

# ***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**

Received and published: 4 December 2020

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<sub>2</sub>, N<sub>2</sub>O, SF<sub>6</sub>, O<sub>2</sub>, and CH<sub>4</sub>. 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.

— Major Comments/Corrections:

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(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<sub>2</sub>O 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.

This concern is especially relevant for the revised dispersion relations for SF<sub>6</sub> and CH<sub>4</sub>. 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 CH<sub>4</sub> 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 SF<sub>6</sub> and CH<sub>4</sub> 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 SF<sub>6</sub>. Similarly, for CH<sub>4</sub> 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.

In short, I do not see anything convincing in the manuscript that the dispersion relation-

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ships produced for SF<sub>6</sub> and CH<sub>4</sub> 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 SF<sub>6</sub> and CH<sub>4</sub> as to that used with CO<sub>2</sub>, 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 SF<sub>6</sub> and CH<sub>4</sub> that cannot be distinguished from current values within your uncertainty.

(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.

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% N<sub>2</sub> reference cross section. But what about the standard deviation of the N<sub>2</sub>/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.

There is an additional problem here in that the reference N<sub>2</sub> 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.

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

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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 CO<sub>2</sub>, N<sub>2</sub>O, SF<sub>6</sub>, 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 CO<sub>2</sub> and SF<sub>6</sub> 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 CO<sub>2</sub> and SF<sub>6</sub>, 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.

(3) The authors should cite previous studies where appropriate. Reference to the n-based 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.

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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.

(4) Figure 9 contains significant errors. The n-based 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.

(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.

— Additional Comments/Corrections:

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

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

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list.

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.

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?

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.

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.

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

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

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?

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

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

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

Line 391: Delete “much”.

Line 392: “Better constrain” relative to what?

Line 412: Change 9b to 9c

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.

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 CH<sub>4</sub> 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

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in that paper. The fact that the fit from the present manuscript is higher for CH<sub>4</sub> simply means that this new fit is not representing the visible data as well as the Wilmouth and Sayres 2020 expression.

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 Sneeep.

Figure 9: It is never stated what the shading represents in this figure.

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

— 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



Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-941>, 2020.

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