Response to Reviewers for "Absolute ozone absorption cross section in the Huggins Chappuis minimum (350– 470 nm) at 296 K" by J. L. Axson
acp-2011-0457

Anonymous Referee #2

We thank the reviewer for useful comments on the manuscript. Listed below are our responses to the comments and the corresponding changes made to the revised manuscript. All page and line numbers refer to the original ACPD manuscript.

- However, the evaluation of the overall uncertainty of their spectrum does not properly combine each contribution to the overall uncertainty, which I would expect to be slightly worse than the stated 2% accuracy in the abstract. The 2% value seems to be based solely on the uncertainty in the O3 concentration (the x-axis of Fig. 5, say): it is not clear what the uncertainty in the extinction coefficient on the y-axis is (3% from the Rayleigh cross-sections? 3% from the repeatability of the calibration? or a combination of the two?), nor how it is combined with the statistical uncertainty of the linear regression (3%, but at wavelengths where the spectrometer would be most sensitive). Each of these uncertainties contributes to the overall uncertainty of the spectrum. It would therefore be helpful for the paper to include an explicit analysis of the overall uncertainty of the cross-section, and to give some indication of the spectral dependence of this uncertainty.

The reviewer has raised an excellent point. We have added a calculation of the precision near the minimum. We have added an explicit calculation of the accuracy. We have added a second calculation of the accuracy based on the discrepancy in overlapping cavity regions. Because the second calculation indicates a poorer accuracy, we have subsequently changed the uncertainty in the abstract.

P. 21664 lines 20 – 24: "[deleted: From the linear fits and standard deviations shown in Fig. 5, we determined a maximum precision of 3% for our O_3 cross sections, although this varies with wavelength because the signal to noise varies with wavelength due to changes in LED intensity and cavity transmission. The 365 nm and 405 nm spectra converge at 384 nm, a region where, as Fig. 2 shows, each channel has somewhat worse signal to noise and where there is only a small region of overlap. Thus, we have the least confidence over this range because of the lower signal to noise in the spectra. The overlap between the two channels spans a small, 1.7 nm region, from 383.4 nm to 385.1 nm.]

From the slope and slope uncertainty in Fig. 5, we calculate precisions of 2.3, 0.7, and 0.5% respectively. Similar linear fits for spectra acquired with the 365 nm channel at 380 nm and 390 nm near the absorption minimum, have precisions of 3.1% and 2.4%, respectively. The absolute accuracy is calculated to be 4% from quadrature addition of the uncertainties in the reflectivity (±3%), O3 concentration (±2%), pressure (±0.5%), and temperature (±0.7%). However, the absolute accuracy can also be evaluated by comparing the cross section differences where the averaged spectral channels overlap. At 386 – 387 nm, near the minimum, observed discrepancies of 1 – 2 × 10^{-24} cm^2 between the 365 nm channel and two 405 nm channels are equivalent to an absolute accuracy of ~30%, but this improves to less than 5% at 395 – 424 nm for the two 405 nm channel measurements, and is 3 – 10% at 424 – 442 nm in the overlap between the 405 nm and 455 nm channels."

P. 21656, line 6: "*The accuracy of the measured cross section is* [deleted: 2] *4 – 30%, with the greatest uncertainty near the minimum.*"

- The FWHM of the Hg calibration lines almost doubles in going from 350 nm (0.27 nm) to 430 nm (0.51 nm). What is the reason for this change in resolution? Are calibration lines (from the Hg/Ar calibration lamp?) actually double or multiple peaks at longer wavelengths, or does the resolution vary in different imaging planes in the spectrometer?

The Hg/Ar lines that we selected for the wavelength calibration are all discrete, narrow electronic transitions. The reviewer is correct that the resolution changes with wavelength because we are using an imaging spectrometer, which images the entrance slit onto the focal plane of the CCD. This is different from the plane grating spectrometers that are typically used for DOAS. We have modified the text:

P. 21659 line 29 – p. 21660 line 2: "*Because the experiment used an imaging spectrometer to image the input light onto the CCD,* the FWHM increased linearly with wavelength (but is constant in frequency space) for the two wavelength determinations."

•The flow rate through the cavity was quite fast (1.0 LPM): was there any evidence of turbulence effects on the spectra? How long did the system take to arrive at a new equilibrium intensity after switching gases, and was this accounted for in the measurement procedure?

We did not observe turbulence effects during the experiments. We have calculated the Reynolds number in the cavities and added the following text:

P. 21661, line 11: "*The experiment was not affected by turbulence because the flow was laminar with a calculated Reynolds number of 13 (1.5 slpm of He in a 2.2 cm diameter tube), and because He has a small refractive index which would minimize any optical affects due to turbulence.*"

•Although there is a balance between optical pathlength and intensity throughput, it is not the case that a sensitivity increase is obtained only for bright sources (p.21657, ll.25-26). When the light source is weak or the cavity finesse is high, the sensitivity of the instrument will be shot-noise limited; nevertheless, even in the shot-noise limited case, the optical cavity still provides a (more modest) improvement over the single-pass absorption measurement (Fiedler et al., Rev Sci. Instrum., 78, 073104, 2007).

We have modified this sentence:

P. 21657, line 24 – 26: "This increased optical path length is balanced by a reduction in intensity throughput, such that the *greatest* sensitivity increase is [deleted: only] realized for [deleted: sufficiently] bright input light sources."

•The precision is stated at the wavelengths close to the centre of each of the cavities and near the LED emission maximum (cf. Fig. 5). However, the most uncertain part of the spectrum (p.12664-5), and the one that diverges most from the Brion spectrum, is around the absorption minimum where the LED output and mirror reflectivities are also markedly lower. What is the overall uncertainty in this region of the spectrum?

Please refer to the response above.

•Despite the difficulty of making it legible in the spectrum, the recent IBBCEAS spectrum of Chen & Venables should be included in Fig. 4 as it strengthens the evidence that the O3 absorption is particularly weak in the Huggins-Chappuis minimum.

We have obtained the Chen and Venables (2011) data and included it in Fig. 4.

• p.21660, l.20: Should be "sccm"

We have changed this.

• p.21660, l.24: "produce"

We have changed this.

p.21660, ll.23-26: Rearrange sentence: the mixing ratio is not a concentration, but could be included in parentheses. The concentration should be stated in molecules cm-3.

P. 21660, lines 22 - 26 now reads: “The O_3 concentration was diluted by a controlled flow of 1.5 standard L min^{-1} (SLPM) of He via a second mass flow controller (Alicat Scientific, MC-5SLPM-D-DB15/5m) to produce O_3 concentration in the range of 1.2×10^{15} – 2.4×10^{16} molecules cm^{-3} (58 – 1178 parts per million (ppm)).”

•p.21661, l.4: omit “easily”. O4 absorption is only likely to be easily measured if the spectrometer is extremely sensitive or if the O2 partial pressure is exceptionally high (tens of bars, as in Greenblat et al.), which is not the case with most prior measurements of the O3 spectrum. (The authors’ precautions are warranted with their spectrometer, of course.)

We have edited this sentence:

P. 21661, lines 2 – 4: “Zero air and O_2 were avoided as bath gases due to the formation of O_4 *(Greenblatt et al., 1990)*, which is observable *with the IBBCEAS instrument* in the 350 – 470 nm region [deleted: (Greenblatt et al., 1990)].”

•p.21661, l.22-24: The symbol “l” (el) for length is indistinguishable from “I” for intensity in the ACPD font. “L” or “d” (as in Eq. (2)) would be preferable.

P. 21661, lines 22 - 24: The symbol for length in Eq. (1) is now d, the same as in Eq. (2)

•p.21663, ll.11-15: Awkward sentence. Rephrase.

P. 21663, lines 11 - 15: The sentence was separated into two sentences and now reads “This accuracy is based on the ±3% accuracy of the Rayleigh N_2 cross sections compared to the measured values (Naus et al., 2000; Sneep et al., 2005) and the 3% repeatability of successive reflectivity measurements. The uncertainty of the Rayleigh scattering cross section for He is similar, but makes a minor contribution to the total uncertainty.”

• p.21666, l.16: “nonlinear” or “non-linear”

We have changed this.

• p.21669, l.12: “O(1D)”

We have changed this.

• Text in Figures 1 and 4 is too small to be readily legible and should be increased.

We had prepared Figures 1 and 4 to span two columns, but they were shrunk by ACPD. We will ask that they appear at the intended larger size in the final proofs.

• Caption: Fig. 1(a): “Also included : : :photodiode”. There is no ozone generator in (a)! Omit sentence or include in figure.

We have edited the caption for Fig. 1(a): “Figure 1. (a) Schematic of the three channel IBBCEAS consisting of LED light sources, optical cavities, and a CCD detector. [deleted: Also included is the O_3 generator consisting of Hg light source and GaP photodiode.]”

• Punctuation: a. p. 21656, l.11: Incorrect? I suggest “investigated; however,” or “investigated, but" b. p.21660, l.16: add comma after 295.8 K c. p.2661, l.14: “254 nm that” d. p.21662, l.19: Incorrect commas e. p.21662, l.26: “reflectivity or, alternatively”

a) P. 21656, l.11: I believe it is the correctly used here.

b) P. 21660, l.16 now reads: "A thermocouple monitored the temperature, which ranged from 295.1 – 295.8 K, and a transducer (Honeywell, PPT0015AXN5V) monitored pressure, which ranged from 820.7 – 830.8 hPa."

c) P. 2661, l.14 now reads: "O_3 concentrations were measured simultaneously at the same acquisition rate as the IBBCEAS spectral measurements using a single-pass absorption measurement at 254 nm *that* consisted of a 10.6 cm glass cell with quartz windows, a mercury penray lamp (UVP 90-0012-01), and gallium phosphide (GaP) photodiode detector (Thorlabs SM05PD7A) with a 254 nm band pass filter (Fig. 1b)."

d) P. 21662, l.19 now reads: "These optical extinctions are more than five orders of magnitude smaller than those that would be observed for O_3 at the same concentration and therefore, any O_4 interferences were considered negligible."

e) P. 21662, l.26 now reads: "Absolute measurement of optical extinction by IBBCEAS requires calibration of the mirror reflectivity, or alternatively total cavity loss."