TERAHERTZ ROTATIONAL SPECTROSCOPY OF THE SO RADICAL

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FT-FIR CW-THZ ³²SO ³⁴SO, ³³SO BACKGROUND

JACKGROUND

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

\rightarrow High resolution pure rotational spectroscopy at higher frequencies

CW-TH

 ^{32}S

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 N



CW-TH2

 ^{32}S

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 N
- Rotational fine structure: spin-spin and spin-rotation couplings

$$J = N + S$$
$$S = 1$$

 \rightarrow rotational energy levels: spin triplets (N>0)





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 N
- **Rotational fine structure:** spin-spin and spin-rotation couplings

$$J = N + S$$
$$S = 1$$

 \rightarrow rotational energy levels: spin triplets (N > 0)



Selection rules: $\Delta N = \Delta J = 1$

FT-FIR CW-THZ

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 N
- Rotational fine structure: spin-spin and spin-rotation couplings

$$J = N + S$$
$$S = 1$$

 \rightarrow rotational energy levels:

spin triplets (N > 0)

• Isotopologues:

³²SO (95 %) $I_{^{32}S} = 0$ ³⁴SO (4.21 %) $I_{^{34}S} = 0$ ³³SO (0.75 %) $I_{^{33}S} = \frac{3}{2}$



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 $20-700 \text{ cm}^{-1}$ 0.6-21 THz
- Benefits from the synchrotron radiation
- "High" resolution $0.001 \text{ cm}^{-1}/30 \text{ MHz}$

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 CW-TH2 ³²SO FT-FIR SPECTROSCOPY AT SOLEIL



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

- Bruker IFS125
- $R = 0.001 \text{ cm}^{-1}$
- Synchrotron radiation
- 20–300 cm⁻¹
- White-type absorption/discharge cell
- Path length: 24m
- 1 A / 980 V (DC)
- flow
- H₂S, He, H₂, air (0.01, 1.15, 0.14, 0.06 mbar)

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FT-FIR GW-THZ GW



- 102 transitions of ³²SO
- 99 lines observed for the 1st time (22 in HIFI spectral windows)
- $31 \le N'' \le 65$
- $44-93 \text{ cm}^{-1}$ (1.3-2.8 THz)

- $SNR \sim 5$
- Accuracy on wavenumber: $0.00007 \text{ cm}^{-1} (\sim 2 \text{ MHz})$
- Unresolved rotational triplets: $31 \le N \le 43$









Accurate frequency determination

Continuous tunability







Continuous tunability









CW-THz

 $^{-32}S($

CW-THZ: CONTINUOUS TUNABILITY



CW-THZ SPECTROSCOPY AT LPCA



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CW-THZ SPECTROSCOPY AT LPCA



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CW-THz

CW-THZ SPECTROSCOPY: TRANSITIONS OF ³²SO



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



• Accuracy on frequency [1]:

$$\Delta(\nu) = \frac{\alpha}{SNR} \sqrt{\Delta x F W H M}$$

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

• $6 \le \Delta(\nu) \le 750 \text{ kHz}$

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

CW-THZ SPECTROSCOPY: ³⁴SO AND ^{33}SO ³⁴SO $N' \leftarrow N'' = 18 \leftarrow 17$ ³³SO $N' \leftarrow N'' = 21 \leftarrow 20$ 0.06 $20 \leftarrow 19$ $21 \leftarrow 20$ $22 \leftarrow 21$ $17 \leftarrow 16$ $18 \leftarrow 17$ $19 \leftarrow 18$ 0.3 0.05 $J' \leftarrow J'' =$ 0.04 $J' \leftarrow J'' =$ Intensity /mV 0.0 $SO_2(v_2)$ ≥_{∃ 0.03} Intensity 0.01 -0.01 -0.1 -0.02758.36 758.37 758.38 758.94 759.35 759.36 893.28 893.65 893.90 758.95 Frequency /GHz Frequency /GHz • Frequency modulation • Frequency modulation ● 716 GHz – 1.338 THz 723 GHz – 978 GHz • 48 transitions • 21 transitions

- $17 \le N'' \le 32$
- $7 \leq SNR \leq 70$
- $13 \leq \Delta(\nu) \leq 220 \text{ kHz}$

• 16 < N'' < 22

• $13 \leq SNR \leq 40$

• $25 \le \Delta(\nu) \le 80 \text{ kHz}$

				Fits
Fit of	THE DATA			
 SPFIT H.M. 1 Fit: ou CW-T availab Compa databa H.S.P. 1 	Y/SPCAT Pickett, J. Mol. Spectrosc. 148, 371 (1991) ar data (FT-FIR + Hz) + all the data ble from the literature arison with CDMS ase Müller, Astron. Astrophys. 370, L29 (2001)	$\begin{array}{c} 3^2 \operatorname{SO} \\ \mathrm{B} \\ \mathrm{D} \\ \mathrm{H} \times 10^9 \\ \lambda \\ \lambda \\ D \\ \lambda \\ N \\ \mathbf{N} $	$\begin{array}{r} {\rm This \ work} \\ 21\ 523.555\ 94\ (17) \\ 0.033\ 915\ 27\ (21) \\ -6.971\ (56) \\ 158\ 254.3915\ (95) \\ 0.306\ 36\ (13) \\ 0.42\ (12) \\ -168.304\ 0\ (20) \\ -0.528\ 2\ (22) \\ 329 \\ 0.77 \\ \hline 21\ 102.731\ 92\ (71) \\ 0.032\ 599\ 9\ (14) \\ -6.53\ (81) \\ 158\ 249.812\ (26) \\ 0.300\ 64\ (24) \\ -164.994\ 0\ (60) \\ -0.511\ 4\ (59) \\ 96 \\ 0.72 \\ \hline 21\ 306.463\ 96\ (85) \\ -0.032\ 322\ 6\ (11) \\ [-7.72139] \\ 158\ 252.16\ (14) \\ 0.304\ 41\ (54) \\ -166.610\ (19) \\ -0.355\ (20) \\ 100 \\ 0.84 \\ \end{array}$	$\begin{array}{c} \text{CDMS} \\ 21 \ 523.555 \ 78 \ (45) \\ 0.033 \ 914 \ 3 \ (11) \\ -7.96 \ (83) \\ 158 \ 254.387 \ (13) \\ 0.306 \ 58 \ (21) \\ \end{array}$
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FIT	OF THE DATA			
		32 SO	This work	CDMS
• SPFIT/SPCAT		B D	$21 523.555 94 (17) \\ 0.033 915 27 (21)$	$21 523.555 78 (45) \\ 0.033 914 3 (11)$
H.M. Pickett, J. Mol. Spectrosc. 148, 371 (1991)		$H \times 10^9$	-6.971 (56)	-7.96 (83)
		λ_D	$\begin{array}{c} 138 \ 254.3913 \ (93) \\ 0.306 \ 36 \ (13) \\ 0.42 \ (12) \end{array}$	$\begin{array}{c} 138\ 234.387\ (13)\\ 0.306\ 58\ (21) \end{array}$
		$\lambda_H \times 10^{\circ}$ γ	0.42 (12) -168.304 0 (20)	-168.305 2 (37)
 Fit: our CW-TH available 	Fit: our data (FT-FIR +	$\gamma_D \times 10^3$ N	-0.528 2 (22) 329	-0.522 1 (87) 66
	CW-THz) + all the data	RMS	0.77	0.65
	available from the literature	В	21 102.731 92 (71)	$21 \ 102.731 \ 24 \ (82)$
9	Comparison with CDMS	D H ×10 ⁹	$0.032 599 9 (14) \\ -6.53 (81)$	0.032 598 8 (13) [-7 501 95]
database		$\lambda \lambda_D$	$158 249.812 (26) \\ 0.300 64 (24)$	$158 249.815 (25) \\ 0.300 25 (78)$
H.S.F	H.S.P. Müller, Astron. Astrophys.	γ^{\prime}	-164.994 0 (60)	-164.996 6 (66)
	370 , L29 (2001)	N	-0.311 4 (33) 96	-0.511 (22)
9	Observation of transitions	³³ SO	0.72	0.63
with ³² SC ³⁴ SC	with higher N values	B D	21 306.463 96 (85) -0.033 232 6 (11)	$21 \ 306.465 \ 2 \ (11)$ -0.033 233 2 (14)
	³² SO: $N''_{\text{max}} = 65$ (29)	$^{\rm H} \times 10^9$	[-7.72139]	[-7.72139]
	$^{34}SO: N''_{max} = 32 (24)$	λ_D	$\begin{array}{c} 136 \ 252.10 \ (14) \\ 0.304 \ 41 \ (54) \\ 166 \ 610 \ (10) \end{array}$	$\begin{array}{c} 133 \ 251.500 \ (4) \\ 0.303 \ 1 \ (12) \\ 166 \ 610 \ (41) \end{array}$
		$\gamma \over \gamma_D imes 10^3$	-100.610 (19) -0.355 (20)	-100.610(41) -0.502(44)
		N RMS	100 0.84	79 0.32

Fп	OF THE DATA			
		32 SO	This work	CDMS
		В	21 523.555 94 (17)	21 523.555 78 (45)
• SPFIT/SPCAT		D	$0.033 \ 915 \ 27 \ (21)$	$0.033 \ 914 \ 3 \ (11)$
H.M. Pickett, J. Mol. Spectrosc. 148, 371 (1991)		$H \times 10^9$	-6.971(56)	-7.96 (83)
		λ	$158 \ 254.3915 \ (95)$ 0 206 26 (12)	$158 \ 254.387 \ (13)$ 0 206 58 (21)
		λ_D	$0.300\ 30\ (13)$	0.300 38 (21)
		$\gamma_H \times 10$	-168.304.0(20)	-168.305 2 (37)
9	Fit: our data (FT-FIR +	$\gamma_D \times 10^3$	$-0.528\ 2\ (22)$	$-0.522\ 1\ (87)$
	$CW(TH_{-}) + -11 + 1 - 1 - + -$	Ň	329	`6 6
	CW-IHZ + all the data	RMS	0.77	0.65
	available from the literature	34 SO		
		В	$21\ 102.731\ 92\ (71)$	$21 \ 102.731 \ 24 \ (82)$
9	Comparison with CDMS	D 1110 ⁹	$0.032\ 599\ 9\ (14)$	0.032 598 8 (13)
		H ×10°	-6.53(81)	[-7 501 95] 159 240 915 (25)
	database	λ_{D}	$0.300\ 64\ (24)$	$0.300\ 25\ (78)$
HSP	HSP Müller Astron Astrophys	γ	$-164.994\ 0\ (60)$	-164.996 6 (66)
		$\gamma_D \times 10^3$	-0.511 4 (59)	-0.511 (22)
	370 , L29 (2001)	Ň	96	43
		RMS	0.72	0.63
0	Observation of transitions	20,20		
	with higher N values	В	$21 \ 306.463 \ 96 \ (85)$	$21 \ 306.465 \ 2 \ (11)$
$^{32}SO:$ $^{34}SO:$	$\frac{3280}{N''} = 65(20)$	н ×10 ⁹	-0.033 232 0 (11)	$-0.033\ 233\ 2\ (14)$
	$N_{\rm max} = 00 (29)$	λ	$158\ 252.16\ (14)$	$158\ 251.960\ (4)$
	$N_{\rm max}^{\prime} = 32 \ (24)$	λ_D	0.304 41 (54)	0.303 1 (12)
т а		γ^{-}	-166.610 (19)	-166.610 (41)
0	Influence on centrifugal	$\gamma_D \times 10^3$	-0.355 (20)	-0.502 (44)
disto	distorsion parameters	N	100	79
	restored parallitotory	RMS	0.84	0.32

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CW-THz

 ^{32}SO



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

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