CM-, MM- AND SUBMM- WAVE SPECTRUM OF ALLYL ISOCYANIDE AND RADIOASTRONOMICAL OBSERVATIONS IN ORION KL AND THE PRIMOS LINE SURVEY

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Outline

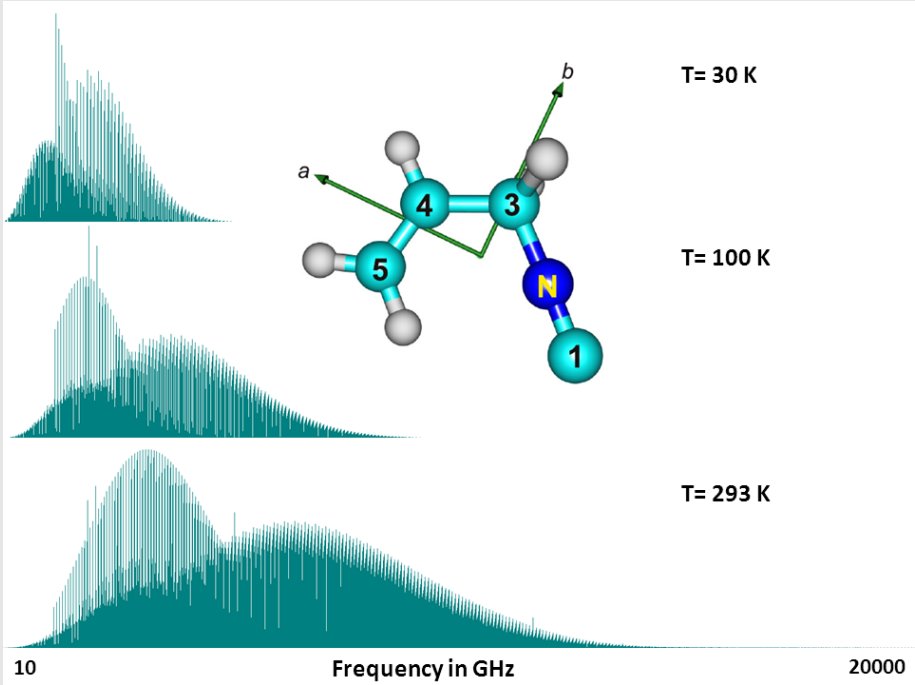
1. On the astronomical level
2. Potential function
3. Previous work on the fundamental states
4. Millimeter- and submillimeter- wave spectrometer in Lille
5. Vibrational excited modes of the Cis conformer
6. Astronomical observation
7. Summary and perspectives

Cyanide and isocyanide molecules in the ISM

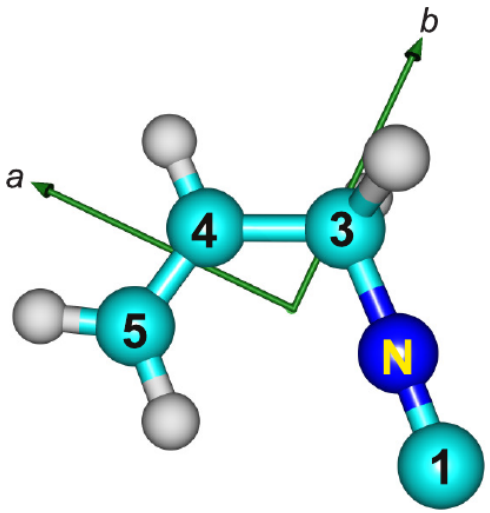
1. Isocyanides are less stable than their nitriles isomers but still are of great interest in the study of the ISM.
2. Many isocyanides were detected in the ISM : HNC ,CH_3NC, $HC\equiv CC$, MgNC, SiNC, AlNC [a].
3. In particular HCN and HNC were detected in the atmosphere of Titan.
4. These detections were primary made thanks to the laboratory work.

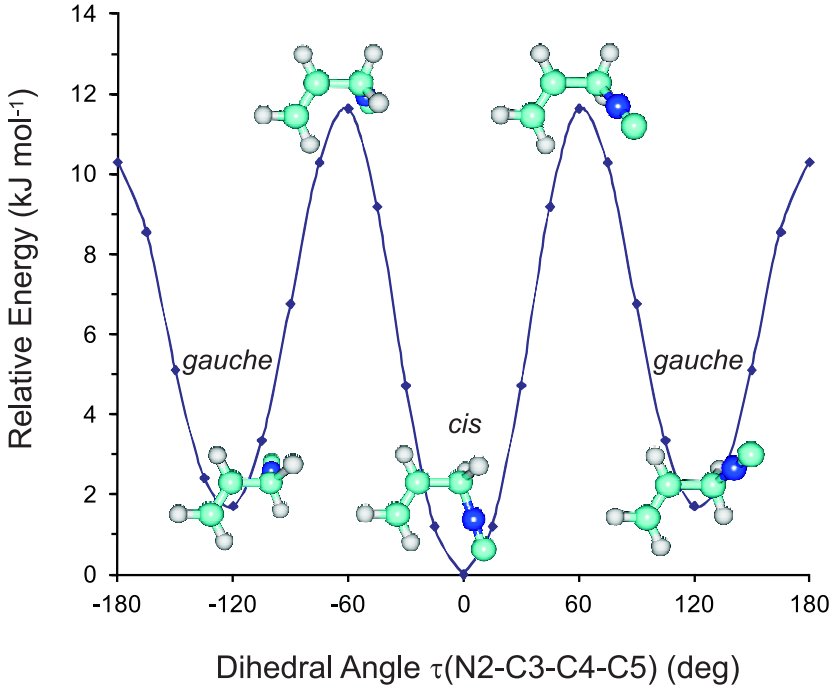
a. Møllendal, H. et al. *J. Phys. Chem. A*, **115** 7978, (2011)

The simulated spectrum of the Cis conformer for different frequencies :



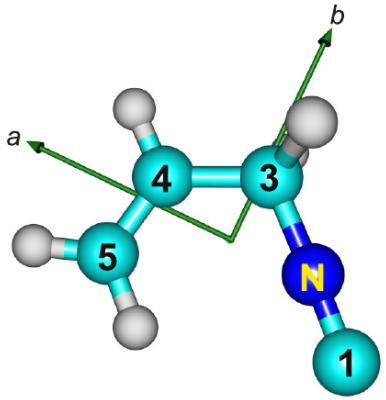
Potential function

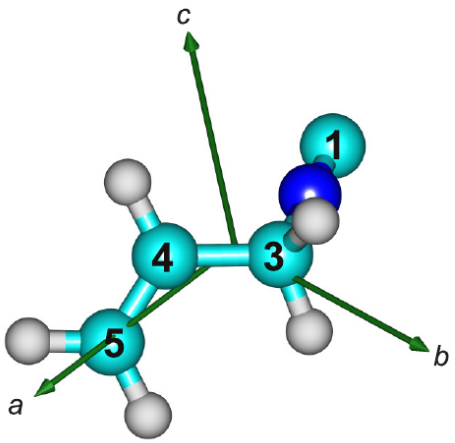




- Allyl isocyanide has two conformers Cis and Gauche with the Cis as the more stable
- The difference in energy between the Cis and Gauche is 142 cm^{-1}
- A large barrier height of 972 cm^{-1} prevents the conversion of the Gauche conformer into the Cis form and hence transitions due to both conformers are observed in the spectra

Conformers Cis and Gauche – Last year's Work



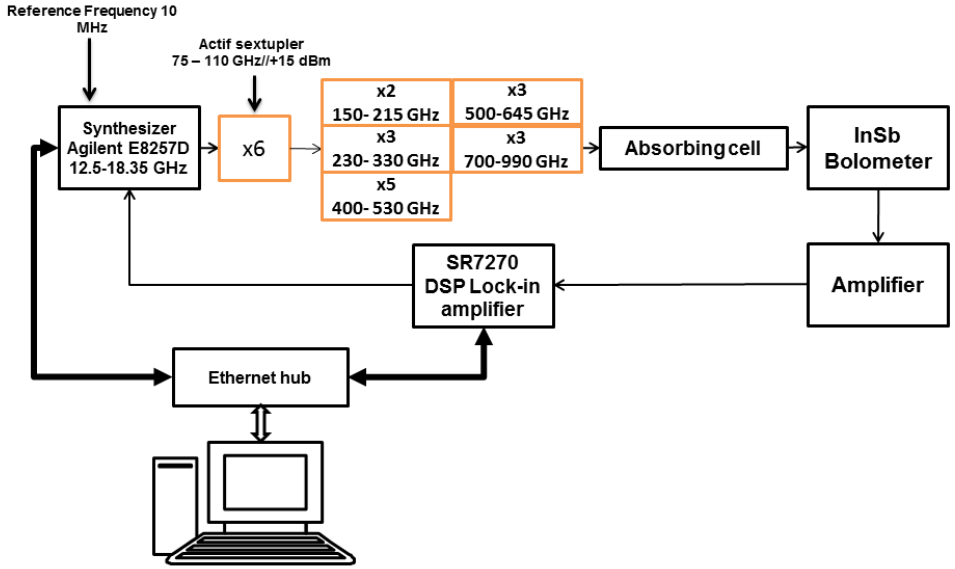


Investigation of the fundamental states

- Spectra were recorded in the range 4-18 GHz with the FTMW in Bilbao [a].
- The nuclear hyperfine structure was resolved only in the micro-wave region and led to the calculation of rotational constants, quadric centrifugal distortion constants and the diagonal operators of quadruple nuclear interaction and this for the Cis and the Gauche conformer.
- The rotational structure of mono-substituted ^{13}C and ^{15}N isotopologs was studied in the micro-wave region.
- Spectra were recorded in the 150-904 GHz range with the Millimeter- and Submillimeter- Wave spectrometer in Lille.
- More than 11000 lines were assigned to the ground states for both conformers.

a. Cocinero, E. et al. *Phys. Chem. Chem. Phys.*, **12**, 12486, 2012

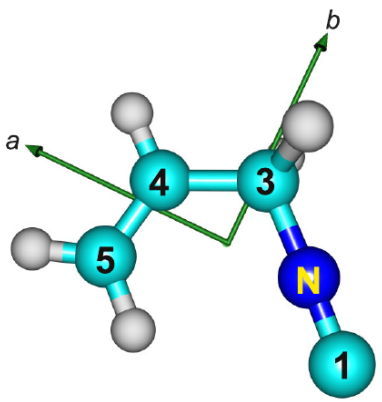
Millimeter- and submillimeter- wave spectrometer in Lille

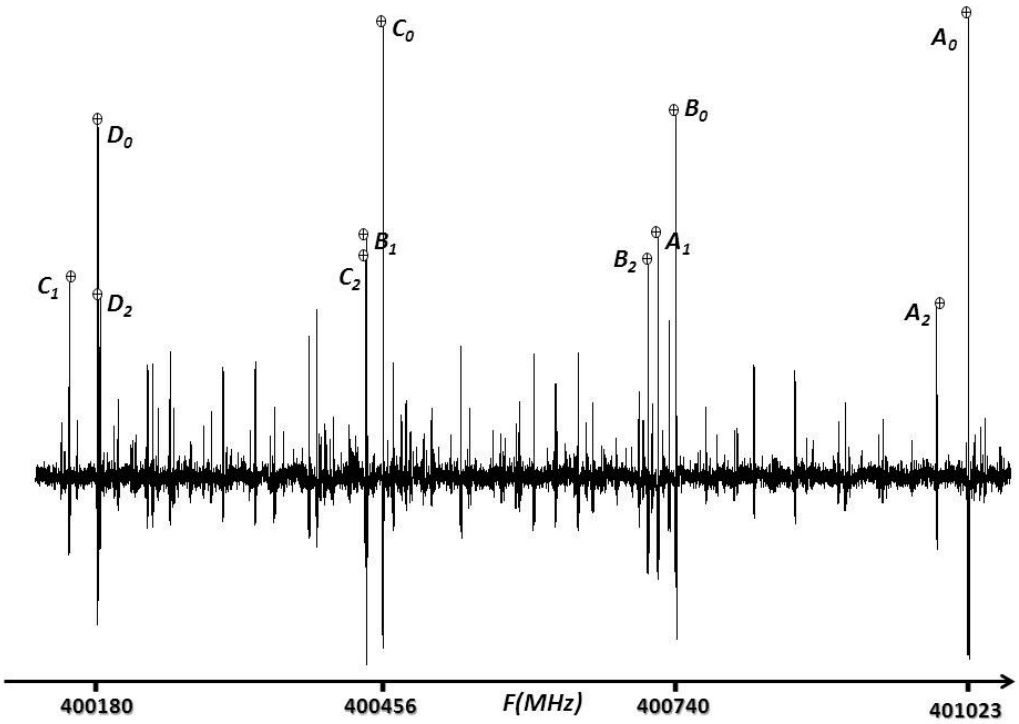


- The 75-990 GHz spectral range shown here was recently extended up to 1.6 THz in a recent improving of the Mm- and Submm- wave spectrometer in Lille.
- The accuracy of an isolated line is better than 30 kHz up to 630 GHz and 50 kHz above.
- The resolution is limited by the Doppler width of the line profile.

Rotational structure of the Cis conformer

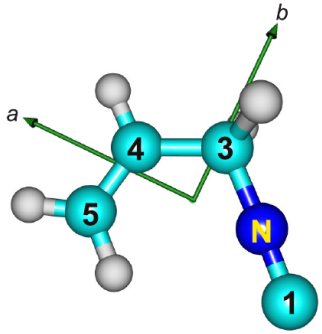
J_{K_c} \ Mode	g.s.	$\nu_1=1$	$\nu_2=1$
$^{66}_{66} \leftarrow {}^{65}_{65}$	A_0	A_1	A_2
$^{65}_{64} \leftarrow {}^{64}_{63}$	B_0	B_1	B_2
$^{64}_{62} \leftarrow {}^{63}_{61}$	C_0	C_1	C_2
$^{63}_{60} \leftarrow {}^{62}_{59}$	D_0	D_1	D_2



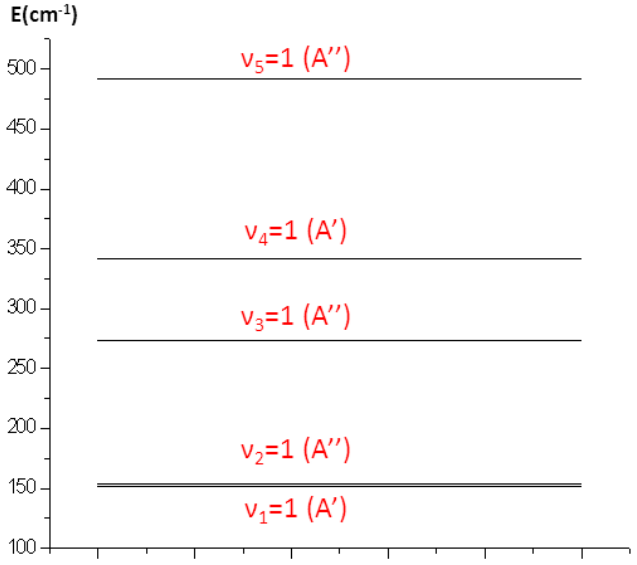


Vibrational structure of the Cis conformer

- Strong satellite lines were also observed in our spectra
- We were especially interested about resolving the rotational structure of ν_1 =1 and ν_2 =1
- Having different symmetries and resonating at very close frequencies, the ν_1 =1 and ν_2 =1 modes interact with both a and b Coriolis-type interactions



$$\Delta E_{12} < 3cm^{-1}$$



$$\Gamma(\nu_1) \otimes \Gamma(\nu_2) = \Gamma(J_{a,b})$$

The Hamiltonian matrix for $\nu_1 = 1$ and $\nu_2 = 1$

$$\begin{pmatrix} H^1_{rot} & H^{Cor}_{\nu_1,\nu_2} \\ H^{Cor}_{\nu_1,\nu_2} & H^2_{rot} + \Delta E_{12} \end{pmatrix}$$

Where ;

$$H^{Cor}_{\nu_1,\nu_2} = i(G_\alpha + G^J_\alpha \overrightarrow{J^2} + G^K_\alpha J^2_z) J_\alpha$$

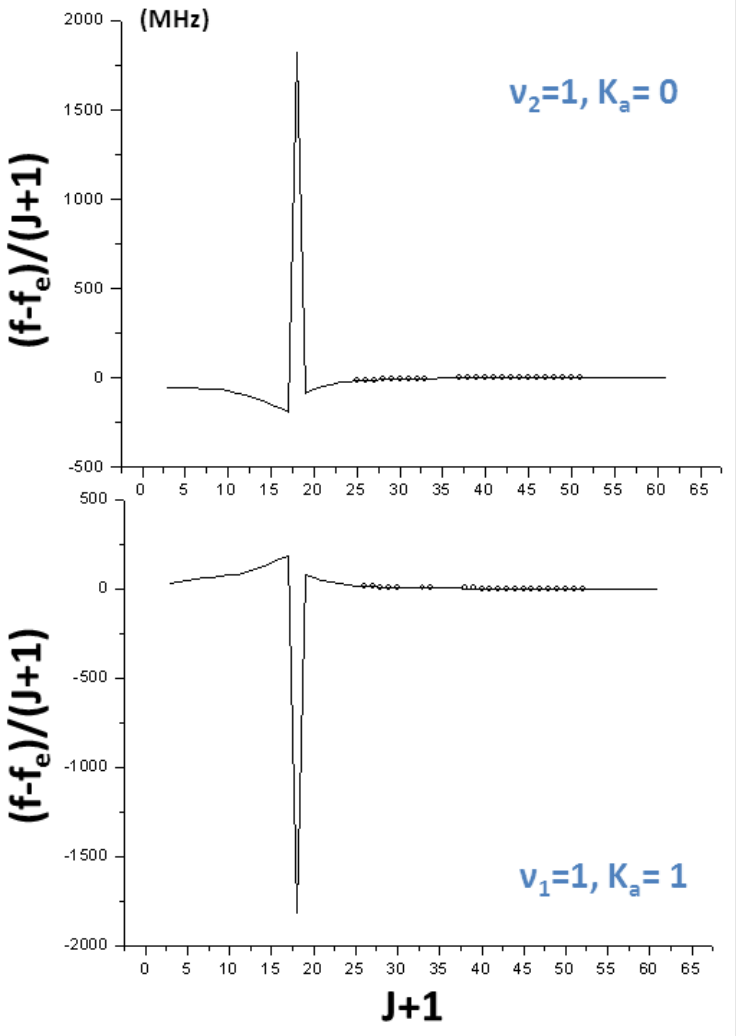
Where ;

$$G_\alpha = \zeta^\alpha_{\nu_1,\nu_2} = \sqrt{2} B^\alpha_e \zeta_{\nu_1,\nu_2} [(\frac{w_1}{w_2})^{1/2} + (\frac{w_2}{w_1})^{1/2}]$$

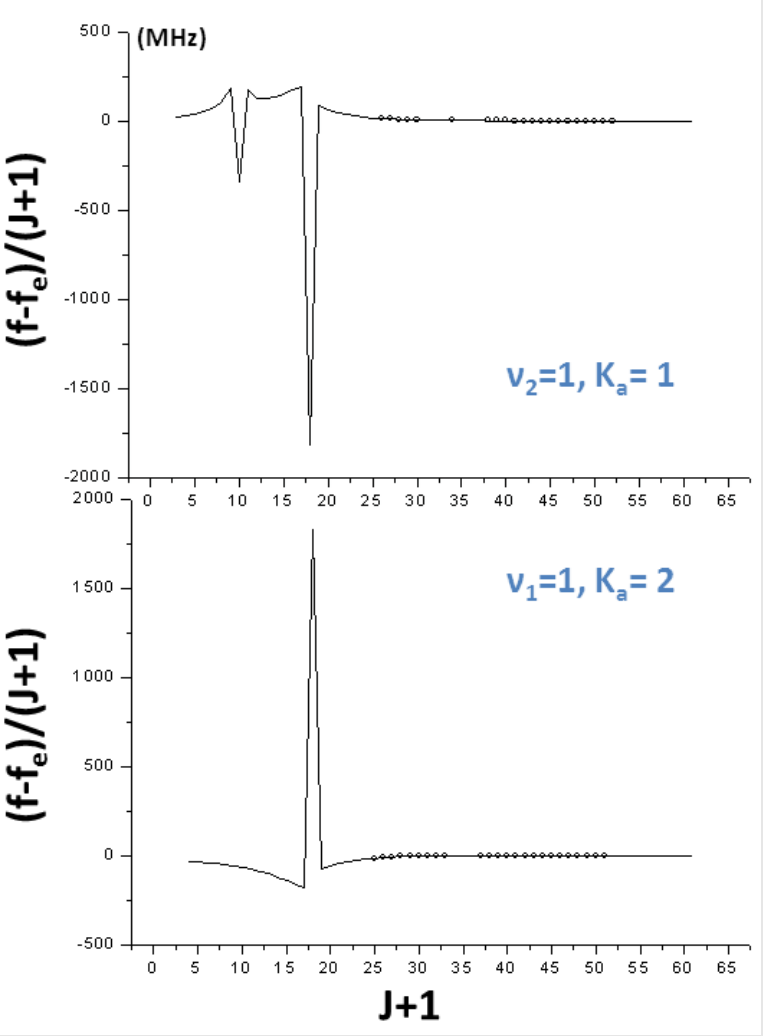
We accomplished the fit using the SPFIT/SPCAT program suite, capable of treating complex Coriolis interactions.

Selective perturbations for R branches associated with the μ_a type transitions

$K_a + K_c = J$



$K_a + K_c = J + 1$



Global fit with SPFIT of the Coriolis Coupling betweet ν_1=1 and ν_2=1

Parameter	ν_1 =1	ν_2 =1	Anhar. freq (B3LYP/6-311++G(3df,2pd))
A/MHz	11560.190(36)	11452.580(34)	
B/MHz	4005.1848(46)	4005.0148(47)	
C/MHz	3023.403965(164)	3025.763632(131)	
Δ_J /kHz	3.45837(122)	3.68089(108)	
Δ_{JK}/kHz	-21.552(57)	-23.140(63)	
Δ_K /kHz	62.84(47)	58.14(43)	
δ_J /kHz	1.19360(61)	1.28664(54)	
δ_K /kHz	5.5335(286)	5.5890(282)	
Φ_J /Hz	0. 004373(78)	0. 006004(69)	
Φ_{JK} /Hz	0.06443(157)	0.05099(143)	
Φ_{KJ} /Hz	-0.6184(53)	-0.4142(54)	
Φ_K/Hz	8.516(132)	8.556(124)	
ϕ_J/Hz	0.002136(39)	0. 002902(35)	
ϕ_{JK}/Hz	-0.008721	-0.008721	
ϕ_K/Hz	0.57674	0.57674	
ΔE_{12}/ MHz	80556. 265(224)		E_2-E_1/MHz=47966.8
G_a/MHz	7319.379(296)		E_2-E_1/cm^{-1}=1.66
G_{Ka}/MHz	-0.2667(62)		E_1/cm^{-1}= 152.22
G_b/MHz	2700.438(101)		E_2/cm^{-1} = 153.88
G_{Jb}/MHz	-0.007158(88)		
G_{Kb}/MHz	0.1396(34)		
J_{MAX},K_{aMAX}	99, 12		
$Freq_{MAX}$ /GHz	630		
Nb lines	3527		
Fit RMS /kHz	31.4		

3527 lines fitted to the experimental accuracy

Partition function and astronomical observations

The expression of the partition function is given by :

$$Q(T)_{tot} = Q(T)_{vib} Q(T)_{rot}$$

where ;

$$Q(T)_{rot} = \sqrt{\frac{\pi}{ABC}\left(\frac{kT}{h}\right)^3}$$

and ;

$$Q(T)_{vib} = \prod_{i=1}^{3N-6} \frac{1}{1 - e^{-E_i/kT}}$$

	Cis		Gauche	
T(K)	$Q(T)_{rot}$	$Q(T)_{vib}$	$Q(T)_{rot}$	$Q(T)_{vib}$
300	74242	7.625	71915	12.261
200	40412	2.961	39145	4.449
150	26249	1.908	25426	2.712
50	5052	1.025	4893	1.135
10	452	1.000	438	1.000

- Neither ally isocyanide nor allyl cyanide have been detected in the line survey about the line confusion limit in the IRAM 30m line survey of Orion KL.
- The upper limit of the column densities was calculated with the MADEX code to be $3.3 \times 10^{14} cm^{-1}$ for the Cis conformer and $1.1 \times 10^{14} cm^{-1}$ for the gauche conformer.

Summary and perspectives

1. In previous work, we analysed the rotational structure of the ground states of both Cis and Gauche conformers up to 905 GHz and about 11000 lines were added to the astronomical database.
2. We calculated the rotational and vibrational partition functions based on the anharmonic frequencies and this for different temperatures.
3. We analysed the Coriolis coupling between ν_1 =1 and ν_2 =1 and determined precisely the value of ΔE_{12}
4. We wish to extend the analysis of ν_1 =1 and ν_2 =1 in order to reach higher K_a quantum number
5. This may demand the analysis of higher vibrational modes due to a possible chain of interactions
6. *This work has recently been accepted to publication for the Astrophysical Journal !*

Not to forget, to thank you for your attention !