THz AND FT-IR STUDY OF 18-O ISOTOPOLOGUES OF SULFUR DIOXIDE

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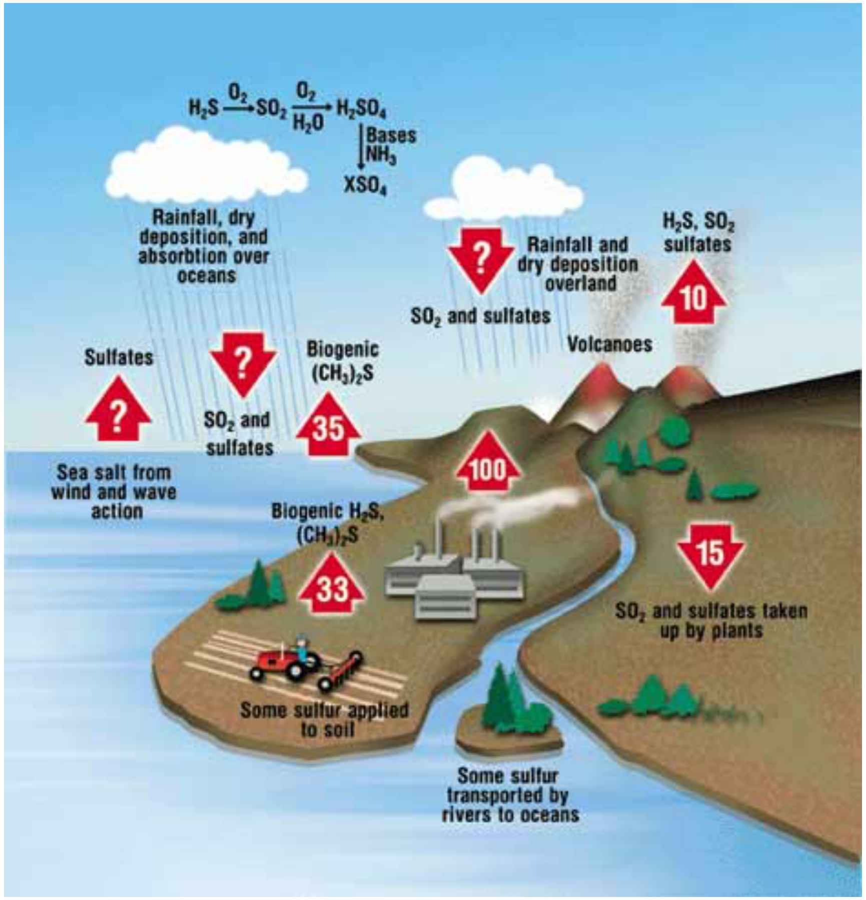
Motivation

- Sulfur dioxide is a molecule which have great interest in differents domains:
- atmospheric:
  - Human activites: mainly coming from burning coal and other fossil
  - Volcanoes (P.J. Wallace,2001, J. Volcanol. Geotherm. Res., 108, 85) and forest fires are the major natural sources

The modern global sulfur cycle. The units in this figure are expressed as teragrams of sulfur.



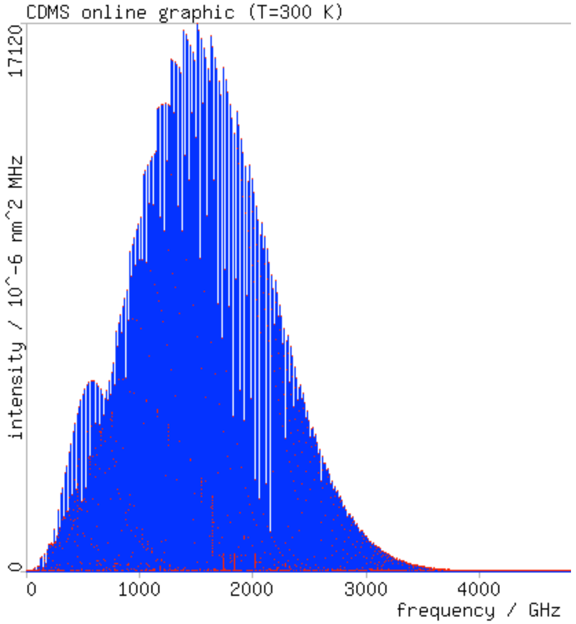
http://mtweb.mtsu.edu/nchong/NS-reactions-atm.htm

Motivation

- planetology chemistry:
  - abundant in Venus an important component of the Io Atmosphere (Nelson et al., 1980, Science 210, 784; Spencer et al., 2005, Icarus, 176, 283)
- Astrophysics:
  - since its first detection in 1975 (Snyder et al., 1975, ApJL, 198, L81) it was found to be ubiquious and abundant in interstellar medium.
  - ^{34}S (Sutton et al. ,1991, ApJS,77, 255) and $^{16}O^{18}O$ (Nummelin et al., 2000, ApJS, 128, 212) isotopologues were detected
- Isotopologs provide informations about atmospheric chemistry and dynamics (P. Bernath, MG02, ISMS 2016)
- ^{16}O species were extensively studied this is not the case of the ^{18}O isotopologues

Previous studies

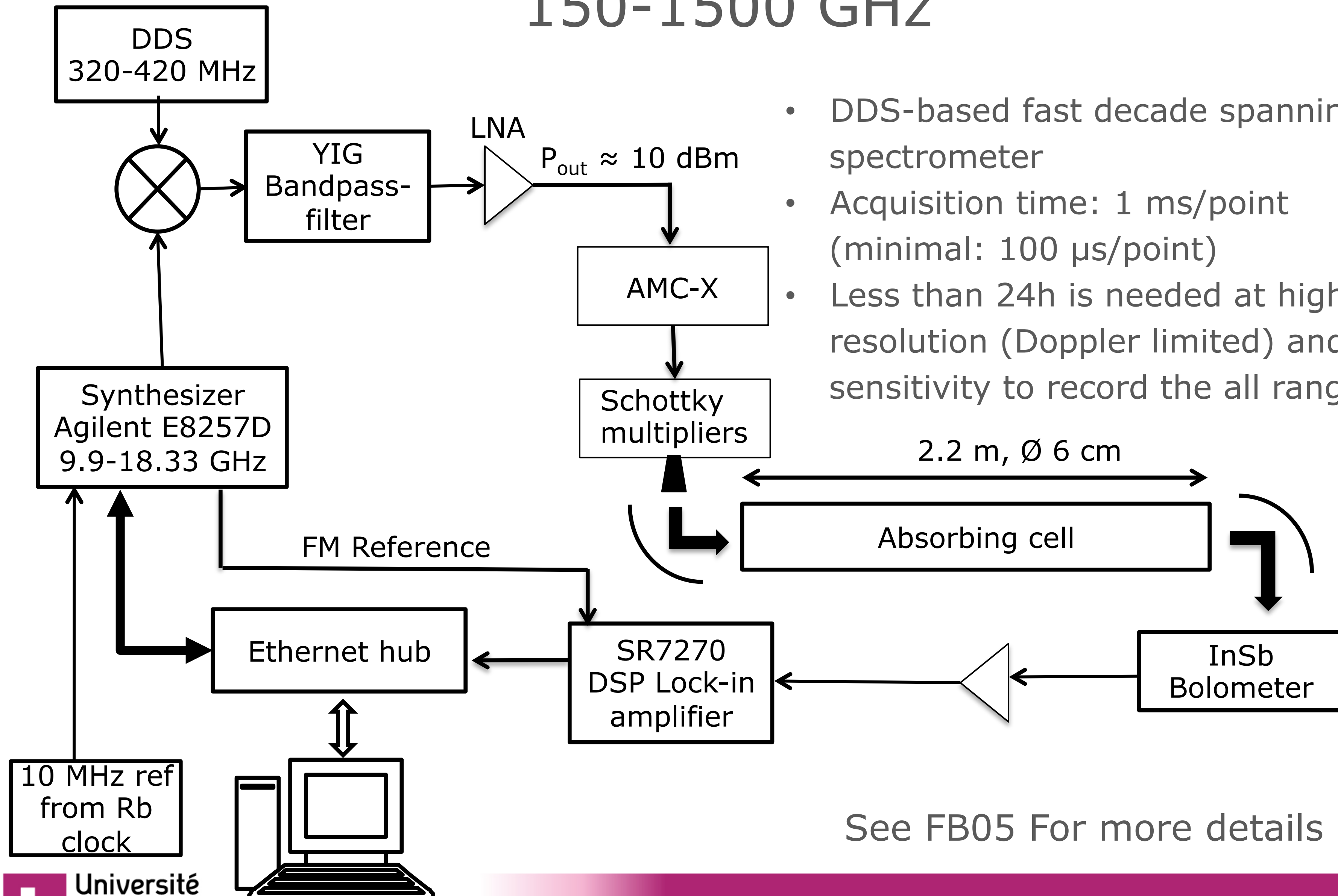
- $S^{16}O^{18}O$
  - Groud state: measurements up to 1050 GHz (Belov et al., 1998, J. Mol. Spectrosc. 191, 17)
  - v_2, v_1, $2v_2$, v_3 : MW spectra up to 60 GHz (Van Riet et al., 1983, Ann. Soc. Sci. Bruxelles, 97, 117)
  - V_2: (IR) + GSCD: Gueye et al., 2016, Mol. Phys., in press



https://www.astro.uni-koeln.de/cgi-bin/cdmsinfo?file=e064502.cat

- $S^{18}O_2$
  - Groud state: measurements up to 145 GHz (Lindermayer, J.; et al., 1985, J. Mol. Spectrosc. 110, 357)
  - v_2, v_1, $2v_2$: MW spectra up to 60 GHz (Van Riet et al., 1983, Ann. Soc. Sci. Bruxelles, 97, 243
  - V_2: (IR) + GSCD: F. Gueye, et al., 2016, Mol. Phys., in press
  - Triad v_1, $2v_2$, v_3 (IR): Ulenikov, et al., 2015, JQSRT 166, 13

Lille's fast solid state device spectrometer 150-1500 GHz

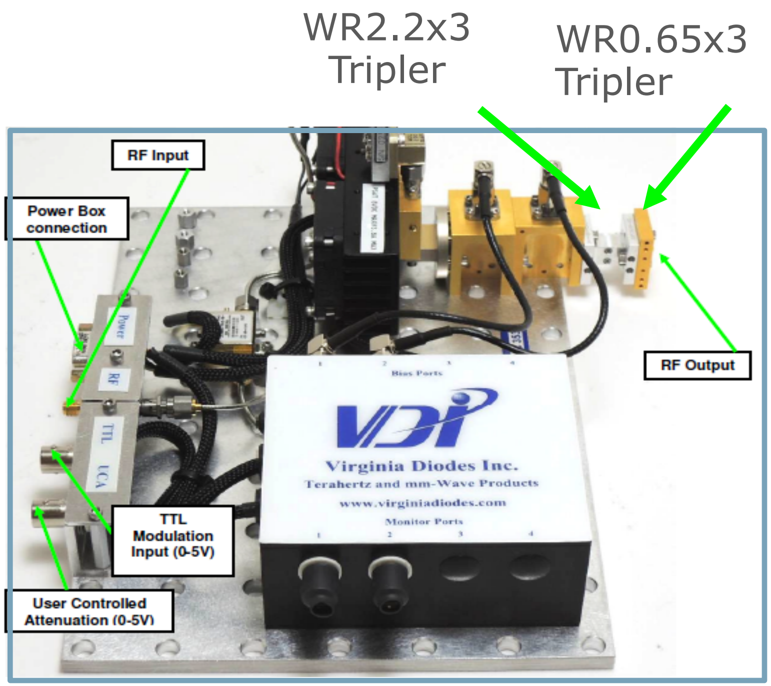


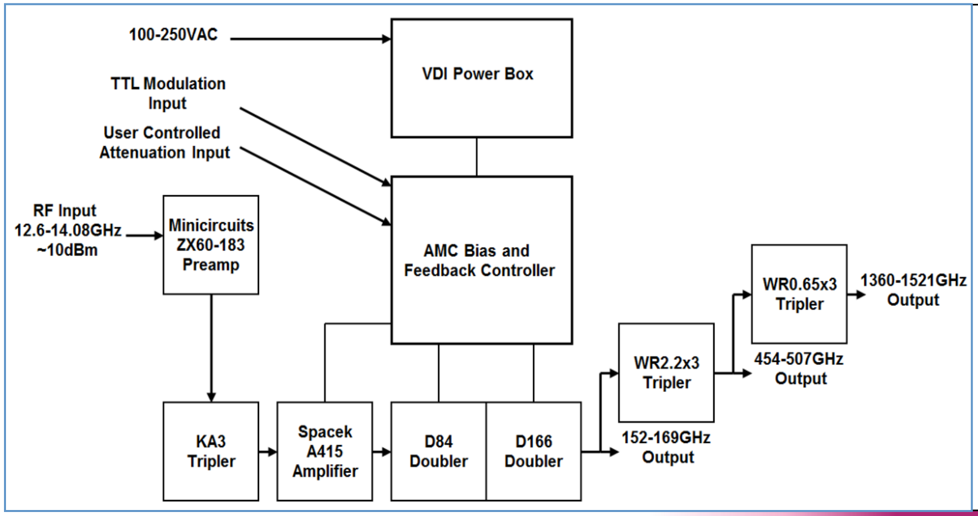
- DDS-based fast decade spanning spectrometer
- Acquisition time: 1 ms/point (minimal: 100 µs/point)
- Less than 24h is needed at high resolution (Doppler limited) and sensitivity to record the all range

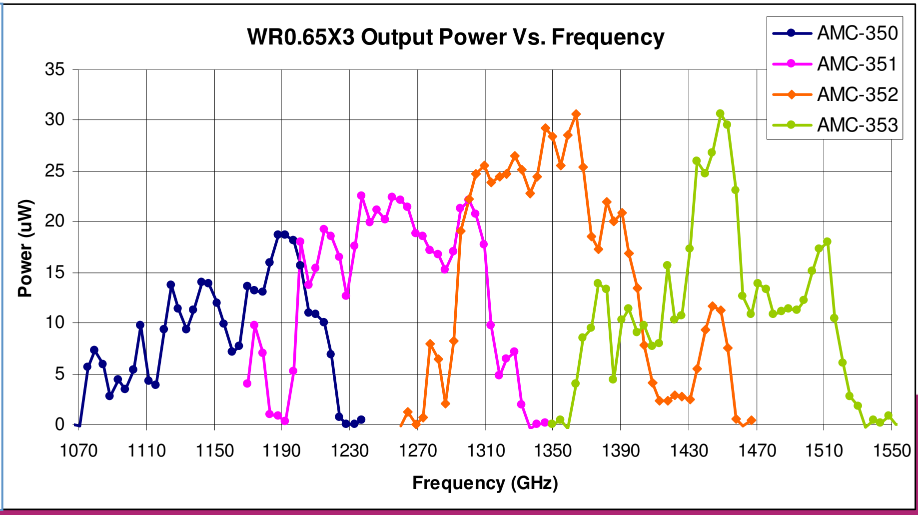
See FB05 For more details

multiplier chain:1.09 -1.5 THz

- The reconfigurable system consists:
  - four active multipliers (x12): 122-134 GHz 134-145/ 145-156 GHz/ 156-169 GHz
  - Followed by two passive triplers: WR2.2x3: 366 – 507 GHz / WR0.65x3: 1090 – 1520 GHz
- full range was recorded into 4 hours
  - frequency step: 0.162 MHz
  - accuracy: better than 50 kHz for isolated lines and 100 kHz poor S/N ratio

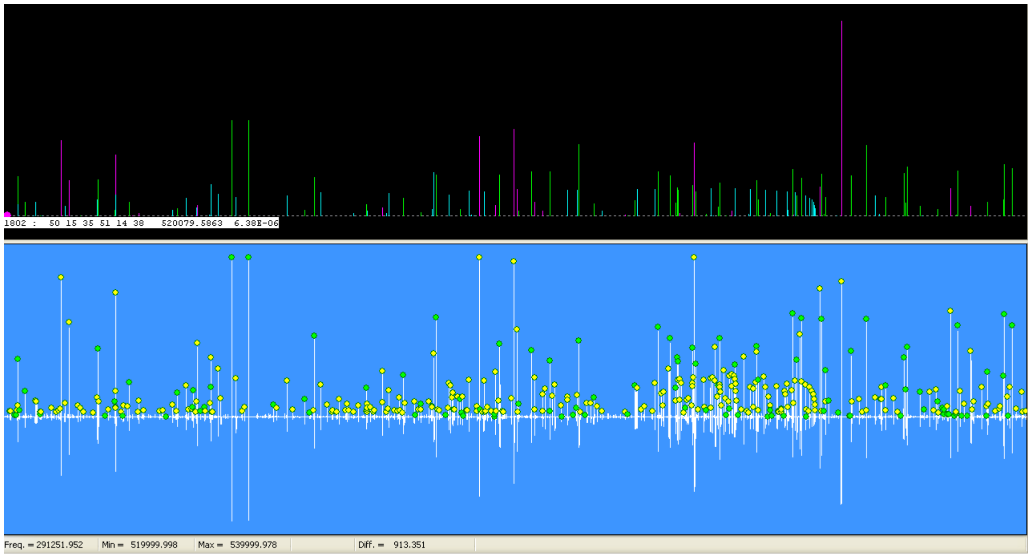






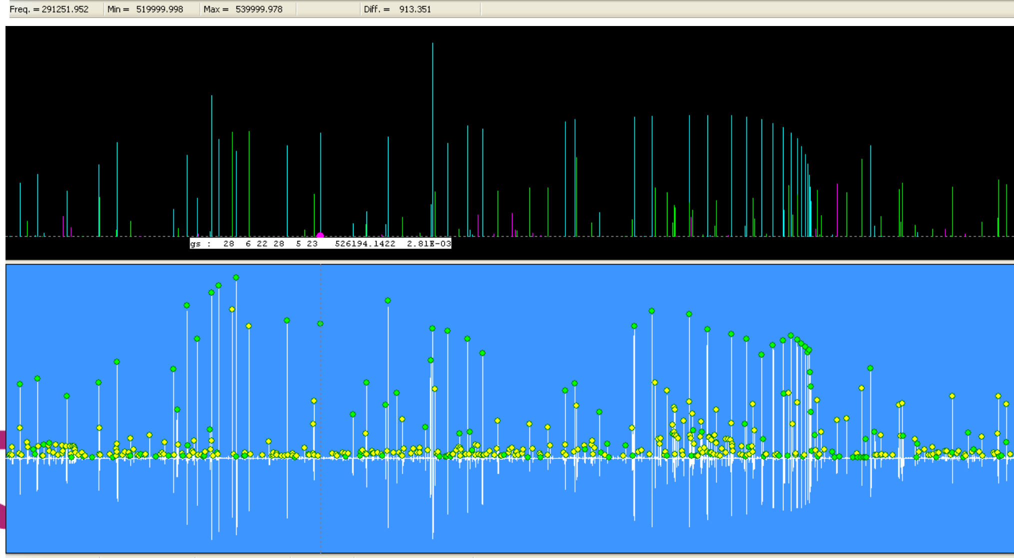
Samples

Samples were provided by L. Manceron, the ones used at Soleil for the v_2=1 studies.



$^{16}O^{18}O$ sample :

$^{16}O_2$: 1 – $^{16}O^{18}O$: 1 – $^{18}O_2$: 0.2



$^{18}O^{18}O$ sample :

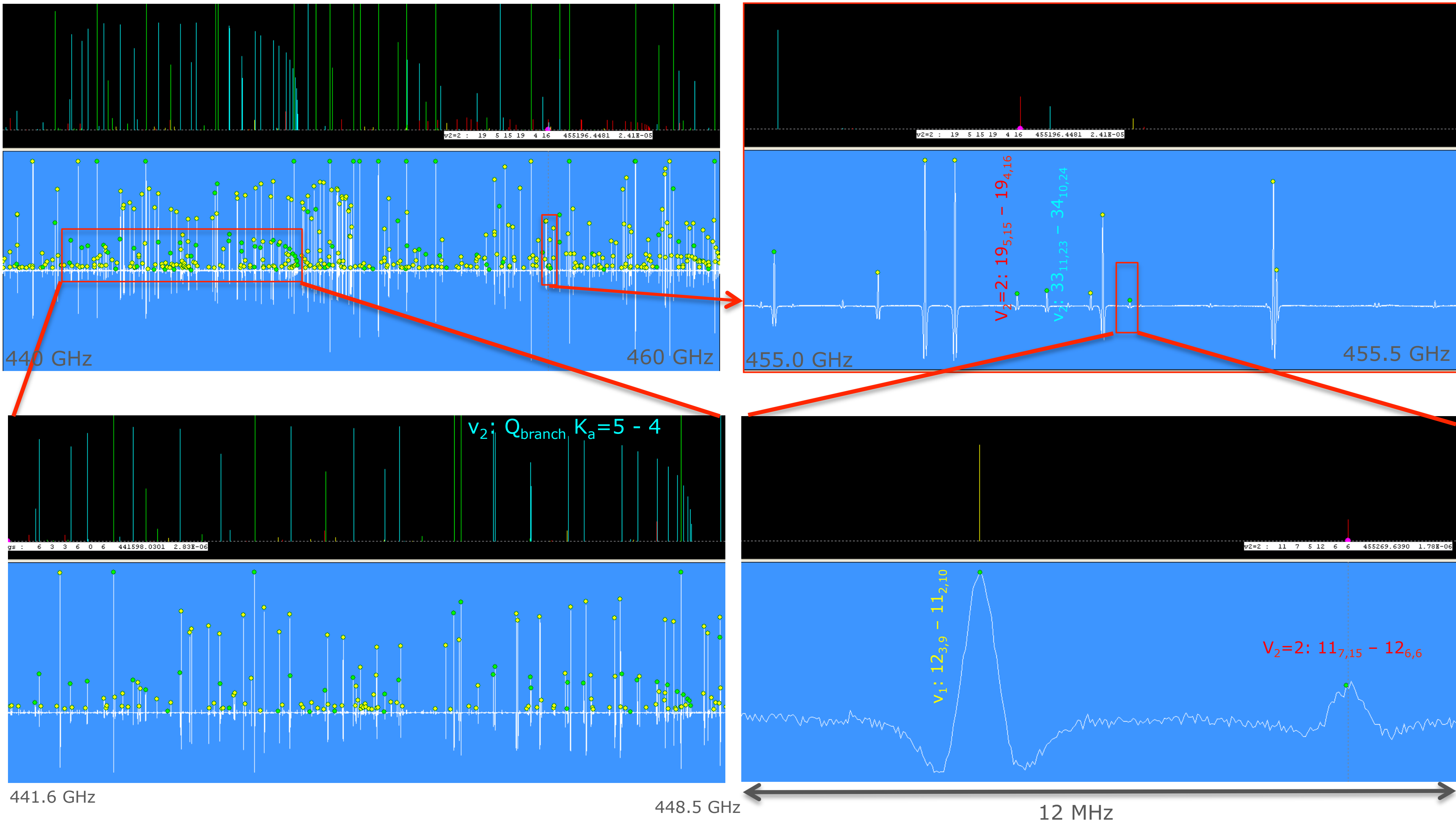
$^{16}O_2$: 0.2 – $^{16}O^{18}O$: 1 – $^{18}O_2$: 1

Analysis

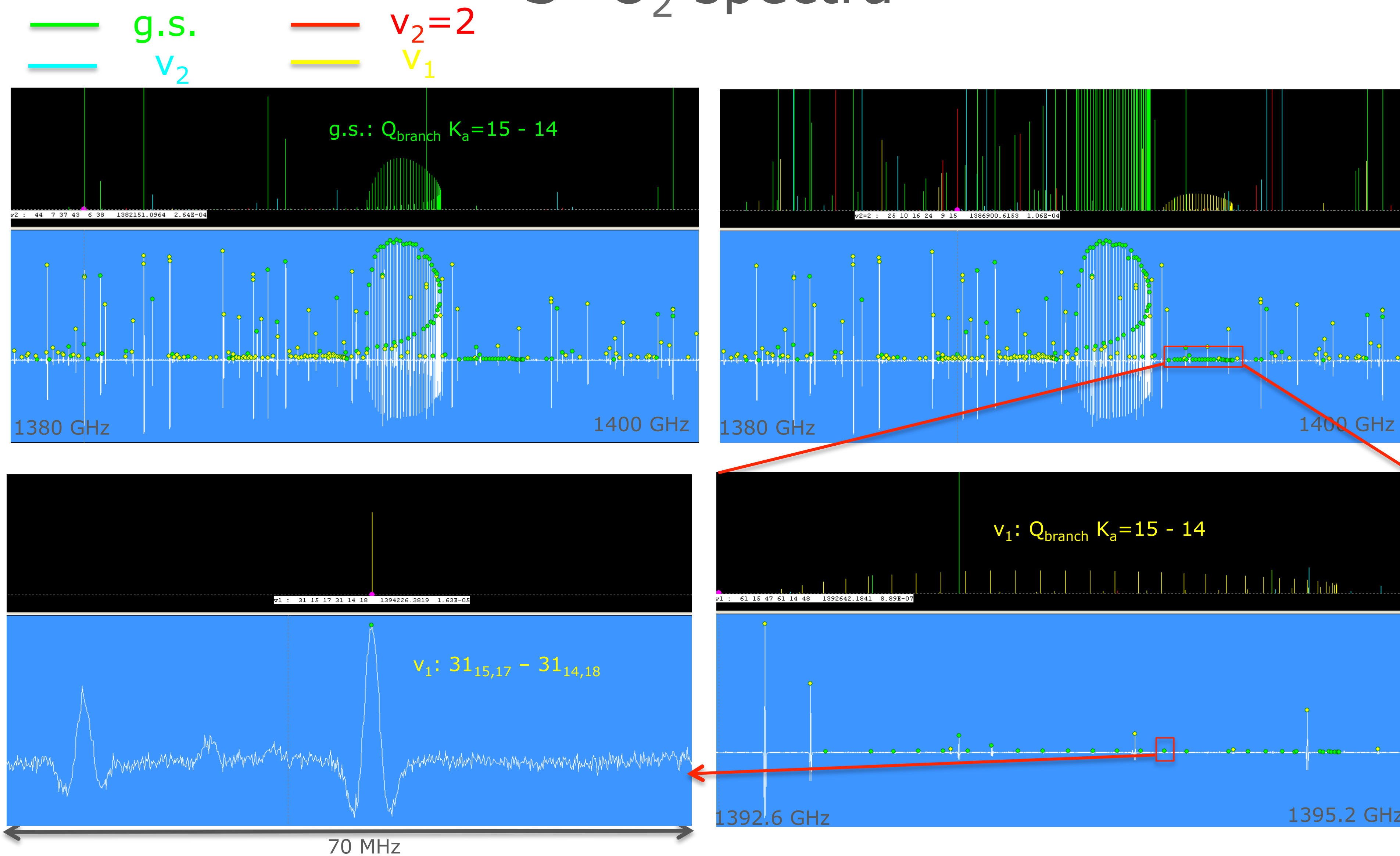
- Major difficulty is the intensity of the excited vibrational states lines. Relative intensity to the ground state ($S^{18}O_2$):
  - v_2 (496.6 cm^{-1}): 9%
  - $2v_2$(992.58 cm^{-1}): 0.9 %
  - v_1 (1101.13 cm^{-1}): 0.5 %
  - v_3 (1362.06 cm^{-1}): 0.1%
- Even if the molecules are near-symmetric tops ($\kappa \approx -0.95$), The Watson-type Hamiltonian in the S reduction was not found to give better results than the usual A reduction (Müller et al, 2005, JMS, 232, 213; F. Gueye, et al., 2016, Mol. Phys. In press).
- Concerning $S^{18}O_2$: due to spin statistic only rotational levels with $K_a + K_c$ even are allowed

$S^{18}O_2$ spectra

g.s. $v_2=2$
v_2 v_1



$S^{18}O_2$ spectra



$S^{18}O_2$ results

$S^{18}O_2$	gs		V_2 (496.59988(1) cm^{-1})	
	This work	Gueye et al.	This work	Gueye et al.
A	57384.92223(23)	57384.9719(102)	58433.21651(26)	58433.26435(109)
B	9170.499205(46)	9170.50915(164)	9172.812474(61)	9172.821299(359)
C	7889.565259(45)	7889.57511(152))	7876.684679(60)	7876.691761(305)
Δ_J *10^3	5.291321(29)	5.29134(135))	5.302110(42)	5.300048(408)
Δ_{JK}*10^3	-101.25971(26))	−101.2824(173)	-105.42690(38)	−105.46073(617)
Δ_K	2.3034889(36	2.303327(106)	2.5421386(36)	2.5420126(569)
δ_J*10^3	1.3077897(60)	1.306840(357))	1.315689(12))	1.315675(159)
δ_K*10^3	21.07997(33)	21.0690(201)	25.57869(56)	25.5519(178)
N_{MW}/N_{IR}	1638/ -	78/1310	948/ -	59 / 635
σ_{MW} (in kHz)	33.5/0.57	125	22.3/0.53	17
σ_{IR} (in MHz)		2.1		1.6

+sextic, octic, decic terms

$S^{18}O_2$ results

$S^{18}O_2$	ν_1 (1101.1368481(27) cm^{-1})		V_2=2 (992.53 cm^{-1})	
	This work	Ulenikov et al.	This work	Van Riet et al.
A	57447.38747(92)	57446.963(12)	59528.20321(98)	59528.3759(669)
B	9127.48028(22)	9127.3495(18)	9174.84111(21)	9174.87594(1093)
C	7852.46600(20)	7856.4677(16)	7863.66153(17)	7863.69203(1051)
Δ_J *10^3	5.27278(16)	5.26939(87)	5.31316(13)	5.47393(4655)
Δ_{JK}*10^3	-98.4031(14)	−102.306(12)	-109.8992(15)	−105.3028(9082)
Δ_K	2.340575(16)	2.34513(17)	2.809081(18)	2.801198(3480)
δ_J*10^3	1.303348(51)	1.31073(29)	1.323715(44)	1.326472(4884)
δ_K*10^3	22.8578(22)	20.914(69)	30.4091(19)	31.2547(2626)
N_{MW}/N_{IR}	456/ -	/	610	70
σ_{MW} (in kHz)	69.1/0.66		89.6/0.75	

+sextic, octic, decic terms

Triad Perturbations

- Perturbations are not treated yet, all the states are fitted as isolated ones.
- Perturbations are not strong: evidence could be found only for high energy levels, at frequencies above 1 THz

$S^{18}O_2$ v_1

J"	Ka"	Kc"	J'	Ka'	Kc'	obs in MHz	o-c (MHz)	acc(MHz)
22	16	6	22	15	7	1485591.8800	-1.0699	0.1000--excl
24	16	8	24	15	9	1485797.5710	-0.9472	0.1000--excl
26	16	10	26	15	11	1486009.3120	-1.1322	0.1000--excl
27	16	12	27	15	13	1486117.1740	-0.7833	0.1000--excl
28	16	12	28	15	13	1486224.9340	-1.1000	0.1000--excl
29	16	14	29	15	15	1486333.5280	-0.7785	0.1000--excl
32	16	16	32	15	17	1486655.6790	-0.7550	0.1000--excl
33	16	18	33	15	19	1486760.9080	-0.6560	0.1000--excl
34	16	18	34	15	19	1486864.0640	-0.8018	0.1000--excl
35	16	20	35	15	21	1486964.9810	-0.9171	0.1000--excl
22	12	10	21	11	11	1487103.3640	0.3530	0.1000--excl
37	16	22	37	15	23	1487158.2470	-1.0818	0.1000--excl
38	16	22	38	15	23	1487249.5990	-1.1851	0.1000--excl
39	16	24	39	15	25	1487336.7050	-1.3791	0.1000--excl
40	16	24	40	15	25	1487419.1800	-1.5472	0.1000--excl
41	16	26	41	15	27	1487496.4200	-1.7798	0.1000--excl
42	16	26	42	15	27	1487568.0350	-1.9415	0.1000--excl
43	16	28	43	15	29	1487633.3660	-2.1536	0.1000--excl
44	16	28	44	15	29	1487691.8690	-2.4106	0.1000--excl
45	16	30	45	15	31	1487743.0920	-2.6027	0.1000--excl
48	16	32	48	15	33	1487846.7400	-3.3319	0.0990--excl

$S^{18}O_2$ v_2=2

J"	Ka"	Kc"	J'	Ka'	Kc'	obs in MHz	o-c (MHz)	acc(MHz)
15	15	1	15	14	2	1447226.9100	0.2382	0.1000--excl
16	15	1	16	14	2	1447309.8750	0.2311	0.1000--excl
17	12	6	16	11	5	1447394.8980	0.0332	0.1000--excl
20	15	5	20	14	6	1447675.0600	0.2739	0.1000--excl
21	15	7	21	14	8	1447773.1120	0.2658	0.1000--excl
22	15	7	22	14	8	1447873.1660	0.2218	0.1000--excl
23	15	9	23	14	10	1447974.9250	0.2088	0.1000--excl
24	15	9	24	14	10	1448077.9740	0.1916	0.1000--excl
25	15	11	25	14	12	1448181.9320	0.1846	0.1000--excl
26	15	11	26	14	12	1448286.3330	0.1332	0.1000--excl
29	15	15	29	14	16	1448598.0790	-0.0545	0.1000--excl
30	15	15	30	14	16	1448699.9250	-0.1849	0.1000--excl
32	15	17	32	14	18	1448897.7340	-0.4151	0.1000--excl
33	15	19	33	14	20	1448992.5650	-0.6225	0.1000--excl
34	15	19	34	14	20	1449084.0560	-0.8071	0.1000--excl
35	15	21	35	14	22	1449171.5380	-1.0874	0.1000--excl
37	15	23	37	14	24	1449332.4030	-1.7280	0.1000--excl
38	15	23	38	14	24	1449404.5870	-2.1094	0.1000--excl
39	15	25	39	14	26	1449470.4040	-2.5887	0.1000--excl
42	15	27	42	14	28	1449623.2630	-4.6533	0.1000--excl
43	15	29	43	14	30	1449657.0990	-5.6090	0.1000--excl
47	15	33	47	14	34	1449694.9150	-4.2174	0.1000--excl
45	15	31	45	14	32	1449697.2570	-5.6462	0.1000--excl
46	15	31	46	14	32	1449705.5210	-1.3591	0.1000--excl

$S^{16}O^{18}O$ results

$S^{16}O^{18}O$	gs		V_2 (507.36541 cm^{-1})	
	This work	Gueye et al.	This work	Gueye et al.
A	59101.17319(29)	59101.18749(213)	60212.86818(35)	60212.85552(573)
B	9724.643944(63)	9724.646003(366)	9726.963224(43	9726.96150(117)
C	8331.560903(59)	8331.563706(334)	8317.255641(47)	8317.257957(785)
$\Delta_J *10^3$	5.905175(38)	5.905781(231)	5.916849(25)	5.912022(953)
$\Delta_{JK}*10^3$	-108.40989(34)	−108.41193(233)	-113.01595(49)	−113.02035(887)
Δ_K	2.4436490(39)	2.4438465(359)	2.7034999(77)	2.7030818(747)
δ_J*10^3	1.487542(10)	1.4873159(835)	1.4962655(98)	1.493238(573)
δ_K*10^3	23.22651(73)	23.2000(887)	28.28696(62)	28.3517(257)
N_{MW}/N_{IR}	2524/ -	338/2033	1338/ -	- / 829
σ_{MW} (in kHz)	46.5/0.97	71	24.1/0.61	
σ_{IR} (in MHz)		2.3		1.2

+sextic, octic, decic terms

$S^{16}O^{18}O$ results

$S^{16}O^{18}O$	v_1 (1124.008 cm^{-1})	
	This work	Van Riet et al.
A	*59144.82282(97)*	59144.9468(630)
B	*9678.35435(26)*	9678.37212(1039)
C	*8291.97717(20)*	8291.99152(970)
Δ_J *10^3	*5.88648(24)*	5.99365(6775))
Δ_{JK}*10^3	*-105.2330(26)*	−103.1861(12718)
Δ_K	*2.480579(17)*	2.476075(4297)
δ_J*10^3	*1.48284(11)*	1.49747(731)
δ_K*10^3	*25.208(13)*	24.7477(2543)
N_{MW}	*450/ -*	119
σ_{MW} (in kHz)	*39.0/0.60*	

+sextic, octic, decic terms

- Lot of lines from Van Riet et al. Should be excluded of the fit
- Like $S^{18}O_2$, small perturbations appear:

J"	Ka"	Kc"	J'	Ka'	Kc'	obs in MHz	o-c (MHz)	acc(MHz
20	14	6	20	13	7	1331617.0150	-0.2268	0.1000--excl
20	14	7	20	13	8	1331617.0150	-0.2268	0.1000--excl
21	14	7	21	13	8	1331692.1840	-0.3724	0.1000--excl
21	14	8	21	13	9	1331692.1840	-0.3724	0.1000--excl
22	14	8	22	13	9	1331767.3390	-0.4154	0.1000--excl
22	14	9	22	13	10	1331767.3390	-0.4154	0.1000--excl
23	14	9	23	13	10	1331841.6170	-0.7064	0.1000--excl
23	14	10	23	13	11	1331841.6170	-0.7064	0.1000--excl
24	14	11	24	13	12	1331914.7650	-0.9638	0.1000--excl
24	14	10	24	13	11	1331914.7650	-0.9638	0.1000--excl
25	14	11	25	13	12	1331986.1360	-1.2773	0.1000--excl
25	14	12	25	13	13	1331986.1360	-1.2773	0.1000--excl
26	14	13	26	13	14	1332055.1510	-1.6466	0.1000--excl
26	14	12	26	13	13	1332055.1510	-1.6466	0.1000--excl
27	14	13	27	13	14	1332121.1690	-2.1109	0.1000--excl
27	14	14	27	13	15	1332121.1690	-2.1109	0.1000--excl
28	14	15	28	13	16	1332183.5510	-2.6852	0.1000--excl
28	14	14	28	13	15	1332183.5510	-2.6852	0.1000--excl
29	14	15	29	13	16	1332241.5920	-3.4282	0.1000--excl
29	14	16	29	13	17	1332241.5920	-3.4282	0.1000--excl
31	14	17	31	13	18	1332341.9740	-5.4016	0.1000--excl
31	14	18	31	13	19	1332341.9740	-5.4016	0.1000--excl

- v_2=2 in progress….

Conclusions and Perspectives

- The rotational spectra of the ground state and the v_2, v_1 and $2v_2$ excited vibrational states were analysed up to 1.5 THz.
- The global analysis Thz+IR measurements concerning v_2 will be done in the next weeks
- Assigning v_3 in the rotational spectra
- New measurements with the AILES Beamline at Synchrotron Soleil will be done in September in the triad range (1000-1500 cm-1) in order to treat properly the perturbation effects combining these measurements with the rotational ones

Aknowledgements

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- And many thanks for your attention