

Submillimeter wave spectroscopy of N-bearing complex organic molecules in Lille

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Outline

• Lille's Fast scan spectrometer

Overview of recent N-bearing COM's projects

Methoxy isocyanate



• Perspective: Radicals

Fast-scan spectroscopy

- To study a molecular spectrum in detail one needs to cover all the frequency range whenever it's possible. Otherwise at least several hudreds of GHz
- Broadband spectra provide sufficient variety of quantum numbers and selection rules
- The goal of the fast-scan: to minimize spectral acquisition time, keeping high sensitivity, resolution, and measurement accuracy.
- Fast-scan: a must-have for the detailed studies of unstable or rare molecular species



Fast frequency sweep with absolute frequency control



Direct digital synthesis

- •Extremely high resolution (up to 10⁻⁶ Hz)
- •Very fast frequency switching (up to 10 ns)
- •Frequency switching with continuous phase
- •The frequency is synthesized: inheriting stability and spectral purity of the reference clock
- •May be used for generating chirp with DDS (Finneran et al. 68th ISMS, WH16)



DDS-based fast scan spectrometer (1st version: BWO's based - 2010)

- Unstable or dangerous species
 - Ethyl and Vinyl-Tellurol (Motiyenko et al. J. Phys. Chem. A, 114, 2794 (2010); J. Phys. Chem. A 114 12202 (2010))
 - Di-isocyanomethane (Motiyenko et al. A&A 544, A82 (2012))
 - Ethylmercury Hydride (M. Goubet et al. J. Phys. Chem. A 116, 5405 (2012))

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Lille's fast solid state device spectrometer 150-1500 GHz (03/2015)





DIY system by R. A. Motiyenko, E. A. Alekseev (Karkhiv, Ukraine)



Fast frequency sweep and spectral measurements



OCS test: spectral purity



Noise tests:CHD₂OH





- Acquisition times are the same: 35 ms per point
- Frequency step is 30 kHz: 20 min per GHz
- No signal to noise ratio difference: the new system is more complex but not noisier

« DDS set up »



- Still very sensitive: 1ms/point is a good compromise
- Test done with solid state detectors less sensitive than bolometer



« DDS set up » with THz chain



No additional noise due to DDS with higher multiplication factor in THz



Lille's fast spectrometer

- Typical: Acq. time 1ms/point 4 acq. per point
- Frequency step from 30 kHz at 150 GHz to 162 kHz above 1 THz
- Cheap system: most expensive part « to speed up » is the filter
- No frequency calibration needed: frequency is always synthesized

We designed a fast decade spanning spectrometer (0.15-1.5 THz). Less than 24h is needed at high resolution (Doppler limited) and sensitivity to record the all range



Outline

Lille's Fast scan spectrometer

Lille's N-bearing COM's projects

Methoxy isocyanate



Perspective: Radicals

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					
AIF	C2H		I-C3H	C4H	I-H2C4	CH2CHCN	HC(O)OCH3	CH3CH2CN	N-bearing				
AICI	C20		C3N	C4Si	C2H4*	CH3C2H	СНЗСООН	(CH3)2O	molecules in TSM				
C2**	C2S		C30	I-C3H2	CH3CN	HC5N	C7H	CH3CH2OH	molecules in 15M				
СН	CH2		C3S	c-C3H2	CH3NC	CH3CHO	C6H2	HC7N					
CH+	HCN		C2H2*	H2CCN	СНЗОН	CH3NH2	CH2OHCHO	C8H					
CN	HCO		NH3	CH4 *	CH3SH	c-C2H4O	I-HC6H *	CH3C(O)NH2					
CO	HCO+		HCCN	HC3N	HC3NH+	Н2ССНОН	CH2CHCHO (?)	C8H–					
CO+	HCS+		HCNH+	HC2NC	HC2CHO	C6H–	CH2CCHCN	C3H6					
СР	HOC+		HNCO	НСООН	NH2CHO	CH3NCO	H2NCH2CN	CH3CH2SH(?)					
SiC	H2O		HNCS	H2CNH	C5N	HC5O 2017	CH3CHNH	CH3NHCHO? 2017					
HCI	H2S		HOCO+	H2C2O	I-HC4H *		CH3SiH3 2017						
KCI	HNC		H2CO	H2NCN	I-HC4N				nis table from: http://				
NH	HNO		H2CN	HNC3	c-H2C3O				ww.astro.uni-koeln.de/				
NO	MgCN		H2CS	SiH4 *	H2CCNH (?)				lms/molecules (10/2017)				
NS	MgNC		H3O+	H2COH+	C5N-								
NaCl	N2H+		c-SiC3	C4H–	HNCHCN								
OH	N2O		CH3 *	HC(O)CN	SiH3CN 2017								
PN	NaCN		C3N-	HNCNH									
SO	OCS		PH3	CH3O									
SO+	SO2		HCNO	NH4+	10 atoms	11 atoms	12 atoms	>12 atoms					
SiN	c-SiC2		HOCN	H2NCO+(?)	CH3C5N	HC9N	c-C6H6 *	HC11N ?					
SiO	CO2 *		HSCN	NCCNH+	(CH3)2CO	CH3C6H	n-C3H7CN	C60 *					
SiS	NH2		H2O2	CH3Cl 2017	(CH2OH)2	C2H5OCHO	i-C3H7CN	C70 *					
CS	H3+ (*)		C3H+		CH3CH2CHO	CH3OC(O)CH3	C2H5OCH3?	C60+ *					
HF	SiCN		HMgNC		CH3CHCH2O								
HD	AINC		НССО										
FeO ?	SiNC												
02	НСР												
CF+	ССР												
SiH ?	AIOH			at 200	malagui	laa haya	boon d	atastad in	the intersteller medium or				
PO	H2O+	•	aimo	St 200	molecu	les nave	been u	elected m	the interstellar medium or				
AIO	H2Cl+		ainau										
OH+	KCN		CIFCU	mstella	r snells	(CDMS))						
CN-	FeCN		A 1										
SH+	HO2	•	AIMO	ost 30 r	iitriie m	olecules	s, which	contain t	ne cyano group (C≡N), nave				
SH	TiO2					(7014)	6						
HCI+	C2N		 been detected in the (ISM) so far Only few species with two nitrogen detected (malonitrile - (CN)₂CH₂??) 										
TiO ΔrH+	Si2C	•											
N2													
NO+ ?	ET TECHNOL	•	Nitrogen chemistry is difficult and widely unknown										

Ethyl cyanide CH₃CH₂CN

Ethyl cyanide, also known as propanenitrile or propionitrile, has been observed in abundance in hot molecular clouds in the range 40–950 GHz (1st ISM detection: Johnson, D. R., et al. 1977, ApJ, 218, 370)



Excited vibrational state study ($v_{bending} = 206 \text{ cm}^{-1}$ and $v_{torsion} = 213 \text{ cm}^{-1}$) of ¹³C species in collaboration with JPL (B. Drouin group)



Formamide NH₂CO

- Formamide (HCONH₂) is the simplest molecule with a peptide bond detected in the interstellar medium (Rubin, R. H., et al. 1971, ApJ, 169, L39)
- it has been shown that of all possible simplest interstellar molecules that contain a peptide bond, formamide is the most stable energetically (Lattelais, et al. 2010, A&A, 519, A30)



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N-methylformamide: CH₃NHCHO

- structural isomer of the known interstellar molecule acetamide, CH₃C(O)NH₂
- Both molecules contain a peptide bond which is the characteristic chemical bond linking amino acids in proteins
- N-methylformamide can also be seen as a partially hydrogenated form of methyl isocyanate, CH₃NCO, which was recently detected in the ISM



- Internal rotation motion with very low barrier value: 55.17 cm⁻¹
- The spectra was measured from 45 to 660 GHz
- The analysis is carried out using the Rho-axis method and the RAM36 code

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Rotational spectroscopy, tentative interstellar detection, and chemical modeling of N-methylformamide*

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So far, so good...

Di-cyanomethane (malonitrile-NC-CH₂-CN) and isocyanomethane:

- Following the first microwave study of a bis-isocyanide derivative diisocyanomethane (Motiyenko et al., A&A 2012, 544 A82)
- No MW study about the cyano-isocyanomethane (CNCH₂CN).
- the most stable isomer malonitrile also reinvistigated:
 - 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.

Acetyl isocyanate (CH₃CONCO)

- 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)
- CH₃COCH₃ is detected since 1987 Sgr B2 (F. Combes et al. A&A, 180, (1987), L13)
- Isocyanate functional group (–NCO) is highly reactive and many chemicals containing isocyanate groups were used for the synthezises of polyurethanes.

Ethyl-isocyanide (CH₃CH₂NC): (A&A in press)

- The few isocyanides detected in the ISM are always isomers of the corresponding : HNC, CH₃NC, HCCNC
- 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 (CH₃CH₂NC) is isomer of one of the most abundant Complex Organic Molecules
- Very badly surprised with the non detection in Orion...



Aminomalononitrile : H₂NCH(CN)₂

- HCN trimer (trimer of the key molecule for ¹⁵N fractionation)
- AMN is a useful intermediate in the synthesis of many heterocyclic systems. Such properties designate AMN as a key compound in prebiotic chemistry and an attractive candidate for the ISM
- The analysis of the rotational spectra of the A conformation has shown that the observed lines exhibit a doublet or quartet structure owing to two large-amplitude motions, C–N torsion and amino group inversion





Figure 3. A part of the experimental spectrum of AMN in the 167–173 GHz frequency range showing (a) the intense series of ${}^{b}R_{1,\pm1}$ transitions and (b–e) a detailed view of selected transitions exhibiting torsion-inversion splittings. For these transitions, the assignment according to irreducible representations of the G_4 molecular symmetry group and the relative intensities are also indicated.



b conformer 6.7 kJ/mol higher in energy

High-Resolution Millimeter Wave Spectroscopy and Ab Initio Calculations of Aminomalononitrile

Roman A Motiyenko,*^{,†} Laurent Margulès,[†] Eugen A Alekseev,[‡] and Jean-Claude Guillemin[¶]

Hydroxyacetonitrile (HOCH₂CN):

- Compete with aminomethanol (NH₂CH₂OH), 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 (CH₂CNH), formaldehyde (CH₂O), hydrogen cyanide (HCN), carbon monoxyde (CO) (Danger G. et al. A&A 549, A93, 2012)
- Detection of aminoacetonitrile in SgrB2(N) (NH₂CH₂CN) (A. Belloche, et al. A&A, 2008, 482 179)



 Methyl isocyanate (CH₃NCO) the most stable energetically structural isomer was detected



Ethanimine (CH₃CHNH)–Propanimine (CH₃CH₂CHNH)

- The aldimines are important to understand amino acids formation process as they appear in reaction scheme of Strecker-type synthesis.
- Methanimine (CH₂NH) was detected in 1973 (Godfrey et al., ApJL, 13, 119 1973)
- Beginning of the projet was studying ethanimine (CH₃CHNH) in 02/2013. But at the same time it was detected in SgrB₂ with Primos survey (Loomis et al., ApJL, 765, L9, 2013)
- We decided to study the next one in the serie: propanimine
- We used a synthesis method to obtain pure samples. E,Z-Ethanimine and E,Z Propanimine has been prepared in the following way : precursors have been slowly vaporized in a reactor containing dry KOH in powder (50 g) in half section and heated to 85-100°C



Propanimine (CH₃CH₂CHNH)

- No spectroscopie studies available up to now
- 2 conformers E and Z:
- Z is the less stable but Z_{conf} μ_a dipole moment is two times the E_{conf} one
 At lab temperature (Boltzman factor is 0.28 for Z_{conf}: intensities are the same
 At ISM temperature (150-250 K): both should be detected





Ethanimine (CH₃CHNH)

- Ethanimine exhibits large amplitude: internal rotation of methyl group.
- Strong coupling between torsion and rotation: $\rho = 0.28$. This as high as acetaldehyde.
- Usually in millimeterwave spectra $^{14}\rm N$ nuclear electric quadrupole hyperfine splittings are no observed with doppler limited resolution or only for high K_a values. (cf. Ethyl cyanide)
- These splittings are enhanced by internal rotation and should be take into account, especially for μ_b type lines.
- Previous studies up to 140 GHz (Lovas et al., J. Chem. Phys. 72, 4964, 1980) and recent CP-FTMW measurements from 6.5 to 40 GHz (Loomis et al., ApJL, 765, L9, 2013) treatment taking account hyperfine spliting not done.



Z_{conf} spectra could be more intense even at ISM temperature



Ethanimine spectra



Future targets

- We were successfull with excited vibrational states, or isotopologues of « weeds »
- Several issues when looking to new molecules
- Difficulty to find the right target despite regular discussions with astrophysics groups
- One way could be the amines, amino acids, amino alcool....
 - laboratory experiments showed that formation of amines and amino acids in the interstellar medium (ISM) is possible
 - only a few molecules with–NH2 group detected in the ISM only two « amines »
- Most of these samples were not commercial, and stable in laboratory conditions



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Astrophysical interest and motivation

- Detection of methyl isocyanate (CH₃NCO) in different object:
 - Orion KL (Cernicharo, et al. 2016, A&A, 587, L4)
 - towards Sgr B2(N) (Halfen, D. T., et al. 2015, ApJ, 812, L5)
 - IRAS 16293-2422 (Ligterink et al. MNRAS (2017) 469 (2))
 - on the comet 67P/C-G (Goesmann, F. et al. 2015, Science, 349)

• CH₃ONCO contains a methoxy CH₃O- radical functional group which has been detected in the ISM towards the cold core B1-b (Cernicharo et al. 2012, ApJ, 759, L43) and may be an important tracer of methanol related chemistry.

NCO + CH₃ → CH₃NCO Belloche et al.(2017) NCO + CH₃O → CH₃ONCO ???

 Follow study of acethyl isocyanate CH₃CONCO (L. Margulès et al, WF10, ISMS, champaign USA 2014)



Experimental details

- Methoxyisocyanate is unstable under room temperature
- Sample synthesized "in situ" by flash vacuum pyrolysis from precursor in the oven at \sim 800 K
- Spectra measured in flow mode
- Pyrex absorption cell





Spectrum of CH₃ONCO

recorded in the millimeter wave range: 75-330 GHz

• Doubler: 150-220 Ghz

152020

152040

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152060

152080

frequency, GHz

152100

152120

152140

- step 36 kHz (usually 30 kHz)
- 10 GHz recorded in ~26 minutes

 ${}^{a}R_{0,1}$ J" = 31 \rightarrow 30

- CH₃OH and HNCO as impurities
- Dipole moments: $\mu_a = 2.32 \text{ D}$ and $\mu_b = 0.24 \text{ D}$





Perturbations in the ground state

 $J'' = 32 \rightarrow 31$ ${}^{a}R_{0,1}$



perturbations have significant effect on the high-resolution spectra observed in all the spectra measured (from J'' = 15 to 70)

Shifts of transitions for the ground state between observed and rigid rotor model ($J'' = 32 \rightarrow 31$):

- - 22 MHz for *K*_a=12
- - 116 MHz for K_a=13
- + 286 MHz for $K_a = 14$



Vibrational modes

Results from Anharmonic force field calculations B3LYP/6-311++(3df, 2pd)

 $E_{v}(cm^{-1})$

350

- Barrier to the internal rotation $V_3 \sim 800$ $cm^{-1} \rightarrow no$ splittings observed
- Up to 7 vibrationally exited states below 250 cm⁻¹: dense spectra!
- Coriolis-type coupling between vibrationa states: ground state and $v_{18}=1$, $v_{18}=1$ and $v_{18}=2$, $v_{18}=2$ and $v_{18}=3$, $v_{18}=3$ and $v_{11}=1 \rightarrow a$ "ladder" of resonances
- The analysis of rotational spectrum is complicated: even the relatively low K_a levels of the ground state are perturbed

 $v_{18} = 59 \text{ cm}^{-1}$

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Skeletal torsion



V₁₁ $= 174 \text{ cm}^{-1} \text{ v}_{17} = 235 \text{ cm}^{-1}$



350

Vibrational modes



- Considering Boltzman distribution, at 300 K, the population ratios of $v_{18}=1 v_{18}=2$ and $v_{18}=3$ are, respectively, 75% ,56%, and 42%.
- In general case low lying vibrational states (below 250 cm⁻¹) shoud be take into accout:
 - may also represent an interest for the astrophysical observations
 - Calculation of the vibrational part of partition function



The Hamiltonian

- The effective Hamiltonian model in a presence of rotational-vibrational interactions was used
- The Hamiltonian for the 5-states (ground state, $v_{18}=1, v_{18}=2, v_{18}=3, v_{11}=1$) coupled fit was constructed in a block matrix form:



where:

- *H*^(rot) standard rotational Watson's S-reduction Hamiltonians
- ΔE energy difference between coupled vibrational levels
- $H^{(Cor)}$ off-diagonal Coriolis interaction terms

$$H^{Cor} = \left(F_{ac} + F_{ac}^{J} \mathbf{P}^{2} + F_{ac}^{K} P_{z}^{2} + ...\right) \left(P_{x} P_{y} + P_{y} P_{x}\right) + \left(F_{bc} + F_{bc}^{J} \mathbf{P}^{2} + ...\right) \left(P_{y} P_{z} + P_{z} P_{y}\right)$$

Papousek, D. & Aliev, M. R. 1982, Molecular vibrational-rotational spectra (Elsevier, Amsterdam New York)



Illustration of the Coriolis interaction





Coriolis coupling between v₁₈=2 and v₁₈=3





Results





global simultaneous fit needed



Results

Parameter	ground state	v ₁₈ =1	v ₁₈ =2	v ₁₈ =3	v ₁₁ =1
A (MHz)	44584.62(39)	41662.23(43)	39203.04(119)	37226.40(56)	46465.19(125)
B (MHz)	2498.23576(47)	2508.13703(62)	2518.35642(140)	2528.8982(51)	2505.80837(223)
C (MHz)	2405.34035(44)	2423.01798(46)	2405.34035(44)	2460.1859(76)	2409.54383(215)
$\Delta_{\sf J}$ (kHz)	0.362714(148)	0.444521(220)	0.54388(33)	0.63023(70)	0.372634(234)
$\Delta_{\sf JK}$ (kHz)	-20.4677(183)	-32.28(58)	-26.26(70)	-40.460(100)	-21.2239(236)
Δ_{K} (kHz)	1.536020904(0)	1.323227535(0)	1.019146667(0)	1.536020904(0)	1.536020904(0)
d ₁ (kHz)	-0.020878(49)	-0.04307(57)	0.016651(268)	0.03676(131)	-0.02277(47)
d ₂ (kHz)	-0.8193(200)E-06	-1.033(106)E-03	1.387(108)E-03		
ΔE , MHz		1516543(223)	2992591(112)	4446796(0)	5037782(0)
Fac, MHz		37.697(39)	-74.39(312)		
Fbc, MHz		1.5958(54)	-1.8883(45)		
Ga, MHz					4748.1(33)
	+ 3 P ⁶ terms	+ 3 P ⁶ terms	+ 3 P ⁶ terms	+ 2 P ⁶ terms	
Number of lines	351	333	125	43	64
rms (MHz)			0.049		
wrms			1.12		



Results

- Asignment and analysis of the ground and lowest vibrationally excited states of methoxy isocyanate, CH₃ONCO, in a presence of strong Coriolis coupling, in the 75 – 330 GHz frequency range
- The catalogue of accurate frequency predictions for the ground state transitions involving J < 70 and $K_a < 13$ will be accessible soon for astronomical observing
- CH₃ONCO was searched in Sgr B2 and Orion KL (J. Cernicharo, private communication)



Simulated spectrum of $\rm CH_3ONCO$ in its ground state at 150 K



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Radical Species

- COM's: route formation is still unknown.
 - Phase-only chemical models could not reproduce produce abundances observed
 - Gaz/Surface model: (UV) irradiation of grain mantle molecules, then the radicals can react on the grain mantles at a temperature of around 20–40K (Garrod, R. T., & Herbst, E. 2006, A&A, 457, 927; Hall et al. A&A, 517, A1, 2010)
 - Recent detection of methyl formate and DME at very cold temperature (10K) in the prestellar core L1689B (Bacmann et al. A&A, 541, L12, 2012)
- The processes involved radicals species not detected yet! Their detection could help a lot astrochemistry



Radical Species

J. M. C. Rawlings et al., Faraday Discuss., 2014, 168, 369

One possible way of forming glycine in such a high density regime would be *via* a three-stage process involving four radicals. The first step would form COOH by simple association of CO and OH:

$$CO + OH + H_2O - COOH + H_2O.$$

$$NH_2 + CH_2 + H_2O \rightarrow NH_2CH_2 + H_2O$$
Not detected in ISM

followed by

Then:

$$NH_2CH_2 + COOH + H_2O \rightarrow NH_2CH_2COOH + H_2O.$$

Or, alternatively,

 $\mathrm{CH}_2 + \mathrm{COOH} + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{CH}_2\mathrm{COOH} + \mathrm{H}_2\mathrm{O}$

followed by

 $CH_2COOH + NH_2 + H_2O \rightarrow NH_2CH_2COOH + H_2O.$



Radical Species

Short time project in Lille: new quartz cell with UV-photolysis

- Photolysis is more selective than DC-discharge
- UV: 4 lamps (300W each!) around the cell





Collaborations

Spectroscopy

- E. Alekseev (Kharkiv, Ukraine)
- B. Drouin, A. Daly, S. Yu, J. Pearson (JPL)
- H.S.P. Müller (Köln)

Synthesis

• J.-C. Guillemin (Rennes)

Theory

• V. Ilyushin (Kharkiv, Ukraine)

Astrophysics

- M. Gérin (Paris)
- J. Cernicharo, B. Tercero (Madrid)
- A. Belloche, K. Menten (Bonn)
- D. Despois, N. Brouillet (Bordeaux)
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