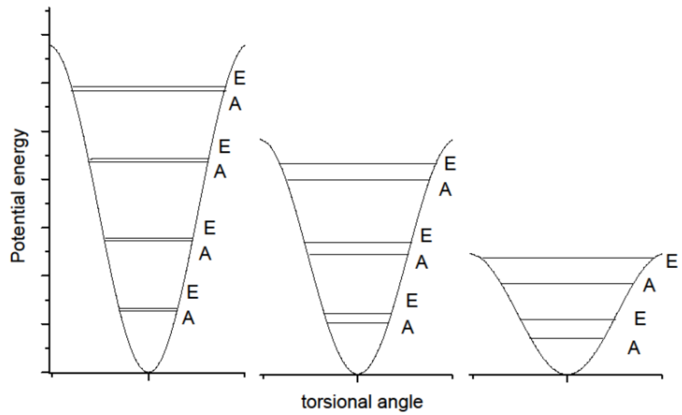
- **Effect of internal rotation on the observed spectra : splitting of the E levels**

Three equivalent positions are possible compared to the molecular frame : the potential function is **periodic**.



The tunneling effect throw the internal rotation barrier **splits each rotational level** into nondegenerated **(A species)** and doubly degenerated (**E species) sublevels.**

The internal dynamics is linked to **the height of the potential barrier:**



<u>Lower is the barrier, larger are the splittings</u>

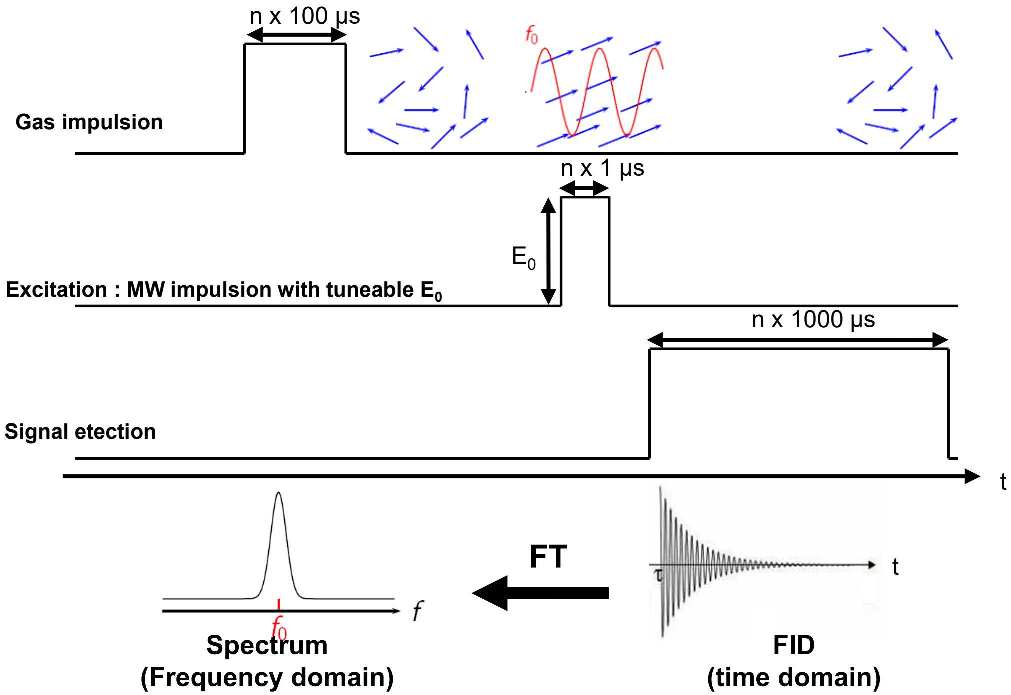
Measurements and data analysis

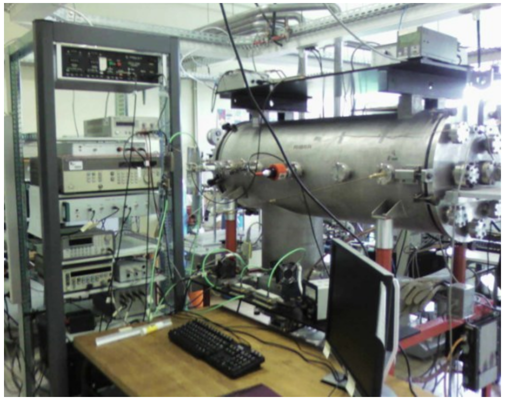
Using the Jet-FTMW spectrometer of the PhLAM (2-20 GHz)


S. Bteich M. Goubet

- **The jet-cooled FTMW spectrometer**
  - **Pure rotational** spectroscopy in the **gas phase cooled by adiabatic expansion (T_{rot}<10K)**

Gas impulsion of 3-NT evaporated in a heated injector (343K) and seeded in Neon gas (2.5bar) ⇨ **short and intense** MW pulse ⇨ **macroscopic polarization** at the **resonant frequency** ⇨ **When the electromagnetic field is cut-off,** the molecules emit **a free induction decay** signal





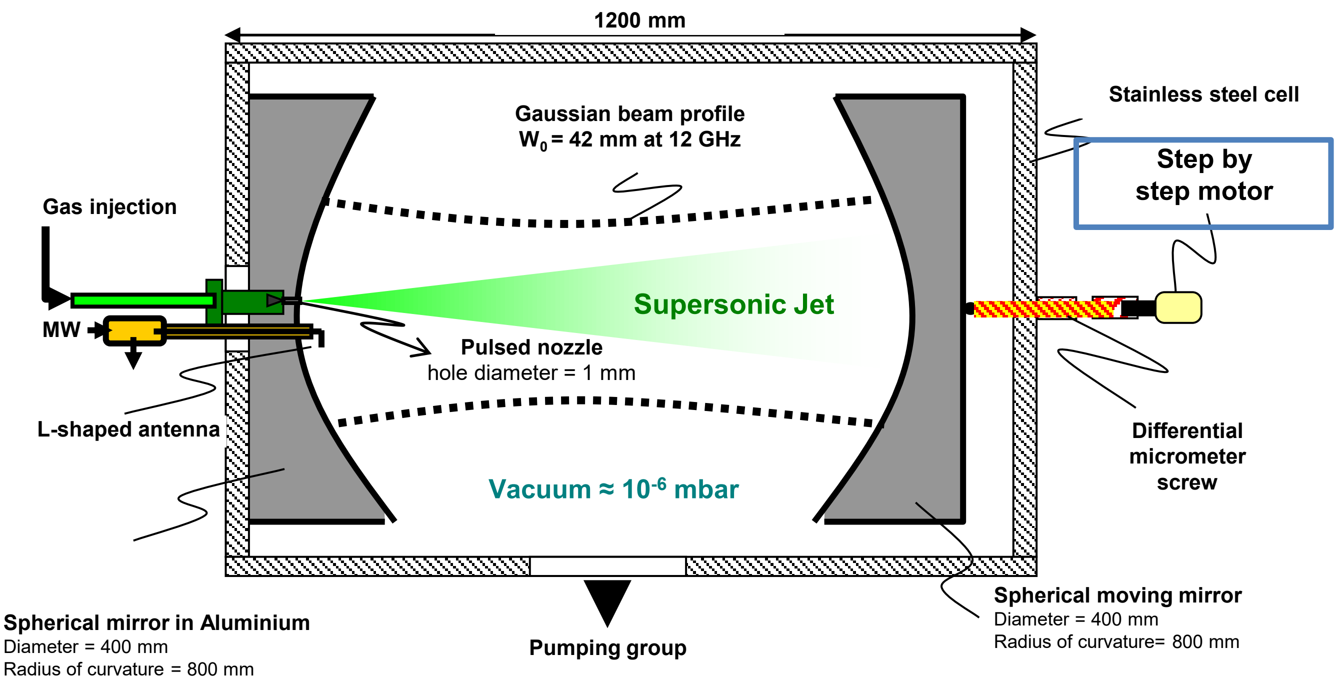
T_{rot}<10K:
Relaxation of the population to the lower rotational states

Measurements and data analysis

Using the Jet-FTMW spectrometer of the PhLAM (2-20 GHz)


S. Bteich M. Goubet

- **Cavity : Perot-Fabry resonator**
  - **Signal amplification** : the mode of the cavity is tuned to be resonant with a molecular transition
  - **Coaxial arrangement** : Doppler doublet (splittings of 70 kHz)



moving the mirror
=
adjust the length of the cavity

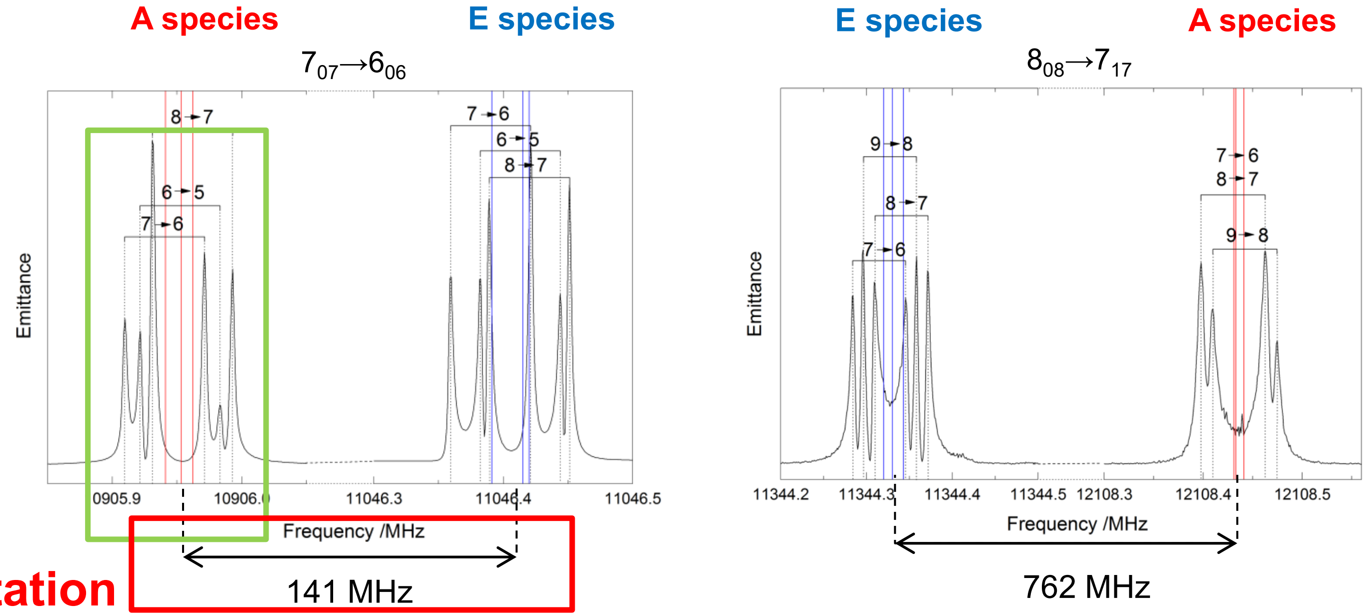
<u>High sensitivity and resolution</u>
Hyperfine structures fully resolved (accuracy of 2kHz)

Measurements and data analysis

Using the Jet-FTMW spectrometer of the PhLAM (2-20 GHz)

- **Results of the MW analysis**

Hyperfine structure Splittings + Doppler splittings



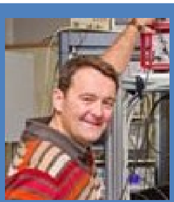
Internal rotation splitting

v_t	sym	J''_{max}	$K''_{a,\ max}$	N^a	RMS /kHz
0	A	11	6	300	1.8
0	E	11	6	260	2.0

Measurements and data analysis

Using the mm-wave spectrometer of the LPCA (70-220GHz)

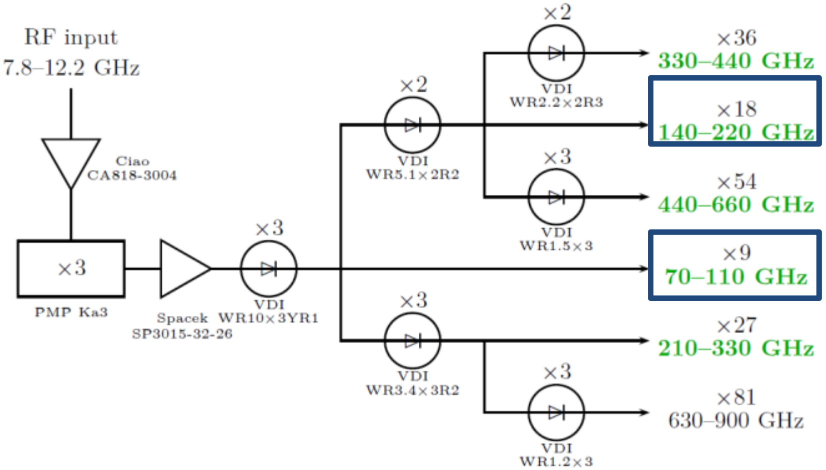

G. Mouret

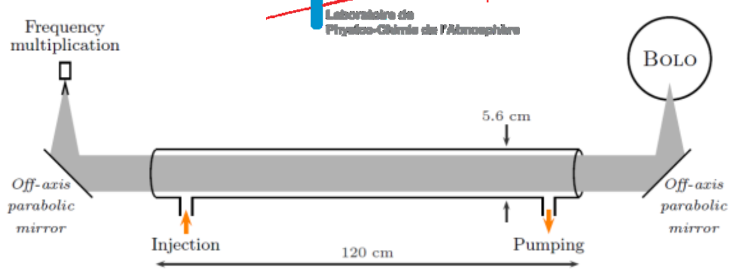

F. Hindle

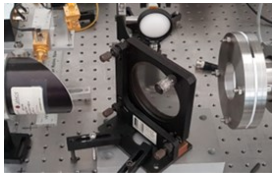

R. Bocquet

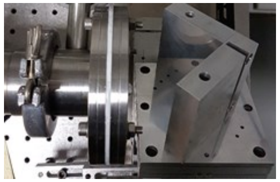
Millimeter-wave room temperature spectrometer (293K)

- **Source**
  - Commercial frequency multiplier chain (VDI)
  - **Electronic source** associated with **multipliers**
- **Cell**
  - Simple or double pass 1.25m absorption cell
  - P= 8μbar (flow)
- **Detection**
  - **Good S/N ratio** : 2F frequency modulation (25.5kHz)
  - **High spectral resolution** (10kHz), Doppler limit.
  - **High sensitivity** : InSb He cooled bolometer (4K)

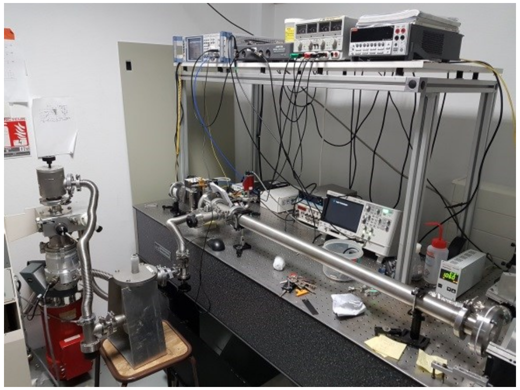





Grid


45° Rooftop

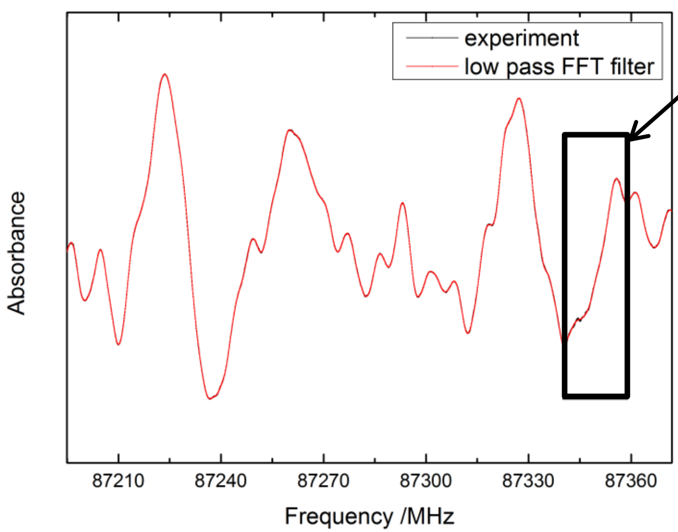
Double pass cell modification:

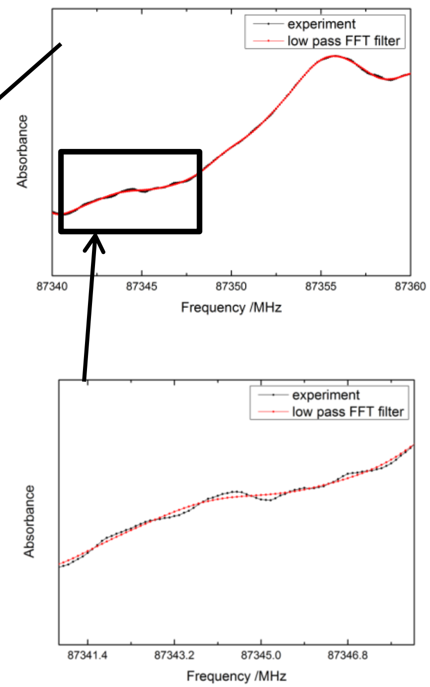


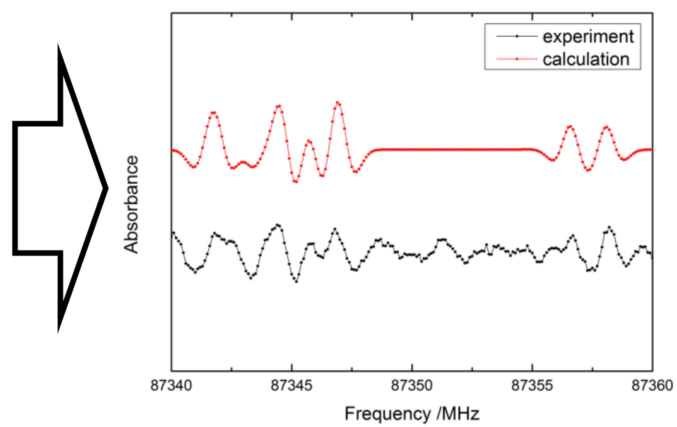
Measurements and data analysis

Using the mm-wave spectrometer of the LPCA (70-220GHz)

- **Millimeter-wave spectrum (70-220 GHz)**
  - **Perot-Fabry** effect arising from **stationary waves**
  - **Weak and congested 2F absorption spectrum of 3NT**





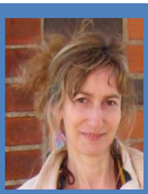


Baseline was reproduced with a FFT filter and then subtracted to reveal the molecular lines

Step : 100kHz
Deviation : 40kHz
Time constant : 200ms
P =8µbar (flow)

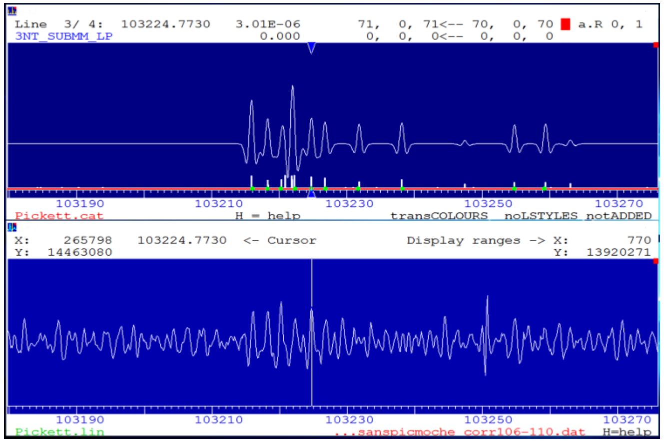
Measurements and data analysis

Using the mm-wave spectrometer of the LPCA (70-220GHz)



I. Kleiner

- **How to analyse the millimeter-wave spectrum ?**
  - **BELGI-Cs-hyperfine :** well adapted to analyse splittings of a low barrier of C_{3v} internal rotor in a C_s molecular frame.
  - **AABS package :** to assign the transitions by comparing the calculated and experimental spectra.



A routine to convert BELGI input/output files in the SPFIT/SPCAT format

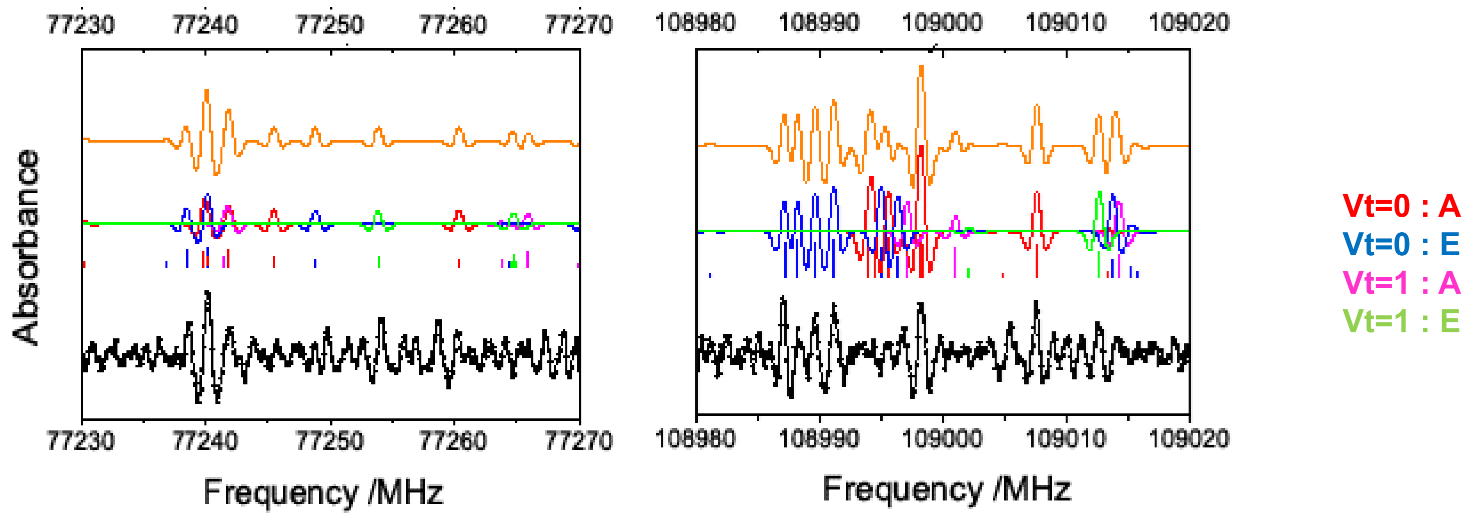
BELGI-Cs-hyperfin ⟺ **SPFIT/SPCAT input/output files** ⟺ **AABS package**

For user-friendly assignments

Measurements and data analysis

Results of the analysis

- **Comparison between the experiment and the calculated spectra**



Most of the lines are weak and blended

Many lines are remaining (excited states)

v_t	sym	J''_{max}	$K''_{a,\ max}$	N^a	RMS /kHz
0	A	74	23	705	93.2
0	E	73	20	517	96.5

v_t	sym	J''_{max}	$K''_{a,\ max}$	N^a	RMS /kHz
1	A	74	8	181	116.1
1	E	74	9	119	109.7

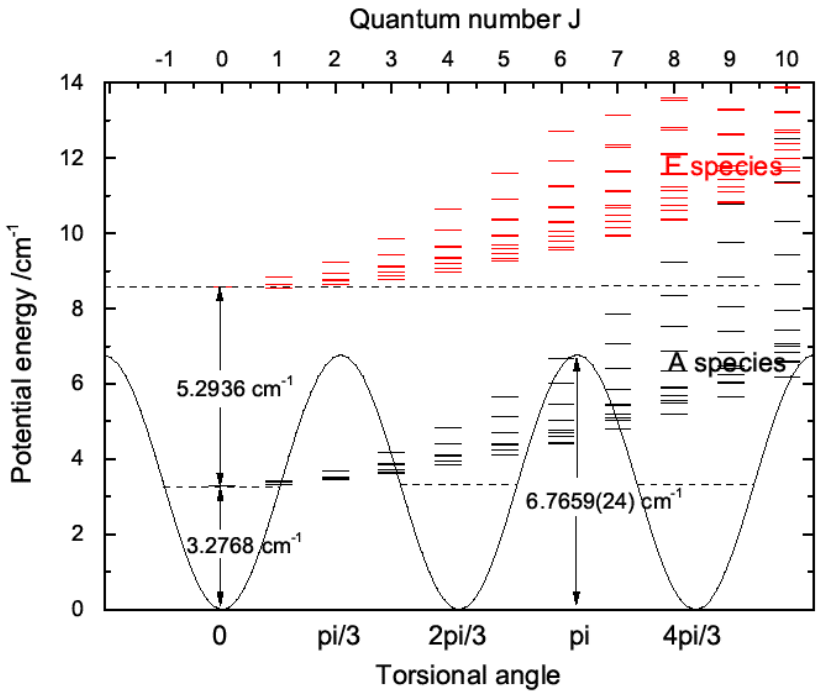
Measurements and data analysis

Results of the analysis

- The global fit of the **ground and first excited torsional states** allowed to determine the **molecular parameters**, the **internal rotation potential** and **bond angles.**

	Unit	BELGI-C_s-hyperfine	Calculated
A	MHz	2662.853(33)	2661.861[a]
B	MHz	982.0909(41)	991.031[a]
C	MHz	721.63029(35)	725.568[a]
V_3	cm^{-1}	6.7659(24)	6.63[b]
V_6	cm^{-1}	0.02333(22)	
ρ	unitless	0.01273920(48)	0.001267[c]
F	cm^{-1}	5.386202(82)	5.4584[c]
θ_{RAM}	deg	−19.18639(74)[d]	−19.318[c]
$\angle(i,a)$	deg	−43.3346(17)[e]	−43.248[c]
unitless standard deviation		MW:0.942[f]/mm-wave: 0.983[f]	

$$V(\alpha) = 1/2V_3(1-\cos(3\alpha)) + 1/2V_6(1-\cos(6\alpha))$$



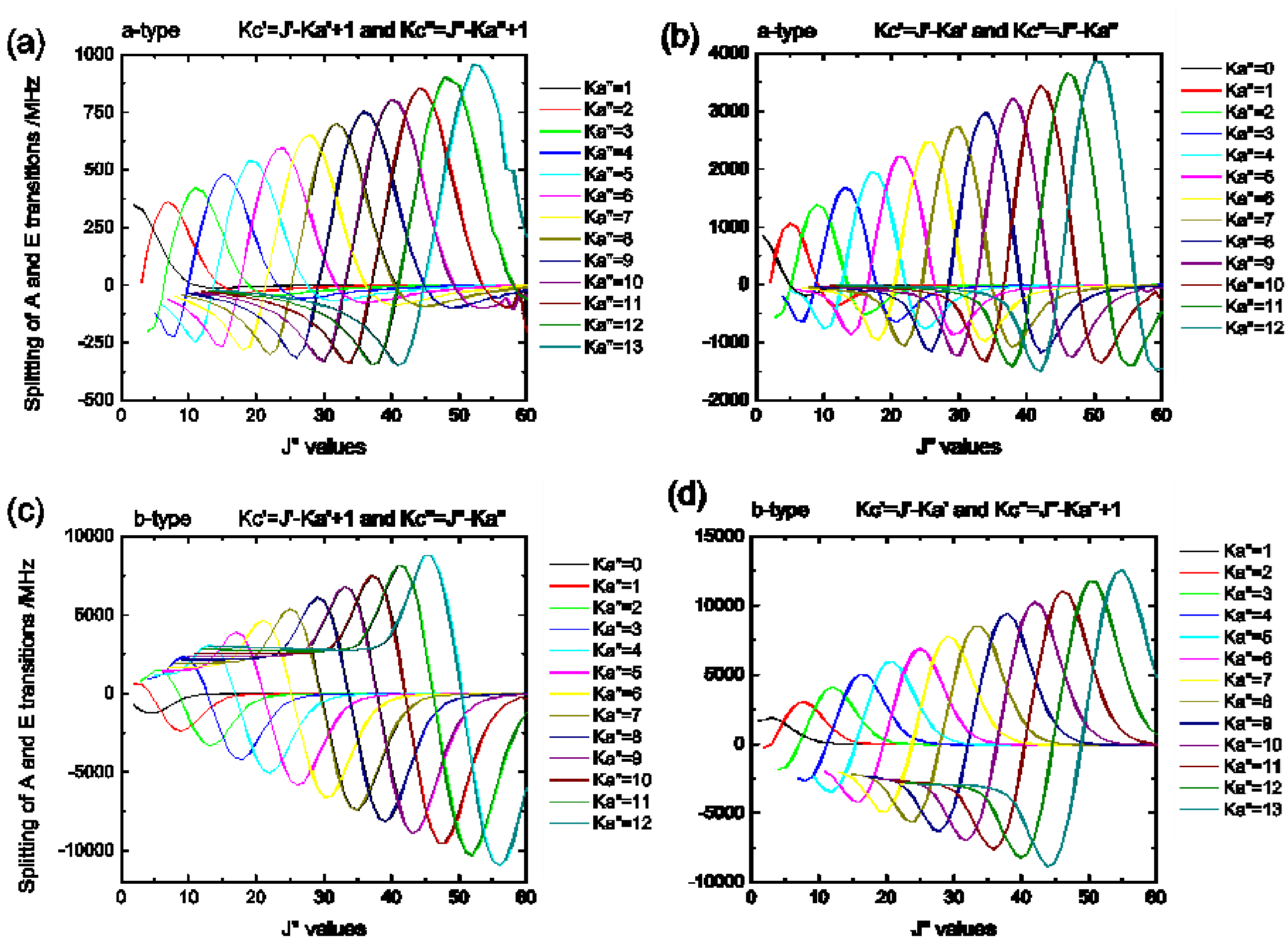
[a]: estimated by adding DFT anharmonicity (B98/CBS) to the MP2 constants at equilibrium (MP2/CBS) (called « hybrid ») + Herschbach corrections
[b]: MP2/CBS level ZPE corrected.
[c]: estimated from « hybrid » rotational constantes, internal I_α and direction cosines of the MP2/cc-pVQZ equilibrium structure.

V_3=6.7659(24) cm^{-1}: free internal rotor

Measurements and data analysis

Results of the analysis

- **Very large internal rotation splittings**

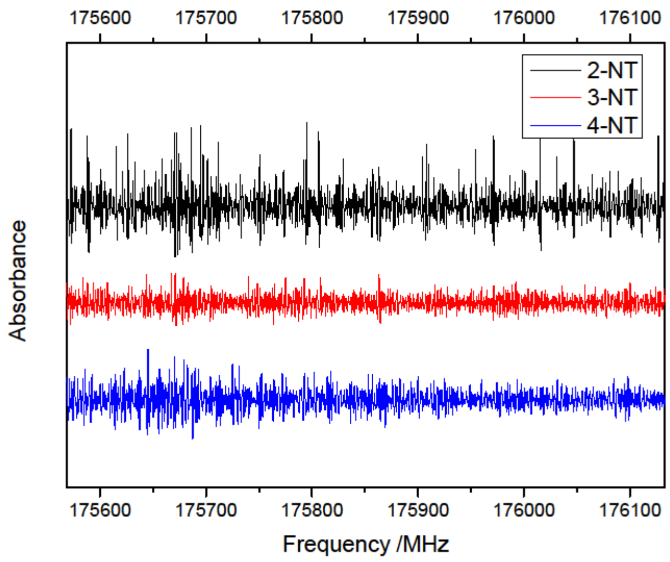


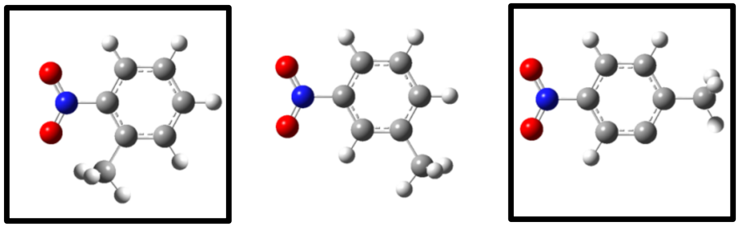
Internal rotation splittings in the mm-wave region : up to 10 GHz

Conclusion and prospects

- A **linelist has been produced** and **the detection limit has been estimated to 600 ppm** for future in situ detection of 3-NT.

- The two other isomers **2-NT and 4-NT have been measured** in the MW and mm-wave regions and the **analysis is in progress**. It will permit to **study the influence of the isomerism** on the internal rotation barrier height.
  - **2-NT** : calculated at 550 cm^{-1}
  - **4-NT** : calculated at 11 cm^{-1}





2-Nitrotoluene 3-Nitrotoluene 4-Nitrotoluene

Work in progress

Thank you for your attention

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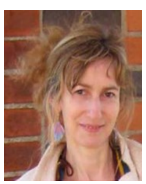
Towards the Detection of Explosive Taggants: Microwave and Millimetre-Wave Gas-Phase Spectroscopies of 3-Nitrotoluene

Anthony Roucou,*[a] Isabelle Kleiner,[b] Manuel Goubet,[c] Sabath Bteich,[c] Gael Mouret,[a] Robin Bocquet,[a] Francis Hindle,[a] W. Leo Meerts,[d] and Arnaud Cuisset*[a]



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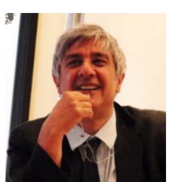

R. Bocquet

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S. Bteich

Collaborations :

- University Paris-Est Créteil, LISA (France)
- University Lille 1, PhLAM (France)
- University of Nijmegen (The Netherlands)

lisa PhLAM Radboud University Nijmegen

Fundings :

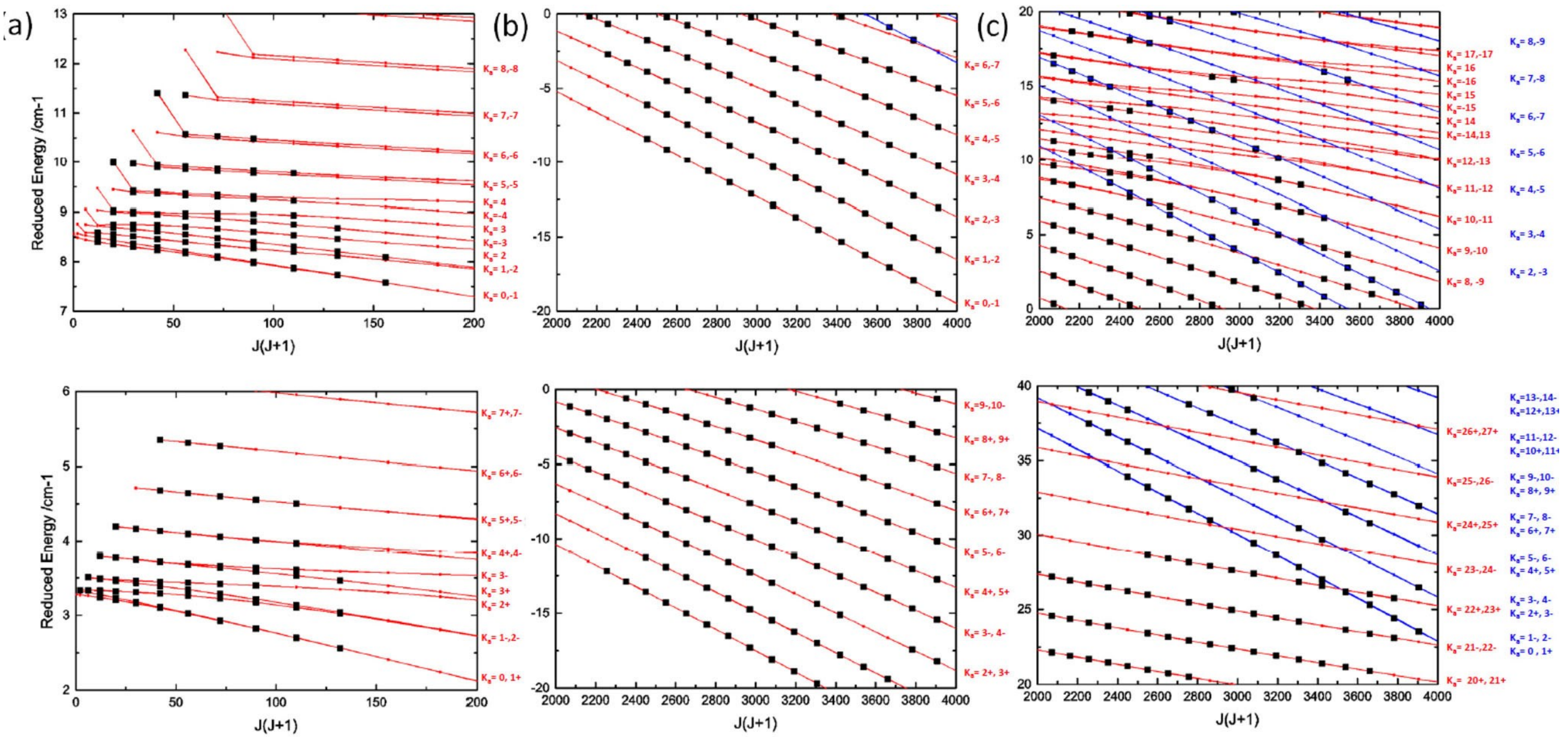
- GdR SPECMO, 3 weeks funded to work at LISA to make a collaboration with Isabelle Kleiner and learn how to use BELGI.

SPECMO cnrs

- The region Haut-de-France and the DGA (french military agency)

Ministère de la Défense DGA Région Hauts-de-France

Questions



Questions

- **How to describe the internal rotation coupling of one C_{3v} top in a C_s molecule :**

$$\boldsymbol{H} = \boldsymbol{H}_{rot} + \boldsymbol{H}_{tors} + \boldsymbol{H}_{dist} + \boldsymbol{H}_{int} + \boldsymbol{H}_{Q}$$

1) Diagonalization of the torsional part of the Hamiltonian in an axis system where torsion-rotation coupling is minimal (Rho Axis Method, RAM) :

$$\boldsymbol{H}_{tors} = \boldsymbol{F}(P_\alpha + \boldsymbol{\rho} P_a)^2 + \frac{1}{2}\boldsymbol{V}_3(1 - \cos(3\alpha))$$

2) Eigenvectors are used to set up the matrix of the rest of the Hamiltonian in RAM :

$$\boldsymbol{H}_{rot} = \boldsymbol{A}_{RAM} P_a^2 + \boldsymbol{B}_{RAM} P_b^2 + \boldsymbol{C}_{RAM} P_c^2 + \boldsymbol{D}_{ab}(P_a P_b + P_b P_a)$$

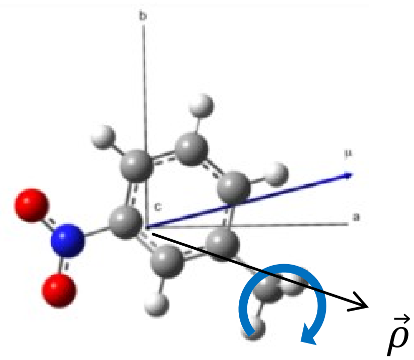
Centrifugal distortion terms :

$\boldsymbol{H}_{dist}$: *usual centrifugal distortion terms*

$\boldsymbol{H}_{int}$: *higher order torsion – rotation coupling terms*

Nuclear quadrupole coupling :

$$\boldsymbol{H}_{Q} = \frac{2f(I,J,F)}{J(J+1)}\left[\boldsymbol{X}_{aa} P_a^2 + \boldsymbol{X}_{bb} P_b^2 - (\boldsymbol{X}_{aa} + \boldsymbol{X}_{bb})P_c^2 + \boldsymbol{X}_{ab}(P_a P_b + P_b P_{\boldsymbol{a}})\right]$$



Low barrier of C_{3v} Internal rotor

⇩

BELGI-Cs-Hyperfine was well adapted