

Reply to the reviewer 1's comment

Before entering the reply section, we express our gratitude to Reviewer 1 for her/his careful and detailed reading of the manuscript and the insightful and helpful comments, which we were pleased to follow up. We believe that addressing all of reviewer's comment should improve a quality of our manuscript. Therefore, we hope to try address all reviewers' comment properly. Please find our reply color-coded as blue between reviewers' comments.

Reviewer #1:

The manuscript provides a detailed discussion of absorption cross-sections using DOAS technology, and the experimental procedures are described comprehensively. However, in its current form, the manuscript requires substantial revision to improve clarity and consistency.

Major Concerns:

1. The manuscript's writing and structure are often confusing, making it difficult to understand the main arguments and methods. A notable example is the inconsistent definition of the hybrid simulation (HS) method for absorption cross-sections (ACSs). For instance, in Lines 163–166:

Hybrid simulation (HS) of ACSs involves converting the reference absorption spectrum from the literature using the instrument function (IF) to simulate how the absorption spectrum would appear if measured by the specific spectrometer.

However, after Section 3.3, the HS method appears to change its definition to include convolution and nonlinear least-squares (NLS) fitting. Throughout the manuscript, the term "HS method" is used multiple times, and it is unclear whether it refers to a standard methodology or a novel approach proposed by the authors, named the hybrid calibration method. More clarity and differentiation are necessary.

- On the major comments:

following the recommendation of the three reviewers who found it difficult to follow the flow of this manuscript, we agreed to split the paper into two parts. The first part is about the hybrid simulation (HS) method and the second part is about the precise measurement (PM) method.

Our proposed Hybrid Simulation (HS) method combines two key steps: first, convolving the reference spectrum with the instrument function (IF) of the spectrometer; and second, applying nonlinear least-squares (NLS) fitting.

This definition of the HS method is consistently applied throughout the revised manuscript to avoid any confusion.

2. Similarly, there is ambiguity regarding the blue line in Figure 5—does it represent the high-resolution cross-section or the convoluted cross-section? The manuscript appears to present conflicting descriptions, which require resolution for accurate interpretation.

- I apologize for the confusion due to the ambiguity in the parameters in the manuscript. We have fixed this problem by making a consistent parameter throughout the new manuscript as follows:

$\sigma(\lambda)_{meas}$: Absorption cross section spectrum measured at wavelength λ

$\sigma(\lambda)_{HS}$: Absorption cross section spectrum simulated using HS approach at wavelength λ

$\sigma(\lambda)_{ref}$: Reference absorption spectrum from literature

The blue line in Figure 5 (now become Figure 3 in the new manuscript) is refers to the reference ACS from literature $\sigma(\lambda)_{ref}$. All others parameters are also corrected accordingly in the graph and the main text.

3. As stated by authors, commonly used cross-sections are either convoluted or experimentally measured. My understanding is that the authors have proposed an innovative method that not only convolutes the high-resolution cross-sections but also applies NLS fitting. This method could potentially be extended to other gases within the same spectral range where experimental cross-sections are unavailable (e.g., Line 295). While this seems a promising innovation, I have reservations about its broader applicability. Absorption cross-sections reported by different studies often exhibit inherent differences, raising doubts about the validity of applying the same correction factor across various studies. To address these concerns, I suggest that the authors provide additional experimental evidence, such as simultaneous measurements of benzene and toluene cross-sections within the same spectral range, comparing the correction factors obtained through separate NLS fittings.

-A comparison experiment between the correction factors obtained using the HS method for benzene and toluene has been performed for the measurement range between 257.9 and 269.6 nm. For the comparison purpose, we made a similar treatment to the both spectra. In this experiment, we use IF at 265 nm for benzene and toluene. However, in the manuscript we used IF at the center wavelength of 248 nm for benzene because in the real application of LP-DOAS we focus on the deep UV range where less strong absorption of other gas species is observed in the range near 248 nm.

Benzene

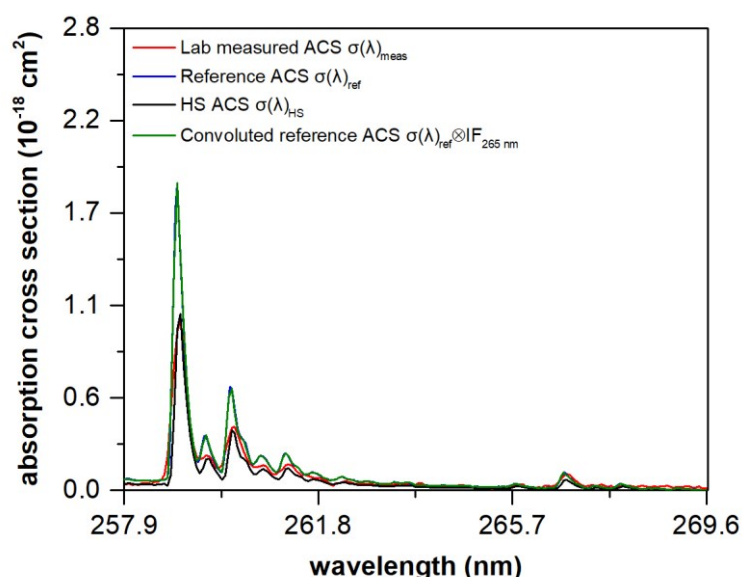


Figure 1. Comparison of the laboratory-measured ACS, the reference literature ACS, and the ACS generated using the HS approach. The convolution alone cannot align the reference ACS spectrum with the measured ACS spectrum. However, applying the HS method improves the fit, as indicated by a reduction in the Sum of Squared Errors (SSE), from 1.6004×10^{-36} before NLS fitting to 4.2574×10^{-37} after NLS fitting.

Table 1. The optimized parameters from NLS fitting from benzene experiment.

Parameter	Value
a (squeezing)	1.001 pixel (0.0635 nm)
b (shifting)	-1 pixel (-0.063 nm)
c (amplitude scaling)	$0.6 \text{ cm}^2 \cdot \text{molecule}^{-1}$

Toluene

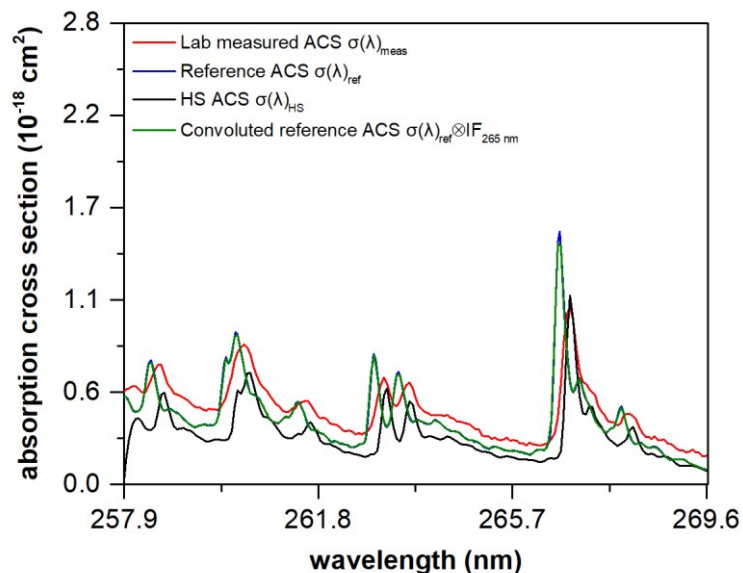


Figure 2. Comparison of the laboratory-measured ACS, the reference literature ACS, and the ACS generated using the HS approach. The convolution alone cannot align the reference ACS spectrum with the measured ACS spectrum. However, applying the HS method improves the fit, as indicated by a reduction in the Sum of Squared Errors (SSE), from 4.5×10^{-36} to 1.45×10^{-36} .

Table 2. The optimized parameters from NLS fitting from toluene experiment.

Parameter	Value
a (squeezing)	1.003 pixel (0.0636 nm)
b (shifting)	-5 pixel (-0.317 nm)
c (amplitude scaling)	$0.68 \text{ cm}^2 \cdot \text{molecule}^{-1}$

We compared the fitting parameters between the two gas species and observed good agreement between the amplitude scaling and squeezing parameters for the HS method. As shown in Figure 1 and Figure 2, when relying solely on convolution, the peak intensity of the convolved reference spectrum does not align well with that of the measured spectrum. However, by applying the HS procedure, the peak intensities of the simulated spectra more closely match the measured spectra. This improvement is reflected in reduced sum of squared errors (SSE) values for both the benzene and toluene measurement spectra. This demonstrates that our approach, which integrates both convolution and nonlinear least squares (NLS) fitting, enhances the accuracy of spectral simulation and is applicable to other gases within the same spectral range where experimental cross-sections are unavailable. Although there is a slight discrepancy of approximately 0.25 nm in the shifting coefficient between the two different literature absorption cross-sections, which may be attributed to variations in experimental conditions, the key parameters—amplitude and squeezing—remain consistent between the two HS simulation results at a same spectral range. The squeezing parameter represents spectral broadening, while the amplitude indicates the depth of absorption (i.e., the optical density of the gas absorber). The shifting parameter, on the other hand, can be effectively determined and corrected using NLS fitting during LP-DOAS retrieval.

4. The correction factors presented in Table 5 are extremely small. Would these corrections not already be manageable within the DOAS fitting process without requiring the proposed methodology? Additional clarification is needed to justify the necessity of this approach.

-In response to the comment regarding the small correction factors in Table 5, we would like to clarify that the amplitude scaling parameter (c), which is critical as it indicates the depth of absorption, was not included in the Table. This parameter represents the optical density of the gas absorber and cannot be fully accounted for through the standard DOAS fitting process alone. The DOAS fitting primarily corrects for absorption features, but it does not directly adjust for the amplitude scaling for the reference spectrum. Therefore, we added this parameter in Table 5 serves to emphasize its importance and to clarify why it is necessary to incorporate our proposed methodology for a more accurate spectral analysis.

Minor Concerns:

1. Figure 5 appears before Figure 3 in the manuscript, which disrupts the logical flow. Please reorder the figures appropriately.

-Thank you for your comments. We now divide the paper into two parts: hybrid simulation (HS) and precise measurement (PM) to make it easier for the reader to follow. Figure 3 will be discussed in the PM part and has been deleted from the first part of the paper.

2. Line 303: The subscripts for (O₂) and (O₃) are incorrect and require revision.

-We have fixed it as suggested.

3. Table 4: The detection limits reported for Trost et al. seem unusually low—three orders of magnitude smaller than other devices. Please verify these values.

-The reason why DL of Trost et al much smaller than other is because the assumed path length is longer than the other work. We will discuss it more detail in the second part of the manuscript. We have deleted the table in the first part of the manuscript because it is related to the PM approach.

4. Table 5: The drift for benzene is reported as (10^{-14}). Such an exceedingly small number raises questions about its significance—please clarify.

-The value is accurate because we have calibrated our spectrometer's wavelength, ensuring precise readings that closely match the literature values. The main difference lies in the amplitude scaling (c) parameter, which we have now included in the new draft.

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