Terahertz Rotational Spectroscopy of the SO Radical

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BACKGROUND

Astrophysical background:

- SO radical observed in a wide variety of astrophysical environments
  (molecular clouds associated with HII regions, center of star formation...)

C.A. Gottlieb, *Astrophys. J.* **184**, L59 (1973);
see T. Klaus, *J. Mol. Spectrosc.* **168**, 235 (1994) and refs. therein

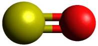
Laboratory background:

- Numerous studies of electronic, vibrational and rotational spectroscopy
- Pure rotational transitions: from the MW to the THz
  (up to 1.9 THz)

see G. Cazzoli, *J. Mol. Spectrosc.* **167**, 468 (1994)
and T. Klaus, *J. Mol. Spectrosc.* **168**, 235 (1994), and refs. therein

→ **High resolution pure rotational spectroscopy at higher frequencies**

SPECTROSCOPY OF SULFUR MONOXIDE



- Fundamental electronic configuration: $\cdots(\pi)^2$ (2 unpaired electrons)
- Ground electronic state $X^3\Sigma^-$
- Convention: Hund's coupling scheme (b)

  Rotational quantum number $\boldsymbol{N}$

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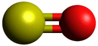
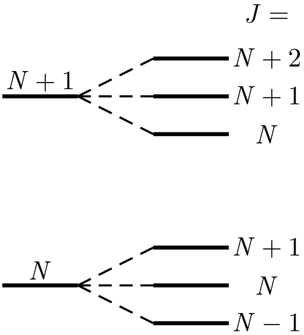
  Rotational quantum number $\boldsymbol{N}$
- **Rotational fine structure:** spin-spin and spin-rotation couplings

$$\boldsymbol{J} = \boldsymbol{N} + \boldsymbol{S}$$
$$\boldsymbol{S} = 1$$

$\rightarrow$ rotational energy levels:

spin triplets $(N > 0)$





SPECTROSCOPY OF SULFUR MONOXIDE

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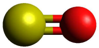

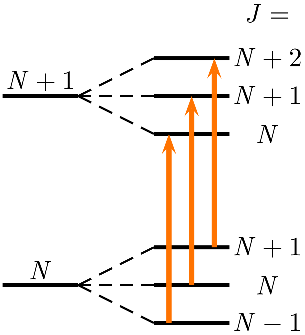

- **Selection rules:**

$$\Delta N = \Delta J = 1$$

SPECTROSCOPY OF SULFUR MONOXIDE

- Fundamental electronic configuration: $\cdots(\pi)^2$ (2 unpaired electrons)
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  $$\boldsymbol{S} = 1$$

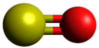
  → rotational energy levels:

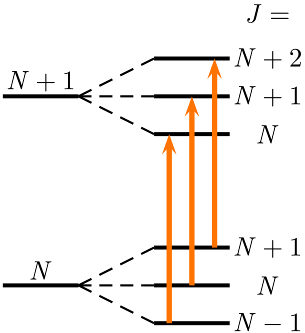
  spin triplets ($N > 0$)
- **Isotopologues:**

  ^{32}SO (95 %) $\boldsymbol{I}_{^{32}S} = 0$

  ^{34}SO (4.21 %) $\boldsymbol{I}_{^{34}S} = 0$

  ^{33}SO (0.75 %) $\boldsymbol{I}_{^{33}S} = {}^3/_2$





- **Selection rules:**

  $\Delta N = \Delta J = 1$

EXPERIMENTAL WORK

Pure rotational spectroscopy of SO radical
in its ground vibrational state

FT-FIR SPECTROSCOPY

SOLEIL synchrotron, AILES beamline

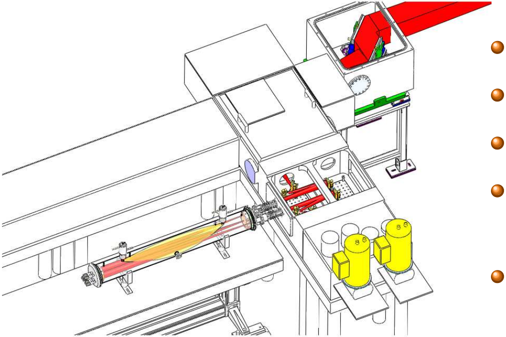
- Broadband technique
  20–700 cm^{-1}
  0.6–21 THz
- Benefits from the synchrotron radiation
- “High” resolution
  0.001 cm^{-1}/ 30 MHz

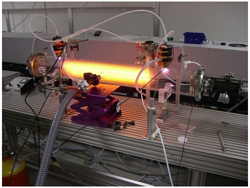
CW-THz SPECTROSCOPY

photomixing technique, LPCA

- monochromatic
- tunable
  0.3–3.3 THz
  10–110 cm^{-1}
- “very high” resolution (resolution limited by the linewidth)

FT-FIR SPECTROSCOPY AT SOLEIL





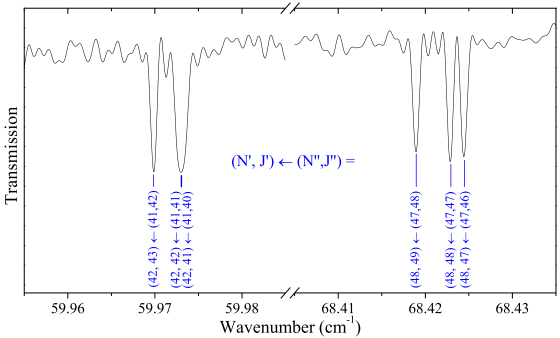
Martin-Drumel et al., *Rev. Sci. Instrum.* **82**, 11 (2011)

- Bruker IFS125
- $R = 0.001\ \mathrm{cm}^{-1}$
- Synchrotron radiation
- 20–300 cm^{-1}

- White-type absorption/discharge cell
- Path length: 24m
- 1 A / 980 V (DC)

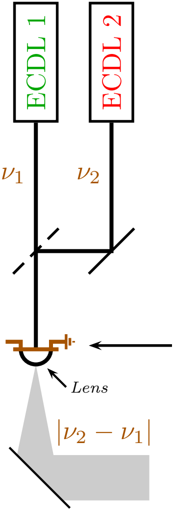
- flow
- H_2S, He, H_2, air (0.01, 1.15, 0.14, 0.06 mbar)

FT-FIR SPECTROSCOPY: OBSERVED TRANSITIONS

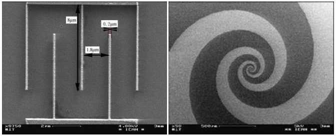


- 102 transitions of ^{32}SO
- 99 lines observed for the 1st time (22 in HIFI spectral windows)
- $31 \leq N'' \leq 65$
- 44–93 cm^{-1} (1.3–2.8 THz)
- $SNR \sim 5$
- Accuracy on wavenumber: 0.00007 cm^{-1} ($\sim$ 2 MHz)
- Unresolved rotational triplets: $31 \leq N \leq 43$

CW-THz SPECTROSCOPY



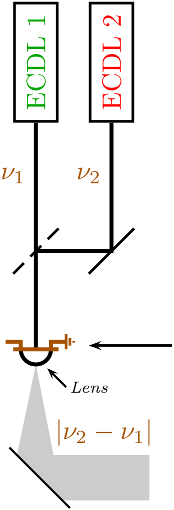
Photomixer



Semi-conductor *Antenna*

0.3 – 3.3 THz

CW-THZ SPECTROSCOPY



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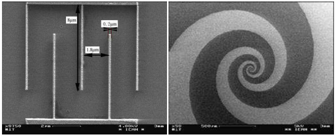


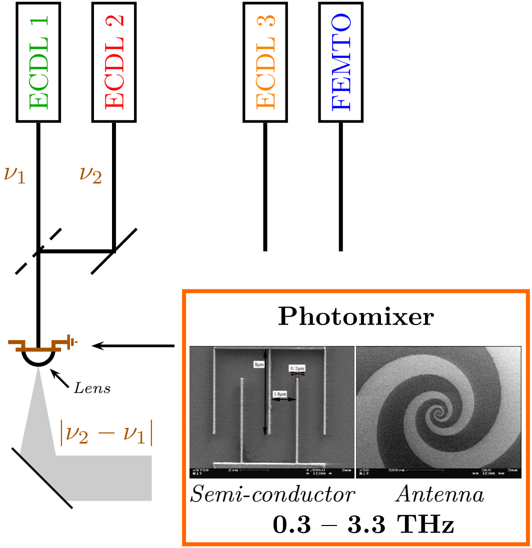
Semi-conductor *Antenna*

0.3 – 3.3 THz

Accurate frequency determination

Continuous tunability

CW-THz SPECTROSCOPY



Photomixer

Semi-conductor *Antenna*

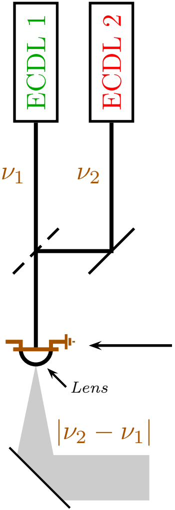
0.3 – 3.3 THz

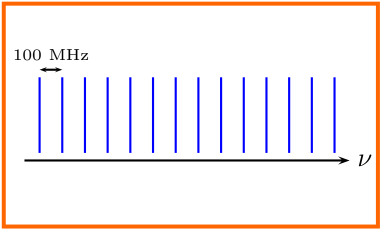
ECDLs 1,2,3 @ 780 nm

Accurate frequency determination

Continuous tunability

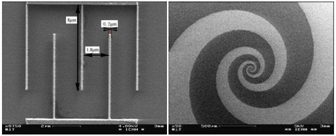
CW-THz SPECTROSCOPY





ECDLs 1,2,3 @ 780 nm

Photomixer



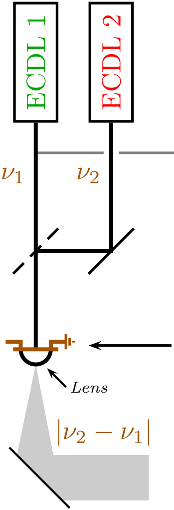
Semi-conductor *Antenna*

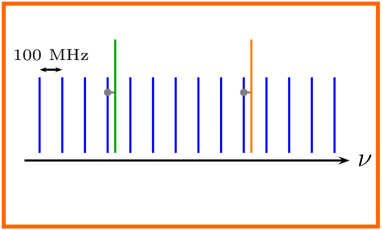
0.3 – 3.3 THz

Accurate frequency determination

Continuous tunability

CW-THz spectroscopy





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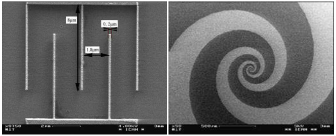
Photomixer



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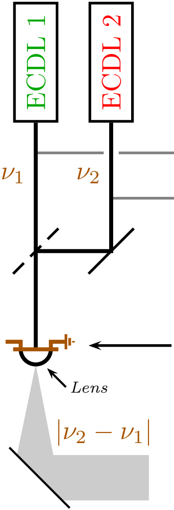
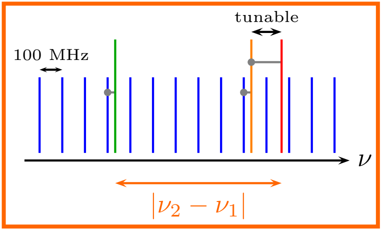
Accurate frequency determination

Continuous tunability

CW-THz SPECTROSCOPY





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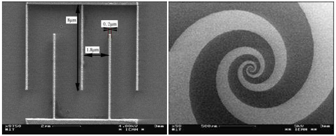
Photomixer



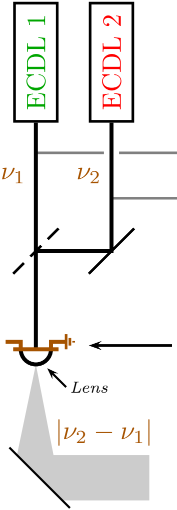
Semi-conductor *Antenna*

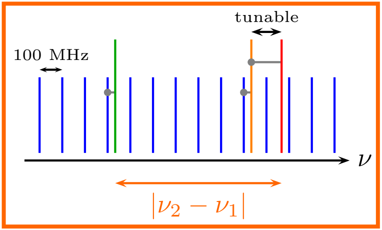
0.3 – 3.3 THz

Accurate frequency determination

Continuous tunability

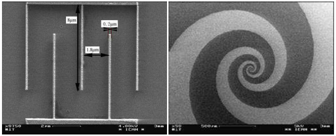
CW-THz spectroscopy





ECDLs 1,2,3 @ 780 nm

Photomixer



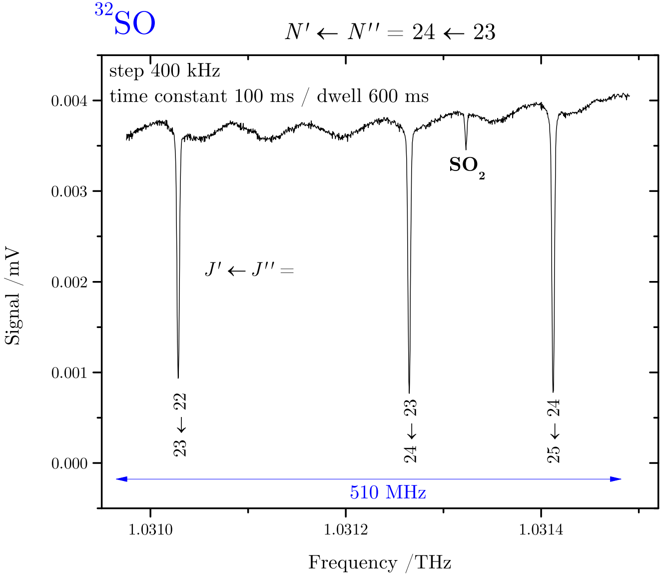
Semi-conductor *Antenna*

0.3 – 3.3 THz

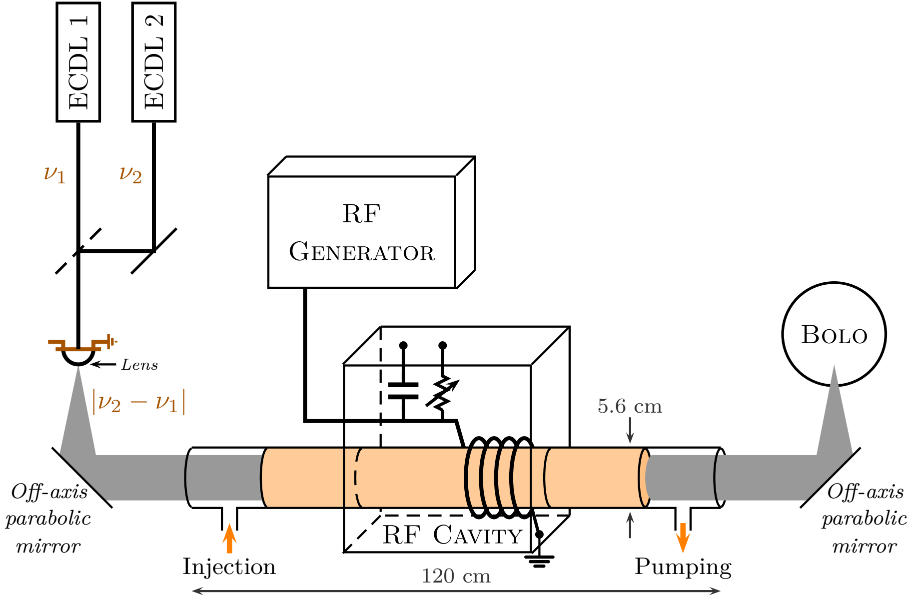
Accurate frequency determination

Continuous tunability
up to 500 MHz

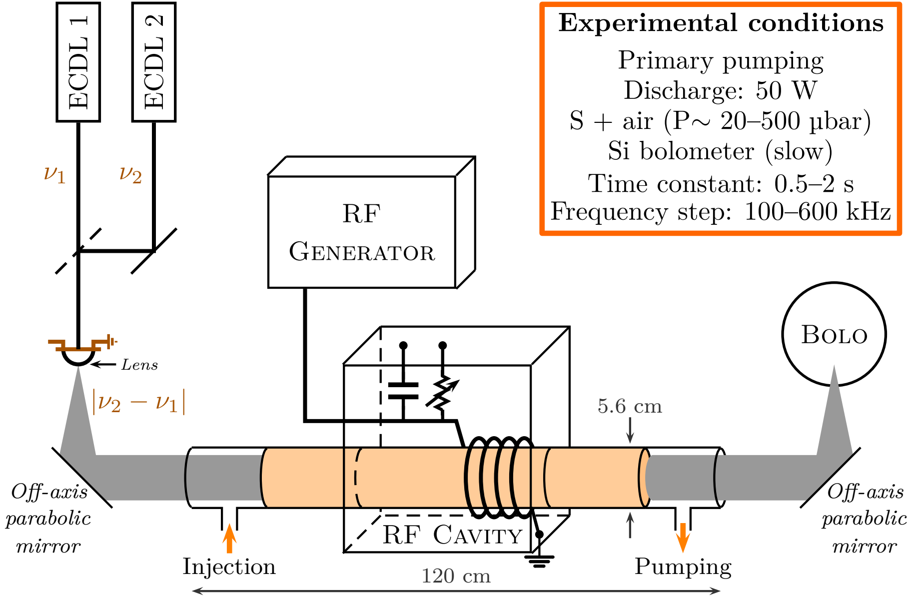
CW-THz: CONTINUOUS TUNABILITY



CW-THz spectroscopy at LPCA



CW-THz SPECTROSCOPY AT LPCA



Experimental conditions

Primary pumping
Discharge: 50 W
S + air (P∼ 20–500 µbar)
Si bolometer (slow)
Time constant: 0.5–2 s
Frequency step: 100–600 kHz

CW-THz SPECTROSCOPY AT LPCA

Modulation

Amplitude (AM): 263 Hz
Frequency (FM): 273 Hz

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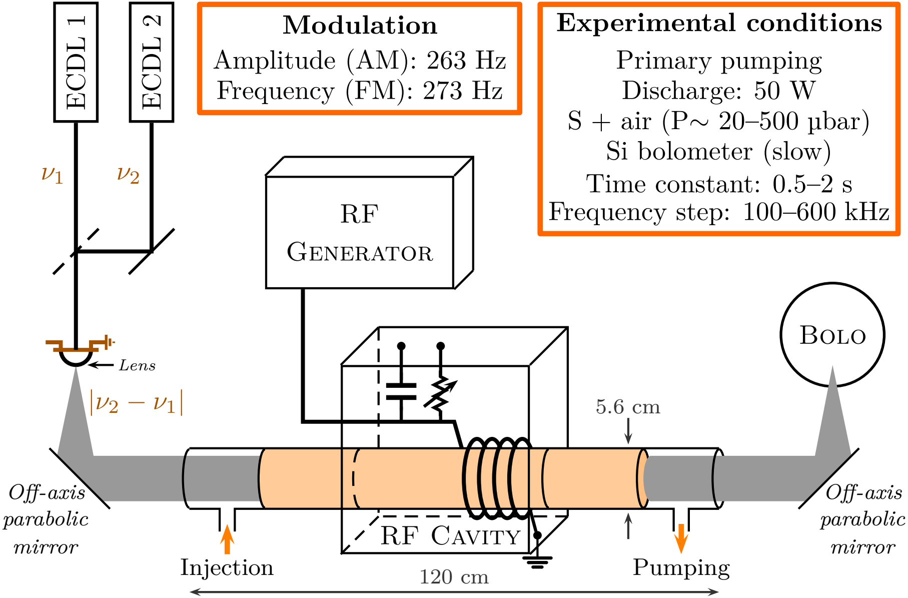
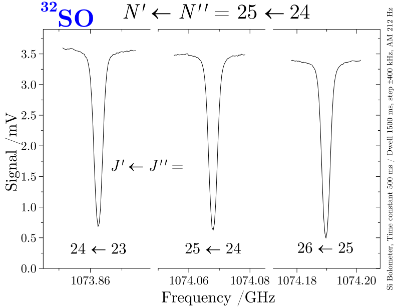
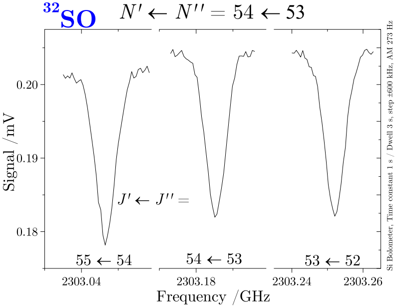
Si bolometer (slow)
Time constant: 0.5–2 s
Frequency step: 100–600 kHz



CW-THz SPECTROSCOPY: TRANSITIONS OF ^{32}SO





- Amplitude modulation
- 731 GHz – 2.511 THz
- 105 transitions
- $16 \leq N'' \leq 58$
- $5 \leq SNR \leq 260$

- Accuracy on frequency [1]:

$$\Delta(\nu) = \frac{\alpha}{SNR}\sqrt{\Delta x FWHM}$$

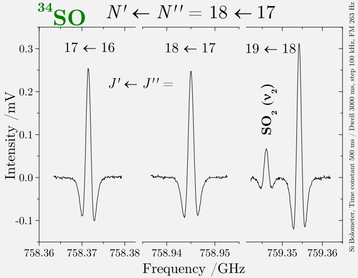
Δx frequency step; α depends on the shape of the line ($\alpha = 2$ here)

- $6 \leq \Delta(\nu) \leq 750$ kHz

[1] Landman D.A. *et al.*, *Astrophys. J.* **261**, 732 (1982)

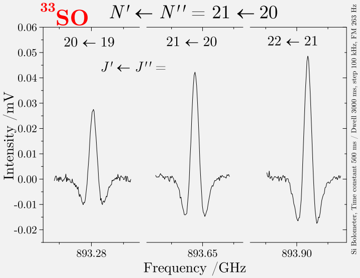
CW-THZ SPECTROSCOPY: ^{34}SO AND ^{33}SO

^{34}SO (4.21 %)



- Frequency modulation
- 716 GHz – 1.338 THz
- 48 transitions
- $17 \leq N'' \leq 32$
- $7 \leq SNR \leq 70$
- $13 \leq \Delta(\nu) \leq 220$ kHz

^{33}SO (0.75%)



- Frequency modulation
- 723 GHz – 978 GHz
- 21 transitions
- $16 \leq N'' \leq 22$
- $13 \leq SNR \leq 40$
- $25 \leq \Delta(\nu) \leq 80$ kHz

Fit of the data

- SPFIT/SPCAT

  H.M. Pickett, *J. Mol. Spectrosc.* **148**, 371 (1991)

- Fit: our data (FT-FIR + CW-THz) + all the data available from the literature

- Comparison with CDMS database

  H.S.P. Müller, *Astron. Astrophys.* **370**, L29 (2001)

^{32}SO	**This work**	**CDMS**
B	21 523.555 94 (17)	21 523.555 78 (45)
D	0.033 915 27 (21)	0.033 914 3 (11)
H $\times 10^9$	-6.971 (56)	-7.96 (83)
λ	158 254.3915 (95)	158 254.387 (13)
λ_D	0.306 36 (13)	0.306 58 (21)
$\lambda_H \times 10^6$	0.42 (12)	
γ	-168.304 0 (20)	-168.305 2 (37)
$\gamma_D \times 10^3$	-0.528 2 (22)	-0.522 1 (87)
N	329	66
RMS	0.77	0.65
^{34}SO		
B	21 102.731 92 (71)	21 102.731 24 (82)
D	0.032 599 9 (14)	0.032 598 8 (13)
H $\times 10^9$	-6.53 (81)	[-7 501 95]
λ	158 249.812 (26)	158 249.815 (25)
λ_D	0.300 64 (24)	0.300 25 (78)
γ	-164.994 0 (60)	-164.996 6 (66)
$\gamma_D \times 10^3$	-0.511 4 (59)	-0.511 (22)
N	96	43
RMS	0.72	0.63
^{33}SO		
B	21 306.463 96 (85)	21 306.465 2 (11)
D	-0.033 232 6 (11)	-0.033 233 2 (14)
H $\times 10^9$	[-7.72139]	[-7.72139]
λ	158 252.16 (14)	158 251.960 (4)
λ_D	0.304 41 (54)	0.303 1 (12)
γ	-166.610 (19)	-166.610 (41)
$\gamma_D \times 10^3$	-0.355 (20)	-0.502 (44)
N	100	79
RMS	0.84	0.32

FIT OF THE DATA

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  H.M. Pickett, *J. Mol. Spectrosc.* **148**, 371 (1991)
- Fit: our data (FT-FIR + CW-THz) + all the data available from the literature
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- Observation of transitions with higher N values
  ^{32}SO: $N''_{\text{max}} = 65$ (29)
  ^{34}SO: $N''_{\text{max}} = 32$ (24)

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N	**329**	**66**
RMS	0.77	0.65
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- Fit: our data (FT-FIR + CW-THz) + all the data available from the literature

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- Observation of transitions with higher N values

  ^{32}SO: $N''_{\max} = 65\ (29)$

  ^{34}SO: $N''_{\max} = 32\ (24)$

- Influence on centrifugal distortion parameters

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B	21 523.555 94 (17)	21 523.555 78 (45)
D	**0.033 915 27 (21)**	**0.033 914 3 (11)**
H $\times 10^9$	**-6.971 (56)**	**-7.96 (83)**
λ	158 254.3915 (95)	158 254.387 (13)
λ_D	0.306 36 (13)	0.306 58 (21)
$\lambda_H \times 10^6$	**0.42 (12)**	
γ	-168.304 0 (20)	-168.305 2 (37)
$\gamma_D \times 10^3$	-0.528 2 (22)	-0.522 1 (87)
$\boldsymbol{N}$	329	66
RMS	0.77	0.65
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B	21 102.731 92 (71)	21 102.731 24 (82)
D	0.032 599 9 (14)	0.032 598 8 (13)
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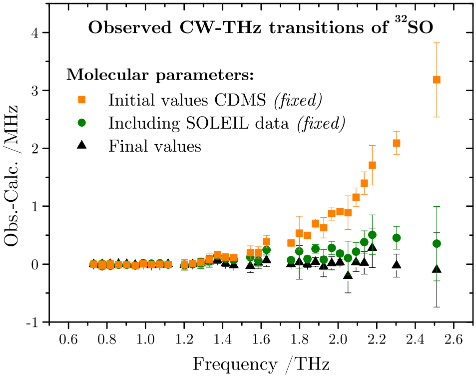
λ	158 252.16 (14)	158 251.960 (4)
λ_D	0.304 41 (54)	0.303 1 (12)
γ	-166.610 (19)	-166.610 (41)
$\gamma_D \times 10^3$	-0.355 (20)	-0.502 (44)
$\boldsymbol{N}$	100	79
RMS	0.84	0.32

SUMMARY



- Complementarity between broadband FT-FIR and CW-THz techniques
- Observation of new pure rotational transitions of ^{32}SO, ^{33}SO, ^{34}SO
- 1st observation of transitions of ^{32}SO and ^{34}SO at frequencies higher than 1.9 and 1.1 THz
- Improvement of the molecular parameters

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