MAX PLANCK INSTITUTE
FOR EXTRATERRESTRIAL PHYSICS

Laboratory spectroscopy of sulphur bearing species

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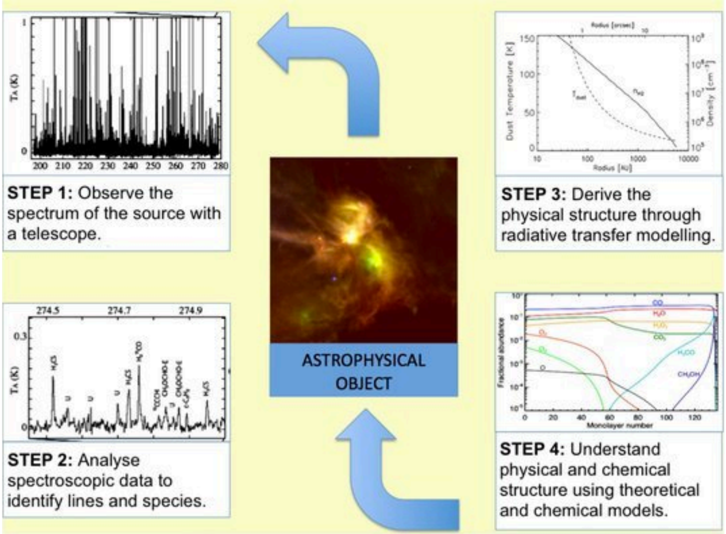

Caselli & Ceccarelli A&ARv 2012

Molecular Spectroscopy for Radioastronomy

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Gas–Phase High Resolution Rotational/Ro–Vibrational
Molecular Spectroscopy for Radioastronomy

Molecular Spectroscopy for Radioastronomy

$\Downarrow$

Gas–Phase High Resolution Rotational/Ro–Vibrational
Molecular Spectroscopy for Radioastronomy

- Stable (COMs) and reactive (ions and radicals) species
- Isotopologues characterisation
- THz extension of low-frequency experiments

Back to Basics – Spectroscopy 101

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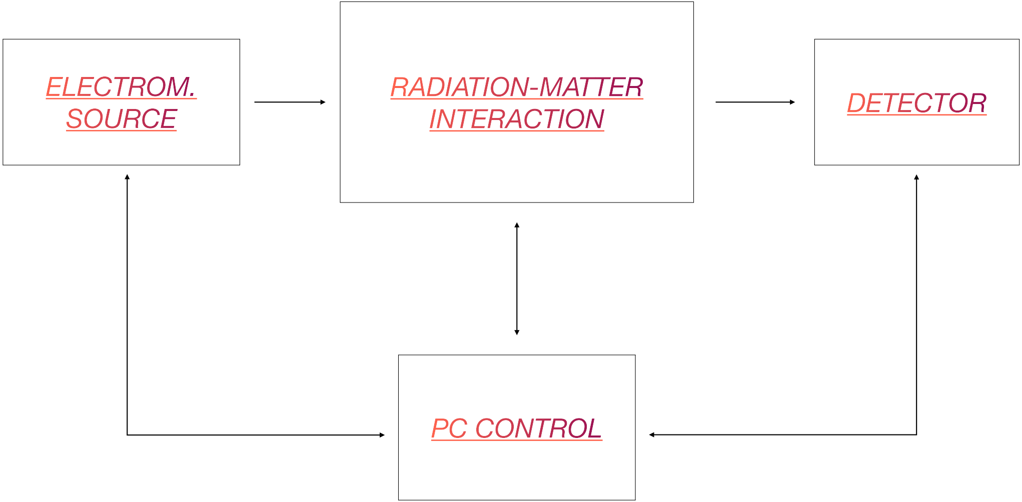
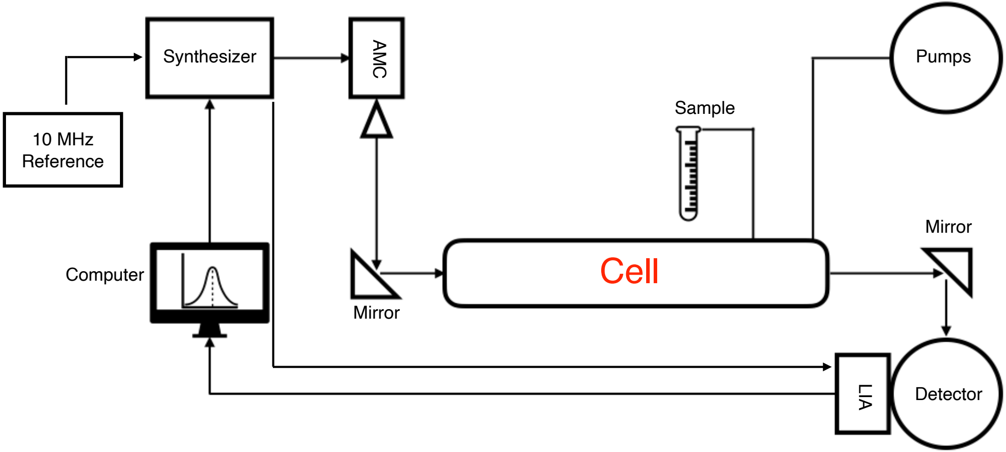


- **SOURCE:**
  - CW in FM from multiplication/amplification of a cm-wave source
  - Broadband Chirped-pulsed, eventually multiplied/amplified – *CP-FTS*
- **GAS RESERVOIR:**
  - Waveguides
  - Absorption Cells – *CASAC*
  - Supersonic free-jet expansion chamber – *CASJet*
- **DETECTORS:**
  - Room temperature Schottky diodes
  - InSB Bolometers (“wet” and “dry”)
  - FTS heterodyne systems

CASAC – Absorption Cell



Several cells are available:

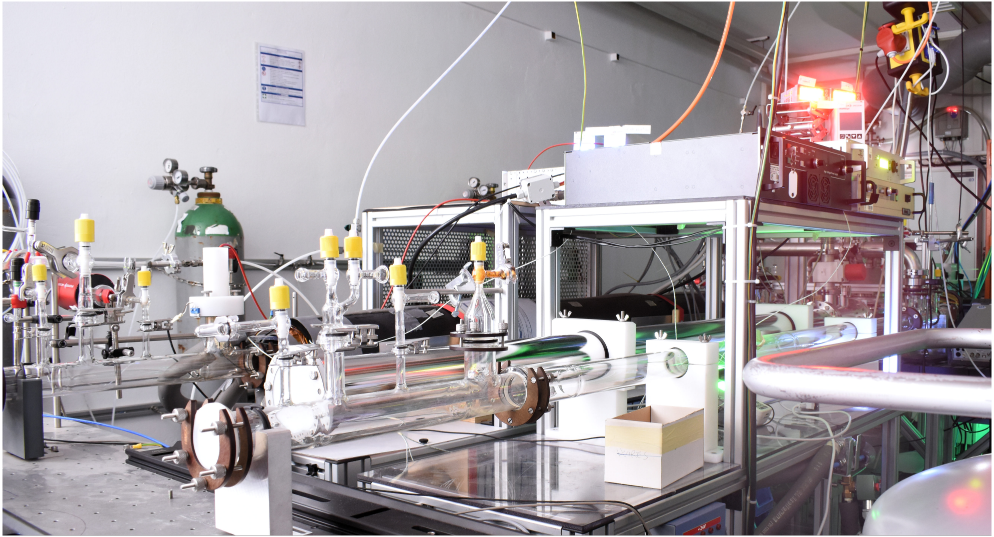
- static cell
- discharge cell
- pyrolysis cell

AMC: amplifier/multiplier chain
LIA: lock-in amplifier

CASAC Experiment – then/now

- Schottky-based active/passive multiplier chain (Virginia Diodes Inc.)
  - 80 GHz – 1.1 THz $\Longrightarrow$ extended to 1.6 THz
- Three absorption cells:
  - Discharge glass tube (3m-long x 5cm-diameter)
  - Pyrolysis glass tube (3m-long x 5cm-diameter)
  - Static Cell (2.5m-long x 10cm-diameter)
- DC discharge (2kW) & solenoid (up to 350 Gauss)
- N_{2L} cooling of the cell
- Pyrolysis oven up to 1500 $^{\circ}$C
- Single and double–pass arrangement
- Cryogenic InSb (QMC) and Schottky diode (Virginia Diodes Inc.) detectors
  Dry cryogenic InSb system w/ cryocompressor
- Diffusion (VHS-6 Agilent) & mechanical (Edwards E2M40) pumps

CASAC Experiment

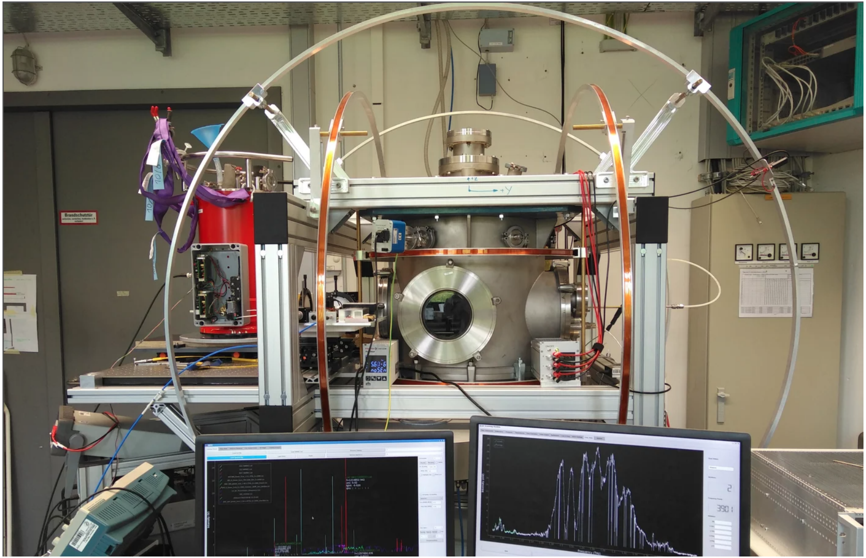


CASJet – Molecular Jet Experiment

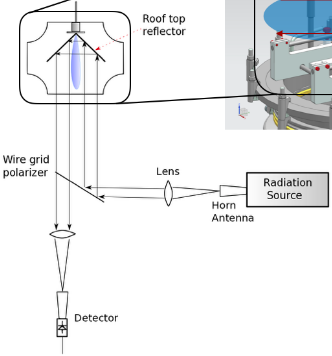
- Supersonic free-jet expansion
- Rotationally cooled molecular beam (as low as $\sim 10\,\mathrm{K}$)
- Pulsed valve (Series 9, Parker Hannifin), 1mm-diameter aperture
- Large diffusion + mechanical pumps (chamber pressure down to 10^{-6}–10^{-7} Torr)
- Same source + detector as CASAC (80–1600 GHz / 4–0.2 mm)

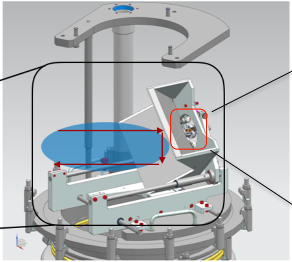
- High-voltage (up to ~ 1.8kV) DC nozzle
- Heating nozzle (up to $\sim 300\,^{\circ}$C)
- Stabilisation in the "zone of silence"

CASJet Experiment

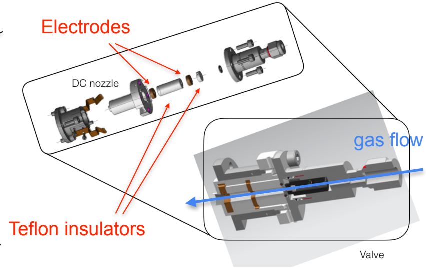


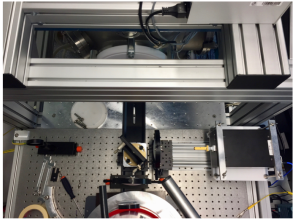
CASJet Experiment

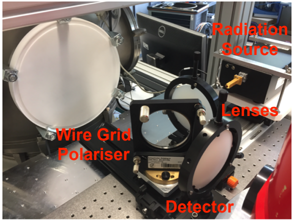




DC-discharge Nozzle





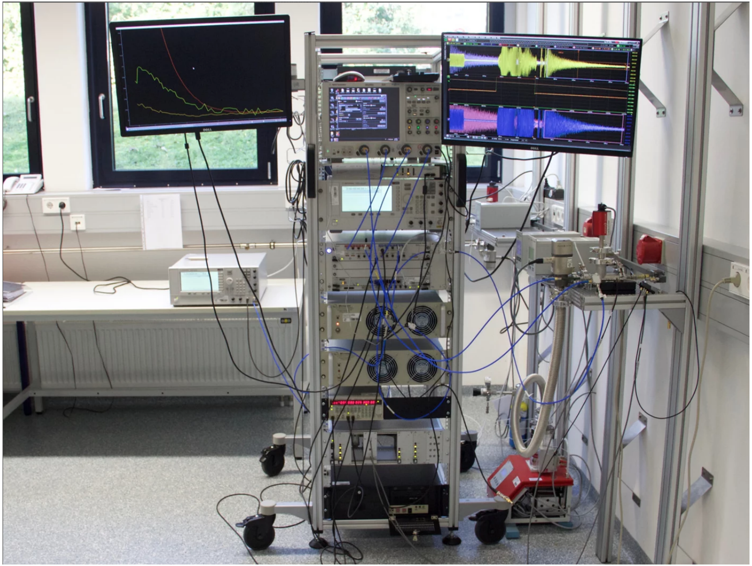


Broadband Chirped-Pulsed Fourier Transform Spectrometer

- 6–26 GHz (20 W and 4 W) / 75–110 GHz (250 mW) / 160–220 GHz ($\sim$ 2 mW)
- Detector noise figures: 6dB @ 26 GHz, 5dB @ 90 GHz, 15-20dB @ 200 GHz
- 5 GHz Arbitrary Waveform Generator (Keysight M8190A)
- FID recorded w/ 25 GHz scope or 2.5 GHz digitiser card
- 2 active x6 multiplier to reach 3mm band
- Mixer with sub-harmonically pumped 3mm local oscillator to reach 2mm band

- Ideal for dense and/or uncertain spectra
- Movable and flexible system

CP-FTS



Some results from the past...

Protonated OCS: what is known

- OCS large proton affinity (632 kJ/mol)
- Isoelectronic with $HOCO^+$
- *N($HSCO^+$)* may be comparable with *N($HOCO^+$)*

Fock & McAllister, ApJL 1982

- Two stable isomers: $HSCO^+$ and $HOCS^+$ (~ 21 kJ/mol higher)
  - $HSCO^+$: $\mu_a = 1.57$ D / $\mu_b = 1.18$ D
  - $HOCS^+$: $\mu_a = 1.52$ D / $\mu_b = 1.64$ D

Wheeler +, JCP 2006

- Higher energy isomer detected in the lab by Ohshima & Endo *(CPL 1996)*
- Laboratory $HSCO^+$ detection in 2007

McCarthy & Thaddeus, JCP 2007

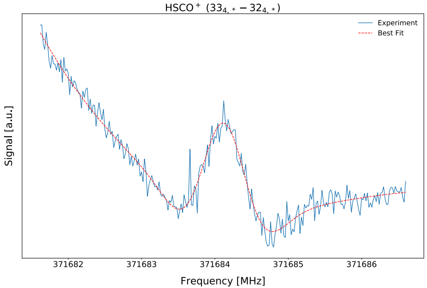
- CASAC experimental conditions:
  - ~ 20 mTorr of OCS (10 %) + H_2 (10 %) + Ar
  - Cell at –90° C
  - Single-pass arrangement
  - "Anomalous" discharge conditions:

    DC = 5mA / 1.5 kV and magnetic field = 200 G

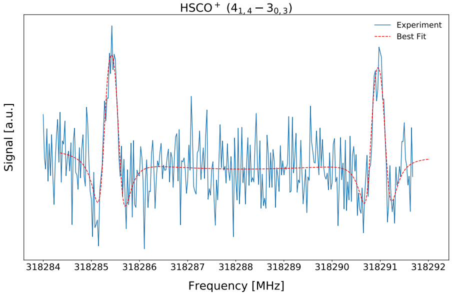
- CASJet experimental conditions:
  - 0.3% OCS in H_2
  - Valve open for 1 ms pulsing at 15 Hz
  - Discharge at 1.5 kV
  - Pressure in chamber few 10s of μTorr

HSCO$^+$: Experimental spectrum

CASAC

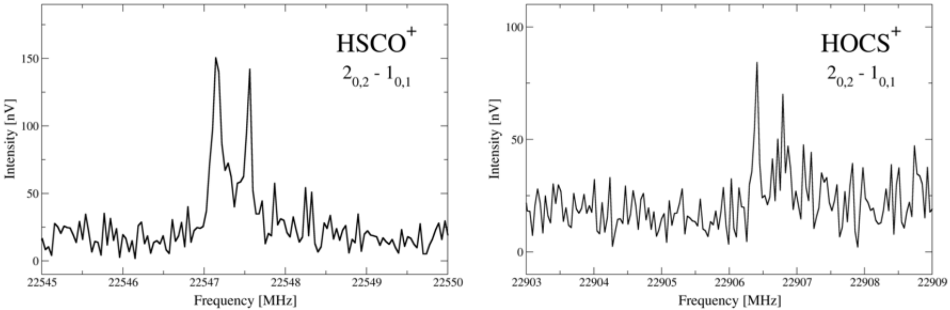


CASJet



Lattanzi+, A&A 2018

CP-FTS + CASJet: First test on ions



- CP-FTS coupled to CASJet
- DC @ 1.5 kV w/ 0.3% OCS in H_2

- $N(HSCO^+)/N(OCS) \approx 3\times10^{-4}$

HCSSH: DITHIOFORMIC ACID

- Sulphur analogue of formic acid, HCOOH
- CS_2 proposed as a major sink of sulphur on dust and ice analogues

e.g. Jiménez-Escobar+ 2014

- CS_2 found in comets, both in comas (visible and UV emission) or *in situ*

Calmonte+ 2016

- CS_2 still undetected in interstellar ices and not detectable by radiotelescopes
- First detection of single substituted formic acid HC(O)SH

Rodríguez-Almeida+ 2021

- Recent detection of double-sulphur species (HS_2) opens new perspectives

Fuente+ 2017

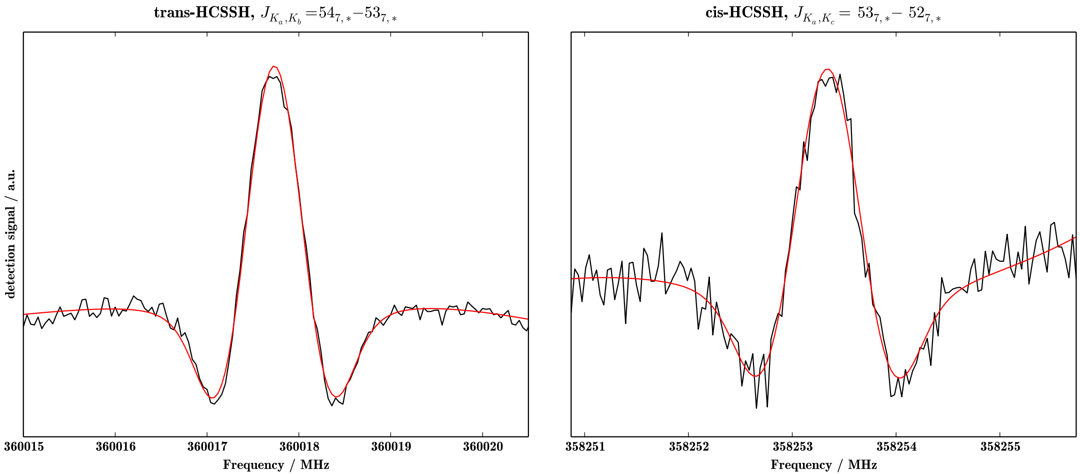
- Two stable isomers: trans-HCSSH and cis-HCSSH (~ 4 kJ/mol higher)
  - trans-HCSSH: $\mu_a = 1.48$ D / $\mu_b = 0.19$ D
  - cis-HCSSH: $\mu_a = 2.08$ D / $\mu_b = 1.64$ D

Prudenzano+ 2018

- Previous cm-wave (up to 40 GHz) spectroscopy by Bak+ 1978

- CASAC experimental conditions:
  - 1:1 mixture of CS_2 and H_2 in Ar for a total pressure of 20-30 μTorr
  - DC = 40mA / 0.8 kV
  - Room temperature
- Measured 204 and 139 new transitions of trans and cis, respectively, up to 478 GHz

HCSSH: Experimental spectrum



Prudenzano+, A&A 2018

Some ongoing projects

D_2CS: DEUTERATED THIOFORMALDEHYDE

- Thioformaldehyde detected in several astronomical regions, including singly and doubly deuterated

e.g. Marcelino+ 2005

- Spectroscopically old microwave transitions available

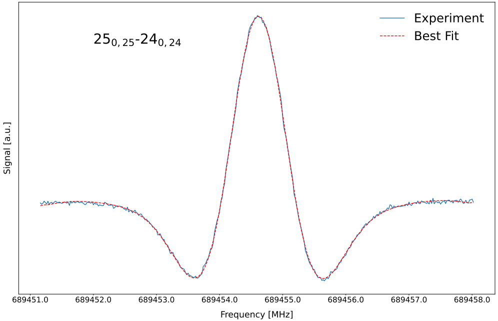
e.g. Cox+ 1982, and *Johnson+ 1971*

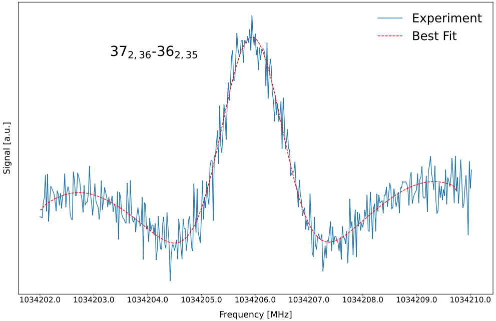
- Database relies on astronomical observations by Marcelino+ 2005
- CDMS: *"Predictions above 200 GHz should be viewed with increasing caution, especially if the calculated uncertainties exceed 0.2 MHz"*

D_2CS: Experiment

- CASAC experimental conditions:
  - 1:6:20 mixture of CS_2 and D_2 in Ar for a total pressure of $\sim 30\,\mu$Torr
  - DC = 40mA / 0.65 kV
  - Cell at -25°C
- Measured more than 150 new rotational transitions in **4 days** up to 1.068 THz

D_2CS: Experimental spectrum





Lattanzi+, in preparation

CH_3NCS: Methyl isothiocyanate

- Sulphur analogue of CH_3NCO, recently detected in ISM

Halfen+ 2015; Cernicharo+ 2016

- Methyl isothiocyanate (CH_3NCS), methyl thiocyanate (CH_3SCN), and, mercaptoacetonitrile (HS–CH_2–CN) are the most thermodynamically stable molecules of C_2H_3NS stoichiometry

Gronowski+ 2016

- Only cm-wave spectrum (< 26 GHz) previously observed

Koput 1986

- Very complex and dense spectrum, with rotational transition from the ground state and various excited torsional and vibrational bending modes

CH_3NCS: Experiment

- *Very* low torsional barrier (V_3=2 cm^{-1}; CH_3NCO: (V_3=21 cm^{-1})

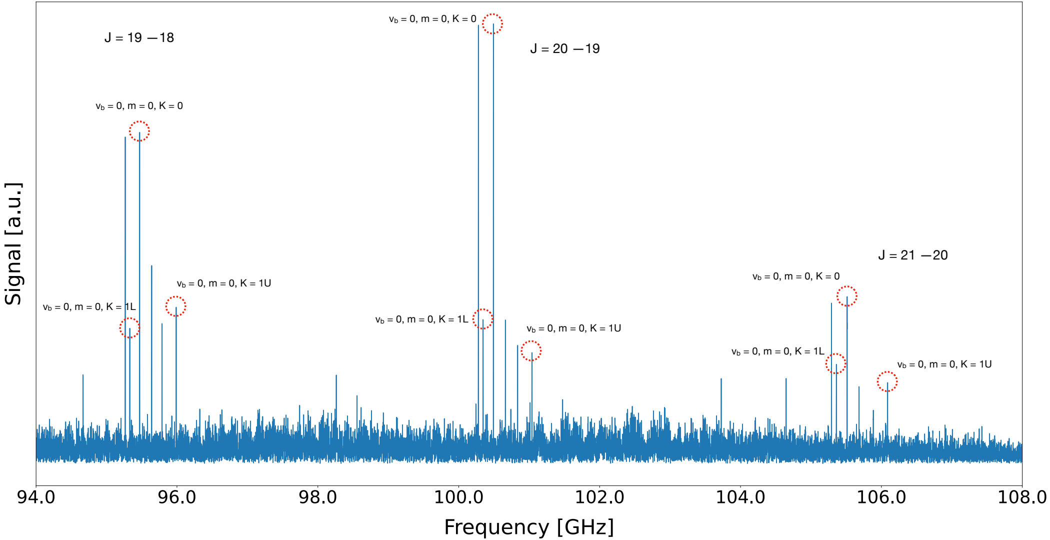
  Koput 1986

- Large dipole moment ($\mu_a = 3.4$ D; CH_3NCO: $\mu_a = 2.9$ D)

  Lett & Flygare 1967 1986

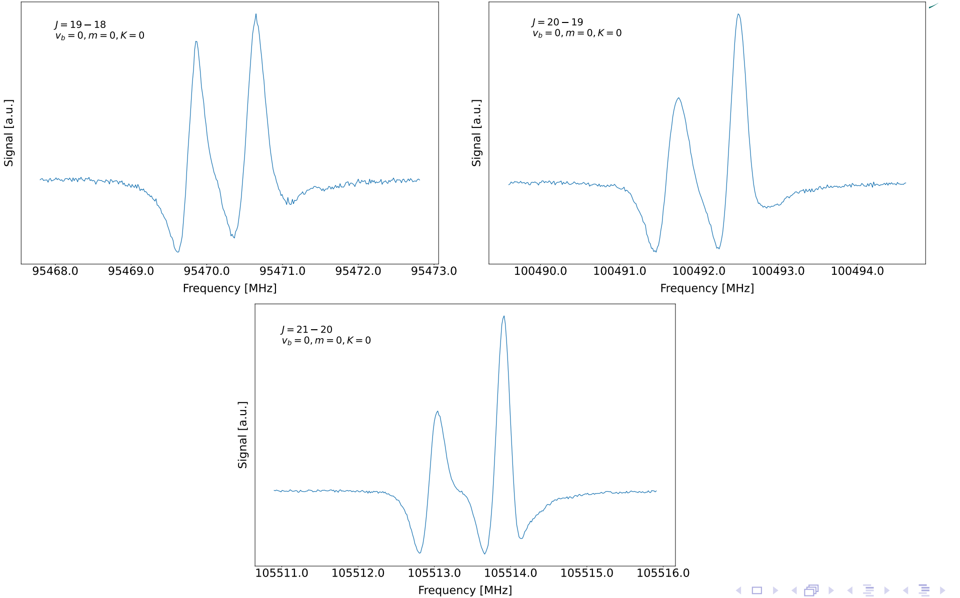
- CASJet experimental conditions:
  - Solid sample: melting point $\sim 37°$C
  - Bubbler at $\sim 80°$C with He flow
  - no DC
- Measured several lines in the 35-125 GHz with a combination of CW in FM and CP-FTS
- Preliminary fit of lower K's available, but **very much work in progress**
- New measurements w/ Heating Nozzle to come "soon"...

CH_3NCS: Experimental spectrum – CASJet + CP-FTS



Tonolo+, in preparation

CH_3NCS: Experimental spectrum – CASJet in CW



Next?

- **Protonated Sulphur Monoxide**: HSO^+
  - Large dipole moment: $\mu_a = 2.87\,\mathrm{D}$ / $\mu_b = 1.07\,\mathrm{D}$
  - Closed-shell molecule: favourable partition function compared to SO
  - Predictions in hand; few scans already performed; testing some candidate lines

- **Protonated thioformaldehyde**: H_2CSH^+
  - Very large dipole moment: $\mu_a = 4.64\,\mathrm{D}$ / $\mu_b = 1.96\,\mathrm{D}$
  - *ab initio* predictions in hand; experiment to start in the next weeks

Conclusions

- Sulphur chemistry still largely to discover
- Sulphur COMs, including isotopic substituted and isomeric forms
- Not always straightforward to pass from Oxygen to Sulphur
- First double-S in ISM opens up new scenarios