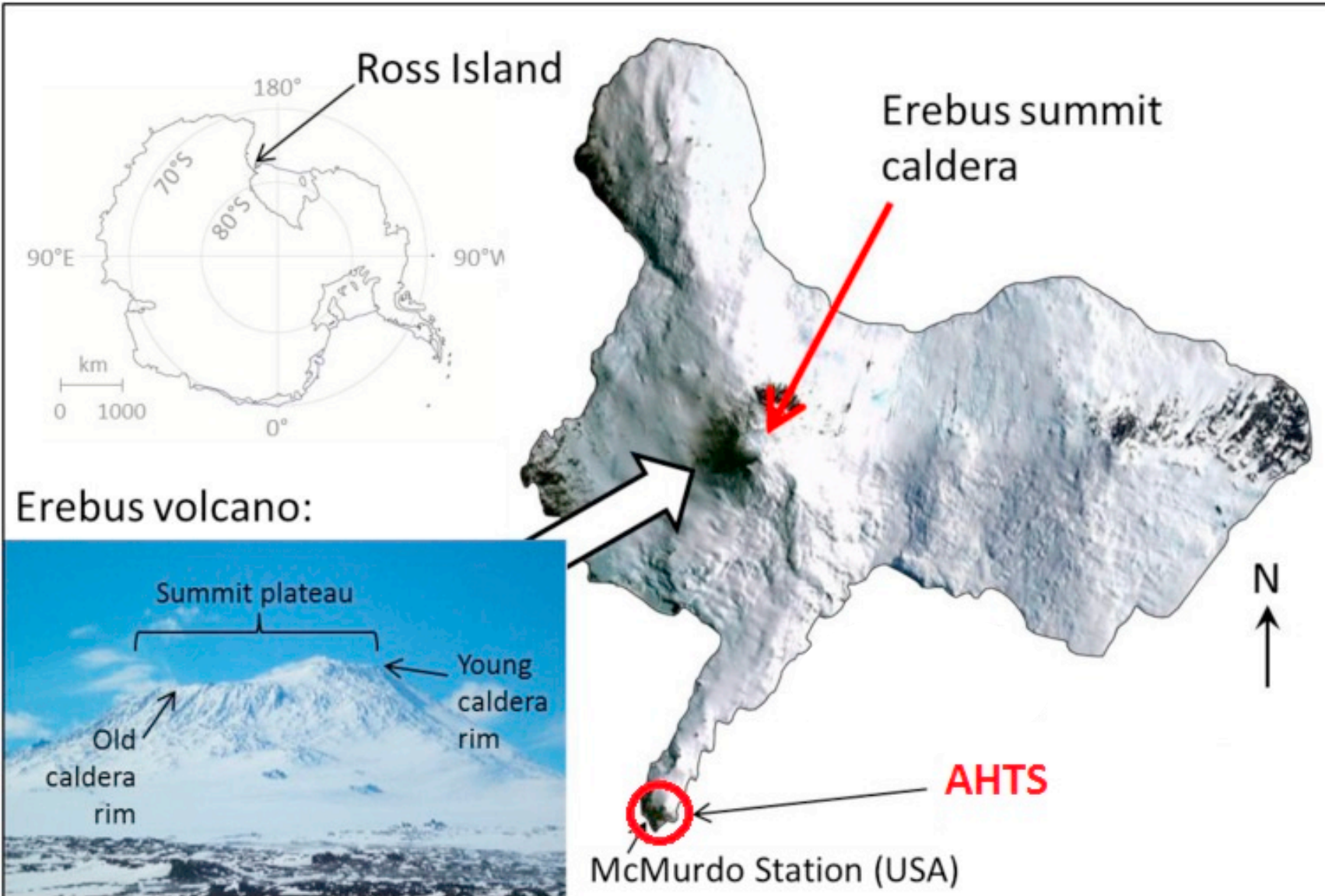


Opportunistic observations of Erebus volcanic plume composition by high resolution solar occultation mid infra-red spectroscopy

Dan Smale (NIWA), Jim Hannigan (UCAR), Mark Murphy (AntNZ), Sanil Lad (AntNZ)



Erebus: Height = 3794 amsl, 37.9 km from Arrival Heights research laboratory (220 amsl). Bearing from AHTS: 20E.
Persistent passive degassing (no explosive events). Phonolitic Volcano (most active in Antarctica). Rich in halogens.
Prior measurements: Zreda-Gostynska (1997): chemical traps, Oppenheimer (2008): Open-path MIR-FTIR,
Boichu (2011): Max-DOAS BrO, NO₂, O₃



Erebus measurements:

- MIR-FTIR system located AHTS. NDACC filters.
- Sun path (day arc) skims the top of Erebus twice a year:
~3rd - 5th April & 6th – 9th September. SZA ~ 84.5, 1130-1215NZST
- Opportunistic (serendipitous?) measurements:
 - Good weather
 - Degassing plume
 - AntNZ tech available to take measurements (among other duties)
- Since 1996, only 7 days, limited filter sets.
- Spectra acquisition time per filter ~ 2mins

Date	Instrument	Res (cm ⁻¹)	Filter set (Lauder ID)
7 th Sept 1996	Bomem DA2	0.02	'3' Non-NDACC
9 th Sept 2001	120M	0.0035	2,3
6 th Sept 2003	120M	0.007	2,3,4,5
5 th April 2009	120M	0.0035	2,3,4,5
5 th April 2018	125HR	0.0035	2,3,4,5,8,A
3 rd April 2019	125HR	0.0035	2,3
5 th April 2019	125HR	0.0035	2,3

20190403



Not the first time....:

GEOPHYSICAL RESEARCH LETTERS, VOL. 25, NO.13, PAGES 2421-2424, JULY 1, 1998

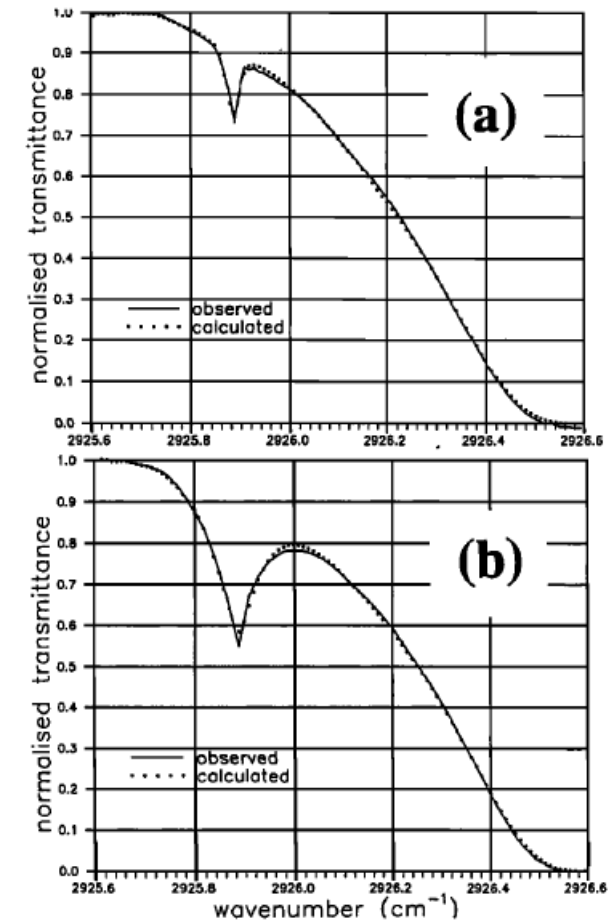
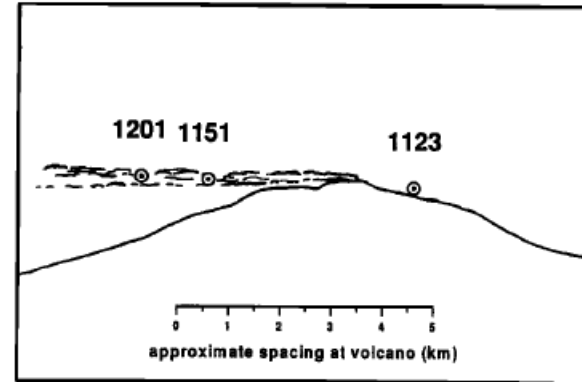
Spectral measurements of HCl in the plume of the Antarctic volcano Mount Erebus

J.G. Keys, S.W. Wood and N.B. Jones

National Institute of Water and Atmospheric Research, Lauder, Central Otago, New Zealand

F.J. Murcray

Physics Department, University of Denver, Colorado



Only other hi-res volcanic plume measurements....:

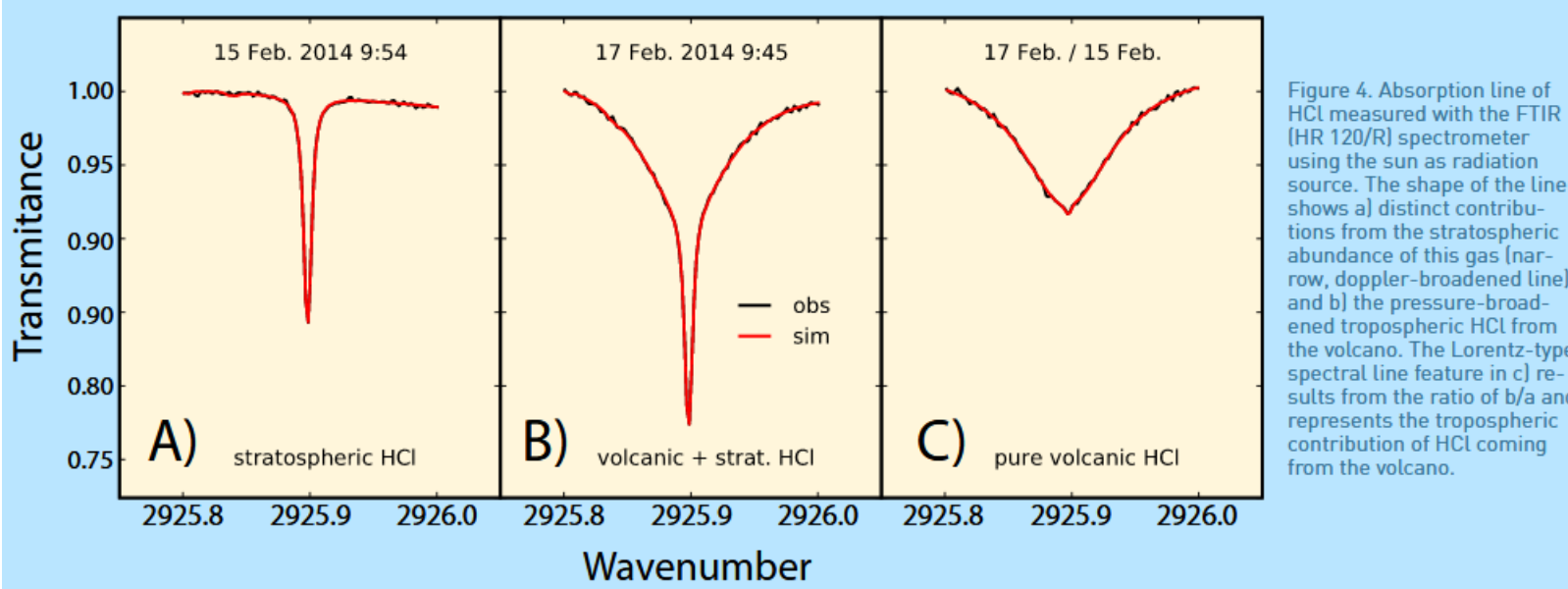


Figure 4. Absorption line of HCl measured with the FTIR (HR 120/R) spectrometer using the sun as radiation source. The shape of the line shows a) distinct contributions from the stratospheric abundance of this gas (narrow, doppler-broadened line) and b) the pressure-broadened tropospheric HCl from the volcano. The Lorentz-type spectral line feature in c) results from the ratio of b/a and represents the tropospheric contribution of HCl coming from the volcano.

.....and fresh off the press, thanks Wolfgang!.....:



1

Variability in the gas composition of the Popocatépetl volcanic plume

Noemie Taquet^{1,*}, Wolfgang Stremme¹, Michel Grutter¹, Jorge Baylón¹,
Alejandro Bezanilla¹, Benedetto Schiavo¹, Claudia Rivera^{1,2}, Robin
Campion³, Thomas Boulesteix⁴, Amiel Nieto-Torres⁵, Ramón
Espinasa-Pereña⁵, Thomas Blumenstock⁶, Frank Hase⁶

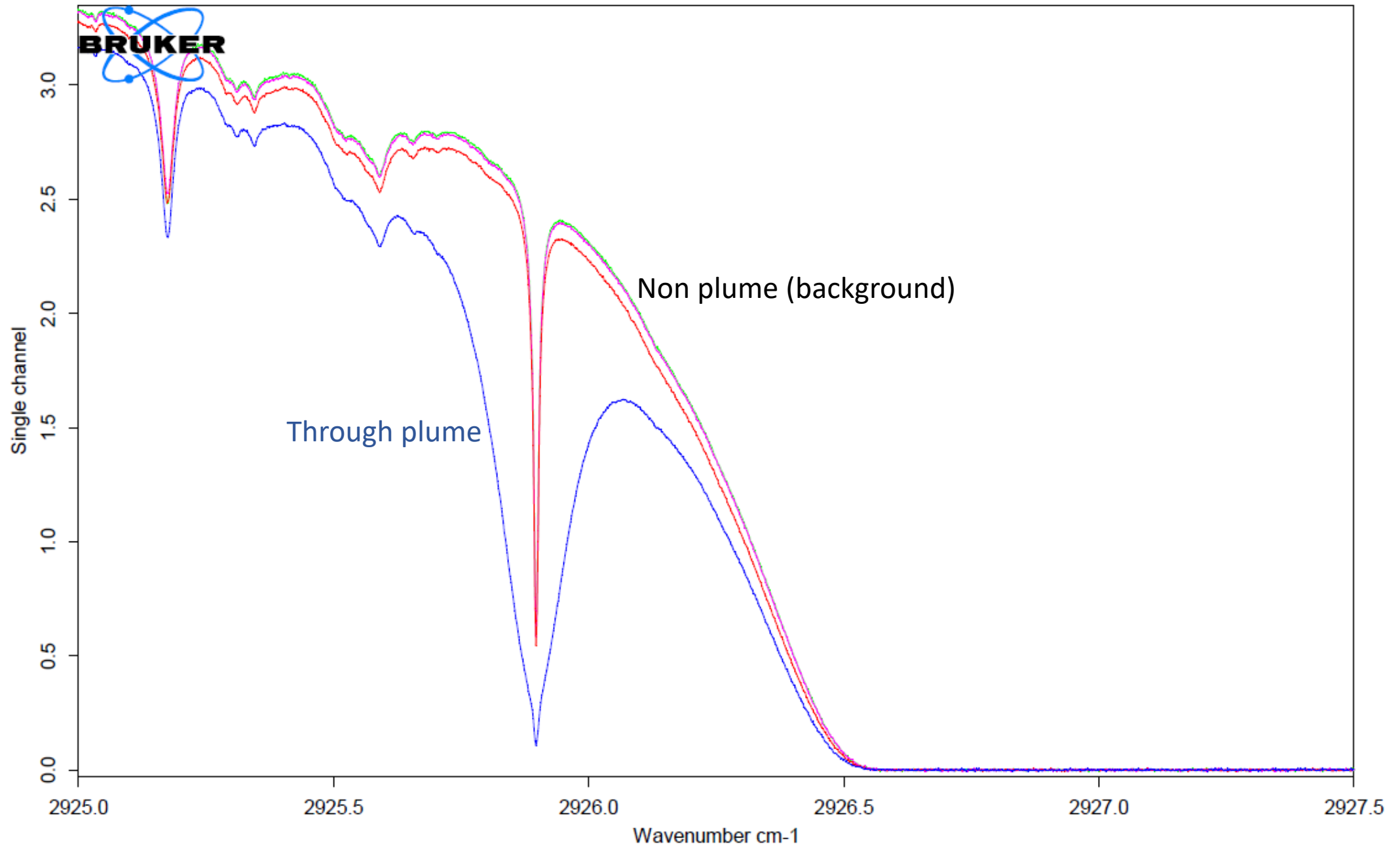
Table 1. Filters, detectors and spectroscopic parameters used for the analysis of SO₂, HCl, HF, SiF₄, and HBr in the Popocatépetl plume from solar absorption measurements (LN2 = liquid nitrogen cooled).

Gas	Filter	Detector	Resolution (cm ⁻¹)	Spectral ranges (cm ⁻¹)
SO ₂	3 & 4	InSb(LN2,DC)	0.1 & 0.005	2480-2520
SO ₂	6	MCT(LN2,AC/DC)	0.1 & 0.005	1080-1250
HCl	3	InSb(LN2,DC)	0.1 & 0.005	2727.0-2728.5; 2775.0-2776.50; 2818.75-2820.35; 2820.75-2822.35; 2843.0-2844.4; 2903.35-2904.85; 2923.0-2924.50; 2925.0-2926.75; 2942.0-2943.5; 2960.3-2961.825; 2962.3-2964.0; 2995.0-2996.5
HCl	Open	InGaAs	0.02	5738.0-5740.0; 5767.0-5767.8; 5779.2-5779.9
HF	1, Open	InGaAs	0.1, 0.0075 & 0.02	3999.0-4003.5; 4036.5-4041.0
SiF ₄	6	MCT(LN2,AC/DC)	0.1	1020.0-1040.0
HBr	3 & 4	InSb(LN2,DC)	0.005	2412.0-2413.75; 2432.0-2433.0; 2451.25-2453.00; 2488.0-2491.0; 2505-2510; 2541.0-2542.75; 2574.0-2576.0; 2589.95-2591.5; 2619.5-2623.0; 2634-2636.5; 2661.5-2664; 2673.9-2676.15; 2686.33-2688.05; 2697.4-2700.0; 2709.6-2710.7

What to do with these measurements?:

- We have 7 days over 20 years...some may say a sparse dataset...So what can we do?
- A test for SFIT4 profile retrievals, can we construct a robust retrieval strategy? Should be able to.
 - Stremme, 2001 (Earth and Planetary Science Letters 301 (2011) 502–510)
used SFIT2 _v394 to analyse low res (0.5cm^{-1}) volcanic plume spectra. Column retrievals of HF, HCl, SiF₄ and SO₂
 - Taquet, 2019,, res =@ 0.02 (HF, HCl), 0.1 cm⁻¹ (SO₂, SiF₄), PROFFIT, v9.6 Column, not profile?
 - Keys, 1996 (GRL), SFIT1, HCl profile scaling.
With the Hi-res spectra can we perform profile retrievals, (instead of apriori profile scaling)?
- If retrievals are successful what can we do?
 - Emission estimates? No. Not sufficient plume or meteorological data to infer any emission rates
 - Species ratios: Yes. A good use. Large number of species absorption features in Hi-res spectra.
- Initially concentrate on HCl and HF: easy targets
 - Prior measurements have detected HCl and HF in the plume
 - Erebus a rich source of halogens
 - Back ground amounts in stratosphere, not common in the troposphere.

What spectra looks like: HCl: 20180405 spectra



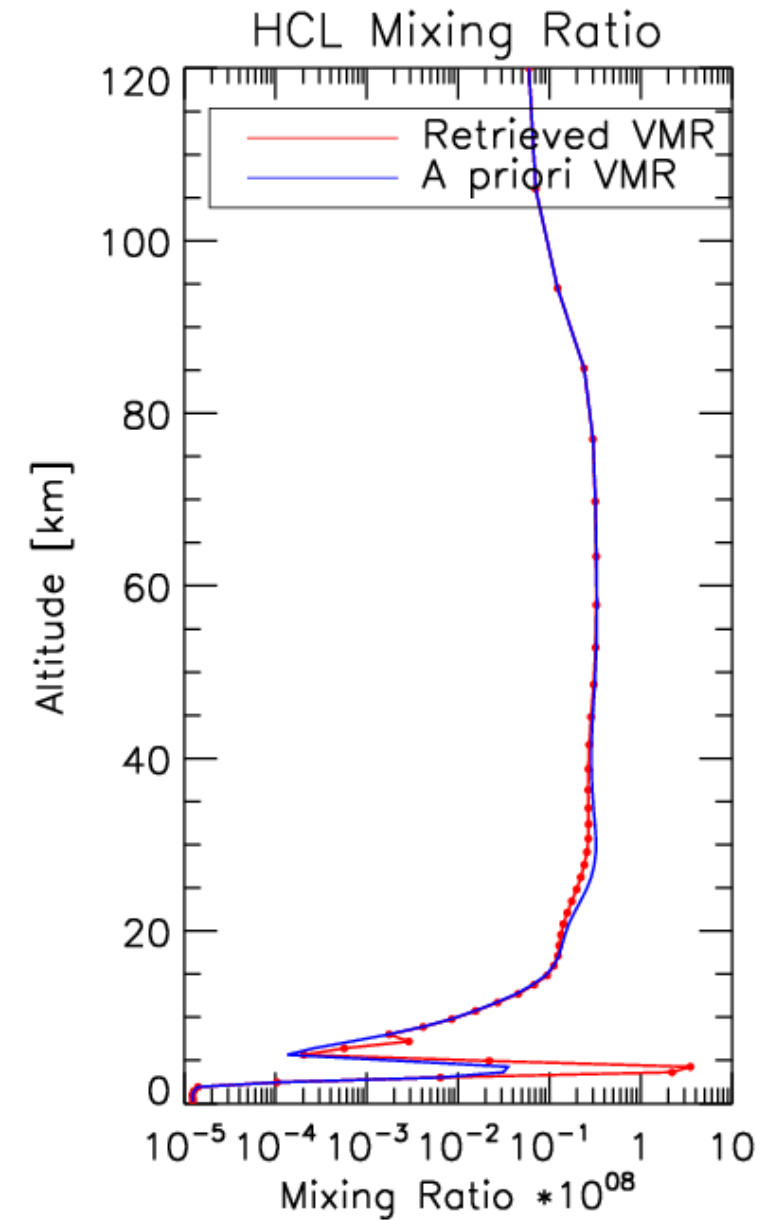
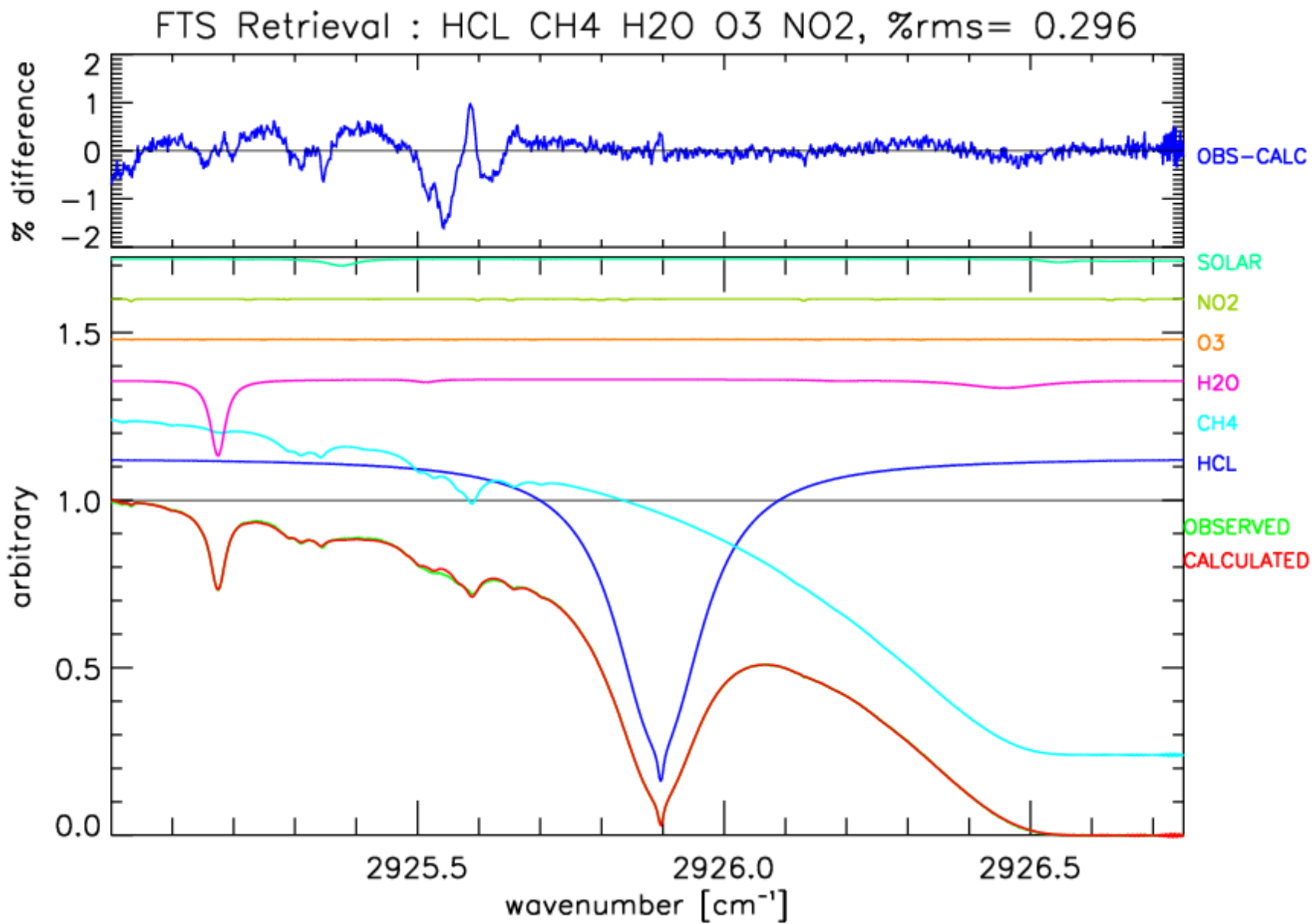
Analysis steps:

- Start with NDACC retrieval strategy as a base.
- NDACC IRWG AHTS station layer used (48 layers 0.2-120km). No need to adapt.
- Expand a single MW. Only single MW required (due to high spectral resolution)
- Two step analysis:
 - Fit background
 - Fit plume spectra (Using background fit as apriori for interfering species and basis for main species)
- Apriori increase (guess) @ lower levels 4-5, 100x-1000x @ 3km, 4km (consistent with Erebus height)
 - (underestimate plume apriori, over estimating leads to retrieval oscillations, as Sa too high)
- Sa Levels 7-12 increased (2.4-4km)
- SNR: spectra specific. ~200-400

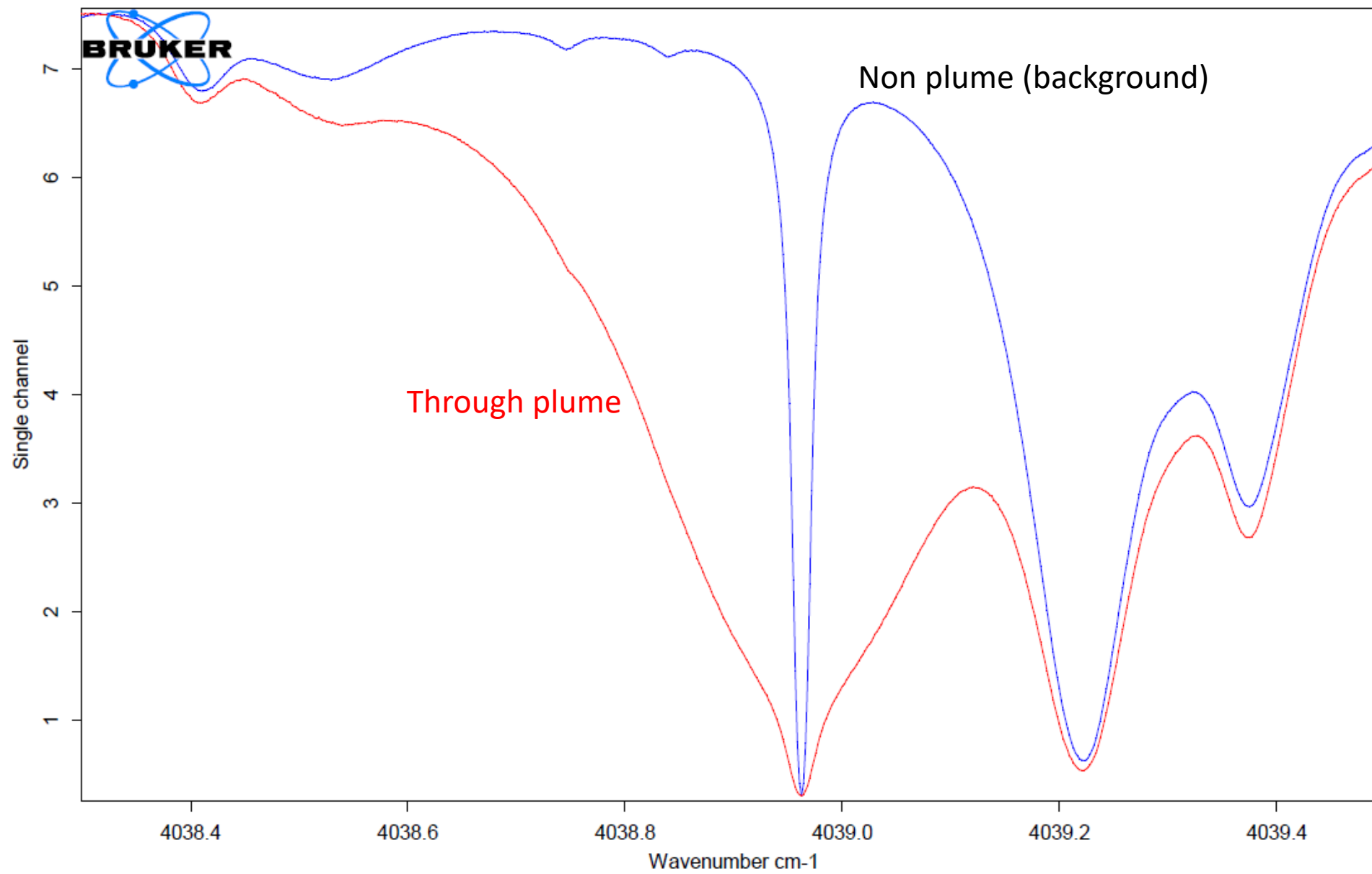
Robust: Same recipe used in all cases, just minor tweaks required. Retrieved profile enhancements at correct height.

gas.profile.HCL.sigma	=	15 HCL	Retrieved amount from state vector:				
0.1 0.1 0.1 0.1 0.1		5.36E-10,	7.53E-10,	9.81E-10,	1.76E-09,	2.50E-09,	
0.1 0.1 0.1 0.1 0.1		2.92E-09,	3.12E-09,	3.21E-09,	3.28E-09,	3.31E-09,	
0.1 0.1 0.1 0.1 0.1		3.26E-09,	3.20E-09,	3.12E-09,	3.01E-09,	2.93E-09,	
0.1 0.1 0.1 0.1 0.1		2.88E-09,	2.88E-09,	2.91E-09,	2.99E-09,	3.12E-09,	
0.1 0.1 0.1 0.1 0.1		3.24E-09,	3.22E-09,	2.99E-09,	2.53E-09,	1.99E-09,	
0.1 0.1 0.1 0.1 0.1		1.59E-09,	1.39E-09,	1.23E-09,	8.70E-10,	4.06E-10,	
0.1 0.1 0.1 0.1 0.1		1.31E-10,	6.66E-11,	2.68E-11,	8.52E-12,	2.41E-12,	
0.1 5.0 5.0 5.0 5.0		1.01E-12,	4.73E-10,	2.58E-10,	1.53E-13,	1.22E-13,	
5.0 5.0 0.01 0.01 0.01		1.27E-13,					
0.01 0.01 0.01							

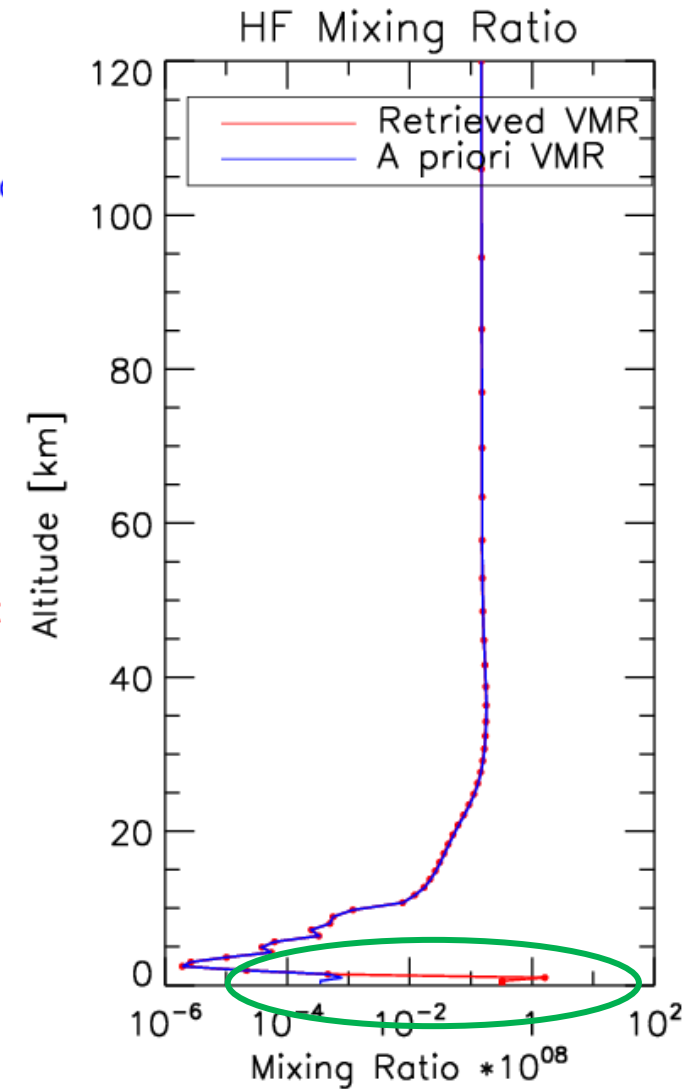
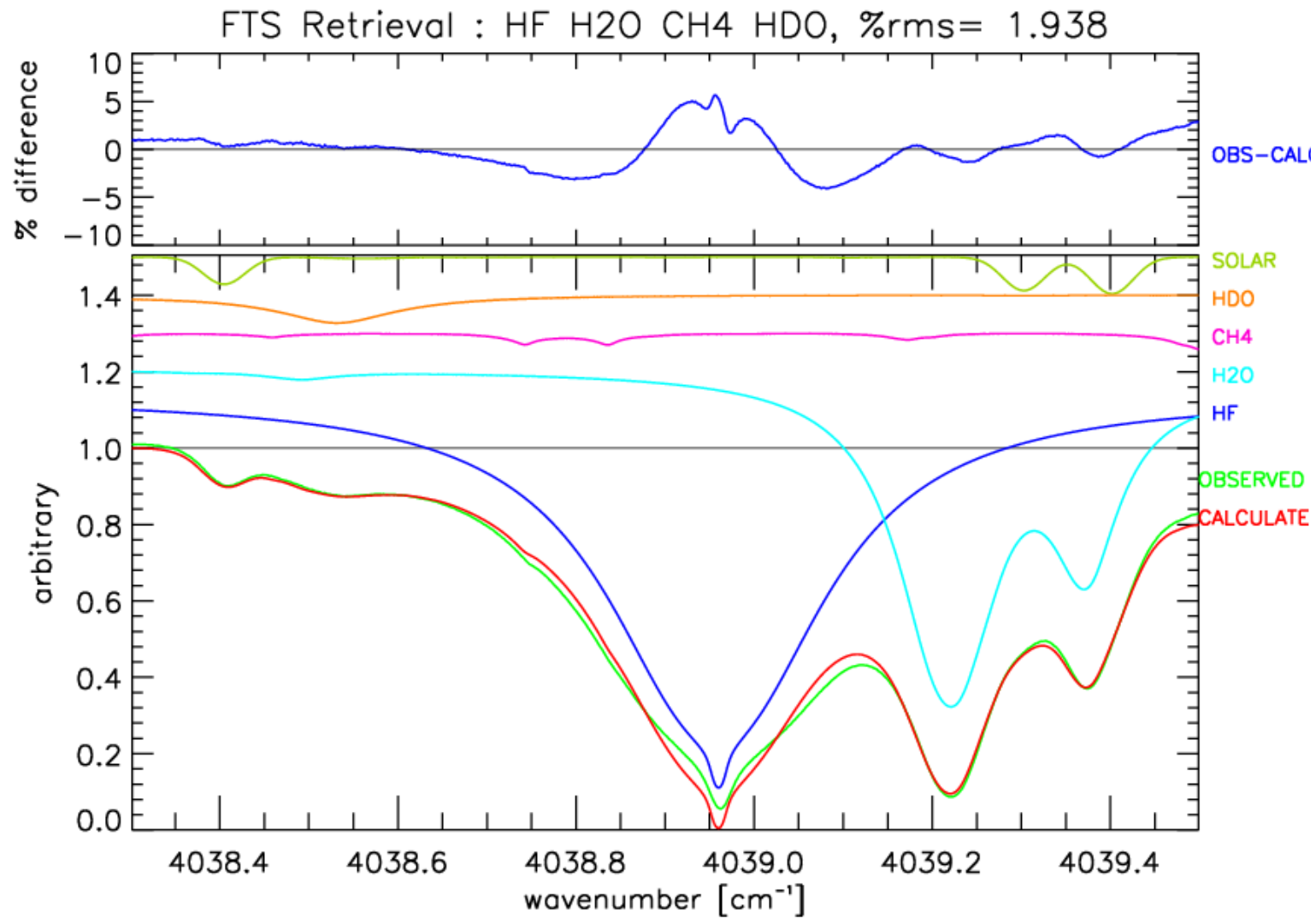
Example: HCL: 20180405 analysis. SFIT4_v0944



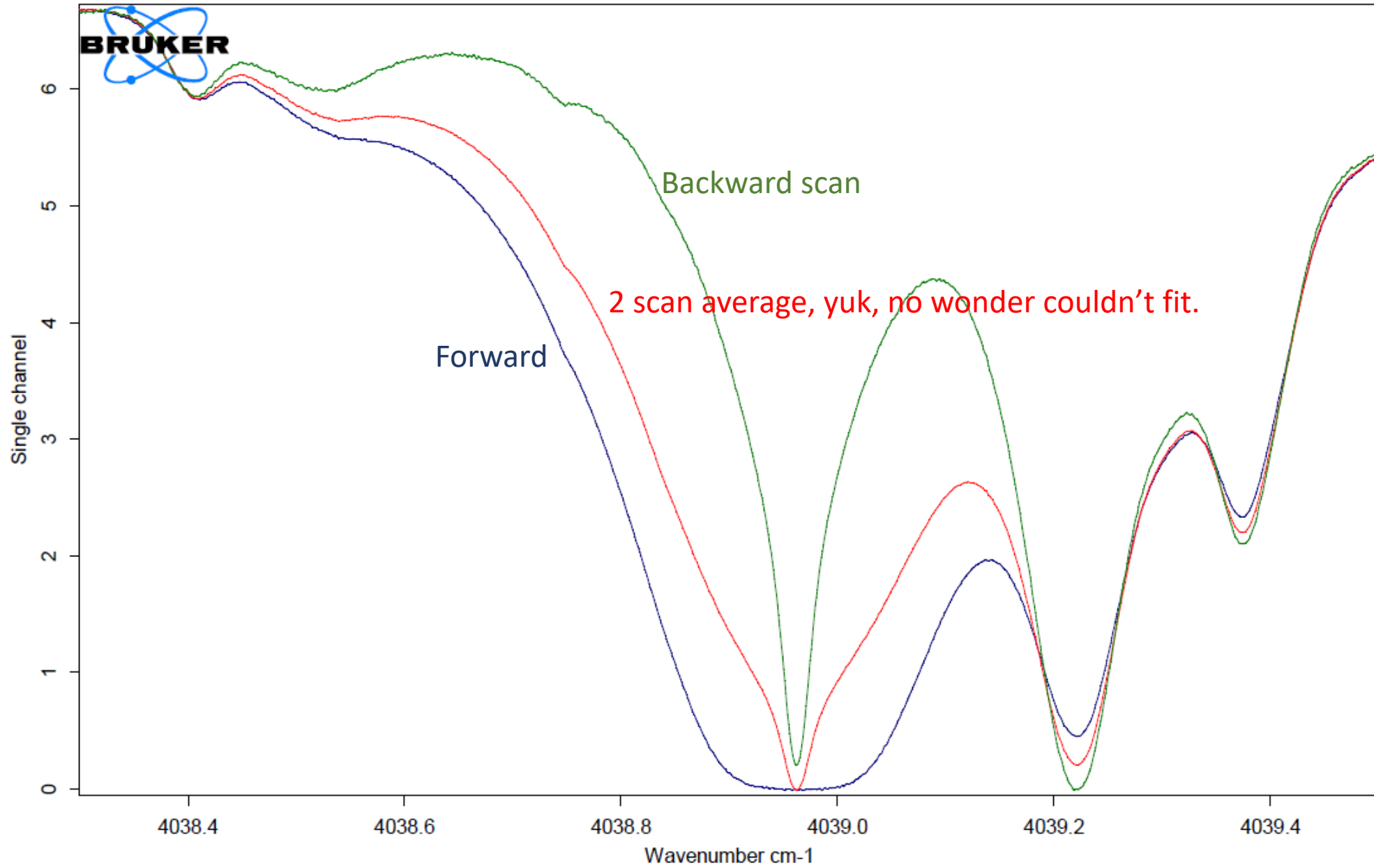
An interesting example: HF: 20180405



20180405: HF Bad fit. Spectra = 2 scan average...

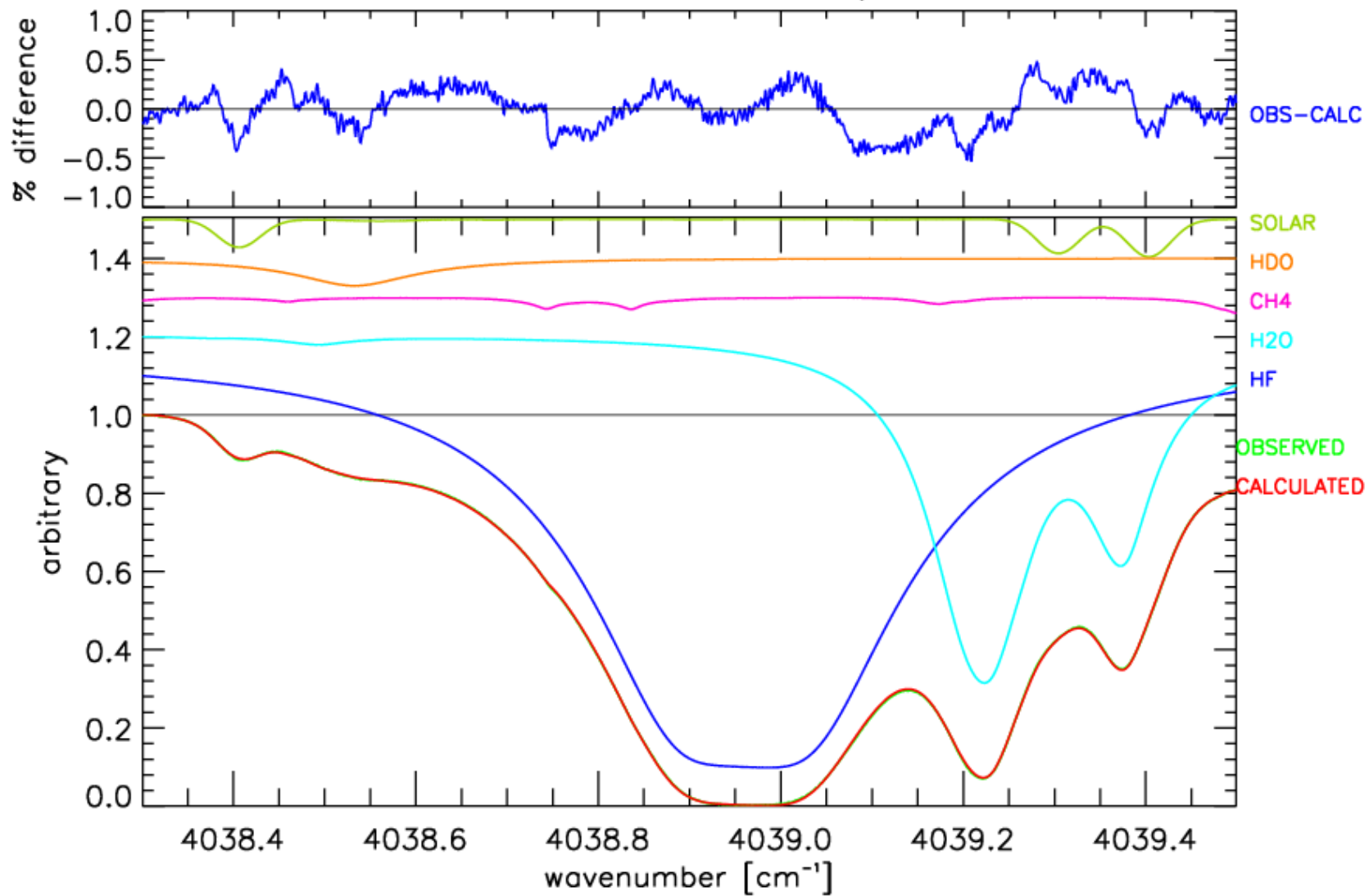


Enhancement altitude too low

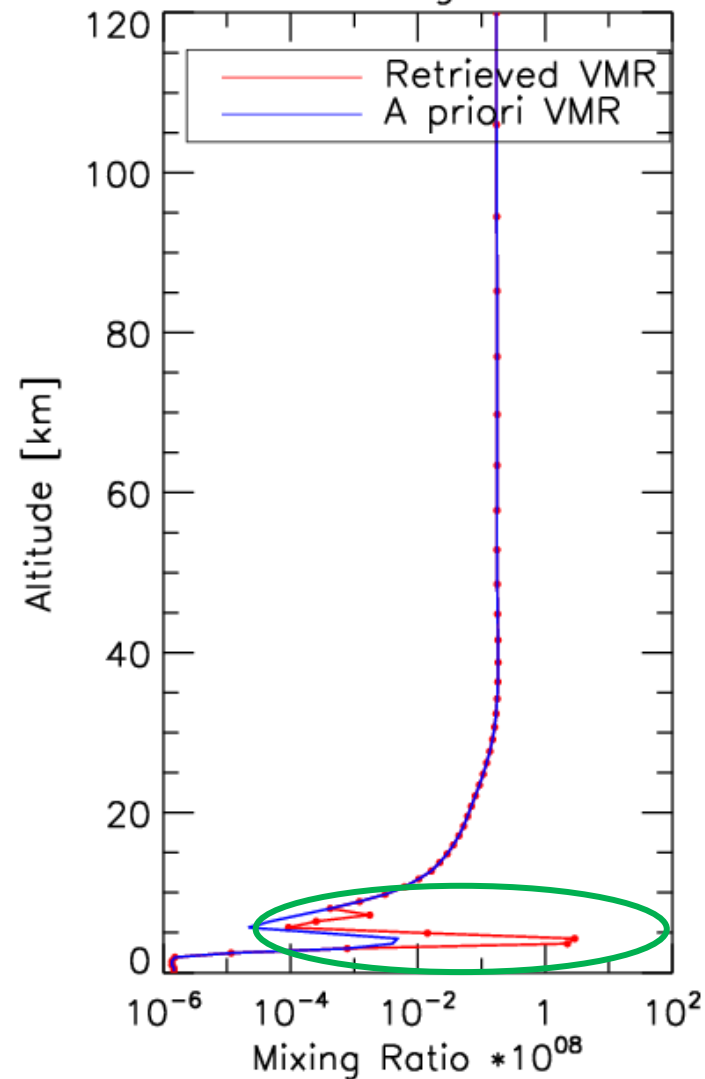


HF 20180405 Forward scan only. Good fit.

FTS Retrieval : HF H2O CH4 HDO, %rms= 0.207



HF Mixing Ratio



Enhancement at correct altitude

Uncertainty analysis:

Using SFIT4 output. Standard error analysis

Same Sb's as in NDACC retrievals except:

temp.random: additional 10K in 2-4km range (guess)

Example: Uncertainties sources (HCl: 20190405, SNR=400) (%):

Smeas= 0.075

Ssmooth= 0.100

Sint1 (retrieval params)= 0.001

Sint2 (intf. spec.)= 0.323

Stemp_sys= 0.227

Stemp_rand= 12.908

SSZA(%)= 0.398

SZeroLev_1(%)= 1.959

SLineInt_HCL(%)= 2.030

SLineTAir_HCL(%)= 0.035

SLinePAir_HCL(%)= 0.068

SEmpPhsFnc(%)= 0.001

SEmpApdFcn(%)= 0.008

Other species spectroscopic uncertainties <0.1%

Single Line:

SLineInt_HCL @ 0.0035cm⁻¹ ~2%

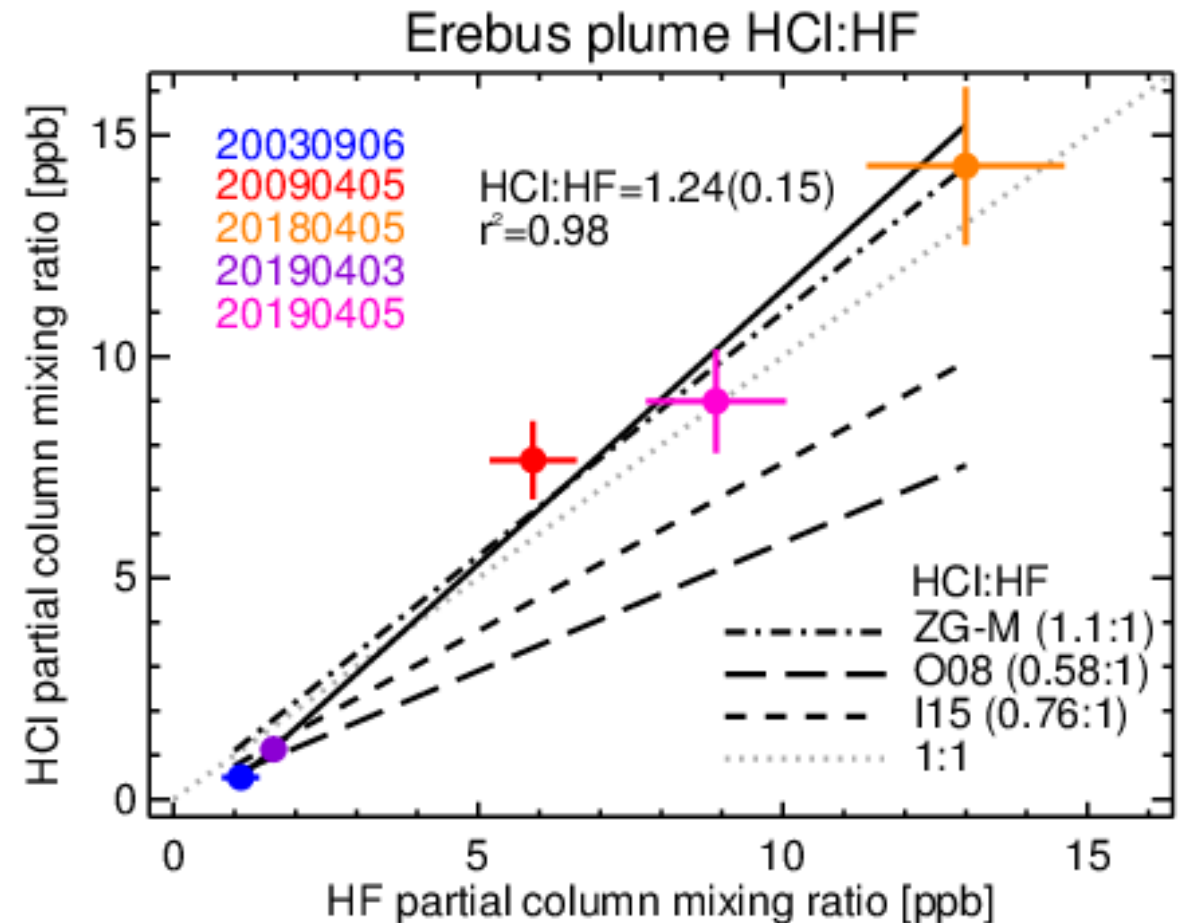
SLineInt_HCL @ 0.007cm⁻¹ ~8%

SLineInt_HCL @ 0.02cm⁻¹ ~40%

Low res: 0.5cm⁻¹ ?% (Multiple lines used in practice)

Results:

- Analysis of HCl and HF: 7 events in total.
Reanalysis of 1996 spectra from Keys
- Look at species ratios (HCl/HF): 5 events
Derived HCl:HF ratio comparable to prior studies.
- Not enough information for emission estimates



Summary:

- First Hi-res spectra of Erebus plume (single absorption line can be analysed)
- SFIT4 profile retrieval technique using a single MW is robust
- Confirmation of HCl:HF ratio in accordance with prior studies.
- Long term sporadic monitoring of Erebus plume composition (continue to take such measurements).
- Future work: retrieval of other species and isotopes:
 - CO₂, H₂O, CH₄, CO, OCS,
 - SO₂ (visually , very little), SiF₄ (visually none)
 - H³⁵Cl, H³⁷Cl
- Currently an opportunistic (serendipitous?) measurement.

Thank you.