Interactive comment on **"Scattering and Absorption Cross-sections of Atmospheric Gases in the Ultraviolet-Visible Wavelength Range (307–725 nm)"** *by* **Quanfu He et al.**

Anonymous Referee #1

The authors report results from a laboratory study using Broadband Cavity Enhanced Spectroscopy (BBCES), supplemented by Cavity Ring Down Spectroscopy (CRDS) to measure Rayleigh scattering cross sections and absorption cross sections, where applicable, for the gases CO_2, N_2O, SF_6, O_2, and CH_4. What's new here is the use of a single mirror to cover a very broad wavelength range for the BBCES studies from 338-725 nm. The topics covered are important and within the scope of ACP, but I have significant concerns that need to be addressed before this paper can potentially be published.

Reply: We thank the Reviewer for the insightfull comments and the careful reading of our manuscript. We appreciate the comments that substantially helped to improve the manuscript.

— Major Comments/Corrections:

(1) The paper makes claims of superiority over prior work that do not appear to be supported by the data. For example, this sentence in the Abstract that is echoed in various other forms in the paper: "This study provides improved refractive index dispersion relations, n-based Rayleigh scattering cross-sections, and absorption cross-sections for these gases." In a few instances, the data from this paper do represent clear improvements over what is already in the literature (e.g., the significantly expanded wavelength range for the N_2O Rayleigh scattering cross sections), but in many cases, the data from this paper can only be stated to be in agreement with past work within the stated uncertainties rather than "improved". The authors should carefully go through the manuscript and make sure they are not overstating the superiority of the present

results over past studies.

Reply: We appreciate the reviewer's concern. As the reviewer suggests, the characterization of an improved dispersion relation is based on the extended wavelength range and continuous nature of the spectra compared to the literature. We have carefully gone through the manuscript to ensure that the language accurately represents cases in which our data agree with the literature and those in which is provides additional measurements. We have rephrased the sentence in the abstract to read "This study provides dispersion relations for refractive indices, n-based Rayleigh scattering cross sections and absorption cross sections based on more continuous and more extended wavelength ranges than available in the current literature.

This concern is especially relevant for the revised dispersion relations for SF6 and CH4. Based on the large spread in the n values from this study (and the range of pink shading, which I assume is the 1-sigma uncertainty) in Figure 9a and 9c, it seems clear that the data from this study do not provide constraint on the dispersion relations to allow distinguishing between the black and green fit lines. Moreover, the Shardanand and Rao data, which have large uncertainties and were intentionally excluded from analyses in earlier studies, only serve to increase the uncertainty of the CH4 fit here rather than decrease it. There are other issues with Figure 9 to be addressed later, but the point here is that the inclusion of the pink points from this study and black dots from Shardanand and Rao do not provide improved dispersion relations for SF6 and CH4 over the existing n-based relations. I find it disconcerting that nearly all of the pink points at wavelengths shorter than 480 nm lie above the fit line for SF6. Similarly, for CH4 nearly all of the pink points shorter than 400 nm are above the fit line except in the region 340–360 nm, where all points lie below the fit line. There appear to be systematic biases as a function of wavelength. Moreover, there is no discussion in Section 3.5 of how the different data sets were weighted to produce the fits.

Reply: We realized that these concerns originate from the fact that the refractive index data were not scaled to the same condition of 288.15K and 1013.25 hPa. The problem was also pointed out by the Reviewer in the later part of the comments. We have

therefore scaled all the data (ours and literature) in the revised manuscript to these conditions to enable better compasrison. After scaling, our data were brought closer to the literature data. See the revised Figure 9 below.

In the revised manuscript, the Shardanand and Rao data, which have large uncertainties, were excluded during the fitting. After adding more data from our study, we weighted all of the data sets equally for fitting, which is different from the approach of Wilmouth and Sayres (2020), where the data sets were differently weighted during the fitting. Our data now lies around the fitted lines and in most cases, it falls well within 1-sigma uncertainty (pink shaded) of our data. Thus, we believe that our data adds constraints for the fitting.

The calculated Rayleigh scattering cross sections using the dispersion relations derived in this study were compared with those derived from previously recommended formulations listed in Table 1 (Figure 9). The difference increases towrds the longer wavelength region between 320 and 725 nm (Figure S4). The average deviations are 0.1%, 0.9%, and 0.1% for SF_6, N_2O, and CH_4, respectively. The derived dispersion relationships agree very well with those of Wilmouth and Sayres (2020), as shown in Figure 9 (c-d).

Thus, we revised section 3.5 due to changes in the data processing. (Line 539-617)

The scaling method of the refractive index can be found in the Methods part "Additionally, the refractive indices of SF_6, N_2O, and CH_4 were calculated based on Equation (1) using cross section results from this study and the King correction factors listed in Table 1. Our measurements were performed under ~295K and ~1020 hPa. However, the calculated refractive indices were scaled to 288.15K and 1013.25 hPa as in previous studies (Sneep and Ubachs, 2005; Wilmouth and Sayres, 2020)."(Line 262-266).

The data weighting during the fitting is described as "For the formulation of the refractive index of CH_4, Wilmouth and Sayres (2020) weighted the data sets from Watson and Ramaswamy (1936) and Cuthbertson and Cuthbertson (1920) equally but gave more weight to their UV measurements when deriving the formulation of the refractive index. In this study, all of the CH_4 data set were weighted equally. The derived

dispersion relation agrees very well with that from Wilmouth and Sayres (2020), as shown in Figure 9 (c-d)." (Line 595-617)
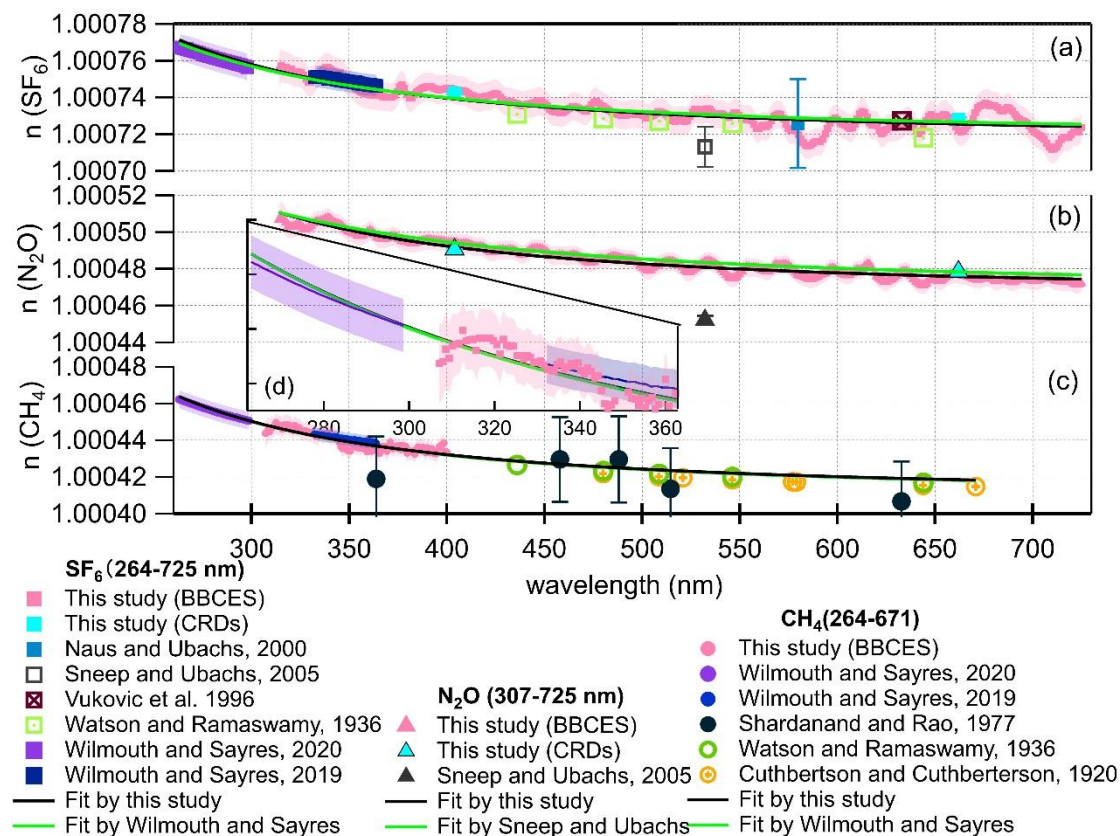

Figure 9. Real refractive index (*n*) for SF₆ (a), N₂O (b), and CH₄ (c). Comparison of Refractive index from this work with previous studies (Cuthbertson and Cuthbertson, 1920; Naus and Ubachs, 2000; Shardanand and Rao, 1977; Sneep and Ubachs, 2005; Vukovic et al., 1996; Watson et al., 1936; Wilmouth and Sayres, 2019, 2020) over the wavelength range of 264–725 nm. The green line represents the dispersion relation given in Table 1. The black line represents the dispersion relation given in Eq. (8–10) derived from a fit to our data and references results. The shading represents 1-σ uncertainty of *n*. The *n* values for Shardanand and Rao (1977), Sneep and Ubachs (2005), Naus and Ubachs (2000) were calculated from their reported Rayleigh scattering cross sections. Refractive index data from Sneep and Ubachs (2005) are not used in the fitting since these results are away from others. Data from Shardanand and Rao (1977) are not used due to large uncertainties. All of the data sets were equally weighted during fitting. Panel (d) is a close-up view of panel (c) in the wavelength range of 264–363 nm.

In short, I do not see anything convincing in the manuscript that the dispersion relationships produced for SF6 and CH4 are "improved" relative to the latest *n*-based

values in the literature, and it is very probable that the relations here are less accurate (see below). I recommend taking a consistent approach for SF6 and CH4 as to that used with CO2, which is to simply say that your results agree with the existing n-based values in the literature, rather than unnecessarily providing new dispersion relationships for SF6 and CH4 that cannot be distinguished from current values within your uncertainty.

Reply: As explained above, we updated the refractive index data for fitting, and all of the data sets are weighted equally during fitting. The derived dispersion relation agrees with that from Wilmouth and Sayres (2020), as shown in Figure 9 (c-d).

The calculated Rayleigh scattering cross sections using the dispersion relations derived in this study were compared with those derived from previously recommended formulations listed in Table 1 (Figure 9). The difference increases towards the longer wavelength in the region of 320–725 nm (Figure S4). The average deviations are 0.1%, 0.9%, and 0.1% for SF_6, N_2O, and CH_4, respectively. Our results based on data at an extended wavelength range support the reference results. Since our results agree well with results from Wilmouth and Sayres, we deleted the word "improved" in the abstract, and now state in the conclusion part that "The derived dispersion relations for SF_6 and CH_4 agree well with those provided by Wilmouth and Sayres (2020)." (Line 636-637)

(2) The accuracy of the Rayleigh scattering cross sections appears to be overstated. In section 2.4, the pressure is stated to be accurate to 0.01% and temperature to 0.1%. While the authors likely have the precision to measure changes in P and T to these levels, this level of accuracy would be surprising. Most pressure gauges are not even capable of 0.01% accuracy. How and where were P and T measured? How were the P and T gauges calibrated to this accuracy? Please provide part numbers for all devices used in the experiments.

Reply: The gas temperature was measured by a K-type thermocouple and the cavity pressure was recorded by a pressure gauge (Precision Pressure Transducer, Honeywell International Inc., MN, USA). The two BBCES channels were connected in series. These two parameters were measured between the two BBCES cavities. The pressure

gauge and the thermocouple were calibrated by the manufacturer. The temperature in our laboratory is very stable, and the daily variations are within ±0.25 °C. The system was operated at a low flow rate, and there is negligible resistance in the system. The stable environment in the lab helped to obtain temperature and pressure data with very small uncertainty. These details were provided in the manuscript as "The gas temperature (K-type thermocouple) and cavity pressure (Precision Pressure Transducer, Honeywell International Inc., MN, USA) were recorded between the two cavities for gas number density (N) calculation." (Line 233-235)

More importantly, the authors appear to be claiming that they have determined the reflectivity of the mirrors with essentially no experimental uncertainty. The 1.03% stated uncertainty in section 2.4 – which is the uncertainty in the effective pathlength, not the mirror reflectivity (please correct this misstatement in line 231) – is almost entirely due to the 1.0% N2 reference cross section. But what about the standard deviation of the N2/He runs? Surely, there was some spread in the data from run to run? And there undoubtedly was a wavelength dependence in the data quality based on mirror reflectivity, mirror transmission, fluctuations in the light source, the amount of light to the detector, etc.

Reply: In this study, the standard error from each measurement was used for the uncertainty calculation. As stated in the Methods part, 150 spectra were recorded for each gas measurement. The standard error of these 150 spectra was used to represent the uncertainty of the light intensity signal measurement. This uncertainly included reflects the variation in the light source, the fluctuations in the cavity and in the spectrometer. The relative uncertainty was ≪0.2%, as stated in the manuscript.

In the revised manuscript, we changed "mirror reflectivity" to "effective pathlength" (Line 313)

There is an additional problem here in that the reference N2 cross section in Table 1 is only valid up to 468 nm. At longer wavelengths, the 1% error should be increased to account for the uncertain extrapolation of this dispersion relation.

Reply: We agree with the Reviewer that the uncertainty of the Rayleigh scattering cross section for N_2 over 468 could be larger than 1%. However, no reference data is available to calculate how big it could be. Thus we added a note in the revised manuscript to explain this issue.

"The uncertainty for the Rayleigh scattering cross section of N_2 is validated up to 468 nm. The uncertainty above this wavelength may be larger than 1%, which is the value used for the calculation in our study. Thus, the uncertainty at wavelengths longer than 468 nm may be underestimated." (Line 321-338)

Most concerning of all with respect to stated uncertainties is that for the individual gases, the authors appear to be defining the 1-sigma uncertainty in their results based on the differences between their values and the existing n-based values. If this was indeed the approach taken, this is wrong and must be corrected. If this was not the approach taken, the method used should be clarified. Lines 262–264 simply state uncertainty values of 1.5%, 1.1%, and 1.5% for CO2, N2O, SF6, respectively, without explanation where they came from – these numbers appear again in the Conclusions Line 434 when these exact same numbers are stated to be the relative difference with the n-based calculations. As I examine the data plotted in Figure 1d, it is clear that the precision of the data in this study is generally quite good. But Figure 1e reveals that the accuracy is substantially worse than the precision. There is nearly +4% to − 4% discrepancy for CO2 and SF6 at some wavelengths relative to the n-based values. Whether or not the n-based values are correct is not the point here – the point is that the n-based values are smooth – so all of this chatter is due to the experimental data in the present paper. For CO2 and SF6, there appears to be a 7% swing just in going from around 590 to 600 nm. And this large error is in the mean values –the variation would be even greater in the individual runs. I suspect that the highly structured reflectivity curve (Figure S1) is creating problems, i.e., systematic biases creating persistent inaccuracies across the wavelength range even though the data reproducibility (precision) is good.

In short, for all the reasons mentioned above, the uncertainties should be completely revisited, more thoroughly explained, and almost certainly increased significantly from

the present values.

Reply: For the measurement of each gas, the light intensity, temperature, and pressure data were acquired 150 times. The standard error of these 150 single measurements was used as the 1-sigma uncertainty of each parameter. The same was done for the following helium measurement. Finally, the uncertainty of the effective pathlength, the uncertainties of the target gas measurement, and the uncertainties of the helium measurement were propagated together to calculate the 1-sigma uncertainty of the extinction cross sections. In the revised manuscript, we added these descriptions: "Each parameter (temperature, pressure, light intensity) was measured 150 times for each gas. The standard error of each parameter obtained from the 150 single measurements was used to calculate the uncertainty." (Line 308-310)

There was a mistake in the original manuscript (Line262-264) about the uncertainty of the CO_2, N_2O, and SF_6. This has been corrected in the revised manuscript as "The mean 1-σ uncertainty of the reported cross sections for all three gases across the 307–725 nm wavelength range is 1.04% for CO_2, 1.05% for N_2O, and 1.04% for SF_6." (Line 361-363)

We agree with the Reviewer that the large discrepancies around 590 to 600 nm are likely correlated with the structured mirror reflectivity. However, it is impossible to quantify how much this would add to the uncertainty of our data. To address this issue, several things were done to evaluate this.

1) First, the relative difference between our measured data and n-based calculations were calculated again and reported in the form of mean±SD. The mean number would give a measure of the bias relative to the n-based measurement and the standard deviation would give a measure of the error about this number. These numbers are now added to the revised manuscript: "The relative difference between our measurements and n-based values are (0.37±1.24)%, (–0.55±1.06)%, (0.91±1.35)% (Mean±SD) for CO_2, N_2O, and SF_6, respectively."(Line 391-393), "our extinction cross sections agree well with the n-based values with an average deviation of (2.81±1.21)%."(Line 475-476),"with an average difference of (0.89±2.18)%."(Line 531), "Comparison of our

measurements with the *n*-based calculations for these gases in the entire wavelength range of this study yields excellent agreement with relative differences of $(0.37\pm1.24)\%$, $(-0.55\pm1.06)\%$, $(0.91\pm1.35)\%$, $(2.81\pm1.21)\%$, and $(0.89\pm2.18)\%$, respectively."(Line 623-626).

2) To evaluate the uncertainty related to the structured mirror reflectivity, we fitted our Rayleigh scattering cross section data and the n-based data to a power function, $\sigma=A\lambda^B$. The difference between these two functions are now shown in Figure 1 panel (f). That would also be a meausure of the uncertainty comparing smooth functions to smooth functions. The change in the varability of the relative difference would represent the influence of the structured mirror reflectivity.We added the following text in the revised manuscript and add panel (f) in Figure 1.

"The relative difference between our measurements and the *n*-based values are $(0.37\pm1.24)\%$, $(-0.55\pm1.06)\%$, $(0.91\pm1.35)\%$ (Mean$\pm$stdev) for CO_2, N_2O, and SF_6, respectively. Variability of the relative difference is due to structure in the mirror reflectivity that does not fully cancel. The wavelength-dependent Rayleigh scattering cross section is generally described in the form of $\sigma = A \times \lambda^B$ In this study, the measured values and the n based data were both fitted to this function. The relative difference between these two fitted functions is shown in Figure 1(f). That would be a measure of the uncertainty comparing smooth functions to smooth functions. The relative differences were $(0.49\pm0.48)\%$, $(-0.41\pm0.30)\%$, and $(0.94\pm0.22)\%$ (Mean$\pm$stdev), for CO_2, N_2O, and SF_6, respectively. The mean values of the relative difference obtained from the fitting function are close to that obtained from the measurements. However, the variabilities are much smaller, which may be related to the cancellation of the influence by the structured mirror reflectivity.." (Line 391-402)

(f)

relative standard deviation of fitting (%) vs wavelength (nm)

— CO$_2$ — N$_2$O — SF$_6$
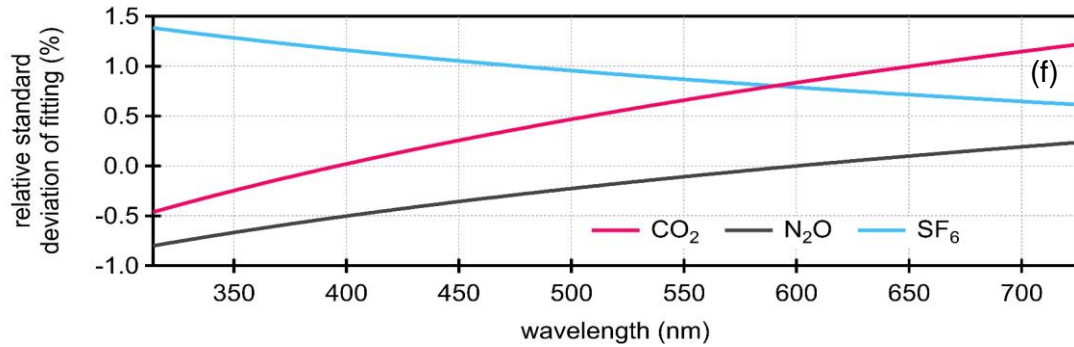
(3) The authors should cite previous studies where appropriate. Reference to the nbased values is made repeatedly throughout the paper for various gases, but it is never stated clearly from which study each of these n-based values originated. I recommend in column 5 of Table 1 that it be highlighted in some way (e.g., asterisk, bold, footnote) which of the listed References the n-based expression in column 2 came from. Also, the source of the n-based expression should be named for each gas at least once in the text and when comparisons are being made.

It would seem appropriate after Lines 80-81 to mention that Wilmouth and Sayres 2020 just published SF6 and CH4 dispersion relationships for the wavelength range 250-650 nm. Lines 90-93, 392-398, and 412-417 all discuss a method of determining new dispersion relationships for SF6 and CH4 in this study that is a copy of the Wilmouth and Sayres 2020 method, but the Wilmouth and Sayres 2020 paper is not credited for the idea that this paper is replicating.

Reply: We thank the Reviewer for this suggestion. In Table 1, we have labeled the source references of the refractive index (Bold) and the King correction factors (Italics) that are used for the n–based calculation. This is also explained in the footnote of Table 1. Moreover, these references were cited in the main text in the Methods part as "or the 307–725 nm wavelength range of this study, the n-based calculated Rayleigh scattering cross sections from largest to smallest are SF$_6$ (Sneep and Ubachs, 2005; Wilmouth and Sayres 2020), N$_2$O (Sneep and Ubachs, 2005), CO$_2$ (Alms et al. 1975; Bideau-Mehu et al. 1973), CH$_4$ (Sneep and Ubachs, 2005; Wilmouth and Sayres 2020), N$_2$ (Bates 1984), O$_2$ (Bates 1984; Sneep and Ubachs, 2005), and He (Abjean et al., 1970; Cuthbertson and Cuthbertson, 1932)." (Line 248-262)

We also added the study by Wilmouth and Sayres in the revised introduction part as "Recently, Wilmouth and Sayres (2020) combined refractive index data in the UV region (264-297 nm and 333-363 nm) and at several single wavelengths in the visible, and they derived the dispersion relation of refractive index for SF_6 and CH_4 in the wavelength range of 264-650 nm. However, more data in the visible range are needed in order to further validate these dispersion relations." (Line 98-102)

In the revised manuscript, the method of determining the new dispersion relationships for SF_6 and CH_4 as described by Wilmouth and Sayres was added to the introduction. (Line 98-102) We also emphasized this in Section 3.5 where we derived the dispersion relation for SF_6 and CH_4. (Line 542-544)

(4) Figure 9 contains significant errors. The n-baqsed data in Figure 9 for the studies of Watson, Cuthbertson, and Vukovic are all plotted incorrectly, causing them to appear much further from the fit lines than they should be. The authors appear to have taken the index of refraction data directly from the papers and did not appropriately convert to the reference temperature of 288.15 K. The authors should also check Figure 8 for accuracy, where the same reference studies are plotted.

Reply: We thank the Reviewer for this comment. We have scaled the refractive index data from Watson and Ramaswamy 1936, Cuthbertson and Cuthbertson 1920, Vukovic et al. 1996 to 288.15 K and 1013.25 hPa. The cross sections were recalculated using the correct temperate and pressure. Figure 8 and Figure 9 were updated in the revised manuscript.

(5) Due to the errors highlighted in point (4) above, the dispersion relationships produced in this study that included the literature index of refraction data are therefore all incorrect. The authors also do not state how they converted their own Rayleigh scattering data to index of refraction, nor the temperature and pressure at which their dispersion equations were defined; these things should be addressed.

Again, once the data themselves are plotted correctly, I see no point in producing new dispersion formulas for SF6 and CH4 that cannot be distinguished from the existing

dispersion formulas within uncertainty. Simply state that the data here agree with existing values, as was done with CO2.

Reply: In the revised manuscript, we added more details about how we converted our scattering cross section data to the refractive index at 288.15K and 1013.25 hPa. "Additionally, the refractive indices of SF_6, N_2O, and CH_4 were calculated based on Equation (1) using cross section results from this study and the King correction factors listed in Table 1. Our measurements were performed under ~295K and ~1020 hPa. However, the calculated refractive indices were scaled to 288.15K and 1013.25 hPa as in previous studies (Sneep and Ubachs, 2005; Wilmouth and Sayres, 2020)." (Line 262-266)

After correction for all of the refractive index data, we derived the dispersion relations for again for SF_6, N_2O, and CH_4 and modified the results and discussion in Section 3.5 accordingly. (Line 539-617)

Wilouth and Sayres (2020) derived the dispersion relations of refractive index based on data in the UV (264-297 nm and 333-363 nm) and in the visible wavelength range. However, we note that only a limited number of data points in the visible wavelength range were used. For SF_6, there is only one data point at 633 nm and for CH_4, there are 12 points. In the present study, however, we obtained many more measurements in the visible wavelength range. Incorporating our results for the formulation of the refractive index is therfore beneficial. Thus, we consider it useful to derive the dispersion relation using our data. We found that the fitting results from our study agree well with the data from Wilmouth and Sayres (2020). We added this discussion in the revised manuscript. "The calculated Rayleigh scattering cross sections using the dispersion relations derived in this study were compared with those derived from previously recommended formulations listed in Table 1 (Figure 9). The difference increases towards the longer wavelength in the region of 320–725 nm (Figure S4). The average deviations are 0.1%, 0.9%, and 0.1% for SF_6, N_2O, and CH_4, respectively. Notably, the difference for N_2O is more significant than for the other two gases. This study uses refractive index data in continuous wavelength ranges of 307–725 nm to derive the dispersion relation, while the formulation for N_2O in Table 1 is derived by Sneep and Ubachs (2005) based on

polarizability measurements at five single wavelengths. For the formulation of the refractive index of CH_4, Wilmouth and Sayres (2020) weighted the data sets from Watson and Ramaswamy (1936) and Cuthbertson and Cuthbertson (1920) equally but gave more weight to their UV measurements when deriving the formulation of the refractive index. In this study, all the CH_4 data sets were weighted equally. The derived dispersion relation agrees very well with that from Wilmouth and Sayres (2020), as shown in Figure 9 (c-d)." (Line 588-617)

— Additional Comments/Corrections:

Line 1 and elsewhere: Cross-sections should not be hyphenated

Reply: We have changed "cross-sections" to "cross sections" in the revised manuscript.

Lines 60–62: It is typical to order references in a list like this chronologically. Add Thalman et al. 2017 (Erratum to 2014 paper) and Wilmouth and Sayres 2020 to this list.

Reply: We added these two references and updated the original reference. (Line 79)

Line 98 and many other places in the manuscript: The authors use "BBCES" as if it were the name of their experimental setup. If the sentence doesn't make sense with "Broadband Cavity Enhanced Spectroscopy" substituted in place of "BBCES", the sentence should be edited.

Reply: We thank the Reviewer for this suggestion. Line 98 using BBCES is correct because the whole paragraph is the introduction of BBCES. We went through the entire manuscript again. We made several changes in the manuscript: 1) Line 306, change "**2.4 Error Propagation for BBCES**" to "**2.4 Error Propagation for Extinction Measurements**", 2) Line 632, change "using BBCES" to "using BBCES and CRDS".

Lines 104-120: Please provide more detail on how the broad wavelength range was filtered and how the data acquisition worked. Did the spectrometer scan through the wavelength range X nm at a time? Were 3 seconds of data acquired at each wavelength per spectrum, or it took 3 seconds to scan the entire range? With light being present

over such a broad wavelength range, how was stray light prevented from impacting the results? It seems like this would have been a problem. For example, did you ever use a longpass filter to block the shorter wavelength light to see if there was still signal present at the detector at the shorter wavelengths due to stray light from the longer wavelengths?

Reply: There are two filters for each BBCES Channel. The UV channel has two filters from Schott Glass: The WG310 filter was used to filter light with wavelength shorter than 310 nm, and a bandpass filter UG11 which has high transmission between 260 and 400 nm. The visible channel also contains two filters: Schott WG 345 was used to filter light with wavelength <345 nm, while a short pass filter (Edmund Optics, 15-261) was used to filter light with wavelength >700 nm. This information was added in Line 136 and Line 140-141.

The spectrometer has a back-illuminated CCD array detector with 1024×56 pixels. This detector records data from $302.15 - 727.29$ nm simultaneously. It does not scan from one wavelength to another. In our experiment, the CCD array was exposed for 3 s to obtain one spectrum. This information was already provided in the manuscript.

We used filters to remove light at both short and long wavelength range (short pass and long pass filters) to match the transmitted light wavelength range with the operating wavelength range of the high-reflectance mirrors. As indicated by the manufacturer, the stray light has a minimal influence on the spectra, e.g., stray light: <0.08% at 600 nm; 0.4% at 435 nm. Moreover, the test suggested by the Reviewer has, indeed, been carried out many times within different wavelength range when we searched for proper filters that fit the high reflection mirrors in the cavity. We did not detect any signal present at the detector at the shorter wavelengths due to stray light from the longer wavelengths.

Line 129: Why not present this equation already solved for R? Section 2: There is an awkward switching between past and present tense throughout. Pick one (ideally past) and stick with it.

Reply: The equation has been changed to show the solved R (Line 170). We went

through Section 2 and changed it to past tense.

Line 155 and many other places: The authors use "CRDS" as if it were the name of their experimental setup. If the sentence doesn't make sense with "Cavity Ring Down Spectroscopy" substituted in place of "CRDS", the sentence should be edited.

Reply: We have checked through the manuscript. The use of "CRDS" is correct.

Line 272: Delete "theoretical". The n-based calculations are based on experimentally determined data.

Reply: This has been corrected in the revised manuscript.

Line 345: Shouldn't 630 nm here be 629 nm, per Line 321?

Reply: Yes, it should be 629 nm. This was corrected.

Lines 346-348: Some of these discrepancies appear quite large, and the explanation given that it is because they are the lowest intensity bands is not entirely true. The band at 532 nm appears smaller than the band and 360 and 380 nm, and yet it agrees well. What the bands with larger discrepancies have in common is not their size, it's that they are all located at wavelengths below 450 nm, while the ones that agree well are all located at wavelengths above 450 nm. Please comment on why this wavelength dependent disagreement might be the case. The text says Thalman and Volkamer 2013 are being plotted, but the legend in the figure says Thalman et al. 2014. Also, why is there no comparison in the text with the most recent Karman 2019 study?

Reply: We thank the Reviewer for raising this question. First, the wavelength ranges where larger discrepancies (344, 360, 380, and 446 nm) appear have lower light intensity than those wavelengths with smaller discrepancies (477, 532, 577, and 630 nm). At a lower light intensity level, a small change in the light source could result in a large change in the determined extinction measurement. This could be one of the reasons why those larger discrepancies occurred. Additionally, the absorption at 344, 360, 380, and 446 nm contribute less to the total extinction as compared to that at 477,

532, 577, and 630 nm. For example, when the cavity is filled with 100% O_2, the absorption at 344, 360, 380, and 446 nm contribute 1.5%, 19.1%, 16.2%, and 12.8% of the total extinction, which are much smaller than those at 477 (64%), 532 (34%), 577 (88%), and 630 nm (90%). The low fraction of absorption may also induce larger discrepancies when apportionment absorption from total extinction. In the revised manuscript, we added more discussion on this: "Moreover, the absorptions at 344, 360, 380, and 446 nm contribute a much smaller fraction of the extinction as compared to that of 477, 532, 577, and 630 nm. Thus larger discrepancies were observed during the apportionment of absorption from extinction." (Line 489-491)

The paper Thalman and Volkamer 2013 should be used here. The Karman et al. 2019 paper explains the updates of the HITRAN collision-induced absorption section data. The O_2-O_2 collision-induced absorption data were taken from Thalman and Volkamer 2013. Thus we only compared the measurement results from Thalman and Volkamer, which is the original study.

Line 355-356: Please add a reference for this first sentence.

Reply: The paper Adel and Slipher, 1934 was added here. (Line 497)

Adel, A. and Slipher, V. M.: The Constitution of the Atmospheres of the Giant Planets, Physical Review, 46, 902-906, 10.1103/PhysRev.46.902, 1934.

Lines 371-373: This sentence is incorrect as written. The interferometer studies obtained index of refraction values, not scattering cross sections.

Reply: This sentence has been revised. We added "and the refractive index" before "of CH_4". (Line 516)

Line 383: It seems like an oversimplification to say that there is "good" agreement here. There are significant discrepancies at many wavelengths.

Reply: Limited data about absorption cross section of CH_4 is avauialble in the literature. In addition, the absorption cross section varies significantly with wavelength. There are large discrepancies between these datasets, and to the best of our knowledge, there is not a recommended data set. Thus we do not discuss the comparison to literature data.

Only a brief description is provided in the manuscript. We revised this sentence to "At most spectral ranges, our results are in better agreement with the results from previous studies by Giver, (1978) and Smith et al.(1990)." (Line 532-534)

Line 391: Delete "much".

Reply: Deleted.

Line 392: "Better constrain" relative to what?

Reply: We derived the dispersion relation expression of SF_6 over a wider wavelength range as compared to previous studies (Wilmouth and Sayres). The word "better" was deleted in the revised manuscript.

Line 412: Change 9b to 9c

Reply: Changed to 8b.

Lines 429-432, Lines 361-363, and Lines 327-332: The BBCES and CRDS agreement is certainly a positive result, but be careful not to overstate what this means (lines 329-331). It's just two wavelengths, and there are clearly significant wavelength-dependent errors in the BBCES data. Moreover, the locations of the CRDS points are all offset from both the fit lines and the BBCES data in Figure 9, suggesting that the CRDS results do not provide any additional constraint on the accuracy of the BBCES results even at these two wavelengths.

Reply: We thank the Reviewer for this comment. We agree that there are wavelength-dependent errors in the BBCES data. The agreement between CRDS and BBCES data at 404 and 662 nm does not guarantee the results at other wavelengths. We have modified this sentence to "This excellent agreement between the instruments further substantiates the BBCES measurements and suggests that the accuracy of the BBCES at these two wavelengths is better than estimated in the error propagation above, where the N_2 refractive index was the largest uncertainty." (Line 462-464)

We scaled the refractive index data to 288.15K and 1013.25 hPa. Now the results from

CRDS agree much better with the results from BBCES as shown in Figure 9.

Line 442-445: This point was made earlier, but to reiterate here, the claims of superiority from this study are not justified. The Wilmouth and Sayres 2020 fit of the UV region for CH4 that is plotted in Figures 9c and 9d was purposefully weighted such that it better represented the existing index of refraction data in the visible region at the slight expense of the UV fit, as described in that paper. A UV-only fit is also presented in that paper. The fact that the fit from the present manuscript is higher for CH4 simply means that this new fit is not representing the visible data as well as the Wilmouth and Sayres 2020 expression.

Reply: We have scaled our refractive index data and literature data in the revised manuscript. By incorporating our revised data into the data used by Wilmouth and Sayres (2020), we derived the dispersion relation for the refractive index of CH4. The Wilmouth and Sayres 2020 fit of the UV region for CH4 that is plotted in Figures 9c and 9d was purposefully weighted such that it better represented the existing index of refraction data in the visible region at the slight expense of the UV fit. In our fit, we added more data points in the wavelength range of 302-400 nm, and we weighted all of the data sets equally. Our fits agree well with that of Wilmouth and Sayres. The calculated Rayleigh scattering cross section from these two fits has a maximum difference of 0.15% and averaged 0.12%. This means that our data do constrain the formulation of the refractive index.

Figure 8: There are many errors in the figure legends. Wilmouth, Watson, and Cuthbertson are all two-author papers, not "et al." Watson is misspelled. Cuthbertson is misspelled. Add a space after Rao. Add a space after Sneep.

Reply: Thanks a lot for the careful reading. These errors have been corrected. The revised figure has been shown below.
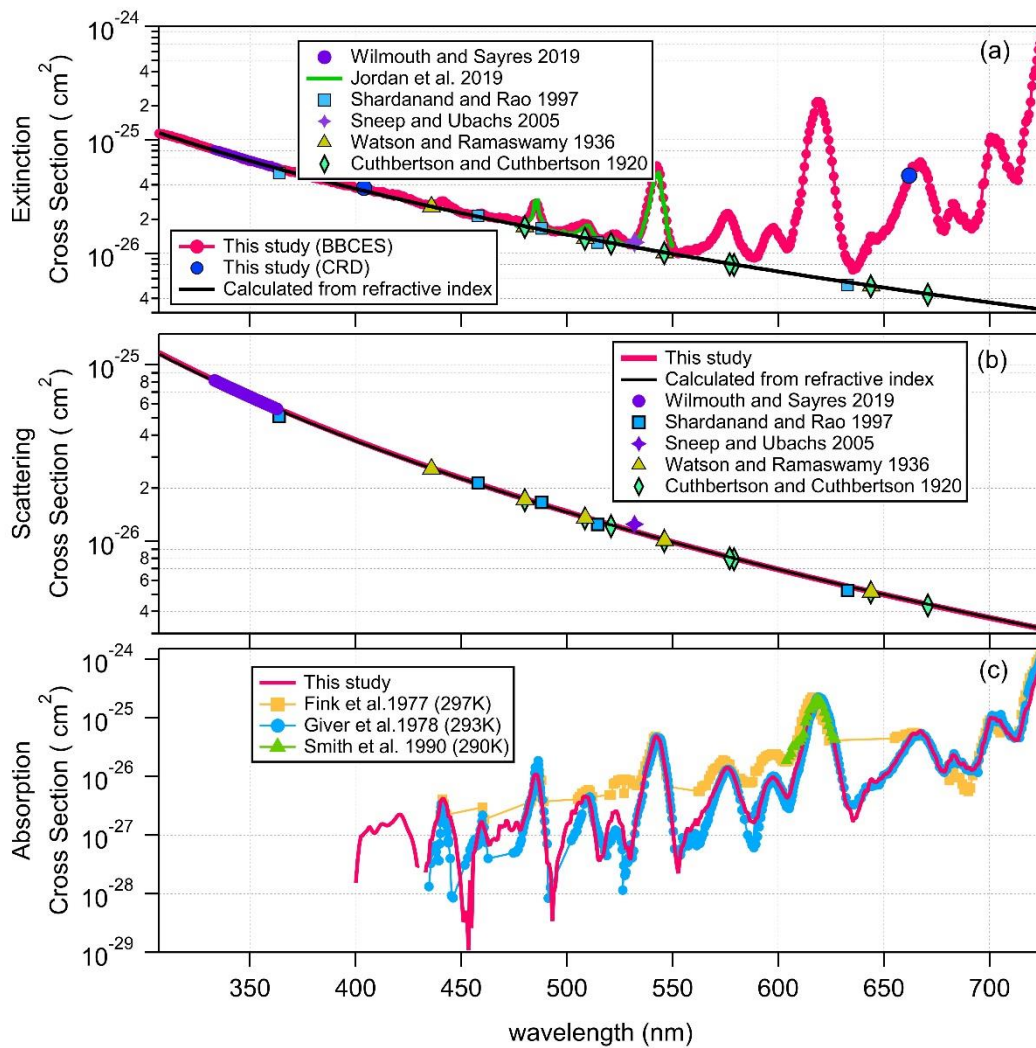
Figure 9: It is never stated what the shading represents in this figure.

Reply: The shading represents the 1-σ uncertainty of the refractive index. This was added to the caption of Figure 9.

Table 1: The He equation is incorrect. There is a missing decimal in 1.8102.

Reply: Corrected.

— Minor Corrections:

Line 22: Delete "and" after 1.5%

Line 31: Delete "as" after either

Line 44: Add "a" after For

Line 53: Change "index" to indices

Line 151: Change "systems" to spectroscopy

Line 152: Change "-validation of" to validate

Line 156: Add "was" after thus

Line 209: Change "overlaps" to overlap

Line 216: Delete "the" after of

Line 235: Change "resulted uncertainty of" to resulting uncertainty in

Lines 306 and 313: Avoid apostrophe "instrument's" – instead say wavelength resolution of the instrument

Line 328: Change "slops" to slopes

Reply: We thank the Review for the careful reading. These have been corrected in the revised manuscript.