Improved Far-IR Ammonia Intensity From Empirical Hamiltonian Model

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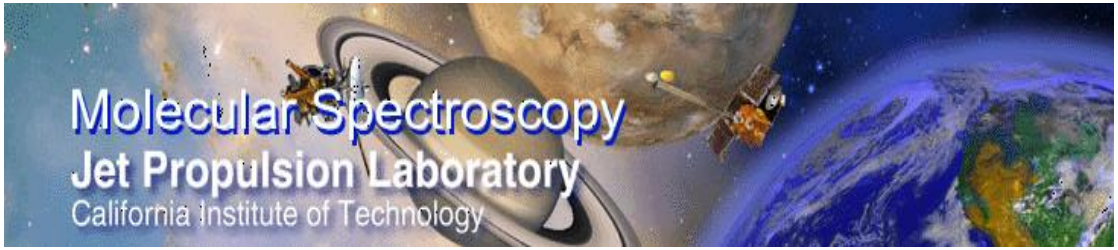

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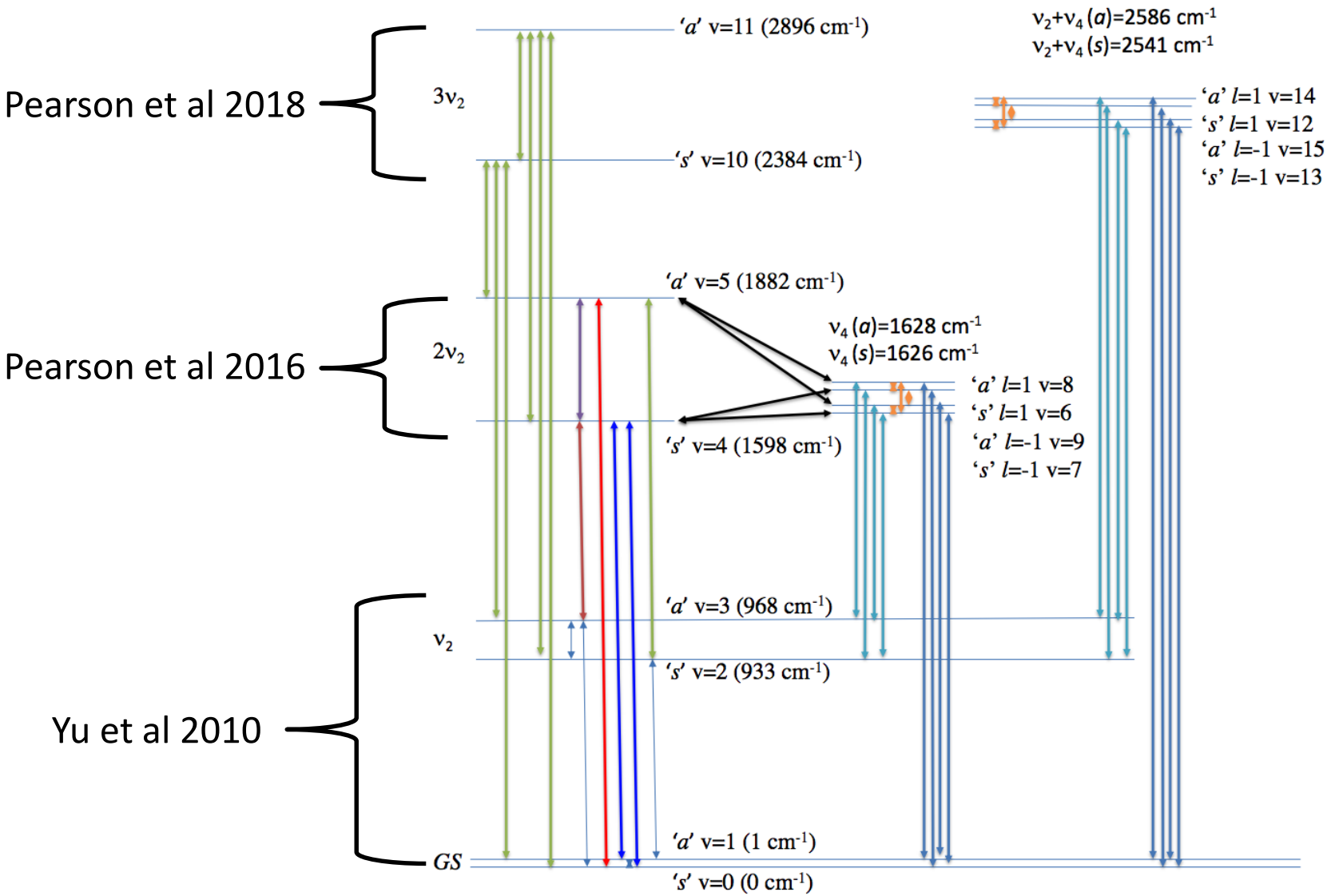
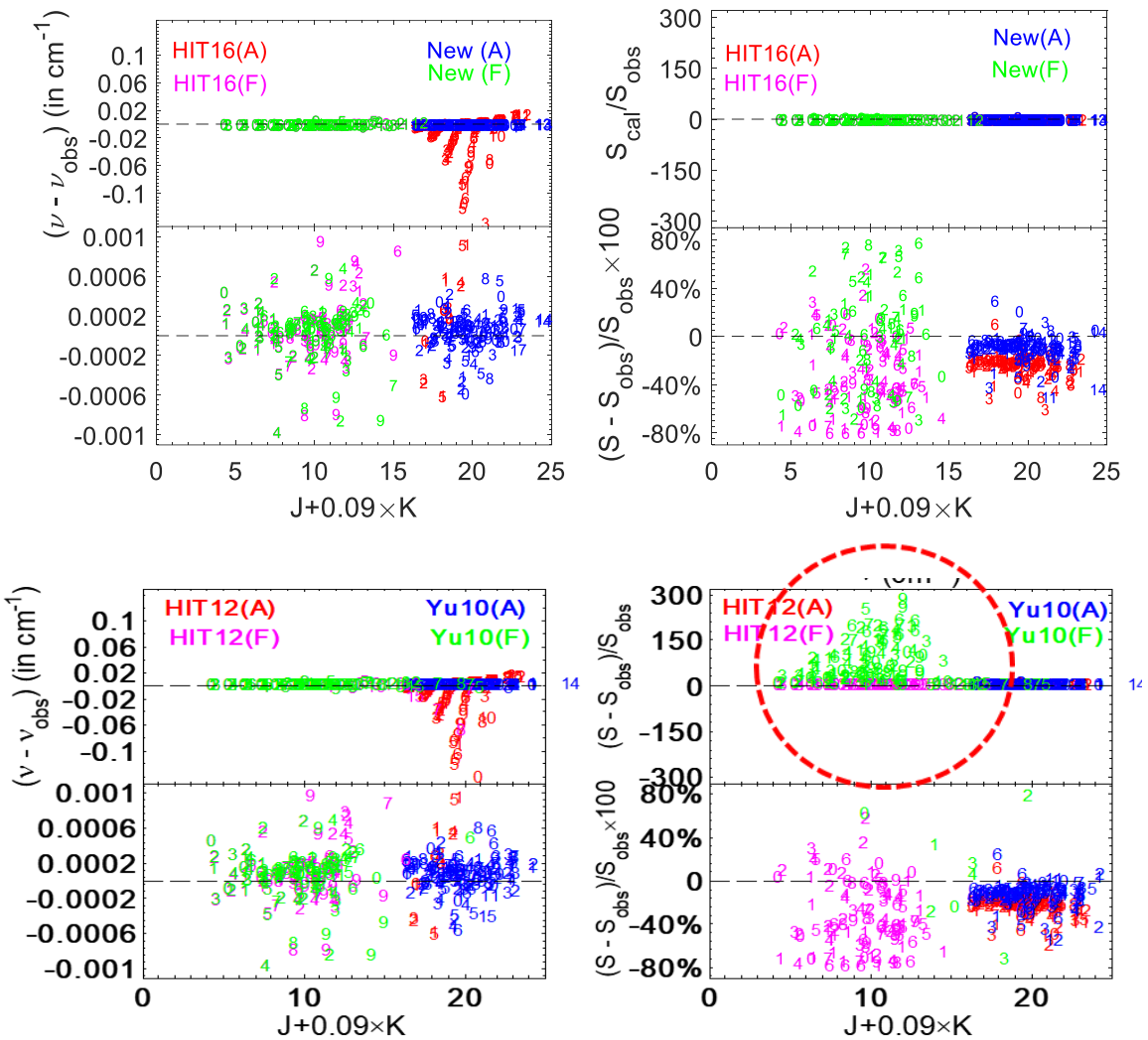
Motivation

- In FE08 of 2016 ISMS, we reported experimental intensity measurements of NH_3 from three Synchrotron SOLEIL spectra in 50-700 cm^{-1}. We used our intensity measurements as standard to evaluate calculations in
  - Yu et al. 2010 (GS and ν2)
  - Pearson et al. 2016 (2ν2 and ν4)
  - HITRAN2012
- In the past year, we improved our intensity predictions and worked on Hamiltonian modeling of 3ν2 and ν2+ν4. This paper reports evaluation of this new work and HITRAN 2016
  - Fix a bug in SPCAT
  - Used dipoles from Yurchenko et al (2009) for bands involving 2ν2 and higher (referred as "ab initio" thereafter)

NH_3 energy levels modeled at JPL



gs(a-s) comparison: HIT16, HIT12, Pr18, Yu10



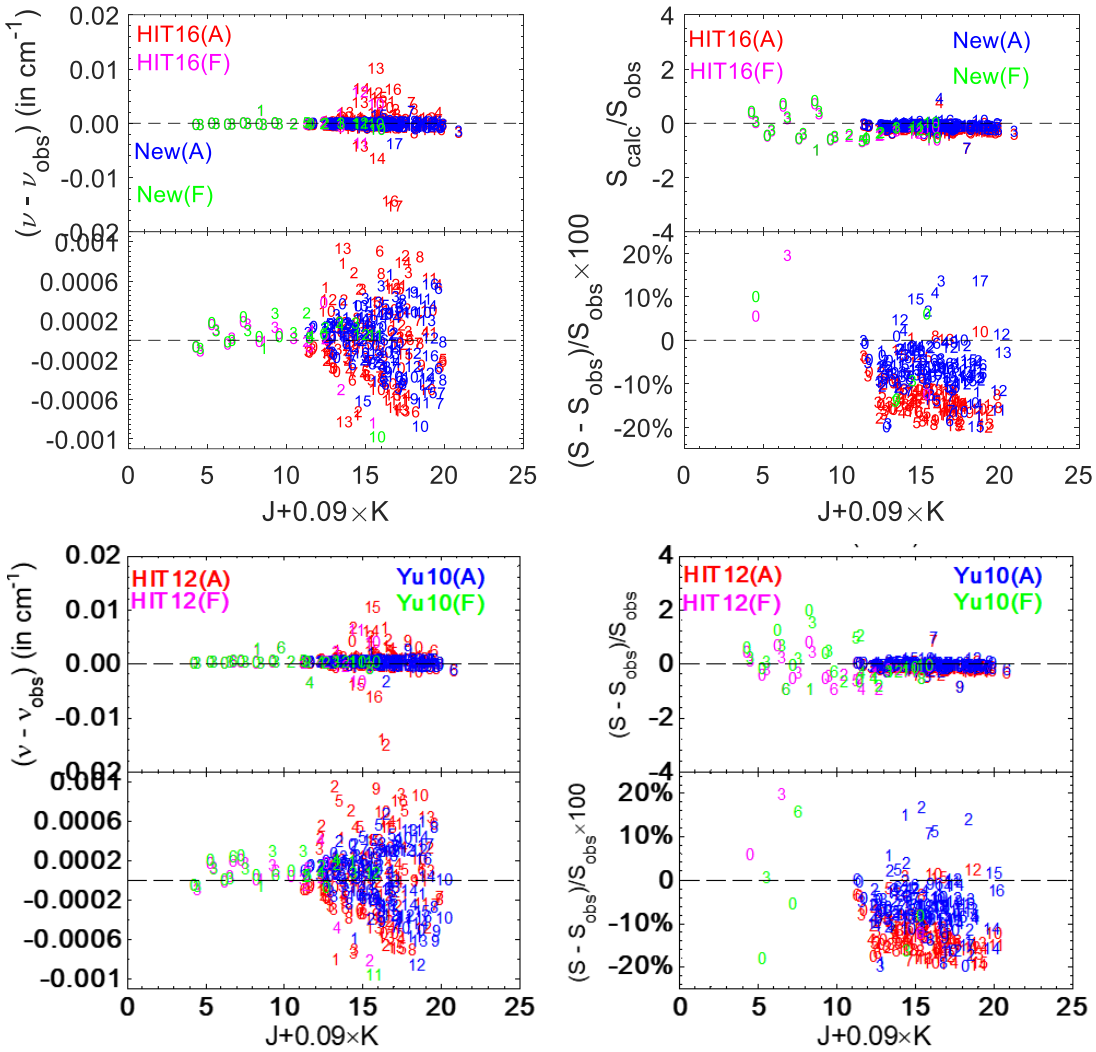
❑ Positions

- No change in Pr18 wrt Yu10: excellent agreement
- HIT16 still shows an offset for high J.

❑ Intensities

- The large intensity offsets seen in Yu10 now fixed in Pr18 by fixing a bug in SPCAT
- Dipole moment used in Pr18 remains the same to Yu10 (from Tanaka et al 1987)

ν_2(a-s) comparison: HIT16, HIT12, Pr18, Yu10



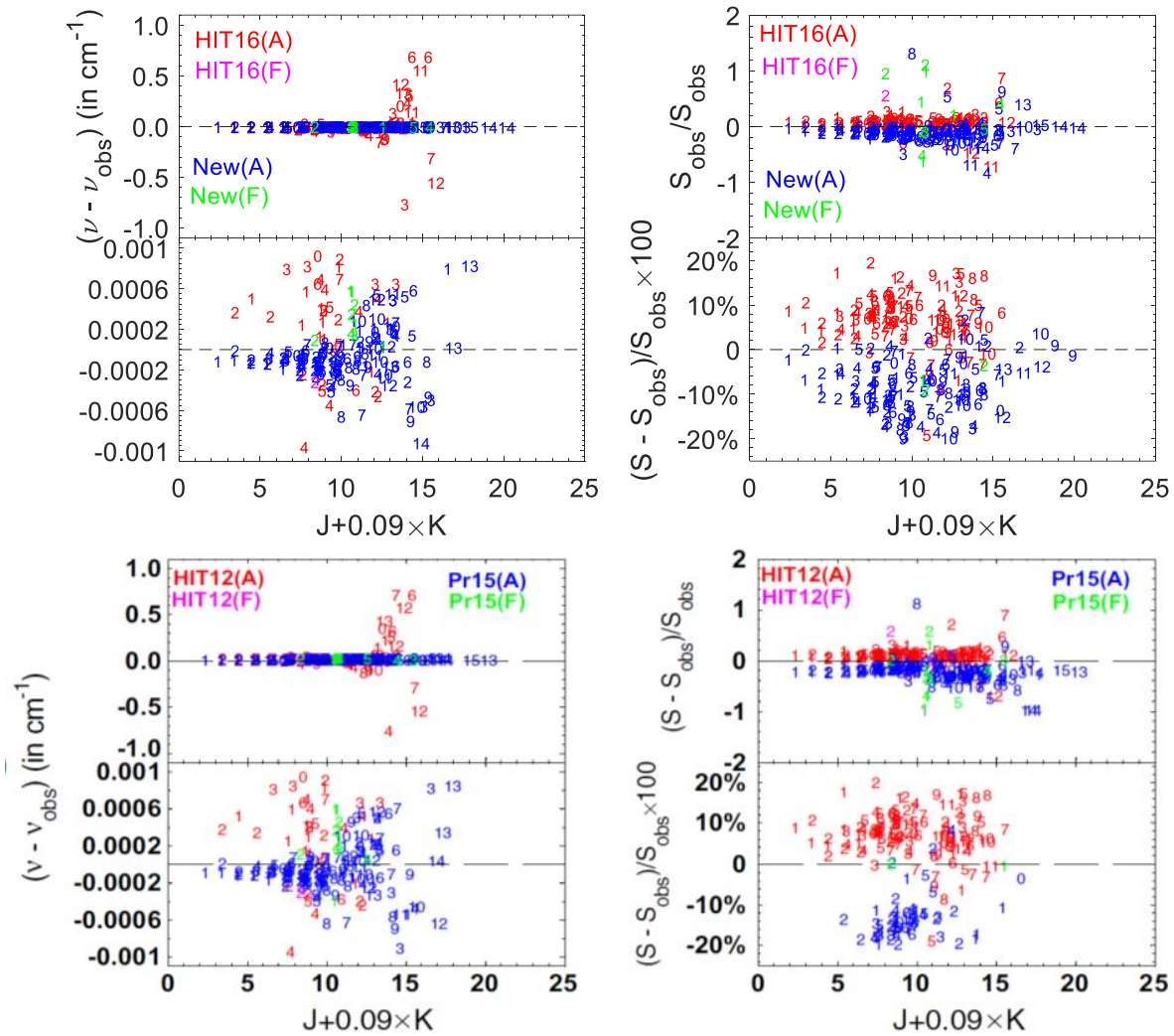
- **Line positions**
  - **No change in Pr18 wrt Yu10**
  - Allowed transitions(**A**)

  →Good agreement with all four but diverging at high J
  - Forbidden transitions(F)

  →sparse but excellent agreement

- **Line intensities**
  - **Pr18 slightly improved for forbidden transitions due to fixing the same bug in SPCAT**
  - **Dipole moment used in Pr18 remains the same to Yu10 (from Ueda&Iwahori 1986)**

$2\nu_2$(a-s) comparison: HIT16, HIT12, Pr18, Pr16



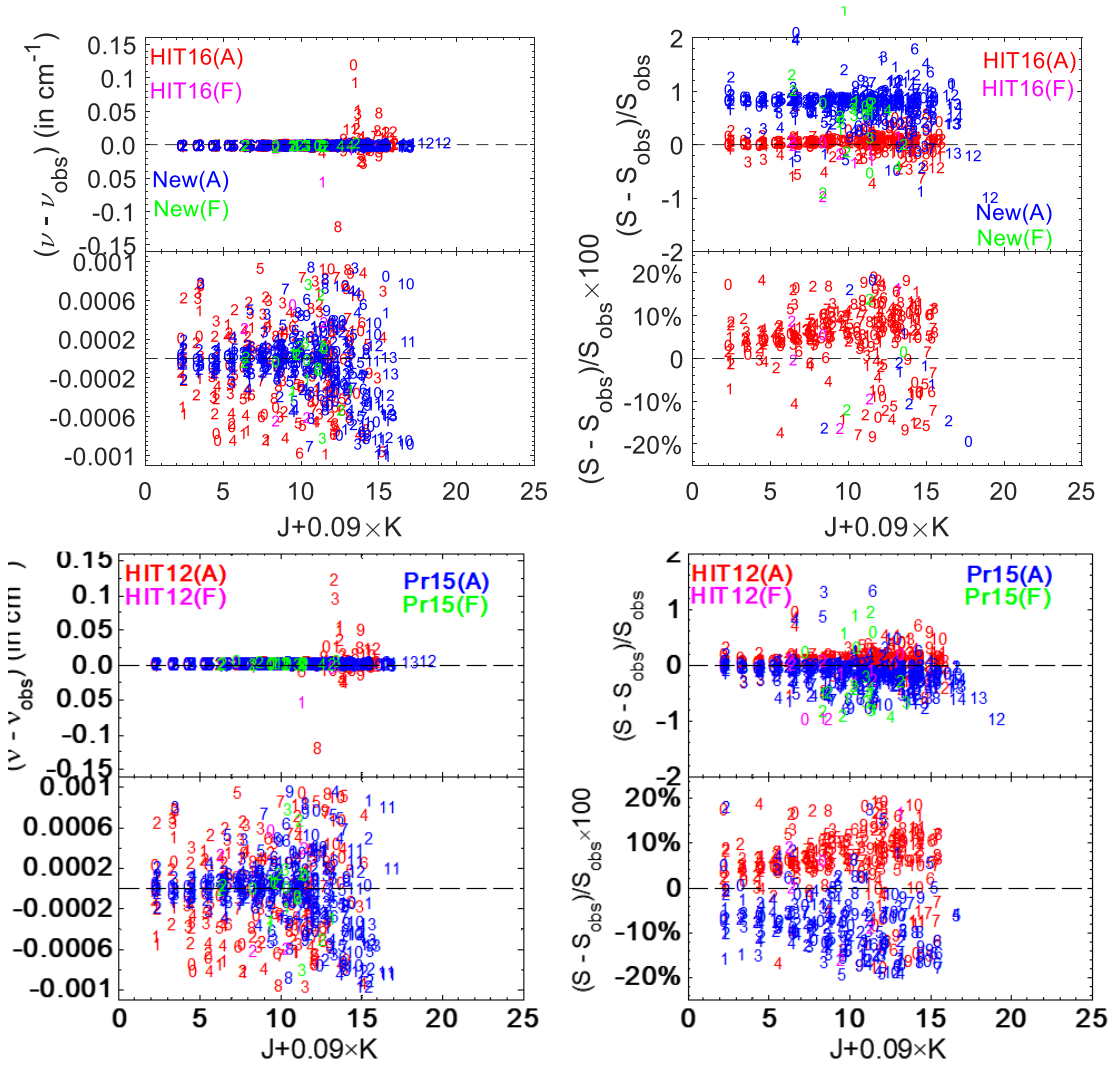
❑ Line positions

- No change in Pr18 wrt Pr16: Excellent agreement
- HITRAN shows some offsets.

❑ Line intensities

- Dipole: 0.9419 D in Pr18 vs 0.83 D in Pr16 (ab initio vs experimental)
- In Pr18 more allowed transitions are identified
- HITRAN and This work show opposite intensity offsets.

ν_4(a-s) comparison: HIT16, HIT12, Pr18, Pr16



❑ Line positions

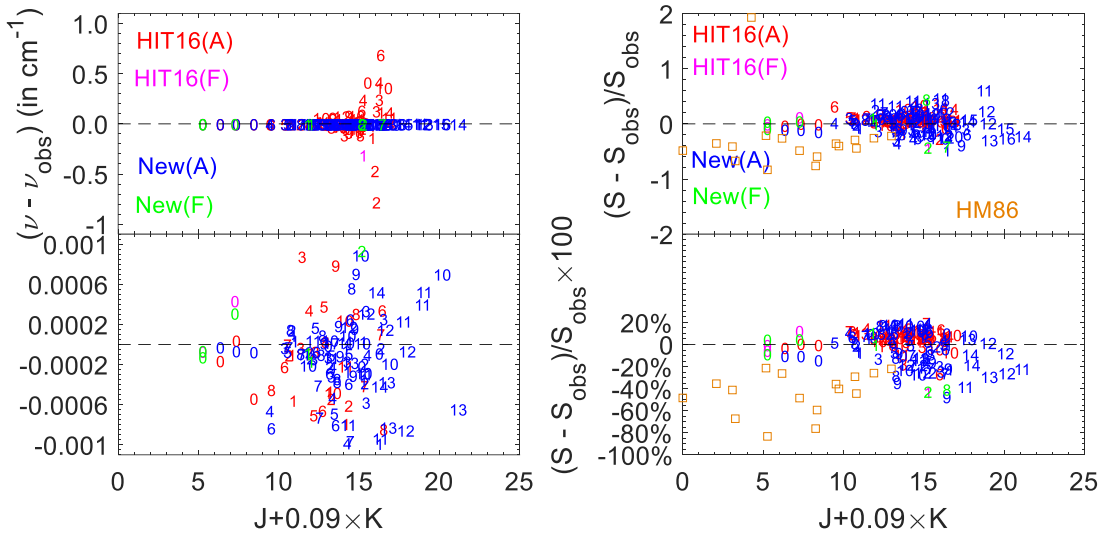
- **No change in Pr18 wrt Pr16**
- Allowed transitions(**A**)

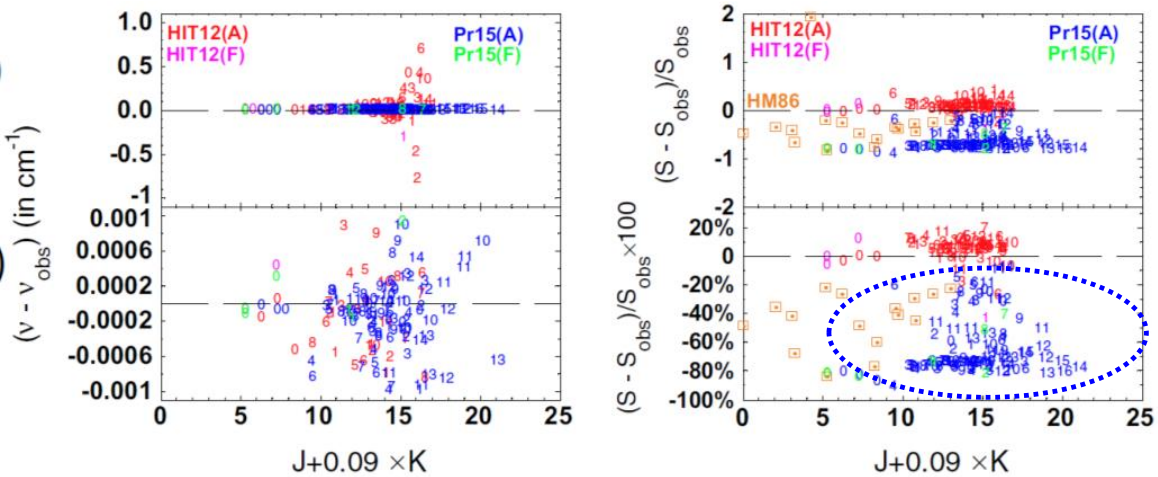
→ Our calculations show better agreement with measurements for all J (i.e. with no outliers).

❑ Line intensities

- **Dipole: 2.0488 D in Pr18 vs 1.459 D in Pr16 (ab initio vs experimental)**
- **For allowed transitions, Pr18 came out worse than Pr16**

$2\nu_2$-ν_2 comparison: HIT16, HIT12, Pr18, Pr16



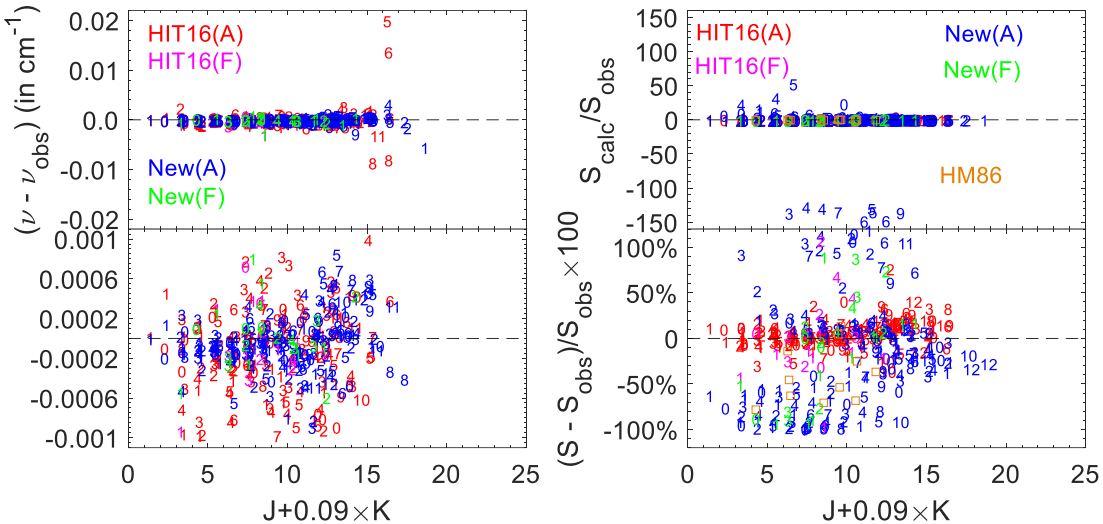


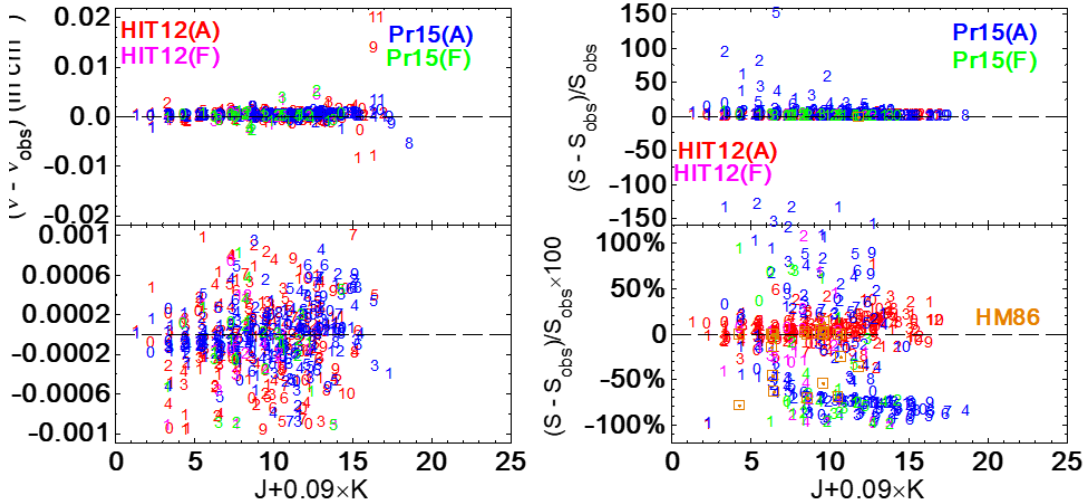
- **Line positions**

No change in Pr18 wrt Pr16: Excellent agreement

- **Line intensities**
  - **Dipole: s-a 0.521/a-s 0.2863 D in Pr18 vs s-a 0.27/a-s 0.27 D in Pr16 (ab initio vs experimental)**
  - **Pr18: intensities for allowed transitions are improved a lot.**

ν_4-ν_2 comparison: HIT16, HIT12, Pr18, Pr16





❑ Line positions

No change in Pr18 wrt Pr16: better than HITRAN for all J

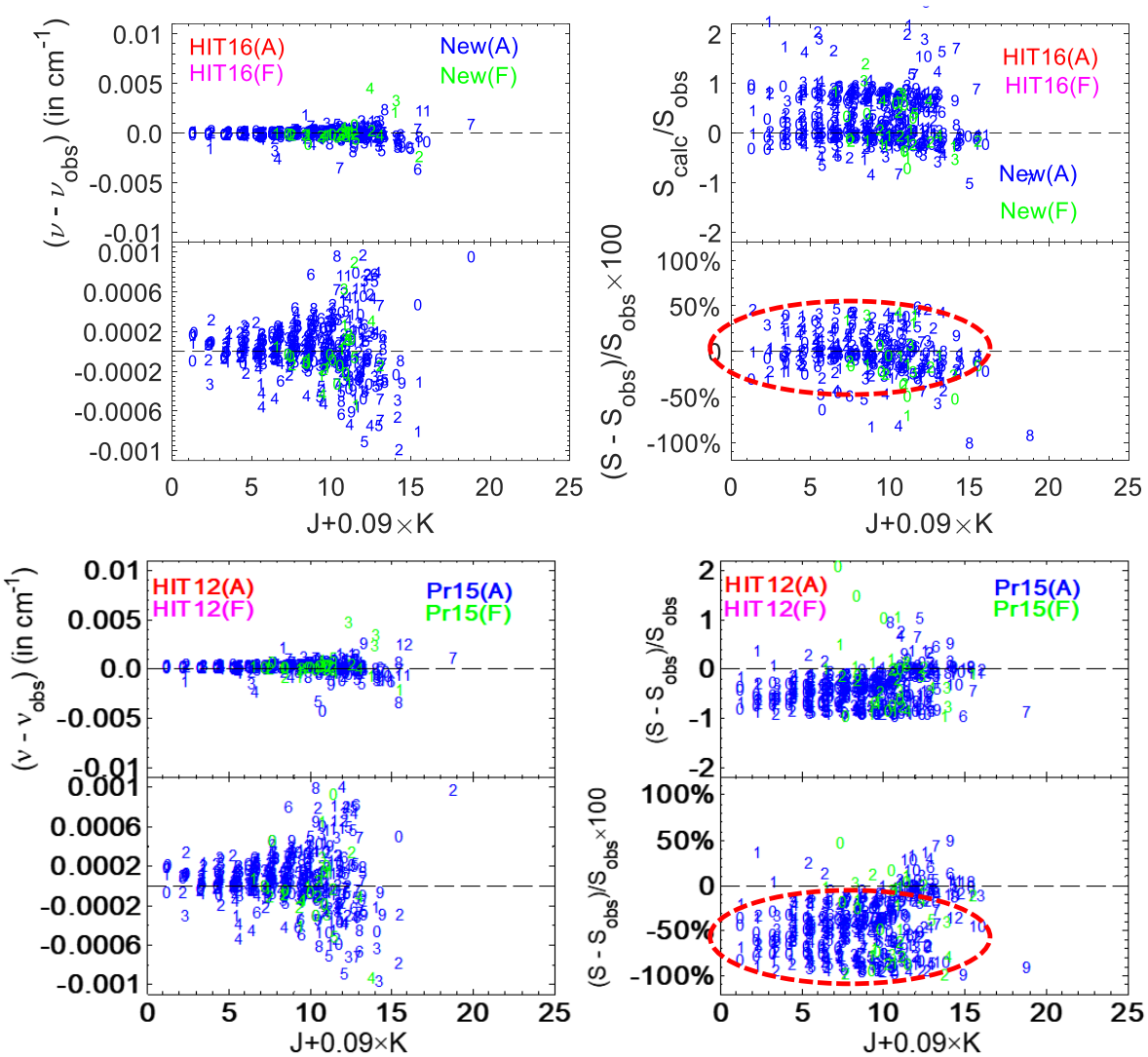
❑ Line intensities

Dipole: s-a 0.521/a-s 0.2863 D in Pr18 vs s-a 0.27/a-s 0.27 D in Pr16 (ab initio vs experimental)

Pr18 show a bit better, but different discrepancy pattern is noticed.

HITRAN shows better agreement with measurements.

ν_4-$2\nu_2$ comparison: HIT16, HIT12, Pr18, Pr16



- **This band Not listed in HITRAN**

Line positions

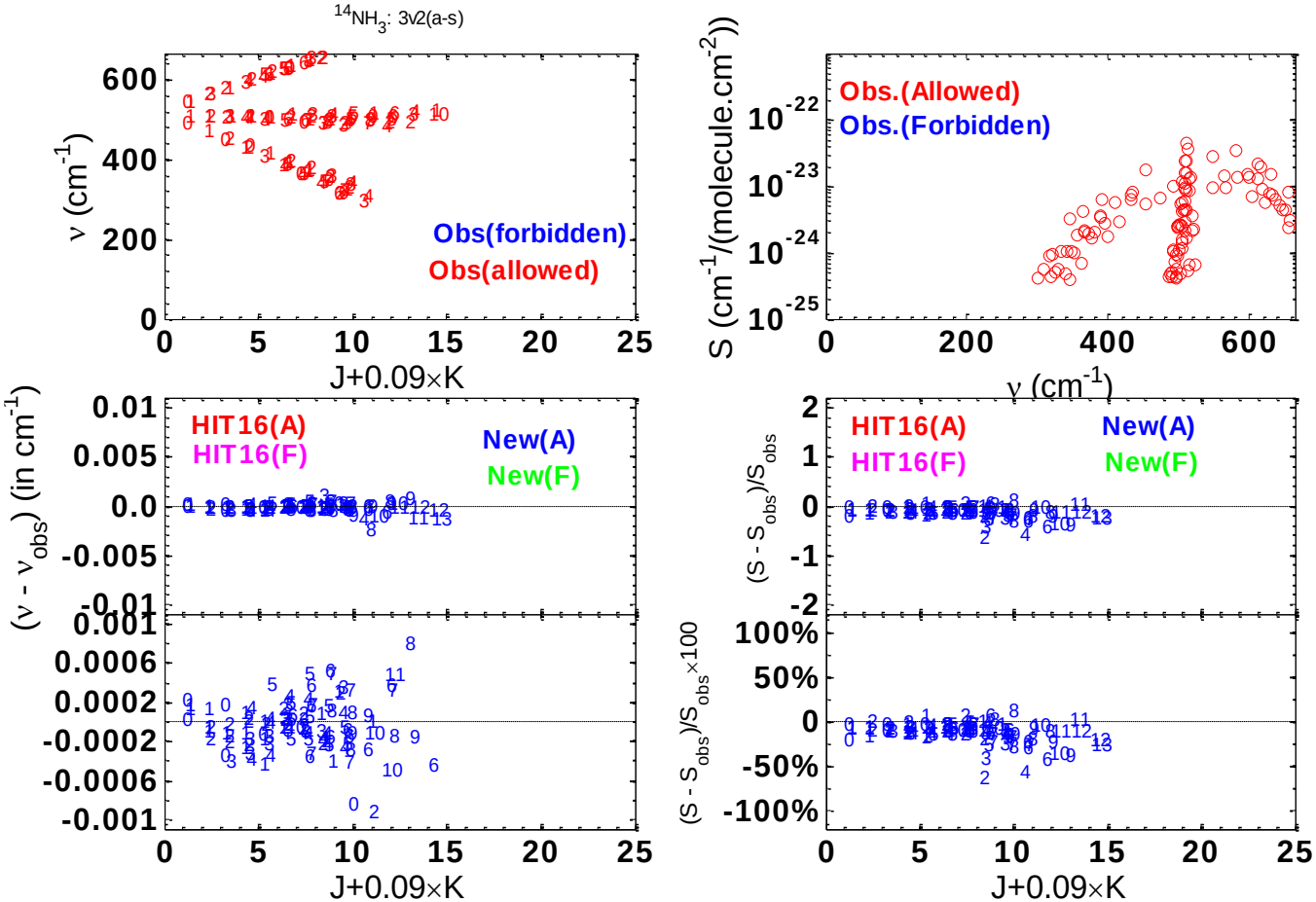
- **No change in Pr18 wrt Pr16: excellent agreement**

Line intensities

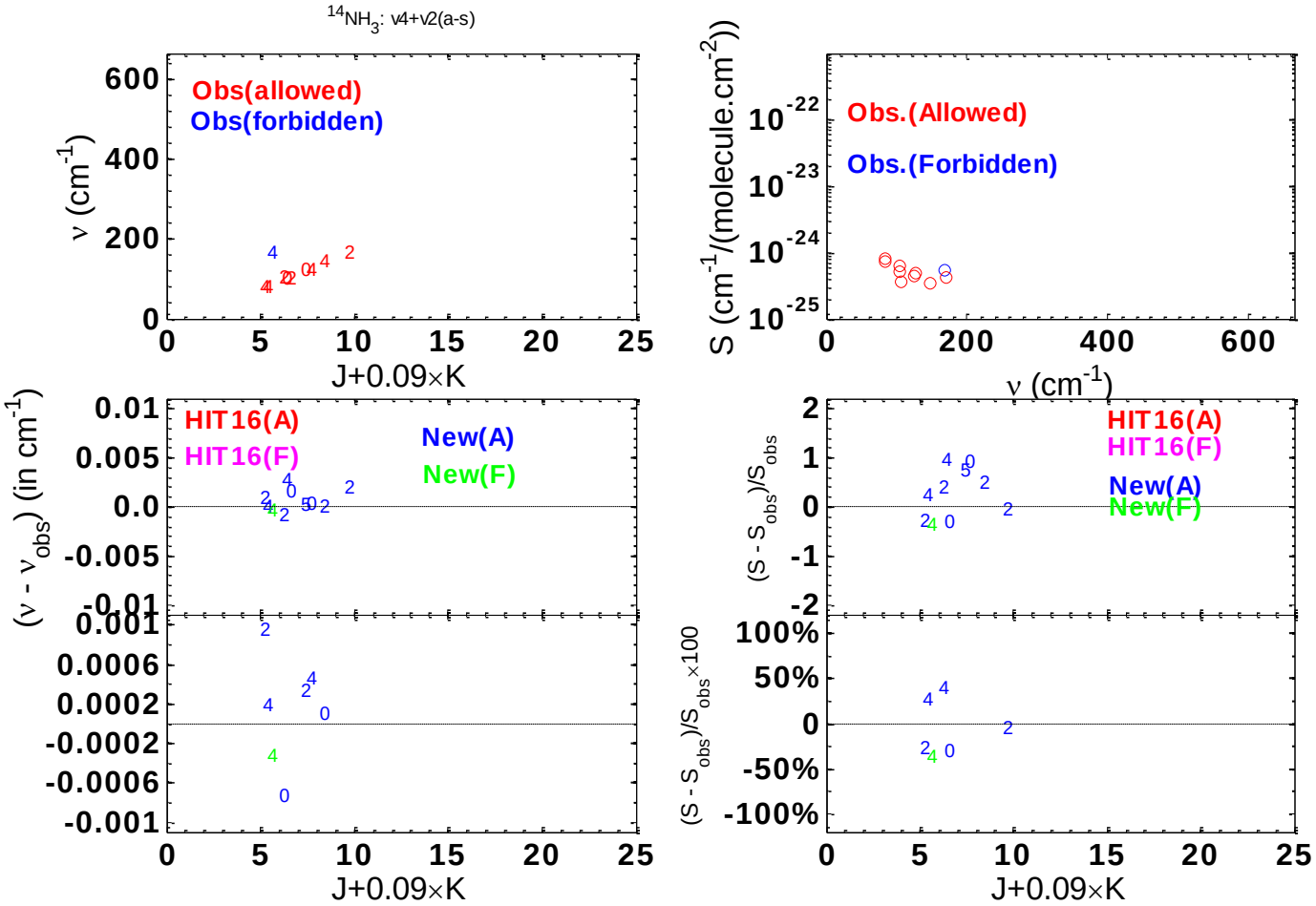
Dipole: 0.0125 D in Pr18 vs s-a 0.05 D in Pr16 (ab initio vs experimental)

New calculations show much better agreement.

$3\nu_2$(a-s) comparison: HIT16, Pr18



$\nu_2+\nu_4$ (a-s) comparison: HIT16, Pr18



Acknowledgements

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