An airborne system for fast measurements of upwelling and downwelling spectral actinic flux densities

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Abstract

This work focuses on the study of the impact of aerosol particles, clouds and surface albedo inhomogeneities on the three-dimensional actinic radiation field. An airborne system for measurements of upwelling and downwelling spectral actinic flux densities is developed and deployed together with microphysical aerosol and cloud droplet instruments as well as an Albedometer during two measurement campaigns.

The first part of this work presents the Actinic Flux Density Meter (AFDM). This instrument allows the measurement of actinic radiation in the ultraviolet and visible wavelength range with a high time resolution of less than one second, which is of special importance for conditions of inhomogeneous clouds. Laboratory measurements are shown and discussed for two different detector principles. A method to correct the nonideal angular response of the optical inlets is presented. Various photolysis frequencies can be derived from the measurements of the spectral actinic flux densities. A parameterization is developed which allows a sufficient determination of the photolysis frequency of ozone even for significant uncertainties of the AFDM in the ultraviolet spectral range.

The second part of this thesis shows several measurement cases under boundary layer cloud conditions and under cloudless conditions with two different aerosol particle concentrations. The dependence of clouds, aerosol particles and the surface albedo on the spectral variability is presented. In addition, simulations from radiative transfer models are compared to measurements and used for the estimation of the influence of clouds and aerosol particles. For one case a slight enhancement of the photolysis frequency compared to aerosol-free simulations is observed in the upper part of the boundary layer. The comparison of actinic flux densities derived from cloud-free conditions and measurements in cloudy situations shows an enhancement in the upper part and above the cloud. A wavelength dependence is found for the enhancement and the reduction of the actinic radiation.
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1 Motivation

Solar radiation is the main driving factor for the atmospheric circulation and chemistry. A life on Earth without solar radiation is impossible. Thereby the knowledge of the interaction between solar energy and atmosphere is of main interest. Studies on the energy budget of Earth are important to investigate the anthropogenic and natural impacts on climate change. On the other hand studies concerning photochemical and biological processes are of interest. For the analysis of air pollution it is essential to understand these atmospheric chemical processes which are initialized by the absorption of solar radiation by an atom, molecule, free radical or ion. These reactions and their frequencies have to be identified. This work considers the interaction between atmosphere and solar radiation regarding to photochemical processes.

The solar radiation is divided into several spectral regions. In terms of photochemistry the ultra-violet (UV) and parts of the visible (VIS) spectral range are important. Radiation with high energy is filtered by the atmosphere. Thereby the stratospheric ozone layer between 20 km and 35 km altitude is of high importance. In this area UV-radiation is absorbed by ozone molecules which dissociate into molecular and atomic oxygen. For this reason UV-radiation up to a wavelength of 290 nm does not reach the Earth’s surface. Consequently, anthropogenic destruction of the ozone layer results in an increase of UV-radiation reaching the surface which causes serious effects on human health (skin, eyes, immune system) and other parts of the biosphere.

The ability to dissociate molecules requires radiation of high energy which merely corresponds to 1% of the solar spectrum (Brasseur and Solomon, 1986). The radiation which is responsible for photodissociation processes is called ” actinic radiation”. The frequency of photodissociation is described by the photolysis frequency. Atmospheric chemistry is strongly driven by the photolysis of trace gases resulting in the production of highly reactive radicals. The hydroxyl- (OH) and peroxyl radical (HO$_2$) are of main interest. OH is the primary oxidizing sink of carbon monoxide, methane and other hycarbons. In addition also a formation of pollutants is possible by reactions of radicals. For example the tropospheric ozone has toxic effects on humans and fauna. The lifetime of trace gases and pollutants strongly depends on the OH-concentration.

Considering the importance of photochemical reactions, chemical transport models need an accurate input of photolysis frequencies ($J$) in order to precisely simulate the photochemical process. In this work the photolysis frequencies of two species are considered in more detail: ozone and nitrogen dioxide, the former being the primary source of OH and the latter the major route for tropospheric ozone formation. However, photolysis frequencies of many other gas species can be determined from measurements with the
instrumentation which is presented in this work. The photolysis frequencies can be directly determined from the actinic radiation. This actinic radiation is influenced by scattering and absorption processes in the atmosphere by gas molecules, aerosol particles and cloud droplets. Clouds and aerosol particles can both enhance and reduce the actinic flux density depending on their optical properties and their position relative to the observation point. Effects of aerosols and clouds on the actinic radiation and photolysis frequency have been discussed by several authors e.g., Liao et al. (1999); Lefer et al. (2003); Tang et al. (2003); Tie et al. (2003); Trentmann et al. (2003). Liao et al. (1999) studied the impact of different aerosols on 14 photolysis frequencies using a one-dimensional radiative transfer model. They found enhancements in the range of 11%-18% for non-absorbing sulfate aerosols in clear sky conditions and a decrease from 6%-11% for absorbing soot aerosols. Airborne measurements presented by Lefer et al. (2003) have shown that the impact of clouds on photolysis frequencies is larger (from -90%...+200%) than of aerosols (±20%). Regarding OH concentrations Tang et al. (2003) used a three-dimensional regional chemical transport model coupled with a radiative transfer model to study the influences of aerosols and clouds on photolysis frequencies and photochemical processes over East Asia and Western Pacific. They determined a reduction of OH by 23% at altitudes below 1 km and an increasing of OH by ~25% above 1 km by clouds. Furthermore the aerosol caused a reduction of OH by ~40% below 1 km, and by ~24% above 1 km. Similar results were reported by Tie et al. (2003). They found an increase of OH by 20% due to clouds compared to the clear sky case. In addition, the ozone concentration increases in the middle to upper troposphere by cloud influence on photolysis rates by about 8%. Their calculations show that with clouds the globally averaged photolysis rates such as $J(O_1D)$, $J(CH_2O)$, and $J(NO_2)$ are enhanced in the troposphere by about 12%-13%.

Measurements of photolysis frequencies are used as important input parameter for chemical box models, and on the other hand measurements are necessary to validate the various radiative transfer models. Particularly airborne measurements of spectral actinic flux densities are still rare. In this regard the quality of the microphysical input data (aerosol particle size distribution, liquid water content) for radiative transfer models is crucial for achieving agreement between calculation and measurements within the range of the inherent measurement/model uncertainties (Ruggaber et al., 1994; Früh et al., 2003; Meloni et al., 2003). Hence the requirements for a successful radiative transfer model validation are reliable measurements of radiation and microphysical properties. In particular for inhomogeneous conditions as in the presence of clouds the time resolution of the measurements plays an important role.

Three different methods to measure photolysis frequencies were used in the past which are introduced in Section 2.3. In contrast to chemical actinometers and filter radiometers, spectrometers measure actinic flux densities directly and thus permit the calculation of photolysis frequencies for various gas species. In recent years mainly ground-based measurements of actinic flux densities using spectrometers were performed as described by several authors (Müller et al., 1995; Eckstein et al., 2003; Edwards and Monks, 2003). For a better understanding of tropospheric processes airborne measurements are required.
First airborne measurements of actinic flux densities using spectrometers were realized by Shetter and Müller (1999) and Shetter et al. (2003b) during the Transport and Chemical Evolution over the Pacific (TRACE-P) - experiment. They used a scanning double-monochromator system covering a spectral range between 280 and 420 nm whose main advantage is a high precision in the UV spectral range. But the time resolution (~10 s) of this system is insufficient regarding the effects of cloud inhomogeneities. For this reason a single-monochromator system called Actinic Flux Density Meter (AFDM) with a time resolution of less than one second was developed in this work. In addition the wavelength range of the AFDM was extended up to 700 nm to provide the determination of photolysis frequencies in the VIS (e.g., the nitrate radical NO₃, glyoxal CHOCHO) and to validate the radiative transfer models in a wider spectral range. The AFDM was applied during two measurement campaigns conducted in 2002 and 2004. These campaigns were part of a project called INfluence of clouds on SPECTral actinic flux in the lower TROposphere (INSPECTRO) which was focused on the characterization of clouds, aerosols and radiation within a defined area. Measurements of the AFDM together with microphysical instruments and an Albedometer (Wendisch et al., 2001) provided a unique possibility to collect crucial parameters for radiative transfer simulations.

The development of the AFDM was based on the experiences in irradiance measurements using the Albedometer. It is also a single-monochromator system and was developed for airborne applications at the Leibniz-Institute for Tropospheric Research (ITF) covering a spectral range between 350 and 1000 nm. Currently the Albedometer spectral range is extended to 2.2 μm. A unique horizontal stabilization system which is essential for irradiance measurements, keeps the optical inlets in a horizontal position during the flight. Wendisch et al. (2001) concluded that an accuracy of the horizontal stabilization of ±0.2° is needed in order to keep the misalignment related uncertainty of the measured irradiances below 1% for solar zenith angles up to 70°. The optical inlets of the AFDM introduced in this work have been mounted jointly with those of the Albedometer. For actinic flux density measurements the horizontal stabilization system ensures a clear separation between the measurements of the upper and lower hemispheres.

Perspectively the AFDM provides a system which can be installed on other platforms such as the new German research aircraft High Altitude and LOnge range research aircraft (HALO). Main objectives of HALO are the investigation of the troposphere and lower stratosphere regarding to chemistry/transport of trace gases, ozone destruction, radiative transfer and precipitation. A number of universities and research institutes is involved in this project so that combined measurement systems are to be deployed on the aircraft. In this context the AFDM together with the Albedometer is planned to be installed on HALO.

This work describes the development of the AFDM using two different types of detectors. Due to the insufficient accuracy in the UV-B spectral range a simple method to derive the ozone photolysis frequency was developed which allows an adequate determination from measured spectral actinic flux densities for lower wavelengths thresholds lower than 310 nm. Furthermore, the application of the AFDM during two measurement campaigns, and comparisons with model simulations are shown.
This work is divided into four major parts. The introduction explains the fundamental definitions of solar radiation, photochemical, microphysical, and optical quantities. Furthermore an overview of the available techniques for the J-determination is given, and the techniques used in this work are introduced. The last part of the introduction describes the field campaigns and the ground-based and airborne instrumentation. Part two introduces the first version of the AFDM, gives a technical description and shows essential calibration procedures. Finally the uncertainties of the system are discussed, and a new parameterization method to estimate the ozone photolysis frequency is presented. With this method an accuracy of better than 10% is achieved. The third chapter introduces the second version of the AFDM and shows its improvement compared to version one. The last part shows measurement examples and an intercomparison of the AFDM with double and single monochromators. Furthermore, clear sky measurements are compared regarding the effects of aerosol and surface albedo inhomogeneities on actinic radiation and photolysis frequencies. The variabilities caused by boundary layer clouds are discussed and compared with model simulations at the end of part 4. Finally, the results are summarized and an outlook is given.
2 Introduction

2.1 Definitions

2.1.1 Atmospheric Radiation Quantities

The atmospheric radiation field is characterized by the spectral radiance \( L(\theta, \Phi, \lambda) \) (in W m\(^{-2}\) sr\(^{-1}\) nm\(^{-1}\)), which represents the radiant energy flux (in W = J/s) through a differential area, perpendicular to the considered direction, into a differential solid angle element \( d\Omega \) per wavelength interval \( \Delta\lambda \). The element of solid angle \( d\Omega \), the incident angle of the radiation \( \theta \) and the azimuth angle \( \Phi \) is shown in Figure 2.1. For atmospheric measurements the solar incident angle \( \theta_s \) is called solar zenith angle, and the solar azimuth angle is named \( \Phi_s \). For laboratory measurements the incidence angle which is the angle between incident radiation and the perpendicular direction with respect to the receiving plane of the optical inlet, is called polar angle \( \theta_p \). Further radiation quantities are derived from the spectral radiance, as the spectral irradiance \( F(\lambda) \) and the spectral actinic flux density \( F_a(\lambda) \).

In contrast to the \( F \) which is a radiant energy flux density in units of W m\(^{-2}\) nm\(^{-1}\), the spectral actinic flux density \( F_a \) is important for photochemical studies. It is also measured in units of W m\(^{-2}\) nm\(^{-1}\). Whereas \( F \) is related to a horizontal plane area, the spectral actinic flux density refers to the unit surface of a sphere (Madronich, 1987). In literature the actinic flux density is often called "actinic flux", which is an inaccurate description. A flux is a temporal change of energy, whereas a flux density is additionally related to a unit area. Also terms like "beam irradiance", "actinic irradiance", "integrated intensity" (McNaught and Wilkinson, 1997), and "average intensity" (Chandrasekhar, 1960) are used.

Eqs. 2.1 and 2.2 give the definitions of \( F \) and \( F_a \):

\[
F(\lambda) = \int_0^{2\pi} \int_{-1}^{1} L(\theta, \Phi, \lambda) \sin\theta \cos\theta \, d\theta \, d\Phi 
\]

\[
F_a(\lambda) = \int_0^{2\pi} \int_{-1}^{1} L(\theta, \Phi, \lambda) \sin\theta \, d\theta \, d\Phi 
\]

Figure 2.1: Geometry
The spectral actinic flux density gives the spectral radiance averaged over all directions of incidence, which is different from the \( \cos \theta \)-weighted irradiance. A conversion of irradiances without knowledge of the \( \theta \)- and \( \Phi \)-dependence of \( L(\theta, \Phi, \lambda) \) into actinic flux densities is only possible with simplifications and assumptions. Here the downwelling and upwelling contributions of the actinic flux density are considered separately. The downwelling portion \( (F_a^\downarrow) \) is the sum of the direct \( (F_{a,0}) \) and the downwelling diffuse \( (F_{a,\text{diff}}) \) parts.

\[
F_a = F_a^\downarrow + F_a^\uparrow = F_{a,0} + F_{a,\text{diff}} + F_a^\uparrow
\]  

with \( F_a^\uparrow \): upwelling actinic flux density. The spectral actinic flux density can be converted from units of \( \text{W m}^{-2} \text{ nm}^{-1} \) into photons \( \text{cm}^{-2} \text{ nm}^{-1} \text{ s}^{-1} \) by:

\[
F_a(\lambda) \left[ \text{photons cm}^{-2} \text{ nm}^{-1} \text{ s}^{-1} \right] = \frac{\lambda}{2\pi \hbar c} 10^{-13} F_a(\lambda) \left[ \text{W m}^{-2} \text{ nm}^{-1} \right]
\]

with \( \hbar = 1.054589 \cdot 10^{-34} \text{ J s} \) (Planck’s constant) and \( c = 2.99792458 \cdot 10^8 \text{ m s}^{-1} \) (speed of light).

### 2.1.2 Photolysis Frequency

The photolysis frequency for a certain atmospheric gas molecule AB is calculated on the basis of the spectral actinic flux density. The process of photodissociation of AB is caused by absorption of photons with energy \( h\nu \):

\[
\text{AB} + h\nu \longrightarrow \text{A} + \text{B}
\]

with \( \nu \): frequency. The speed of the reaction complies with the photolysis frequency \( J(\text{AB}) \). The temporal change of the molecule concentration is determined by:

\[
-d[\text{AB}]/dt = J(\text{AB}) \cdot [\text{AB}]
\]

with \([\text{AB}]\): concentration of molecule AB and \( t \): time in s. \( J(\text{AB}) \) represents the probability of dissociation of a molecule AB per unit time. \( J(\text{AB}) \) depends on the intensity of the radiation, the ability of the molecule to absorb radiation and the probability to dissociate into its components A and B. \( J(\text{AB}) \) (in units of \( \text{s}^{-1} \)) is given by:

\[
J(\text{AB}) = \int_0^\infty \sigma_{\text{AB}}(\lambda, T) \cdot \phi_{\lambda}(\lambda, T) \cdot F_a(\lambda) \cdot d\lambda.
\]

In this equation \( \sigma_{\text{AB}} \) stands for the spectral absorption cross section (in units of \( \text{cm}^2 \)) of the molecular species AB and \( \phi_{\lambda} \) represents its spectral quantum yield (dimensionless). The quantum yield \( \phi(\lambda) \) of a photochemical reaction is defined as the number of events (e.g., molecules formed or destroyed) divided by the number of absorbed photons of a particular wavelength in the same time period. Both molecular parameters depend on the absolute temperature \( T \) (in K) and are mostly determined experimentally in the laboratory.
2.1 Definitions

2.1.3 Microphysical Quantities

For radiative transfer calculations quantities are required which can be derived from the number size distribution of aerosol and/or cloud particles. The size distribution is parameterized as an $n$-modal lognormal function:

$$
\frac{dN}{d\log d_p} = \sum_{i=1}^{n} \frac{N_i}{\sqrt{2\pi} \log \sigma_i} \cdot \exp \left[ - \frac{(\log d_p - \log \bar{d}_{p,i})^2}{2 \log^2 \sigma_i} \right]
$$

(2.8)

with $\frac{dN}{d\log d_p}$ [cm$^{-3}$] representing the logarithmic particle number size distribution; $d_p$ [μm] the particle diameter; $n$ the number of modes, $N_i$ [cm$^{-3}$] the integrated number concentration in mode $i$; $\bar{d}_{p,i}$ [μm] the geometric mean particle diameter of mode $i$; and $\sigma_i$ the geometric standard deviation of mode $i$. From the size distribution microphysical properties can be derived, e.g. the liquid water content $LWC$ [g m$^{-3}$] of the cloud droplets and the effective radius $R_{e,f}$ [μm]. These quantities are defined as follows:

$$
LWC = \frac{4\pi}{3} \rho \int_{0}^{\infty} \frac{dN}{d\log d_p} (d'_p) \cdot d'_p^3 \cdot d \log d'_p
$$

(2.9)

$$
R_{e,f} = \frac{\int_{0}^{\infty} \frac{dN}{d\log d_p} (d'_p) \cdot d'_p^2 \cdot d \log d'_p}{\int_{0}^{\infty} \frac{dN}{d\log d_p} (d'_p) \cdot d'_p \cdot d \log d'_p}
$$

(2.10)

with $\rho$: density of water in g cm$^{-3}$.

2.1.4 Optical Properties

The optical properties of gas molecules, aerosol particles and cloud droplets determine their ability to scatter and absorb solar and terrestrial radiation. These are the spectral volume extinction coefficient $\sigma_{ext} (λ)$ [m$^{-1}$], the single scattering albedo $ω_0 (λ)$, and the scattering phase function $p(λ, \vartheta)$ with the scattering angle $\vartheta$. The spectral volume extinction coefficient is the sum of the scattering and absorption coefficients ($\sigma_{scat}$, $\sigma_{abs}$):

$$
\sigma_{ext} = \sigma_{scat} + \sigma_{abs}
$$

(2.11)

The optical thickness $τ(λ)$ serves as vertical coordinate and is a non-dimensional measure of the extinction of radiation for a vertical path between an elevation $z$ and the top of atmosphere (TOA), as:

$$
τ(λ, z) = \int_{z'}^{\infty} \sigma_{ext}(λ)(z')dz'
$$

(2.12)

The total optical thickness is the sum of the optical thickness of aerosol particles $τ_{aer}$, gas molecules $τ_g$, and cloud droplets $τ_d$. Ice clouds and precipitation are not considered in this work. An approximate characterization of the aerosol size distribution is obtained from the spectral behaviour of the aerosol particle optical thickness. The Ångström formula (Ångström, 1929) describes this relation:

$$
τ_{aer}(λ) = β_λ λ^{-α_λ}
$$

(2.13)
2 Introduction

$\alpha$ is a measure for the aerosol size distribution and ranges between 0.5 and 2.5 (Junge, 1952). Large values of $\alpha$ indicate a dominant contribution to the aerosol optical thickness from small particles relative to larger ones. $\beta$ describes the aerosol extinction coefficient at a wavelength of 1 $\mu$m and ranges typically between 0 and 0.5 (Bokoye et al., 1997). For shortwave radiation the extinction coefficient of droplets ($\sigma_{ext}$) is estimated from the LWC and $R_{eff}$ (Paltridge and Platt, 1976; Stephens, 1978):

$$\sigma_{ext} = \frac{3}{2} \frac{LWC}{\rho R_{eff}} \quad .$$

From 2.12 and 2.14 an estimation follows for the optical thickness:

$$\tau_d = \frac{3}{2} \int LWC \, dz \quad .$$

The single scattering albedo is defined as the ratio of the scattering to the extinction coefficient. If an aerosol particle or cloud droplet does not absorb, the single scattering albedo is unity, whereas values less than one indicate absorption of radiation. The phase function $p(\theta)$ describes the probability of incoming radiation being scattered in the direction $\theta$. In radiative transfer models often a single parameter is used - the so called asymmetry parameter $g$. This parameter describes the fraction of light which is scattered in the forward versus backward direction. It is described by an average cosine of the scattering angle $\theta$ weighted by the phase function $p(\theta)$ (Lenoble, 1993):

$$g = \langle \cos \theta \rangle = \frac{\int_{-1}^{+1} \cos \theta \, p(\cos \theta) \, d \cos \theta}{\int_{-1}^{+1} p(\cos \theta) \, d \cos \theta} \quad .$$

2.2 Solar Radiation and Atmospheric Photochemistry

2.2.1 The Electromagnetic Spectrum

The energy of the sun is the main driving factor of nearly all processes in the atmosphere. The sun also causes photochemical reactions. The spectrally integrated solar extraterrestrial irradiance ($F_0$) incident to the top of atmosphere (TOA) is about 1367 W m$^{-2}$ (Fröhlich and Brusa, 1981).

The spectrum of the electromagnetic radiation spans many orders of magnitude. It runs from the dimension of Angstrom (gamma - and x-rays) to a wavelength range of several kilometers. The classification of the electromagnetic spectrum is displayed in Figure 2.2. In this work only solar radiation between 290 and 700 nm wavelength range is considered, which comprises the ultra-violet (UV) and the visible (VIS) spectral range. This spectral range covers more than 50% of the extraterrestrial irradiance (9% UV, 48% visible). The UV spectral range is divided into three sub-ranges: (i) UV-A (315..400 nm), (ii) UV-B (280..315 nm), and (iii) UV-C (100..280 nm). The influence of radiation on biological systems increases with radiant energy. UV radiation has a higher energy than the radiation in the visible spectral range.
2.2 Solar Radiation and Atmospheric Photochemistry

2.2.2 Atmospheric and Extraterrestrial Factors

In this work the influence of several parameters on the atmospheric actinic flux density field is investigated. The downwelling radiation reaching the Earth’s surface is about 50% lower than the extraterrestrial irradiance at the TOA (see Figure 2.3). Atmospheric radiation is influenced by scattering, absorption and reflection processes. Molecules absorb energy in certain wavelength bands of water vapor (H₂O), oxygen (O₂) and carbon dioxide (CO₂). O₂ and N₂ absorb in different wavelength bands mainly below 200 nm wavelength. Therefore high frequency radiation, as X-Rays, does not reach the Earth surface. The absorption bands of ozone (O₃) are between 220 and 300 nm (Hartley bands), weaker absorption bands are between 300 and 350 nm (Huygens bands). The ozone in the stratosphere causes a strong absorption of UV -radiation which results in a reduction of UV radiation below 350 nm. The position of the so-called atmospheric cutoff around 300 nm depends on the variability of the total ozone column (TOC) in Dobson Units (DU) and the solar zenith angle (SZA).

Figure 2.3: Solar spectrum at the TOA and at the surface.

In addition to absorption, the extinction of solar radiation is also determined by scattering
processes. Scattering of photons on molecules or atoms with diameters less than the wavelength of the incident radiation can be approximated by Rayleigh scattering laws (Young, 1982). Rayleigh scattering is more effective for short wavelengths due to the strong wavelength dependence of the scattering which is proportional to $1/\lambda^4$. Small particles tend to scatter light equally into the forward and backward directions. For larger particles, as cloud droplets and aerosol particles the scattered energy is increasingly concentrated in the forward direction. This scattering on particles with sizes comparable to or larger than the wavelength is described by Mie theory (Bohren and Huffman, 1983).

The impact of aerosol particles on the attenuation of radiation strongly depends on their optical properties, whereby the size and shape of the aerosol particles and its chemical composition determine the extinction. Hygroscopic particles swell at high relative humidity, and hence absorb and scatter more radiation than at lower humidity.

Clouds have a fundamental influence on solar radiation. Not only the cloud cover is important but also the spatial distribution of clouds and their optical properties. The temporal and spatial cloud variability causes significant variations of the solar radiation. Clouds can both decrease and increase solar radiation in broken cloud conditions. The spectral ratio of actinic flux densities in homogenous cloud conditions to clear sky conditions shows a decrease with increasing wavelength. That means a more effective absorption of radiation by clouds in the visible and infrared spectral range. Scattering processes dominate cloud extinction in the UV spectral range.

Furthermore the spectral surface albedo (ratio of spectral upwelling and downwelling irradiance), which is defined as the ratio of reflected to incident irradiances, has an impact on the solar radiation field. The influence is wavelength-dependent and decreases with decreasing wavelengths. At high surface albedo values (e.g., in the case of snow cover) the backscattering of radiation leads to an increase of solar radiation.

In addition to the influence of the altitude also extraterrestrial parameters have an impact on the radiation. The most crucial parameter is the solar zenith angle (SZA). Further parameters which influence the radiation are the distance between Earth and Sun, and the variability of emitted radiation by the Sun.

### 2.2.3 Photochemical Reactions

Solar radiation initiates different photochemical reactions in the atmosphere. Photodissociation yields reactive products which catalyze new reactions. Trace gases and pollutants, for example hydrocarbons and oxides of nitrogens, are degraded in the atmosphere, other gases such as ozone are produced. These chemical processes proceed in radical chains. The hydroxyl radical (OH) is one of the most important radical in the Earth’s atmosphere. It initiates a multitude of reactions. Therefore the lifetime of trace gases and pollutants depends strongly on the OH-concentration. A simplified OH-cycle is displayed in Figure 2.4.

The primary source for the OH radical in the clean and polluted atmosphere is the photolysis of oxygen by UV radiation at wavelengths less than 320 nm (see left branch of the OH-cycle in Figure 2.4), which leads to an excited oxygen atom, $O(\text{^1D})$, and molecular oxygen:
Figure 2.4: OH-cycle

\[ O_3 + h\nu \rightarrow O(^1D) + O_2 \]  \hspace{1cm} (R-2.1)

Excited \( O(^1D) \) atoms are either deactivated to their ground state or react with water vapor to form hydroxyl radicals:

\[ O(^1D) + H_2O \rightarrow 2\ OH \]  \hspace{1cm} (R-2.2)

Reaction of \( O(^1D) \) with water vapor plays an important role in the lower troposphere due to the much higher water content, particularly in cloudy conditions. In polluted areas other sources also form OH through photodissociation, such as nitrous acid, HONO. HONO is present mostly during the nighttime and photolyzed during the daytime:

\[ \text{HONO} + h\nu \rightarrow \text{OH} + \text{NO} \hspace{0.5cm} (\lambda < 400\ \text{nm}) \]  \hspace{1cm} (R-2.3)

About 70% of OH reacts with carbon monoxide, CO and forms the peroxyl radical \( \text{HO}_2 \) which together with OH is called HO\(_2\) (see Figure 2.4). Redundant energy is absorbed by a mediator molecule M:

\[ \text{CO} + \text{OH} \rightarrow \text{H} + \text{CO}_2 \]  \hspace{1cm} (R-2.4)

\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \]  \hspace{1cm} (R-2.5)

The formation of ozone depends on the concentration of nitrogen oxide (NO) and nitrogen dioxide (NO\(_2\)), which together are called NO\(_x\). In the presence of large concentrations of NO the oxidation of CO leads to ozone formation because the peroxyl radical rapidly reacts with NO and forms OH and NO\(_2\). These NO\(_2\) photolyses at daylight below a wavelength of 420 nm and forms ozone:

\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]  \hspace{1cm} (R-2.6)

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \]  \hspace{1cm} (R-2.7)
In reaction (R-2.4)-(R-2.7) OH, HO₂, NO, and NO₂ act as catalyst. In a NO-poor environment the ozone destruction dominates:

\[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \]  \hspace{1cm} (R-2.9)

In general the formation of ozone is much faster than its destruction because the HO₂ reacts 4000 times faster with NO (R-2.6) than with O₃ (R-2.9). Besides reacting with NO and O₃ the peroxyl radical can also react with itself and produces the hydrogen peroxide molecule, H₂O₂ (right branch of the OH-cycle in Figure 2.4):

\[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]  \hspace{1cm} (R-2.10)

which plays a major role in the sulphuric acid formation. Additionally, H₂O₂ forms OH via its photolysis below 420 nm wavelength:

\[ \text{H}_2\text{O}_2 + h\nu \rightarrow \text{OH} + \text{OH} \]  \hspace{1cm} (R-2.11)

A further source of the hydrogen radical is the photolysis of formaldehyde below a wavelength of 370 nm:

\[ \text{HCHO} + h\nu (+2\text{O}_2) \rightarrow 2\text{HO}_2 + \text{CO} \]  \hspace{1cm} (R-2.12)

Formaldehyde is formed by the reaction of the hydroxyl radical with methane (CH₄), the second major reaction partner of OH besides CO.

\[ \text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O} \]  \hspace{1cm} (R-2.13)

\[ \text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2 \]  \hspace{1cm} (R-2.14)

\[ \text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \]  \hspace{1cm} (R-2.15)

\[ \text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 \]  \hspace{1cm} (R-2.16)

When NO is present, the sources and sinks of the peroxyl radical are the same as the sources and sinks of hydroxyl radical, whereby the timeframe of the transfer between each other is some seconds. The oxidation of methane via HCHO and CO to CO₂ yields the following net results:

a) in NO-poor environments a net loss of HOₓ.

b) in NO-rich environments a net gain of OH and ozone. As mentioned before the concentration of NOₓ plays an important role. The last reaction listed here shows the removal of NO₂ with the help of OH and the formation of nitric acid, HNO₃:

\[ \text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M} \]  \hspace{1cm} (R-2.17)

All reactions constitute a very complex cycle: the OH concentration influences the concentration of various trace gases, whereby the OH concentration itself depends on the ozone concentration and the available radiation. Ozone formation and destruction are coupled with the available catalyst NOₓ and so on.

To understand the link between all chemical processes there is a need to know the rate of these reactions and therefore it is necessary to measure photolysis frequencies in the atmosphere under different atmospheric conditions.
2.2.4 Uncertainty of the Molecular Data

Uncertainties in the published molecular data of the quantum yield and the cross section are the major source of uncertainty in derived photolysis frequencies. This section summarizes the different sources of molecular data, in particular $\sigma$ and $\phi$ of ozone and NO$_2$ photolysis.

**Ozone** Uncertainties of the $J$-values of ozone due to problems in the molecular data $\sigma$ and $\phi$ were investigated by several authors (Michelsen et al., 1994; Müllner et al., 1995; Blindauer et al., 1996; Shetter et al., 1996; Kraus and Hofzumahaus, 1998). Cantrell et al. (2003) and Hofzumahaus et al. (2004) show that the absorption cross sections of ozone reported by several authors (Bass and Paur, 1985; Molina and Molina, 1986; Malicet et al., 1995; Daumont et al., 1992) are in good agreement, in particular in the shorter wavelength range with deviations of ± 2% ($\lambda < 315$ nm), while somewhat larger deviations (± 8%) were observed at longer wavelengths with ($\lambda > 320$ nm). Hofzumahaus et al. (2004) calculated $J$-values using the same quantum yield (Talukdar et al., 1998) and different absorption cross sections. The overall agreement was within 1-3%.

In case of the O$^1$D quantum yield the published data differ significantly as shown by Cantrell et al. (2003). Figure 2.5 (after Cantrell et al., 2003) displays quantum yields published by different authors (DeMore et al., 1994, 1997; Sander et al., 2000; Talukdar et al., 1998; Matsumi et al., 2002). The spectral data of $\phi$ differ in particular for longer wavelengths ($\lambda > 310$ nm) and for $\lambda < 305$ nm. General recommendations that were valid until 1997 (DeMore et al., 1994) set the upper threshold of $\phi$ below 320 nm. Recent publications show non-zero $\phi$-values at larger wavelengths due to two processes: (i) photodissociation of vibrationally excited ozone molecules up to 325 nm, and (ii) spin-forbidden dissociation beyond 325 nm (Matsumi et al., 2002). This spectral extension of $\phi$ is often called as ”tail” in literature and was also shown by Bauer et al. (2000). A small $\phi$ at long wavelengths can significantly contribute to $J$ as a result of an increasing actinic flux density, even for a rapidly decreasing $\sigma$ at $\lambda > 320$ nm. Several revisions of $\phi$ were published by the National Aeronautics and Space Administration / Jet Propulsion Laboratory (NASA/JPL). $\phi$ recommended in the JPL-report of 1997 (DeMore et al., 1997) differs from those reported in JPL94 (DeMore et al., 1994) by including the contribution from the photolysis of vibrationally excited ozone. The latest JPL-reports of 2000 and 2003 (Sander et al., 2000, 2003) contain the contribution of spin-forbidden O$^1$D formation in the ozone photolysis. The recommendation for $\phi$ of Sander et al. (2003) is taken from the review of Matsumi et al. (2002). Exemplarily, Cantrell et al. (2003) quote a difference of $8\%$ between $J$-values derived by DeMore et al. (1997) and Sander et al. (2000) for large SZA. Using $\phi$ data published by Matsumi et al. (2002) $J$ is $4\%$ higher than calculated with DeMore et al. (1997).

In addition, the temperature dependence of $\phi$ is obvious in Figure 2.5 considering the plotted $\phi$-values derived from Talukdar et al. (1998) at a temperature of 273 K and 318 K. With increasing temperatures $\phi$ increases at wavelengths above 310 nm. The uncertainty in the ozone absorption cross section is quoted as $3\%$ (Molina and Molina, 1986), while uncertainties in the quantum yield for the formation of O($^1$D) can be up to 10%
2 Introduction

![Graph](image)

Figure 2.5: Quantum yields of O¹D formation from O₃ photolysis at 298 K determined by different authors after Cantrell et al. (2003). \( \phi \) by Tahukdar et al. (1998) is plotted for 273 K and 318 K to point out the strong temperature influence.

(Shetter et al., 1996; Hofzumahaus et al., 1999). An assumed error of 10% of the quantum yield together with a 3% error in the absorption cross section data, the root mean square error propagated in \( J(O¹D) \) is calculated with 10%.

NO₂ There are also uncertainties of \( \sigma \) and \( \phi \) in NO₂ photolysis. Cantrell et al. (2003) calculated ratios of cross sections for NO₂ as measured by Harder et al. (1997), Schneider et al. (1987) and recommended by the International Union of Pure and Applied Chemistry (IUPAC) to those recommended by JPL (DeMore et al., 1997) and measured by Davidson et al. (1988) as displayed in Figure 2.6. The IUPAC recommendation is based on data from several studies (Mérieux et al., 1995, 1997; Coquart et al., 1995; Vandaële et al., 1996, 1998; Jenouvrier et al., 1996; Harder et al., 1997; Yoshino et al., 1997; Burrows et al., 1998). The structure in the ratios in the wavelength range 345-425 nm is explained by mismatch of absorption peaks due to differences in wavelength calibration and spectrometer resolution which does not affect \( J(NO₂) \) significantly. Figure 2.6 shows that the deviation of \( \sigma_{\text{Harder}}/\sigma_{\text{Davidson}} \) and \( \sigma_{\text{IUPAC}}/\sigma_{\text{Davidson}} \) averages +7% and +5%, respectively, in the wavelength range between 348 and 424 nm. Whereas \( \sigma_{\text{Schneider}} \) is 5% lower than \( \sigma_{\text{Davidson}} \) in the same wavelength region.

The quantum yield data of NO₂ photolysis were published by Gardner et al. (1987) (JPL recommendation of 1997; DeMore et al., 1997), Roehl et al. (1994), and Troe (2000) (IUPAC recommendation). These data agree very well below 390 nm (less than 5% deviation). Between 390 and 410 nm the average ratios were given in Cantrell et al. (2003) with \( \phi_{\text{Troe}}/\phi_{\text{Gardner}} = 1.12 \) and \( \phi_{\text{Troe}}/\phi_{\text{Gardner}} = 1.11 \).

Kraus and Hofzumahaus (1998) calculated systematic uncertainties in photolysis frequency of several species (O₃, NO₂, HCHO, H₂O₂, HONO, and CH₃CHO) using different literature data quoted in the recommendations by DeMore et al. (1994), Atkinson et al. (1992), Martinez et al. (1992), Harwood and Jones (1994), Mérieux et al. (1995), and Roehl et al. (1994). Table 2.1 summarizes their studies and gives the total uncertainty of
2.3 Available Techniques to Measure Actinic Radiation

Figure 2.6: Ratioed cross sections for NO₂ (after Cantrell et al. (2003))

the $\sigma \cdot \phi$ calculated by the Gaussian error propagation ($\sqrt{\sum \text{Error}^2}$).

<table>
<thead>
<tr>
<th>Photolysis frequency</th>
<th>Error $\sigma$ (%)</th>
<th>Error $\phi$ (%)</th>
<th>Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J(\text{O}^1\text{D})$</td>
<td>±3</td>
<td>±10</td>
<td>±10</td>
</tr>
<tr>
<td>$J(\text{NO}_2)$</td>
<td>±6</td>
<td>±10</td>
<td>±12</td>
</tr>
<tr>
<td>$J(\text{HCHO})$</td>
<td>±10</td>
<td>±12</td>
<td>±16</td>
</tr>
<tr>
<td>$J(\text{H}_2\text{O}_2)$</td>
<td>±25</td>
<td>- *</td>
<td>±25</td>
</tr>
<tr>
<td>$J(\text{HONO})$</td>
<td>+2 /-17</td>
<td>- *</td>
<td>+2 /-17</td>
</tr>
<tr>
<td>$J(\text{CH}_3\text{CHO})$</td>
<td>±5</td>
<td>±20</td>
<td>±21</td>
</tr>
</tbody>
</table>

Table 2.1: Estimated uncertainties in photolysis frequencies (T= 298 K). Data published by Kraus and Hofzumahaus (1998). * Quantum yield is unity.

In this work molecular data of several sources are used, which are summarized in Appendix A.

2.3 Available Techniques to Measure Actinic Radiation

There are three major principles to derive photolysis frequencies: (i) chemical actinometry (Bahe et al., 1979; Dickerson et al., 1982; Bairai and Stedman, 1992; Shetter et al., 1992; Kelley et al., 1995; Müller et al., 1995), (ii) filter radiometry (Junkermann et al., 1989; Brauers and Hofzumahaus, 1992; van Weele et al., 1995; Wendisch et al., 1996), and (iii) spectroradiometry (Müller et al., 1995; Kraus and Hofzumahaus, 1998; Hofzumahaus et al., 1999; Shetter and Müller, 1999; Jäkel et al., 2005). Each method is described and evaluated in the following sections.

2.3.1 Actinometers

Photolysis frequencies (no actinic flux densities) can be measured using chemical actinometers. Such types of instruments to measure $J(\text{NO}_2)$ have been successfully applied
since the 1970’s. Chemical actinometry is a direct method; photochemical reactions are monitored in a quartz photolysis reactor, either a flow-tube or a bulb. The reactor contains a known concentration of a photochemical reactive compound which is exposed to sunlight. For a $J(\text{NO}_2)$ chemical actinometer, detection is usually conducted via a reaction of NO following photochemistry inside the reactor. A O$_2$ rich mixture is used wherein NO$_2$ is photodissociated by sunlight (see R-2.7). The formed oxygen atoms react to form ozone (see R-2.8), and the NO formed is used as a measure of the extent of photodissociation of the NO$_2$.

$J(O^1D)$ measurements were applied by Müller et al. (1995). These authors used an O$_3$/N$_2$O mixture where O($^1$D) reacts with N$_2$O to form N$_2$ (O($^1$D) + N$_2$O → N$_2$ + O$_2$) or NO (O($^1$D) + N$_2$O → NO + NO). The concentration of N$_2$ is measured by gaschromatography before and after exposure of radiation. Therewith $J(O^1D)$ was calculated from the N$_2$ formation rate.

Actinometers do not require the uncertain molecular parameters (quantum yield and absorption cross section). However, the chemical actinometry is a process-specific method and limited to one molecular species per instrument. The relatively large time responses (on order of a minute to an hour) and the large size and weight of these systems make them less suitable for fast flying aircraft.

### 2.3.2 Filter Radiometers

Filterradiometry is a technique where the spectrally integrated solar actinic flux density is measured in a confined spectral interval. Filter radiometers have been employed to determine photolysis frequencies of NO$_2$ (Junkermann et al., 1989; Brauers and Hofzumahaus, 1992; Volz-Thomas et al., 1996) and O$_3$ (Bahe et al., 1979; Dickerson et al., 1982; Junkermann et al., 1989; Hofzumahaus et al., 1992; Shetter et al., 1996; Wendisch et al., 1996). Typically, the instrumental response is determined by comparison to chemical actinometers. The input optics of a filter radiometer consists of a series of frosted hemispherical quartz domes that act as diffuser with a nearly isotropic response. A quartz light guide directs the photons through a pair of optical filters to a detector (e.g., a photodiode). A set of band pass filters is used to emulate the spectral sensitivity of the molecule specific product of the absorption cross section and the quantum yield. That means that the relative spectral sensitivity of the instrument corresponds to the relative product $\sigma \cdot \phi$. Ideally, the signal of a filter radiometer is directly proportional to the photolysis frequency. However, in practical applications the spectral response of the radiometer does not match exactly the shape of the product $\sigma \cdot \phi$. As a result the relationship between $J(O^1D)$ and the radiometer signal exhibits non-linearities as the spectral distribution of the UV flux density changes with TOC and SZA.

Based on a comparison with a chemical actinometer Junkermann et al. (1989) have estimated the uncertainties to be less than 10% at SZA < 50° and about a factor of two at SZA = 70° for $J(O^1D)$. Therefore correction functions were employed. Moreover, Bohn et al. (2004) tested the correction for the effect of ambient temperatures on $J(O^1D)$ due to the temperature dependence of $\sigma$ and $\phi$. Bohn et al. (2004) estimated relative errors
between 10% and 15% depending on SZA. 

The uncertainty of the filter radiometric technique depends critically upon the choice of band pass filters which also assumes an accurate knowledge of the spectral course of the molecular parameters $\sigma$ and $\phi$. Accordingly, a filter radiometer can only refer to a single photolysis process. However, the response time is faster (on the order of 1 second) than that of actinometers. In addition the instrumentation is small, lightweight, compact and therefore better suited for airborne operations than actinometers.

### 2.3.3 Spectroradiometers

Spectroradiometers measure directly the spectral actinic flux densities. Using Eq. 2.7 the photolysis frequency is derived. Consequently, the photolysis frequency can be determined for any molecule for which the absorption cross section falls within the wavelength range measured by the spectroradiometer. The instrument sensitivity is calibrated using standard light sources traceable to a reliable primary standard (e.g., Physikalisch-Technische Bundesanstalt or National Institute of Standards and Technology). For accurate $J$ values an exact wavelength calibration is needed. This is accomplished by scaling the spectra with known emission lines from low-pressure lamps or to the Fraunhofer structure in observed spectra.

The radiation is collected with an optical inlet. The collected light is transmitted to a monochromator where the photons are detected as a function of wavelength with a photomultiplier tube (mostly used for scanning monochromator) or a photodiode array (usually applied to multi-channel spectrometer). Alternatively a Charge Coupled Device (CCD) detector as in this work is used. The methods of optical collection vary from flat plate devices with a cosine angular response to hemispherical optical inlets with an isotropic angular response. Flat plate devices are sensitive to irradiance and require a number of complex corrections in order to determine actinic flux density (Madronich, 1987; Ruggaber \textit{et al.}, 1993; van Weele \textit{et al.}, 1995; Cotte \textit{et al.}, 1997; Kazadzis \textit{et al.}, 2000; McKenzie \textit{et al.}, 2002; Webb \textit{et al.}, 2002a,b; Kylling \textit{et al.}, 2003). Isotropic hemispheric optics monitor actinic flux densities directly (Junkermann \textit{et al.}, 1989). The difference between irradiances and actinic flux densities is displayed exemplarily for a measured profile of the upwelling and downwelling components of both quantities for clear sky conditions (Figure 2.7). The scatterplots show a poor correlation between $F_a^\downarrow$ and $F_d^\downarrow$ (plus signs).

For the upwelling components (circles) a better correlation (coefficient of determination $R^2=0.86$) was found. However, the profiles of the ratios (Figure 2.7b) indicate a stronger variation for the upwelling component ($2.55\pm0.17$; $\sim 7\%$) than the downwelling component ($1.84\pm0.17$; $\sim 2\%$). Obviously, the correlation between both radiation quantities strongly depends on the complexity of the atmosphere, in fact on the specific angular dependence of the diffuse fraction. That’s why the variation of the upwelling ratio is more significant than the downwelling ratio, whereby the variable scattering properties of the surface albedo and the atmosphere between surface and aircraft determine the variability of the upwelling ratio. One can imagine that for cloudy conditions an acceptable conversion between irradiances and actinic flux densities is nearly impossible.

From its definition the actinic flux density refers to a $4\pi\ sr$ geometry. In general the
Figure 2.7: (a) Scatterplot of upwelling and downwelling $F$ and $F_a$ both measured at a wavelength of 600 nm for a profile flight (see Chapter 5.3.1) between 100 and 1200 m altitude. (b) Vertical profile of the ratio $F_a/F$ for the upwelling and downwelling components at 600 nm wavelength.

Actinic flux density is separately measured for each hemisphere with two hemispheric optical inlets, one upward-looking, the other one downward-looking. Eckstein et al. (2003) developed a spectrometer system with a $4\pi$ optical inlet. In case of ground-based measurements mostly the downwelling fraction complies with the total actinic flux density, unless the surface albedo is high and the upwelling fraction becomes important. Hence, ground-based measurements are often restricted to measurements using an upward-looking optical inlet.

First actinic flux density measurements using a double monochromator system with a photomultiplier for detection were described by Hofzumahaus et al. (1999) and Shetter and Müller (1999). Both scanning spectroradiometers recorded the actinic flux densities in the spectral range between 290 and 420 nm with a wavelength resolution of 1 nm. Scanning spectrometer typically cover a spectrum every 10-90 seconds (Lefer et al., 2001). The time-consuming scanning procedure leads to a distortion of the spectrum in particular for inhomogeneous clouds or surface albedo. Also, due to moving parts within the spectrometer system the wavelength stability is not always warranted especially during airborne measurements. In practice monochromators not only isolate a particular spectral component from all other wavelengths but they also transmit residual ”out-of-band” wavelengths, which is known as stray light. A quantity of the reduction of stray light is called ”stray light rejection”. The main advantage of using a double monochromator instead of a single monochromator is the high stray light rejection which is critical for accurate actinic flux measurements in the UV-B spectral region. The stray light is more a problem for the photodiode-array-based instruments (Eckstein et al., 2003; Edwards and Monks, 2003). Diode array instruments do not have the necessary stray light rejection to
determine accurately actinic flux densities below 300 nm. The main benefit of that kind of spectrometer is the high time resolution with less than 1 second (Jäkel et al., 2005) and the mechanical stability due to a fixed grating. The uncertainty of $J$-values derived from spectroradiometer measurements depends on the uncertainty of the actinic flux density measurement. On the other hand, the accuracy of the literature values of the molecule parameters $\sigma$ and $\phi$ is critical as well (see Section 2.2.4).

2.3.4 Techniques Used in This Work

The preceding sections have shown that spectroradiometers are preferable for the determination of photolysis frequencies of different species. For atmospheric conditions of high variability multi-channel spectrometer provide the best capability to perform airborne measurements. Admittedly the treatment of the stray light contribution influences the uncertainty of actinic flux density measurements and consequently the derived $J$-values. This work presents spectrometers with a conventional photodiode array (PDA) detector based on the Albedometer (Wendisch et al., 2001) which was developed at IFT. The Albedometer was constructed for airborne measurements of spectral downwelling and upwelling irradiances. It uses the same multi-channel spectrometer technique than the Actinic Flux Density Meter AFDM-PDA, which is introduced in this work. Differences between these two instruments are the spectral ranges and the optical inlets. The latter realizes the different weighting of the incident radiation to obtain irradiances (cos-weighting) or actinic flux densities (isotropic weighting). The second part of this work presents a new generation of multi channel spectrometer using a more sensitive Charge Coupled Device (CCD) detector which improves the capability of airborne actinic flux density measurements. A similar spectrometer system was recently developed by the ARIM-group (Atmospheric Radiation Investigations and Measurements) of the National Center of Atmospheric Research (NCAR) in Boulder, USA. The AFDM-CCD system is able to measure $F_o$ with a time resolution of less than 300 ms. Furthermore the increase of the spectral resolution causes an improvement of the results. Both instruments were tested during two measurement campaigns, which are introduced in the following section.

2.4 The INSPECTRO Field Campaigns

2.4.1 Overview

This work contains field measurement examples of two measurement campaigns which were conducted within the scope of the INfluence of clouds on SPECtral actinic flux in the lower TROposphere (INSPECTRO) - project, which is funded by the European Union. The IFT participation has been partly supported by the Deutsche Forschungsgemeinschaft (DFG). The overall objective of INSPECTRO is to study the variability of actinic radiation and its implications for photochemistry in the lower troposphere, mainly in cloudy conditions. INSPECTRO combines space-based, aircraft and ground-based measurements as
well as simulations with one- and three-dimensional radiative transfer models to characterize the radiation field in the presence of clouds (Thiel et al., 2005; Kylling et al., 2005). A first campaign (INSPECTRO-1) was held in East Anglia, UK in September 2002. Small-scale variations of the three-dimensional actinic radiation field were studied within an area of 20x20 km², which is shown in Figure 2.8a. The edge points of the flight box are T1-T3 and M4. Measurements of the actinic flux density, the irradiance and aerosol and cloud properties were made from four ground stations (M1-M4) and by four different aircraft. Furthermore chemical measurements of radicals were performed by the University of East Anglia at M1. This data included peroxy radicals (RO₂+HO₂) measured with a Peroxy Radical Chemical Amplifier (PERCA) and nitric oxide (NO) measured using a chemiluminescence technique. A VEHICLE-mounted Lidar System (VELIS) (Gobbi et al., 2000) was situated at M1. Measurements from VELIS were used to retrieve the aerosol particle height and the cloud fraction. At the beginning of the campaign an intercomparison of the radiation instruments was performed. Reference spectrometers for irradiance and actinic flux density measurements travelled to all locations to check the stability of each instrument during the campaign. Four aircraft (two Partenavia, one Cessna, one Ultralight) equipped with instrumentation for microphysical and radiative measurements were operated from Norwich airport. The main flight tracks run circular along the edge of the flight boxes.

Figure 2.8: (a) Measurement area of the INSPECTRO-1 campaign held in September 2000. M1-M4 stations for ground-based measurements, T1-T3 stands for turning point of the aircraft measurements. (b) Measurement area of the INSPECTRO-2 campaign held in May 2004. The points M1-M5 mark the stations for the ground-based radiation measurements, B stands for the position of the tethered balloon.

A second campaign (INSPECTRO-2) was held in the Straubing area, Germany (May 2004). Ground-based measurements and flight patterns covered an area of 50x50 km² which is a typical grid box size used e.g., in regional and mesoscale chemical transport
models. The focus of this campaign was the characterization of the radiation field and its variability over the scale of a single model pixel. Instrumentation was similar to the one used in INSPECTRO-1. Two Partenavias and one Cessna participated on the campaign. In addition a tethered balloon in combination with the Airship-borne Cloud Turbulence Observation system (ACTOS) was used for vertical measurements of cloud properties (Siebert et al., 2003).

The measurement area of INSPECTRO-2 is shown in Figure 2.8b. The outer black line represents the border of the area. Compared to the flat surface of the East Anglia the Straubing area is marked by an uneven ground with parts of the Bavarian Forest with altitudes of about 1000 m, in the north of the river Donau, and a flat ground surface in the southern part. The measurement area was divided into two measurement boxes bounded by the Donau. One Partenavia measured in the northern part, the other one performed measurements in the southern box. The red line in Figure 2.8b shows a typical track of a measurement flight. Clouds are quite inhomogeneous in their spatial and temporal distribution. To take the three-dimensional (3-D) distribution of the clouds into account the circular flight pattern from the first campaign was replaced by a more randomized pattern in order to collect cloud droplet data over a larger area.

Ground-based measurements of irradiances and actinic flux densities were performed on several stations (M1-M5, see Figure 2.8b). The tethered-balloon was based at the center of the measurement area (position B in Figure 2.8b). An intercomparison of all spectrometers was performed in the first week of the campaign. In the course of the campaign reference spectrometers for irradiance and actinic flux density measurements travelled to all stations to check the stability of the other spectrometers.

### 2.4.2 Platform and Instrumentation

**Aircraft** A small research aircraft (Partenavia P68B) was used to perform airborne measurements presented in this work. A photo of the two-engine, unpressurized aircraft is shown in Figure 2.9. The maximum aircraft speed ranges between 60 and 80 m s$^{-1}$, the aircraft ceiling is 4000 m. The Partenavia is equipped with meteorological, avionic, radiation, and microphysical instruments (Keil et al., 2001). The temperature and relative humidity is measured by Vaisala sensors, the flight altitude is deduced from pressure measurements by a Pitot sonde with a precision of ± 20 m. Aircraft attitude data (pitch and roll angle) are derived from the AHZ system (see Section 3.1.1). The geographical coordinates are measured by a GPS.

**Radiation Measurements** During both INSPECTRO campaigns radiation measurements were performed with the Albedometer and the AFDM. The AFDM-PDA was used during INSPECTRO-1 to measure $F_d^\uparrow$ and $F_a^\uparrow$. During INSPECTRO-2 the AFDM-CCD measured the downwelling actinic flux density and the AFDM-PDA the upwelling actinic flux density. A detailed description of the AFDM is given in Chapters 3 and 4. The Albedometer measures spectral upwelling and downwelling irradiances in a wavelength range between 290 and 1000 nm with a full width at half maximum (FWHM) ≈ 2-3 nm using two multi-channel spectrometer (MCS) for simultaneous detection of the
upwelling and downwelling spectral radiation (Wendisch et al., 2001). The surface albedo was determined from airborne measurements using the method described by Wendisch et al. (2004). An overall uncertainty for the spectral irradiance measurements is estimated with ± 4% for wavelengths between 400-770 nm and ±6% for λ ≤ 400 nm and λ ≥ 770 nm (Wendisch and Mayer, 2003). The angular response of both horizontally stabilized optical inlets are weighted by the cosine of the incidence angle. The nonideal angular response of the optical inlets quantified in the laboratory was corrected in the data analysis as described by Wendisch (2003).

**Microphysical Measurements** In addition to the radiation instrumentation the Partenavia was equipped with various instruments for measurements of particle and drop size distributions and concentrations during INSPECTRO-1. The aerosol particle size distribution of aerosol particles with a diameter between 0.1 and 10 μm was measured with a Passive Cavity Aerosol Spectrometer Probe, PCASP-X (manufactured by Particle Measuring Systems, USA). The isokinetic particle inlet mounted on the top of the aircraft (see Figure 2.9) has a droplet separator (Maser et al., 1994) for in-cloud aerosol measurements. Details of the calibration and the data procession are reported by Keil et al. (2001). The droplet microphysical sensors were mounted below the wings of the Partenavia (see Figure 2.9). The distance to the propeller is more than 4 meters, where the flow is supposed to be undisturbed. A Particle Volume Monitor, PVM-200A (manufactured by Gerber Scientific, Inc., USA) was used to measure the Liquid Water Content (LWC) and the effective radius (R_eff) for droplets with a diameter between 2 and 35 μm and a LWC ≤ 10 g m⁻³. A Modified Fast Forward Scattering Spectrometer Probe, M-Fast-FSSP, (Schmidt et al., 2004) mounted next to the PVM-100A was employed for measurements of the size distribution of droplets with a diameter between 2 and 50 μm. A Fast-FSSP developed
by Brenguier et al. (1998) was mounted beneath the opposite wing and measured the size
distribution of droplets in the same range as the M-Fast-FSSP. The main difference
between the Fast-FSSP and the M-Fast-FSSP is the data acquisition which was changed
such that the sampling volume can be adjusted after the measurements (Schmidt et al.,
2004). $R_{eff}$ and LWC were derived from the droplet size distribution applying Eqs. (2.9
and 2.10). A further LWC instrument, a Nevzorov hot-wire probe (manufactured by
SkyTech Research, Inc, Canada), was employed. This probe was mounted outside the
cabin window and measures the LWC and the total water content (TWC) (liquid plus
ice water content) of clouds in the range between 0.003 g m$^{-3}$ and 3 g m$^{-3}$.
During the INSPECTRO-2 campaign the Partenavia was equipped with the PCASP-X,
PVM-100A, Nevzorov hot-wire probe and for several flights with the M-Fast-FSSP.
3 Actinic Flux Density Meter (AFDM) - Photodiode Array (PDA) Detector

This chapter introduces the spectrometer system that was applied during the two INSPECTRO measurement campaigns. After a presentation of the instrumental setup the results of the instrumental characteristic are discussed which determine the capability of the system to measure actinic flux densities and to derive photolysis frequencies. Parts of the results presented in this section have been published by Jäkel et al. (2005). Pictures of the aircraft and the optical inlets of the AFDM and the Albedometer were shown on the cover of the January issue of Applied Optics (see Figure 3.1).

3.1 Setup and Performance

The AFDM-PDA comprises two separate measurements units (one for the downward, the other for upwelling actinic flux density measurements) each consisting of three components: (i) optical inlet, (ii) fiber optical cables, and (iii) multi-channel spectrometer (MCS). The MCS modules consist of photodiode array (PDA) detectors. A general overview of the setup of the AFDM-PDA is presented in Figure 3.2. There are two hemispheric collectors (manufactured by meteorologie consult, Königstein, Germany) one upward-, the other one downward-looking. The sum of the two spectral actinic flux densities from the upper hemisphere ($F_{u}^{1}$) and the lower hemisphere ($F_{u}^{1}$) yields

Figure 3.1: Cover of the 20 January 2005 issue of Applied Optics which shows the Partenavia P68B and the optical inlets of the AFDM and Albedometer.
the spectral actinic flux density \( (F_a) \). Both optical inlets are mounted together with the Albedometer inlets on the same horizontal stabilization system thus keeping the inlets in a horizontal position during aircraft attitude changes. The cos-optical inlets for the irradiance measurements indicated as \( I^\downarrow \) and \( I^\uparrow \) in Figure 3.2. They are connected to the Albedometer unit which is no more described here. A personal computer is used for data acquisition.

![Diagram](image)

Figure 3.2: Scheme of the AFDM (actinic flux density meter) - PDA version, MCS: Multi-Channel Spectrometer, \( A^\downarrow \): isotropic optical inlet for downwelling and \( A^\uparrow \) for upwelling actinic flux density measurements, DAS: data acquisition

### 3.1.1 Horizontal Stabilization System

The horizontal stabilization system assures the separation of downwelling and upwelling actinic flux densities. The system consists of two parts: (i) the measurement unit for the actual roll and pitch angles, and (ii) the active horizontal adjustment. (i) On accelerated platforms like an aircraft usual inclination sensors which use the Earth’s gravity vector are not applicable, because they cannot distinguish between the Earth’s gravity vector and the acceleration vector of the moved platform. Therefore an artificial horizon (AHZ) (developed by iMAR GmbH, St. Ingbert, Germany) is applied which determines the aircraft attitude angles. The artificial horizon consists of three linear servo-acceleration sensors, which deliver the aircraft velocity and position, and three fiber optical gyroscopes for the angle rates. Furthermore, supporting informations from a global positioning system (GPS) are used to compensate temporal drifts of the acceleration sensors and of the fiber optical gyroscopes. (ii) Two separate two-dimensional tilt stages, which are connected with the optical inlets, consist of two servo-motors which realize the horizontal adjustment of the optical inlets with an accuracy of \( \pm 0.2^\circ \) in a range of \( \pm 6.0^\circ \). Further details are described by Wendisch \textit{et al.} (2001).

### 3.1.2 Isotropic Optical Inlets

The setup of the hemispheric actinic inlets \( A^\downarrow \) and \( A^\uparrow \) is similar to the dome arrangement described by VoIz-Thomas \textit{et al.} (1996). The inlets consist of a set of frosted quartz
domes. Multiple refraction and reflection lead to a nearly isotropic angular response of the inlets with regard to the incident radiation. That means that optical inlets are supposed to exhibit on isotropic sensitivity. A photo of the AFDM optical inlets together with the cosine optical inlets of the Albedoimeter is given in Figures 3.3a and b. The distance between the irradiance and the actinic inlets is about 30 cm. Both inlets are connected via a black painted shadowing construction, which serves as an artificial horizon to reduce the radiation from the opposite hemisphere. A larger and consequently heavier shadow ring would reduce the distortion of the measurements due to radiation from the opposite hemisphere even more efficiently. But the size and mass of this shadowing construction is limited by the capability of the horizontal stabilization system. To avoid condensation within the optical inlets a cartridge filled with silica gel is used.

### 3.1.3 Spectrometer-PDA

The spectrometers and the isotropic optical inlets are connected with optical fibers (distributed by Prinz Optics GmbH, Stromberg, Germany) with a length of three meters (monofibers with a diameter of 600 μm). Each end has a Standard Mechanical Adapter (SMA), the end connecting with the spectrometer is mechanically revised compared to conventional SMA couplings. It allows to plug the optical fibers into the spectrometers in the same position. A fixed coupling assures a low uncertainty due to re- and disconnections of the optical fibers. Optical fibers operate by total internal reflection. They consist of a core material with high refractive index and a cladding of lower refractive index. The transmittance of each fiber is determined by the choice of the core and the cladding. The so called UV-enhanced optical fibers of the AFDM system transmit best in the UV spectral range due to the fused silica core with high OH content and the silica cladding.

The MCS-PDA modules (manufactured by Zeiss GmbH, Jena, Germany) have a fixed grating for wavelength splitting and a photodiode array (manufactured by Hamamatsu, Japan) with 512 pixels for detection.

Figure 3.3: Actinic (right arrows) and irradiance (left arrows) optical inlets mounted on the top (a) and the on the bottom (b) of the aircraft.
within the wavelength range between 280 and 700 nm. Both spectrometers are mounted in ceramic bodies, therefore thermal and mechanical stability are warranted (see Figure 3.4). The light passes through an entrance slit (70 μm) and is dispersed by a flat field diffraction grating (248 lines/mm), which is blazed (optimized efficiency degree) at 450 nm (VIS region). In addition to its dispersive function, the grating images the entrance slit on the PDA as shown by the light path in Figure 3.4.

The function of the PDA detector is based on the following principle: Silicium photodiode arrays consist of multiple photodiode elements, formed in a linear arrangement. Photodiodes are semiconductors and each individual pixel is connected to a parallel capacitor. Charges (electron-hole pairs), produced by light hitting a diode, are stored in the capacitors.

The electronics behind the PDA works nearly simultaneously for both MCS using a multiplexer. Two different integration times between 50 and 6000 ms can be adjusted. Typical scan times are between 250 and 1200 ms depending on atmospheric conditions. The activation of the multiplexer and the analysis of the signals are performed by a PC card (manufactured by tec5 GmbH, Oberursel, Germany). Between the photodiode array and the PC card the Front End Electronics is placed, that is responsible for the control signal generation of the diode array, and digitalization of the analog video signal.

![Diagram](image)

Figure 3.4: Optical path within the MCS-PDA. Sketch adapted from Zeiss.

### 3.1.4 Offset

The overall offset consists of the dark current signal plus an electronic noise and a stray light contribution. The dark current arises from thermally generated electrons in the PDA and depends on the temperature. Compared to the electronic noise the stray light and dark current depend on the integration time. Stray light describes undesirable signals originated from other wavelengths or from misguided light within the instrument caused
Figure 3.5: Temperature dependence of the d+e current: (a) MCS-PDA\(^\dagger\), (b) MCS-PDA\(^\dagger\)

by e.g., reflections on the spectrometer walls. Furthermore the signal to noise ratio as a parameter of the instrumental precision is discussed in this context.

**Dark Current Signal and Electronic Noise** The sum of dark current and electronic noise is measured when the optical inlet is completely obscured. In the following this measurement is called "d+e measurement", its signal is the "d+e current". The number of thermally generated electrons are subject to randomized variations. This variation influences the d+e current. Therefore it is advisable to consider a mean of several d+e measurements. The wavelength-dependence is studied by d+e measurements using different integration times and temperatures. Exemplarily, a wavelength averaged d+e current of 454 counts was measured with a standard deviation std of ±4 counts during one second integration time (MCS\(^\dagger\)), which means a spectral variability of less than 1%. Because of this low spectral variability the wavelength dependence of the d+e signal can be neglected. The dark current depends strongly on the temperature. It can not be measured separately from the electronic noise, which does not depend on the integration time. Figure 3.5 shows the temperature-dependent d+e currents of both spectrometers measured for different integration times. The d+e current is averaged over the whole wavelength range (280 - 700 nm), its standard deviation is represented by the error bars. As expected the d+e current is positive correlated with the integration time and increases with temperature. Despite different absolute values of the d+e current their relative increase with temperature is similar for both spectrometers. Exemplarily, between 18° and 28°C a factor of 1.98 is determined for 800 ms. This factor decreases nearly linear with decreasing integration time. The temperature-dependence of the d+e current increases with increasing integration times. The electronic noise is estimated from the linear regressions of the d+e current plot using this function: d+e current\(t\) = \(t\) \cdot slope + electronic noise, whereby \(t\) stands for the integration time. A distinct dependence from the temperature is not found.

**Stray Light** The stray light of the two spectrometers was quantified using spectral cutoff filters (LOT Oriel, Germany). VIS long-wave pass filters (cutting wavelengths \(\lambda\): 400
nm, 500 nm, 600 nm, 700 nm) have been employed. $\lambda_c$ is defined as the wavelength where the spectral transmission yields 50%. Such filters block radiation of wavelengths less than $\lambda_c$. A rejection of radiation of $\geq 99\%$ is reached at $0.9\lambda_c$. If the spectrometer measures a signal which differs from the d+e current below $0.9\lambda_c$, then the difference between the measured counts and the d+e current using a long-wave pass filter with $\lambda_c$ is defined as the stray light signal. This measurement method is called "stray light measurement" in the following text. Such stray light measurements can be performed under atmospheric conditions using the Sun as light source or in the laboratory using a lamp.

Figure 3.6a shows the signals of the photodiode array spectrometer MCS-PDA$^+$ derived from the stray light measurements in the laboratory using a 1000 W lamp (d+e current is substracted). The results for MCS-PDA$^+$ are similar. Therefore they are not shown. In addition the lamp signal without filter is plotted in Figure 3.6a. The measurement suggests that the filter blocks the light near $0.9\lambda_c$.

Figure 3.6b displays the stray light measurement in a limited wavelength range (280-430 nm) because the contribution of stray light above 430 nm is lower than 1% and hence stray light can be neglected for higher wavelengths. A closer look on this spectral ranges shows a slight wavelength-dependence of the stray light signal only.

The percentage contribution of stray light to the lamp signal varies in this case from 30% in the UV-B range up to less than 1% for wavelengths above 430 nm (see Figure 3.6c). An influence of the integration time on the percentage stray light contribution was not observed due to the linearity of the intensity e.g., a doubling of the integration time causes a doubling of the intensity (stray light and lamp signals).

Figure 3.6: (a) Stray light measurements of the AFDM-PDA between 280-700 nm using a 1000 W lamp; linear scale. (b) Spectral relative contribution of stray light measurement to lamp measurement without filter; logarithmic plot, (c) Stray light measurement of the MCS-PDA between 280-430 nm; logarithmic plot.

Signal to Noise Ratio  The precision of spectrometer measurements is defined by the noise of the measured signals for constant measurement conditions. A quantitative mea-
The signal-to-noise-ratio ($SNR$) which is defined by:

$$SNR = \frac{\sum Y}{\sigma_Y}$$

with: $\bar{Y}$ = the average of the counts and $\sigma_Y$ = its standard deviation. The precision of a spectrometer measurement is defined as $1/SNR$. It gets smaller with an increased $SNR$. Using a lamp for the measurement of $SNR$ causes an additional noise contribution due to lamp uncertainties which contributes to the instrumental noise. Therefore $d+e$ measurements were performed instead to quantify the instrumental $SNR$. The $SNR$ of the AFDM-spectrometers was determined by the mean and standard deviation of 1000 $d+e$ measurements at 20°C room temperature using different integration times (50-500 ms). The results of these measurements show average values $\bar{Y}$ of 200–400 counts (depending on integration time) and an almost constant $\sigma_Y$-value of 2 counts which was independent on integration time and wavelength. Hence the $SNR$ is only affected by the averaged signal. Since the $d+e$ current is nearly wavelength-independent, the $SNR$ shows no wavelength dependence either. Figure 3.7a displays the correlation between mean signal $\bar{Y}$ and $SNR$ averaged over the wavelength. The $SNR$ varies between 120 and 240 depending of the integration time (Figure 3.7b) which corresponds to a precision of 1-2% independent on wavelength.

![Graph](image)

Figure 3.7: $SNR$ of MCS-PDA$^\dagger$ and MCS-PDA$^\dagger$ as a function of (a) the averaged signal measured for integration times between 50 ms and 500 ms and (b) integration time. The error bars indicate the standard deviation of the wavelength-averaged mean signal and mean $SNR$.

The limit of detection, also called noise equivalent irradiance ($NEI$), describes the lowest actinic flux density which can be measured. $NEI$ is determined by the standard deviation of the $d+e$ current $\sigma_Y$ and is calculated with:

$$NEI = \frac{\sigma_Y}{D}$$

with: $D$=spectrometer sensitivity (conversion factor between counts and actinic flux density) and $\sigma_Y$=2 counts. $NEI$ depends on the wavelength due to the wavelength-dependence of the sensitivity (see Chapter 3.2). The results are shown in Figure 3.8.
3.1 Setup and Performance

Apparently $NEI$ is largest for low wavelengths, that means that the capability of spectral measurements is reduced compared to higher wavelengths. Comparing $NEI$ of both spectrometers, a better detection limit of the AFDM-PDA$^\dagger$ is noticeable $[\overline{NEI} = (6 \pm 3) \cdot 10^{-5} \text{ W m}^{-2} \text{ nm}^{-1}, \overline{NEI}^\dagger = (16 \pm 10) \cdot 10^{-5} \text{ W m}^{-2} \text{ nm}^{-1}]$.

![Graph](image)

Figure 3.8: Wavelength-dependent detection limit $NEI$ of spectrometer AFDM-PDA$^\dagger$ and AFDM-PDA$^\dagger$. 
3.2 Calibration and Data Correction

The measured signal [counts] depend on the pixel number of the MCS and have to be converted into spectra and units of the actinic flux density [W m$^{-2}$ nm$^{-1}$]. Moreover, it is necessary to consider the angular response of the optical inlets in the data procedure. In the following three essential calibrations are discussed with regard to the procedures listed in Table 3.1.

<table>
<thead>
<tr>
<th>Calibration</th>
<th>Data Correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. spectral calibration (spectral lamps)</td>
<td>(de)convolution of measured spectra</td>
</tr>
<tr>
<td>• pixel number $\rightarrow \lambda$</td>
<td></td>
</tr>
<tr>
<td>• determination of slit function and FWHM</td>
<td></td>
</tr>
<tr>
<td>2. absolute calibration (1000 W lamp)</td>
<td>• determination of correction functions</td>
</tr>
<tr>
<td>• counts $\rightarrow$ actinic flux density</td>
<td>depending on atmospheric conditions</td>
</tr>
<tr>
<td>3. determination of angular response $Z_P$</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1: Overview of calibration data correction procedures.

3.2.1 Spectral Calibration

The spectral calibration provides (i) the assignment of each pixel of the photodiode array to a specific wavelength, and (ii) the determination of the spectral slit function. This function represents the spectral line shape output for monochromatic input. The wavelength assignment given by the manufacturer was checked with Penray spectral lamps, mercury (Hg(Ar)) and Neon (Ne), (LOT, Germany) with known emission lines given in Table 3.2. Differences between the spectral calibration given by the manufacturer and own laboratory measurements were observed. Therefore a new polynomial fit of third order was created. The final parameter $(b_0, b_1, b_2, b_3)$ of the polynomial fit of spectrometer MCS-PDA$^4$ and MCS-PDA$^5$, defined by:

$$\lambda = b_0 + b_1 \cdot x + b_2 \cdot x^2 + b_3 \cdot x^3$$

are summarized in Table 3.3, with $x$ representing the pixel number. In addition the standard deviation (sdv) of each parameter and the coefficients of determination (R$^2$) of the polynomial fit are given. Figures 3.9a and 3.9b show the differences of the expected peak (Penray lamp) and the measured peaks derived from the data of the manufacturer and the own parameterization. Except for one single peak the difference between the
3.2 Calibration and Data Correction

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MCS-PDA† Value</th>
<th>MCS-PDA† sdv</th>
<th>MCS-PDA† Value</th>
<th>MCS-PDA† sdv</th>
</tr>
</thead>
<tbody>
<tr>
<td>(b_0)</td>
<td>278.65935</td>
<td>0.45759</td>
<td>278.77747</td>
<td>0.3215</td>
</tr>
<tr>
<td>(b_1)</td>
<td>0.83164</td>
<td>0.00785</td>
<td>0.82971</td>
<td>0.00553</td>
</tr>
<tr>
<td>(b_2)</td>
<td>-1.37941E-5</td>
<td>3.32615E-5</td>
<td>-1.00107E-6</td>
<td>2.35787E-5</td>
</tr>
<tr>
<td>(b_3)</td>
<td>-1.47382E-9</td>
<td>4.0607E-8</td>
<td>-2.11668E-8</td>
<td>2.90133E-8</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.99</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.3: Spectral lines of the mercury (Hg(Ar)) and neon (Ne) spectral lamp for pixel-wavelength assignment.

![Graph](image)

Figure 3.9: Difference between expected and measured peak wavelengths derived from Zeiss and new parameterization of pixel-wavelength assignment. a) for spectrometer MCS-PDA†, b) for spectrometer MCS-PDA†

expected peak and the new fit is lower than 0.25 nm, whereas the difference of the Zeiss fit increases with increasing wavelength up to a value of 3 nm.

Each spectrometer has its own spectral slit functions, because it measures a weighted integral in a certain spectral range instead of a discrete wavelength. Since measurements of different instruments are compared it is necessary to de-convolute the measured spectra. For this objective a Gaussian fitting curve was adapted to each measured spectral line. Figure 3.10a shows one example of a spectral line measured with the Hg (Ar) emission lamp. A set of full width at half maximum (FWHM) values was calculated from the different Gaussian fits of each spectral line. The results are listed in Table 3.4. No distinct spectral dependence of the FWHM was revealed, which is displayed in Figure 3.10b. The wavelength averaged FWHM of the two spectrometers of the MFDM was calculated with 2.7 ± 0.4 nm and 2.6 ± 0.4 nm, respectively.

3.2.2 Absolute Calibration

The relation between the measured spectral counts \(I(\lambda)\) and the actinic flux density \(F_a(\lambda)\) is given by:

\[
I(\lambda) = D(\lambda) \cdot F_a(\lambda) .
\]
3 Actinic Flux Density Meter (AFDM) - Photodiode Array (PDA) Detector

<table>
<thead>
<tr>
<th>Peak Wavelength</th>
<th>FWHM MCS-PDA$^+$</th>
<th>MCS-PDA$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.73</td>
<td>3.44</td>
<td>3.12</td>
</tr>
<tr>
<td>302.15</td>
<td>-</td>
<td>3.45</td>
</tr>
<tr>
<td>365.02</td>
<td>2.76</td>
<td>2.56</td>
</tr>
<tr>
<td>404.66</td>
<td>2.40</td>
<td>2.24</td>
</tr>
<tr>
<td>435.84</td>
<td>2.38</td>
<td>2.30</td>
</tr>
<tr>
<td>546.07</td>
<td>2.50</td>
<td>2.44</td>
</tr>
<tr>
<td>614.31</td>
<td>3.06</td>
<td>3.02</td>
</tr>
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<td>650.65</td>
<td>2.31</td>
<td>2.46</td>
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<td>585.25</td>
<td>3.10</td>
<td>2.39</td>
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<td>594.48</td>
<td>2.79</td>
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</tr>
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<td>671.7</td>
<td>3.05</td>
<td>2.76</td>
</tr>
<tr>
<td>692.95</td>
<td>3.00</td>
<td>2.79</td>
</tr>
</tbody>
</table>

Table 3.4: Measured FWHM of different emission lines for MCS-PDA$^+$ and MCS-PDA$^+$.  

$D(\lambda)$ spectral sensitivity. Its inverse is the absolute calibration function. For $\theta = 0^\circ$, the equivalence of spectral irradiance $F(\lambda)$ and the spectral actinic flux density $F_a(\lambda)$ is valid. That implies that the spectral sensitivity can be determined by using a standard irradiance lamp with known irradiance values $F(\lambda)$ according to the following equation:

$$D_0(\lambda) = \frac{I(\lambda)}{F(\lambda)}.$$  \hspace{1cm} (3.5)\

$D_0(\lambda)$ describes the spectral sensitivity at $\theta = 0^\circ$ for measurements of direct signals. The absolute calibration was performed with a standard irradiance 1000 W lamp (traceable to the Physikalisch Technische Bundesanstalt - PTB). The standard irradiance is certified for a distance of 700 mm between the lamp and the receiver. For an accurate determination of the distance a virtual plane has to be introduced. An equivalent plane receiver with the assumption that the optical inlet behaves like a plane receiver that is irradiated at normal incidence. By assuming that the irradiance is proportional to the inverse square of the distance

$$I(\lambda) = const(d_0 + \Delta d)^{-2}$$  \hspace{1cm} (3.6)\

the signals for different relative distances $d_0 + \Delta d$ between lamp and optical inlet are measured. Afterwards the inverse of the root of these signals $I(\lambda)^{-1/2}$ is plotted as a function of the distances. $\Delta d$ is extrapolated from the linear fit $I(\lambda)^{-1/2} = 0$. An example of such measurements is shown in Figure 3.11. With the help of the intersection of the regression lines with the abscissa the position of the virtual receiving plane is determined. A wavelength-averaged distance between receiving plane and dome top of 21±1 mm was obtained by this procedure for both optical inlets of the AFDM.
3.2 Calibration and Data Correction

Figure 3.10: (a) Spectral Hg(Ar) line measured with the MCS-PDA<sup>↓</sup> spectrometer. (b) Calculated FWHM at different emission lines for MCS-PDA<sup>↓</sup> and MCS-PDA<sup>↑</sup>.

Figure 3.11: Determination of the receiving plane of the optical inlet measuring the up-welling actinic radiation (inlet A<sup>↑</sup>). The different lines represent the linear regressions of the measured signal (+) for different pixel numbers.

After the calculation of the receiving plane position the correct distance between standard irradiance and optical inlet is determined. To adjust the lamp and the optical inlet in the same horizontal plane a laser, which marks the optical axis, and a mirror are used. The mirror placed in front of the inlet is adjusted such that it reflects the laser beam exactly in the center of the laser. First of all, the optical inlet, which is mounted on a rotating table, is moved such that the optical axis meets the dome top of the optical inlet and the optical axis is parallel to the body of the optical inlet. After that the lamp is mounted on the optical table within the laser beam, which is illustrated in Figure 3.12.

The optical bench covered by a tent that consists of black cloth (to minimize reflected radiation from the walls). Additionally a baffle is used to receive direct radiation from the lamp only. According to the lamp certificate the irradiance standard is heated over a
period of 30 minutes to stabilize the temperature and to get a constant output. The lamp current has to be slowly increased (over a period of about one minute) until it reaches 8.1000±0.0001 A, as advised in the lamp manual. The calibration consists of three steps: After heating the lamp, the spectra are measured twenty times with an integration time of two and five seconds. A next scan series is done with a long wave pass filter ($\lambda_c = 320 \text{ nm}$) which blocks the UV radiation of the lamp to determine the stray light contribution afterwards. A last scan series is done with a covered optical inlet to measure the d+e current of the spectrometer. In general a measured spectrum includes a d+e current level and a stray light signal. This stray light signal is calculated from the difference between filter signal and d+e current. The averaged signal in the UV spectral range confirms with the stray light. By calculating the difference of the averaged direct, d+e current and straylight signal the offset level is removed and the calibration factors are obtained using Eq. 3.5.

3.2.3 Angular Response of Optical Inlets

**Laboratory Measurements of the Angular Response** The relative angular response function $Z_P$ of the two actinic optical inlets was measured in the laboratory for different azimuth ($\Phi$) and polar ($\theta_P$) incidence angles using:

$$Z_P(\theta_P, \Phi, \lambda) = \frac{I(\lambda, \theta_P, \Phi)}{I(\lambda, \theta_P = 0^\circ, \Phi)} .$$

$I(\lambda, \theta_P, \Phi)$ represents the measured signal of the direct contribution (without diffuse radiation) in counts/second. An ideal isotropic optical inlet would show a $Z_P$ of unity between 0 and $90^\circ$ polar angle. For polar angles larger than $90^\circ$ $Z_P$ would drop down to a value of 0.

The measurement setup is similar to Figure 3.12. To determine the influence of the cosine optical inlet on the angular response of the isotropic optical inlet the angular response calibration was performed with both inlets and the shadow ring construction shown in Figures 3.3a and b. A slight azimuthal dependence ($\leq 2\%$) results from shadowing effects.
The effect appears when the cosine optical inlet is between radiation source and isotropic optical inlet at large polar angles.

Figure 3.13a shows the wavelength-averaged relative angular response \( Z_P \) of \( A_\parallel \) and \( A_\perp \) as a function of the polar angle \( \theta_P \) for a fixed azimuth angle. The vertical bars represent the standard deviation. The curves show that both \( A_\parallel \) as well as \( A_\perp \) receive a certain amount of radiation from the opposite hemisphere (\( \theta_P > 90^\circ \)). If no corrections are applied the actinic flux density would therefore be overestimated by up to 35\%. The fraction of downwelling radiation is usually higher than the upwelling fraction in the atmosphere. Hence, the non-ideal isotropic angular response is important in particular for \( A_\perp \) which is crucially influenced by the radiation from the upper hemisphere.

Figure 3.13b illustrates the wavelength dependence of \( Z_P \) for a polar angle of 40° and 70°. A maximum deviation between the measured and ideal angular response of about ± 5\% (for a polar angle of 70°) is quantified.

![Relative Angular Response](image)

Figure 3.13: (a) Relative angular response \( Z_P \) of the optical inlets \( A_\parallel \) and \( A_\perp \) as function of polar angle \( \theta \). \( Z_P \) is wavelength-averaged (vertical bars represent the standard deviation). (b) shows \( Z_P \) as a function of wavelength \( \lambda \) for two different polar angles, 40° and 70°.

**Correction of Atmospheric Measurements**  The deviations from the ideal isotropic angular response of the optical inlets are corrected similar to the method described by Hofzumahaus *et al.* (1999) in which, however, the correction was restricted to the downward component only. In this study both the downwelling and upwelling components of the actinic flux density are measured and thus have to be corrected separately.

The differential solid angle \( d\Omega \) is defined by:

\[
d\Omega = \sin\theta \, d\theta \, d\Phi \quad .
\]  

(3.8)

The incident radiation is related to the spectral signals using Eqs. (2.2), (3.4), and (3.8) by:

\[
dI(\lambda) = D(\lambda) \, L(\theta, \Phi, \lambda) \, d\Omega \quad .
\]  

(3.9)
$D(\lambda)$ depends on the sensitivity of the detector and the characteristic of the optical inlet. $D_0(\lambda)$, which is measured in the laboratory, and $D(\lambda)$ are related as follows:

$$D(\theta, \Phi, \lambda) = D_0(\lambda) \cdot Z_P(\theta, \Phi, \lambda)$$  \hspace{1cm} (3.10)

with $Z_P(\theta, \Phi, \lambda)$ representing the relative angular response function. For an ideal isotropic optical inlet applies: $Z_P(\theta, \Phi, \lambda) = 1$. By inserting Eq. (3.10) in Eq. (3.9) it follows:

$$dI(\lambda) = D_0(\lambda) \cdot Z_P(\theta, \Phi, \lambda) \cdot L(\theta, \Phi, \lambda) \cdot d\Omega$$ \hspace{1cm} (3.11)

In the atmosphere the entrance optics integrate the radiances over all angles of incidence. Spectral signals are given by:

$$I(\lambda) = D_0(\lambda) \int Z_P(\theta_s, \Phi_s, \lambda) \cdot L(\theta_s, \Phi_s, \lambda) \cdot d\omega$$ \hspace{1cm} (3.12)

By introducing the dimensionless function $Z_H$ the following relation between the signal and actinic flux density is obtained:

$$I(\lambda) = D_0(\lambda) Z_H F_a(\lambda)$$ \hspace{1cm} (3.13)

$$Z_H = \frac{1}{F_a} \int_{4\pi} Z_P(\theta_s, \Phi_s, \lambda) \cdot L(\theta_s, \Phi_s, \lambda) \cdot d\omega$$ \hspace{1cm} (3.14)

$Z_P$ is unity for an isotropic optical inlet. From this and Eq. (3.14) it follows that $Z_H = 1$.

$$I_{\text{ideal}}(\lambda) = D_0(\lambda) F_a$$ \hspace{1cm} (3.15)

The comparison of Eq. 3.13 and Eq. 3.15 shows that $Z_H$ describes the correction function of a non-ideal isotropic inlet.

In the atmosphere the incoming radiance $L$ is the sum of the direct $L^d_0$, the diffuse downward $L^d_{\text{diff}}$, and the diffuse upward $L^\uparrow$ radiance:

$$L = L^d_0 + L^d_{\text{diff}} + L^\uparrow.$$ \hspace{1cm} (3.16)

The correction method assumes that the distribution of $L^d_{\text{diff}}$ and $L^\uparrow$ are isotropic. That implies:

$$L^d_0 = F^d_{\alpha,0} \delta(\theta_0, \Phi_0),$$ \hspace{1cm} (3.17)

$$L^d_{\text{diff}} = \frac{F^d_{\alpha, \text{diff}}}{2\pi},$$ \hspace{1cm} (3.18)

$$L^\uparrow = \frac{F^\uparrow}{2\pi},$$ \hspace{1cm} (3.19)

where $L^d_0$ and $F^d_{\alpha,0}$ are the spectral radiance and the actinic flux density of the direct radiation from the direction $(\Phi_0, \theta_0)$ of the radiation source. $\delta$ represents a Dirac delta function, and the direction of the arrows denotes the upwelling ($\uparrow$) and downwelling ($\downarrow$) component of $L$ and $F_a$. By inserting Eq. (3.16) in Eq. (3.14) it follows:

$$Z_H = \frac{1}{F_a} \int_{4\pi} Z_P(\theta_s, \Phi_s, \lambda)(L_0 + L^d_{\text{diff}} + L^\uparrow) \cdot d\omega.$$ \hspace{1cm} (3.20)
It follows with Eqs. (3.17)-(3.19) and Eq. (3.20):

\[
Z_H = \frac{1}{F_a} \int_{4\pi} Z_P(\theta_s, \Phi_s, \lambda) F_{a,0}^\dagger \delta(\theta_o, \Phi_o) \, d\Omega \\
+ \frac{1}{F_a} \int_{4\pi} Z_P(\theta_s, \Phi_s, \lambda) F_{a,0} \frac{F_{a,\text{diff}}^\dagger}{2\pi} \, d\Omega \\
+ \frac{1}{F_a} \int_{4\pi} Z_P(\theta_s, \Phi_s, \lambda) \frac{F_a^\dagger}{2\pi} \, d\Omega
\]  

(3.21)

Eq. (3.21) can be written as:

\[
Z_H = \frac{F_{a,0}^\dagger}{F_a} Z_P(\theta_s, \Phi_s, \lambda) \\
+ \frac{F_{a,\text{diff}}^\dagger}{F_a} \frac{1}{2\pi} \int_{UH} Z_P(\theta_s, \Phi_s, \lambda) \, d\Omega \\
+ \frac{F_a^\dagger}{F_a} \frac{1}{2\pi} \int_{LH} Z_P(\theta_s, \Phi_s, \lambda) \, d\Omega,
\]  

(3.22)

where \(UH\) means the upper and \(LH\) the lower hemisphere. The first term includes the fraction of the direct to the total actinic flux density \((F_{a,0}^\dagger / F_a)\), the second describes the downward diffuse fraction \((F_{a,\text{diff}}^\dagger / F_a)\) and the third term represents the upwelling fraction \((F_a^\dagger / F_a)\). In contrast to the correction method presented by Hofzumahaus et al. (1999) \(Z_H\) is considered for the downwelling and upward looking optical inlet separately. \(Z_H\) for optical inlet \(A^\dagger\) and \(A^\uparrow\) differ in the reference hemisphere. Hence, in case of inlet \(A^\dagger\) \((A^\uparrow)\) the fractions correspond to the upper (lower) hemisphere. The following equation describes the correction functions \(Z_H^\dagger\) for optical inlets \(A^\dagger\):

\[
Z_H^\dagger = \frac{F_{a,0}^\dagger}{F_a} Z_P(\theta_s, \Phi_s, \lambda) + \frac{F_{a,\text{diff}}^\dagger}{F_a} \frac{1}{2\pi} \int_{UH} Z_P(\theta_s, \Phi_s, \lambda) \, d\Omega \\
+ \frac{F_a^\dagger}{F_a} \frac{1}{2\pi} \int_{LH} Z_P(\theta_s, \Phi_s, \lambda) \, d\Omega,
\]  

(3.23)

The fraction of the direct component to the upwelling actinic flux density is 0. Thus, Eq. (3.22) for optical inlet \(A^\uparrow\) is reduced to:

\[
Z_H^\uparrow = \frac{F_{a,\text{diff}}^\dagger}{F_a} \frac{1}{2\pi} \int_{UH} Z_P(\theta_s, \Phi_s, \lambda) \, d\Omega + \frac{1}{2\pi} \int_{LH} Z_P(\theta_s, \Phi_s, \lambda) \, d\Omega.
\]  

(3.24)

In the following the parameters \(\alpha, \beta,\), and \(\gamma\) are introduced. They consider the portion of the direct \(F_{a,0}\), the upward \(F_a^\dagger\) and the diffuse downward \(F_{a,\text{diff}}^\dagger\) to the actinic flux density \(F_a\) of the corresponding hemisphere. Table 3.5 displays the parameters \(\alpha, \beta, \) and \(\gamma\) for each of the two actinic optical inlets. The final correction functions \(Z_H\) for the downwelling and upwelling components are given by Eq. (3.25) and (3.26):

\[
\text{for } A^\dagger \\
Z_H^\dagger = \alpha^\dagger Z_P(\theta_s, \Phi_s, \lambda) + \frac{\beta^\dagger}{2\pi} \int_{LH} Z_P(\theta_s, \Phi_s, \lambda) \, d\Omega \\
+ \frac{\gamma^\dagger}{2\pi} \int_{UH} Z_P(\theta_s, \Phi_s, \lambda) \, d\Omega
\]  

(3.25)
Table 3.5: Parameter of correction function $Z_H$

\[
\begin{array}{c|c}
Z_H^\dagger & \alpha^\dagger = \frac{F_{\alpha}^\dagger}{F_\alpha^\dagger} \\
\beta^\dagger & \beta^\dagger = 1 \\
\gamma^\dagger = 1 - \alpha^\dagger & \gamma^\dagger = \frac{F_{\alpha}^\dagger d\Omega}{F_\alpha^\dagger d\Omega}
\end{array}
\]

for $A^\dagger$

\[
Z_H^\dagger = \frac{\gamma^\dagger}{2\pi} \int_{U_H} Z_P(\theta_S, \Phi_S, \lambda) d\Omega + \frac{1}{2\pi} \int_{L_H} Z_P(\theta_S, \Phi_S, \lambda) d\Omega. \quad (3.26)
\]

The measured spectral actinic flux densities (upwelling and downwelling) are divided by the respective $Z_H$-values in order to perform the correction. For overcast conditions $\alpha^\dagger$ is 0 within and below the cloud.

To calculate a set of wavelength-dependent correction functions $Z_H$, the parameters $\alpha$, $\beta$ and $\gamma$ are determined as a function of a) solar zenith angle, b) altitude above ground, c) surface and cloud albedo, and d) cloud cover. The parameters in Table 3.5 were calculated for solar zenith angles in the range between $45^\circ$ and $65^\circ$ in steps of $5^\circ$. The SZA range complies with the values observed during the measurement INSPECTRO-1 campaign. Calculations were carried out with the Discrete-Ordinate Method (DISORT), a plane-parallel radiative transfer model (Stamnes et al., 1988) which was run by Anke Kniffka (University of Leipzig). The calculations were performed for three surface and cloud albedo values. For the surface albedo a wavelength averaged value of 0.08 was used which was derived from respective surface albedo measurements. An overcast case was simulated using a cloud top albedo of 0.9. For broken cloud conditions an intermediate albedo of 0.6 was chosen. For the correction of measurements below or within clouds, a cloud simulation using a surface albedo of 0.08 and placing a cloud layer between 1 and 2 km was used.

Figures 3.14a and 3.14b display the resulting correction functions $Z_H^\dagger$ for optical inlet $A^\dagger$. A clear wavelength dependence for all $Z_H^\dagger$ is obvious. The $Z_H^\dagger$ plotted in Figure 3.14a applies to an altitude of 2 km and a surface albedo of 0.08. There are only small deviations ($\pm$ 3%) between the different $Z_H^\dagger$-values for different solar zenith angles ($45^\circ$ and $60^\circ$).

The altitude and albedo dependence of $Z_H^\dagger$ is illustrated in Figure 3.14b. Here a fixed solar zenith angle of $45^\circ$ was chosen. The correction functions are plotted for an albedo of 0.08 (surface albedo) and 0.9 (cloud top albedo), respectively, and for an altitude above the surface of 0 km and 2 km. The altitude dependence increases with decreasing albedo. Furthermore the correction functions increase with increasing albedo, because of an increasing signal portion from the lower hemisphere. For example the measured actinic flux density above a compact cloud layer may have an error of up to 8%.

Figure 3.15 shows the wavelength-dependent correction function $Z_H^\dagger$ of $A^\dagger$ for different altitudes and albedo values. In comparison with the correction functions of $A^\dagger$, $Z_H^\dagger$ generally decreases with an increasing albedo which results from the increasing portion of
3.2 Calibration and Data Correction

Figure 3.14: Correction factor $Z_H$ of the optical inlet $A^\dagger$ as a function of the wavelength $\lambda$. (a) shows the correction factor for an altitude of 2 km above the ground-surface which has a wavelength-averaged albedo of 0.08 at two solar zenith angles, SZA (45°, 60°). In panel (b) $Z_H$ is plotted for 0 km and 2 km altitude and a cloud top albedo (CTA) of 0.9 and a surface albedo (SA) of 0.08 at a solar zenith angle of 45°.

the diffuse downward to the actinic flux density of the lower hemisphere. Because the part of the actinic flux from the upper hemisphere is much higher than from the lower hemisphere, the relative error due to non-ideal angular response is significantly larger for $A^\dagger$ (for an albedo of 0.08 up to 35%). However the actinic flux density, $F_a = F_a^\dagger + F_a^\uparrow$, is less dependent on the upwelling part for a small albedo. The dependence of the correction function $Z_H$ of both optical inlets in the overcast case is nearly similar to the other cases, except for azimuth and zenith angles because of the isotropic assumption in the model simulation.

Figure 3.15: Correction factor $Z_H$ of the optical inlet $A^\dagger$ as a function of wavelength $\lambda$ for a surface albedo of 0.08 and two cloud albedo values (0.9, 0.6) in 1 km and 2 km altitude.
3.2.4 Data Evaluation Procedure

For the evaluation of the measured signals (counts) the following procedure is applied: (i) the offset has to be defined. The wavelength independence of the drift current and stray light signal simplifies the determination of the offset. The stray light signals as well as the dark current and electronic noise are considered by subtracting an average signal of all counts between 280 and 290 nm from each spectrum. (ii) After subtracting the offset the calibration function $1/D_0$ is multiplied with the counts to get the actinic flux density in units of W m$^{-2}$ nm$^{-1}$. The calibration functions determined in the laboratory are modified with regard to the sensitivity of the AFDM in the field. For this purpose secondary calibrations were carried out using different 200 W lamps during the field campaigns and in the laboratory. In this way uncertainties due to dis- and reconnecting of fiber optical cables between the laboratory calibrations and the field measurements are taken into account. (iii) Next the data are corrected with regard to the non-ideal angular response. The correction function $Z_p$ depends on the SZA, flight altitude above ground, surface albedo, and cloudiness. According to these parameters the correction function is applied to the actinic flux density spectrum. (iv) Since the spectra are compared to measurements of other instruments, the spectra are deconvoluted by the SHICRIVM-code (Slaper et al., 1995) considering the slit function of the AFDM. Figure 3.16 illustrates the stepwise data evaluation.

![Figure 3.16](image)

**Figure 3.16**: Data evaluation steps. (a) Original measured spectral signals and signals after offset subtraction (step i). (b) Actinic flux density spectra after applying of calibration (step ii) function, correction function (step iii), and deconvolution (step iv).
3.3 Measurement Uncertainties

The following discussion gives an overview of the AFDM uncertainties with respect to (i) the measurement uncertainty of the actinic flux density, and (ii) the uncertainty of the photolysis frequencies integrated from the actinic flux density measurements.

3.3.1 Actinic Flux Densities

The AFDM has proven to work accurately within 305 to 700 nm wavelength. Due to low counting statistics the sensitivity of the actinic flux density drops below 305 nm. For this reason the determination of the offset causes significant uncertainties in this spectral range because the accuracy of distinction between noise and signals coming from the light source is very low. Comparisons with radiative transfer simulations have shown that the agreement between model and measurement drops significantly below 305 nm as shown in Figure 3.17. Measurements of the AFDM-PDA are compared to one-dimensional simulations which were modeled with the uvspec-model (Mayer and Kylling, 2005). The measurements were taken on day 030901 in clear sky conditions for several SZA (34°, 51°, 62°). The simulations were performed without any information about the aerosol particle properties on this day. Therefore uncertainties resulting from insufficient input data for the aerosol conditions have to be taken into account for the evaluation of the results. However, the lower limit of the reliable spectral range of the AFDM-PDA can be estimated by these simulations. The atmospheric UV cutoff marks a significant increase of solar radiation with wavelength over several orders of magnitudes. Its position is determined by the SZA and the TOC which are crucial model input data. The TOC data stem from Total Ozone Mapping Spectrometer (TOMS) measurements, the SZA is directly calculated from the time and geographical position. The simulated and measured down-welling actinic flux density spectra differ mainly in the lowest wavelengths (see Figure 3.17a), where the measured spectral $F_{\alpha}^\downarrow$ is larger than the simulated. The ratio shown in Figure 3.17b displays the sharp drop of the agreement between simulation and measurement below 305 nm for each SZA. Therefore the lower limit of the reliable spectral range of the AFDM-PDA was set to 305 nm.

The main sources of measurement uncertainties of the AFDM-PDA are quantified in Table 3.6. The largest uncertainty arises from the absolute calibration. The temporal drift of the absolute calibration and the uncertainty due to disconnection and reconnection of the measurement setup, in particular the fiber optics, is continuously observed with the transfer calibration during the field campaign. The connections between the fibers and the spectrometers as well as between the fibers and the optical inlets are maintained during the field measurements. For the transfer lamps an uncertainty of $\pm$3% is estimated for a wavelength range above 400 nm. Below 400 nm the lamp signal is low and therefore the uncertainty drastically increases below 400 nm. Figure 3.18 displays results of transfer calibrations performed during a field campaign. A spectral average of lamp spectra measured on 5 days of the campaign (09/12/02, 09/13/02, 09/15/02, 09/22/02, and 09/28/02) was determined. The noise of the ratio increases with lower wavelengths due to the lower lamp signals in this spectral range. Overall the ratios vary between $\pm$3%
and show no temporal dependence.

The determination of the certified distance from the irradiance standard to the receiving plane of the optical inlet leads to an uncertainty of less than ±1%. In addition to the absolute calibration the spectral calibration represents the second major uncertainty in the UV spectral range. The manufacturer specifies an absolute wavelength accuracy of about 0.3 nm for the MCS-PDA. To calculate the related uncertainty, spectra were shifted by 0.3 nm, similar to Eckstein et al. (2003). The ratio of the original spectra and the shifted spectra was calculated, and an uncertainty of ±5% in the UV range and of less than ±1% in the VIS range was observed. The error due to the non-ideal angular response was considered in the angular correction of the data depending on various parameters. A remaining uncertainty for that kind of correction can only be estimated. In Hofzumahaus et al. (1999) an uncertainty of ±1% is specified. However, with regard to the complex calculations of the angular correction functions an uncertainty of ±2% is estimated in this study. These results yield a total uncertainty estimate of ±8% in the UV range and ±5% in the VIS range, calculated with Gaussian error propagation.

<table>
<thead>
<tr>
<th>Source of Error</th>
<th>UV range (305-400 nm)</th>
<th>VIS range (400-700 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>calibration lamp uncertainty</td>
<td>±5%</td>
<td>±3%</td>
</tr>
<tr>
<td>transfer lamp uncertainty</td>
<td>±3%</td>
<td>±3%</td>
</tr>
<tr>
<td>determination of receiving plane</td>
<td>&lt; ±1%</td>
<td>&lt; ±1%</td>
</tr>
<tr>
<td>wavelength calibration</td>
<td>±5%</td>
<td>±1%</td>
</tr>
<tr>
<td>remaining angular response error</td>
<td>±2%</td>
<td>±2%</td>
</tr>
<tr>
<td>total uncertainty</td>
<td>±8.0%</td>
<td>±4.9%</td>
</tr>
</tbody>
</table>

Table 3.6: Estimated measurement uncertainties
3.3 Measurement Uncertainties

Figure 3.18: Ratio of mean spectra and single lamp spectra measured with transfer lamp 
#2 on several days in September 2002.

3.3.2 Photolysis Frequencies

Uncertainty due to Spectral Range Limitations The reliable spectral range of the 
AFDM-PDA version was quoted with 305-700 nm. For this reason the AFDM-PDA 
capability to determine photolysis frequencies is mainly restricted to gas species with 
significant contributions of quantum yield, absorption cross section and actinic flux density 
above 305 nm wavelength, as for example NO2, H2O2, CH2O and NO3. Figures 3.19 a-d 
display spectral photolysis frequencies defined as: 
\[ J(\lambda) = F_a(\lambda) \cdot \sigma(\lambda) \cdot \phi(\lambda) \] 
of these four species calculated for SZA = 20° and 60°. The actinic flux densities stem from 
model simulations performed with the uvspec model from the libradtran package (Mayer 
and Kylling, 2005). Note that the wavelength ranges in Figure 3.19 are different. The 
vertical lines mark the 305 nm wavelength. In addition Figure 3.19e depicts the spectral 
photolysis frequency of ozone. Different from the other four species it is obvious that 
\( J(0^1D) \) determined by a limited spectral range causes distinctiv uncertainties.

In the following the uncertainty of \( J \)-calculations caused by the limitation of the spectral 
range is quantified by the ratio of the calculated \( J \)-value using the spectral range between 
290 and 700 nm and the limited spectral range (here \( \lambda_{505} = 305 \) nm):

\[ \epsilon_{\lambda_{505}} = \frac{\int_{290nm}^{700nm} F_a \cdot \sigma \cdot \phi \, d\lambda}{\int_{\lambda_{505}}^{700nm} F_a \cdot \sigma \cdot \phi \, d\lambda} \]  

Input to the model are profiles from the U.S. standard atmosphere (Anderson et al., 1986). 
The aerosol particle single-scattering albedo and asymmetry parameter were set to 0.98 
and 0.75, respectively regarding to the input values which were used by Kylling et al. 
(2005) for clear sky simulations for the INSPECTRO-1 campaign. The surface albedo 
was taken from aircraft measurements with the Albedometer during the INSPECTRO-1 
campaign (here called "green"), from Feister and Grewe (1995) for snow conditions 
surface. Albedo data for sea from Bowker et al. (1985) were also used. The aerosol op-
Figure 3.19: Spectral photolysis frequencies of (a) NO₂, (b) H₂O₂, (c) CH₂O, (d) NO₃, and (e) O₃ calculated for 20° and 60° SZA. The vertical lines mark the 305 nm wavelength.

spectral thickness was scaled by the Ångstroem coefficients. The radiative transfer equation was solved by the DISORT algorithm. The solver was run in 16-stream mode. The extraterrestrial spectrum was used from the modified spectrum of Kurucz (1992), which was averaged over 1 nm intervals.
\( \alpha_{\text{M}_{\text{C}}} = 305 \text{ nm} \) was calculated for two extreme cases where the highest and lowest uncertainties in photolysis frequency determination due to the limited spectral range of the AFDM-PDA are expected. Case A includes modeled spectra at SZA = 0° and 250 DU TOC and case B was calculated at SZA = 80° and TOC = 350 DU. Table 3.7 summarizes the calculated \( \alpha_{\text{M}_{\text{C}}} \)-values (-100\%) of both cases A and B for the photolysis frequencies of \( \text{NO}_2 \), \( \text{H}_2\text{O}_2 \), \( \text{CH}_2\text{O} \), \( \text{NO}_3 \) and ozone. Apart from the ozone photolysis all listed photolysis frequencies can be measured with the AFDM-PDA accepting an uncertainty of 6%, even though the spectral range is limited on spectral measurements above 305 nm.

<table>
<thead>
<tr>
<th>Species</th>
<th>Case A (0°, 250 DU)</th>
<th>Case B (80°, 350 DU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J(NO₂)</td>
<td>0 %</td>
<td>0 %</td>
</tr>
<tr>
<td>J(H₂O₂)</td>
<td>6 %</td>
<td>0 %</td>
</tr>
<tr>
<td>J(CH₂O) + h\nu → H₂ + CO</td>
<td>1 %</td>
<td>0 %</td>
</tr>
<tr>
<td>J(CH₂O) + h\nu + (2O₂) → H₂ + CO</td>
<td>6 %</td>
<td>0 %</td>
</tr>
<tr>
<td>J(NO₃)</td>
<td>0 %</td>
<td>0 %</td>
</tr>
<tr>
<td>J(O¹D)</td>
<td>60 %</td>
<td>2 %</td>
</tr>
</tbody>
</table>

Table 3.7: Calculated uncertainties of photolysis frequencies.

**Uncertainty due to FWHM and Spectral Resolution**  In addition to the reliable spectral range, two further spectrometer-dependent characteristics influence the accuracy of photolysis frequency determination: (i) the spectral resolution of the spectrometer that corresponds to the pixel distance of the photodiode array, and ii) the FWHM, which depends on the slit width of the MCS.

In the following the uncertainty of photolysis frequency determination is studied for \( J(\text{O}^1\text{D}) \) which is highly sensitive to the spectral resolution and FWHM. For this purpose modeled actinic flux density spectra for two different atmospheric conditions and different spectral resolutions are used. The input parameter of the uvspec model are similar to the input used before apart from the spectral resolution of the extraterrestrial spectrum, SZA, and TOC. For this study the actinic flux density spectra are computed using the extraterrestrial spectrum with 0.1 nm resolution (Kurucz, 1992). Thus the modeled spectra can be adjusted to any spectral resolution above 0.1 nm. Exemplarily, \( J(\text{O}^1\text{D}) \)-values are compared which are derived from actinic flux density spectra with a spectral resolution of 0.1 nm, 0.5 nm, 0.8 nm, and 1.0 nm. Furthermore the simulated spectra are convoluted with different slit functions according to FWHM’s in the range of 0.2-3.0 nm with 0.2 nm stepwise. Two different SZA and TOC values are chosen to take the position of the atmospheric cutoff into account. Case A (SZA = 0°, TOC = 250 DU) considers an atmospheric cutoff positioned at lower wavelengths than case B (SZA = 60°, TOC = 320 DU). The results of this study are shown in Figure 3.20. Figure 3.20a and b display the derived photolysis frequencies as a function of the FWHM for case A and B. The gray stars mark the AFDM-PDA specifications of the FWHM (2.6 nm) and spectral resolution (0.8 nm). Two main features are noticeable: First \( J(\text{O}^1\text{D}) \) increases with increasing FWHM, and second an increased spectral resolution which corresponds
to a lower pixel distance results in higher \(J(O^1D)\)-values.

![Graphs showing \(J(O^1D)\)-values as a function of FWHM for different cases and resolutions.](image)

Figure 3.20: \(J(O^1D)\)-values as a function of FWHM for (a) case A: calculation for TOC = 250 DU and SZA = 0°, and (b) case B: calculation for TOC = 320 DU and SZA = 60°. (c), (d) display ratios of \(J(O^1D)\)-values determined by spectra convoluted with different slit functions \((J(O^1D)_{\text{FWHM}=x\text{nm}})\) and \(J(O^1D)\) determined by the non-convoluted actinic flux density spectrum with 0.1 nm spectral resolution \((J(O^1D)_{\text{FWHM}=0\text{nm}})\) as a function of FWHM for case A and B. The gray stars represents the AFDM-PDA specifications.

Figures 3.20c and d display the ratios of \(J(O^1D)\)-values derived from convoluted spectra \((J(O^1D)_{\text{FWHM}=x\text{nm}})\) for each spectral resolution (0.1 nm - 1 nm) and the standard spectrum \((J(O^1D)_{\text{FWHM}=0\text{nm}})\). The standard spectrum refers to the non-convoluted spectrum calculated with 0.1 nm spectral resolution. The ratios are plotted as a function of FWHM for four spectral resolutions and the two cases A (Fig. 3.20c) and B (Fig. 3.20d). Deviations between ±5% are found. However the range of uncertainty is larger in case B.

The influence of the FWHM on \(J(O^1D)\) originates from the level of smoothing and attenuation of the spectral absorption lines in the actinic flux density spectrum. Simulated spectra (in the wavelength range 320-340 nm) convoluted with 0.6 nm and 2.0 nm FWHM are shown in Figure 3.21a. This simulation is based on the data input of Case B and was calculated for a spectral resolution of 0.8 nm. The attenuation of the absorption lines
caused by the smoothing for a convolution with 2.0 nm FWHM is obvious. Hence, the integrated actinic flux density derived from the convoluted spectrum with a lower FWHM is lower than the integrated $F_a$ of the convoluted spectrum with a higher FWHM. In addition the smoothing of the atmospheric cutoff with increasing FWHM causes an increase of $J(O^1D)$. The impact of the spectral resolution on $J(O^1D)$ results from the artificial broadening of the spectral absorption lines. Even though the level of broadening strongly depends on the position of the wavelength grid. This broadening is shown in Figure 3.21b. The simulated spectra with resolutions of 0.1 nm and 1.0 nm plotted between 320 and 240 nm wavelength show different spectral courses. The broadening of the absorption lines leads to a decrease of the integrated actinic flux density.

Figure 3.21: (a) Actinic flux density spectra calculated for a spectral resolution of 0.2 nm and convoluted with FWHM of 0.6 nm and 2.0 nm. (b) Spectra simulated for spectral resolutions of 0.1 and 1.0 nm convoluted with FWHM = 0.2 nm. The simulation input corresponds to Case B.

The studies presented above have shown that a high-resolution spectrometer with a small FWHM is advantageous, particularly for $J(O^1D)$-determination due to the influence of the spectral absorption lines and the strong increase of radiation by several orders of magnitudes within a small wavelength range in the UV spectral range. With regard to the AFDM-PDA characteristics (FWHM $\approx$ 2.6 nm, $\Delta \lambda \approx$ 0.8 nm) the uncertainty of $J$-measurements is estimated with $\pm2\%$ depending on the studied gas and the atmospheric conditions.
3.4 \( J(0^1D) \) Parameterization

One of the most important photolysis frequencies is that of ozone, \( J(0^1D) \) (see Chapter 2.2.3). The wavelength range below 305 nm plays a significant role in the ozone photolysis (see Table 3.7). The AFDM-PDA is not capable to determine \( J(0^1D) \) without significant uncertainties. Therefore the missing portion due to the limited spectral range \( \varepsilon_{\lambda_c} \) is parameterized. \( \varepsilon_{\lambda_c} \) depends mainly on the position of the atmospheric cutoff which is introduced in the following Section 3.4.1. In addition, the \( \varepsilon_{\lambda_c} \)-sensitivity in terms of several parameters, e.g., temperature, TOC, SZA, and LWC is investigated in Section 3.4.2. A specific parameterization of \( \varepsilon_{\lambda_c} \) is presented for the AFDM-PDA with a threshold wavelength \( \lambda_c \) of 305 nm. This parameterization is generalized by the parameter \( \lambda_c \) to correct \( J(0^1D) \) also for other threshold wavelengths.

3.4.1 Atmospheric Cutoff

The atmospheric cutoff wavelength is determined by the increase of solar radiation over several orders of magnitudes around 300 nm wavelength. Below this spectral range the absorption of radiation by ozone serves as filter for high-energy radiation reaching the Earth surface.

The more the atmospheric cutoff is shifted toward higher wavelengths the smaller becomes \( \varepsilon_{\lambda_c} \), whereas the spectral position of the atmospheric cutoff is correlated with SZA and TOC, or the slant ozone column \( (S) \) which combines the TOC and SZA as follows:

\[
S = \text{TOC} \cdot \sec \theta \quad . \tag{3.28}
\]

In this work the position of the atmospheric cutoff wavelength \( \lambda_c \) is determined by the slope of the actinic flux density spectrum. Examplarily a modeled \( F_a \) spectrum calculated for TOC = 250 DU and SZA = 40° is displayed in a logarithmic plot (black line) in Figure 3.22. The wavelength region of strong increase of \( F_a \) over several orders of magnitude is shaded. In addition the dashed line represents the calculated slope of the logarithmic actinic flux density. The position of the atmospheric cutoff wavelength \( \lambda_c \) (black dot) complies with the wavelength position of the slope defined with:

\[
\text{slope} = \frac{\Delta \log F_a}{\Delta \lambda} \quad . \tag{3.29}
\]

reaching the threshold 0.04 (black horizontal line). This threshold was determined by the author and results from various simulations which studied the slopes of the actinic flux density in the spectral region of the atmospheric cutoff.

The position of \( \lambda_c \) is studied as a function of the SZA, TOC, and cloud cover. Figure 3.23a displays \( \lambda_c \) as a function of SZA for TOC = 260 (350) DU and two cloud cases: cloudless (black full circles and full triangles) and overcast (red open circles and open triangles).

In general the atmospheric cutoff wavelength increases with SZA. For SZA above 60° \( \lambda_c \) of the cloudless and overcast cases are different in particular for TOC = 260 DU. This correlation is also noticeable in Figure 3.23b which shows the atmospheric cutoff wavelength versus TOC. Obviously the increase of the atmospheric cutoff wavelength
3.4 \( J(\text{O}^1\text{D}) \) Parameterization

![Logarithmic plot of modeled spectral actinic flux density with TOC = 250 DU, SZA = 40° (black line). The dashed line represents the slope of logarithmic \( F_a \).](image1)

Figure 3.22: Logarithmic plot of modeled spectral actinic flux density with TOC = 250 DU, SZA = 40° (black line). The dashed line represents the slope of logarithmic \( F_a \).

![Atmospheric cutoff wavelength \( \lambda_c \) as a function of (a) SZA, (b) TOC and (c) slant ozone column for cloudless (gray) and overcast (black) condition.](image2)

Figure 3.23: Atmospheric cutoff wavelength \( \lambda_c \) as a function of (a) SZA, (b) TOC and (c) slant ozone column for cloudless (gray) and overcast (black) condition.

with TOC is considerably less distinctive than the SZA dependence. The dependence on the slant ozone column is plotted in Figure 3.23c and shows that the atmospheric cutoff wavelength increases with \( S \). The shift of the atmospheric cutoff is caused by the increasing ozone absorption for (i) large TOC, and (ii) large SZA because the light path through the atmosphere becomes longer.

### 3.4.2 Sensitivity Studies

In the following \( \varepsilon_{\lambda_c} \) depending on \( S \) and \( \lambda_G \) is calculated with respect to different atmospheric conditions e.g., pressure, temperature, aerosol, surface albedo, and LWC. \( \varepsilon_{\lambda_c} \) is calculated separately for the upwelling and downwelling actinic flux density. Table 3.8 summarizes the input for the model calculations. Each data set consists of calculations for a TOC between 250 and 350 DU in 10 DU steps and SZA values between 0 and 80° (10° steps), which results in 99 spectra for each altitude.
Table 3.8: Model input data. When cloud cover = 8, then a LWC profile measured at the INSPECTRO campaign is used with a cloud layer between 0.4 and 1.0 km. Calculations for the cloudy case are carried out for 4 different altitudes one above the layer (2 km), two within (0.6, 0.9 km) and one below (0 km).

The results are plotted in Figures 3.24a-h for a threshold wavelength of 305 nm according to the upper limit of AFDM-PDA reliable spectral range. Besides the variable parameter the other parameters were fixed for this study with $T = 12^\circ C$, TOC = 300 DU, LWC = 0 g/m$^3$, particle single-scattering albedo $\omega_o = 0.98$, asymmetry parameter $g = 0.75$, surface albedo="land". Temperature, SZA, TOC and consequently the slant ozone column (Figure 3.24 a-d) show a significant influence on the calculated $\varepsilon_{\lambda_{oc}}$-values. It is noticeable that the variation of $\varepsilon_{\lambda_{oc}}$ with SZA is more distinctive than the variation of $\varepsilon_{\lambda_{oc}}$ with TOC. The influence of the temperature is related to the dependence of the O$^1$D quantum yield on $T$ which leads to a lower $\varepsilon_{\lambda_{oc}}$ at high temperatures due to the spectral broadening of $\phi$ towards higher wavelengths. In addition $\varepsilon_{\lambda_{oc}}$ is plotted against the LWC based on measurements during a cloud penetration (Figure 3.24e). The results show a more or less constant course of $\varepsilon_{\lambda_{oc}}$. The variation of the particle single scattering albedo and the asymmetry parameter in Figures 3.24f and g have no influence on the calculated $\varepsilon_{\lambda_{oc}}$. Figure 3.24h displays the $\varepsilon_{\lambda_{oc}}$ dependence on the SZA for three types of surface albedos: snow covered surface, land, and sea surface. Obviously, the impact of the surface albedo is negligible. The $\varepsilon_{\lambda_{oc}}$ values for a snow covered surface (high albedo) deviates not more
than 3% from $\varepsilon_{\lambda_G}$ calculated for low albedo surfaces.

![Graphs showing various parameters vs. SZA, TOC, LWC, and asymmetry parameter](image)

Figure 3.24: Set of $\varepsilon_{\lambda_G}$-values (threshold wavelength = 305 nm) as a function of (a) SZA, (b) TOC, (c) slant total ozone, (d) temperature, (e) LWC, (f) particle single scattering albedo $\omega_0$, (g) asymmetry parameter $g$, and (h) surface albedo.

### 3.4.3 Parameterization for $\lambda_G = 305$ nm

The comparison between $\varepsilon_{\lambda_G}$-values calculated for the upwelling component and the downwelling component yields the same result. Hence all data of both components (about 3000
data points) are used to find a parameterization of \( \varepsilon_{\lambda_G} \) for \( \lambda_G = 305 \) nm of the form:
\[
\varepsilon_{305\,nm,\,para} = x_0 + S \cdot x_1 + S^2 \cdot x_2 + S^3 \cdot x_3 + S^4 \cdot x_4 + T \cdot x_5 + T^2 \cdot x_6
\]

(3.30)

with: \( T=\) temperature, \( S=\) slant ozone column.

The results of the parameterization are summarized in Table 3.9. The correlation coefficient is calculated to 0.992. Several combinations using less parameters were checked and resulted in correlation coefficients between 0.968 and 0.991.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Coefficient</th>
<th>Standard Error</th>
</tr>
</thead>
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<td>0.00652154</td>
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<td>( x_1 )</td>
<td>-0.005943</td>
<td>3.5766E-05</td>
</tr>
<tr>
<td>( x_2 )</td>
<td>7.4461E-06</td>
<td>6.2573E-08</td>
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<td>( x_3 )</td>
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<td>( x_4 )</td>
<td>7.478E-13</td>
<td>9.6874E-15</td>
</tr>
<tr>
<td>( x_5 )</td>
<td>-0.00192127</td>
<td>3.5427E-05</td>
</tr>
<tr>
<td>( x_6 )</td>
<td>6.5686E-06</td>
<td>1.8847E-06</td>
</tr>
</tbody>
</table>

Table 3.9: Coefficients of Eq. 3.30, which parameterized \( \varepsilon_{\lambda_G} \) for \( \lambda_G = 305 \) nm depending on SZA, TOC and \( T \).

### 3.4.4 Generalized Parameterization

The parameterization of \( \varepsilon_{\lambda_G} \) presented in Section 3.4.3 is valid for \( \lambda_G = 305 \) nm. For other threshold wavelengths this parameterization results in increasing uncertainties in \( J(O^1D) \) determination. Therefore it is necessary to find a generalized parameterization which includes the dependence of \( \lambda_G \). \( \varepsilon_{\lambda_G} \) were calculated with varying \( \lambda_G \) between 290 and 310 nm (1 nm step width) for all data sets given in Table 3.8.

The contour plot in Figure 3.25 displays the dependence of \( \varepsilon_{\lambda_G} \) on the threshold wavelength \( \lambda_G \) and the slant ozone column \( S \). Note that the scaling of \( \varepsilon_{\lambda_G} \) is not linear. Exemplarily \( \varepsilon_{\lambda_G} \) ranges between 1.6 and 1.04 in case of a threshold wavelength of 305 nm that complies with the lowest reliable threshold of the AFDM-PDA. Since an error of 5\% (\( \varepsilon_{\lambda_G}=1.05 \), thick line in Figure 3.25) \( J(O^1D) \) may be acceptable the determination of \( J(O^1D) \) with threshold wavelengths below 298 nm do not influence the \( J \)-value significantly. But with an increasing threshold wavelength \( \varepsilon_{\lambda_G} \) increases considerable in particular at low slant ozone columns which corresponds to low SZA. For the generalized parameterization of \( \varepsilon_{\lambda_G} \) Eq. 3.30 was extended to:
\[
\varepsilon_{\lambda_G,\,para} = x_{0,\lambda_G} + S \cdot x_{1,\lambda_G} + S^2 \cdot x_{2,\lambda_G} + S^3 \cdot x_{3,\lambda_G} + S^4 \cdot x_{4,\lambda_G} + T \cdot x_{5,\lambda_G} + T^2 \cdot x_{6,\lambda_G}
\]

(3.31)

with: \( T=\) temperature, \( S=\) slant ozone column.

The set of the coefficients \( x_{0,\lambda_G}, \ldots, x_{6,\lambda_G} \) is parameterized as a function of the threshold wavelength \( \lambda_G \). The results of the 5th order polynomial fit:
\[
x_{j,\lambda_G} = \sum_{i=0}^{5} a_i \cdot \lambda_G^i
\]

(3.32)
Figure 3.25: Contour plot of $\varepsilon_{\lambda G}$ as a function of slant ozone column $S$ and threshold wavelength $\lambda_G$ for downwelling actinic flux density. The thick line represents a $\varepsilon_{\lambda G}$ of 1.05.

are summarized in Table 3.10 with $j = 0...6$ and $\lambda_G$=threshold wavelength. The coefficients of determination $R^2$ are 0.99.

The coefficients $a_i$ in Eq. 3.32 are tested against the $\varepsilon_{\lambda G}$ derived from the model calculation. The ratio of "true" $\varepsilon_{\lambda G}$ and parameterized $\varepsilon_{\lambda G,\text{para}}$ complies with the ratio of "true" $J(\text{O}^1\text{D})$ and parameterized $J(\text{O}^1\text{D})_{\text{para}}$. Figure 3.26 displays the frequency plot of the ratio of "true" $\varepsilon_{\lambda}$ versus parameterized $\varepsilon_{\lambda G,\text{para}}$ in 2% bins. The distribution shows a nearly symmetric characteristic with a mean value of 1.00±0.03.

Figure 3.26: Frequency plot of the ratio of "true" $\varepsilon_{\lambda G}$ versus parameterized $\varepsilon_{\lambda G}$

The plot of $\varepsilon_{\lambda G}$ versus $\varepsilon_{\lambda G,\text{para}}$ (Figure 3.27) indicates the uncertainty of the parameteri-
3 Actinic Flux Density Meter (AFDM) - Photodiode Array (PDA) Detector

<table>
<thead>
<tr>
<th>(x_0, \lambda_G)</th>
<th>(x_1, \lambda_G)</th>
<th>(x_2, \lambda_G)</th>
<th>(x_3, \lambda_G)</th>
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<tr>
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<td>4.7405007890E+00</td>
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</tr>
<tr>
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<td>4.1050416471E+01</td>
<td>-5.2738442782E-02</td>
<td>2.9046984901E-05</td>
</tr>
<tr>
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<td>1.7275983349E-04</td>
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<td>(a_3) 8.0758872798E-03</td>
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</tr>
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<td>(a_4) -2.6861585063E-04</td>
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<td>-1.0897318622E-09</td>
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<td>(a_5) 3.5320160863E-07</td>
<td>-1.1165498119E-09</td>
<td>1.4308135120E-12</td>
<td>-7.8673630485E-16</td>
</tr>
</tbody>
</table>

Table 3.10: Coefficients of Equation 3.32

tion. Despite a value of \(R^2 = 0.99\) the scatterplot displays significant deviations of \(\varepsilon_{\lambda_G, \text{para}}\) particularly for high \(\varepsilon_{\lambda_G}\)-values. It means that the uncertainty of the method increases with increasing threshold wavelength. Generally \(\varepsilon_{\lambda_G}\) and \(\varepsilon_{\lambda_G, \text{para}}\) agree quite well up to 304 nm threshold wavelength within a \(\pm 2\%\) error range.

The parameterization provides the opportunity to determine \(J(O^1D)\)-values with instruments that have a limited accuracy within 290 and 310 nm wavelength. It was shown that even a calculation of \(J(O^1D)\) with a threshold wavelength=298 nm is possible without any parameterization during adequate atmospheric conditions within a tolerable 5\% error range. The agreement of \(\varepsilon_{\lambda_G}\) and \(\varepsilon_{\lambda_G, \text{para}}\) for all cases is acceptable with a mean \(\varepsilon_{\lambda_G}/\varepsilon_{\lambda_G, \text{para}} = 1.00 \pm 0.03\). However, the uncertainty of this method increases with (i) increasing threshold wavelengths, and (ii) low temperatures linked with a large SZA and a high TOC. Up to now the ability of the parameterization was tested against modeled spectra and a modeled atmosphere. In the following Section the method is applied to measurements in real atmospheric conditions.

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Figure 3.27: Scatterplot of $\varepsilon_{\lambda G}$ versus parameterized $\varepsilon_{\lambda G, \text{para}}$. Individual dots depict every 10th pair of $(\varepsilon_{\lambda G}, \varepsilon_{\lambda G, \text{para}})$.

### 3.4.5 Experimental Test of the $J(O_1D)$ Parameterization

Ground-based measurements of actinic flux densities using the AFDM-PDA and a double monochromator system were performed on Marshall Field near Boulder, Colorado in collaboration with the radiation group of the National Center of Atmospheric Research (NCAR). During a three-month visit funded by NCAR, several spectrometer systems were characterized in the laboratory and compared in the field. Among others, a double monochromator spectrometer called Scanning Actinic Flux Spectroradiometer (SAFS) owned by NCAR participated. It was described in Shetter and Müller (1999); Shetter et al. (2003a); Lefer et al. (2001). The SAFS instrument is usually deployed on aircraft and participated in the International Photolysis frequency Measurement and Model Intercomparison (IPMMI) conducted at Marshall Field in 1998 (Cantrell et al., 2003; Bais et al., 2003; Shetter et al., 2003b). The main components of the SAFS are an optical inlet, a UV optical fiber bundle, a double monochromator, and a photomultiplier tube with a four-channel signal amplifier. The FWHM of the double monochromator is 1.0 nm. The acquisition time for a 280 nm to 420 nm spectrum is 10 seconds wavelengths steps of 1.0 nm. A measurement uncertainty of ±6% in the UV-B and ±4.8% in the UV-A was estimated in Shetter and Müller (1999).

The absolute calibration of the AFDM-PDA and the SAFS were performed using a 1000 W NIST (National Institute of Standards and Technology) traceable quartz-tungsten-halogen lamps. Drifts in the instrument sensitivity were checked during the intercomparison using a set of 250 W transfer calibration lamps.

The optical inlets of the spectrometer were mounted on the roof of a container shown in Figure 3.28. Measurements were taken on several days in September 2003. The photolysis frequencies of ozone were determined using the absorption cross section of Daudmont et al. (1992). Quantum yield data were taken from the JPL report 2003 (Sander...
et al., 2003) based on Matsumi et al. (2002). Compared to the SAFS, the AFDM-PDA measured actinic flux density spectra with a higher time resolution of 300 ms. For this reason averaged spectra of 10 seconds were calculated. From these spectra $J(O^1D)$-values were derived by means of the parameterization method which was applied for a threshold wavelength of 305 nm. $J(O^1D)$-values of the SAFS were provided by NCAR. They used the same quantum yield. The absorption cross section data stem from the recommendation by the IUPAC (Atkinson et al., 1999) which are based on the data of Molina and Molina (1986). Uncertainties of $J(O^1D)$ which are determined with $\sigma$ given by Molina and Molina (1986) and Daumont et al. (1992) are negligible as shown by Cantrell et al. (2003). They calculated $J(O^1D)$ for different SZA and obtained ratios of 0.994. However, differences in the application of the integration method to derive $J$-values after Eq. 2.7 may lead to uncertainties in the results. In addition the different wavelength resolutions of both spectrometers are a source of uncertainty with respect to the integration of $F_a(\lambda)$.

Examples of a diurnal pattern of $J(O^1D)$ derived from AFDM-PDA and SAFS measurements are displayed in Figure 3.29 for three days. A minimum value of SZA of 35° occurred around 13:00 local time (solid lines). On these days TOC ranged between 266 DU and 277 DU. Clear sky conditions were observed in the morning of all days, whereas some cumulus clouds influenced the diurnal pattern of $J(O^1D)$ in the afternoon of day 030901 and 030905. The diurnal pattern of day 030904 shows a lack of data around noon. The ratios between $J(O^1D)$ derived from the AFDM-PDA and the SAFS of each day are plotted in Figure 3.29b, d, and f. The range of $\pm10\%$ is marked by a gray area. In general a good agreement was found within the $\pm10\%$ range. For a SZA $>70^\circ$ the parameterization method leads to $J(O^1D)$-values which are out of $+10\%$ deviation. In addition a decrease of the ratio is noticed in the course of the day.

This slope is not observed in the diurnal pattern of the $J(NO_2)$ ratio (see Figure 3.30b). $J(NO_2)$ was determined using the molecule data recommended by JPL 2003 (Sander et al., 2003). The agreement of the SAFS and AFDM-PDA results is within the $\pm10\%$ range during clear sky conditions. In contrast to $J(O^1D)$ the different sample times of both spectrometers lead to a significant differences in cloudy conditions as shown in Figure 3.30b around 15:00 local time. Due to the fact that the decrease of the ratio is not observed in the $J(NO_2)$ values this decrease is not explainable by possible obstacle effects. Solely the optical inlets which were mounted in a distance of about 50 cm may have a slight effect on the field of view. However, a slope of the ratio is not explainable by this effect.

The daily variation of the TOC may influence the results of the parameterization. A
3.4 \( J(O^1D) \) Parameterization

Figure 3.29: Diurnal pattern of \( J(O^1D) \) derived from AFDM-PDA and SAFS spectrometer measurements for three days. The ratios of the \( J(O^1D) \)-values are plotted in (b), (d) and (f). In addition the SZA is shown and gray area marks a ratio of \( pm1.10 \).

decrease of the ratio corresponds to decreasing \( J(O^1D) \)-values derived from the AFDM-PDA, which may caused by an undersized correction factor \( \varepsilon_{\lambda_{G}} \). This correction factor may result from a higher assumed TOC (taken from TOMS data) than the actual one. The overpass of the satellite which measures the TOC was around 11:00 local time. A typical diurnal pattern of TOC shows a maximum in the afternoon under clear sky conditions. For this reason the measured TOC does not correspond to the maximum TOC reached on the day, and the correction factor \( \varepsilon_{\lambda_{G}} \) is not undersized. In addition a variation of the TOC with a maximum in the afternoon does not cause a systematic decrease of the \( J(O^1D) \)-ratio. A variation of 10 DU would yield an \( \varepsilon_{\lambda_{G}} \) uncertainty of 3% which is lower than the 10% decrease of the ratio in the course of the day (for SZA<70°). Consequently uncertainties in the assumed TOC can partly explain the decrease. A comparison of actinic flux densities measured with both spectrometers may be necessary to investigate the slope.

In the following the parameterization method is applied for several threshold wavelengths \( \lambda_{G} \) in the range between 305 nm and 310 nm on the actinic flux densities measured on day 030901 for SZA<70°. Figure 3.31a shows a scatterplot of the \( J(O^1D)_{SAPS} \) versus
Figure 3.30: Same as Figure 3.29 for $J(\text{NO}_2)$ (day 030901).

$J(\text{O}^1\text{D})_{AFDM-PDA}$, whereby the $J(\text{O}^1\text{D})_{AFDM-PDA}$ data stem from the parameterization for $\lambda_G=305$ nm, 307 nm, 308 nm, and 310 nm. The black solid line represents an ideal agreement. The deviation from the solid line is lowest for $\lambda_G = 305$ nm. For higher threshold wavelengths the slope of the regression lines decreases, as shown in Table 3.11. From this it follows that the ratio $J(\text{O}^1\text{D})_{AFDM-PDA}/J(\text{O}^1\text{D})_{SAFS}$ increases with increasing $J(\text{O}^1\text{D})$. This is also shown in the frequency plots of the $J(\text{O}^1\text{D})$-ratio in Figure 3.31b. The frequency distribution of the ratios do not show a symmetric characteristic resulting from the diurnal pattern of the ratio (see Figures 3.29b, d, f). A drift of the maximum to higher ratios is noticed for an increasing $\lambda_G$. Furthermore the distribution for $\lambda_G$ exhibits the largest broadness compared to lower threshold wavelengths. However, the parameterized $J(\text{O}^1\text{D})$-values for $\lambda_G > 306$ nm do not show significant differences (see Figure 3.31b).

In general the parameterization method to derive $J(\text{O}^1\text{D})$ has proven to work under atmospheric conditions. The method is limited to SZA lower than 70°. The uncertainty of the method increases with the threshold wavelength. For higher $\lambda_G$ the parameterized $J(\text{O}^1\text{D})$-values seem to be underestimated in particular for low SZA. For this cases the correction factors $\varepsilon_{\lambda_G,\text{param}}$ are in the range of four.

<table>
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<tr>
<th>$\lambda_G$</th>
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<th>306 nm</th>
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</tbody>
</table>

Table 3.11: Slope of the regression lines in scatterplot 3.31a for different threshold wavelengths $\lambda_G$. 

3 Actinic Flux Density Meter (AFDM) - Photodiode Array (PDA) Detector
Figure 3.31: (a) Scatterplot of $J(O^1D)_{SAFS}$ versus $J(O^1D)_{AFDM-PDA}$. The single dots depict every 50th pair of the correlation. The black line represents the 1:1 curve. (b) Frequency plot of the ratio of $J(O^1D)_{AFDM-PDA}$ versus $J(O^1D)_{SAFS}$. 
4 Actinic Flux Density Meter (AFDM)  
- Charge Coupled Device (CCD) Detector

4.1 General Description

The first part of the work presented a new and fast airborne system to measure upwelling and downwelling actinic flux densities in the range between 305 nm and 700 nm with an uncertainty of ± 8% in the UV spectral range and ± 4.9% in the VIS spectral range. Various photolysis frequencies as \( J(\text{NO}_2) \), \( J(\text{H}_2\text{O}_2) \), \( J(\text{HCHO}) \), or \( J(\text{NO}_3) \) can be directly derived from the AFDM-PDA measurements. Also \( J(\text{O}^1\text{D}) \)-values, which are among the most crucial photolysis frequencies, can be derived from AFDM-PDA measurements using a parameterization method. However, measurements of the actinic flux density below 305 nm is not possible within an acceptable range of uncertainty due to low sensitivities of the photodiodes in the UV-B and a high stray light contribution. The aim of the second part was to revise the AFDM with a new detector unit with a higher sensitivity in the UV-B spectral range. Upwelling radiation is measured with the AFDM-PDA further on. The downwelling measurement unit is equipped with a new spectrometer and a modified optical inlet. The following sections describe the main improvements of the AFDM and discuss its characterization.

4.1.1 Optical Inlet

The optical inlet \( A_d \) used in the AFDM-PDA setup is additionally equipped with a band-pass filter (UG5) which reduces the sensitivity mainly in the visible spectral range. The UG5 transmission ranges from 89% at wavelengths around 350 nm to 0.7% at 580 nm. The new CCD has a sensitivity (maximum in VIS range) which is one order of magnitude higher than the PDA detector. That would lead to a fast saturation of the detector in the VIS range even during measurements with low integration times (20 ms). Hence, the main purpose of this bandpass filter is the adjustment of the sensitivity considering the whole wavelength range with respect to the available solar radiation. The influence of the filter on the AFDM capability by decreasing the sensitivity within the VIS range is not crucial. The second advantage using the UG5 filter is the reduction of stray light which originates from larger wavelengths. The spectrometer of the revised AFDM includes a Charge Coupled Device (CCD) detector.
4.1.2 Spectrometer - CCD

The CCD is a two-dimensional matrix of photodiodes (532 x 64 pixel) which covers a wavelength range of about 260-680 nm. A higher sensitivity improves the ability of UV measurements. Figure 4.1 shows the schematic picture of the MCS-CCD. The module consists of a spectrometer body with a flat field grating (248 lines/mm), which is blazed at 250 nm, a fiber cross section converter with SMA connector and 20 μm entrance slit in order that the FWHM is reduced compared to that of the AFDM-PDA (70 μm entrance slit). Furthermore the CCD detector of Hamamatsu is thermoelectrically cooled by a Peltier element to reduce the noise of the signals and to improve the d-e current temporal stability. The condition for such a cooling is a dry environment within the spectrometer body, particularly for windowless spectrometer systems which have the main advantage of a reduced stray light signal compared to detectors with window. Hence, the spectrometer body is sealed after flushing with CO₂. The preamplifier is integrated in the spectrometer housing. The remaining operating electronics (Front End Electronics and cooling electronics) is mounted in an additional housing. A picture of the AFDM-CCD system shows Figure 4.2.

Figure 4.1: Sketch of the MCS-CCD module used in the AFDM-CCD version (after Zeiss).

Figure 4.2: Picture of the AFDM-CCD. Left housing (A) includes the electronics, the right one (B) the spectrometer which is connected via an optical fiber (C) with the optical inlet (D).

The CCD consists of an array of photodiodes that are connected with each other (line
by line and column by column). Thereby charges can be shifted from pixel to pixel (see Figure 4.3). CCDs are array detectors with metal-oxide-capacitors. During the illumination a charge (electron-hole pair) connected with a voltage is initiated. The read out algorithm is slightly different from the PDA due to the additional dimension of the CCD array. The charges of each column are pixelwise shifted to a register on the edge parallel to the light collecting rows. This process of summing the charge is called vertical binning. The charge in the register is moved horizontally by one pixel, so that the charge on the endmost pixel of the register is moved into the amplifier. After the signal amplification by a analog-digital-converter the charges are converted into electrical signals.

![Figure 4.3: Sketch of the CCD detector.](image)

Table 4.1 summarizes the main technical differences between the AFDM-PDA and AFDM-CCD.

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<thead>
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<th>AFDM-CCD</th>
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<td>-</td>
<td>UG5</td>
</tr>
</tbody>
</table>

Table 4.1: Comparison between AFDM-PDA and AFDM-CCD

### 4.1.3 Offset

**Dark Current and Electronic Noise** The treatment of the AFDM-CCD offset is more delicate than that of the AFDM-PDA. The integration time dependence of the d+e current is shown for different wavelengths (300 nm, 400 nm, 500 nm, 600 nm) in Figure 4.4a. The linear regressions of the d+e current (given with: d+e current = integration time ·
dark current + electronic offset) are used to determine the electronic offset. The spectral electronic offset corresponds to the extrapolated value of the linear regression lines at an integration time of 0 ms. Wavelength-averaged value of 1970 counts with a standard deviation $\sigma_y = 3$ counts was calculated which means a spectral variability of <1%. After subtracting the electronic offset from the d+e current a dark current remains which is wavelength-dependent and shows a strong pixel-to-pixel variation (see Figure 4.4b). The spectral variability of the dark current ($\approx 7\%$) is higher than that of the electronic offset. To determine the spectral variability of the overall offset the sum of electronic offset and dark current is crucial. In this case a spectral variability of 3% was calculated for the wavelength averaged d+e current measured for an integration time of 1000 ms (AFDM-PDA $\sigma < 1\%$). In contrast to the AFDM-PDA the wavelength dependence is not negligible.

![Figure 4.4(a)](image)

![Figure 4.4(b)](image)

Figure 4.4: (a) Integration time dependence of the d+e current plotted for different wavelengths. The error bars indicate the standard deviation of the averaged spectra (average of 1000 single spectra). (b) Dark current plotted as a function of wavelength for four integration times (60 ms, 100 ms, 200 ms, and 300 ms).

Consequently, the dark measurement offset must be considered in a different way compared to the AFDM-PDA offset. The assumption of a wavelength-independent offset would lead to uncertainties. The temporal stability of the offset is warranted due to the cooling of the CCD-system which was checked with d+e measurements for different temperatures in the laboratory. There are two possibilities to consider the wavelength-dependence. The first one requires spectral dark measurements for every integration time which is subtracted from each measured spectrum. The second possibility uses a 100 ms dark current multiplied by the integration time ratio. Finally, the measured spectrum is subtracted by the sum of the revised dark current and the electronic noise. During the field campaign INSPECTRO-2 the first method was applied. D+e measurements were performed before and after each flight for different integration times which were used...
during the flight. A deviation of the d+e currents (for each integration time) in the range of <1% was observed in the whole course of the campaign.

**Stray Light** Stray light measurements were performed under atmospheric conditions on the roof of IfT and in the laboratory. Atmospheric measurements of the stray light contribution have the advantage that the spectral course of the stray light is measured in real conditions. Furthermore the atmosphere itself serves as filter below the atmospheric cutoff. A comparison with laboratory measurements would expose a dependence of the spectral course of the stray light on the radiation source.

Long wave pass filters (320 nm, 380 nm, 500 nm, 700 nm) were used to determine the contribution of the stray light. Figure 4.5a shows the spectral stray light measurements derived from data with different long wave pass filters. Additionally the sun spectra is displayed. As long as the light source is the sun and the atmosphere serves as a long wave pass filter with a cutoff wavelength about 290 nm, the stray light of a measured sun spectra agrees with the signal measured between 270 and 290 nm after offset subraction. In this wavelength range the stray light in this spectral range should be the same for all measurements independent of the filter. However, a difference is noticeable in particular between the sun spectrum and spectra measured with filter \( \lambda_c = 380 \text{ nm}, 500 \text{ nm} \) and 700 nm. This problem has two causes. (i) First, the measured signal using a filter results in a generally lower signal due to the decrease of the transmission ability of the filter even in the spectral range higher than \( \lambda_c \). (ii) The broader the filter range is, the more the integrated signal decreases. It is quite evident that lower signals causes lower stray light. Therefore the stray light of the filter spectrum measurement is diminished compared to the stray light signal of the solar spectrum.

For a better comparision the filter spectra are scaled to the solar spectrum so that the spectra are in agreement within the spectral range where the cutoff filters don not block the solar radiation. The fraction of each filter spectrum on the solar spectrum is plotted in Figure 4.5b. The stray light signal impacts the total signal mainly in the UV spectral range below 315 nm. Between 315 and 520 nm the stray light contribution is less than 1%. Above 520 nm it increases again to 10% due to the decreased sensitivity of the AFDM-CCD in this range (see Section 4.2.2). The measurement using the filter with \( \lambda_c = 700 \text{ nm} \) shows the wavelength-dependence of the stray light signal. Therefore the influence of the stray light contribution on photolysis frequencies is studied for three different approaches of its correction. The first method (A) determines the stray light contribution by averaging the signal offset between 270 and 290 nm. Thus method A assumes a spectrally constant stray light contribution. The second approach (B) defines a wavelength-dependent stray light signal. For that purpose the stray light measurement with \( \lambda_c = 700 \text{ nm} \) is used as a reference stray light spectrum. It is scaled to the stray light signal determined between 270 and 290 nm. Method C does not correct the stray light at all.

Figure 4.6a displays a time series of \( J(O^1D) \) measurements with the AFDM-CCD using these three stray light correction methods. The measurements stem from the INSPECTRO 2 - campaign conducted in Straubing, Germany. The spectral downwelling actinic
flux densities measured with 100 ms integration time (afterwards averaged over 3 seconds) were performed on the ground at SZA between 33° and 35°. The variations of $J(O_1 D)$ are caused by the influence of clouds during the course of the measurements. $J(O_1 D)$ calculated with method B differs only slightly from $J(O_1 D)$ obtained by method A. Figure 4.6b shows a mean ratio between the two methods of less than 0.98 (solid line with triangles) which means a deviation of < 2%. As Figure 4.5 has shown the stray light signal between 270 and 320 nm decreases by about 30%. Calculating an averaged signal between 270 and 290 nm consequently leads to a higher mean stray light signal than it would arise between 290 and 320 nm wavelength. For this reason the approach of a constant stray light signal leads to a slight decrease of the spectral actinic flux density due to the increased stray light signal within the responsible $J(O_1 D)$ spectral range. The comparison of method B and method C shows a significant difference in the $J(O_1 D)$-values. An overestimation of +11% is noticed when the Sun was not covered by clouds. For lower actinic flux densities the influence of the stray light decreases as it is deducible from the decrease of the ratio between method A and method B during the period of a covered sun disk displayed in Figure 4.6b. The methods were also tested for the determination of NO2 photolysis frequencies. All three methods yield the same $J(NO_2)$-values, because the contribution of the stray light on the overall signal is less than 1% above 315 nm wavelength, and the responsible spectral range for $J(NO_2)$ measurements is between 300 and 420 nm. In terms of the negligible deviation between $J(O_1 D)$ determined with method A and B it does not seem necessary to consider the stray light as wavelength-dependent. The comparison between the spectral actinic flux densities derived with both methods shows deviations below 310 nm (up to 15%) and around 580 nm wavelength (2%) displayed in Figure 4.7. The reason of the distinct deviation below 310 nm is the decrease of the
Figure 4.6: (a) Time series of $J(O^1D)$-values measured with the AFDM-CCD using three methods of stray light correction. Method A: constant stray light signals, method B: wavelength-dependent stray light signals, and method C: no stray light correction. (b) Ratio of method C and method B as well as ratio of method A and method B.

spectral stray light signals up to 320 nm. The assumption of constant stray light which neglects this slope yields larger stray light signals. For this reason the wavelength dependence of the stray light is not negligible with regard to $F_a$.

Figure 4.7: Spectral ratio of measured $F_a$ evaluated with method A and method B.

The variation of the spectral stray light structure was studied in the laboratory. Generally a lamp spectrum differs significantly from the solar spectrum. Therefore one would expect a change in the stray light structure if it were influenced by the spectrum of the radiation source. The 1000 W standard irradiance was placed as close as possible in front of the optical inlet of the AFDM-CCD. The INSPECTRO 2 spectra were evaluated with the stray light distributions measured in the laboratory and were compared with spectra analyzed with the stray light spectrum obtained from the atmospheric measurement. A difference of ±3% was derived mainly in the first nm of the actinic flux density spectrum. For wavelengths above 304 nm the difference decreases to less than 1%. In addition $J(O^1D)$-values calculated with both stray light distributions were compared. Here an overall difference of less than 2% was obtained which justifies the use of a predefined stray light spectrum from the laboratory for the data evaluation.
Signal to Noise Ratio $SNR$ The signal-to-noise-ratio is quantified for integration times between 5 ms and 300 ms. Different from the AFDM-PDA the standard deviation $\sigma_Y$ of the CCD measurements depends on the integration time as shown in Figure 4.8a. 1000 d+e measurements for each integration times are averaged, and afterwards the mean spectrum is averaged over all wavelengths. The error of the latter calculation is considered by the standard deviation and marked by the vertical bars within the Figure 4.8a. The integration time-dependence of $\sigma_Y$ has an effect on the $SNR$. The $SNR$ of the AFDM-CCD decreases with integration time (see Figure 4.8b) which is different from the $SNR$ behaviour of the AFDM-PDA (see Figure 3.7b).

![Figure 4.8](a) Correlation between standard deviation of mean signal and integration time. Vertical error bars indicate the standard deviation of the wavelength average. (b) $SNR$ dependence on integration time.

A calculation of $NEI$ is not well-defined due to the variation of $\sigma_Y$. Figure 4.9 displays calculated $NEI$ for two assumed $\sigma_Y$ (3 counts, 5 counts). The range of the detection limit is increased compared to $NEI$ of the AFDM-PDA system. The main reason of this feature is the use of the UG5 filter in the optical inlet which leads to a very low sensitivity within the VIS spectral range. In the UV-B range an improvement of the $NEI$ is achieved by an order of one magnitude independent from the chosen $\sigma_Y$.

4.2 Calibration and Data Processing

4.2.1 Spectral Calibration

Similar to Section 3.2.1 spectral emission lamps are used to define the FWHM and the pixel-wavelength assignment of the spectrometer. The Hg(Ar) and Neon lamp measurements approved the assignment given by the manufacturer Zeiss. A polynomial fit (Eq. 3.3) assigns a particular pixel to a wavelength of the AFDM-CCD system with the following parameters: $b_0 = 260.377$, $b_1 = 0.803854$, $b_2 = -2.84802E-06$, and $b_3 = -1.67086E-08$. The 532 pixels conform to a wavelength range between 260 and 680 nm with a pixel
Figure 4.9: Wavelength-dependent detection limit $NEI$ of the AFDM-CCD calculated for two different standard deviations (3 counts, 5 counts).

distance of 0.8 nm. The reliable wavelength range is quoted by Zeiss with 273 to 677 nm. Due to the 20 $\mu$m entrance slit the FWHM is decreased to 1.53±0.21 nm. This alone improves the $J$(O$^1D$) accuracy to 2-4% (see Fig. 3.20) compared to the AFDM-PDA accuracy.

4.2.2 Absolute Calibration

The absolute calibration of AFDM-CCD is performed with a 1000 W standard irradiance as described in Chapter 3.2. To improve the calibration accuracy the procedure is carried out with two calibration distances: The first set of measurements in the calibration distance of 700 mm as given in the lamp manual and a second set in a closer distance (≈ 400 mm) between lamp and optical inlet. The latter one increases the signal magnitude, which helps to improve the accuracy of the sensitivity measurement in particular in the low-sensitive spectral region of the CCD. Each set of measurements consists of a series of lamp scans $I_{lamp}(\lambda)$, filter scans with a long wave pass filter F320, and d+e measurement $I_{d+e}(\lambda)$. The stray light signal $I_{SL}(\lambda)$ is derived from the difference of filter signals and d+e measurement. As shown previously the stray light is slightly wavelength-dependent. Thus the F320 filter measurement serves as a reference signal to scale the F700 filter measurement to the stray light level which is derived between 270 and 305 nm wavelength using long wave pass filter F320. The spectral direct signal calculated with:

$$I_{dir}(\lambda) = I_{lamp}(\lambda) - I_{d+e}(\lambda) - I_{SL}(\lambda)$$

is determined for both distances. In this way a scaling factor is derived which links the measurements of "near" and "far" calibration. The factor is calculated by dividing the direct signals for each pixel. In theory the ratio should be constant and independent of wavelength. But due to the low sensitivity in particular below 320 nm and above 520 nm the measured scaling factor is noisy. Hence the final scaling factor is determined by measurements between 370 and 430 nm wavelength. Now the scaling factor enables a
conversion of the "near" direct signals to direct signals at the 700 mm distance. Finally, the revised "far" signals are used to determine the calibration factors using Eq. 3.5. The calibration factors are displayed in Figure 4.10. A large calibration factor means a low sensitivity. Comparing the spectral courses of the PDA- and CCD-sensitivity a clear difference becomes obvious. The sensitivity of each AFDM system reflects not only the sensitivity of the spectrometer itself, it also includes the transmittance characteristic of the optical inlet and the optical fiber. In this way the different spectral courses of the PDA- and CCD-sensitivities can partly be explained by the transmittance characteristic of the optical inlet. As discussed in Section 4.1.1 the optical inlet of the AFDM-CCD is equipped with a bandpass filter. An optical inlet without filter would increase the sensitivity by two magnitudes around 600 nm wavelength. With regard to the determination of $J(O_1^1D)$ the range between 290 nm and 320 nm is important. There a clear improvement of the AFDM-CCD sensitivity by at least one order of magnitude is noticeable.

![Figure 4.10: Calibration factors of the AFDM-PDA, AFDM-PDA, and AFDM-CCD spectrometer.](image)

**Measurement Uncertainties** The calibration uncertainties are similar to that of the AFDM-PDA version, with a total uncertainty of 8.0% in the UV-range and 4.9% in the VIS spectral range. Comparisons with precise double monochromator measurements (see Section 5.1.2) have shown that the reliable spectral range of the AFDM-CCD was improved in the UV range. In contrast to the AFDM-PDA which had a reliable spectral range above 305 nm, the new system provides reliable results above 300 nm. With regard to photolysis frequencies the AFDM-CCD the parameterization method needs not to be applied. An uncertainty caused by this parameterization was given with 5%. The assumption of a wavelength-independent straylight results in an uncertainty of 2% with respect to $J(O_1^1D)$. In contrast, $J(NO_2)$ is not affected by this assumption.
4.2.3 Data Evaluation

The data evaluation of the AFDM-CCD measurements is similar to the procedure described in Section 3.2.4 for the AFDM-PDA. The main difference is the treatment of the offset. As discussed in Section 4.1.3 and 4.1.3, the offset of the AFDM-CCD is wavelength-dependent. For each spectrum the offset must be subtracted which is measured after each flight by a measurement. The stray light spectrum is determined by scaling a predefined spectral stray light distribution (atmospheric stray light measurement with $\lambda_c = 700$ nm). The measured signals between 270 and 290 nm are averaged and compared to the average of the predefined spectral stray light spectrum calculated for the same wavelength range. By applying the scaling factor (ratio of both averages) the current stray light spectrum is derived which is subtracted from the signals, so that the offset is completely removed from the measurement.

To improve the quality of the measurement the starting point of the spectrum, the lowest $\lambda$, is defined by the slope of the spectrum. Using a fixed starting wavelength, uncertainties may arise mainly for measurements at large SZA. Low signals at low sun and a limited detection capability due to noise (see Section 4.1.3) can lead to an overestimation of the actinic flux density in the UV-B range (see Figure 4.11). The gray curve in Figure 4.11 illustrates the actinic flux density defined by a dynamic start wavelength. The dashed black line represents a spectrum which is determined by the subtraction of the d+e current and stray light signal using a fixed start wavelength of e.g., 290 nm. The overestimation of the actinic flux density using a fixed wavelength start affects the determination of photolysis frequencies, mainly $J(O_3)$, and leads to an overestimation of $J$-values.

![Figure 4.11: Actinic flux density spectra determined by a fixed start wavelength (290 nm, black curve) and a flexible starting point (gray curve).](image)

The capability of the AFDM-CCD is discussed in the following chapter. In the beginning of Chapter 5 an intercomparison between the AFDM-CCD and several other double- and single monochromator systems is presented.
5 Measurement Examples

This chapter presents airborne measurement examples of the AFDM-PDA and AFDM-CCD system for clear sky and boundary layer cloud conditions and investigates the impact of surface and cloud top albedo, aerosol and cloud inhomogeneities on the measured actinic flux densities and photolysis frequencies. At the beginning the results of an intercomparison between several spectrometer systems are shown.

5.1 Intercomparison of Actinic Radiation Measurements

5.1.1 Overview

As part of the INSPECTRO-2 campaign an instrumental intercomparison of actinic flux density measurements was performed with high precision double monochromators, photodiode array instruments and the AFDM-CCD (Thiel et al., 2005). Irradiance and actinic flux density spectrometers were placed on the airport of Straubing as shown in Figure 5.1. Here measurements of two Bentham Double Tripplegrating Monochromator (DTM) 300

![Image](image-url)

Figure 5.1: Intercomparison of various spectrometers during INSPECTRO-2.

instruments and three photodiode array instruments are compared to measurements of the AFDM-CCD which was installed on the aircraft. The instruments are summarized in Table 5.1. Both Bentham DTM 300 instruments scanned one spectrum within 21 minutes with 0.5 nm resolution between 290 and 500 nm, which means 3 seconds per 0.5 nm step. The PDA instruments and the AFDM-CCD measured actinic flux density spectra with higher time resolution. Exemplarily the DEM and DED instrument yielded one spectrum within 10 seconds, the AFDM-CCD measured with 200 ms integration time. The spectra of the AFDM-CCD were averaged over a period of 3 s according to the stepwise of the
double monochromator scanning series. Hence over 400 AFDM-CCD spectra were taken during these 21 minutes. PDA and AFDM-CCD spectra were converted to 0.5 nm wavelength steps. For a comparison artificial spectra of the PDA’s and the AFDM-CCD were generated. For each time given for each wavelength step of the double monochromator a syncing AFDM-CCD (PDA) spectral actinic flux density was selected. It requires an exact time synchronisation of all instruments, particularly for fast changing atmospheric conditions. During the intercomparison the sky coverage was mainly more than 6 octa with periods of rain. Therefore some uncertainties due to the insufficient time synchronisation has to be considered in the data interpretation. In addition the different FWHM of all instruments ranging from 0.64 to 2.5 nm were considered by using the SHICRIVM algorithm (Slaper et al., 1995) to homogenize all spectra to a FWHM of 1 nm. One actinic flux density spectrum was taken per hour by the double monochromator during the intercomparison. Finally, 32 spectra taken on five days were used for the in the following comparison of actinic flux density spectra and photolysis frequencies.

### 5.1.2 Actinic Flux Densities

First, single actinic flux density spectra are compared. Exemplarily $E_a(\lambda)$ are plotted for a small and large SZA in Figures 5.2a and b. Figure 5.2a shows the artificial spectra of the PDA spectrometers, the AFDM-CCD as well as the ATI and GBM spectrum in a logarithmic plot measured on day 040506 (10:30 - 10:51 a.m.) at SZA = 33°. The spectral range is between 298 and 310 nm considering the most critical range. For longer wavelengths all results agree within a ±10% range. The double monochromator spectra are considered as the measurement with the lowest uncertainty in the UV-B spectral range due to their high quality of stray light rejection. The start wavelength of the DED and DEM spectra are shifted to higher wavelength compared to the double monochromator spectra. An overestimation of the actinic flux density due to stray light is noticed for the GBS spectrum. The AFDM-CCD spectrum shows an underestimation below 299 nm compared to the ATI and GBM spectra. The reason is the problematic determination of the offset. The offset is calculated by the difference of two signals with a high number of counts (measured signal minus d+e current). A reduction of the dark current by decreasing the cooling temperature would improve the determination of the offset. The cooling temperature is limited by the Peltier element. With an increased temperature difference the Peltier element produces more heat itself, which is not removed completely.
5.1 Intercomparison of Actinic Radiation Measurements

For large SZA between 71° and 76° actinic flux density spectra between 302 nm and 320 nm are plotted in Figure 5.2b. The measurement performed on day 040510 (4:30 - 4:51 p.m.) shows a shifting of the start wavelengths towards higher wavelengths due the impact of the larger SZA. Compared to the DEM and DED spectrometers the AFDM-CCD follows best the spectra of the double monochromators towards lower wavelengths. The ratios of the actinic flux density spectra of all spectrometer (X) and the ATI double monochromator for both measurements are plotted in Figures 5.2c and d. The gray area represents a deviation of ±10%. Excepting wavelength-dependent features all spectra agree above 305 nm (for SZA = 33°) and 315 nm (for SZA ≥ 71°), respectively within the ±10% range. This spectral features possibly originate from (i) an unsufficient 0.5 nm interpolation of the spectra, or (ii) from an inexact time synchronisation, or (iii) uncertainties in the wavelength calibration. The ratio between the double monochromator spectra and the AFDM-CCD spectrum clearly shows the increased uncertainty of the AFDM-CCD below 300 nm wavelength (Figure 5.2c). In Figure 5.2d the ratio of the double monochromator spectra and the AFDM-CCD spectrum indicates a shift of the reliable spectral range towards higher wavelengths. However, compared to PDA-spectrometers the increased sensitivity of the AFDM-CCD leads to better results.

![Figure 5.2](image)

Figure 5.2: (a) and (b) show spectral actinic flux density spectra measured at a SZA of 33° and around 74° with all spectrometers. (c) and (d) present the spectral ratios of all spectrometers (X) referred to the ATI spectra for both SZA. The range of ±10% is marked by a gray area.

The diurnal pattern of the ratios between double monochromator and AFDM-CCD is studied. For this purpose these ratios were calculated for each measurement (all in all 32 ratios). Figure 5.3 shows the ratios for different wavelengths from 300 nm up to 350 nm. Additionally the SZA is plotted. Again a range of ±10% is marked by a gray area. Beside the dependence on the SZA also atmospheric conditions influence the accuracy of the AFDM-CCD measurements. For large SZA and overcast conditions the intensity of the downwelling radiation is reduced in order that a higher sensitivity of the detec-
The increase of the agreement between AFDM-CCD and both double monochromators with increasing wavelength is obvious. Exemplarily for 300 nm the ratio between GBM and AFDM-CCD ranges between 0.7 and 1.4, whereas for 301 nm the ratios are mostly concentrated around the ±10% range. One has to keep in mind that wavelength shifts and time synchronisation problems may have an impact on these results. A closer look on Figure 5.3a shows that even the differences between both double monochromators for 300 nm can reach 10%.

Figure 5.3: Ratios of double monochromator (ATI/GBM) and AFDM-CCD measurements for different wavelengths (gray area: ±10% range). In addition the SZA is plotted as a solid line in this figure.
5.1.3 Photolysis Frequencies

Photolysis frequencies of ozone and NO₂ were calculated from the corrected AFDM-CCD and PDA spectra and from the double monochromator spectra. The same quantum yield and absorption cross section data were applied to calculate these J-values. The use of \( J(\text{NO}_2) \) and \( J(\text{O}^1\text{D}) \) investigates the AFDM-CCD capability to determine \( J \)-values in the UV-A and UV-B compared to the PDA and double monochromator measurement method. Figure 5.4 shows the \( J(\text{NO}_2) \) and \( J(\text{O}^1\text{D}) \) measured with the AFDM-CCD versus the \( J \)-values derived from the PDA instruments and the double-monochromators. The red line marks an agreement of 100%. The data pairs of each correlation are approximated by a linear fit which is marked by a color according to the symbol color of the compared instrument. The best agreement of \( J(\text{O}^1\text{D}) \) is found for the double monochromators ATI and GBM data (see Figure 5.4a). Both fits closely match with the 1:1 curve. \( R^2 \)-values are calculated with 0.999 (GBM and ATI). Figure 5.4b shows the correlation between the \( J(\text{NO}_2) \) data. An improvement of the correlations is obvious. \( J(\text{NO}_2) \) is mainly affected by the actinic flux density measured in the UV-A spectral range. Hence the improvement is caused by the better agreement of the \( F_a \) measurements in this spectral range. Coefficients of determination between 0.995 and 0.999 were determined. The coefficients of determination and the slopes of the linear regression are summarized in Table 5.2.

![Figure 5.4](image)

Figure 5.4: (a) Correlations between \( J(\text{O}^1\text{D}) \) measured with different spectrometers and \( J(\text{O}^1\text{D}) \) derived from AFDM-CCD measurements. (b) The same as (a) for \( J(\text{NO}_2) \). The red line marks the 1:1 curve.

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<td>DED</td>
<td>1.056</td>
<td>0.983</td>
<td>1.062</td>
<td>0.998</td>
</tr>
</tbody>
</table>

Table 5.2: Slope of the linear regressions and coefficients of determination of the correlation plots which are shown in Figure 5.4.
In addition, the ratios of the $J$-values derived from AFDM-CCD/DED/DEM/GBM/GBS measurements and the $J$-values of the ATI were calculated. A time series of the ratios is plotted in Figure 5.5. A range of ±10% is marked by a gray area in Figure 5.5. The smallest deviation of $J(O^1D)$-values are found for the GBM and AFDM-CCD comparison. The highest deviation is detected for the comparison with the GBS data which are yield higher $J(O^1D)$-values than the all other instruments. Figure 5.5b displays the ratio of the $J(NO_2)$-values. Nearly all ratios are within the ±10% range whereby the best agreement was found for the GBM and AFDM-CCD each with a mean ratio of 0.99 (±0.01).

![Figure 5.5](image)

Figure 5.5: (a) Ratios of $J(O^1D)$ measured with different spectrometers and $J(O^1D)$ derived from ATI measurements. (b) The same as (a) for $J(NO_2)$. Again, the ±10% is marked by a gray area.

### 5.1.4 Evaluation of the AFDM-CCD

An intercomparison between the AFDM-CCD and other spectrometer systems which are based on single and double monochromator techniques was performed regarding to actinic flux density spectra and photolysis frequencies. An improved agreement was found between the AFDM-CCD and the double monochromators (ATI/GBM) compared to the agreement between single monochromators with PDA detectors and the ATI/GBM (see Figure 5.2). Thereby the lower threshold of the reliable spectral range of the AFDM-CCD is shifted to higher wavelengths depending on SZA and atmospheric conditions. However, the increase of the sensitivity allows a determination of $J(O^1D)$ without any parameterization as shown in Figure 5.5a. In contrast to other single monochromator spectrometers the AFDM-CCD shows an agreement with the GBM within ±10% independent from the intensity of the downwelling actinic flux density. Also for $J(NO_2)$ the AFDM-CCD shows an agreement with the double monochromator systems in the range of ±5% (Figure 5.5b).
5.2 Radiative Transfer Calculations

In the following measured actinic flux densities and photolysis frequencies are compared to radiative transfer simulations. These simulations were performed by Anke Knippka (University of Leipzig) using a 3-D radiative transfer model called Spherical Harmonic Discrete Ordinate Method - SHDOM (Evans, 1998). The input data contain the optical properties of aerosol particles, cloud droplets, and air molecules (Knippka and Trautmann, 2004). The aerosol particles are considered in the following way: From the size distribution determined by PCASP-X measurements the scattering and absorption properties are calculated by Mie-theorie. For the simulations shown here a maritime aerosol type is assumed due to the fact that the measurement area is situated near the coast of the North Sea. The scattering by air molecules is considered by Rayleigh scattering, whereby the molecule scattering cross section is calculated by an empirical formula of Nicolet (1984). The absorption of ozone plays a major role in the atmosphere, particularly for the UV spectral range. Therefore the ozone properties are considered carefully. The absorption cross section of ozone is assumed as altitude-and temperature-dependent (Daumont et al., 1992). The vertical profile of the number concentration for the ozone molecules is used from McClatchy et al. (1971) and scaled by satellite (GOME, ERS-2) measurements of the ozone column. Further properties are considered by the standard atmosphere reference of McClatchy et al. (1971). These standards are classified by the region and season of the year. With respect to the presented comparisons the aerosol layer was separated into vertical layers. The aerosol parameters were averaged within each layer and thus assumed as horizontal homogeneous in order that SHDOM was run in 1-D mode.

Cloud droplets can be considered in two ways. First, the measured size distributions (Fast-FSSP data) are used to apply the Mie-theory. Second, since data of the effective radius and LWC are available the parameterization after Slingo (1989) can be applied.

5.3 Clear Sky Conditions

5.3.1 Actinic Flux Density Profile Measurements

This section presents vertical profiles of AFDM measurements under different aerosol conditions. Similar airborne profile measurements in clear sky conditions were reported by e.g., Volz-Thomas et al. (1996), Wendisch et al. (1996), Früh et al. (2000), Hofzumahaus et al. (2002), Balis et al. (2003), and Meloni et al. (2003).

Clear sky measurements were performed on day 020912 during INSPECTRO-1 and on day 040520 during INSPECTRO-2. The photos in Figure 5.6 give a rough impression of the aerosol conditions on both days. Photo 5.6a indicates a low aerosol particle concentration. In addition some cumulus clouds were noticed near the horizon, which did not influence the clear sky radiation measurements. Photo 5.6b gives an idea of the aerosol conditions on day 040520. It was taken above the boundary layer and implies that the aerosol particle concentration is much higher than on day 020912.

The atmospheric conditions on both days differed significantly. Figure 5.7 illustrates the temperature and aerosol particle concentration profiles measured on board of the Parte-
navia with a Vaisala sensor and the PCASP-X, respectively. The flight altitude complies with the height above sea level. For a better comparison these altitudes were subtracted by the surface height. During INSPECTRO-1 the surface height roughly fitted with the sea level but for the INSPECTRO-2 campaign the surface height strongly varied. Therefore the surface height was determined along the flight path using a digital elevation model (kindly provided by Deutsches Zentrum für Luft- und Raumfahrt, DLR).

The temperature profile shows a quite linear decrease of the temperature with altitude on day 040520 (0.7 K / 100 m). An inversion is noticed in the temperature profile of day 020912 in 1200 m altitude. Above this inversion the temperature profile remains nearly constant. The aerosol particle concentration shown in Figure 5.7b approves the visual observations from Figure 5.6. Comparing the aerosol particle concentrations of both days a factor of 10 is found below 1500 m altitude. The boundary layer on day 040520 is more pronounced than on day 020920. Their upper limits are around 1400 m (day 020912) and 2000 m (day 040520). Lidar measurements using the VELIS instrument have shown an aerosol optical thickness of 0.1 (day 020912) and 0.3 (day 040520) at 532 nm wavelength.

The vertical extinction coefficient $\sigma_{\lambda_{ext}}$ plotted in Figure 5.7b shows maximal values (0.15 km$^{-1}$) at 250 m altitude for case A, whereas for case B $\sigma_{\lambda_{ext}}$ increases with altitude (up to 1800 m) to a maximal value of 0.8 km$^{-1}$.

In the following vertical profile measurements of $F_a$ on both days with different aerosol particle concentration are discussed. The low aerosol concentration case is called A, the high aerosol concentration case is B. The measurements were taken under 53° SZA (day 020912) and 45° SZA (day 040520). Therefore they are not directly comparable. Comparing irradiances measured at different SZA the irradiance spectra are often scaled to the same SZA using the scaling factor: $\cos(SZA_1)/\cos(SZA_2)$. This assumption is acceptable due to the fact that irradiances are dominated by the direct component. For actinic flux densities the contribution of the diffuse component plays a major role. Hence the validity of the assumption was tested for nearly clear sky conditions at SZA between 42.5° and 51.8° during an one hour measurement (10:00 - 11:00 local time). For this purpose a $F_a$ spectrum measured at SZA = 42.5° was scaled to different SZA considering the SZA of
the other measured actinic flux densities. The ratio of scaled and original spectral $F_\alpha$ are plotted in Figure 5.8 for $\lambda = 320$ nm, 420 nm, 520 nm and 620 nm. Apart from the 320 nm ratio the deviation is significant and increases with an increasing difference between SZA$_1$ (here: $42.5^\circ$) and SZA$_2$ ($42.5^\circ-51.8^\circ$). A difference of $8^\circ$ which corresponds to the SZA difference of day 020912 and day 040520 would yield a deviation of about 10%. For this reason a scaling on the same SZA is not applied in this work.

Integrated upwelling and downwelling actinic flux densities were calculated from all measured spectra during the descent profile flight on day 020912 and the ascent profile flight on day 040520. $F_\alpha$-spectra were integrated in three spectral regions: (i) VIS: 490-495 nm, (ii) UVA: 350-355 nm, and (iii) UVB: 305-310 nm.
**Case A - Low Aerosol Particle Concentration** The vertical profile of the integrated actinic flux densities are plotted in Figure 5.9. In addition the aerosol particle concentration is presented (black dotted line) that shows a decrease with altitude in three steps at around 500 m, 1100 m and 1400 m. The slope (variation of \( F^\downarrow_\alpha \) with altitude) of the increase of the downwelling actinic flux density (Figure 5.9a) is only slightly affected by the aerosol particle concentration. The highest variability is observed for the lowest altitudes (below 500 m). There the inhomogeneity of the aerosol particle concentration leads to a high variability in the downwelling actinic flux density. The highest relative increase of \( F^\downarrow_\alpha \) over the whole profile (0-1600 m) is found for the UV-B spectral range. Figure 5.9b illustrates \( F^\downarrow_\alpha \) and the aerosol particle concentration as a function of altitude. The increase of \( F^\downarrow_\alpha \) with altitude in the UV-A and UV-B spectral ranges is about a factor of 6 with the highest increase in the UV-A spectral range. In the VIS \( F^\downarrow_\alpha \) increases by a factor of 2. Variabilities of the aerosol particle concentration as well as the variability of the surface albedo causes a much higher variability of \( F^\downarrow_\alpha \) than observed for \( F^\downarrow_\alpha \). The spectral surface albedo derived from the albedometer measurements shows values of 0.02 - 0.04 in the range between 290 and 500 nm. Above the upper limit of the boundary layer the slope of \( F^\downarrow_\alpha \) reaches a maximum in the VIS.

Table 5.3 compares the slopes calculated for the UV-B, UV-A and VIS spectral ranges between 100 m and 1600 m altitude. In addition Table 5.3 contains the ratio of standard deviation (sdv) and averaged profile which represents a measure of variability. The increase of the upwelling actinic flux density is much higher than the increase of the downwelling component. Moreover, this slope is steepest for shorter wavelengths. The variability of the upwelling component is mainly affected by the surface albedo and is a factor of 10 higher than that of the downwelling component. A spectral dependence of the variability is also noticed (highest for lower wavelengths).

<table>
<thead>
<tr>
<th>Slope (Factor)</th>
<th>( F^\downarrow_\alpha ) (UV-B)</th>
<th>( F^\downarrow_\alpha ) (UV-A)</th>
<th>( F^\downarrow_\alpha ) (VIS)</th>
<th>( F^\downarrow_\alpha ) (UV-B)</th>
<th>( F^\downarrow_\alpha ) (UV-A)</th>
<th>( F^\downarrow_\alpha ) (VIS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sdv/mean (%)</td>
<td>1.21</td>
<td>1.14</td>
<td>1.04</td>
<td>5.62</td>
<td>6.60</td>
<td>2.04</td>
</tr>
</tbody>
</table>

Table 5.3: Slope and ratio of standard deviation (sdv) and average actinic flux density for the profile of \( F^\downarrow_\alpha \) and \( F^\uparrow_\alpha \) between 100 m and 1600 m altitude.

In the following measured profiles (index "meas") of \( J(\text{NO}_2) \) and \( J(\text{O}^1\text{D}) \) are compared to simulated profiles (index "sim"). The simulations were performed by A. Kniffka (Leipzig University) using SHDOM. A value of 0.1 (at 532 nm) for the optical thickness of the aerosol layer indicates the marginal impact of aerosols regarding to radiation measurements. The TOC was given with 269 DU. The surface albedo was deduced from aircraft Albedometer measurements which were revised by the method described by Wendisch et al. (2004).

The simulations were conducted for two aerosol conditions. First, using the aerosol properties as measured and described above. Second, the extinction by aerosol particles was excluded from the calculation in order that the influence of aerosols with respect to photolysis frequencies can be studied. The \( J \)-values were derived from the simulated spectra using the same molecular data (\( \sigma \) and \( \phi \)).
5.3 Clear Sky Conditions

Figure 5.9: Integrated downwelling (a) and upwelling (b) actinic flux densities (UV-B, UV-A, VIS) and aerosol particle concentration on day 020912.

Figure 5.10 shows the comparison of simulated (with and without aerosol) and measured $J$(O$^1$D) and $J$(NO$_2$) profiles. The measurement uncertainty is shown as horizontal error bars. These uncertainties are based on measurement uncertainties of the AFDM. Uncertainties of the molecular data are neglected because they affect both the measured and simulated profiles. Both simulated profiles show nearly the same results which suggests the negligible influence of the aerosol for this case. The effect of the vertical aerosol inhomogeneity is obvious in the increased variability of the measured $J$-values mainly in the lowest altitudes below 500 m. The measured values are systematically larger than the simulated values (4% $J$(NO$_2$) up to 6% $J$(O$^1$D)). But they agree within the range of measurement uncertainties.

**Case B - High Aerosol Particle Concentration** In the following, profiles of $F_a$ and $J$-values under high aerosol particle concentrations are studied. The vertical profiles shown in Figure 5.11 are plotted for altitudes above sea level. Considering the orography (altitude above sea level minus surface height) as vertical coordinate would lead to much noisier profiles. Moreover the optical inlets of the AFDM receive actinic flux densities of a $2\pi$ hemisphere and consequently a mixed signal of the reflection properties of the orography. The profile of the aerosol particle concentration can be subdivided into 3 sections: (i) an area of maximal concentration, below 800 m, (ii) a decreasing range of concentration between 800 m and 2000 m, and (iii) the area above the boundary layer, above (2000 m). The surface albedo ranges between 0.01 and 0.06 (290 - 500 nm) and is slightly different from the surface albedo of case A. In addition the SZA is higher in case A. Consequently a direct comparison of the absolute values of $F_a$ between both cases is not possible.
Figure 5.10: Vertical profiles of measured and simulated J-values $J(\text{O}^1\text{D})$ (a) and $J(\text{NO}_2)$ (b). The simulated photolysis frequencies were derived from spectra which were calculated with and without aerosols. The horizontal bars indicate the measurement uncertainty.

The slope of the $F_a$ increase with altitude is influenced by these areas of different aerosol particle concentrations where the highest slope of $F_a^\dagger$ is found in the lowest altitudes (see Figure 5.11). Furthermore the highest increase between 600 m and 2100 m altitude is noticed in the UV-B spectral range as shown in Table 5.4. Comparing the slopes of case A and case B in all spectral ranges a difference is found for the UV-B and the UV-A spectral range. The increase of $F_a^\dagger$ is about 8 % higher for case B compared to case A. Whereas in the VIS spectral range a nearly similar increase is observed. Also the variabilities differ slightly with higher variabilities for case B, which may caused by the stronger inhomogeneity of the aerosol particle concentration.

<table>
<thead>
<tr>
<th></th>
<th>$F_a^\dagger$(UV-B)</th>
<th>$F_a^\dagger$(UV-A)</th>
<th>$F_a^\dagger$(VIS)</th>
<th>$F_a^\dagger$(UV-B)</th>
<th>$F_a^\dagger$(UV-A)</th>
<th>$F_a^\dagger$(VIS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope (Factor)</td>
<td>1.31</td>
<td>1.23</td>
<td>1.05</td>
<td>5.51</td>
<td>5.20</td>
<td>2.70</td>
</tr>
<tr>
<td>sdv/mean (%)</td>
<td>7.5</td>
<td>5.4</td>
<td>1.6</td>
<td>35</td>
<td>36</td>
<td>24</td>
</tr>
</tbody>
</table>

Table 5.4: Same as Table 5.3 but for day 040520 and a vertical profile between 600 m and 2100 m altitude.

Furthermore the $F_a^\dagger$(VIS) profile shows an interesting feature. Below the upper limit of the boundary layer a small enhancement region (see the accolade in Figure 5.11) compared to the region above the boundary layer is noticed. Similar effects are observed on the upper part of cloud layers.

$F_a^\dagger$ shows a more distinctive influence of the aerosol particle concentration than $F_a^\dagger$. Near the upper limit of the boundary layer a significant change of the increase is noticed. Above the boundary layer the increase of $F_a^\dagger$ is lower than within the aerosol layer. As for case A there is a spectral dependence of the slope with higher values for lower wavelengths. Comparing the $F_a^\dagger$-slopes of both cases a stronger increase of $F_a^\dagger$ for case A is observed in the UV-B and UV-A. Whereas for the VIS spectral range case B shows a stronger increase.
5.3 Clear Sky Conditions

Figure 5.11: Integrated downwelling (a) and upwelling (b) actinic flux densities (UV-B, UV-A, VIS) and aerosol particle concentration on day 040520.

As for case A measured profiles of $J(\text{NO}_2)$ and $J(\text{O}^1\text{D})$ are compared with simulations. In this calculation a rural aerosol type was assumed. The spectral surface albedo was also changed with regard to Albedo meter measurements. Figure 5.12 shows the measured and simulated $J(\text{O}^1\text{D})$ and $J(\text{NO}_2)$ profiles. For both species the simulated $J$-values using an aerosol-free atmosphere are slightly lower than the results from the aerosol simulation (3%). Dickerson et al. (1997) and He and Carmichael (1999) also found enhancements of the photolysis frequency within the boundary layer as a result of highly scattering aerosols. The comparison with the measured profile indicates even a larger enhancement for higher altitudes. In the lower part of the boundary layer $J(\text{NO}_2)_{\text{meas}}$ intersects the aerosol-free profile. Also the simulated profiles show a convergence with decreasing altitudes albeit with a much weaker occurrence than observed between measurement and simulation. However, in general the agreement between $J(\text{NO}_2)_{\text{meas}}$ ($J(\text{O}^1\text{D})_{\text{meas}}$) and $J(\text{NO}_2)_{\text{sim}}$ ($J(\text{O}^1\text{D})_{\text{sim}}$) is within the range of uncertainty but close to the lower limit in particular for higher altitudes.

5.3.2 Horizontal Actinic Flux Density Data

The influence of aerosol- and surface albedo inhomogeneities on actinic flux densities measured along horizontal flight paths is studied in the following sections. Case A and B refer to the same flight days as in Section 5.3.1.

Case A - Low Aerosol Particle Concentration First, horizontal flight legs in an atmosphere with low aerosol particle concentration (case A) are considered. The first leg covers spectral measurements above sea, the second one above land as shown in Figure...
5 Measurement Examples

Figure 5.12: The same as Figure 5.10 but for case B.

5.13. Both flight legs have a length of 10 km to make them comparable with regard to their variability. The flight altitude was 2000 m with a negligible aerosol particle concentration of less than 20 particle/cm³ > 0.1 μm. Figure 5.14a displays the averaged downwelling actinic flux density measured above land (black line) and above sea (blue line). The vertical error bars indicate the standard deviation (sdv), which is very low. A measure of the relative variability is the ratio of sdv and average. This ratio which is also plotted in Figure 5.14a (dashed lines) shows no distinct wavelength dependence. The increase below 320 nm is caused by the increasing measurement uncertainty of the AFDM-PDA for lower wavelengths and thus no effect of the $F_a^\dagger$ variability.

The averaged upwelling actinic flux densities are shown in Figure 5.14b. Both averaged spectra differ in their spectral course due to the reflection properties of the surface. The spectral shape of the surface albedo is clearly noticed in the spectral course of $F_a^\dagger$ measured above sea and land. The influence of the vegetation is found in the measured land spectra above 500 nm wavelength. In contrast to the relative variability of $F_a^\dagger$, $F_a^\dagger$ shows a higher variability with a clear wavelength dependence, which mostly increases with wavelength. One would expect a lower relative variability above sea than above land which is a mixture of pasture and farmland because a flat gray surface albedo of the sea and the more wavelength-dependent albedo of land surfaces. But Figure 5.14 does not show this behavior. There are two possible reasons: (i) Whitecaps caused by wind were observed on the sea. These irregular whitecaps increase surface reflection and leads to a higher variability than a calm sea. (ii) The second more likely reason is the influence of the land, because the flight track above sea was flown near the coastline. Hence, the downward-looking optical inlet, which integrates $F_a^\dagger$ over the whole lower hemisphere, receives also reflected radiation from the land surface whether the fraction is quite small. This fraction would decrease with increasing distance to the coastline. In fact an increase of $F_a^\dagger$ is noticed (7% at 350 nm wavelength), which maybe is an effect of the increasing distance of the land.
5.3 Clear Sky Conditions

Figure 5.13: Flight pattern on day 020912. The dashed line marks the coastline. The grey line indicates the flight path. The two thick lines show the two selected flight legs, one above sea (between M2 and T1) and the other one above land (between M1 and M3). A SZA of 56° was calculated.

Case B - High Aerosol Particle Concentration  Measured spectra of horizontal flight legs are compared for the high aerosol case B for different altitudes. Figure 5.15a shows the measurement area of INSPECTRO-2. 10 km flight legs were chosen regarding to their spatial position. The surface height in the area which was selected and shown in the enlargement (Figure 5.15b) is nearly uniform with ~ 360 m above sea level. For this reason variabilities of the actinic flux density due to the surface height can be neglected.

The three flight legs labeled with X, Y and Z were flown in three altitudes above sea level and during different SZA. Table 5.5 summarizes the conditions of the flight legs. The SZA of all flight legs differ significantly. Consequently, first of all the downwelling actinic flux density is influenced by this quantity as shown in Figure 5.16a. Two effects compete against each other: the altitude dependence and the SZA dependence. Despite a higher flight altitude the averaged $F_{\alpha}^h$ measured in 1500 m is lower than in 700 m due to the higher SZA in 1500 m. The averaged spectrum of the 2700 m flight leg is higher than the spectrum of 700 m altitude in face of a higher SZA. In this case the lower aerosol particle concentration plays a major role and dominates the magnitude of the downwelling actinic flux density.

The relative variabilities also plotted in Figure 5.16 show a slight increase with increasing wavelength. Furthermore the relative variability is lowest for the highest altitude which is above boundary layer. In the other two altitudes, particularly in 700 m, the horizontal inhomogeneity of the aerosol distribution influences $F_{\alpha}^h$. In comparison to case A the
5 Measurement Examples

Figure 5.14: Averaged downwelling and upwelling actinic flux densities measured above land and sea ((a): downwelling, (b): upwelling). The error bars indicate the standard deviation (sdv), the dashed lines show the ratio of the sdv and the average $F_a$.

<table>
<thead>
<tr>
<th>Flight Leg</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZA ($^\circ$)</td>
<td>48</td>
<td>39</td>
<td>57</td>
</tr>
<tr>
<td>Altitude (m)</td>
<td>2700</td>
<td>1500</td>
<td>700</td>
</tr>
<tr>
<td>$N$ (particles/cm$^3$)</td>
<td>30$\pm$7</td>
<td>2000$\pm$130</td>
<td>2200$\pm$300</td>
</tr>
</tbody>
</table>

Table 5.5: Conditions during flight legs X, Y and Z.

The relative variability of case B is slightly higher.

A different behavior shows the relative variability of the upwelling actinic flux densities (Figure 5.16b). Compared to case A the relative variability measured in 1500 and 2700 m is significantly smaller than the measured variability above land of case A. One possible reason is the increasing homogeneity of the reflection properties at high aerosol particle concentrations. Features of the surface albedo above land dissipate by the aerosol layer below. In the lowest altitude the upwelling actinic flux density is mainly determined by the surface reflection properties which are quite inhomogeneous as shown by the relative variability of $F_a^U$.

5.4 Boundary Layer Clouds

5.4.1 Profile Flight Patterns

Enhanced $F_a$ Values near Cloud Top Measurements in stratiform cloud layer conditions were performed on two days during the INSPECTRO-1 campaign (day 020914 and day 020915). Several vertical profiles were flown on day 020915 as shown in Figure 5.17. This figure illustrates the altitude of the aircraft (black line) during the flight track and the mean cloud extent of the cloud layer (dashed line) which was between 1300 and 1700 m. The SZA decreased from 52$^\circ$ to 48$^\circ$. All ascending and descending profiles are labeled (#1 ... #9); the arrows denote its direction. These profiles were measured along the edges of the measurement area (cf. Figure 5.14).
Figure 5.15: (a) Flight pattern on day 040520 during the INSPECTRO-2 campaign. The circled area indicates the measurement area where three flights were selected. (b) Enlargement of the dashed area. The thick black line, the dashed one and the thick grey line denote the three flight legs X, Y and Z.

The downwelling actinic flux density integrated between 490 and 495 nm \( F_{\alpha}^L(VIS) \) is plotted as function of time in Figure 5.18. In addition the LWC measured with the PVM-100A is shown (gray areas). Mostly adiabatic LWC profiles are observed. A more detailed study of the LWC-profiles referring to this cloud layer is given by Schmidt (2004). In general lowest \( F_{\alpha}^L(VIS) \) values were measured below the cloud, whereas \( F_{\alpha}^L(VIS) \) increases with increasing altitude. Apart from profile #6 all profiles show a maximal \( F_{\alpha}^L(VIS) \) just below the cloud top. As far the downwelling radiation enters the cloud the downward diffuse component is increasing due to multi-scattering. In addition the direct component still has a significant fraction on the total downwelling actinic flux density. Consequently, it results in an enhancement of the downwelling actinic flux density which depends on SZA and wavelength. In the following this enhancement is quantified with:

\[
\text{Enhancement} = \left( 1 - \frac{F_{\alpha}(\text{above cloud})}{F_{\alpha}(\text{maximal})} \right) \times 100\% . \quad (5.1)
\]

For smaller SZA the enhancement is more distinct than for larger SZA (Trautmann et al., 1999). Furthermore the enhancement decreases with decreasing wavelength. The enhancement of \( F_{\alpha}^L(VIS) \) derived for each profile is summarized in Table 5.6. Similar enhancements were observed during tethered-balloon measurements by de Roode et al. (2001) and Vila-Güereu de Arellano et al. (1994). They found a maximal enhancement of 12% for the downwelling actinic flux density depending on SZA and cloud optical thickness. Theoretical considerations about the enhancement were described by Madronich (1987), van Weele and Duykerke (1993), and Los et al. (1997).

With regard to photolysis frequencies the wavelength-dependence of the enhancement...
Figure 5.16: Averaged downwelling and upwelling actinic flux densities measured in 2700 m, 1500 m and 700 m altitude ((a): downwelling, (b): upwelling). The error bars indicate the standard deviation (sdv), the dashed lines show the ratio of sdv and the average.

Figure 5.17: Flight pattern on day 020915 during the INSPECTRO-1 campaign. The altitude (solid line) and SZA (dotted line) is plotted as function of time. The dashed lines mark the mean cloud top and cloud base, #1...#9 label the vertical profiles.

plays a fundamental role which is illustrated for profile #2 (Figure 5.19). The vertical profiles of the integrated downwelling and upwelling actinic flux densities ($F_{\alpha}$ (VIS), $F_{\alpha}$ (UV-A), $F_{\alpha}$ (UV-B)) are plotted together with the LWC. $F_{\alpha}^\uparrow$ of all three spectral ranges show a nearly constant course below the cloud layer, whereas the downwelling component decreases with altitude. Within the cloud layer $F_{\alpha}^\uparrow$ and $F_{\alpha}^\downarrow$ strongly increase with increasing altitude. Above the cloud $F_{\alpha}^\uparrow$ remains nearly constant, whereas $F_{\alpha}^\downarrow$ slightly increases. This significant altitude dependence of $F_{\alpha}^\uparrow$ above the cloud layer may have been caused by scattering processes near cloud top which effect an increase of downwelling radiation compared to regions more far away from the cloud top. Kylling et al. (2005) compared 1-D model simulations performed with the uspec model and measurements using the AFDM-PDA and found also a decrease of $F_{\alpha}^\downarrow$ with altitude above the cloud layer.

In the visible spectral range $F_{\alpha}^\downarrow$ (VIS) has a small maximum near the cloud top, which is more significant for the downwelling component (see Figure 5.19a). Comparing the magnitudes of the enhancement in the VIS, UV-A and UV-B a reduction of the enhancement
Table 5.6: Enhancement of $F_{a}^{\uparrow}(\text{VIS})$ in the upper part of the cloud layer compared to the region above the cloud.

![Figure 5.18: LWC (gray areas) and integrated downwelling actinic flux density (red line) as the function of time.](image)

is noticed, particularly between the UV-A (enhancement $\sim 4\%$) and the VIS (enhancement $\sim 11\%$) spectral range. The reason for this wavelength dependence is the increasing production of diffuse light due to multiple scattering in the upper region of the cloud. Figure 5.20 points up exemplarily the proportions of $F_{a}^{\downarrow}$, $F_{a,\text{dif}}^{\downarrow}$, and $F_{a,0}$ of a profile through a cloud layer between 600 m and 1060 m altitude which were simulated for a SZA of 48°. The simulations stem from SHDOM calculations. The VIS spectral range of $F_{a}^{\downarrow}$ is mainly determined by the direct component, whereas the UV range is affected by the diffuse component. Since the direct contribution converts to diffuse light the increase of the diffuse light for the VIS spectral range is more significant than for the UV-A range. For the upwelling components an enhancement in the upper part of the cloud is not obvious. In terms of photolysis frequencies as $J(\text{NO}_2)$ and $J(\text{O}^1\text{D})$ only a slight enhancement is observed near the upper part of the cloud (Figure 5.19d,e). The $J$-profiles look very similar to that one of the UV-A and UV-B spectral range.

**Comparison with Model Simulations** The model simulations presented in Figure 5.20 refer to microphysical measurements performed on day 020914. In contrast to day 020915 this day was not influenced by cirrus clouds. In the presence of inhomogeneous cirrus clouds it is difficult to conduct radiative transfer simulations without further information about microphysical properties of the cirrus and its distribution. Therefore a comparison of measurements and simulations is presented for a cirrus-free case using a descending profile measurement through a stratus layer on day 020914.

With respect to the presented comparison the cloud layer was separated into vertical layers. As for the aerosol studies the droplet parameters were averaged within each layer and thus assumed as horizontal homogeneous. A value of 0.027 for the optical thickness
Figure 5.19: (a)-(c) Integrated upwelling and downwelling actinic flux densities of three spectral ranges (VIS, UV-B, UV-A) and LWC (gray area) measured during profile #2. (d)-(e) Profiles of the downward and upward component of $J(\text{NO}_2)$ and $J(\text{O}^1\text{D})$.

Figure 5.20: Profiles of $F_{a,i}^\downarrow$, $F_{a,dif}^\downarrow$, and $F_{a,0}$ for 310 nm, 350 nm, and 490 nm. Cloud top and cloud base are marked by dashed lines.
of the aerosol layer indicates the marginal impact of aerosols regarding to radiation measurements which were mainly affected by the cloud droplets. The TOC was given with 283 DU. Both methods for the treatment of droplets were applied, which gave very similar results. Here the results of the Slingo parameterization are shown.

The vertical profile measurement of the actinic flux density and the LWC are displayed in Figure 5.21. Actinic flux densities profiles were exemplarily studied for individual wavelength in the UV-B (310 nm), the UV-A (350 nm), and the VIS (490 nm) spectral range according to the spectral ranges which were defined for the integration of \( F_a \) previously. 

For the comparison an integration of simulated \( F_a \) is not advisable due to the wavelength resolution of the SHDOM model (5 nm step width). The LWC profile shows values of up to 0.6 gm\(^{-3}\) on the top of the cloud layer that has a thickness of 400 m with cloud top (bottom) at 1000 m (600 m).

Figure 5.21a presents the measured and simulated downwelling actinic flux density at 310 nm wavelength. The horizontal bars indicate the measurement uncertainty. The small enhancement as already observed in Figure 5.19 in the upper part of the cloud layer appears here as well. Whereas the simulation (dashed line) does not show this feature. The inhomogeneity of the cloud top plays a role for the size of the peak. For a more inhomogeneous cloud top a peak may appear even for \( F_a^{\downarrow} \) in the UV-B spectral range due to scattering processes between cloud parts. Hence the structure of the cloud layer in the model maybe is insufficient regarding to the cloud top. Furthermore, the simulations are outside the measurement uncertainties above 800 m altitude. Beneath that altitude the agreement is nearly within the measurement uncertainty.

For 350 nm and 490 nm wavelength (Figure 5.21b) measured and simulated upwelling actinic flux densities agree within measurement uncertainties over the whole vertical profile apart from the lowest altitudes. In this range the horizontal cloud inhomogeneity could be the reason for the differences. An enhancement of the simulated \( F_a^{\downarrow} \) near cloud top is visible for 490 nm wavelength, whereas the measured profile also shows a peak for 350 nm. However, this measured peak is most significant for 490 nm, which is slightly shifted vertically compared to the simulations due to the fact that the cloud top heights used in the model simulation were averaged over the whole measurement area.

Figures 5.21c and d show the measured and simulated upwelling actinic flux density profiles for 310 nm, 350 nm and 390 nm. The agreement of the measured and simulated profiles at 310 nm and 490 nm is almost within the measurement uncertainty. A significant enhancement near cloud top is not noticed for the measured profile.

**Comparison with Simulated \( F_a \) for Clear Sky Conditions** In addition, clear sky model simulations using SHDOM model were performed to investigate the influence of clouds.

The impact of aerosol particles is negligible due to low concentrations similar to the aerosol conditions on day 020912 (cf. Figure 5.7b). Apart from the area near and above cloud top the measured \( F_a^{\downarrow} \) is decreased compared to clear sky conditions (see Figure 5.21. Above the cloud radiation is reflected due to the high cloud top albedo. This reflected radiation is backscattered by air molecules which causes an increase of the downwelling radiation. For all wavelengths the simulated clear sky profiles are lower than the simulated cloudy
profile above the cloud, which was expected. Below the altitude of enhancement (around 1000 m) the attenuation of the downwelling actinic flux density increases quickly with decreasing altitude compared to the clear sky profile. With regard to the ratio of $F^{\downarrow}_{a}$ in cloudy case and in clear sky case a wavelength dependence is noticed. The ratio for 490 nm is lower than for the UV-B spectral range, particularly above the cloud (1.3 vs. 1.8 in 1000 m altitude). Wavelength-dependent effects were already reported by several authors e.g., Crawford \textit{et al.} (1999) and Jäkel \textit{et al.} (2005). For cloudy conditions the increase of $F^{\downarrow}_{a}$ is stronger for the UV spectral range because of the increase of diffuse radiation, which influences the UV range more than the VIS spectral range. For the same reason the decreasing $F^{\uparrow}_{a}$ compared with that in the clear sky is more effective for longer wavelengths. Compared to clear sky simulations $F^{\downarrow}_{a}$ is higher above 700 m altitude (see Figures 5.21a, b). Below that altitude the clear sky simulations are higher. In this region the downward-looking optical inlet receives most radiation from the surface which is much darker than clouds. In addition the reflected radiation from the ground depends on the incoming radiation which is attenuated compared to the clear sky case. Therefore one would expect lower values of $F^{\downarrow}_{a}$ than in clear sky conditions below the cloud. The ratio of $F^{\downarrow}_{a}$ in cloudy and clear sky conditions differs from the results for the $F^{\uparrow}_{a}$ ratios. For the upwelling component the ratio is much higher above and within the cloud. The wavelength dependence is inverse to the downwelling component ratio. The reason is the wavelength dependence of the albedo which determines the spectral course of the upwelling actinic flux density. For clear sky conditions the spectral albedo increases with wavelength between 310 nm and 490 nm (Wendisch \textit{et al.}, 2004; Webb \textit{et al.}, 2004). In contrast, the spectral albedo is nearly wavelength-independent above and within clouds (Webb \textit{et al.}, 2004). Therefore the ratio of the upwelling components in cloudy and clear sky conditions increases with wavelengths. Below the cloud the wavelength dependence of the ratio is nearly negligible caused by the same spectral course of the albedo. Table 5.7 summarizes the ratios of cloudy measurements and clear simulations for different wavelengths (310 nm, 350 nm, 490 nm) and different altitudes (300 m, 800 m, 1000 m, 1100 m).

<table>
<thead>
<tr>
<th>Component/Altitude</th>
<th>1100 m</th>
<th>1000 m</th>
<th>800 m</th>
<th>300 m</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F^{\downarrow}_{a}$ (310 nm)</td>
<td>1.7</td>
<td>1.8</td>
<td>0.7</td>
<td>0.38</td>
</tr>
<tr>
<td>$F^{\downarrow}_{a}$ (350 nm)</td>
<td>1.4</td>
<td>1.5</td>
<td>0.6</td>
<td>0.31</td>
</tr>
<tr>
<td>$F^{\downarrow}_{a}$ (490 nm)</td>
<td>1.2</td>
<td>1.3</td>
<td>0.5</td>
<td>0.28</td>
</tr>
<tr>
<td>$F^{\downarrow}_{a}$ (310 nm)</td>
<td>4.6</td>
<td>4.6</td>
<td>1.7</td>
<td>0.3</td>
</tr>
<tr>
<td>$F^{\downarrow}_{a}$ (350 nm)</td>
<td>6.0</td>
<td>5.7</td>
<td>2.0</td>
<td>0.2</td>
</tr>
<tr>
<td>$F^{\downarrow}_{a}$ (490 nm)</td>
<td>10.8</td>
<td>11.2</td>
<td>3.5</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 5.7: Ratios of measurements in cloudy conditions and clear sky simulations for downwelling and upwelling components of $F_{a}$ (310 nm, 350 nm, 490 nm) in different altitudes.
Figure 5.21: Upwelling and downwelling actinic flux densities at 310 nm, 350 nm and 490 nm wavelength measured and simulated for a vertical profile through a stratus cloud layer (day 020914). In addition clear sky simulations are plotted. (a) 310 nm, $F_a^\downarrow$, (b) 350 nm and 490 nm, $F_a^\downarrow$, (c) 310 nm, $F_a^\uparrow$, (b) 350 nm and 490 nm, $F_a^\uparrow$.

5.4.2 Horizontal Measurements

**Variability above Boundary Layer Clouds**  The upwelling actinic flux density measured above clouds is crucially influenced by the macro- and microphysical homogeneity of clouds. In case of cirrus-free conditions the variabilities of the downwelling component measured above a boundary cloud layer is negligible. For that reason just the variability of $F_a^\uparrow$ is studied here. The measurements which are presented were performed on day 020913 and 020914 during INSPECTRO-1. The photos in Figure 5.22 display the cloud conditions on both days. The left one shows a stratuscumulus cloud layer with a vertical extent between 1900 and 3500 m and an estimated optical thickness $\tau_d$ of 6 derived from
5 Measurement Examples

$LWC$ and $R_{eff}$ measurements which were used in Eq. 2.15. The flight altitude was 1600 m. A photo of the compact stratus cloud layer is shown in Figure 5.22b. An optical thickness of 38 was determined. Measurements were taken in an altitude of 2800 m. The cloud layer had a cloud base (top) height of 550m (1000 m).

![Photographs of the cloud conditions on day 020913 (left) and 020914 (right).](image)

Figure 5.22: Photographs of the cloud conditions on day 020913 (left) and 020914 (right).

Figure 5.23 shows an example of averaged spectra of $F_a^\uparrow$ in the presence of overcast and scattered cloud layers. Both averaged spectra were calculated for flight legs of 10 km length. The SZA during the flight periods were nearly the same (50°-53°), which means an approximately 4-7% difference for the upwelling actinic flux density. The error bars in Figure 5.23 indicate the standard deviations of the averaged spectra and show the variability of $F_a^\uparrow$, whose relative spectral values are plotted with dashed lines. The variability above the scattered cloud layer is clearly higher than above the stratus cloud. Comparing the relative variabilities of both cases a factor of ~ 15 is noticed. Above the stratus cloud layer the relative variability is nearly wavelength-independent because of the spectral gray cloud albedo of a compact cloud layer (Webb et al., 2004). Whereas above the stratocumulus layer the variability slightly increases with increasing wavelength due to the wavelength dependence of the surface which was partly seen through the stratocumulus cloud layer.

**Variability within Boundary Layer Clouds** The variability of the actinic flux density within clouds strongly depends on the distribution of the cloud droplets. The size distribution of the droplets and the $LWC$ are the crucial parameters. The variability and the averaged spectra of the downwelling and upwelling actinic flux density during a flight track through the cloud layer (day 020914) are shown in Figure 5.24. The flight track which is considered here includes measurements between 10:37 UTC and 10:59 UTC and complies with a complete circle around the measurement area (see Figure 5.14). The SZA ranged from 50.3°-51.6°. As expected the difference between the downwelling and upwelling component is much smaller than observed during the clear sky case. In contrast to clear sky conditions $F_a^\uparrow$ is increased, whereas $F_a^\downarrow$ is decreased due to scattering processes within the cloud layer. The relative variabilities of both components range around 0.085 and 0.11, respectively which complies a nearly similar variability. A distinctive wavelength
Figure 5.23: Averaged upwelling spectral actinic flux density measured above a stratus layer and above a scattered cloud layer at mean SZA of 50° and 53°, respectively. In addition the ratio of standard deviation and average is plotted (dotted lines).

dependence is not noticed, that results in a wavelength-independent influence of cloud inhomogeneities on the actinic flux density. However, the influence of the water vapour absorption bands appears slightly in the relative variability plot of the downwelling component (around 595 nm and 650 nm), where higher variabilities are found.

Figure 5.24: Averaged upwelling and downwelling spectral actinic flux densities measured within a compact stratus cloud layer. The dashed lines indicate the spectral ratio of sdv and average.

In the following, the effects of 3-D cloud structures on the solar radiative transport within a cloud layer is studied in terms of cloud radiative smoothing. The radiative smoothing is investigated by applying the power spectrum analysis. The power spectra are considered regarding to measurements of upwelling and downwelling actinic flux densities in the VIS and UV-B spectral range for the flight leg within the cloud layer of day 020914. Power
spectra give a plot of the proportion of a signal’s power falling within given frequency bins. In this case the frequency is taken from a time series of $F_a$ measurements which corresponds to a spatial course calculated from the true air speed (TAS) of the aircraft. In the past such power spectra were applied on satellite data of upwelling radiation reflected by cloud layers (Boers et al., 1988; Calahan and Snider, 1989).

The power spectrum of a $F_a$ series $\text{Pow}_{F_a}$ is calculated by the absolute square of the Fourier transformed actinic flux density. $F_a$ is scale-invariant for:

$$\text{Pow}_{F_a}(k) \sim f^{-\beta}$$

(5.2)

where $f$ is the wave number (frequency), $r = 1/f$ and $\beta$ the slope. $\beta$ indicates the smoothness of the $F_a$ distribution. The smoothness increases with increasing $\beta$ (Marshak et al., 1995). A scale break is defined as a transition in power law behavior from $f^{-\beta_1}$ to $f^{-\beta_2}$ and is caused by a change in physical processes that impact the variability at the corresponding scale.

Schmidt (2004) studied the power spectra of upwelling and downwelling irradiances for the same flight leg within in clouds as in this work. He noticed a typical scale break at about 0.07 Hz ($\sim 1$ km with TAS $\sim 70$ m/s) which indicates the so-called radiative smoothing. For higher frequency a power law of $f^{-3.28}$ was found, whereas for lower frequencies the variability of the irradiances followed the Kolmogorov’s -5/3 law of the LWC. For smaller scales (frequencies) the variability is lost due to horizontal photon transport. Further studies regarding to radiative smoothing were performed by e.g., Calahan and Snider (1989), Marshak et al. (1995) and Schröder (2004). Calahan and Snider (1989) considered variabilities above a stecoculus cloud layer using satellite measurements. They found that for scales larger than 200 m the radiation energy spectrum follows the one of the LWC, while at smaller scales it exhibits a much smoother behaviour with $f^{-3.8}$.

The power spectra of the upwelling and downwelling $F_a$ for the VIS and UV-B spectral range are shown in Figure 5.25. A scale break is noticed at 0.15 - 0.2 Hz ($\sim 350-450$ m with TAS $\sim 70$ m/s) for the downwelling component. Whereby the slope for lower frequencies follows the -5/3 law of the LWC. For higher frequencies $\beta$ increases to a value of 5.8 (UV-B) and 4.6 (VIS) which indicates a stronger smoothness. The upwelling component (see Figures 5.25b and d) shows a scale break at $\sim 0.3$ Hz ($\sim 2.3$ km) with $f^{-3.0}$ and $f^{-3.2}$. That means that the variability of $F_a^{\uparrow}$ follows the variability of the LWC for a broader range of frequencies than $F_a^{\downarrow}$.

Compared to the radiative smoothing of upwelling and downwelling irradiances which have shown similar results concerning slope and scale break, a difference between both component is noticed for $F_a$. The slope for $F_a^{\downarrow}$ is much larger than for $F^{\uparrow}$, whereas for $F_a^{\uparrow}$ $\beta$ is somewhat lower than for $F^{\uparrow}$. Table 5.8 summarizes the results of the power spectrum analysis.
Figure 5.25: Power spectra of upwelling and downwelling actinic flux densities in the VIS and UV-B spectral range for the flight leg within the cloud layer of day 020914.

<table>
<thead>
<tr>
<th>Component</th>
<th>$F_a^{\uparrow}(\text{UV-B})$</th>
<th>$F_a^{\uparrow}(\text{VIS})$</th>
<th>$F_a^{(500 \text{ nm})}$</th>
<th>$F_a^{(500 \text{ nm})}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scale Break (Hz)</td>
<td>0.2</td>
<td>0.15</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>$\beta$</td>
<td>5.8</td>
<td>4.6</td>
<td>3.3</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Table 5.8: Scale break position and slopes for smaller scales derived from power spectra analysis for $F_a$ and $F$ measurements performed within a cloud layer. Results of $F$ analysis are taken from Schmidt (2004).
6 Summary

This work presented the development, testing and application of a spectrometer system which measures upwelling and downwelling actinic flux densities in the UV and VIS spectral range. From spectrometer measurements various photolysis frequencies can be derived, which is the main benefit compared to filter radiometer measurements which are restricted to photolysis frequencies of one specific gas species. A system called Actinic Flux Density Meter (AFDM) was designed for airborne applications. Two different detector principles (a PDA and a CCD) were tested and characterized. The AFDM was deployed during two measurement campaigns. Results have shown the influence of surface and cloud albedo, aerosol and cloud inhomogeneities. The measurements were compared with simulations. Furthermore a parameterization was developed which allows the determination of one of the most crucial photolysis frequencies, $J(\text{O}^1\text{D})$, using spectrometer measurements even with insufficient accuracy in the UV-B spectral range.

The Actinic Flux Density Meter - PhotoDiode Array (AFDM-PDA)

The AFDM consists of two identical single monochromator spectrometers with a PDA detector. Each spectrometer is connected via optical fibers with optical inlets which have a nearly isotropic angular response. Nevertheless a correction method is required to minimize the uncertainties caused by measuring radiation of the opposite hemisphere. If no corrections were applied, the upwelling actinic flux density may be overestimated by as much as 35% depending on albedo, altitude, SZA and cloud conditions. Both inlets are horizontally stabilized in order to be able to distinguish between both hemispheres. The reliable spectral range of the AFDM-PDA is within 305-700 nm. In the past airborne measurements of upwelling and downwelling actinic flux densities were mainly based on scanning double monochromators covering a spectral range between 280 and 420 nm. By using the AFDM-PDA a broader range can be covered in order to determine photolysis frequencies of gas species which dissociate in a wavelength range larger than 420 nm (for example $J(\text{NO}_3)$). Below 305 nm the sensitivity of the PDA drops so that the low-intensity radiation of the UV-B spectral range is not detected with sufficient accuracy. The overall uncertainty of the AFDM-PDA was estimated with ±8.0% in the UV range and ±4.9% in the VIS range. Despite a lower threshold of 305 nm various photolysis frequencies can be derived directly from the actinic flux density ($J(\text{NO}_2)$, $J(\text{H}_2\text{O}_2)$, $J(\text{HCHO})$, $J(\text{NO}_3)$) within a range of 6% as shown by model simulations.

For the formation of the hydroxyl radical OH the photolysis of ozone by UV radiation below 320 nm is the primary source. Hence the photolysis frequency of ozone is of main in-
Simulations have shown that a direct determination of $J(O^\text{I})$ from AFDM-PDA measurements would lead to uncertainties up to 60%. For this purpose a parameterization method was developed and tested during a comparison with results of a double monochromator system. The parameterization is based on data of the SZA, temperature and total ozone column. Furthermore this method was generalized for an application for other threshold wavelengths below 311 nm. As a result $J(O^\text{I})$ derived from double monochromator systems and the parameterized AFDM-PDA data agreed within ±10% for SZA lower than 70°. Tests of the parameterization method on simulated spectra yielded an uncertainty of ±5%.

For airborne measurements in fast changing atmospheric conditions such as in the presence of clouds a high temporal resolution of the measurements is required. Conventional double monochromator spectrometers have a time resolution of more than 10 s depending on the scanning steps and wavelength range. Whereas the AFDM-PDA provides a time resolution of less than 1 s. For airborne measurements this means a spatial resolution of ~60 m, assuming an average aircraft velocity of 60 m/s. The high temporal resolution and its mechanical stability (no moving parts) are the main advantages of the AFDM-PDA. For UV-B measurements the actinic flux density measurements with this system are not reliable due to its low sensitivity and its high stray light contribution in this spectral range. Therefore a new detector was tested during the second part of the work.

The Actinic Flux Density Meter - Charge Coupled Device (AFDM-CCD)

The spectrometer system for measurements of the downwelling actinic flux density was replaced by a spectrometer with a CCD detector with a higher sensitivity in the critical UV-B spectral range (more than one order of magnitude). Comparisons with $J(O^\text{I})$-values derived from double monochromator measurements have shown that $J(O^\text{I})$ is directly derivable from AFDM-CCD measurements without parameterization.

In contrast to the AFDM-PDA the AFDM-CCD is thermoelectrically cooled by a Peltier element to reduce the noise of the signals and to improve the d+c current temporal stability. The latter is important because of its wavelength dependence. The study of SNR gave an improvement of the detection limit in the UV-B by an order of one magnitude compared to that of the AFDM-PDA.

A comparison of actinic flux densities measured by the AFDM-CCD and two double monochromators has shown that the reliable spectral range strongly depends on the intensity of the radiation. For low SZA (30°) the lower threshold is around 300 nm. Furthermore the time resolution was reduced below 300 ms, which means a higher spatial resolution.

Measurement Examples

The AFDM was deployed during two measurement campaigns within the European IN-SPECTRO project. The first campaign took place in East Anglia (UK), the second one in Bavaria (Germany).
During INSPECTRO-1 low aerosol conditions dominated, whereas in Bavaria higher aerosol particle concentrations were measured. Profile measurements of the actinic flux densities in clear sky conditions were presented and related to profiles of the aerosol particle concentration. The slope of the increase with altitude and the variability of integrated $F_a^\uparrow$ and $F_a\downarrow$ in the UV-B, UV-A and VIS spectral range were compared. The highest variability of $F_a^\uparrow$ was found in the lower part of the boundary layer in the UV-B range (5%). In this spectral range also the relative increase of radiation with altitude (slope factor) was highest. For $F_a^\uparrow$ the UV-A has shown the highest variability (34%) and largest slope factor (6.6) which was nearly similar to the UV-B range. As for the downwelling component the lowest variability was calculated for the VIS range. The vertical profiles in high aerosol concentrations gave similar spectral dependencies of the variabilities and slopes. Compared to low aerosol conditions a higher variability was found within the boundary layer for all spectral ranges. Also the slope of $F_a^\uparrow$ was larger. The slope of $F_a\downarrow$ above the aerosol layer has shown a significant decrease compared to the slope within the layer. An interesting feature was noticed for $F_a\downarrow$ (VIS). Below the upper limit of the boundary layer a small enhancement region compared to the region above the boundary layer was observed. This confirms theoretical considerations which were made by e.g., Madronich (1987) and van Weele and Duynkerke (1993).

Radiative transfer simulations were performed to investigate the influence of the aerosol. These simulations realized for aerosol-free and aerosol-loaded atmospheres. The latter case used aerosol properties derived from measurements. A nearly negligible impact of the aerosol was found on the vertical profiles of $J(O_{1D})$ and $J(NO_2)$ for the low aerosol case, whereas for the high aerosol particle concentration case the measured profiles were larger than the aerosol-free simulated profiles in the upper part of the boundary layer. A weaker enhancement (3%) was also noticed between the $J$-profiles simulated for aerosol-free conditions and $J$-profiles simulated for high aerosol concentrations.

In addition to vertical profiles also horizontal variabilities of the actinic flux density in clear sky conditions were presented for both aerosol conditions. The variability of $F_a^\uparrow$ caused by surface albedo inhomogeneities of land and sea surfaces was studied. A spectral dependence was found with increasing variabilities for longer wavelengths (from 2% to 12%). The impact of the land surface on $F_a^\uparrow$ was noticed for measurements above sea. For high aerosol particle concentrations the variabilities in different altitudes (two within, one above the boundary layer) was studied. As expected the highest variabilities were found for the lowest altitude. The spectral dependence of the relative variability of $F_a^\uparrow$ in the middle and above the boundary layer was lower than observed for low aerosol conditions. Most likely the increasing homogeneity of the reflection properties at high aerosol particle concentrations caused this effect.

The main focus of the field campaigns was on the influence of cloud inhomogeneities on $F_a$. For this purpose several vertical profile measurements through stratiform boundary layer clouds were measured. As already reported in literature enhancements of $F_a$ in the upper part of the cloud layer compared to the region above the cloud were observed. These enhancements reached values up to 11% for the VIS spectral range. For shorter wavelengths this enhancement decreased. The measured profiles of upwelling and down-
welling actinic flux densities were compared to 1-D radiative transfer simulations. As far as possible the input data for the model stem from additional microphysical aerosol particle and cloud droplet measurements on the aircraft. The surface albedo was deduced from the Albedometer measurements. For the UV-A and VIS range the agreement between measured and simulated $F_a^{\uparrow}$ was within the measurement uncertainties, whereas the measured $F_a^{\downarrow}$ at 310 nm above the cloud layer was higher than the simulated (≈ 20%). Probably reflection properties of the cloud above the layer are underestimated by the model. However, within and below the cloud the agreement was improved. The agreement between the upwelling components was almost within the measurement uncertainties. The simulated profiles follow the measured profiles quite well in a ±10% range. In addition, the measurements were compared to clear sky simulations in order to derive the influence of clouds. $F_a$ and photolysis frequencies show a significant enhancement above and near cloud top (more than 80% for the downwelling component, up to a factor of 11 for the upwelling component). This enhancement of $F_a^{\downarrow}$ was largest for the UV-B spectral range due to the increase of diffuse radiation which influences the UV range more than the VIS range. The reduction of radiation by clouds was nearly wavelength-independent. The strongest reduction of $F_a^{\downarrow}$-values was observed near the ground (decrease of ≈ 80%). Variability studies of $F_a^{\downarrow}$ above a compact stratus cloud layer and a stratocumulus layer have shown a much higher variability (factor of 10) for the stratocumulus case. In both cases the wavelength-dependence was nearly negligible. The relative variability above the stratus layer was even lower than observed for clear sky conditions. Horizontal measurements within this compact boundary layer have also shown a wavelength-independent variability. A scale analysis was performed which yielded a scale break around 400 m spatial resolution for the downwelling component. For larger scales the radiation follows the variability of the liquid water content. For the upwelling component a scale break near above 2 km was noticed. For lower scales the variability of $F_a^{\uparrow}$ is smaller than the variability of $LWC$ caused by horizontal photon transport.

**Outlook**

In the near future the AFDM and the Albedometer will deployed during the SAharan Mineral dUst ExperiMent (SAMUM). Among other things the layer absorption can be derived from parallel irradiance and actinic measurements. Data from the INSPECTRO campaigns are still in the analyzing process. First publications are submitted (Kylling et al., 2005) or in preperation (Thiel et al., 2005). The main objective is the simulation of complex cloud situations using 1-D and 3-D radiative transfer models. For this reason a method is desired which reproduces the cloud fields from measured microphysical parameters. Scheirer and Schmidt (2004) presented such a new approach. These cloud fields are used as input for 3-D simulations. Detailed studies of the comparisons between measured and simulated actinic flux densities are in progress.
Appendices
A Molecular Data

In this work molecular data of several sources were applied. Table A.1 summarizes the references of the quantum yield and absorption cross section data which were used.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Absorption cross section</th>
<th>Quantum yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>for the parameterization part</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$<em>2$ + h$</em>\nu$ → NO + O($^3$P)</td>
<td>Merienne et al. (1995)</td>
<td>DeMore et al. (1997)</td>
</tr>
<tr>
<td>H$_2$O$<em>2$ + h$</em>\nu$ → OH + OH</td>
<td>DeMore et al. (1997)</td>
<td></td>
</tr>
<tr>
<td>O$<em>3$ + h$</em>\nu$ → O($^1$D) + O$_2$</td>
<td>DeMore et al. (1997)</td>
<td>Talukdar et al. (1998)</td>
</tr>
</tbody>
</table>

| Reaction                          |                          |               |
|----------------------------------|                          |               |
| for the comparison part          |                          |               |
| NO$_2$ + h$_\nu$ → NO + O($^3$P) | Sander et al. (2003)     | Sander et al. (2003) |
| O$_3$ + h$_\nu$ → O($^1$D) + O$_2$ | Daumont et al. (1992)  | Atkinson et al. (1999) |

| Reaction                          |                          |               |
|----------------------------------|                          |               |
| for the measurement example part |                          |               |
| NO$_2$ + h$_\nu$ → NO + O($^3$P) | Merienne et al. (1995)   | Troe (2000)   |
| O$_3$ + h$_\nu$ → O($^1$D) + O$_2$ | Daumont et al. (1992)  | Matsumi et al. (2002) |

Table A.1: Overview of used molecular data
# B Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>m s⁻¹</td>
<td>speed of light</td>
</tr>
<tr>
<td>d</td>
<td>m</td>
<td>distance</td>
</tr>
<tr>
<td>D</td>
<td>counts / (W m⁻² nm⁻¹)</td>
<td>spectrometer sensitivity</td>
</tr>
<tr>
<td>D₀</td>
<td>counts / (W m⁻² nm⁻¹)</td>
<td>spectrometer sensitivity at θ = 0°</td>
</tr>
<tr>
<td>dₚ</td>
<td>µm</td>
<td>particle diameter</td>
</tr>
<tr>
<td>dₚᵢ</td>
<td>µm</td>
<td>geometric mean particle diameter</td>
</tr>
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<td>F</td>
<td>W m⁻² nm⁻¹</td>
<td>spectral irradiance</td>
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<tr>
<td>F₀</td>
<td>W m⁻² nm⁻¹</td>
<td>spectral extraterrestrial irradiance</td>
</tr>
<tr>
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<td>W m⁻² nm⁻¹ or photons cm⁻² nm⁻¹ s⁻¹</td>
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<td>↓</td>
<td>downwelling component</td>
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<td>AHZ</td>
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<tr>
<td>DISORT</td>
<td>DIScrete ORdinate method</td>
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<tr>
<td>DEM</td>
<td>Digital Elevation Model</td>
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<tr>
<td>DTM</td>
<td>Double Tripplegrating Monochromator</td>
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<tr>
<td>DLR</td>
<td>Deutsches Zentrum für Luft- und Raumfahrt</td>
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<td>FWHM</td>
<td>Full Width at Half Maximum</td>
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<td>GPS</td>
<td>Global Positioning System</td>
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<tr>
<td>HALO</td>
<td>High ALtitude and LOng range research aircraft</td>
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<td>INSPECTRO</td>
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<td>IUPAC</td>
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<tr>
<td>LOT</td>
<td>Laser, Optic, Technology</td>
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<tr>
<td>MCS</td>
<td>Multi-Channel Spectrometer</td>
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<tr>
<td>NEI</td>
<td>Noise Equivalent Irradiance</td>
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<tr>
<td>NASA</td>
<td>National Aeronautics and Space Administration</td>
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<td>PC</td>
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<td>PCASP-X</td>
<td>Passive Cavity Aerosol Spectrometer Probe</td>
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<tr>
<td>PDA</td>
<td>PhotoDiode Array</td>
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<td>PERCA</td>
<td>Peroxy Radical Chemical Amplifier</td>
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<td>PVM</td>
<td>Particle Volume Monitoring</td>
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<td>Surface Albedo</td>
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<td>Signal-to-Noise-Ratio</td>
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<td>Solar Zenith Angle</td>
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<td>TOA</td>
<td>Top Of Atmosphere</td>
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<td>TOMS</td>
<td>Total Ozone Mapping Spectrometer</td>
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<td>TRACE-P</td>
<td>Transport and Chemical Evolution over the Pacific</td>
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<td>UV</td>
<td>ultra-violet spectral range</td>
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<td>VELIS</td>
<td>VEHICLE-mounted LIDAR System</td>
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<td>VIS</td>
<td>VISIBLE spectral range</td>
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