

We thank the reviewer for his or her careful review of our paper. In the following, we restate each comment followed by our response. As Referee 1 raised similar questions about measurement uncertainty, we will partly refer to our response to Referee 1 where suitable.

C1: At UV wavelengths the absolute stability of Xe-arc lamps is limited. Since the lamp intensity in absence of absorbers affects the retrieval accuracy in this paper, the authors employ a separate spectrometer/CCD detector to reduce potential for such error. However, it remains unclear what the benefit of this rather expensive solution is for the absolute accuracy in the ultimate data products. Are such measures indeed needed? What benefit do they bring? How stable is the lamp a-priori? What is the relative accuracy at which I<sub>0</sub> is characterized from measuring out-of-band light? What is the improvement in precision in the drift-corrected I<sub>0</sub>? The error in drift-corrected I<sub>0</sub> is necessarily larger than the relative accuracy at which I<sub>0</sub> is measured. Has this uncertainty been propagated into the final data product?

R1: This comment seems to suggest that the additional hardware (cf. comment 10) was used to monitor the stability of the lamp. This was not the case: The reason for the absorption measurement at 320 nm was to quantify the concentrations of O<sub>3</sub> and the ketones. The concentration is necessary to calculate the cross-section from the absorption (or extinction) coefficient measured between 335 and 375 nm (that is, the IBBCEAS spectrum). Any method could therefore have been used to quantify the concentration of the absorbing species. The approach we pursued, based on the absorption at 320 nm, is feasible in this study because (a) all the species absorb about an order of magnitude more strongly at 320 nm than they do above 335 nm, and (b) the literature cross-sections are well-established at this wavelength. An advantage of the approach followed here is that the exact same sample is interrogated by the single-pass (320 nm) and the IBBCEAS (335 to 375 nm) absorption measurements; the effect of sample losses to apparatus surfaces can therefore be ignored (as we point out in the Discussion on p.4586, 1.18 and in response to comment 1 of Referee 1).

Nevertheless, it is perhaps not surprising that some confusion could have arisen with regard to the separate absorption measurements because the performance of the spectrometer is *dramatically* different at 320 nm and in IBBCEAS region. The spectrometer sensitivity is directly influenced by the mirror reflectivities (cf. Eq. (1)): in the maximum reflectivity region of the mirrors (335 to 375 nm), the high reflectivity results in a long effective pathlength of light ( $L_{\text{eff}} = d / (1 - R)$ ) in the empty cavity. In our system, for example, the effective pathlength is about 0.5 km at 353 nm ( $R = 0.996$ ). In contrast, most of the light traverses the sample once only at 320 nm ( $R = 0.41$ ) and the pathlength through the sample is shorter by over two orders of magnitude.

We believe much of this information is stated or implied in the relevant paragraph of the Experimental section (p. 4576, 1.7). However, as both referees seem to have misunderstood the 320 nm absorption measurement, some clarification of its role is warranted to distinguish it from the IBBCEAS spectra. Accordingly, we have changed

“The concentration of absorber in the cavity was quantified from the single-pass absorption at 320.1 nm in the O<sub>3</sub> and ketone experiments. These species have moderate...” (p.4574, 1.7)

to

“The concentration of absorber must be known to calculate the absorption cross-section. Although any analytical method could be used to quantify the concentrations of O<sub>3</sub> and the ketones, here we exploit the single-pass absorption at 320.1 nm to determine the concentration of the absorber. At this wavelength, which falls outside of the high reflectivity region of the optical cavity mirrors, most light traverses the sample once (a pathlength of 2 m). In contrast, the spectrometer is dramatically more sensitive between 335 and 375 nm where the reflectivity is at a maximum and the effective pathlength of light is about 0.5 km. (The effective pathlength in the absence of sample extinction is given by  $d/(1 - R)$ , where  $d$  is the mirror separation and  $R$  is the mirror reflectivity). The IBBCEAS measurement is therefore about two orders of magnitude more sensitive than the 320 nm (single-pass) measurement. Ozone and ketone have moderate...”

The reviewer is quite correct that the additional spectrometer is an expensive solution. In principle, it would be straightforward to combine both the single-pass and the IBBCEAS measurements in a single spectrometer using, for instance, a two-way fibre bundle. That solution was not possible at the time of our experiments, however.

C2: A geometrical description what portion of the measurement light is used for characterizing I0 would be interesting. Is the overall noise photon shot noise limited in this system, or what factors are limiting noise?

R2: Information about dimensional considerations and the stability of optical cavities can be found in a general text dealing with lasers or optical cavities (e.g., Demtröder, *Laser Spectroscopy*). This topic is rarely addressed explicitly in papers using optical cavities for measuring spectra. A notable exception (which we cite) is Fiedler et al. (2007), where it is the focus of the paper. Nonetheless, we consider this topic to be outside of the scope of this paper.

As the optical cavity rejects most light of interest, this type of spectrometer is generally close to the shot noise limit.

C3: The authors measure R at 353nm, and specify the error as 7% based on the range of ozone cross-sections at that wavelength. It is further said that the error at other wavelengths can not be quantified, yet later it is said that the error can be up to 20%. The 7% are necessarily a lower limit. In principle the accuracy at other wavelength can be assessed from comparing with literature cross sections, or e.g., SO<sub>2</sub>. On reading on the authors later mention on P4850 1 11 about the potential use of SO<sub>2</sub>, but then

do not appear to exploit this further. What attempts have been made to improve knowledge of the wavelength dependence of the mirror? To what degree is the fundamental need for such knowledge of R to calculate cross section values based on independent information measured here, vs. literature data.

R3: This is a valuable comment on the wavelength dependence of the mirror reflectivity and its impact on the overall uncertainty. We refer to our response to comment 1 of Referee 1 and to the new section (3.3) where this issue is addressed. The uncertainty in the reflectivity away from 353 nm is revisited in the Discussion, where (as per the referee's suggestion) comparison with literature spectra suggests a larger uncertainty at short wavelengths.

The aim of the SO<sub>2</sub> absorption spectrum in this paper was to demonstrate that the IBBCEAS spectrometer gives reasonable agreement with literature spectra across the 335 to 375 nm region. We have used SO<sub>2</sub> as a calibration gas in a different spectrometer, but in the current paper we simply wanted to alert interested readers to its potential as a convenient calibrant in the near-UV.

The wavelength-dependence was determined using Rayleigh scattering (cf. p.4577, 1.13 and Fig. 2b). Apart from using known gas absorptions, other approaches to determining the mirror reflectivity have been demonstrated, including cavity-ringdown characterisation of the reflectivity (Meinen et al., "Using a high finesse optical resonator to provide a long light path for differential optical absorption spectroscopy: CE-DOAS", *Atmos. Chem. Phys. Discuss.*, 8, 10665–10695, 2008) and the use of a low-loss optic (Varma et al., 2009). Nevertheless, absorption or scattering measurements remains the most common method of charactering the mirror reflectivity for broadband optical cavity spectrometers.

C4: How have the various error sources been propagated into the final error that is given as 10-15%? This seems somewhat low, given that the mirror alone is uncertain already to 7%. At which precision is the trace gas concentration known? And how certain is I<sub>0</sub> (see comment 1)? What error sources are treated as systematic, and what sources of error are treated as statistical? Is retrieval error dealt with as the 1-sigma fit error, or at a 2-sigma absolute accuracy level, which is 6 times larger than the former?

R4: As in R3, the measurement uncertainty and the issues raised in this comment are addressed in our response to comment 1 of Referee 1 and to the new section (3.3), which explicitly deals with each contribution to the (lower limit) uncertainty at 353 nm. Equations (4) and (5) treat all sources of error as effective standard deviations (in accordance with NIST Technical Note 1297 "Guidelines for Evaluating and Expressing the Uncertainty of NIST measurement results"), which are combined according to the law of propagation of uncertainty. The mirror reflectivity, which is clearly the major source of uncertainty in both the extinction coefficient and the absorption cross-section, affects the measurement result in a systematic way, whereas intensity fluctuations are random sources of noise. The total uncertainty and the retrieval error are expressed as 1σ uncertainties.

C5: P4579, l 27: How can a concentration of SO<sub>2</sub> have units of % ?

R5: We agree that more precise wording is required and have accordingly changed “overall concentration of SO<sub>2</sub>” to “SO<sub>2</sub> mole fraction of the sample gas (at similar ambient pressures)”. The sentence (p.4579, l.27) now reads:

“The SO<sub>2</sub> mole fraction of the sample gas is about 0.039% in our spectrometer compared to pure SO<sub>2</sub> and 1% SO<sub>2</sub> in N<sub>2</sub> of Vandaele and Bogumil respectively”

C6: The discussion of UV LEDs is interesting. The authors seem to imply that in the UV Xe-arc lamps are advantageous over LEDs. How does the absolute accuracy of Xe-arc lamps compare to UV LEDs? See Thalman and Volkamer, 2010 AMT for a comparison at visible wavelengths. It would be timely to include a discussion about lamp stability and attainable noise levels at UV wavelengths, and compare them with the visible spectral range.

R6: Our discussion compares arc lamps to LEDs in the context of measuring reference spectra in the UV and near-UV (from p.4585, l.22). The specific advantages of arc lamps for this study are (a) broad spectral output and (b) useful intensity at short wavelengths (below 350 nm, say). Neither of these characteristics are met by current near-UV LEDs and we therefore did not believe a more detailed discussion of the choice of light source was necessary.

Nevertheless, we are aware of the advantages of LEDs for many applications: using LEDs, our group first extended the broadband cavity method into the near-UV (cf. Gherman et al., 2008). As Fig. 2 in the Gherman paper shows, the 365 nm LED has a narrower range (ca. 10 nm, FWHM) with a usable lower wavelength limit of 355 nm. Shorter wavelength LEDs have about two orders of magnitude lower output power than at 365 nm (cf., www.roithner-laser.com) and are nowhere near being competitive with Xe arc lamps. We think that these points are addressed by the sentence (p.4586, l.1), but have added the following sentence:

“High power LEDs are not yet available below 365 nm.”

at p.4585, l.27 to emphasise that suitable LED technology is not yet available.

We are not sure what the referee means by “absolute accuracy”: we presume what is meant is the stability of the arc lamp, which we quantified earlier in terms of short-term fluctuations as well as long-term drift (p.4575, l.20). The Thalman and Volkamer paper compares several LEDs and an arc lamp in the blue region of the spectrum, but significant differences compared to the near-UV are (a) the very high power of blue LEDs (180 to 1300 mW) as well as the broader output of the blue LEDs (ca. 20 nm, FWHM). At blue wavelengths, LEDs have clear advantages as light sources over arc lamps. In general, the overall sensitivity of this type of spectrometer depends on (a) the light source and (b) the detector sensitivity, (c) the mirror reflectivity, and (d) cavity length. As only the cavity length is independent of wavelength, we contend that a comparison between different spectral ranges would not be particularly meaningful.

C7: The paper would benefit from a quantitative argument based on theory that sets the experimental conditions probed (gas extinction) in context with the cavity extinction of the empty cavity. For each gas, how does the range of trace gas extinctions compare to that of mirror loss?

R7: A quantitative comparison of cavity extinction compared to mirror losses is an important consideration in optimising an instrument for trace gas detection, as we have discussed elsewhere (e.g., Gherman et al., 2008) and as other groups have presented theoretically (e.g., Platt et al., “Broadband Cavity Enhanced Differential Optical Absorption Spectroscopy (CE-DOAS) – applicability and corrections”, *Atmos. Meas. Tech.*, 2, 713–723, 2009). In the present article, where the spectrometer is used to determine weak absorption cross-sections, the ratio of cavity extinction to mirror losses is not particularly important as long as the extinction is large enough to be measured. We note also that any such comparison between gas extinction and mirror losses would be difficult owing to the strongly varying spectral dependence of the absorption for the gases considered here (cf. also our response to comment 7 of Referee 1).

C8: P4585, l 12: ‘We note in passing that whereas our measurements were obtained under steady-state conditions with low BrO concentrations’. What do the authors mean to imply from this statement? How stable was their BrO concentration?

R8: Our aim was to contrast the differences in the BrO concentrations between our work (low, relatively constant concentrations) and those in the literature (high, short-lived BrO concentrations). We have accordingly changed “higher BrO concentrations” to “higher instantaneous BrO concentrations” to clarify the BrO temporal dependence of previous studies. The stability of the BrO concentration (as indicated by the retrieved fit coefficients) is estimated from the standard deviation from a running average of the concentration and is explicitly stated in p.4585, l.9.

C9: P4586, l24ff: ‘In comparison to numerous literature spectra, the IBBCEAS spectra have significantly lower noise and also display linear absorption behaviour for weak absorptions.’ This statement really is a claim of ‘precision’ and does not imply ‘accuracy’ of the measurements. However, the following statement, that ‘the spectra reported here are to be preferred to most prior spectra’ requires accuracy not precision to support. It hence remains to be supported by a fully transparent treatment of experimental error (comment 4). Unless the authors can make a credible claim for ‘absolute accuracy’ to be better than previous literature data, this claim should be removed.

R9: The referee is correct that the distinction between precision and accuracy is important in the context of claims such as the one we made above. That our spectrometer remains sensitive to absorption at these wavelengths is demonstrated by the linear absorption

behaviour for extremely weak absorptions (cf. Fig. 2a and 7a). The cross-section is determined from the slope of these curves (and Eq. (1)), while the precision arises from measurement-to-measurement variations in the slope. The accuracy of the cross-section is now described by a full statement of the experimental uncertainty associated with the cross-section in the new section 3.3 (“Uncertainty of cross-sections”) which, we believe, fulfills the criteria of a “fully transparent treatment of experimental error”, and the Discussion indicates that our spectra below 340 nm are less accurate. Again, this treatment applies at 353 nm and is a lower limit; an estimate of higher uncertainty at the limits of the IBBCEAS spectra is indicated in revisions to the Discussion (cf. response 1 to Referee 1).

C10: Do the two caveats listed in the following sentences imply that the authors do not trust their characterization of  $I_0$ ? What use is then the separate hardware? And if indeed the mirror is off up to 20% at 330nm, how the authors claim an accuracy of 10-15% for most cases?

R10: The separate hardware was not used to characterise the intensity but to quantify the concentration (cf. R1). We have, however, set a lower uncertainty on the absorption coefficient based on the small offset in the ketone spectra (cf. reply to comment 1 of Referee 1). The uncertainty in the mirror reflectivities increases at the limits of the IBBCEAS spectrum, so there is no contradiction between 20% as an upper limit and 10-15% for most cases, as we endeavour to make clear in the Discussion (cf. response to comment 1 of Referee 1).