

Figure S1 Full width half maximum ($\text{FWHM} = 2 \times \text{width} \times (\ln(2))^{1/2}$) values calculated for sharp peaks in the Hg(Ne) calibration source and 50 μm spectrometer slit width. The error bars represent 1σ of the Gaussian peak fitted to each line in the lamp spectrum.

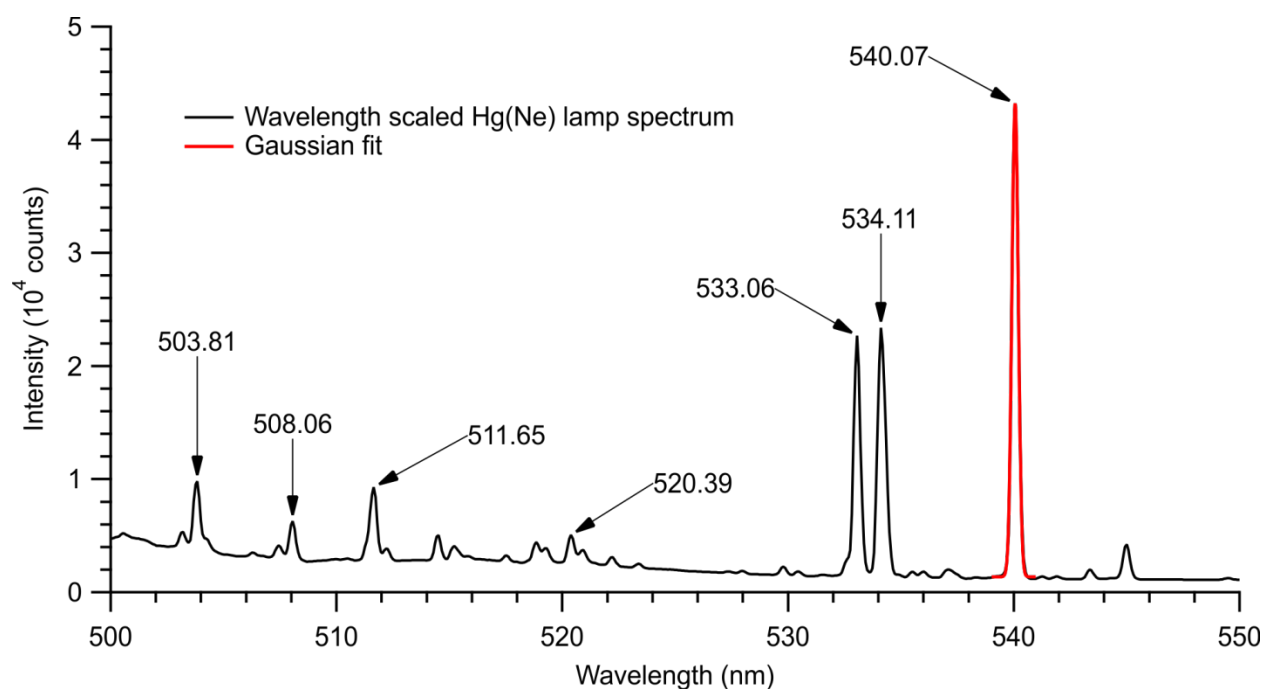


Figure S2 Wavelength calibrated Hg(Ne) lamp spectrum recorded using Acton SP2156 spectrograph equipped with PIXIS 100B CCD camera. The spectrum was produced by the average of 120 one second scans.

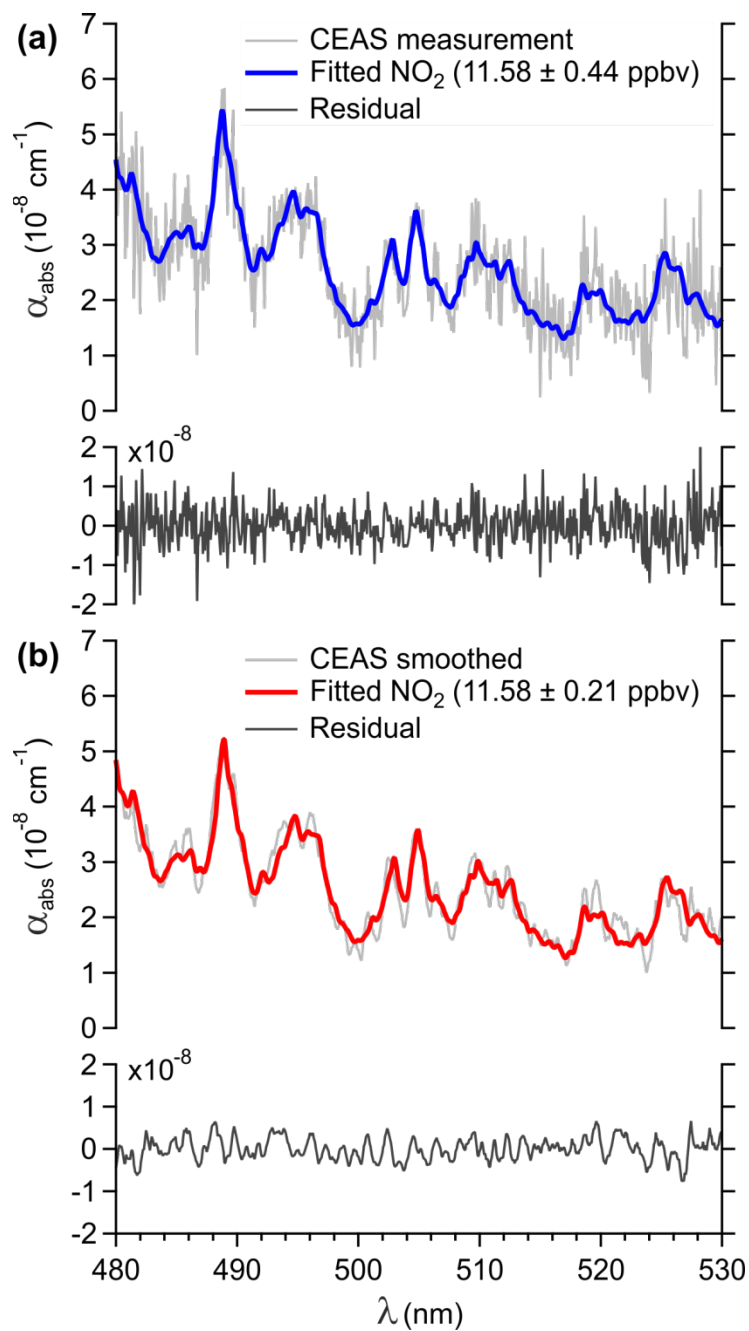


Figure S3 Example of fitted spectra for **a)** NO_2 without smoothing and **b)** NO_2 with smoothing using a fourth degree polynomial Savitzky-Golay (1964) filter.

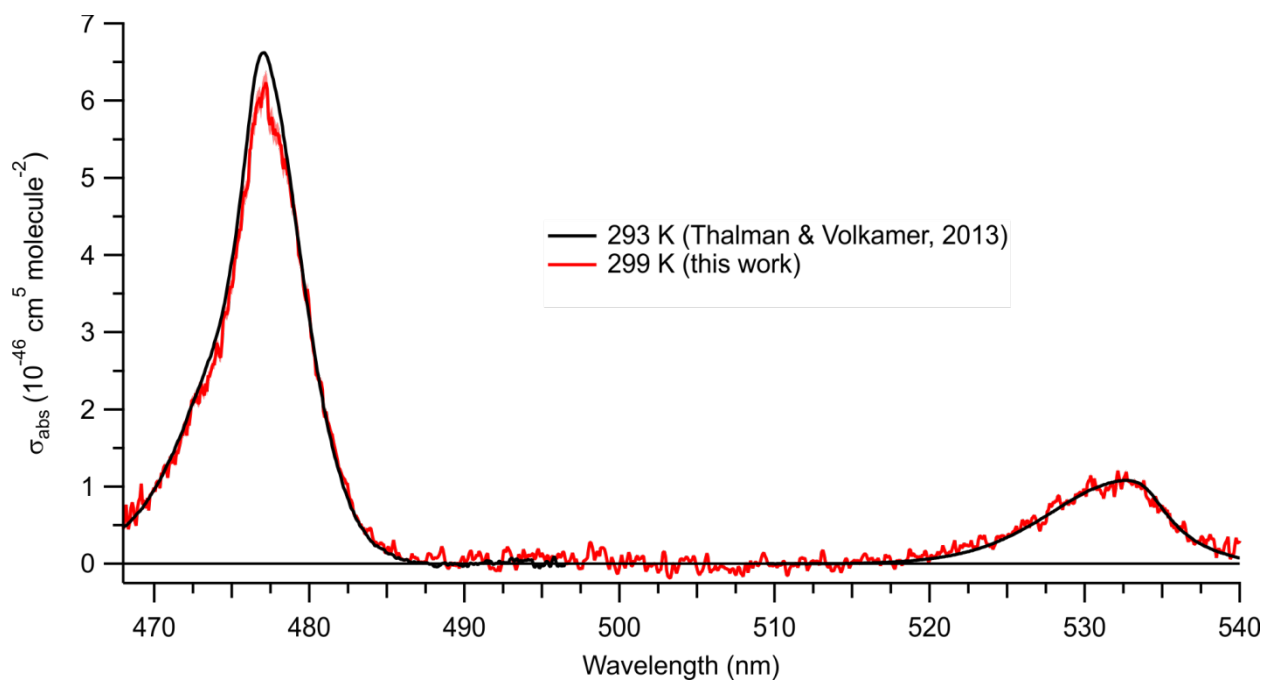


Figure S4 Room-temperature absorption cross-section of O₄, calculated from the data shown in Figure 4c. Data from (Thalman and Volkamer, 2013) are superimposed.

Table S1. Selected absorption cross-sections of O₄ at room temperature in the recent literature.

Reference	Peak $\sigma(477 \text{ nm})$	Peak $\sigma(532 \text{ nm})$
	($10^{-46} \text{ cm}^5 \text{ molecule}^{-2}$)	($10^{-46} \text{ cm}^5 \text{ molecule}^{-2}$)
(Greenblatt et al., 1990)	6.3 ± 0.6	1.0 ± 0.1
(Newnham and Ballard, 1998)	8.3 ± 0.8	1.2 ± 0.4
(Hermans et al., 1999)	6.6	1.1
(Sneep and Ubachs, 2005)	-	1.01 ± 0.03
(Sneep et al., 2006)	6.60 ± 0.06	-
(Thalman and Volkamer, 2013)	6.6 ± 0.1	1.09 ± 0.06
This work	6.2 ± 0.5	1.08 ± 0.09

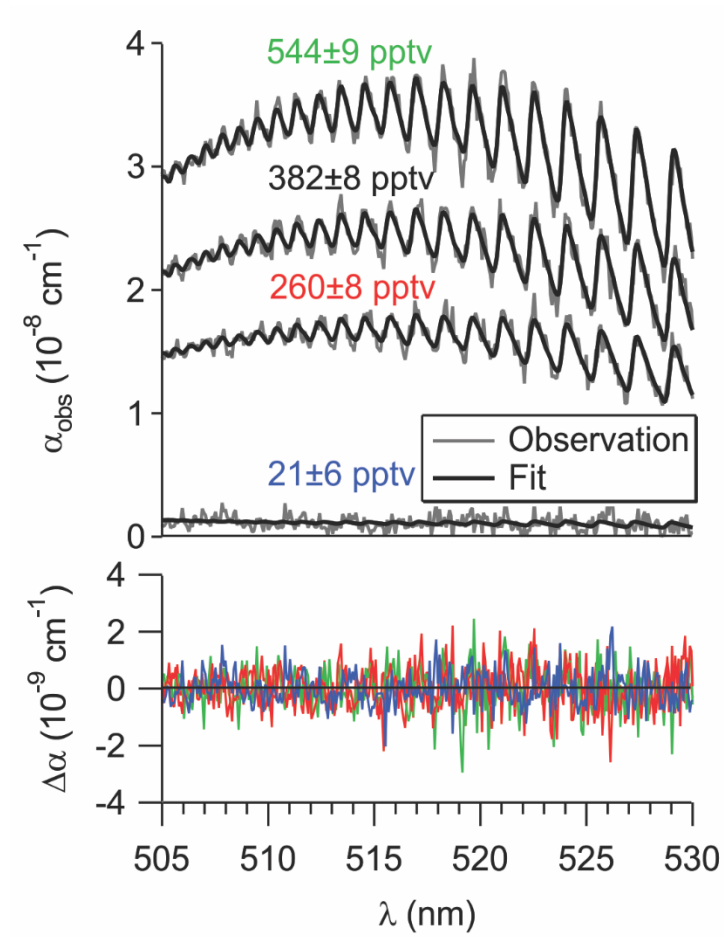


Figure S5 Examples of spectral fits of laboratory generated I_2 at different mixing ratios. The absorption cross-sections by Spietz et al. (2006) and a third-order polynomial were used. The bottom panel shows the fit residuals, colour-coded by the mixing ratio labels above.

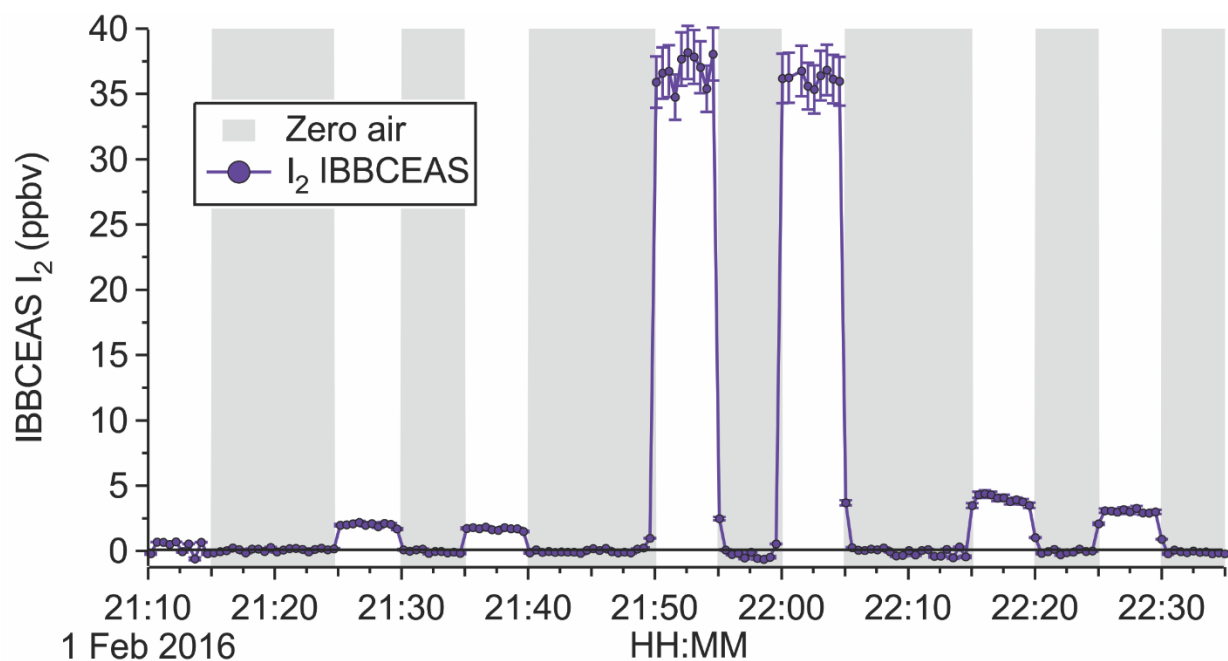


Figure S6 Time series of sample CEAS retrievals while sampling laboratory generated I₂. The grey underlay indicates times when the instrument sampled zero air. Iodine was delivered from four permeation tubes of different wall thickness, which were exchanged during the zeroing periods while the diffusion chamber output was bypassed.

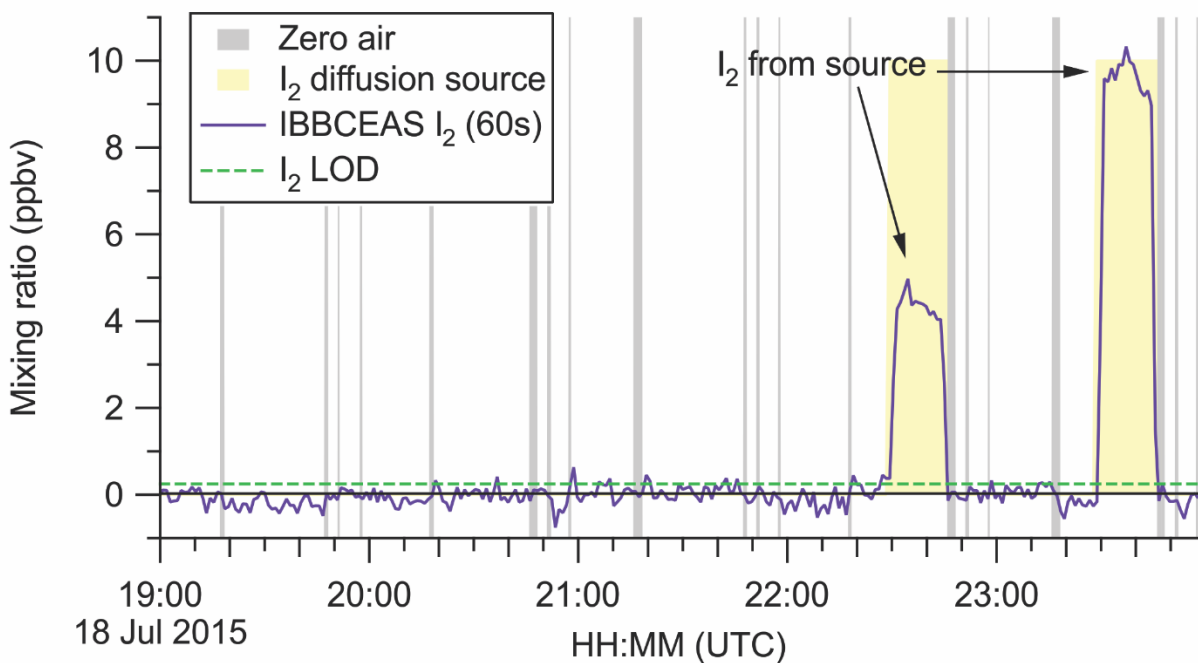


Figure S7 Time series of ambient air I_2 measurements during the ORCA campaign. The green dashed line represents the 2σ LOD for I_2 . The grey shaded areas indicate periods when the CEAS sampled zero air. The yellow shaded areas indicate times when the CEAS sampled I_2 from a permeation which was controlled to a temperature of 40 °C at 22:30 and 55 °C at 23:30 UTC.

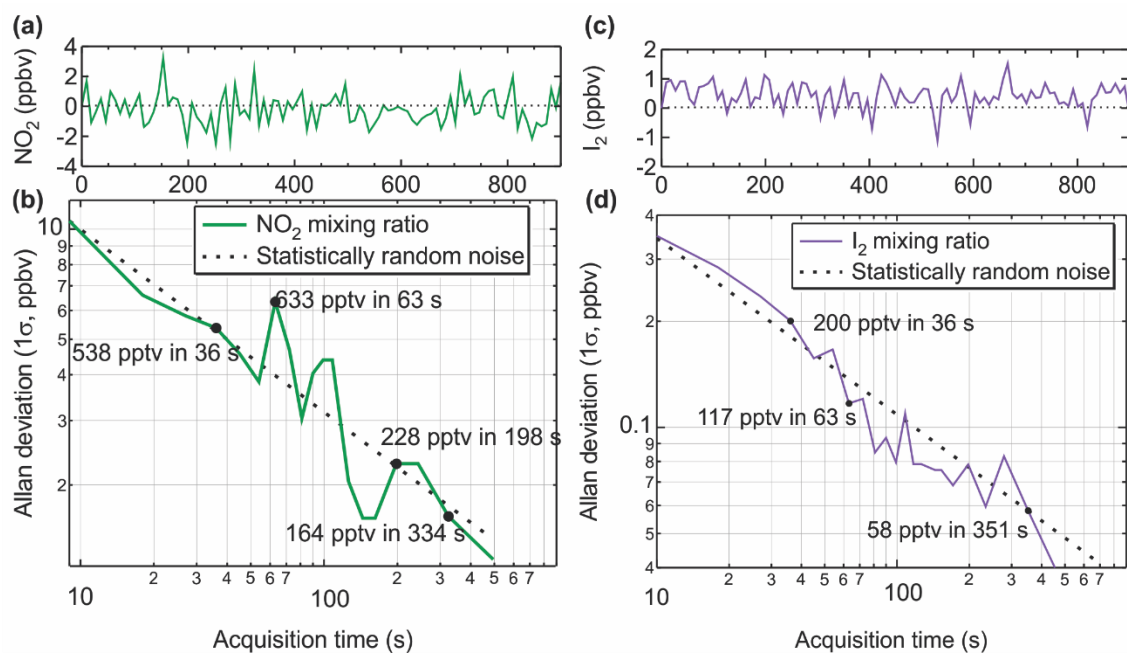


Figure S8 Data collected while the CEAS continuously sampled zero air during the ORCA campaign at a sample cell pressure of 467 hPa, flow rate of 5 slpm, and at a temperature 290 K. **(a)** Time series of NO_2 mixing ratios. **(b)** Allan deviation plot of the above data. **(c)** Time series of I_2 mixing ratios. **(d)** Allan deviation plot of the above data.

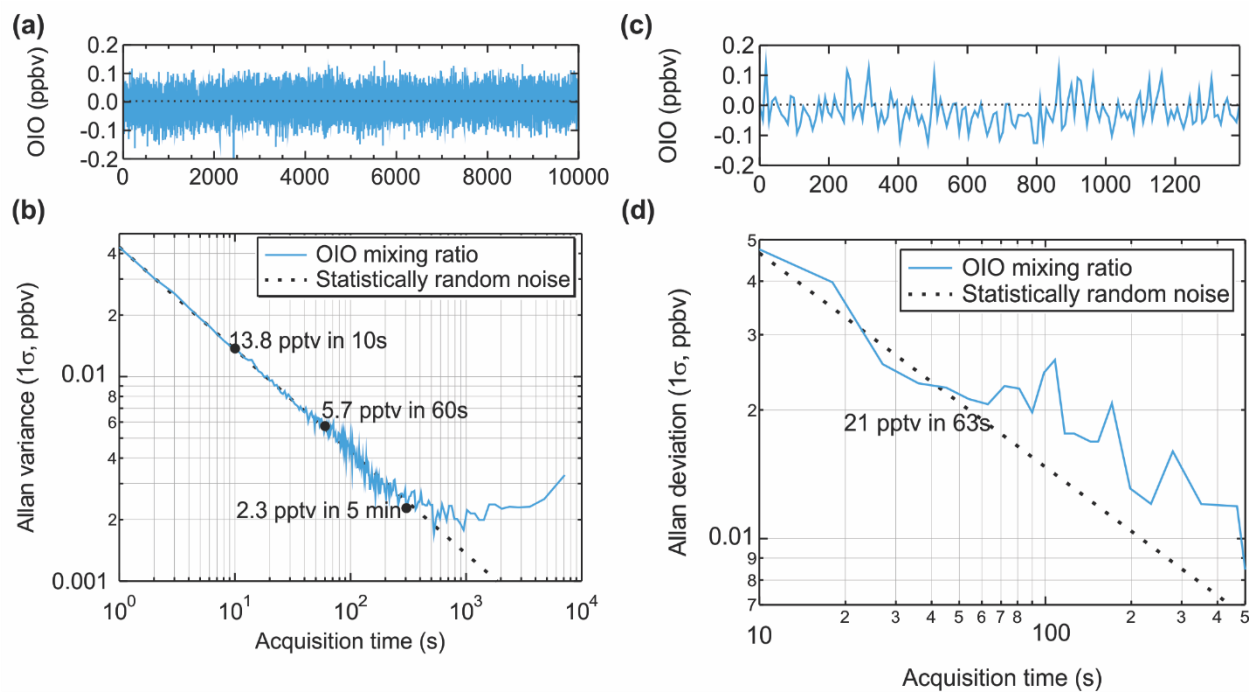


Figure S9 (left hand side) Data collected while the CEAS continuously sampled zero air in the laboratory at a sample cell pressure of 890 hPa, flow rate of 1.5 slpm, and at a temperature 298 K. **(a)** Time series of OIO mixing ratios. **(b)** Allan deviation plot of the above data. (right hand side) Data collected while the CEAS continuously sampled zero air during the ORCA campaign at a sample cell pressure of 467 hPa, flow rate of 5 slpm, and at a temperature 290 K. **(c)** Time series of OIO mixing ratios during ORCA. **(d)** Allan deviation plot of the above data.

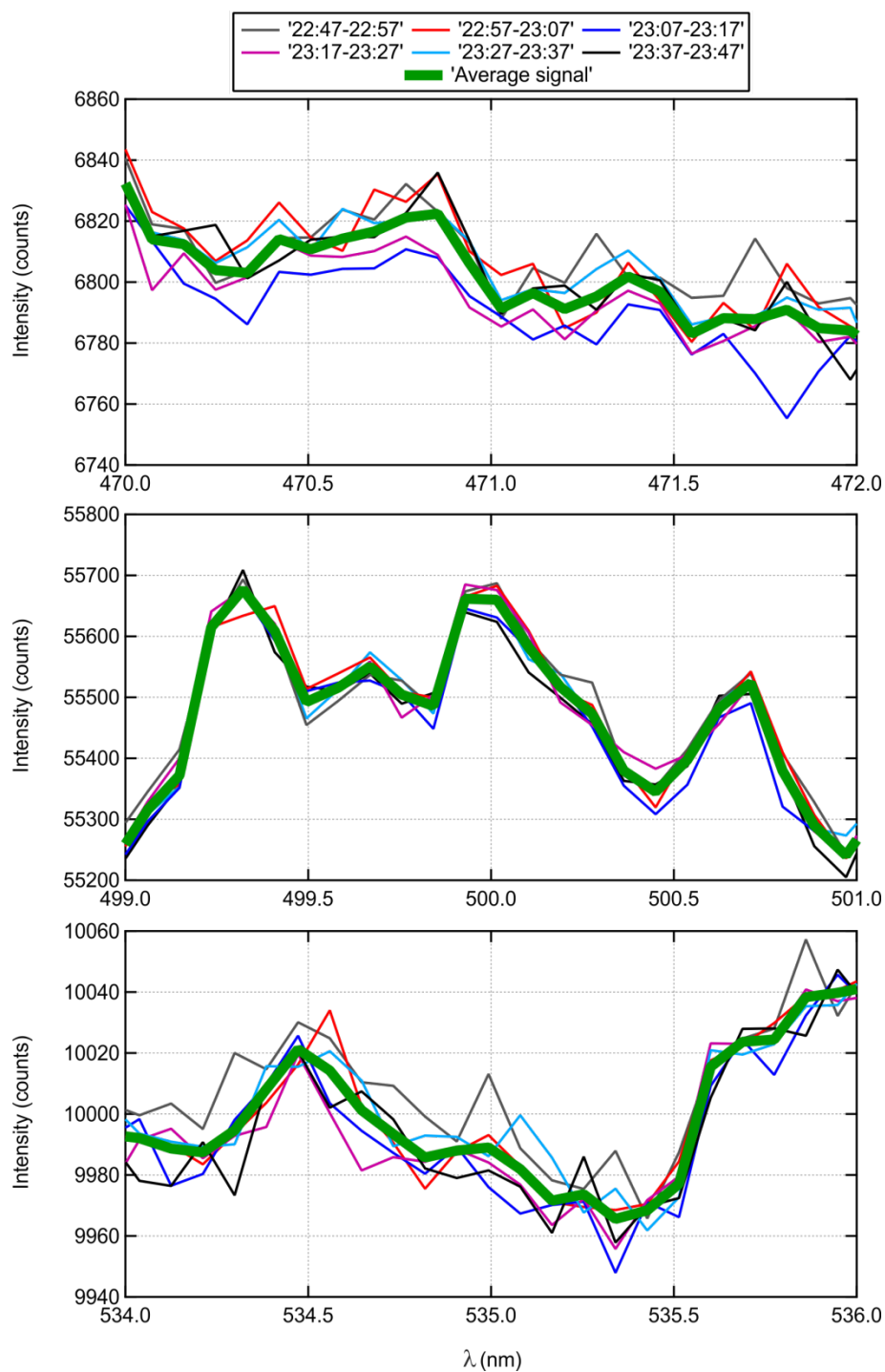


Figure S10 Intensity of light exiting a cavity filled with zero air. Three different wavelength regions within the emission spectrum of the LED (M505L3) operated at 30.0 ± 0.1 °C are shown. The stability of the emission profile was monitored over a 60 min interval with a LED warm up time of 30 min prior to measurements. Each trace represents a 10 min average while the thick green trace shows 60 min average.

References

- Greenblatt, G. D., Orlando, J. J., Burkholder, J. B., and Ravishankara, A. R.: Absorption Measurements of Oxygen Between 330 and 1140 nm, *J. Geophys. Res.*, 95, 18577–18582, 10.1029/JD095iD11p18577, 1990.
- Hermans, C., Vandaele, A. C., Carleer, M., Fally, S., Colin, R., Jenouvrier, A., Coquart, B., and Mérienne, M.-F.: Absorption cross-sections of atmospheric constituents: NO₂, O₂, and H₂O, *Environm. Sci. Poll. Res.*, 6, 151-158, 10.1007/bf02987620, 1999.
- Newnham, D. A., and Ballard, J.: Visible absorption cross sections and integrated absorption intensities of molecular oxygen (O₂ and O₄), *J. Geophys. Res.-Atmos.*, 103, 28801-28815, 10.1029/98JD02799, 1998.
- Savitzky, A., and Golay, M. J. E.: Smoothing and Differentiation of Data by Simplified Least Squares Procedures, *Anal. Chem.*, 36, 1627-1639, 10.1021/ac60214a047, 1964.
- Sneep, M., and Ubachs, W.: Direct measurement of the Rayleigh scattering cross section in various gases, *J. Quant. Spectrosc. Radiat. Transfer*, 92, 293-310, 10.1016/j.jqsrt.2004.07.025, 2005.
- Sneep, M., Ityaksov, D., Aben, I., Linnartz, H., and Ubachs, W.: Temperature-dependent cross sections of O₂-O₂ collision-induced absorption resonances at 477 and 577 nm, *J. Quant. Spectrosc. Radiat. Transf.*, 98, 405-424, 10.1016/j.jqsrt.2005.06.004, 2006.
- Spietz, P., Gómez Martín, J., and Burrows, J. P.: Effects of column density on I₂ spectroscopy and a determination of I₂ absorption cross section at 500 nm, *Atmos. Chem. Phys.*, 6, 2177-2191, 10.5194/acp-6-2177-2006, 2006.
- Thalman, R., and Volkamer, R.: Temperature dependent absorption cross-sections of O₂-O₂ collision pairs between 340 and 630 nm and at atmospherically relevant pressure, *Physical Chemistry Chemical Physics*, 15, 15371-15381, 10.1039/c3cp50968k, 2013.