Fluorescence Detection of Atmospheric SO₂ Using Excitation by NO- γ -Bands

F. Michels, C. Zetzsch, and F. Stuhl *

Ruhr-Universität, Physikalische Chemie I, Bochum

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A method previously applied for the detection of NO was modified to also monitor SO₂. With this method SO₂ is excited by NO- γ -bands ($A^2 \Sigma^+ \rightarrow X^2 \Pi_r$) and is detected by its subsequent fluorescence in the wavelength region from 300 to 400 nm. The results indicate a linear detection range from 4 ppb to 100 ppm in air using a time response of 100 s. The interferences from some atmospheric constituents were investigated.

Introduction

Recently, it has been shown that NO can be sensitively detected by fluorescence subsequent to excitation by light of the NO- γ -bands [1]. Sulfur dioxide also absorbs light in the wavelength region of the NO- γ -band emission ($200 \text{ nm} \lesssim \lambda \lesssim 250 \text{ nm}$). It has been previously demonstrated that SO₂ fluoresces when excited by Zn (213.8 nm) and Cd (228.8 nm) lines [2] and by light from a deuterium lamp-filter combination ($205 \text{ nm} < \lambda < 225 \text{ nm}$) [3]. Since SO₂ is one of the major air pollutants and since detection methods capable of monitoring more than one atmospheric constituent are desirable, we have studied the feasibility to also detect SO₂ using excitation by NO- γ -bands.

Experimental

In the present study the experimental set up is the same as that used for the detection of NO [1]. Therefore only the major features will be described here. The detector consists of three parts: a lamp to produce NO- γ -bands, a fluorescence cell including a flow system to mix SO₂, and a detection system to monitor the intensity of the fluorescence.

Emission of NO- γ -bands is generated in a microwave discharge in mixtures of flowing air and argon. Light from this lamp is focused into the fluorescence cell through an optical filter (Schott R 220). The reaction cell can be evacuated to less than 1×10^{-5} torr. For the detection of SO₂ the cell was constantly purged with mixtures of pure dry air and SO₂. These

mixtures of air and SO₂ were prepared in a flow using a calibrated 5-cm-SO₂-permeation tube (NBS-SRM No 1626). The permeation tube was contained in a thermostat at a constant temperature slightly higher than room temperature. The overall flow was regulated by needle valves and measured by calibrated flowmeters (Rota). Using the full ranges of the available flowmeters, SO₂ mixing ratios ranging from 130 ppb to 10 ppm could be obtained. Only a part of the flowing gas mixture was used to purge the cell. This way the SO₂ mixing ratio could always be kept constant when changing the pressure in the fluorescence cell. In some experiments air was replaced by N₂ or by O₂. In order to add H₂O vapor to SO₂/air mixtures the flow was first fed through a saturator containing liquid H₂O at a temperature of 298 K and then fed through a condensator at lower temperature to control the H₂O pressure. To study interferences from other species known to be present in the atmosphere a number of gases (NO, CH₄, C₂H₆, C₃H₈, C₄H₁₀, C₂H₄, C₃H₆, toluene) were introduced into the flow. These gases were usually injected into a bulb, which was constantly purged by the SO₂/air flow. This way concentrations of about 500 ppm were added initially which subsequently decreased with a time constant of about 30 s. Since NO is known to fluoresce by excitation of the γ -bands [1], NO/air mixtures were prepared in the fluorescence cell as previously [1].

Fluorescence of SO₂ was observed by a photomultiplier through a coloured glass (Schott UG1) which transmits the wavelength interval from about 300 to 400 nm. Photon counting was applied throughout these measurements. For the measurement of SO₂ in ambient air the ratio mode of the photon counter was used. For this purpose a second

* On sabbatical leave at NOAA, Aeronomy Laboratory, and CIRES, University of Colorado, Boulder, Colorado 80303.

Reprint requests to Prof. Dr. F. Stuhl, Physikalische Chemie I, Ruhr-Universität, D-4630 Bochum, Germany.

photomultiplier (RCA 1P28) was used to monitor the intensity of the exciting NO- γ -bands. The fluorescence signal was thus registered in reference to the intensity of the incident light. This way, a better long term stability was achieved. Further details of the detection method have been reported elsewhere [1, 4].

Results

Preliminary experiments at low SO₂ concentrations using a static mixing procedure indicated poor reproducibility and non-linear behavior of the fluorescence signal. It is very likely that efficient adsorption processes cause these undesirable effects. All further experiments were therefore performed under flow conditions. This way, a reproducible signal was obtained. However, after a change in [SO₂], it took at least 20 min until a constant signal was reached. To obtain a signal for [SO₂] = 0 the fluorescence cell had to be purged with clean air for about 5 hours. In spite of this large time constant for the sampling the electronic time constant was chosen to be 100 s; hence the change of the signal with time could be easily observed.

The influence of different amounts of air on the fluorescence intensity of SO₂ was investigated for a constant pressure of 1×10^{-4} torr SO₂. A Stern-Volmer plot of the result is shown in Figure 1. In

Fig. 1. The inverse of the relative fluorescence intensity $I(M)/I(M)_0$ plotted vs. the pressure of M (M = dry air). The intensity $I(M)_0$ was determined at $[M]_0 = 700$ torr dry air. The SO₂ pressure was constant at 1×10^{-4} torr.

this plot the signal is normalized for a pressure of air of 700 torr, since, at this pressure, the fluorescence signal could be determined with higher precision. The half quenching pressure for the SO₂ fluorescence obtained from this figure is 882 torr.

Similar plots obtained for the addition of N₂ and of O₂ resulted in half quenching pressures of 1567 and of 325 torr, respectively. Both these values combined yield a value of 888 torr in very good agreement with the half quenching pressure obtained in Figure 1. These quenching data and those reported in the literature are compared in Table I. The low quenching efficiency of air allows the detector to be operated at relatively high pressures. Therefore all the following experiments were done with air at a pressure of about 720 torr.

Table I. Half quenching pressure, $P_{1/2}$, for the quenching of the SO₂ fluorescence.

Constituent of air	This work ^a	Ref. [3] ^b
N ₂	1567	1333
O ₂	325	373
air (calculated)	888	877
air (measured)	882	862
H ₂ O	(19) ^c	16.5) ^c

^a [SO₂] = 1 to 3×10^{-4} torr. ^b [SO₂] = 10^{-1} torr.

^c Non-linear Stern-Volmer plot.

Water is present in ambient air at variable concentrations. Stern-Volmer plots for the addition of water to SO₂/air mixtures were found to be non-linear. Figure 2 displays the relative intensity of the fluorescence signal as a function of the pressure of H₂O. In this figure the signal is normalized for the absence of H₂O. H₂O was added to 200 ppb (circles) and to 365 ppb (squares) SO₂ in air at 720 torr. Included in this figure are two bars representing the range of previous data obtained by

Fig. 2. The relative intensity of the fluorescence as a function of added H₂O. The intensity in the absence of H₂O was taken as a reference. Experimental conditions: ○ 200 ppb SO₂ in 720 torr air; □ 365 ppb SO₂ in 720 torr air. The range of data previously measured [2] is indicated by bars.

Fig. 3. Calibration curve of the SO₂ detector in a double logarithmic plot. The fluorescence intensity is given in number of photon pulses per sec. and the concentration is given by the mixing ratio. The overall pressure was 720 torr and the time constant was 100 s. The detection limit (three standard deviations of the background signal) is indicated by the dashed line. The average background signal is subtracted. The fluorescence signal for the addition of NO is included.

Schwartz et al. [2] using a Cd lamp. The data of Fig. 2 show that the fluorescence signal is reduced by a factor of 2 at 100% and by a factor of 1.03 at 50% relative humidity at 20 °C air temperature.

Figure 3 displays the dependence of the fluorescence intensity on the mixing ratio of SO₂ in dry air. It is evident from this figure that the intensity of the fluorescence is linearly dependent on the concentration of SO₂ in the range from 130 ppb to 7 ppm. A number of similar linear plots were obtained for slightly different experimental arrangements (using different light collection efficiencies of the detection system). Also, a linear relationship was obtained using the ratio mode of the photon counter. At the low concentrations of Fig. 3 a linear dependence of the fluorescence intensity on the concentration is expected since self-quenching by added SO₂ is a negligible process. Furthermore, it can be shown that the amount of light absorbed by SO₂ is linearly dependent on [SO₂] at these low concentrations. Because of these reasons we have represented the calibration curve of Fig. 3 by a straight line with the slope one. In this figure the average background signal has been subtracted. This background signal

was about 120 pulses s⁻¹ and was caused by both the dark current of the photomultiplier and by a weak unknown fluorescence. The linear extrapolation of the calibration curve in Fig. 3 is equal to three times the standard deviation (3σ) of the background signal at a mixing ratio of 4 ppb SO₂ (dashed line). This value provides a measure for the detection limit of the present apparatus when using a time constant of 100 s.

Recently it has been shown that NO fluoresces efficiently at about 250 nm when excited by NO-γ-bands [1]. We have therefore investigated the interference of fluorescing NO on the detection of SO₂. Figure 3 shows the fluorescence signal for the addition of NO obtained in the wavelength region from 300 to 400 nm. From these data it can be seen that NO fluoresces about 100 times weaker than SO₂ at the same mixing ratio. A similar result was obtained previously by Okabe et al. [5]. Moreover, Okabe et al. have added a number of gases to their system using irradiation by Zn and Cd lamps and have found no significant interference by the gases studied [5]. In the present investigation we have added CH₄, C₂H₆, C₃H₈, C₄H₁₀, C₂H₄, C₃H₆ and have observed no interfering fluorescence. C₇H₈ (toluene) was found to interfere less than NO did.

All other tropospheric constituents are present at relatively low mixing ratios. Those with mixing ratios greater than 1 ppm are usually present at constant mixing ratios. Furthermore they do not absorb light of the incident NO-γ-band irradiation. Therefore these trace gases are considered not to interfere with the detection of SO₂ in tropospheric

Fig. 4. Measurement of SO₂ mixing ratios in ambient air during the period of Nov. 29, 1977, to Dec. 2, 1977. Sampling site was Building NC at the Ruhr University Bochum. Time constant used: 100 s; air temperature: ≈ 5 °C.

air. Minor trace gases (<1 ppm) are not likely to be able to quench the fluorescence or to decrease the incident light intensity by absorption because of their low concentrations.

To demonstrate the feasibility of the present method we have monitored ambient air at the Ruhr-University Bochum. The measured mixing ratios of SO₂ during three consecutive days (Nov. 29 until Dec. 2, 1977) are shown in Figure 4. It should be noted that during these days the outside temperature was always less than 5 °C and hence the humidity (Fig. 2) is not expected to influence the data very much. Figure 4 shows that mixing ratios of up to 0.25 ppm SO₂ (corresponding to $\approx 0.7 \text{ mg m}^{-3}$) were observed.

Discussion

The present detection method permits NO and SO₂ to be monitored simultaneously in polluted air. In air irradiated by NO- γ -bands fluorescence of NO is monitored at $(250 \pm 10) \text{ nm}$ and fluorescence of SO₂ is monitored in the wavelength region from 300 to 400 nm. Thus either two photomultiplier/filter combinations or one photomultiplier with two alternating filters can be used to measure NO and SO₂ at the same time. Since the most favorable pressures for the detection of NO (35 torr) and of SO₂ (>720 torr) are different, a pressure of about 300 torr in the fluorescence cell should be chosen as a compromise for the simultaneous detection. This way the detection limit (3σ) will stay below about 10 ppb for both gases. Also the interference in the detection of SO₂ by H₂O will become much smaller. A linear response for both constituents has been shown for up to 10 ppm. The long time constant we observe for the signal is very likely to be due to surface processes in the sampling lines and in the fluorescence cell. Different materials and a heated system can possibly decrease the time constant.

Recently Okabe and coworkers [2, 6] have developed a fluorescence method capable of monitoring both NO and SO₂ using irradiation by the Zn 213.8 nm line. The fluorescence was detected in

the wavelength region from about 230 to 420 nm. The reported detection limits of this method are: 10 ppb (signal to noise ratio = 1) NO in N₂; 0.5 ppm NO in air; and 8.6 ppb (standard deviation 29%) SO₂ in air. Since SO₂ can interfere when NO is monitored, the use of different wavelength regions for the detection of SO₂ and of NO fluorescence has been considered [6]. This method has been used for the measurement of NO in standard reference mixtures of NO in N₂ and for the measurement of SO₂ in air, stack gases and automobile exhaust.

Okabe and coworkers have also studied the feasibility of exciting SO₂ by the Cd 228.8 nm line [2] and by a 216 nm deuterium source [3]. However, from the published work, none of these methods seems to be more favorable for air monitoring than the excitation by the Zn line. Previously Zolner et al. [7] have excited SO₂ by a flash lamp and have monitored SO₂ by its fluorescence. The detection limit of this method has been reported to be 0.5 ppm.

The excitation and fluorescence processes of SO₂ have been described by Okabe and coworkers in detail [2, 3, 5, 6] and will not be discussed here. These authors have studied the influence of a number of gases on the fluorescence signal. In the present study we have repeated some of their experiments at about 10³ times lower concentrations of SO₂ and find reasonable agreement with their results.

The mixing ratios observed in ambient air (Fig. 4) were compared with those obtained by the Landesanstalt für Immissionsschutz NRW [8] at the air monitoring station Bochum-Stadtmitte. Considering the distance of 6 km between the two sampling sites the agreement was found to be satisfactory. A maximum value of 0.7 mg m^{-3} , for example, was measured at both sites at the same time.

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