

Ultraviolet radiation and photochemistry in clouds: observations and modelling

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Abstract

Ultraviolet (UV) radiation plays a key role in the chemistry of the troposphere since it is in these wavelengths of the solar spectrum that radiation breaks molecules into reactive atoms and free radicals by photodissociation. It is for that reason that the Institute for Marine and Atmospheric Research Utrecht (IMAU) started in 1990 a research project within the frame of the Dutch National Research Programme on Air Pollution and Climate Change (NRP). The strategy of the research project was to combine measurements and model calculations in order to determine accurate photodissociation rates for chemical species. The study focused on the actinic flux, a radiometric quantity which determines the photodissociation rates for chemical species. Measurements and model calculations were focused on study the behaviour of the actinic flux under the presence of clouds and for various ground albedo.

1. INTRODUCTION

In the troposphere key chemical species such as ozone, hydrogen peroxide and nitrogen dioxide are dissociated by sunlight in the ultraviolet spectral region. As UV radiation passes through the atmosphere it is modified by absorption and scattering by gases and aerosols. In addition, UV radiation and therefore the effects on chemical species are influenced by the solar zenith angle, the ground albedo and the presence of clouds (Figure 1).

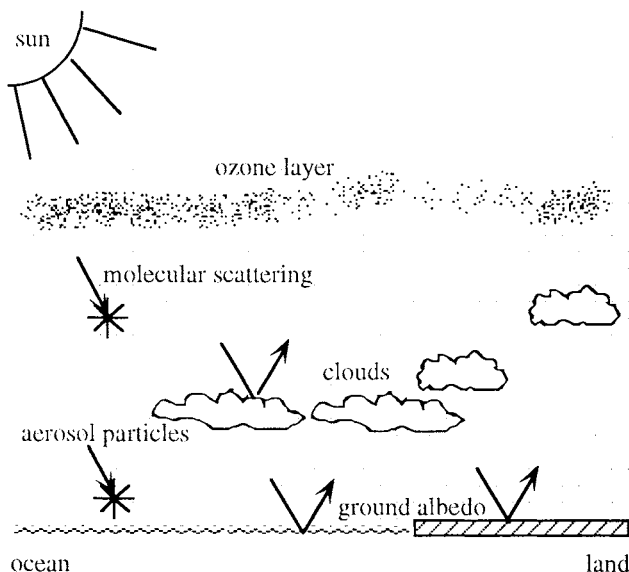


Figure 1. The physical processes relevant for the transfer of UV radiation in the atmosphere.

The photodissociation rates for chemical species i (J_i) can be derived from

$$J_i(\lambda, T) = \int \sigma_i(\lambda, T) \phi_i(\lambda, T) F(\lambda) d\lambda \quad (1)$$

where $\sigma_i(\lambda, T)$ is the absorption cross section and $\phi_i(\lambda, T)$ is the quantum yield. Both quantities are properties of the chemical species and are dependent on the wavelength λ and the temperature T . However, the actinic flux F is a radiometric quantity which is defined as the radiance integrated over all solid angles, i.e. over 4π , per unit area. Consequently, the actinic flux differs from the usually measured irradiance E , which is the radiance incident on a horizontal surface per unit area [1] and [2].

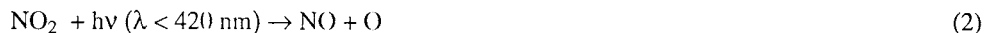
Vertical profiles of actinic flux measured under clear and cloudy conditions by means of a tethered-balloon are presented. The measurement campaign was carried out during the Atlantic Stratocumulus Transition EXperiment (ASTEX) [3]. The strategy of ASTEX is based on a combination of modelling activities and satellite, airborne, ship and surface observations. Therefore, the campaign yielded complete and detailed meteorological, oceanographic and atmospheric chemistry data sets.

In addition to the above-mentioned observations, ground level measurements of actinic flux were taken at different locations in the world: Azores, Antarctica and De Bilt (The Netherlands). These observations were made to study the influence of ground albedo in the actinic flux and consequently in the photodissociation rates.

A comparison was made between the actinic flux measurements and radiative transfer calculations performed with a δ -Eddington model [1] and [2]. The comparison shows that these observational data are an excellent basis for the evaluation of radiative transfer models in the UV-A spectral region, i.e. between 315 and 400 nm.

2. PHOTO-ELECTRIC DETECTOR TO MEASURE ACTINIC FLUX

The actinic flux was measured with a photo-electric detector developed at IMAU [4]. This instrument measures the incoming radiation from all directions (actinic flux), whereas the standard UV radiometer measures only the UV radiation falling on a horizontal plate (irradiance). Briefly, the instrument consists of six diodes covered by diffuse filters, projecting from a cylinder, and arranged perpendicular to each other. The directional response of the photo-electric detector deviates less than 5% from perfect isotropy. The instrument covers the spectral range 330 to 390 nm. It is in this range that e.g. NO_2 photodissociates in the following way:



where $h\nu$ denotes the radiation incident on a molecule, M is the molecule which absorbs the excess of energy and NO , O_2 and O_3 are nitric oxide, oxygen and ozone, respectively. The photodissociation of NO_2 is key reaction in the formation of O_3 in the troposphere.

The photo-electric detector was calibrated against the irradiance measured by a UV-radiometer. The instrument measures the total and direct downward irradiance at 367 nm. To calibrate the photo-electric detector, all the incoming radiation has to be diffuse. Under this condition, the actinic flux is linearly related to the irradiance. The unit of the actinic flux measurements is $\text{W m}^{-2} \text{ nm}^{-1}$. The instrument was designed to be used under a tethered balloon but can as well be used to make surface measurements.

3. ACTINIC FLUX MEASUREMENTS AND MODEL RESULTS

The first actinic flux measurements were carried out within the framework of ASTEX [5]. The observations were made between 1 and 30 June 1992 on Santa Maria island (36.99° N, 25.17° W), the Azores. More than 34 tethered-balloon soundings were carried out. Figure 2 shows the measured vertical profiles of actinic flux. These observations are compared with model calculations performed with the above mentioned δ -Eddington model. The cloud characteristic input necessary for the model calculations was provided by other research groups participating in ASTEX. For the same zenith angle the vertical profile of actinic flux is also calculated under clear sky conditions. An excellent agreement is found between the observations and the model calculations. The figure also shows the different behaviour of the actinic flux (photodissociation rates) under cloud and clear sky conditions. Under clear sky conditions, a slightly increasing tendency for the actinic flux in the whole atmospheric boundary layer is observed.

Under cloud conditions, the actinic flux values are lower below the clouds than in a cloud-free sky because part of the radiation is shielded by the cloud. Inside the cloud the actinic flux increases almost linearly. Above the cloud the value of actinic flux was found to be higher than on a clear day because the cloud albedo has a higher value than the albedo of Earth's surface. Both observations and model calculations show that the different vertical profiles are dependent on the solar zenith angle and the cloud optical depth.

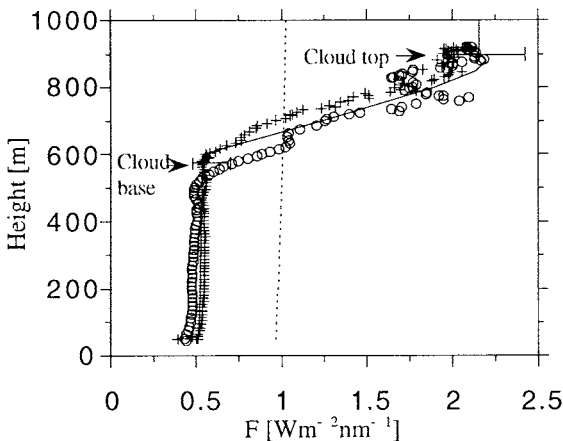


Figure 2. Observed vertical profiles of actinic flux: crosses represent upsonding; open circles downsonding. Solid line is the vertical profile calculated with the model under the presence of a cloud. Dotted line is the vertical profile for a clear sky situation.

At ground level actinic flux measurement were taken in the Azores, Antarctica (74.58° S, 11.12° W) and De Bilt (52.00° N, 5.18° W) [6]. The measurements at the different locations were all performed around the summer solstice. Figure 3 shows the different behaviour of actinic flux compared with the standard radiometric quantity global radiation G (irradiance) under clear sky conditions at different sites. The figure shows the large effect that the high surface albedo (about 0.9) has on the actinic flux measurements. The albedo on the other two sites was 0.05.

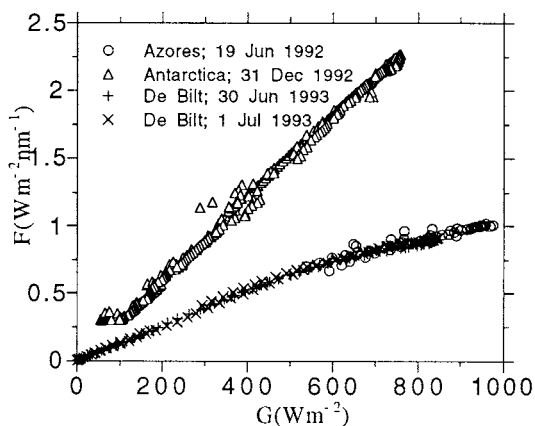


Figure 3. Measured UV actinic flux as a function of measured global radiation for clear sky conditions.

In summary, both measurements and model calculations stress the necessity to describe accurately clouds and take ground albedo into account to obtain accurate photodissociation rates for chemical species. Based on these measurements and model calculations, a parameterization which describes the influence of clouds and ground albedo on photodissociation rates was developed [7]. This parameterization can be readily implemented in atmospheric chemistry models.

5. REFERENCES

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