Detection of Halogens by CIMS

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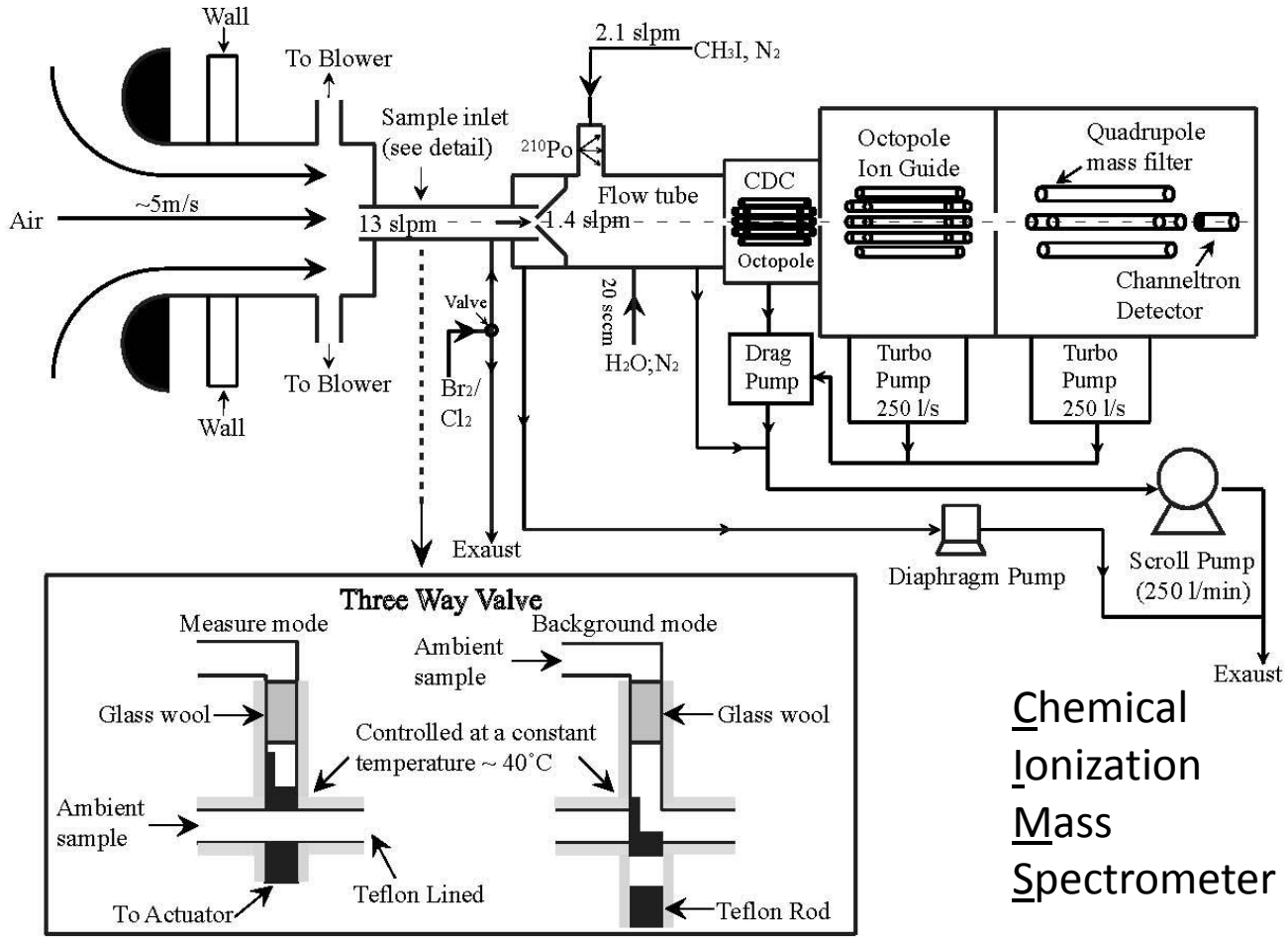
CIMS detection of halogens



Chemical Ionization Mass Spectrometer

Ion Chemistry for Detection of Halogens

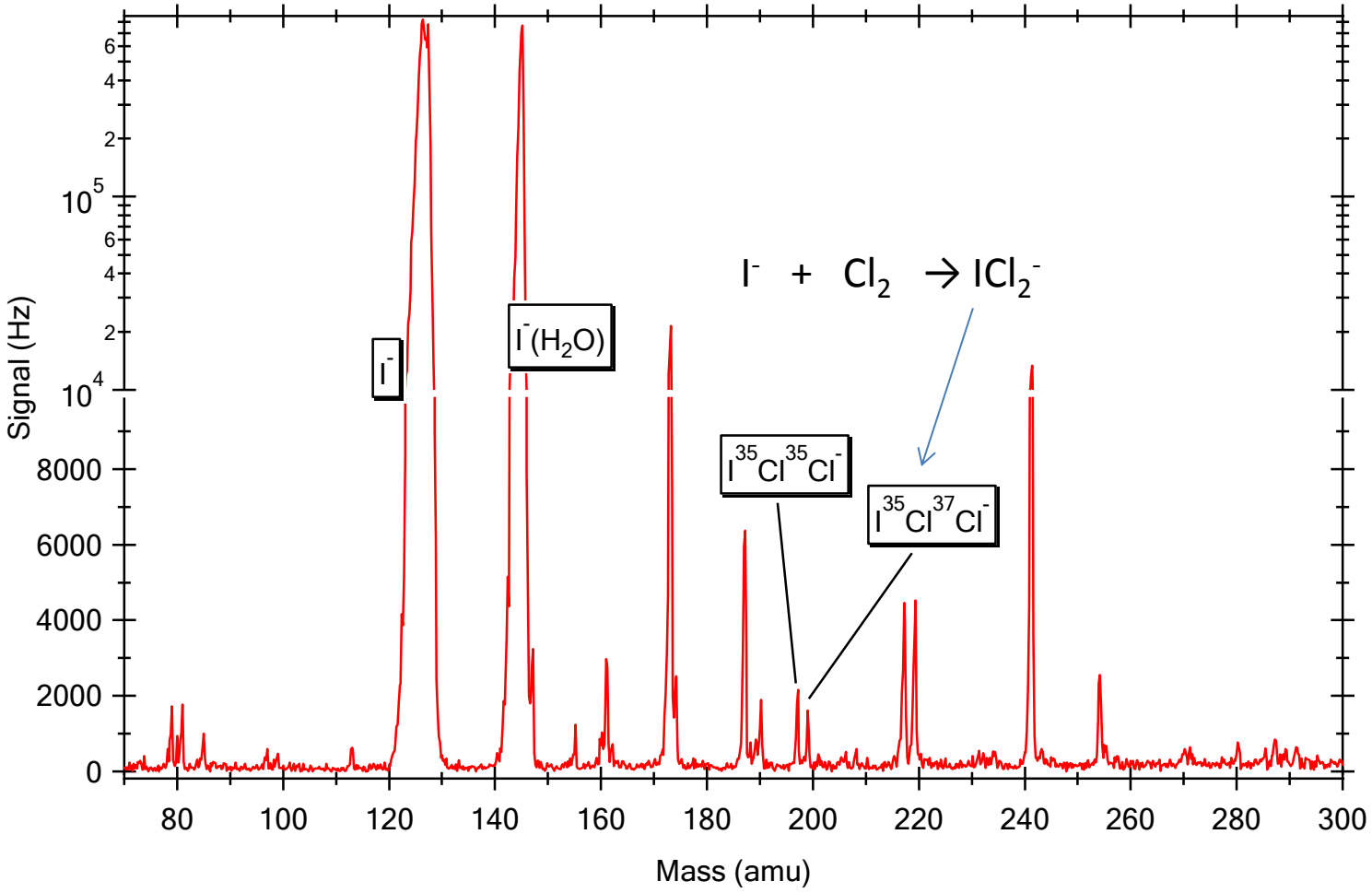
Tri-Halide "type" and/or association reactions

$$I^- + Cl_2 \rightarrow ICl_2^-$$
$$I^- + Br_2 \rightarrow IBr_2^-$$
$$I^- + BrCl \rightarrow IBrCl^-$$
$$I^- + ClO \rightarrow IClO^-$$
$$I^- + BrO \rightarrow IBrO^-$$
$$I^- + HOBr \rightarrow I(HOBr)^-$$

(Neuman et al., JGR, 2010, Liao et al., JGR, 2011, and 2012, Pratt and Shepson)

All reactions are more efficient at higher water levels. e.g. dominant channel w/ Cl_2 at low water is Cl^-.

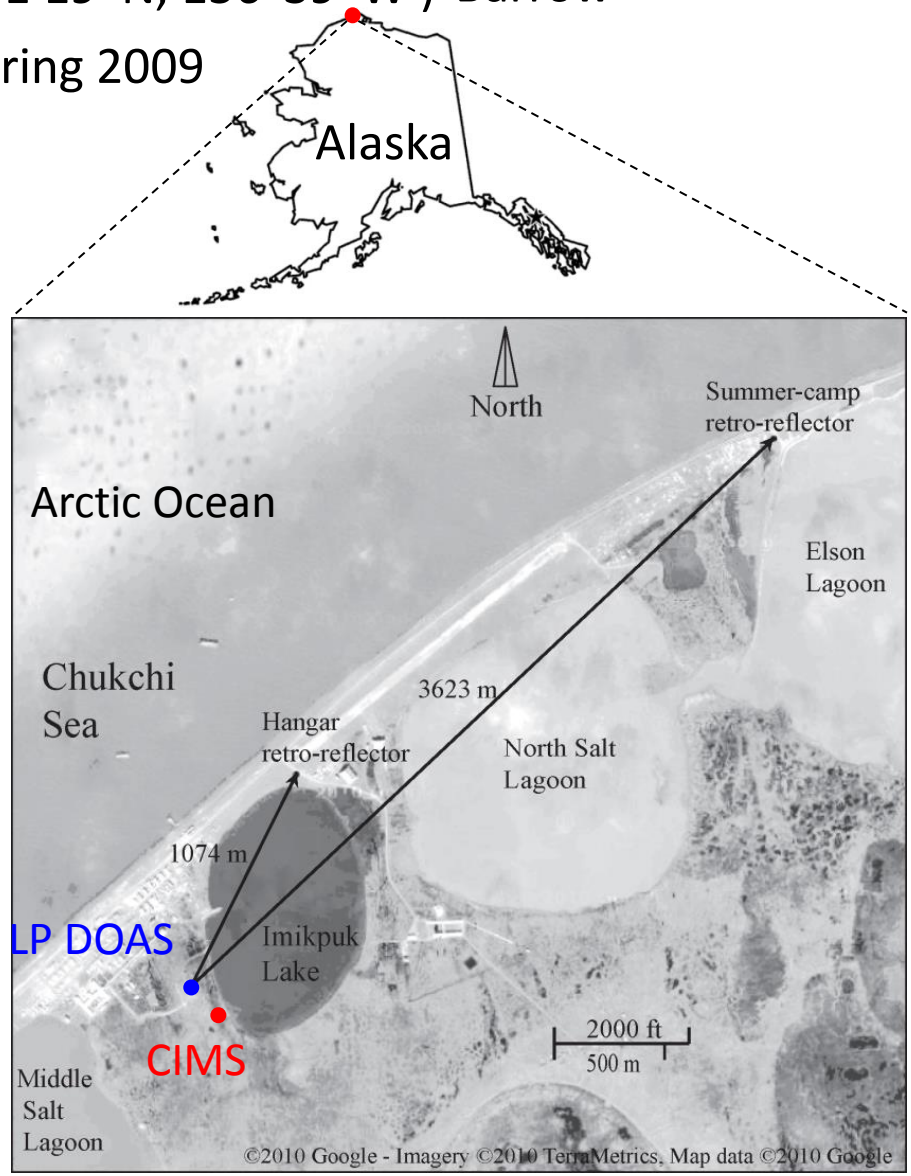
Mass Spectra from Barrow



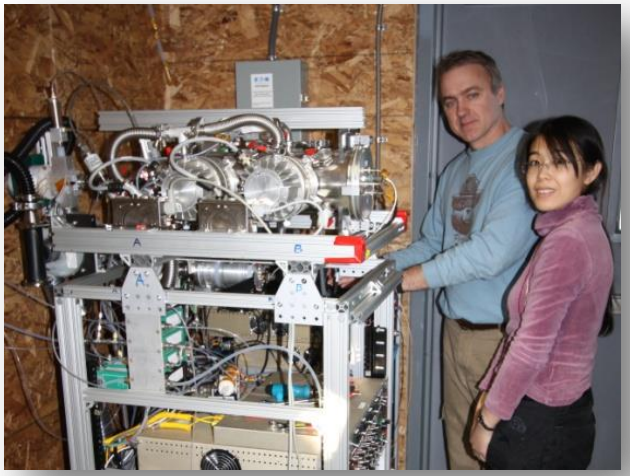
Barrow, AK (OASIS-09)

(71°19′ N, 156° 39′ W) Barrow

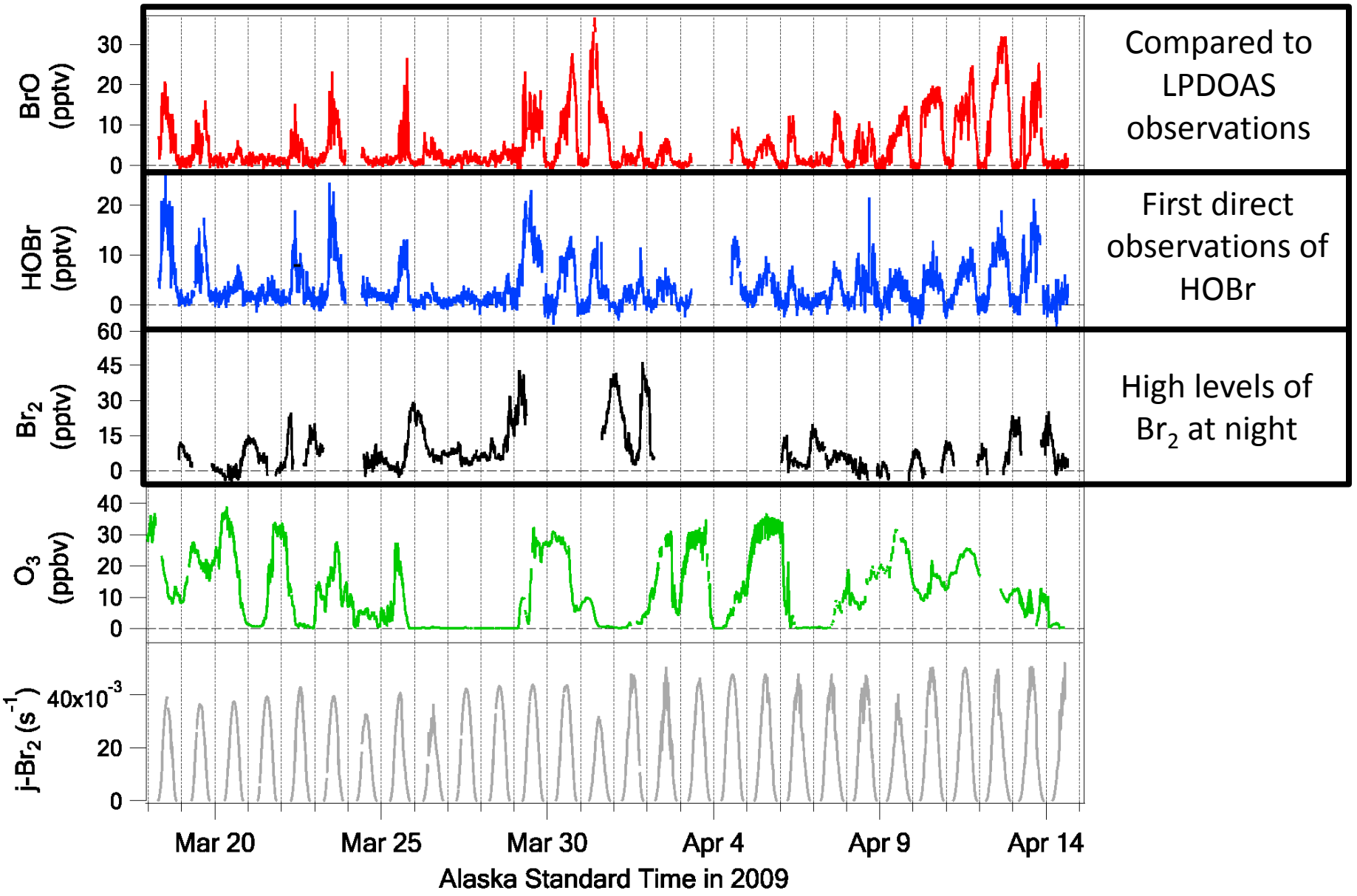
Spring 2009



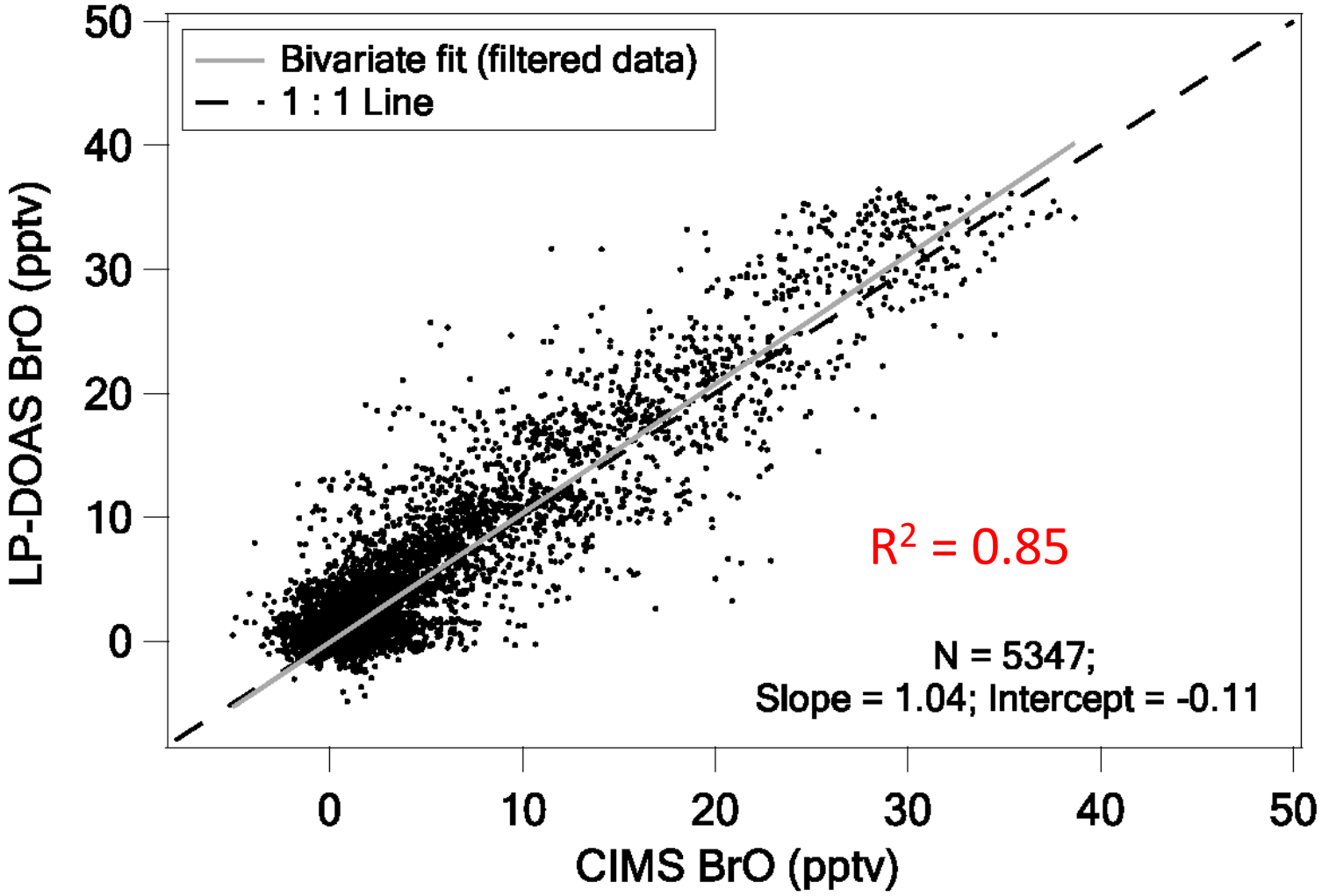
Chemical ionization mass spectrometer



Observations of BrO, HOBr and Br_2 by CIMS

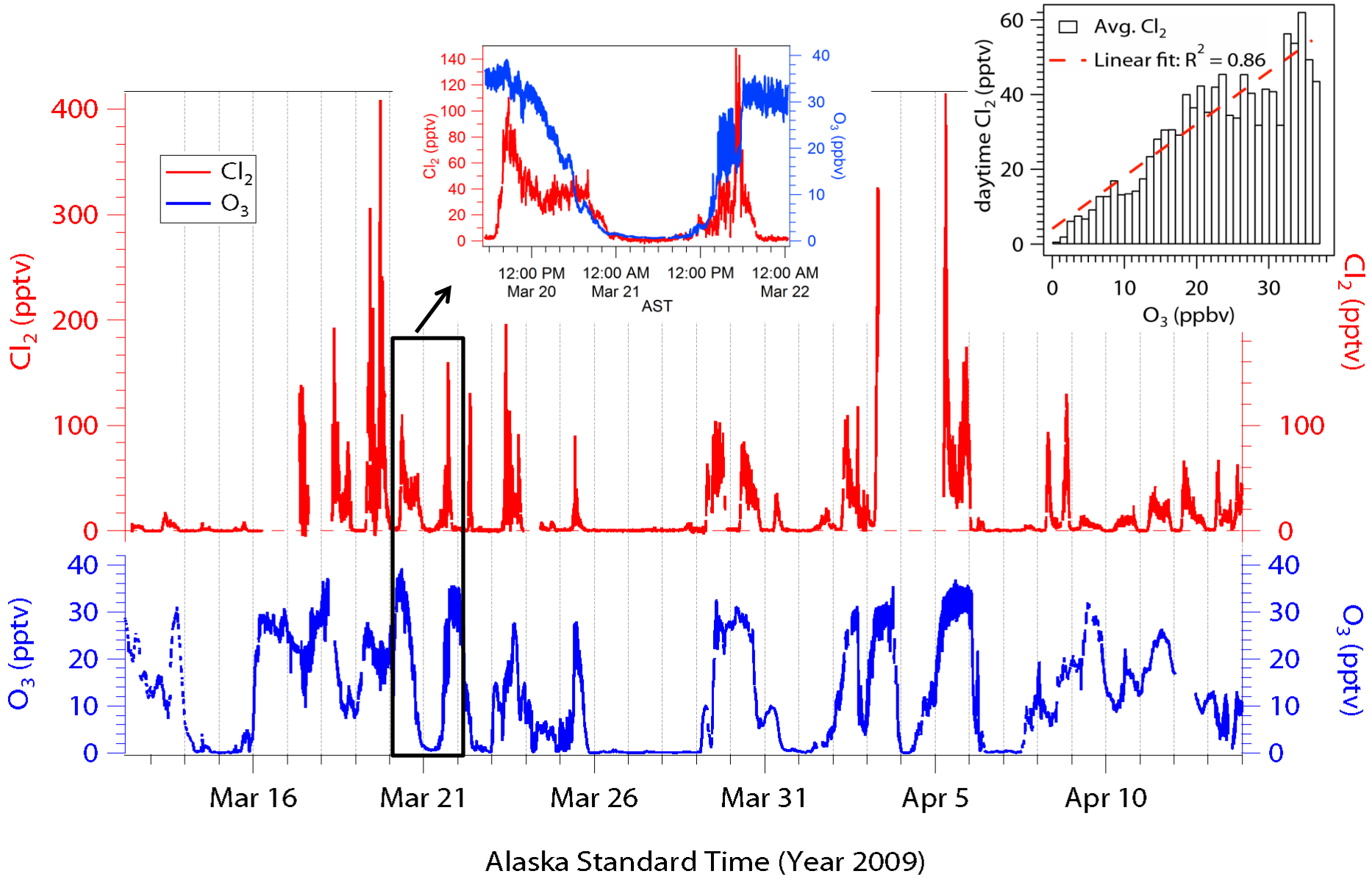


BrO measurement comparison



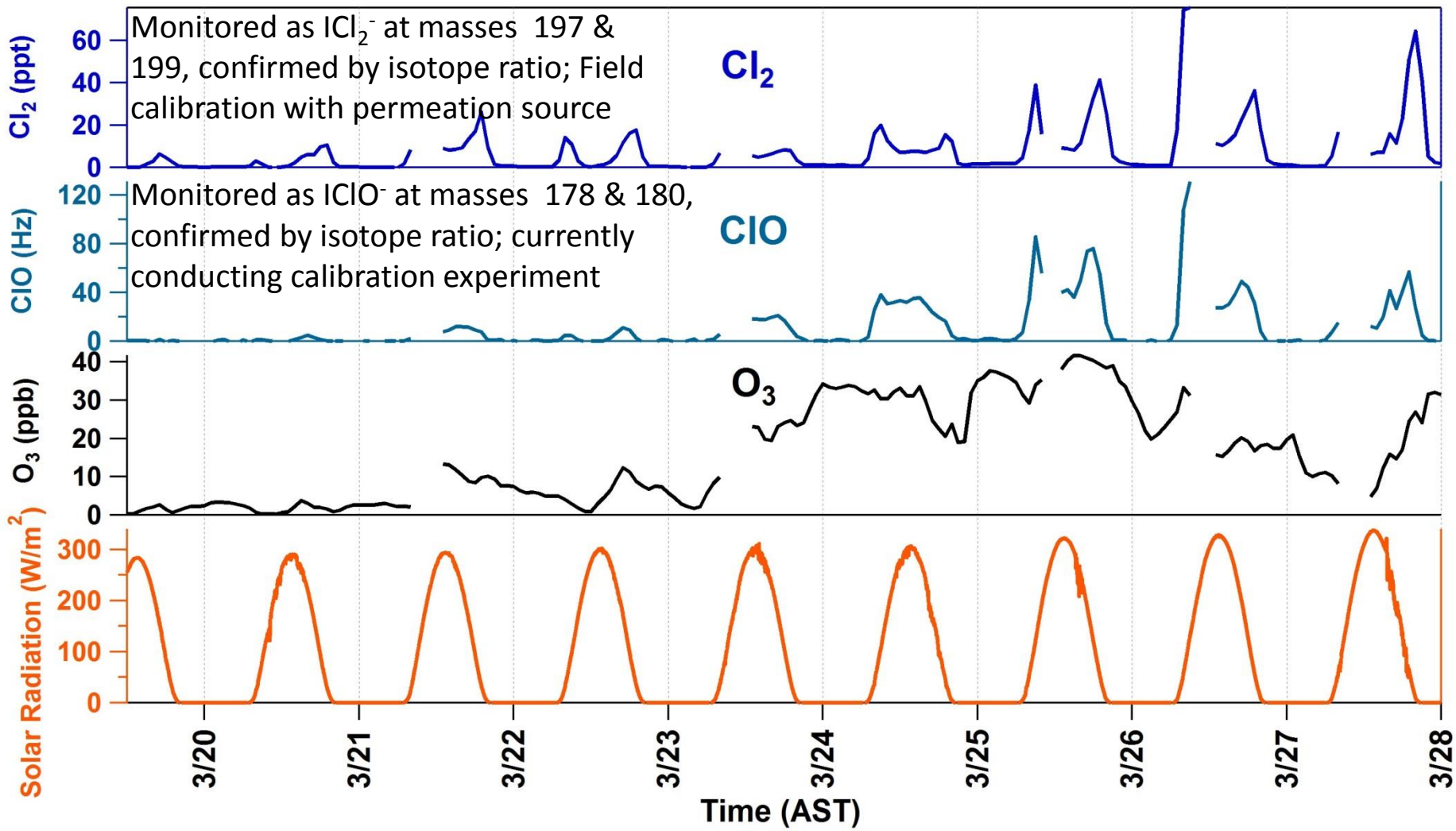
BrO measurements from the CIMS were in excellent agreement with a nearly co-located LP-DOAS, especially at moderate wind speeds (3 m/s <ws < 8 m/s) and low NO (NO < 100 pptv) conditions. [*Liao et al.*, 2011]

High levels of Cl_2 observed in presence of Ozone and Sunlight



BRomine, Ozone, and Mercury EXperiment (BROMEX)
CIMS Deployment to Barrow, Alaska, March 2012

$I(H_2O)_n^-$ as reagent ion



- Cl_2 correlated with solar radiation and ozone similar to Liao et al. observations

Kerri Pratt, Kyle Custard, & Paul Shepson, Purdue University

Halogens by CIMS for CONTRAST

- We can detect a wide variety of inorganic halogens – BrO, ClO, etc.
- CONTRAST environment for BrO will be challenging due to bromine partitioning (i.e. low O_3 favoring Br atoms). We will focus on high altitude measurements.
- GV inlet will convert HOBr to Br_2. We will take advantage of this impact to detect the sum of these species during night time flights to take best shot at inorganic bromine .
- Other molecules available with this ion chemistry – HO_2NO_2, formic and acetic acid.