The SOLEIL view on sulfur rich oxides: The ν_3 mode of S_2O revisited

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Outline

Previous high-res IR / MW studies of S_2O

SOLEIL study

The ν_3 mode and the $\nu_3 + \nu_2 - \nu_2$ hot band

and associated mmw study

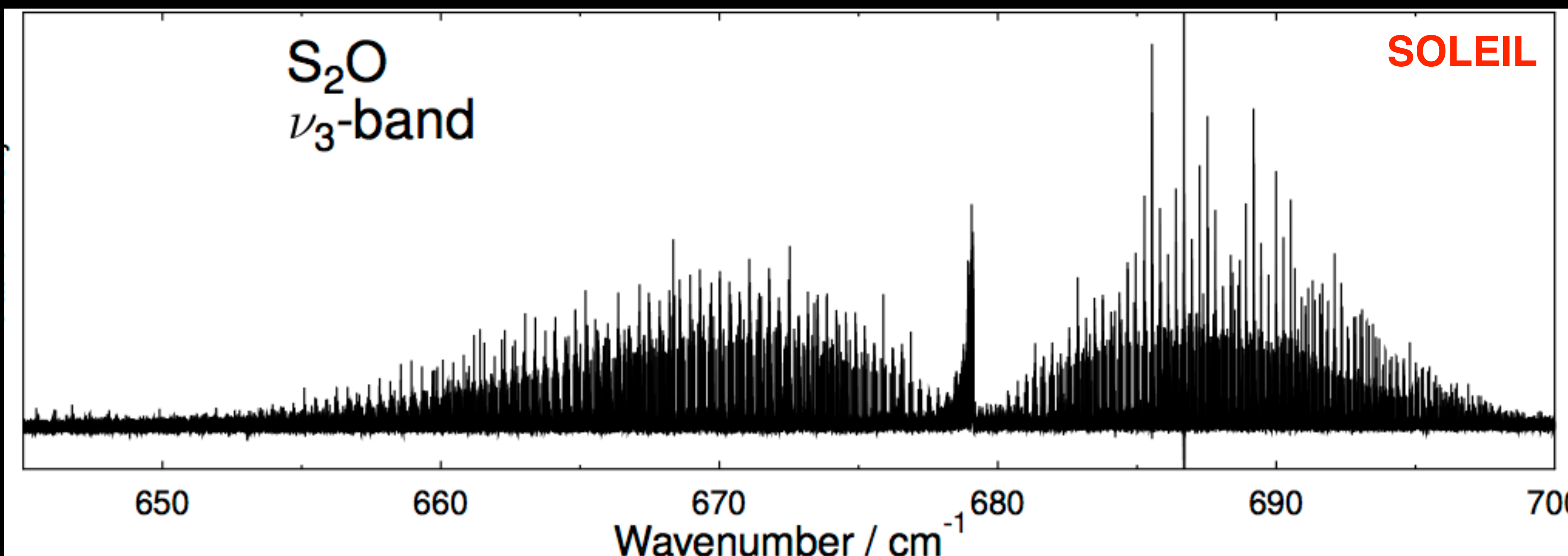
ASAP analysis of IR spectra

Prospects

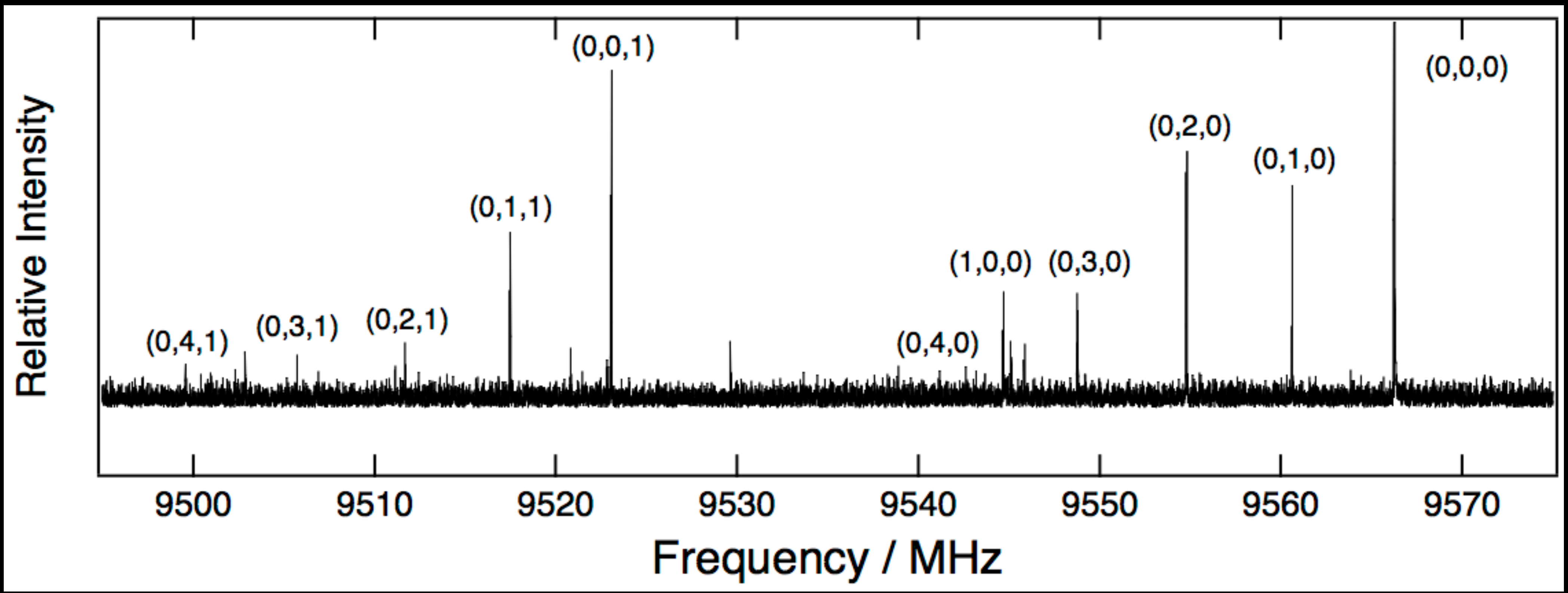
Previous studies: IR

All three fundamental vibrational modes observed

$\nu_{1(\text{S-O-stretch})}$: 1166 cm^{-1} (Lindenmayer and Jones 1985)
$\nu_{2(\text{S-S-O-stretch})}$: 380 cm^{-1} (Martin-Drumel et al. 2015)
$\nu_{3(\text{S-S-stretch})}$: 679 cm^{-1} (Lindenmayer et al. 1986)



Previous studies: FTMW vib. satellite pattern



$J = 1_{0,1} - 0_{0,0}$

Total of 15 vibrational states observed in SO_2 discharge

Thorwirth et al. (2006)

Previous studies: FTMW

S. Thorwirth et al. / Journal of Molecular Structure 795 (2006) 219–229 221

Table 1
Experimental microwave transition frequencies of S_2O in the ground vibrational and first excited vibrational states (MHz) and residuals *o–c* (kHz, global fit)

Transition	(0,0,0)	*o–c*	(1,0,0)	*o–c*	(0,1,0)	*o–c*	(0,0,1)	*o–c*
$2_{1,2}-3_{0,3}$	7635.6394(20)	0.3	7331.3709(20)	0.8	8209.2989(20)	0.4	7790.6101(20)	−0.7
$1_{0,1}-0_{0,0}$	9566.2535(20)	0.1	9544.6729(20)	−1.1	9560.6089(20)	−0.2	9523.0528(20)	0.3
$5_{0,5}-4_{1,4}$	13258.9405(20)	−1.3	13522.6729(20)	1.0	12696.7339(30)	−0.1	13009.9395(20)	−0.6
$1_{1,1}-2_{0,2}$	17728.9092(20)	1.3	17404.1709(20)	0.5	18303.6572(20)	0.7	17838.2598(20)	0.3
$2_{1,2}-1_{1,1}$	18580.7120(20)	0.8	18536.0606(20)	0.8	18562.4414(20)	−0.5	18496.9815(20)	1.5
$2_{0,2}-1_{0,1}$	19126.3106(20)	0.4	19083.0557(20)	−0.2	19114.9600(20)	0.3	19039.9707(20)	−0.6
$2_{1,1}-1_{1,0}$	19684.4688(20)	0.2	19642.8037(20)	−0.8	19680.1709(20)	1.0	19595.3956(20)	0.0
$3_{1,3}-2_{1,2}$	27867.1533(20)	1.2	27800.1163(20)	0.7	27839.7100(20)	0.1	27741.5938(20)	−0.6
$3_{0,3}-2_{0,2}$	28673.9805(20)	0.5	28608.8594(20)	−0.6	28656.7998(20)	−0.1	28544.6299(20)	1.1
$3_{1,2}-2_{1,1}$	29522.7061(20)	2.2	29460.1465(20)	−0.1	29516.2178(20)	0.6	29389.1348(20)	0.6
$2_{1,1}-2_{0,2}$	37965.2618(20)	−1.6	37600.3555(20)	−0.2	38542.6973(20)	−1.3	37982.8711(20)	−0.1
$4_{0,4}-3_{0,3}$	38203.1016(30)	1.4	–		–		–	
$3_{1,2}-3_{0,3}$	38813.9883(20)	0.9	–		–		–	

Table 2
Vibrational satellites of S_2O (MHz) and residuals (kHz, global fit)

Transition	(0,2,0)	*o–c*	(0,3,0)	*o–c*	(0,4,0)	*o–c*	(0,5,0)	*o–c*
$1_{0,1}-0_{0,0}$	9554.7837(20)	0.3	9548.7769(20)	0.8	9542.5869(20)	0.0	9536.2154(20)	0.1
$2_{1,2}-1_{1,1}$	18543.8360(20)	−0.8	18524.9034(20)	2.8	18505.6387(20)	0.3	18486.0557(20)	0.7
$2_{0,2}-1_{0,1}$	19103.2500(20)	−0.2	19091.1797(20)	−1.1	19078.7500(20)	−1.1	19065.9610(20)	0.5
$2_{1,1}-1_{1,0}$	19675.4814(20)	−0.4	19670.3985(20)	0.4	19664.9131(20)	0.5	19659.0196(20)	0.5
$3_{1,3}-2_{1,2}$	27811.7657(20)	−0.3	27783.3272(20)	−0.5	27754.4004(20)	−2.1	27725.0000(30)	2.1
$3_{0,3}-2_{0,2}$	28639.0889(20)	−0.8	28620.8477(20)	−1.0	28602.0762(20)	−0.1	28582.7725(20)	1.0
$3_{1,2}-2_{1,1}$	–		–		29493.2285(30)	−0.1	29484.3584(20)	−0.2
$4_{1,4}-3_{1,3}$	37074.9727(30)	3.2	37036.9883(30)	−0.3	36998.3613(30)	−1.3	36959.1016(30)	0.2
$4_{0,4}-3_{0,3}$	38156.0215(20)	1.9	38131.4414(20)	−1.4	–		38080.2149(30)	2.1

Transition	(0,6,0)	*o–c*	(0,7,0)	*o–c*	(0,8,0)	*o–c*	(0,1,1)	*o–c*
$1_{0,1}-0_{0,0}$	9529.6607(20)	−0.4	–		9516.0034(20)	−0.1	9517.4732(20)	0.7
$2_{1,2}-1_{1,1}$	–		–		–		18478.7461(20)	−0.2
$2_{0,2}-1_{0,1}$	19052.8086(20)	0.3	19039.2930(20)	−0.9	19025.4180(20)	1.3	19028.7461(20)	−1.3
$2_{1,1}-1_{1,0}$	–		–		–		19591.3193(20)	0.3
$3_{1,3}-2_{1,2}$	–		–		–		27714.2022(20)	−1.8
$3_{0,3}-2_{0,2}$	28562.9336(20)	−0.1	28542.5606(20)	−1.4	–		28527.6328(20)	−0.1
$3_{1,2}-2_{1,1}$	–		–		–		29382.9805(30)	1.3

Transition	(0,2,1)	*o–c*	(0,3,1)	*o–c*	(0,4,1)	*o–c*
$1_{0,1}-0_{0,0}$	9511.7027(20)	−0.6	9505.7456(20)	1.1	9499.5962(20)	0.5
$2_{1,2}-1_{1,1}$	18460.1621(20)	−0.2	18441.2344(20)	1.3	18421.9620(20)	−1.5
$2_{0,2}-1_{0,1}$	19017.1495(20)	1.1	19005.1748(20)	1.0	18992.8213(20)	−1.6
$2_{1,1}-1_{1,0}$	19586.8340(20)	−1.5	19581.9365(30)	−2.2	–	
$3_{0,3}-2_{0,2}$	28510.0830(20)	−0.1	28491.9805(20)	1.7	28473.3203(30)	1.2

FTMW and MMW / SubMMW study (up to 470 GHz, Thorwirth et al. 2006)

Previous studies: FTMW

Table 1
Experimental microwave transition frequencies of S_2O in the ground vibrational and first excited vibrational states (MH and residuals *o–c* (kHz, global fi

Transition	(0,0,0)	*o–c*	(1,0,0)	*o–c*	(0,1,0)	*o–c*	(0,0,1)	*o–c*
$2_{1,2}$–$3_{0,3}$	7635.6394(20)	0.3	7331.3709(20)	0.8	8209.2989(20)	0.4	7790.6101(20)	−0.7
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$4_{0,4}$–$3_{0,3}$	38203.1016(30)	1.4	–		–		–	
$3_{1,2}$–$3_{0,3}$	38813.9883(20)	0.9	–		–		–	

Table 2
Vibrational satellites of S_2O (MHz) and residuals (kHz, global fit)

Transition	(0,2,0)	*o–c*	(0,3,0)	*o–c*	(0,4,0)	*o–c*	(0,5,0)	*o–c*
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$3_{1,2}$–$2_{1,1}$	–		–		29493.2285(30)	−0.1	29484.3584(20)	−0.2
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$2_{1,1}$–$1_{1,0}$	–		–		–		19591.3193(20)	0.3
$3_{1,3}$–$2_{1,2}$	–		–		–		27714.2022(20)	−1.8
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$3_{1,2}$–$2_{1,1}$	–		–		–		29382.9805(30)	1.3

Transition	(0,2,1)	*o–c*	(0,3,1)	*o–c*	(0,4,1)	*o–c*
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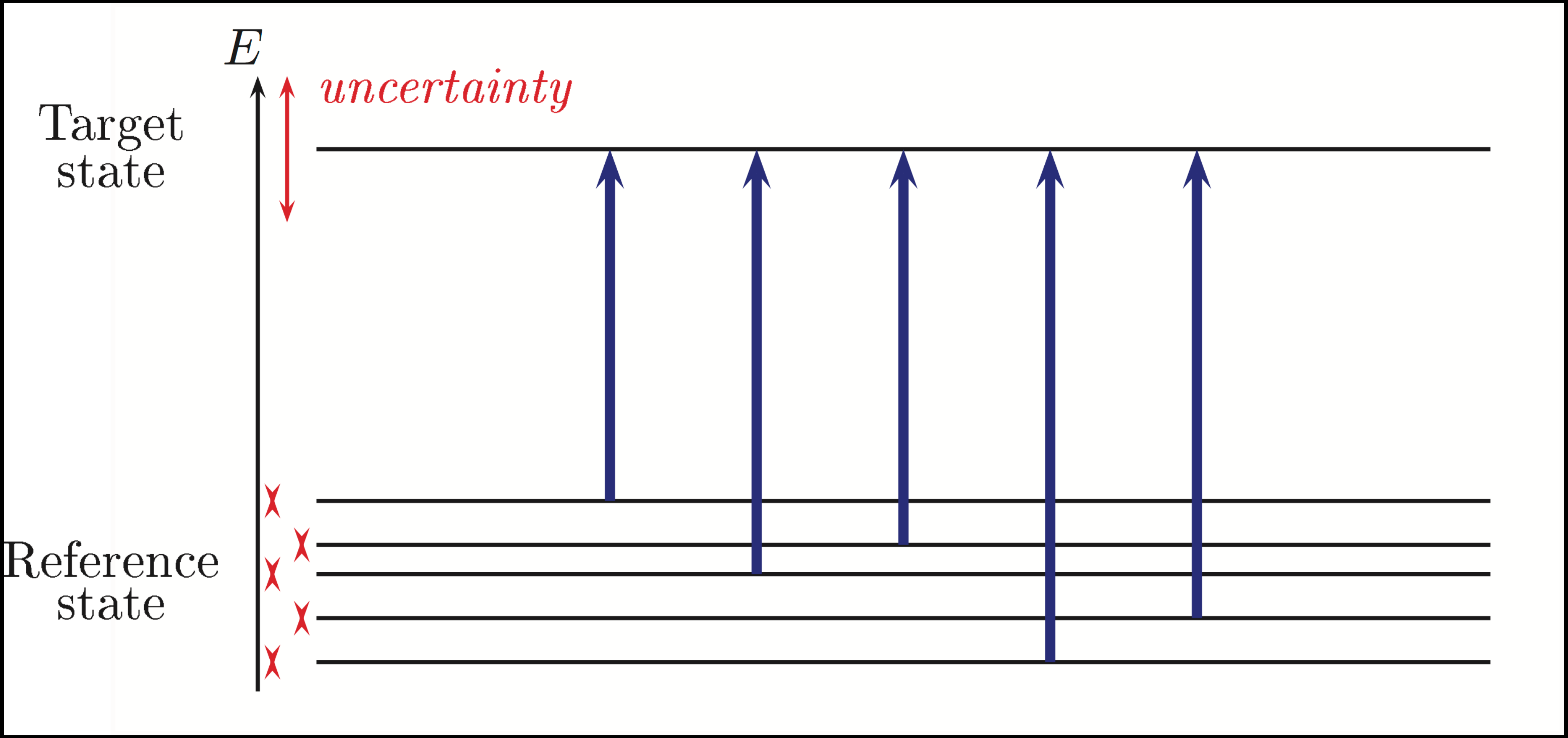
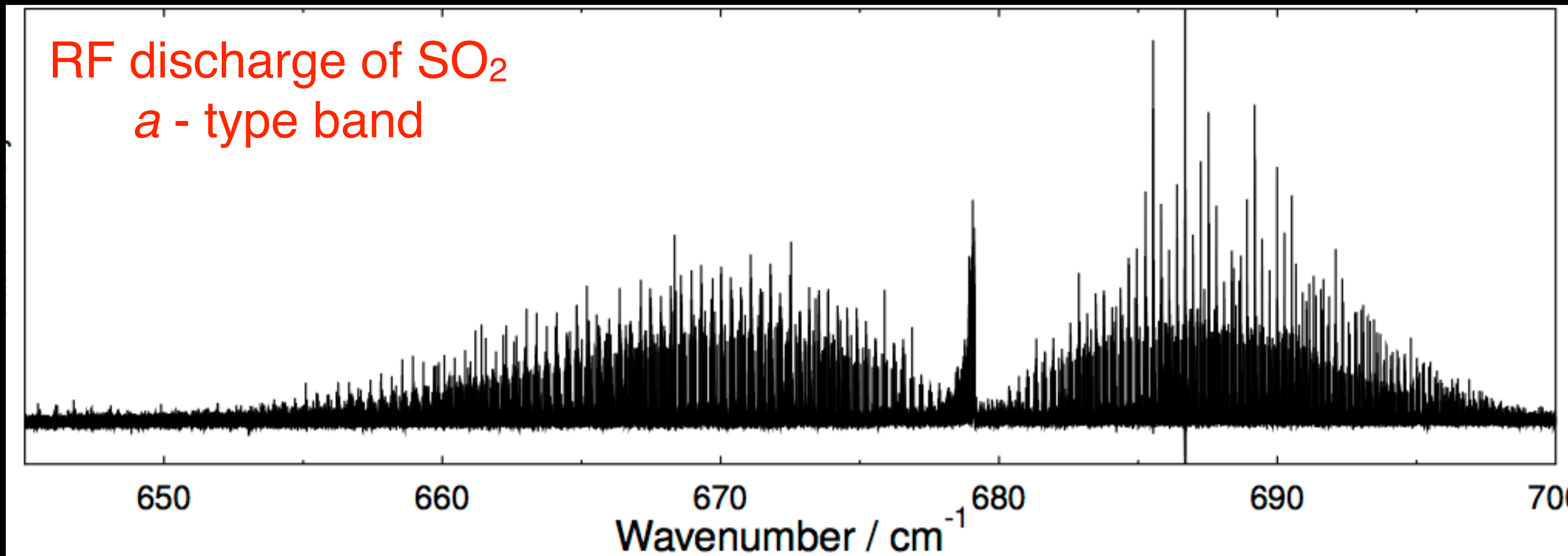
FTMW and MMW / SubMMW study (up to 470 GHz, Thorwirth et al. 2006)

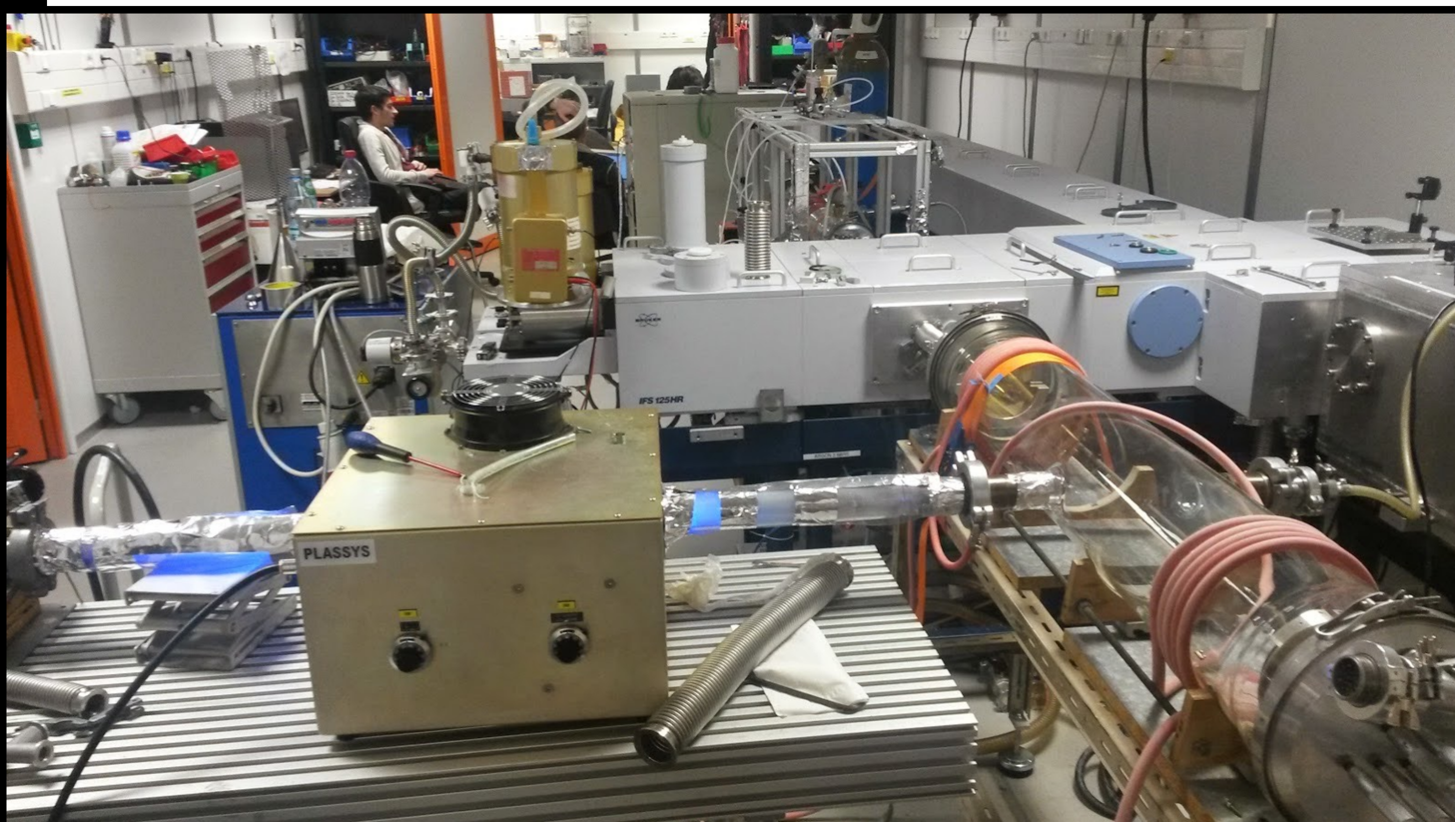
Previous studies: Mmw / Submmw

(0,0,0) state observed up to 470 GHz:
Good description of the "reference state" for ASAP



The ν_3 mode of S_2O revisited with SOLEIL



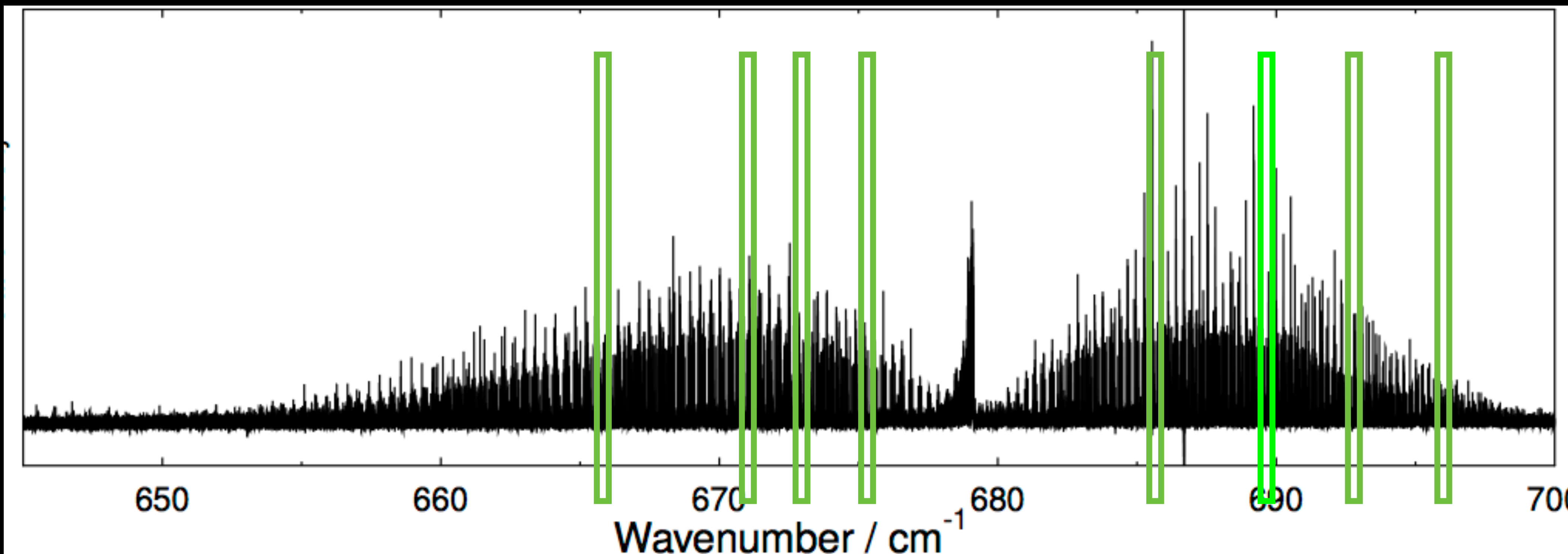


White-type cell
30m pathlength

The ν_3 mode of S_2O revisited with SOLEIL

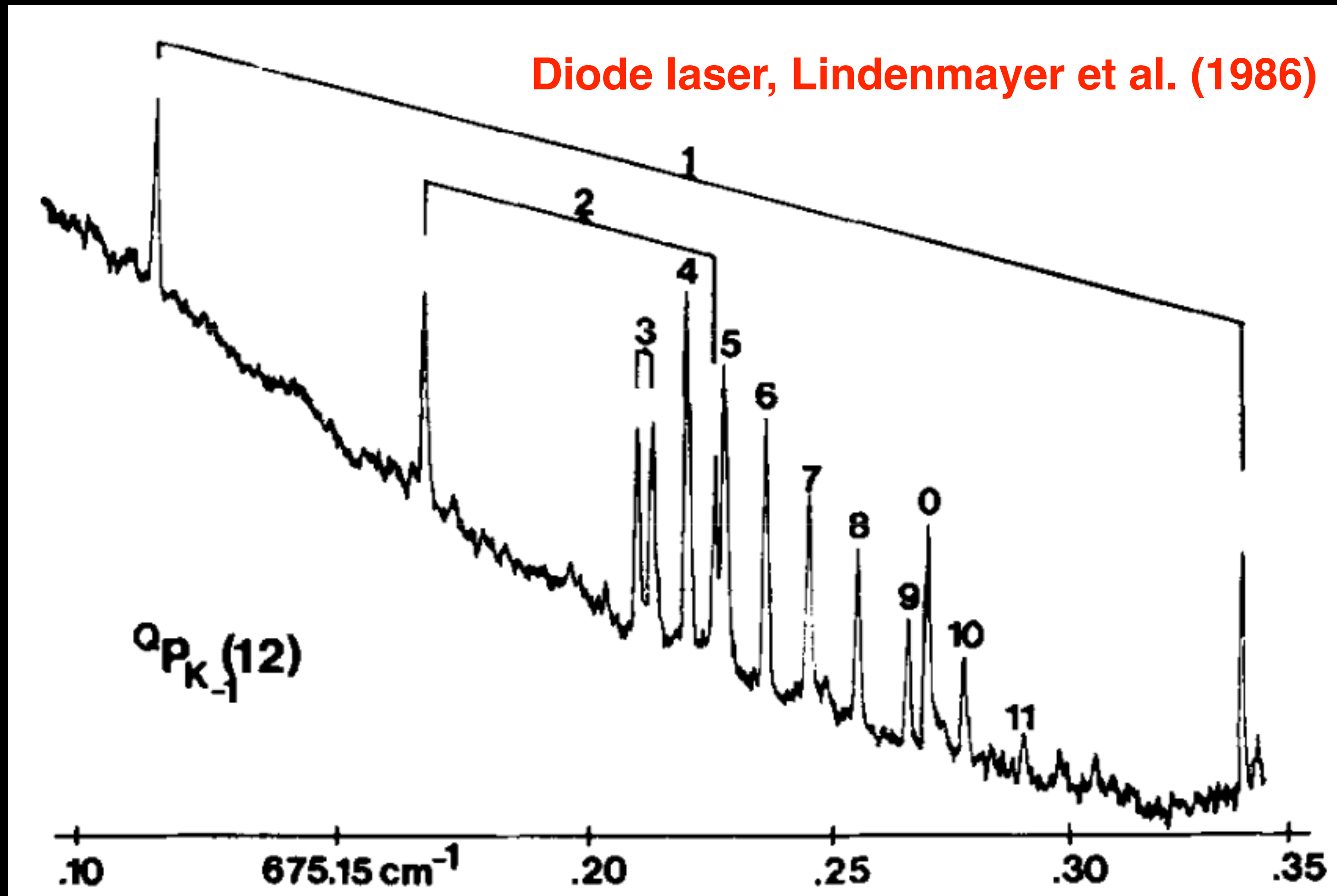
RF discharge of SO_2

a - type band



Diode laser, Lindenmayer et al. (1986)

“Old” vs. new


Diode laser, Lindenmayer et al. (1986)
1
2
3
4
5
6
7
8
0
9
10
11
$^{Q}P_{K_{-1}}(12)$
.10
675.15 cm^{-1}
.20
.25
.30
.35

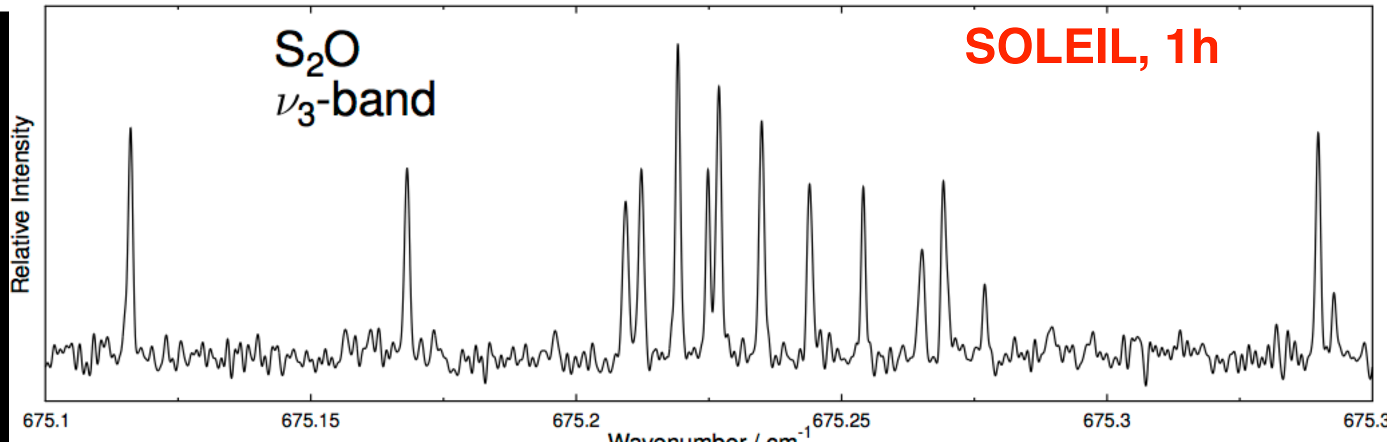

S_2O
ν_3-band
SOLEIL, 1h
Relative Intensity
675.1
675.15
675.2
675.25
675.3
675.35
Wavenumber / cm^{-1}

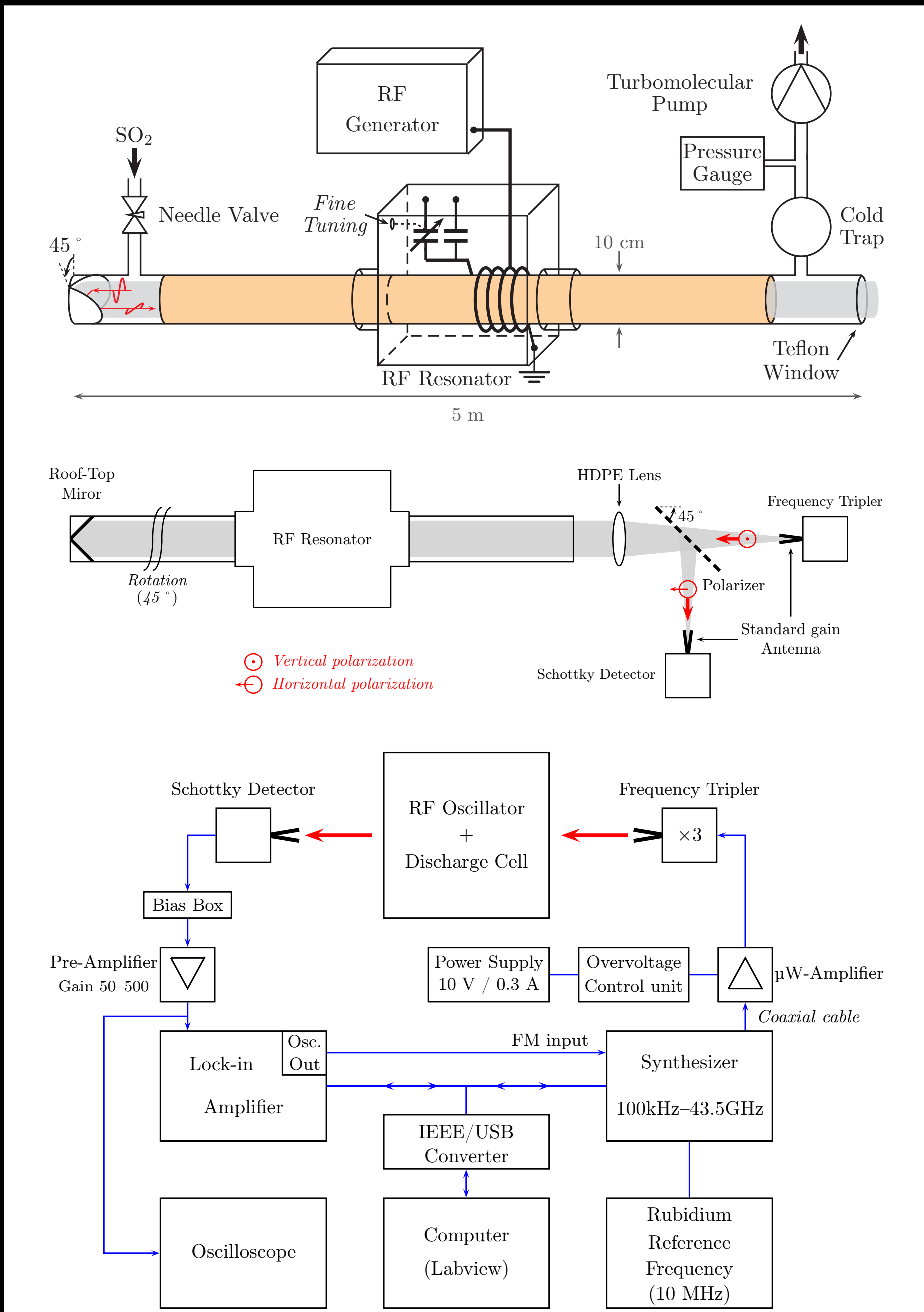
TABLE IV

Rotational and Distortion Constants Determined for $^{32}S_2{}^{16}O$ (in GHz)

	(000)	(100)	(010)	(001)
A	41.915426(11)	41.537208(45)	42.479669(30)	41.915368(49)
B	5.0590985(11)	5.0490555(67)	5.0597847(51)	5.0361446(74)
C	4.5071612(11)	4.4956140(69)	4.5008537(44)	4.4868797(70)
$\Delta_J \cdot 10^6$	1.8860(12)	1.9001(14)	1.968(46)	1.8835(16)
$\Delta_{JK} \cdot 10^5$	-3.2090(39)	-3.2482(41)	-3.15(11)	-3.2090(44)
$\Delta_K \cdot 10^3$	1.19735(69)	1.18142(71)	1.2890(64)	1.20937(69)
$\delta_J \cdot 10^7$	3.4460(19)	3.498(10)	3.554(27)	3.4341(92)
$\delta_K \cdot 10^5$	1.2178(29)	1.219(14)	1.264(29)	1.226(20)
$H_{KJ} \cdot 10^9$	-4.51(54)[a)]	-4.51(54)[a)]	b)	-4.51(54)[a)]
$H_K \cdot 10^8$	9.0(16)[a)]	9.0(16)[a)]	b)	9.0(16)[a)]
ν_0 (cm^{-1})		1166.453885(69)		679.136537(92)

a) = assumed to have same value in all three states, all other sextic terms constrained to zero; b) = constrained to zero.

Lindenmayer et al. (1986)



Martin-Drumel et al. (2015)

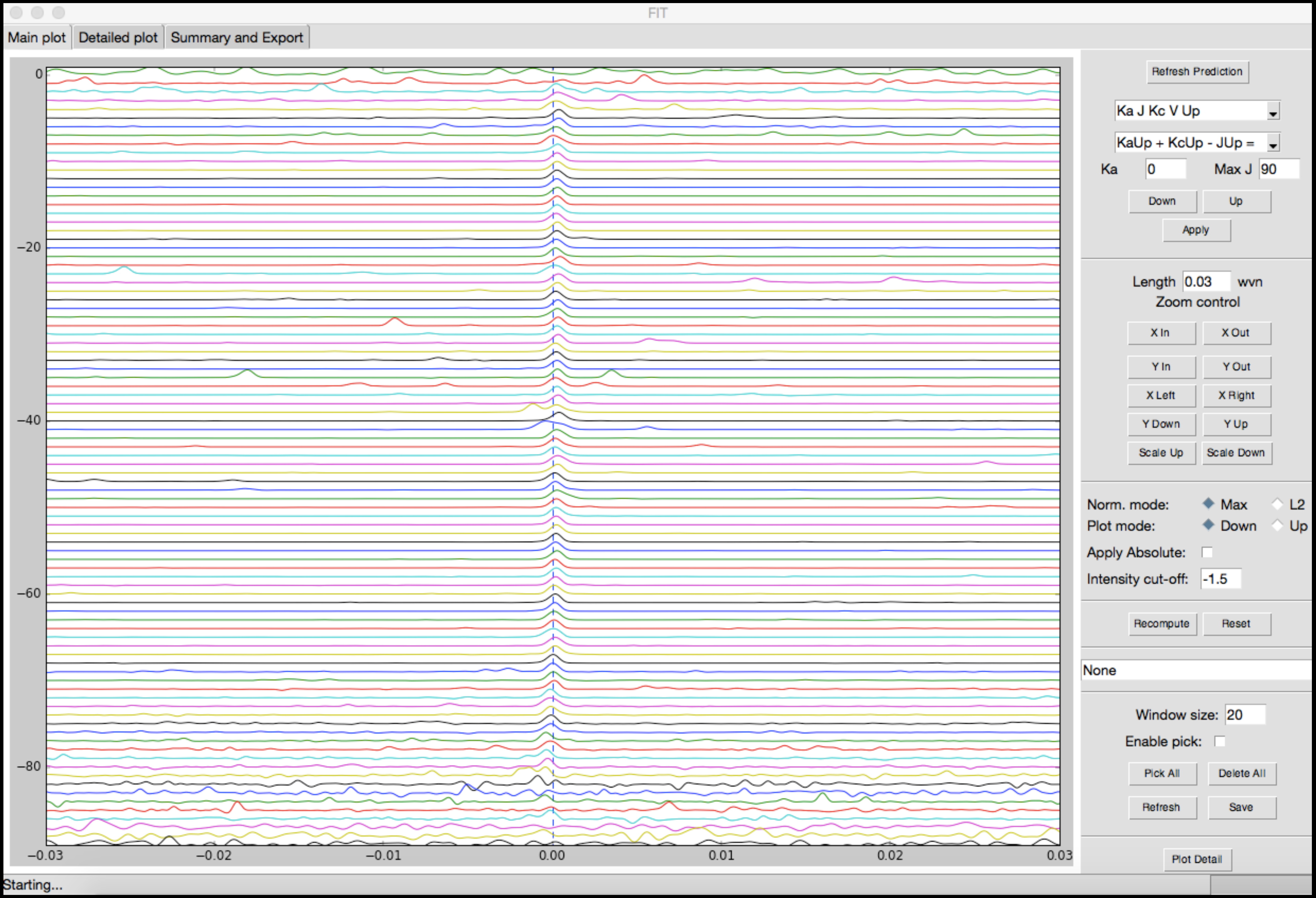
Prior to ASAP analysis:

A little bit of "cheating"

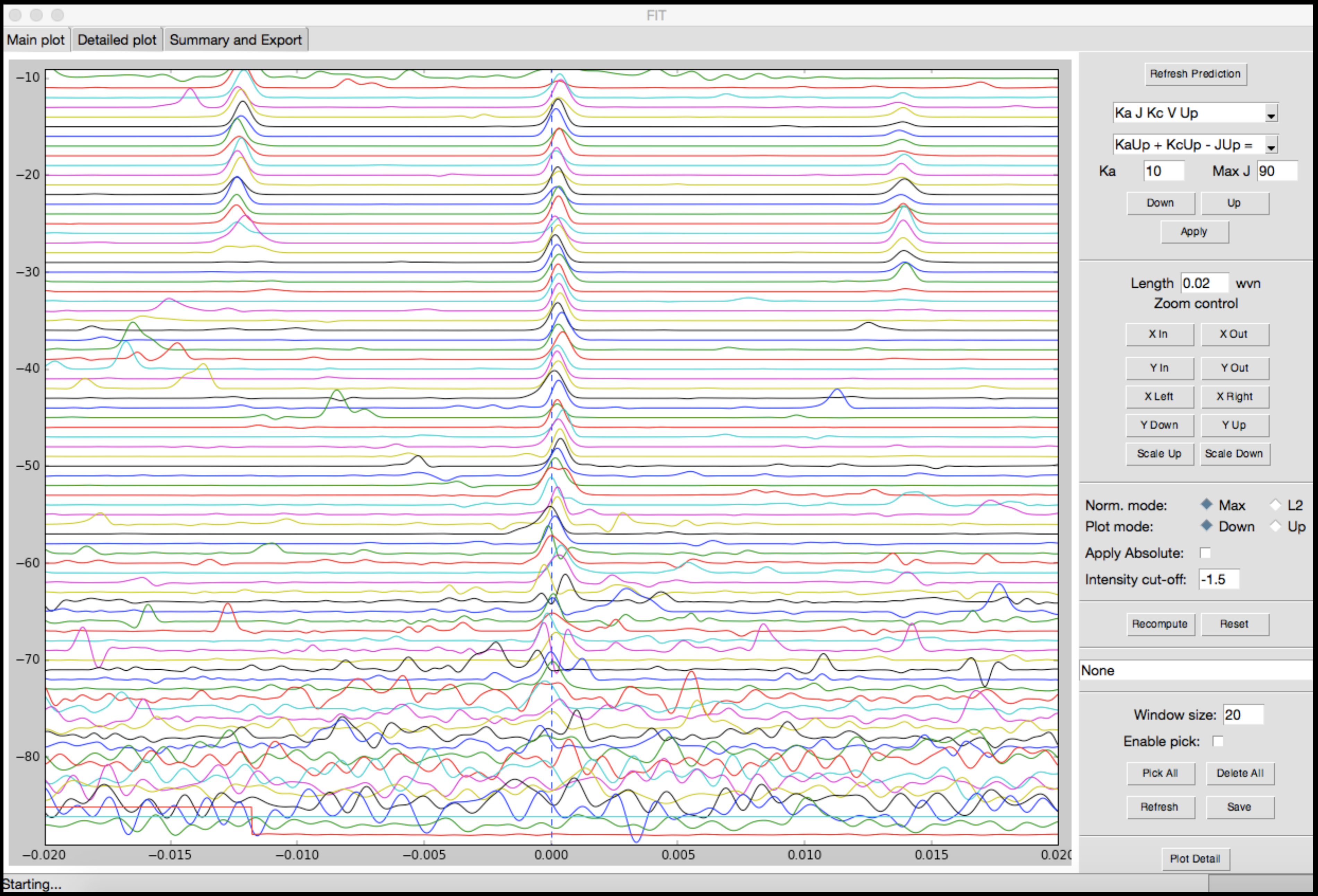
Mmw-measurements of (0,0,1) vibrational satellites in the 257 to 278 GHz regime $J \leqq 29$ and $K_a \leqq 19$

Target state characterized "comparably well"

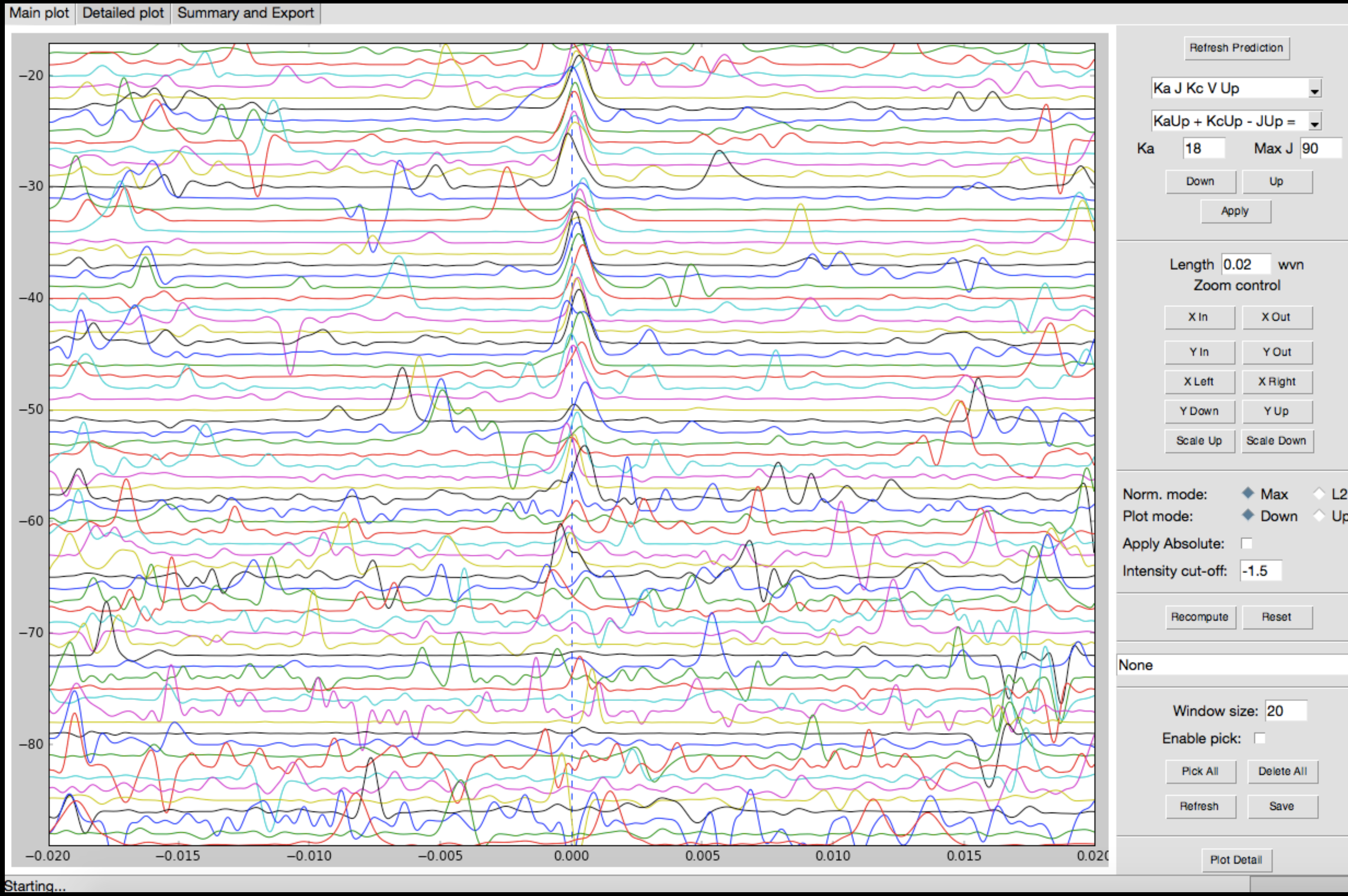
Assignment procedure: ASAP
K_a = 0 at the very start



Assignment procedure: ASAP
K_a = 10 at the very start



Assignment procedure: ASAP
K_a = 18 at the very start



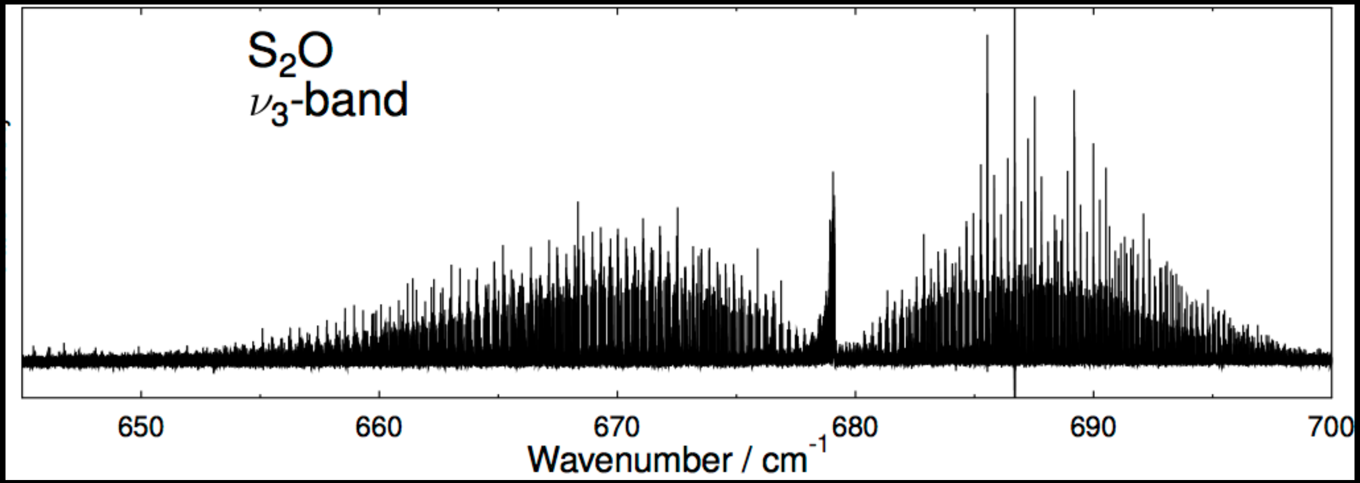
New data for the (0,0,1) state

MMW study at Cologne:

some 70 Lines from 257 to 278 GHz

SOLEIL / ASAP:

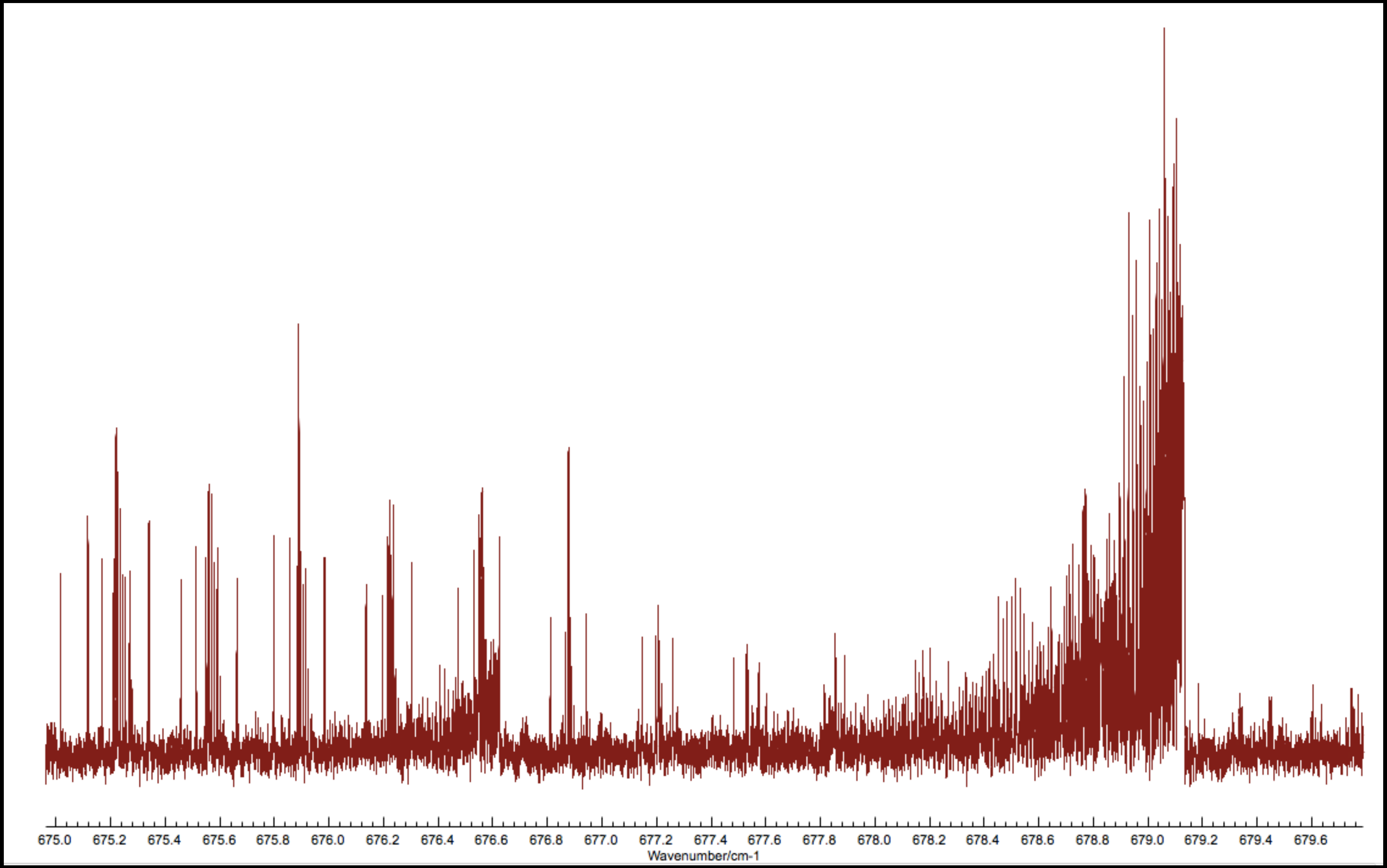
full band observed
2240 energy levels with $J \leqq 84$ and $K_a \leqq 20$



Parameter sets

Parameter	Lindenmayer et al. (2006) (0, 0, 1)	this study (0, 0, 1)
A_v	41915.368(49)	41915.51769(80)
B_v	5036.1446(74)	5036.16425(18)
C_v	4486.8797(70)	4486.89604(21)
$\Delta_{Jv} \times 10^3$	1.8835(44)	1.89320(11)
$\Delta_{JKv} \times 10^3$	−32.090(44)	−32.1260(17)
Δ_{Kv}	1.20937(69)	1.213303(33)
$\delta_{Jv} \times 10^3$	0.34341(92)	0.344670(62)
$\delta_{Kv} \times 10^3$	12.26(20)	12.426(24)
$\Phi_{Jv} \times 10^9$	⋯	1.049(20)
$\Phi_{JKv} \times 10^9$	⋯	51.1(62)
$\Phi_{KJv} \times 10^6$	⋯	−4.971(25)
$\Phi_{Kv} \times 10^3$	⋯	0.12591(19)
$\phi_{Jv} \times 10^9$	⋯	0.515(11)
$\phi_{JKv} \times 10^9$	⋯	17.5(48)
$\phi_{Kv} \times 10^6$	⋯	5.86(58)
$L_{KKJv} \times 10^9$	⋯	0.673(24)
$L_{Kv} \times 10^9$	⋯	−18.25(31)
$\tilde{\nu}$ / cm^{-1}	679.136537(92)	679.1364116(36)

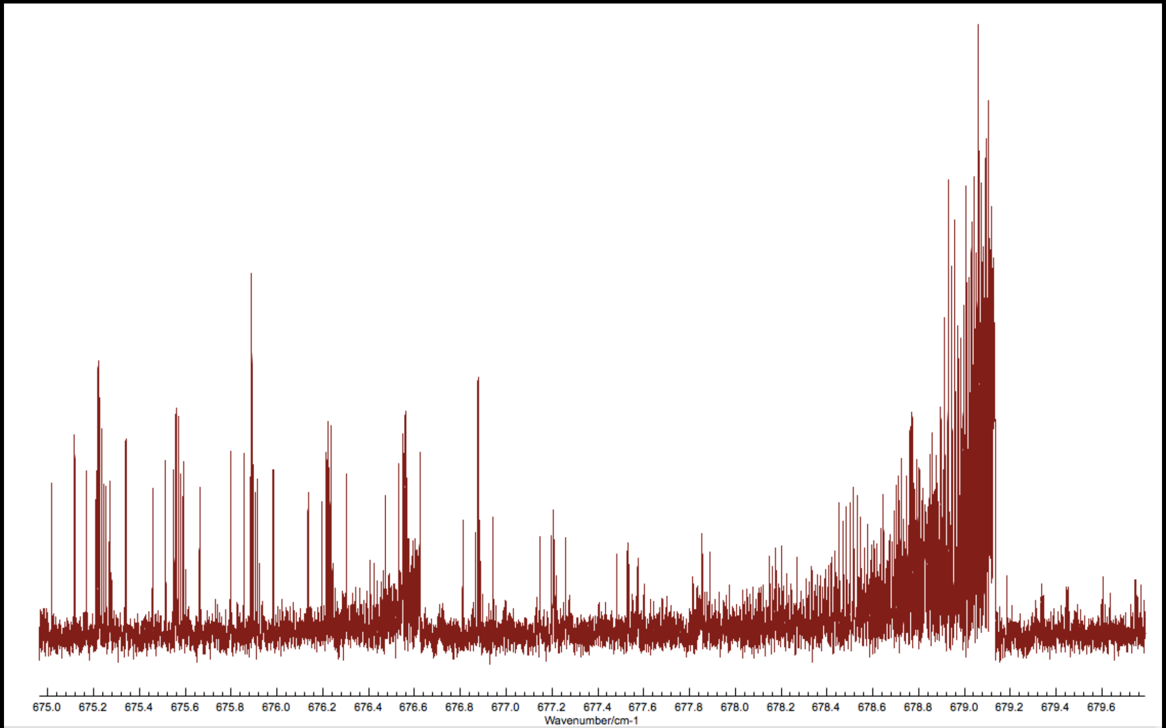
Digging deeper: the $\nu_3 + \nu_2 - \nu_2$ hot band



The $\nu_3 + \nu_2 - \nu_2$ hot band: Prior knowledge and initial guess

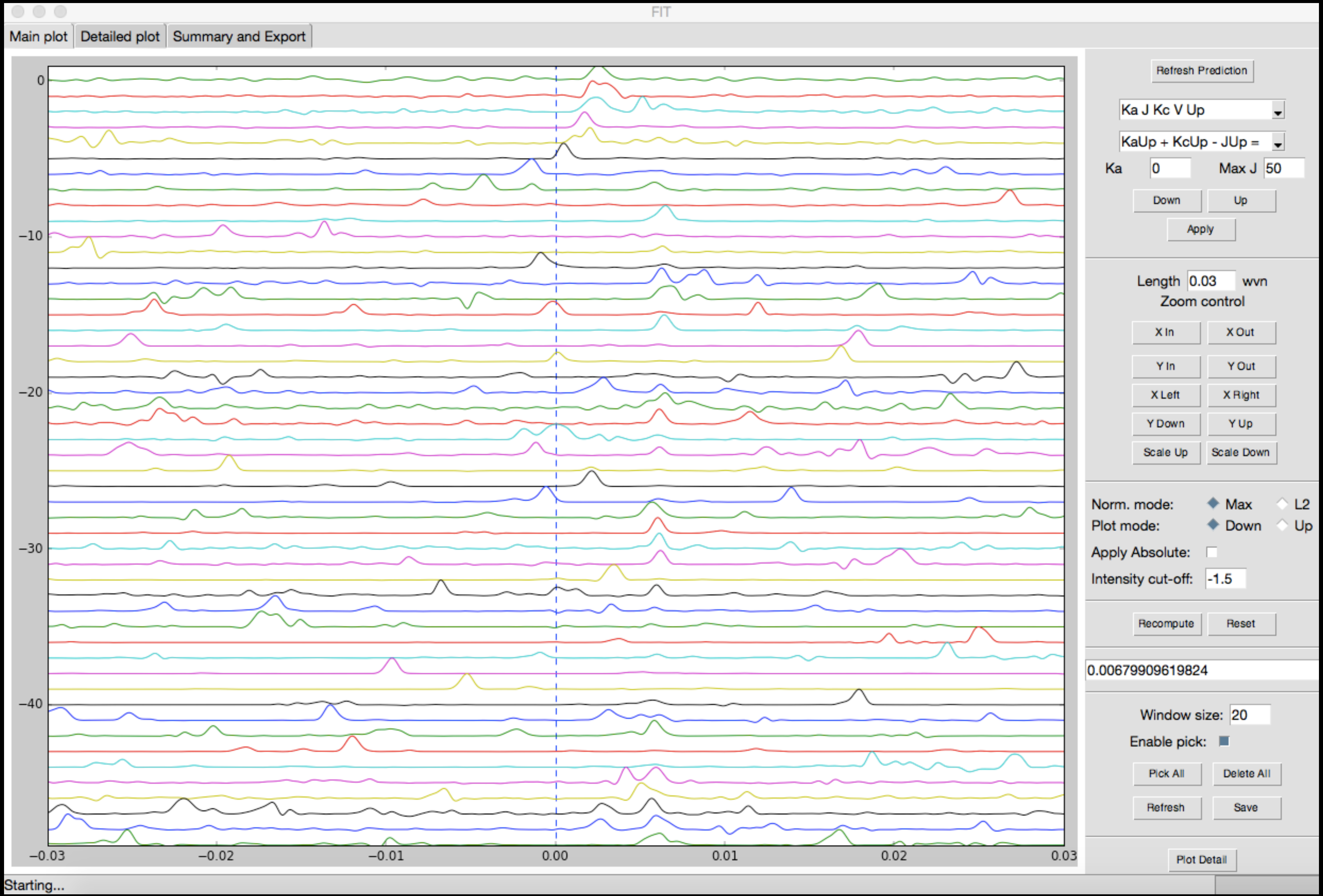
(0,1,0) very well characterized
Seven FTMW lines in (0,1,1):
⇒ three rotational constants and one cd term

Band center estimate from spectrum

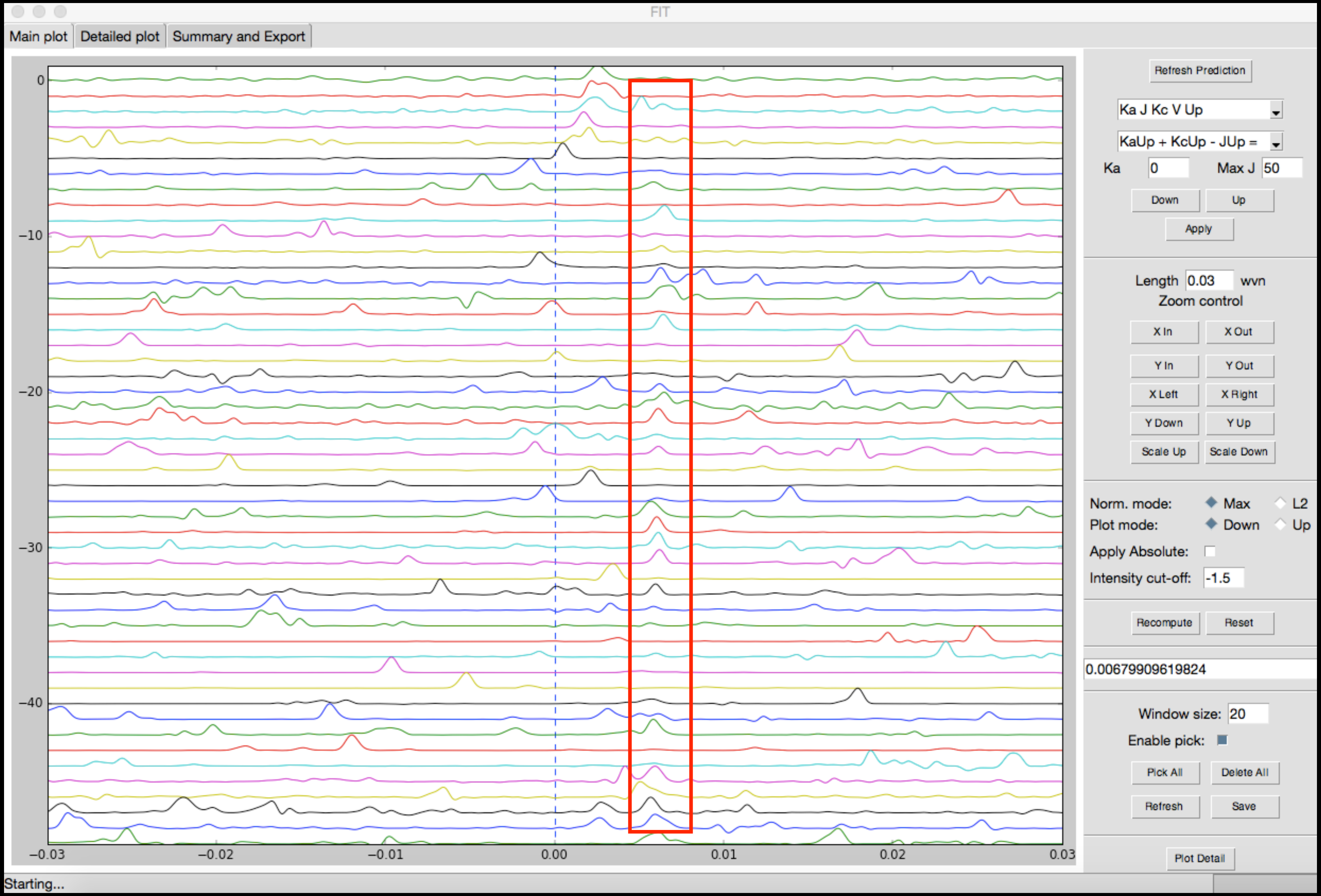


Estimate of full set of quartic cd-terms for (0,1,1) state from (0,0,1) and (0,1,0)/(0,0,0) states, sextic terms kept fixed at (0,0,1)

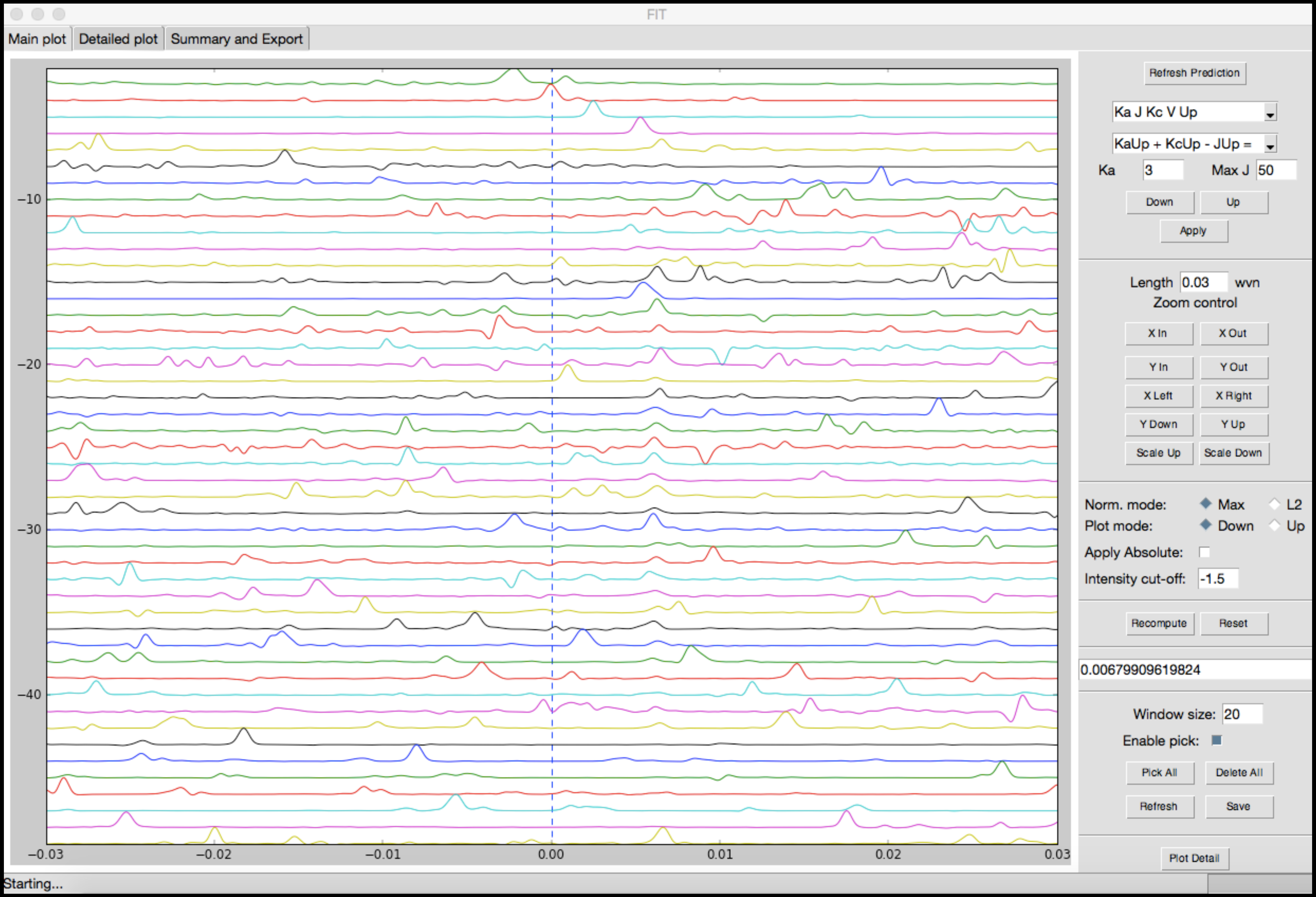
The $\nu_3 + \nu_2 - \nu_2$ hot band: ASAP and $K_a = 0$



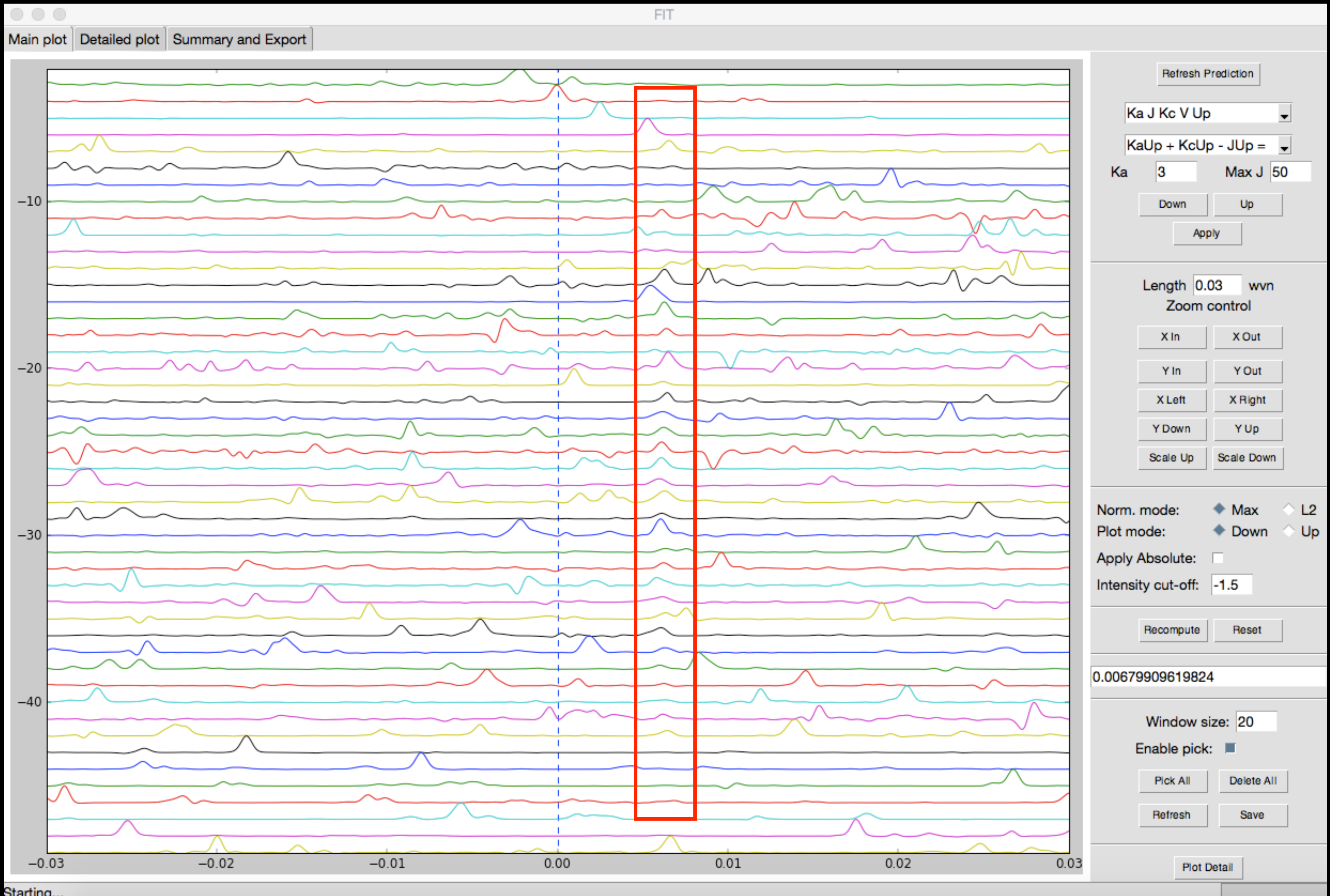
The $\nu_3 + \nu_2 - \nu_2$ hot band: ASAP and $K_a = 0$



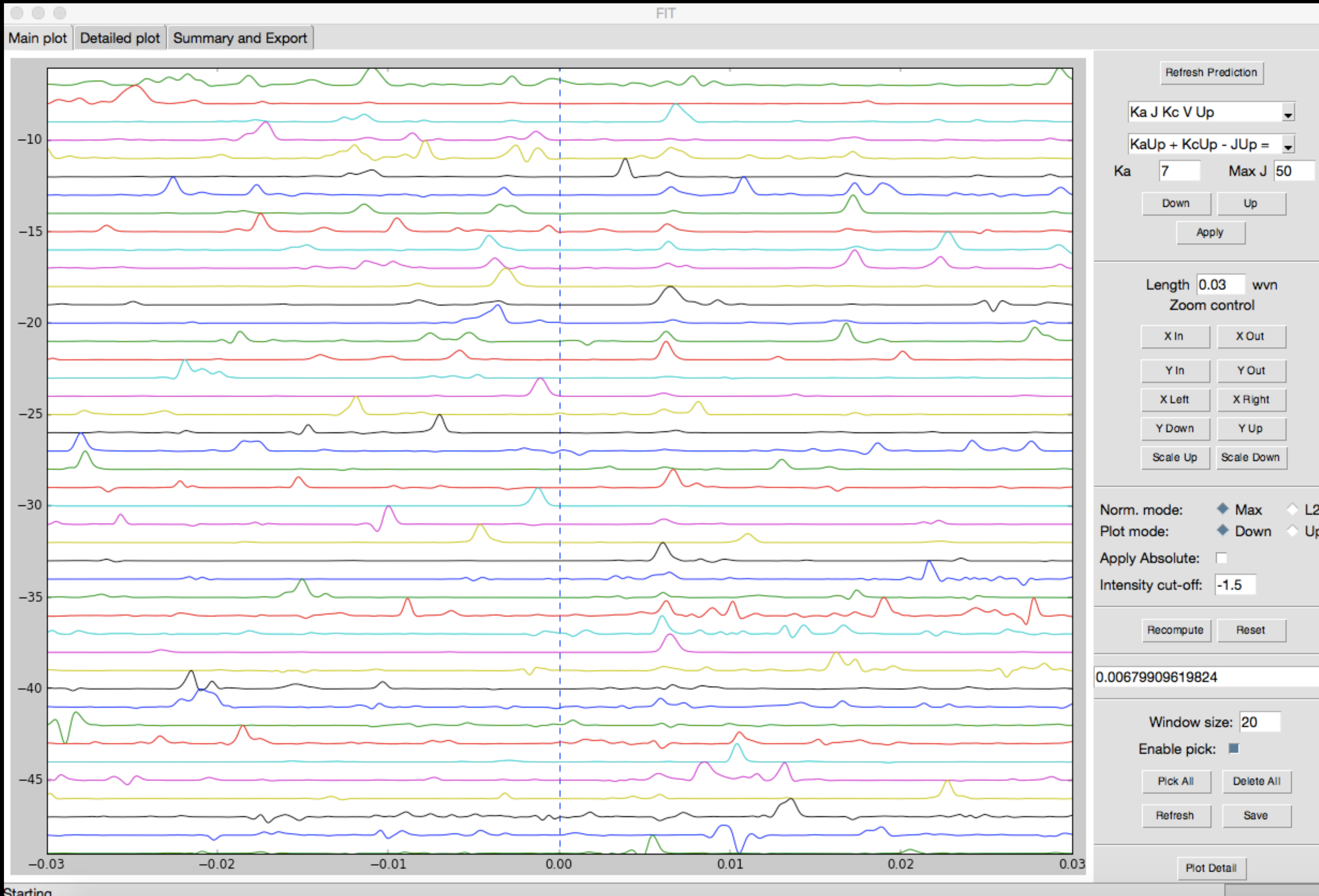
The $\nu_3 + \nu_2 - \nu_2$ hot band: ASAP and $K_a = 3$



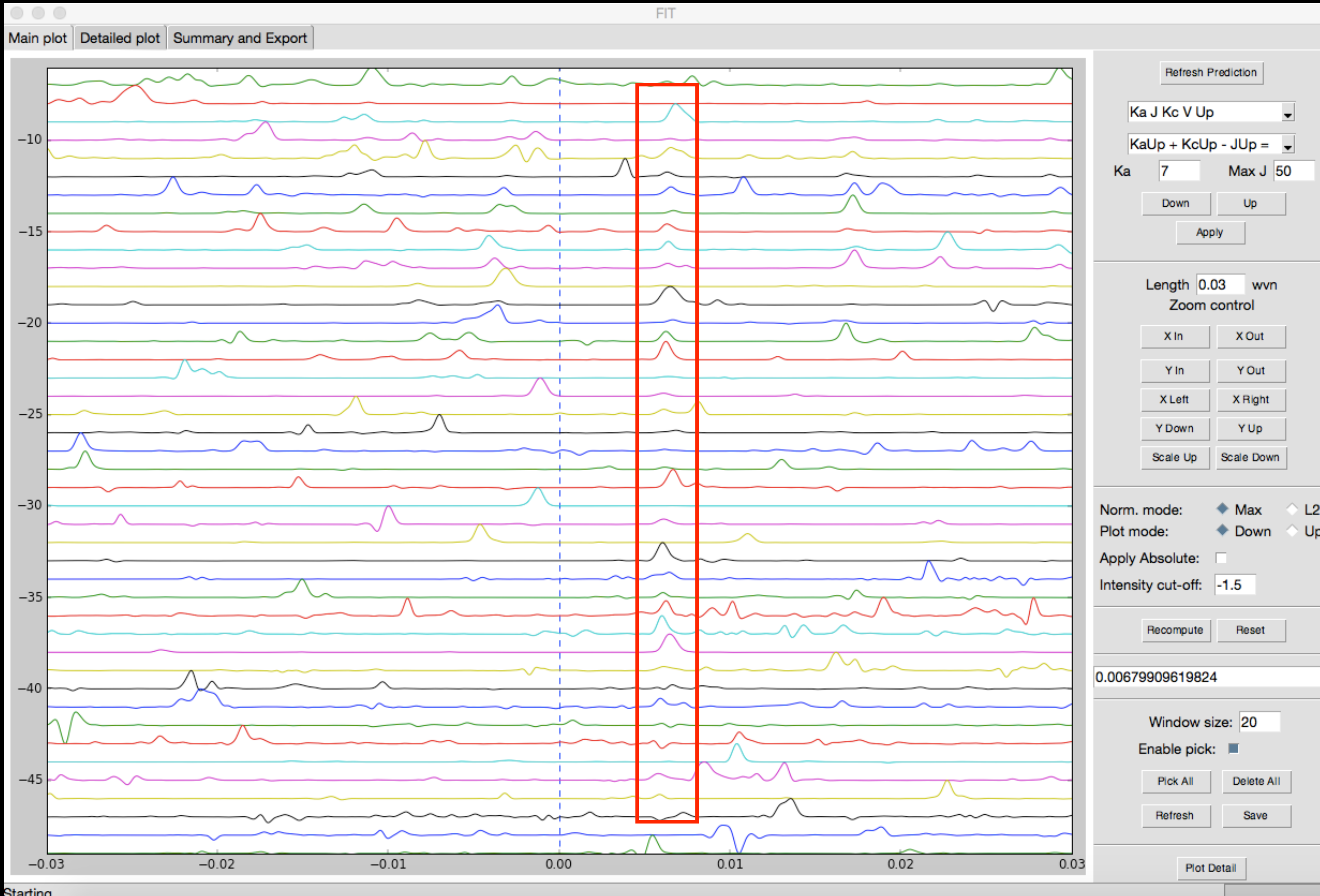
The $\nu_3 + \nu_2 - \nu_2$ hot band: ASAP and $K_a = 3$



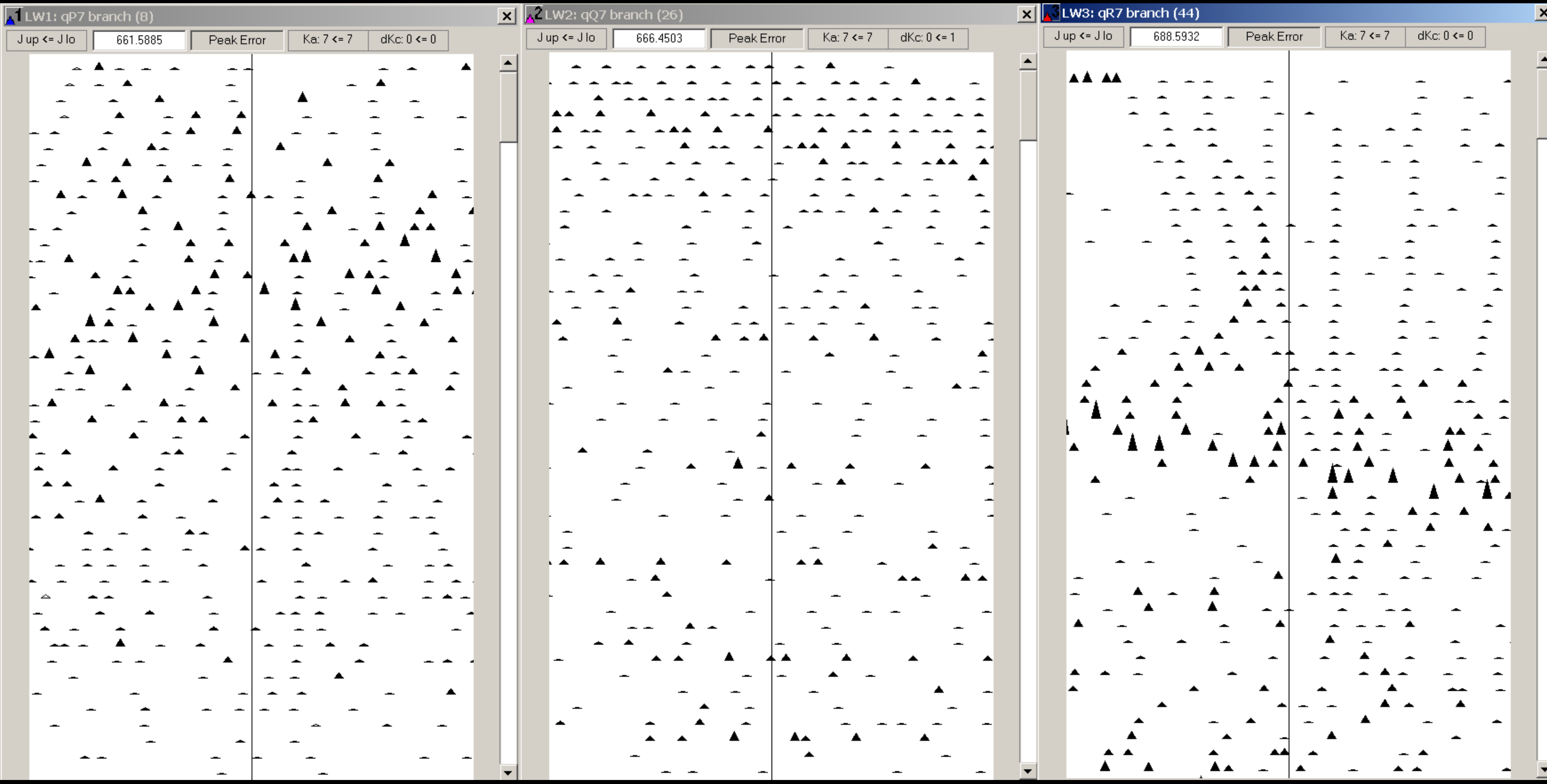
The $\nu_3 + \nu_2 - \nu_2$ hot band: ASAP and $K_a = 7$



The $\nu_3 + \nu_2 - \nu_2$ hot band: ASAP and $K_a = 7$



The $\nu_3 + \nu_2 - \nu_2$ hot band: LWWa at $K_a = 7$

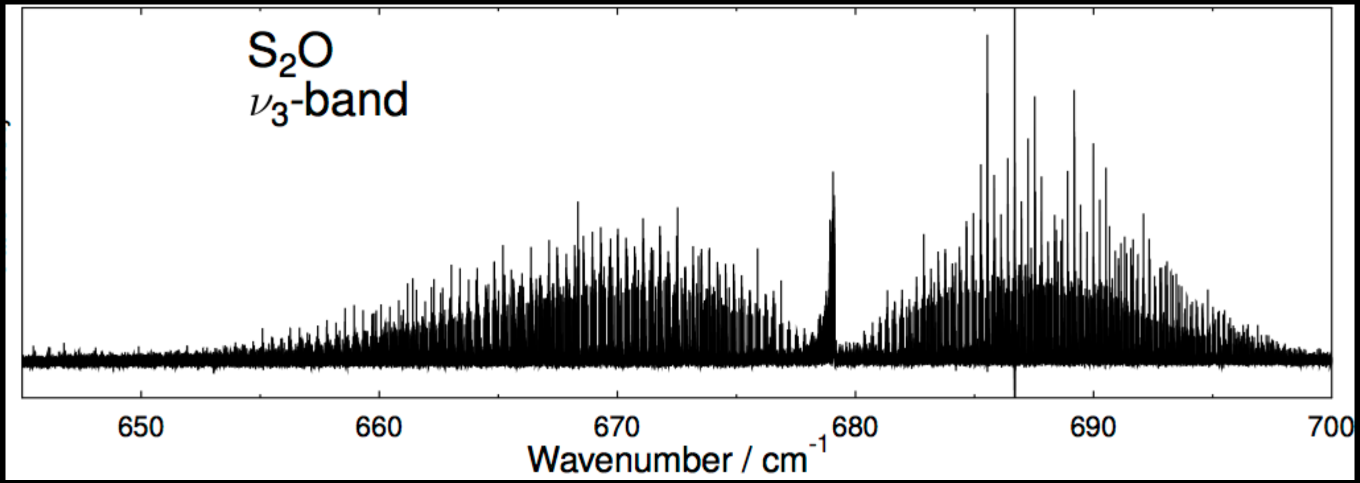


P **Q** **R**

New data for the (0,1,1) state

SOLEIL / ASAP:

485 energy levels with $J \leqq 64$ and $K_a \leqq 11$

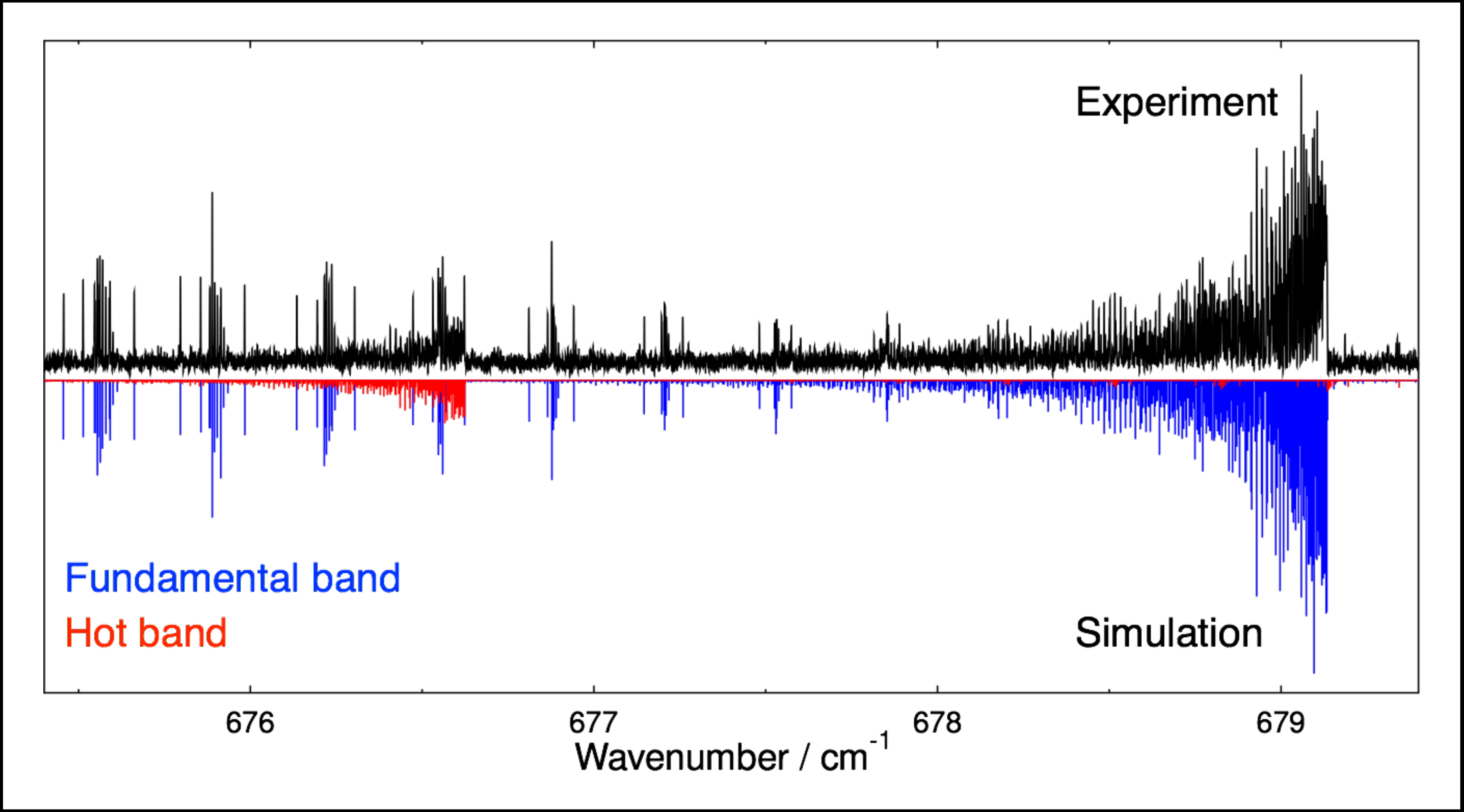


Parameter sets

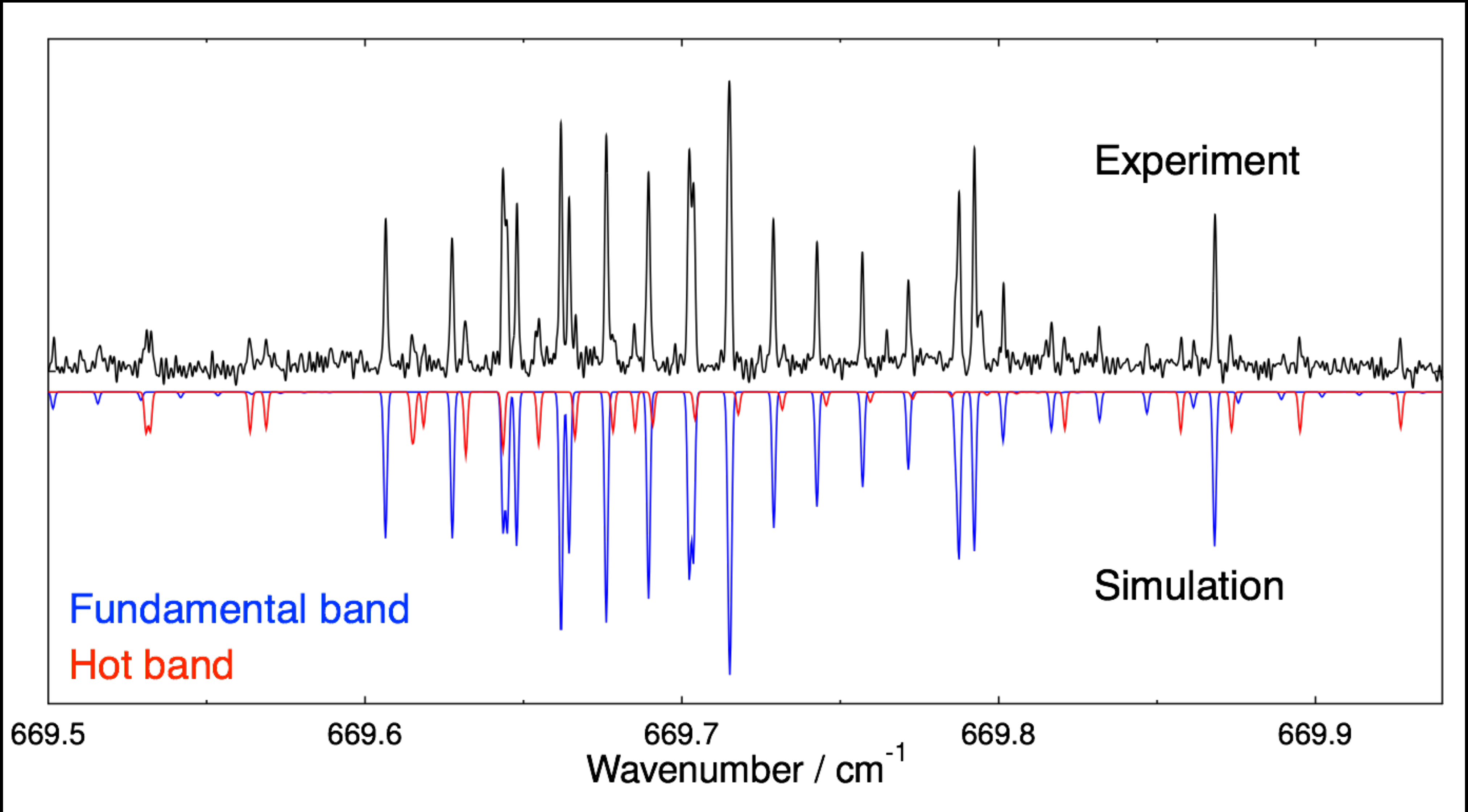
Parameter	Lindenmayer et al. (2006) (0, 0, 1)	this study (0, 0, 1)	Thorwirth et al. (2006) (0, 1, 1)	this study (0, 1, 1)
A_v	41915.368(49)	41915.51769(80)	42480.4(68)	42480.497(44)
B_v	5036.1446(74)	5036.16425(18)	5036.91332(73)	5036.91810(48)
C_v	4486.8797(70)	4486.89604(21)	4480.56649(73)	4480.56215(47)
$\Delta_{Jv} \times 10^3$	1.8835(44)	1.89320(11)	···	1.90242(68)
$\Delta_{JKv} \times 10^3$	−32.090(44)	−32.1260(17)	−33.34(58)	−33.193(59)
Δ_{Kv}	1.20937(69)	1.213303(33)	···	1.31011(45)
$\delta_{Jv} \times 10^3$	0.34341(92)	0.344670(62)	···	0.34857(25)
$\delta_{Kv} \times 10^3$	12.26(20)	12.426(24)	···	14.382(83)
$\Phi_{Jv} \times 10^9$	···	1.049(20)	···	1.042(165)
$\Phi_{JKv} \times 10^9$	···	51.1(62)	···	···
$\Phi_{KJv} \times 10^6$	···	−4.971(25)	···	−4.78(66)
$\Phi_{Kv} \times 10^3$	···	0.12591(19)	···	···
$\phi_{Jv} \times 10^9$	···	0.515(11)	···	···
$\phi_{JKv} \times 10^9$	···	17.5(48)	···	···
$\phi_{Kv} \times 10^6$	···	5.86(58)	···	···
$L_{KKJv} \times 10^9$	···	0.673(24)	···	···
$L_{Kv} \times 10^9$	···	−18.25(31)	···	···
$\tilde{\nu}$ / cm^{-1}	679.136537(92)	679.1364116(36)	···	1056.936446(21)

Fluorescence: 1056(5)
T. Müller et al. (1999)

Simulation of band centers



Simulation *P*-branch



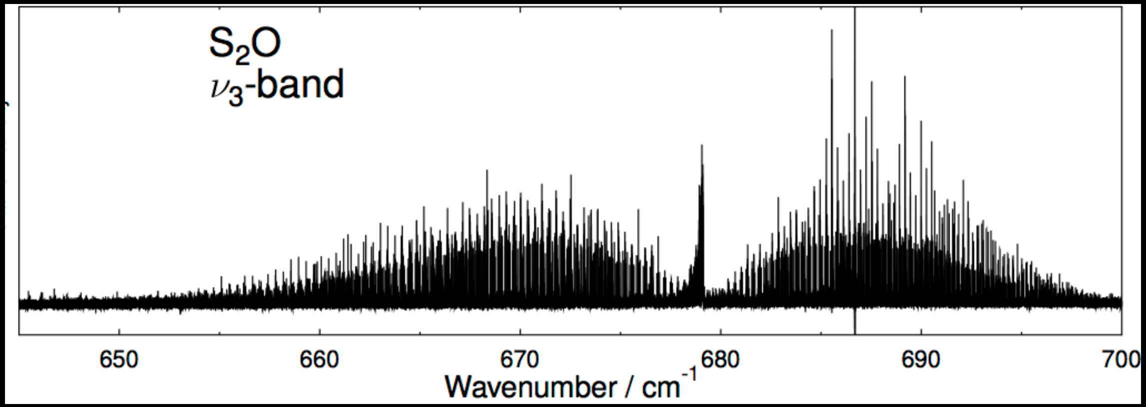
Conclusions and prospects

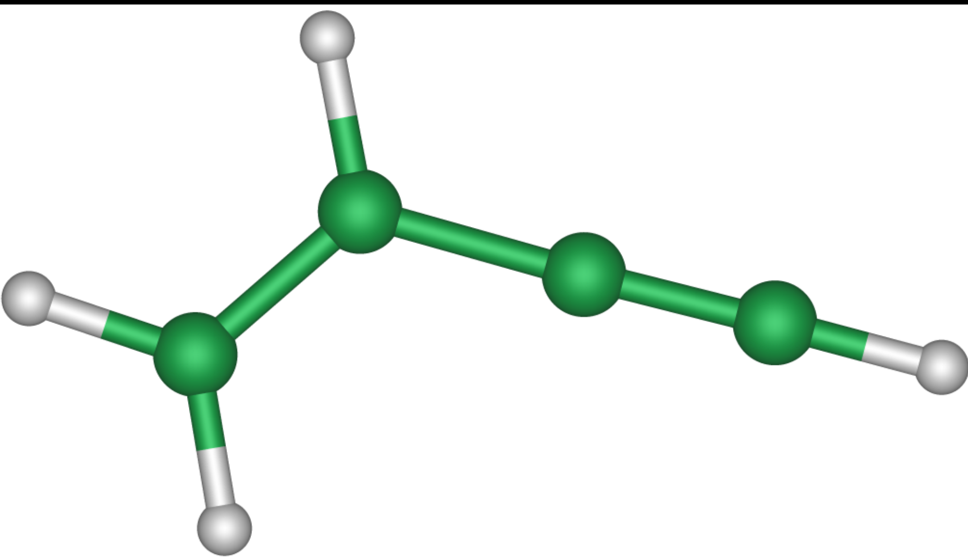
ASAP analysis of S_2O successful

Follow-up (sub)mmw measurements of S_2O

General application of ASAP analyses
of high-res spectra

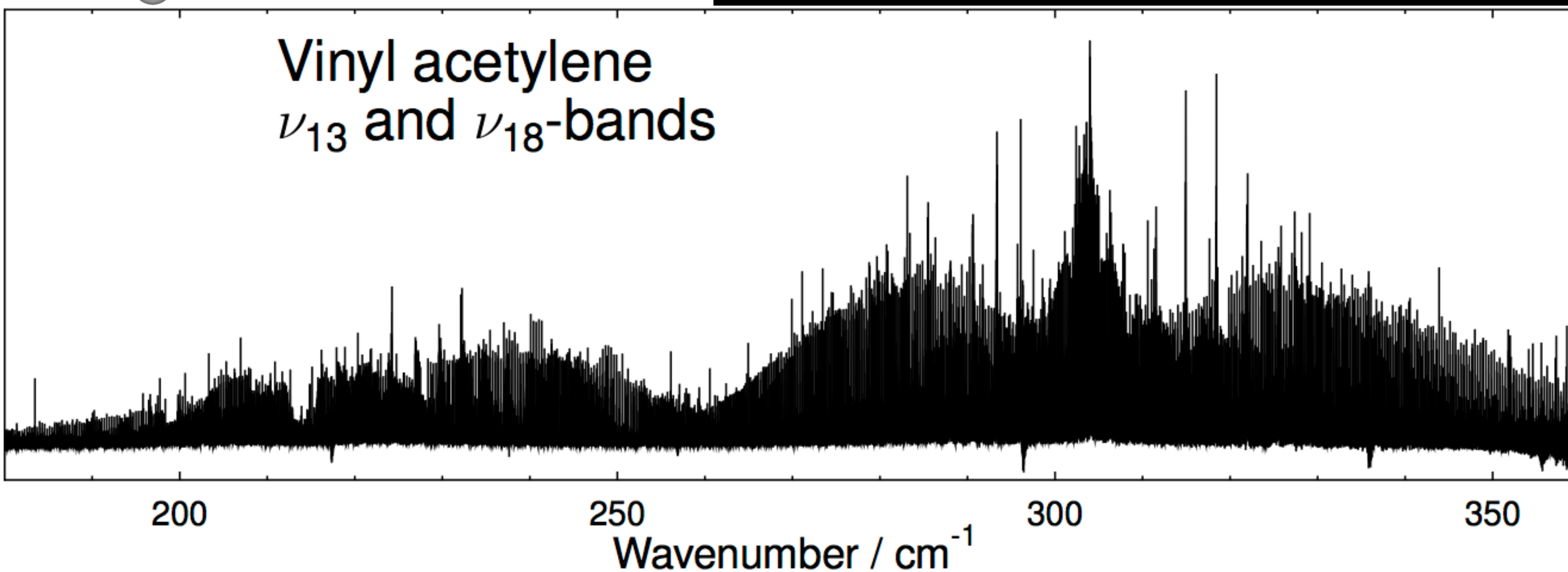
Check your files for “lost” data



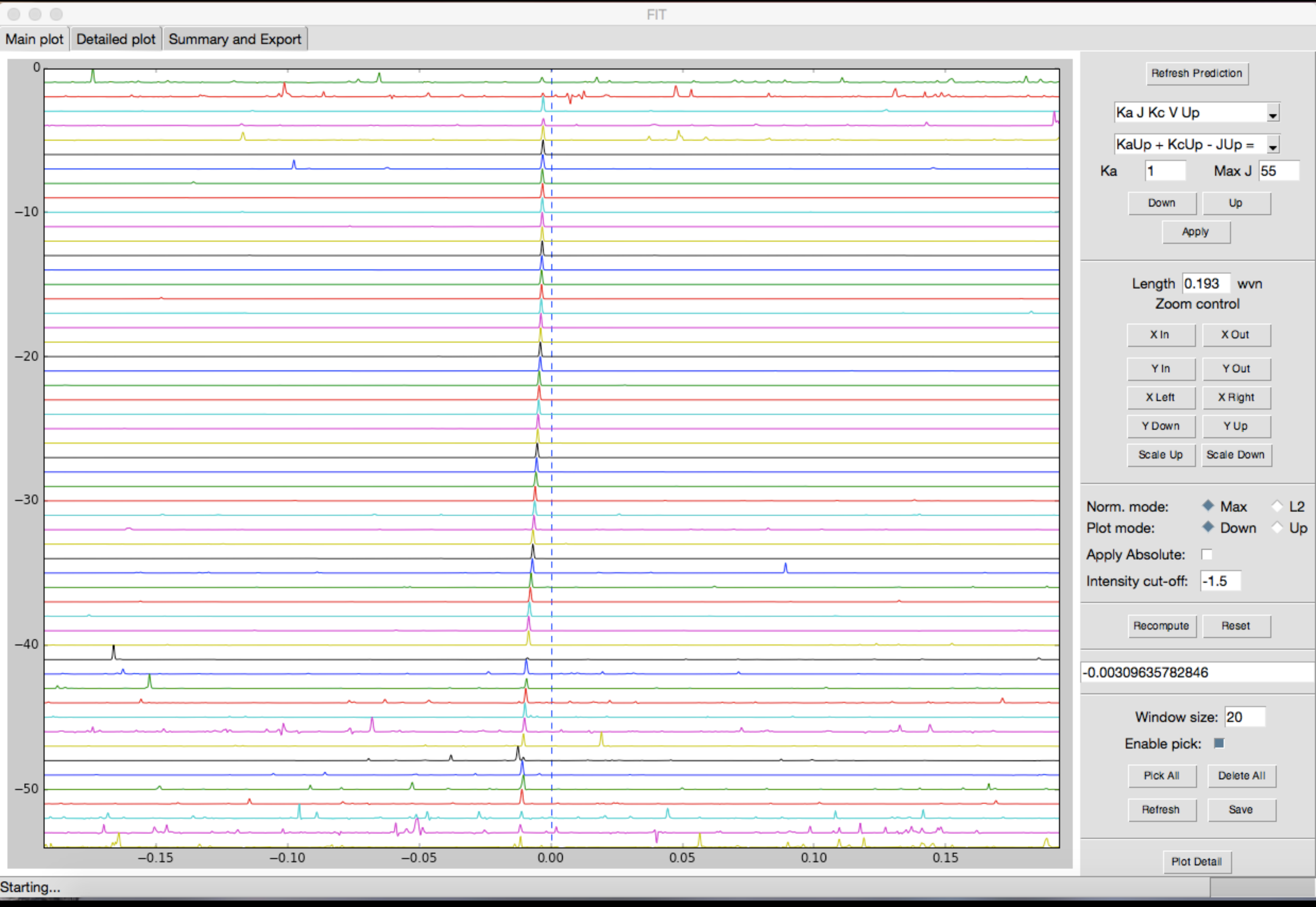


Vinyl acetylene FTIR-spectrum

taken at JLU Gießen
more than ten years ago
(Thorwirth, Lichau, Mellau, Müller et al.)



ASAP and the ν_{13} band of vinyl acetylene



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Thank you!

Outline

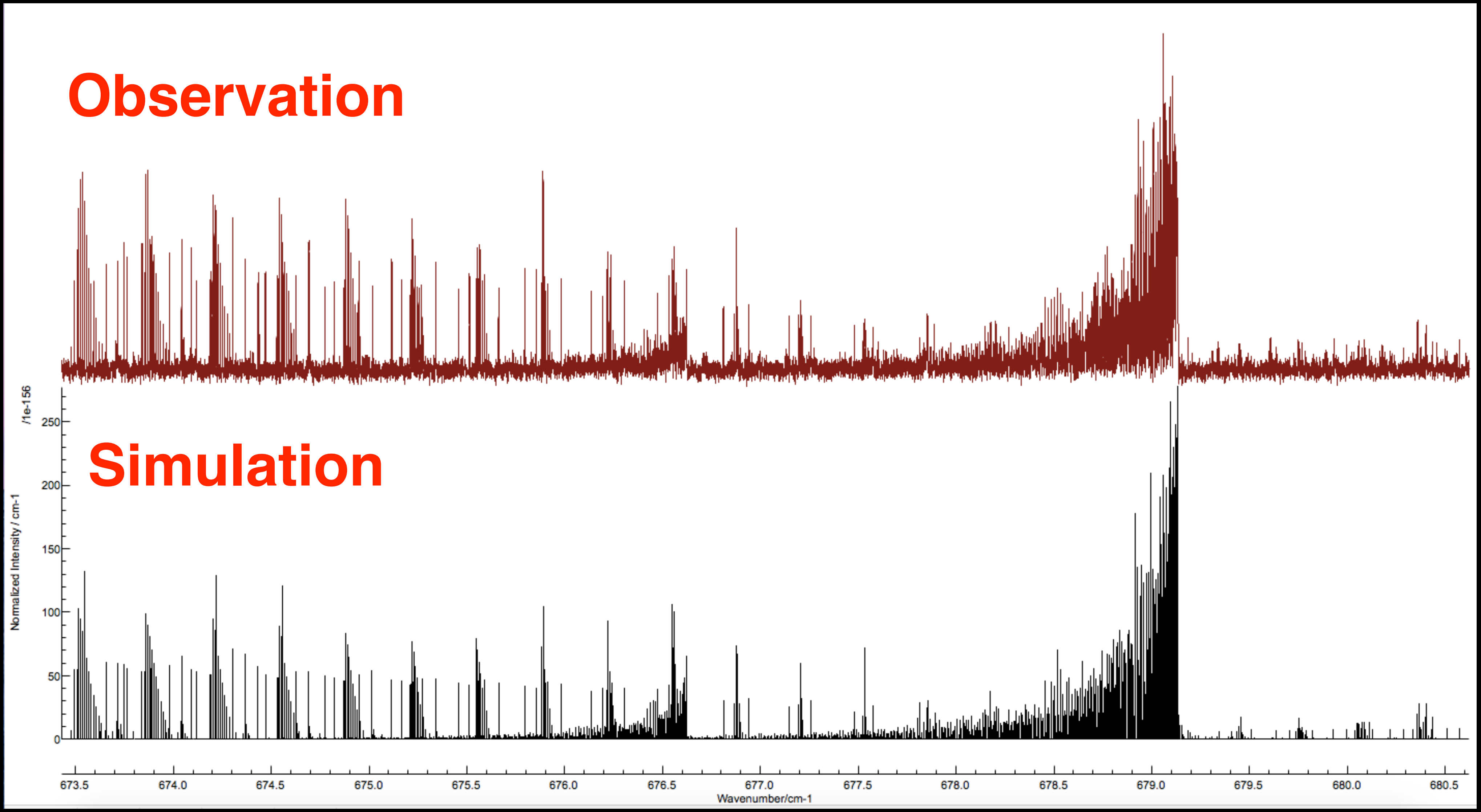
Motivation

Previous studies of S_2O

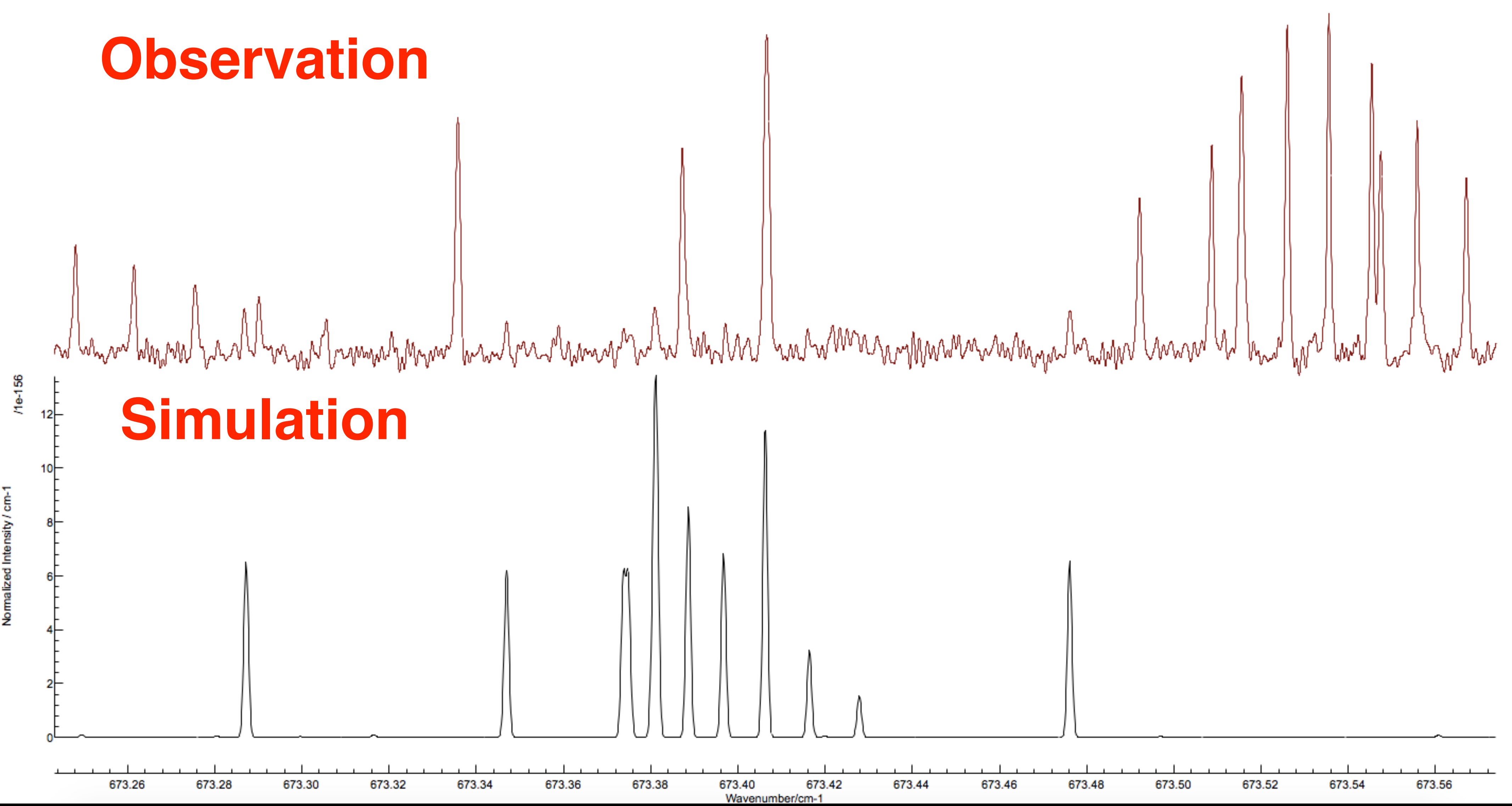
SOLEIL study

Prospects

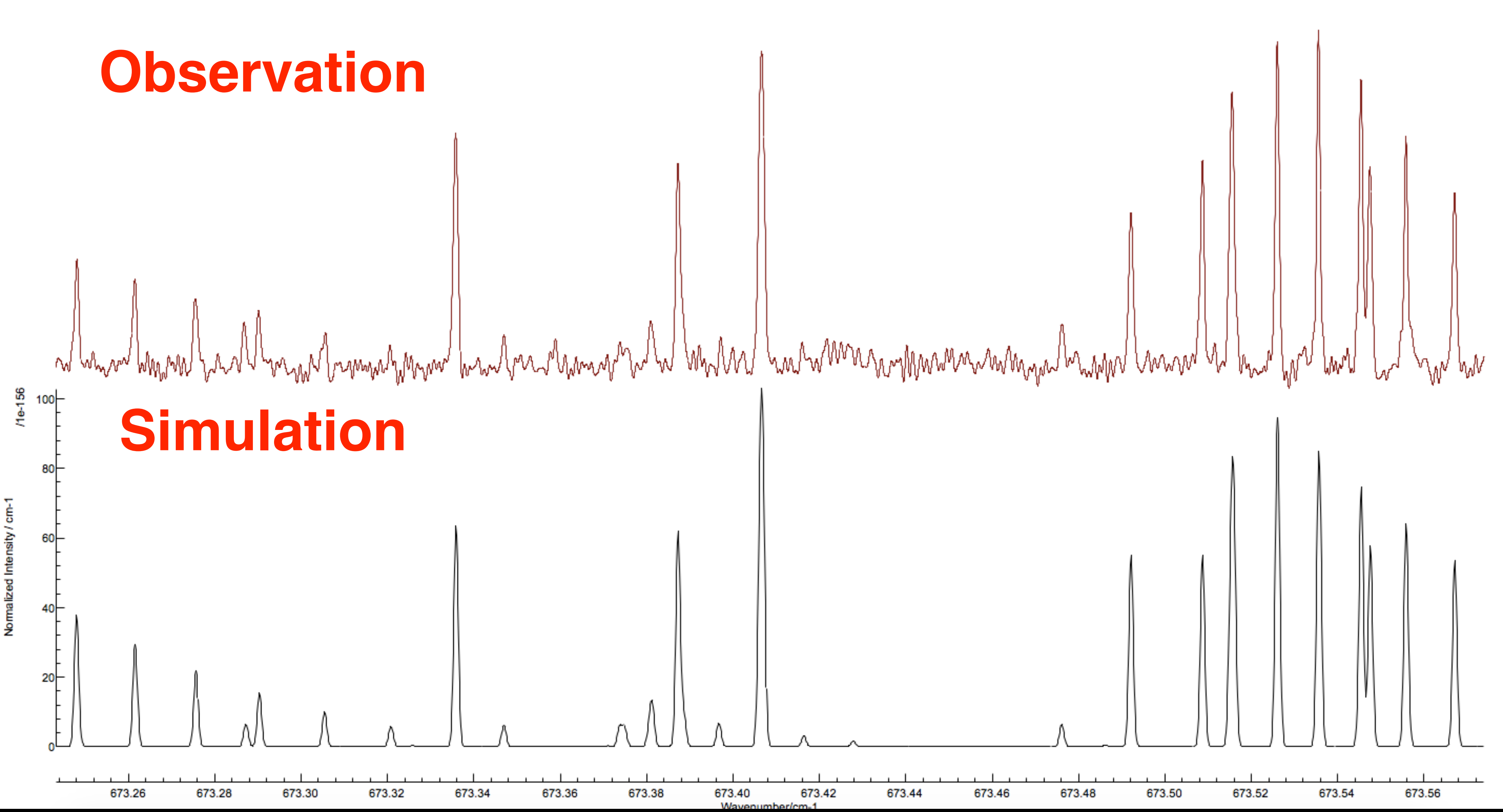
FInally: Observation vs. Simulation



FInally: Observation vs. Simulation



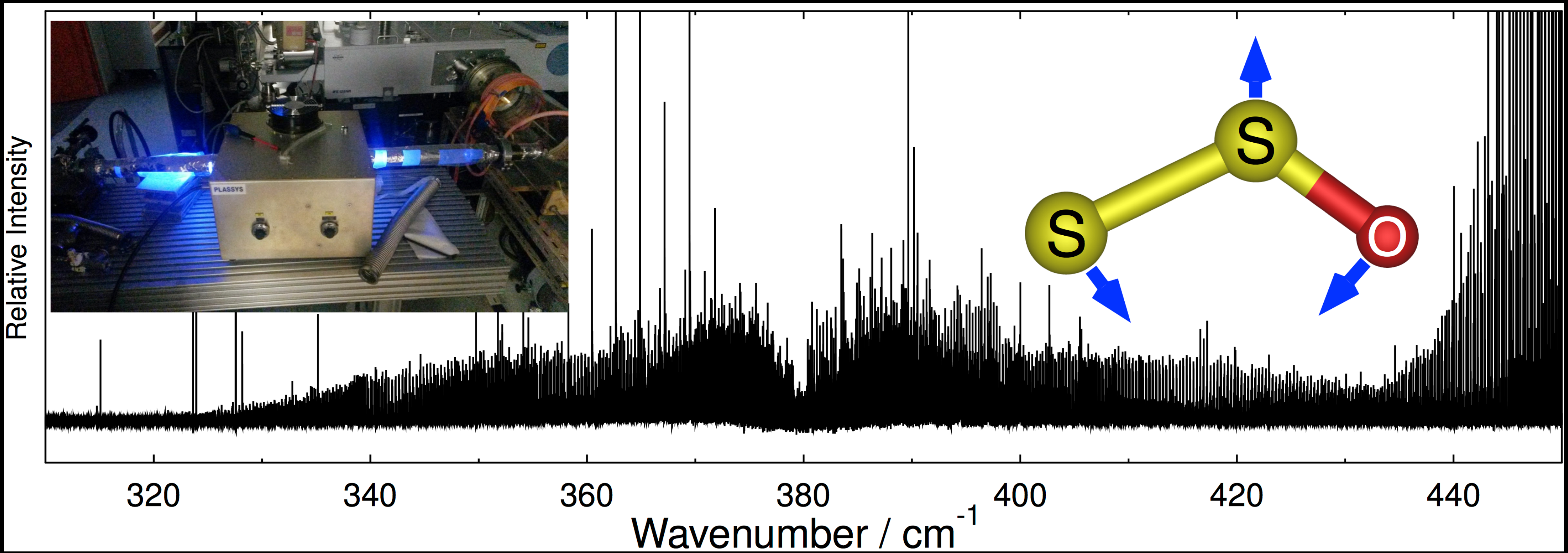
FInally: Observation vs. Simulation



Previous studies: IR

All three fundamental vibrational modes observed

$\nu_{1(\text{S-O-stretch})}$: 1166 cm^{-1} (Lindenmayer and Jones 1985)
$\nu_{2(\text{S-S-O-stretch})}$: 380 cm^{-1} (Martin-Drumel et al. 2015)
$\nu_{3(\text{S-S-stretch})}$: 679 cm^{-1} (Lindenmayer et al. 1986)



Martin-Drumel et al. (2015)