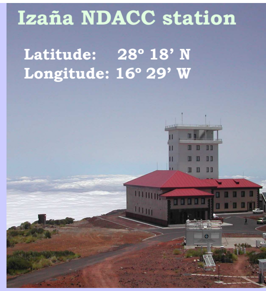

Detection of IO in subtropical Free Troposphere.

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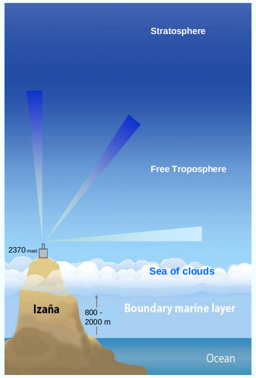
RASAS II spectrograph at Izaña Observatory

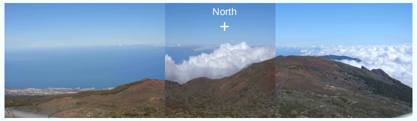


Izaña Observatory

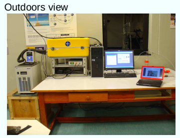
Izaña Observatory is located at 28ºN in the north-subtropical belt.

Vertical temperature profile around the station is dominated by the contrast of humid and cold trade winds in superficial layers and the general circulation of upper layers resulting in an strong thermal inversion below the height of the station. As result, pollution and most of the marine aerosols are trapped under the level of the observatory, keeping observations from Izaña unperturbed by marine boundary layer.

Panoramic of the pointing view of the instrument, the composition shows an irregular situation when sea of cloud is non-existing (except in the central and right picture). Usually, the height of sea of clouds ranges between 800 and 2000m.



Outdoors view



Indoors view

Instrumental settings

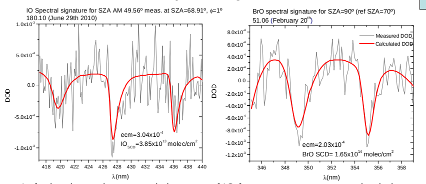
- Technique: UV-visible MAXDOAS
- Light input: Fused Silica fiber bundle.
- FOV: 1º
- Spectrograph: Andor Shamrock SR-163
- Grating: Holographic 1200 grooves/mm blazed at 300nm.
- Detector: Andor iDus.
- Detector temperature: - 40 ºC.
- Resolution: 0.6 nm FWHM.
- Spectral range: 400-515 nm.
- Oversampling factor: 8 nm/pixel
- Thermal regulation: ± 0.05ºC.
- Elevation angles: -1º, 0º, 1º, 2º, 3º, 5º, 10º, 30º, 70º and 90º.
- Azimuth angle= 0º (to North).

IO Retrieval

Settings for IO retrieval

- Spectral interval: 417-440 nm.
- IO: Spiezt et al. 2005, at 298K.
- Glyoxal: Volkamer et al. 2004, at 296K.
- H_2O: HITRAN.
- NO_2 XS: Van Daele et al.,1998, at 220 and 294 K. I0 corrected.
- O_3 XS: Bogumil et al., 2000, at 223 and 243 K. I0 corrected.
- O_4 XS: Greenblatt et al., 1990.
- Ring: Ratio of a high resolution solar (Kurucz) and Raman spectra (provided by IASB).
- Offset correction: Inverse of reference.

IO spectral signature

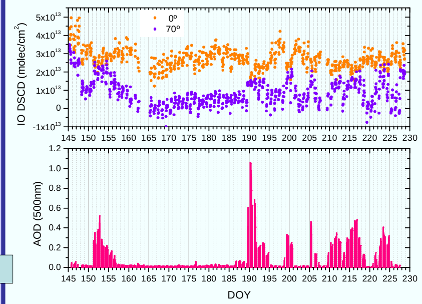


Left plot shows the spectral signature of IO for a spectrum measured pointing to horizon at SZA 70º analysed with a zenith reference at SZA 50º. IO DSCD is $3.85x10^{13}$ molec/cm^2 for an error fit of $3.0x10^{-4}$. For this particular case signal-to-noise ratio is 0.86. Right plot shows the spectral signature of another DOAS instrument measuring BrO, at the same location, as reference. For two zenith spectra at SZA 90º and 70º signal-to-noise ratio is 1.5.

Although the IO retrieval shows twice the noise than BrO one, the three bands of IO absorption between 415 and 440 nm are observed.

Day to day evolution based on 3 month of data.

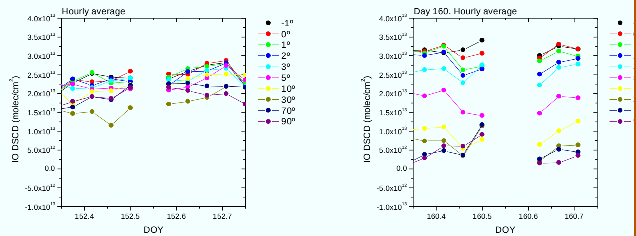
Spectra from the end of May to mid-August have been analysed using a single reference (day 180, SZA =49.56º). Differences between horizontal (0º) and 70º elevation geometries (upper plot) are reduced on Saharan event conditions due to changes in th path because of increasing of multiple scattering. Plot of cloud-screened Aerosol Optical Depth (AOD) at 500 nm obtained by AERONET-CIMEL photometer (lower plot) illustrates the optical conditions of the studied period, where values as large as 1 are observed.



Under these conditions uncertainties on th way make useless any attempt of inversion. Clear and clean days show a pe nearly constant DSCD density of 2. molec.cm^{-2}, with little day-to-day variation.

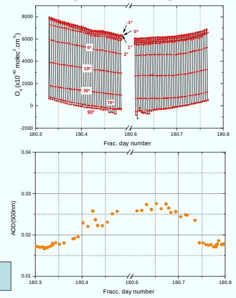
An example of dusty day (day 152, AOD=0.5 clean one (day 160, AOD=0.02) results elevation angles are shown. Data are avera every hour to reduce short term va

Further work has to be carried out to try to av difficulties of IO measurements encountered the dust conditions in order to detect if th concentration increases found recently ove during Saharan outbreaks (Williams et al., result in IO concentration increase.



Diurnal evolution of IO DSCD

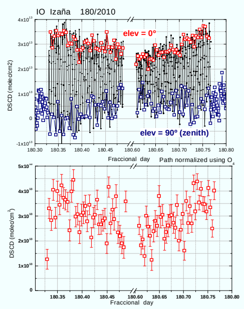
Optical characterization of atmosphere day 180 (June 29th 2010)



Aerosol optical depth diurnal evolution from AERONET at Izaña.

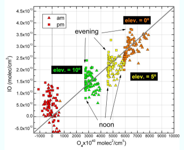
AOD remains all day at low values with slightly increase in the afternoon, also observed in O_4 DCSD (see upper plot).

Diurnal evolution of IO DSCD day 180 (June 29th 2010)



IO diurnal evolution has been normalised to a constant path by using O_4 data. Assuming that horizontal path (elevation=0º) is that of the level of the observatory, a minimum in IO is observed at noon. The same results have been observed by Friess et al. (2010) over Neumayer (Antarctica) in the MBL and has been attributed to reaction with HO_2 produced in the daytime by photolysis of O_3 and subsequent reaction with water (Martínez et al., 2010).

DSCD for day 180. Zenith measurements (blue circles) and horizontal (red circles)



IO increases linearly with O_2 indicating larger concentrations at lowest levels (probably from direct MBL ventilation or organic compound transformation in the Free Troposphere).

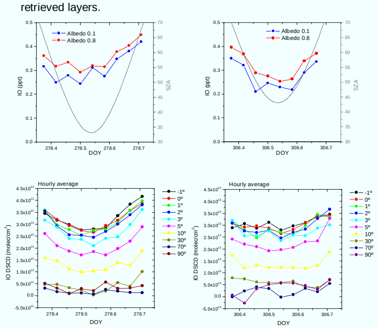
Vertical profile retrieval

A linear maximum a posteriori solution (Rodgers, 2000) is used to obtain a vertical profile:

$$\hat{\mathbf{x}} = \mathbf{x}_a + (\mathbf{K}^T \mathbf{S}_\varepsilon^{-1} \mathbf{K} + \mathbf{S}_a^{-1})^{-1}$$

Where $\mathbf{x_a}$ is a linear IO a priori profile from 0.2 ppt at 1 km linearly decreasing to 0.01 pptv at 5 km, $\mathbf{S_a}$ is the error covariance matrix for $\mathbf{x_a}$ and y are the DSCDs with error covariance $\mathbf{S_\varepsilon}$.

K is a weighting function matrix describing the sensitivity of the measurements to changes in the concentrations of IO in each of the retrieved layers.



K is determined using the NIMO full spherical Monte Carlo radiative transfer model. The model simulates backward photon trajectories from the instrument to the TOA and the photon radiances are adjusted for each measurement geometry by creating adjoint trajectories at each scattering location. An opaque cloud layer is simulated at 1km with an albedo of 0.1, and a linearly decreasing aerosol profile is used in the RT with an optical depth of 0.024 at 430nm. The retrieval was performed from 1-5 km with a layer height of 50 m.

Two plots at the top show vmr of IO for the retrieval layer at the height of the station for two selected days, 278 (October 5th) and 306 (November 2nd). Bottom plots show the measured IO DSCD hourly averaged for the same days.

For these particular days vmr ranges between 0.2 and 0.4 ppt. Similar results are obtained by estimating the optical path from direct O_4 measurements.

Diurnal variation for both days shows an "U" shape typical from places where chemical destruction (e.g. HO_2 + IO) of IO at midday dominates over its formation (Martínez et al., 2010).

References.

Friess et al., Atmos. Chem. Phys., 10, 2439-2456, 2010.

Martínez et al., Atmos. Chem. Phys., 10, 3759-3773, 2010.

Rodgers RC, Inverse methods for atmospheric soundings: Theory and practise. World Scientific Publishing, 2000.

Williams et al., JGR, vol 112, Do7302, doi:10.1029/2005/JD006702, 2007.

Acknowledgements.

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Summary and conclusions.

- A new MAXDOAS instrument operating in the visible has been settled at Izaña station in Febru 2010.
- Iodine monoxide has been unequivocally detected with a signal-to-noise ratio of 0.8-0.9 in the Subtropical Free Troposphere.
- Three months of measurements between May and August 2010 is shown. IO has been detecte everyday above the detection limit in the Free Troposphere.
- Clear and clean days show a persistent nearly constant DSCD density of $2.5x10^{13}$ molec.cm^{-2}, little day-to-day variation.
- Under Saharan dust conditions enhancement in multiple scattering perturbs the optical path di the measurements interpretation.
- Preliminary estimation of IO vmr in the Free Troposphere, using a linear maximum *a posteriori* to retrieve vertical profiles, ranges between 0.2 and 0.4 ppt at the height of the station.
- IO vmr diurnal variation shows an "U" shape with a minimum around noon problably related to chemistry. Same shape is observed in the DCSD norrmalised to a constant path using O_4 measurements.