**Atmospheric
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Interactive comment on "Iodine monoxide in the north subtropical free troposphere" *by* O. Puentedura et al.

Anonymous Referee #2

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The manuscript entitled 'Iodine monoxide in the north subtropical free troposphere' by Puentedura et al. describes the first measurements of the iodine monoxide (IO) radical in the free troposphere. Measurements are performed by MAX-DOAS, and the data are interpreted on the basis of radiative transfer modelling calculations. IO concentrations are estimated on the basis of a simple approach using O_4 as an indicator for the atmospheric light path.

Previous modelling studies have shown that halogen radicals potentially have a large impact on the chemical balance and the oxidative capacity of the free troposphere, even if they are present in very small amounts. Therefore the novel findings presented in this paper are of very high relevance for our understanding of atmospheric chemistry and the topic fits well in the scope of ACP. However, I have several concerns

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which are described in the general comments below and which should be addressed before considering a publication in ACP. In particular, the method for determination of the detection limits and the way the data are averaged requires substantial revision. Furthermore, the way the effect of clouds on the radiative transfer is treated in the model simulations is too simplistic.

General comments:

I would appreciate a more detailed presentation of related work and a more detailed discussion of the findings resulting from the measurements. The conclusions section mainly contains technical information, but no discussion on possible sources of IO in the free troposphere and its impact on photochemistry. IO, as well as many of its organic precursors, is a very short- lived substance, and it is believed that the presence of IO is restricted to the boundary layer since its lifetime is too short to reach higher altitudes. Therefore, the question how this reactive species can reach the free troposphere should be discussed on the basis of previously published studies. What are the sources and lifetimes of IO precursors, and is it possible that reactive iodine reaches the free troposphere? What are possible organic or inorganic mechanisms resulting in a production of reactive iodine? The results of Williams et al.

2007

are only mentioned briefly, but his findings regarding a possible inorganic release of iodocarbons from Saharan dust are of great relevance here. They strongly support the findings from the MAX-DOAS measurements and should be discussed in much more detail.

The methods for determination of the errors and detection limits of the spectral analysis of IO appear to be too optimistic. Prior to the analysis, the spectra were smoothed using a 4-pixel boxcar average, and the authors claim that this leads to a reduction in RMS error (P27839, L9ff). Indeed, the apparent reduction in RMS residual is about 55% if a 4 point boxcar average is applied to a normally distributed noise spectrum,

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while the smoothing leads to a reduction of the optical density of IO of only about 5%. Although the residuals look better, a smoothing neither leads to a reduction of the true spectral noise nor to an improvement of the true signal-to-noise ratio and the fit errors. Usually, the error in retrieved slant column density is determined by DOAS retrieval algorithms under the assumption that the error in intensity is independent for each pixel. This assumption does not hold if the spectra are smoothed prior to the analysis. Consequently, a correction factor needs to be applied to the fit errors and the detection limits in order to provide a realistic estimate of the true error. This is discussed in detail by Stutz and Platt [1996]. This correction needs to be applied to the measurements (alternatively, the spectra can be analysed without smoothing), and their significance needs to be re-assessed on the basis of a realistic estimate of the detection limits.

The estimation of IO mixing ratios and the subsequent discussions are mainly based on the daily averaged IO dSCD at $5°$ elevation angle which are shown in the middle panel of Fig. 3. For the averaging, all data below the detection limit has been excluded (P27842, L21f). This leads to an artificial increase in the average value, and means that the 'average' is automatically above the detection limit. For example, on day 162 all measurement except one at $5°$ elevation angle appears to be above 1×10^{13} molec/cm^2, but the 'average' of the DSCD is above 1.5×10^{13} molec/cm^2. From visual inspection of the data presented in Fig. 3, it seems that the true daily average is significantly below the reported values, since many hourly values at $5°$ elevation angle are very close to zero and were therefore omitted. Again, the question arises to which degree the measurements presented here are significant.

Radiative transfer modelling: If I understand it right, an opaque cloud cover with an albedo of 0.8 means that no light can penetrate the interior of the cloud and the atmosphere below. As a result, the box AMFs shown in Fig. 6 appear to be zero below the cloud top height. This is an unrealistic scenario, since a significant fraction of the light observed from above comes from inside the cloud, and it is well known that the light paths inside a cloud can become very long, resulting in an enhancement of the

airmass factor due to multiple scattering. Useful conclusions on the sensitivity inside and below the cloud can only be drawn if the optical properties of the cloud (optical density, phase function, etc.) are modelled realistically.

Specific comments:

P27835, L14: Regarding the measurements of Mahajan et al. (2010), it is not clear what is meant with 'local biogenic activity is supposed not to have an important impact'. Iodocarbon measurements show that biogenic emission of iodinated precursors from biogenic activity takes place (although it is insufficient to explain the measured IO concentrations), and it is concluded that other iodine compounds must be emitted from the ocean surface. It is not clear, if this missing source is of biological origin or not. Again, the introduction is too short and sources for iodine radicals and its impact on atmospheric chemistry should be explained in much more detail.

P27835, L24ff: The reference for Grossmann et al. (2011) is missing, and I was not able to get hold of this paper. If this should be unpublished data, please remove the paragraph.

P27835, L29: Reference for Butz et al. (2008) is missing.

Section 2: Specify the measurement period, which is mentioned later on several times in the manuscript.

P27836, L21f: 'A persistent sea of clouds...'; add 'at Tenerife' to the end of the sentence (otherwise one might think that the sea of clouds appears everywhere).

P27837, L4: I cannot see how molecules like CO_2 and H_2O are 'absorbed or destroyed'. CO_2 is a stable molecule. For water vapour, it is obvious that concentrations at higher altitudes are lower since (1) water vapour is removed by condensation in the cloud, and (2) at constant relative humidity, the water vapour concentration strongly depends on temperature.

Section 3.1: Specify the FOV of the instrument here. If I understand it right, there is

no real entrance optics but only a tube that leads to a very large FOV. Why isn't a lens used as entrance optics, which should limit to FOV to less than 1 degree as for most DOAS instruments?

P27837, L24: Specify where the dry nitrogen was pumped through (I guess the detector housing).

P27838, L19: Is there a practical reason why spectra are accumulated for the time required for the Sun to move from $90°$ to $90.2°$?

Section 5: The authors use a simple approach to determine IO concentrations from slant column density measurements of IO and O_4. I believe that this method is very useful, but its restrictions should be discussed: Equation (1) is strictly fulfilled only if the dSCDs of O_4 and IO are proportional to each other, which means that the vertical profiles IO and O_4 need to have the same shape (and thus the same total airmass factor).

P27842, L27: What is meant by 'extra absorption'?

P27843, L7ff: The definition of the MBLPI is difficult to understand. Please clarify. Is this a common meteorological quantity, and if so, can you provide references?

P27843, L21ff: This paragraph presents important conclusions and should therefore be moved to the Conclusions section.

P27843, L17ff: Again, IO concentrations can only be inferred from the comparison of O_4 and IO dSCDs if the IO vertical profile has the same shape as the O_4 profile. The conclusion that 'observed increases in the DSCDs must be due to larger IO concentrations' (L22) is therefore not necessarily true.

The Conclusions section is too short and far too technical. I would appreciate a discussion of possible sources of IO, its possible impact on the chemistry of the free troposphere and the question whether IO might be of importance in the FT on a global scale.

The last sentence of the conclusions is unclear. What is the 'previously proposed explanation of the existence of a mechanism that introduces significant amounts of IO precursors during such events'?

Technical corrections:

P28839, L25: Remove 'photon'.

P27840, L9, and P27841 L3: The measurement period is not mentioned anywhere in the manuscript. Specify, e.g., in Section 2.

P27840, L14: Replace 'in successive' with 'in the following denoted as'.

P27840, L19: '... up to 6-7 km with an AOD(500 nm) of up to 1...'

P27840, L21: '... increase in multiple scattering...'

P27842, L9: insert 'height' after 'observatory'.

P27842, L19: insert 'that' after 'ensure'.

P27842, L20: replace 'calculations of' with 'estimates of the'.

P27844, L4: O_4 is considered not to be an O_2 dimer, but rather an O_2 collision complex.

P27843, L15, and P27844, L17: replace 'Saharan events' with 'Saharan dust events' or 'Saharan dust outbreaks'.

Figure 3: Use the same colour for the $0°$ and $5°$ elevation angle in upper and middle panel.

Figure 4: Please add error bars to the IO dSCDs

References:

Stutz, J., and U. Platt, Numerical analysis and estimation of the statistical error of differential optical absorption spectroscopy measurements with least-squares methods, Appl. Opt., 35, 6041-6053, 1996.

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