HOx isotopes

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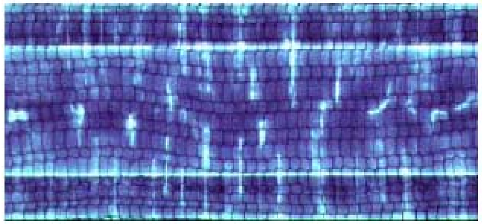
Pasadena, CA
March 3, 2005

HOx isotopes:
Photolysis - Fluorescence detection of HDO/H_2O

Excimer Lamp Photolysis

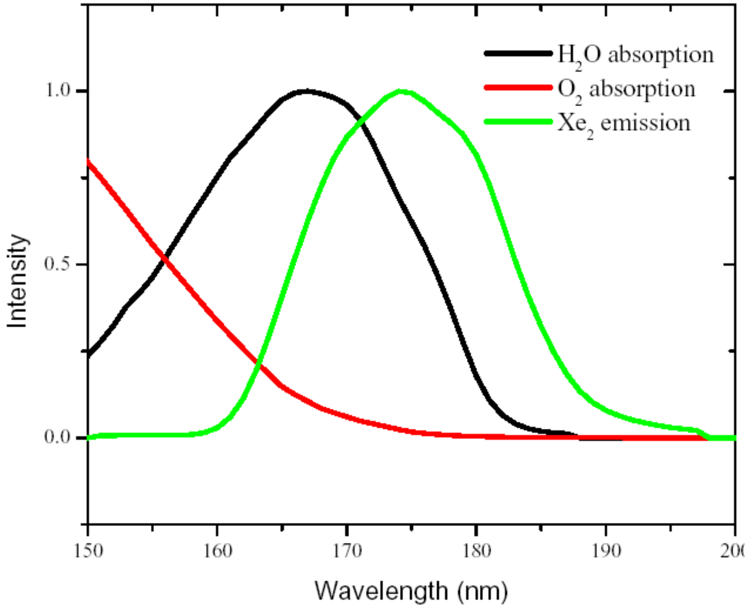


$H_2O + h\nu \rightarrow H + OH$

$HDO + h\nu \rightarrow H + OD$

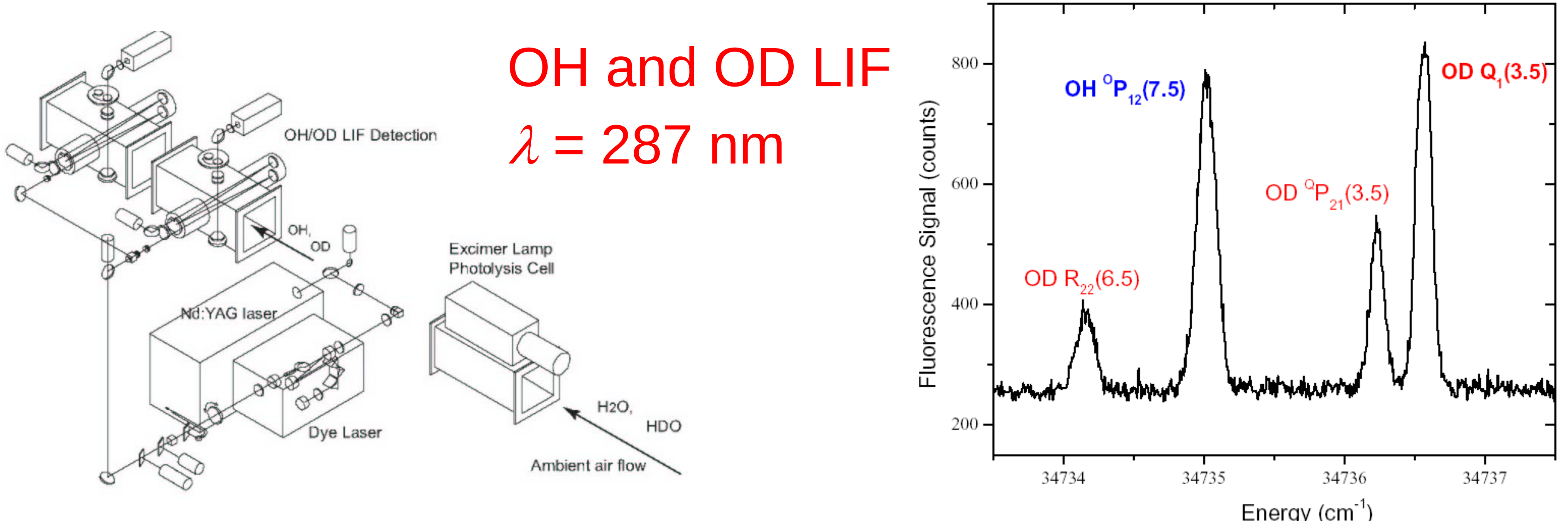
$h\nu$ = 8W

λ = 172 nm



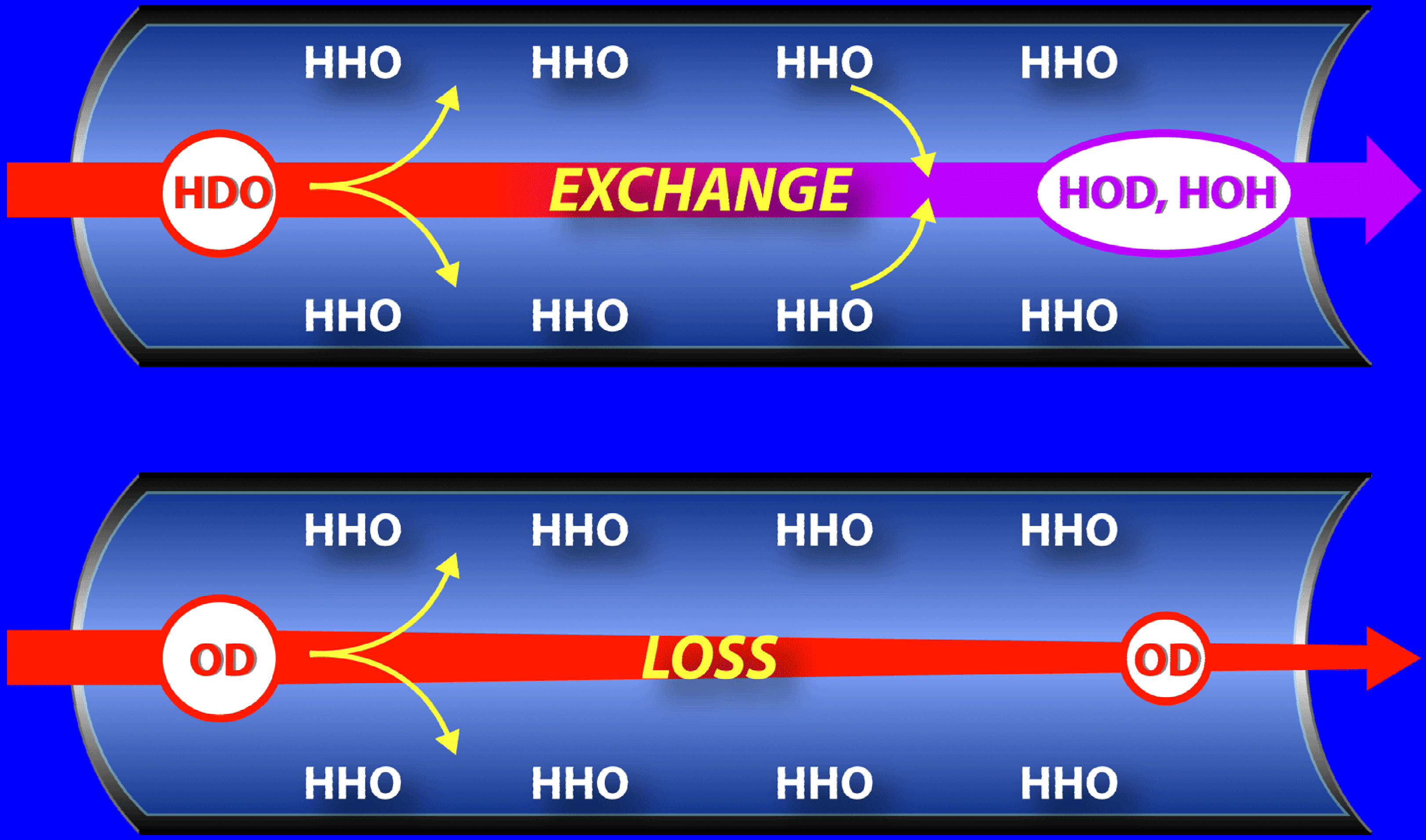
OH and OD LIF

λ = 287 nm

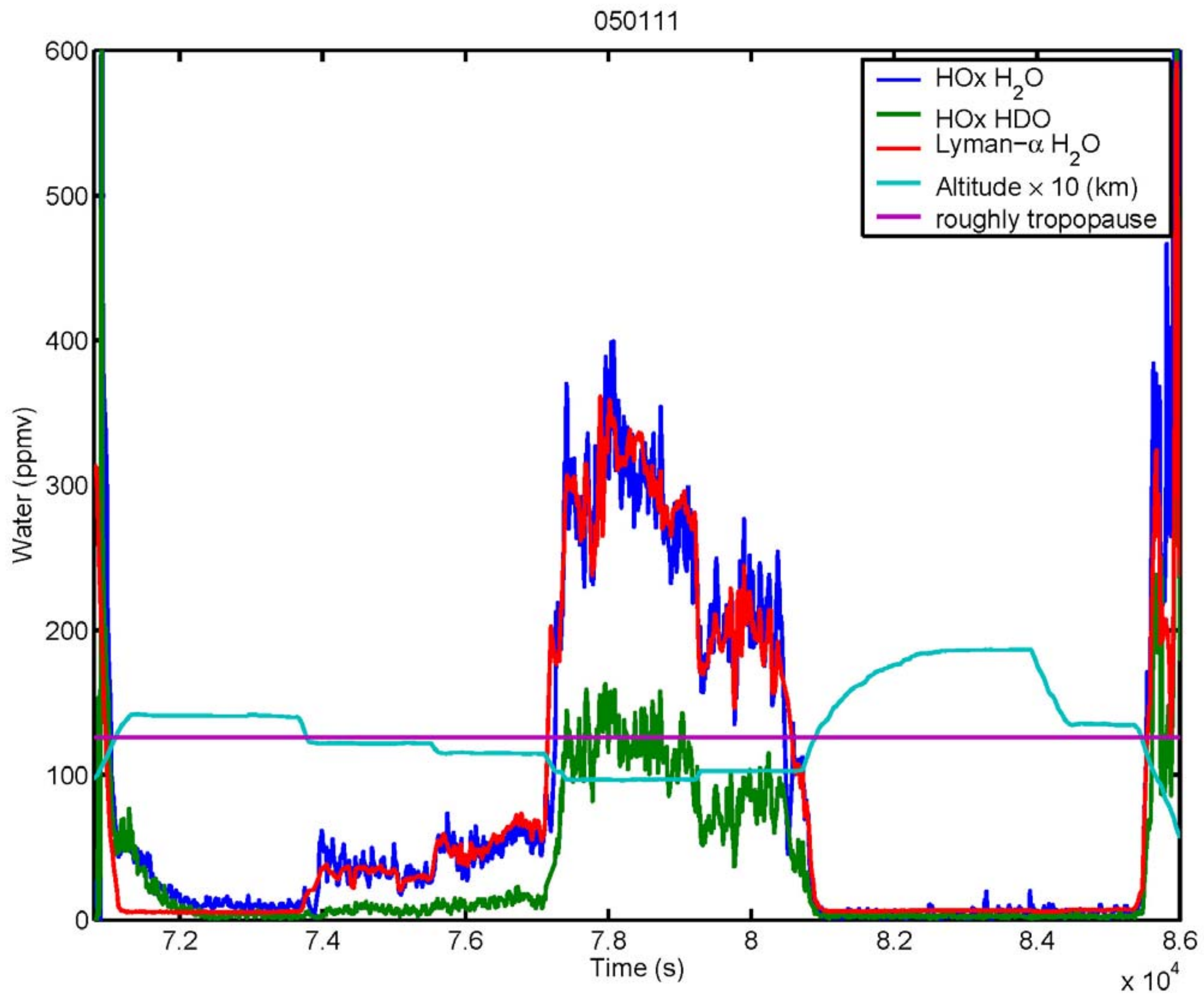


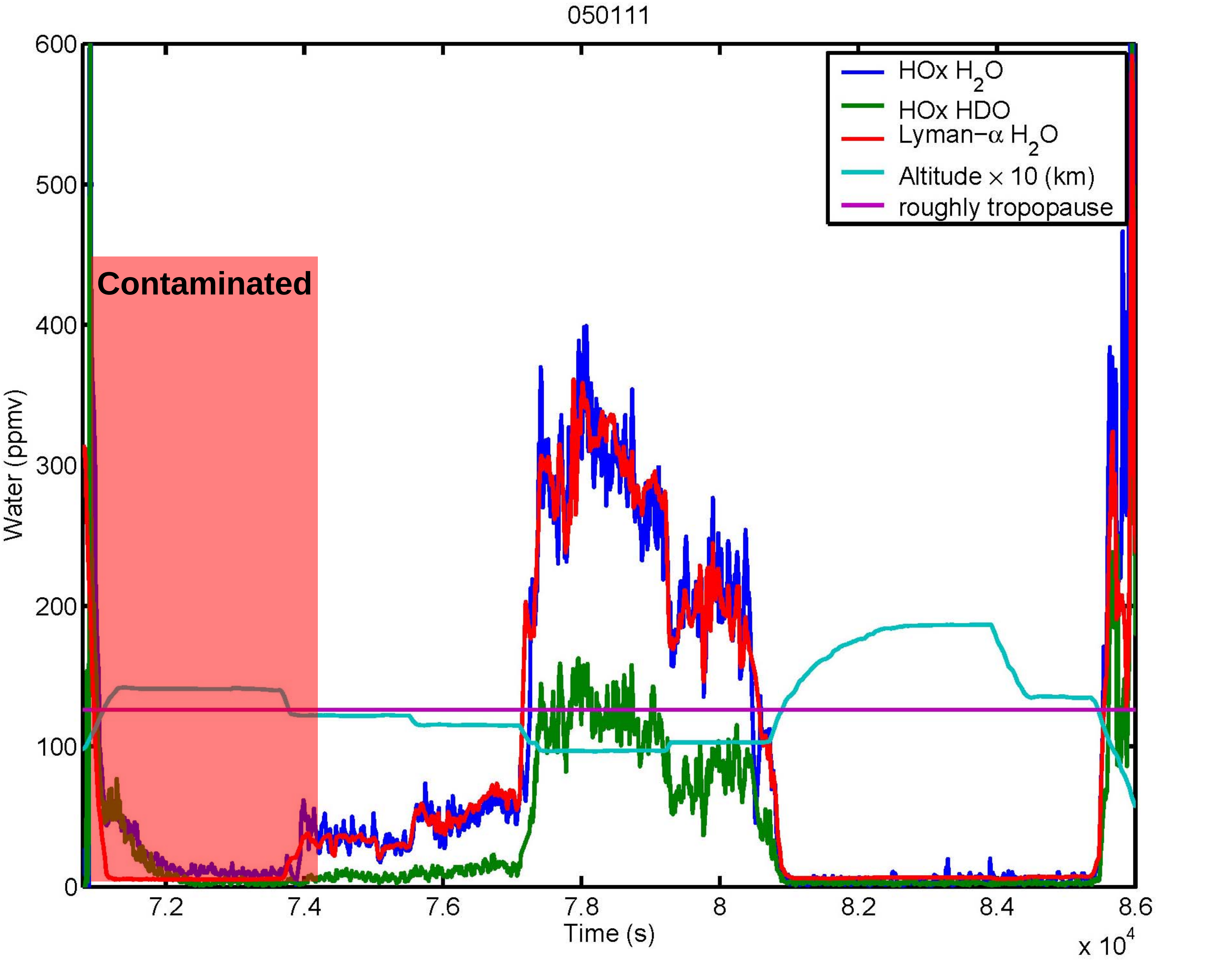
Radical vs. Molecular Sampling

Molecular water exchanges with walls. OH and OD radicals are lost irreversibly



Preliminary Flight Results

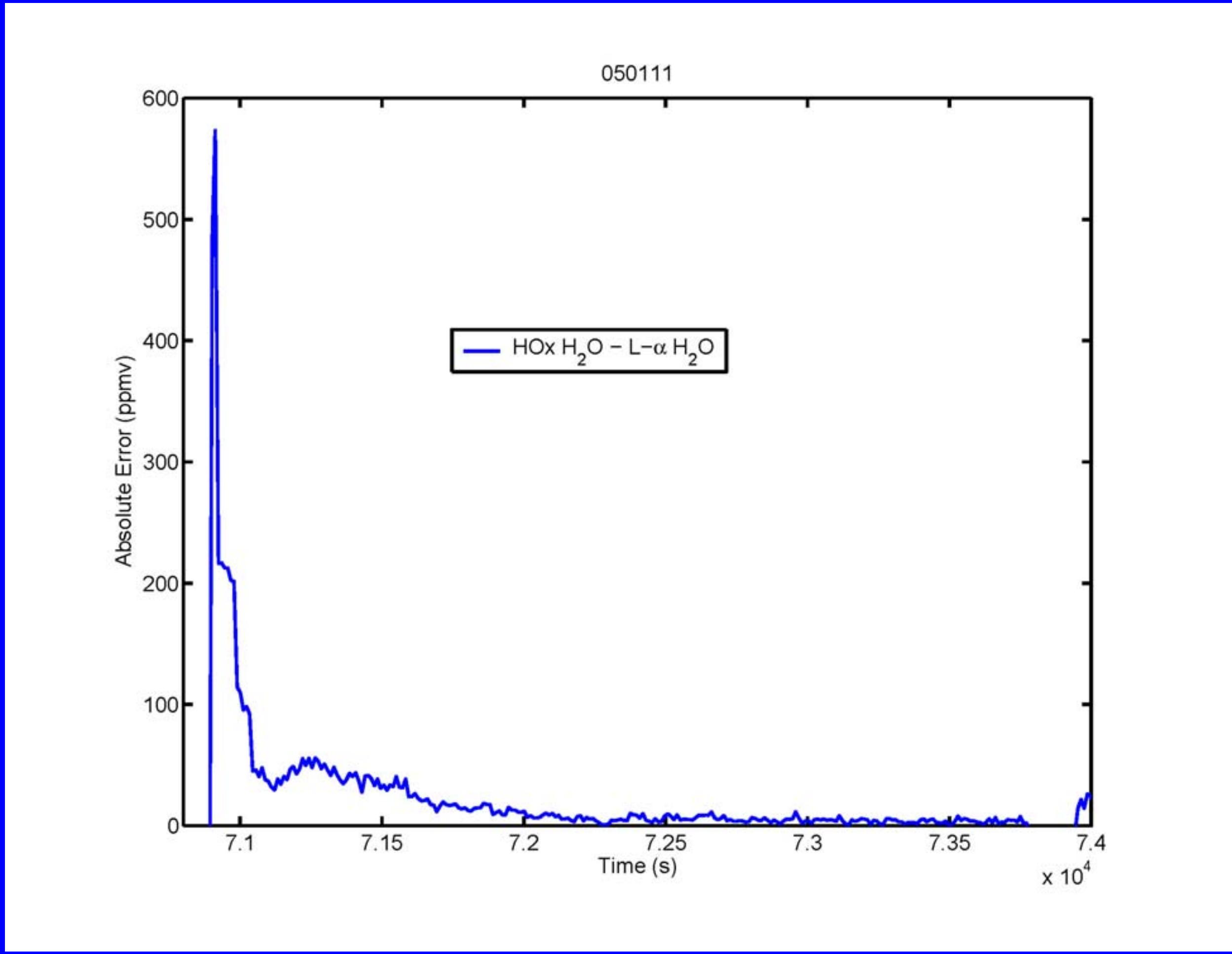



050111
HOx H2O
HOx HDO
Lyman−α H2O
Altitude × 10 (km)
roughly tropopause
Contaminated
Water (ppmv)
Time (s)
x 10^4
0
100
200
300
400
500
600
7.2
7.4
7.6
7.8
8
8.2
8.4
8.6

Residual Water During Ascent

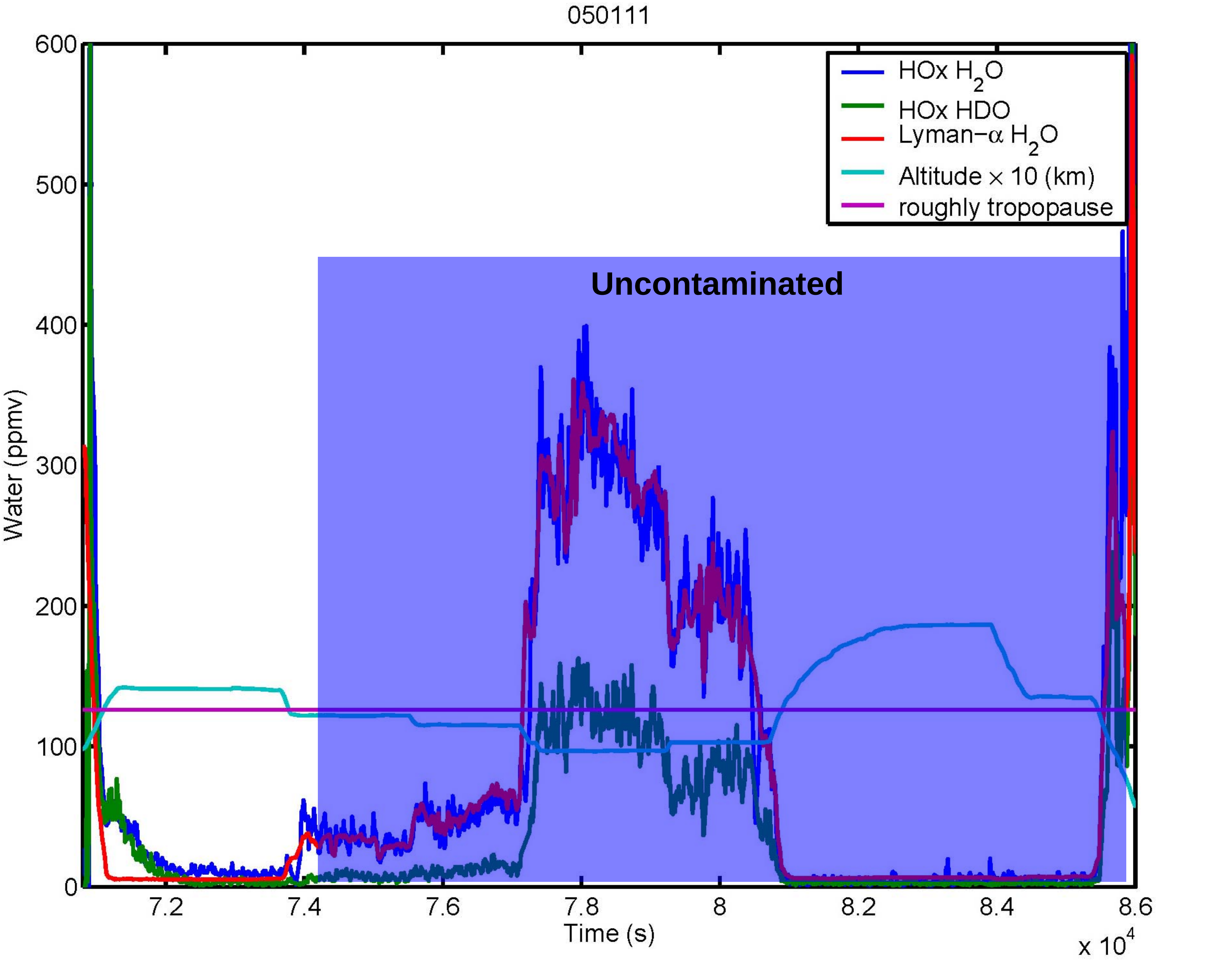
Water source =
$4x10^4$ ppmv s $H_2O \times 150\ cm^3/s$ flow = $6\ cm^3\ H_2O$ = $1.5x10^{20}$

Inlet: A = $100\ cm^2$, 1 ML = $1x10^{15}\ cm^2 \rightarrow 1000$ ML H_2O



Potential Water sources

- Nearest neighbors:
- Total water inlet
- Landing gear
- Fuselage



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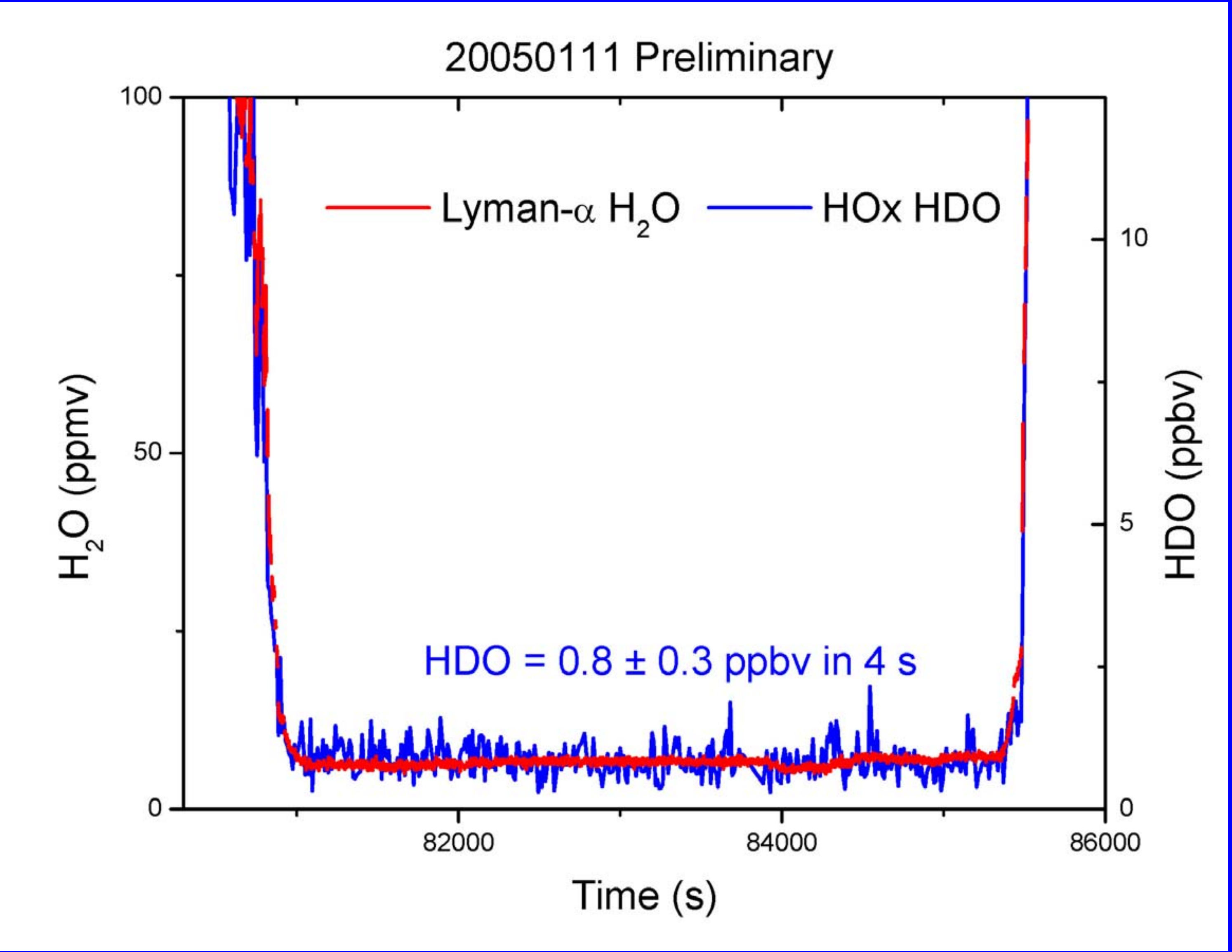
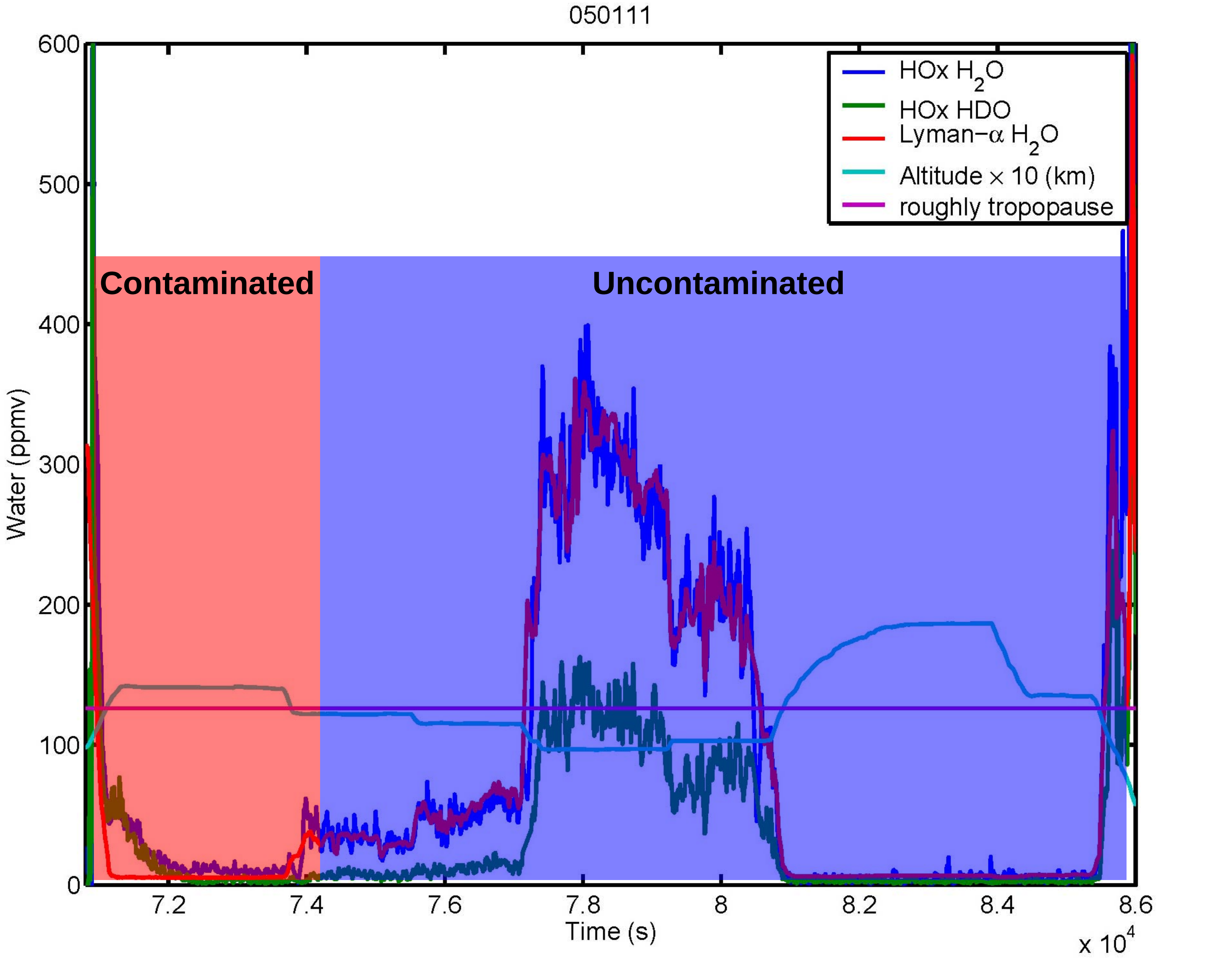


In this stratospheric leg the measurement demonstrates a fast time response and good signal to noise



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0
100
200
300
400
500
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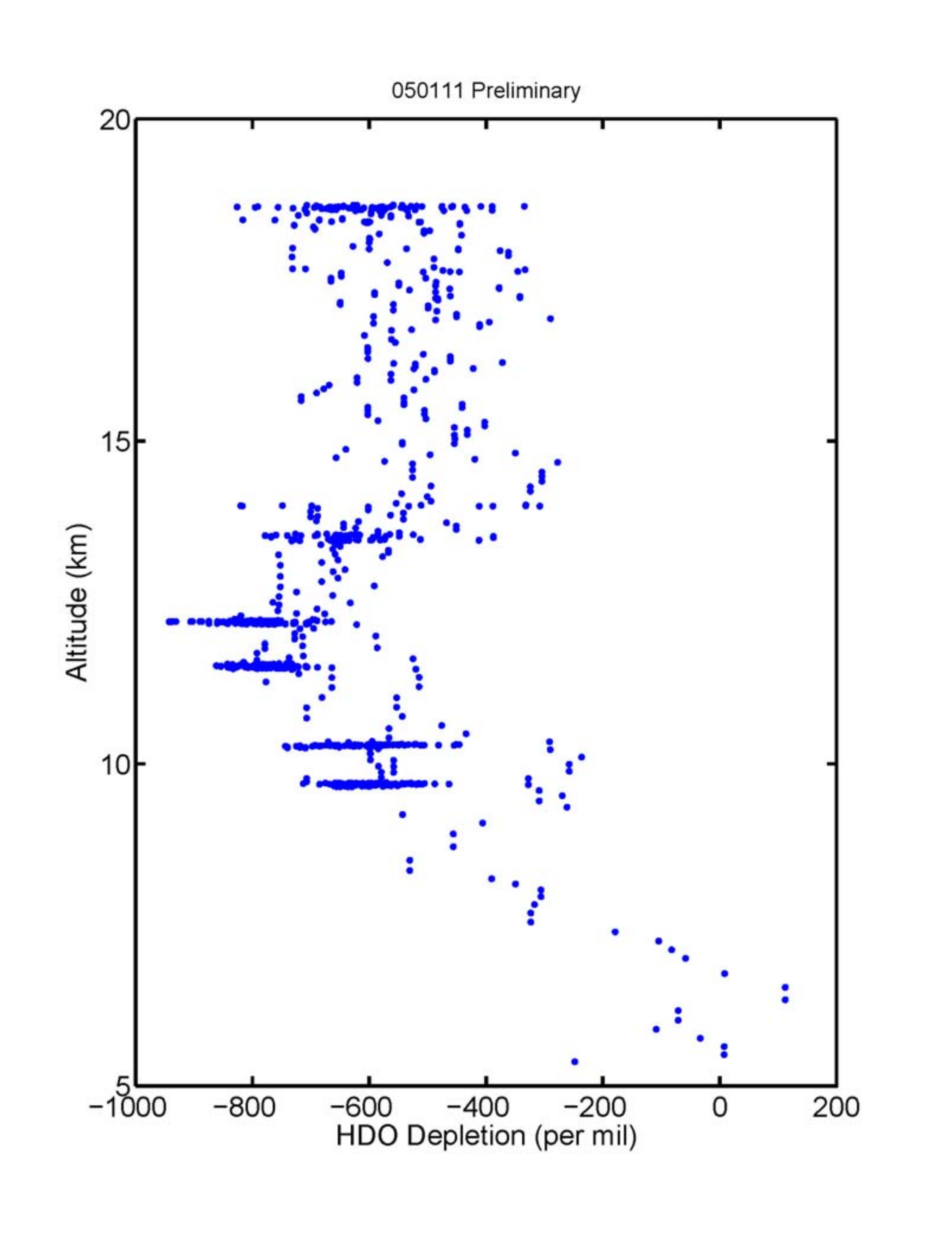
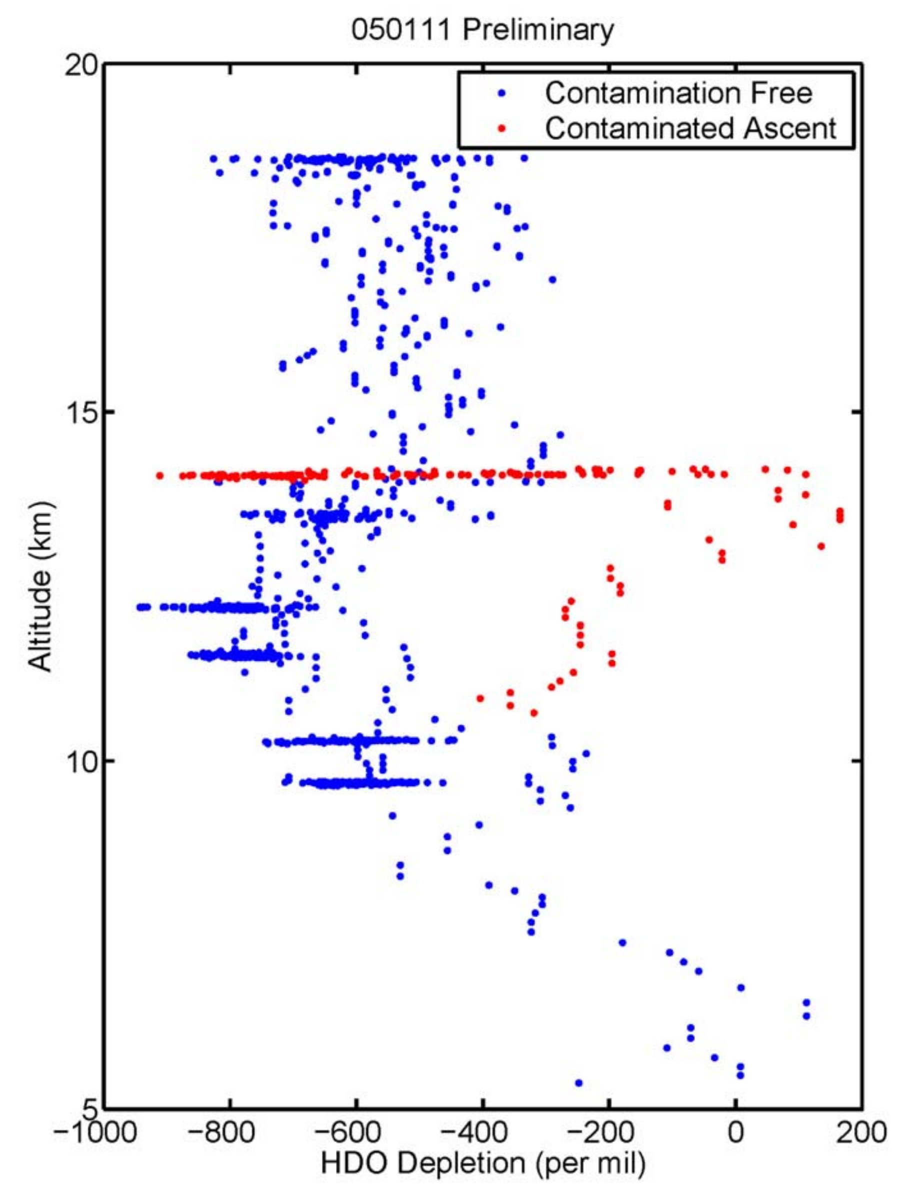
7.2
7.4
7.6
7.8
8
8.2
8.4
8.6

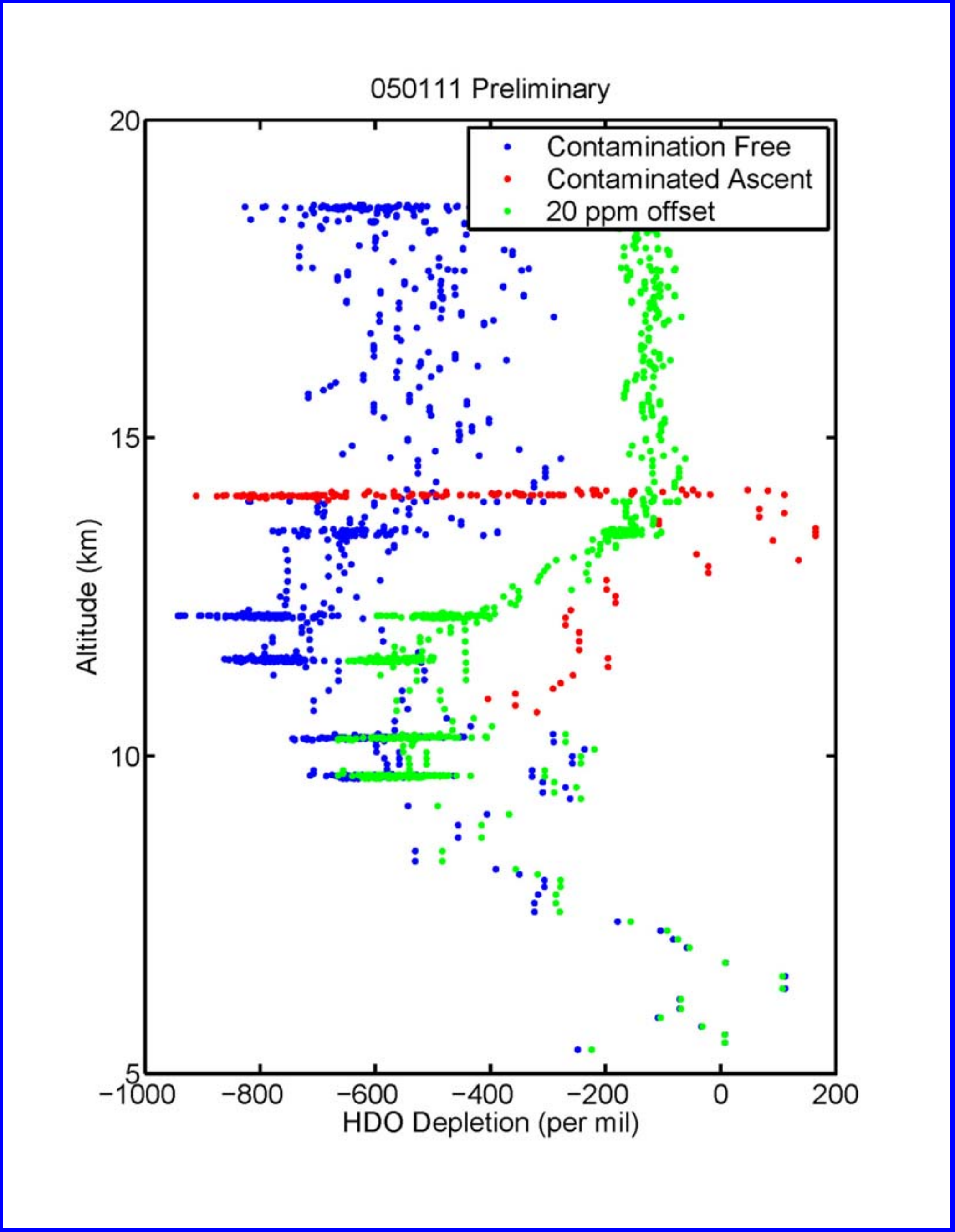
Uncontaminated Profile



Contaminated Ascent



20 ppm Offset Added to Both H_2O and HDO

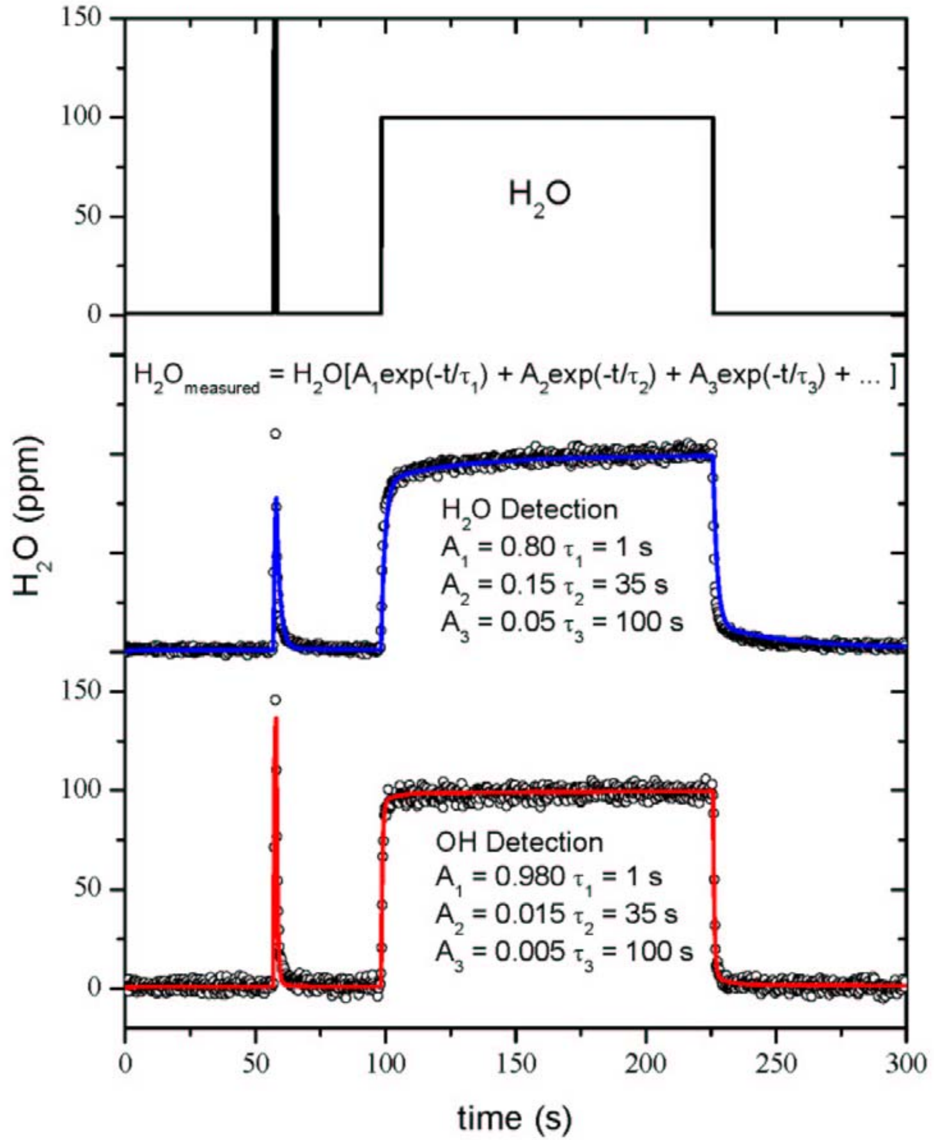


Summary

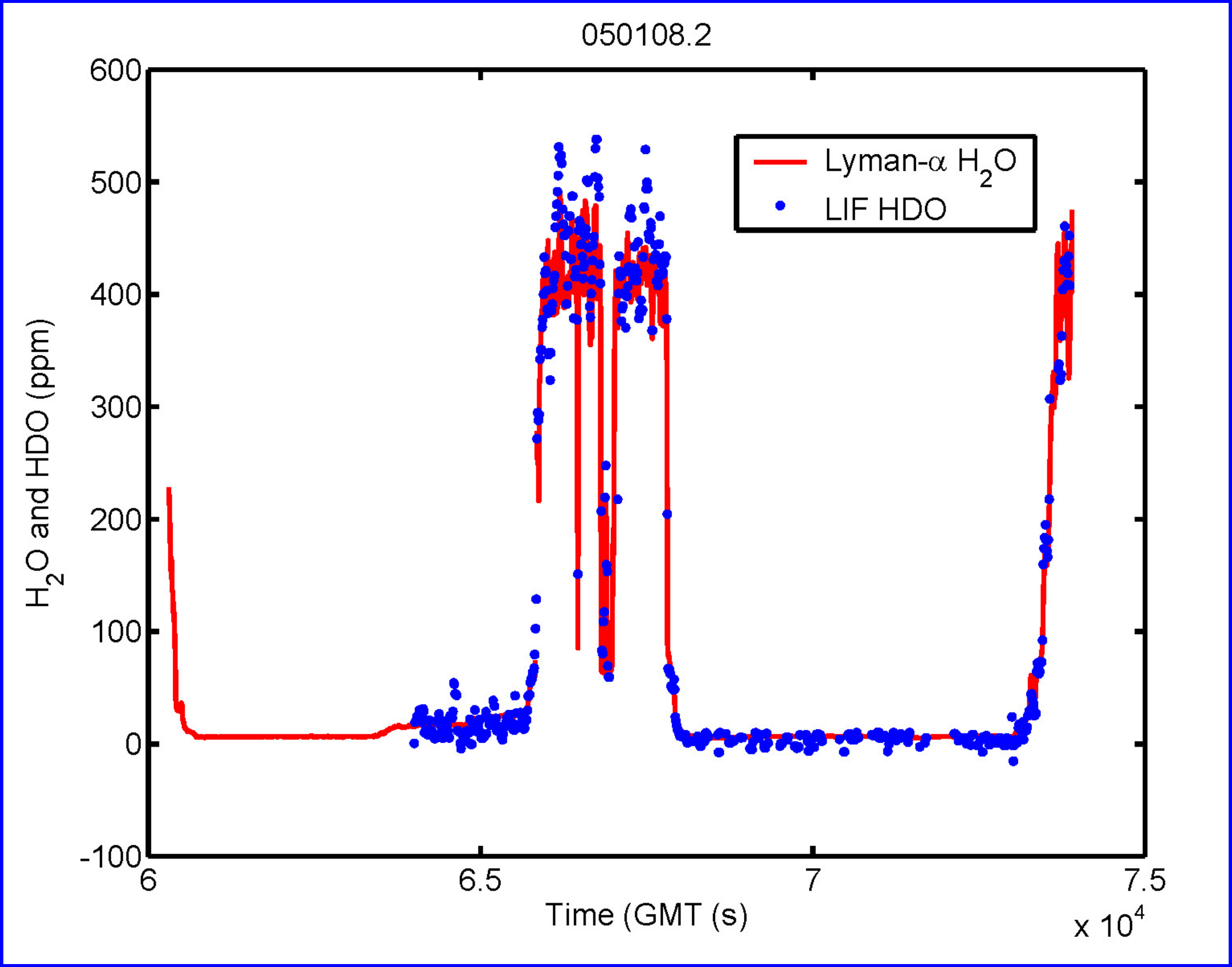
- Flight data high points:
  - Hoxotope worked as well in flight as in the lab
  - Fast time constant in $H2O$ and HDO sampling
  - Absence of unexplained artifacts
  - Good accuracy
  - Reasonable signal to noise (HDO ± 250 pptv/4s)
- Post flight schedule:
  - Calibration: 5% (50 per mil)
  - Sensitivity: factor of 5 for moderate effort

- Thanks to NASA IIP, NASA WB57, Harvard Engineering

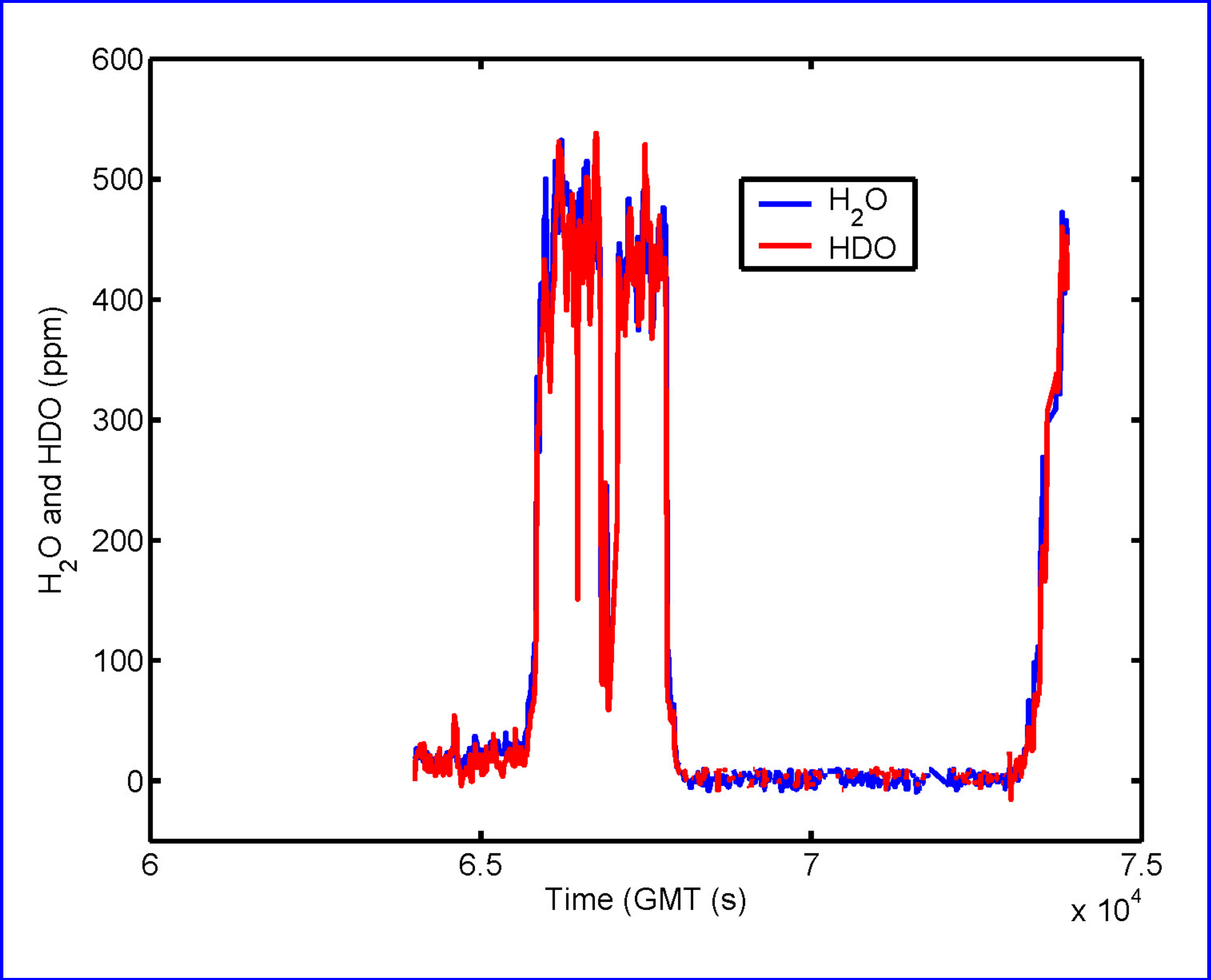
Laboratory Time Constant

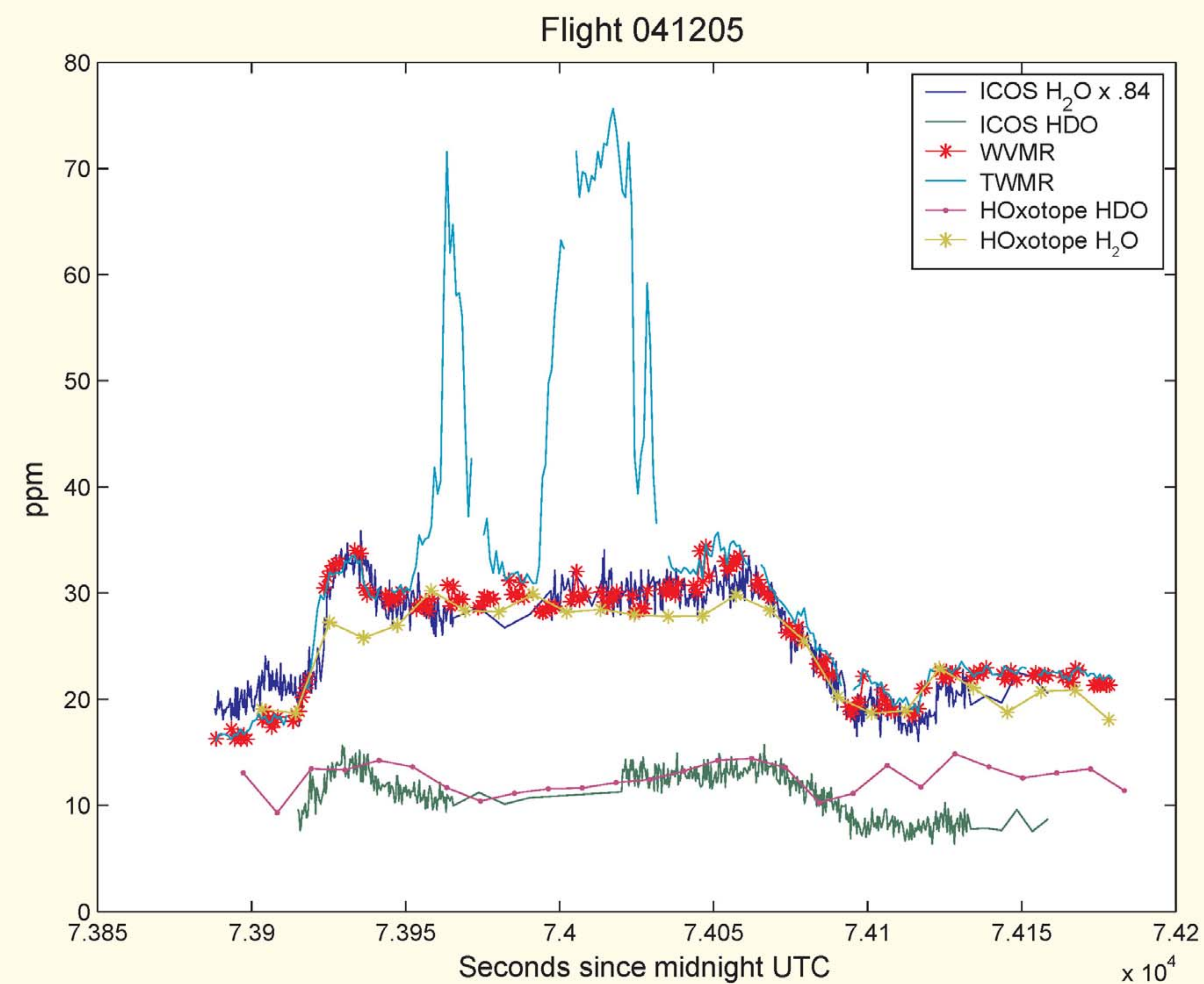


Test flight 050108 Comparison to Lyman-α



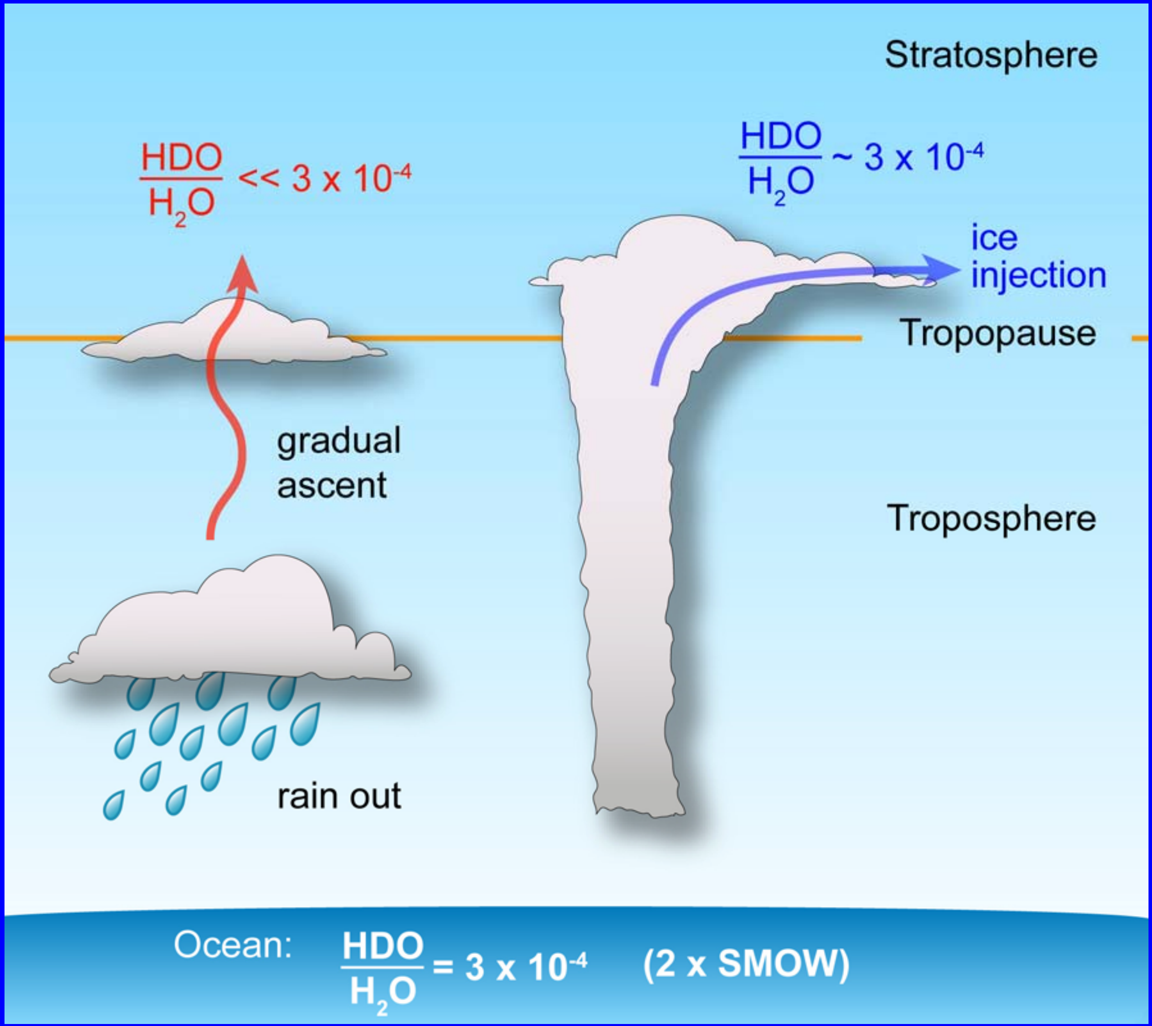
Test Flight 050108 H_2O and HDO




Flight 041205
ppm
Seconds since midnight UTC
x 10^4
ICOS H2O x .84
ICOS HDO
WVMR
TWMR
HOxotope HDO
HOxotope H2O
0
10
20
30
40
50
60
70
80
7.385
7.39
7.395
7.4
7.405
7.41
7.415
7.42

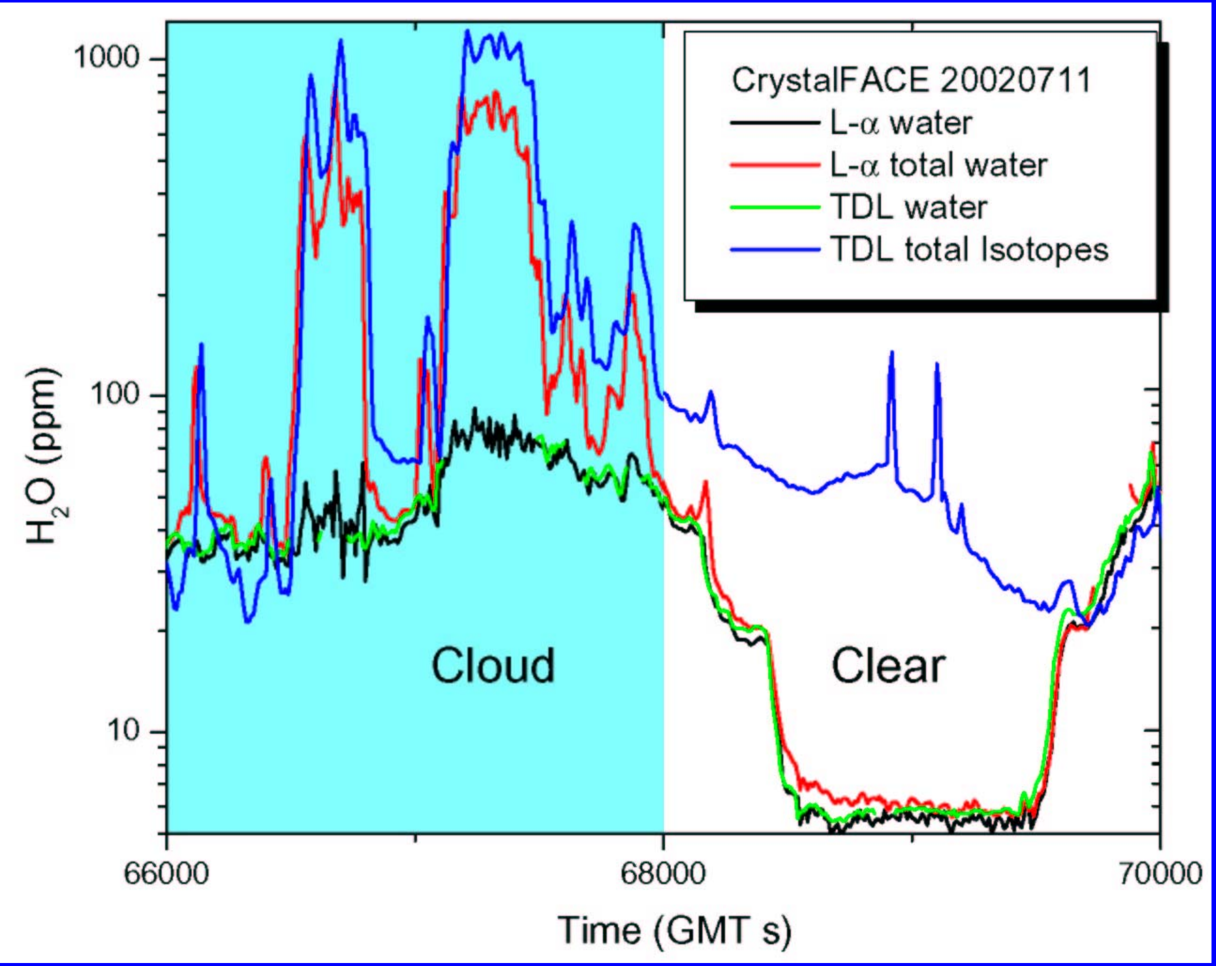
Motivation I: Water isotopes are valuable *in situ* tracers

- HDO condenses more readily than H_2O
- Rainout leads to HDO depletion
- Ice injection can make the stratosphere “Heavy”
- *In situ* water isotope measurements can offer a tracer for the condensation history of air parcels

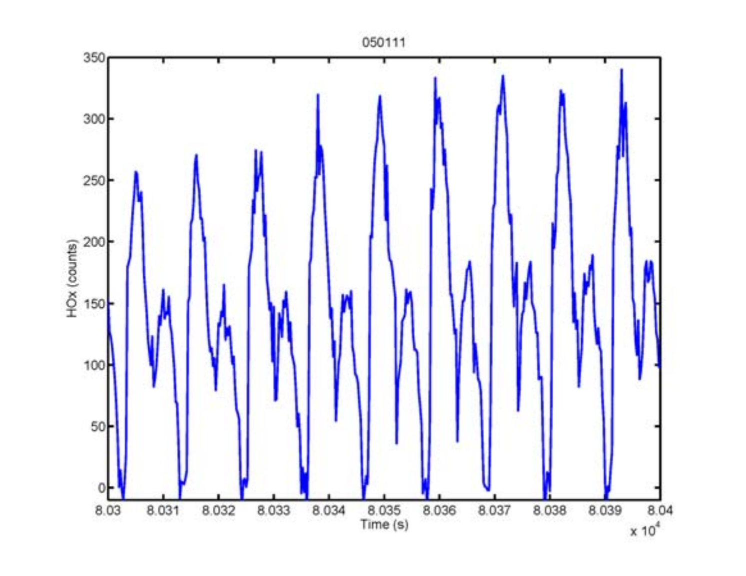


Motivation II: In situ water isotope instruments require validation

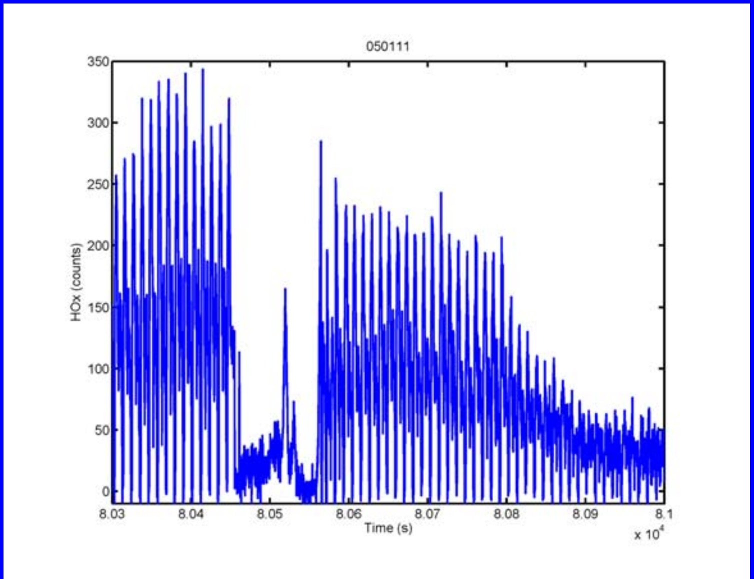
- We expect instrument artifacts to contaminate water measurements.
  - Sampling
  - Optical
  - Software analysis
- Independent measurements can help identify artifacts.

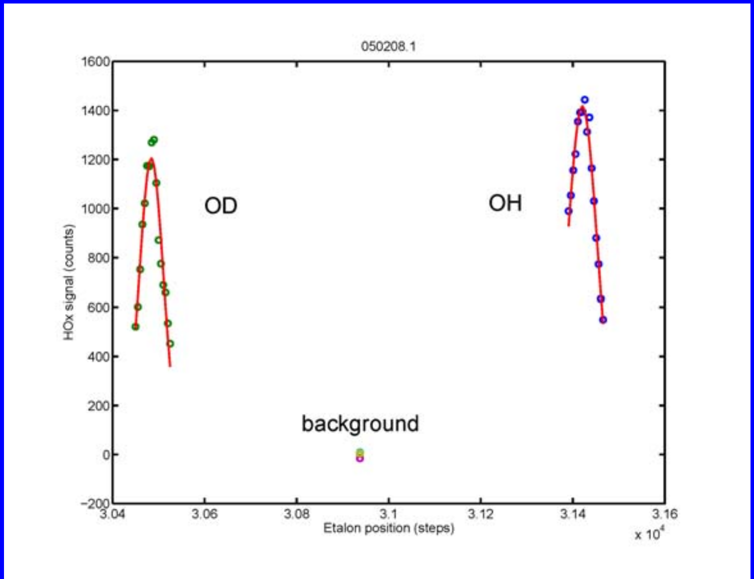


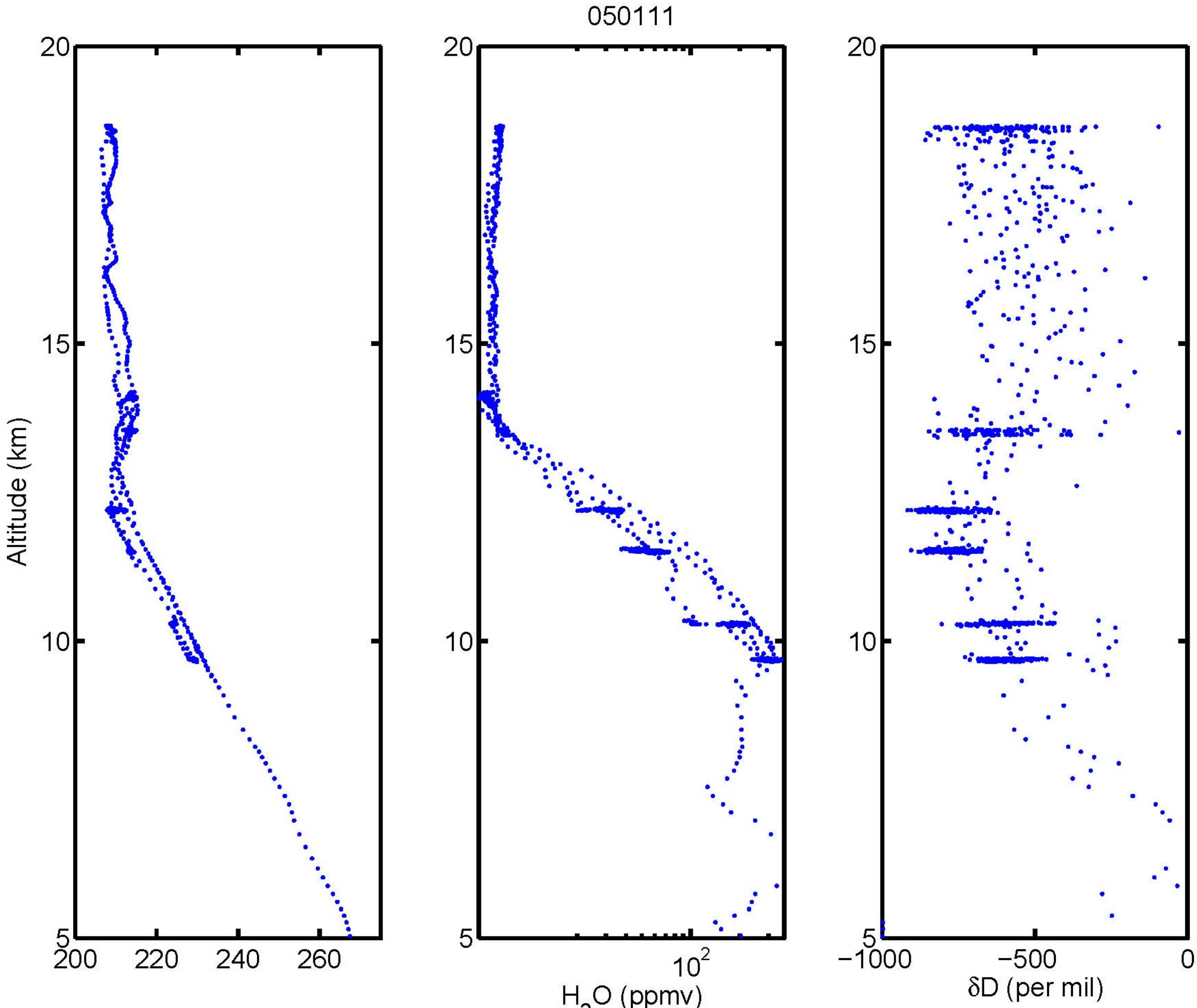
Data acquisition



- OD and OH lines are scanned alternately (4 s) with background (2 s)
- OD and OH line positions are determined from real-time fits
- Post flight analysis:
  - Least squares fit of each line to get [OD] and [OH]
  - Multiply by cal factor to get [HDO] and [H_2O]







050111
Altitude (km)
20
15
10
5
200
220
240
260
H2O (ppmv)
10^2
δD (per mil)
−1000
−500
0