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Concentration evaluation method using broadband absorption spectroscopy for sulfur dioxide monitoring

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We report on an approach for sulfur dioxide monitoring using broadband absorption spectroscopy in the ultraviolet spectral range. The method was applied in real-time measurements and has the advantage of straightforward data evaluation, limited susceptibility for interference from other gases, and low degree of complexity compared with other real-time optical detection techniques having the same precision. Concentration measurement is demonstrated at atmospheric pressure, which is of interest for pollution emission monitoring, yielding a detection limit of about 1 ppm with 3 s integration time. Comparison is made with low pressure measurements for validation of the accuracy of the method. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2211299]

The absorption spectroscopy technique is a fast and sensitive method used for the detection of many atmospheric gases and pollutants. The technique has been widely employed in the midinfrared spectral region (2–15 μm), where numerous species of interest have fundamental vibrational absorption bands, and in the near-infrared region (0.6–2 μm), where weaker overtone and combination bands occur. Most atoms and molecules also have strong electronic transitions in the ultraviolet (UV) spectral region (200–400 nm).[1] The linestrengths of these transitions are several orders of magnitude larger than the ones of rovibrational transitions in the infrared.[2]

Sulfur dioxide (SO_2) is a primary air pollutant and has a strong transition in the UV spectral region. Typical background concentrations of SO_2 in air are very low, e.g., 0.13 ppm according to the EU standards for hourly limit value for the protection of human health,[3] however, much higher SO_2 concentrations are present, for example, in industrial environments. Major anthropogenic sources of atmospheric SO_2 include power plants that burn high-sulfur coal, paper and pulp industries, petroleum refineries, industrial processes for roasting of nonmetallic ores, and incineration of solid waste—particularly of hazardous and medical wastes.[4,5] At present, many techniques, such as differential optical absorption spectroscopy (DOAS),[6,7] correlation spectroscopy (COSPEC),[8,9] differential absorption lidar (DIAL),[10–12] and tunable diode laser absorption spectroscopy (TDLAS) techniques[13] are used for monitoring SO_2 in air.

In this letter, a concentration evaluation method based on a formula deduced from Beer—Lambert's law is introduced. Real-time SO_2 pollution monitoring based on broadband absorption spectroscopy in the UV region is performed. The simple structure of the data evaluation method increases the convenience of application and reduces the complexity of the technique.

The setup for real-time monitoring of SO_2 is shown in Fig. 1. A broadband 30 W deuterium lamp (Beijing Union Optics-Electronic Co. 5601) was operated as a UV light source and a quartz lens of 75 mm focal length was used to collimate the exiting light. The light beam passed through a 35-cm-long gas cell equipped with quartz windows at Brewster angle and filled with a certain amount of SO_2. The transmitted light was carefully focused by a quartz lens of 145 mm focal length into a multimode optical fiber (Ocean Optics Inc. OFLV-200-1100) coupled to a high-resolution spectrometer (resolution of ~0.1 nm), composed of a monochromator and a 2048 element charge-coupled device (CCD)-array detector (Ocean Optics Inc. HR2000). The signal from the CCD detector was transmitted to a personal computer. The spectrometer control, together with the real-time data collection and evaluation were performed automatically using a software written in VISUAL BASIC language. The sampling time of the CCD detector was adjusted in order to obtain a good signal-to-noise ratio and high-resolution integrated spectra.

Using the Beer-Lambert law, the ratio between the received radiation intensity $P_t(\lambda)$ and the original intensity $P_o(\lambda)$ can be written as[14]

$$\frac{P_t(\lambda)}{P_o(\lambda)} = R(\lambda)\exp\{[-\sigma(\lambda)NL] + \alpha(\lambda)\}, \qquad (1)$$

where $\sigma(\lambda)$ is the absorption cross section of the gas, N is the concentration of the gas, L is the absorption path length, $\alpha(\lambda)$ is the absorption coefficient of other gases, and $R(\lambda)$ is the dissipation due to refraction, diffraction, and scattering of the gas. For two particular wavelengths λ_1 and λ_2, Eq. (1) can be written as

$$\frac{P_t(\lambda_1)}{P_o(\lambda_1)} = R(\lambda_1)\exp\{[-\sigma(\lambda_1)NL] + \alpha(\lambda_1)\}, \qquad (2)$$

$$\frac{P_t(\lambda_2)}{P_o(\lambda_2)} = R(\lambda_2)\exp\{[-\sigma(\lambda_2)NL] + \alpha(\lambda_2)\}. \qquad (3)$$
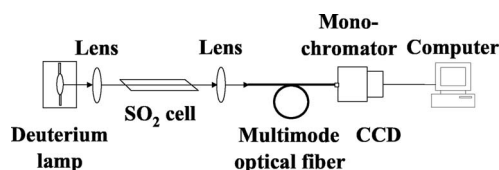

FIG. 1. Experimental setup for real-time monitoring of SO_2.

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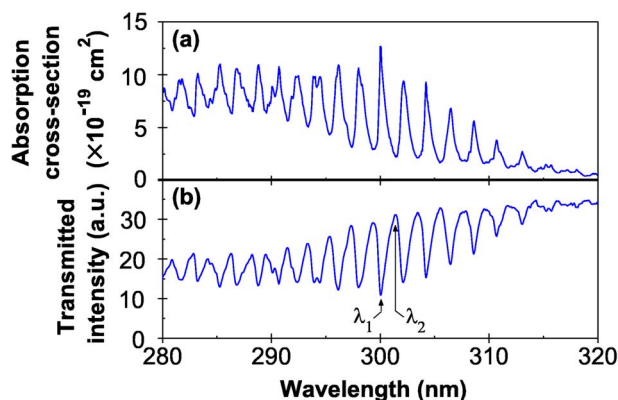[b]Electronic mail: zhangzhiguo@hit.edu.cn

FIG. 2. (Color online) (a) The absorption cross section of SO_2 obtained with a Fourier transform spectrometer (Ref. 15). (b) Absorption spectrum recorded by a CCD-equipped spectrometer after that broadband UV light from a deuterium lamp was passed through a gas cell containing SO_2 at atmospheric pressure and with a concentration of 1460 ppm. λ_1 and λ_2 are marked with arrows in the figure.

Division by terms of Eqs. (2) and (3) yields a formula for the average SO_2 concentration according to

$$N = - \frac{\ln[P_t(\lambda_1)/P_t(\lambda_2)]}{[\sigma(\lambda_1) - \sigma(\lambda_2)]L}, \qquad (4)$$

which is the key expression used in the proposed broadband absorption spectroscopy evaluation method. In Eq. (4) the original intensity at the two wavelengths $P_o(\lambda_1)$ and $P_o(\lambda_2)$ cancel due to the negligible variation of the source intensity within a limited wavelength range (~ 1 nm). In our measurements $\alpha(\lambda)$ was neglected due to the small difference of absorption cross section for other gases at the two selected wavelengths, and because the low concentration of other gases compared to SO_2. Additionally, the effect of the dissipation $R(\lambda)$ from other gases and dust is washed out by calculating the intensity ratios.

To detect molecular SO_2 it is suitable to utilize the strong absorption band in the wavelength range around 300 nm. As shown in Fig. 2(a),[15] the absorption cross section of SO_2 around 300 nm changes rapidly. The two wavelengths λ_1 and λ_2 are chosen at the on-/off-resonance pair 300.02 and 301.39 nm, respectively, to achieve maximum contrast. Thus, the gas concentration can be obtained directly by measurement of the received radiation intensities $P_t(\lambda_1)$ and $P_t(\lambda_2)$, respectively, and by insertion of the tabulated values of the absorption cross section $\sigma(\lambda_1)$ and $\sigma(\lambda_2)$ at the above two wavelengths.[16,17] The strength of Eq. (4) consists in the possibility of acquiring the absolute gas concentration directly without the need of a reference spectrum for the data evaluation, like in the case of the DOAS technique. Furthermore, the robustness and straightforwardness of our method simplifies the data evaluation compared to other gas sensing techniques.

Figure 2(b) shows a typical SO_2 spectrum recorded around 300 nm using the above setup. The selected on/off wavelengths are marked with arrows in the figure. Comparison can be made with the Fourier transform interferometer spectrum shown in Fig. 2(a).[15] The measurement was performed on a certified mixture of 1460 ppm SO_2 in dry air at atmospheric pressure.

In order to determine realistic estimates of the performance of the broadband SO_2 spectrometer, the detection
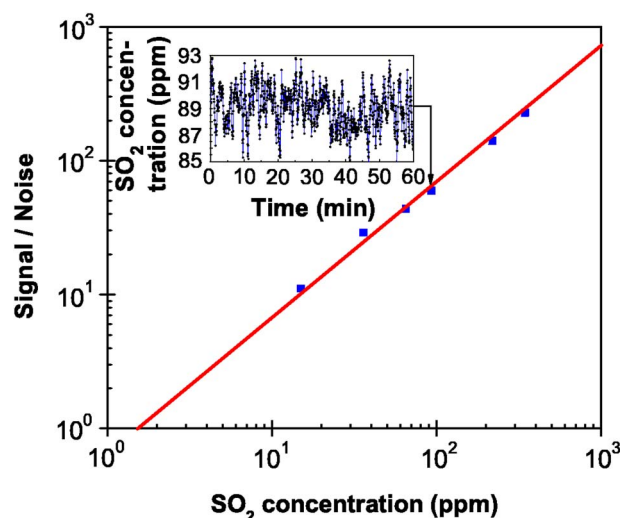

FIG. 3. (Color online) Signal to noise vs SO_2 concentration in ppm. Linear extrapolation leads to a minimum detectable concentration of ~ 1 ppm (SNR=1). Data were collected with a stable gas mixture in a sealed sample cell at atmospheric pressure. Insert: long-time recording of a 89 ppm SO_2 concentration for assertion of the system stability.

limit was derived from the statistical fluctuations of the signal over time. A series of six different fixed SO_2 concentrations were chosen, and for each measurement 300 data samples were acquired at a rate of 0.3 Hz. Figure 3 shows the dependence of the measured signal to noise for decreasing SO_2 concentrations. The rms noise is essentially independent of concentration, with an average value corresponding to about 1.5 ppm. The Beer—Lambert law can be linearized for low gas concentrations, and this explains the observed linear decrease of the absorption signal. The extrapolated minimum detectable concentration is estimated to be ~ 1 ppm and is limited by thermal noise in the detector. The sensitivity obtained is comparable to that of commercially available instruments used for continuous emission monitoring.[18] It should be noted that data points were acquired with only 3 s integration time. However, the response time of the system is in the order of 100 ms, depending on the amount of light available.

Finally, we investigated the long-term stability of the system over 1 h, as shown in the insert of Fig. 3. The SO_2 concentration was 89 ppm with an evaluated standard deviation of 1.6 ppm, which implies a measurement precision of about 1.8%.

In the case of polluted air with very high SO_2 concentrations, the absorption path length L can be shortened to avoid saturation of the absorbed signal. Oppositely, in the case of very low gas concentrations, the measurement sensitivity can be enhanced by averaging over periods longer than 10 s or by increasing the absorption path length (i.e., in cross-stack monitoring, path lengths of $1-3$ m are feasible in single-pass arrangements). Our spectrometer was tested in field for measurement of SO_2 in flue gas emitted from a coal-fired boiler in Harbin, China, and the typical concentrations recorded were in the range of $100-200$ ppm. The relatively high values obtained can be explained by the high sulfur content of bituminous coal used in China.

Pressure can affect the absorption spectrum of the gas due to collisional broadening effects. In order to evaluate its influence on the SO_2 concentration measurement, the absorption spectra of the gas was recorded at atmospheric and at
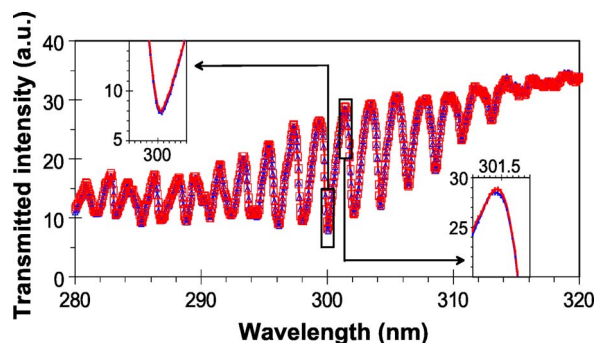
FIG. 4. (Color online) Recorded spectra of SO_2 at 1.2 mbars (squares) and at ambient atmospheric pressure (triangles).

low (1.2 mbars) pressure for a gas concentration of 1757 ppm (4691 mg/m³). As expected from theoretical considerations, the two spectra basically overlap, as shown in Fig. 4. Thus, for the present spectral resolution of 0.1 nm, pressure does not affect the concentration evaluated using this technique.

Temperature can also influence the line shape of the absorption spectrum due to the Doppler effect. The present laboratory measurements were performed at room temperature and therefore no corrections were required. However, in many practical circumstances gases are monitored at much higher temperatures, and this effect becomes dominant. A thorough analysis of the temperature effect on the proposed concentration evaluation method is presented in Ref. 19.

We have demonstrated the applicability of a novel concentration evaluation method based on broadband absorption spectroscopy. Recorded spectra around 300 nm were used for real-time evaluation of the SO_2 concentration in a cell. The detection limit of the system in the present configuration was evaluated to be about 1 ppm with 3 s integration time. The absorption spectra were measured at both low and atmospheric pressures, and it was found that pressure does not influence the results of the concentration evaluation using the present setup. The influence of gas absorption interferences, and scattering effects from other gases and dust may be neglected when using this data evaluation method. The complexity and cost of a commercial product utilizing the proposed method are estimated to be lower than for other real-time detection techniques with the same performance.

The capability of real-time measurement of SO_2, easy data evaluation, low cost, and comparatively high measurement precision are the advantages of the technique presented here. The dynamic range of the spectrometer CCD currently used was 2×10^8. However, with a higher dynamic range of the CCD array, which can become available through the fast development of semiconductor materials, the signal-to-noise ratio and the accuracy of this technique may be improved further, leading to an expanded application range of this technique.

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