HIGH RESOLUTION 2D INFRARED SPECTROSCOPY: A NEW WAY TO ASSIGN NEAR INFRARED PEAKS

ISMS

Mini-symposium: Infrared Spectroscopy in the JWST Era

Tuesday, 2023-06-20, 01:45 PM

Medical Sciences Building 274

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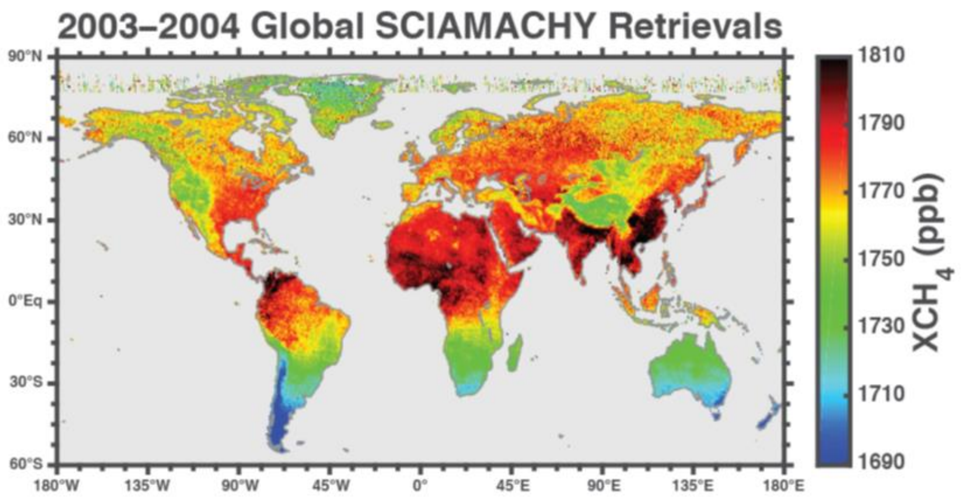
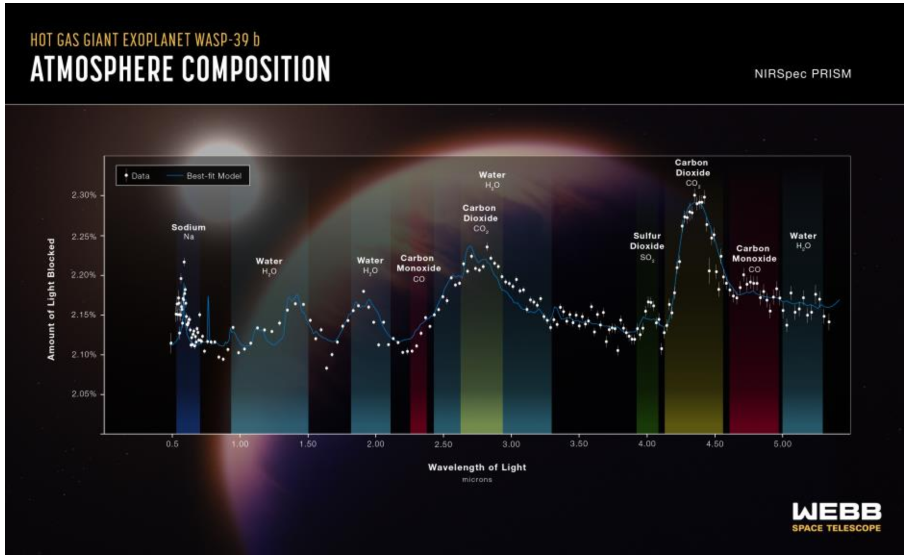
Near Infrared Spectroscopy

- Remote detection and identification of molecules and for studying their environments (e.g., temperature)
- NIR spectrometers are small, sensitive, inexpensive, robust, no moving parts, etc.
- However, peaks in the NIR region are difficult to interpret
  - Polyads due to overlapping overtone and combination bands cause congestion and mixing
  - Peak assignments can be difficult or questionable, which can affect the accuracy of temperature measurements

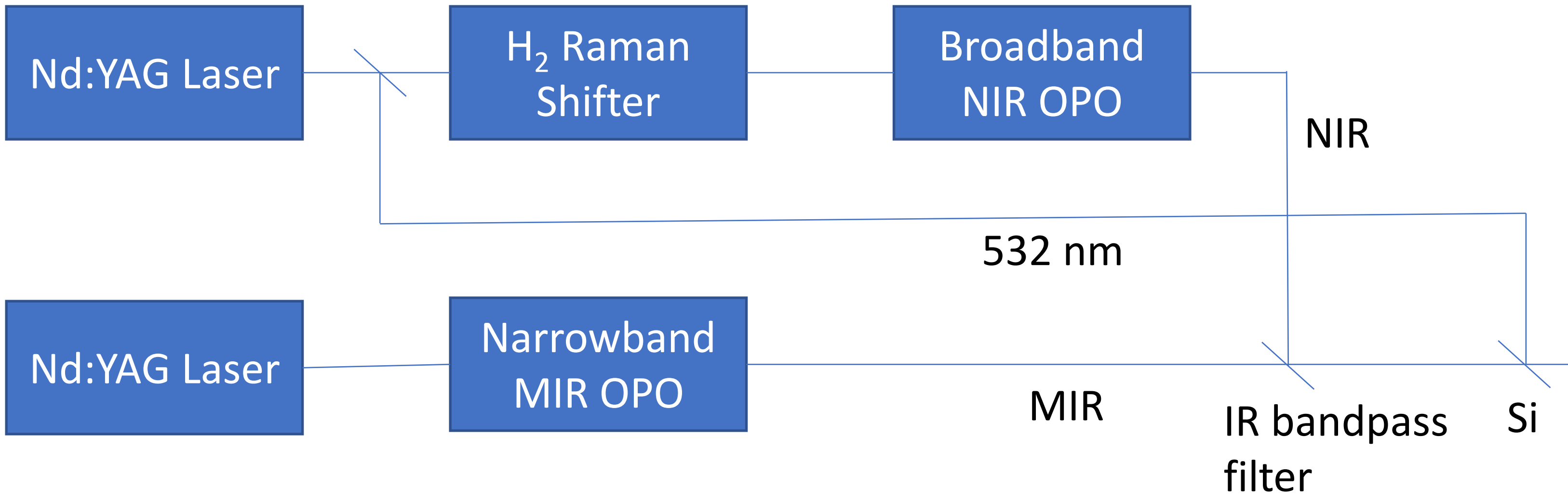


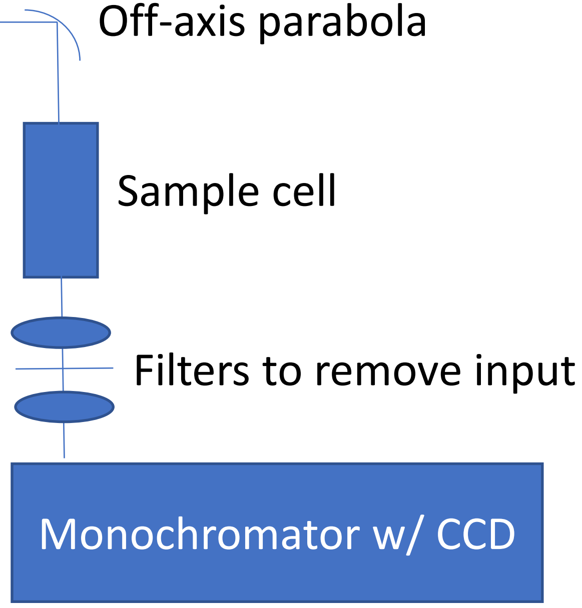
Satellite monitoring of greenhouse gases



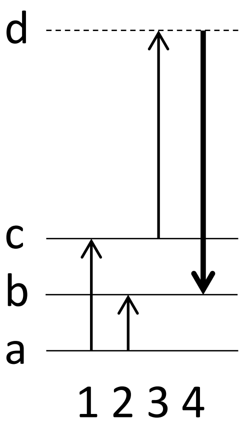
JWST has recorded NIR spectra identifying atmospheric gases on exoplanets.
www.nasa.gov /feature/goddard/2022

2D Rovibrational spectrometer

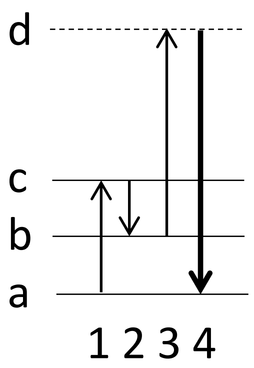




DOVE-IR



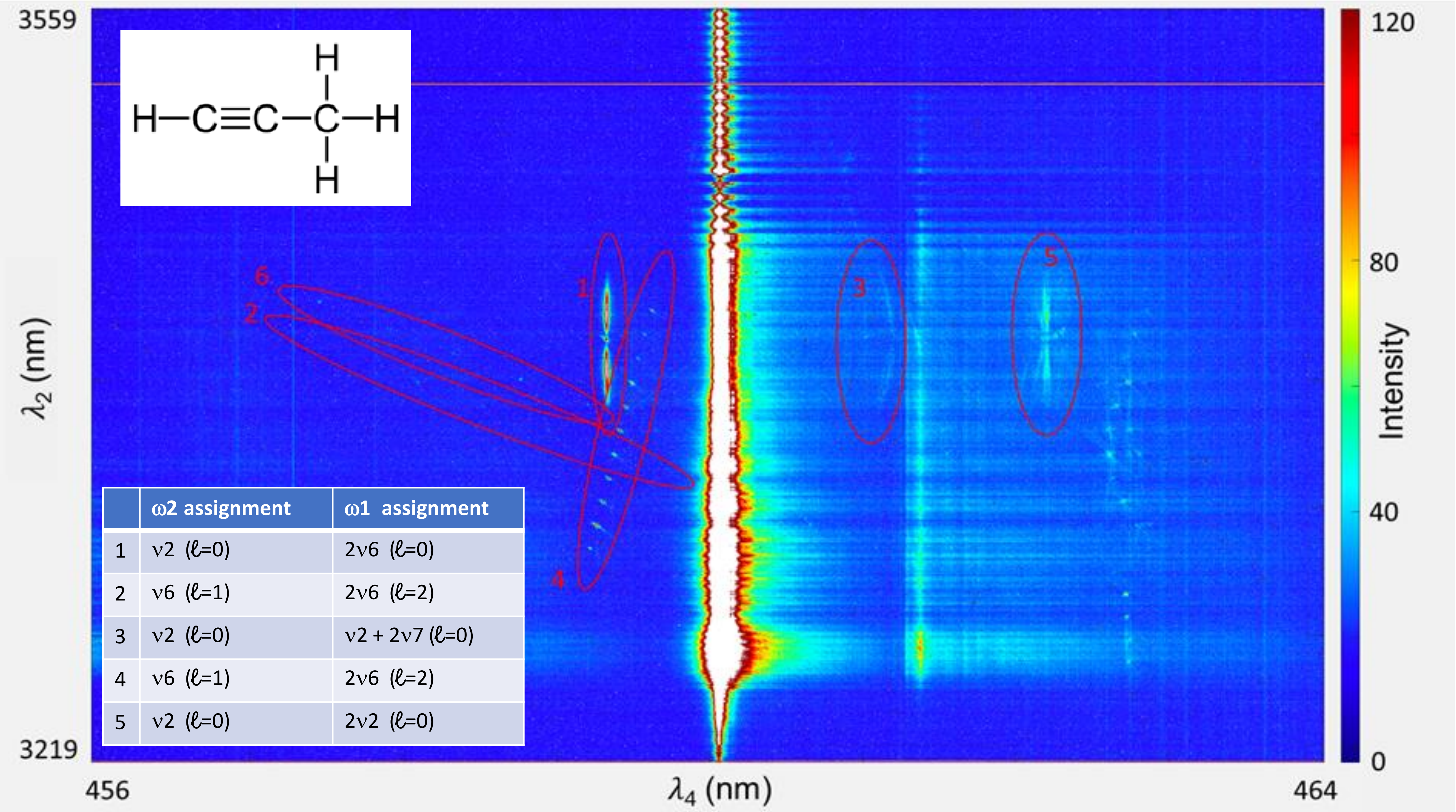
DOVE-Raman



1. Near IR input (6000-8000 cm^{-1})
2. Mid-IR input (3000-4000 cm^{-1})
3. Visible input
4. Visible **output**

a. Ground (initial) level
b. Fundamental XH stretch (X=C, N, O)
c. Overtone XH stretch
d. Virtual level

$$\omega 4 = \omega 1 - \omega 2 + \omega 3$$



	ω2 assignment	ω1 assignment
1	ν2 (ℓ=0)	2ν6 (ℓ=0)
2	ν6 (ℓ=1)	2ν6 (ℓ=2)
3	ν2 (ℓ=0)	ν2 + 2ν7 (ℓ=0)
4	ν6 (ℓ=1)	2ν6 (ℓ=2)
5	ν2 (ℓ=0)	2ν2 (ℓ=0)

Spectroscopy of Ammonia

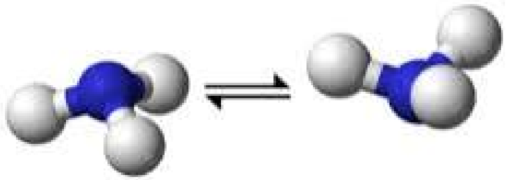
- Deacon Nemchick, NASA JPL
- Keeyoon Sung, NASA JPL

Remote temperature sensor. (Atmospheric window 1.5μ)

Detected in/on:

- Atmospheres of Jupiter, Saturn, Neptune, Titan
- Comets
- Molecular clouds
- Brown dwarfs

	s	a
$\nu 1$ (a1):	3336.2,	3337.2 cm^{-1}
$\nu 2$ (a1):	932.5,	968.3
$\nu 3$ (e):	3443.6,	3443.9
$\nu 4$ (e):	1626.1,	1627.4

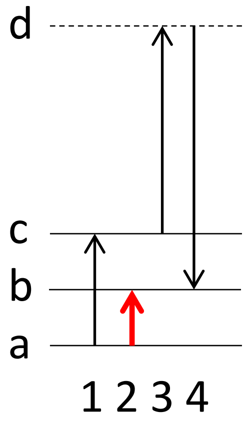


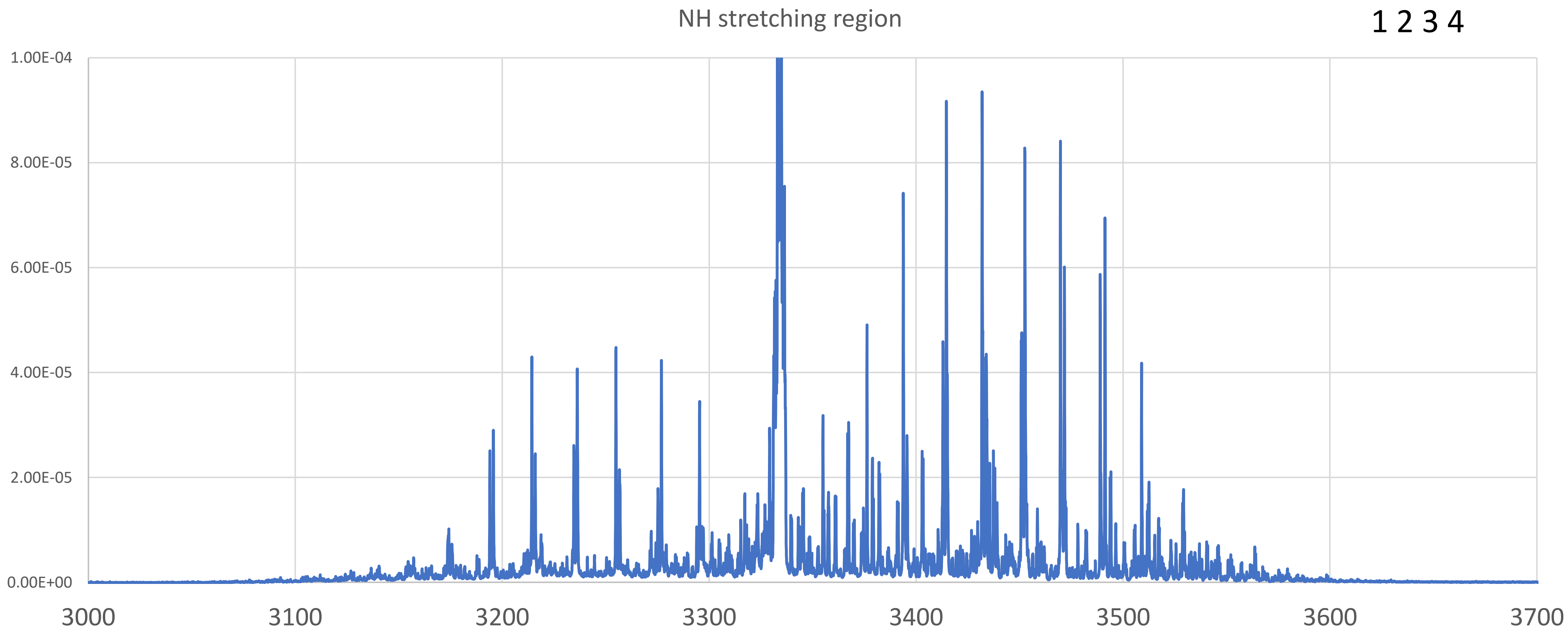
- Symmetric rotor with an umbrella inversion
- Very well studied. HITRAN database includes current assignments

Keeyoon Sung, Linda R. Brown, Xinchuan Huang, David W. Schwenke, Timothy J. Lee, Stephen L. Coy, Kevin K. Lehmann, "Extended line positions, intensities, empirical lower state energies and quantum assignments of NH3 from 6300 to 7000cm−1", JQSRT 113, 2012, 1066-1083.

Mid-IR spectra of ammonia

HITRAN assignments: ν1, ν3, 3ν2, 2ν4, 2ν2+ν4, 4ν2, plus 13 hot bands

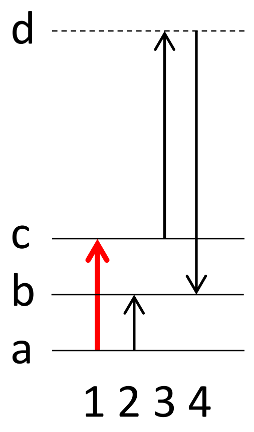


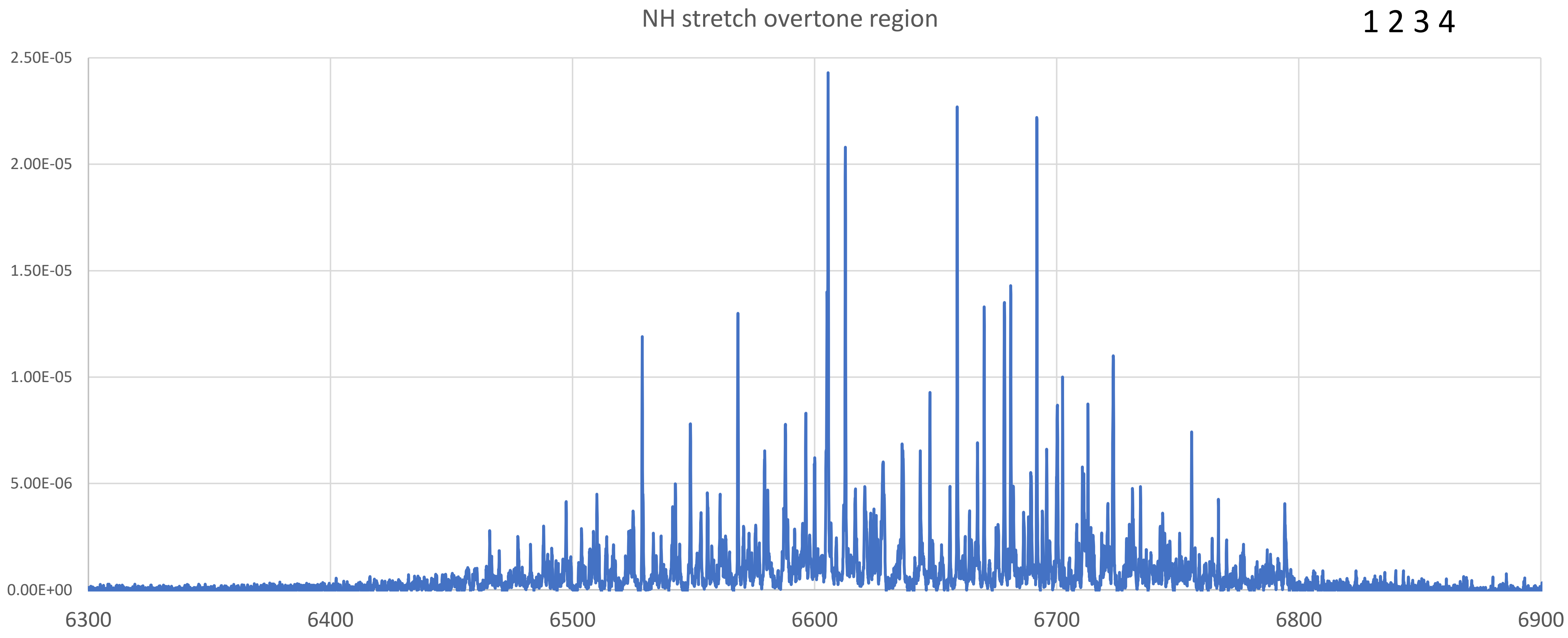


FTIR spectrum from PNNL database

NIR spectrum of ammonia

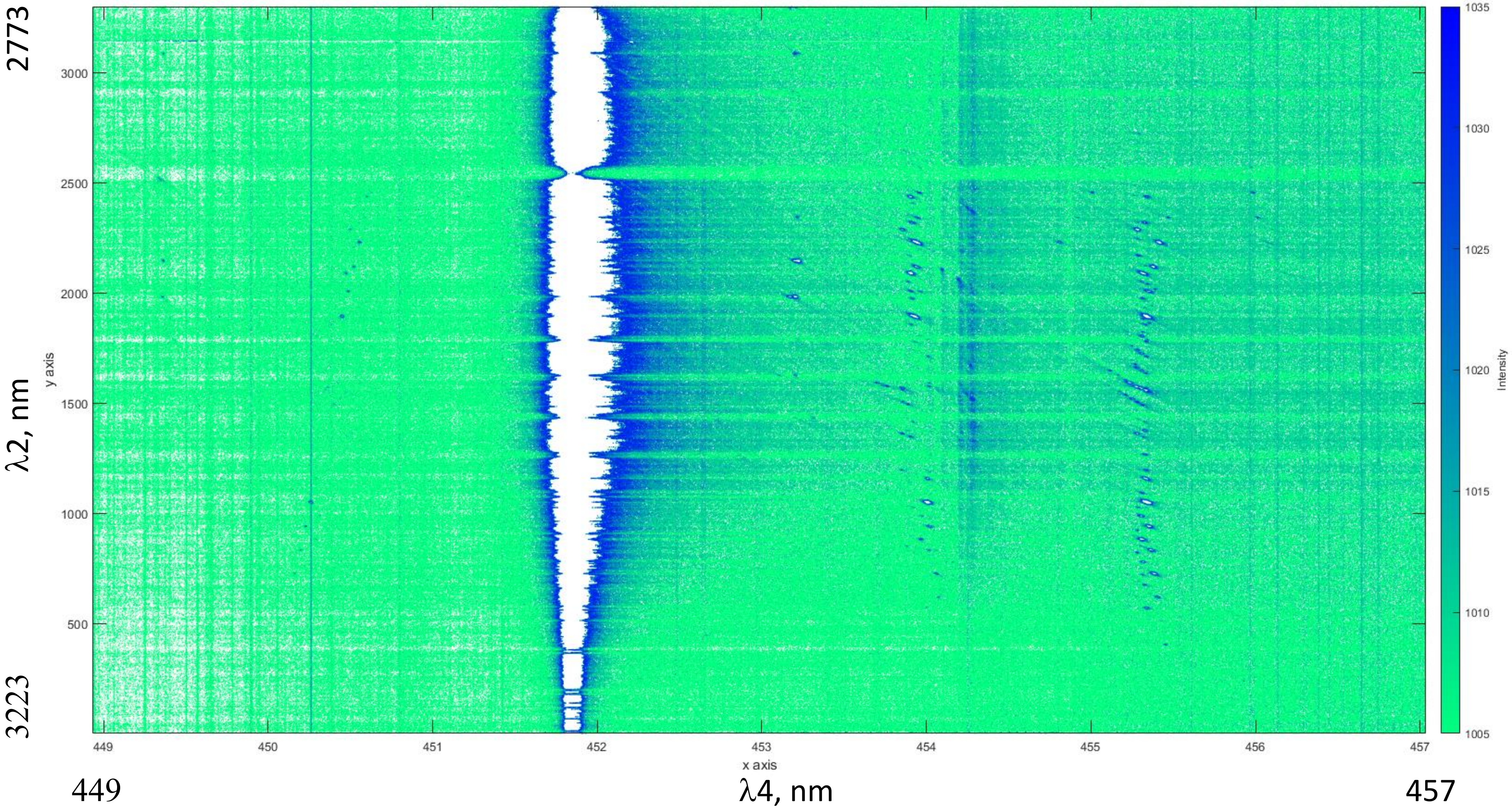
HITRAN assignments: 2ν3, 4ν4, ν3+2ν4, 2ν2+3ν4, 3ν2+ν3, 5ν2, ν1+2ν4, ν1+ν3, ν1+3ν2, 2ν1



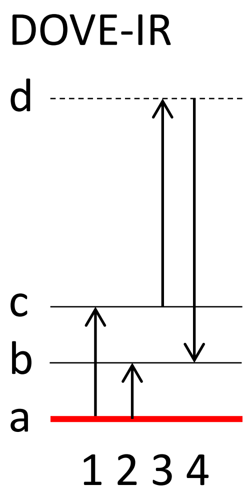


FTIR spectrum from PNNL database

052623a1, ammonia
Noise 1000: Outlier 1035, 0.003nm/sec, 2 sec integration, flashed 769.050 and 789.350 nm



Limitations due to the required common level



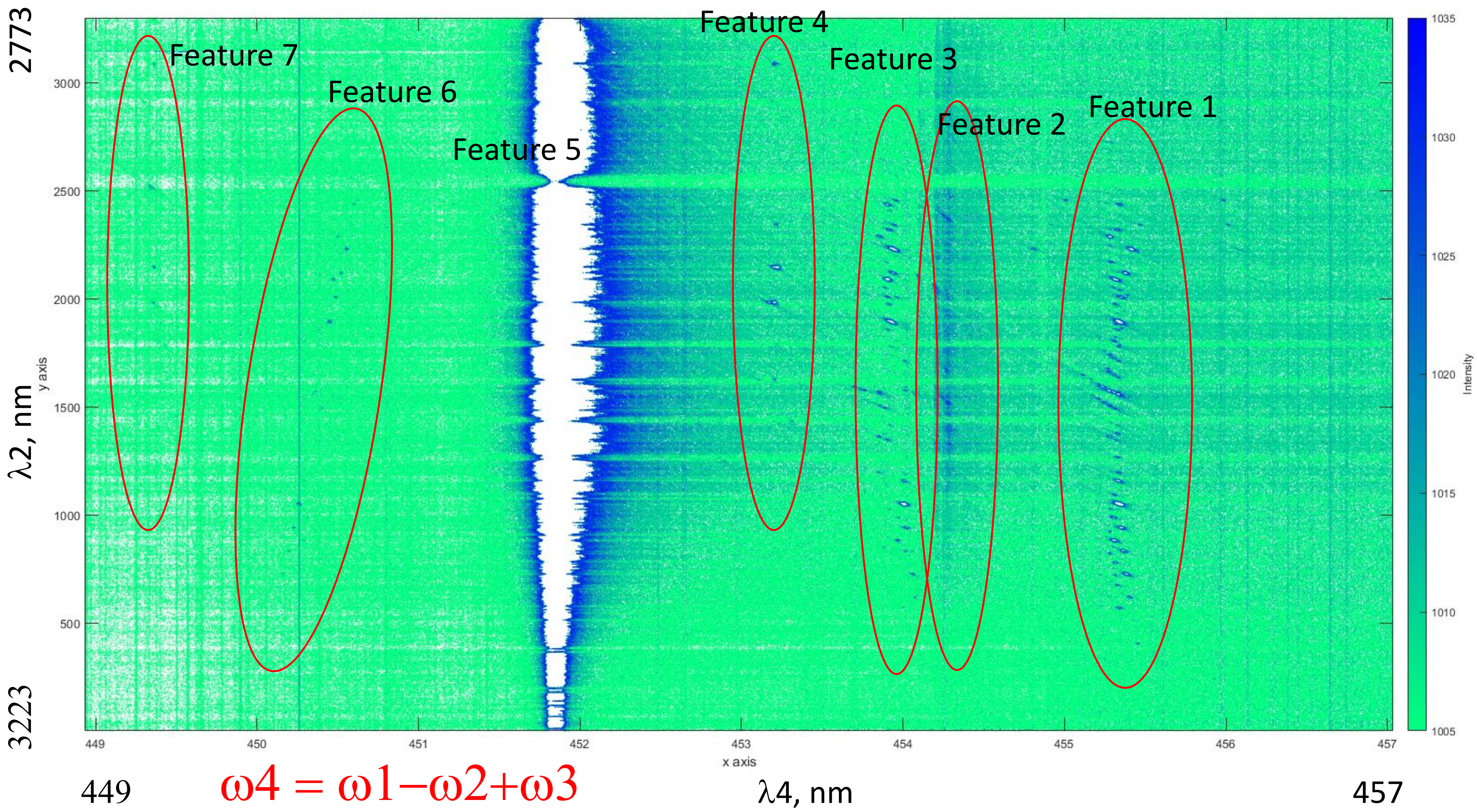
1. Near IR input
2. Mid-IR input
3. Visible input
4. Visible **output**

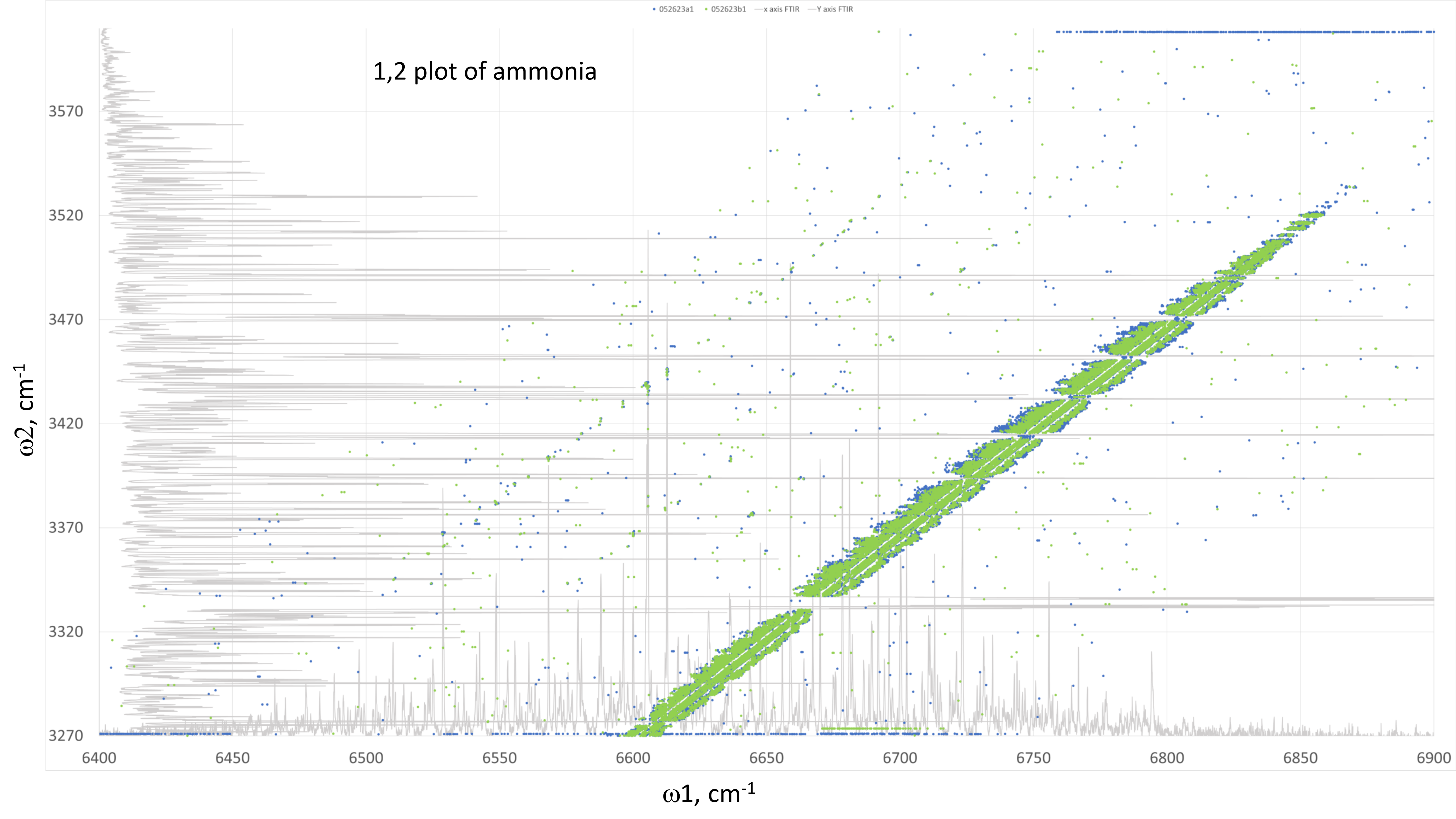
2D peaks must have the exact same J”, K”, symmetries, etc. in the ground (initial) state.

Therefore, the x,y coordinates of each peak identify two transitions with the same lower level

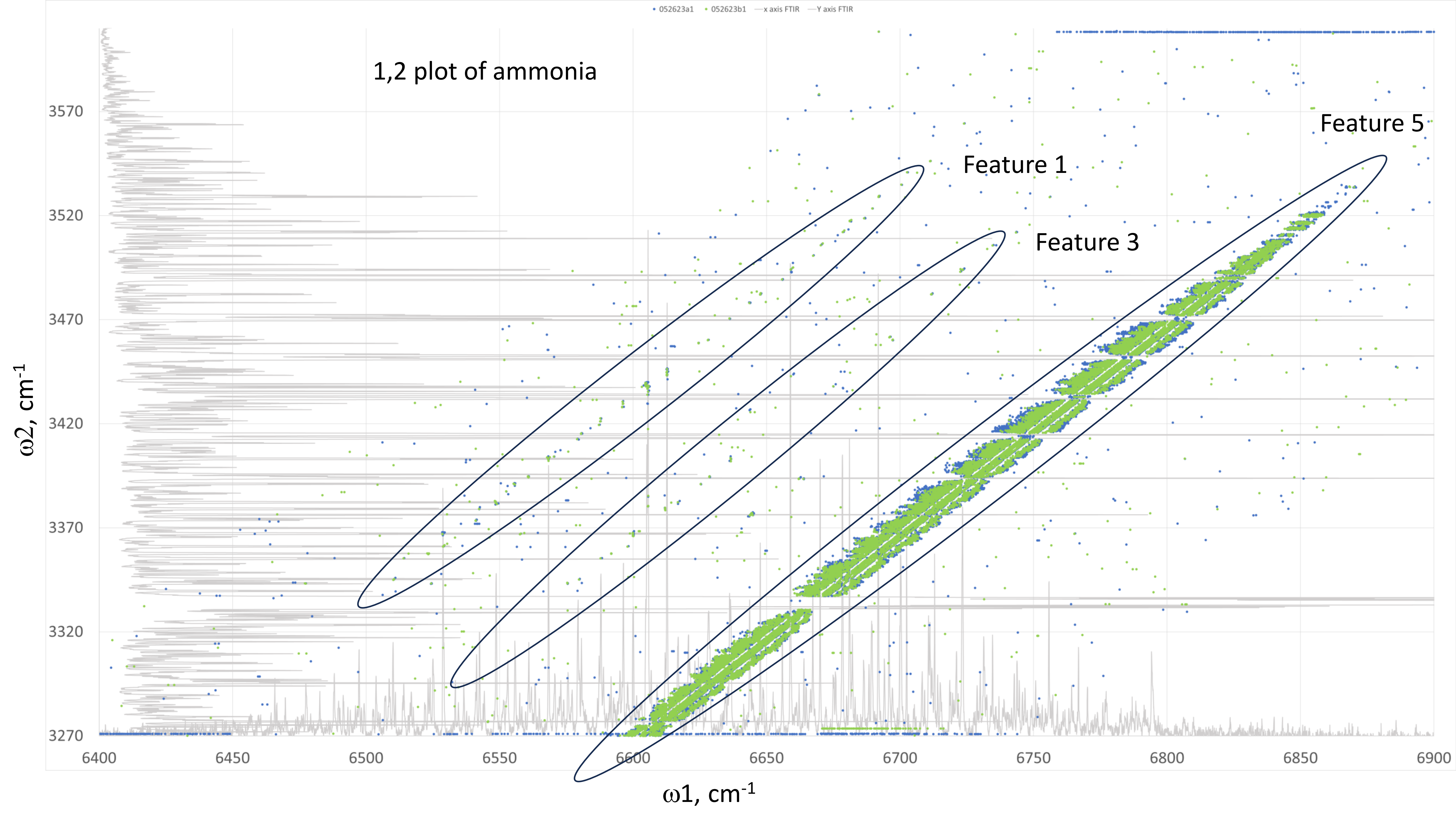
Transitions to other levels can occur, but they don’t contribute to the generation of the coherent FWM beam, nor to the peaks in the 2D spectrum.

052623a1, ammonia
Noise 1000: Outlier 1035, 0.003nm/sec, 2 sec integration, flashed 769.050 and 789.350 nm





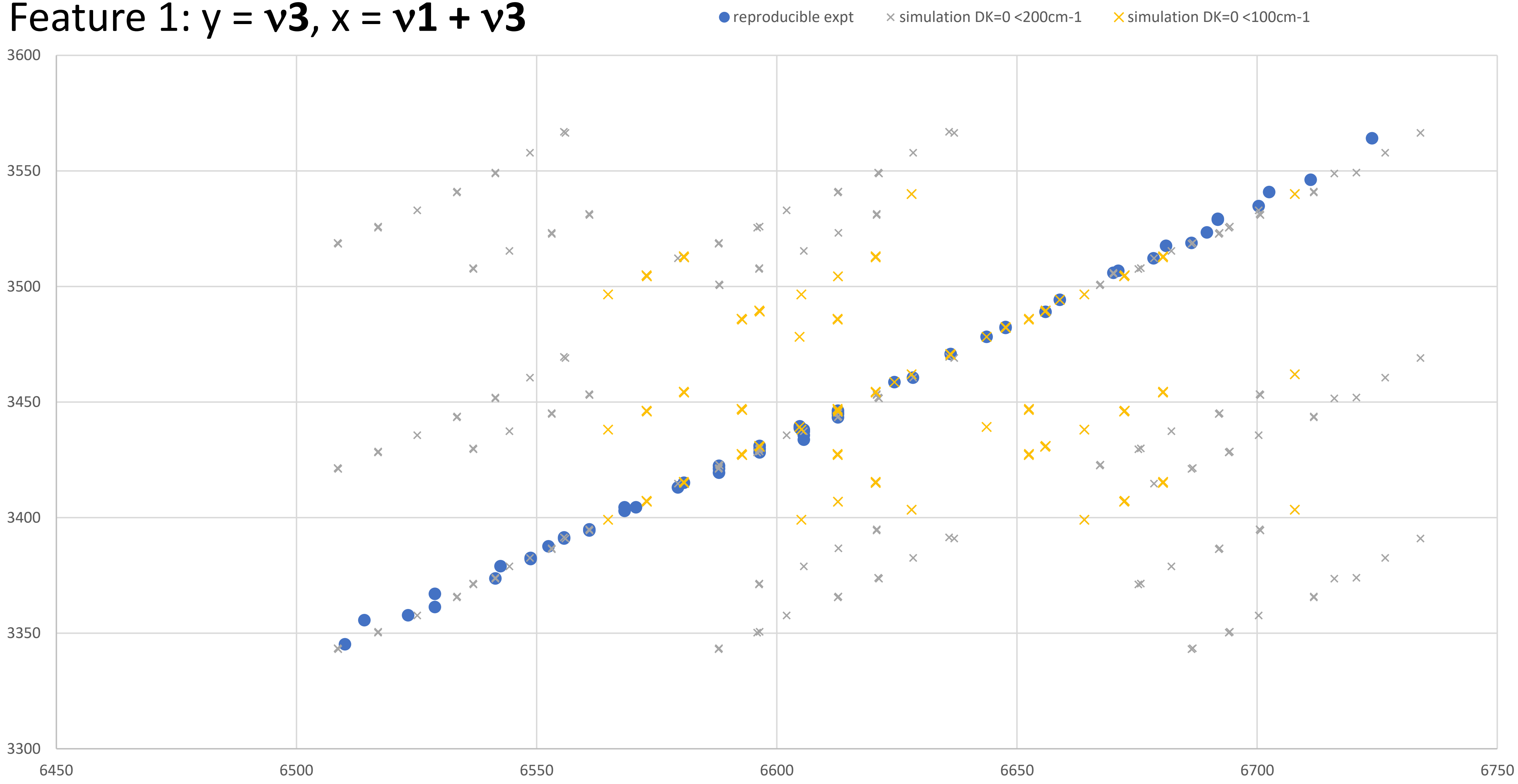
052623a1
052623b1
x axis FTIR
Y axis FTIR
1,2 plot of ammonia
ω2, cm-1
ω1, cm-1
3570
3520
3470
3420
3370
3320
3270
6400
6450
6500
6550
6600
6650
6700
6750
6800
6850
6900



052623a1
052623b1
x axis FTIR
Y axis FTIR
1,2 plot of ammonia
Feature 1
Feature 3
Feature 5
ω2, cm-1
ω1, cm-1
3570
3520
3470
3420
3370
3320
3270
6400
6450
6500
6550
6600
6650
6700
6750
6800
6850
6900

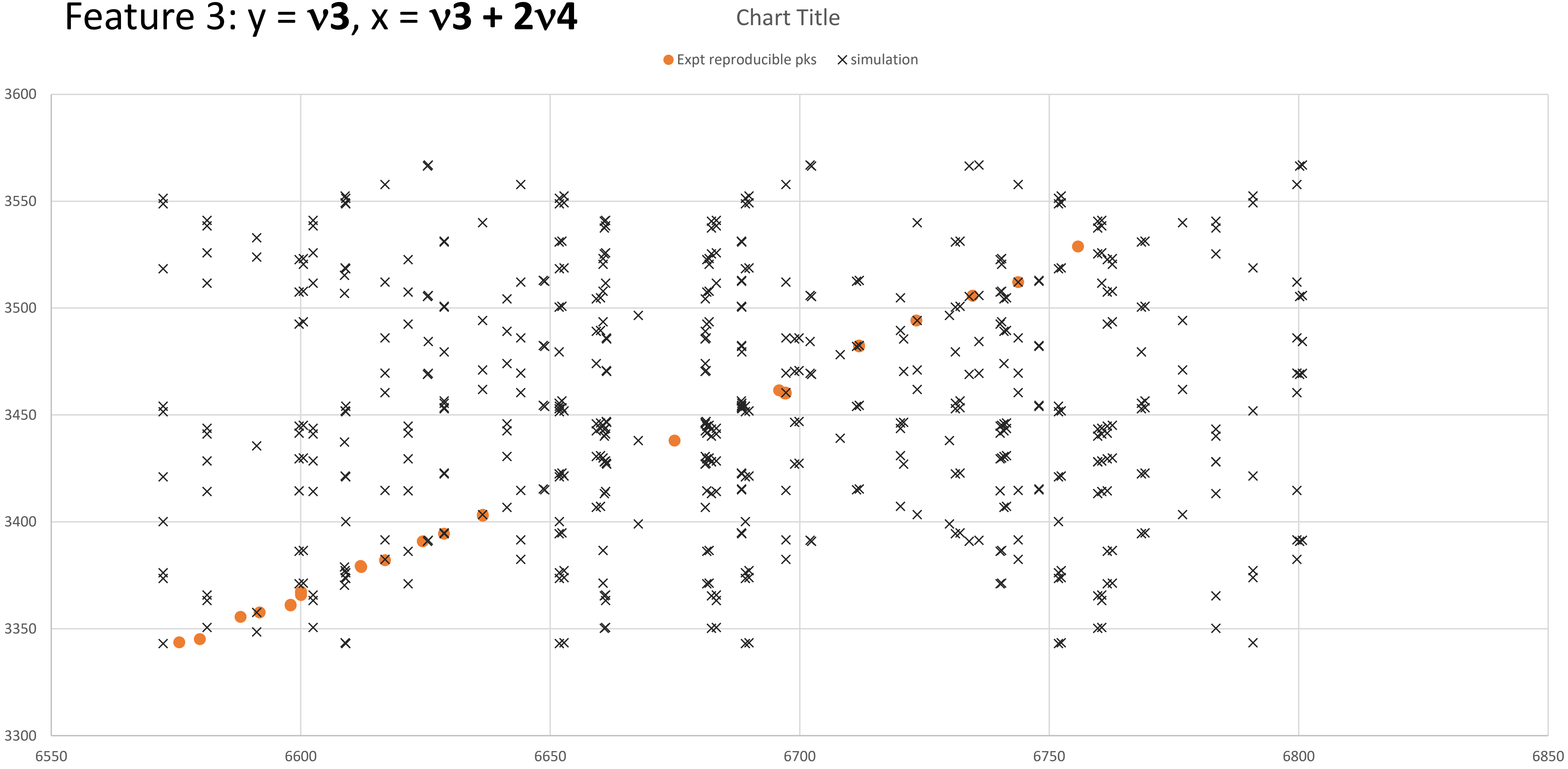
Hitran simulation vs experiment for Feature 1

Feature 1: y = **ν3**, x = **ν1 + ν3**



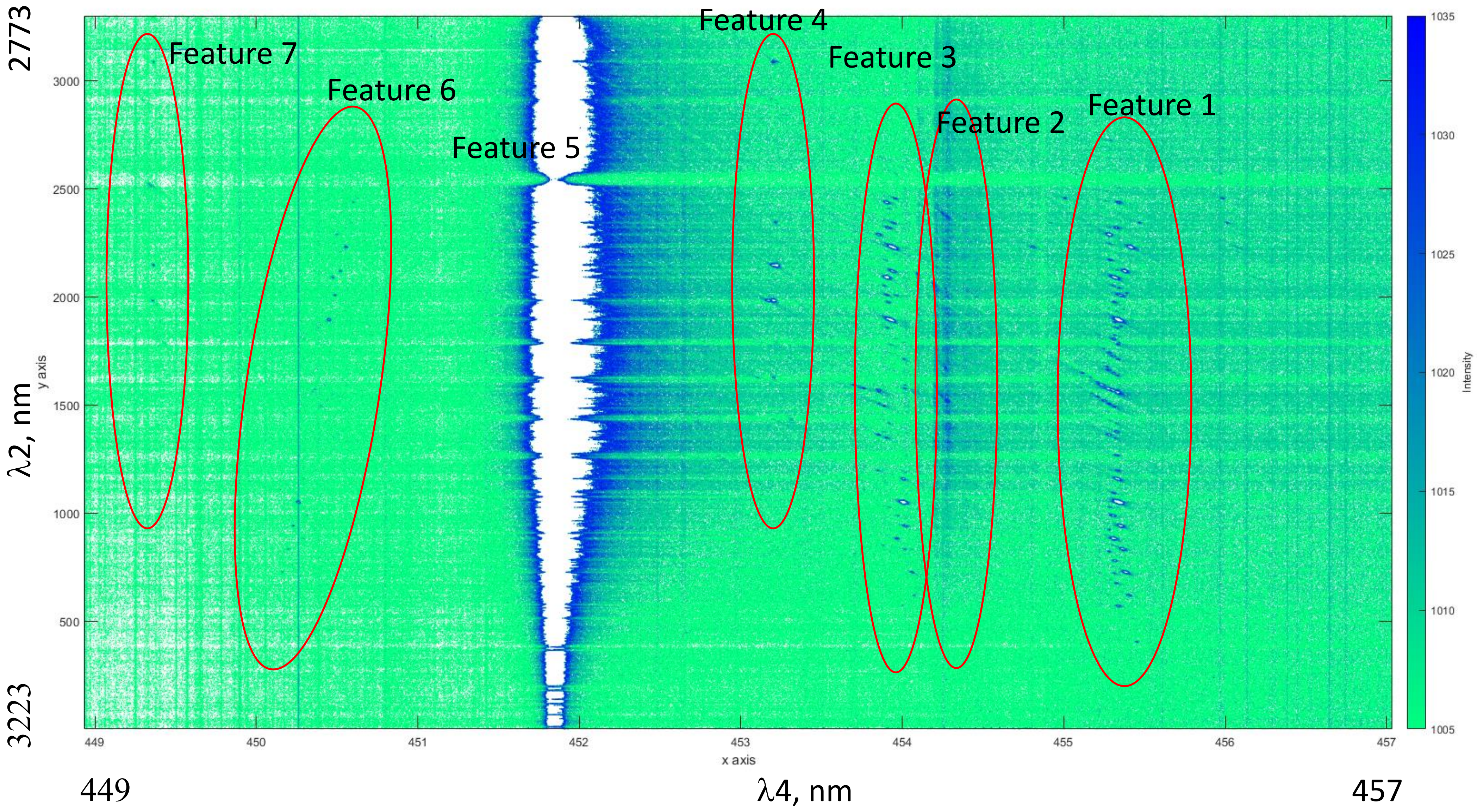
Hitran simulation vs experiment for Feature 3

Feature 3: y = **ν3**, x = **ν3 + 2ν4**



052623a1, ammonia
Noise 1000: Outlier 1035, 0.003nm/sec, 2 sec integration, flashed 769.050 and 789.350 nm

Feature 1: ν3 and ν1 + ν3
Feature 3: ν3 and ν3 + 2ν4
Feature 4: ν1 and ν1 + ν3
Feature 5: Coherent Raman of ν1



Conclusions

- Experimental 2D spectra partially agree with the corresponding HITRAN simulation. Need to further explore selection rules and tendencies. Also need to improve the instrument so that we can possibly observe weaker peaks.
- Peaks that are entangled in conventional IR spectra appear spatially separated by their coupled vibrational modes in 2D rovibrational spectra
- Peaks are limited:
  - Their vibrations must be coupled
  - Limited by common level requirements
  - Follow multiple selection rules (two IR and one Raman).
- Within each feature:
  - All peaks involve the same vibrational levels
  - All peaks come from the same FWM process
  - All peaks involve the same set of selection rules

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