

Interactive comment on “Absolute ozone absorption cross section in the Huggins Chappuis minimum (350–470 nm) at 296 K” by J. L. Axson et al.

Anonymous Referee #2

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The paper presents a new absorption cross-section of ozone in the near-ultraviolet measured using a three channel incoherent broadband cavity-enhanced absorption spectroscopy instrument. Ozone has an extremely small cross-section in this region and, as a result, agreement between prior literature spectra in this region is really rather poor. Although a single, weak absorption cross-section is not intrinsically exciting (and such weak absorptions would generally be insignificant in the atmosphere), O₃ is a special case owing to its exceptional importance in atmospheric photochemistry and radiative transfer. The paper provides strong evidence that the O₃ absorption in the Huggins-Chappuis minimum is weaker than most previous spectral measurements indicate. Their spectrum agrees closely with another recent and highly sensitive

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spectrum (Chen & Venables) as well as the Brion (1998) spectrum on which the 2006 JPL recommendation is based. The authors also examine O₃ absorption under humid conditions and find no evidence for absorption of O₃.H₂O clusters, which have been proposed as long-wavelength precursors of OH.

Axson et al. give careful attention to the experimental details of the spectral measurement, including calibration of the mirror reflectivity, quantifying the ozone concentration, and to potential sources of uncertainty. As a result, their spectrum is convincingly shown to be both sensitive and accurate, and is likely to provide the definitive spectrum of O₃ at these wavelengths. 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.

Some clarification is warranted in parts of the work:

1. 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?
2. The flow rate through the cavity was quite fast (1.0 LPM): was there any evidence of

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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?

3. 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).

4. 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?

5. 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.

Minor technical corrections:

1. p.21660, l.20: Should be "sccm"
2. p.21660, l.24: "produce"
3. 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.
4. 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.)

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surements of the O₃ spectrum. (The authors' precautions are warranted with their spectrometer, of course.)

5. 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.
6. p.21663, ll.11-15: Awkward sentence. Rephrase.
7. p.21666, l.16: "nonlinear" or "non-linear"
8. p.21669, l.12: "O(1D)"
9. Text in Figures 1 and 4 is too small to be readily legible and should be increased.
10. Caption: Fig. 1(a): "Also included . . . photodiode". There is no ozone generator in (a)! Omit sentence or include in figure.
11. 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,"

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