A Photolysis Scheme for Photochemical Modelling of the Troposphere and Lower Stratosphere

A contribution to subproject GLOREAM

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Summary

A scheme for calculation of photolysis rates in the troposphere and lower stratosphere has been developed. The scheme accounts for zenith angles greater than 90° and includes the effects of clouds. Absorption cross sections and quantum yields are taken from the most recent evaluations. For application in photochemical models the photolysis rates are pre-calculated for different altitudes, surface albedos, ozone profiles and columns, cloud optical depths and cloud types, and sun zenith angles. The zenith angle dependence is fitted to a three parametric analytical function to reduce storage. Calculations with the new scheme indicate the importance of photolysis of some halogenated species and NO_3 at zenith angles greater than 90°. The vertical distribution of ozone is of comparable importance as the ozone column. Comparison with results from other published schemes including schemes presently used by the authors indicate differences by more than a factor of 2 for some species.

Introduction

Interest in photochemical processes in the tropopause region requires a good description of photolysis in numerical models, including a good vertical resolution up to the lower stratosphere. The present scheme has been developed for the combined use in two different photochemical models; a Lagrangian aircraft plume model (Pleijel, 1998) and an Eulerian, 3D, photochemical model based on the MATCH model (Robertson et al., 1999; Langner et al., 1998). These models will be used separately and combined to study the effects of aircraft emissions on atmospheric chemistry (see Pålsson et al., 2002, this issue). Model calculations are made for extended periods, months to years, and an efficient and accurate estimate of the photolysis rates is therefore required.

Results

The photolytic rate constants were calculated with the help of a two-stream version of the Phodis model (Kylling et al., 1995). The absorption cross-sections and quantum yields were updated according to the latest CODATA and IUPAC evaluations (DeMore et al., 1997, DeMore et al., 2000, Atkinson et al., 1997). The model atmospheres for 45 and 60°N, for both summer and winter (Anderson et al., 1986), were used for the calculations. The ozone profiles of standard atmospheres were scaled with varying total ozone columns. For the cloud-free sky the photolytic rates were calculated for solar zenith angles, Θ, between 0 and 97° with a 1° step. Planar geometry was used for angles below 70°.

The functional dependency of the calculated photolytic rate constant of species *i* at altitude *z*, on solar zenith angle were fitted with a 3-parametric exponential function:

$$J_{i,z} = A_{i,z} * \exp(-B_{i,z}/(\cos \Theta^{+}_{z} + C_{i,z})) \quad (1)$$

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Where Θ^+ is a zenith angle modified by the effect of the Earth curvature for a given altitude:

$$\Theta^+_z = \Theta - \xi_z * \sin\Theta, \qquad (2)$$

ξ_z is the zenith angle at dawn/dusk at altitude *z* reduced by 90°. This method avoids numerical problems when Θ is crossing 90°. Table 1 shows ξ_z and the shift of dawn and dusk due to the Earth curvature for different altitudes and declination angles. In Figure 1 the photolytic rates are plotted against the solar elevation angle (90°- Θ) for six different atmospheric profiles and two different altitudes. The differences indicate that the vertical distribution of ozone has at least as much importance on photolysis as the total ozone column of the profile (for total ozone columns see figure caption). The results also show that for some halogenated species and NO_3, the photolysis beyond 90° zenith angle may be of importance.

Table 1. Zenith angle reduced by 90° ξ_z (degrees) at dawn/dusk at different altitudes *z* (km) and delay of dawn and dusk ΔH (min) for these altitudes and fo two different declination angles Δ.

z	ξ_z (deg.)	ΔH(min) $\Delta = 0^o$	$\Delta = 23.5^o$
5	2.27	15.40	14.12
10	3.21	21.78	19.97
15	3.93	26.68	24.46
20	4.53	30.82	28.25
35	5.99	40.79	37.39

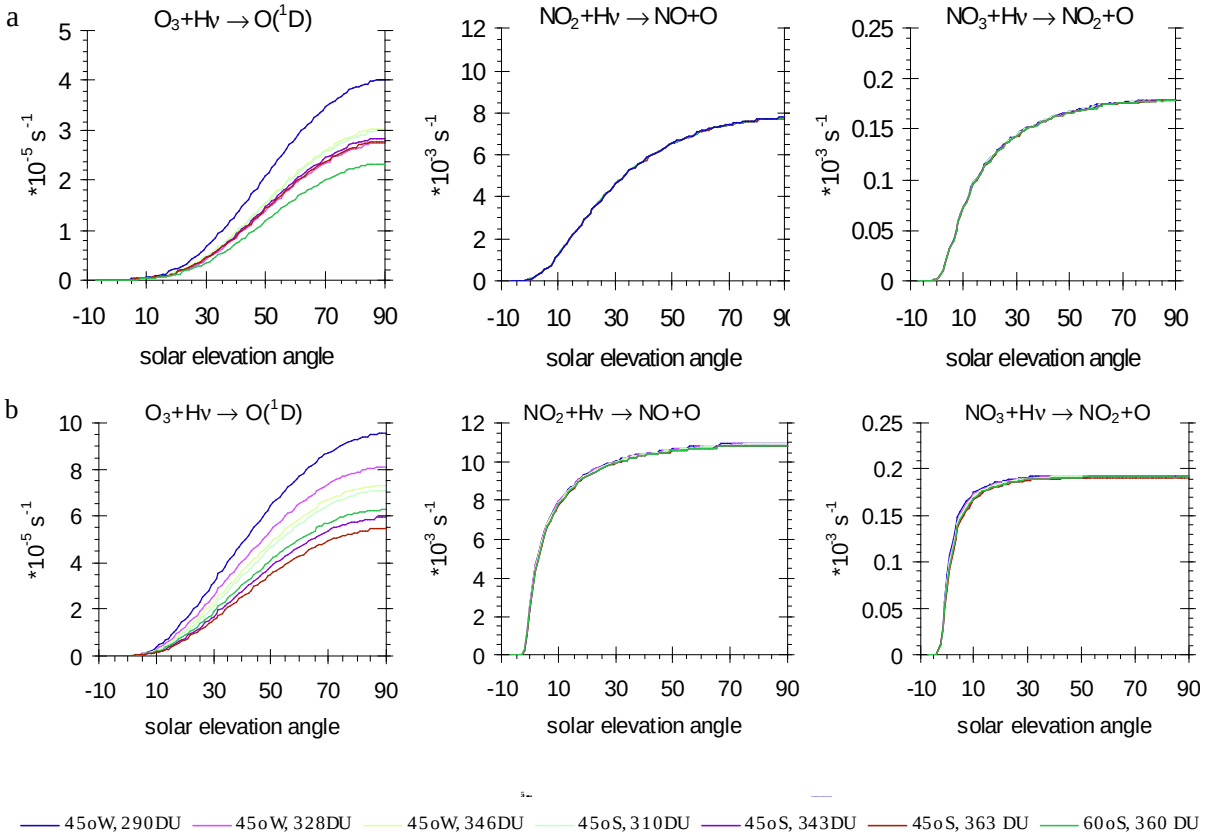

Figure 1. Photolytic rates at Earth surface a) and at 35 km altitude b) plotted against solar elevation angle for different atmospheric profiles, (W=winter, S=summer), latitudes and ozone columns.

The new photolytical rates were compared with three sets used in other models: EMEP (Barrett et al., 1995), MOCCA (Sander and Crutzen, 1996), and an older scheme used in IVL's aircraft-plume model (Pleijel, 1998 and references therein). The best agreement was obtained with rates used in the MOCCA model. Those rates were calculated with the PAPER model (Landgraf and Crutzen, 1998) using the latest absorption cross-sections and the AFGL atmospheric profiles (Anderson et al., 1986). However, those rates were available only for the ground level. Agreement with the other two models was not as good. The maximum differences were of about a factor of 2. Figure 2 shows comparison with the rates used in the EMEP model, which are also those used in the MATCH model so far. These rates were also calculated with the PHODIS model, some specifics of the calculations can however differ from our calculations.

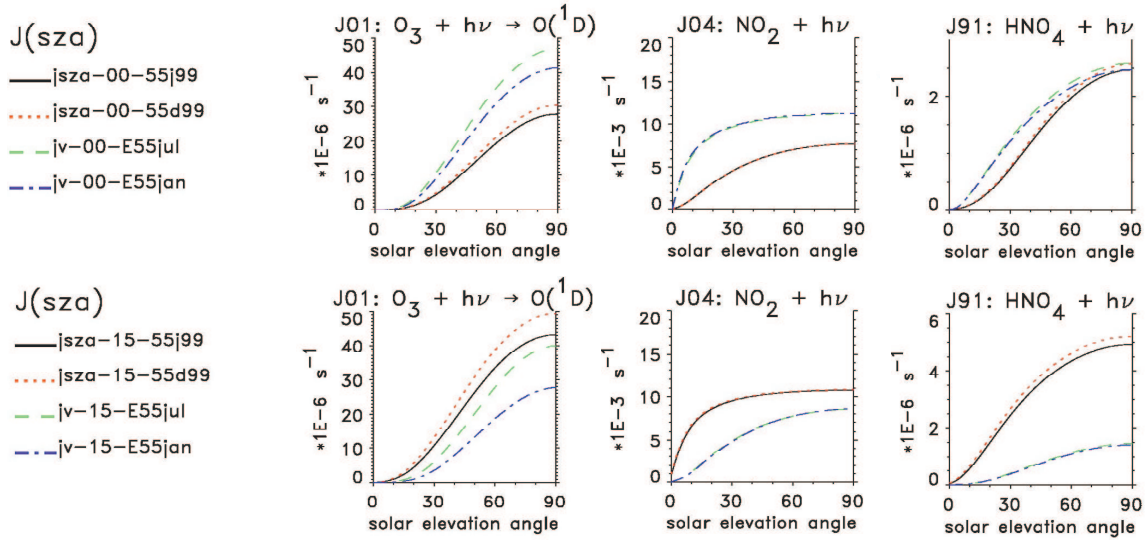

Figure 2. Comparison of the photolytic rates presented in this work (jsza) with those used in the EMEP model (jv) at the Earth surface (-00) and at 15 km altitude (-15) for two atmospheric profiles: mid-latitude winter (55d99 and E55jan) and mid-latitude summer(55j99 and E55jul).

The effects of clouds on photolytic rates were investigated with the model. Effects of the cloud height, cloud optical depth (τ_N), and distribution of the liquid water in the vertical column were studied. The results showed that τ_N has the major influence and that the below-cloud photolytic rates vary very little with varying height of clouds. The ratio J_{cloud}/J_{clear_sky} above the cloud can then be related to the distance from the cloud top. The effect of the distribution of liquid water along the vertical column for clouds with the same τ_N is shown in Figure 3. It can be seen that the effect is small at cloud-free altitudes. The main difference is at altitudes for which outside-cloud rates are compared with inside-cloud rates.

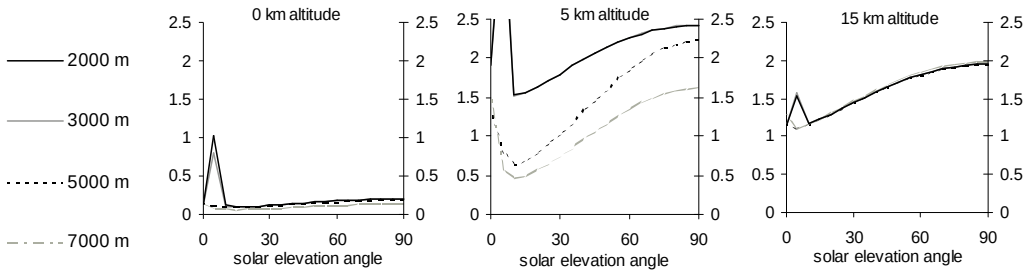

Figure 3. Comparison of the J_{cloud}/J_{clear_sky} ratio of the NO2 →NO+O reaction for four cloud cases, all have τ_N=100 and cloud thickness as indicated in the figure legend. The ratios are for the mid-latitude summer atmospheric profile.

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