The SOLEIL view on sulfur rich oxides
The S_2O bending mode ν_2 at 380 cm^{-1} and its analysis using an Automated Spectral Assignment Procedure (ASAP)

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[2]Max-Planck-Institut für extraterrestrische Physik, Garching, Germany
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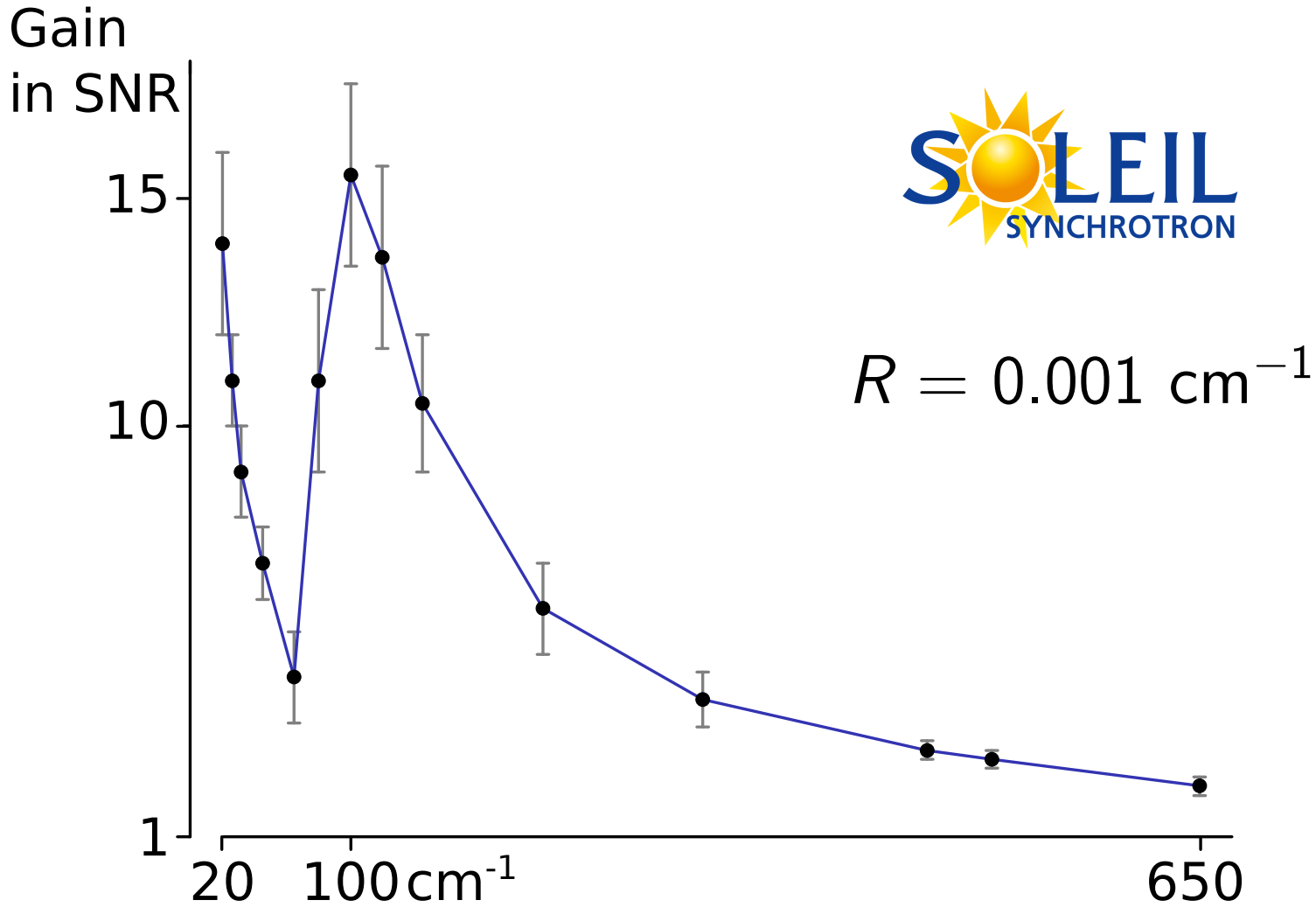
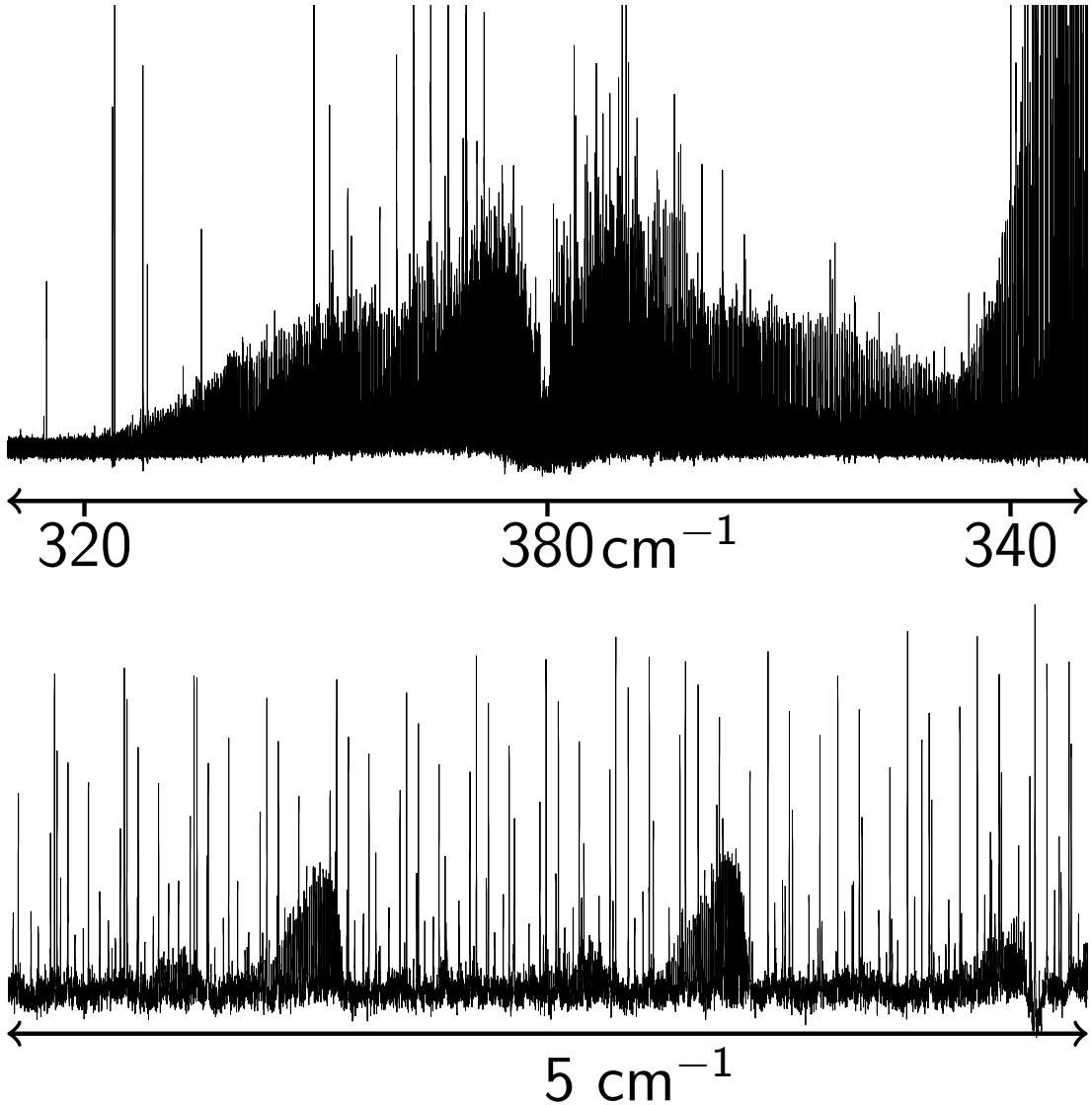
[5]SOLEIL Synchrotron, L'orme des Merisiers, Saint-Aubin, France

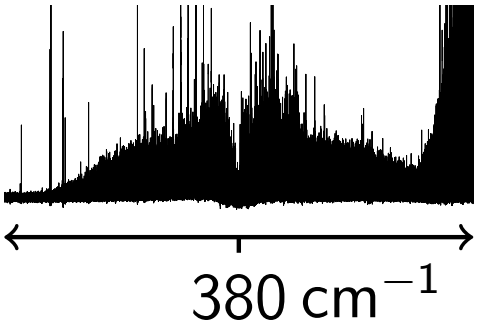
24 h with synchrotron radiation are months using classic sources

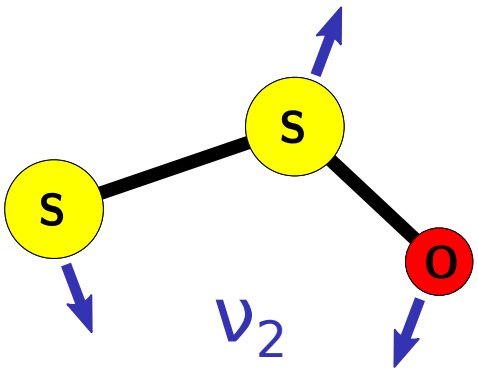


But the analysis of dense spectra is still time consuming



The ν_2 band of S_2O has been investigated





High resolution FIR spectrum[1]

SOLEIL

R=0.001 cm^{-1}

post-RF discharge

Semi-automatic analysis

[1] see talk RB08 by S. Thorwirth

A semi-automatic assignment procedure has enable a fast analysis of the spectrum

Automated
Spectral
Assignment
Procedure

- largely automated approach
- analysis of the ν_2 band of S_2O in only a few hours

The S_2O bending mode ν_2 at $380\,cm^{-1}$ and its analysis using ASAP

Principle of the ASAP

Study of the ν_2 mode of S_2O

Discussion on the procedure

ASAP: straightforward analysis of ro-vibrational spectra

One of the two vibrational state has to be well characterized

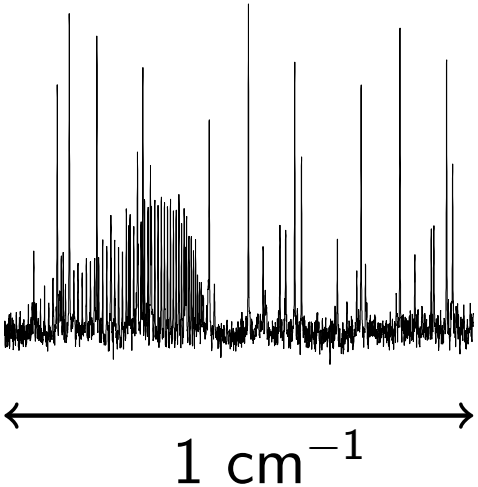
- Reference state
- Target state

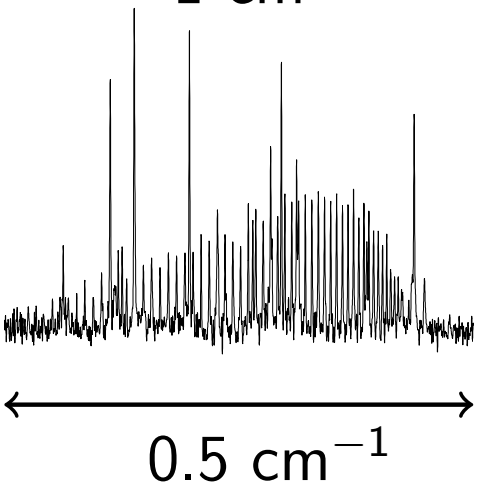
Determination of the energy levels in the target state

The ν_2 band of S_2O is a good test case

- Dense spectrum
  - *a*- and *b*-type transitions
  - hot band(s)

The ν_2 band of S_2O is a good test case



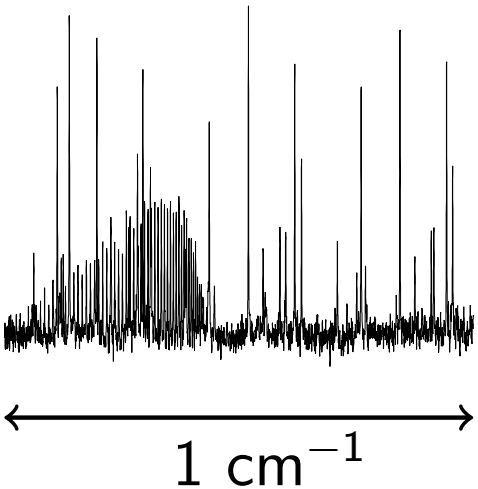


Dense spectrum

- *a*- and *b*-type transitions
- hot band(s)

Fully resolved

The ν_2 band of S_2O is a good test case



Dense spectrum

- *a*- and *b*-type transitions
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Fully resolved

Previous investigations in the MW and sub-mm[1]

- ground state
- vibrational satellites

[1] Tiemann, 1974; Thorwirth, 2006

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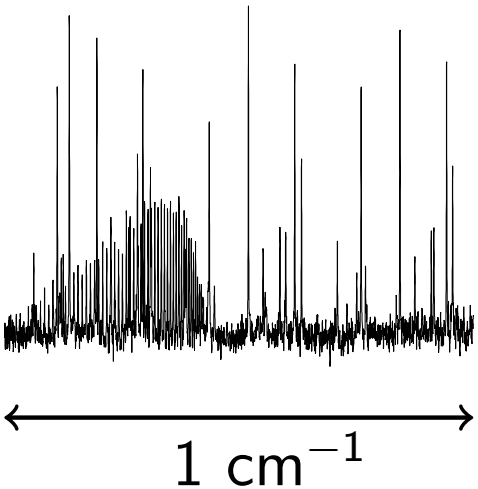

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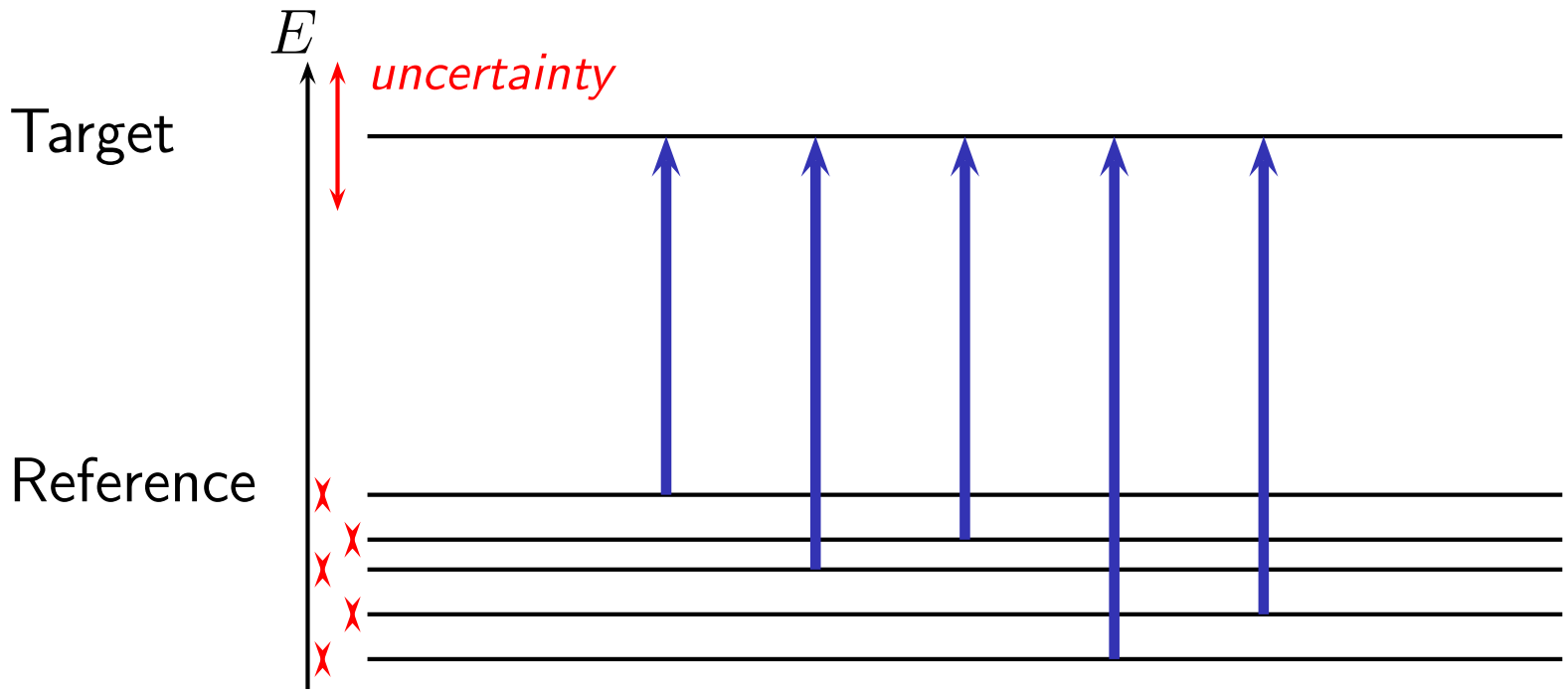
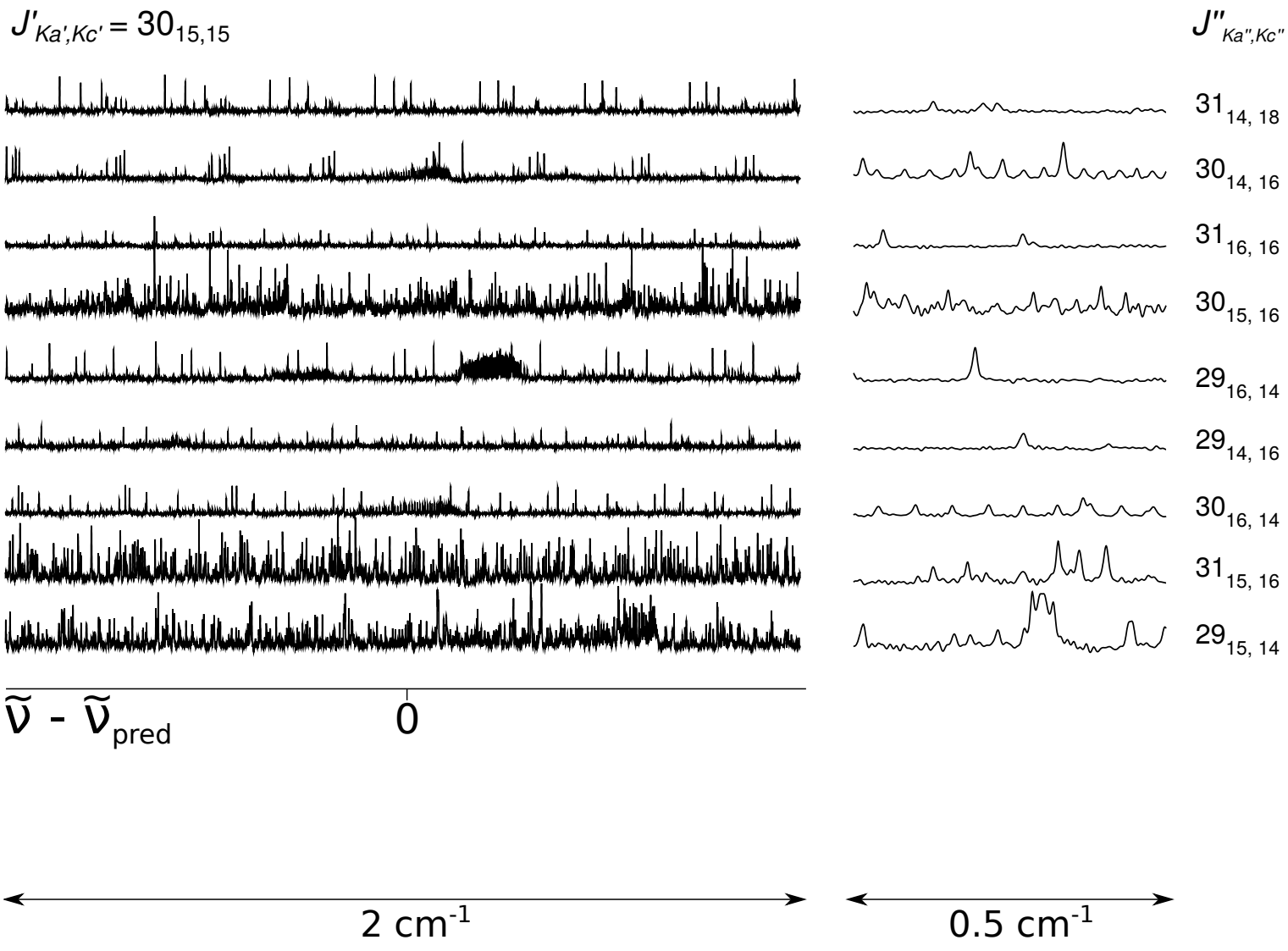
Transitions sharing a target energy level are shifted by the same amount



The cross-correlation plot features a strong peak



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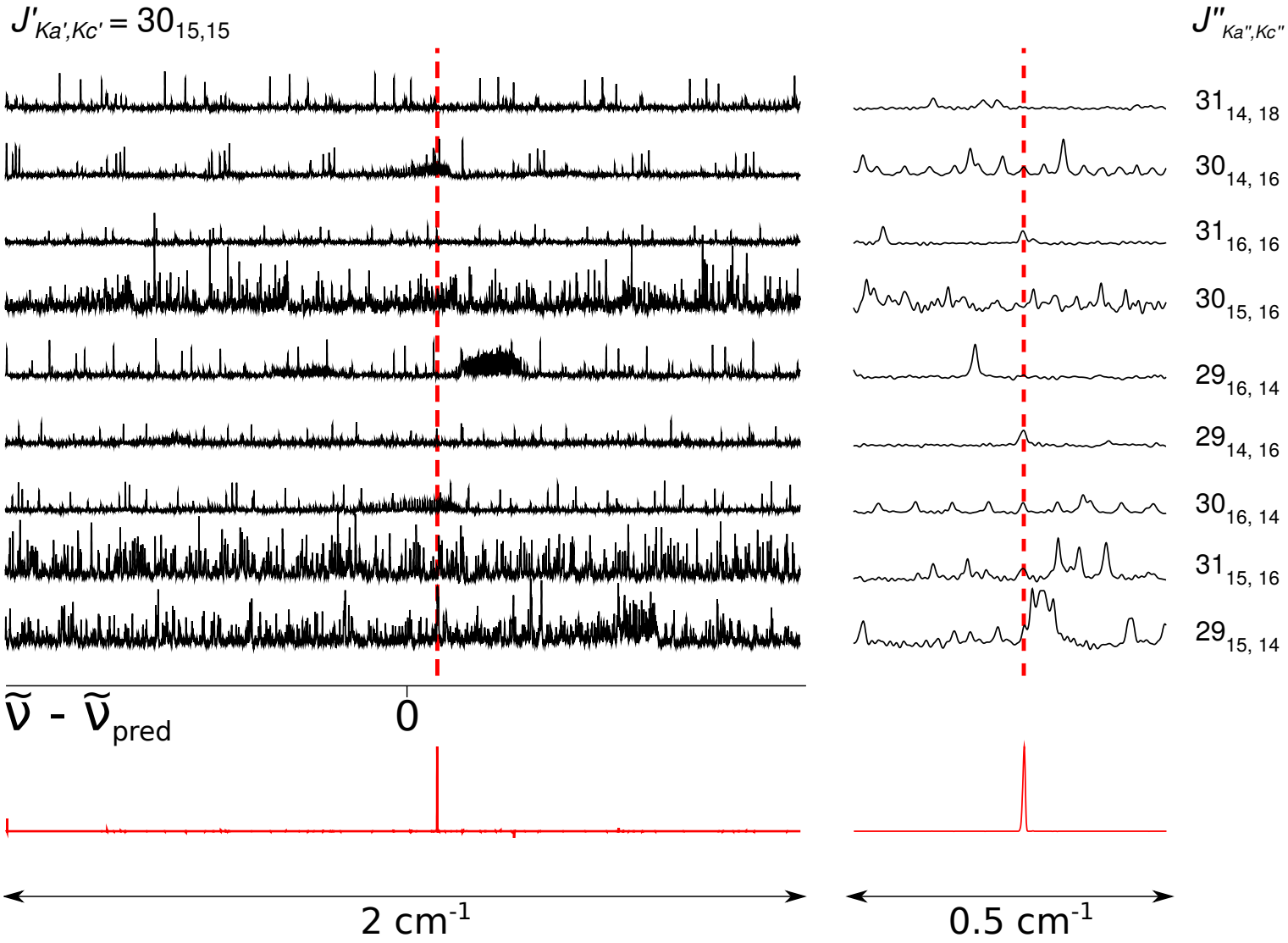
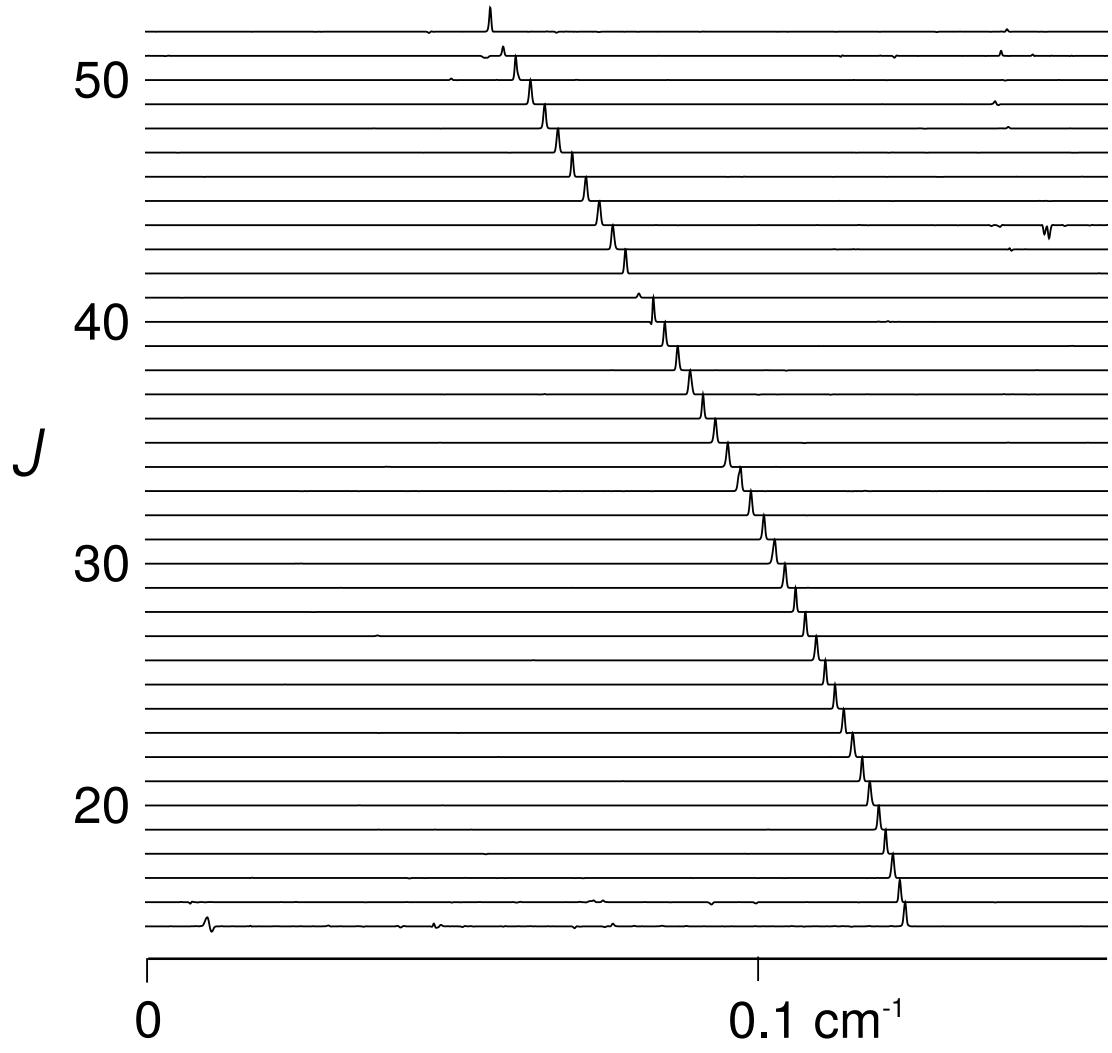
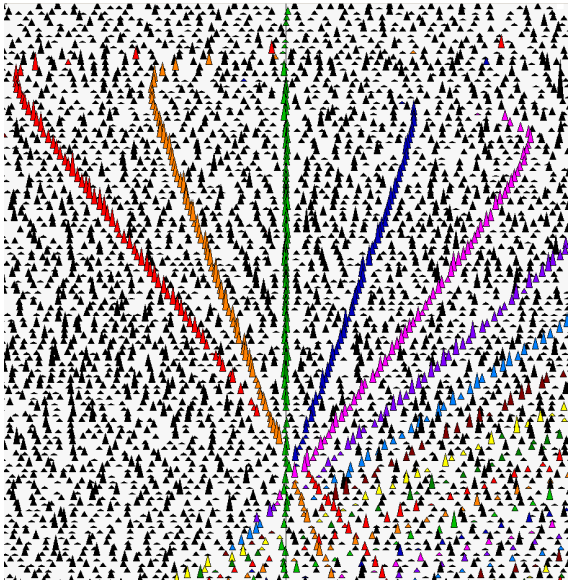


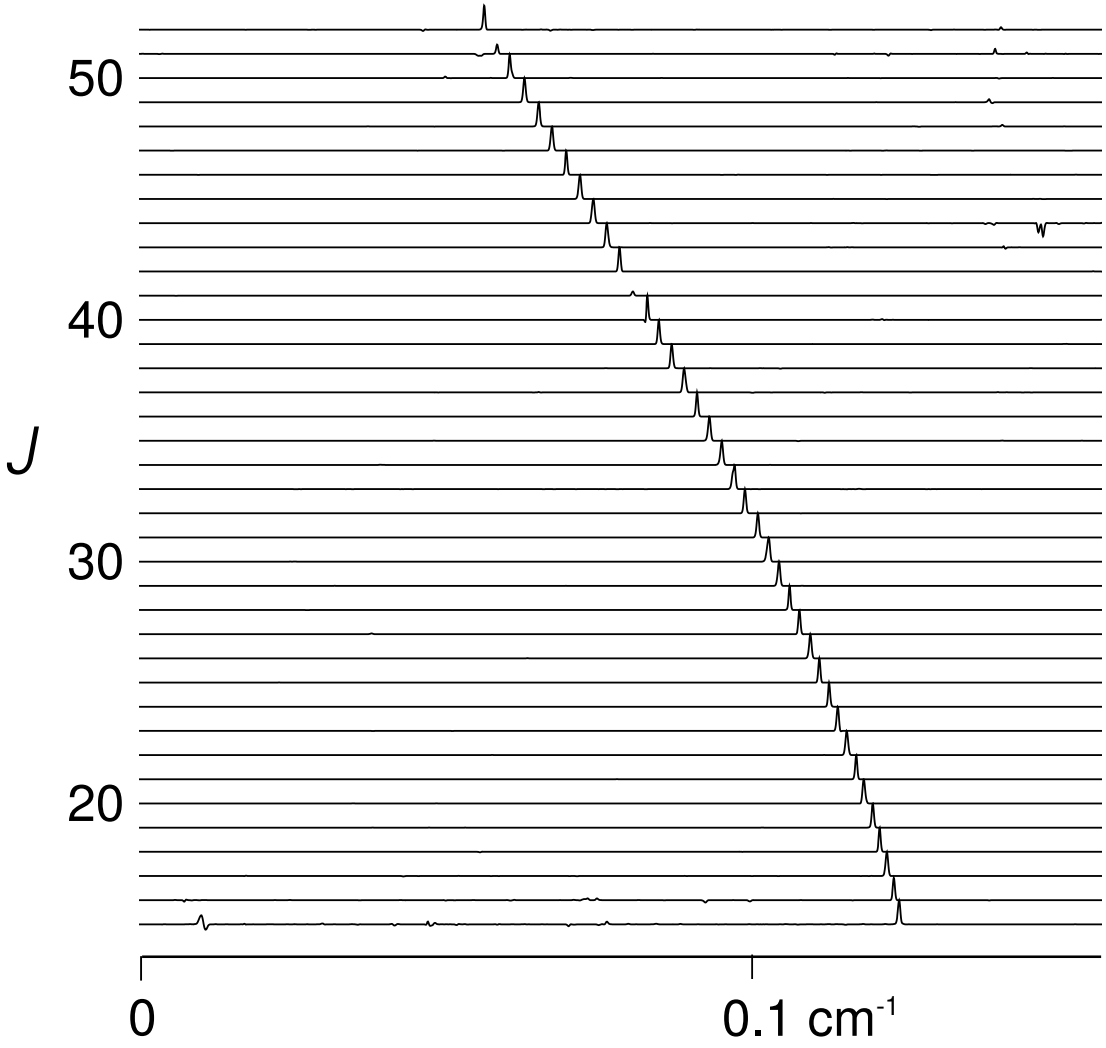
A trend with J is visible for the cross-correlation plots



$K_a = 15,\ K_a + K_c = J$

A trend with J is visible for the cross-correlation plots





$K_a = 15,\ K_a + K_c = J$

The ν_2 band of S_2O has been analyzed using ASAP

ν_2 band

- Reference: (0,0,0)
- Target: (0,1,0)

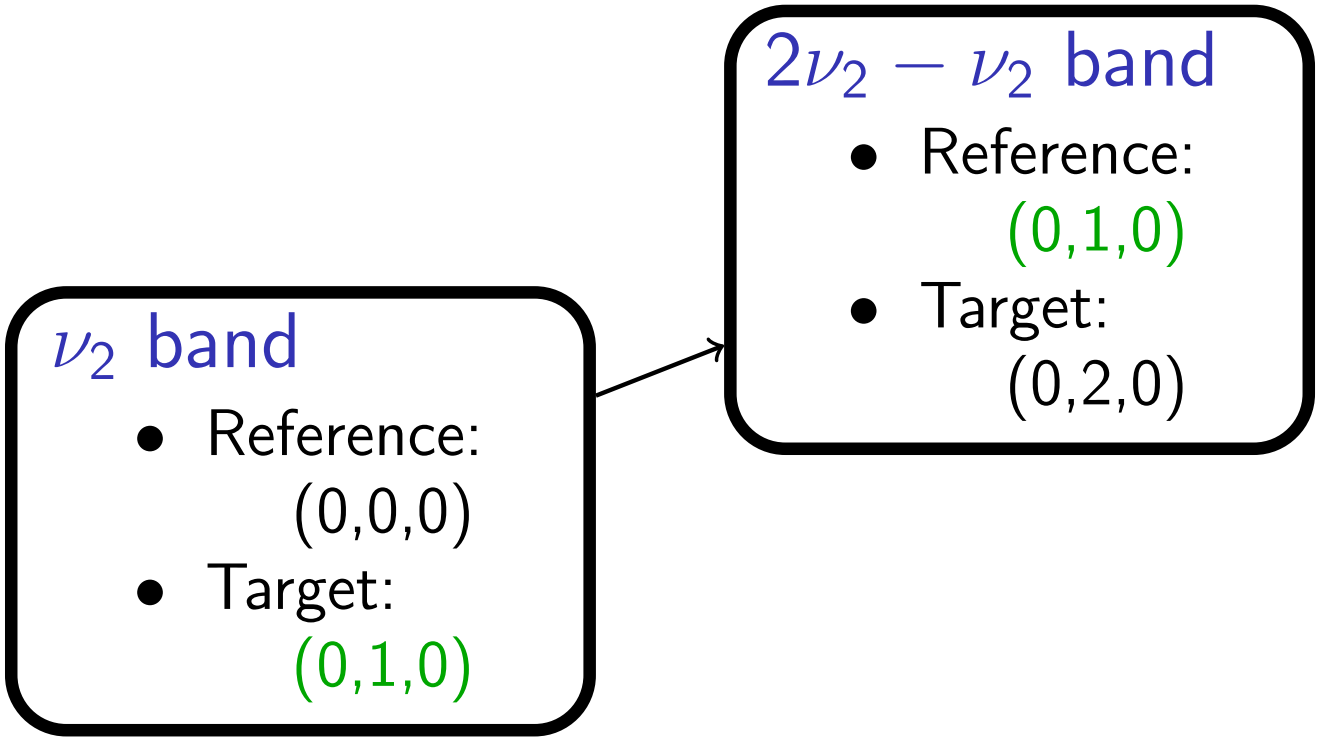
$\sim$2000 energy levels

$J \leq 84$, $K_a \leq 24$

$(J \leq 5,\ K_a \leq 1)$[1]

[1] Thorwirth, 2006

The ν_2 band of S_2O has been analyzed using ASAP



~1500 energy levels
$J \leq 73$, $K_a \leq 19$
$(J \leq 4,\ K_a \leq 1)^1$

~2000 energy levels
$J \leq 84$, $K_a \leq 24$
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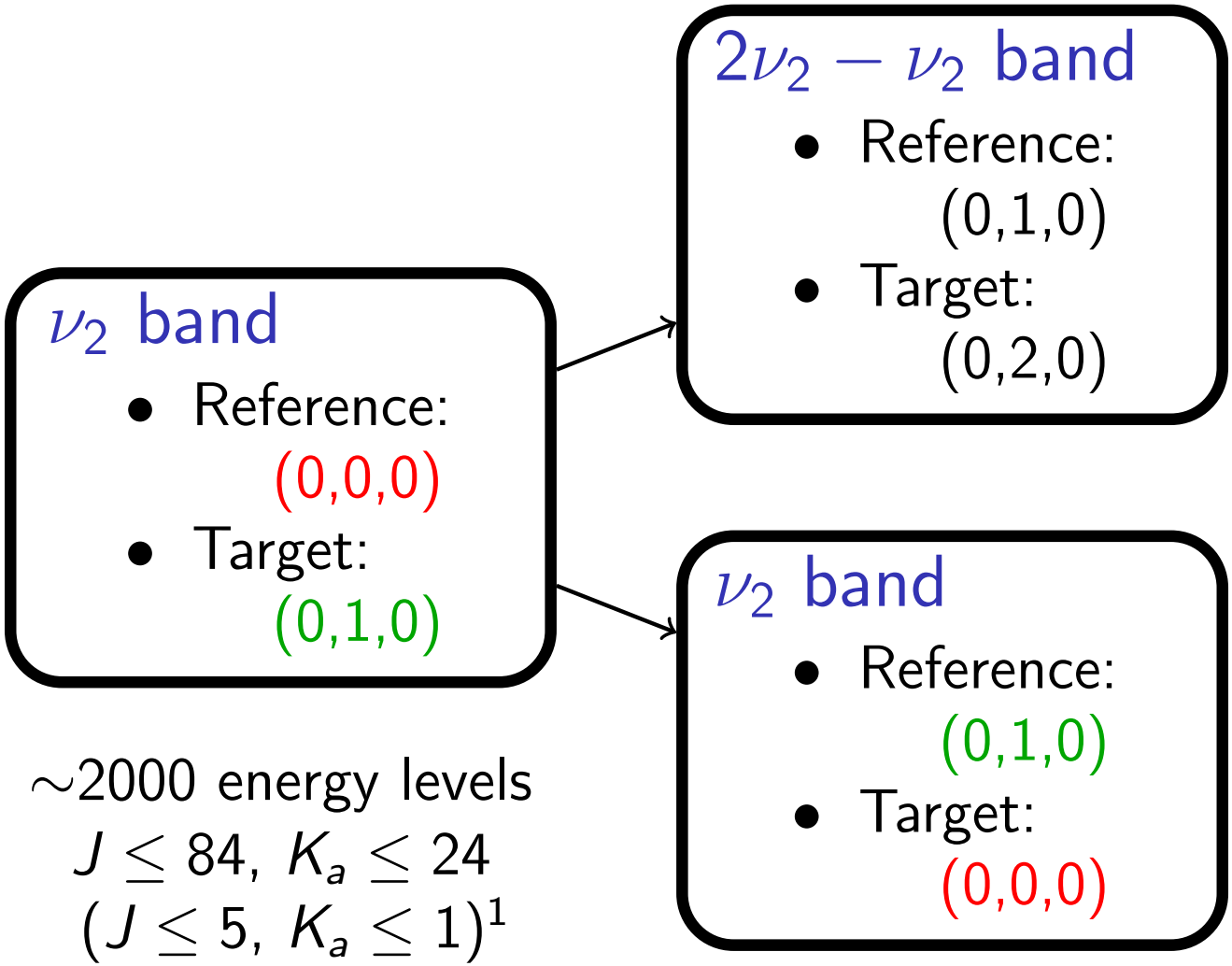

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~2000 energy levels
$J \leq 84$, $K_a \leq 24$
$(J \leq 5,\ K_a \leq 1)^1$

~2000 energy levels
$J \leq 83$, $K_a \leq 24$
$(J \leq 76,\ K_a \leq 22)^1$

[1] Thorwirth, 2006

Vibrational satellites have been measured

RF experiment[1]

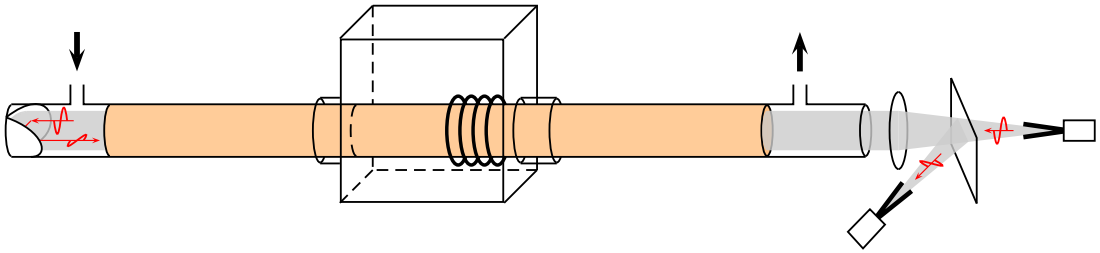
$\leq$ 500 GHz

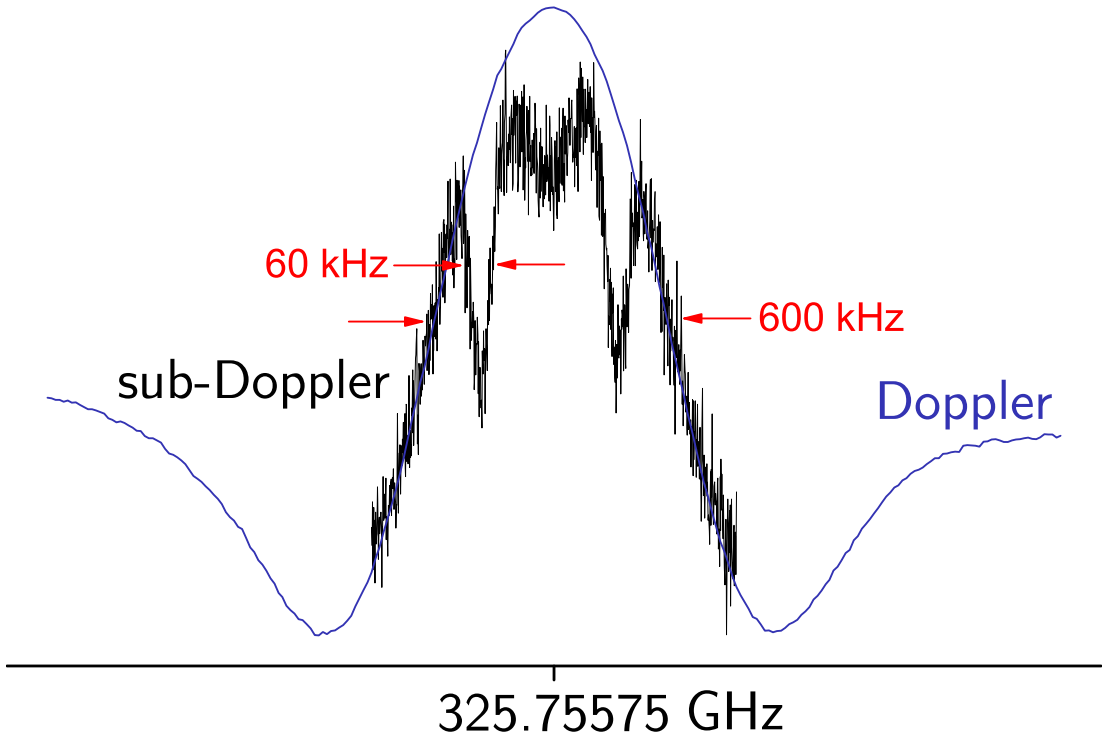
(0,1,0)

- 450 lines
- $J \leq 60$
- $K_a \leq 29$

(0,2,0)

- 150 lines
- $J \leq 56$
- $K_a \leq 19$





[1] see talk RB08 by S. Thorwirth

Accurate molecular parameters have been derived

Least-squares fit

SPFIT/SPCAT[1]

pure rotation, ro-vibration[2]

(0,0,0), (0,1,0), (0,2,0)

$\sigma = 1.02$

Accurate constants

CD up to the octic terms

$$\tilde{\nu}_2 = 380.310367(3)\ \text{cm}^{-1}$$

$$2\tilde{\nu}_2 - \tilde{\nu}_2 = 380.07577(1)\ \text{cm}^{-1}$$

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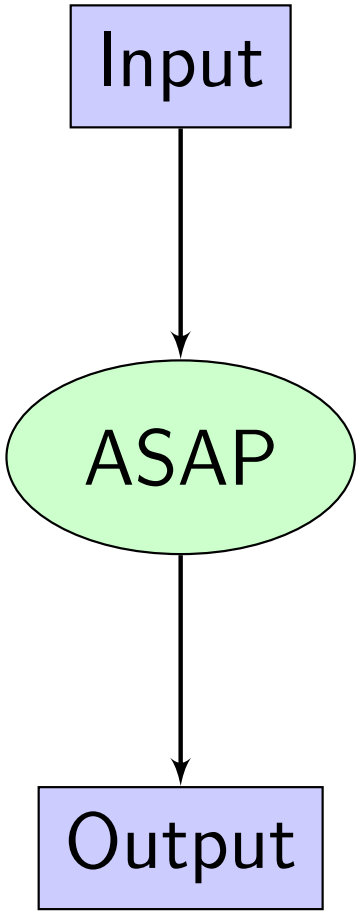
[1] Pickett, 1991

[2] Meschi, 1959; Cook, 1973; Tiemann, 1974; Lindenmayer, 1985, 1986; Thorwirth, 2006

ASAP allows a rapid determination of the energy levels of a vibrational state



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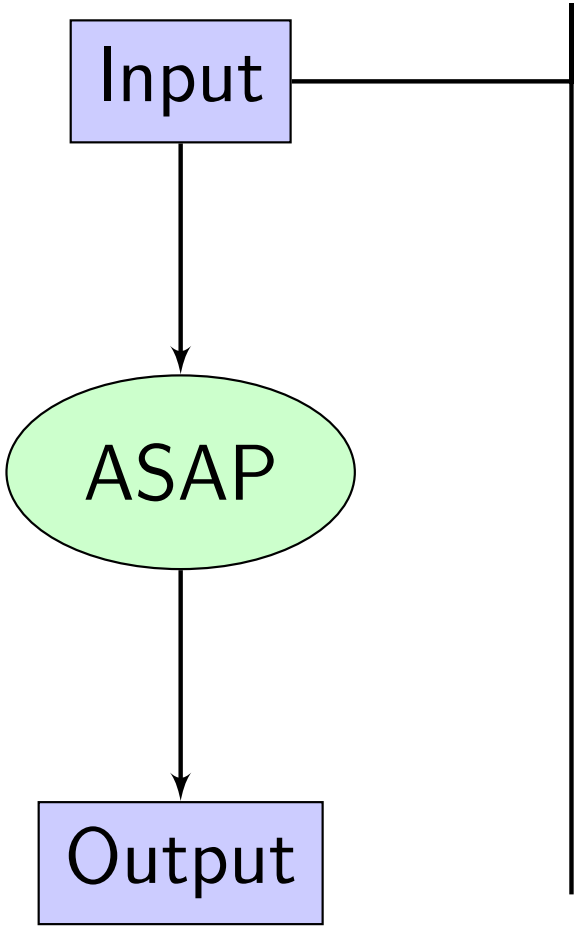


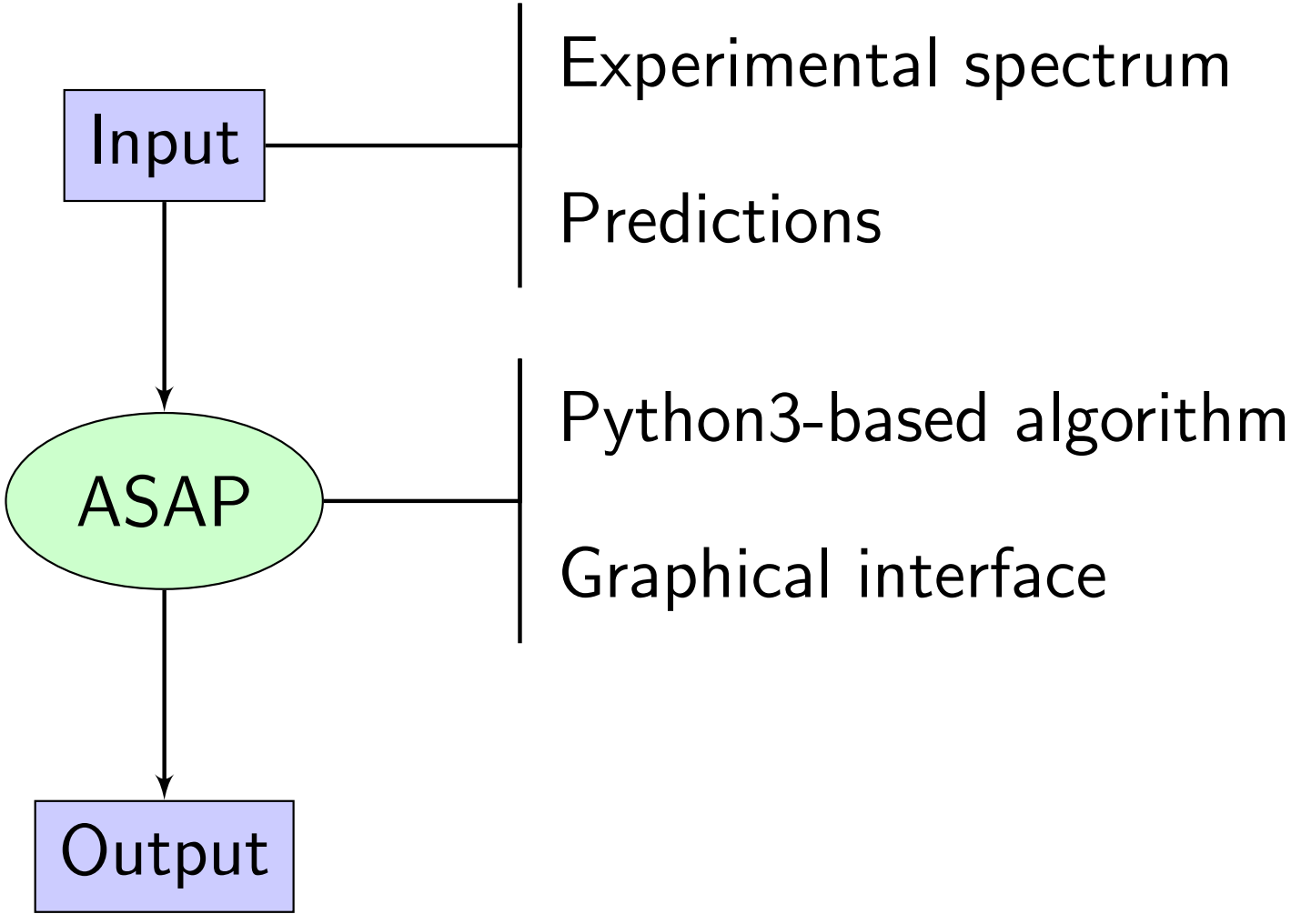
Experimental spectrum

- absorbance
- calibrated
- post-zero filled
- no peak-finder required

Predictions

- transitions (.cat)
- energy levels (.egy)

ASAP allows a rapid determination of the energy levels of a vibrational state



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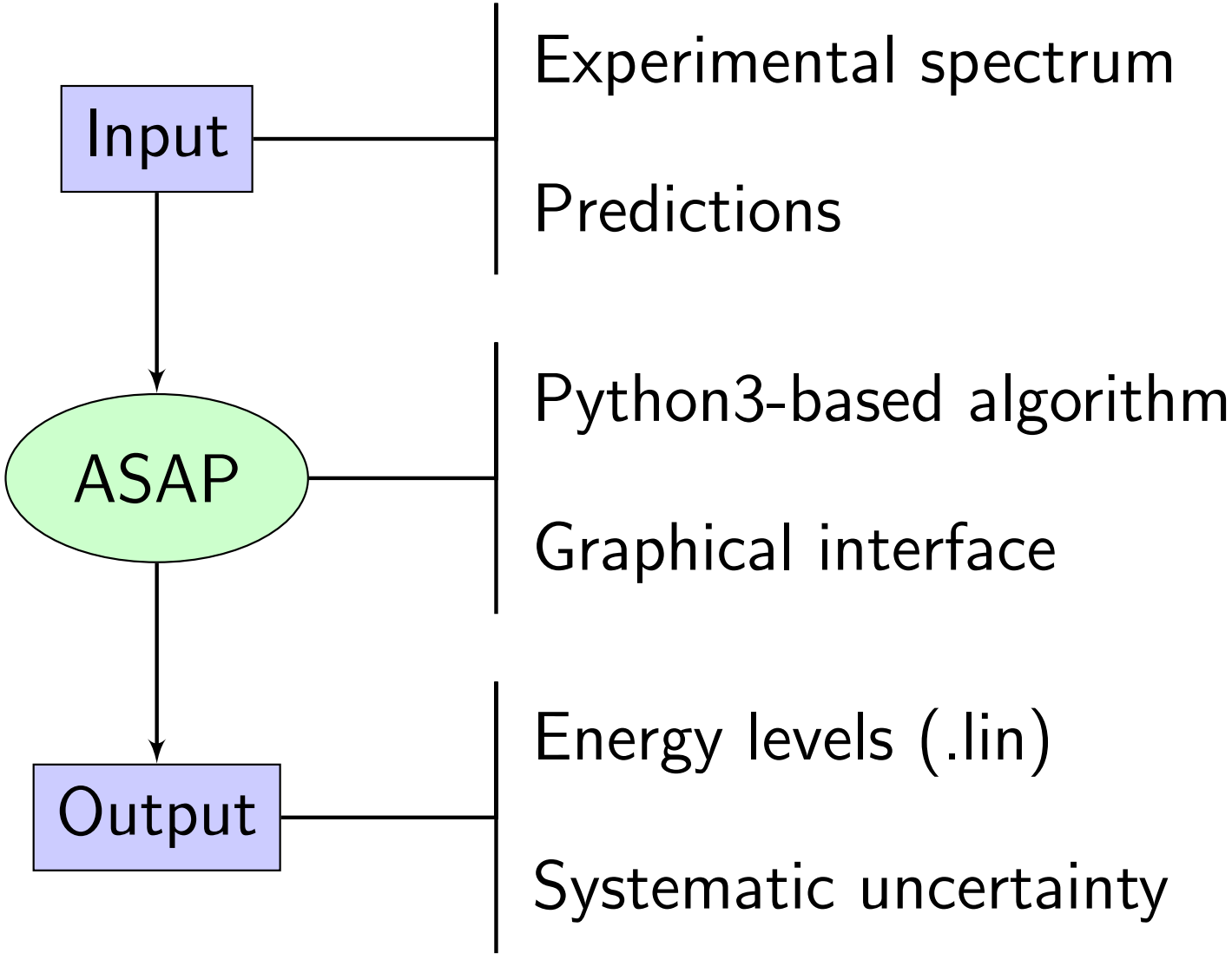

The S_2O bending mode ν_2 at 380 cm^{-1} and its analysis using ASAP

A new semi-automatic assignment method has been developed

successfully applied to the analysis of the ν_2 band of S_2O

An improved list of molecular parameters has been derived for S_2O

Some features of ASAP warrant further discussion

Up to which spectral density would the procedure work?

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Up to which spectral density would the procedure work?

What if only few spectral portions can be cross-correlated?

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Energy levels or ro-vibrational transitions?

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What about the uncertainties?

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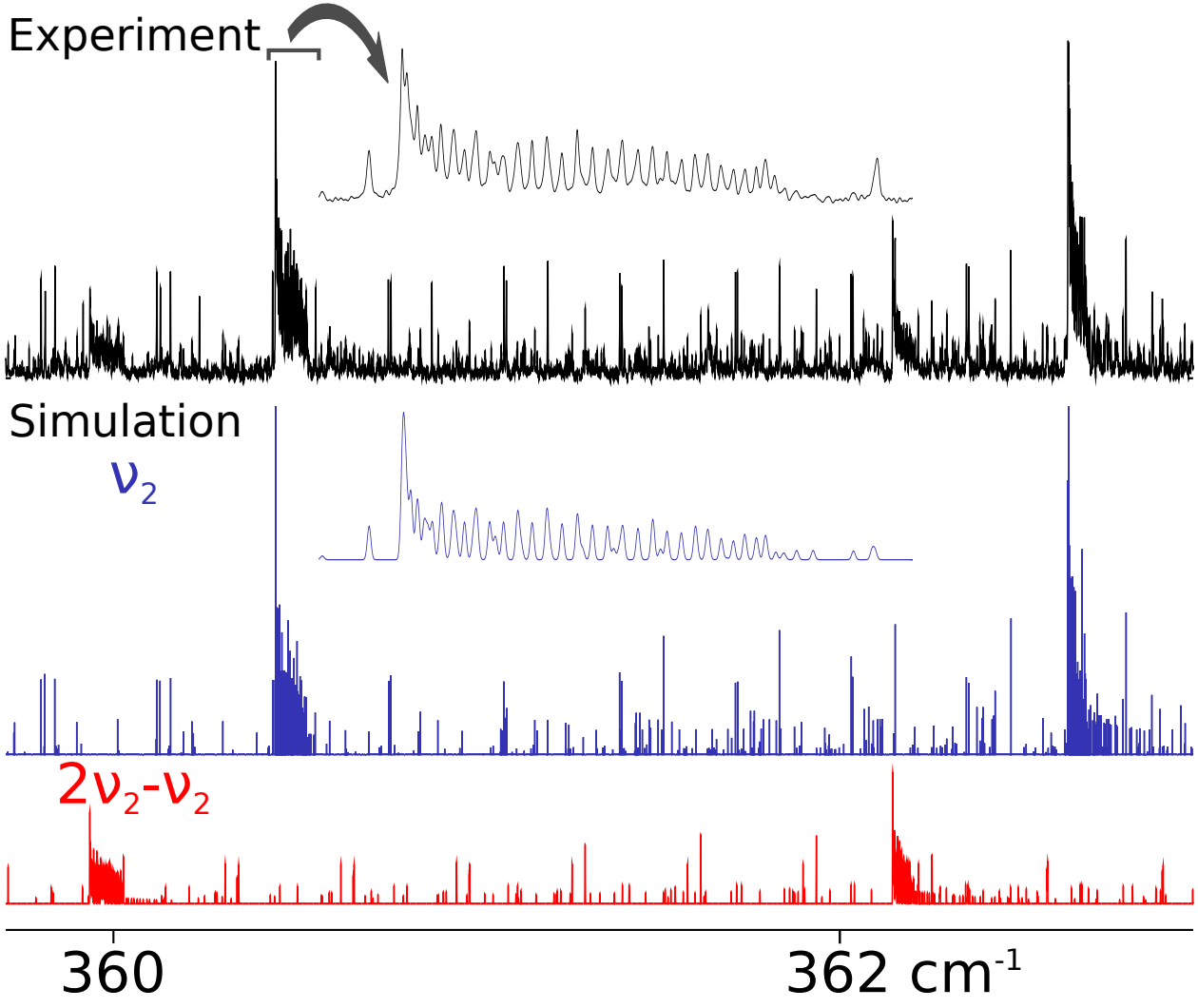
Energy levels or ro-vibrational transitions?

What about the uncertainties?

Towards full automation?

The ν_2 band of S_2O has been analyzed using ASAP in only a few hours



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