SUBMILLIMETER-WAVE SPECTROSCOPY OF NITROGEN CONTAINING MOLECULES OF ASTROPHYSIC INTEREST

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Interest of the studies: ISM search

2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms
H2	C3*	c-C3H	C5*	C5H	C6H	CH3C3N	CH3C4H
AlF	C2H	l-C3H	C4H	l-H2C4	CH2CHCN	HC(O)OCH3	CH3CH2CN
AlCl	C2O	C3N	C4Si	C2H4*	CH3C2H	CH3COOH	(CH3)2O
C2**	C2S	C3O	l-C3H2	CH3CN	HC5N	C7H	CH3CH2OH
CH	CH2	C3S	c-C3H2	CH3NC	CH3CHO	C6H2	HC7N
CH+	HCN	C2H2*	H2CCN	CH3OH	CH3NH2	CH2OHCHO	C8H
CN	HCO	NH3	CH4*	CH3SH	c-C2H4O	l-HC6H*	CH3C(O)NH2
CO	HCO+	HCCN	HC3N	HC3NH+	H2CCHOH	CH2CHCHO (?)	C8H-
CO+	HCS+	HCNH+	HC2NC	HC2CHO	C6H-	CH2CCHCN	C3H6
CP	HOC+	HNCO	HCOOH	NH2CHO		H2NCH2CN	
SiC	H2O	HNCS	H2CNH	C5N			
HCl	H2S	HOCO+	H2C2O	l-HC4H*			
KCl	HNC	H2CO	H2NCN	l-HC4N			
NH	HNO	H2CN	HNC3	c-H2C3O			
NO	MgCN	H2CS	SiH4*	H2CCNH (?)			
NS	MgNC	H3O+	H2COH+	C5N-			
NaCl	N2H+	c-SiC3	C4H-				
OH	N2O	CH3*	HC(O)CN				
PN	NaCN	C3N-	HNCNH				
SO	OCS	PH3?	CH3O				
SO+	SO2	HCNO					
SiN	c-SiC2	HOCN					
SiO	CO2*	HSCN					
SiS	NH2	H2O2					
CS	H3+*	C3H+					
HF	H2D+, HD2+						
HD	SiCN						
FeO?	AlNC						
O2	SiNC						
CF+	HCP						
SiH?	CCP						
PO	AlOH						
AlO	H2O+						
OH+	H2Cl+						
CN-	KCN						
SH+	FeCN						
SH	HO2						
HCl+							

10 atoms	11 atoms	12 atoms	>12 atoms
CH3C5N	HC9N	c-C6H6*	HC11N
(CH3)2CO	CH3C6H	C2H5OCH3?	C60*
(CH2OH)2	C2H5OCHO	n-C3H7CN	C70*
CH3CH2CHO			

This table from: http://www.astro.uni-koeln.de/cdms/molecules (07/2014)

Aminoacetonitrile: Belloche et al., A&A, 2008, 482, 179

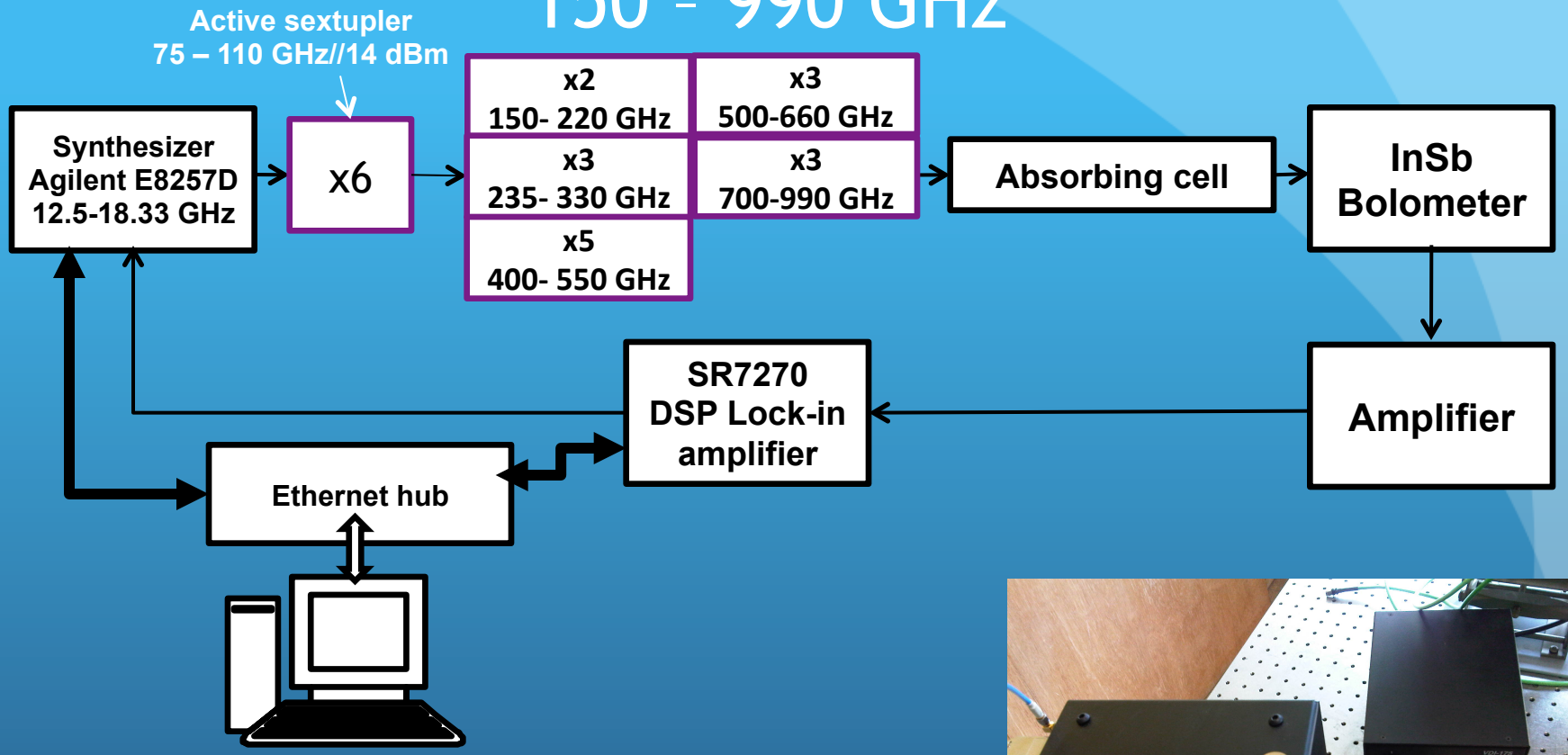
Carbodiimide: B. A. McGuire et al, 2012, ApJ 758, L33

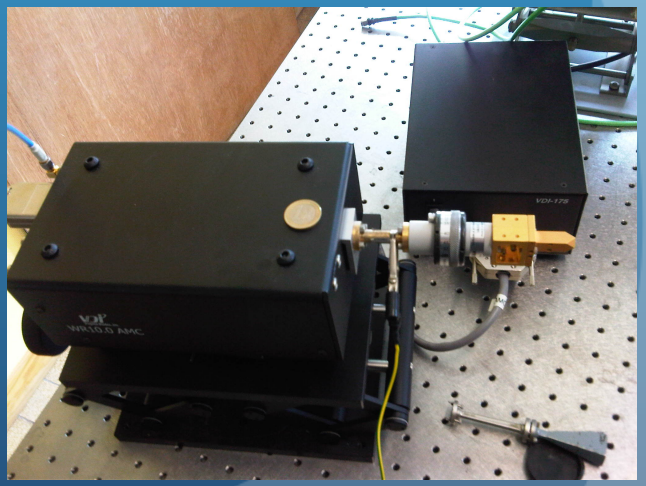
- Almost 30 nitrile molecules, which contain the cyano group (C≡N), have been detected in the (ISM) so far
- Except these two species, no molecules with two nitrogen detected
- Nitrogen chemistry is difficult and widely unknown

Last nitrile studies in Lille

- **Ethyl-isocyanide (CH_3CH_2NC)**: The few isocyanides detected in the ISM are always isomers of the corresponding : HNC, CH_3NC, HCCNC
- **Di-cyanomethane (malonitrile-NC-CH_2-CN) and isocyanomethane**: Following the first microwave study of a bis-isocyanide derivative diisocyanomethane (Motiyenko et al., A&A 2012, 544 A82)
- **Hydroxyacetonitrile ($HOCH_2CN$)**: Compete with aminomethanol (NH_2CH_2OH), a glycine precursor, through the Strecker synthesis (Danger G. et al., ApJ 756, 11, 2012)
- **Acetyl isocyanate** (CH_3CONCO)
  - Isocyanic acid, HNCO, was among the very early molecules to be detected in space
  - OCN^- is assumed to be in the grains (K. Demyk et al. A&A, 339 (1998), 553)
  - CH_3COCH_3 is detected since 1987 Sgr B2 (F. Combes et al. A&A, 180, (1987), L13)

Solid state sources spectrometer: 150 – 990 GHz





- Very compact
- power : 50 μw – 5mW)
- Broad band : Assigment easier with series, like in I. R.
- Full coverage with high resolution in 5 days

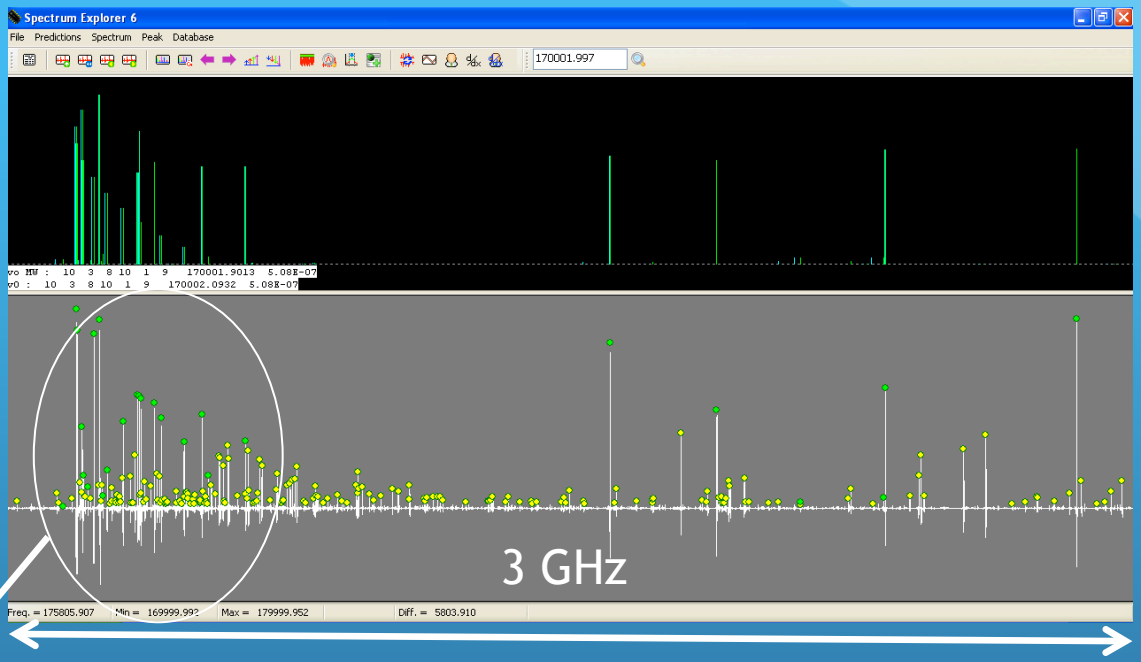
Ethyl-iscocyanide (CH_3CH_2NC)

- Isocyanides molecules are poorly studied mainly due Spectroscopy of isocyanides is often complicated by difficulties in synthesis and kinetic instability of many of them
- Ethyl-iscocyanide (CH_3CH_2NC) is isomer of one of the most abundant Complex Organic Molecules. The study was limited to MW domain up to 40 GHz. (Kruger et al., Z. Naturforsch. 1992, A47, 1067), making the prediction inaccurate in the millimeter-submillimeter wave domain.

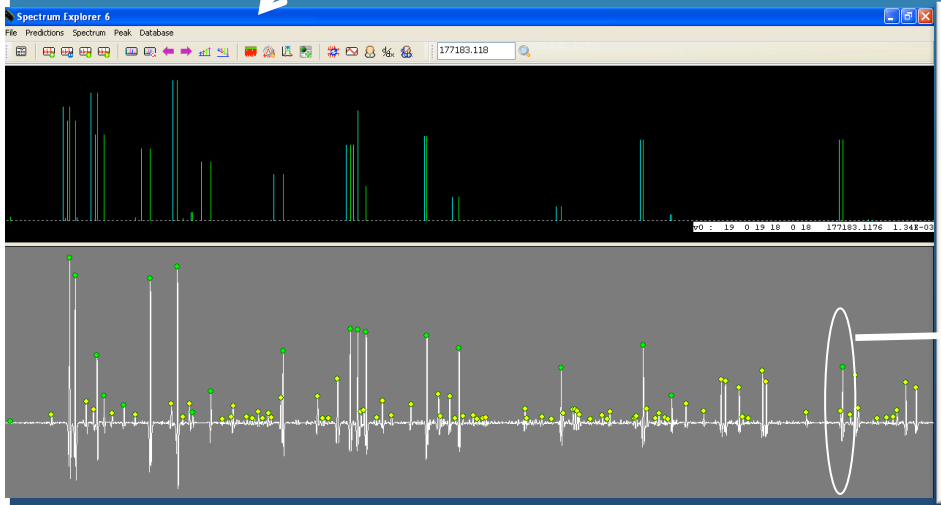
Ethyl-isocyanide: results

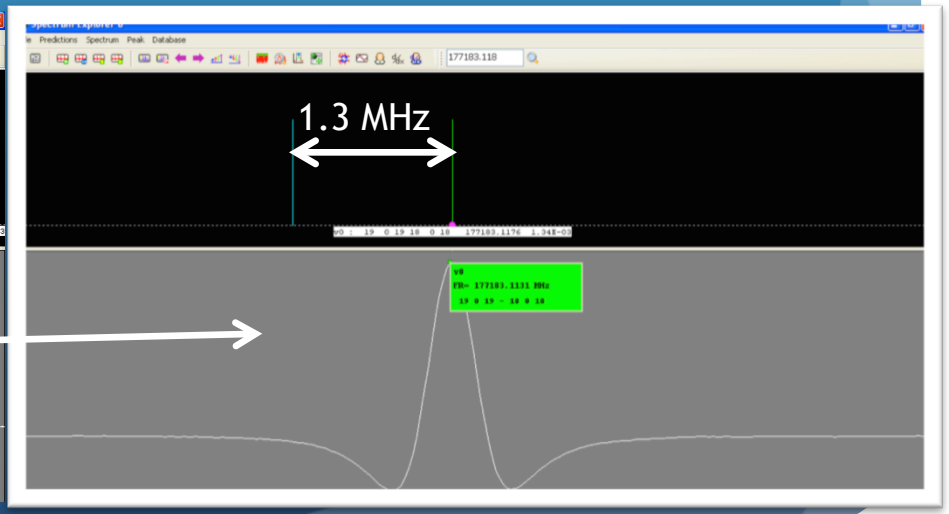
Pred from MW

Pred from new data



Relatively stable compound: the range 150-990 GHz was recorded





Despite this new job, no detection in ORION…

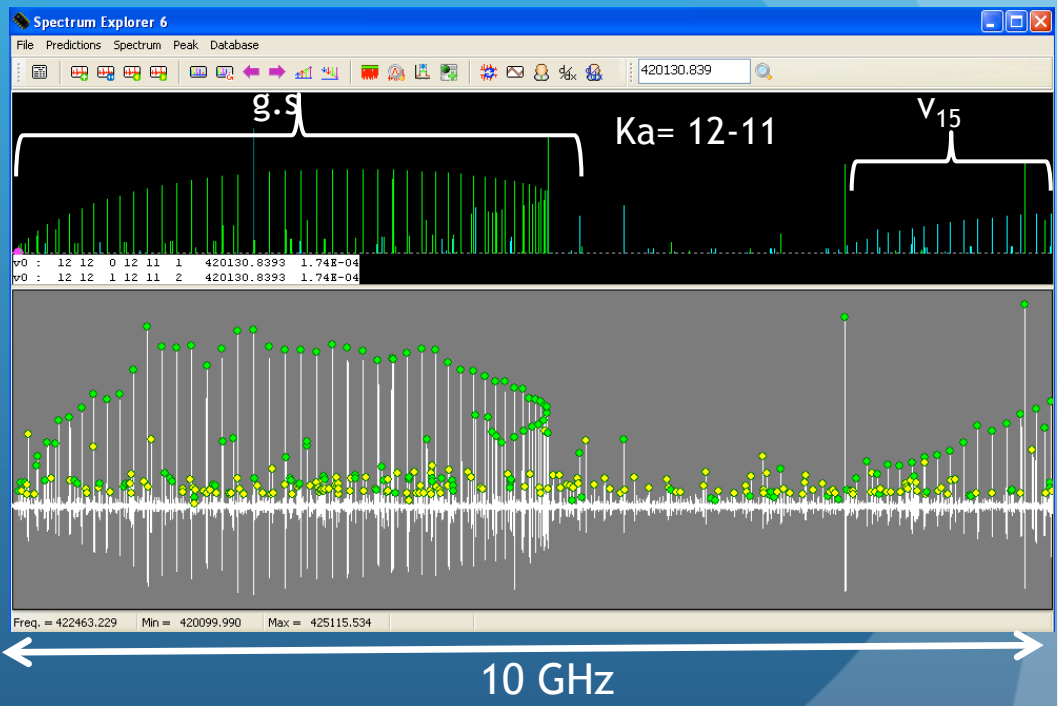
dicyanomethane (malonitrile) and isocyanomethane

- No MW study about the cyano-isocyanomethane ($CNCH_2CN$).
- We decided also to reinvestigate the most stable isomer malonitrile for two reasons:
  - Study is limited to 240 GHz (Burie et al. 1982, J. Phys. 43, 1319)
  - Spin statistic we put in evidence in the diisocyanomethane study was not took into account.

Isocyanomethane : spectra

- The sample is unstable, it can explode on heating (if t° > −10°C). A flow was used, the optimal temperature of evaporation was found to be close to −25°C.

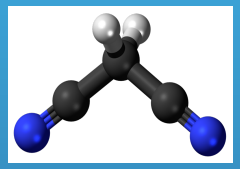
- The dipole moment : μ_a= 0. 2 D - μ_b= 3.7 D - μ_c= 0
- Spectra is mainly Q branch series
- 110-180 GHz range
- 5-10 GHz windows located in the Q-branches regions from 200 to 640 GHz

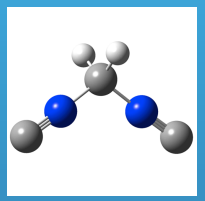


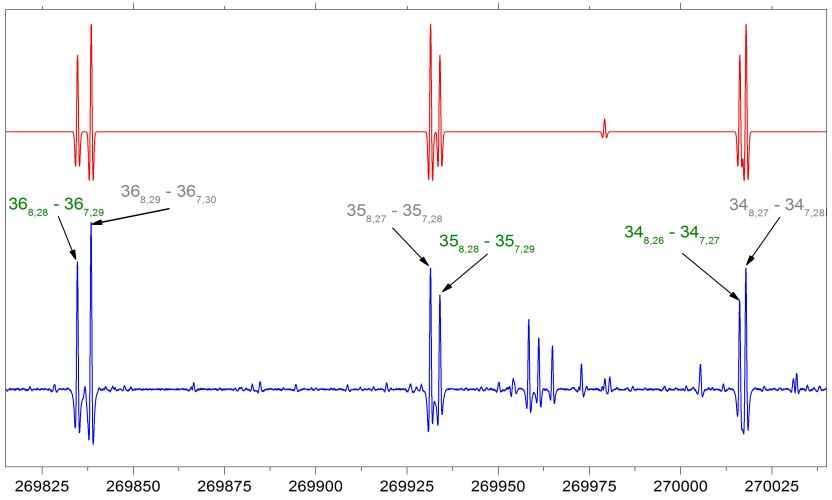
- Malonitrile which is a stable and commercial sample: 150-660 GHz

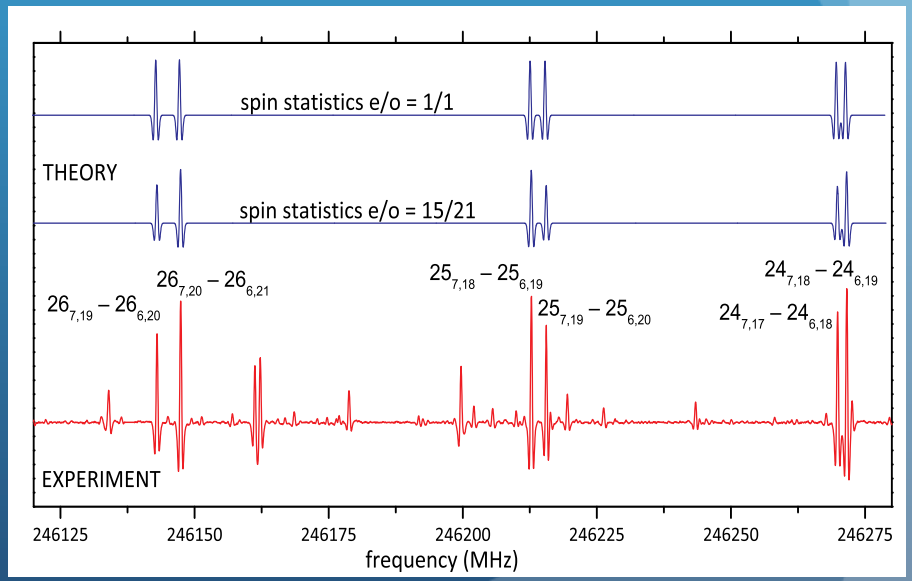
Dicyanomethane (Malonitrile) : results

- As for di-isocyanomethane, spin statistic have an influence on the intensity of the lines
- This should be take into account in case of ISM detection



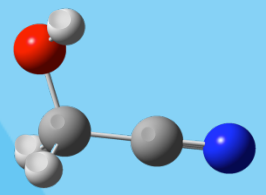






Motiyenko et al., A&A 2012, 544 A82

Hydroxyacetonitrile



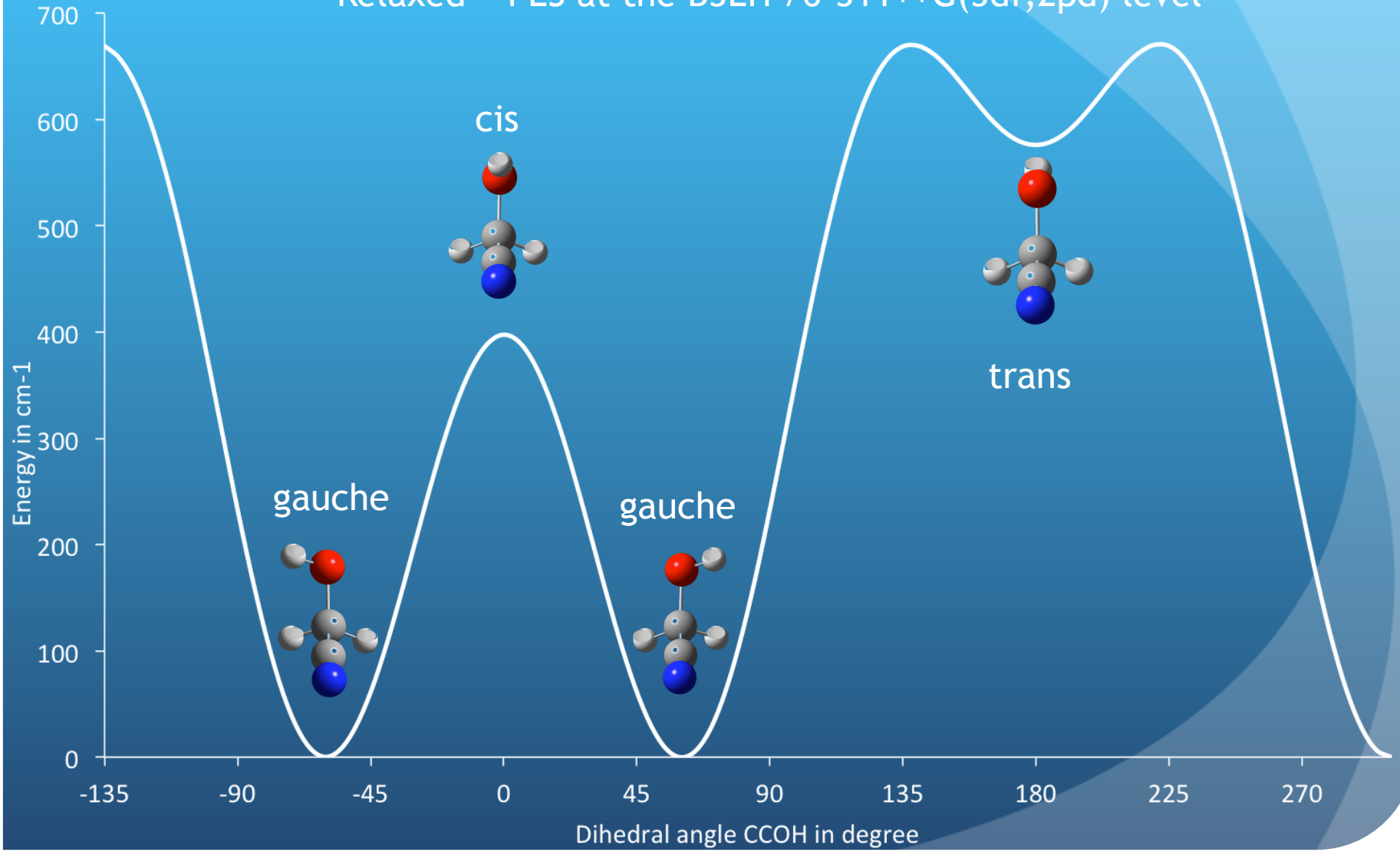
- Detection of aminoacetonitrile in SgrB2(N) (NH_2CH_2CN) (A. Belloche, et al. A&A, 2008, 482 179)
- 3-hydroxy propionitrile ($HOCH_2CH_2CN$) recently investigate in the millimeter save domain (Braakman et al, 2010, JMS, 262, 100). In this paper : « Hydroxyacetonitrile ($HOCH_2CN$) would have been another natural target » (not commercial, high vapor pressure)
- Compete with aminomethanol (NH_2CH_2OH), a glycine precursor, through the Strecker synthesis (Danger G. et al., ApJ 756, 11, 2012)
- Its photochemistry leads to the formation of formylcyanide (CHOCN), ketenimine (CH_2CNH), formaldehyde (CH_2O), hydrogen cyanide (HCN), carbon monoxyde (CO) (Danger G. et al. A&A 549, A93, 2012)

Previous study

- IR work in solid Argon at 14-17 K (not the torsional motion) (Mielke et al, *J. Phys. Chem.* 1989, *93*, 558-564)
- Only one spectroscopic study in the microwave domain up to 50 GHz (also $DOCH_2CN$): Cazzoli et al. J. Chem. Soc., Faraday Trans. 2, 1973,69, 569)
  - 56 lines for both sub-states up to $J = 8$ and $K_a = 3$
  - the standard deviation of the fit is nearly 500kHz, but a good starting point for our analysis
  - Derived Energy difference between the torsional substates (no μ_c lines): 110 700 MHz same order of magnitude as our value!
  - Torsional equilibrium angles found from potential function analysis was 56°angles: *ab initio* value determined is 60°

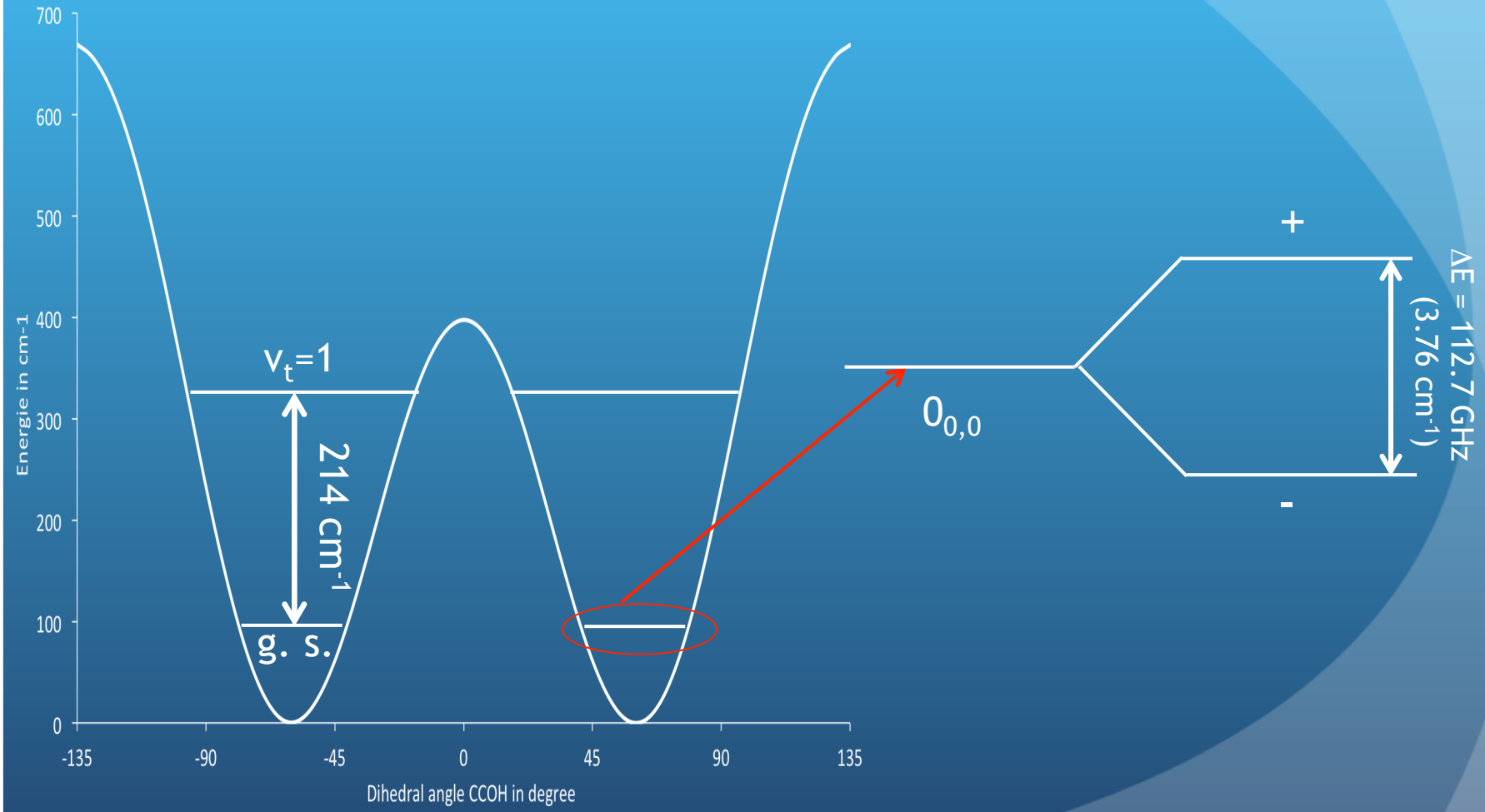
Internal rotation of the hydroxyl group

« Relaxed » PES at the B3LYP/6-311++G(3df,2pd) level



Internal rotation of the hydroxyl group

- Tunneling between the two equivalent gauche configurations split each rotational levels.



Analysis

- We used the same method as for Ethanetellurol (R. A. Motiyenko et al., JPC A, 114, 2794, 2010). Analysis was done considering coriolis interactions between the two substates. The Picket RAS formalism was used (H. M. Pickett, *J. Chem. Phys.*, **56**, 1715, 1972) :

$$H_{\mathrm{RAS}} = \sum_{\nu=0}^{1} |\nu\rangle \left(E^{\nu} + H_R^{\nu}\right) \langle\nu| + \left[|0\rangle\langle 1| + |1\rangle\langle 0|\right] H_I \quad ,$$

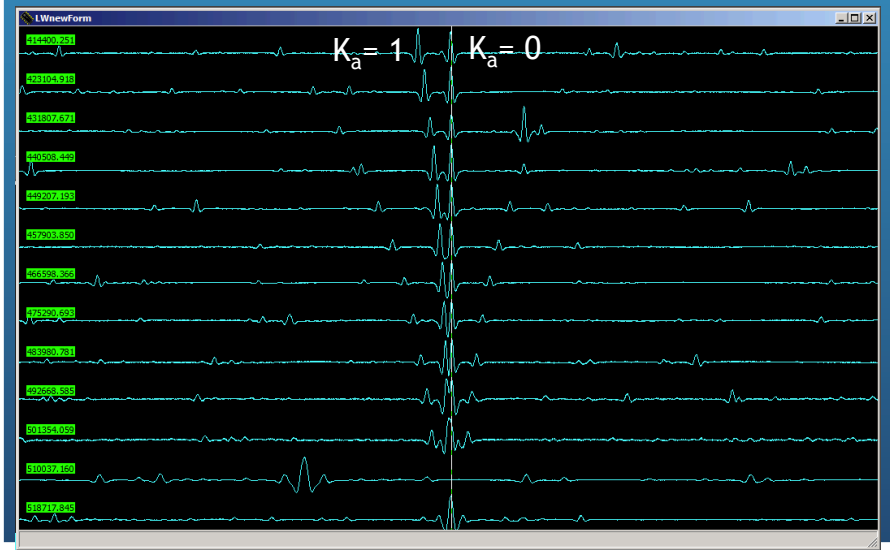
- H_I: Coriolis interaction terms F_{bc}, F_{ac}
- H_R: Watson S-reduction in the I^r representation Hamiltoniann.
- The rotational dependence of the energy difference has been expressed as (D .Christen and H.S.P. Mülller, Phys. Chem. Chem. Phys., 5, 3600, 2003)

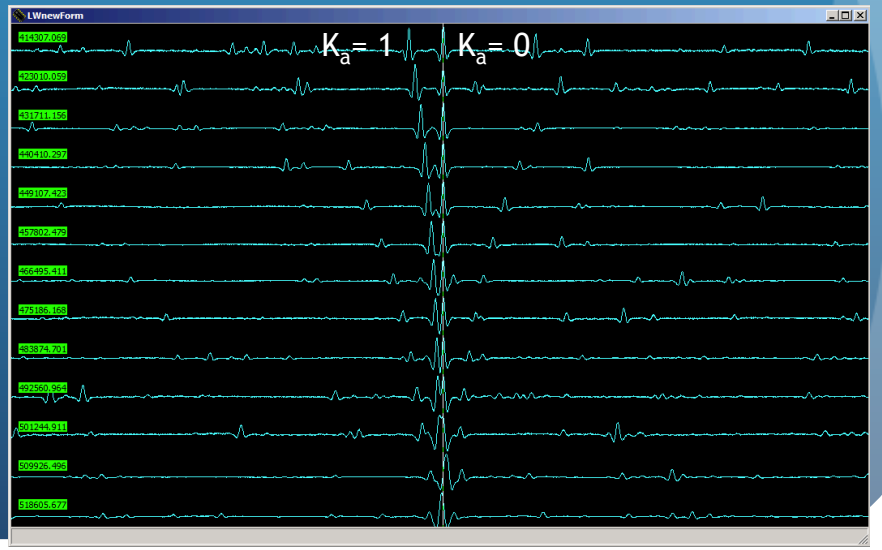
$$\begin{aligned} H_{\Delta} = {} & E^{*} + E_J^{*}\boldsymbol{J}^2 + E_K^{*}J_z^2 + E_2^{*}\left(J_+^{\,2} + J_-^{\,2}\right) + D_{ac}^{*}\left(J_aJ_c + J_cJ_a\right) \\ & + E_{JJ}^{*}\boldsymbol{J}^4 + E_{JK}^{*}\boldsymbol{J}^2J_z^2 + E_{KK}^{*}J_z^4 + E_{2J}^{*}\boldsymbol{J}^2\left(J_+^{\,2} + J_-^{\,2}\right) \\ & + E_4^{*}\left(J_+^{\,4} + J_-^{\,4}\right) + \ldots \end{aligned}$$

Analysis

- First prediction from MW measurements with two separate states.
  - Even for the K_a=0 lines, difficult to assign unambigously the + substates lines in the low frequency range (up to 300 Ghz)
  - Surprisely: at high frequency (from 400 to 650 GHz) for both subtates the Ka=0 lines and Ka=1, Kc=J are not so perturbed. This permits to fix rotational constants and distortional terms

- substate « Loomis Wood Diagram » + substate

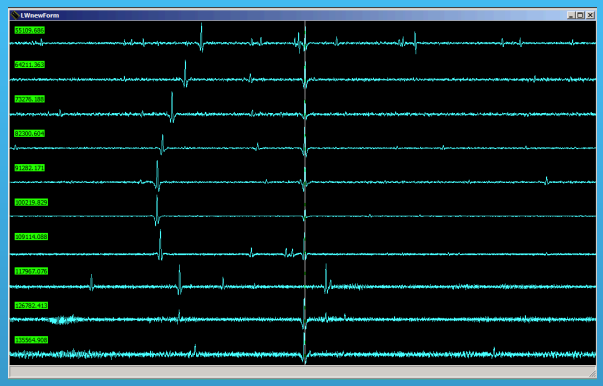




Analysis

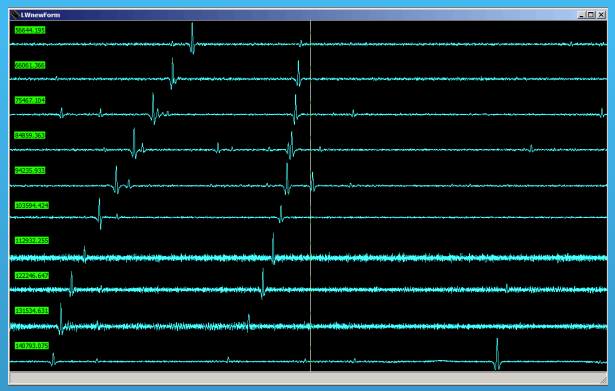
$K_a = 0$

\+ -



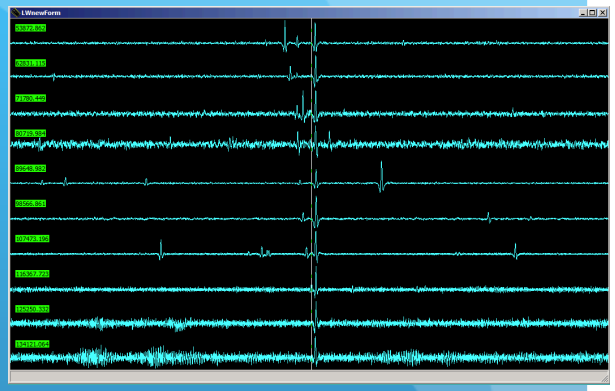
$K_a = 1$, $K_c = J-1$

\+ -



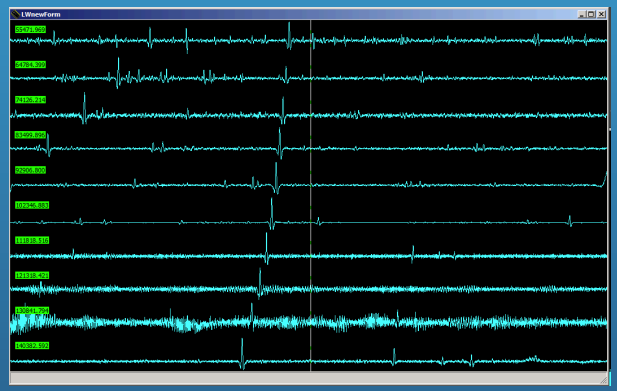
$K_a = 1$, $K_c = J$

+:? -



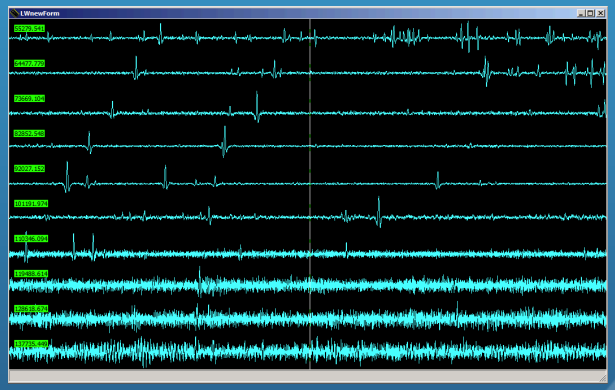
$K_a = 2$, $K_c = J-2$

+:? -



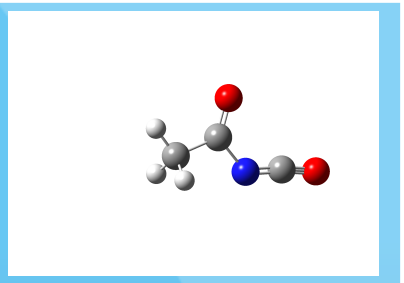
$K_a = 2$, $K_c = J-1$

+:? -:?



- Second step: global fit
  - Coriolis term was adjusted « by hand » with keeping ΔE constant
  - Assigning $\Delta V = \pm 1$ lines

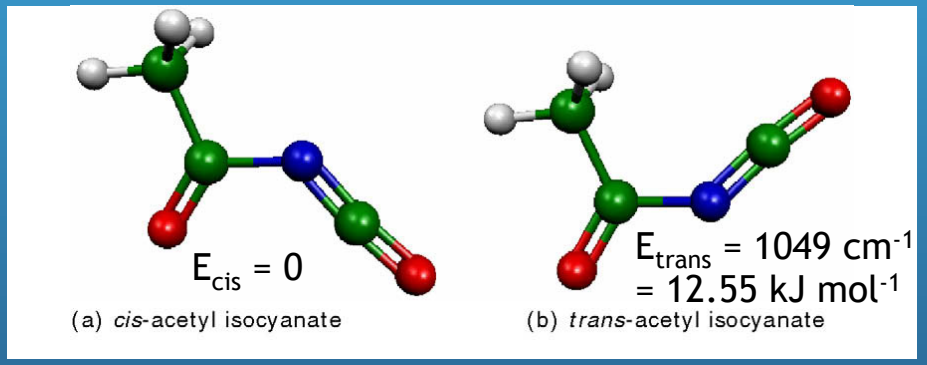
Acethyl isocyanate



- cis and trans isomerism:
  - most molecules with a conjugated double- bond structure seem to prefer the trans conformations (acrolein and derivatives of butadiene…).
  - Even the more analogous vinyl isocyanate prefer the trans configuration (C. Kirby, H.W. Kroto JMS. 70 (1978) 216.)
  - However, for vinyl azide it has been shown by relative intensity measurements of microwave spectra that the cis form is the more stable
  - the cis form is the more stable conformer in the gas, but the trans form is the stable form in the solid (K.A. Krutules, et al., J. Mol. Struct. 293 (1993) 23.)
- Isocyanate functional group (–NCO) is highly reactive and many chemicals containing isocyanate groups were used for the synthezises of polyurethanes.

Previous studies

- MW spectra up to 40 GHz (B.M. Landsberg et al. J.C.S. Faraday, 76, 1208, 1980):
  - J_{max}=23 and $K_{a,max}$= 3
  - Dipole moment (Stark measurements): μ_a=0.954D μ_b=1.48D
  - 1st order internal rotation parameters determined
- MW spectra of $CD_3C(O)NCO$ and $^{13}CH_3C(O)NCO$ (Y. Uchida et al. J. Mol. Spectrosc. 256, 163, 2009)
  - Ab initio calculations
  - Molecular structure

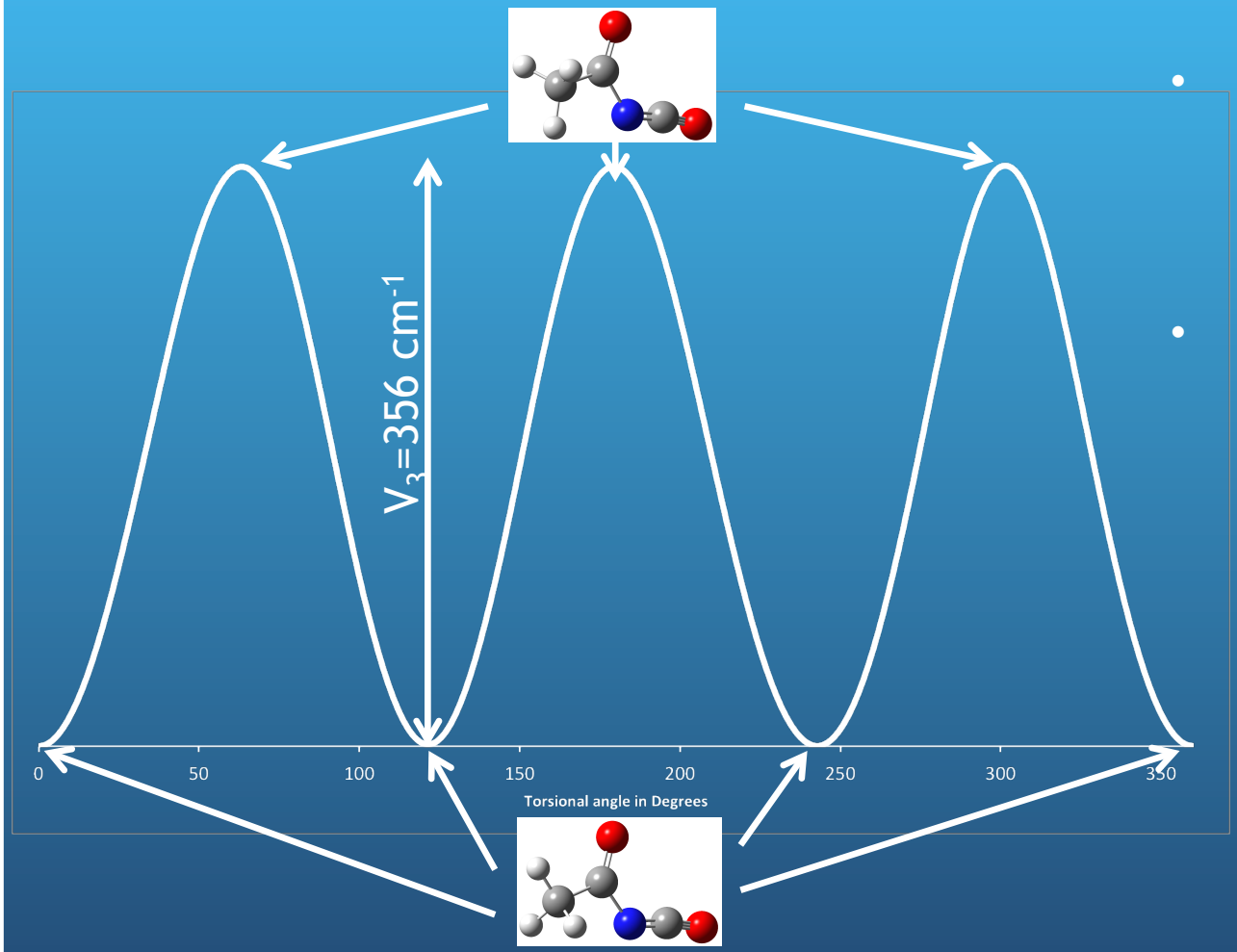


	V_3 in cm^{-1}	ρ
$HCOOCH_3$	373	0.08
CH3(ONCO	356	0.06

Similar case to methyl formate, should not be too difficult….

CH_3 internal Rotation

Methyl group is C_{3v} symmetry : $V(\alpha) = \frac{V_3}{2}(1 - \cos 3\alpha) + \frac{V_6}{2}(1 - \cos 6\alpha) + \ldots$

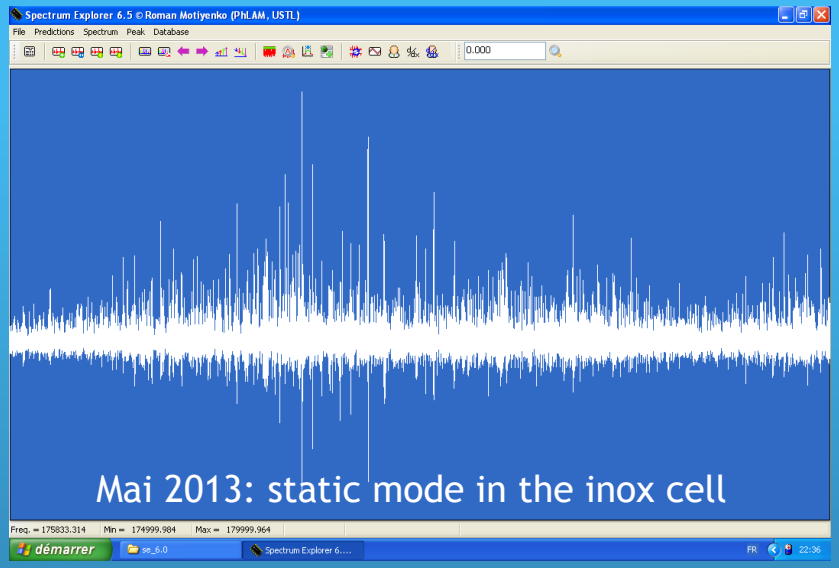


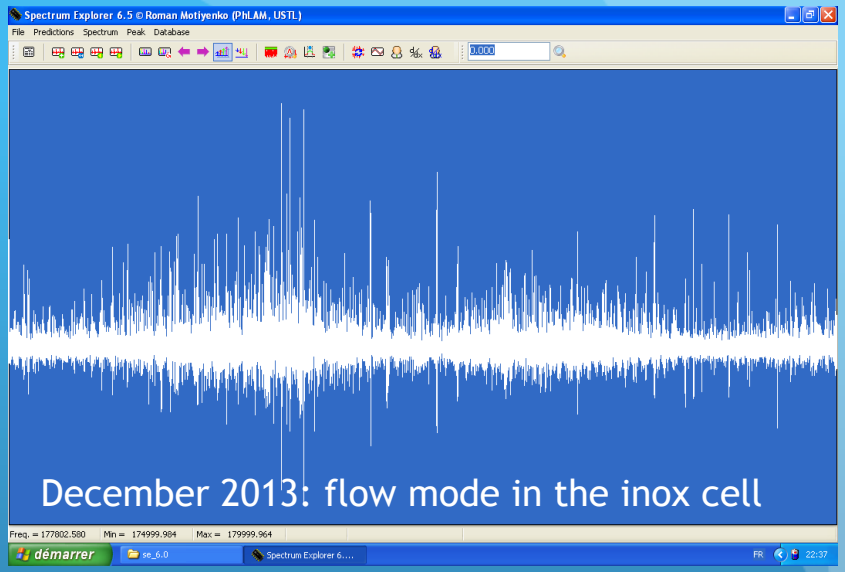
- Due to tunnel effect, the transitions are splitted into two components: A and E
- The code used in these studie is « RAM36-code » from V. Ilyushin (Karkhov-Ukraine). The former name comes from the Toluene study (V. Ilyushin et al. J. Mol. Spectrosc 259, 26, 2010)

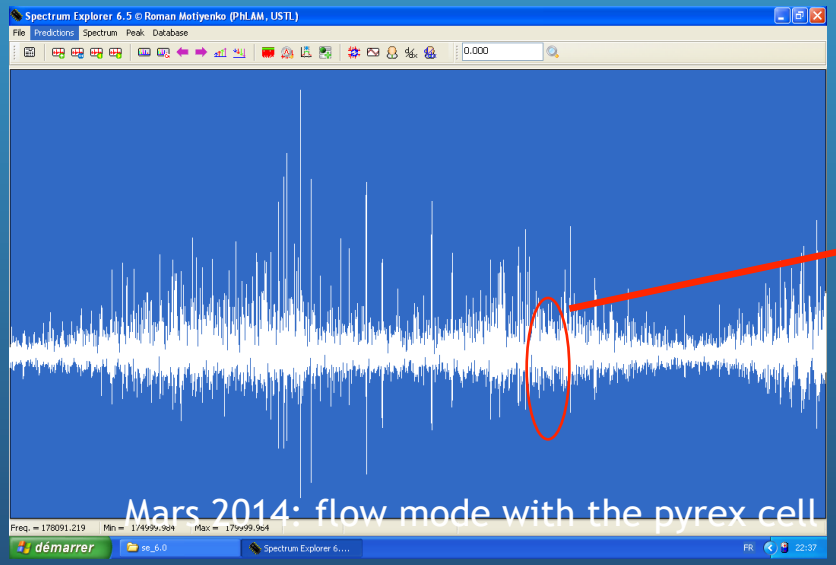
Experimental details

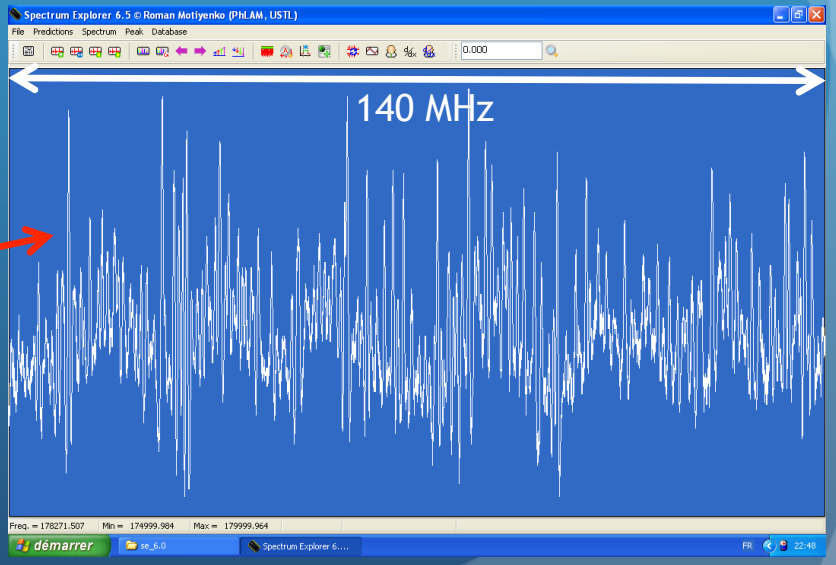
- The synthesis is well known: Acetyl isocyanate was prepared by the reaction of acetyl chloride with silver cyanate (***Rodd's Chemistry of Carbon Compounds*** (Elsevier, **Amsterdam, 2nd edn, 1965), vol. I, part C, p. 360**)
- The compound is relatively stable, could be stored in the fridge (-20°C) for months, but the spectra obtained have poor signal to noise ratio. We thought it was reactive with metal, it was recorded 3 times
  - Mai 2013: static mode in the inox cell
  - December 2013: flow mode in the inox cell
  - Mars 2014: flow mode with the pyrex cell

175-180 GHz spectra





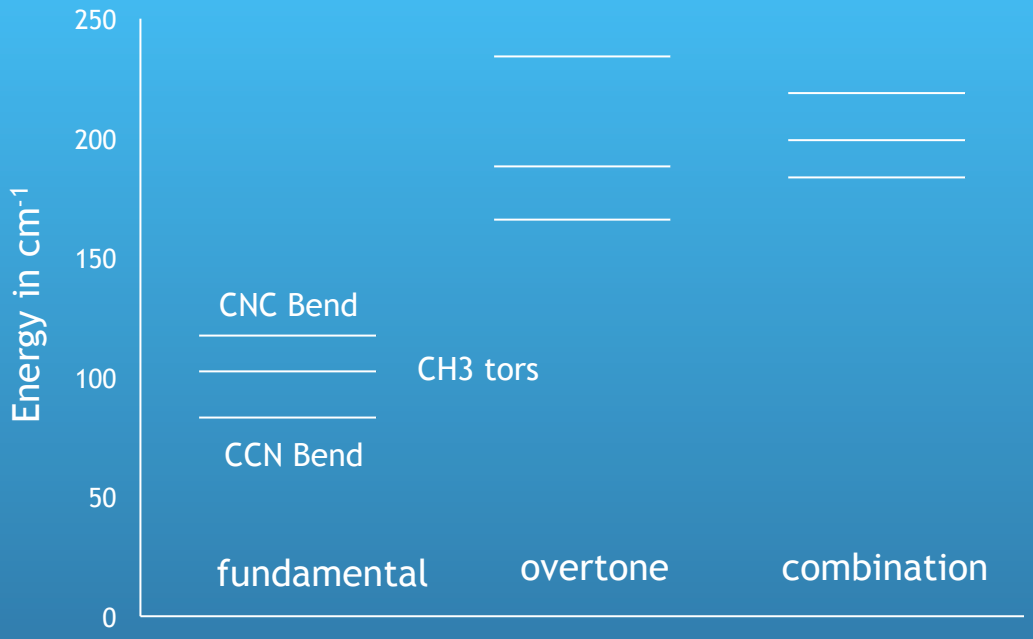




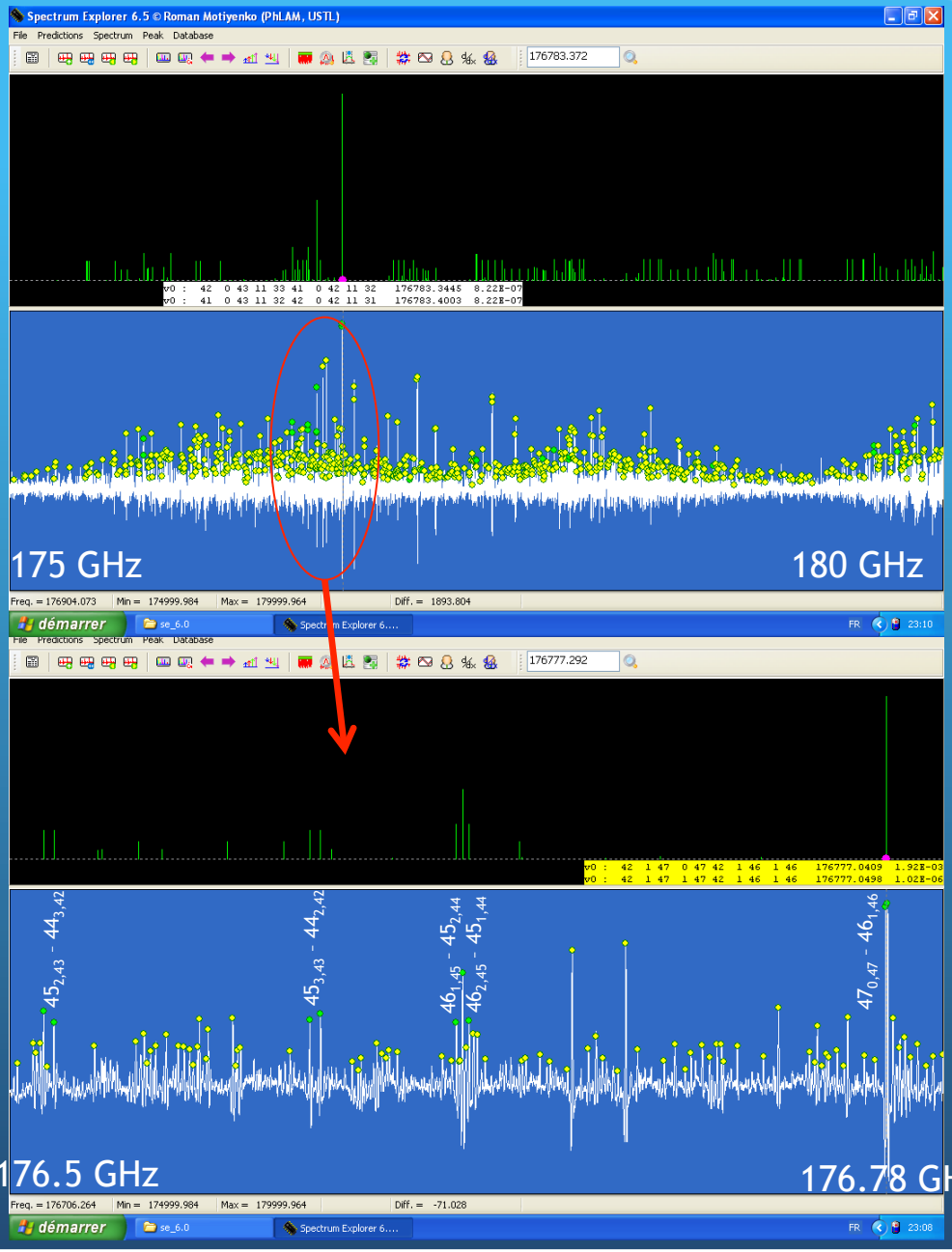
Not noise but huge number of lines!

Vibrational energy levels up to 250 cm^{-1}

(from B3LYP/6-311G++(3df,2pd) anharm force field)



- 9 energy levels below 250 cm^{-1}: floppy!
- In particular 3 levels at 83, 102 ans 117 cm^{-1}, spectra difficult to assign
  - Dense spectra: relative intensity to g.s. are from 67 to 57%
  - Levels are interacting together and with g.s.
- In fact this « floppy » behaviour is logic if we are coidering the very floppy case HNCO!



Assignement

- The most intense line don't have great signal to noise ratio
- Intensity decrease fastly with K_a, close to prolate limit case

Conclusions

- These works will help potential detection with the ALMA powerfull facility
- In case of detection: this could improve the knowledge about the ratio cyano/isocyano in the ISM and help the understanding of the unknown nitrogen chemistry
- Hydroxyacetonitrile: Spectroscopy of one target molecule for exobiology is done up to 0.5 THz
- Acethyl isocyanate:
  - Assignment is still in progress for higher K_a values and up to 450 GHz
  - Treatment of the bending and torsional modes could be possible in the near future: V.V. Illyushin, I. Kleiner and J. Hougen are coding the interactions…

Collaborations

- B. Tercero, J. Cernicharo - Departamento de Astrofiisica, Centro de Astrobiologica CAB, CSIC-INTA, Madrid, Spain
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