

## DEVELOPMENT OF MULTI-AXIS DIFFERENTIAL OPTICAL ABSORPTION SPECTROSCOPY SYSTEM AND ITS APPLICATION IN MEASURING ATMOSPHERIC NO<sub>2</sub> VOLUME MIXING RATIO IN HANOI

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**Abstract.** *Monitoring the concentration and distribution of nitrogen dioxide NO<sub>2</sub> in urban environment is of great interest because of the importance of this gaseous pollutant in affecting air quality. In this paper we present the development of a multi-axis differential optical absorption spectroscopy instrument capable of sensitively detecting NO<sub>2</sub>. The instrument collects the sun light scattered by the air molecules and aerosols in the atmosphere and measures the spectrum using a portable spectrometer of high sensitivity. The viewing direction of the instrument is controlled through a motor and can be changed continuously. Data analysis of the measured spectra allows us to simultaneously determine the differential scint column density of NO<sub>2</sub> and oxygen dimer O<sub>4</sub>. From the accurately known concentration of O<sub>4</sub>, the effective optical path length of scattered sun light near the horizontal direction could be derived, which in turn provides an estimate the concentration of NO<sub>2</sub>. The measured data show that the concentration of NO<sub>2</sub> near ground surface in the early afternoon in Hanoi is about ~ 1.5 ppb. We also present the detection of formaldehyde HCHO and possible detection of glyoxal CHOCHO. Our sensitive instrument offers the possibility to monitor the concentration of other molecular species of interest in urban environment of Hanoi.*

Keywords: volume mixing ratio.

Classification numbers: 42.40.Pa; 43.28.+h.

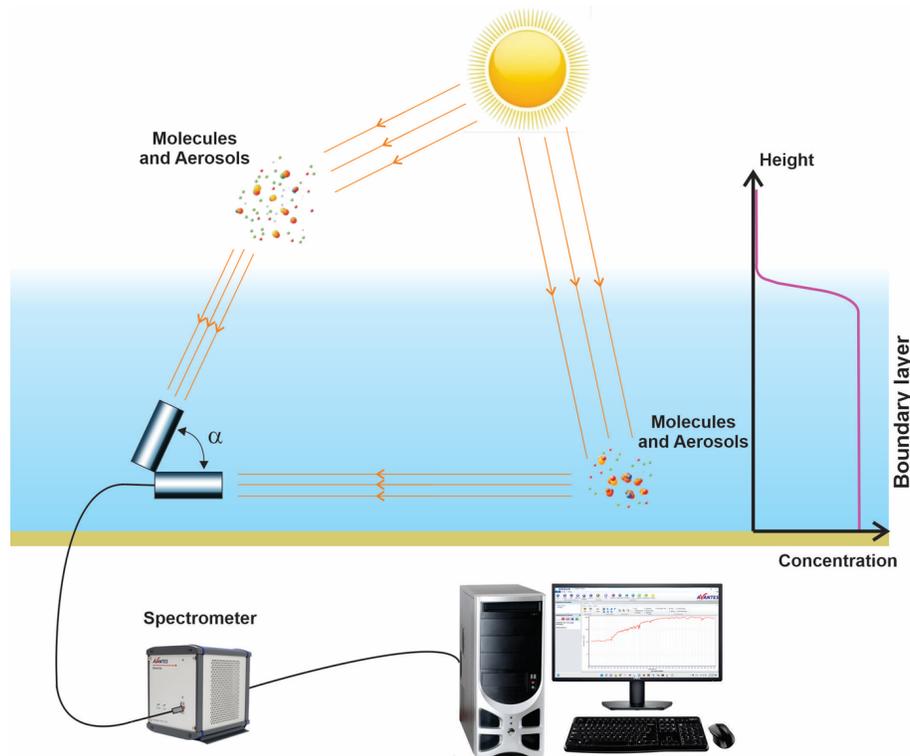
## I. INTRODUCTION

Trace gases such as  $\text{NO}_2$ ,  $\text{SO}_2$  or ozone play a very important role in the physio-chemical processes which determine the state of the atmosphere. These gases are generated through natural routes and anthropogenic activities might adversely affect human health and are currently recognized as the cause of atmospheric pollution in urban environment. As a result, the detection and monitoring of the pollutant trace gases have attracted the attention of the scientific community, regulatory agency and the general public. For more than two decades the differential optical absorption spectroscopy (DOAS) method [1–5] has been widely used to retrieve the concentration and spatial distribution of trace gases in the atmosphere either on the ground or from space-based platforms. The DOAS technique relies on the identification and determination of minute absorption features of trace gases imprinted on the broad band continuum emission from an artificial light source such as Xenon lamp (active DOAS) or from natural light sources such as the Sun or the Moon (passive DOAS). The spectrally resolved absorption features serve as finger prints to identify the presence of trace gases and allow the retrieval of their concentration with very high sensitivity, usually in the sub-ppb range, if the light path in the atmosphere is precisely known. More recently, the technique of multi-axis DOAS has become widely used and allowed the retrieval of vertical profiles of aerosol together with the trace gases in the atmosphere [2–8]. This technique relies on the measurement of the UV and visible sky spectrum representing scattered sun light at different elevation angles. For directions close to the horizon, the increase in path length of the scattered sun light results in enhanced sensitivity to trace gases located near the surface [6, 7]. This method has been widely adopted to used to investigate the horizontal and vertical distribution of trace gases important to atmospheric physical chemistry and air pollution. Our group at the Institute of Physics has undertaken the development of a multi-axis DOAS instrument, for the first time in Vietnam, with the aim to study atmospheric pollutants in Hanoi city. In this paper, we describe in detail our instrument and report some initial measurements with the main focus on estimation of  $\text{NO}_2$  volume mixing ratio.

## II. MULTI-AXIS DOAS INSTRUMENT AND DATA ANALYSIS

The measuring principle using our multi-axis DOAS instrument is shown in Fig. 1. The sun light scattered by the air and aerosols in the atmosphere is collected by a small quartz telescope with an objective lens of 50 mm in diameter and focal length of 100 mm. An optical fiber with a core diameter of 200  $\mu\text{m}$  is used to receive and transport the collected light to the spectrometer. Thus the field of view of the instrument is approximately 0.2 mm/100 mm or 0.11 degree. The telescope is mounted on a two-axis rotating platform, thus allowing measurements at different azimuthal and elevation angles. The motion of the platform is actuated through ac servo motors controlled through a microcontroller. For light detection we make use of the compact and portable spectrometer Avaspec-HSC1024x58TEC-EVO from Avantes covering the wavelength range from 250 nm to 630 nm with a spectral resolution of  $\sim 0.9$  nm. The spectrometer temperature is controlled, allowing highly stable and good quality data. The large wavelength coverage of the selected spectrometer also allows the instrument to cover the absorption features of many different molecular species present in the atmosphere. An observation sequence consists of a measurement  $I(\lambda)$  taken at an elevation angle of  $1^\circ$  by averaging 5000 spectra, each with an integration time of 100 ms and a reference spectrum  $I_0(\lambda)$  taken in a similar manner toward sky zenith. The short

integration time is used to minimize the electronic noises that might affect the quality of the collected data. The measured spectra are automatically obtained and saved on a computer connected to the spectrometer through USB interface.



**Fig. 1.** Principle of multi-axis DOAS measurement. Pollutants and other molecular species present in the atmosphere produce absorption features in the spectrum of scattered sun light.

To analyse the DOAS data we use the usual Lambert law, which expresses the relation between the measured spectra as follows [1, 9]:

$$I(\lambda) = I_0(\lambda) \exp \left[ - \sum \sigma_i^d(\lambda) \cdot dSCD_i + P(\lambda) \right], \quad (1)$$

where  $dSCD_i$  is the differential scint column density of trace gas  $i$  between the two directions,  $P(\lambda)$  is the low order polynomial determined through fitting process,  $\sigma_i^d(\lambda)$  is the narrow absorption features of the molecular species  $i$ . The main spectral window is selected to between 450 nm and 495 nm covering the absorption features of  $\text{NO}_2$ , oxygen dimer  $\text{O}_4$  and water vapor  $\text{H}_2\text{O}$ . The absorption cross sections of molecular species present in the atmosphere and the corresponding fitting spectral windows are summarized in Table 1. The absorption cross sections of the molecular species are taken from Refs. [9–14]. In addition, the Ring effect [15] due to rotational Raman scattering in the atmosphere is also taken into account as recommended in the data analysis of CINDI (Cabauw Intercomparison Campaign of Nitrogen Dioxide measuring Instruments) inter-comparison measurement campaign [13]. The spectral fitting and retrieval of the differential scint

**Table 1.** Spectral windows used for our data analysis.

Gas species	Fitting window (nm)	Reference
NO <sub>2</sub>	450-495	[10]
O <sub>4</sub>	450-495	[12]
O <sub>3</sub>	450-495	[11]
H <sub>2</sub> O	450-495	[13]
Ring	450-495	[14]
Formaldehyde (HCHO)	335-360	[11]
Glyoxal (CHOCHO)	450-495	[15]

column density of trace gases dSCD are done offline using the QDOAS software developed at the Belgium Institute for Aeronomy [5]. The data reduction involves: first, wavelength calibration and spectral resolution are determined through comparison with a standard high resolution solar spectrum; second, spectral fitting of Eq. (1) is performed to remove the low order polynomial  $P(\lambda)$  and retrieve the differential scant column density  $dSCD$  of each molecular species.

### III. RETRIEVAL OF NO<sub>2</sub> CONCENTRATION

The measured DOAS spectrum at low elevation presents the absorption signal close to the surface. As such a measurement is highly sensitive to the near surface trace gases. The effective light path or effective length from the last scattering in the observation direction is mainly limited by the atmospheric visibility, i.e. the scattering by air molecules and aerosol particles [6–8]. If the concentration of a molecular species is known in advance the effective light path could be estimated. Sinreich *et al.* [6] and Wang *et al.* [7] developed and applied a method to estimate the effective light path when the aerosol loading in the atmosphere is moderate, using the retrieved O<sub>4</sub> dSCD obtained from DOAS analysis for 1o elevation. The effective light path  $L$  is given as:

$$L = \frac{dSCD_{O_4}}{n_{O_4}}. \quad (2)$$

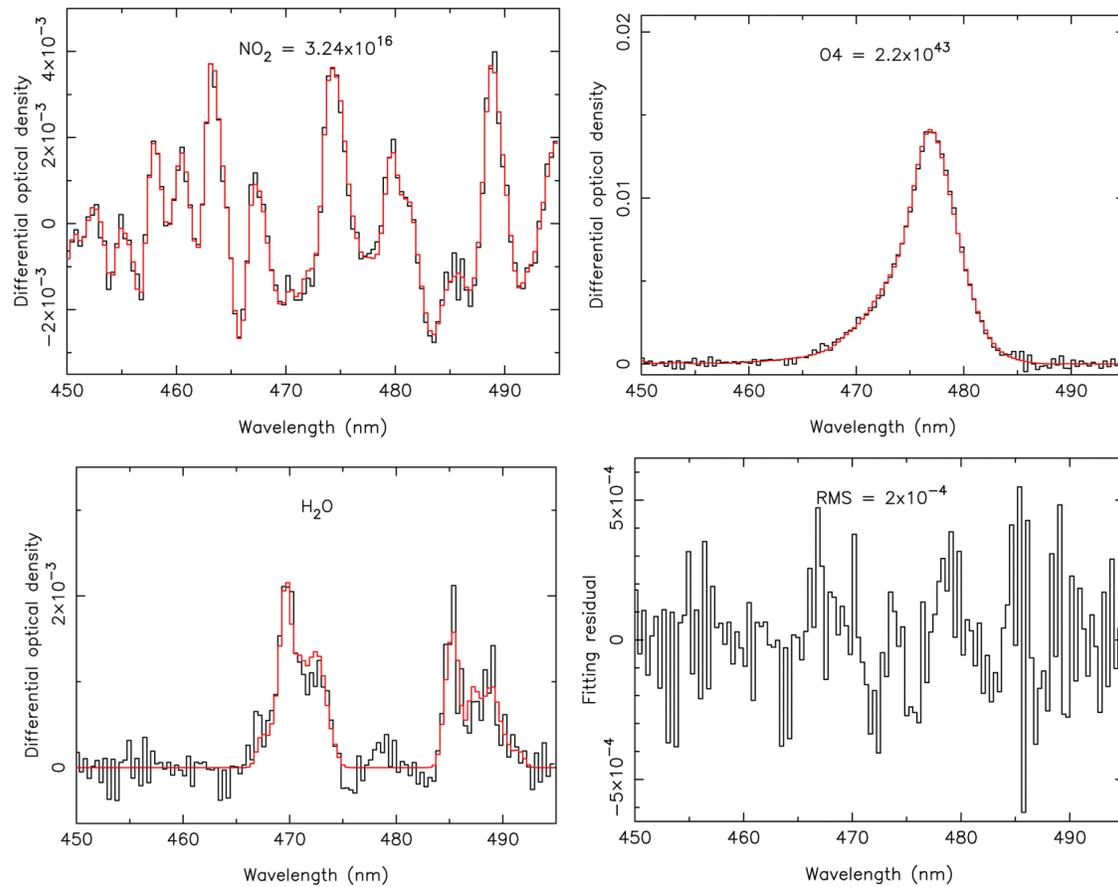
The near surface concentration of O<sub>4</sub>, which is proportional to the square of oxygen concentration, could be calculated using local atmospheric temperature and pressure. However, for the sake of simplicity, we adopt a value for  $n_{O_4}$  of  $2.79 \times 10^{37}$  molecules<sup>2</sup> cm<sup>-6</sup> as used in [7]. Accordingly, the O<sub>4</sub> dSCD as retrieved in the DOAS analysis is expressed in unit of molecules<sup>2</sup> cm<sup>-5</sup>. Using the derived effective light path  $L$  we can estimate the concentration, and therefore the volume mixing ratio of other trace gases such as NO<sub>2</sub> from their  $dSCD$ :

$$n_{NO_2} = dSCD/L. \quad (3)$$

As suggested in Refs. [6, 7] the above equation could be used directly to derive the concentration of NO<sub>2</sub> if the distribution profile of NO<sub>2</sub> is similar to that of O<sub>4</sub>. However, for atmospheric pollutants the concentration is usually highest near the surface and decreases rapidly with height and mainly confined within the atmospheric boundary layer. A small (from about 0.6 to unity) correction factor depending on the distribution of trace gases and aerosol particles is usually introduced in the above equation [7]. Currently we lack the detailed knowledge of the distribution of NO<sub>2</sub> in Hanoi and the exact value of the correction factor remains uncertain. Therefore, for the

sake simplicity, in this paper we assume a correction factor of unity and use Eq. 3 to derive the concentration of  $\text{NO}_2$ .

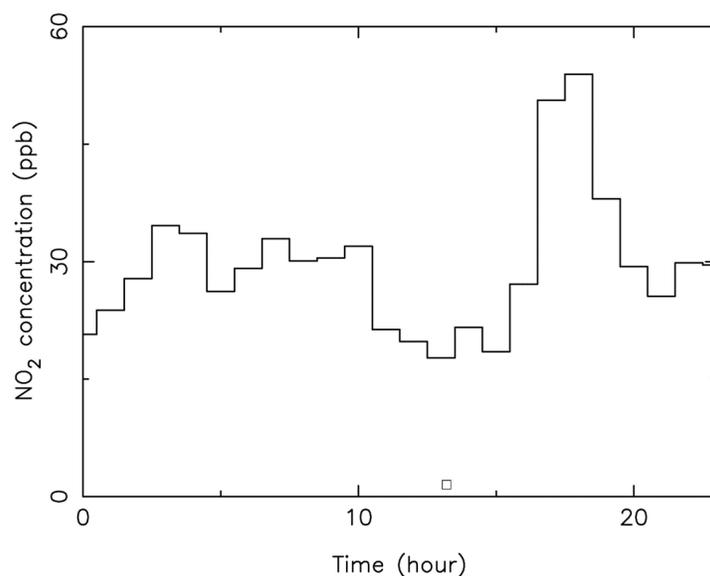
#### IV. RESULTS AND DISCUSSION



**Fig. 2.** Fitting results obtained for data on 4 May 2022 at 13:10 pm local time. The black line represents the data while the red line represents the theoretical differential absorption model best matched to the data. The residual of the fitting is low with  $\text{RMS} = 2 \times 10^{-4}$  over the spectral window indicating a good data quality.

In Fig. 2 we show an example of the analysis of  $\text{NO}_2$ ,  $\text{O}_4$  and water vapor, for the day 4th May 2022 at 1:10 pm local time. The instrument is located on the 7th floor ( $\sim 20$  m above ground level) of the 2H building in the 18 Hoang Quoc Viet campus of the Vietnam Academy of Science and Technology. The telescope is pointed to the East and the solar zenith angle at the time of observation is  $72.7^\circ$ . The DOAS fitting exhibits satisfactory results with low residual rms of  $2 \times 10^{-4}$ . Absorption features with strength in the range of  $10^{-3}$  could be relatively easy to detect, attesting to the sensitivity of our multi-axis DOAS instrument. The derived differential column density

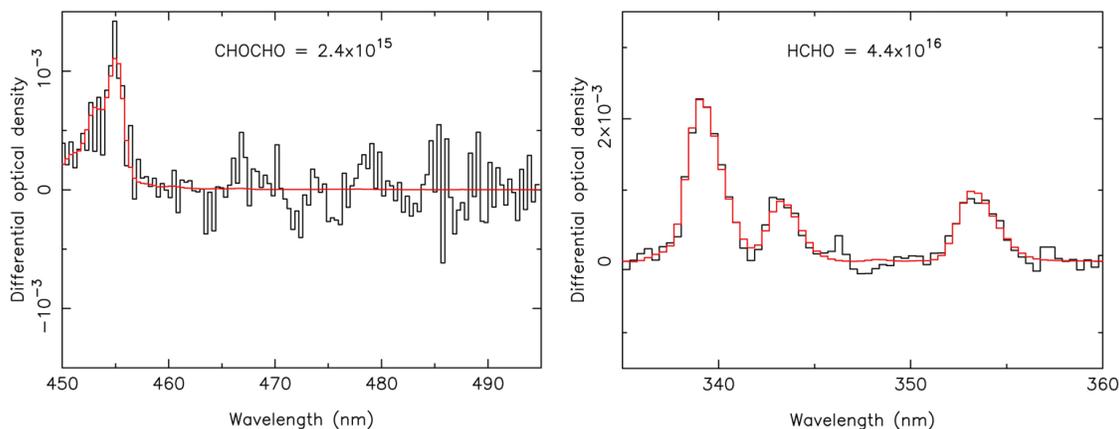
of oxygen dimer  $O_4$  is  $2.2 \times 10^{43} \pm 2.7 \times 10^{41}$  molecules<sup>2</sup> cm<sup>-5</sup> from the absorption feature at 477 nm. Using the above mentioned near surface concentration of  $O_4$ , we obtain an effective path length of approximately 7.9 km. The measured *dSCD* of  $NO_2$  is  $3.24 \times 10^{16} \pm 4.7 \times 10^{14}$  cm<sup>-2</sup>, resulting in a near surface concentration or volume mixing ratio of approximately  $1.5 \pm 0.02$  ppb. The high signal to noise ratio of the data results in very small statistical error in the derived *dSCD* and allows a very sensitive detection of  $NO_2$ . For comparison, we note that the level of sensitivity (about 1.5% noise level in term of slant column density of  $NO_2$ ) of our instrument is similar to that obtained with the instrument developed by Romanian group [4] for the detection of  $NO_2$ .



**Fig. 3.** Hourly averaged concentration of  $NO_2$  measured by monitoring station (histogram) and the DOAS measurement (small square at 1:10 pm).

We note that in several previous works such as the study carried out in the city of Vienna (Austria), the comparison between the in-situ measurements with DOAS analysis indicates that the in-situ measurements always show higher concentration, up to 3 – 5 times or higher, of  $NO_2$  [2]. This fact is understood as the averaging effect of  $NO_2$  concentration over the long effective path length sampled by the multi-axis DOAS method. In Fig. 3 we show the hourly averaged concentration of  $NO_2$  measured by the Center for Environmental Monitoring (CEM, 556 Nguyen Van Cu street, Hanoi), which is quite close to the line of sight of our multi-axis DOAS system, together with our DOAS measurement. As can be seen clearly in Fig. 3, traffic related variation of  $NO_2$  concentration is quite evident, especially during the afternoon rush hour from 5.00 pm to 7.00 pm. Our DOAS data is a factor of 10 lower than that measured by monitoring station. Several factors could explain this large difference: the monitoring station is located near ground level and by a main road with busy traffic, therefore should show elevated level of  $NO_2$ . In addition, the line of sight of our multi-axis DOAS system is several 10 m to 100 m above the ground level with averaging effect over the entire effective length of 7.9 km covering the West Lake and the Red River, leading to a significantly lower concentration of  $NO_2$ .

The spectral window between 450 nm and 495 nm also contains a feature of glyoxal CHOCHO with possible detection as shown in Fig. 3. In the 335 – 360 nm window the DOAS analysis indicates the presence of formaldehyde HCHO with good signal to noise ratio (see Fig. 4). These molecules are known to be important in the photochemistry of the atmosphere, especially in urban environment. We will present further analysis of these important trace gases in a future publication.



**Fig. 4.** Detection of glyoxal and formaldehyde in Hanoi on 4 May, 2022 data taken at 13:10 pm local time. The black line represents the data while the red line represents the theoretical differential absorption model best matched to the data.

## V. CONCLUSION

We have presented the multi-axis DOAS instrument recently developed at the Institute of Physics and the procedure to analyze the observed data. We showed that the instrument performed well and allowed the detection of several important trace gases, namely  $O_4$ ,  $NO_2$ , water vapor and formaldehyde together with a possible detection of glyoxal CHOCHO. Using a well tested methodology based on the estimate of optical path length of scattered sun light in the atmosphere, we derived the near surface mixing ratio of  $NO_2$  of 1.5 ppb with high sensitivity. Our work represents the first direct measurement of trace gases in the atmosphere above Hanoi using spectroscopic method with high sensitivity and broad capability. We plan to use our instrument to monitor the seasonal variation of trace gases in the atmosphere.

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