



**A simple formulation  
of the CH<sub>2</sub>O  
photolysis quantum  
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E.-P. Röth and  
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# A simple formulation of the CH<sub>2</sub>O photolysis quantum yields

E.-P. Röth<sup>1</sup> and D. H. Ehhalt<sup>2</sup>

<sup>1</sup>Institute for Energy and Climate Research (IEK-7: Stratosphere), Research Center Jülich, Jülich, Germany

<sup>2</sup>Institute for Energy and Climate Research (IEK-8: Troposphere), Research Center Jülich, Jülich, Germany

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Correspondence to: E.-P. Röth (e.p.roeth@fz-juelich.de)

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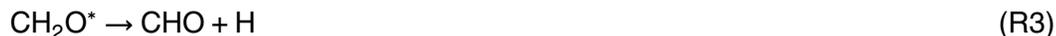


## Abstract

New expressions for the various wavelength – dependent photolysis quantum yields of  $\text{CH}_2\text{O}$ ,  $\Phi_j$ , are presented. They are based on combinations of functions of the type  $A_j/(1 + \exp[-(1/\lambda - 1/\lambda_{0j})/b_j])$ . The parameters  $A_j$ ,  $b_j$ , and  $\lambda_{0j}$  which have a physical meaning are obtained by fits to the measured data of the  $\Phi_j$  available from the literature. The altitude dependence of the photolysis frequencies resulting from the new quantum yield expressions are compared to those derived from the  $\Phi_j$  recommended by JPL and IUPAC.

## 1 Introduction

Formaldehyde,  $\text{CH}_2\text{O}$ , is an important trace gas in the atmosphere. It is formed as an intermediate in the oxidation of methane and non-methane hydrocarbons, and destroyed by the reaction with OH and by photolysis in the near ultraviolet. The photolysis involves several channels. Following the excitation (Reaction R1),  $\text{CH}_2\text{O}^*$  can decay into purely molecular products (Reaction R2), or into products that in the atmosphere lead to the eventual formation of hydroperoxy radicals,  $\text{HO}_2$ , (Reactions R3 and R4). The quenching Reaction (R5) and fluorescence (Reaction R6) can influence the quantum yields of the product channels.



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As it turns out the molecular channel, Reaction (R2), provides the by far largest source of molecular hydrogen, H<sub>2</sub>, in the atmosphere (Ehalt and Rohrer, 2009). The radical channels, Reactions (R3) and (R4), that generate HO<sub>2</sub> radicals, enhance local photochemistry. Finally each destruction of a CH<sub>2</sub>O molecule – including that by OH – eventually results in a carbon monoxide molecule, CO. As a consequence CH<sub>2</sub>O is also an important source of CO in the atmosphere.

Recognizing the importance for atmospheric chemistry the quantum yields of the CH<sub>2</sub>O photolysis were measured early on and by various authors (see Sander et al., 2011; Atkinson et al., 2006, and the internet version IUPAC (2013) for summaries).

The quantum yield  $\Phi_{\text{mol}}$  of the molecular branch (Reaction R2) was usually measured by monitoring the H<sub>2</sub> production while scavenging the H atoms to prevent their contribution to the H<sub>2</sub> production (e.g. Moortgat et al., 1978; Horowitz and Calvert, 1978). The formation of the molecular products via the reaction path of a roaming H atom (see e.g. Bowman and Shepler, 2011; and Christoffel and Bowman, 2009) was not known then and is not included explicitly in our list of reactions but it is included in Reaction (R2), and its quantum yield is part of the measured  $\Phi_{\text{mol}}$ .

Reactions (R3) and (R4) form the radical channel with the combined quantum yield  $\Phi_{\text{rad}}$  which in some cases was investigated directly by measuring the products, H and CHO (e.g. Smith et al., 2002; Gorrotxategi et al., 2008; Tatum Ernest et al., 2012).

The fluorescence quantum yield (Reaction R6) was measured by Miller and Lee, 1978, in the wavelength range 290 to 360 nm. Its maximum at 353 nm is less than 3.5 % and it is less than 1 % at the other wavelengths considered. It will, therefore, be neglected here. We know of no measurements below 290 nm.

The total quantum yield  $\Phi_{\text{tot}}$ , i.e. the fraction of the decay of excited formaldehyde, CH<sub>2</sub>O\*, into products other than its ground state, was derived from the CO production. By definition  $\Phi_{\text{tot}}$  is the sum of the quantum yields of the molecular and the radical channel:

$$\Phi_{\text{tot}} = \Phi_{\text{mol}} + \Phi_{\text{rad}} \quad (1)$$

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Moortgat et al. (1983) have also measured the wavelength dependence of  $\Phi_{\text{rad}}$  at 220 K. Given the experimental variance in those admittedly sparse data, Eq. (3) also fits the measured  $\Phi_{\text{rad}}$  at 220 K quite well (not shown here). Thus, as far as the experimental data on  $\Phi_{\text{rad}}$  are concerned, Eq. (3) covers the temperature range of 220 to 300 K relevant for atmospheric modeling and there is no immediate need to introduce a temperature dependence. On the other hand, theoretical considerations suggest the inclusion of the internal energy of the CH<sub>2</sub>O molecule, and this can be easily done: following Troe (2007) one can add a term  $3kT$  (appropriately scaled) to  $1/\lambda$  in the left hand term of Eq. (3). In Sect. 5, Discussion, we will investigate the impact of this  $T$  dependence (see Eq. 12) on the altitude profile of the respective photolysis frequency. In principle, another weak  $T$  dependence can arise through the parameter  $b$ . That dependence could be easily accommodated by replacing  $b$  by  $(b_0 + b_1T)$  should future  $\Phi_{\text{rad}}$  measurements provide enough information to warrant such a step.

The present formulation of Eq. (3) with constant parameters  $b$  – i.e.  $b$  independent of  $\lambda$  – forces the decrease to be nearly symmetrical around the respective  $\lambda_0$ . This is not necessarily realistic. Again, if future measurements or theoretical considerations should prove the need, an asymmetry could be easily accommodated by allowing  $b$  to depend on  $\lambda$ .

Finally, we note, that a line structure could be superimposed on Eq. (3) without difficulty. For the moment we refrain from doing so for two reasons. (1) As Tatum Ernest et al. (2012) showed even the strong feature in  $\Phi_{\text{rad}}$  at 321 nm would change the photolysis frequency in the atmosphere,  $j_{\text{rad}}$ , by only  $-4\%$ , because it coincides with a strong minimum in the absorption coefficient of CH<sub>2</sub>O. Thus the error possibly introduced by its neglect is comparatively small (see discussion below). (2) The measurements of  $\Phi_{\text{rad}}$  by Smith et al. (2002), and Gorrotxategi et al. (2008) contain data points close to 321 nm which fall right on the average  $\Phi_{\text{rad}}$  given by Eq. (3). They were made with sufficient resolution to resolve the feature at 321 nm and are therefore somewhat at variance with the finding of Tatum Ernest et al. (2012).

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Figure 1 also contains the recommended wavelength dependences of  $\Phi_{\text{rad}}$  given in the evaluations by JPL (Sander et al., 2011) and IUPAC (2006). The reason for the choice of IUPAC (2006) over IUPAC (2013) is that the former data, which were first published in 2002 and remained in the internet until 2012, had many users in the past and possibly still has at present. Further included is the theory-based dependence derived by Troe (2007); it covers only the restricted wavelength range from 310 to 350 nm. As a quantitative measure of the quality of these fits we here add the coefficient of determination  $c$ . In the present case this is identical to the correlation coefficient between fitted and measured data. These correlation coefficients are:  $c = 0.821$  (IUPAC, 2006);  $c = 0.840$  (Troe, 2007);  $c = 0.898$  (JPL, 2011); and  $c = 0.905$  (this work); that is the quality of these various fits does not differ drastically.

### 3 The total quantum yield

There are more direct measurements for  $\Phi_{\text{tot}}$  and its dependence on  $\lambda$  than for  $\Phi_{\text{mol}}$ . To obtain higher accuracy we, therefore, first obtain a fit for  $\Phi_{\text{tot}}(\lambda)$  and then use Eq. (1), i.e.  $\Phi_{\text{mol}} = \Phi_{\text{tot}} - \Phi_{\text{rad}}$  for a fit of  $\Phi_{\text{mol}}(\lambda)$ . That fit is later compared to the measured dependence of  $\Phi_{\text{mol}}$  on  $\lambda$ .

The available measurements of  $\Phi_{\text{tot}}(\lambda)$  at 300 K temperature and 1013 hPa pressure are reproduced in Fig. 2. The values of  $\Phi_{\text{tot}}$  at 355 and 353 nm were obtained by interpolating the respective Stern–Volmer plots given by Moortgat et al. (1979, 1983) to the pressure of 1 atm. The  $\Phi_{\text{tot}}$  values at  $\lambda < 340$  nm are pressure independent. The measured  $\Phi_{\text{tot}}(\lambda)$  exhibits three regions: a plateau between 290 and 330 nm, a steep decrease to zero at longer wavelengths, and a weak decrease to  $\Phi_{\text{tot}} \sim 0.8$  at shorter wavelengths. The average measured  $\Phi_{\text{tot}}$  in the plateau is  $1.06 \pm 0.09$  – not significantly different from 1 – the maximum possible value. Therefore, in the fit we will fix this value to unity. The separation of the two decreases by a plateau with  $\Phi_{\text{tot}} = 1$  also means that it is possible to fit these two regions of decrease separately and independently of each other.



Our fit yields the parameters  $\lambda_{0,i}$  and  $b_i$  of Table 2. In this case  $\lambda_{0,i}$  has a somewhat different meaning than before. Here,  $\lambda_{0,i}$  not only depends on the threshold energy of the reaction involved, but also on the quenching efficiency with which energy is drained from the excited  $\text{CH}_2\text{O}$  molecule. But as before  $\lambda_{0,i}$  represents the inflection point in the decrease of  $\Phi$ , at least for  $M = M_0$ .

The fit of  $\Phi_{\text{tot}}$  for the short wave decrease relies on our model Eq. (2) and yields the parameters listed in Table 2.

The equation for  $\Phi_{\text{tot}}(\lambda)$  over the full wavelength range therefore is:

$$\Phi_{\text{tot}} = \frac{1}{1 + \exp\left(\frac{-(1/\lambda - 1/347.1)}{5.7 \times 10^{-5}}\right)} \left(M/M_0\right) - \frac{0.20}{1 + \exp\left(\frac{-(1/\lambda - 1/284.3)}{3.5 \times 10^{-5}}\right)} \quad (6)$$

with  $\lambda$  given in nm.

We have not been able to find a ready explanation for the experimentally observed weak decrease of  $\Phi_{\text{tot}}$  at shorter wavelengths in the literature. We note, however, that  $\lambda_{0,s} = 284.3$  corresponds closely to the heat of formation for reaction Eq. (4) (see Sect. 2).

Following the arguments by Troe (2007) we assume the temperature dependence of  $\Phi_{\text{tot}}(\lambda)$  to be negligible. But here again, our fitting functions could readily be modified to include a  $T$  dependence.

$\Phi_{\text{tot}}(\lambda)$  from Eq. (6) is also shown in Fig. 2. It compares favorably to the measured data of  $\Phi_{\text{tot}}$ . For additional comparison Fig. 2 also contains the recommended wavelength dependences of  $\Phi_{\text{tot}}$  given in the evaluations by JPL (Sander et al., 2011) and IUPAC (2006). Further included is the dependence derived from Troe's (2007)  $\Phi_{\text{mol}}$ ; it covers only the restricted wavelength range from 310 to 370 nm. Just as Eq. (6), the  $\Phi_{\text{tot}}(\lambda)$  from JPL and that based on Troe (2007) agree well with the measurements. An exception are the recommended values from IUPAC (2006) which clearly deviate from the measurements in the range  $330 \text{ nm} < \lambda < 350 \text{ nm}$ . The consequence of this deviation on the coefficient of determination is relatively small:  $c = 0.913$ , whereas the

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others are: JPL,  $c = 0.959$ ; Troe,  $c = 0.944$ ; present,  $c = 0.956$ . In IUPAC (2013) this deviation is removed; the corresponding  $c$  is 0.924.

#### 4 The quantum yield of the molecular channel

Since  $\Phi_{\text{mol}}$  is given by  $\Phi_{\text{tot}} - \Phi_{\text{rad}}$ , it could be simply obtained from the difference of Eqs. (6) and (3). Explicitly:

$$\Phi_{\text{mol}} = \Phi_{\text{tot}} - \Phi_{\text{rad}} = \frac{1}{1 + \exp\left(\frac{-(1/\lambda - 1/347.1)}{5.7 \times 10^{-5}}\right)} (M/M_0) - \frac{0.20}{1 + \exp\left(\frac{-(1/\lambda - 1/284.3)}{3.5 \times 10^{-5}}\right)} - \frac{0.72}{1 + \exp\left(\frac{-(1/\lambda - 1/328.0)}{5.2 \times 10^{-5}}\right)} + \frac{0.38}{1 + \exp\left(\frac{-(1/\lambda - 1/278.4)}{4.7 \times 10^{-5}}\right)} \quad (7)$$

On the other hand  $\Phi_{\text{mol}}$  can be obtained by a direct fit to the measured data. This requires a combination of only three functions of the Eq. (2) type and the fit results in:

$$\Phi_{\text{mol}} = \frac{1}{1 + \exp\left(\frac{-(1/\lambda - 1/345.2)}{6.2 \times 10^{-5}}\right)} (M/M_0) - \frac{0.75}{1 + \exp\left(\frac{-(1/\lambda - 1/325.3)}{3.9 \times 10^{-5}}\right)} + \frac{0.24}{1 + \exp\left(\frac{-(1/\lambda - 1/274.2)}{2.3 \times 10^{-5}}\right)} \quad (8)$$

Equation (8) makes the implicit assumption that the short wave decreases in  $\Phi_{\text{tot}}$  and  $\Phi_{\text{rad}}$  (second and fourth term in Eq. 7) have the same  $\lambda_{0,s}$  and  $b_s$ . The estimated  $1\sigma$  errors along with the fit parameters are listed in Table 3.

In Fig. 3  $\Phi_{\text{mol}}(\lambda)$  from Eq. (8) is compared to the measured data on  $\Phi_{\text{mol}}(\lambda)$ . The latter consist of direct measurements of  $\Phi_{\text{mol}}$  by Moortgat et al. (1979, 1983), and data

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concerns the temperature dependence of  $\Phi$ . Given the experimental uncertainties we have refrained from providing  $T$  dependences for the  $\Phi$ 's. But there are temperature dependences in the literature, which could be incorporated in our formulation (Atkinson et al., 2006; Troe, 2007; Sander et al., 2011). Below we will incorporate such a temperature dependence in  $\Phi_{\text{rad}}$  to test the sensitivity of the corresponding photolysis frequencies of  $\text{CH}_2\text{O}$  to the vertical temperature profile.

In addition the question of line structure in  $\Phi_{\text{rad}}$  needs eventually to be resolved.

Of major interest to the atmospheric chemist is the impact of this new formulation of  $\Phi$  on the atmospheric photolysis frequencies of  $\text{CH}_2\text{O}$ . That photolysis frequency  $j$  is given by:

$$j = \int_0^{\infty} \Phi(\lambda) \sigma(\lambda) F_{\lambda}(\lambda) d\lambda \quad (9)$$

i.e. it also depends on the absorption cross-section,  $\sigma(\lambda)$ , of  $\text{CH}_2\text{O}$ , and the local actinic photon flux density  $F_{\lambda}(\lambda)$ . For our calculations of  $j$  we will use the absorption spectrum measured by Gratien et al. (2007). It is, by the way, also slightly temperature dependent; the respective function can be found in Röth et al. (1997). The atmospheric actinic photon flux density consists of down-welling and up-welling contributions, and depends of course on the solar zenith angle and altitude. It was calculated by the radiative transfer program ART (Röth, 2002) using the extraterrestrial solar flux from WMO (1985). All three factors under the integral strongly vary with wavelength,  $\lambda$ . (To various degrees they also vary with altitude.) As an example Fig. 4 shows  $\sigma(\lambda)$ ,  $F_{\lambda}(\lambda)$ , and  $\Phi_{\text{mol}}(\lambda)$  at 30 km altitude and  $33^\circ$  solar zenith angle. We particularly notice the sharp cutoff in  $F_{\lambda}(\lambda)$  around  $\lambda = 320$  nm caused by the absorption of solar UV in the ozone layer at lower wavelengths. This means that below 30 km altitude the exact form of the  $\Phi_i$  at  $\lambda < 300$  nm has little influence on the various photolysis frequencies. Figure 4 further indicates how much the long-wave decrease of  $\Phi_{\text{mol}}$  is shifted towards longer wavelengths at the air density at 30 km altitude. In fact, this shift is so large that the

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long-wave cutoff of the integrand in Eq. (9) is no longer determined by  $\Phi_{\text{mol}}$ , as it is at low altitudes, but rather by the absorption spectrum of  $\text{CH}_2\text{O}$ . Hence, at altitudes above 30 km the exact form of the decrease in  $\Phi_{\text{mol}}$  and  $\Phi_{\text{tot}}$  at the longer wavelengths has no influence on the respective photolysis frequencies.

Given the  $\Phi_j$  from Eqs. (11) to (13),  $\sigma(\lambda)$  from Gratien et al. (2007) along with vertical temperature and density profiles of the US standard atmosphere (NOAA, 1976) we can calculate the vertical profiles of the photolysis rates. They are shown in Fig. 5. The shaded areas mark the  $1\sigma$  error bounds of the  $j_j$  profiles based on the errors of the fitting parameters for  $\Phi_j$  given in Sect. 5. As to be expected, all  $j_j$  increase with altitude. In the case of  $j_{\text{rad}}$  that increase is essentially due to the vertical change in  $F_\lambda(\lambda)$ , since our  $\Phi_{\text{rad}}$  is neither temperature nor pressure dependent and thus independent of altitude, and the slight temperature dependence of  $\sigma(\lambda)$  makes a minor contribution only.  $j_{\text{tot}}$  and  $j_{\text{mol}}$ , however, are significantly modified by the density dependence in  $\Phi_{\text{mol}}$ .

In Fig. 5 we also demonstrate the impact of a possible temperature dependence in  $\Phi_{\text{rad}}$ . The temperature dependence is introduced by adding the term  $(300 - T)(3k/hc)$  in the appropriate dimensional units to  $1/\lambda$  in the first term of Eq. (3) (see Troe, 2007, and Sect. 2).

$$\Phi_{\text{rad}} = \frac{0.74}{1 + \exp\left(\frac{-(1/\lambda + (300 - T)(3k/hc) - 1/327.4)}{5.4 \times 10^{-5}}\right)} - \frac{0.40}{1 + \exp\left(\frac{-(1/\lambda - 1/279.0)}{5.2 \times 10^{-5}}\right)} \quad (10)$$

That means: only the long-wave decay in  $\Phi_{\text{rad}}$  is considered to be temperature dependent. Here  $k$  is the Boltzmann constant,  $h$  the Planck constant, and  $c$  the speed of light. As Fig. 5 shows a temperature dependence of this size clearly has a significant impact on  $j_{\text{rad}}$  and by virtue of  $\Phi_{\text{mol}} = \Phi_{\text{tot}} - \Phi_{\text{rad}}$  also on  $j_{\text{mol}}$ . The effect is largest at around 15 km, the height of the temperature minimum, and about  $-9\%$  for  $j_{\text{rad}}$ , respectively ca.  $+6\%$  for  $j_{\text{mol}}$ . The temperature at 15 km is 220 K, i.e. the temperature shifts in  $j_{\text{rad}}$  and  $j_{\text{mol}}$  correspond to a temperature difference of 80 K. Apparently a correct formulation

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of the  $T$  dependence of  $\Phi_{\text{rad}}$  could lead to a significant improvement in the predicted vertical profiles of  $j_{\text{rad}}$  and  $j_{\text{mol}}$ .

$j_{\text{tot}}$  remains unaffected by the proposed temperature dependency. In fact, even assuming a temperature dependence of the kind above for the long-wave decay of  $\Phi_{\text{tot}}$  would have comparatively little impact on the  $j_{\text{tot}}$  profile. It would be masked by the air density dependence of  $\Phi_{\text{tot}}$ : just as at lower densities, the exact form of the long-wave decay in  $\Phi_{\text{tot}}$  no longer influences  $j_{\text{tot}}$ , so can its temperature dependence no longer influence  $j_{\text{tot}}$ .

Finally, in Fig. 6, we compare the photolysis frequencies based on this work's quantum yields to those calculated with the quantum yields recommended by IUPAC (2006) and JPL (Sander et al., 2011). The JPL recommendation includes an explicit temperature dependence for  $\Phi_{\text{rad}}$ . In addition, both, JPL and IUPAC (2006), treat the density dependence of  $\Phi_{\text{mol}}$  in terms of atmospheric pressure, which introduces a further temperature dependence. Both temperature effects are included in the calculation of the respective  $j_i$  profiles. The comparison demonstrates that even at present – without a representation of the temperature dependence – our  $\Phi_i$  provide vertical profiles of the photolysis frequency which agree well with those based on  $\Phi_i$  from the JPL recommendation – for all  $j_i$  and both solar zenith angles considered. The comparison with the data from Atkinson et al. (2006) is less favorable, especially for  $j_{\text{mol}}$ . This reflects the differences between  $\Phi_{\text{mol}}(\lambda)$  given here and that recommended by JPL on the one hand to that recommended by Atkinson et al. (2006) on the other, which were already apparent in Figs. 2 and 3. The new quantum yields recommended by IUPAC in 2013 give photolysis rates which lie slightly above our curves for  $j_{\text{mol}}$ , just outside the error bounds.

Although the derived  $j_i$  profiles as well as the fits to the measured  $\Phi_i$  (Figs. 1–3) based on the JPL recommendation and on the present work appear reasonably equivalent, we feel our formalism to be advantageous: since it consistently formulates the wavelength dependence of  $\Phi_i$  in terms of  $1/\lambda$ , its fitting parameters are in units of energy, and represent, or are close to, molecular parameters, notably threshold

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energies, which are often available and can serve as guides. Moreover, the formulation in units of energy makes it easy to introduce temperature dependences should future measurements or theoretical considerations demand it. For the same reasons our formalism should provide a useful template for the formulation of the  $\Phi_i$  for the isotopologues of formaldehyde and likewise for the photolysis quantum yields of many other molecules.

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**Table 1.** Coefficients of the quantum yield function for the radical channel and  $1\sigma$  errors of Eq. (3).

Coefficient	value	error
$A_l$	0.72	$\pm 0.01$
$\lambda_{0,l}$	328.0 nm	$\pm 0.6$ nm
$b_l$	$5.2 \times 10^{-5} \text{ nm}^{-1}$	$\pm 0.6 \times 10^{-5} \text{ nm}^{-1}$
$A_s$	0.38	$\pm 0.03$
$\lambda_{0,s}$	278.4 nm	$\pm 0.8$ nm
$b_s$	$4.7 \times 10^{-5} \text{ nm}^{-1}$	$\pm 1.1 \times 10^{-5} \text{ nm}^{-1}$

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**Table 2.** Coefficients of the total quantum yield function and 1 $\sigma$  errors of Eq. (6).

Coefficient	value	error
$A_l$	1.0	fixed
$\lambda_{0,l}$	347.1 nm	$\pm 0.7$ nm
$b_l$	$5.7 \times 10^{-5} \text{ nm}^{-1}$	$\pm 0.8 \times 10^{-5} \text{ nm}^{-1}$
$A_s$	0.20	$\pm 0.01$
$\lambda_{0,s}$	284.3 nm	$\pm 0.9$ nm
$b_s$	$3.5 \times 10^{-5} \text{ nm}^{-1}$	$\pm 1.4 \times 10^{-5} \text{ nm}^{-1}$

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**Table 3.** Coefficients of the quantum yield function for the molecular channel and  $1\sigma$  errors of Eq. (8).

Coefficient	value	error
$A_l$	1.0	fixed
$\lambda_{0,l}$	345.2 nm	$\pm 0.8$ nm
$b_l$	$6.2 \times 10^{-5} \text{ nm}^{-1}$	$\pm 1.7 \times 10^{-5} \text{ nm}^{-1}$
$A_m$	0.75	$\pm 0.03$
$\lambda_{0,m}$	325.3 nm	$\pm 0.6$ nm
$b_m$	$3.9 \times 10^{-5} \text{ nm}^{-1}$	$\pm 0.5 \times 10^{-5} \text{ nm}^{-1}$
$A_s$	0.24	$\pm 0.05$
$\lambda_{0,s}$	274.2 nm	$\pm 3.3$ nm
$b_s$	$2.3 \times 10^{-5} \text{ nm}^{-1}$	$\pm 2.1 \times 10^{-5} \text{ nm}^{-1}$

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**Table 4.** Recommended quantum yield functions for use in atmospheric chemistry models (wavelength  $\lambda$  in nm).

$$\Phi_{\text{rad}} = \frac{0.74}{1 + \exp\left(\frac{-(1/\lambda - 1/327.4)}{5.4 \times 10^{-5}}\right)} - \frac{0.40}{1 + \exp\left(\frac{-(1/\lambda - 1/279.0)}{5.2 \times 10^{-5}}\right)} \quad (11)$$

$$\Phi_{\text{tot}} = \frac{1}{1 + \exp\left(\frac{-(1/\lambda - 1/346.9)}{5.4 \times 10^{-5}}\right)} (M/M_0) - \frac{0.22}{1 + \exp\left(\frac{-(1/\lambda - 1/279.0)}{5.2 \times 10^{-5}}\right)} \quad (12)$$

$$\Phi_{\text{mol}} = \frac{1}{1 + \exp\left(\frac{-(1/\lambda - 1/346.9)}{5.4 \times 10^{-5}}\right)} (M/M_0) - \frac{0.74}{1 + \exp\left(\frac{-(1/\lambda - 1/327.4)}{5.4 \times 10^{-5}}\right)} + \frac{0.18}{1 + \exp\left(\frac{-(1/\lambda - 1/279.0)}{5.2 \times 10^{-5}}\right)} \quad (13)$$

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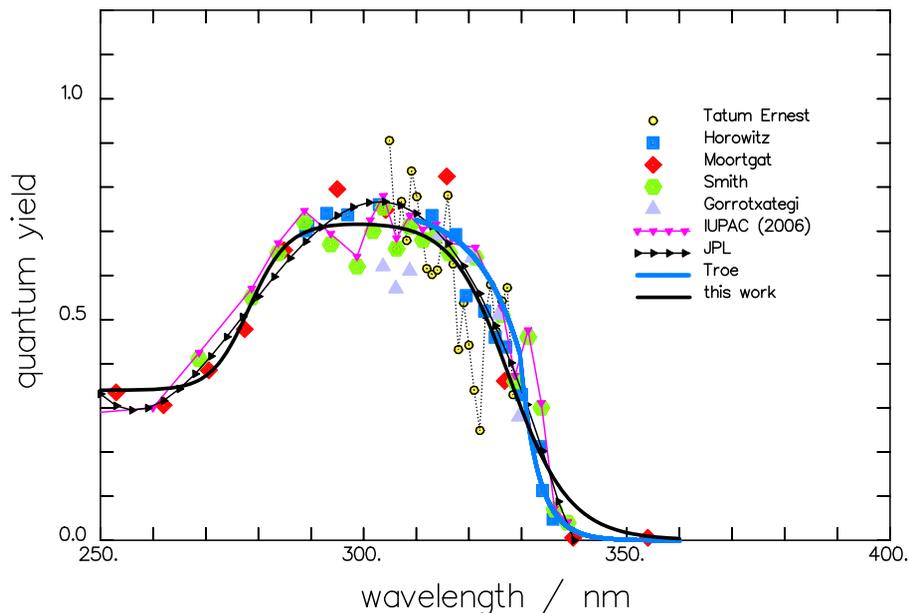
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**Table 5.** Coefficients and  $1\sigma$  errors of the equations in Table 4, along with the coefficients of determination  $c$  for the quantum yield functions. These parameters result from a global fit of all data, as described in Sect. 5.

	coefficient	value	error
$\Phi_{\text{rad}}$ $c = 0.904$	$A_l$	0.74	$\pm 0.01$
	$\lambda_{0,l}$	327.4 nm	$\pm 0.5$ nm
	$b_l$	$5.4 \times 10^{-5} \text{ nm}^{-1}$	$\pm 0.5 \times 10^{-5} \text{ nm}^{-1}$
	$A_s$	0.40	$\pm 0.04$
	$\lambda_{0,s}$	279.0 nm	$\pm 1.3$ nm
	$b_s$	$5.2 \times 10^{-5} \text{ nm}^{-1}$	$\pm 2.4 \times 10^{-5} \text{ nm}^{-1}$
$\Phi_{\text{tot}}$ $c = 0.951$	$A_l$	1.0	fixed
	$\lambda_{0,l}$	346.9 nm	$\pm 0.5$ nm
	$b_l$	$5.4 \times 10^{-5} \text{ nm}^{-1}$	$\pm 0.3 \times 10^{-5} \text{ nm}^{-1}$
	$A_s$	0.22	$\pm 0.02$
	$\lambda_{0,s}$	279.0 nm	$\pm 1.3$ nm
	$b_s$	$5.2 \times 10^{-5} \text{ nm}^{-1}$	$\pm 2.4 \times 10^{-5} \text{ nm}^{-1}$
$\Phi_{\text{mol}}$ $c = 0.934$	$A_l$	1.0	fixed
	$\lambda_{0,l}$	346.9 nm	$\pm 0.5$ nm
	$b_l$	$5.4 \times 10^{-5} \text{ nm}^{-1}$	$\pm 0.3 \times 10^{-5} \text{ nm}^{-1}$
	$A_m$	0.74	$\pm 0.01$
	$\lambda_{0,m}$	327.4 nm	$\pm 0.5$ nm
	$b_m$	$5.4 \times 10^{-5} \text{ nm}^{-1}$	$\pm 0.5 \times 10^{-5} \text{ nm}^{-1}$
	$A_s$	0.18	$\pm 0.02$
	$\lambda_{0,s}$	279.0 nm	$\pm 1.3$ nm
	$b_s$	$5.2 \times 10^{-5} \text{ nm}^{-1}$	$\pm 2.4 \times 10^{-5} \text{ nm}^{-1}$

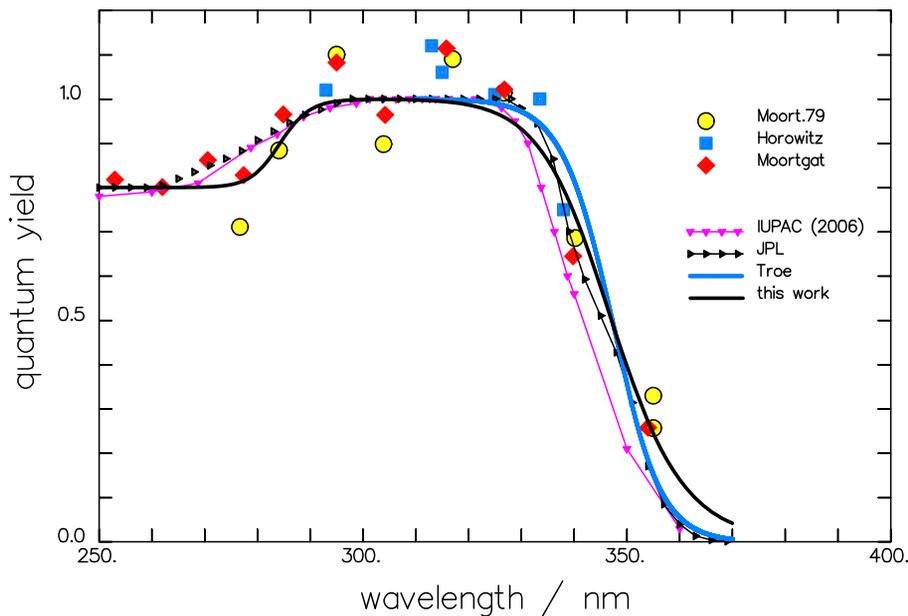
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**Figure 1.** Spectrum of the quantum yield of the radical channel of the  $\text{CH}_2\text{O}$  photolysis at room temperature. Measured data used for the fit are indicated by the large full symbols (Horowitz and Calvert, 1978; Moortgat et al., 1983; Smith et al., 2002; Gorrotxategi Carbajo et al., 2008). The present fit and the theoretical curve from Troe (2007) are given by full lines. Recommended data are represented by small symbols connected by a thin line: JPL (Sander et al., 2011); IUPAC (2006). The line structure observed by Tatum Ernest et al. (2012) is indicated by open circles and a dotted line.

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**Figure 2.** Spectrum of the quantum yield of the total  $\text{CH}_2\text{O}$  photolysis at room temperature. Measured data used for the fit are indicated by the large full symbols (Moort.79: Moortgat and Warneck, 1979, Horowitz and Calvert, 1978; Moortgat et al., 1983). The present fit and the theoretical curve from Troe (2007) are given by full lines. Recommended data are represented by small symbols connected by a thin line: JPL (Sander et al., 2011); IUPAC (2006).

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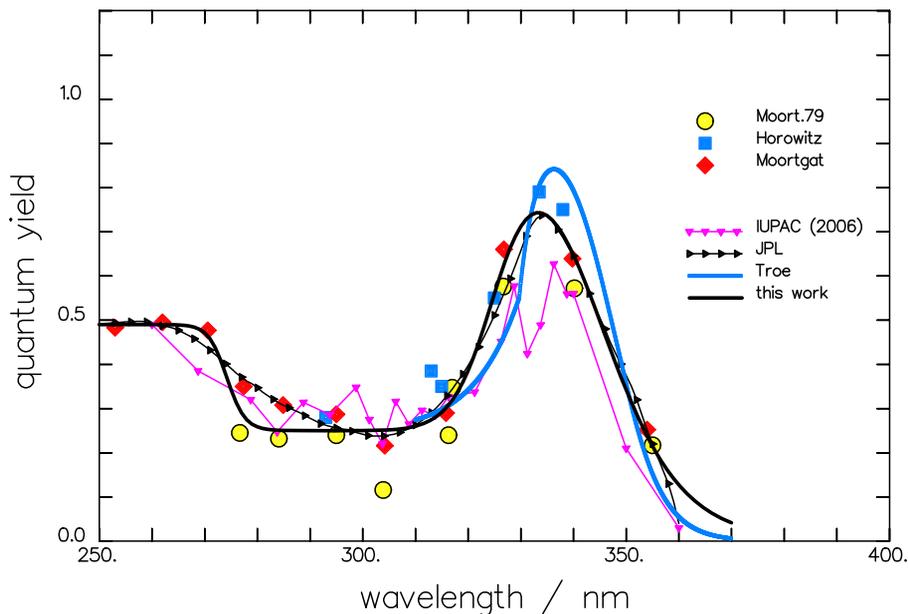
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**Figure 3.** Spectrum of the quantum yield of the molecular branch of the  $\text{CH}_2\text{O}$  photolysis at room temperature. Measured data used for the fit are indicated by the large full symbols (Moort.79: Moortgat and Warneck, 1979, Horowitz and Calvert, 1978; Moortgat et al., 1983). The present fit and the theoretical curve from Troe (2007) are given by full lines. Recommended data are represented by small symbols connected by a thin line: JPL (Sander et al., 2011); IUPAC (2006).

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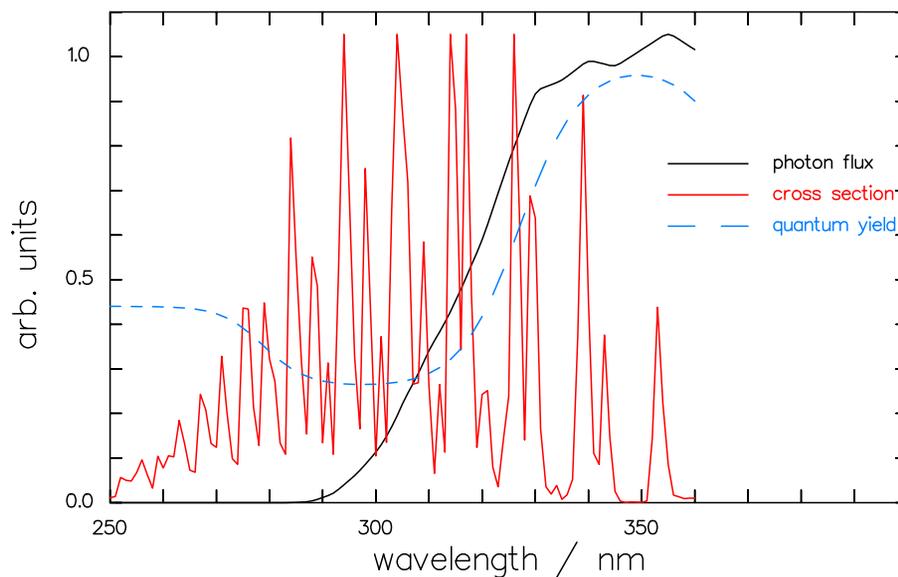
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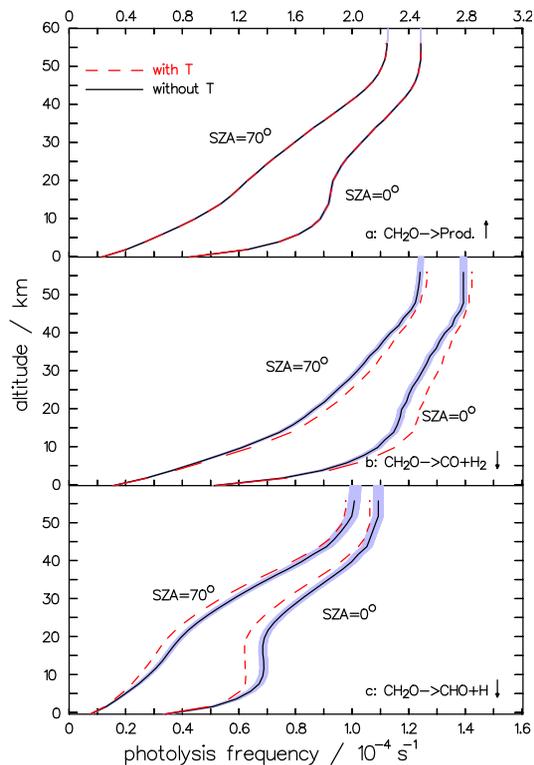
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**Figure 4.** Spectra of the actinic photon flux density (WMO, 1985), the optical absorption cross section (Gratian et al., 2007) and the quantum yield  $\Phi_{\text{mol}}$  at 30 km altitude, 33° solar zenith angle, 227 K.

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**Figure 5.** Impact of a temperature dependent quantum yield,  $\Phi_{\text{rad}}$ , on the altitudinal profile of the photolysis of formaldehyde: total photolysis **(a)**, molecular channel **(b)**, and radical channel **(c)**. The dashed line indicates the impact of the temperature dependence of  $\Phi_{\text{rad}}$  given by Troe (2007). The shaded areas mark the  $1\sigma$  error bounds of the profiles based on the errors of the fitting parameters for the present quantum yields. The frequencies are depicted for two solar zenith angles (SA). (The arrows point to the related ordinate).

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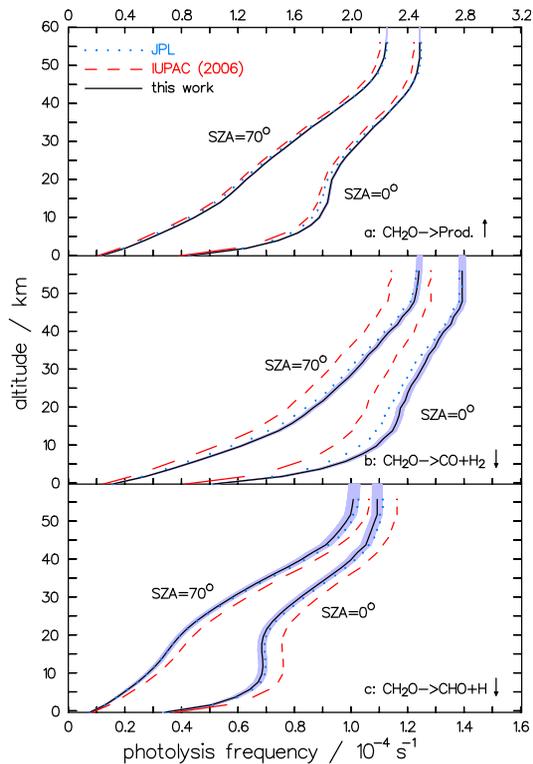
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**Figure 6.** Comparison of the altitudinal profiles of the photolysis frequencies of formaldehyde from JPL (Sander et al., 2011); IUPAC (2006) and the present work: total photolysis **(a)**, molecular channel **(b)**, and radical channel **(c)**. The frequencies are depicted for two solar zenith angles (SZA). The shaded areas mark the  $1\sigma$  error bounds of the profiles based on the errors of the fitting parameters for the present quantum yields. (The arrows point to the related ordinate).

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