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 #1

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.

• I did not find the rationale for the study, as presented in the introduction and briefly summarized in the conclusions, to be especially compelling. Perhaps the authors can provide a more complete discussion of why further measurements are needed to improve on the existing literature. I concede that there are discrepancies in the published absorption cross sections for ozone in this region, but are the discrepancies at a level that matters for atmospheric applications in a region of such weak absorption? The introductory paragraph mentions that weak UV absorption features can matter for tropospheric radical production, but the latest JPL-NASA tables [1] do not consider O(1D) quantum yields from ozone photolysis at wavelengths longer than 328 nm, and it seems unlikely that O(1D) formation will extend as far as 360 nm with any significant quantum yield. Are the cross sections in the region studied in this paper used in any satellite retrievals of ozone profiles? If so, the measurement of the temperature dependence of the absorption cross sections would appear to be an important next step in this study, as is hinted in the conclusions.

The reviewer has raised a good point. The introduction did not justify the practical need for accurate measurements of the weak O_3 absorption cross-section. We have added the following text to address this concern:

P. 21657 line 4: "*Measurement of the weak O_3 absorption cross-section has practical importance for two reasons. First, satellites use the adjoining Huggins and Chappuis bands for direct retrievals of O_3, relying on the strongly varying differential cross-section (see Kroon et al. (2011) and references therein). Second, quantifying weak O_3 absorptions is necessary for satellite retrievals of other trace gases in this spectral region. For example, at 404 nm O_3 and NO_2 cross-sections have been previously reported to be 1.49×10^{-23} molecules^{-1} cm^2 (Fuchs et al., 2009) and 5.9×10^{-19} cm^2 (Voigt et al., 2002). For an O_3 column abundance of 8×10^{18} molecules cm^{-2} (~300 Dobson units) and an NO_2 column abundance of 4×10^{15} molecules cm^{-2} (Burrows et al. 1999), the optical extinctions of the two molecules are 1×10^{-4} and 2×10^{-3}, respectively, and the O_3 extinction is both structured and significant (5% at 404 nm) in comparison to that of NO_2. Furthermore, literature cross sections at 404 nm vary from 1.5×10^{-23} to 7×10^{-23} cm^2 molecule^{-1}, or 5 to 30% of the NO_2 column extinction for these conditions. More accurate O_3 measurements are therefore required across its absorption minimum."*

• The reference on page 21659 to "effective path lengths (i.e. e-1)" may be cryptic to those not familiar with CEAS spectroscopy methods and could be spelled out more clearly.

We have clarified the definition of effective path length in the text:

P. 21659 line 5 – 7: "*In cavity enhanced absorption spectroscopy, the effective path length can be defined as equal to an e^{-1} decay of light from the cavity. From this definition,* the corresponding effective path lengths [deleted: (i.e. e-1)] were 4.0 km, 17 km, and 14 km respectively, when the *three* cavities contained pure helium (He)."

• I did not follow the exact meaning of the discussion on page 21665 of the comparison between spectra from the 405-nm cavity: specifically, what is meant by "the two wavelengths were interpolated"?

We had intended to explain that the spectra were interpolated to the same wavelength scale before averaging. However, we agree with the reviewer that this sentence is confusing. We have edited the paragraph:

P. 21665 lines 9 – 14: [deleted: To average t] *T*he two sets of 405 nm spectra over the region from 380 nm to 427.9 nm *were averaged* [deleted:, the two wavelengths were interpolated]. [deleted: This left out a portion of the 405 nm spectra from 427.9 nm to 441.3 nm.] To obtain the full spectral coverage from 380 – 441.3 nm, the difference in the spectrum from 380 nm to 427.9 nm and the spectrum from 427.9 nm to 441.3 nm, was added to the latter to account for the averaging."

• How significant was the difference between the spectra obtained from 380-427.9 nm and 427.9-441.3 nm that was used as a correction to the latter (page 21665)?

The difference was 1.55×10^{-24} cm^2 or 2% difference, which is within the error range of the spectrum.

• In figure 4, there appears to be a small wavelength offset between the structured features reported in the Brion (1998) and the current spectra. Can the authors comment further on the accuracy of the wavelength scales for the two studies?

The reviewer has raised a useful point. We have examined the uncertainty in our wavelength calibrations and modified the text. In addition, we have changed the manuscript to state vacuum wavelengths throughout, both for our analysis and the literature:

P. 21659 lines 27- 28: The wavelength calibration of the spectrometer was determined using an Hg/Ar calibration lamp with [deleted: lines at 334.15, 404.66, 407.78, and 435.83] *vacuum wavelengths of 334.24, 404.77, 407.90, and 435.96* nm (*Sansonetti et al., 1996), and is accurate within 0.5 nm.*

To ensure the accuracy of the comparison, we have reviewed the spectra that we obtained from the Mainz Spectral Database. Brion et al. 1998 states a wavelength uncertainty of 0.1 – 0.7% at 350 – 420 nm. This corresponds to an uncertainty of 0.4 – 2.8 nm at 400 nm. The paper does not specify whether the spectra are reported for vacuum or air wavelengths. We have added the following text:

P. 21664 lines 12 – 15: "Fig. 4 shows the O_3 absorption cross section measured at 295 K and 820 hPa, together with previously measured cross sections (Burkholder et al., 1994; Brion et al., 1998; Burrows et al., 1999; Voigt et al., 2001; Bogumil et al., 2003; Fuchs et al., 2009; Chen et al., 2011) obtained from the Mainz Spectral Database and plotted for vacuum wavelengths. *The Burkholder et al. (1994), Fuchs et al. (2009), and Chen and Venables (2011) spectra were corrected from air to vacuum wavelength using Eqn. (1) in Ciddor (1996). The wavelength scale reported by Brion et al. (1998) is not specified.*"

We additionally updated Table 1 and added the following footnotes:

"[1] λ_{air} converted to λ_{vacuum} using Ciddor (1996) Eqn. (1).
[2] Wavelength scale not specified.
[3] Cross-section reported at λ_{vacuum} = 404.1 nm."