High resolution spectroscopy of large molecules

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mm and submm spectroscopy in Lille

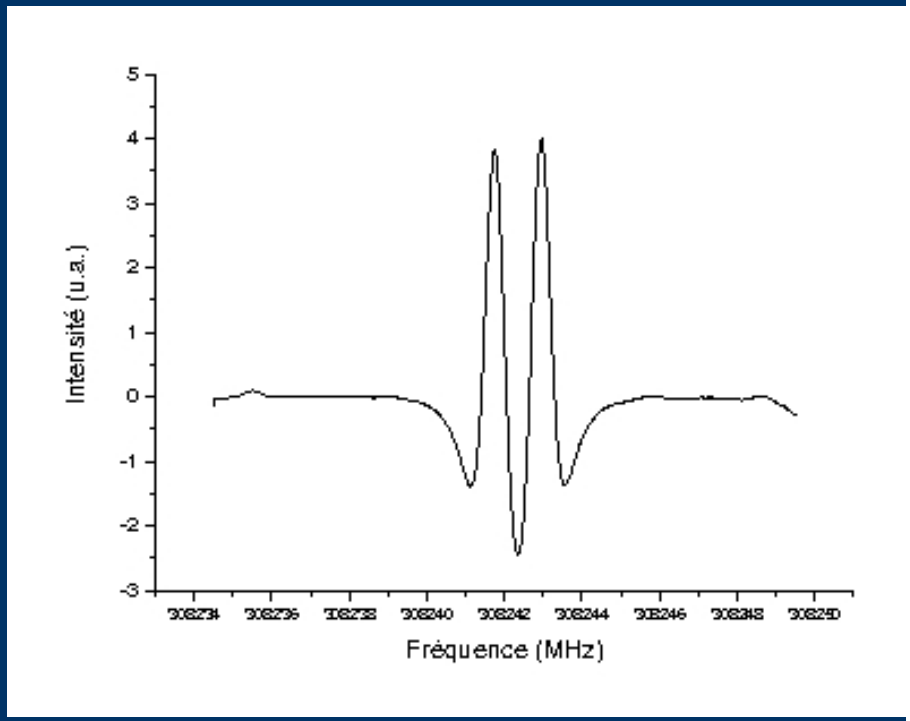
- Large wavelength coverage
  - 8-20 GHz with the FTMW spectrometer SIMO
  - 150-600 GHz with BWOs
  - 600 GHz-2.5 THz with the sideband molecular laser spectrometer
- High spectral resolution : 50 kHz
- Stable molecules, radicals, ions can be studied
- Outline of the talk :
  - mm wave study of istotopologues of methyl formate and propionitrile
  - THz study of urea
  - Toward larger molecules

Methyl formate : $HCOOCH_3$

- Dense and intense rotational spectrum
- Internal rotation of the methyl group splits each rotational line into a doublet (A and E)
- Abundant species in molecular clouds, more than 900 transitions have been identified in interstellar spectra
- Ground state: 3000 lines assigned up to 608 GHz (Plummer et al. 1984, 1986; Ogata et al. 2004)
- First torsionally excited state studied in the 7-200 GHz, up to J=18 and K_a =7 (Ogata et al. 2004)
- $DCOOCH_3$ studied up to 377 GHz and J=30 (Oesterling et al. 1995)

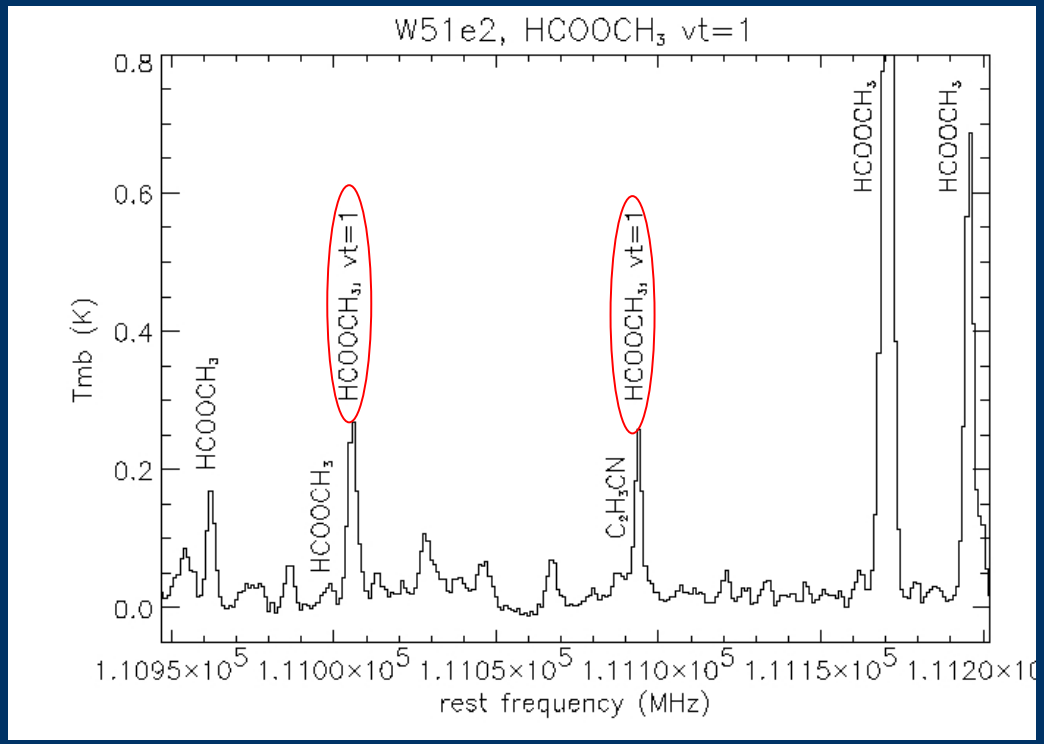
^{13}C methyl formate : H^{13}COOCH$_3$

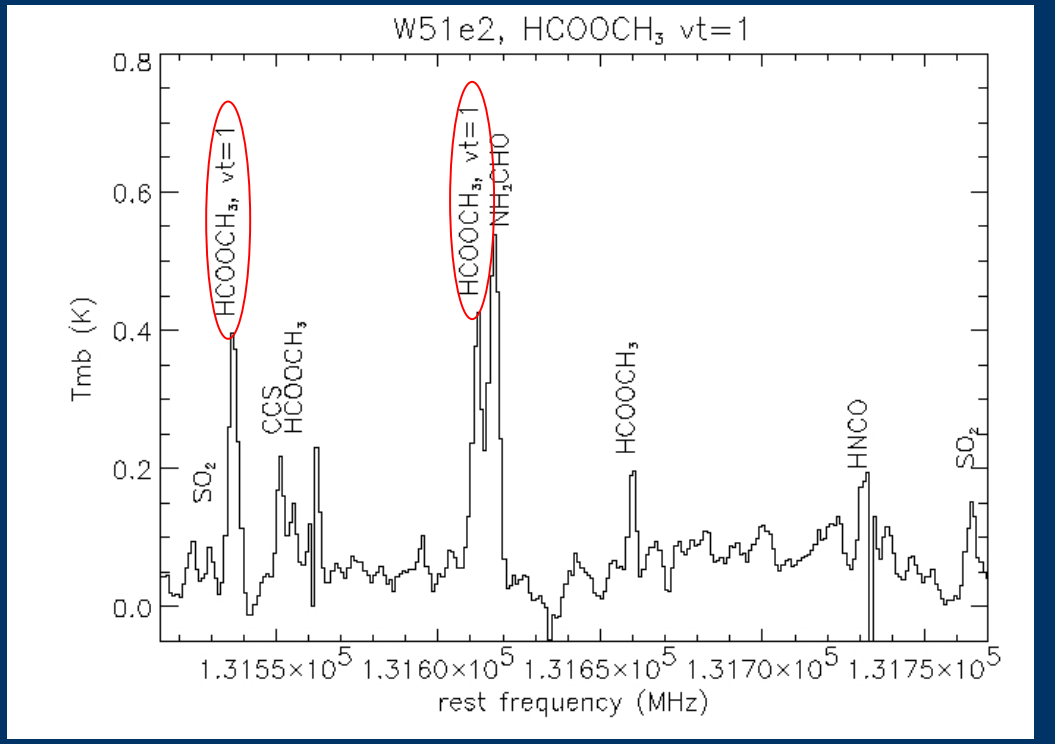
- Measurements in the frequency range 7 – 610 GHz
- 290 transitions for the A species up to J=58 and K_{max}=24
- 260 transitions for the E species up to J=58 and K_{max}=24
- Separate analysis for the A and E species + global analysis
- Willaert et al. J. Mol. Spec., in press



Torsionally excited $HCOOCH_3$ in W51e2

- IRAM 30m antenna observations





Torsionally excited $HCOOCH_3$ in W51e2

- Estimated abundance and temperature: (waiting for new data coming soon!)
  - Ground state : 35 lines observed, 8<J<35, T_{rot} = 200K, N=1.6x10^{16} cm^{-2}
  - Vt=1 state : 4 lines, T=200K , N=1.2x10^{16} cm^{-2}

J'	Ka'	Kc'	J''	Ka''	Kc''		Eup cm-1	Measured freq. (MHz)	Observed freq. (MHz)
12	0	12	11	0	11	A	163.8	131536.624	131536.95
12	0	12	11	0	11	E	163.8	131612.344	131612.09
9	1	8	9	1	7	E	153.4	111094.105	111094.01
9	3	7	8	3	6	E	156.4	111005.617	111005.83

Propionitrile CH_3CH_2CN

- Abundant in molecular clouds (10^{15}-10^{17} molecules/cm^2), more than 500 lines observed in interstellar spectra (Lovas catalog)
- Rich and intense rotational spectrum, large dipole moment (μ_a=3.85 , μ_c=1.23 D), studied up to 610 GHz, J<70, K_a<36 (Lovas 1982, Pearson et al. 1994, Fukuyama et al. 1996)
- The excited torsional (212.7 cm^{-1}) and in-plane bend (206.5cm^{-1}) state studied up to 422 GHz and observed in SgrB2 (Mehringer et al. 2004)

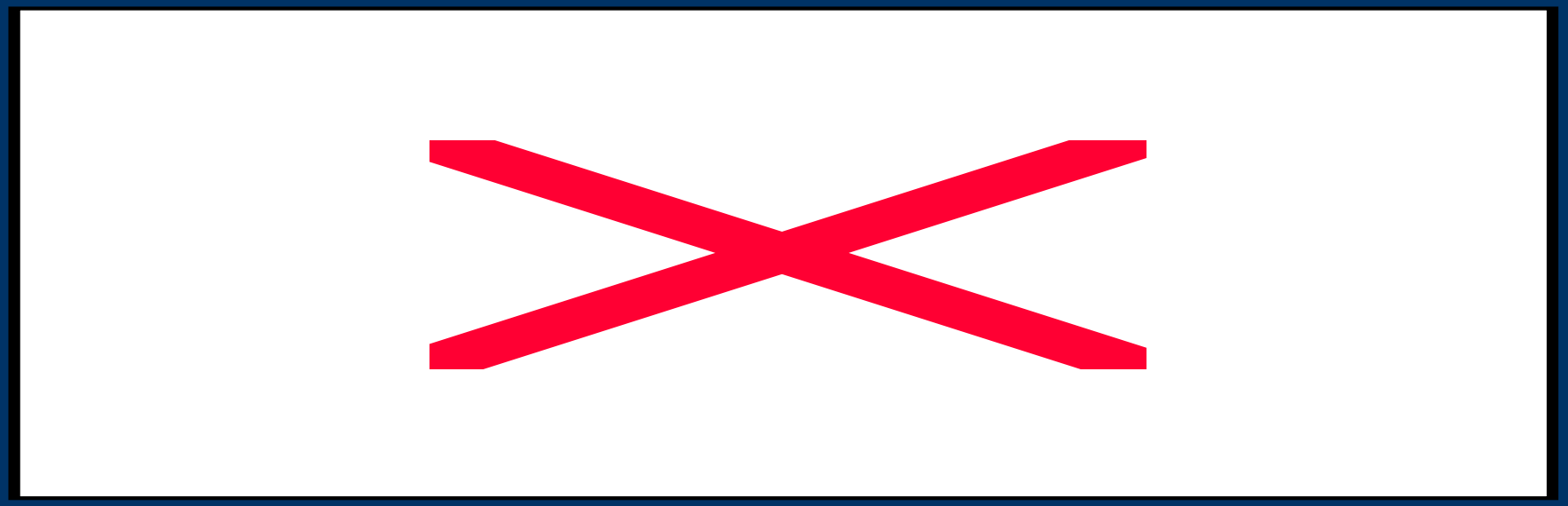
^{13}C substituted CH_3CH_2CN

- $^{13}CH_3CH_2CN$, $CH_3{}^{13}CH_2CN$, $CH_3CH_2{}^{13}CN$
- Intense rotational spectra, large dipole moment (μ_a=3.84 , μ_c=1.37 D)
- Previous studies by Heise et al 1973 in the 8-40 GHz frequency range
- Studied in the range 8-60 GHz at Kiel (H. Mäder) and 150-300 GHz, 150 to 200 assigned transitions up to J=35 and K_a=20 for each species (Demyk et al. in prep)

^{13}C substituted CH_3CH_2CN : new set of spectroscopic constants

Comparison with JPL predictions

- JPL data are extrapolated from Heise measurements in the 8-40 GHz range. Line frequencies are predicted up to J=10



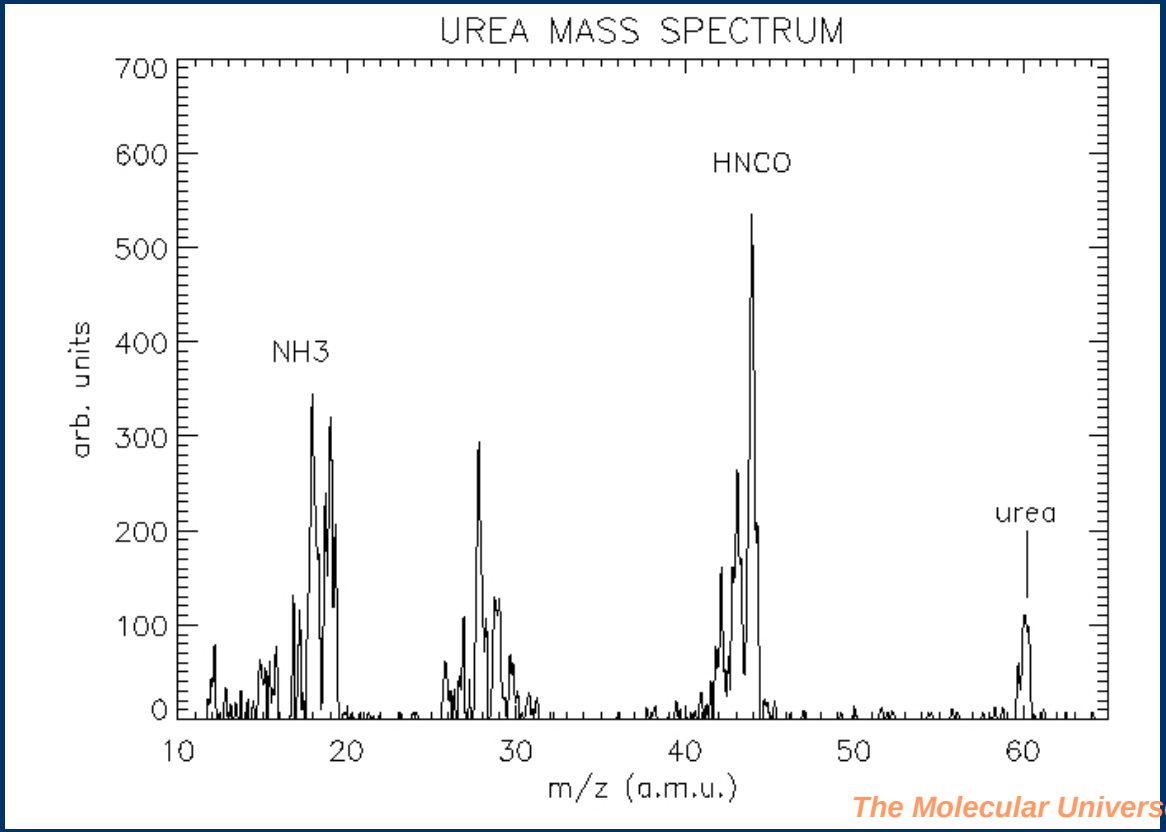
- The new set of constant allows to predict line frequency with an accuracy better than 1 MHz up to ~500 GHz for intense lines and J < 35 (emission maximum at about 337 GHz for T_{rot} = 200K)

Urea $(NH_2)_2CO$ (in progress)

- Not yet observed in mm and submm interstellar spectra
- Possible detection at 6μm in the ices around deeply embedded protostellar objects (Raunier et al. 2004)
- Experimental study of the rotational spectrum by Kretschmer et al. 1996 in the 8-19 GHz frequency range, measurements in Kharkov (V. Iluyshin, E. Alekseev) up to 220 GHz
- Measurements in Lille above 600 GHz

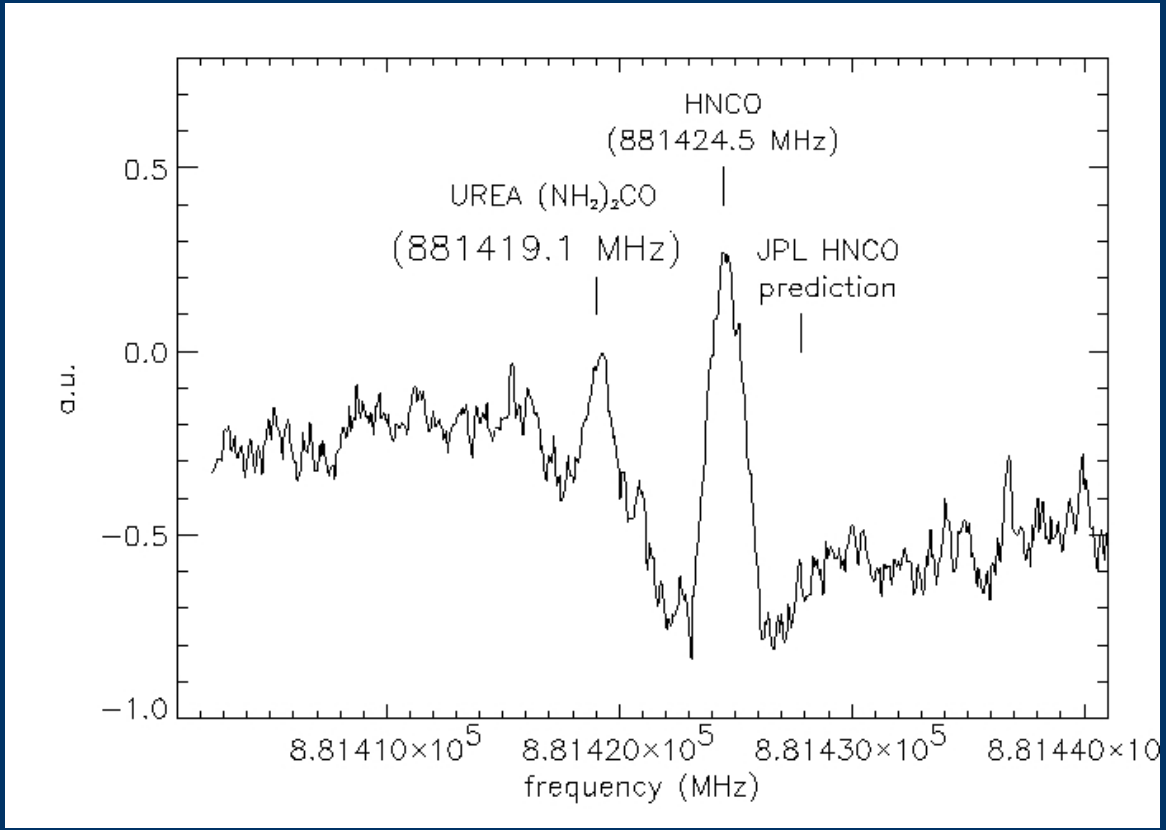
Urea $(NH_2)_2CO$ (in progress)

- Solid at room temperature
- Melting point : 135°C
- Decompose into HNCO and NH_3 above 152°C

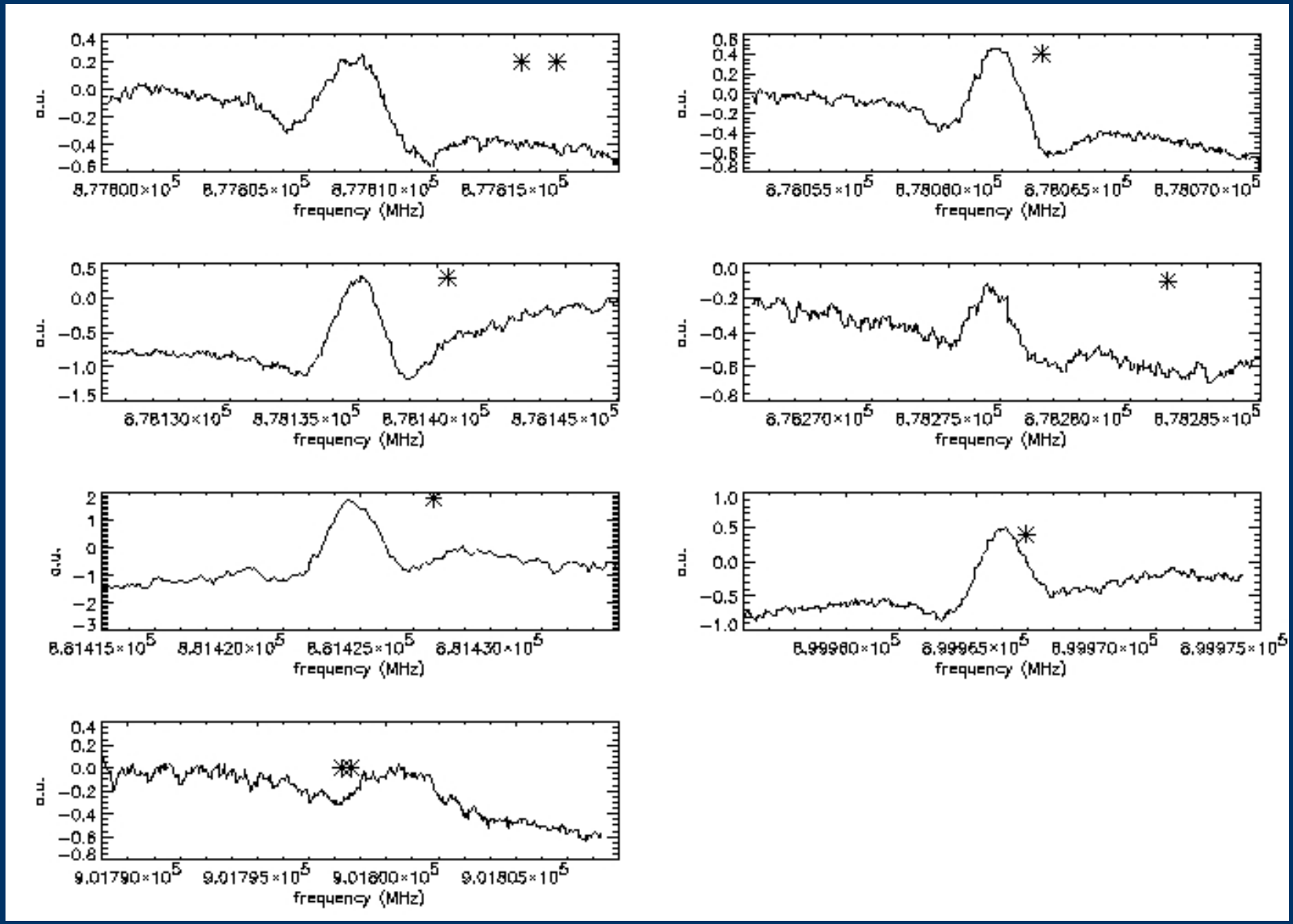


Urea $(NH_2)_2CO$ (in progress)

- Tentative detection of one transition @ 881419.1 MHz 41(33,8) 40(32,9)

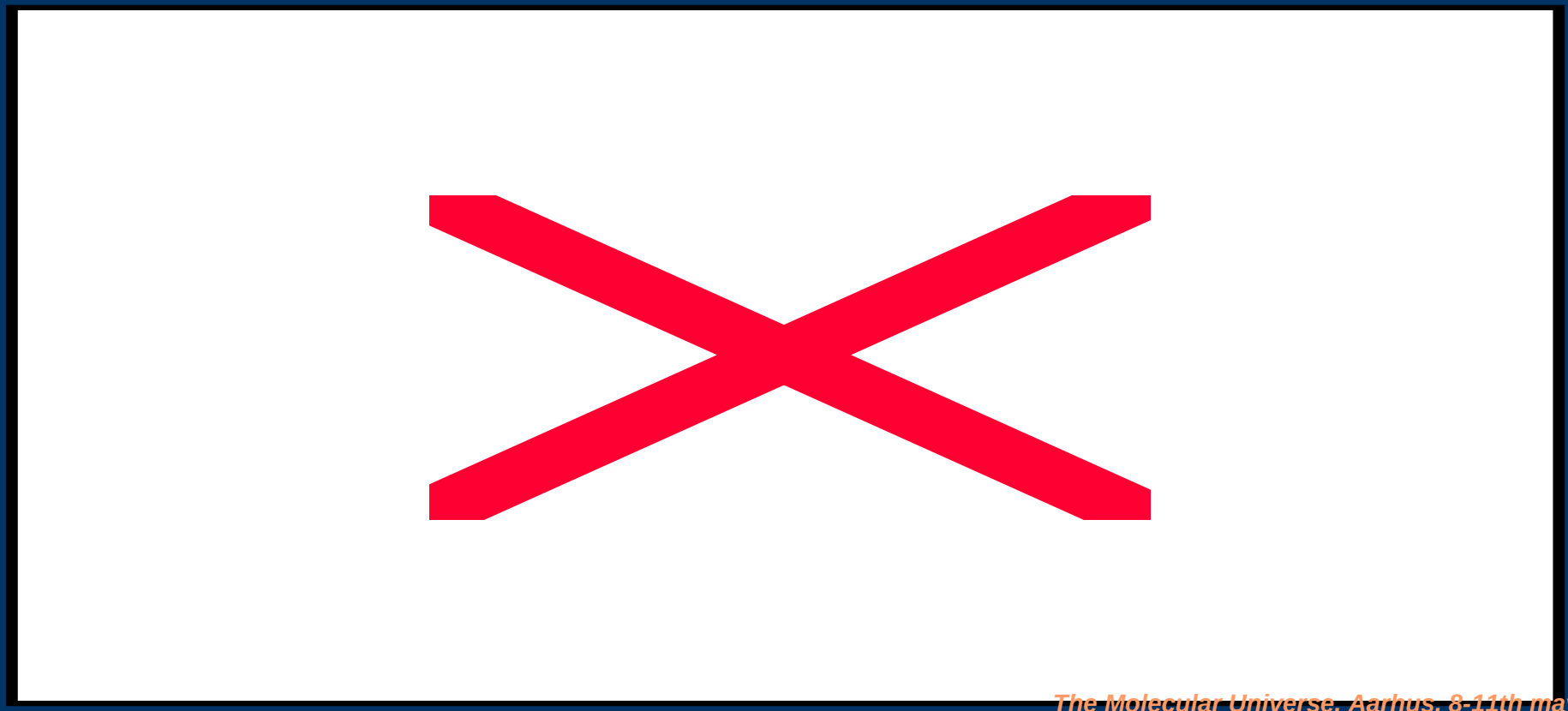


HNCO



HNCO

- JPL data are extrapolated from measurements in the 8-220 GHz range (Hocking et al. 1975)
- FTIR measurements are from Niedenhoff et al. 1995

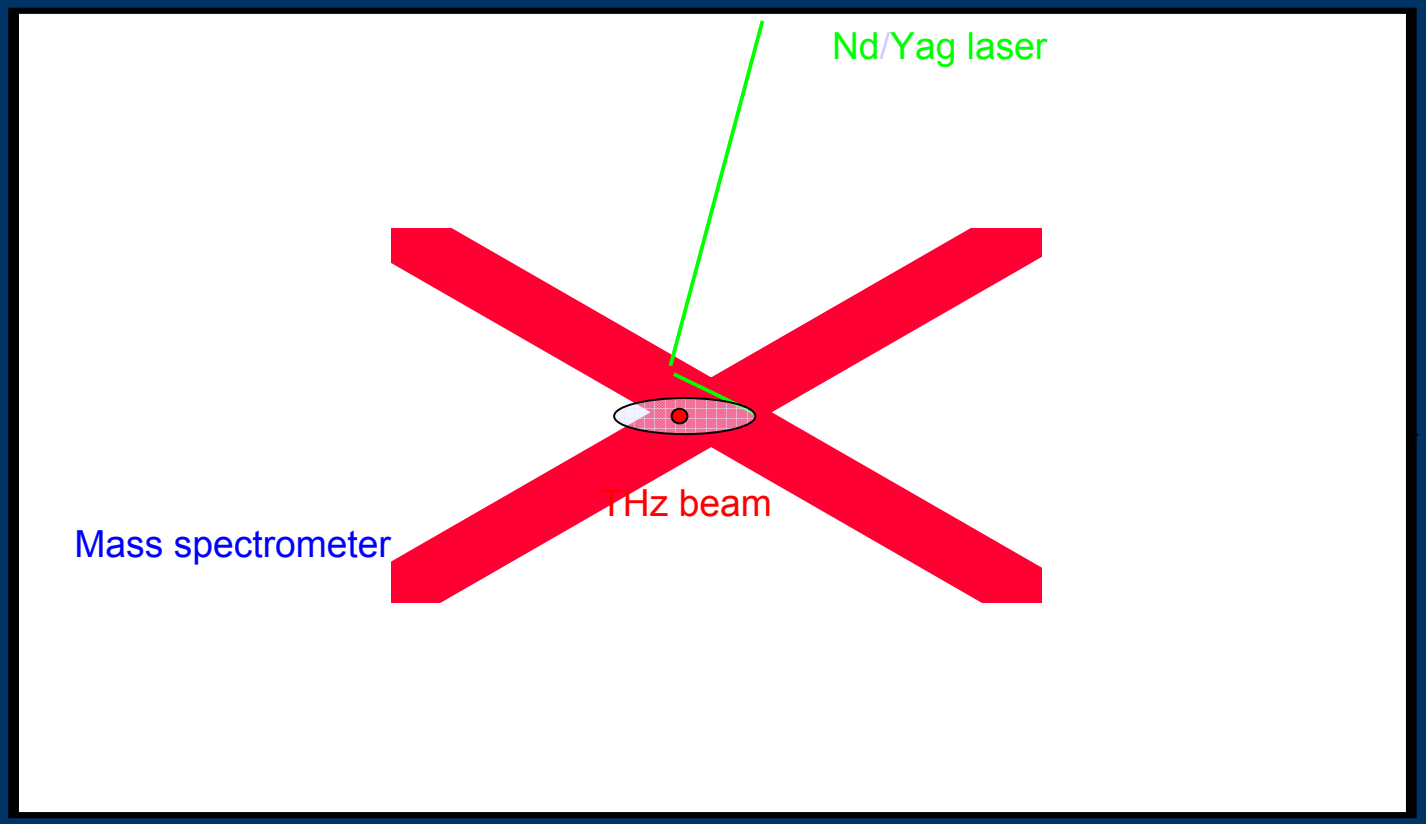


THz spectroscopy of very large molecules

- Study the low frequency torsional and vibrational mode in flexible molecules such as PAHs
- Identification of the molecules from the rotational structure of these modes
- High level ab-initio calculations needed to estimate rotational constants and band positions
- Preliminary measurements with FTIR spectroscopy if possible
- High spectral resolution on the sideband molecular laser THz spectrometer in Lille

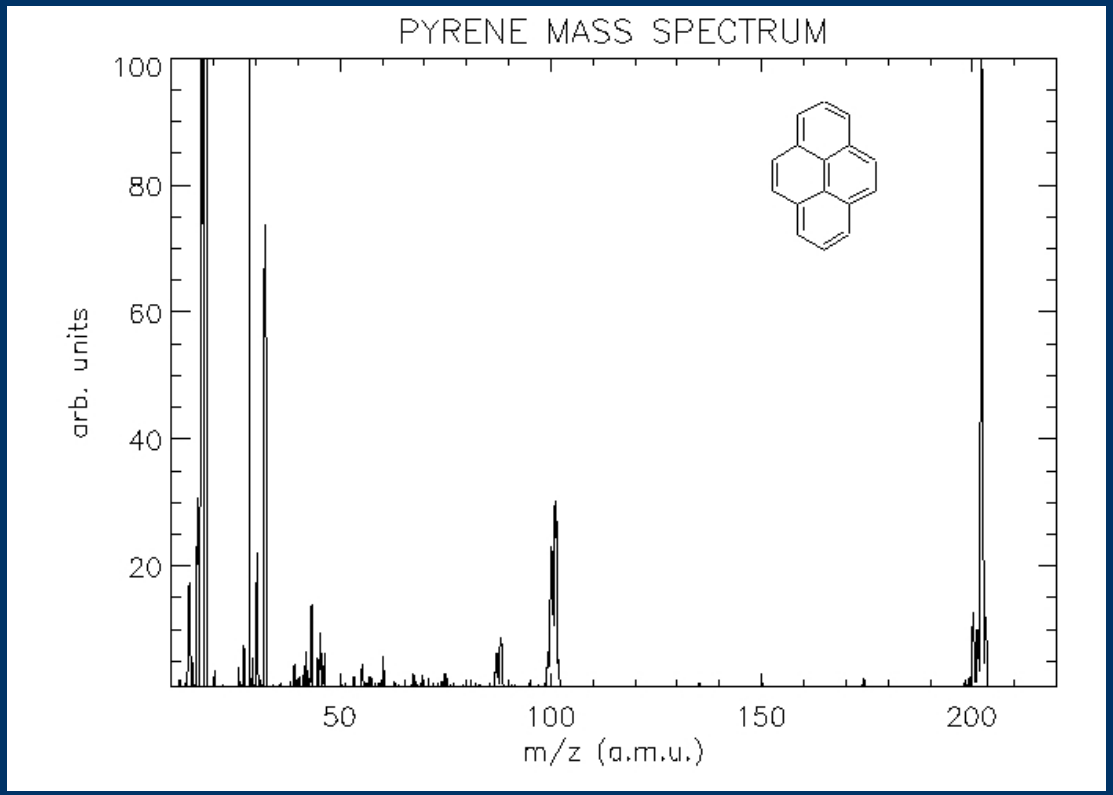
THz spectroscopy of very large molecules

- Production into the gas phase via laser desorption with a Nd:Yag laser @ 1064, 532, 366 or 234 nm, 25 mJ, quadrupole mass spectrometry to control the process



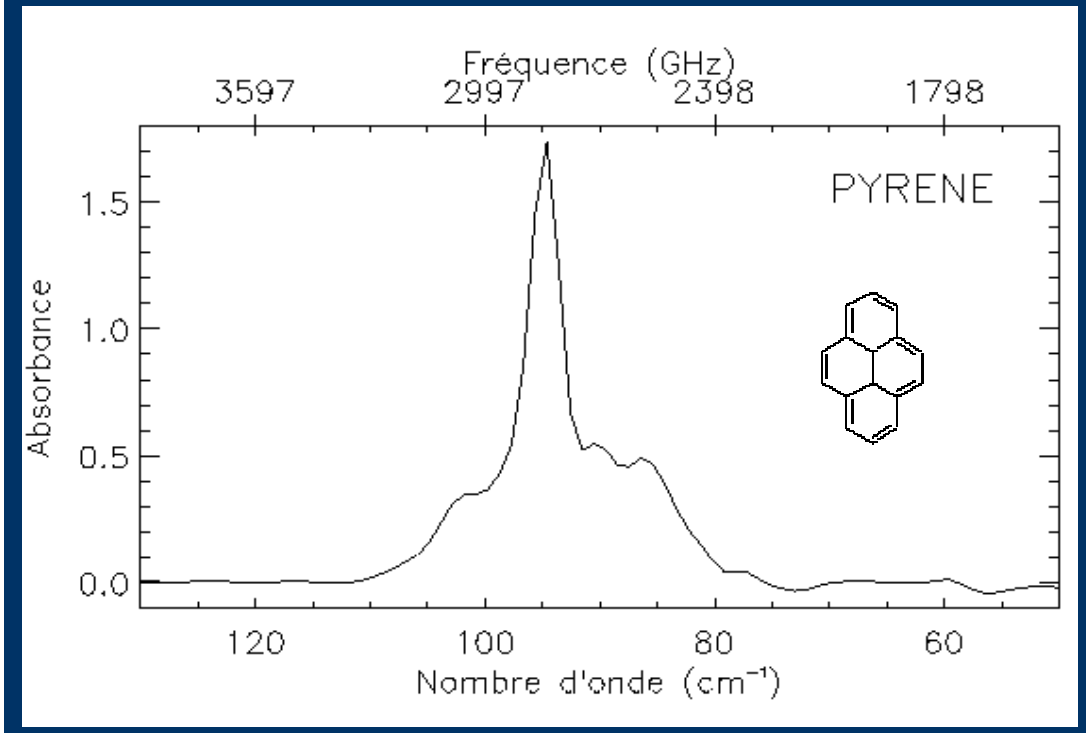
Low frequency mode in pyrene

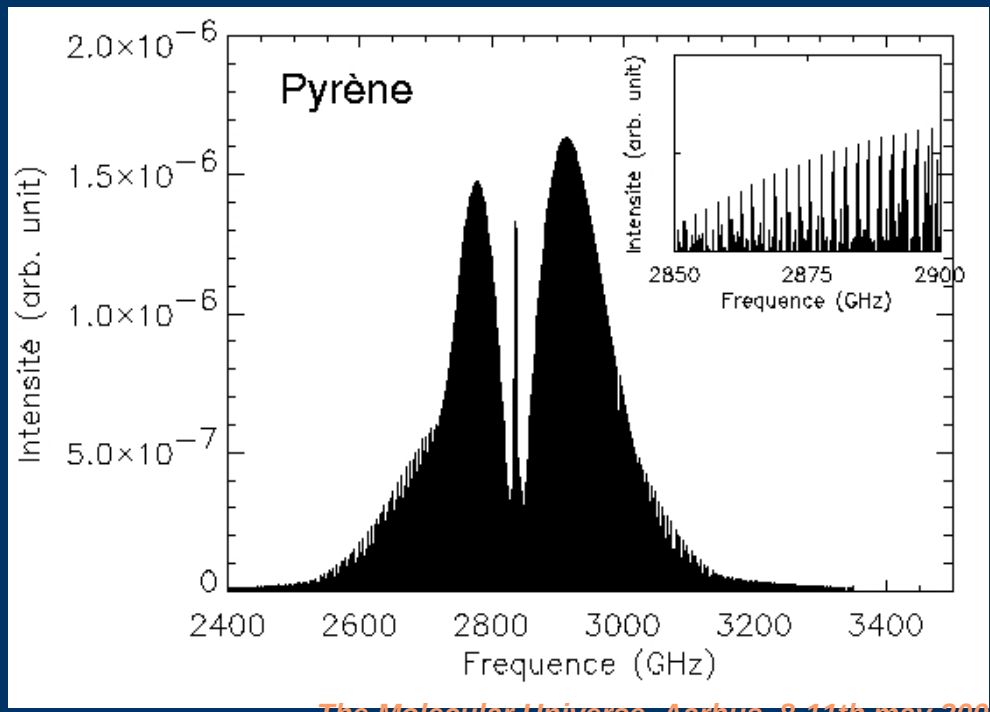
- **Band at 101.13 cm^{-1} (3031.9 THz); A=1009.93 MHz, B=554.90 MHz, C=358.13MHz**
- **Pyrene ($C_{16}H_{10}$) desorbed @532nm, 15Hz, 25mJ**



Low frequency mode in pyrene

- **Emission spectrum of pyrene recorded at LPPM (Orsay) (M. Vervloet, O. Pirali) with high resolution FTIR spectrometer**
- **Calculated rotational structure of the vibrational mode at 101 cm^{-1}**





Other possible candidates for spectroscopic studies :

- **Pentacene ($C_{22}H_{14}$) : mode at 39.16 cm^{-1} (1174 GHz), A=1319.86 MHz, B=117.34 MHz, C= 107.76 MHz**
- **Crysene ($C_{18}H_{12}$) : mode at 50.90 cm^{-1} (1526 GHz) and 78.51cm^{-1} (2354 GHz); A=1257.58 MHz, B=262.56 MHz, C= 217.06 MHz**
- **Acridine ($C_{13}H_9N$) : mode at 95.09 cm^{-1} (2850 GHz), A=2153.25 MHz, B=465.12 MHz, C= 382.49 MHz**

Other species studied in Lille

- C_2H_4 (ethylene) global analysis (A. Fayit)
- $H_2NCH=CHN$ (aminopropenenitrile) 4-80 GHz (H. Mollendal, J. Demaison, J. Avilez-Moreno, T. Huet)
- H_2CS, 4-80 GHz (H. Mollendal, J. Demaison)

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