Analysis of an ^{18}O and D enhanced lab water spectrum using variational calculations of $HD^{18}O$ and $D_2{}^{18}O$ spectra

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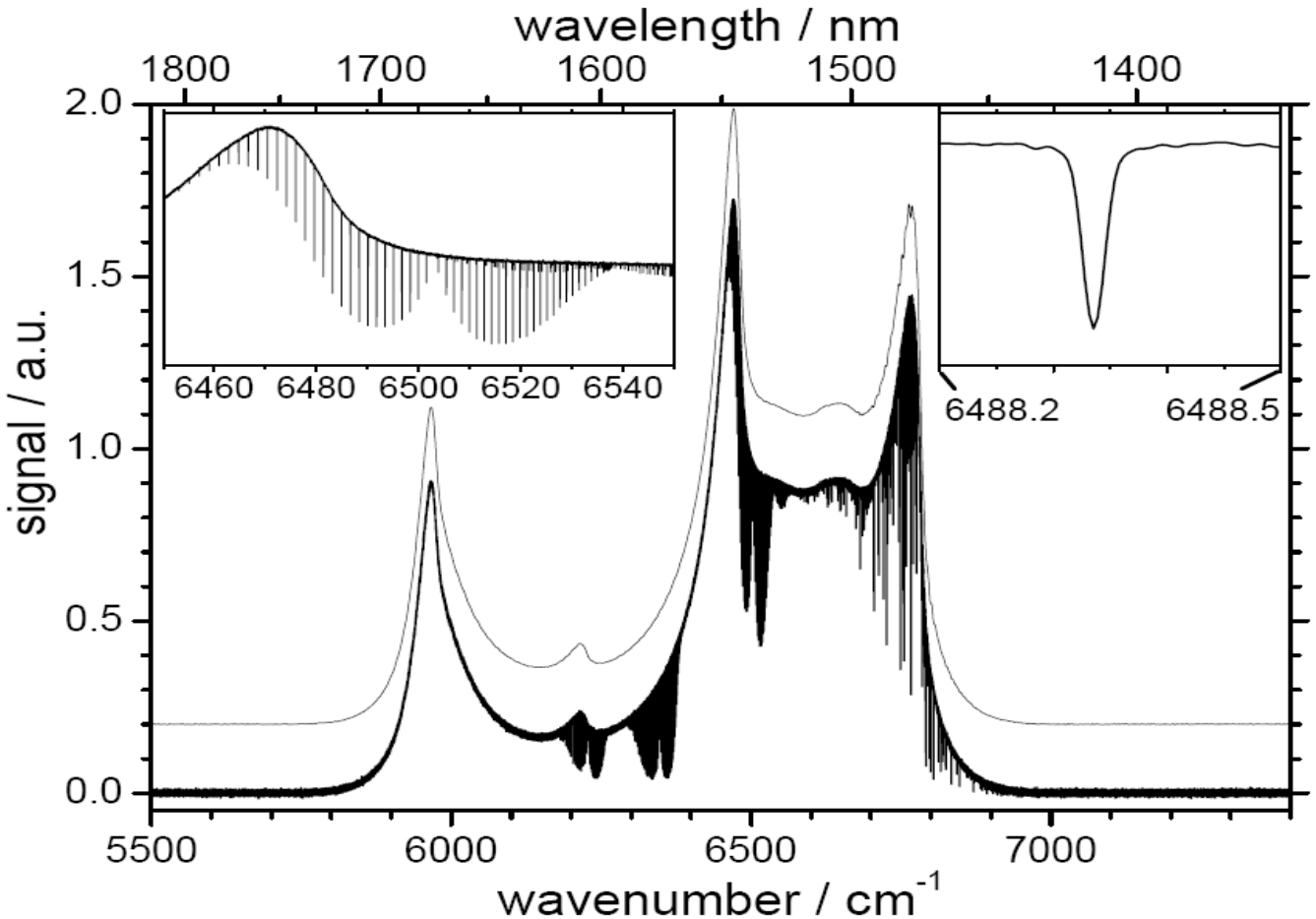
Experimental data courtesy of J. Orphal and A. Ruth (2008)

HDO P.E.S and variational line list courtesy of Boris Voronin et. al. (2009)

D_2O line list courtesy of Sergei Shirin et. al. (2007)

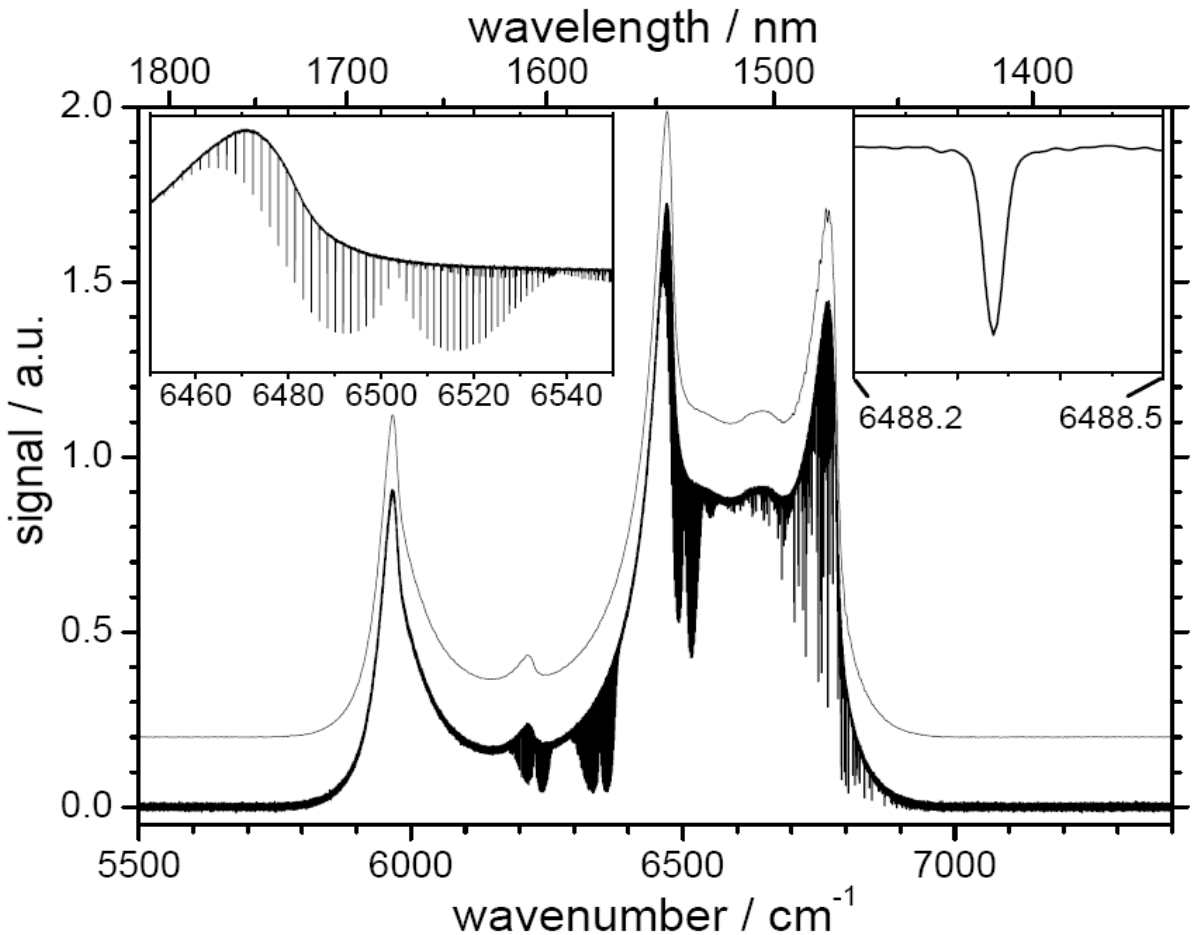


Summary of Experimental Data

Mixture of rare isotopologues: 12.4 mbar <u>pure</u> $H_2{}^{18}O$ and 8.0 mbar $D_2{}^{16}O$

Precision of 0.002-0.004 cm^{-1} (strong isolated lines & low signal to noise).

Spectral resolution of 0.02 cm^{-1} over spectral range 5800-7000 cm^{-1} recording 4738 peaks.



J. Orphal and A. Ruth. Optics Express, 16, 23 (2008), 19232.

Background Theory

Analysis based on three different types of line lists

Experimental line lists

Observed spectra previously assigned.
Documented in various databases with traditional rigid rotor + normal mode quantum numbers.

Semi empirical line lists

e.g MARVEL a procedure used to invert transition position data to provide semi empirical energy levels. These can then be used to predict line lists.
MARVEL energy levels and transitions are currently being documented by the IUPAC task group for water.

Variational Calculations

Calculations based on the diagonalisation of exact Hamiltonians.
e.g DVR3D program suite.
Based on rigorous QN's so only provides J and Γ.

What have we got?

A mixture of all possible isotopologues in the approximate proportions below, based purely statistical reasoning. This ignores fractionation effect which are small.

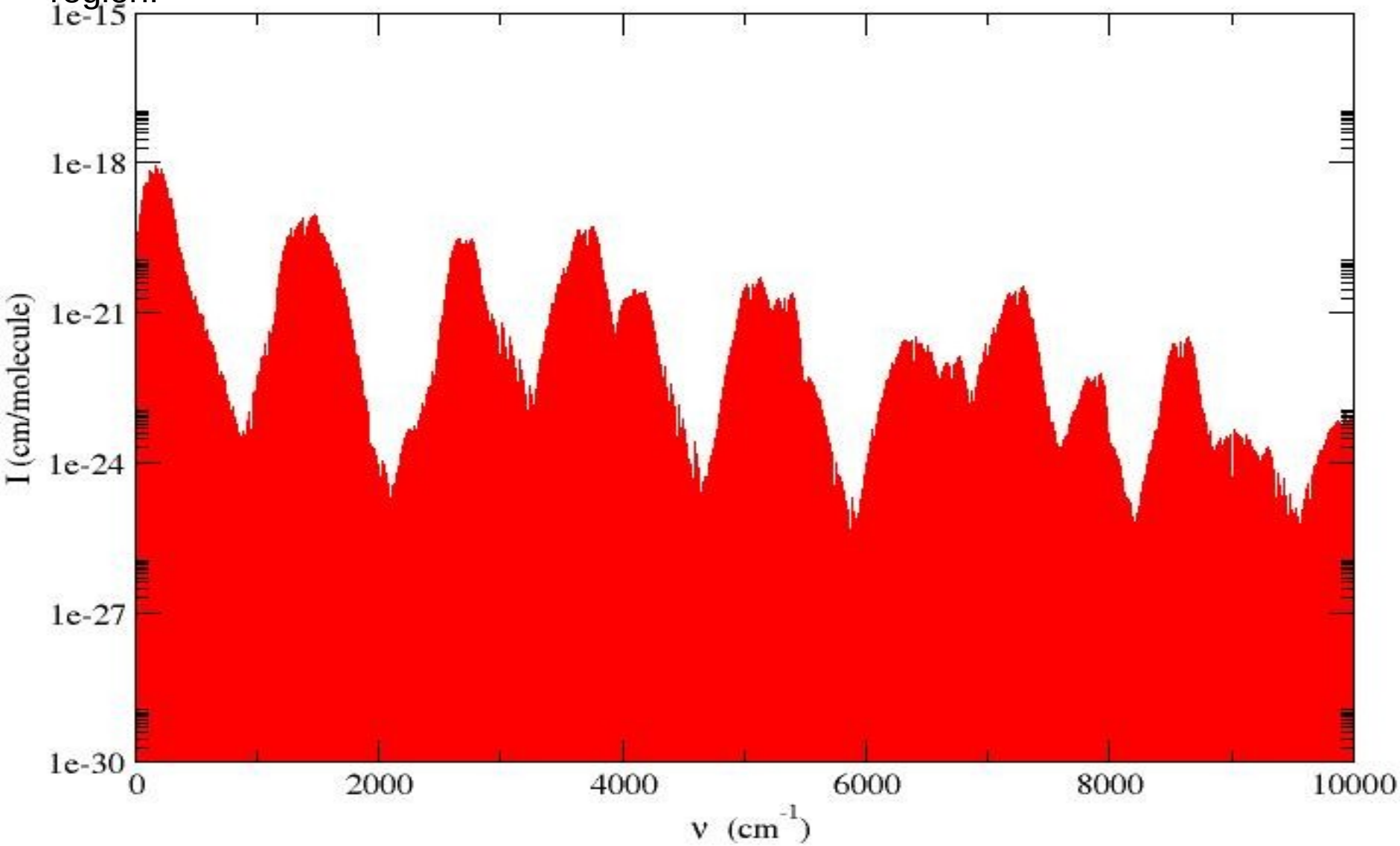
$H_2{}^{16}O$	14.5%	0.997317	HITRAN
$H_2{}^{18}O$	22.5%	0.00199983	HITRAN MARVEL+DVR3D (LODI et. al.)
$HD^{16}O$	18.6%	0.000310693	VTT (Variational Calcs.)
$HD^{18}O$	29.0%	6.23003e-07	TOMSK (PS)
$D_2{}^{16}O$	6.0%	2.4197e-08	SHIRIN (Variational Calcs.)
$D_2{}^{18}O$	9.3%	4.9e-11	TOMSK (PS)

Likely that there are significant $HD^{18}O$ and $D_2{}^{18}O$ features.

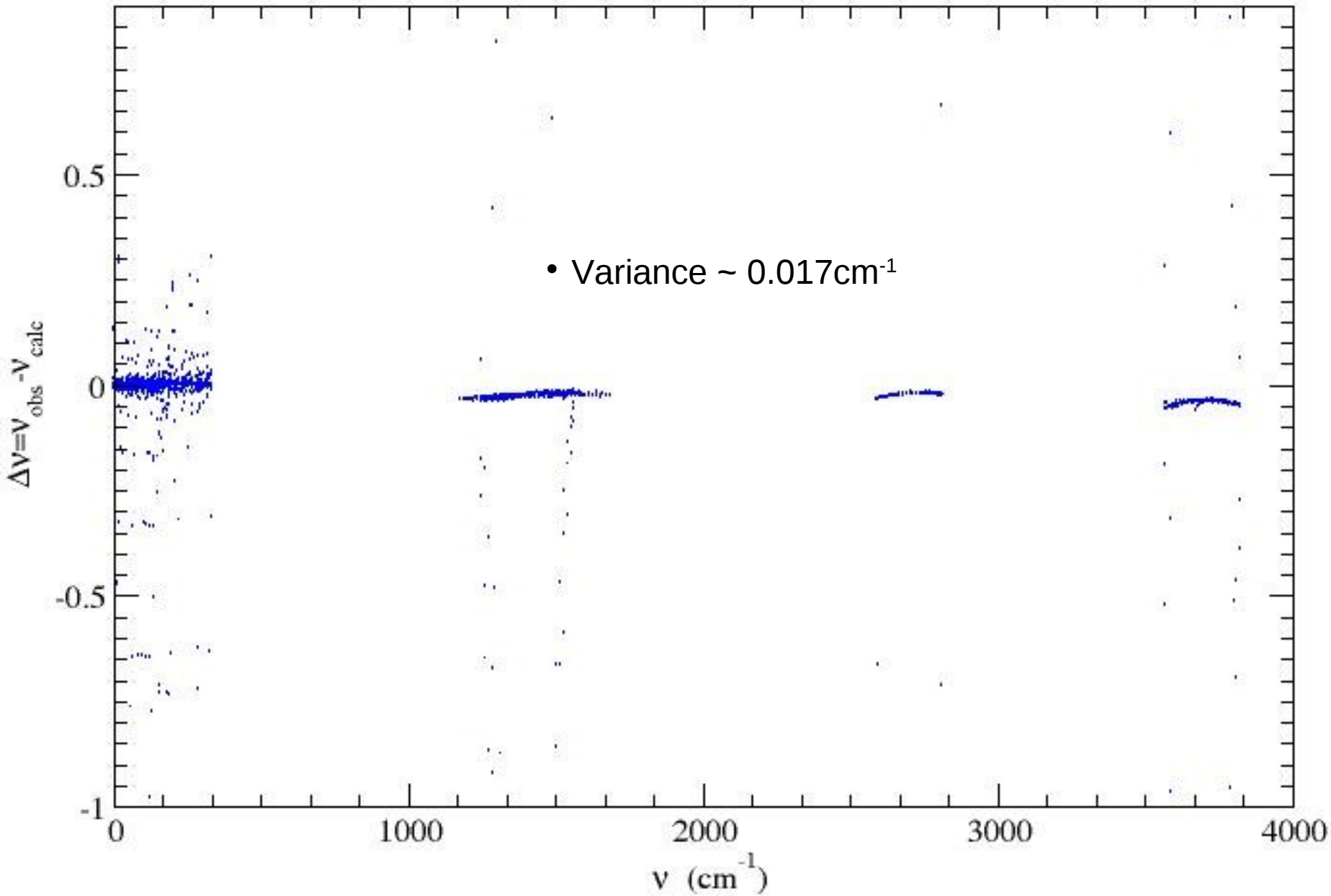
Yurchenko et. al. J. Chem. Phys. 128, 044312 (2008).
Shirin et. al. JQSRT 109, 549 (2008).

Calculations for $HD^{18}O$

- Using PES from VTT and the DVR3D suite a $HD^{18}O$ line-list produced.
- Intensities and positions were compared against HITRAN in the lower frequency region.

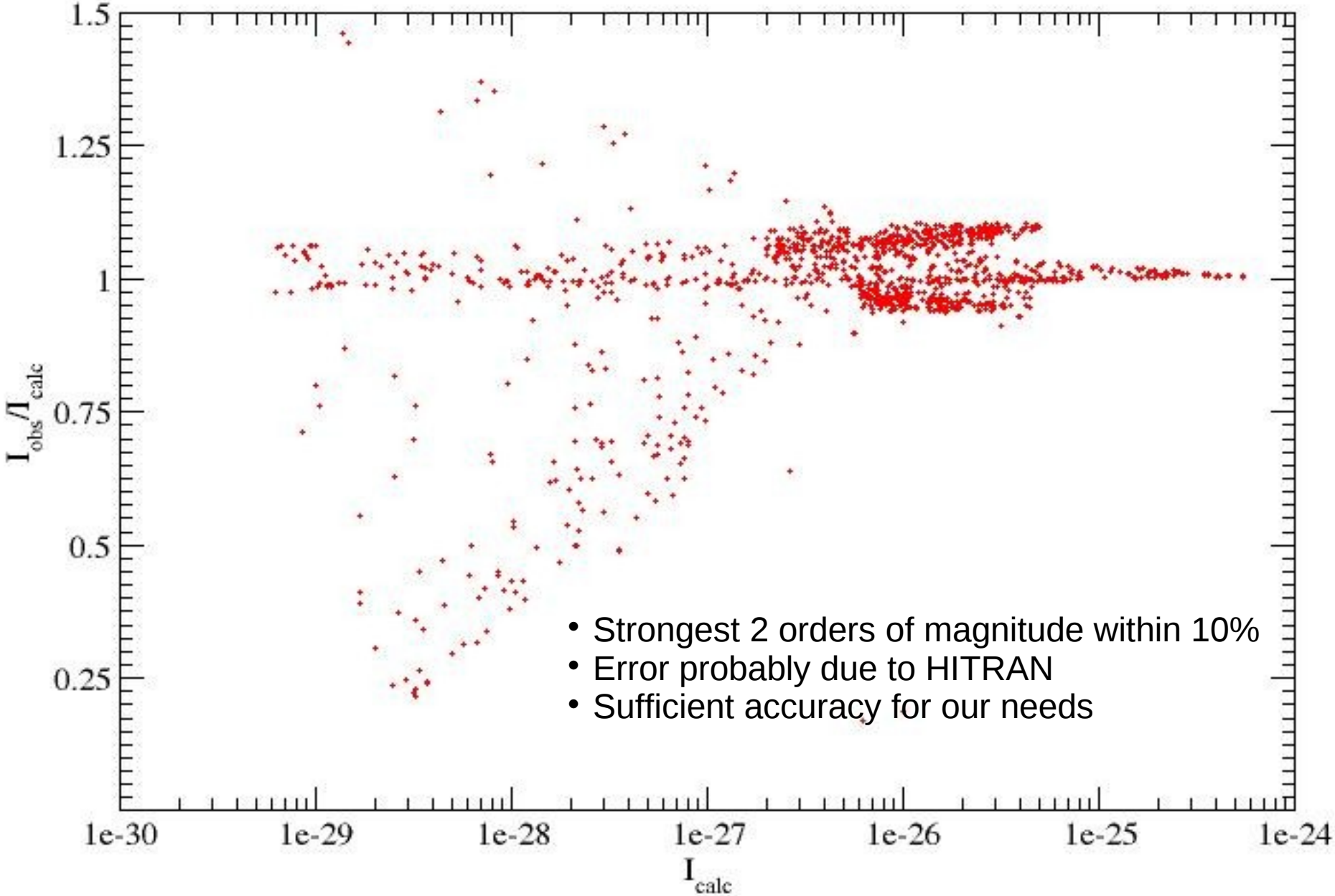


Position Errors



- Variance ~ 0.017cm^{-1}

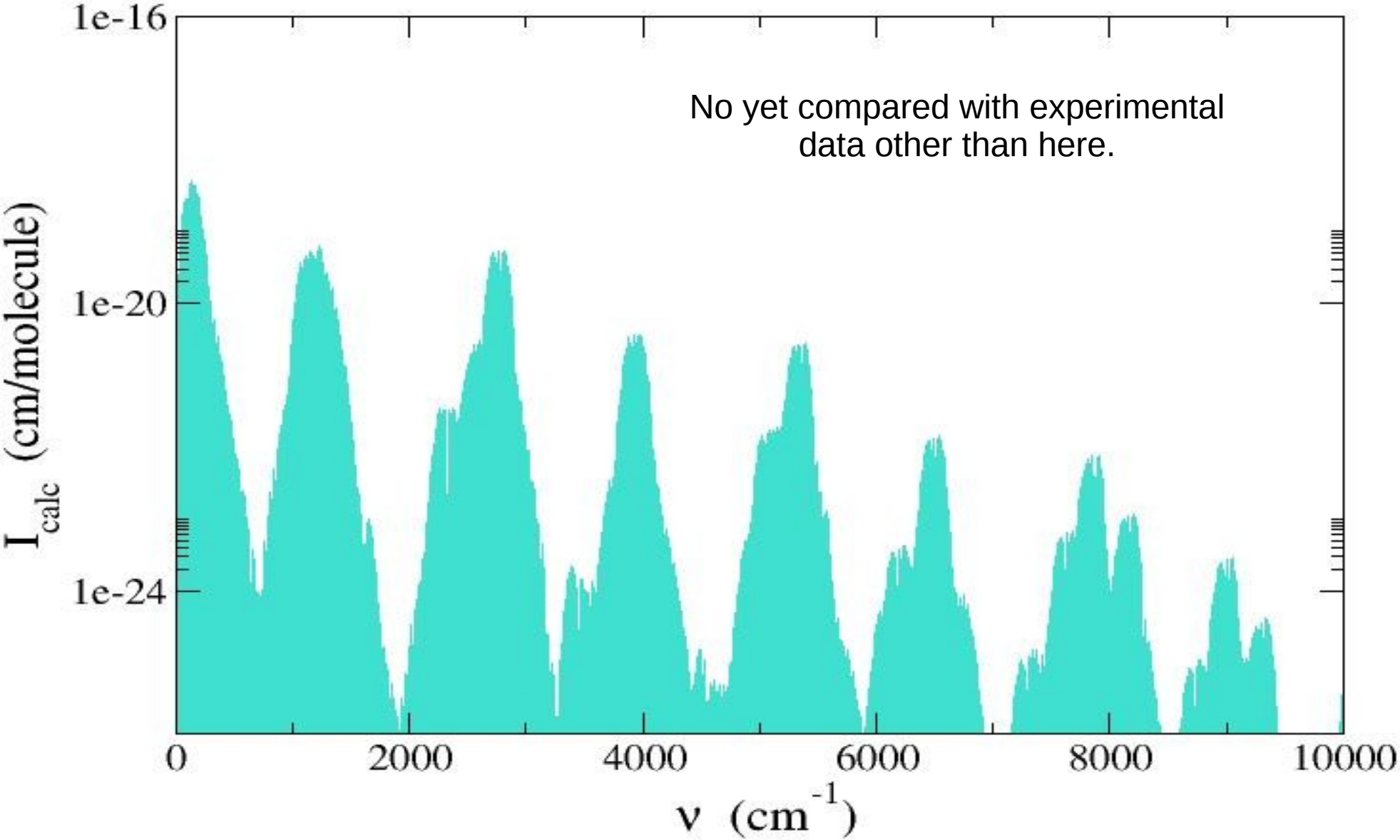
Intensity Ratios



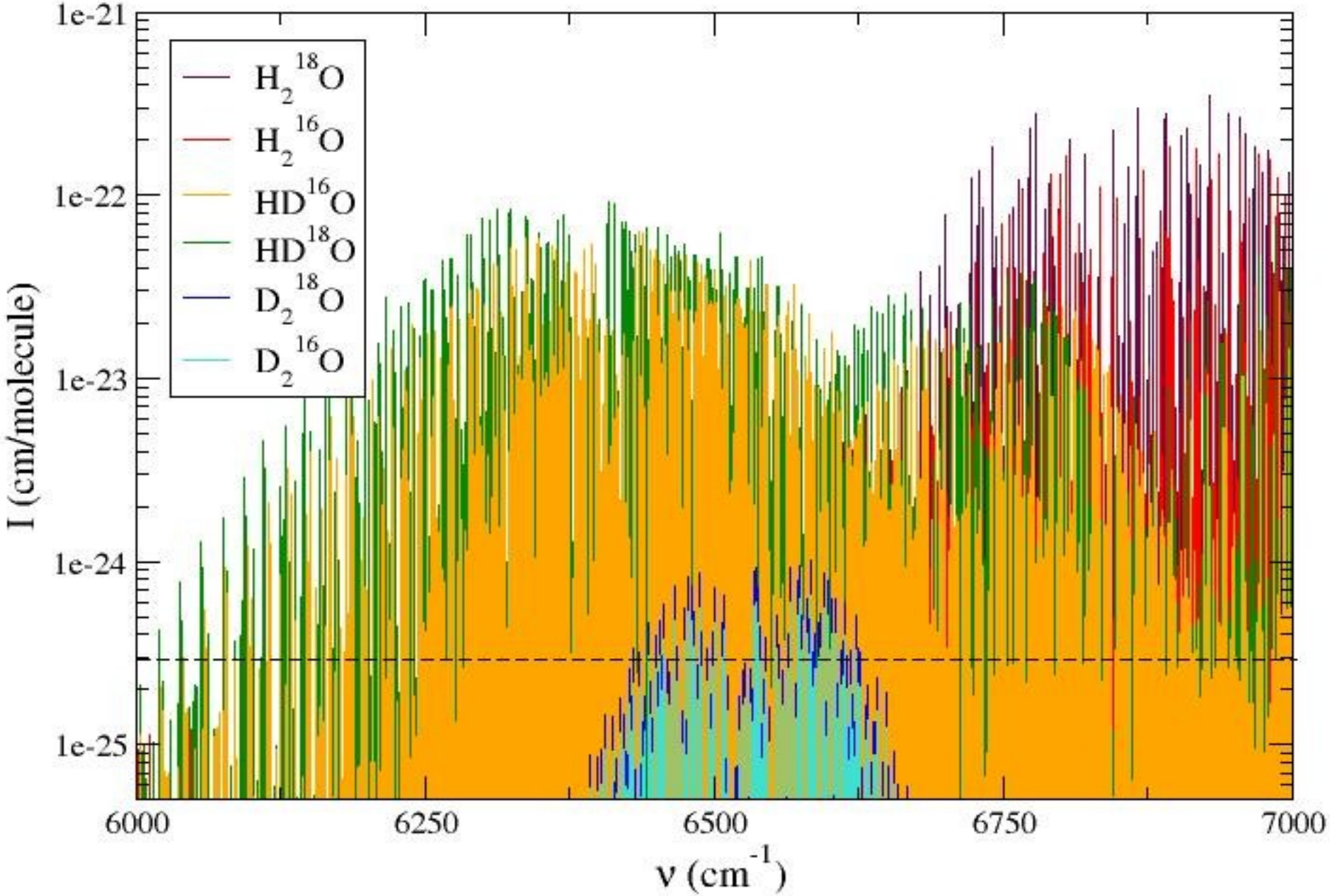
- Strongest 2 orders of magnitude within 10%
- Error probably due to HITRAN
- Sufficient accuracy for our needs

Calculations for $D_2{}^{18}O$

- Using PES from Shirin et. al. and the DVR3D suite a $D_2{}^{18}O$ line-list was produced.
- Quality was verified during analysis of the experiment.



Combining the 6 Isotopologues



Assigning the Spectrum

Line lists were sufficiently accurate to make reliable assignments, which are subsequently checked using CD's where possible.

Line intensities were scaled by their approximate concentrations.

Intensity cut off applied to all the data at 3E-25 cm/molecule.

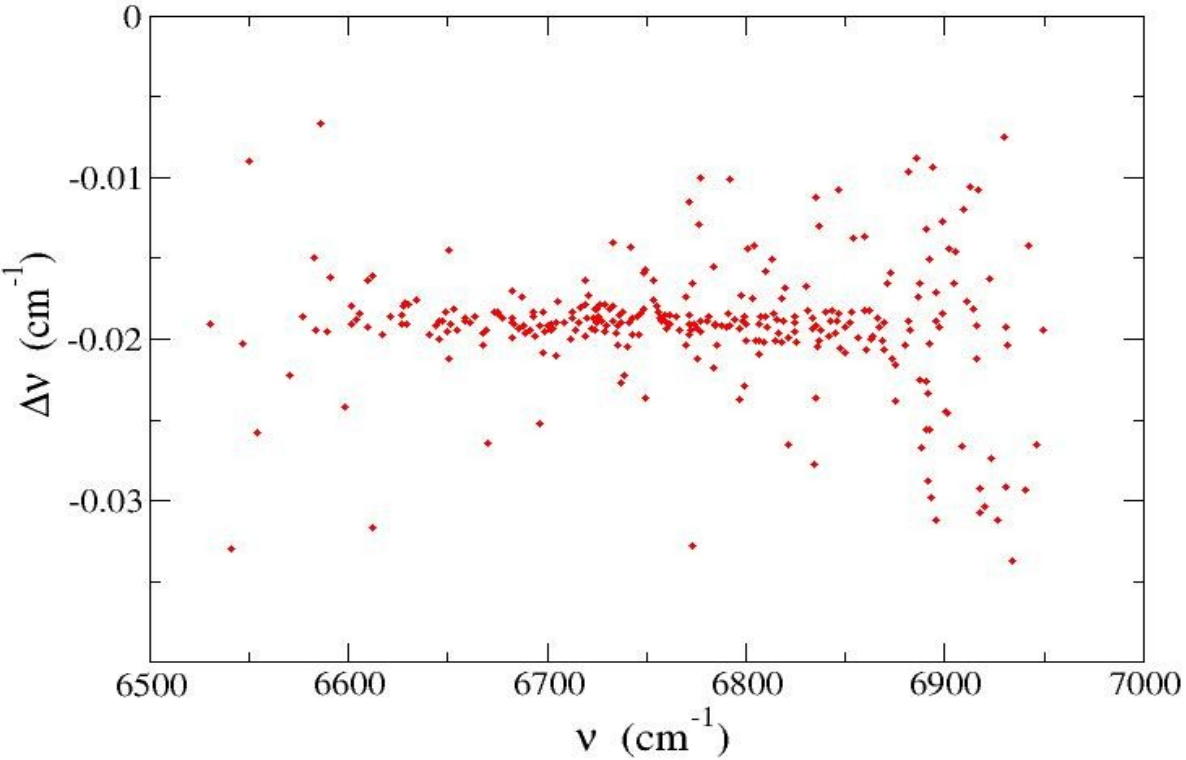
HITRAN intensities have to be divided by their natural abundance.

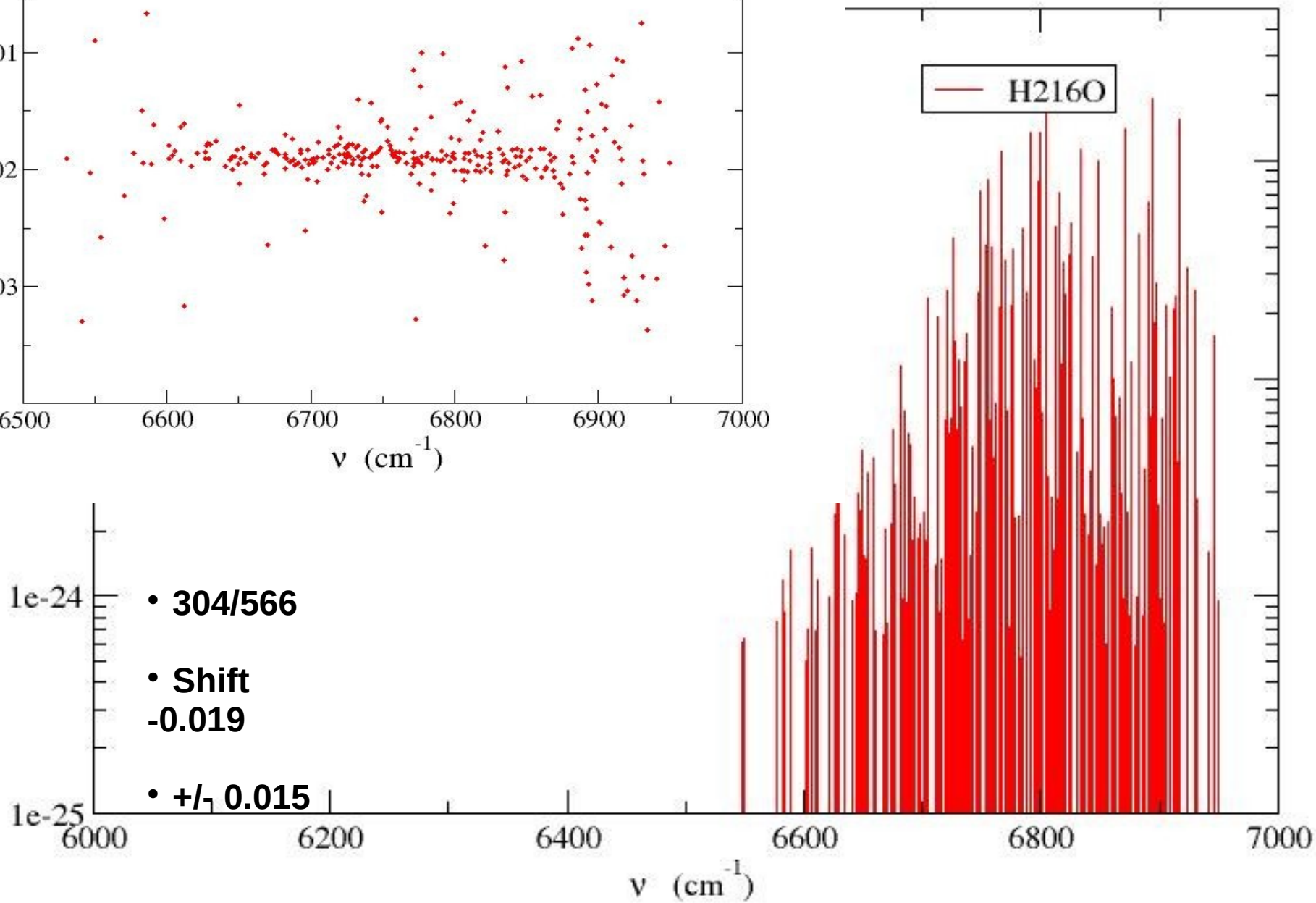
Gives 5472 lines in total above intensity threshold compared to the 4738 observed.

Assigned $H_2{}^{16}O$ then $H_2{}^{18}O$ then $D_2{}^{16}O$ (SHIRIN) then $D_2{}^{18}O$ and then $HD^{16}O$ (VTT) and then $HD^{18}O$.

Recalibration of positions was required.

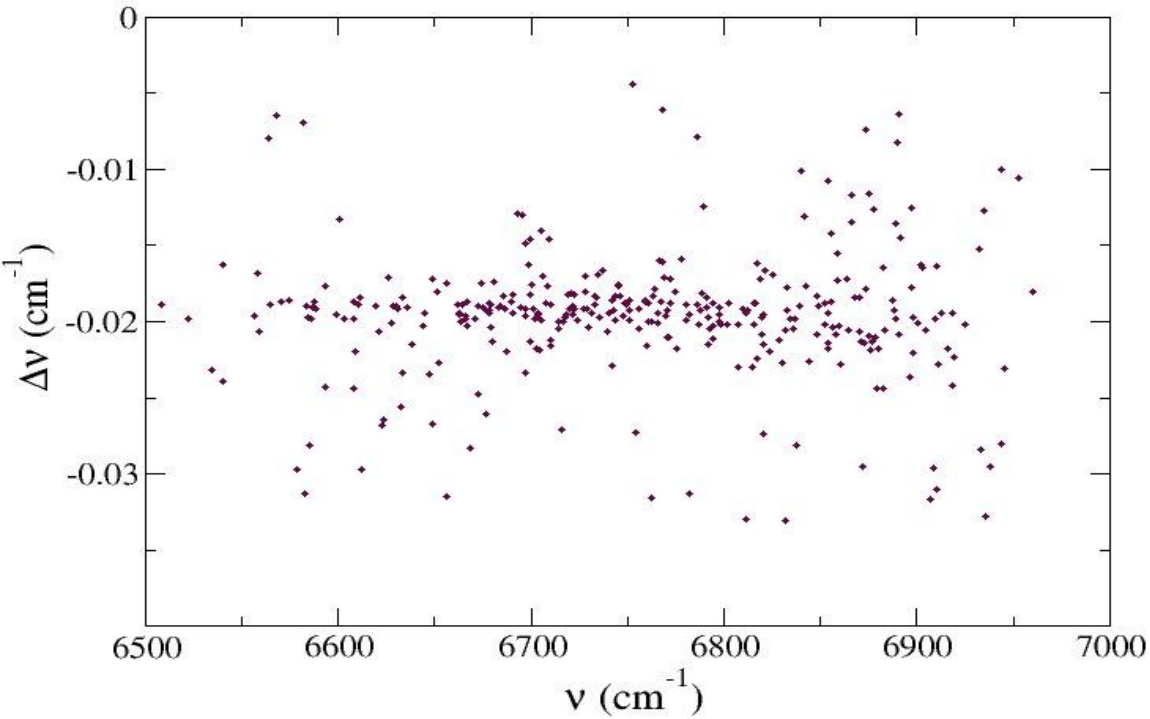
$H_2{}^{16}O$

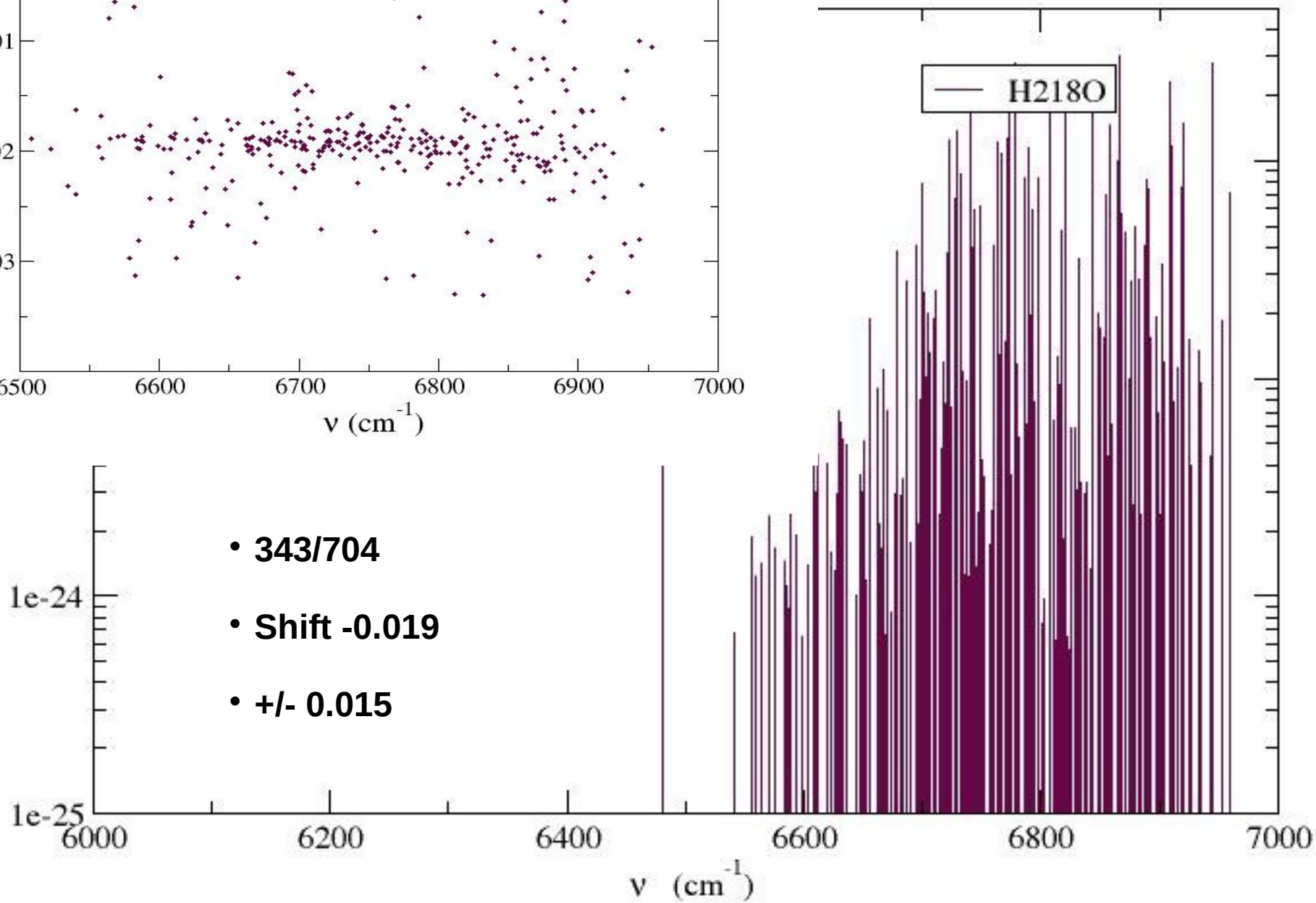




- **304/566**
- **Shift -0.019**
- **+/- 0.015**

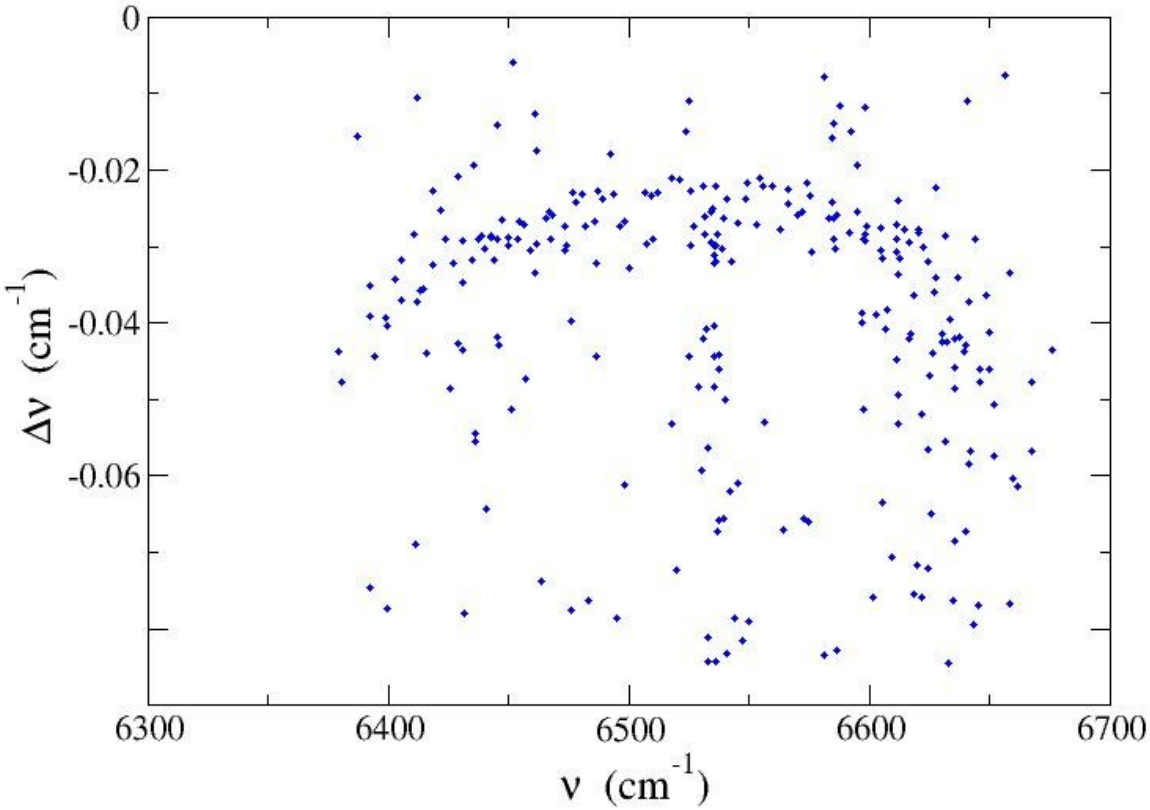
$H_2{}^{18}O$

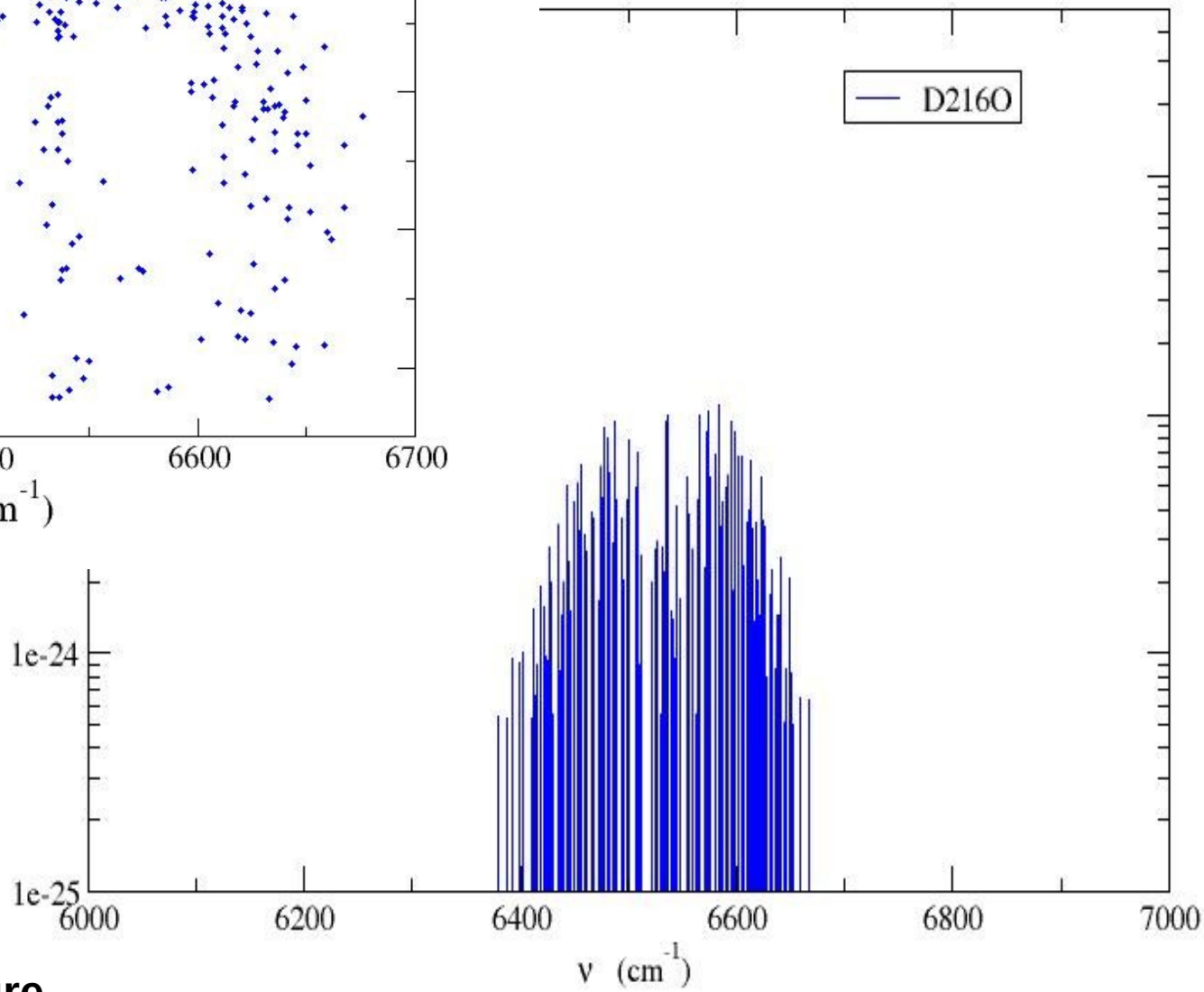




- **343/704**
- **Shift -0.019**
- **+/- 0.015**

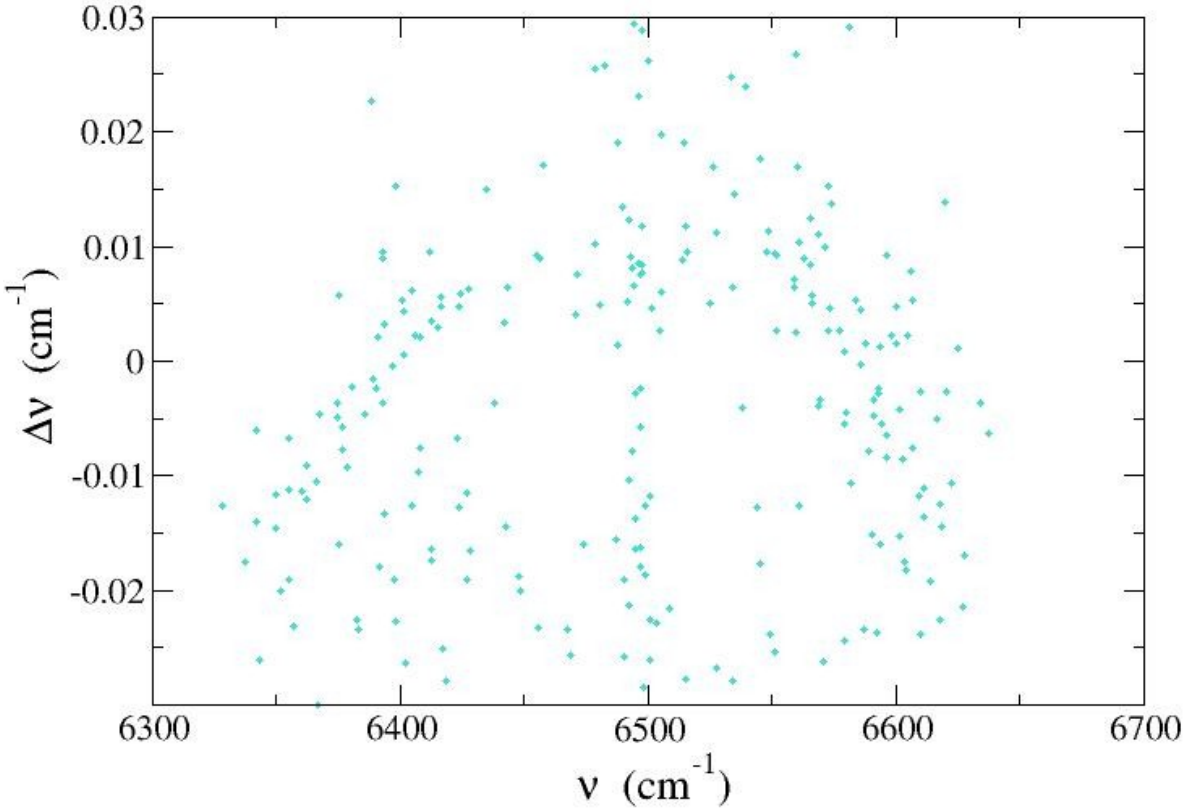
$D_2{}^{16}O$

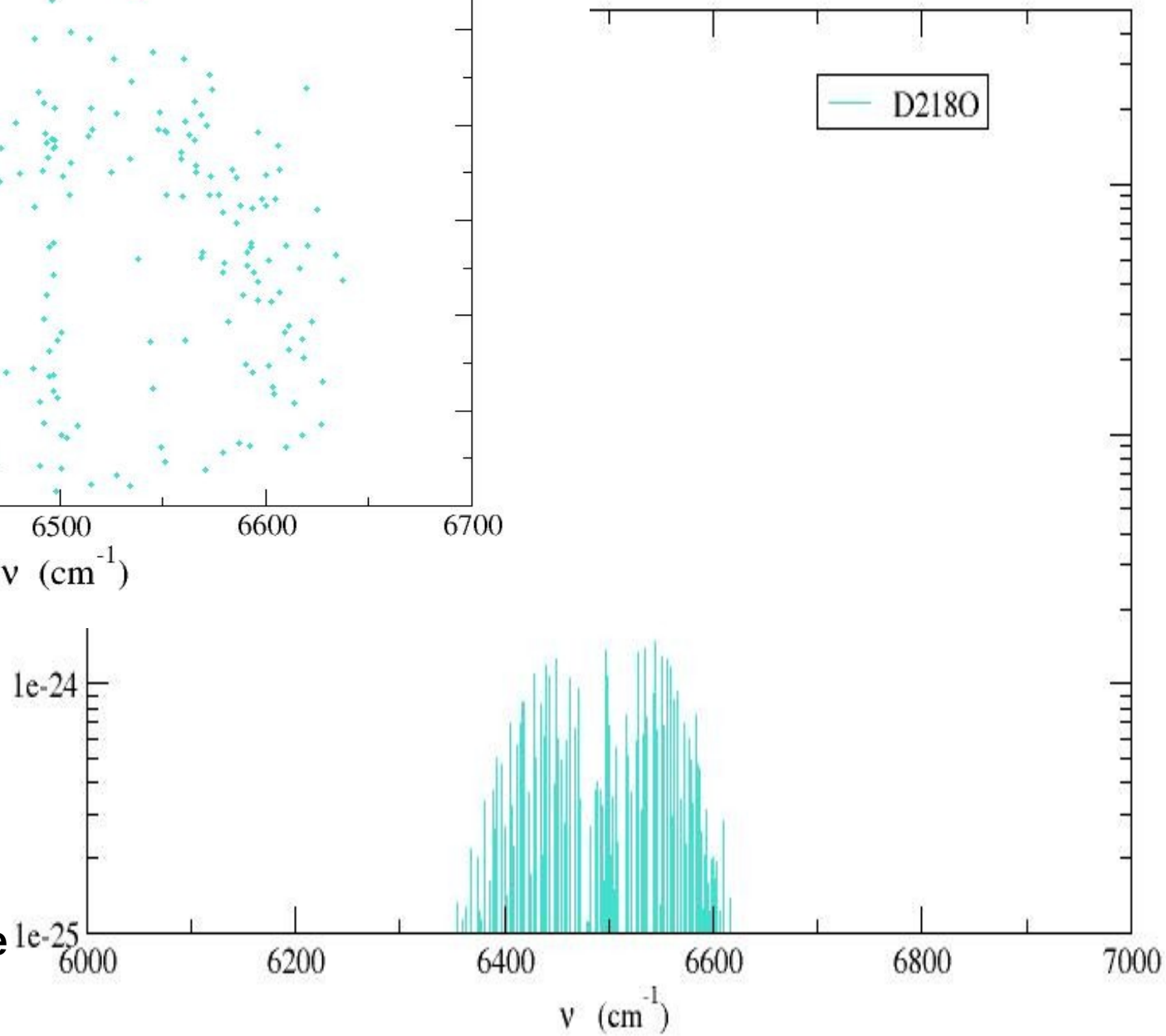




- **265/295**
- **Shift of -0.045**
- **~ Band errors.**
- **+/- 0.04**
- **Rotational structure**

$D_2{}^{18}O$

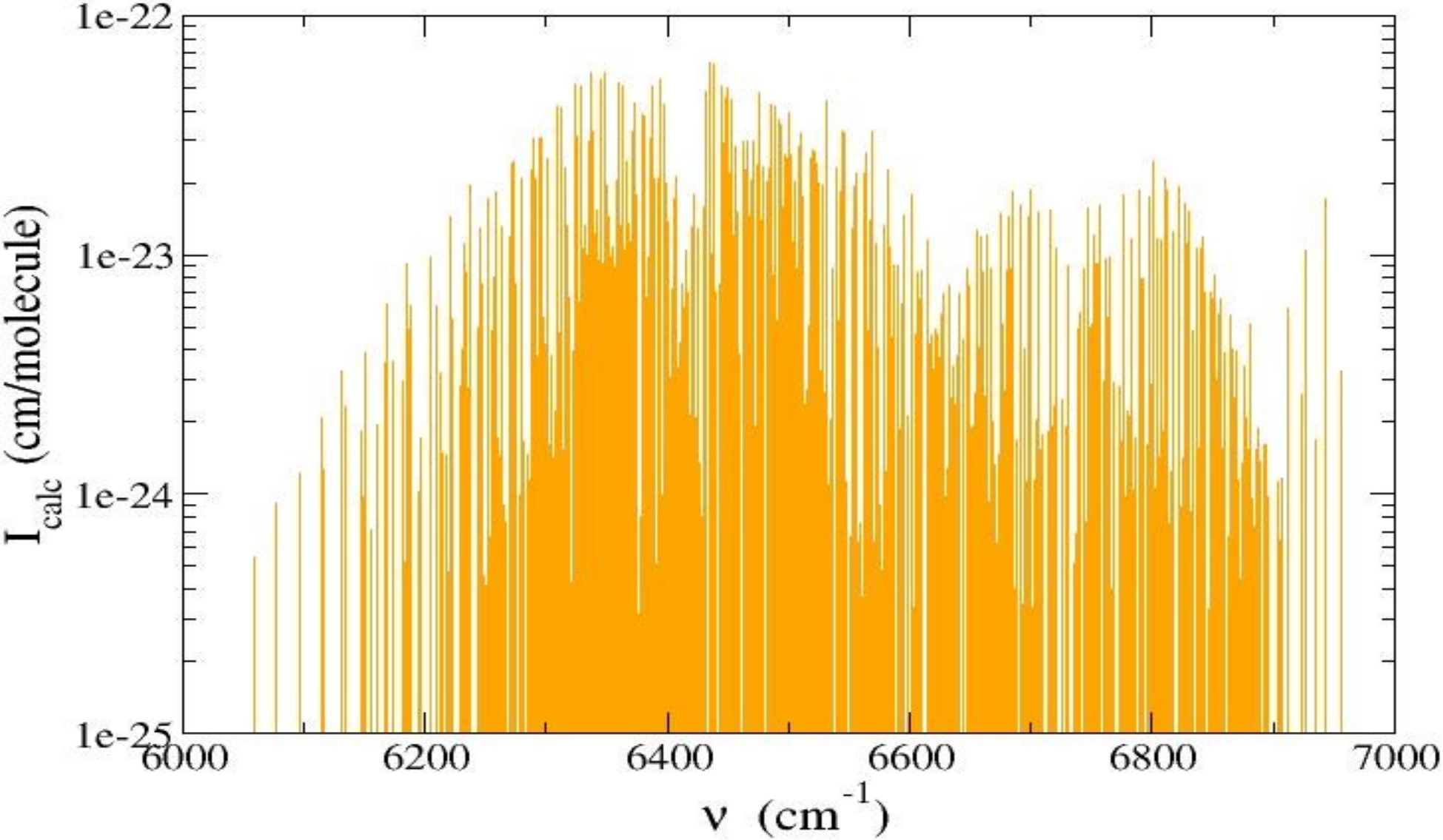




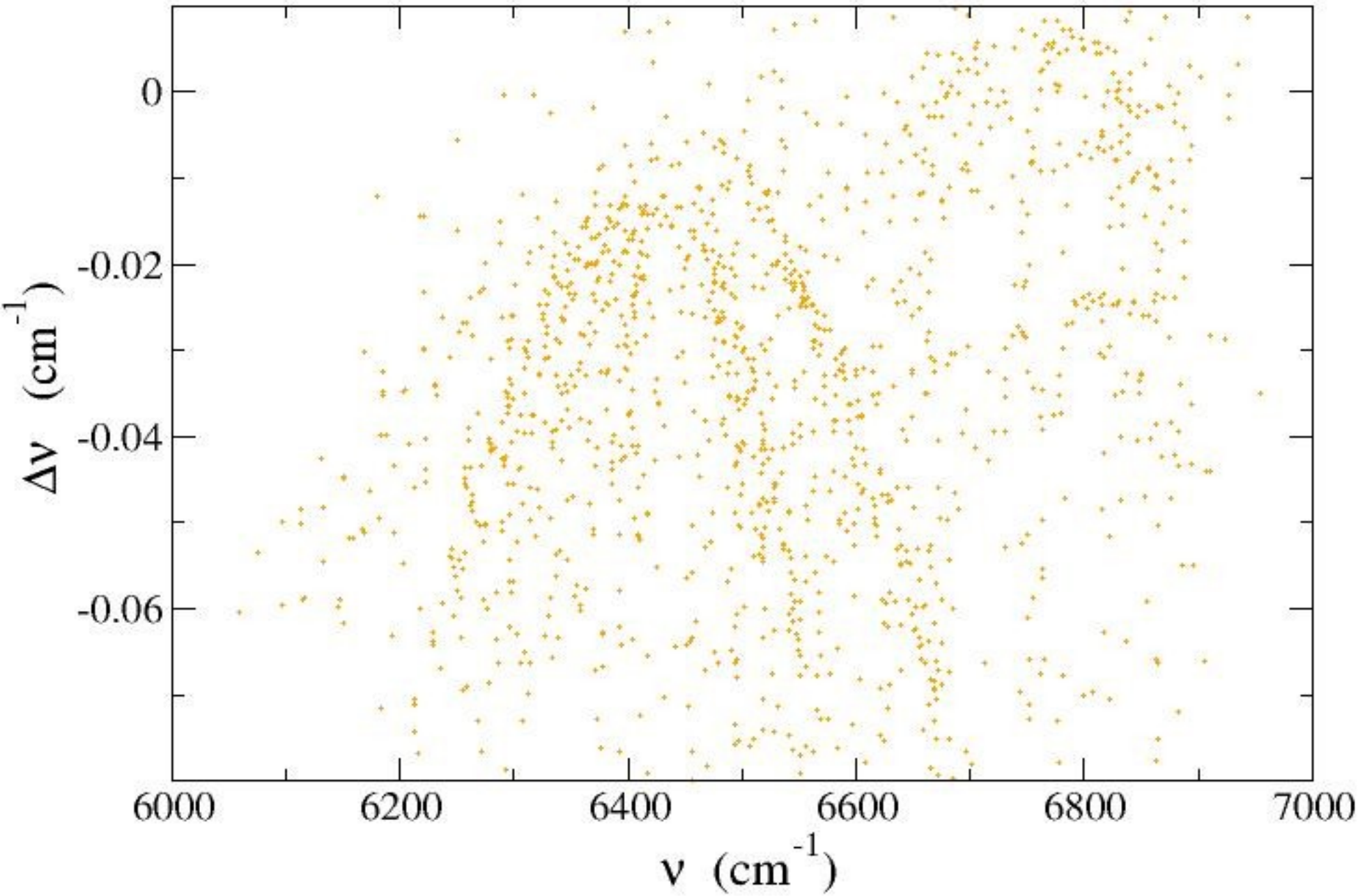
- **233/337**
- **No shift required**
- **Rotational structure**

$HD^{16}O$ Lines

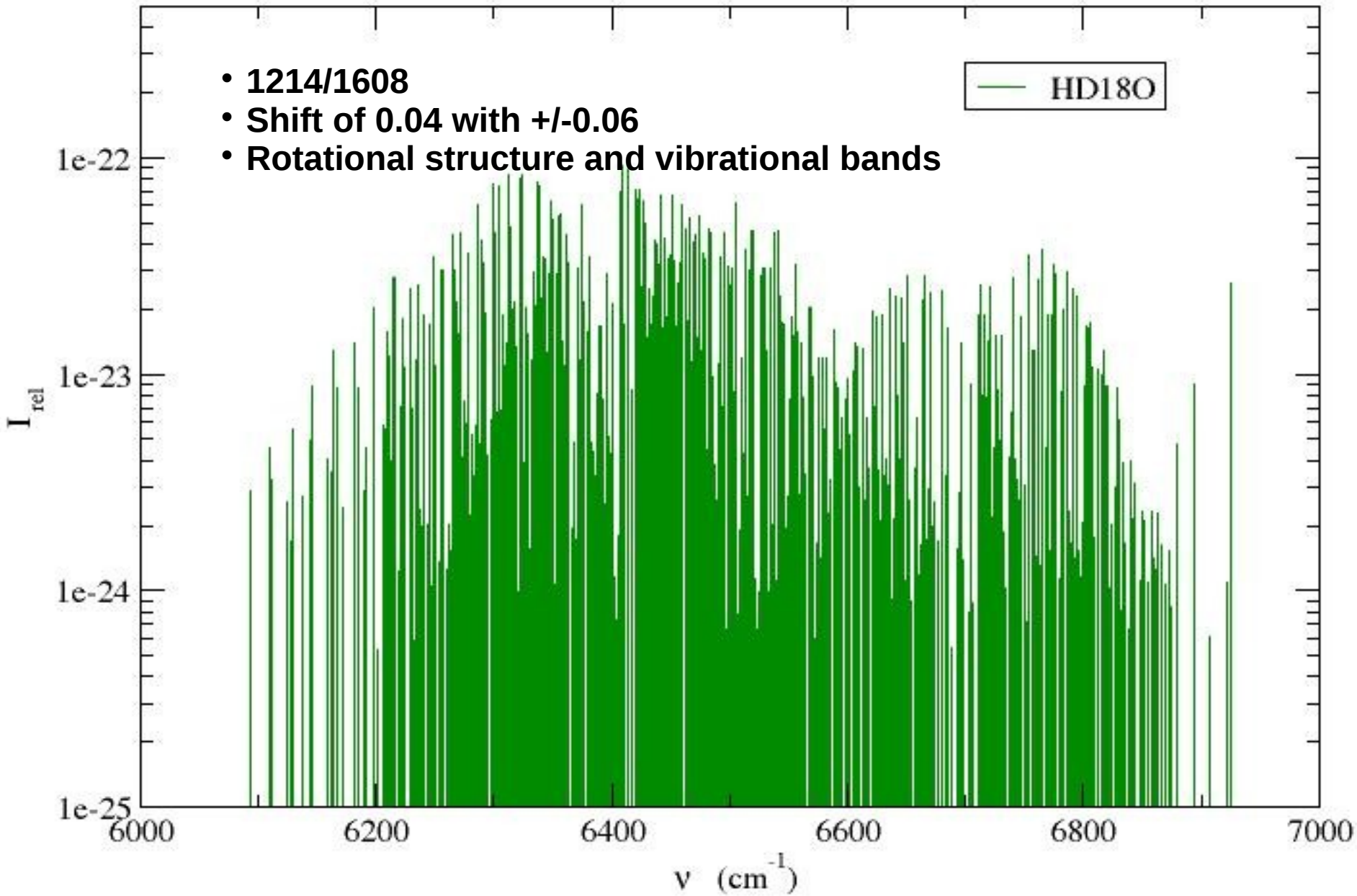
- **1284/1692** +/- **0.045** with a constant shift of **0.035.**
- This compares well with VTT band errors.
- Rotational structure and vibrational bands.



$HD^{16}O$ Residuals

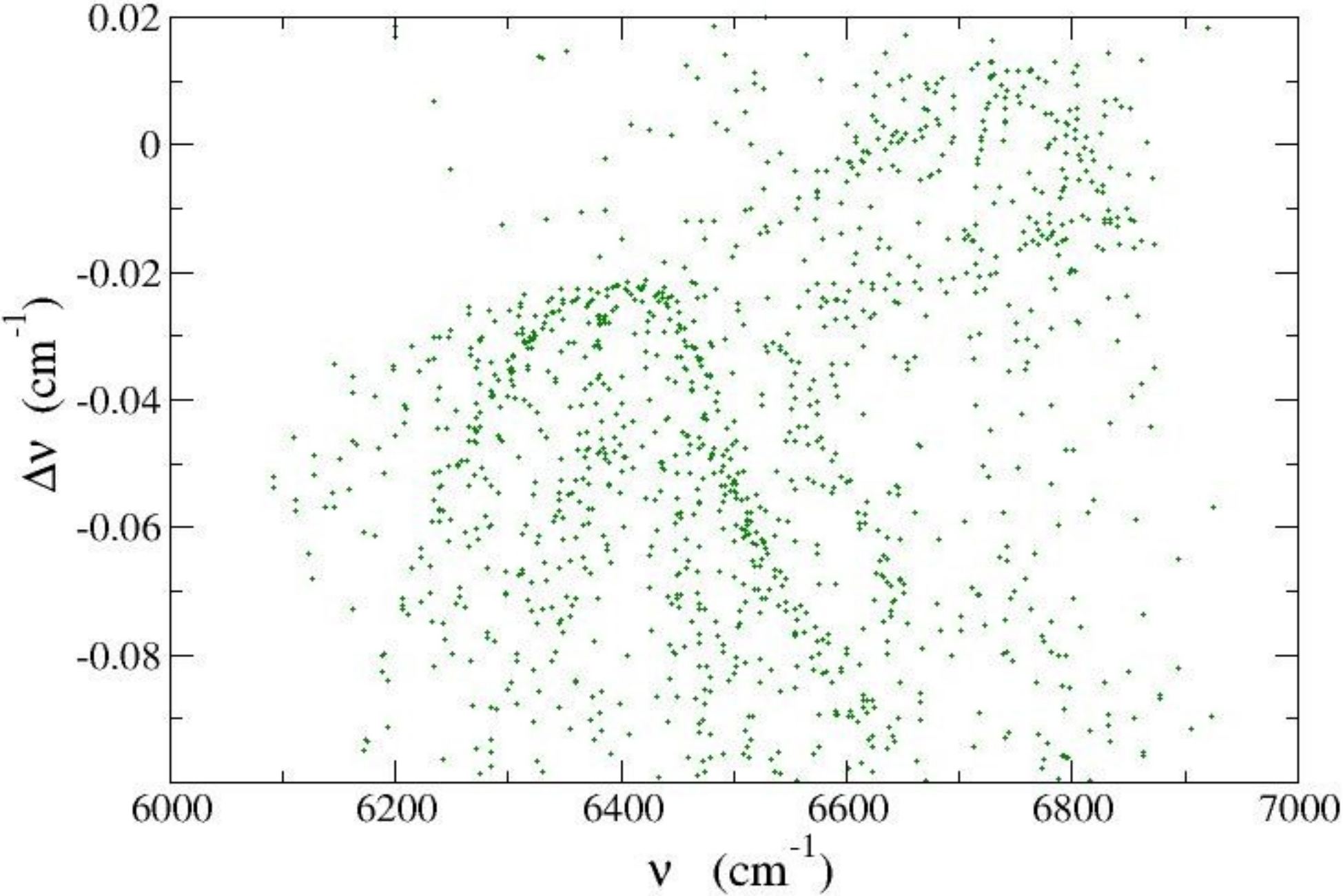


$HD^{18}O$ Lines



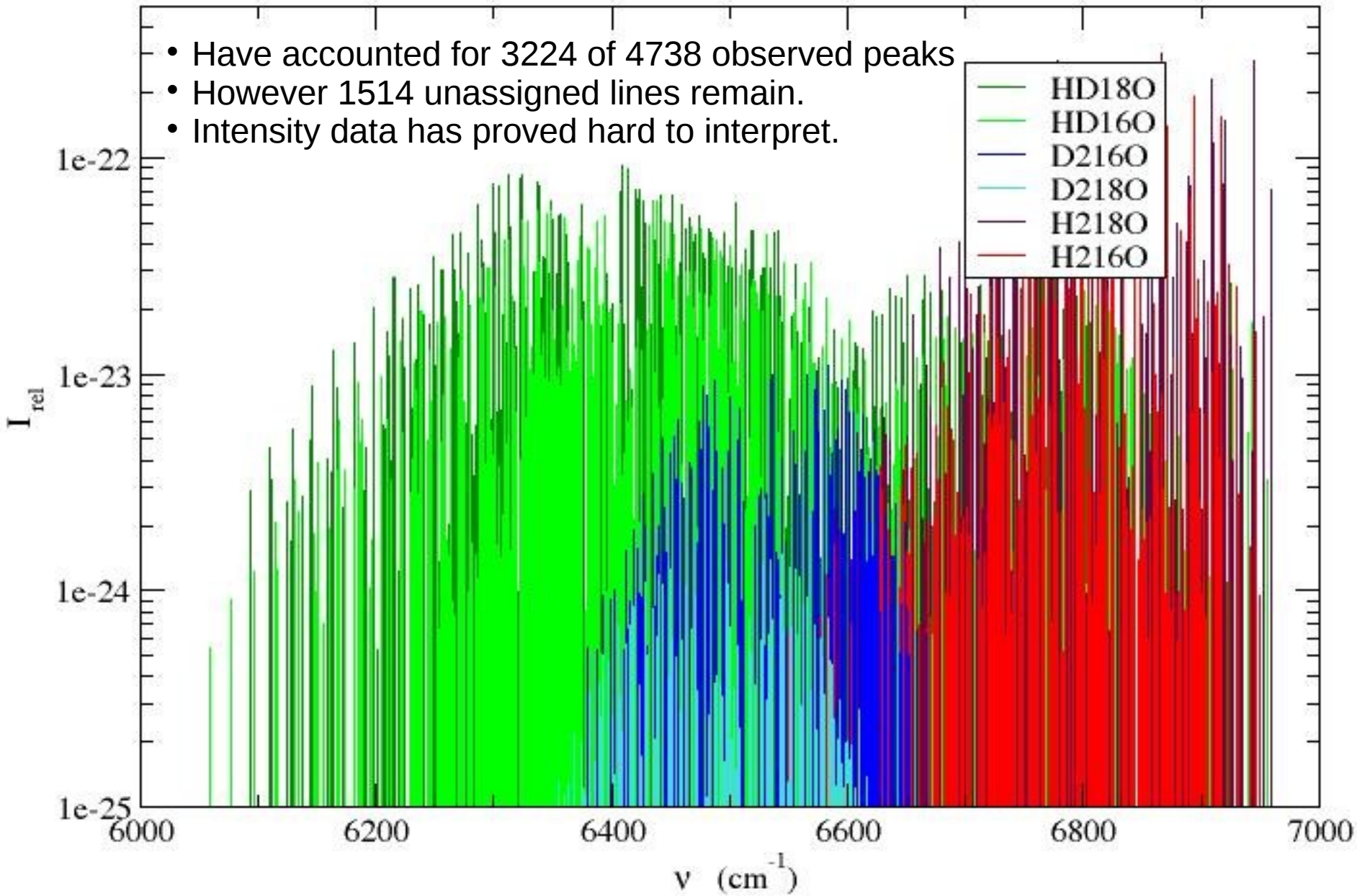
- 1214/1608
- Shift of 0.04 with +/-0.06
- Rotational structure and vibrational bands

$HD^{18}O$ Residuals

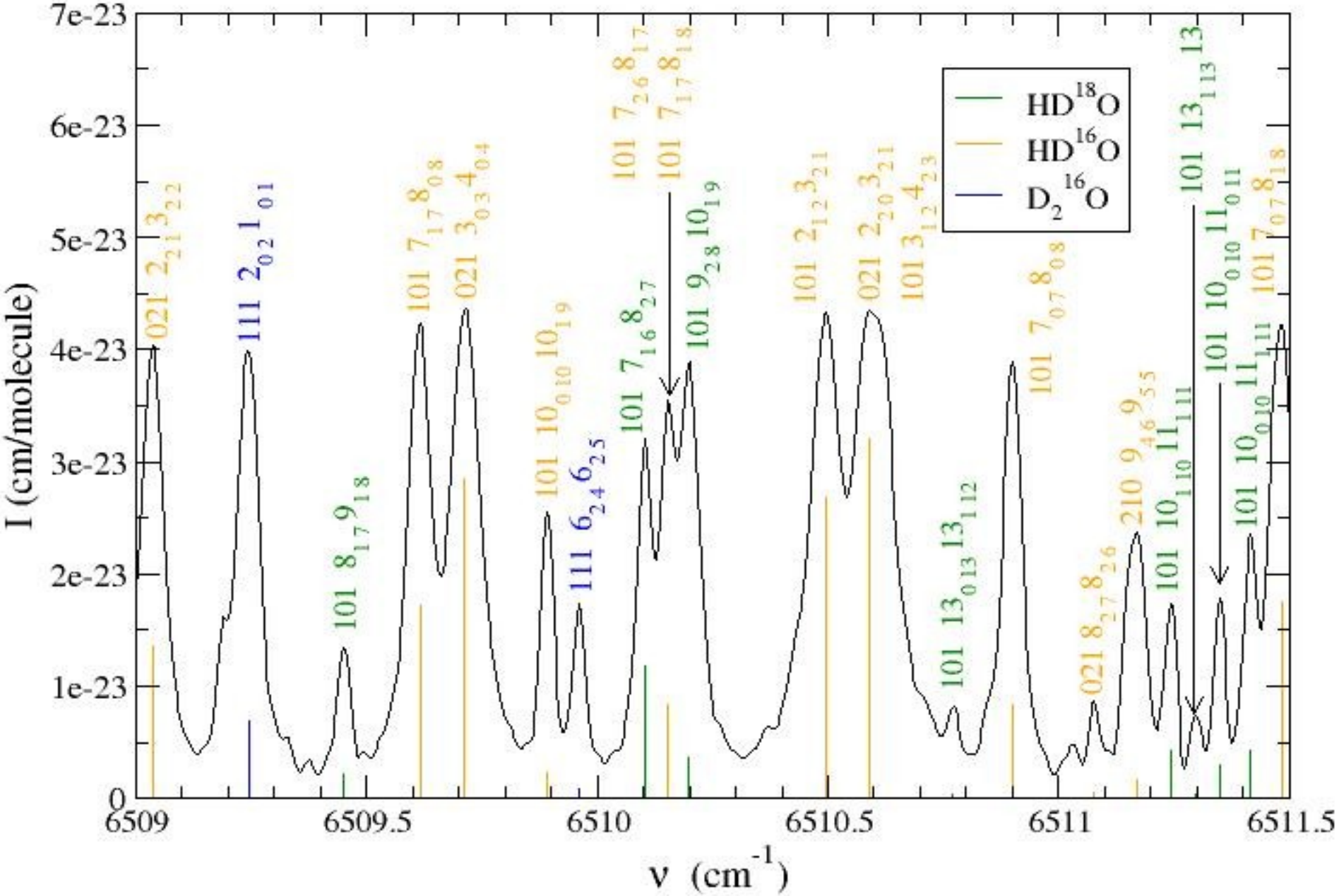


Putting it all together

- Have accounted for 3224 of 4738 observed peaks
- However 1514 unassigned lines remain.
- Intensity data has proved hard to interpret.

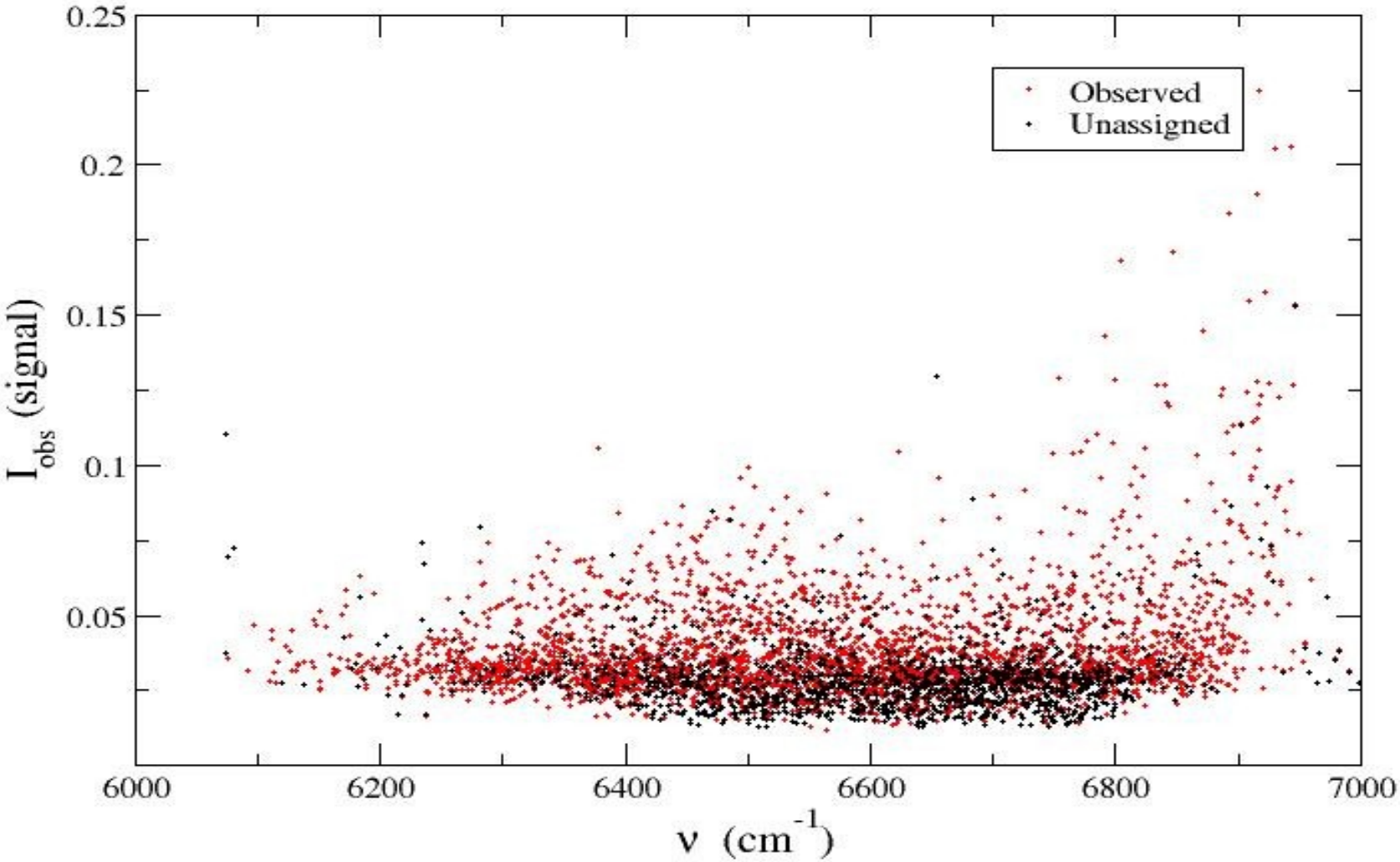


Example Assignment Region



What remains?

- Have removed the vast majority of strong observed lines.
- Remaining strong lines have been checked against strongest $H_2{}^{17}O$ lines without success. “Sticky” species could still be present.
- Can not expect to account for ALL weak lines there are very many of them and intensity data is hard to interpret.



New Assignments and Energy levels

All assignment have been checked via CD's using empirical lower energies.
Agreement in upper levels was required to beat 0.1 cm^{-1}
This produces empirical upper levels which we have also been documented.

- **$H_2$0**

- No new observations.

- **$HD^{16}O$ and $HD^{18}O$**
-
- Lines can be compared with IUPAC. Also *Mikhailenko et. al. JQSRT 113, 653 (2012).*
- Results in 426 newly observed lines for HD18O.
- Only 26 newly observed lines for HD16O.
- 88 new energy levels for HD18O but only 5 for HD16O.

- **$D_2{}^{16}O$ and $D_2{}^{18}O$**

- No IUPAC yet published.
- Significant observations by *Ormsby et. al. J. Mol. Spect. 158, 109 (1993)* for D216O.
- Also D218O lines from recent work of *Mikhailenko et. al. JQSRT 113, 653 (2012).*
- No new D216O assignments.
- 218 new observations for D218O.
- 103 new energy levels.

A New Publication

Subsequent to the completion of this work Mikhailenko et. al. published analysis of a similar spectrum in this region.

Significant overlap **AND** agreement between the two studies.

Detailed comparison with their work reveal 36 $HD^{18}O$ lines and 38 $D_2{}^{18}O$ lines unique to our work.

Hopefully this work will be accepted by JMS shortly!

Thanks for Listening

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