

Supplementary material

Measurement of the absorption cross-sections of sulfur compounds in the 180-270 nm region considering nonlinear effects

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Part 1: Theoretical explanation of the nonlinear effect

The conditions for the application of Lambert-Beer law, whether measuring the concentration of solutions or gases, are that the incident light is parallel monochromatic and perpendicularly illuminated. However, the detector actually receives multicolored light during the measurement. Based on the principle of additivity of multicolor light intensities, we give a theoretical explanation for the linear deviation of the Lambert-Beer law with respect to resolution and concentration, as shown in Eq. S1. The exact derivation of Eq. S1 is described in the literature [1].

$$A_s = \sum_{n=1}^N A_n = 0.4343k_\alpha CL \sum_{n=1}^N \sigma(\lambda_{1n}) + \sum_{n=1}^N \lg \frac{I_{0n}(\lambda_{1n}) + I_{0n}(\lambda_{2n})}{I_{0n}(\lambda_{1n}) + I_{0n}(\lambda_{2n}) \times \exp[(\sigma(\lambda_{1n}) - \sigma(\lambda_{2n}))k_\alpha CL]} \quad (\text{S1})$$

A_s is the sum of absorbance; λ_{1n} , λ_{2n} are two different wavelengths received by the n th detector, respectively; $\sigma(\lambda)$ is the absorption cross-section at λ ; C is the concentration of the substance; and L is the effective optical range.

Let:

$$\begin{cases} A_l = 0.4343k_\alpha CL \sum_{n=1}^N \sigma(\lambda_{1n}) \\ A_d = \sum_{n=1}^N \lg \frac{I_{0n}(\lambda_{1n}) + I_{0n}(\lambda_{2n})}{I_{0n}(\lambda_{1n}) + I_{0n}(\lambda_{2n}) \times \exp[(\sigma(\lambda_{1n}) - \sigma(\lambda_{2n}))k_\alpha CL]} \end{cases} \quad (\text{S2})$$

A_l is the linear part of Lambert-Beer law; A_d is the source of the deviation from linearity. Absorbance (A_s) and total column concentration (CL) show a linear relationship only when the light received by the detector has the same absorption cross-section ($A_d = 0$). From A_d , it can be found that the linear deviation is negatively correlated with the resolution (value) and positively correlated with the column concentration. The nonlinear effect is the result of insufficient spectral resolution. Therefore, a direct means of reducing the deviation from linearity is to increase the resolution. However, the resolution of the spectrometer cannot be increased indefinitely

making $\sigma(\lambda_{1n}) = \sigma(\lambda_{2n})$. Therefore, the column concentration (CL) should be made as small as possible in order to keep the error within allowable limits (A_d can be ignored.) at a fixed resolution. At this point, the absorbance was considered to be linearly related to the column concentration.

Part 2: Sample collection process

The ex-factory quality of the four standard gases SO_2 , CS_2 , H_2S and OCS used by us were 1497 ppm, 101 ppm, 96 ppm and 205 ppm respectively. The standard gases and their high purity nitrogen (99.99%) used throughout the experiments were supplied by Nanjing Tianze Gas Co., Ltd. The standard gases produced by this company are in accordance with the standard QBW:TZ0190. The relative extended uncertainty of the concentration of the standard gas is 2% (clearly marked on the production certificate of the standard substance).

A gas distributor (GC400, Tunkon) supplied by Tunkon Electric Co., Ltd. is used, which consists of one dilution channel and four sample channels. Each channel inside the gas distributor is actually adjusted by an independent MFC mass flow controller to adjust the process flow, and after uniform mixing is able to output a complex mixture of gases with different concentrations of each component. In this experiment, high purity nitrogen is passed into the dilution channel and standard gas can be passed into any of the sample channels to mix with the dilution gas. Finally, the mixed gas is passed into the sample cell at a flow rate of 1L/min. The maximum achievable dilution ratio of the instrument is 500:1, and the accuracy of the gas distribution is $\pm 0.5\%$ F.S.

Part 3: Comparative analysis of SO_2 absorption cross-section

Numerous research groups in previous studies have carried out measurements of SO_2 absorption cross-section at different resolutions and temperatures. We compared the results of their data measured at different resolutions under room temperature conditions, as shown in Fig. S1. Theoretically, the higher the resolution the larger the

absorption cross-section obtained. However, we found in Fig. S1(a) that the data obtained by Olive [2] at 0.13 nm is much smaller than that obtained by Ahmedkumar [3] at 0.2 nm. The absorption cross-section obtained by Wu [4] at a high resolution (0.05 nm) is also much smaller than the data obtained in Fig. S1(b) at 0.1 nm. In addition, the obtained data at 0.1 nm resolution are different, as shown in Fig. S1(b). This shows that most researchers used high concentrations for the calculation of absorption cross-sections in order to improve the signal-to-noise ratio of the spectra, ignoring the serious impact of high concentrations on the nonlinear effects. Thus, the absorption cross-section obtained at high resolution is smaller than the data obtained at low resolution in Fig. S1. The specific experimental conditions under which the relevant studies in the figure were performed are shown in Table S1.

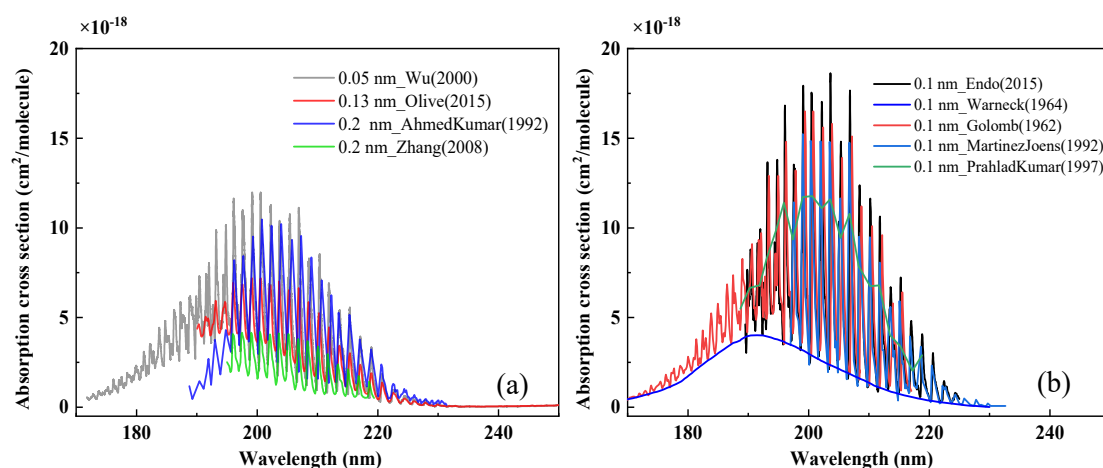


Fig. S1 UV absorption cross-section of SO₂

Table S1. Summary of SO₂ absorption cross-section

Researchers (Year)	Measured region (nm)	Resolution	Experimental conditions		Maximum values (cm ² /molecule)
			Temperature	Pressure	
C. Y. Robert Wu (1981) [5]	208-228 299-340	0.06 nm	294 K	0.01-40 Torr	8.0×10 ⁻¹⁸ (208.5 nm)
Olive (2015) [2]	190-306	0.13 nm	298 K	--	7.20×10 ⁻¹⁸ (203.64 nm)
Zhang (2008) [6]	195-219.4	0.2 nm	298 K	101.3 kPa	4.12×10 ⁻¹⁸ (203.58 nm)
Warneck (1964) [7]	135-230	0.1 nm	298 K	--	4.02×10 ⁻¹⁸ (190.4 nm)

Golomb (1962) [8]	106-217	0.1 nm	298 K	--	15.6×10^{-18} (202.41 nm)
PrahladKumar (1997) [9]	188-219	0.1 nm	300 K	--	11.77×10^{-18} (200.6 nm)
S. M. AHMED (1992) [3]	188-231 278.7-320	0.2 nm	298 K	0.1-0.35 Torr	10.47×10^{-18} (200.8 nm)
Martinez (1992) [10]	197-240	0.1 nm	300 K	100 Torr	15.80×10^{-18} (203.56 nm)
Yoshiaki Endo (2015) [11]	189.5-225	0.1 nm	293 K	0.1-2.3 Torr	18.6×10^{-18} (203.62 nm)
Stark (1999) [12]	198-220	0.00054 nm	295 K	0.07-0.12 Torr	4.0×10^{-17}
Yoshiaki Endo (2022) [13]	206-220	$\sim 1 \text{ cm}^{-1}$	295 K	--	2.0×10^{-17} (207 nm)
C. Y. Robert Wu (2000) [4]	171.7- 189.7	0.05 nm	295 K	1 Torr	11.98×10^{-18} (199.2 nm)

Part 4: Comparative analysis of CS₂ absorption cross-section

Similarly, previous studies regarding CS₂ were organized, as shown in Fig. S2. In the figure, it can be seen that CS₂ and SO₂ appear to be in the same situation. To put it differently, there is a large difference in the absorption cross-sections obtained even at the same resolution. Their specific experimental conditions are shown in Table S2. When comparing the data in Table S2, we found that both Ahmedkumar [14] and Xu [15] performed their experiments at ultra-low pressures. However, Zhang et al. [16] performed their experiments at standard atmospheric pressure. Due to the large difference in pressure in the three experimental environments, the experimental results can be different. However, in the main body of the article, we compared the absorption cross-section obtained using a spectrometer at 0.23 nm with that obtained at 0.1 nm [16] (both at standard atmospheric pressure) and found the same conclusions as those obtained above after analyzing SO₂ in Part 2.

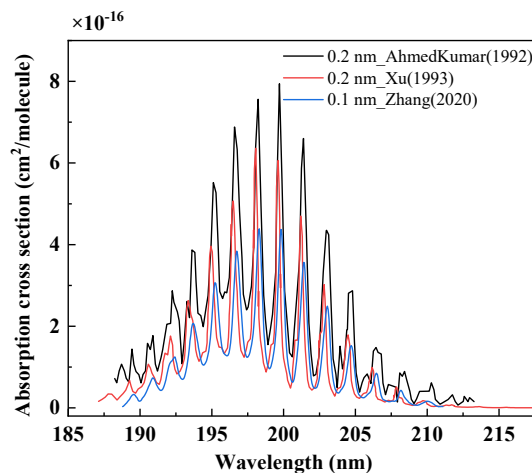


Fig. S2 UV absorption cross-section of CS₂.

Table S2. Summary of CS₂ absorption cross-section

Researchers (Years)	Measured region (nm)	Resolution	Experimental conditions		Maximum values (cm ² /molecule)
			Temperatur e	Pressure	
S M AHMED (1992) [14]	188-213	0.2 nm	298 K	1-5 mTorr	7.94×10 ⁻¹⁶ (198.0 nm)
Huan Xu (1993) [15]	187-230	0.2 nm	300 K	10-100 Torr	6.3×10 ⁻¹⁶ (198.0 nm)
Y.G. Zhang (2020) [16]	188-215	0.1 nm	298 K	101.3-101.5 kPa	4.5×10 ⁻¹⁶ (198.1 nm)

Part 5: Comparative analysis of H₂S and OCS absorption cross-section

The results of the database studies related to H₂S and OCS are shown in Fig. S3. The specific conditions under which the experiment was conducted are shown in Tables S3 and S4. As can be seen from the figure and tables, the results of the measurements are essentially the same even when the absorption cross-sections are measured at different resolutions. This indicates that the absorption characteristics of H₂S and OCS are different from the oscillatory type of spectra such as SO₂ and CS₂, and that a lower spectrometer resolution is sufficient to meet the requirements of a broad band absorption spectrum. Therefore, the concentration does not have a large effect on the measurements of the absorption cross-section.

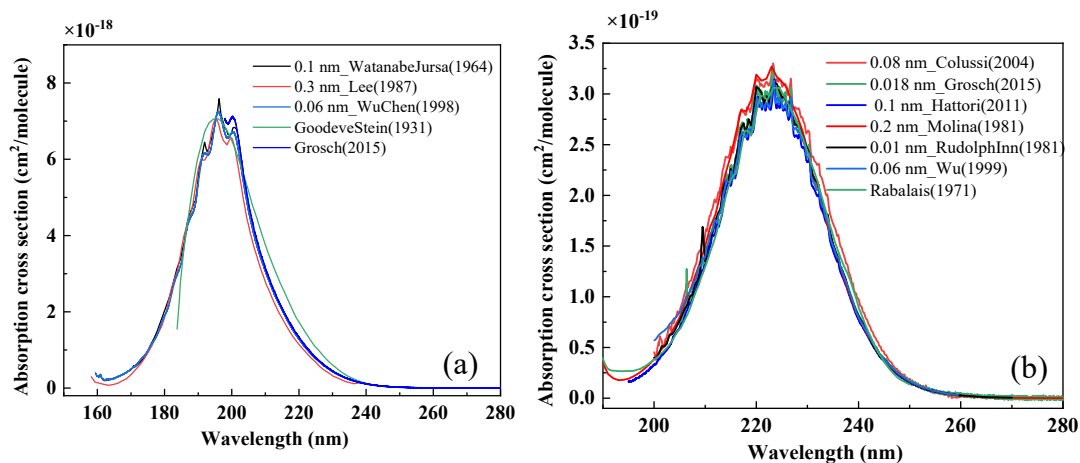


Fig. S3 (a) UV absorption cross-section of H₂S; (b) UV absorption cross-section of OCS

Table S3. Summary of H₂S absorption cross-section

Researchers (Years)	Measured region (nm)	Resolution	Experimental conditions		Maximum values (cm ² /molecule)
			Temperature	Pressure	
GoodeveStein (1931) [17]	183.7-270.6	--	298 K	--	7.09×10 ⁻¹⁸ (195.37 nm)
K. Watanabe (1964) [18]	160.2-209.4	0.1 nm	298 K	--	7.59×10 ⁻¹⁸ (196.24 nm)
Lee (1987) [19]	158-238	0.3 nm	295 K	--	7.10×10 ⁻¹⁸ (195.28 nm)
Grosch (2015) [20]	198-370	0.018 nm	294.8 K	--	7.13×10 ⁻¹⁸ (200.27 nm)
WuChen (1998) [21]	160-260	0.06 nm	295 K	0.02-100 Torr	7.26×10 ⁻¹⁸ (195.88 nm)

Table S4. Summary of OCS absorption cross-section

Researchers (Years)	Measured region (nm)	Resolution	Experimental conditions		Maximum values (cm ² /molecule)
			Temperature	Pressure	
L.T. Molina (1981) [22]	185-300	0.2 nm	295 K	300 Torr	3.19×10 ⁻¹⁹ (223.5 nm)
C. Y. ROBERT WU (1999) [23]	200-260	0.06 nm	295 K	0.02-100 Torr	3.0×10 ⁻¹⁹ (222.0 nm)
H. Grosch (2015) [24]	200-360	0.018 nm	295 K	101.3 kPa	3.25×10 ⁻¹⁹ (223.0 nm)

Colussi (2004) [25]	200-260	0.08 nm	298 K	2-10 mbar	3.3×10^{-19} (223.3 nm)
Hattori (2011) [26]	195-260	0.1 nm	295 K	133 mbar	3.14×10^{-19} (223.52 nm)
RudolphInn (1981) [27]	200-270	0.01 nm	297 K	2.5-90 Torr	3.11×10^{-19} (223.5 nm)
Rabalais (1971) [28]	125-250	--	298 K	10^{-4} Torr	3.06×10^{-19} (223.26 nm)

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