Referee 2

Initial review of "Scattering and Absorption Cross-sections of Atmospheric Gasses in the Ultraviolet-Visible Wavelength Range (307 -725nm)" by Quanfu He, Zhen Fang, Ofir Shoshamin, Steven S. Brown and Yinon Rudich.

The research presented in the manuscript is interesting, and certainly relevant to the journal Atmospheric Chemistry and Physics. it is somewhat unfortunate that nitrogen is used for the calibration of the mirror reflectance, as nitrogen itself is a highly interesting gas for these type of measurements. However, the manuscript needs to be improved significantly before it is ready for publication.

Reply: We thank the reviewer for these important comments. These comments helped a lot to improve our manuscript. We agree with the reviewer that nitrogen by itself a highly interesting gas for Rayleigh scattering cross-section measurement. However, we need one gas that has significantly larger extinction cross-sections than He to calibrate our BBCES. The previous study by Thalman et al. (2013) has pointed out that their CRD measurement agrees with the *n*-based calculation within 1%. It is noted that N_2 is widely used for the calibration of BBCES to measure extinction/scattering/absorption of various gases.

I have doubts about the direct measurements of the oxygen absorption bands presented rather prominently in the abstract (the delta and gamma overtone bands and the B-band) should be included at all. The spectral resolution of the instrument is simply not suitable to produce a meaningful result for these bands. I interpreted the 0.8 nm resolution statement as a FHWM value, and produced a plot of high resolution cross sections of oxygen (HITRAN; modelled concentration is 21% O_2 in N_2 at 1018hPa and 294K and includes pressure and temperature broadening) and overplotted a Gaussian spectral response function with FWHM of 0.8 nm, see figure 1. This combination cannot produce a meaningful result. The range of absorption cross sections spans several orders of magnitude within the spectral response of the instrument. In a CRDS setup this would lead to a multi-exponential decay, an underdetermined problem. I'm not sure the situation of interpreting the output of a BBCES instrument when a wide range of absorptions is present within a spectral pixel is any better. At best the result depends on the spectral resolution, making it far less useful to others. Also note that this is before taking any broadband collision induced effects into account, but that is probably the least of your worries in this case. Taking out these three figures leaves enough material for an article that is worth publishing, so I do not see this as a significant drawback or a hindrance to the publication of the remaining results. The other features (O_2-O_2 absorption and Rayleigh scattering) have spectral features that are much wider than 0.8 nm, and as such can be investigated with this instrument. I'm not enough of an expert to judge the methane absorption features in this spectral range, but I would consider these suspect as well.

This means a substantial rewrite of section 3.3, to reduce the section on how the O_2-O_2 absorption was isolated from the oxygen absorption and Rayleigh losses.

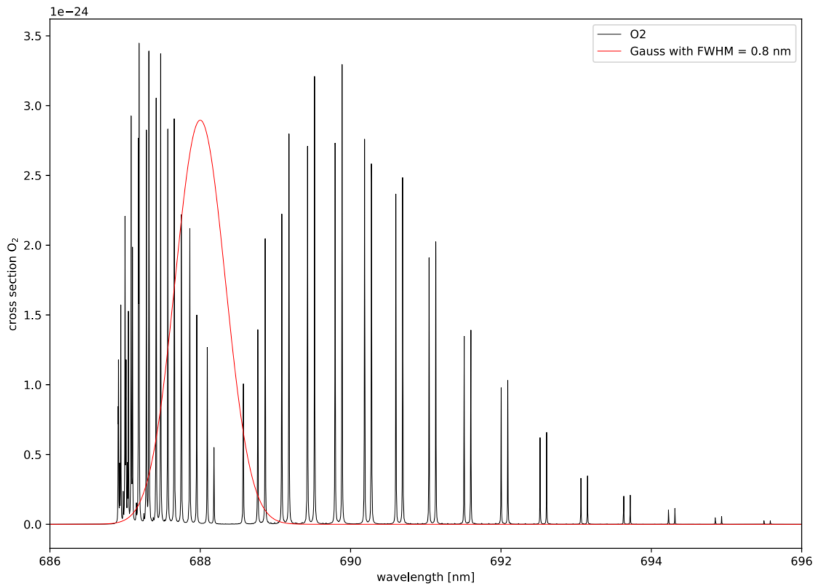

Figure 1: Oxygen B-band absorption cross sections from HITRAN. The modelled concentration is 21% O_2 in N_2 at 1018hPa and 294K and includes pressure and temperature broadening. In red a Gaussian spectral response function with FWHM of 0.8 nm in shown.

Reply: We thank the reviewer for this constructive comment. We agree with the reviewer that due to the low instrument wavelength resolution and the discrete structured of the B, γ, and δ bands, the absorption cross-sections measured for these bands are less useful to others. Thus we accepted the Reviewer’s suggestion and deleted all of the results regarding O_2 absorption bands. We also revised the abstract and the conclusion section. It is noted, though that the data for the broad unstructured O_2-O_2 collision-induced absorption bands and the Rayleigh scattering cross-sections are still valid and useful. The agreement between our results (Rayleigh scattering and O_2-O_2 absorption cross-sections) and literature data validates our method. We prefer to keep this information in the manuscript. Detailed changes are as follows,

We added the following text in Section 3.3 “These absorption bands can only be resolved by a high-resolution spectrascopic technique. Absorption cross-sections of the B, γ, and δ bands were convoluted from the HITRAN database (Gordon et al., 2017) by considering the temperature, pressure, and instrument’s wavelength resolution. The wings of the oxygen lines also show a quadratic dependence on the pressure due to pressure broadening. However, due to the minimal O_2 absorption contribution below 680 nm and the low instrument wavelength resolution, the extinction cross-section of the O_2 monomer can be treated as linearly correlated with the O_2 concentration. Moreover, the extinction cross-section of the O_2 monomer is linearly correlated with the O_2 concentration and the O_2–O_2 absorption cross-section is correlated with the square of the O_2 concentration. Therefore, these cross-sections can be retrieved from measurements at different O_2 concentrations. Moreover, the O_2–O_2 CIA cross-section is correlated with the square of the O_2 concentration. Therefore, the two cross-sections can be retrieved from measurements at different O_2 concentrations. Due to the discrete structured absorption bands and the instrument’s wavelength resolution, the range of absorption cross-sections spans several orders of magnitude within the spectral response of the instrument, limiting the relevance of the absorption cross-sections for other researchers. These results are not further discussed here. However, the data for broader, unstructured CIA of O_2–O_2 are still useful for various applications. (Line 308-322)

We deleted the following sections, "Absorption cross-sections of O_2 absorption bands were measured directly at 579 nm ($1.8\pm0.3\times10^{-27}$ cm^2), 629 nm ($6.4\pm0.3\times10^{-27}$ cm^2), and 688 nm ($2.69\pm0.08\times10^{-26}$ cm^2)." (Line 23-24), "but positive values for O_2 B band absorption" (Line 345), "The extinction cross-section data between 307–550 nm and 650–680 was further used to derive the refractive index of O_2 and then extrapolate it to the entire wavelength range for calculating the Rayleigh scattering cross section. The absorption cross-section was then calculated as the difference between the extinction cross-section and Rayleigh scattering cross-section. Three absorption peaks corresponding to the molecular oxygen B band at 688 nm, γ overtone band at 629 nm, and δ overtone band at 580 nm were found and the determined absorption cross-sections at their center wavelengths are $(2.69\pm0.08)\times10^{-26}$, $(6.4\pm0.3)\times10^{-27}$, and $(1.8\pm0.3)\times10^{-27}$ cm^2, respectively. The absorption cross-sections contribute 81%, 24%, and 8.0% to the extinction of each wavelength. These fractions are consistent with the estimation by Thalman and Volkamer (2013)." (Line 351-360), and "Absorption cross-sections of the molecular oxygen bands (δ, γ and B) were derived directly at 579 nm ($1.8\pm0.3\times10^{-27}$ cm^2), 629 nm ($6.4\pm0.3\times10^{-27}$ cm^2), and 688 nm ($2.69\pm0.08\times10^{-26}$ cm^2), respectively." (Line 452-454)

There is no available high-resolution spectroscopy data for CH_4 below 869 nm from the HITRAN database. Previous studies by Fink et al. (1977), Giver et al. (1978), and Smith et al. (1990), have determined the absorption bands of CH_4 at wavelength resolution of 1, 0.05-0.06, 0.025 nm, respectively. The latter two studies' wavelength resolution is sufficient for quantitative spectral studies of individual vibrational-rotational lines of CH_4 (Giver et al. 1978, Smith et al. 1990). The observed absorption bands are smooth, unstructured, and the spectral features are substantially broader than 0.8 nm. Therefore, these absorption features can be investigated by our BBCES. Moreover, the BBCES measured extinction coefficients at 334, 485.28, 542.56, 619.31, and 701.32 nm that significantly linearly correlated with the CH_4 concentration, with $R^2>0.9988$. Our results also agree well with the literature results. Thus, we keep the results for CH_4 in the manuscript. We add the following sentence "Previous high resolution spectroscopy studies have identified smooth and unstructured absorption bands across the UV-visible range (Giver, 1978; Smith et al., 1990). The spectral features are substantially broader than 0.8 nm, thus the absorption by CH_4 can be measured by our BBCES." in Line 216-219.

Please note that at line 286 it is mentioned that the extinction cross section of the oxygen monomer is linearly correlated with the oxygen concentration. Be very careful with that statement, as as the wings of the oxygen lines also show a p2 dependence due to pressure broadening.

Reply: We thank the reviewer for this comment. The absorption from the γ overtone at 629 nm and the δ overtone band at 580 nm contribute a fraction (<20%) to the total absorption. Our experiments use different mixing ratios of oxygen in He at a constant total pressure and temperature. The change in the wings of the O_2 molecular absorption spectrum would therefore be the exchange of pressure broadening for O_2 self broadening. The average pressure shifts measured for the B and γ bands are −0.0087 and−0.0095 cm^{-1} atm^{-1}, respectively (Barnes and Hays, 2002). The self-broadening collision coefficients for the γ overtone have been determined from the absorption line width and were found to vary from 0.055 to 0.037 cm^{-1} atm^{-1} (Mélières et al., 1985). The O_2 partial pressure changed from 0.1 to 1 atm during our experiment while the totoal pressure is constant. The resulted broadening are withing the spectra resolution of this study. Thus the pressure broadening effect for wings of the oxygen lines has a small contribution to the strong O_2-O_2 CIA peak centered at these two wavelengths. As we can see from the results, the absorption cross-sections for Rayleigh scattering and O_2-O_2 CIA dericed by this method are in good agreement with literature data, thus our method provide reliable results. For data processing, the extinction cross-section can be treated as linearly correlated with the O_2 concentration. We clarified this in the revised manuscript as "The wings of the oxygen lines also show a quadratic dependence on the pressure due to pressure broadening. However, due to the small contribution of O_2 absorption below 680 nm and the low instrument wavelength resolution, the extinction cross-section of the O_2 monomer can be treated as linearly correlated with the O_2 concentration." (Line 311-315)

Barnes, J. E., and Hays, P. B.: Pressure Shifts and Pressure Broadening of the B and γ Bands of Oxygen, J. Mol. Spectrosc., 216, 98-104, https://doi.org/10.1006/jmsp.2002.8689, 2002.

Mélières, M. A., Chenevier, M., and Stoeckel, F.: Intensity measurements and self-broadening coefficients in the γ band of O_2 at 628 nm using intracavity laser-absorption spectroscopy (ICLAS), J. Quant. Spectrosc. Radiat. Transf., 33, 337-345, https://doi.org/10.1016/0022-4073(85)90195-5, 1985.

At the end of section 3.3 there is a contradiction: on line 326 the 630 nm is listed as within 1.1% of Thalman and Volkamer (2013), while on line 333 the same wavelength is listed as this method cannot derive the cross-sections of CIA of O_2-O_2 at 630 and 688nm". Either alter the statement or explain better what is going on here.

Reply: As described in the methods section, two methods are used to derive the absorption cross-sections of O_2-O_2 CIA. Method1: by performing 2nd polynomial fitt to the concentration-dependent extinction coefficients to get the absorption cross-sections of O_2-O_2 absorption (Line 197-205). Method2: Only using the extinction coefficient data from 100% O_2 measurement (Line 206-214). We subtracted the scattering cross-section of O_2 from the measured total extinction to get the absorption cross-sections. However, the O_2 absorption bands at 580, 630, and 690 nm overlap with those of O_2–O_2 collisions. Thus only by using 100% O_2 measurement, we can not derive the absorption cross-sections of O_2-O_2 at these wavelengths. In line 326, we describe the results from Method1, while in line 333, the results from Method 2 are described.

I should note there that I don't have access to He et al., 2018, so some of my remarks may have been covered there. However, some details on the experimental setup should be mentioned briefly here as an aid to the reader. I'll indicate what I'd like to see added in the technical remarks below.

In the method section a lot of the equipment is mentioned. I'm missing some crucial information on the pressure sensor, the temperature probe and how the gas was mixed at specific mixing ratios, and the error introduced there. I do not see any discussion of the wavelength calibration. For the CRDS this is likely inherent in the used source (not mentioned here either) but for the BBCES the calibration method for the spectrometer should at least be mentioned.

Reply: The temperature sensor is a K-type thermocouple, and the pressure sensor is a Precision Pressure Transducer from Honeywell. The wavelength of the spectrometer was calibrated using an HG-1 Mercury lamp within the wavelength range of 296.728 and 738.393 nm. The way we mixed the gas was described in Line 147-149. The precision of the mass flow controllers is 0.5 mL min^{-1}. When the total flow rate is 500 mL min^{-1}, the uncertainty of the gas concentration (10-100%) varies from 0% to 1.0% (See table below). Specifically, when the gas concentration is within 20-80% or 100%, the uncertainty is below 0.5%. We included this uncertainty in the error propagation process for measurements of CH_4+He and O_2+He. We added this information in the revised manuscript.

Table 1. Uncertainty of the gas concentration introduced by mixing.

Percentage (%)	10	15	20	25	30	35	40	45	50	60	70	80	90	100
Uncertainty (%)	1.0	0.68	0.52	0.42	0.36	0.32	0.30	0.29	0.28	0.17	0.36	0.13	1.0	0

Line 180-181 “The gas temperature (K-type thermocouple) and cavity pressure (Precision Pressure Transducer, Honeywell International Inc., MN, USA) were recorded for gas…”

Line117-119 “Before gas measurement, the wavelength of the spectrometer was calibrated using an HG-1 mercury argon calibration light source (Ocean Insight, USA) within the wavelength range of 302.15−727.29 nm.”

Line238-241 “The precision of the mass flow controllers is 0.5 mL min^{-1}. When the total flow rate is 500 mL min^{-1}, the resulted uncertainty of the gas concentration (10-100%) varies from 0% to 1.0%. Thus, the overall 1-σ uncertainty of extinction coefficients measured for CH_4+He and O_2+He varies from 1.1% to 1.5%.”

In section 2.2 I'm missing some details on the CRDS technique. There are a lot of methods to initiate a ring down of an optical cavity, and this details is down of an optical cavity, and this details is not in the description. The reference (Bluvshtein et al., 2012) uses a 20 Hz Nd:YAG laser, whereas here the manuscript reads: Over 1000 decay time measurements are monitored and averaged on a second basis", suggesting that a much faster laser system was employed here.

Reply: The CRDS at 404 nm used in this study is similar to that described in Bluvshtein et al., 2012, and it is the same system shown in Bluvshtein et al., 2016. We are now using a 110mW diode laser (iPulse, Toptica Photonics, Munich, Germany) instead of a Nd:YAG laser as the light source. The diode laser is modulated to 1383 Hz at 50% duty cycle. We added more details of the CRDS in the revised manuscript.

“…measurement can be found in Bluvshtein et al. (2016) and He et al. (2018). Briefly, diode lasers (110 mW 404 nm diode laser, iPulse, Toptica Photonics, Munich, Germany; 120 mW 662 nm diode laser, HL6545MG, Thorlabs Inc., NJ, USA) are used as the light source of these CRDS. The 404 nm and 662 nm lasers are modulated at 1383 Hz and 500 Hz with a 50% duty cycle. The diode lasers are optically isolated by quarter waveplates (1/4 λ) and polarizing beam splitters to prevent damage to the laser head by back reflections from the highly reflective CRDS mirror. The back-reflected light beam is directed into a photodiode, which serves as an external trigger source. Light transmitted through the back mirror of the cavity is collected by an optical fiber and detected by a photomultiplier tube (PMT), which samples at a rate of 10 to 100 MHz. The time-dependent intensity data is acquired with a 100MHz card (PCI-5122, National Instruments, USA) and processed by a data acquisition software in Labview. An exponential curve is fitted to…" (Line 161-172)

In the conclusion (line 446 to 449) a reference is made to a wavelength range that is not part of this study at all. On line 441 nitrogen is explicitly mentioned as a gas of interest for atmospheric observations in particular for Lidar analysis, also including a wavelength that is outside the scope of the article. While I appreciate the outlook for future studies, please explicitly mark these statements as such, as they are not part of the conclusions of this study.

Reply: Thank you for this suggestion. We added one sentence at the end of the conclusion part. "In the future, gas extinction measurements at extended wavelengths (near-infrared) and for additional gases (e.g., N_2) will expand the spectroscopic applications in atmospheric studies." (Line 490-491)

Finally, the choice of colours hinders accessibility for many colourblind people. There are combinations of colours for use in figures that will make the results more readable for colourblind people. Printing in black and white will quickly show where the use of colours should be improved.

Reply: We updated the colors in the figures and used different symbols for different data sets.

Figure 1, data sets in panel a,b,c are mainly differentiated by marker shape. We kept the colors of the markers but enlarged the size of the markers. The colors in panel c and d are improved. We also use different markers for different data sets.

Figure 4, we used different markers for extinction coefficients at different wavelengths.

Figure 8, we changed the colors in panel c and used different symbols for those three data sets.

Figure 9, we updated the colors and used different symbols for the data points.

Figure S1 and Figure S4, we updated the colors of the traces and used different line styles.

Figure S3, we changed the colors of the markers and used different symbols.

1. Specific remarks

Line 43: please refer to the original year of publication in the reference (1899), not the year of the re-issue of the collected papers. Anyone familiar with the subject matter will be confused by Strutt 2009, but at the same time know immediately what Strutt 1899 is.

Reply: This reference was changed to the original one. (Line 43)

Strutt, J. W.: XXXIV. On the transmission of light through an atmosphere containing small particles in suspension, and on the origin of the blue of the sky, London, Edinburgh Dublin Philos. Mag. J. Sci., 47, 375-384, 10.1080/14786449908621276, 1899.

Line 50 (and several other locations throughout the manuscript): really weird line breaks.

Reply: These line breaks were fixed. (Line 51)

Line 74: Nitrogen should have subscript "2" not "e".

Reply: "N_e" was changed to "N_2". (Line 74)

Line 99 in the Methods section: I found Bluvshtein et al., 2016 (doi:10.5194/amt-9-3477-2016) to be the end point of a chain of references for the method that starts with the two that are mentioned. I suggest to use this reference (in addition or instead of). Sending readers into a rabbit hole to chase the methods is not nice.

Reply: The BBCES system has two channels. The first publication describing the $BBCES_{UV}$ channel (307-350 nm) is by Washenfelder et al., (2016), who used it to determine nitrogen dioxide and formaldehyde. Bluvshtein et al. (2016) used this system for aerosol light extinction measurements. These two papers were cited here, and we delete Bluvshtein et al. (2017). (Line 101)

Bluvshtein, N., Flores, J. M., Segev, L., and Rudich, Y.: A new approach for retrieving the UV–vis optical properties of ambient aerosols, Atmos. Meas. Tech., 9, 3477-3490, 10.5194/amt-9-3477-2016, 2016.
Washenfelder, R. A., Attwood, A. R., Flores, J. M., Zarzana, K. J., Rudich, Y., and Brown, S. S.: Broadband cavity-enhanced absorption spectroscopy in the ultraviolet spectral region for measurements of nitrogen dioxide and formaldehyde, Atmos. Meas. Tech., 9, 41-52, 10.5194/amt-9-41-2016, 2016.

Line 226: In the results and discussion I read: The reflectivity of the cavity mirrors, measured across the entire range using the difference in Rayleigh scattering of N_2 and He, was very stable throughout the experiments". I expect to find this in the method section, how this was determined.

Reply: Reflectivity measurements were repeated every three samples measurements. The average peak reflectivity of the $BBCES_{UV}$ mirrors was 0.99933, with a 1σ uncertainty of 0.000006 at 330 nm. The average peak reflectivity of the $BBCES_{Vis}$ mirrors was 0.9999550, with a 1σ uncertainty of 0.0000006 at 657.9 nm.

In method Section 3.1, we added "Reflectivity measurements were repeated every three samples measurements to track the stability of the system." in Line 139-140

In Section 3.1, we added the 1σ uncertainty for the reflectivity. "The mean peak reflectivity of the $BBCES_{UV}$ mirrors was 0.999328±0.000006 (672±6 ppm) at 330 nm, with a corresponding effective optical pathlength of 1.40±0.01 km. The reflectivity curve of the $BBCES_{Vis}$ is much more structured, with reflectivity ranging between 0.999224±0.000010 and 0.9999550±0.0000006 (45 776±10 ppm < loss < 776 45±0.6 ppm)…" Line 249-253

Line 231: the reflectivities and the losses have their relative order inter-changed, please maintain order for readability.

Reply: We changed "(45 ppm < loss < 776 ppm)" into "(45 776±10 ppm < loss < 776 45±0.6 ppm)" Line 252-253

Line 285: It is worthwhile to note what transitions of the O_2-O_2 absorption features occur here, and especially that both molecules leave the interaction in an electronically excited state, at least for the shorter wavelengths.

Reply: The transitions of the O_2-O_2 absorption features around 688, 629, and 580 nm are ${}^1\Sigma_g^+(\nu = 1)$, ${}^1\Delta_g + {}^1\Delta_g$ $(\nu = 0)$, and ${}^1\Delta_g + {}^1\Delta_g$ $(\nu = 1)$, respectively. This is added in Line ** as "…overlap with O_2–O_2 CIA bands of are ${}^1\Sigma_g^+(\nu = 1)$, ${}^1\Delta_g + {}^1\Delta_g$ $(\nu = 0)$, and ${}^1\Delta_g + {}^1\Delta_g$ $(\nu = 1)$, respectively. These absorption bands…" (Line 306-307)

2. Figures and captions

Line 466: Caption does not match labels in Figure. Given the magnitude of the signal in the figure, the error is in the caption, not the figure.

Reply: The caption is now revised as "Figure 1. Rayleigh scattering cross-sections of CO_2 (a), SF_6 (b), and N2O (c). Panel (d) shows the relative standard deviations…"

Figure 3: missing units on the axes.

Reply: We put the unit in the figure caption "Figure 3. Correlations between the extinction coefficients (unit, cm^{-1}) measured by the BBCES and CRDS."

Figure 4: consider listing tabular material in a table rather than a figure legend.

Reply: We listed the fitted coefficients in a table next to the figure.

Figure 5: the unit of panel (c) cannot be correct, there must be a density involved here.

Reply: The unit is now revised as "cm^5 $molecules^{-2}$".

Figure 6: the methane percentage is mentioned, but not the cell density for 100% methane concentration.

Reply: We added the cell density for 100% methane concentration in the caption as "The number concentration of 100% methane was 2.50143×10^{19} molecules cm^{-3}."

Figure 6 & 7: suggest to add markers to figure 6 indicating where the wavelengths are that are shown in figure 7.

Reply: Thank you for this suggestion. We added vertical lines to indicate the wavelengths that are shown in Figure 7. We also illustrated in the figure caption as "The selected wavelengths are shown in Figure 6 by vertical lines."

Figure S3: missing units on the axes

Reply: We provide the unit in the figure caption.

Figure S4: in black white the traces look identical.

Reply: We changed the colors and line style of the traces.