

Interactive comment on “In situ detection of atomic and molecular iodine using resonance and off-resonance fluorescence by lamp excitation: ROFLEX” by J. C. Gómez Martín et al.

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We would like to thank both reviewers for their helpful and enriching comments that we address in detail below (comments are shown in bold, our response in normal typescript)

Report 1 (T. Hanisco)

This paper describes the design, calibration, and operation of a new instrument
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that detects atomic and molecular iodine using atomic resonance fluorescence and molecular fluorescence. The authors provide a very thorough and detailed description of the fluorescence detection technique including characteristics of the iodine lamp used to excite iodine atoms and molecular iodine. This section is especially informative and will be a valuable contribution to the scientific literature. The operation of the instrument including the calibration method that uses a combination of photolysis and broadband cavity ringdown is described completely and effectively. Overall, this is a well written paper that meets all of the requirements for publication. I recommend this paper for publication after these minor comments are addressed.

General comments:

It is not clear in the paper how the loss of I atoms on the wall of the flow tube or on the orifice affects the calibration and the measurement. There is a brief mention of the loss of I atoms on the smallest pinhole on page 3819 lines 1-3. The fact that I atom recombination is observed on the smallest pinhole suggests that the same process is occurring elsewhere in the system, on walls of tubing and solenoid valves, especially. This loss could be significant - from the drawing, there are lots of surfaces for this recombination to occur. Is it significant? What evidence do you have that this recombination is understood?

We thank the reviewer for this detailed comment. Actually, the manuscript is lacking a more thorough discussion of wall losses in the inlet. One third of the inlet is made by the 3 way solenoid PTFA valve (8 cm tube length), which is a very important piece of the instrument, since it enables shifting from background to direct sampling mode automatically using a programmed routine. Other techniques to acquire the iodine free background signal (e.g scavenging by an excess of reactant) present more complications than potential wall or chemical losses derived from a longer inlet.

Potential I and I₂ losses during calibration could result in the loss of sensitivity and/or over/underestimation of the sensitivity factors. Three scenarios can be considered:

1) I atoms and I₂ are lost in the walls. Then, the measurement of the photolysis efficiency $\Phi = \Delta_{\Phi}[I_2]/[I_2] = \Delta_{\Phi}S(I_2)/S(I_2)$ is not affected by I₂ wall losses. If wall losses stay constant between calibrations and field measurements, the implication would be a decreased sensitivity ($\gamma < 1$ in equations 1 and 2). But if losses were larger in the field (e.g. due to deposition of water and sea salt aerosol), the sensitivity obtained in the lab would overestimate that in the field.

2) I atoms recombine in the walls with unit I₂ yield. Since this process would depend on I atom concentration, it would be much slower at low I atom concentrations (e.g. ambient concentrations). This means that the γ factor for I₂ would be larger for calibrations, resulting in an overestimation of sensitivity towards I₂. The loss of I atoms in this process would not directly affect the calibration validity (scenario 1), but the decrease of the observed photolysis efficiency $\Phi = \Delta_{\Phi}S(I_2)/S(I_2)$ due to I₂ regeneration would imply an underestimation of the iodine atom concentration at the pinhole $[I] = 2\Phi[I_2] > 2\Phi_{obs}[I_2]$, and therefore an underestimation of the sensitivity factor C_I .

A noticeable dependence of $\Phi = \Delta_{\Phi}S(I_2)/S(I_2)$ on $[I_2]$ (i.e. of $[I]$) is expected if wall-assisted I atom recombination plays a role. However, $\Phi = \Delta_{\Phi}S(I_2)/S(I_2)$ is constant up to 10 ppb, when slight bending of the Φ curve is observed as recombination in the photolysis cell starts playing a role (since we measure Φ for every $[I_2]$, I atom recombination in the photolysis cell does not affect the measurements). To give an idea about the sensitivity of Φ towards $[I_2]$ through inlet recombination, we estimate that the inlet effective recombination rate coefficient should be as high as $1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to produce a 30% decrease of the observed Φ for 5 ppb of I atoms. For a recombination rate coefficient of $2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ the change of the $\Phi(5\text{ppb})$ value due to inlet recombination would stay within the observational error (10%).

On the other hand S_I vs. $[I] = 2\Phi[I_2]$ remains fairly linear in the range of concentrations considered. Therefore we are confident that I atom recombination on the inlet walls is not significant.

3) I atoms and I₂ are lost in the inlet walls, but some I atoms recombine (a mix of cases

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1 and 2). For atomic iodine wall losses imply only a sensitivity loss. Since the loss of I₂ in the walls could balance partially the wall-assisted I atom recombination, the observed $\Phi = \Delta_{\Phi}S(I_2)/S(I_2)$ would be more or less close to the real Φ depending on the ratio of the I₂ loss and I recombination rates. Note that in this case I₂ wall losses would be actually helping to reduce the biases of C_I and C_{I_2} , and that the constant Φ already rules out an important role of I atom recombination.

In order to estimate wall losses during calibration, two approaches can be used:

1) Vary the flow rate through the fluorescence cell in order to vary the residence time of the sample in the inlet. For a particular pinhole (diameter is fixed) this can only be done by changing the exhaust tube section using the throttle valve, and therefore implies a change in pressure in the cell. Pressure change implies an increase of gas density, fluorescence quenching and O₂ and I atom absorption. These processes can be modelled by introducing them explicitly in equation 2. Estimates for the wall loss rate and fluorescence quenching rate can be deduced by fitting to the experimental data shown in figure 4 (top panel). From this exercise a quenching rate coefficient of $4.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ and a wall loss rate of 9 s^{-1} are derived. The latter implies a loss of 17% of iodine atoms in the inlet. A similar modelling of the pressure dependence of the I₂ fluorescence signal (see Exton and Balla, 2004) gives a somewhat lower loss rate, although due to multi-wavelength excitation the uncertainties in the O₂ and I₂ cross sections make such estimate much more uncertain.

2) Perform calibrations with different inlet lengths and infer the wall loss rate from the difference in the sensitivity factors. We are currently doing these experiments with a range of inlet lengths and pinhole materials in order to maximize the γ values.

In order to account for and keep track of possible field-specific wall losses, the instrument is calibrated frequently in the field. We expect that the effects of potential changes in the nature of the inlet surface are accounted for in the variability of the calibration.

Even if the recombination has a small effect on the calibration, can you be sure

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that it also has a small effect in the measurement of I atoms in ambient air? What about the conversion of other iodine species (e.g. IO)? Are they converted to I or I₂ in the sample inlet?

The residence time of an air parcel in the inlet (20 ms) is way to short to allow any chemical losses of I by reaction with ambient trace gases (e.g. with itself, O₃, NOx) or recycling of I from the IO self reaction or BrO+IO.

Another concern that I have is the loss of I atoms to species other than molecular iodine. If any oxidizer is present (O, O₃, OH, etc) iodine oxides will be produced. These species are notorious for sticking to flow tube walls. In the calibration system, the use of the Xe lamp could easily produce these oxidizers, especially if there is UV light present. Is the lamp filtered? These species are not included in Equation 4. Do you have any evidence to support the absence of these species? If not, how big of an effect might you expect from their presence?

The photolysis lamp (LOT-ORIEL, 1000W, OF) has a very small output below 260 nm. The photodissociation thresholds for O₂ and H₂O are respectively 242 nm and 246 nm, and therefore potentially interfering concentrations of O₃ and/or OH are not expected.

Detailed comments:

p. 3807 In 4-12 and p. 3825 In 3 -12. The lamp self-absorption will also decrease the sensitivity of the 178 nm line. In fact, this could be a major part of the reason that the resonance fluorescence of I is so much less sensitive than Cl in your case. Have you tested to see if the 178 nm line is self-absorbed? I would expect that the fluorescence in Ar shown in Fig 3 would have a peak at a lower temperature than in air if the 178 nm line were not already self-absorbed.

We will improve the discussion about the lamp output by including some aspects of atomic emission which have not been taken into account in the manuscript.

The statistical weights (g) of the states involved and their relative population play a role in the apparent line intensity (Brown and Carrington, 1969). The 178 nm and 183 nm

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iodine lines originate in states of the same multiplet $5p^4(^3P_2)6s(^2[2]_J)$ with $J=3/2$ ($g=4$) and $J=5/2$ ($g=6$) respectively. Assuming equilibrium at the kinetic temperature of the gas ($T=900K$, Spietz et al, 2001), the relative population of the multiplet would be 1:15. This balances the ratio of oscillator strengths of 15:1 and brings the expected relative intensity (1) closer to the one observed (0.5) (note however that the assumption of thermal equilibrium is not necessarily appropriate in this context). This is in clear contrast to the chlorine case where: (a) the statistical weight of the state originating the strongest transition at 118 nm ($J=5/2$) is larger and (b) the energy splitting between the two spin-orbit levels in the $3s^23p^4(^1D)4s(^2D)$ state originating the 118 nm doublet is extremely small, and as a consequence the $J=5/2$ state is significantly populated at the temperature of the plasma ($T=800K$, Schwab and Anderson, 1980).

Figure 1, upper panel, shows that the 178 nm line intensity responds to SBT (vapour pressure) changes. The optimal SBT for the 178 nm line is close to the optimal SBT for the 183 nm line, for which the former is still weaker than the latter (ratio 0.5). When the optical thickness of the emitting and reabsorbing layers within the lamp is large, the relative intensities of the multiplet lines may differ from the theoretical values indicated above as a result of unavoidable self absorption (Brown and Carrington, 1969). Therefore our statement in p.3807, line 9, that self absorption is partly the reason for the weak 178 nm line observed is still valid, although for the optimal SBT it is not the only or major reason for it.

p. 3821 In 15-22. This is the first (and only?) mention of measurement uncertainty that I found. It should be expanded here or elsewhere in the paper. What is the relative error from these individual terms? What is the typical uncertainty in the calibration? Is an estimate of wall loss included?

The uncertainty in the I₂ calibration factor C_{I_2} is typically 17%, arising from the I₂ concentration uncertainty (16%) and the random error of the least squares calibration fit (5%). The uncertainty of the I₂ concentration measurement encompasses the uncertainties of mirror reflectivity calibration (3%), effective path length (8%), reference ab-

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sorption cross sections (12%) and linear least squares spectral fitting (6%). The error quoted in page for C_{I_2} was set to 2σ by mistake: it should be 0.8×10^{-9} . The most important contributions to uncertainty of the I atom calibration factor C_I (20%) are the uncertainty of C_{I_2} (17%) and of the I_2 photolysis efficiency measurement (10%), and the random error of the least squares calibration fit (4%). Inlet wall losses are not included in the estimated uncertainty, although from the discussion above we think they are not significant in calibration experiments. An uncertainty breakdown table will be included in the revised manuscript.

p. 3825 ln 8 – 14. Have you adjusted the pressure to show that it is the O_2 absorption that removes the 178 nm signal? If so, just state this. This paragraph is too wordy.

Also, the emission line at 178 nm is about 6 times weaker than the emission at 184 nm.

The paragraph must be re-written. The lamp used for recording the dispersed fluorescence spectrum in figure 1c, had a smaller 178/183 intensity ratio than the lamp whose emission spectrum is shown in figure 1a, for reasons related to state population and optical thickness of the reabsorbing layer inside the lamp, as discussed above. Therefore, the discussion in p 3825, lines 8-14 is unnecessary. We have done some experiments using N_2 as carrier gas, but besides an overall increase of fluorescence we could not discern an increase of the 178 nm line intensity relative to that of the 183 nm. Another aspect to this is that although optimal SBT for the 183 nm line is not far from the 178 nm optimal SBT, the overlap between the emitter and absorber line at 178 nm may be not optimal.

Miscellaneous: You might be interested to know about similar detection method for Cl and Cl₂: Wilmouth et al, J. Phys. Chem., 2009.

This reference was included in an early draft of the paper. We removed the text where the reference was inserted for concision. We will consider including it again in the

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manuscript.

I_2 adsorbed on molecular sieves provides a low vapor pressure source for I atom resonance lamps. It can operate above 300 K without running the lamp deep.

We thank the reviewer for this suggestion.

Typos:

p3825 ln 3; 2825 ln 14; 3827 ln 7; Table 1 the superscript “g” should be “h”

Fig. 1 is too small. It has a lot of good information, but it is hard to read. Consider splitting it into two figures.

Fig. 2. Indicate where the sample intake is.

These comments will be addressed.

Report 2 (Anonymous Referee)

General Comments:

This manuscript describes the design and performance of a new instrument to make in situ measurements of atomic and molecular iodine. The instrument design is focused in particular on observations in the marine boundary layer. In general, the paper is well written, thorough and contains a significant amount of detailed information about the technique, its development and implementation. The content of the manuscript seems entirely appropriate for publication in AMT and I recommend publication after the authors address the comments below.

Specific Comments:

p. 3805-6: The discussion of previous uses of resonance fluorescence for detection of atmospheric halogen species seems to imply an analogy between the measurements of Cl and Br and that of I. To my knowledge, there have been no measurements of ambient halogen atoms in the troposphere; those reported in

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the literature were for observations made in the middle stratosphere [Anderson et al., 1977 and Anderson et al., 1980].

As the reviewer says, we are implying such analogy, since the techniques are closely related, but we are not saying that Cl or Br atoms have been measured in the troposphere. However Bale et al. (2008) did measure 20 ppt of atomic iodine in the MBL. We will reword this paragraph to avoid misunderstanding.

p. 3807 and Figure 1: There has been considerable work done in the past on the effects of self-absorption in atomic resonance light sources. I recommend that the authors look at the work of, for example, Linevsky and deHaas (J. Chem. Phys., 77, 6060, 1982) and Braun and Carrington (J. Quant. Spectrosc. Radiat. Transfer, 9, 1133, 1969). These authors discuss the theoretical basis of self-absorption and also provide a framework for characterizing it. In particular, I am concerned that the authors are using a lamp temperature of 243 K for their calculations. This may be the external temperature of the lamp, but it is not likely to be the temperature of the emitters within the lamp, so the Doppler width and overlap with the absorbers in the flow system will be incorrect.

Our study does not attempt to characterise self absorption of lines inside the iodine light source. Note that SBT=243 K is the temperature of the spot contact between the Peltier element and the side branch of the lamp, and not the emission temperature of the source, which was estimated by Spietz et al. (2001) to be around 900 K for a similar iodine RF system. The only purpose of the cold point contact is controlling the I₂ vapor pressure inside the lamp. Emission temperature is not used in any calculation. Calculated line shapes are not required. The system is optimised empirically (Fig 3) by finding the optimum SBT (as a proxy of vapour pressure of the emitter inside the lamp), i.e a compromise between emitter density and self absorption inside the lamp, such that the overlap with the absorption line in the fluorescence chamber is maximized. On the other hand, sensitivities are determined empirically using a photochemical calibration technique (p. 3808, lines 1-4).

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We will try to adequate the terminology employed in the text to the existing theoretical framework, as suggested by the reviewer.

Figure 1, panel b: There are quite large differences among the three I₂ absorption cross-sections shown here. What are the implications of those differences for the measurement technique?

There are no implications of discrepancies between the I₂ cross sections. The cross sections are displayed only to better illustrate the absorption stage of the molecular fluorescence technique. For instance, the increase in SBT implies a decrease of the intensity of the 183 nm line and an increase of the intensity of the 206 nm line. However, the I₂ cross section at 206 nm is small and therefore the increase of the intensity of the atomic line at this wavelength may not compensate the intensity decrease at 183 nm. In fact, figure 2 shows that I₂ fluorescence starts decreasing at 270K. Thus, relative I₂ absorption cross sections are used to calculate normalised I₂ absorption factors (see equation 2) and to compare them to the integrated dispersed fluorescence collected by using a spectrometer +CCD system (figure 1C) and the I₂ fluorescence collected by the ROFLEX detector (comparison is displayed in figure 3, bottom panel). But again these semi-quantitative comparisons are presented just for illustration of the principles in which the technique is based. Since the display of the three literature cross sections is unnecessary and does not contribute neither to the understanding of the method nor to the calculations, we will consider showing just one of them.

p. 3808: Can the atomic I lamp photolyze I₂?

No. Even assuming that the lamp integrated irradiance is equal to the radiofrequency discharge power (21W), and that the entire output of the lamp is collimated towards the fluorescence chamber, considering that the residence time of an I₂ molecule within the lamp beam would be of the order of 10 ms, the I₂ photolysed fraction would be below 1%. This conservative upper limit would imply 2 ppt of iodine for every ppb of I₂, which is negligible compared to the 200-500 ppt of I from the photolysis of 1 ppb I₂ in

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the calibration cell.

p. 3810: Is it more advantageous to keep the I atom resonance axis at a vacuum (via pump) than to purge it with some gas (such as N₂ or Ar)?

Yes. As long as access to electricity is granted, it is more convenient carrying a small pump than having to carry a cylinder of purging gas, which would have to frequently be replaced by a new cylinder.

p. 3814: I am not clear on the procedure for calibrating the absorption path reduction. How well can this be done? That is, the authors quote a reduction of 14%, but how well is that value known?

After a measurement of the I₂ concentration carried by the main flow through the cavity, the mirror purging flow (600 sccm on each side) was shut and the main flow was slightly increased to compensate for that. Then the I₂ concentration was measured again. This procedure was repeated several times in order to account for any I₂ or lamp drifts by reference interpolation. The ratio of the concentrations derived with and without purging flow is the path reduction factor quoted in the paper, which has an uncertainty of about 8%.

p. 3820: The calibrations described here are carried out at very large mixing ratios compared to those measured in the atmosphere. How have the authors established that these calibrations are linear and absolute?

The minimum mixing ratio that could be reached with this set up was 300 ppt. This concentration was actually reached with the I₂ trap closed, just from wall degassing after previous experiments where larger mixing ratios were obtained by passing a flow between 0.1 and 3 sccm through the I₂ reservoir and diluting it in 10 slm of synthetic air. I₂ is extremely sticky, and all surfaces get covered with it. After shutting the I₂ reservoir walls keep degassing slowly for hours. 300 ppt are admittedly not very frequent in the atmosphere, but we have detected up to 350 ppt of I₂ in a recent campaign (see

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section 4.4 and figure 11) Also, a recent paper (Huang et al, 2009) reports similarly high I₂ mixing ratios in Mweenish Bay near Mace Head (Ireland). I₂ calibrations are linear over more than 2 orders of magnitude and intercepts are close to zero, so there is no reason to think that linearity does not hold for the low concentration range.

The smallest mixing ratio of atomic iodine considered was 100 ppt, about one order of magnitude larger than expected in the coastal MBL. Admittedly, lower mixing ratios could have been reached by reducing the photolysis beam using an iris, especially in view of the enhanced sensitivities obtained in recent optimisation experiments (see above). However, lower photolysis efficiencies also imply larger uncertainties. In view of the linearity of atomic iodine calibrations over 2 order of magnitudes and the zero intercepts, we believe the calibrations can be safely used in the atmospheric range of mixing ratios.

p. 3824, lines 14-17: It would seem that the differences in optimal pressure are related to the use of different atomic lines whose line broadening characteristics vary.

This paragraph will need rewording, since we do not have an explanation for the discrepancy with Bale et al. (2008) about the optimal pressure for I atom detection. We mentioned the use of the interference filter in p 3824 implying what the reviewer is saying. However, both emission (lamp) and absorption (sample) line profiles are Doppler-dominated, with Lorentz widths smaller by one order of magnitude in both cases. A pressure change in the range 10-100 Torr is not expected to make a significant difference in line shape. In addition, it is likely that the output of the microwave lamp employed by Bale et al showed a line intensity ratio 183/178 similar to the one observed in our lamps and in other studies (Hikida et al., 1983; Loewenstein and Anderson, 1985; Aleksandrov et al., 1985, NIST atomic spectra database) due to the characteristics of the 5p⁴(³P₂)6s (²[2]_J) multiplet.

A simple de-excitation model, combined with O₂ absorption of excitation and fluoresced radiation, shows that the pressure dependence of the fluorescence signal observed by

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our instrument between 10 and 100 Torr, with a broad maximum around 70 Torr (figure 4), is consistent with a quenching rate coefficient of $4.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for air, whereas the quenching rate coefficient should be $1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ to obtain a fluorescence maximum at 20 Torr as reported by Bale et al. (2008) This suggests that Bale et al. could have had an I atom loss at higher pressures.

p. 3824, lines 18-19: Note that there may only be one prior in situ measurement for BrO (not Br atoms), but there are numerous observations of tropospheric and boundary layer BrO made by DOAS. Also, there is recent work by Greg Huey at Georgia Institute of Technology to use CIMS for measuring BrO (in situ) from airborne platforms.

This sentence must be re-worded. As it is, it seems to imply that Avallone's instrument was designed for Br atom detection and that it was the only existing device capable of BrO detection in the MBL. What we meant is that Avallone's instrument is the only previous in situ device for BrO detection in the boundary layer. Of course, there are many other observations of BrO in the boundary layer, but the only device related and comparable to ROFLEX from a technical point of view is the resonance fluorescence instrument developed by Avallone et al.

The instrument of Avallone et al. was indeed designed only for BrO. Addition of NO to the sampled air resulted in nearly stoichiometric generation from the ambient BrO of Br atoms, which are then subsequently detected by resonance fluorescence. The instrument would have been able in principle of measuring ambient Br atoms as well, if a method for removing the background Br atoms would have been implemented. But in any case the instrument of Avallone et al. detects Br atoms by fluorescence, and therefore a comparison to our I atom fluorescence detection technique can be done.

Section 5.2: While I think it is useful to talk about the potential importance of interferences in a measurement, I think this section is unnecessary. In section 4.2, the authors state that they have found no interference from water vapor or nitrogen oxides. Why then spend more than two pages discussing the theoretical

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background of how these species might interfere?

Section 5.3: This section also seems redundant with information presented earlier in the manuscript.

We will consider reducing these sections and removing any redundant information.

Figure 8: In the manuscript text, the authors note the size of their background signals (a few hundred counts each for I and I₂). So, how in the calibration procedure can the signals be zero (or even negative) at zero concentration of I (and I₂)?

Figure 8 shows plots of background corrected signal $S = S_T - S_b$ (i.e. only fluorescence, see eq. 6) vs. mixing ratio for I₂ and I (upper and lower panel respectively). Therefore, the intercept is zero or close to zero, and not close to the background count rate S_b . Missing subscript T in S in the first two lines of section 4.3. (page 18) may have contributed to this confusion. In any case, we have not observed negative signals after background correction.

Technical Comments:

p. 3804, line 17 – write out “marine boundary layer (MBL)”, since this is the first time the term is used.

p. 3805, lines 8-9 – this sentence is awkwardly written and the meaning is not very clear.

p. 3805, lines 26-28 – this sentence is redundant with information given earlier in the paragraph.

p. 3806, line 2 – the phrase “for the detection of atomic iodine” is redundant and can be removed.

p. 3810, line 13 – “below” not “bellow”

p. 3818, line 5 – I am not sure what the “factor of 4 increase” relates to

p. 3818, line 8 – “major” not “mayor”

p. 3822, line 19 – “major” not “mayor”

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p. 3825, line 3 – “below” not “bellow”

p. 3825, line 13 – no “d” on Schumann

p. 3829, line 5 – “major” not “mayor”

Figure 3: write out “SBT” in this caption

Figure 4: The figure caption and the labels on the top panel do not seem to agree.

Figure 10: It is difficult to discern which line is meant by the “thick line” – in my copy, it looks like the spectrum for the old lamp is thicker than for the new one.

Table 1: The final footnote should be “h” not “g”.

All these minor corrections will be addressed.

Table 1: The Br atom reference here should probably be to Brune et al., 1989, where the RF technique was first described.

To our knowledge, the RF technique for Br was reported for the first time by Brune and Anderson in 1986, although there may be an earlier paper by the same group of which we are not aware. The Br reference in table 1 has been chosen on purpose, since the intention was not compiling references reporting a first detection, but referring to a few relatively recent papers where all the parameters included in the table are explicitly reported. We will try to make this clearer for the reader.

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 3803, 2010.