

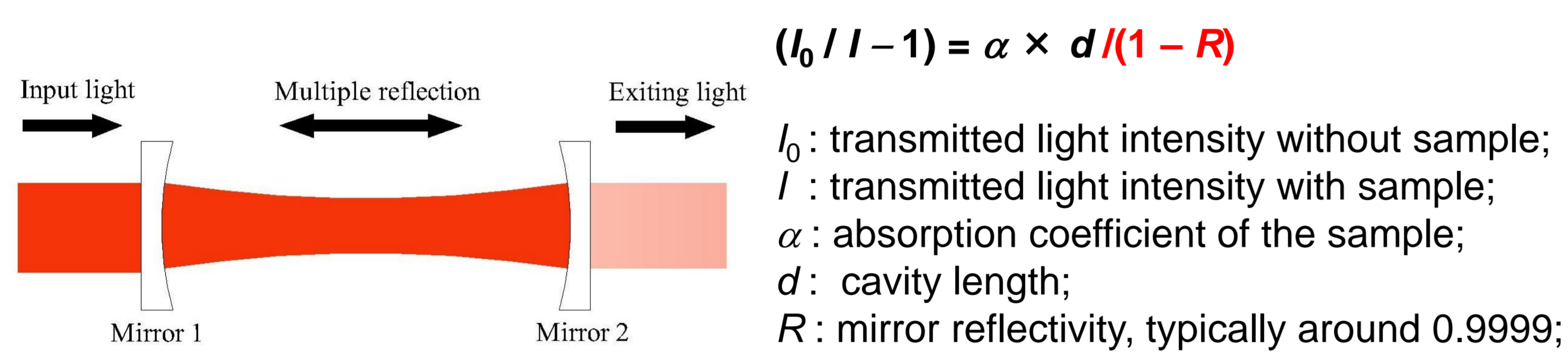
Measurement of IO levels during the CAST campaign using broadband cavity enhanced absorption spectroscopy

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Abstract Iodine monoxide has been regarded as an important radical involved in ozone destruction in the remote marine boundary. Here we report results from aircraft measurements of IO using broadband cavity enhanced absorption spectroscopy on board the UK FAAM BAe-146 atmospheric research aircraft during the CAST campaign during Jan-Feb 2014. 1σ sensitivity of ~ 1.5 ppt Hz $^{-1/2}$ on the surface level was achieved, and instrument baseline (corresponding to zero [IO]) was obtained by injection of ~ 40 ppb nitric oxide into the sample gas. No clear absorption feature was observable from spectra by eye with up to 100 s averaging, pointing to very low mixing ratios ($< \sim 0.5$ ppt) of IO over the sampled area. A small positive bias (~ 0.3 ppt) of IO against the baseline signal during NO titration was obtained in the statistical histogram of retrieved IO from average of each straight and level run, but little altitude dependence was noted. In summary, our observation appears to support the existence of IO in the remote marine boundary layer at sub-ppt levels, but the limited sensitivity precludes us from quantifying spatial gradients more accurately.



Principle – cavity enhanced absorption spectroscopy



Pathlength L enhancement factor: $1/(1 - R) = 10,000$ if $R = 0.9999$.

Instrument – the airborne LED-based broadband cavity enhanced absorption spectrometer



- The instrument was designed to fit onto two mountable 19" racks that are mountable to the UK FAAM BAe-146 atmospheric research aircraft;
- The instrument is featured by using high-power light emitting diodes (LEDs) as light source;
- Wavelength-sensitive components, namely the LEDs, the high-reflectivity mirrors and light detectors, can be easily adapted to cover the entire UV-vis range;

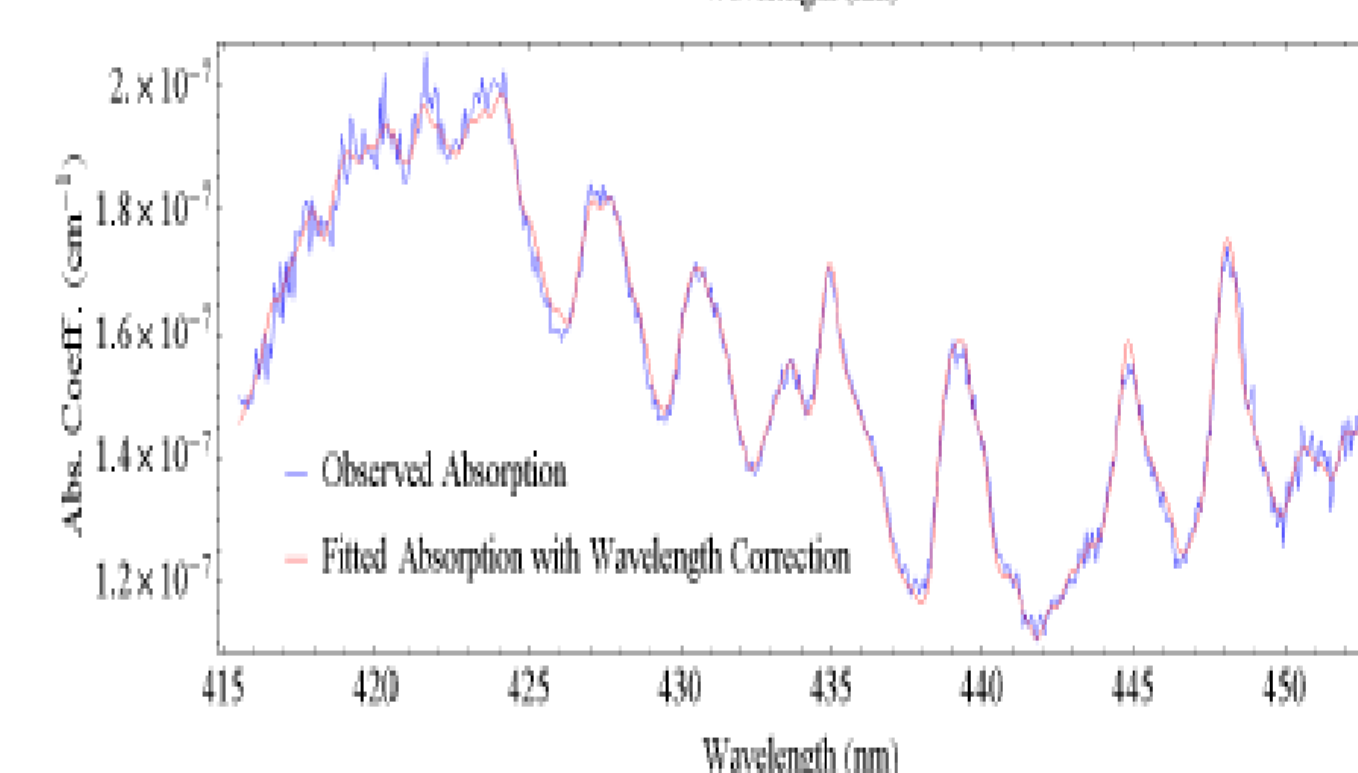
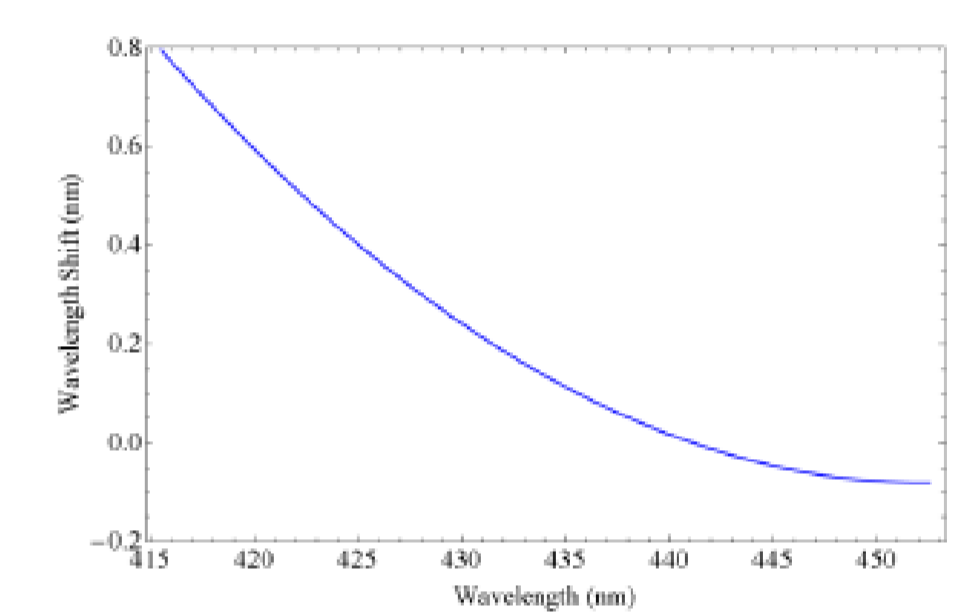
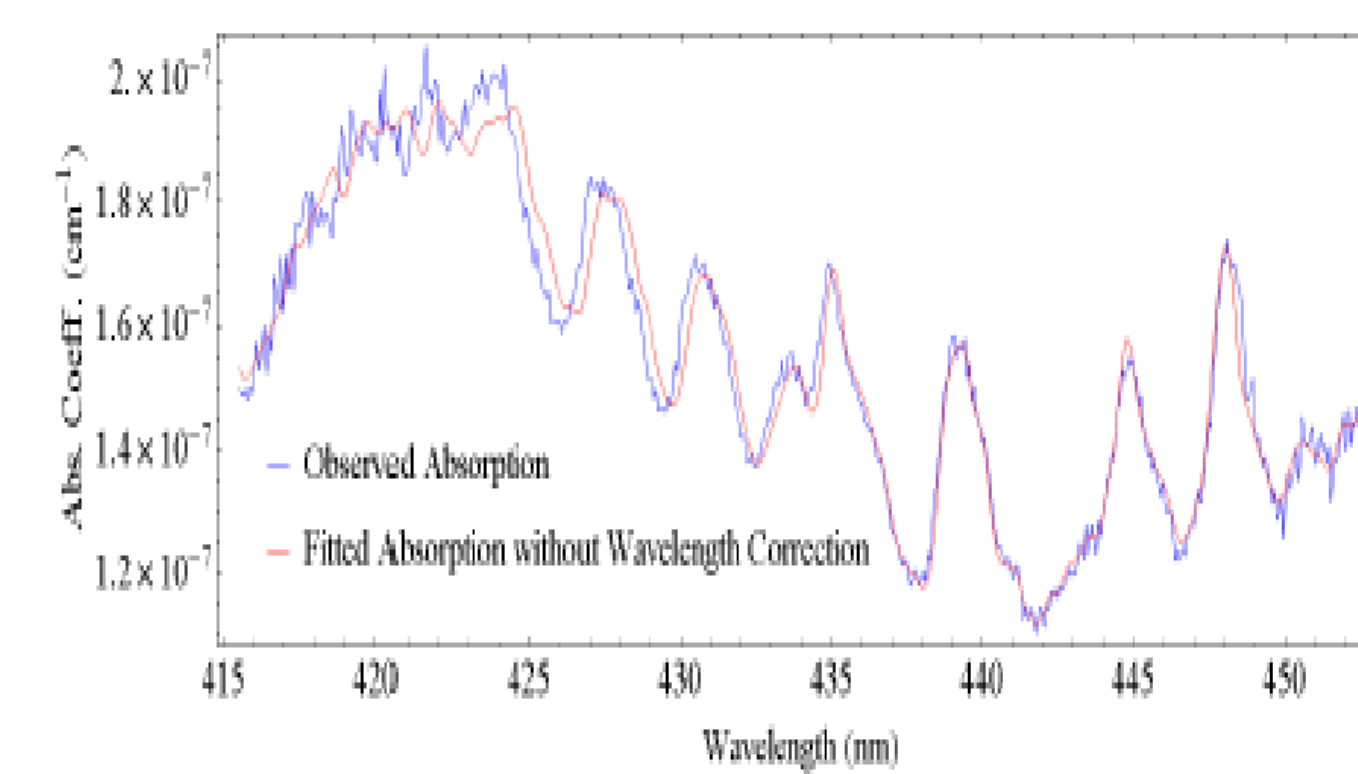
Measurement strategy

Chemical zero: by periodic injection of ~ 40 ppb NO in the sample gas to completely titrate away IO through:
 $\text{IO} + \text{NO} \rightarrow \text{I} + \text{NO}_2$; $\text{I} + \text{NO} \rightarrow \text{INO}$;

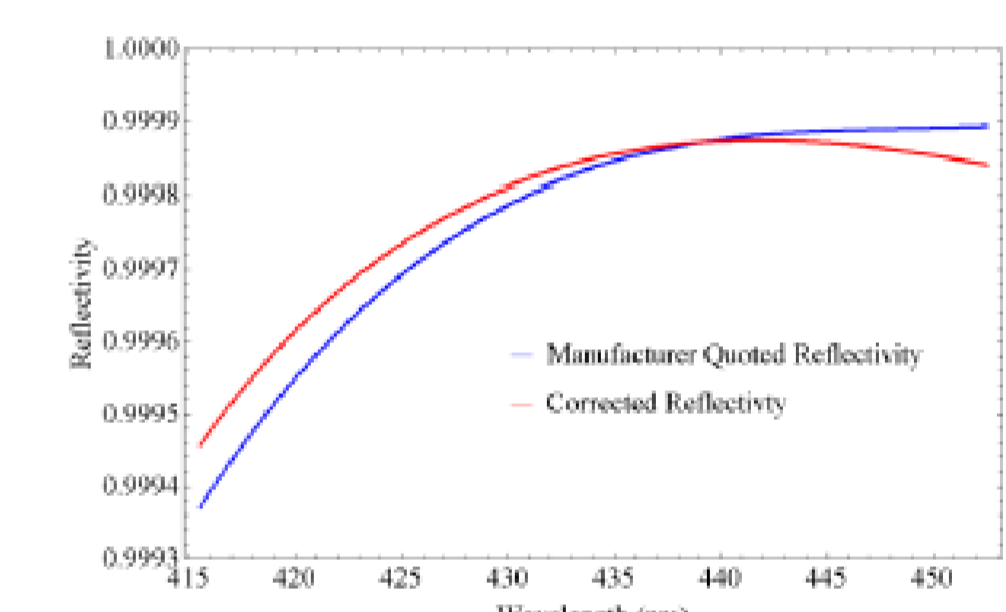
Monitoring wavelength range: 415 – 452 nm;
 LED: APG2C-435 (Roithner), with peak emission at 435 nm;
 Spectrometer: Ocean Optics QE65000, configured for 410 – 482 nm;
 Cavity mirrors: Layertec, peak reflectivity $R \sim 0.99985$ @ ~ 445 nm;

Verification of Instrument performance via NO_2 absorption:

Correction for spectrometer wavelength drift:

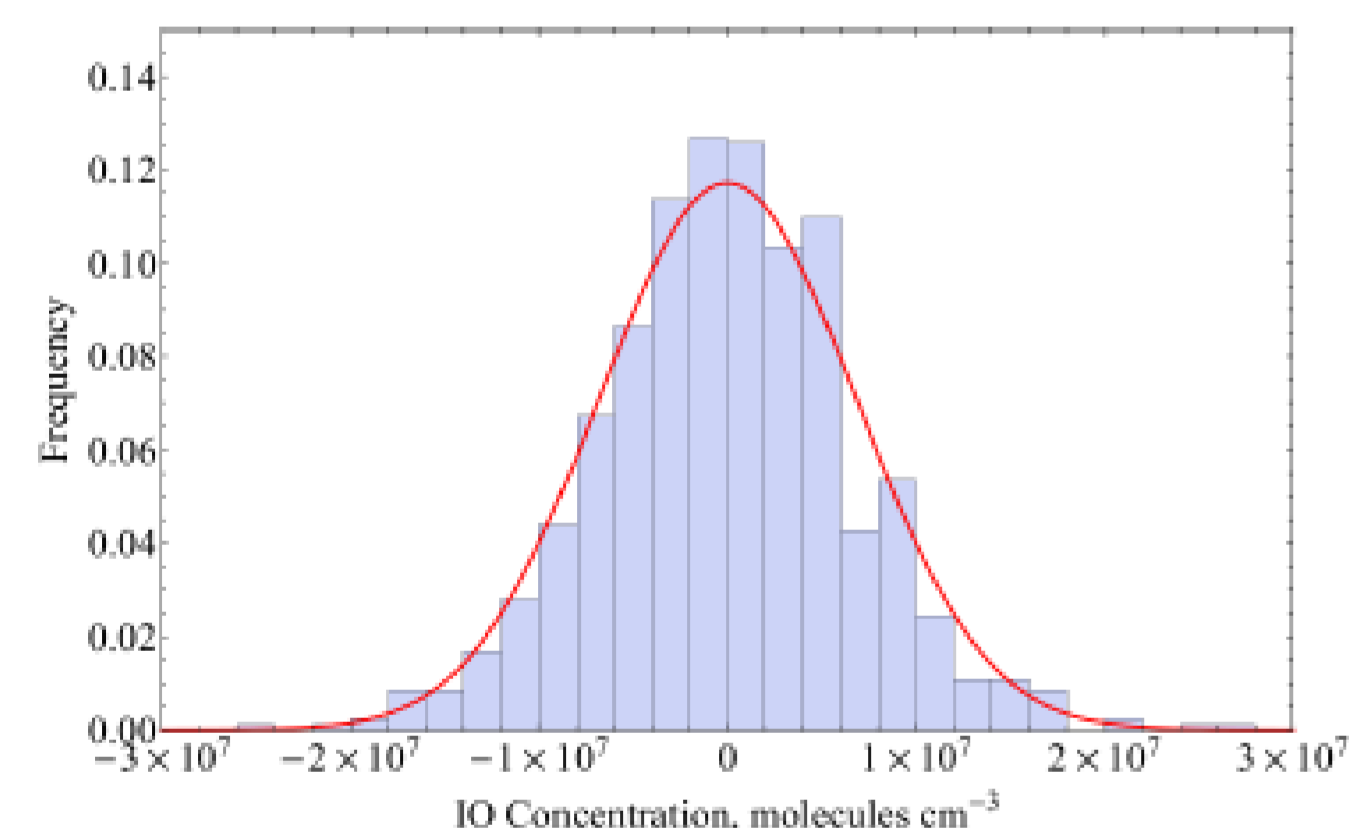


Correction for change of mirror reflectivity curve:



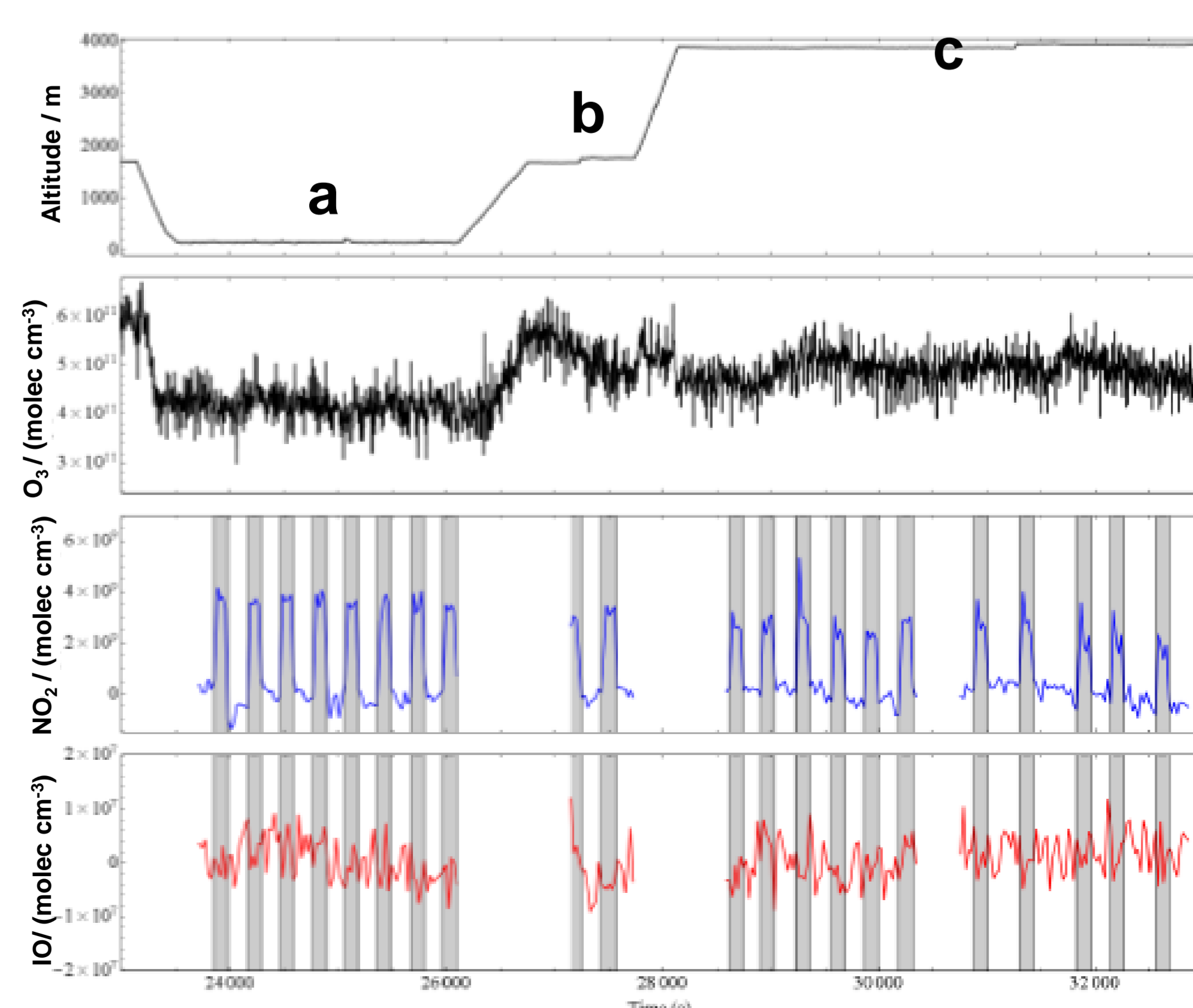
Measurement sensitivity and example time series

Sensitivity test



The left graph shows statistical histograms of retrieved IO concentrations from 25 s averaged spectra where the NO titration was on. Overlaid red line is the fit of histogram with Gaussian function which yields a standard deviation (1σ) of $\sim 7.5 \times 10^6$ molec cm^{-3} , corresponding to a detection limit of ~ 1.5 ppt Hz $^{-1/2}$ at surface pressure level.

Example time series of flight B828

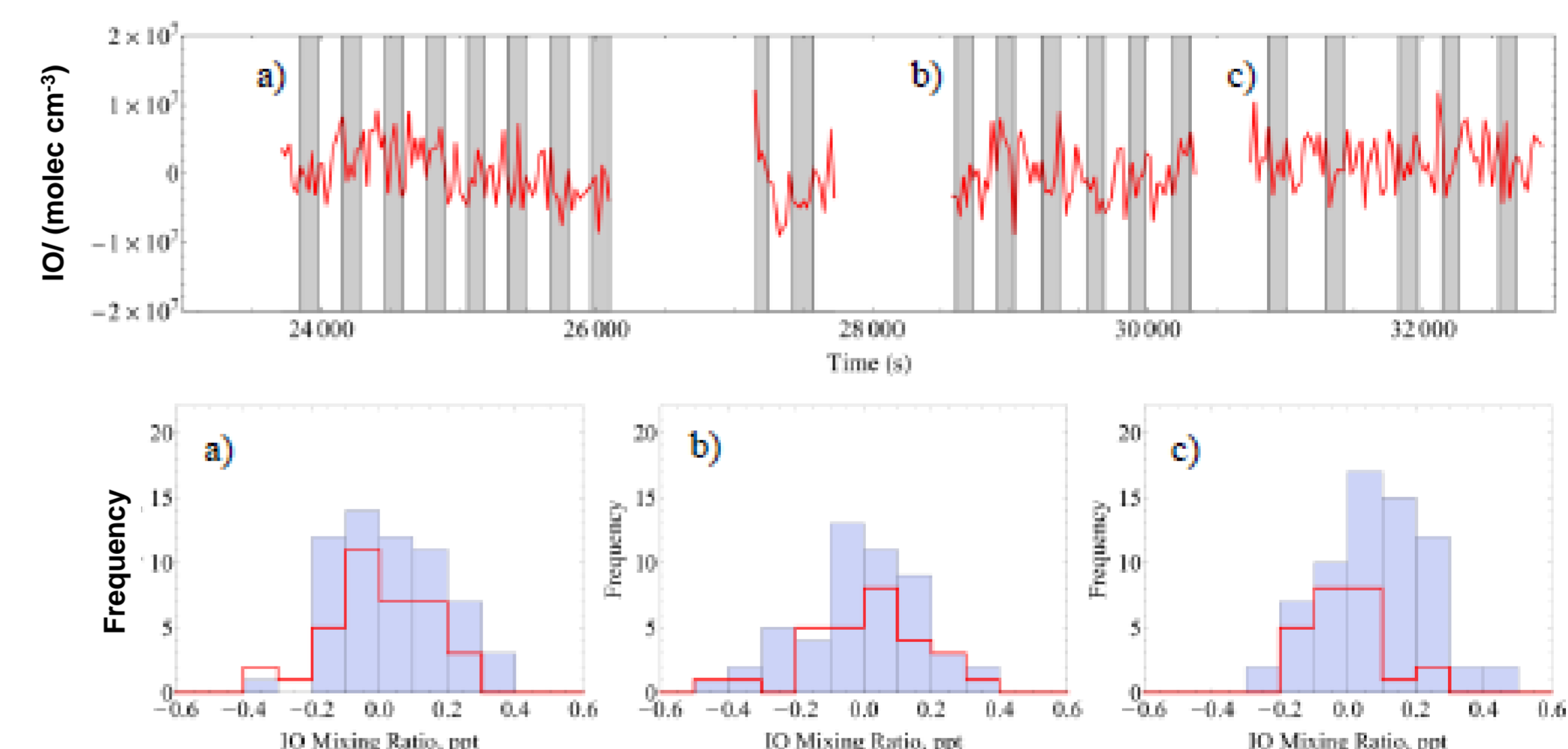


The left graph shows flight altitude, ozone number density as well as retrieved NO_2 and IO number densities during the three SLRs at different altitudes during flight B828.

The shaded area suggests periods when NO titration was turned on. Formation of NO_2 from reaction between the injected NO and ambient O_3 is clearly visible as spikes in the time series. Retrieved IO "signal" during these periods were taken as "zero" and was referenced to by the NO-off periods.

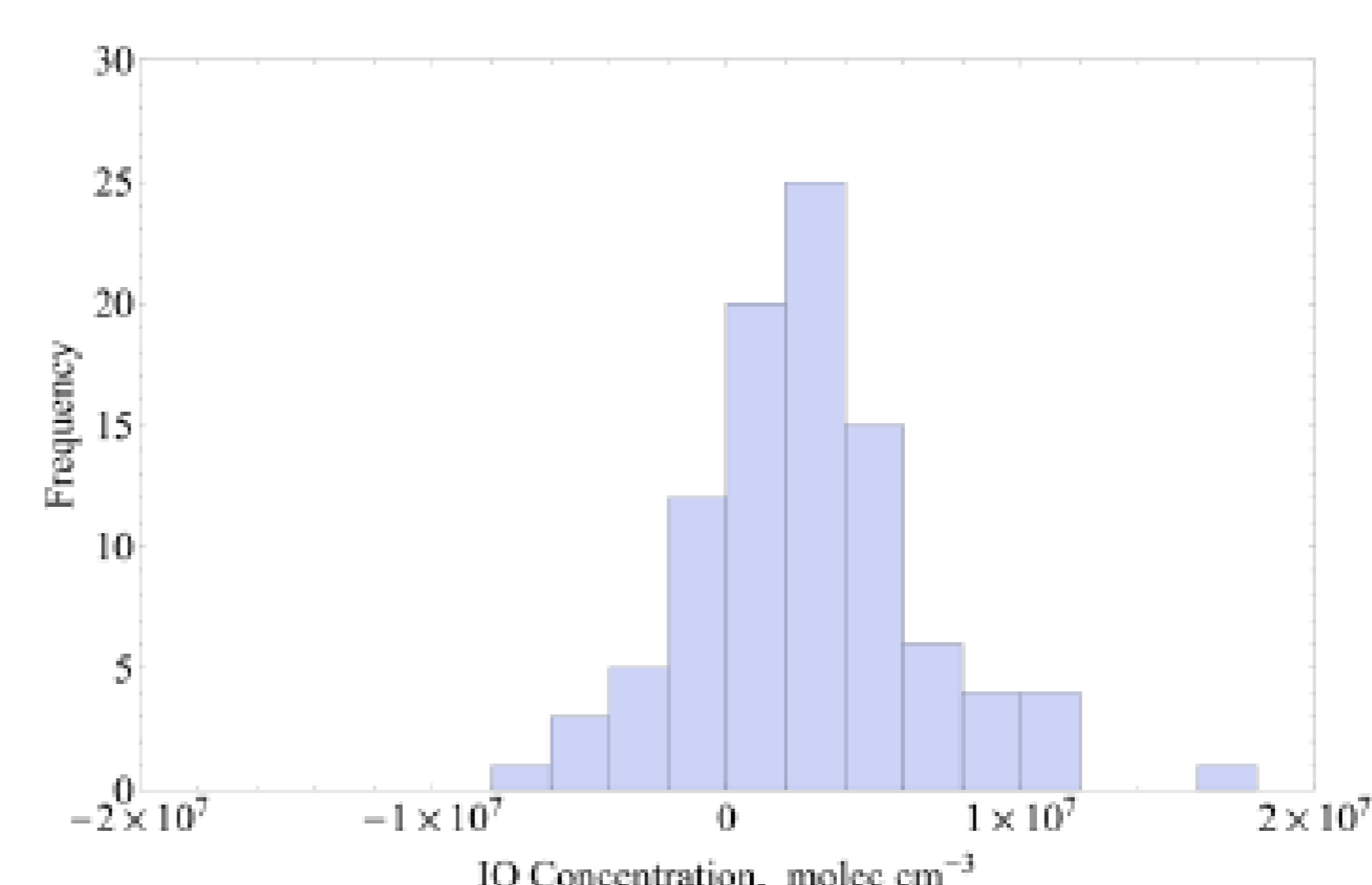
IO levels – from individual flight to entire campaign

B828



Above shows the time series of retrieved mixing ratios of IO at three different SLRs during flight B828 (also see left), together with the histogram of retrieved IO when NO titration was off (blue columns) and that of IO when NO titration was on (overlaid red lines). Comparison of the two appears to show positive bias of < 0.2 ppt, yet with little altitude dependence.

Campaign summary



Left shows the histogram of retrieved IO (referenced to the baseline from NO titration) from 97 level runs during the entire CAST campaign. The distribution seems to skew towards positive values of IO at sub-ppt level. Further analysis of altitude dependence (not shown) however shows no clear trend. More analysis will be carried out when complementary measurement data are available.