

We thank Referee 1 for his or her comments and careful review of the paper. As both referees indicated that greater detail on the measurement uncertainty was required, we have addressed this matter extensively in our response to comment 1 of Referee 1. Other responses to the referee's comments are listed below.

C1: There is no in depth discussion of the error budget. As this paper tries to promote the use of a new method, it should include a detailed discussion on errors. Some issues to discuss here : effects of the determination of R , effect of the lamp drift and fluctuations, effect of photodissociation, adsorption on the walls and on the mirrors, : : : The only discussion is p 4586, L 15, but does not go deep enough. L17 : 'typically around 10% to 15%, acceptable for many application': a complete analysis of the error budget would give more precise numbers. Is it true that 10 to 15 % of inaccuracy on cross section is acceptable?

R1: As a more in-depth discussion of the uncertainty of the measurement was raised by both referees, we have added a new section (3.3) to explicitly quantify the uncertainty and have also extended our comments on this matter in the Discussion (see below). The new section addresses the uncertainties in determining R , the lamp drift and fluctuations, and how these contribute to the overall uncertainty. We note that this addition does not significantly modify our earlier assessment of the measurement uncertainty –the uncertainty in the mirror reflectivity remains the dominant source of noise in most cases. Based on the lamp stability (see our observations in Section 3.3 and in the Discussion, p.4587, as well as Referee 2, comment 10), we put a lower limit on the uncertainty of the extinction measurement (and hence on the absorption cross-sections, depending on the concentration). This lower limit is most relevant to the long-wavelength region of the 2-butanone and 2-pentanone spectra where the absorption is very weak and only a single concentration was used to calculate the cross-section.

Because the single-pass measurement directly quantifies the concentration across the optical cavity at any instant, sample losses to photolysis or to adsorption inside the cavity can be ignored (as stated in on p.4586, l.22).

We strive to make clear that the *uncertainty is a lower limit that applies at 353 nm*; the uncertainty is necessarily larger towards the long- and short-wavelength limit of the spectrum and we try to put an estimate on the uncertainty at the short-wavelength limit by comparison with literature cross-sections (as suggested by Referee 2 in comment 3). As the overall uncertainty depends on wavelength, we express the uncertainty as a range of values.

Whether or not an uncertainty of 10-15% is acceptable clearly depends on the application. For the particularly weak spectra reported here, an uncertainty of 15% is considerably smaller than the divergence shown between the literature spectra (e.g., in Figs 5, 7, and 8, and R7) and therefore, we believe, significantly improves our knowledge of these cross-sections.

The new section reads:

2.3 Uncertainty of cross-sections

The uncertainty of the absorption cross-sections was estimated using standard uncertainty propagation. The uncertainty in the extinction coefficient, $\Delta\varepsilon$, was common to all spectra and was evaluated from Eq. (1):

$$\begin{aligned}\Delta\varepsilon^2 &= \left| \frac{\partial\varepsilon}{\partial d} \right|^2 \Delta d^2 + \left| \frac{\partial\varepsilon}{\partial(1-R)} \right|^2 \Delta(1-R)^2 + \left| \frac{\partial\varepsilon}{\partial I_0} \right|^2 \Delta I_0^2 \\ &= \varepsilon^2 \left(\frac{\Delta d}{d} \right)^2 + \varepsilon^2 \left(\frac{\Delta(1-R)}{1-R} \right)^2 + \left(\frac{1-R}{d} \right)^2 \left(\frac{\Delta I_0}{I} \right)^2\end{aligned}\quad (4)$$

where Δd , $\Delta(1-R)$, and ΔI_0 are the uncertainties in the mirror separation, the mirror reflectivity term, and the intensity. Here $(1-R)$ and d are systematic sources of uncertainty, whereas the intensity term contributes randomly to the final uncertainty. The relative uncertainties in Eq. (4) are 7% for $(1-R)$ at 353 nm, 0.5% for d , and less than 1% for short-term intensity fluctuations. The overall uncertainty in the extinction measurement at 353 nm is therefore around 7% and is clearly dominated by the uncertainty in the mirror reflectivity. However, the characterisation of the lamp intensity appears to understate the longer-term drift in the intensity, as seen in the small offset at long wavelengths in the spectra of 2-butanone and 2-pentanone (where the absorption is expected to be effectively zero). On the basis of this evidence, the intensity contribution to the uncertainty is estimated to be around $5 \times 10^{-7} \text{ cm}^{-1}$.

The uncertainty in the absorption cross-sections must furthermore account for the uncertainty in the concentration of each species (ΔN):

$$\left(\frac{\Delta\sigma}{\sigma} \right)^2 = \left(\frac{\Delta\varepsilon}{\varepsilon} \right)^2 + \left(\frac{\Delta N}{N} \right)^2\quad (5)$$

We estimated ΔN from the standard deviation of the literature cross-sections at 320 nm (Table 1), together with a 1.1% uncertainty in the single-pass absorption measurement. The uncertainties in the concentrations are 3% for O_3 , 4% for acetone, 3% for 2-butanone and 3% for 2-pentanone. The overall uncertainties in absorption cross-sections are thus 8% (O_3), 8% (acetone), 10% (2-butanone) and 8% (2-pentanone).

We emphasize that this uncertainty applies to the absorption cross-section at 353 nm and is necessarily a lower limit. The uncertainty is expected to be larger at the long and short wavelength limits of the IBCEAS spectrum. The uncertainty will therefore be revisited in the Discussion section to place a more conservative estimate on the overall uncertainty in the absorption cross-section.

The Discussion has expanded the sentence:

“In the results here (and in prior IBBCEAS studies), this uncertainty is typically around 10% to 15% and acceptable for many applications.” (p.4586, 1.17)

to:

“In the results here, this uncertainty is 8 to 10% at 353 nm but increases towards the long and short-wavelength limits of the spectra owing to the uncertainty in the $(1 - R)$ term. Below 340 nm, our spectra were 10 to 20% lower than previously reported absorption cross-sections, suggesting that the mirror reflectivity was overestimated at the short wavelength limit and that our spectra are less accurate in this region. Taking the wavelength-dependence of the uncertainty into account, we estimate the uncertainty in our cross-sections above 340 nm to range from 10 to 15%, which is acceptable for many applications and in line with the uncertainty in prior IBBCEAS studies.”

As the last two sentences of the Discussion (p.4587, 1.3) repeat much of the above, we have modified them to:

“...BrO, O₃, and Br₂ spectrum. Secondly, the accuracy of the absorption measurement tends to be worse at the limits of the high reflectivity region of the cavity mirrors, as we observe below 340 nm.”

As the above extension to the Discussion facilitates if the reader has already been alerted to this issue, the following sentence was added to section 3.2 (p.4581, 1.4):

“Below 340 nm, our cross-sections are 10 to 20% smaller than the literature values, probably because the mirror reflectivity is overestimated at short wavelengths.”

C2: Different wavelengths are indicated throughout the paper which leads to a certain confusion. For example: in the description of the set-up (p 4576, L1) ; 335-375 nm. For SO₂: 345-420 nm For O₃: not said but from the plot : 350-376 nm For Ketones: 335-355 nm The make the reading particularly difficult. Moreover if the instrument is sensitive in a certain spectral range, say 335-375 nm, why not give the measurements for all species on this entire interval, even if the cross section falls to 0.0. This would be a good way to test the sensitivity of the instrument towards lamp drift, for example. Then there is the 320 nm used for calibration, and is not in the domain. It would be interesting to have the plots showing this wavelength in each case. If you are using this wavelength for calibration, I assume you know the R value at that wavelength ?

R2: We agree that the different wavelength ranges are unclear and unnecessary and have accordingly modified Figs. 4, 5, 7, and 8 to extend from 335 to 375 nm as per the referee's suggestion. (The referee made no reference to the spectral range of Fig. 9 – the absorption spectrum and fit of Br₂, O₃, and BrO. This figure aims to compare a fit of the literature cross-

sections to the experimental spectrum. The spectral interval of the fit was selected to give good sensitivity to all three components; extending the fit window to 375 nm would weight more heavily the Br₂ contribution to the fit. Accordingly, we made no change to this figure.)

We do not consider the 320 nm measurement to be a part of the IBBCEAS system (also see our response to Referee 2, comment 1). The single-pass (320 nm) measurement used literature cross-sections to quantify the concentration, not the other way around. Including the cross-section at 320 nm on the spectrum would only show the literature data; this would not be particularly meaningful and could mislead the reader to confuse the literature data with the new cross-sections reported here (335 to 375 nm).

The mirror reflectivity at 320 nm was stated as about 42% (p.4576, 1.15; see also R4 below), which implies that only a small fraction of the light makes more than one pass through the sample.

C3: Resolution of the instrument: p 4575, L18 ‘approximately’ is not enough for such observations. Resolution is one of the critical parameters for cross sections. True values, deduced from measurements of the ILS should be given. Is this resolution constant on the whole spectral interval ?

R3: The relevant sentence (p.4575, 1.18) was been modified to be more precise:

“The uncertainty of the wavelength calibration was about 0.02 nm and the average resolution was 0.31 nm (25 μm slit width) and 0.55 nm (100 μm slit width) as determined from emission lines at 334 nm and 365 nm.”

The resolution of the spectrograph showed a small dependence on wavelength, typically below 10% in the spectral region of interest.

C4: Discussion on the mirror calibration (P 4578, L 11) a/ I am confused again by the use of the different wavelengths : 320 nm to scale the cross section, 353 nm to determine the R(@353nm) ? Again what about R(@320 nm) b/ ‘the cross section used was the average of four literature values: : : ‘ : what was the standard deviation ? Would be interesting to have this value on plot 5, from which it is not clear if the value @ 353 nm is given. If it is the utmost point at the left, then the values from the literature are not identical (considering the logarithmic scale of the plot) What is the impact of this average value on the precision of the measurement.

R4: (a) The 320 nm measurement was not mentioned at all in this section (2.2), although we did use an average of the well-established literature cross-sections at both 320 and 353 nm. The literature cross-sections were put to different uses, however: at 320 nm the aim was to quantify the absorber; at 353 nm the goal was to determine the mirror reflectivity. To clarify

this matter, the relevant paragraph in the Experimental section has been expanded (see R1 to Referee 2).

Nevertheless, we should state how the reflectivity at 320 nm was measured and have therefore modified

“As the cavity mirrors have a reflectivity of 42% at 320 nm,” (p.4576, l.15)

to

“As the cavity mirrors have a reflectivity of 42% at 320 nm (as measured in a UV-visible spectrometer),”

(b) The standard deviation of the literature cross-sections is stated as 7% (p.4578, l.14). We have modified Fig. 5 to show this standard deviation as an error bar at 353 nm. The mirror reflectivity, which was determined periodically between experiments, is a systematic contribution to the uncertainty and does not affect the measurement precision.

C5: It would help the reading if there was a table (or several tables, one for each species) summarizing some instrumental parameters (range, resolution, temperature, : : :) for the literature data.

R5: We have incorporated this helpful suggestion by adding Table 1 (see below) to the paper and referring to it in the text.

C6: p 4582, L 17: ‘ (Fig 7) exhibits lower noise over this region’ : I do not see a lot of noise on the data from the literature. In Fig 7, several data sets of the literature are plotted, but no reference to their experimental parameters (see rmq 5) or discussions are given in the text.

R6: We have removed this statement (p.4582, l.17). The sentence now reads:

“Our spectrum is in reasonable agreement with these spectra.”

The experimental parameters will be listed in the new table (cf. R5 above).

C7: No quantitative analysis of the comparisons is presented. The authors speak of good or less good agreement, but do not provide % difference or absolute differences.

R7: This comment is readily implemented in the paper for O₄ and SO₂ based on a comparison of absorption peak heights. Accordingly, we have added the following sentences:

“The magnitudes of the five largest absorption features above 350 nm were 28% larger than the average literature cross-sections, although around half of the difference (8.2×10^{-23} cm² average) can be explained by our generally higher baseline (4.2×10^{-23} cm² higher on average).”

and

“within 9% of the average literature value for the O₄ cross-section peak, ”

For the spectra of O₃ and the ketones, however, we doubt the value of such a comparison because differences within each spectrum are very large in relative terms. Two issues arise concurrently in these spectra: first, the absorption cross-section falls by an order of magnitude over 10 to 15 nm; second, many of the literature spectra are close to the limits of their instrumental sensitivity. This latter assertion we base on the large discrepancies between different ozone cross-sections above 365 nm, the constant, unrealistic absorption of acetone at longer wavelengths in the spectra of Martinez, Yujing, and Meyrahn, and the negative absorption of Horowitz for 2-pentanone in Fig. 8b.

For instance, if we take the standard deviation of all the spectra (including ours) as one measure of how closely the data agree, we find that for O₃ the standard deviation is about 15% of the mean at 360 nm but 70% at 370 nm. A direct comparison of spectra is even worse: for example, the Burrows spectrum is about 30% higher than ours at 360 nm but 300% larger at 370 nm! Similar examples could be given for the ketones.

All this information is conveyed by the figures. We therefore believe that the current qualitative discussion is more appropriate for these spectra and is to be preferred to an artificial quantitative comparison.

C8: Comments on the Plots They should all cover the entire sensitive spectral interval of the instrument, including the 320 nm used for calibration Fig 4: it is not enough to plot the maxima of the convoluted spectra, the values in the holes will be also modified by the convolution Fig 6: last sentence of the caption is not clear

R8: The first part of this comment reiterates C2 – see our response above.

Fig 4: We wanted to show the literature data at their original resolution and signal-to-noise ratio, but included the convoluted maxima of the literature data to facilitate a meaningful comparison with our spectrum. We have nevertheless followed the referee’s suggestion and plotted the convoluted literature spectra.

Fig. 6: we have changed the last sentence of the caption to:

“To facilitate comparison with the literature maxima, our measured spectrum was shifted downwards by the offset of the Gaussian fit.”

In addition, we note that we have made a correction to Fig. 2b: The mirror reflectivity at 353 nm stated on the figure should be “ $R = 0.9960$ ”.

Author (Year)	Temp. [K]	Wavelength [nm]	Resolution [nm]
<u>Sulfur dioxide</u>			
Bogumil et al. (2003)	293	239-395	0.26
Vandaele et al. (2009)	298	227-420	0.03
<u>Ozone</u>			
Bogumil et al. (2003)	293	230-1075	0.26
Voigt et al. (2001)	293	230-851	0.027
Burrows et al. (1999)	293	230-794	0.2-0.4
Brion et al. (1998)	295	350-830	0.01
<u>Acetone</u>			
Yujing et al. (2000)	298	240-350	0.04
Wollenhaupt et al. (2000)	296	220-346	0.16
Gierczak et al. (1998)	298	215-349	0.5
Martinez et al. (1992)	300	202-355	0.5
Hynes et al. (1992)	298	253.7-360	2
Meyrahn et al. (1986)	298	275-368	1.8
<u>2-Butanone</u>			
Yujing et al. (2000)	298	240-350	0.04
Martinez et al. (1992)	300	202-355	0.5
<u>2-Pentanone</u>			
Horowitz et al. (1999)	298	210-360	0.07
Martinez et al. (1992)	300	202-354	0.5

Table 1. Instrumental parameters of literature absorption cross sections.