Sulfur Dioxide Fluorescence Imaging

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Abstract Sulfur dioxide is an ideal tracer to study the partitioning of the resistance of gas transfer across the water interface between air and water because the pH value in water controls the effective solubility of sulfur dioxide. Friman and Jähne [1] already demonstrated that it is possible to measure sulfur dioxide concentration profiles with laser induced fluorescence (LIF), but the best excitation wavelength under standard atmospheric conditions was not known. Here, we report the result of our investigation to select the best excitation wavelength for sulfur dioxide fluorescence to reach maximum intensity with the lowest possible absorption.

Keywords Sulfur Dioxide, Fluorescence Imaging

1 Introduction

Fluorescence imaging has two specific advantages. Firstly, it allows to measure concentration fields. The simplest setup is to stimulate the fluorescence by a light sheet to obtain a planar cross-section of a 3-D concentration field. Secondly, by using the right combination of the stimulation wavelength and spectral range, it is very specific and can be tuned to measure the fluorescence of a single chemical component. Therefore fluorescence imaging has become very useful in life sciences, fluid dynamics and combustion research. In this paper we describe fluorescence imaging of sulfur dioxide. It nicely demonstrates that all details must carefully be considered to set up an optimal measuring system.

Our interest in sulfur dioxide is caused by the fact that sulfur dioxide is an ideal tracer to study the partitioning of the resistance of gas transfer across the air-water interface. The dimensionless solubility expresses how much of a dissolved species is contained per volume unit in water as compared to air. The solubility of a volatile species or gas in water decides whether it can be transported more easily in water or in air. A species with a low solubility experiences a high concentration difference in water compared to the concentration difference in air, because not much of the dissolved species can be transported by a volume element in water. The transport experiences then a high resistance, i. e., concentration difference in water. In this case the transport processes in water control the speed of transfer and not those in the air space. For a high solubility in water, it is the other way round. At a wind-driven water surface the transition between water-side to air-side control occurs at a solubility between 500 and 1000 [2, 3].

The physical solubility of sulfur dioxide is about 29 at room temperature [4]. At pH-values larger than 1, sulfur dioxide reacts with water to form hydrogen sulfite. Therefore, the effective solubility increases tenfold per pH-value (Figure 1, top). At pH values higher than 4.5, the solubility reaches such high values that sulfur dioxide is transported better in water than in air. At a pH-value of about 3.3, the air-side and water-side resistances are expected to be equal, which means that the transfer is about half as fast as at high pH-values with pure air-side and negligible water-side resistance. Niegel [5] verified this in a small linear wind-wave facility (Figure 1, bottom).

The transfer resistance can therefore be shifted from water-side to air-side control when the pH-value changes from 2.5 and 4.5 and any ratio of the transfer resistance between air and water can be set by the pH-value. This allows a detailed investigation of the partitioning of the transfer resistance between air and water, which has not yet been performed at all. Of special interest is the direct measurement of the concentration sulfur dioxide reaches in air right at the water surface. This value directly yields the partitioning ratio of the resistance between air and water. It has never been observed yet to which extend this ratio fluctuates and which parameters control these fluctuations.

Such a measurement, however, requires to measure vertical sulfur dioxide profiles in the air down to the wavy water surface using a fluorescence technique. Friman and Jähne [1, 6] demonstrated that it is
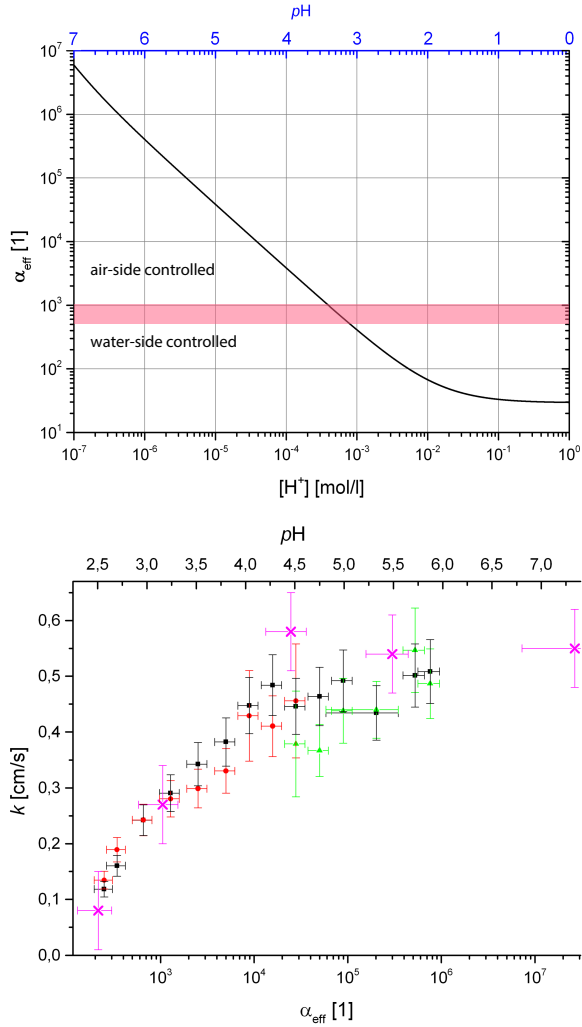
Figure 1: Top: Effective solubility of sulfur dioxide depends on the pH-value of water; Bottom: Measured transfer velocities of sulfur dioxide at different pH-values in a small wind-wave facility [5].
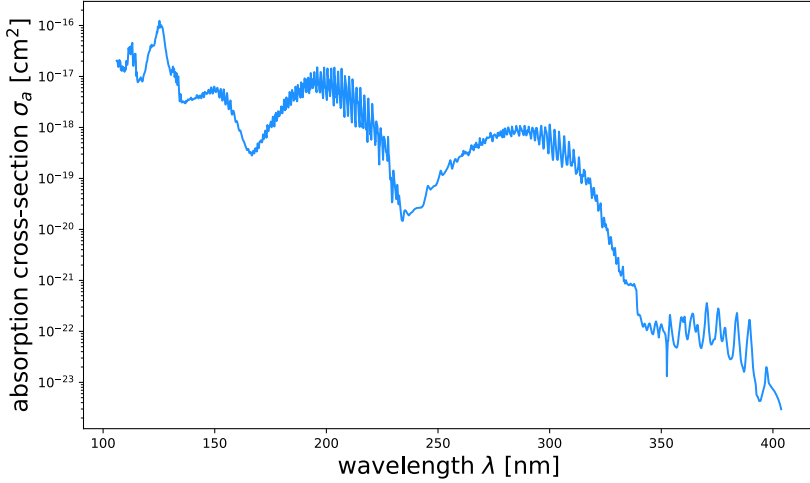
Figure 2: UV absorption spectra of sulfur dioxide (absorption cross-section) at wavelengths from 100 to 400 nm [7].

possible to measure sulfur dioxide concentration profiles with laser induced fluorescence (LIF), although only a suboptimal fixed excitation wavelength of 223.7 nm was available. Because sulfur dioxide has a complex absorption spectrum, the best excitation wavelength was unknown. Competing processes such a fluorescence quenching or dissociation of the sulfur dioxide molecule lower the fluorescence quantum yield and must be considered.

The paper is organized as follows. Section 2 reviews the knowledge about the absorption spectra and fluorescence of sulfur dioxide. Then the setup to measure sulfur dioxide fluorescence is explained (Section 3) and the results are discussed in Section 4.

2 Sulfur Dioxide Absorption Spectra and Fluorescence

Sulfur dioxide has a complex absorption spectrum in the UV (Figure 2), which is caused by electronic transitions together with changes of the vibration and rotation state. Measurements of sulfur dioxide by ab-
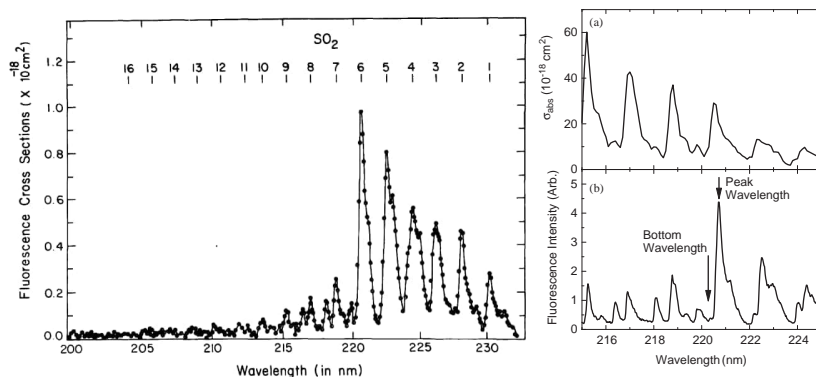
Figure 3: Left: Fluorescence absorption cross-section measured at 5–13 µbar pure sulfur dioxide [8]; right: Absorbance and fluorescent intensity of 10 ppbv sulfur dioxide in air at 13 mbar [10].

sorption spectroscopy are possible in the band between 260 and 310 nm or with a tenfold increased sensitivity in the deep UV around 200 nm. It is known from literature [8] that the quantum yield of sulfur dioxide fluorescence excited in the weaker second absorption band between 260 and 310 nm is low even in pure sulfur dioxide gas at low pressures. The quantum efficiency for fluorescence is only high in this band at high temperatures. Sick [9] used it for fluorescence imaging of sulfur dioxide in flames.

In the deep UV, radiation can dissociate the sulfur dioxide molecule. Hui and Rice [11] observed that the high quantum efficiency for fluorescence at 0.13 mbar decreases from about one at 225.8 nm down to zero at 215.24 nm by this effect. This is in agreement with the findings of Ahmed and Kumar [8], who observed that the fluorescence absorption cross-section (absorption cross-section times fluorescence quantum yield) shows a strong decrease (Figure 3, left), even though the absorption cross-section still increases.

Matsumi et al. [10] used fluorescence to measure atmospheric sulfur dioxide concentrations. They found a maximum fluorescence intensity with an excitation wavelength of 220.8 nm (Figure 3, right). The pressure in the measuring chamber was reduced to 13 mbar.

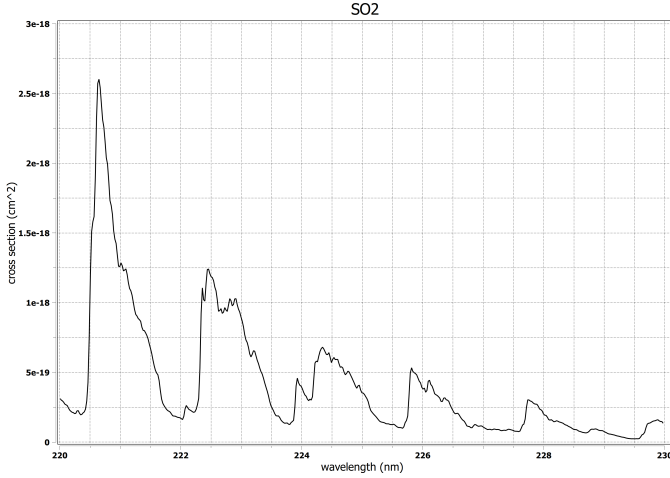No data about sulfur dioxide fluorescence could be found in air at

Figure 4: Absorption spectrum of sulfur dioxide from [12] smoothed to the line width of the InnoLas SpitLight Compact OPO-355, data collection by [13].

atmospheric pressures. Therefore the optimum excitation wavelength under this condition was unclear and a new investigation was required.

3 Experimental Setup

Fluorescence was excited by an InnoLas SpitLight Compact OPO-355 with UV extension to tune the excitation wavelength between 220 and 230 nm with a pulse energy of about 4 mJ at 20 Hz. Within this wavelength range, the pulse energy of the OPO remained constant. As an absorption reference we used the measurements from Rufus et al. [12] as made available by the MPI Mainz UV-VIS spectral atlas [13]. The high-resolution data were smoothed to the line width of the OPO (Figure 4). The absorption cross-section at 220.7 nm is about ten times larger than at 227.8 nm.

A flow of 20 NL/min of dry air set by a mass flow controller was mixed with a flow of 28.8 NmL/min of sulfur dioxide set by a second mass flow controller to obtain a sulfur dioxide concentration of 1440 ppm in air at atmospheric pressure. The mixed flow was directed
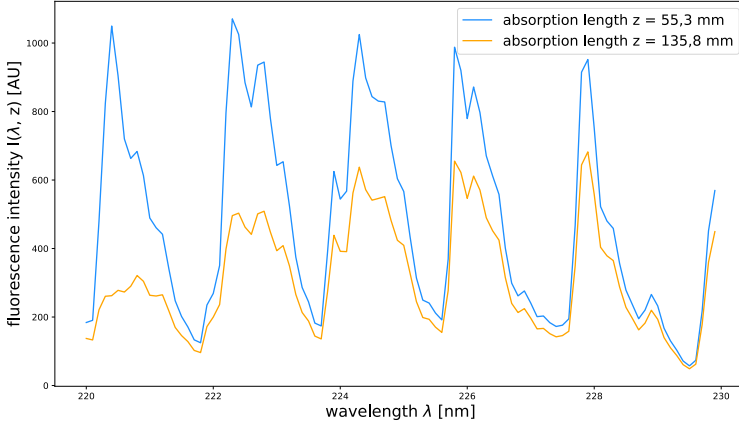
Figure 5: Fluorescence spectrum of sulfur dioxide in air measured by Beronova [14] at absorption lengths of 55.3 mm and 135.8 mm.

through a Duran glass tube with a diameter of about 6 cm. The OPO laser beam entered the tube at one end through a quartz glass window and the fluorescent light was imaged with a PCO edge 4.2 UV back illuminated UV sensitive camera using a Linos inspec.x 2.8/50 UV-VIS APO prototype lens. The imaging system covered an absorption distance between 55.3 mm and 135.8 mm, i. e., a laser beam length of 80.5 mm. Further details about the experimental setup can be found in Beronova [14].

4 Results and Discussion

In contrast to Matsumi et al. [10] (Figure 3), we found that the fluorescence intensity is about the same at all absorption peaks after the laser beam intensity has already been attenuated slightly by an absorption distance of 55.3 mm at 1440 ppm sulfur dioxide concentration (Figure 5). After a further distance of 80.5 mm, the fluorescence is even about two times higher at 227.8 nm than at 220.8 nm, because the absorption there is significantly lower (Figure 4).

For experiments in wind-wave facilities the laser beam has to travel

a distance of about 1 m in air before it reaches the water surface. In this experiments it is planned to use sulfur dioxide concentrations of only 100 ppm. Therefore laser beam experiences about the same attenuation and the absorption peak at 227.8 nm is the then the best choice for maximum fluorescence intensity close to the water surface.

It could be demonstrated that sulfur dioxide fluorescence measurements are possible in air at atmospheric pressure and an optimum excitation wavelength of 227.8 nm was be found. The higher fluorescence intensity at higher wavelengths in contrast to the results of Matsumi et al. [10] (Figure 3) is obviously caused by additional fluorescence quenching because of more frequent collisions of sulfur dioxide with other molecules in air. The quenching appears to be higher at lower excitation wavelengths.

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