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Differential Optical Absorption Spectroscopy (DOAS) Measurements of Ozone in the 280-290 nm Wavelength Region

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The differential absorption structure of the ozone spectrum between 250 and 330 nm has been investigated in order to determine the optimal wavelength region to be utilized for active differential optical absorption spectroscopy (DOAS) measurements. Considering aspects of atmospheric attenuation and interference from other species as well as the magnitude of the differential absorption cross section, an interval around 283 nm was found to be a good candidate for this application. This result was also verified during 12 months of continuous ozone monitoring in an urban environment.

Index Headings: Differential optical absorption spectroscopy; Ozone; Atmospheric measurement.

INTRODUCTION

The presence of ozone is one of the critical factors in the study of the photochemistry of the atmosphere. Consequently, accurate monitoring methods are needed for ozone as well as for other trace gases. Several optical techniques based on the Beer-Lambert law have been developed for this purpose.[1-3] Differential optical absorption spectroscopy (DOAS) has proved to be one of the most promising ones for active long-path absorption measurements in the troposphere.[4] In the DOAS application, the light from a broad-band xenon high-pressure lamp is transmitted through up to several kilometers of the atmosphere. The light is received and analyzed with the use of a fast scanning device to eliminate the influence of air turbulence.

The accuracy of the DOAS technique is vitally dependent on an accurate determination of the differential absorption cross section for the studied species. To ensure maximum sensitivity, it is also important to determine the optimal wavelength region to be utilized, particularly with regard to maximal differential cross section, minimum atmospheric attenuation, and minimum interference from other species. The ozone absorption in the UV region has been measured several times to establish the absolute absorption cross section,[5-9] and many monitoring techniques use the structure of the Hartley bands (200-300 nm) or the Huggins bands (300-360 nm). This is also the case for DOAS, where a part of the Huggins bands, around 328 nm, is the most commonly used wavelength region for ozone measurements.[4] However, we have investigated the possibility of using the low-energy tail of the Hartley bands, with absorption features which can be enhanced by the evaluation algorithms used in DOAS. This wavelength region (280-285 nm) has proved to be a very good alternative to the Huggins band (328 nm). The Hartley bands around 250 nm have the strongest differential cross section in the UV region, but this spectral range is difficult to use for long-path measurements due to the higher atmospheric attenuation. The differential absorption spectra of O_2, SO_2, and NO_2 in the 250-330 nm wavelength region have also been studied in order to estimate interference problems.

In the next section the laboratory experiment for determining the differential absorption cross section is described. The results are discussed in the following section. Results from 12 months of continuous DOAS measurements of ozone concentrations in the center of the city of Jönköping (pop. 60,000), with the use of the 280-285 wavelength range, are next discussed. Here a 750-m light path was used together with a retroflector setup, giving a total measurement path of 1500 m. Experience from this field test shows that the higher atmospheric attenuation in this wavelength region is not a problem for moderate lengths of the light path.

EXPERIMENTAL TECHNIQUE

Experimental Setup. The experimental setup is shown in Fig. 1. A 150-W xenon arc lamp (Hamamatsu L2273) was used, which has a broad emission spectrum with enough UV light to enable measurements through hundreds of meters in the atmosphere. This type of light source is well fitted for the DOAS application except for measurements around 450 nm, where it has some sharp emission lines. The light was focused into a two-meter-long White cell with a volume of 140 L.[10] The White cell has an f-number of about 15, with MgF_2-coated aluminum mirrors. In this experiment the folded path in the cell was 32 m. After the White cell the beam was collimated with a lens and then focused into a spectrometer to match its f-number. The spectrometer used was a Spex 500 M unit with an f-number of 4. It is equipped with a rotating slotted disk setup replacing the exit slit.[4] The measurement time for each scan of the spectrum is 10 ms. The grating has 1200 grooves/mm and blaze at 300 nm. The width of the entrance slit was 100 μm and the slotted disk on the exit side has 100-μm slits. The spectrum was masked in the focal plane to cover approximately 40 nm. For synchronization of the wavelength scale of individual scans, a trigger signal was used—ob-

FIG. 1. Experimental setup.

FIG. 2A. The absorption spectrum of ozone around 238 nm (solid line) with fitted polynomial (dashed line).

FIG. 2B. Absorption spectrum of ozone after normalization (e.g., division) with fitted polynomial and logarithmic transformation.
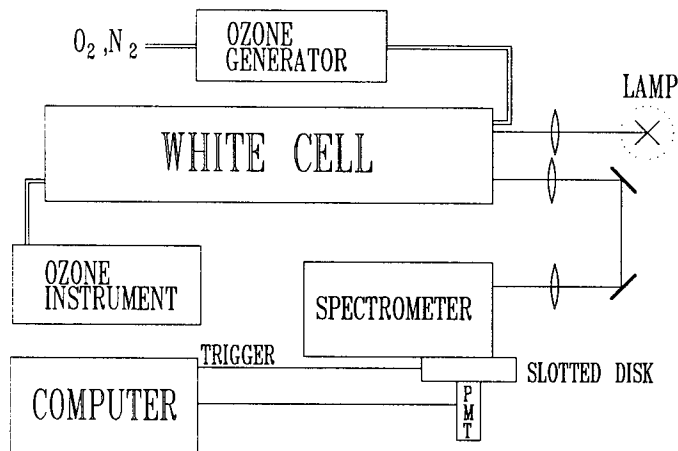
tained when the slit passes an infrared light barrier close to the edge of the mask. The spectrum was scanned as the disk rotated, but since the slit was vertical only in the middle of each scan, the resolution varied from 0.23 nm in the middle to 0.53 nm at both ends of the spectrum. An EMI 9558 QA photomultiplier tube was used as a detector, and the signal was amplified and sent to an IBM-compatible AT computer with a custom-made MCA (multichannel analyzer) plug-in card with a 12-bit ADC dividing each scan into 1000 channels. After 30,000 scans had been accumulated, during 5 min, the data were transferred to the computer for signal processing. In order to obtain absorption spectra of ozone, spectra were recorded when the White cell was flooded with different mixtures of ozone and oxygen (2–8 ppm of ozone, 298 K, 1 atm). These spectra were afterwards adjusted for oxygen absorption and instrumental features by division with a spectrum recorded when the cell was flooded with pure oxygen. The ozone/oxygen mixtures were achieved by passing oxygen through an electrical discharge chamber. The mixing ratio was monitored with a Dasisbi Model 1008-AH ozone instrument. However, this unit was not used for absolute measuring of the ozone concentration, but only to monitor when the mixing ratio in the White cell had reached equilibrium. The true ozone concentration was calculated from the absorption spectra (see below). Absorption spectra of nitrogen dioxide and sulphur dioxide were recorded by inserting small reference cells in front of the White cell.

Determination of the Ozone Concentration. The technique used to calculate the ozone concentration in the White cell setup is based on the absolute absorption cross sections published by Molina and Molina.[9] The absolute ozone absorbance as a function of the wavelength for each mix of ozone and oxygen was obtained by dividing a spectrum recorded at this mixing ratio with a pure oxygen reference spectrum taken before ozone was added to the White cell. The ozone concentration corresponding to each spectrum was then calculated and averaged from the Beer-Lambert law at 10 different wavelengths in the 275–295 nm interval, with the use of absolute absorption cross sections.[9] The absolute error due to electronic and mechanical drift in the experimental setup was estimated by comparing reference spectra taken before and after each run, yielding a differential cross section accuracy
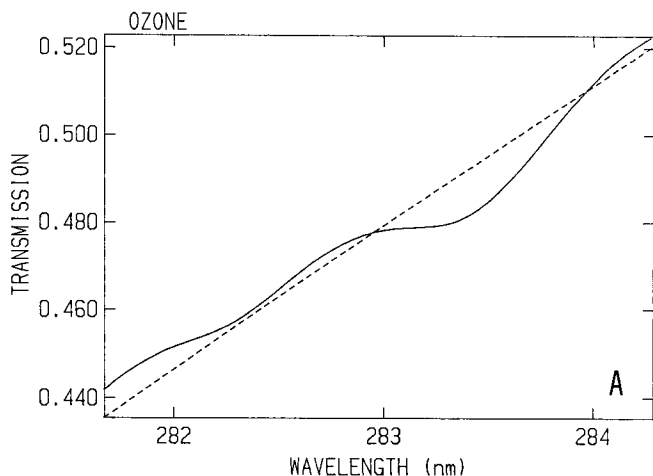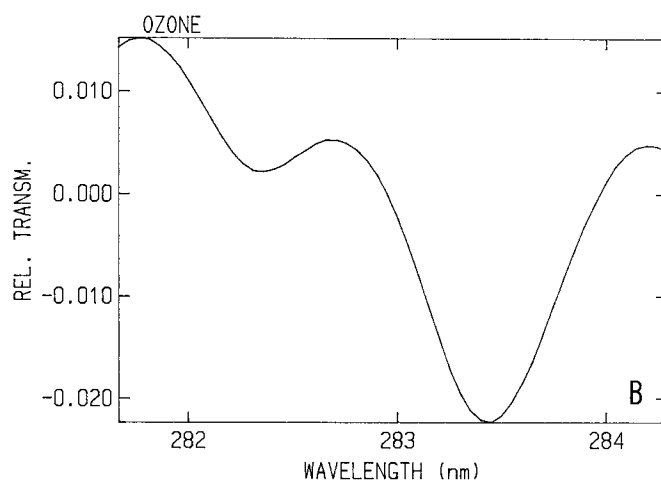
within 5%. The wavelength scale of the DOAS spectrometer was calibrated with reference to several emission lines of mercury between 250 and 305 nm.

Determination of Differential Absorption Cross Sections. The determination of the differential absorption cross section for ozone in the DOAS application was evaluated according to the algorithms described by Platt and Perner.[4] First the zero signal offset, due to a dc offset in the pre-amplifier and the dark current from the PM tube, is calculated and subtracted from the "raw" spectrum. The resulting spectrum is then divided with a reference spectrum recorded before ozone is added. This is to compensate for instrument-specific features as well as the differential absorption structure from oxygen. The result is the absolute absorption spectrum of ozone which, as already mentioned above, was used for calculating the corresponding ozone concentration. Then, a fifth-order polynomial is fitted to a portion of the spectrum. By normalizing (e.g., dividing) the spectrum with the resulting polynomial, we achieve a high-pass filtering which enhances the differential structure in this part of the spectrum. Figure 2A shows the absorption spectrum of ozone, around 283 nm, together with the fitted polynomial. Finally, in order to calculate the differential ab-
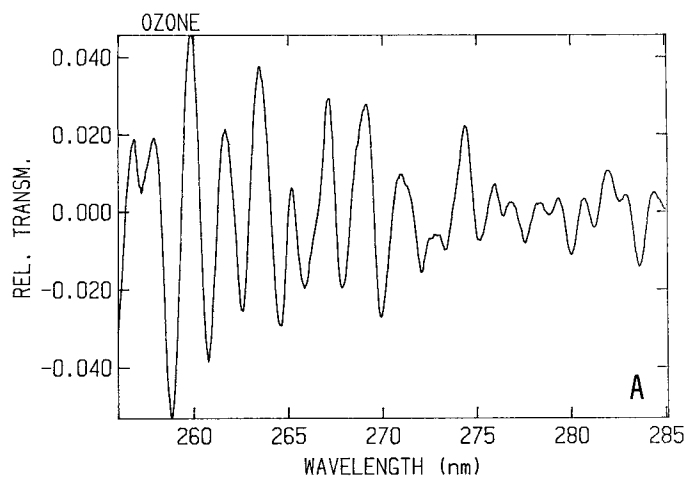
FIG. 3A. The differential absorption spectrum of ozone in the 255–285 nm region.
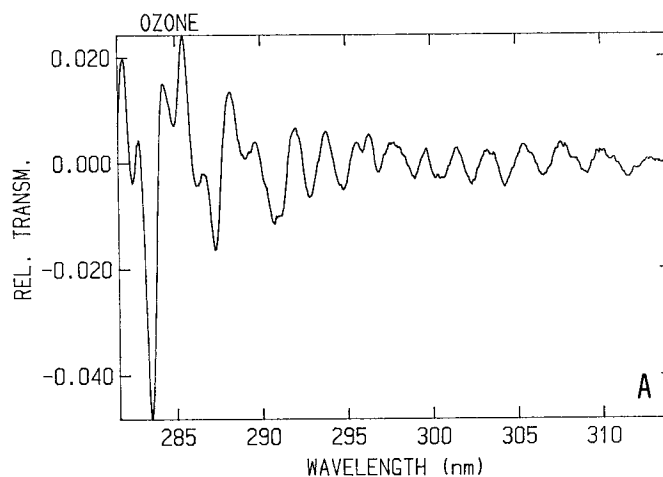

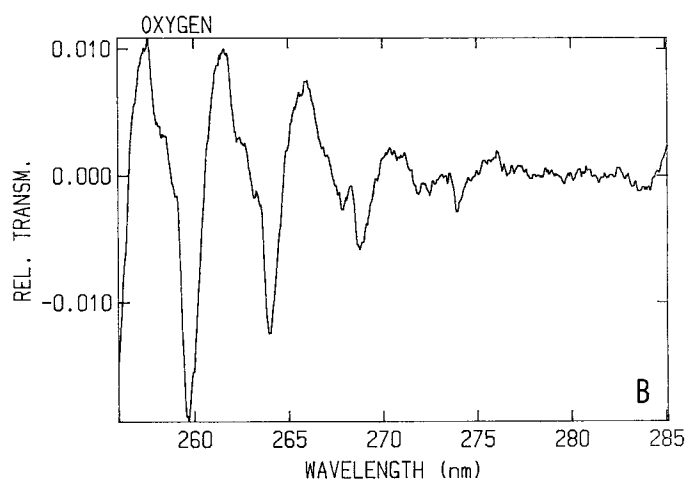FIG. 4A. The differential absorption spectrum of ozone in the 281–314 nm region.

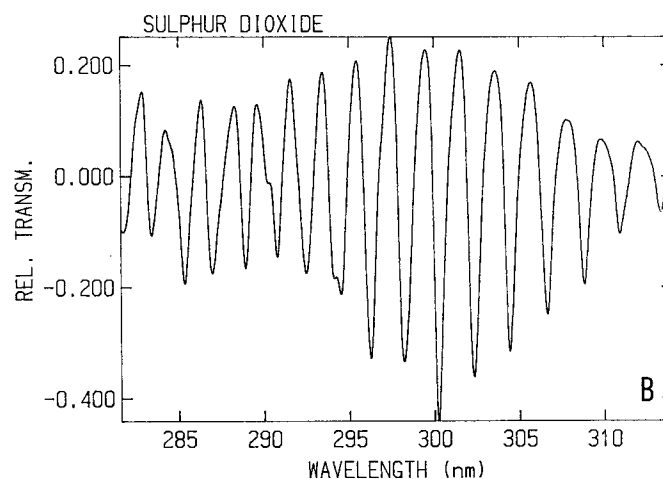FIG. 3B. The differential absorption spectrum of oxygen in the 255–285 nm region.

FIG. 4B. The differential absorption spectrum of sulphur dioxide in the 281–314 nm region.

sorption cross section from the Beer-Lambert law, a logarithmic transformation of the spectrum is made. Figure 2B shows the resulting absorption spectrum of ozone after normalization and logarithmic transformation. The correlation spectra of oxygen, sulphur dioxide, and nitrogen dioxide were evaluated with the same algorithm, except that the raw spectra were divided with nitrogen spectra.

RESULTS AND DISCUSSION

When one is determining the most feasible wavelength region to be used in the DOAS application, it is not only the magnitude of the differential absorption that has to be taken into account. Two almost equally important parameters, when the sensitivity is being determined, are the atmospheric attenuation and possible interference from other trace gases.

Differential Absorption. The strongest differential absorption in the whole wavelength range from 250 to 330 nm was obtained in the Hartley bands around 259 nm [see Figs. 3A (32 m, 4.6 mg/m^3), 4A (32 m, 13.3 mg/m^3), and 5A (32 m, 40.0 mg/m^3)]. The calculated differential cross section was here $53.6 \cdot 10^{-20}$ cm^2/molecule. In the

Huggins bands, the differential cross section at 328 nm was measured to $0.7 \cdot 10^{-20}$ cm^2/molecule (0.3 nm spectral resolution). This gives a theoretical detection limit of 11.2 μg/m^3 (1 km light path, least detectable optical density = 10^{-4}). The maximum differential absorption cross section of ozone in the intermediate range, 275 to 310 nm, was found at 283 nm (see Figs. 3A and 4A). The differential cross section was here evaluated to $10.7 \cdot 10^{-20}$ cm^2/molecule. This gives a theoretical detection limit of 0.7 μg/m^3 (1 km light path, least detectable optical density = 10^{-4}). The main cause of uncertainties in these values is in the determination of the ozone concentration. The calculated differential cross section is also likely to vary somewhat with the chosen mathematical evaluation algorithm (e.g., the order and the interval of the fitted polynomial)—which makes it important to use the same algorithm for the atmospheric spectrum as for the correlation spectra.

Atmospheric Attenuation. The differential absorption band around 259 nm is the strongest in the UV region; however, it is also the wavelength range that shows the strongest atmospheric attenuation. This fact, together with the decreasing efficiency of the light transmitting and receiving system at shorter UV wavelengths, results
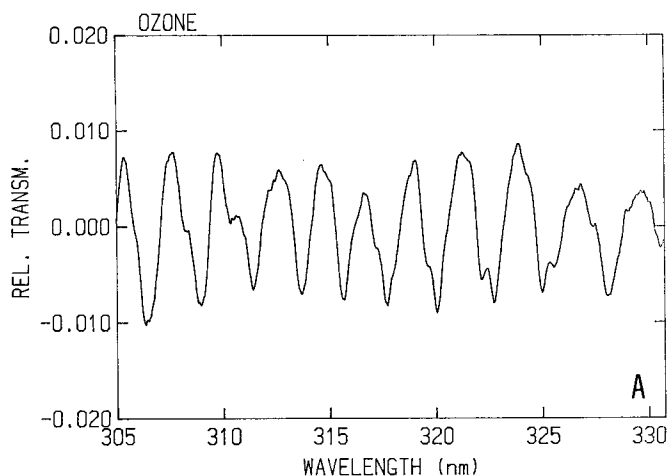
FIG. 5A. The differential absorption spectrum of ozone in the 305–330 nm region.
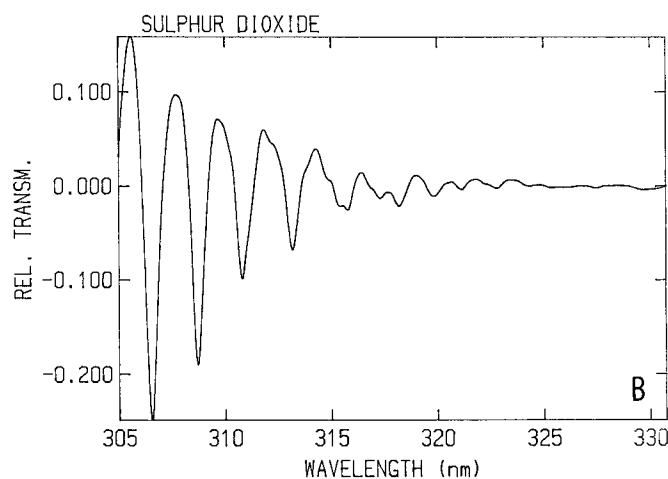

FIG. 5B. The differential absorption spectrum of sulphur dioxide in the 305–330 nm region.
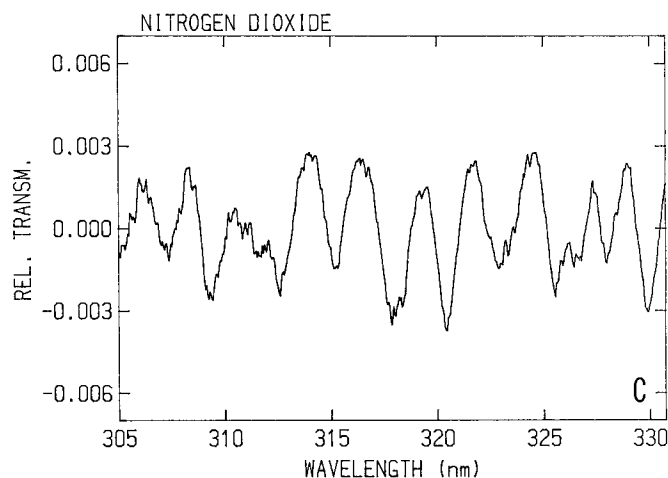

FIG. 5C. The differential absorption spectrum of nitrogen dioxide in the 305–330 nm region.

FIG. 6. Atmospheric spectrum (solid line) recorded in Lund and correlated with an O_3 and SO_2 calibration spectrum (dashed line). The spectrum corresponds to 161 $\mu g/m^3$ of O_3 and 2.5 $\mu g/m^3$ of SO_2.

in an unfavorable signal-to-noise ratio. The Huggins bands around 328 nm have so far been the most commonly used wavelength region for ozone measurements with DOAS.[4,11,12] A major reason for this approach is that at-
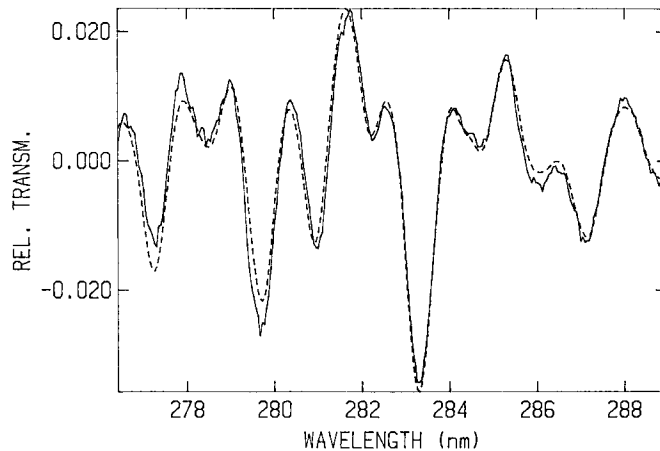
mospheric attenuation is, in this case, a minor problem, except with the case of extreme weather conditions or very long pathlengths. The third alternative discussed in this paper, the low-energy tail of the Hartley bands around 283 nm, is five times weaker than the differential absorption structure at 259 nm. However, the attenuation features of the atmosphere, as well as instrument performance in this wavelength region, are clearly in its favor. Field tests have shown that the signal-to-noise ratio, with the use of the absorption structure around 283 nm, is not a problem for light paths up to at least 2–3 km. The differential absorption cross section is also ten times stronger in this region than in the popular region around 328 nm.

Interferences. Due to its high abundance, oxygen is always to be taken into account in terms of interference. The Herzberg bands of oxygen interfere strongly below 270 nm [see Fig. 3B (32 m, 100% O_2)] and that fact, together with the high atmospheric attenuation, is the reason why the strongest Hartley bands of ozone are normally not used for long path absorption spectroscopy measurements. Sulphur dioxide has a strong absorption head centered around 300 nm. This means that it interferes strongly with parts of the Huggins bands [see Fig. 4B (1 cm, 3% SO_2)]. However, above 325 nm the SO_2 absorption is drastically reduced [see Fig. 5B (1 cm, 3% SO_2)]. In the mid part of the Huggins bands, the interference from nitrogen dioxide starts to be noticeable [see Fig. 5C (1 cm, 1% NO_2)]. The increasing NO_2 absorption, together with the decreasing ozone absorption with wavelength, is the reason for the compromise of using the wavelength region around 328 nm for ozone monitoring with DOAS. Here the interferences from SO_2 and NO_2 are quite weak, although their differential structures here are similar to those for ozone. We have studied the possibility of measuring ozone at 283 nm, and the only major interference problem in this wavelength interval discovered so far is from sulphur dioxide (see Fig. 4B). This interference is, however, quite weak and could be handled by means of multiple regression analysis where a SO_2 calibration spectrum is fitted together with the ozone calibration spectrum when one is evaluating the ozone concentration from each atmospheric spectrum. The
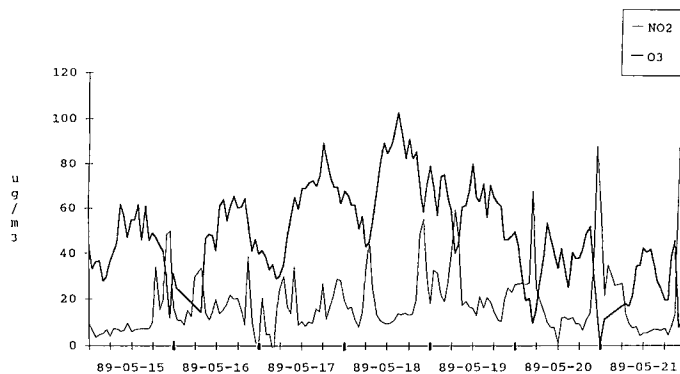
FIG. 7. DOAS measurements of O_3 and NO_2 during one week in May in the center of Jönköping. The total length of the measurement path was 1500 m.

ozone spectrum and the SO_2 spectrum proved to have a correlation coefficient of less than 0.01 for the interval 276 to 287 nm, compared with more than 0.3 for the interval 320 to 327 nm or -0.27 for the interval 324 to 330 nm. This result recommends the choice of multiple regression as a solution for the interference problem.

APPLIED ATMOSPHERIC DOAS MEASUREMENTS OF O_3 USING THE DIFFERENTIAL ABSORPTION AROUND 283 nm

Figure 6 shows an atmospheric spectrum (solid line) recorded during an ozone episode in the vicinity of the city of Lund (pop. 60,000) at 2.15 pm on 26 March 1990. The spectrum was recorded with the same DOAS setup used in the laboratory studies with a measurement path of 2000 m. The spectrum was afterwards evaluated with respect to O_3 and SO_2. The dashed line is the sum of two correlation spectra, yielding an ozone concentration of 161 $\mu g/m^3$ and a SO_2 concentration of 2.5 $\mu g/m^3$. Twelve months of continuous ozone monitoring was performed in the city of Jönköping along a 750-m-long path in a retroflector setup (total measurement path = 1500 m). These measurements were carried out with a system similar to the one used in the laboratory studies, except for the use of a different spectrometer, the Spex 1870c Minimate (focal length {entrance} = 0.22 m; focal length {exit} = 0.34 m; f-number = 4, grating = 600 grooves/mm; blaze = 300 nm; spectral resolution = 8–9 Å). With this system the wavelength interval 270 to 370 nm was covered in each scan, making possible concurrent measurements of O_3 (280–290 nm), SO_2 (290–310 nm), and NO_2 (350–370 nm). Figure 7 shows one hour mean values of O_3 and NO_2 measured during one week in January. The anticorre-

lation between NO_2 and O_3, due to oxidation of primary emitted (traffic) NO to NO_2, is clearly shown. The detection limits in these measurements were estimated to be about 2–3 $\mu g/m^3$ for ozone and 1 $\mu g/m^3$ for NO_2. The experience from this campaign is that there are no major problems with the use of the 283-nm absorption structure in the DOAS application for moderate lengths of the measurement path and for moderate ozone concentrations.

CONCLUSION

The differential absorption structure of ozone in the wavelength interval 280 to 290 nm can be considered to be as good a candidate for DOAS measurements as the already established region around 328 nm in the Huggins bands. Our value of the maximum differential cross section is estimated to be within 5%, but is likely to vary somewhat with the mathematical evaluation algorithm. Field measurements have shown that the higher atmospheric attenuation in this wavelength region is not a problem for moderate lengths of the light path (at least up to 2–3 km). However, due to the strong absorption in stratospheric ozone this wavelength region cannot be used for passive DOAS measurements using sky radiation.

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