

HIGH RESOLUTION THz AND FIR SPECTROSCOPY OF SOCl_2

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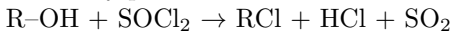
^bISMO, CNRS, University of Paris XI, Orsay, France;
SOLEIL Synchrotron, AILES beamline, Gif-sur-Yvette, France



THIONYL CHLORIDE (SOCl_2)

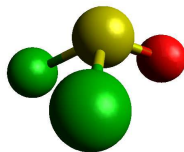
- **Industrial compound:**

extremely powerful oxidant



role in lithium batteries

global production > 10 000 tons/year



- **Environmental impact:**

extremely volatile inorganic compound

reacts rapidly with water

tropospheric lifetime: a few minutes (hydrolysis $\rightarrow \text{HCl} + \text{SO}_2$)

T. J. Johnson, *J. Phys. Chem. A* **107**, 6183 (2003)

- **Defense application:**

precursor of nerve agents



SPECTROSCOPIC BACKGROUND

- Fundamental modes determined by gas phase vibrational spectroscopy (Raman, IR)
D. E. Martz, *J. Chem. Phys.* **22**, 1193 (1954)
- High resolution measurements: restricted to pure rotational transitions in the MW (up to 25 GHz)
see H. S. P. Müller, *J. Chem. Soc. Faraday Trans.* **90**, 3473 (1994)
and refs. therein

Objectives:

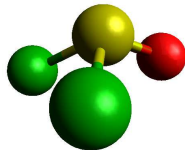
- High resolution FT-FIR ro-vibrational spectroscopy
- Pure rotational spectroscopy at frequencies higher than 25 GHz

SPECTROSCOPY OF SOCl_2

- C_s point group
(pyramid, one plane of symmetry)
- 6 fundamental vibrational modes
(all IR and Raman active)

$$\Gamma = 4A' + 2A''$$

5 modes lying in the FIR



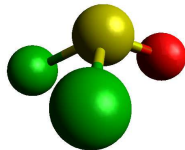
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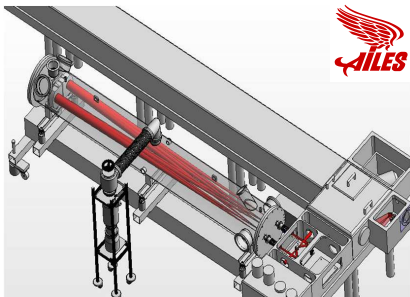
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5 modes lying in the FIR

- Asymmetric rotor ($\kappa = -0.4484$)
- Small rotational constants
→ rich rotational / ro-vibrational spectrum
- Symmetry plane = bc inertial plane
Pure rotational spectrum:
 b - and c -type transitions of comparable intensity
- Nuclear quadrupole splitting pattern (2 identical nuclei)



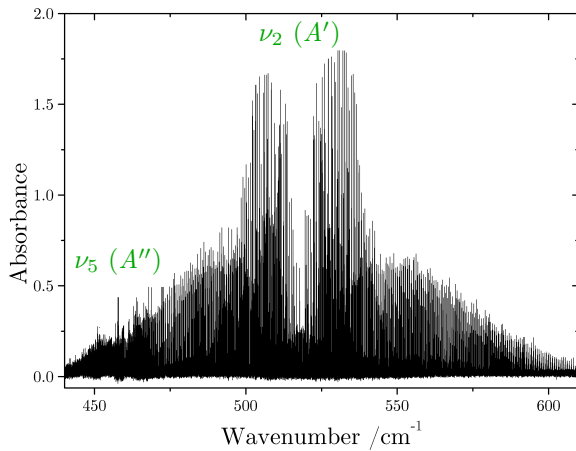
FT-FIR SPECTROSCOPY AT SOLEIL



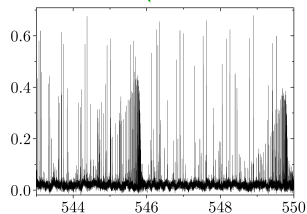
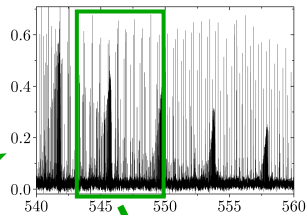
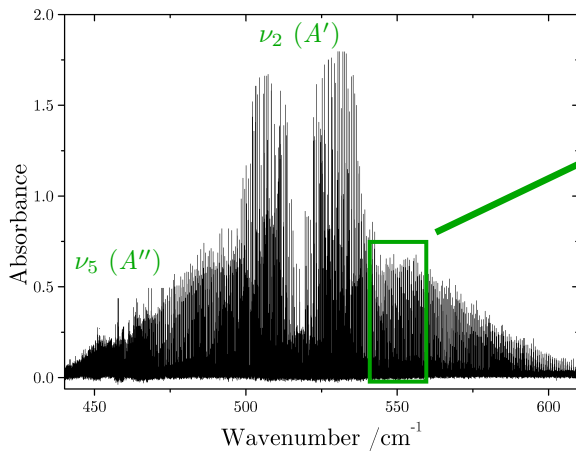
O. Pirali et al., *J. Chem. Phys.*
136, 024310 (2012)

- Bruker IFS125
- $R = 0.001 \text{ cm}^{-1}$
- Synchrotron radiation
- $20\text{--}700 \text{ cm}^{-1}$
- White-type absorption cell
- Absorption path length:
150 m
- 2 FIR spectra
- $P(\text{SOCl}_2) = 5 \text{ }\mu\text{bar}$
 $P(\text{SOCl}_2) = 56 \text{ }\mu\text{bar}$

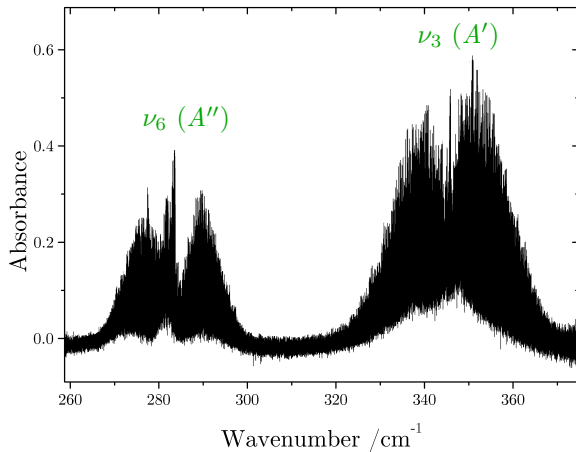
5 μ BAR SPECTRUM



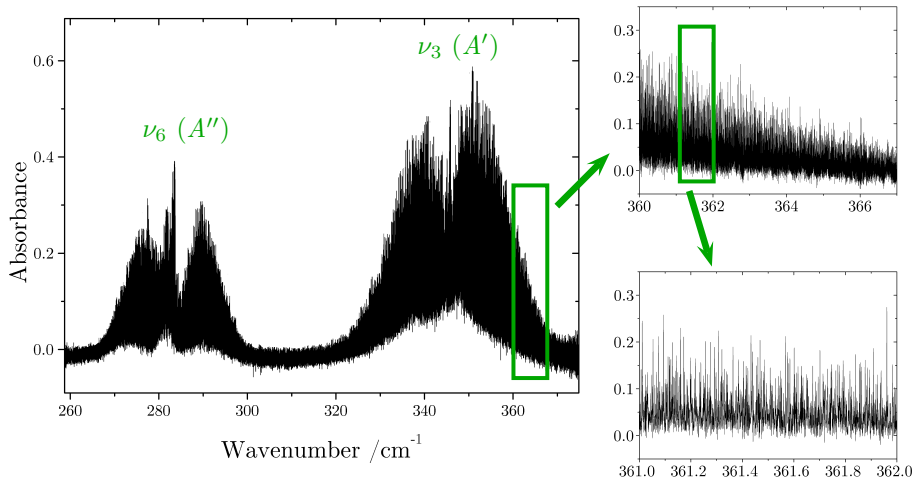
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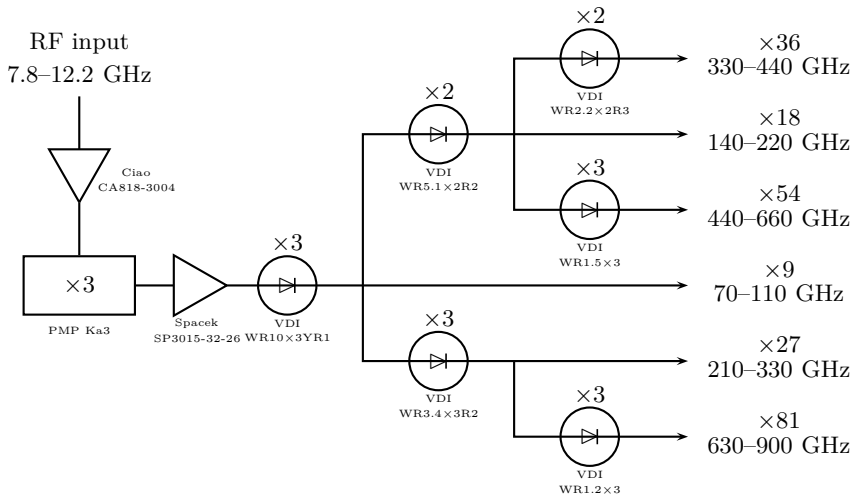
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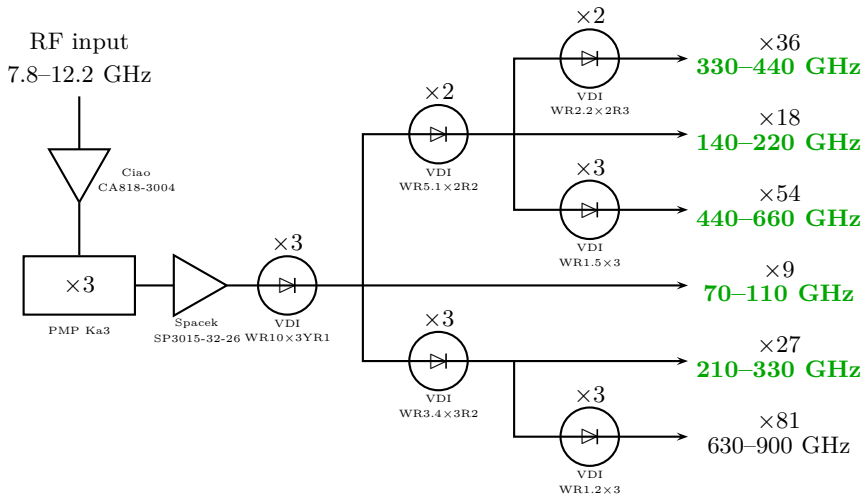


THz SPECTROSCOPY (FREQUENCY MULTIPLIER)



- Commercial frequency multiplier chain (VDI)
- 6 bands \rightarrow 70–110, 140–900 GHz

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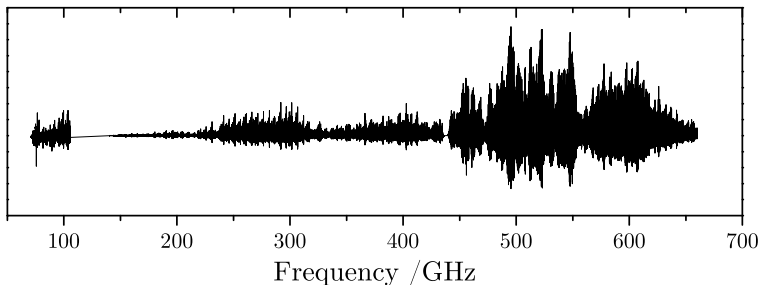


- Commercial frequency multiplier chain (VDI)
- 6 bands \rightarrow 70–110, 140–900 GHz

This work: 70–110, 140–660 GHz

THz SPECTRUM OF SOCl_2

- 1 m long single path cell
- InSb bolometer
- Frequency modulation (60 kHz)
- Time constant 10 ms (dwell 60ms)
- Frequency step 100 kHz
- Flow of SOCl_2 at $P \sim 15 \mu\text{bar}$



ANALYSIS OF THE SPECTRUM

- First prediction based on MW data

[1] J. Burie, *Compt. Acad. Sci. (Paris), Ser. B* **271**, 331 (1968),
G. Journal, PhD thesis, University of Lille, France (1969)

[2] H. S. P. Müller, *J. Chem. Soc. Faraday Trans.* **90**, 3473 (1994)

- Use of the LWWa software

W. Lodyga, *J. Mol. Spectrosc.* **243**, 182 (2007)

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	[1]	[2]	This work	Total
N	98	262*	9221	9581
J''_{\max}	76	4	109	109
$K''_{a_{\max}}$	25	2	49	49
$unc.$ /MHz	0.5	0.0005–0.0010	0.05–0.1	0.0005–0.5
RMS /MHz	0.42	0.00042	0.0809	0.0949
RMS error	0.64	0.79	1.08	1.06

*Observation of the hyperfine components

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ROTATIONAL AND CENTRIFUGAL DISTORSION CONSTANTS

	This work	Ref. [2]
A	5086.748 213 (12)	5086.748 209 (47)
B	2822.530 105 (11)	2822.530 125 (49)
C	1960.313 912 4 (89)	1960.313 918 (41)
$\Delta_J \times 10^3$	1.125 149 1 (52)	1.126 5 (15)
$\Delta_{JK} \times 10^3$	-2.226 927 (69)	-2.233 7 (52)
$\Delta_K \times 10^3$	6.985 72 (19)	6.992 4 (44)
$\delta_J \times 10^3$	0.394 382 2 (24)	0.394 59 (67)
$\delta_K \times 10^3$	1.247 324 (59)	1.252 6 (80)
$\Phi_J \times 10^9$	0.417 79 (73)	
$\Phi_{KJJ} \times 10^9$	5.632 (16)	
$\Phi_{KKJ} \times 10^6$	-0.043 325 (93)	
$\Phi_K \times 10^6$	0.060 82 (16)	
$\phi_J \times 10^9$	0.223 45 (35)	
$\phi_{JK} \times 10^9$	1.021 (12)	
$\phi_K \times 10^6$	0.015 546 (84)	
$L_{KKJJ} \times 10^{12}$	0.135 (23)	
$L_{KKKJ} \times 10^{12}$	0.246 (50)	
$L_K \times 10^{12}$	-0.521 (38)	
$l_{KKJ} \times 10^{12}$	0.230 (13)	
$l_K \times 10^{12}$	-0.182 (35)	

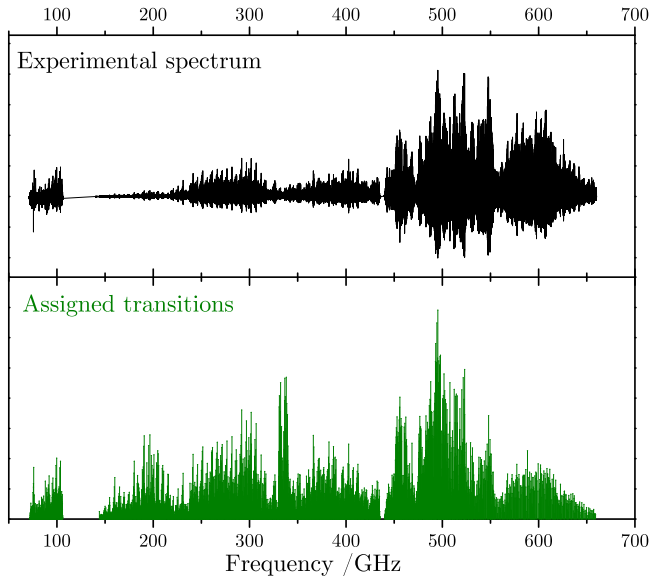
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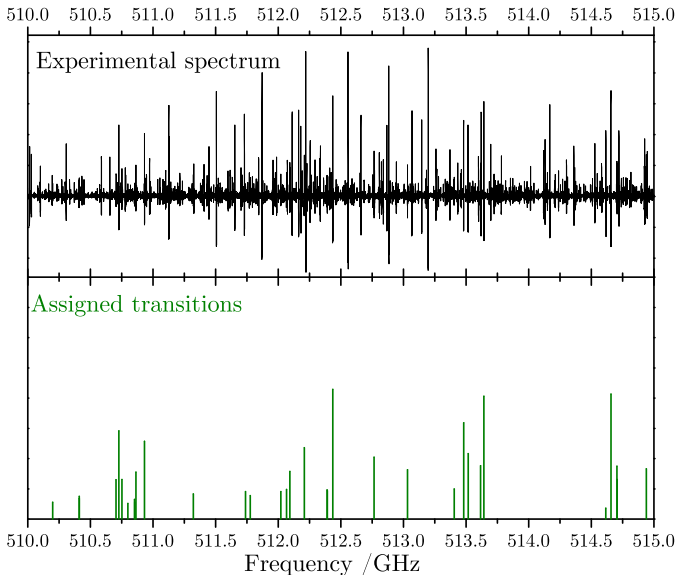
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CONCLUSION AND PROPECTS

^{35}Cl (75.77 %), ^{37}Cl (24.23 %)
 ^{32}S (95.02 %), ^{34}S (4.21 %), ^{33}S (0.75 %)

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Conclusion:

- Assignment of pure rotational transitions of $^{32}\text{SO}^{35}\text{Cl}_2$ up to 660 GHz (previously $f < 25$ GHz)
- Significant contribution to the list of observed transitions
- Improvement of SOCl_2 molecular parameters

Prospects:

- FT-FIR: Assign the ro-vibrational transitions (ν_2 to ν_6)
- THz: Assign the pure rotational transitions of the isotopologues
- THz: Search for transitions within excited vibrational states