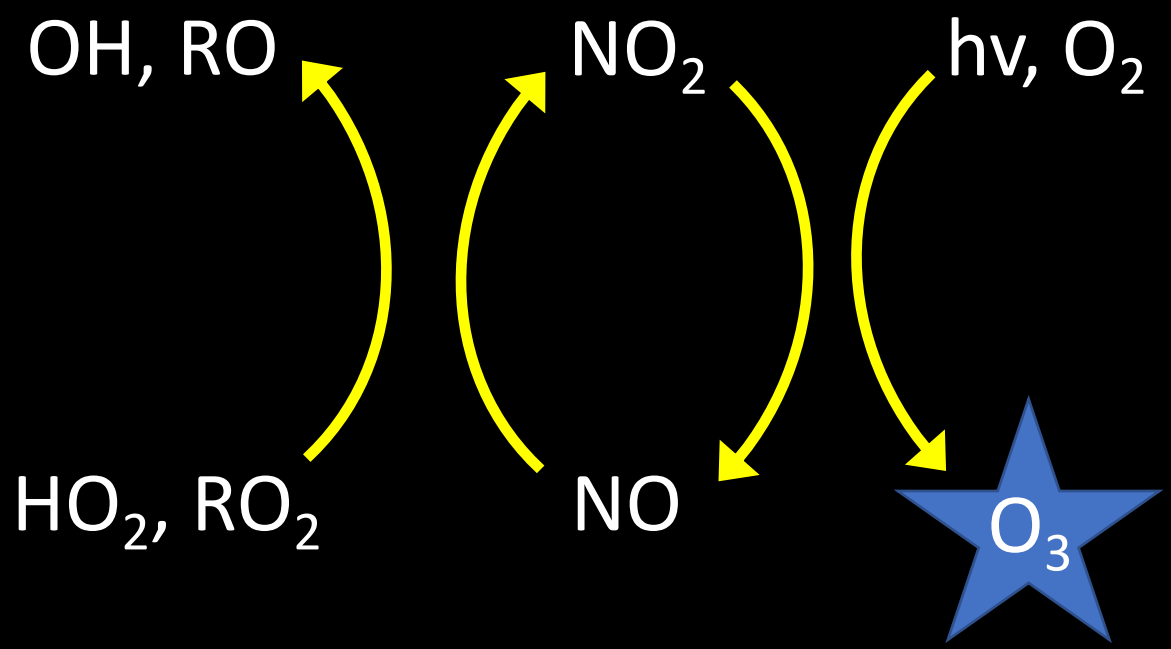
Single-Photon LIF: A new benchmark for measurements of atmospheric nitric oxide

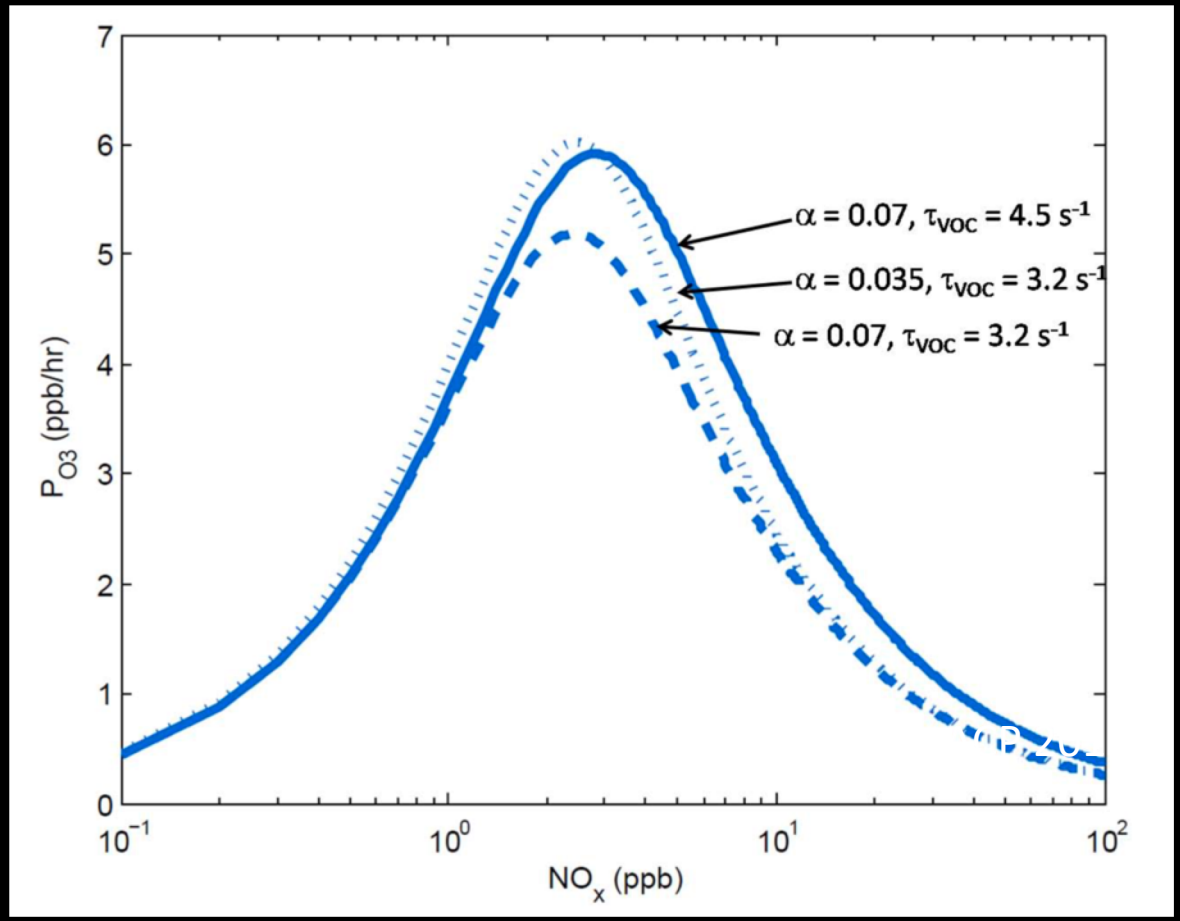
Andrew Rollins, NOAA/CSL

- New spectroscopic technique for measuring NO well suited for aircraft or monitoring applications
- Significantly lower uncertainties at NO < ~20 ppt compared to chemiluminescence
- Potential for real-time measurements of NO isotope ratios

NO: Central to tropospheric ozone production

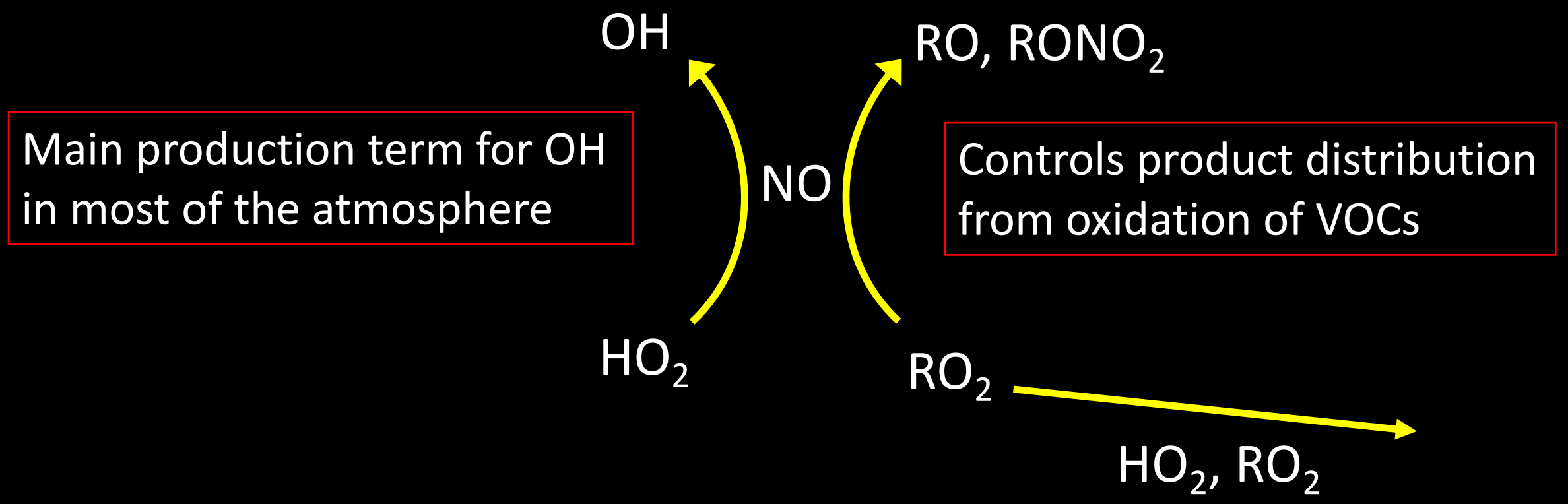


Air quality control strategies hinge on understanding O_3 production chemistry and sources of NO_x



Farmer et al, ACP 2011

NO: Central to OH production and VOC degradation



Need for measurements of very low NO

"The inter-model differences in tropospheric OH burden and vertical distributions are mainly determined by the differences in the nitrogen oxide (NO) distributions"

	NO pptv			
	750	500	250	Tp
CESM1-CAM4Chem	9	4	12	13
CESM1-WACCM	9	5	12	12
CMAM	17	4	17	26
EMAC-L47MA	8	4	11	14
EMAC-L90MA	8	5	11	17
GEOSCCM	9	5	13	13
MOCAGE	26	14	17	20
MRI-ESM1r1	10	5	20	32
SOCOL3	48	10	14	25

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https://doi.org/10.5194/acp-19-13701-2019

Atmosp
Chei
and Ph

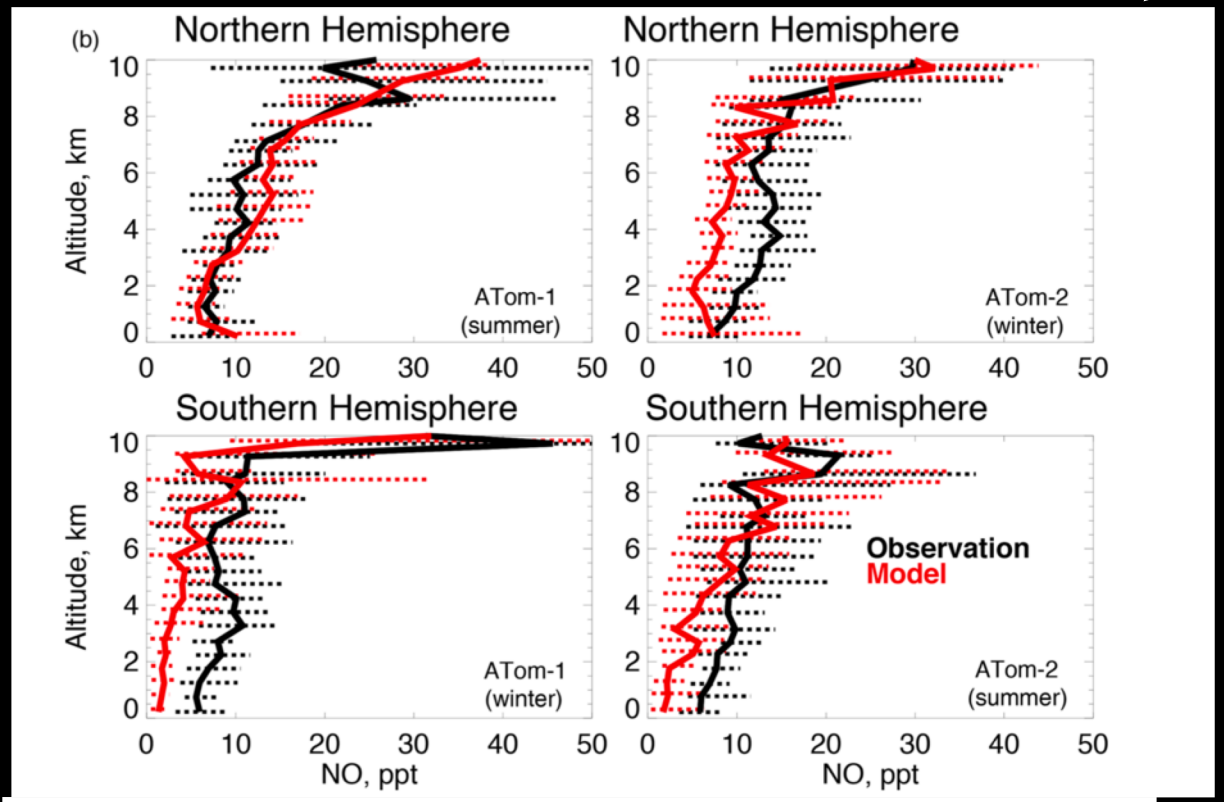
Inter-model comparison of global hydroxyl radical (OH) distributions and their impact on atmospheric methane over the 2000–2016 period

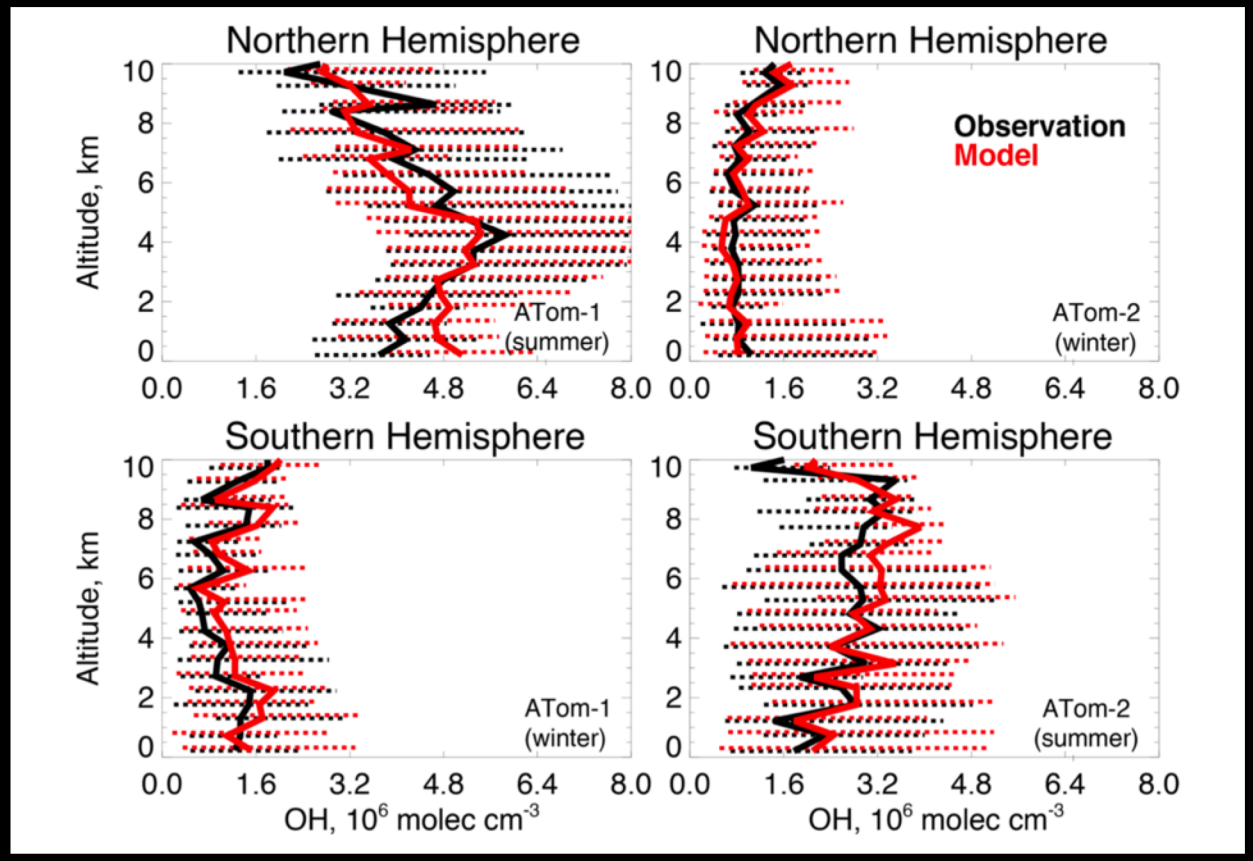
Yuanhong Zhao[1], Marielle Saunois[1], Philippe Bousquet[1], Xin Lin[1,a], Antoine Berchet[1], Michaela I. Hegglin[2], Josep G. Canadell[3], Robert B. Jackson[4], Didier A. Hauglustaine[1], Sophie Szopa[1], Ann R. Stavert[5], Nathan Luke Abraham[6,7], Alex T. Archibald[6,7], Slimane Bekki[8], Makoto Deushi[9], Patrick Jöckel[10], Béatrice Josse[11], Douglas Kinnison[12], Ole Kirner[13], Virginie Marécal[11], Fiona M. O'Connor[14], David A. Plummer[15], Laura E. Revell[16,17], Eugene Rozanov[16,18], Andrea Stenke[16], Sarah Strode[19,20], Simone Tilmes[12], Edward J. Dlugokencky[21], and Bo Zheng[1]

Need for measurements of very low NO

NO

OH





Atmos. Chem. Phys., 20, 7753–7781, 2020
https://doi.org/10.5194/acp-20-7753-2020

Atmospheric Chemistry and Physics
Open Access
EGU

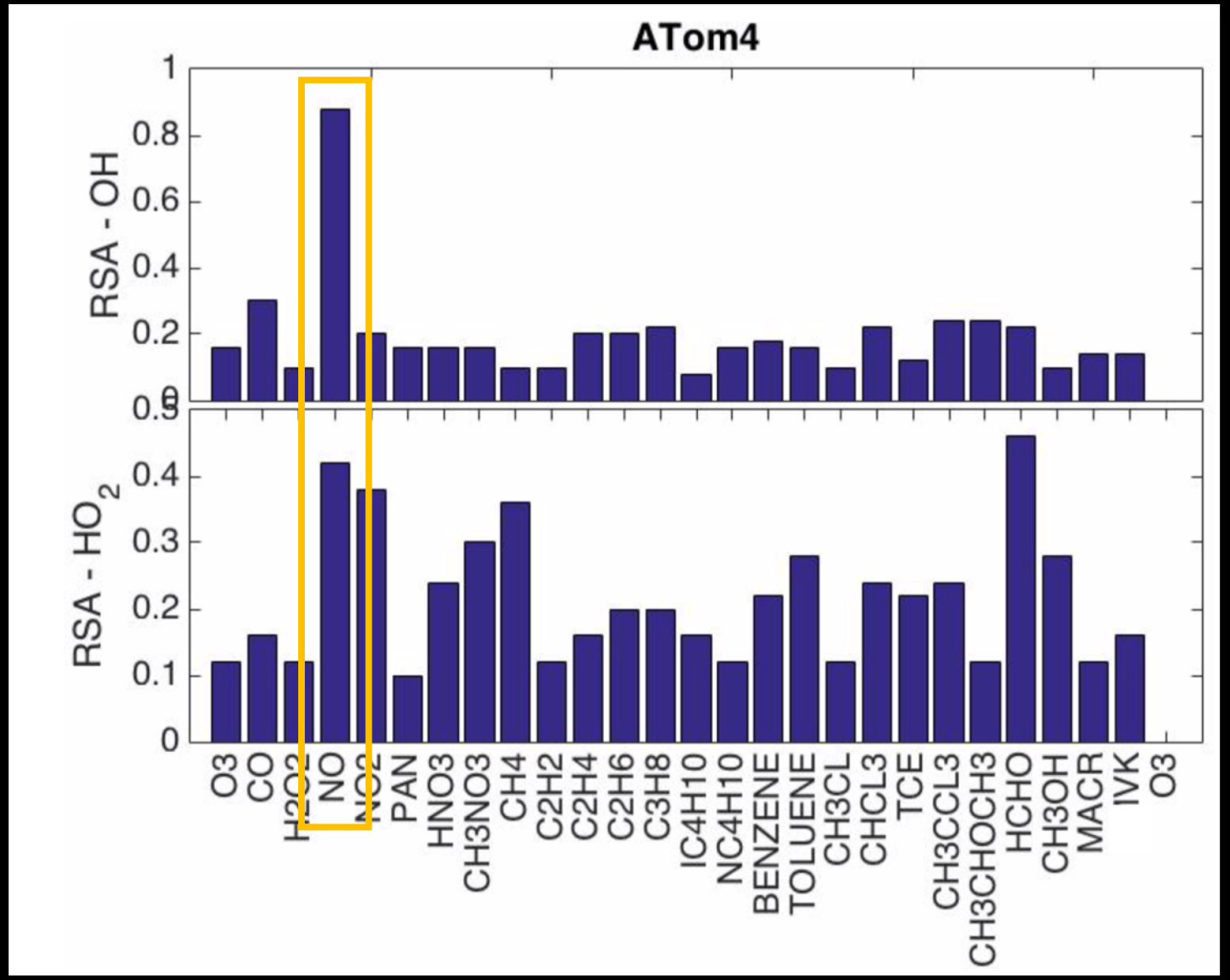
Constraining remote oxidation capacity with ATom observations

Katherine R. Travis[1,a], Colette L. Heald[1,2], Hannah M. Allen[3], Eric C. Apel[4], Stephen R. Arnold[5], Donald R. Blake[6], William H. Brune[7], Xin Chen[8], Róisín Commane[9], John D. Crounse[10], Bruce C. Daube[11], Glenn S. Diskin[12],

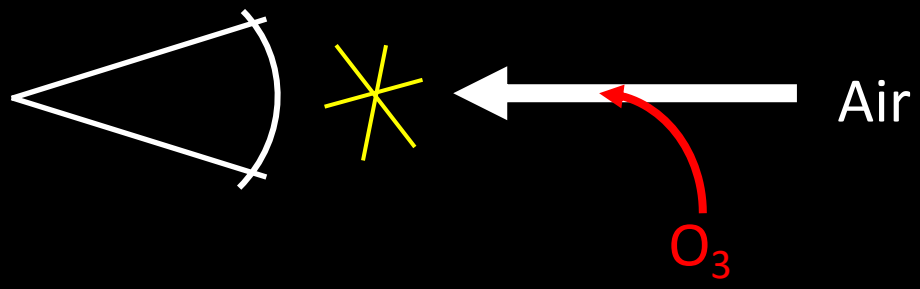
Need for measurements of very low NO

Figure from David Miller, Penn. State

Sensitivity of modeled OH to ATom measurement uncertainties



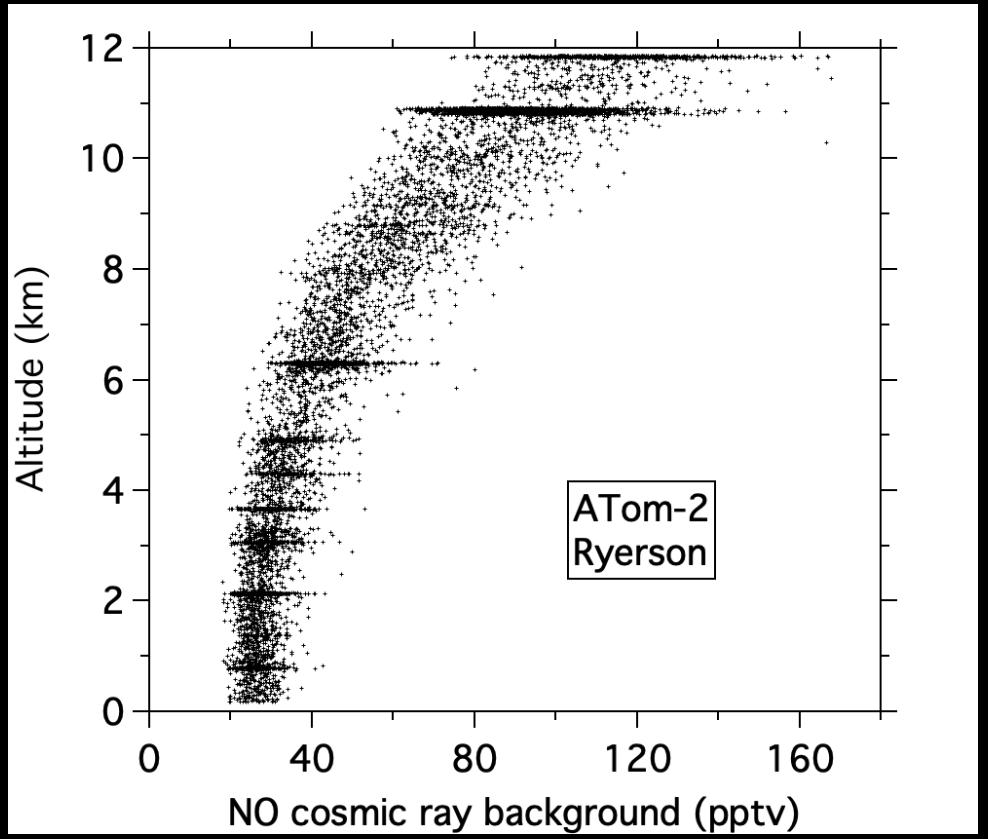
Chemiluminescence: Ridley et al 1972, 1974, …



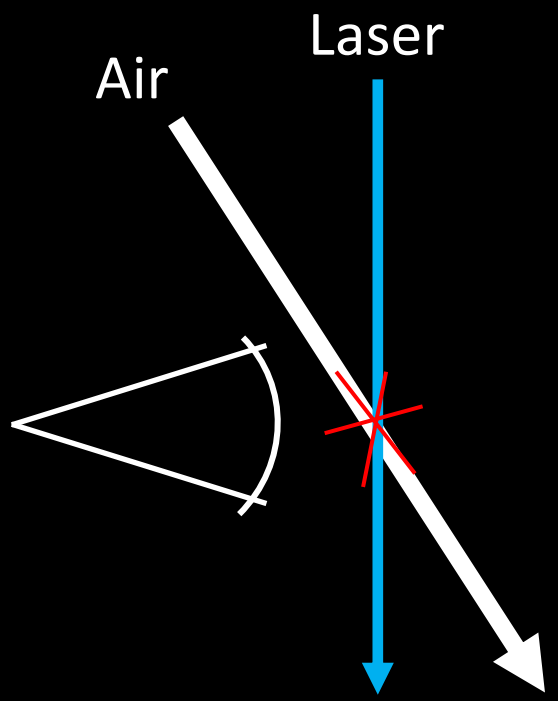
$NO + O_3 \rightarrow NO_2^*$

$NO_2^* \rightarrow NO_2 + h\nu$ ($\lambda > 650$ nm)

- Typical signal rates 5-10 cps / ppt
- Typical background 500-1000 cps
- Cosmic ray background varies with altitude and latitude
- O_3 related background decreases during operation



Laser Induced Fluorescence

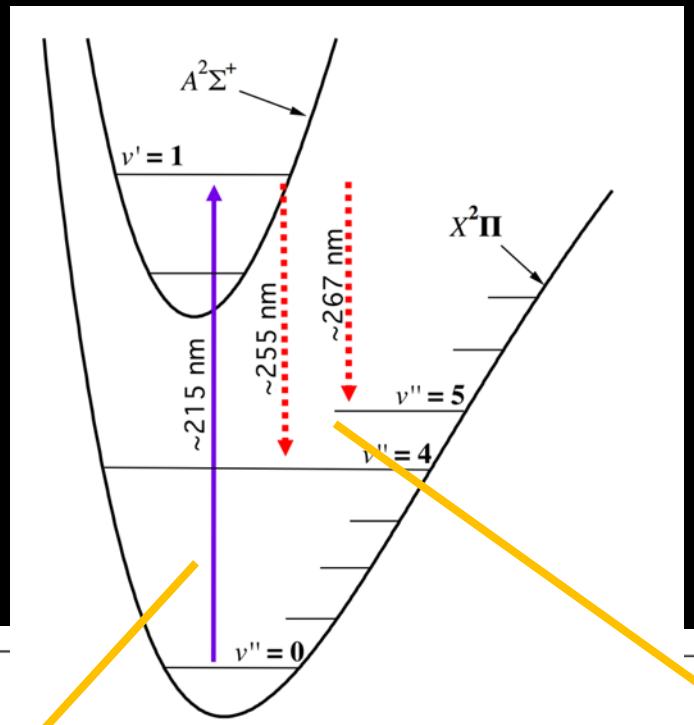


$NO + hv \rightarrow NO^*$

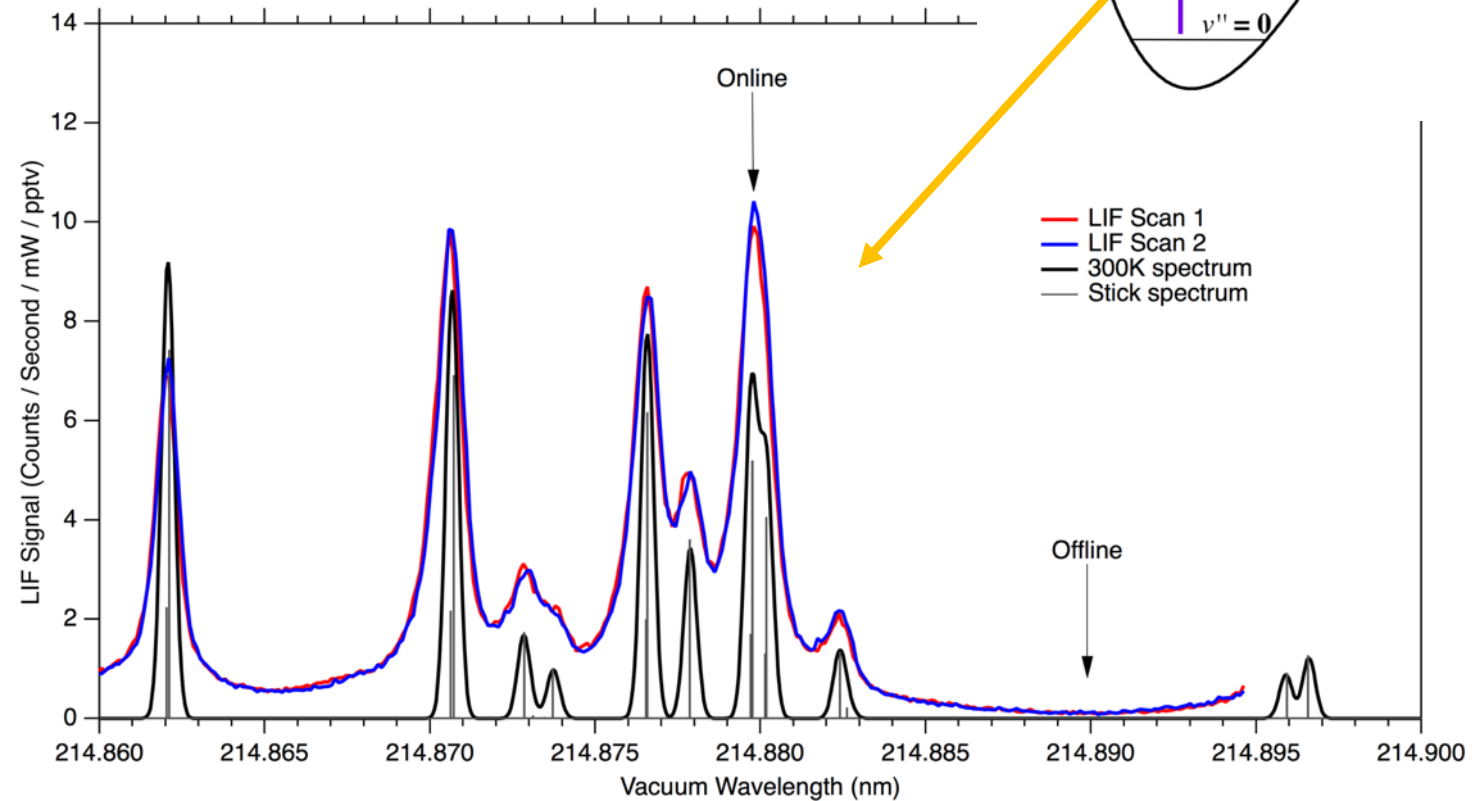
$NO^* \rightarrow NO + hv'$

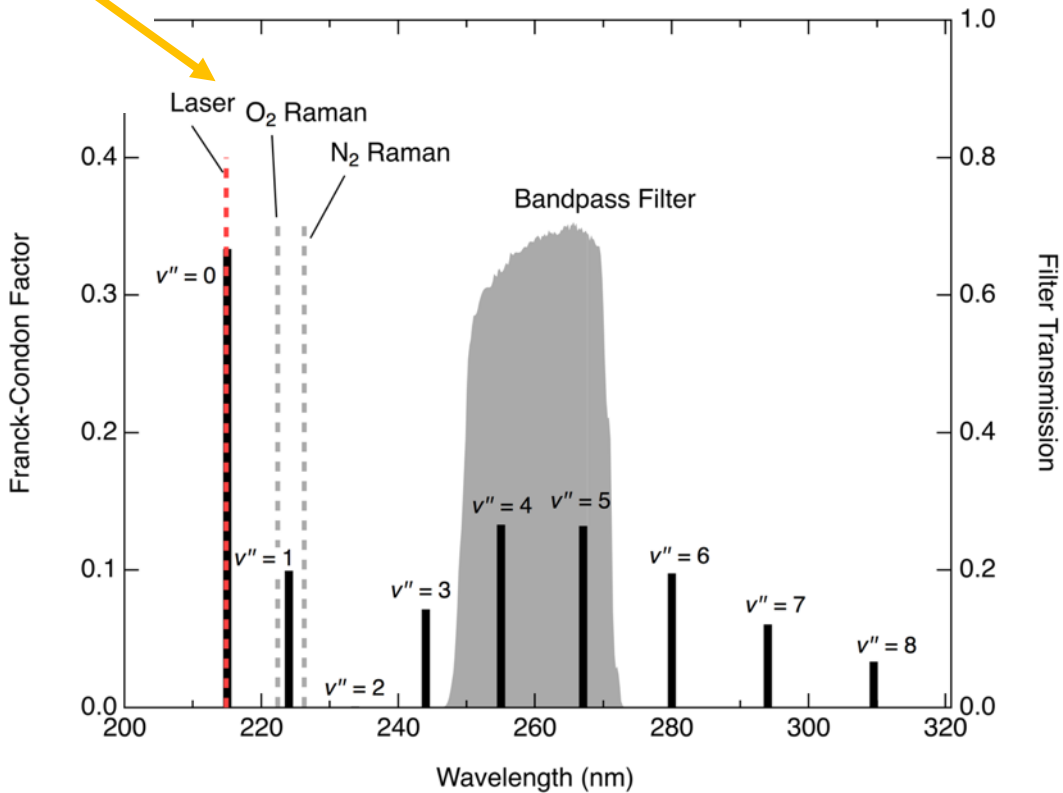
- Typical signal rate 10 cps / ppt
- Typical background 10 cps
- Background is low and relatively stable throughout operation

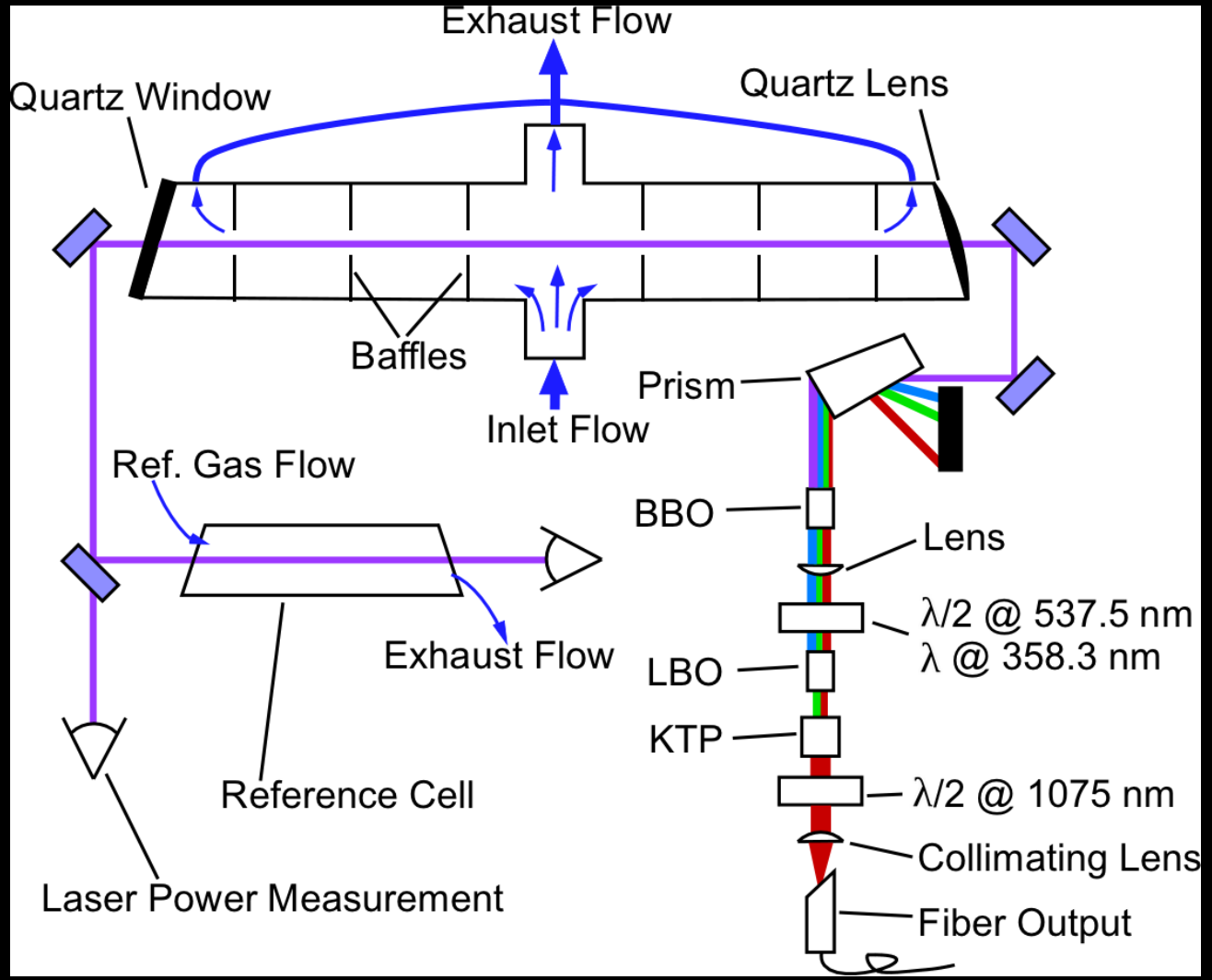
Laser Excitation

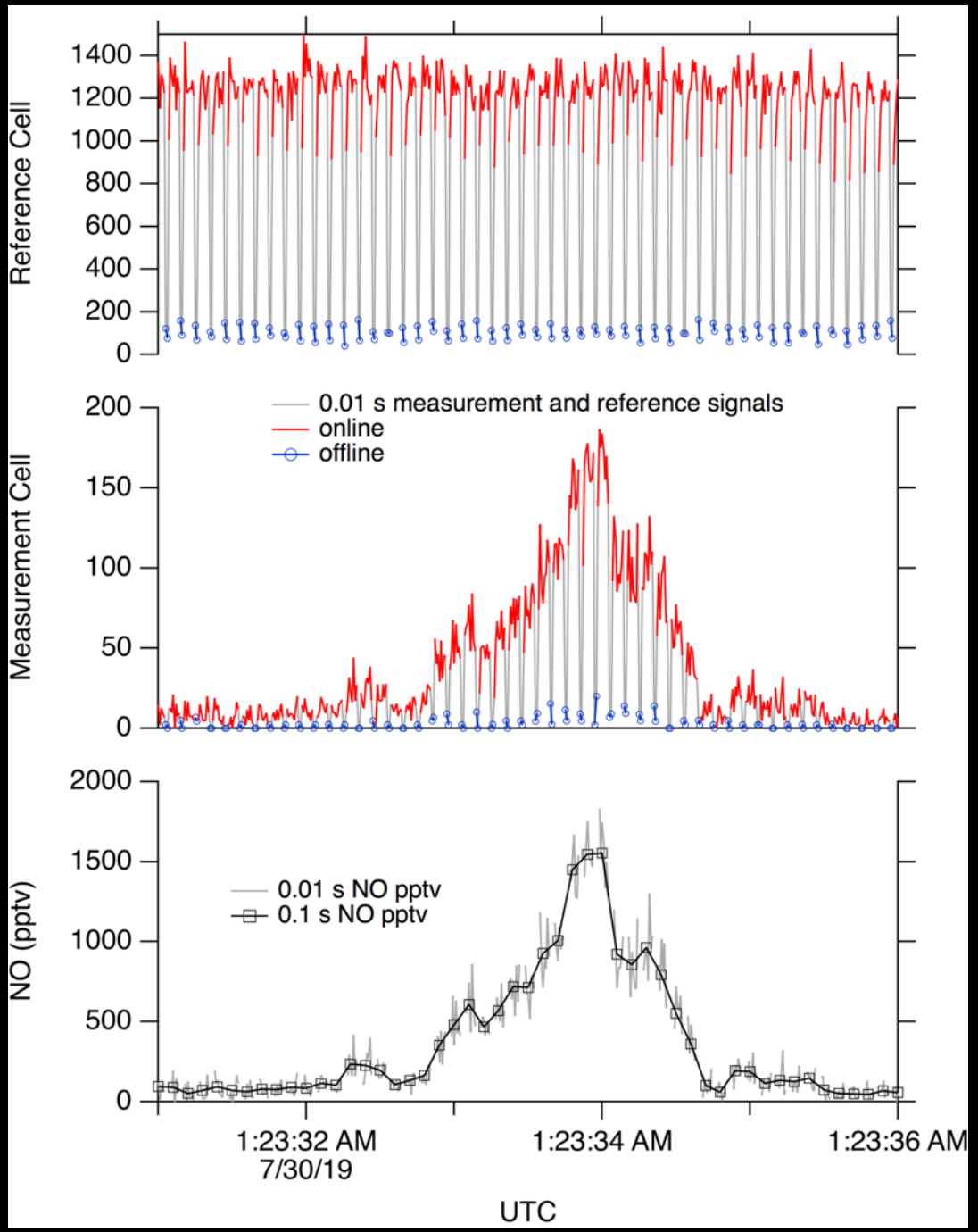


Fluorescence Detection



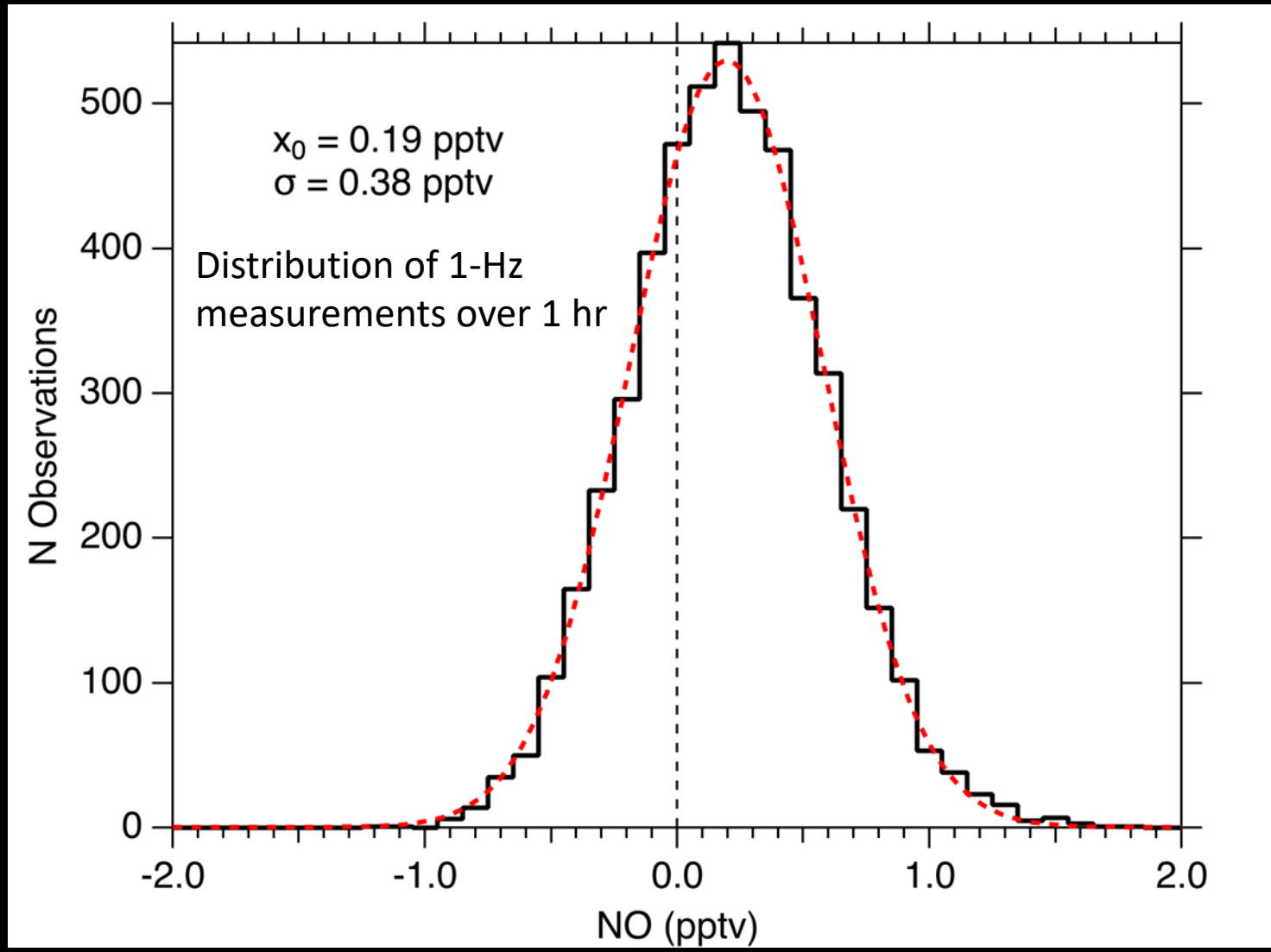



Exhaust Flow
Quartz Window
Quartz Lens
Baffles
Inlet Flow
Prism
Ref. Gas Flow
BBO
Lens
λ/2 @ 537.5 nm
λ @ 358.3 nm
Exhaust Flow
LBO
KTP
Reference Cell
λ/2 @ 1075 nm
Collimating Lens
Laser Power Measurement
Fiber Output


Reference Cell
1400
1200
1000
800
600
400
200
0
Measurement Cell
200
150
100
50
0
0.01 s measurement and reference signals
online
offline
NO (pptv)
2000
1500
1000
500
0
0.01 s NO pptv
0.1 s NO pptv
1:23:32 AM
7/30/19
1:23:34 AM
1:23:36 AM
UTC

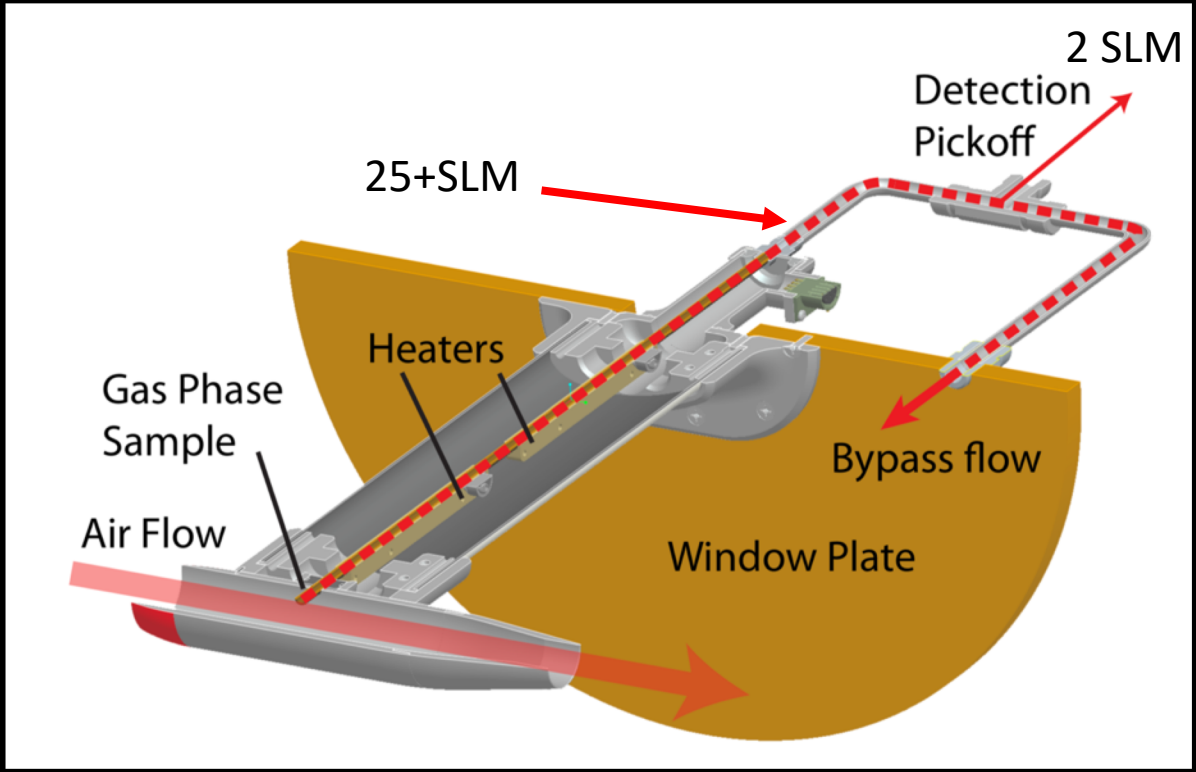
Detection limit / artifact test

- NO is calculated using online – offline without any other zero determination
- Laboratory measurements of chemically scrubbed ($KMnO_4$) zero air indicate sampling artifact is < 0.2 ppt.
- 2σ 1 Hz detection limit < 1 ppt



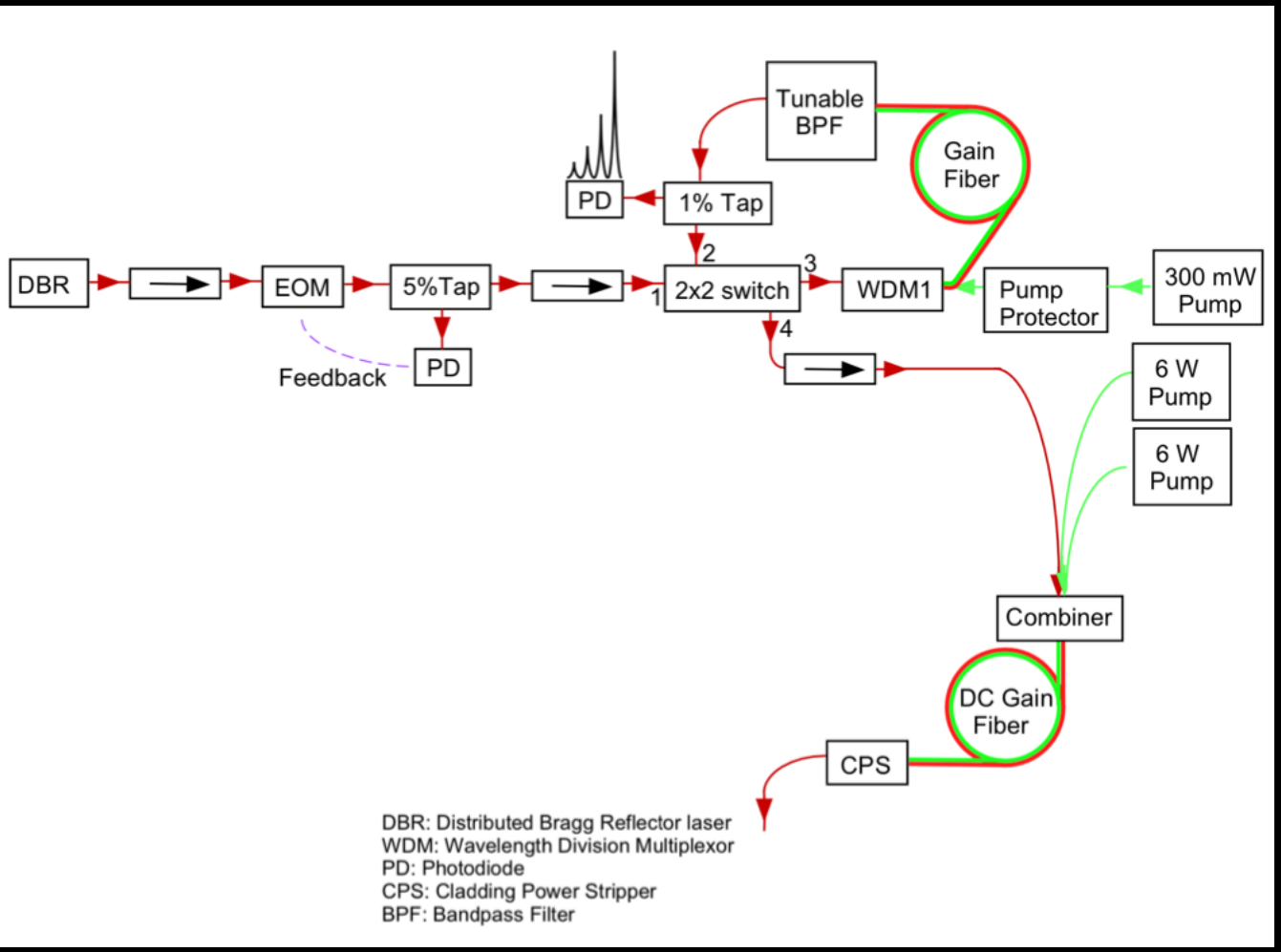
DC-8 rack installation of two-channel LIF instrument Deployed during FIREX-AQ, July/August 2019

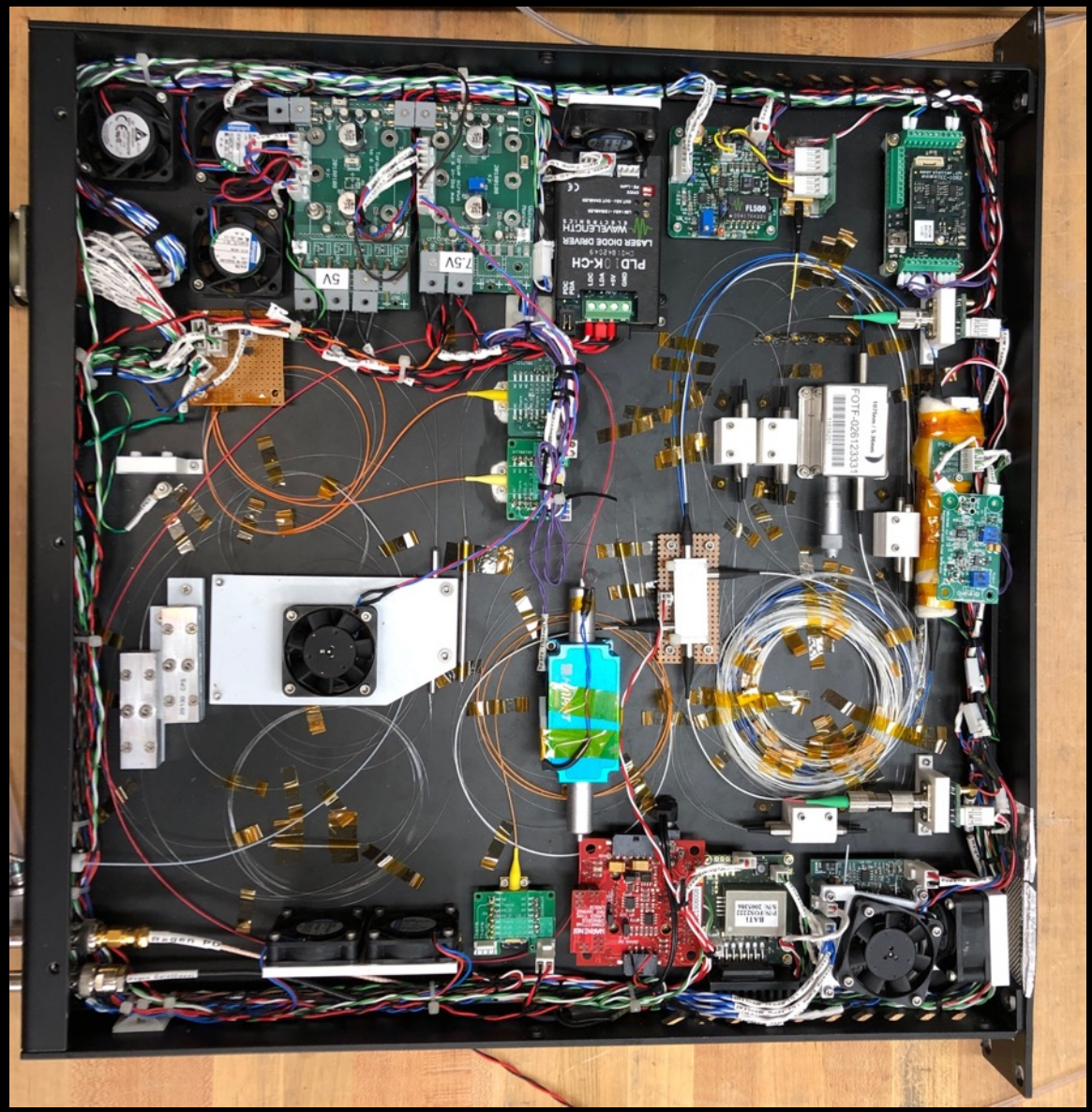
- ~20” vertical rack space
- 110 lbs
- 2-sigma detection limit for 1s integration is ~ 1 ppt
- Accuracy 6 – 10 % depending on humidity
- For FIREX, shared inlet with ISAF



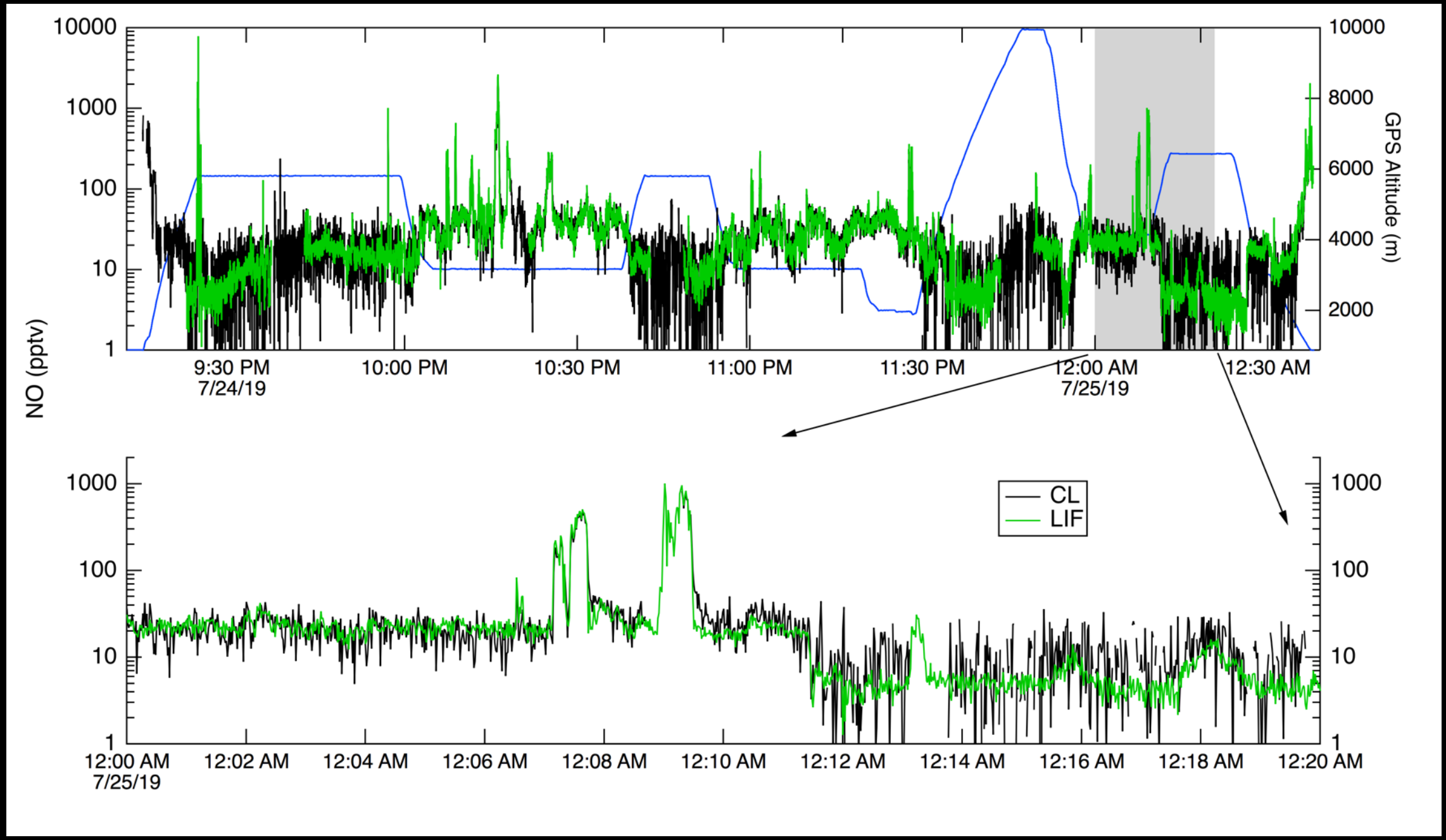
Fiber Laser system

Custom-built fiber laser system produces ~ 1 mW @ 215 nm

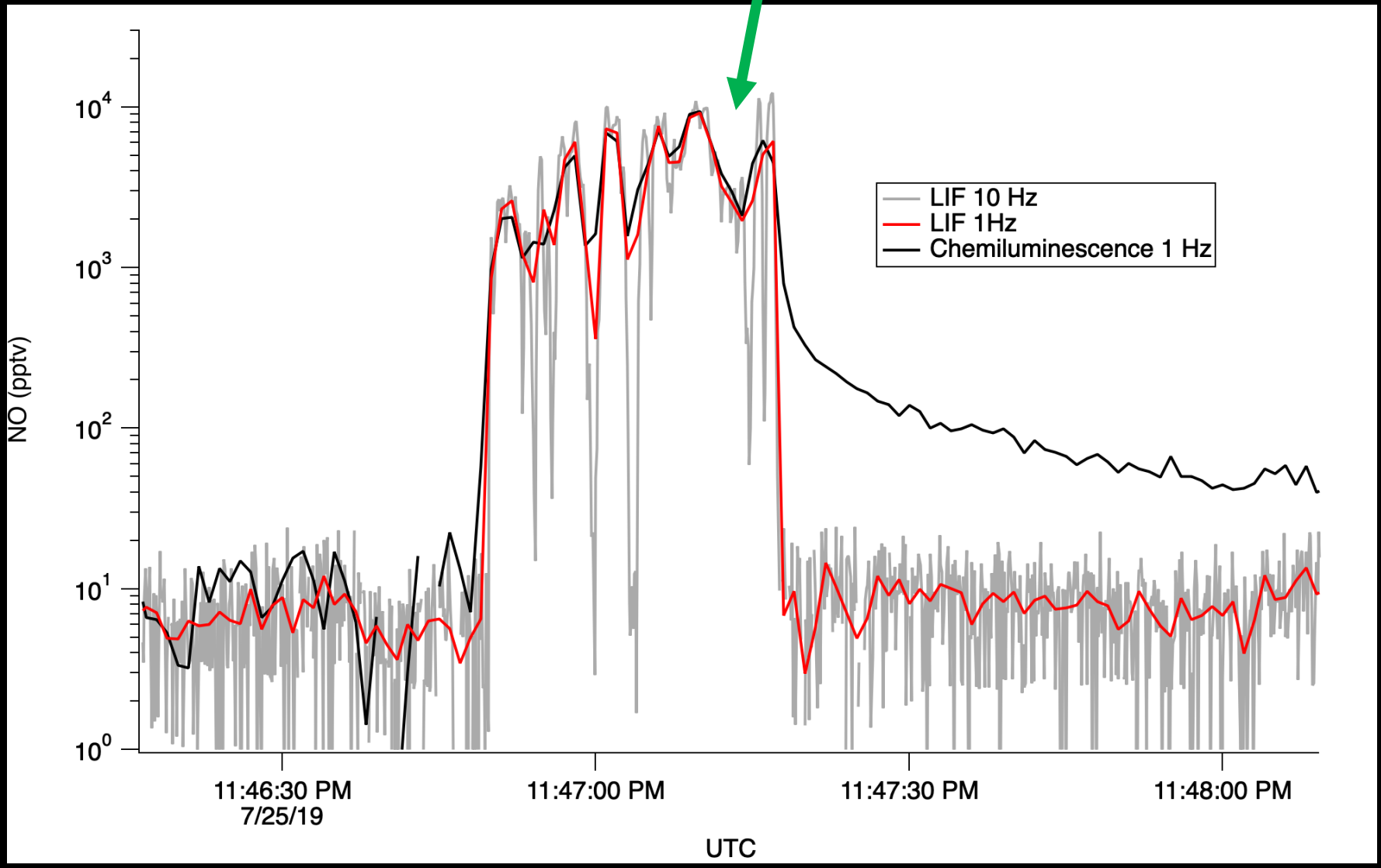




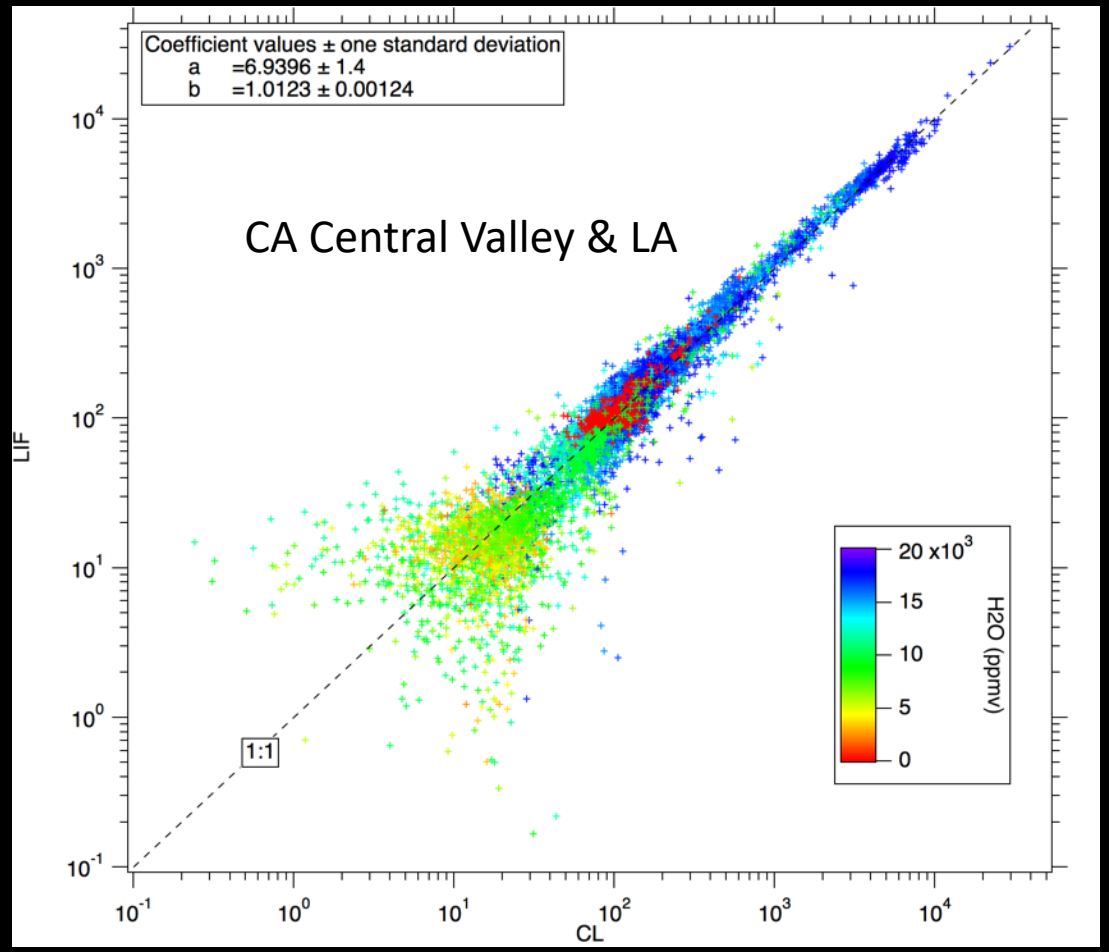
FIREX Comparison with Ryerson CL Instrument on DC-8

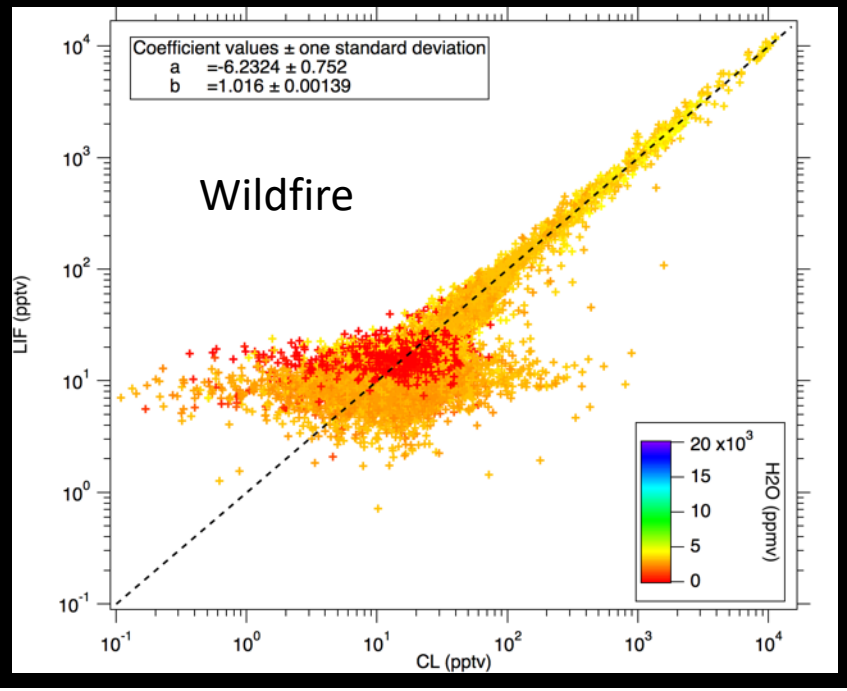


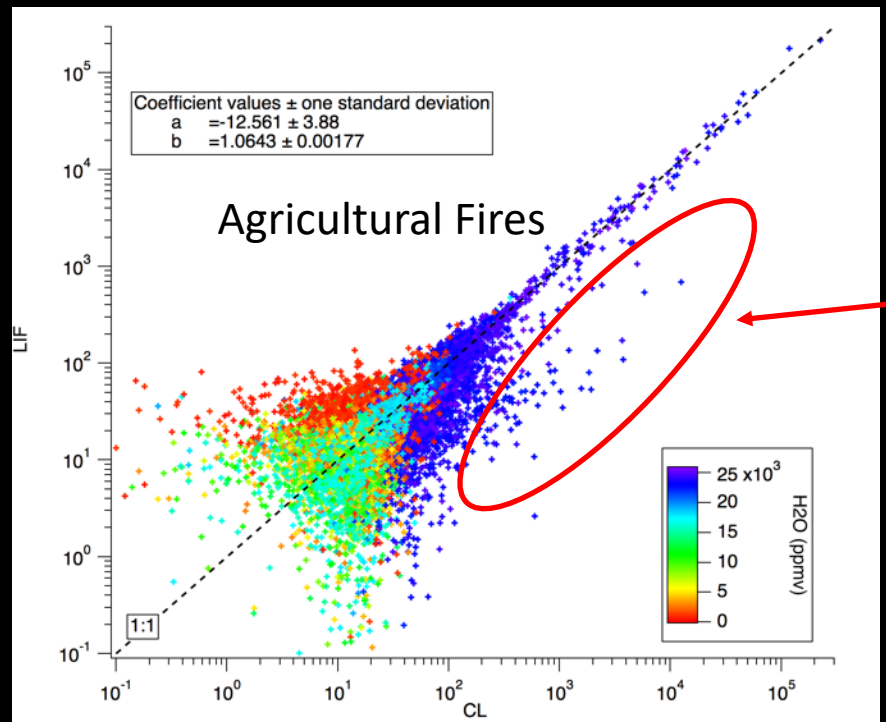
FIREX Comparison with Ryerson CL Instrument on DC-8



FIREX Comparison with Ryerson CL Instrument on DC-8



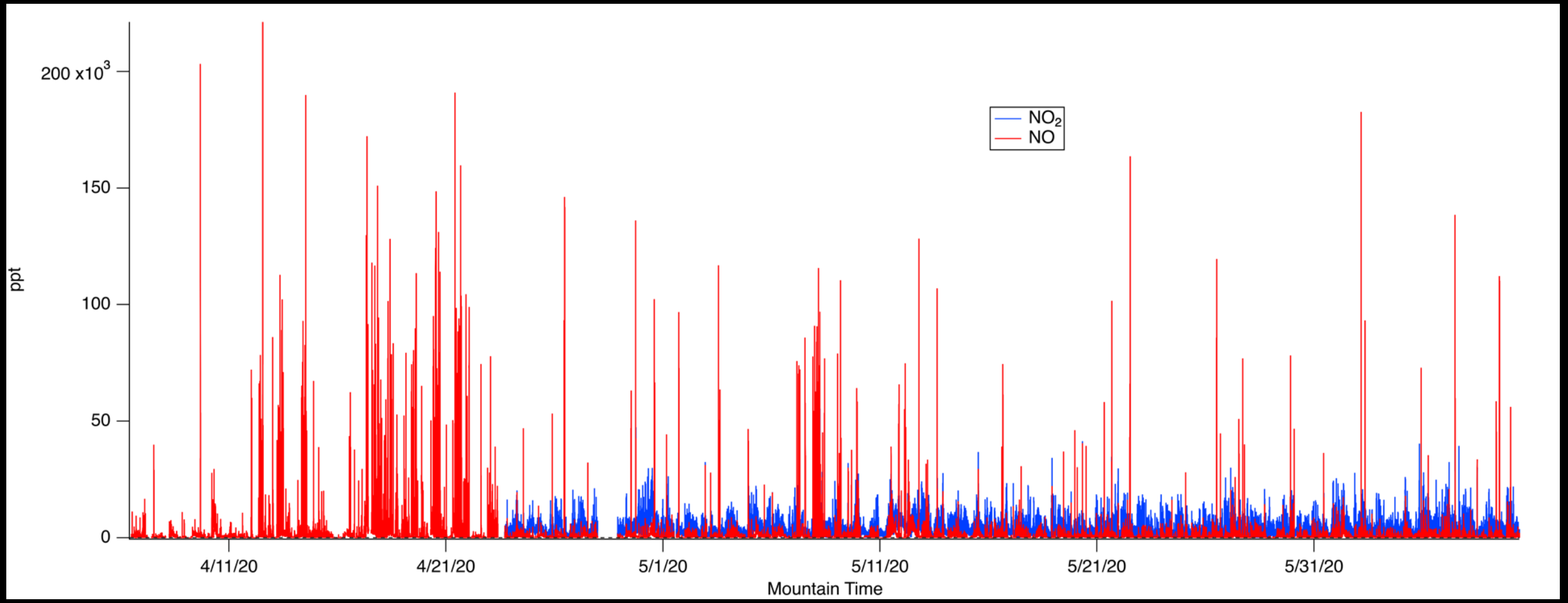




CL Time Response

Long-Term / Monitoring Use

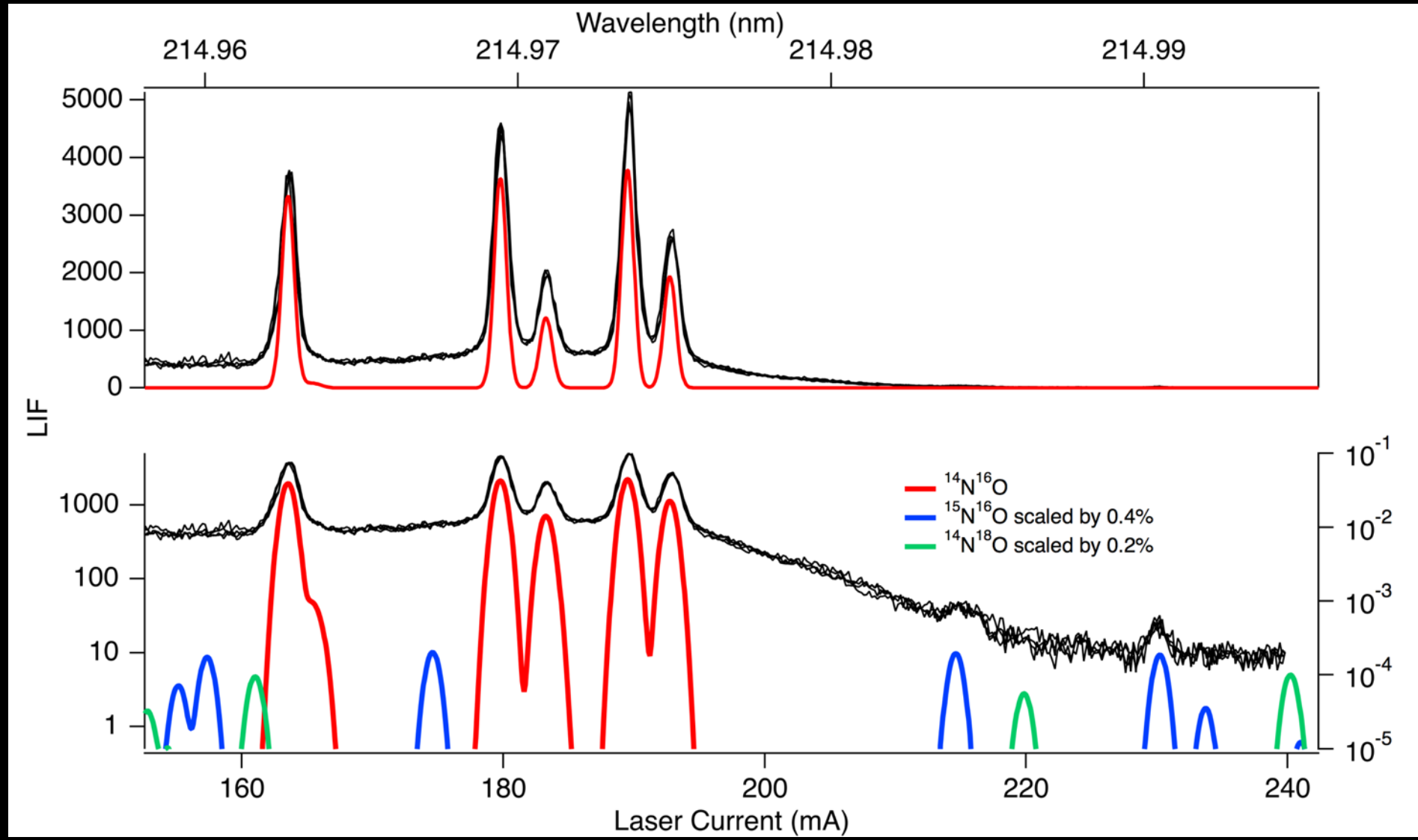
Instrument used in 2-channel mode to measure NO and NO_2 for continuous operation > 2 months during CSL COVID-AQS



Ongoing work: NO isotopologues

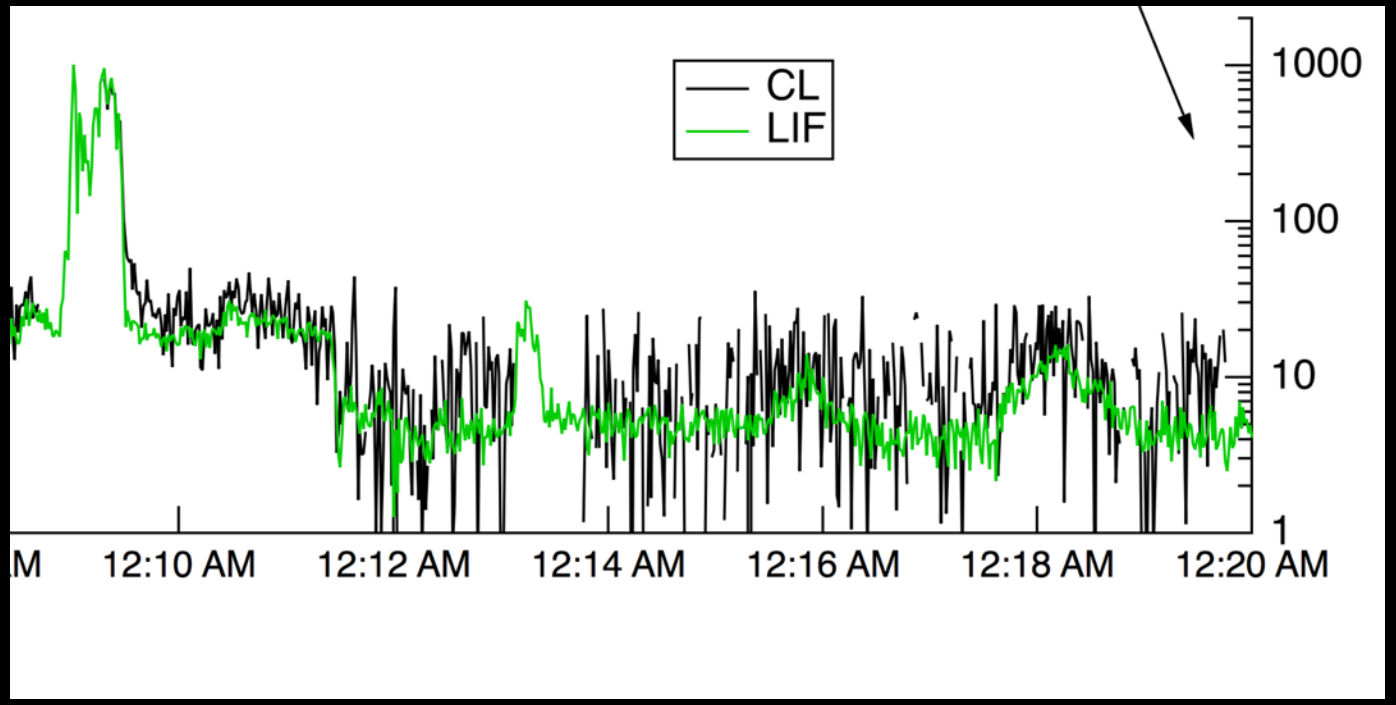
^{15}N : NOx sources

^{18}O: Peroxy radical chemistry



Summary

- New single-photon LIF scheme developed and demonstrated on DC-8 to be a reliable alternative to chemiluminescence
- SP-LIF has practical advantages over CL including size, weight, operator effort and consumables
- Detection limit is < 1 ppt for 1 s integration
- Background, and potential uncertainties due to background are < 1 ppt
- Potential for NO isotope ratio measurements



Thanks!
- Tom Ryerson
- Ilann Bourgeois
- Jeff Peischl
- Steve Brown
- Pam Rickly