

Spectral fine-structure in the polarisation of skylight

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Abstract. High-spectral resolution polarisation measurements of the clear daylight sky reveal an unexpected rich spectral fine-structure in the polarisation superimposed on the more familiar broad-band continuum. This polarisation spectrum shows the spectral fingerprints of scattering and absorption processes which is illustrated with radiative transfer calculations. In particular, radiative transfer calculations suggest the potential of high-spectral resolution polarimetry within absorption bands for remote sensing of aerosol vertical distribution, which is relevant to the Earth's radiation budget and ozone hole chemistry. In addition, the presence of spectral fine-structure in the polarisation of skylight also has relevance to radiance measurements performed with polarisation sensitive spectrometers, such as the space-based GOME instrument.

Introduction

Traditionally, polarisation observations of the daylight sky are being performed using broad-band spectral filters [Coulson, 1988]. The so measured polarisation is explained by scattering by air molecules [Rayleigh, 1871; Chandrasekhar, 1950], aerosol scattering [Coulson, 1988], and surface reflection [Chandrasekhar, 1950]. Hence, it has been commonly assumed that the skylight polarisation exhibits pure broad-band spectral behaviour in contrast with the spectrally rich radiance spectra. However, in 1970 Lenoble predicted [Lenoble, 1970] that for diffusely reflected radiation in a homogeneous Rayleigh atmosphere, the polarisation in absorption bands should be higher due to enhanced single scattering compared to the polarisation outside the absorption band. Recently, a few polarisation measurements of diffusely transmitted radiation were reported [Stammes *et al.*, 1994; Preusker *et al.*, 1995] confirming that the polarisation of skylight indeed shows variation on a high-spectral resolution scale when observed within an absorption band. In these measurements a sharp

change in the polarisation at 761 nm, corresponding to a molecular absorption band of oxygen, was observed. It was proposed by Stammes *et al.* [1994] that increasing oxygen absorption favours scattering of sunlight at higher altitudes in the atmosphere, and that this results in a change of the polarisation with wavelength reflecting the variation of scatterers with altitude. The studies by Stammes *et al.* and Preusker *et al.* were, however, limited to the wavelength region from 650 to 850 nm. In the present work we extended the wavelength region to the visible and ultra-violet to cover the range from 300 to 800 nm. As a result, much more spectral structure was observed which coincides with solar Fraunhofer lines and molecular absorption bands of ozone (O₃), oxygen (O₂) and water vapour (H₂O).

Experimental

The polarisation measurements have been performed with the ground-based Global Ozone Monitoring Experiment Bread Board Model (GOME BBM). The GOME BBM is a four-channel grating spectrometer covering the ultra-violet (UV), visible (VIS) and near-infrared (NIR) wavelength range (240 - 790 nm), with a 0.17-0.33 nm spectral resolution, equivalent to GOME on board the ERS-2 satellite [ESA, 1995]. Each channel has a 1024-diode array detector which is cooled to 236 K to reduce detector noise. Due to the strong UV absorption by O₃ in the Earth's atmosphere the ground-based measurements are limited at the short-wavelength end to 305 nm. The polarisation is determined through relative measurements; therefore no radiometric calibration of the GOME BBM is needed. Radiometric and spectral stability is achieved by operating the GOME BBM in vacuum and stabilising the optical bench temperature. Atmospheric radiation collimated by a lens, passes through a rotatable Glan-Thompson polariser, and is focused onto a fibre bundle. The resulting field-of-view is approximately 2°. The fibre bundle transports the light to the spectrometer while scrambling the polarisation of the light, thereby eliminating the influence of the polarisation sensitivity of the spectrometer on the polarisation measurements. Atmospheric radiation measurements can be performed for any part of the sky as the optics and fibre bundle are fed into a remote control telescope mount. The degree of linear polarisation [Hansen and Travis, 1974] henceforth referred to as the polarisation, is determined by measuring the atmospheric radiation with the polariser under three different orientations, chosen 60° apart. Typical integration times for the individual radiation measurements are 10

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to 100 seconds resulting in a total integration time of at most a few minutes for each polarisation spectrum. The measurement site is located in a surrounding of vegetation and buildings.

Results and discussion

All observations presented here have been obtained on April, 7, 1997, which was a cloud-free day. The polarisation of the zenith sky was measured in the morning for three different solar zenith angles (SZAs) and is shown in Figure 1. The polarisation measured in zenith decreases with rising sun, which is consistent with the angular behaviour of polarisation by Rayleigh scattering, having its maximum at 90° scattering angle. The spectral appearance of the polarisation is similar for different SZA. All curves show a wealth of spectral fine-structure, particularly in the UV and the NIR. In the following, we will present a qualitative discussion of the observed spectral behaviour of the polarisation on the basis of radiative transfer calculations presented in Figure 2 for a pure molecular atmosphere and an atmosphere with aerosol added, for two wavelength-independent surface albedos, namely a black surface ($A_s = 0.0$) and a highly reflecting surface ($A_s = 0.4$).

The radiative transfer code used fully includes multiple scattering and polarisation [De Haan et al., 1987]. Molecular absorption is included in the model for O_3 in the UV and the VIS (Huggins and Chappuis bands respectively) and for O_2 around 761 nm (A band), because these are the most prominent absorbers in the observed wavelength region. A Mid-Latitude Summer atmosphere [McClatchey et al., 1972] consisting of 32 plane-parallel homogeneous layers is used, where the column density of O_3 is fixed to 300 DU, as measured at KNMI, De Bilt, on April, 7, 1997. For the aerosol-added atmospheres, the total aerosol optical thickness

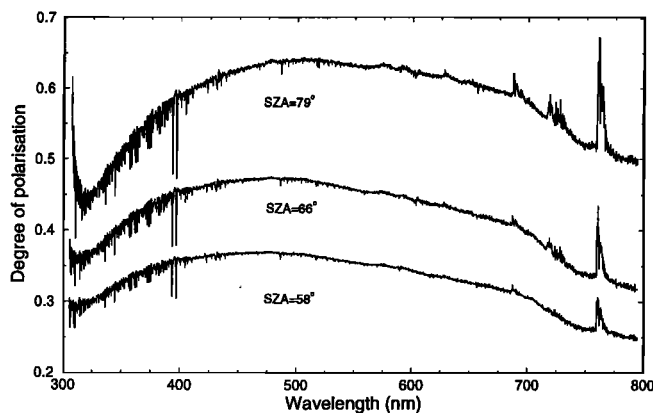


Figure 1. The degree of linear polarisation of the cloud-free zenith sky as a function of wavelength from 305 to 794 nm, for three values of the solar zenith angle (SZA), as measured at SRON, Utrecht, The Netherlands (52.1°N , 5.2°E) on the morning of April, 7, 1997. Superimposed on the broad-band continuum, spectral fine-structure in the polarisation is observed.

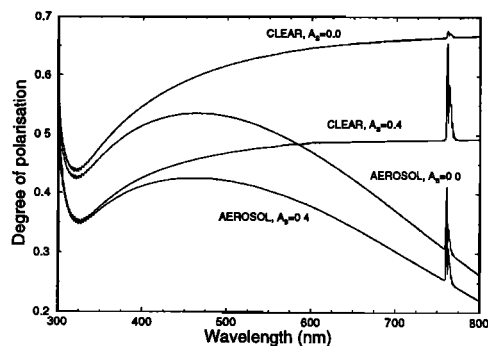


Figure 2. The degree of linear polarisation of the zenith sky for a solar zenith angle of 66° as calculated with the doubling-adding method [De Haan et al., 1987]. Calculations are shown for a pure molecular atmosphere, denoted by "Clear", and an atmosphere with aerosol added, denoted by "Aerosol". In both cases the calculations are performed for two different surface albedos, $A_s=0.0$ and $A_s=0.4$.

is 0.08 at 500 nm, determined from direct sun measurements with the GOME BBM on April, 7, 1997. The aerosol vertical distribution is adapted from the WMO aerosol profiles [WMO, 1983], with the aerosol distributed over four homogeneous layers ranging from 0 - 2 km, 2 - 12 km, 12 - 30 km and 30 - 100 km. In the troposphere, up to 12 km, we assumed dust-like aerosol [WMO, 1983] which is consistent with the aerosol size retrieved from the direct sun measurements, with optical thickness of 0.075. Above 12 km, the atmosphere contains background stratospheric aerosol [WMO, 1983] ($75\% \text{H}_2\text{SO}_4$ in water) with optical thickness 0.005. The scattering properties of the aerosols are calculated using Mie-theory [Van De Hulst, 1957]. The surface reflection is assumed to be isotropic and depolarising which is considered adequate for modelling polarisation of diffusely transmitted radiation.

The calculations in Figure 2 illustrate the various radiative transfer processes causing, respectively, the broad-band and narrow-band spectral features in the polarisation. At wavelengths near 300 nm, the radiation arises predominantly from single scattering because of the strong O_3 absorption, resulting in a high degree of polarisation. With increasing wavelength, the polarisation drops because O_3 absorption decreases and multiple scattering becomes more important. Beyond $\lambda \sim 320$ nm a smoothly increasing polarisation is apparent which is due to the wavelength dependence of the Rayleigh scattering optical thickness. In the hypothetical case of a pure molecular atmosphere without any reflection from the surface ($A_s = 0.0$), the polarisation will tend to its single scattering value near the long wavelength end of the spectrum. The addition of aerosols to the atmosphere model reduces the polarisation across the entire spectrum (Fig. 2), but most pronounced at longer wavelengths, which agrees with our observations. Model calculations further show that a high surface albedo leads to depolarisation of sky-

light [Chandrasekhar, 1950]. Therefore, we attribute the sharp decrease in polarisation observed above 700 nm (Fig. 1) to the reflection of surrounding vegetation which has indeed a high albedo in the NIR [Bowker et al., 1985].

The spectral fine-structure observed in the UV coincides with solar Fraunhofer lines as demonstrated in Figure 3 which shows a comparison of the ground-based polarisation measurements with the space-based GOME measurement of the extra-terrestrial solar spectrum. This suggests that most of the observed UV fine-structure is related to the Ring effect [Grainger and Ring, 1962; Brinkmann, 1968]. This phenomenon is known from radiance spectra where the depths of solar Fraunhofer lines observed in skylight are smaller than those observed in direct sunlight. Different explanations of the Ring effect have been put forward [Kattawar et al., 1981], but it is now generally accepted that inelastic rotational Raman scattering is the major cause of the Ring effect [Solomon et al., 1987; Fish and Jones, 1995; Joiner et al., 1995]. Raman scattering by N₂ and O₂ shifts the wavelengths and has a depolarising effect, resulting in less polarised light in the dark Fraunhofer lines which agrees with our observations. Because Raman scattering is not included in our radiative transfer calculations, the polarisation fine-structure corresponding to the Fraunhofer lines does not show up in Figure 2. The model calculations show some polarisation spectral fine-structure around 310 nm coinciding with the spectral fine-structure of O₃ absorption. In the measurements this structure is hidden by the stronger Ring lines. The characteristic broad-band O₃ absorption in the UV, however, is clearly visible (Figure 1, SZA=79°) in the polarisation below 310 nm.

Towards longer wavelengths molecular scattering, including rotational Raman scattering, becomes much less important (λ^{-4}). Nevertheless, some very pronounced

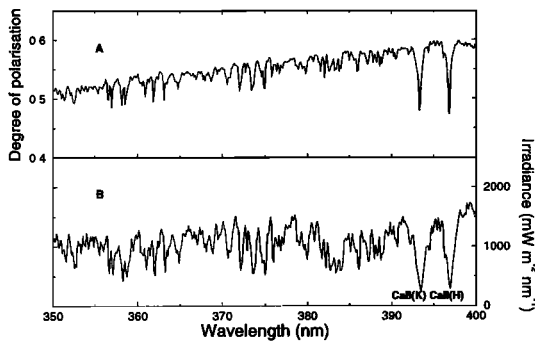


Figure 3. The UV part of the zenith sky polarisation spectrum for SZA = 79° is shown in more detail (top). The spectral fine-structure in the measured polarisation coincides closely with the Fraunhofer lines in the extra-terrestrial solar irradiance spectrum (bottom). The latter has been measured on April, 7, 1997, by GOME on ERS-2. Even the smallest spectral features in the polarisation coincide with Fraunhofer lines, which demonstrates the precision ($\sim 10^{-3}$) of the measurements.

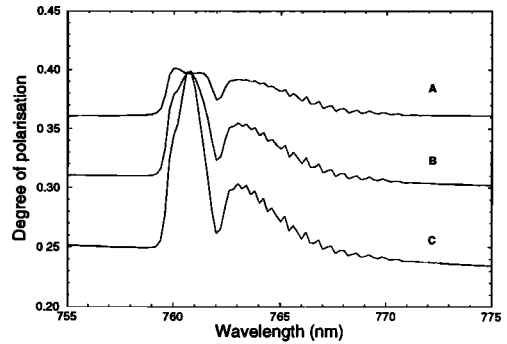


Figure 4. The degree of linear polarisation of the zenith sky as calculated for the O₂-A band for three different aerosol profiles with a fixed aerosol optical thickness of 0.08 at 500 nm. Curve (A) represents an atmosphere with all aerosol in the troposphere using dust-like aerosol, curve (C) an atmosphere with all aerosol in the stratosphere using background stratospheric aerosol, and curve (B) an atmosphere with 50% of the aerosol in the troposphere and 50% in the stratosphere. Here the solar zenith angle is 66° and A_s = 0.4.

spectral fine-structure in the polarisation is observed in the NIR. These features coincide with molecular absorption bands of H₂O around 725 nm, and of O₂ around 761 nm (A band) and 687 nm (B band). Radiative transfer calculations of the O₂-A band, illustrated for a realistic case by the curve "Aerosol, A_s=0.4" in Figure 2, show that the polarisation of the zenith sky outside the band is mainly determined by single and multiple scattering in the dense lower atmospheric layers, containing molecules and tropospheric aerosols, and by surface reflection. However, for high absorption optical thicknesses inside the O₂-A band, the zenith sky polarisation is dominated by radiation that has taken the shortest path through the atmosphere, and thus has been singly scattered in the tenuous upper atmospheric layers by molecules or stratospheric aerosols [Stammes et al., 1994; Stam et al., 1997], resulting in a higher polarisation in this particular case. In other words, with increasing O₂ absorption optical thickness inside the band, the zenith sky radiation has been scattered at increasing altitudes. Because different scattering processes dominate inside and outside the O₂-A band, the polarisation will generally be different. The sensitivity of the polarisation in the O₂-A band for the vertical distribution of aerosol is further illustrated in Figure 4, where calculations are shown for three model atmospheres with equal total aerosol optical thickness at 500 nm but with different aerosol profiles, ranging from all aerosol in the troposphere to all aerosol in the stratosphere. The large differences between the polarisation inside and outside the band suggest the potential of using high-spectral resolution polarisation measurements of the O₂-A band to obtain aerosol profiles.

Conclusions and implications

Here for the first time spectral fine-structure in the polarisation of skylight from the ultra-violet to the

near-infrared has been presented. This spectral fine-structure is due to two different processes : (1) Atmospheric gas absorption, especially by O₂ and H₂O. This process is most clear in the visible and near-IR, but also in the UV (O₃). (2) The Ring effect. This process is most clear in Fraunhofer lines in the UV.

We have shown using radiative transfer calculations that the high-spectral resolution polarisation measurements in the O₂-A band potentially offer a new method for remote sensing of aerosol in the Earth's atmosphere, combining the advantages of polarimetry and spectrometry. Polarimetry has a high measurement accuracy and is sensitive to aerosol microphysics [Hansen and Travis, 1974; Mishchenko and Travis, 1997] as has been demonstrated recently for the Earth's atmosphere [Herman et al., 1997; Deuzé et al., 1997].

In addition, we want to point out the implications of our findings for interpretation of radiance measurements by the space-based GOME spectrometer. GOME is a polarisation sensitive spectrometer measuring the solar radiation backscattered by the Earth's atmosphere with high-spectral resolution. It measures the polarisation of the incoming light with three broad-band polarisation filters to account for the instrument polarisation sensitivity. However, since the spectral resolution of the polarisation measurements is much lower than the spectral resolution of the radiance measurements, polarisation spectral fine-structure, as observed in the present work, is thereby neglected. Consequently, errors are introduced in the absolute radiances of the solar Fraunhofer lines and strong molecular absorption bands. This should be realised for interpretation of these and future spectroscopic measurements.

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