



# Far-infrared $^{14}\text{NH}_3$ line positions and intensities measured with submm and FT-IR spectroscopy

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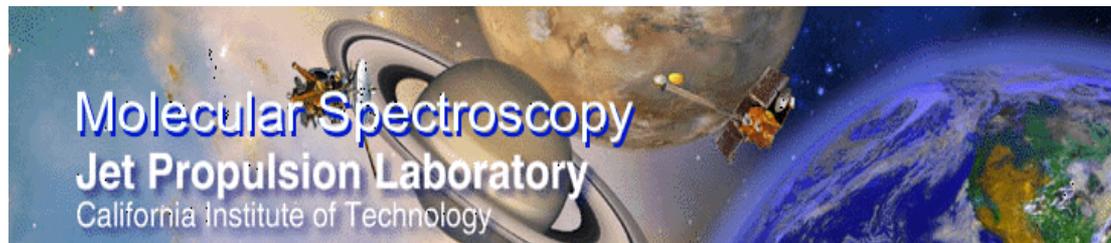
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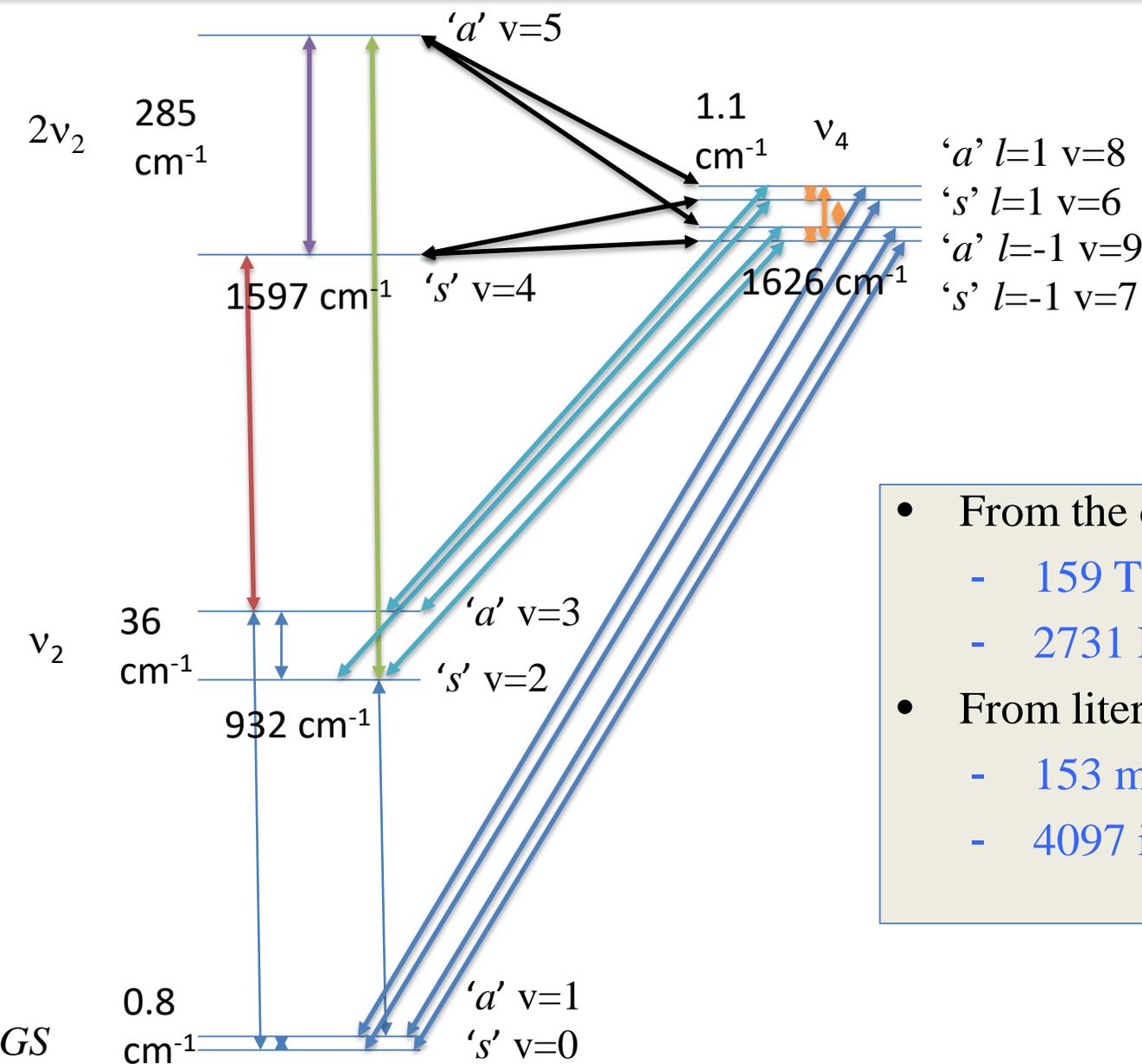
# Outline



- Results on modeling  $\text{NH}_3$   $2\nu_2$  and  $\nu_4$  line positions to experimental accuracy
- Results on  $\text{NH}_3$  experimental line intensities in FIR and their comparisons to models and HITRAN
- What we have learned from the current work

**More details in Pearson et al 2016, JCP (in press) and Sung et al 2016, JMS (in press)**

# Lines included in our Hamiltonian modeling of $2\nu_2$ and $\nu_4$



- From the current work
  - 159 THz transitions
  - 2731 FTIR transitions
- From literature
  - 153 microwave transitions
  - 4097 infrared transitions

# Summary of sources for our new data on line positions



	JPL	Synchrotron SOLEIL	
Instrument	FMSS	FTS	FTS
Frequency range	0.38 – 2.03 THz;	50 - 700 $\text{cm}^{-1}$	50 - 700 $\text{cm}^{-1}$
Absorption or emission	Absorption	Emission	Absorption
Resolution	Doppler limited	0.004 $\text{cm}^{-1}$	0.0011 $\text{cm}^{-1}$
Optical path (m)	1 m	0.7 m	180 m
Gas pressure	30 - 500 mTorr	10 Torr	1 Torr
Gas temperature	300 K	~900K	300K
Experimental accuracy	200 kHz	0.001 $\text{cm}^{-1}$	0.0006 $\text{cm}^{-1}$

\* The two FTS spectra from Synchrotron SOLEIL were recorded in 2010 and used in our data analysis of the ground state and  $\nu_2$  state of  $\text{NH}_3$  (Yu et al. 2010)

# Fit statistics for datasets involving $2\nu_2$ and $\nu_4$ of NH<sub>3</sub>

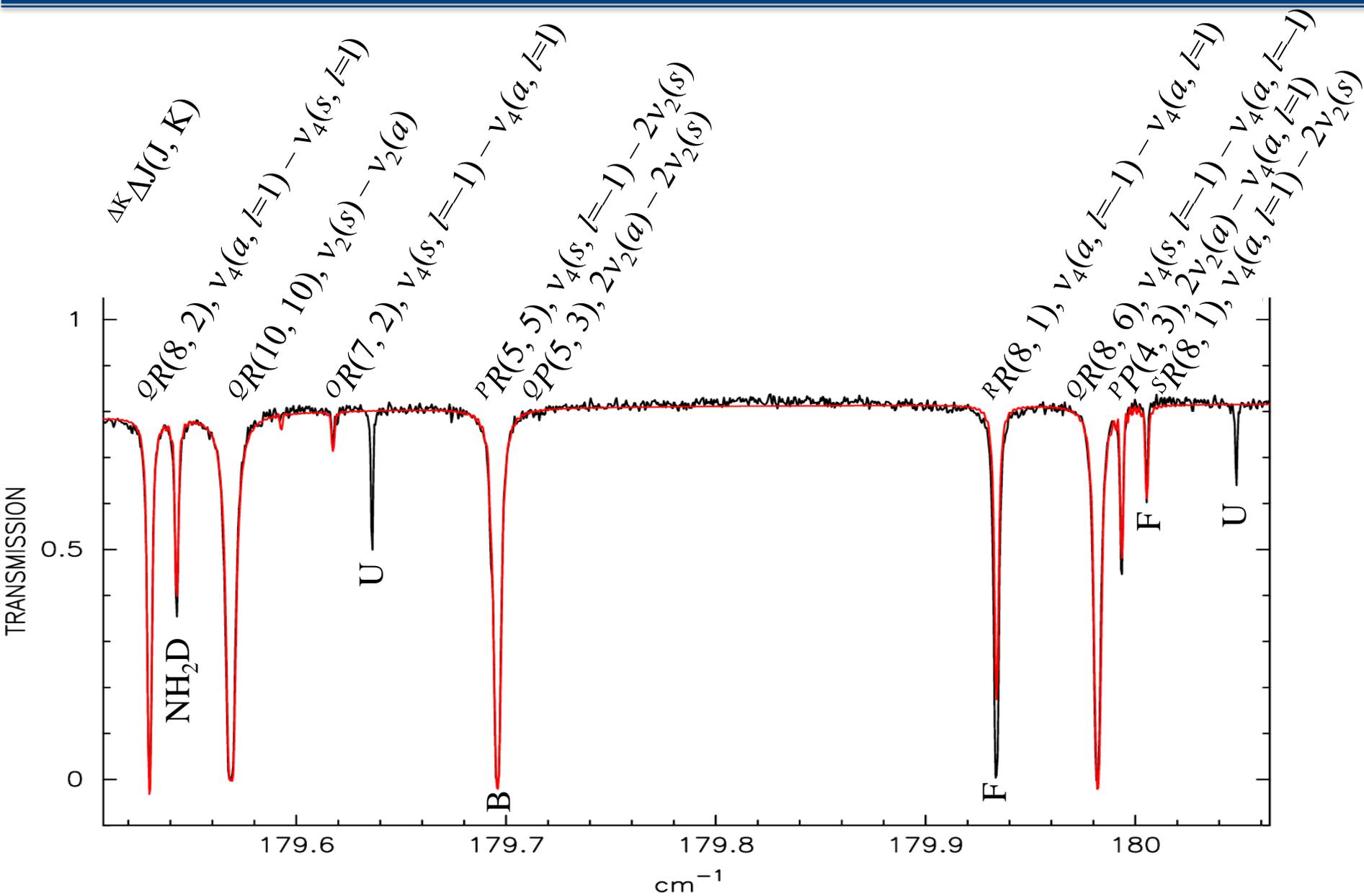


Reference	Band type	Experimental				Model			
		# of reported lines	$J''$ range	$K''$ range	Uncertainty (MHz)	RMS (MHz)	Reduced RMS	Average residual (MHz)	# of excluded line
Cohen 1974 [30]	$\nu_4$ inversion	50	1-15	1-15	0.005-0.3	0.167	1.839	0.027	0
Bischel 1976 [64]	$2\nu_2$ inversion	1	5	4	0.1	0.075	0.751	-0.075	0
Cohen 1980 [31]	$\nu_4$ inversion	18	5-10	3-7	0.02-0.05	0.102	2.283	-0.015	0
Sasada 1982 [32]	$\nu_4$ inversion/ $2\nu_2$ - $\nu_4$	12	3-11	1-11	0.05	0.093	1.857	-0.042	2
Sasada 1992 [5]	$\nu_4$ inversion/ $2\nu_2$ - $\nu_4$	79	1-14	0-14	0.05	0.089	1.773	-0.004	5
Present work	$\nu_4$ inversion/ $2\nu_2$ - $\nu_4$	159	0-13	0-11	0.2	0.387	1.935	0.011	0
					(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )		
Present work	$\nu_4$ , $2\nu_2$ inversion/ $2\nu_2$ - $\nu_4$	2731	1-19	0-19	0.0006-0.005	0.001	1.227	0.000	0
Nereson 1978 [34]	$2\nu_2$ - $\nu_2$	24	1-12	1-11	0.002	0.002	0.940	0.001	0
Sattler 1981 [35]	$2\nu_2$ - $\nu_2$	6	4-10	2-9	0.0002	0.000	0.855	0.000	1
Sattler 1981 [36]	$2\nu_2$ - $\nu_2$	16	1-11	1-11	0.0002-0.0003	0.000	0.386	0.000	0
Urban 1984 [29]	$\nu_4$	927	1-18	0-18	0.0005-0.03	0.004	0.848	0.000	16
Weber 1984 [48]	$\nu_4$ and $2\nu_2$	176	1-13	0-13	0.00013-0.004	0.001	1.100	0.000	0
Hermanussen 1986 [38]	$\nu_4$ - $\nu_2$ and $2\nu_2$ - $\nu_2$	223 <sup>a</sup>	0-15	0-13	0.003	0.003	1.023	0.000	0
Papousek 1986 [49]	$2\nu_2$	72	3-12	2-12	0.001	0.002	1.559	0.000	3
					0.00007-				
Sasada 1986 [33]	$2\nu_2$ - $\nu_2$	135	1-12	0-12	0.00025	0.000	1.348	0.000	0
D'Cunha 1987 [37]	$2\nu_2$ - $\nu_2$	194	1-11	0-11	0.001	0.001	1.193	0.000	4
Lellouch 1987 [50]	$\nu_4$ and $2\nu_2$	455 <sup>b</sup>	1-14	0-14	0.0003	0.001	1.946	0.000	0
Sasada 1992 [5]	$\nu_4$ and $2\nu_2$	700	0-15	0-15	0.0002-0.00175	0.001	2.541	0.000	16
Chu 1994 [40]	$2\nu_2$ - $\nu_2$	12	1-12	0-11	0.0002	0.000	1.038	0.000	0
Cottaz 2000 [6]	$\nu_4$ and $2\nu_2$	1203	0-16	0-16	0.0003	0.000	1.205	0.000	6

<sup>a</sup> 131 new assignments were made from this work.

<sup>b</sup> 305 new assignments were made from this work.

# Observed and simulated spectrum



# NH<sub>3</sub> FIR intensity: motivations and data acquisition

## ❖ Primary objectives

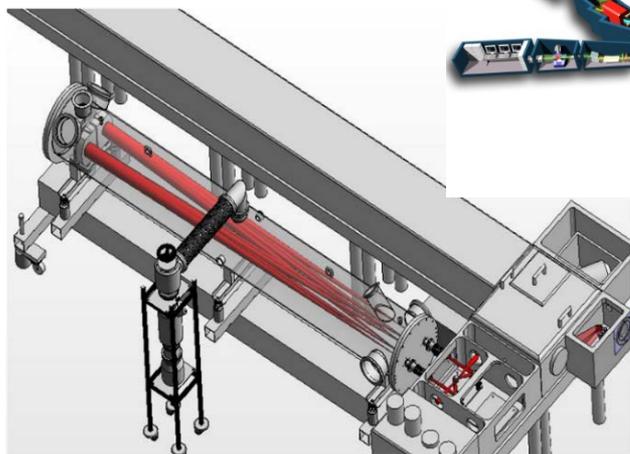
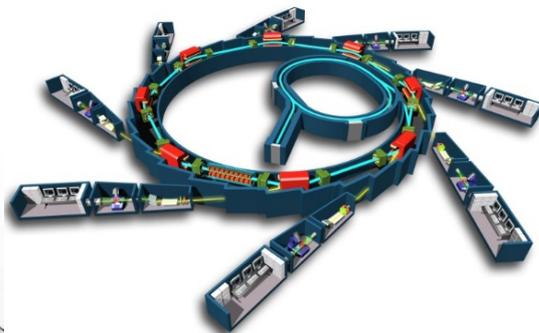
- Measuring weak lines with intensity of  $\sim 10^{-22}$  cm/molecule (100 times weaker than GS lines), esp.  $\Delta K=3$  forbidden transitions
- Validation of calculations

*Yu et al. 2010; Pearson et al. 2016; HITRAN*

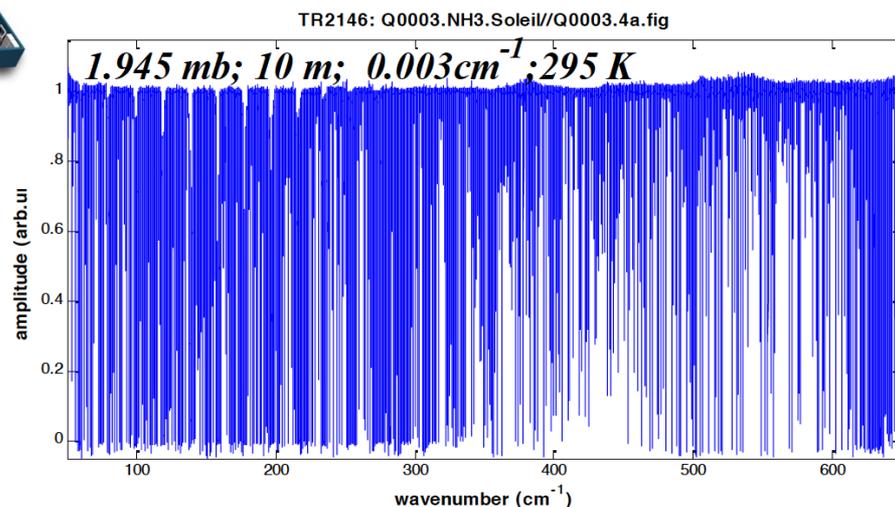
## ❑ Experimental conditions

Gas samples	Normal sample
Spectral region	50 – 660 cm <sup>-1</sup>
Resolution(B)	0.003 cm <sup>-1</sup>
Pressures	2.0, 6.0 mbar
Path lengths	10, 80 m
Temperatures	295 K

## ❖ Data acquisition



2.52 m base White cell



# NH<sub>3</sub> line positions and intensities



## ❖ Spectrum fitting

- ✓ Voigt profile assumed
- ✓ *sinc* function with FOV correction
- ✓ Non-linear curve fitting
- ✓ One spectrum at a time
- ✓ Line position, intensity, self-pressure broadening, simultaneously retrieved

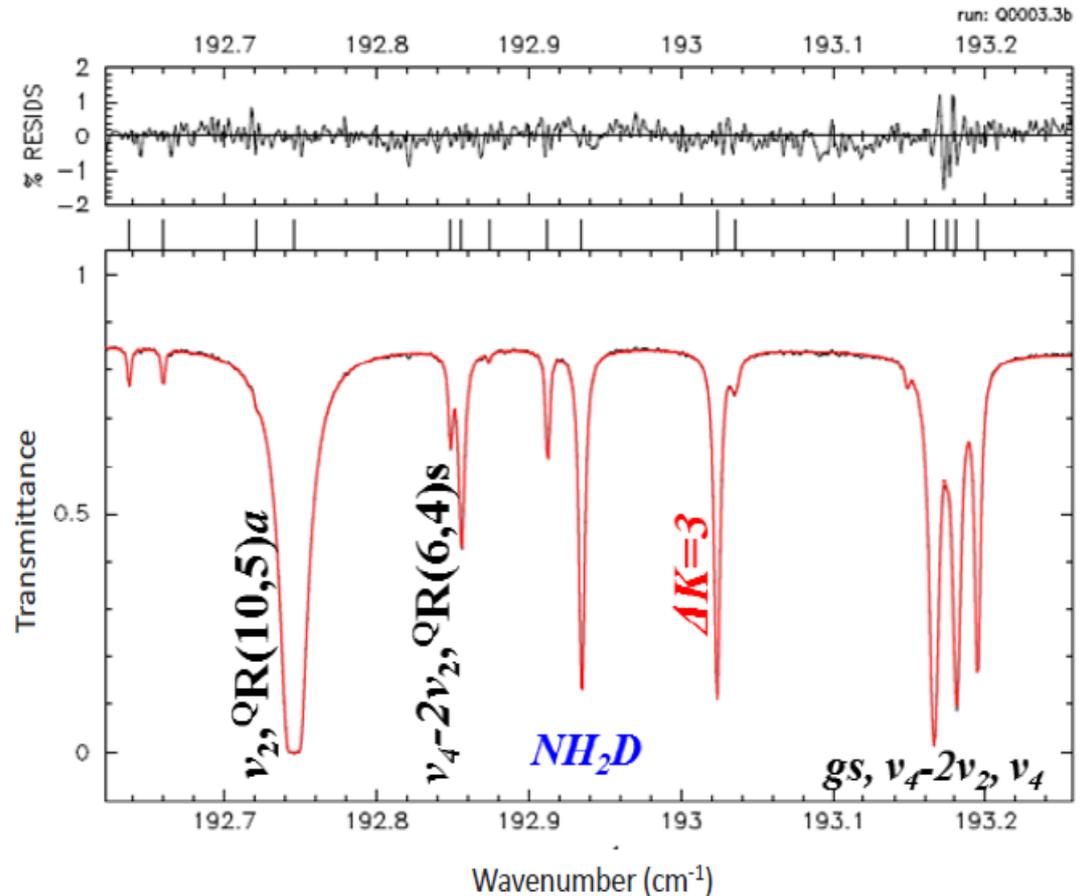
## ❖ Averaging the measurements

- Grouping within 0.5\*resolution
- Positions, intensities, widths were averaged
- Compiled into one set of list
- ~ 4820 lines were retrieved

## ❖ Frequency calibration

- 18 isolated water features
- HITRAN as standards
- freq. accuracy  $\geq 0.0002 \text{ cm}^{-1}$

## ❖ Residuals = Observed - Calculated





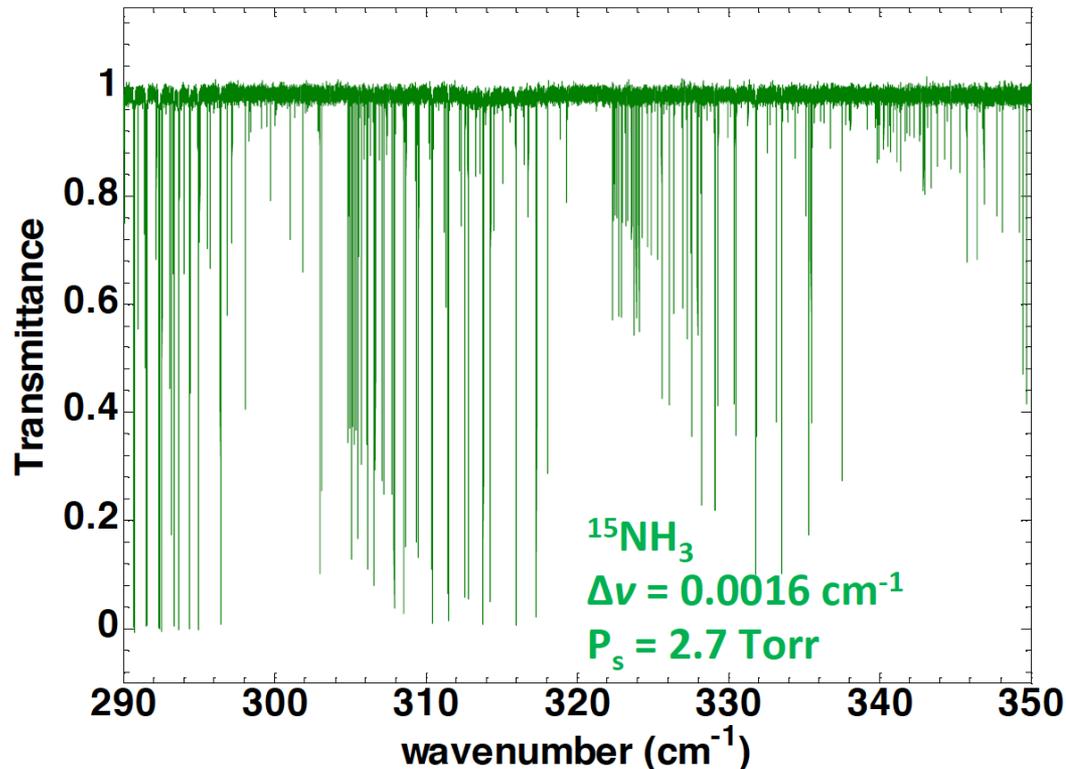
# Spectroscopic sample characterization

## □ Filtering out contaminated species

- H<sub>2</sub>O – 343 lines (HITRAN)
- <sup>15</sup>NH<sub>3</sub> – 455 lines (<sup>15</sup>NH<sub>3</sub> spectrum from SOLEIL)
- NH<sub>2</sub>D – 530 lines (CDMS; <http://www.cdms.de>)
- <sup>14</sup>NH<sub>3</sub> – most of the remaining lines

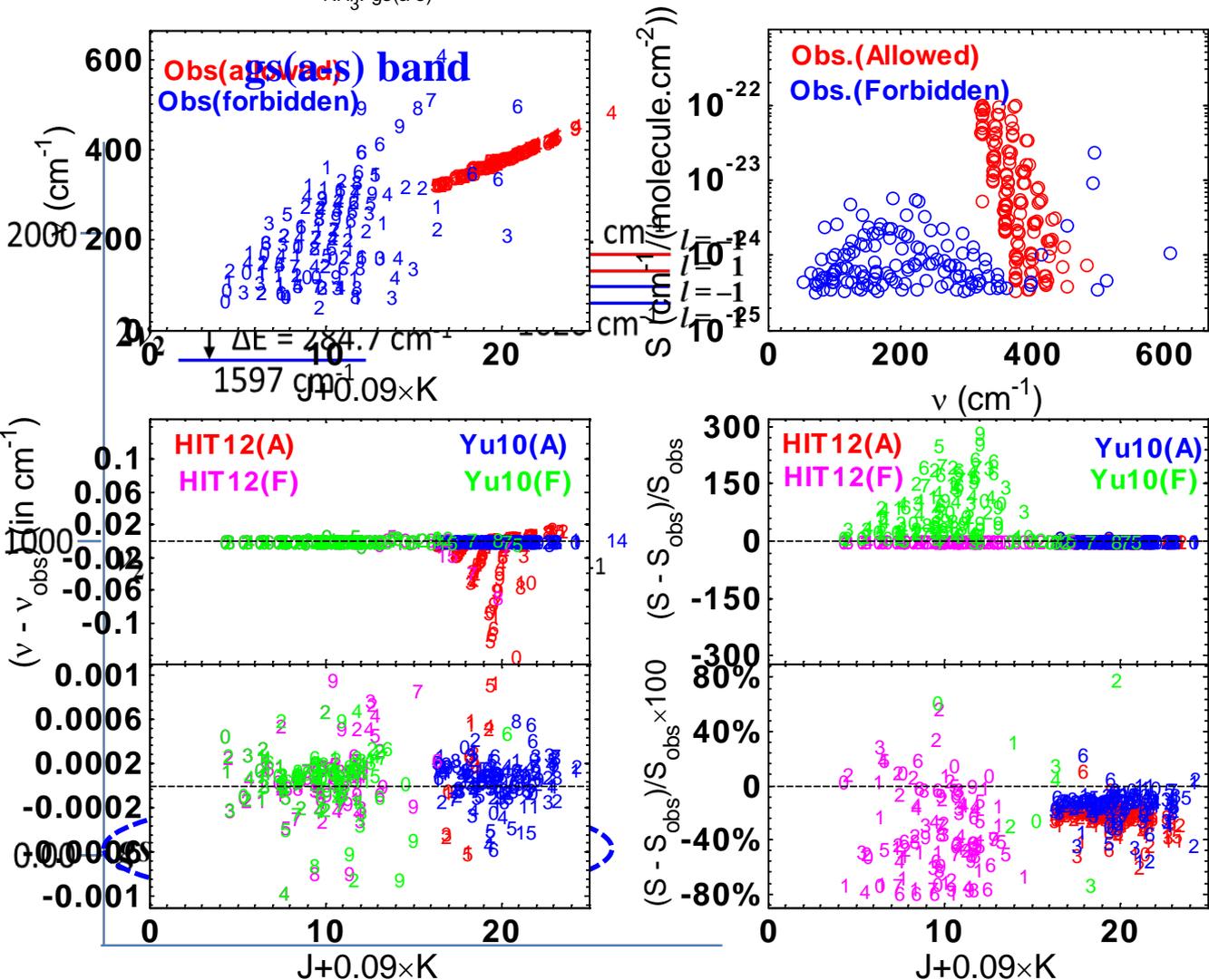
## □ Abundances

- H<sub>2</sub>O (0.2%)
- <sup>15</sup>NH<sub>3</sub> (0.33%)
- NH<sub>2</sub>D (0.037%)
- Total impurity = 0.57%



# Results and Comparison: gs(a-s)

$^{14}\text{NH}_3$ : gs(a-s)



## Line positions

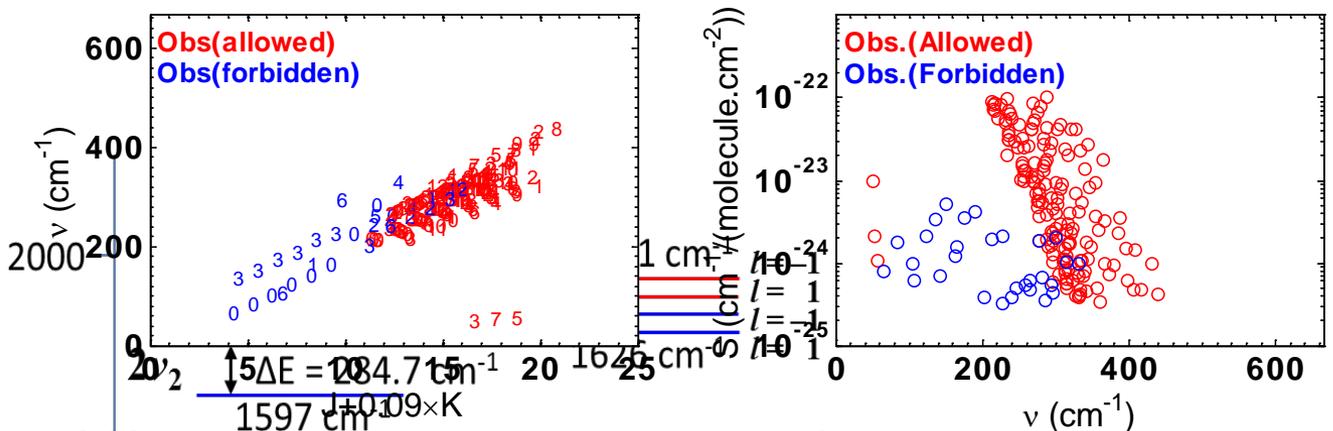
- Allowed transitions (A)
- Excellent agreement with both
- Forbidden transitions (F)
- Deviation at high J from H12

## Line intensities

- (A): high J lines
- (F): intermediate J lines
- (A): Measured low
- (F): Yu et al. shows large offsets, up to by a factor of 300.

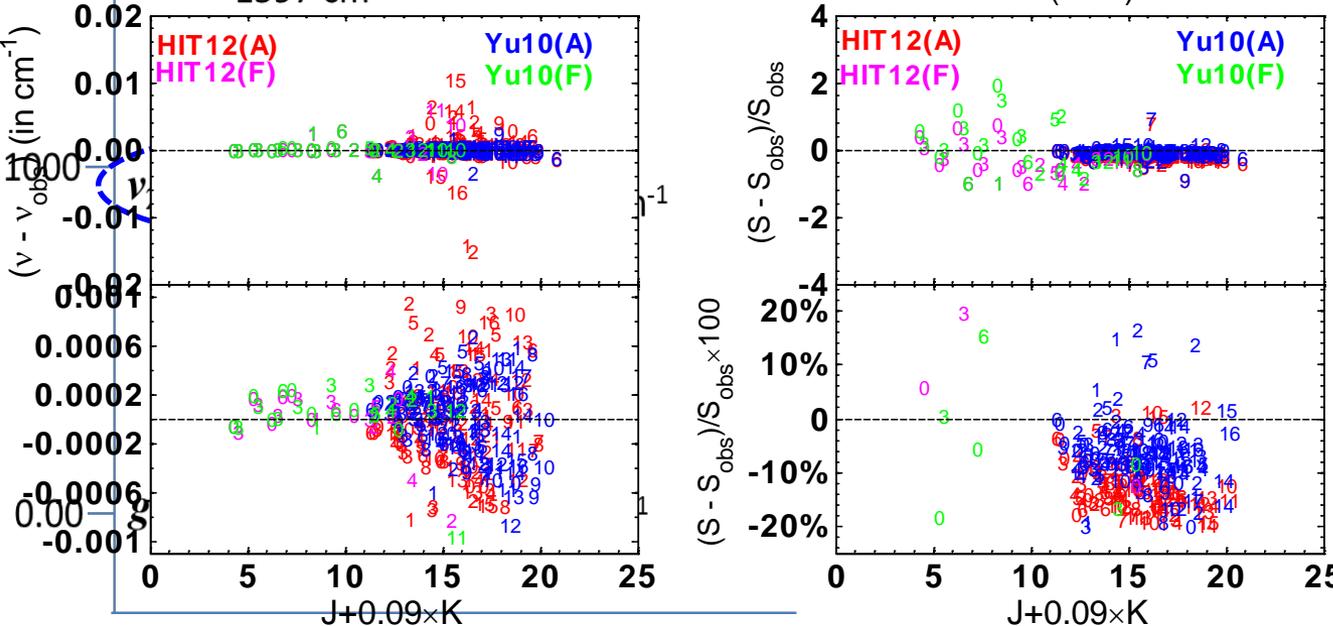
# Results and Comparison: $\nu_2(a-s)$

$^{14}\text{NH}_3$ :  $\nu_2(a-s)$



## □ Line positions

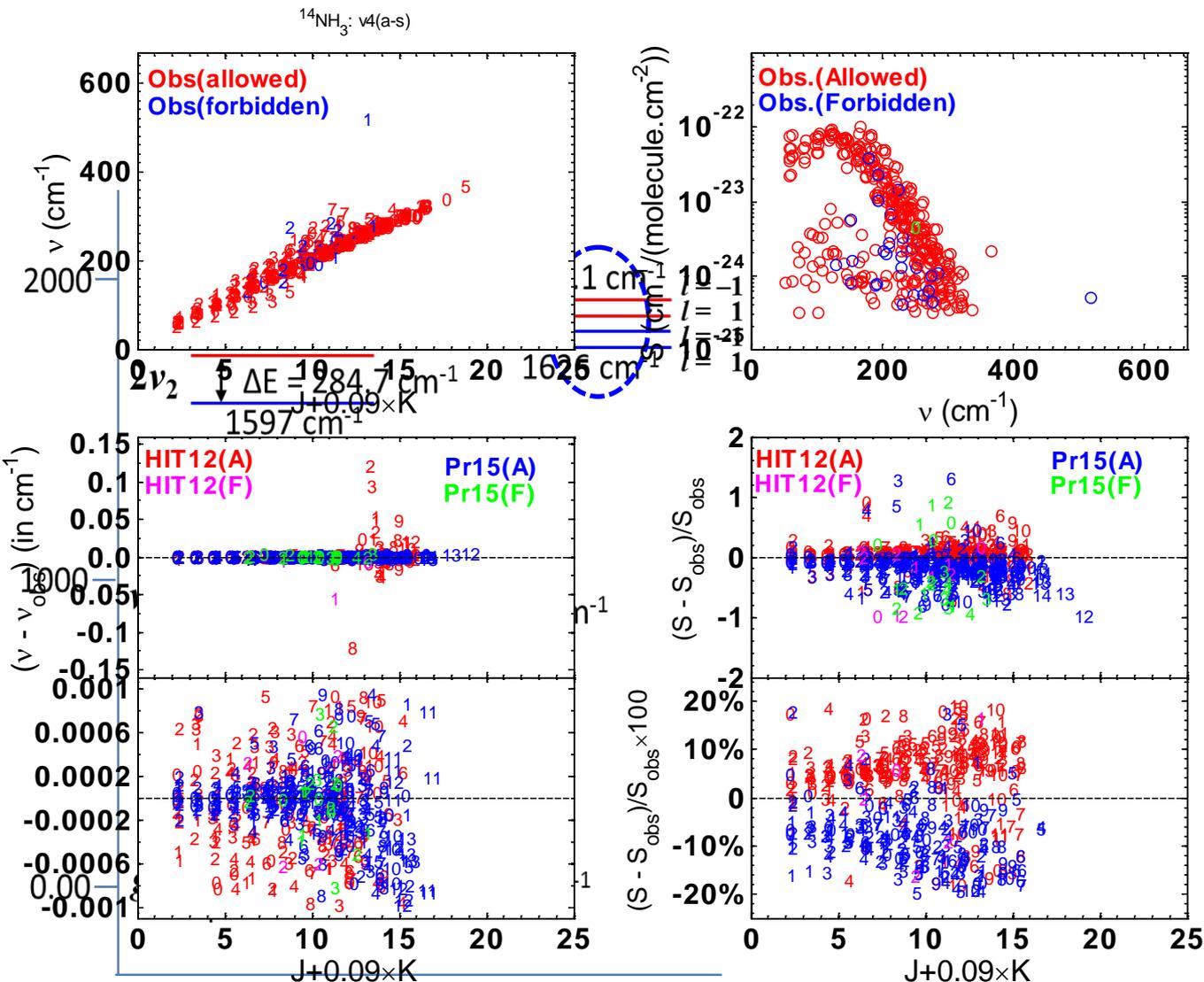
- Allowed transitions(A)
- Good agreement with both
- but diverging at high J lines
- Forbidden transitions(F)
- sparse but excellent agreement



## □ Line intensities

- (A): Agree better with Yu et al.
- (F): Agree better with HITRAN

# Results and Comparison: $\nu_4$ (a-s)



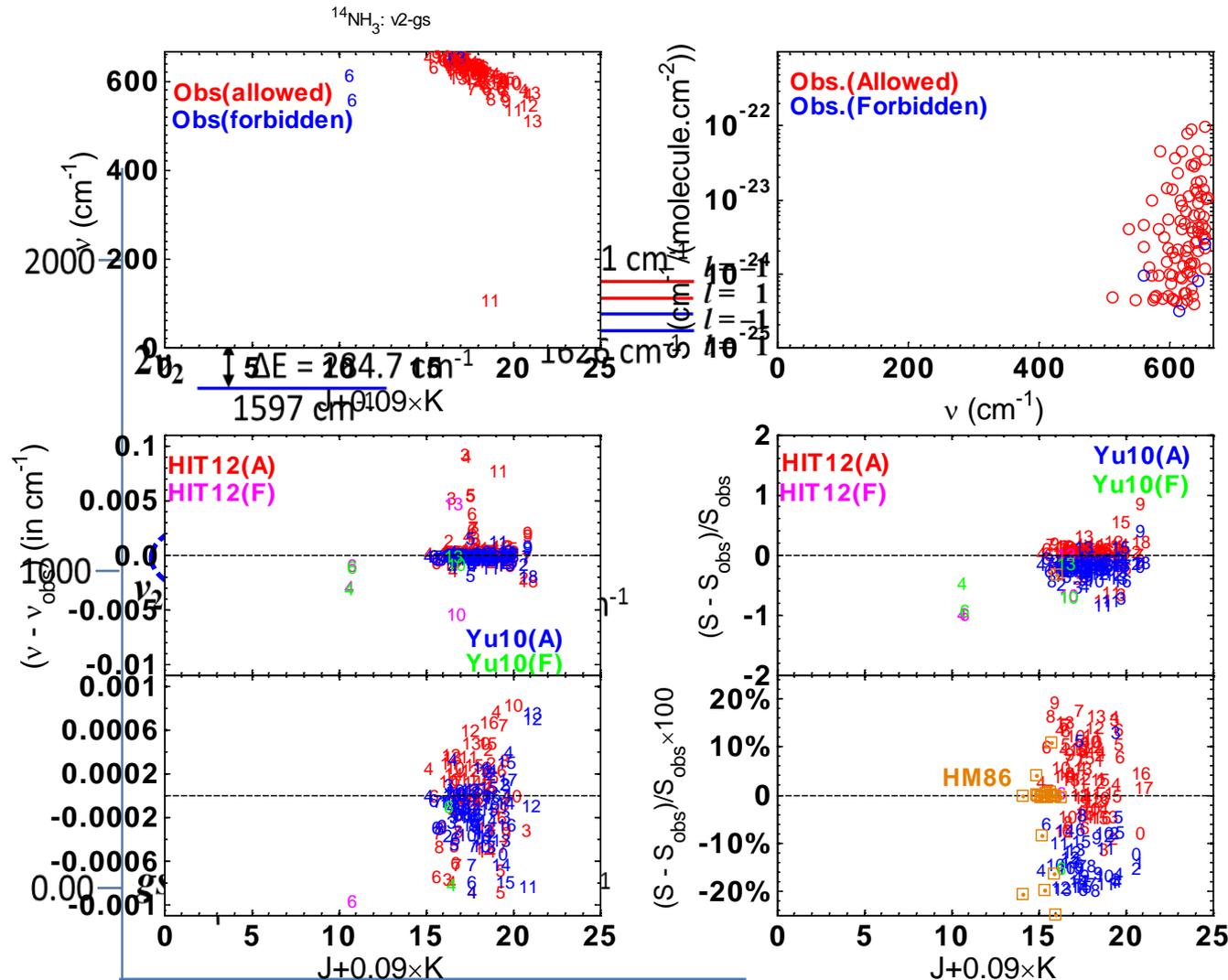
## Line positions

- Allowed transitions(A)
- Excellent agreement with both.
- Forbidden transitions(F)
- Excellent agreement

## Line intensities

- (A): Good agreement in general, but, progressively diverging toward high J lines
- (F): outliers from predictions

# Results and Comparison: $\nu_2 - \text{gs}$



Only high J lines from P-branch captured

Line positions

- Allowed transitions(A)

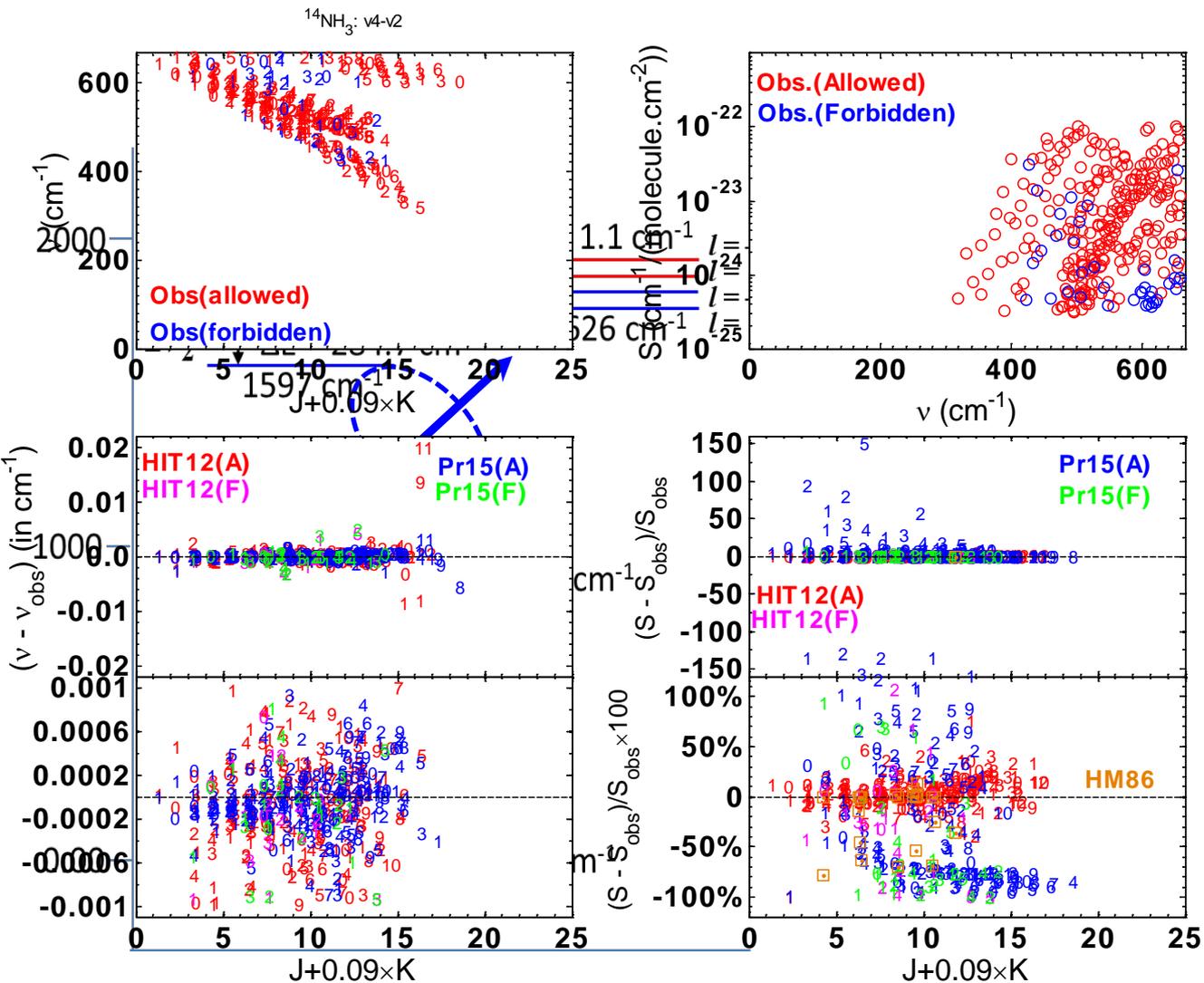
→ Very good except a few outliers.

Line intensities

(A): Agree better than HITRAN

Also compared with HM86 (Hermanussen et al. 1986)

# Results and Comparison: $\nu_4 - \nu_2$



## Line positions

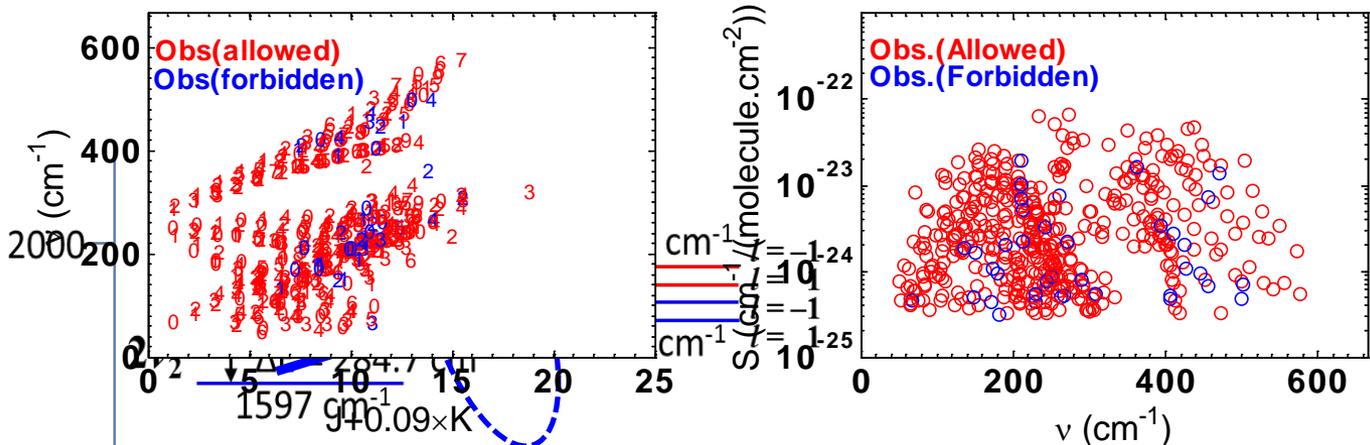
- Allowed transitions(A)
  - Forbidden transitions(F)
- Excellent agreement

## Line intensities

- (A): Much better agreement with HITRAN, esp. low J lines
- Also compared with HM86:  
(Hermanussen et al. 1986)

# Results and Comparison: $\nu_4 - 2\nu_2$

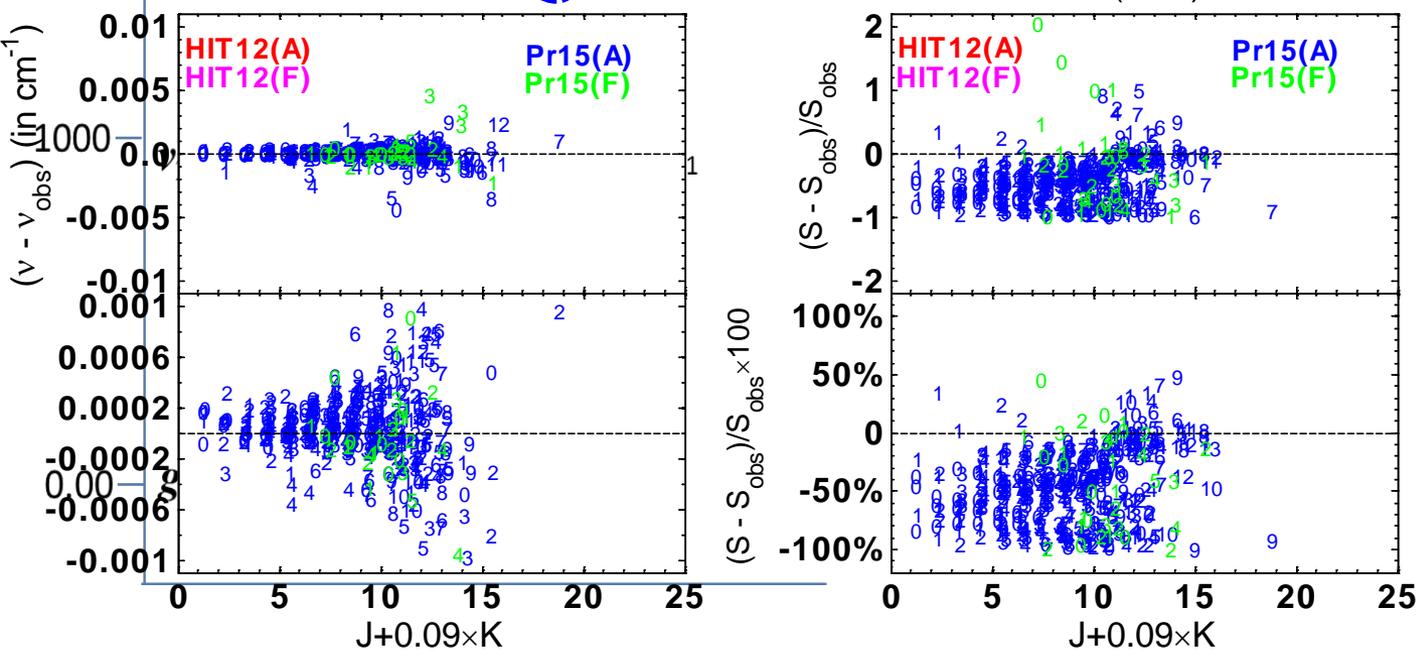
$^{14}\text{NH}_3$ :  $\nu_4 - 2\nu_2$



This band  
Not listed in HITRAN

Line positions

- Allowed transitions(A)
  - Forbidden transitions(F)
- Excellent agreement



Line intensities

(A): Measured low  
with large spread on K  
(F): Sparsely measured  
for high J lines and  
randomly scattered



# Compiled line parameters

#	Bands	#Meas.(A; F)	J range	K range	RMS(v)cm <sup>-1</sup>	RMS(%dS)
1	<i>gs (a-s)</i>	152; 140	16 ≤ J ≤ 24	0 ≤ J ≤ 22	0.00014	8.1
2	<i>v<sub>2</sub> (a-s)</i>	156; 29	11 ≤ J ≤ 19	0 ≤ J ≤ 18	0.00010	7.2
3	<i>2v<sub>2</sub>(a-s)</i>	164; 12	2 ≤ J ≤ 18	1 ≤ J ≤ 18	0.00019	6.0
4	<i>v<sub>4</sub>(a-s)</i>	365; 30	2 ≤ J ≤ 17	2 ≤ J ≤ 17	0.00013	7.4
5	<i>v<sub>2</sub> - gs</i>	94; 4	14 ≤ J ≤ 19	0 ≤ J ≤ 18	0.00016	6.1
7	<i>2v<sub>2</sub> - v<sub>2</sub></i>	109; 8	6 ≤ J ≤ 19	0 ≤ J ≤ 18	0.00013	6.7
9	<i>v<sub>4</sub> - v<sub>2</sub></i>	259; 38	1 ≤ J ≤ 17	1 ≤ J ≤ 15	0.00021	8.0
8	<i>v<sub>4</sub> - 2v<sub>2</sub></i>	445; 42	1 ≤ J ≤ 17	1 ≤ J ≤ 17	0.00013	6.4
	Total	Meas.	2835	$3 \times 10^{-25} \leq S \leq 1 \times 10^{-22}$ cm/molecule 0 – 2 % 849 2 – 5 % 568 5 – 10 % 293		
Assigned		2047				
Allowed(A)		1744				
Forbidden(F)		303				
Unassigned		788	<sup>14</sup> NH <sub>3</sub> , NH <sub>2</sub> D (?)			



# What we have learned from the current work (I)

## The Hamiltonian (1/2)

$$H = H_{diag} + H_{nondiag}$$

Diagonal is with respect to inversion  $\psi_i^s(\rho)$  or  $\psi_i^a(\rho)$

$$H_{diag} = H_0 + H_2 + H_{4d} + H_{6d} + \dots$$

$H_0 = E_i$  Solution of inversion problem

$$H_2 = B(\rho)J^2 + (C(\rho) - B(\rho))J_Z^2$$

$$H_{4d} = -D_J(\rho)(J^2)^2 - D_{JK}(\rho)J^2J_Z^2 - D_K(\rho)J_Z^4$$

$$H_{6d} = H_J(\rho)(J^2)^3 + H_{JK}(\rho)(J^2)^2J_Z^2 + H_{KJ}(\rho)J^2J_Z^4 \\ + H_K(\rho)J_Z^6 + \eta_3(\rho)(J_+^6 + J_-^6)$$

Note constants are different for a and s inversion states

## The Hamiltonian (2/2)

$$H_{nondiag} = H_3 + H_{4nd} + H_5 + H_{6nd} + \dots$$

$$H_3 = i\beta(\rho)(J_+^3 - J_-^3)$$

$$H_{4nd} = \alpha(\rho)[J_+^3 + J_-^3, J_z]_+$$

$$H_5 = i\beta_J(\rho)J^2(J_+^3 - J_-^3) + i\beta_K(\rho)[J_z^2, J_+^3 - J_-^3]_+$$

$$H_{6nd} = \alpha_J(\rho)J^2[J_+^3 + J_-^3, J_z]_+ + \alpha_K(\rho)[J_+^3 + J_-^3, J_z^3]$$

Where  $[A, B]_+ = AB + BA$

Ground state and  $v_2$  were solved with  $H_3=H_5=0$

Can be solved with  $H_{4nd}=H_{6nd}=0$  just as well

One set for each  $s$  and a pair



## Contact transformation (1/2)

Can make a unitary Transform of the form:

$$\tilde{H} = e^{-iS} H e^{iS}$$

Can define the following

$$S_3 + S_5 = i s_3 [J_+^3 - J_-^3] + i s_{5J} J^2 [J_+^3 - J_-^3] + i s_{5K} [J_+^3 - J_-^3, J_z^2]$$

$$S_4 + S_6 = s_4 [J_+^3 + J_-^3, J_z] + s_{6J} J^2 [J_+^3 + J_-^3, J_z] + s_{6K} [J_+^3 + J_-^3, J_z^3]$$

Where

$$S = S_3 + S_4 + S_5 + S_6$$

$S_3, S_{5J}, S_{5K}, S_4, S_{6J}, S_{6K}$  are chosen according to Watson



## Contact transformation (2/2)

### The transformed Hamiltonian

$$\tilde{H}_0 = H_0$$

$$\tilde{H}_2 = H_2$$

$$\tilde{H}_3 = H_3 + i[H_0, S_3]_\rho$$

$$\tilde{H}_4 = H_4 + i[H_2, S_3]_R + i[H_0, S_4]_\rho$$

Where H and S are both products for rotation R and inversion  $\rho$

$$H = \dots + H_\rho(\rho)H_R(R) + \dots$$

$$S = \dots + S_\rho(\rho)S_R(R) + \dots$$

Can choose  $S_3$  or  $S_4$  to make either  $\tilde{H}_3$  or  $\tilde{H}_4$  vanish

If the orders of magnitude of the terms satisfy “smallness”



## Ground state and $\nu_2$

- Ground and  $\nu_2$  fit with  $\tilde{H}_3=0$ 
  - Transformations are different in ground and  $\nu_2$
  - Form of transformation:  $S_3 + S_5 = iS_3[J_+^3 - J_-^3] + iS_{5J}J^2[J_+^3 - J_-^3] + iS_{5K}[J_+^3 - J_-^3, J_Z^2]$  which is  $\Delta K=3$
  - Transform scrambles the meaning of “K” in ground state relative to  $\nu_2$  results in  $\Delta K=3, 6, 9$  contributions
  - Transformed dipoles moment are now needed
- Contact transformation depends on  $\rho$  in each state
- Two choices to get intensities right:
  - Transform dipoles or
  - Solve in a common  $\rho$ -axis



## Other states

- GS and  $\nu_2$  do fit but  $\Delta K=3$  intensities are poor
- $2\nu_2/\nu_4$  and higher
  - States are no longer isolated
  - Magnitude of inversion very different (path of atoms different)
  - One set of transformations cannot remove  $H_3$  and  $H_5$  in all states
  - “smallness” will be violated in one or more states
  - Fits poor with parameters in  $H_3$  and  $H_5$  set to zero
  - Intensities are worse than fits
- At a minimum one  $\rho$ -axis can be defined so that the others are relative. I.e. must fit the  $H_3$  and  $H_5$  terms
- Care must be taken in vibrational bands to use the same axis system or transform the dipoles accordingly

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