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Intercomparison of the influence of tropospheric clouds on UV-visible absorptions detected during the NDSC intercomparison campaign at OHP in June 1996

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Abstract. The influence of tropospheric clouds on zenith sky light (or brief ZSL-DOAS) measurements of stratospheric gases is investigated. From a large set of intercomparison studies including six simultaneously operated UV/visible spectrometers, the zenith sky absorptions of O_3, O_4, NO_2, and H_2O are found to increase considerably under the investigated Cumulonimbus (Cb) cloud. The accuracy of the inferred visible O_3 absorptions, however, are affected by interfering H_2O absorptions. The increased cloudy sky absorptions are attributed to increased pathlengths due to multiple Mie scattering and hence interstitial gaseous absorptions inside the cloud. The absorptions detected for chemically inert gases like O_4 (and H_2O) are found to be inconsistent with those detected for NO_2 and O_3. This finding indicates that O_3 and NO_2 are modified by cloud related transport or chemical processes.

1. Introduction

In recent years ZSL-DOAS has been developed into a powerful tool to remotely monitor the fate of several stratospheric constituents (O_3, NO_2, BrO, OClO, ..) [e.g., *Noxon,* 1978]. For useful stratospheric studies, however, accuracy on the level of a few percent in the measured total column amounts is required.

After the first pioneering study of Noxon [1978], only recently it has been argued that tropospheric clouds (either by radiative transfer (RT), cloud chemical processes, or by transport processes due to clouds) may affect these spectroscopic measurements (denoted herein as "cloud effects" or "CE"), reported to occasionally be as large as ~10% in total O_3 [e.g., *Brewer and Kerr,* 1973; *Van Roozendael et al.,* 1994; *Erle et al.,* 1995; *Wagner et al.,* 1998]. Although RT processes - which are likely to cause such influences - have been recently described [*Pfeilsticker et al.,* 1998a,b, hereafter denoted PF98ab], their magnitude and significance in ZSL-DOAS are still to be determined.

The uncertainty associated with RT related CE is mainly due to the low tropospheric concentrations of the gases of interest i.e., of O_3, NO_2, and BrO. Therefore, fluctuations in the absorption path or change in the tropospheric concentrations are expected to modify only slightly the total atmospheric absorptions of the investigated species, and consequently it was speculated whether CEs are detectable, or possibly could have been caused by spectral retrieval problems, i.e., retrieval of O_3, NO_2 and O_4 in the visible spectral region during cloudy sky Cb conditions when H_2O absorptions are very strong.

ZSL-DOAS measurements, however, can also contribute to the cloud absorption controversy [e.g., *Kerr et al.,* 1995] either by investigating the spectroscopy of UV/visible absorbers or cloudy sky photon pathlengths [*Pfeilsticker et al.,* 1997; PF98ab; *Solomon et al.,* 1999].

In view of still existing RT uncertainties for cloudy sky conditions, intercomparison studies including several simultaneously operated ZSL-DOAS instruments appeared to be warranted. Results of such a study conducted within the framework of the NDSC (Network for the Detection of Stratospheric Change) June 1996 intercomparison campaign held at the Obsèrvatoire de Haute Provence (OHP, 43.9°N, 5.7°E) are reported.

2. Methodology

The presented data are collected by a subgroup of participants from the intercomparison campaign: the Belgian Institute for Space Aeronomy, (IASB), the Instituto Nacional de Tècnica Aeroespecial (INTA), the Norwegian Institute for Air Research (NILU), the Institut für Umweltphysik, University of Bremen (Uni-Bre), the Service D'Aèronomie du CNRS operating a SAOZ (Systèm d'Analyse par Observations Zénithales) CNRS2-instrument, and the Institut für Umweltphysik, University of Heidelberg with an UV (IUPuv) and a visible (IUP-vis) instrument. Instrumental details as well as the standard retrieval techniques of the individual groups have already been described by Roscoe et al. [1999].

A frequent feature of early summer weather at OHP is clear sky mornings followed by strong vertical convection and the formation of optically thick, vertically extended precipitating Cb clouds in the afternoons. Also,

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southwesterly winds frequently prevailed whereby OHP is often downwind of several major cities (Marseille, Nice, Avignon) and industrial areas (in the Rhone valley) which gave rise to elevated NO_x concentrations. Likewise, due to the lightning inside Cb-clouds, interstitial NO_2 could have been formed [e.g., *Huntrieser et al.*, 1998].

Comparisons of CEs detected prior to this study revealed that another major source of uncertainty is the spectral interference due to increased cloudy sky H_2O vapor absorption features in the visible band interfering with the differential optical absorption features of O_3 (at 505nm), O_4 (at 478nm) and NO_2 (at 448nm). Such spectral interferences are mainly due to oversaturated H_2O absorption lines not properly considered in low resolution spectrometry and improper temperature corrections due to inadequate spectroscopic assignments of some visible H_2O lines in the HITRAN96 library (C. Camy Peyret, priv. comm., 1998). Accordingly different spectral retrievals covering different wavelength intervals (denoted by a1 - a5, b1 and b2) are chosen to avoid spectral interferences.

In the a1 retrieval, each group was free to use their own standard wavelength interval and retrieval technique (i.e., the mathematical code and the degree of the fitting polynomial) [for details see Roscoe et al., 1999]. Other retrievals included the following regions; (a2) 450nm to 550nm, (a3) 450nm to 497nm, (a4) 442nm to 497nm, (a5) 442nm to 467nm. In most spectral retrievals (a1 to a5) each of the groups was allowed to use their own cross section spectra [as specified in Roscoe et al., 1999]. The H_2O cross sections were derived for each instrument by degrading the 273K HITRAN96 library high resolution H_2O [*Rothman et al.*, 1992] to the resolution of the instrument. A b1 test was also conducted on spectra from June 14', where the participating groups used a common set of cross sections in their standard (a1) wavelength interval. The Bremen and IASB groups also performed a b2 retrieval for the interference-free detection of NO_2 in the wavelength interval from 403nm to 429nm for June 14'. Also, the IUP operated an instrument in the UV where water vapor does not absorb and hence the results can serve as an independent check for the results obtained from the observations in the visible.

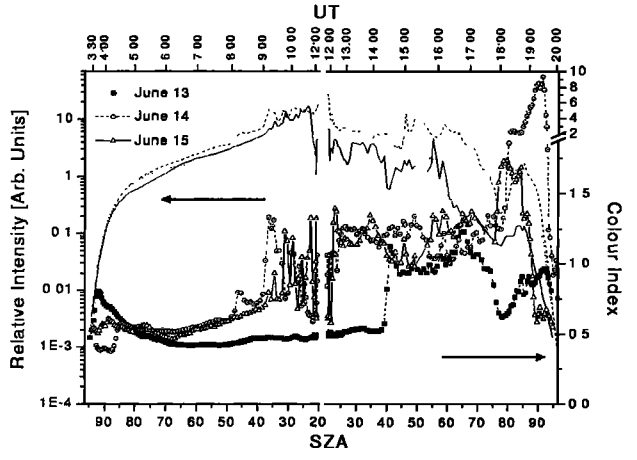

Figure 1. Intensity (lines) and CI (symbols) (see text) for June 13, 14, and 15, 1996. For the mostly clear sky conditions during the mornings, the CI follows a smooth function versus time or SZA. During the afternoons the occurrence of Cb clouds causes a variable whitening of the spectra and variations in the CI.

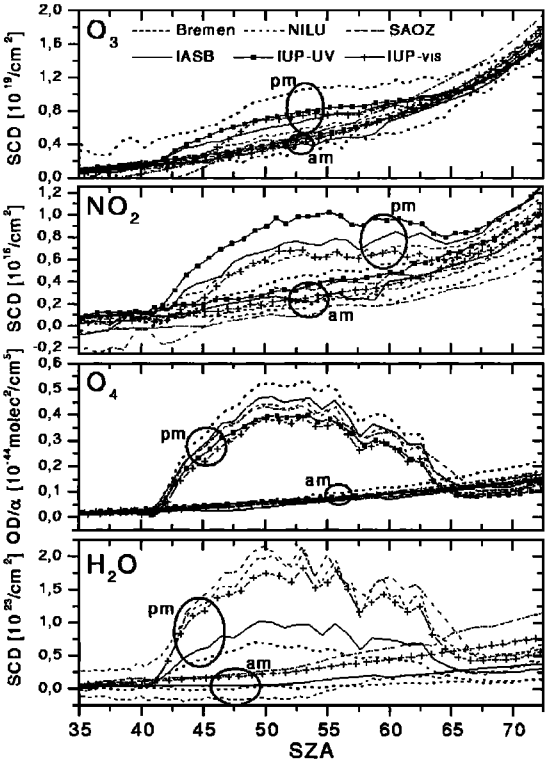

Figure 2. Slant column densities (SCD) measured by the different instruments during the afternoon of June 13, 1996. A Cb cloud was located over the measuring site between 14:00 UT and 18:30 UT. For the evaluation each group used their standard (a1) retrieval.

Daily high sun reference spectra [as specified in Roscoe et al., 1999] were simultaneously recorded with all instruments and used to ensure a true intercomparison for a systematic comparison. Note, that since not all instruments covered the same maximum wavelength range (from 403nm to 550nm) not all groups could participate in all individual retrieval test runs. Likewise, instrumental problems prevented some groups from contributing to all measurements (e.g., SAOZ and NILU on June 14' or INTA on June 15').

3. Observations

Here, the data recorded on June 13, 14 and 15, 1996 are intercompared. The presence of clouds above the measuring site (i.e., within the FOV of each of the instruments) is discernable from the relative zenith radiance as well as from the color index (CI), defined here as the radiance ratio of the light received at 682nm and 388nm (Figure 1). Clearly, the smooth increase of the zenith radiance indicated clear skies during the morning, i.e., 4 UT to 14 UT on June 13', from 4 UT to 8 UT on June 14', and 4 UT to 9 UT on June 15'. In contrast, the actuating zenith radiance indicated cloudy skies during the afternoons. The coinciding CI values indicated that blue (clear) skies prevailed during the mornings and white (cloudy) skies during the afternoons.

From the well known relationship between cloud transmission and cloud optical thickness (τ_c) [e.g., *Cahalan et al.*, 1994], the decrease in zenith radiance

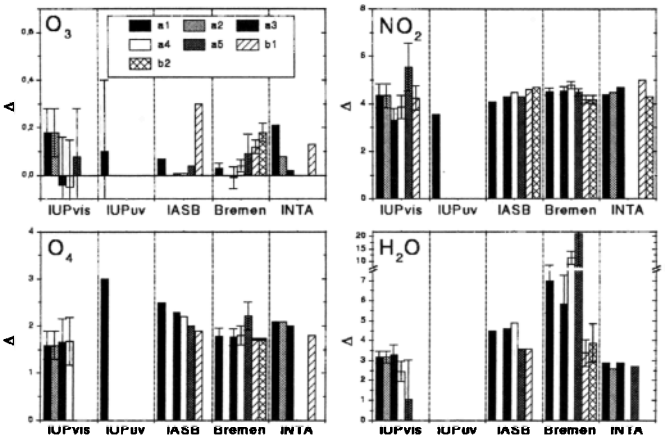

Figure 3. Derived absorption enhancements ($\Delta_{\mathtt{meas}}$) for O_3, NO_2, O_4 and H_2O for the different spectral retrievals (a1, a2, a3, a4, a5, b1, and b2) used to evaluate the thunderstorm observation on June 14, 1996, 18:00 UT, SZA=78.1°.

(when compared to the clear sky morning observations) can be used as a proxy to derive τ_c overhead. Accordingly, the largest observed drop in the zenith radiance (by more than a factor of 10) reveals that Cb clouds could have had $\tau_c \geq 100$.

For example, larger slant column densities (SCD) for O_3, NO_2, O_4 and H_2O for each of the instruments (using the standard a1 retrieval) are detected for the cloudy part of the afternoon (within the range of solar zenith angles (SZA) from 42° to 65°) than for the clear sky morning on June 13 (Figure 2). The best agreement is seen for the relative absorption increase of O_4. Since O_4 is photochemically inert, its increased absorption clearly indicates increased geometrical pathlengths due to multiple Mie scattering inside clouds. Of major concern, however, was the poor agreement between the retrieved SCDs of O_3, NO_2, and H_2O. Since H_2O does not absorb in the UV, but the IUPuv instrument also observed increased absorptions of O_3, and NO_2, the CE detected at visible wavelengths can not solely be attributed to spectral retrieval problems i.e., H_2O interference.

In order to avoid that differences in the values of the absorption cross sections used by the participants giving rise to further discrepancies in the retrieved SCDs, cloud enhancement "$\Delta_{\mathtt{meas}}$" values are compared. For a particular fixed SZA the $\Delta_{\mathtt{meas}}$ is defined as follows:

$$\Delta_{\mathtt{meas}} = \frac{\mathtt{SCD_{obs}}}{\mathtt{SCD_{clear}}} - 1 = \frac{\mathtt{OD_{obs}}}{\mathtt{OD_{clear}}} - 1 \qquad (1)$$

with $\mathtt{SCD_{obs}}$, $\mathtt{OD_{obs}}$ being the actual retrieved SCD or optical density (OD), respectively, and $\mathtt{SCD_{clear}}$, $\mathtt{OD_{clear}}$, the parameters expected for clear sky. The latter parameters ($\mathtt{SCD_{clear}}$ or $\mathtt{OD_{clear}}$) are determined from the measured values detected at the same SZA during the respective morning. In the case of H_2O, O_4 and O_3 this is assumed to be justified since for all three gases, possible diurnal variations are assumed to be much smaller than the detected CEs. In the case of NO_2, the $\Delta_{\mathtt{meas}}$ values are inferred by additionally accounting for the diurnal variation of the stratospheric NO_2 column amount using the result from a photochemical model calculation [*Nevison et al.*, 1996].

4. Results and Discussion

The Δ values for NO_2 and O_4 (excluding IUPuv) agree between all groups for all analysis within the error bars (Figure 3 and 4). In contrast, the results for O_3 and H_2O are very variable due to either spectral interference or missing lines for H_2O. Clearly, the CE detected for the visible and UV absorptions of the photochemically stable trace gas O_4 indicate that CE can not solely be attributed to spectral retrieval problems or changed trace gas concentrations within the cloud. Therefore, our observations indicate that due to multiple Mie scattering inside the cloud the pathlength and hence the absorptions of interstitial gases are increased [e.g., PF98ab]. It is therefore of interest whether for the probed Cb clouds the result for any of the gases are consistent, or whether possible inconsistencies are caused either by photochemical processes (for O_3 and NO_2), or by transport of polluted air masses from the PBL into the cloud interior or by NO_x production by lightning [e.g., *Huntrieser et al.*, 1998, *Winterrath et al.*, this issue].

For this purpose, the measured $\Delta_{\mathtt{meas}}$ values are compared with calculated $\Delta_{\mathtt{calc}}$ values for each gas using the relation of the geometrical path length enhancement as function of τ_c [PF98ab] in the photon diffusion approximation for optically thick Cb clouds $\tau_c \geq 1/(1-g)$:

$$\frac{< L_T >}{H_c} = (1-g) \times \tau_c^{\gamma-1} \approx \mathtt{AMF_{cloud}} \qquad (2)$$

with $< L_T >$ being the mean geometrical path for the transmitted light, H_c the vertical cloud extension, g ($\approx$ 0.85) the asymmetry factor for Mie scattering, γ ($\approx$ 1.75) the Lévy index for Cb clouds [Pfeilsticker, 1999], and $\mathtt{AMF_{cloud}}$ the air mass factor (AMF) for the cloudy part of the troposphere. The $\Delta_{\mathtt{calc}}$ is estimated from:

$$\Delta_{\mathtt{calc}} = \frac{(\mathtt{AMF_{cloud}} - \mathtt{AMF_{clear}}) \times \mathtt{VCD_{trop}}}{\mathtt{SCD_{clear}}} \qquad (3)$$

with $\mathtt{AMF_{clear}}$ being the clear sky AMF for that part of the troposphere which otherwise is filled with clouds, and $\mathtt{VCD_{trop}}$ the tropospheric vertical column amount of a trace gas (Table 1).

For this calculation, the cloud top and bottom were taken as provided by a meteorological report from the Deutscher Wetterdienst, τ_c ($= H_c/\lambda_{\mathtt{Mie}}$) was calculated

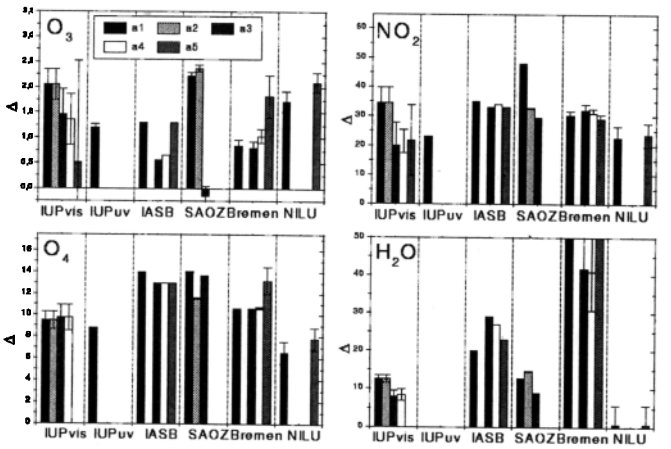

Figure 4. same as Figure 3, but for the thunderstorm observation on June 15, 1996, 17:00 UT, SZA=68°.

Table 1. Inferred and Calculated Cloudy Sky Absorption Enhancements (Δ).

Date/Time (UT)	Cloud Bottom/ Top (km)	AMF_{cloud}	ΔH_2O		ΔO_4		ΔO_3		ΔNO_2	
			calc	meas	calc	meas	calc	meas	calc	meas
June 13, 15:00 SZA=50 7°	2 3-9.1	15.5	18±6 0	11±5.0	6.9±3	10±2	0 5±0.1	0.4±0.1	7.1±3	2 5±0.5
June 14, 18:00 SZA=78 1°	2.3-9 2	13.8	3.5±1 5	5.0±2.0	1.63±0 3	1.9±0.3	0.13±0.1	0.1±0.1	1.89±0 2	4.5±0.5
June 15, 17:00 SZA=68°	2.2-10 1	17 2	23±10	30±20	9.0±3	11±2	0 43±0.2	1 1±0.5	5.9±1.5	30±6.0

For the assumptions, which went into the calculations, see the text. The cloud bottom was estimated from the reported temperature and humidity profiles, and the cloud top height from the METEOSAT IR-imagery (provided by the Deutscher Wetterdienst). AMF_{cloud} was calculated using equ. 2. The standard deviation of the Δs inferred from the measurements are due to standard deviation of all measurements from the mean. The inferred Δs and their uncertainties were calculated from equ. 3 with the assumed parameters as discussed in the text and their uncertainties.

by assuming a mean free path for Mie scattering, λ_{Mie} (= 14.1m) as specified by Stephens [1979], a VCD_{trop} for O_3 (about 35 Dobson units) measured by daily ECC O_3 profile soundings at the nearby located Gap/France and for NO_2 a $VCD_{trop} = 5 \times 10^{15}/cm^2$ (330 ppt) an upper limit inferred from the morning observations, and stratospheric SCD_{clear}s as detected.

For the Δ of H_2O and O_4, a fair agreement exists for all three observations but the Δ for O_3 agree only for June, 13 and 14. On June 15 the lower Δ for O_3 indicates that interstitial O_3 is probably increased in (or due to) the Cb cloud on June 15 [see Winterrath et al., this issue]. For NO_2, the calculated Δs do not agree on either day. While the lower NO_2 may indicate low interstitial NO_2 (below 330 ppt) - tentatively because of a low tropospheric NO_2 background or some removal in the Cb cloud, the larger observed than calculated Δ clearly indicates an increase of interstitial NO_2. This may tentatively imply either NO_x production due to lightning inside the thunderstorm cloud increasing the interstitial NO_2, or that NO_x-rich air masses were vertically transported from the PBL into the interior of the thunderstorm cloud [e.g., *Huntrieser et al.*, 1998], a conclusion that is discussed in detail by Winterrath et al. (this issue) for our observation.

When scaled to climatological relevant cloud cover, the detected CE indicate that tropospheric clouds can adversely affect the zenith sky observation of stratospheric gases on a percent level (in either direction), a conclusion basically in agreement with the findings of PF98ab.

ZSL-DOAS measurements can thus provide new information on cloudy sky geometrical pathlengths [PF98ab; *Pfeilsticker*, 1999], cloudy sky SW absorption [*Pfeilsticker et al.*, 1997; *Solomon et al.*, 1999] and in-cloud chemical processes [*Winterrath et al.*, this issue].

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