A simple formulation of the CH$_2$O photolysis quantum yields

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Abstract. New expressions for the wavelength-dependent photolysis quantum yields of CH$_2$O, $\Phi_j$, are presented. They are based on combinations of functions of the type $A_i/(1+\exp[-(1/\lambda - 1/\lambda_0_i)/b_i])$. The parameters $A_i$, $b_i$, and $\lambda_0_i$ which have a physical meaning, are obtained by fits to the measured $\Phi_j$ data available from 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, CH$_2$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), CH$_2$O* can decay into purely molecular products (Reaction R2), or into products that in the atmosphere lead to the eventual formation of hydroperoxy radicals, HO$_2$, (Reactions R3 and R4). The quenching Reaction (R5) and fluorescence Reaction (R6) can influence the quantum yields of the product channels.

CH$_2$O + h$\nu$ $\rightarrow$ CH$_2$O* (R1)
CH$_2$O* $\rightarrow$ CO + H$_2$ (R2)
CH$_2$O* $\rightarrow$ CHO + H (R3)
CH$_2$O* $\rightarrow$ CO + H + H (R4)
CH$_2$O* + $M \rightarrow$ CH$_2$O + $M^\#$ (R5)
CH$_2$O* $\rightarrow$ CH$_2$O + h$\nu'$ (R6)

As it turns out, the molecular channel, R2, provides by far the largest source of molecular hydrogen, H$_2$, in the atmosphere (Ehhalt and Rohrer, 2009). The radical channels, R3 and R4, that generate HO$_2$ radicals, enhance local photochemistry. Finally each destruction of a CH$_2$O molecule – including that by OH – eventually results in a carbon monoxide molecule, CO. As a consequence, CH$_2$O is also an important source of CO in the atmosphere.

Recognizing the importance for atmospheric chemistry, the quantum yields of the CH$_2$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 $\Phi_{mol}$ of the molecular branch R2 was usually measured by monitoring the H$_2$ production while scavenging the H atoms to prevent their contribution to the H$_2$ 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; Christoffel and Bowman, 2009) was not known then and is not included explicitly in our list of reactions but it is included in R2, and its quantum yield is part of the measured $\Phi_{mol}$.

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

The fluorescence quantum yield (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 $\Phi_{tot}$, i.e., the fraction of the decay of excited formaldehyde, CH$_2$O*, into products other than its
The measured wavelength dependences of the quantum yields are usually given in tabular form (see e.g., Atkinson et al., 2006; IUPAC, 2013). For \( \Phi_{\text{rad}} \), a fit by a fourth-order polynomial (see Sander et al., 2011) also exists. To provide a more handy tool for atmospheric modeling we propose to use sums of energy-dependent functions of the type

\[
\frac{A}{1 + \exp\left(-\frac{(1/\lambda - 1/\lambda_0)}{b}\right)}
\]

(2)

to fit \( \Phi_{\text{mol}} \) and \( \Phi_{\text{rad}} \). These functions are well-suited to map smooth transitions. They allow to include pressure and temperature dependences. And the resulting parameters are few and have a physical meaning: in particular, \( 1/\lambda_0 \) corresponds to the threshold energy of the respective reaction; \( b \) describes the width of the transitions. Moreover, the formalism should also provide a useful template for the formulation of the analogous \( \Phi_i \) for the isotopologues of formaldehyde. In particular, we hope to eventually construct expressions of the quantum yields for CHDO for which – apart from the threshold energies and a few isotope fractionation factors – no direct measurements exist.

Our analysis of the quantum yields will be based on the data filed by JPL (Sander et al., 2011) and IUPAC (2006) omitting all measurements whose wavelength dependencies deviate strongly from the forms recommended by JPL or IUPAC (e.g., McQuigg and Calvert, 1969; Clark et al., 1978; Tang et al., 1979, for \( \Phi_{\text{rad}} \)). Likewise, if measured data appear in several publications by the same authors, only the latest data were considered. Not all data are independent of each other, as some measurements (Smith et al., 2002; Pope et al., 2005; Tatum Ernest et al., 2012) are relative and normalized to absolute quantum yields (DeMore et al., 1997; Sander et al., 2011). This influences the uncertainty range of the parameters \( A_i \), whose \( 1\sigma \) errors might be somewhat larger than indicated in the respective equations.

First, in Sects. 2 to 4, we will fit the measured wavelength dependences of the various \( \Phi \) separately and compare them to those reported in literature. In a second step, after having convinced ourselves that the parameters from the separate fits that should correspond to each other are indeed similar in value, we attempt a simultaneous fit of all \( \Phi \) in Sect. 5.

2 The quantum yield of the radical channel

Most publications on the formaldehyde photolysis deal with the radical channel (R3) – notably: Horowitz and Calvert (1978), Moortgat et al. (1983), Smith et al. (2002), Gorrotxategi Carbajo et al. (2008), and Tatum Ernest et al. (2012). Nearly all of these measurements were made at room temperature, and experiments and theory indicate that there is no pressure dependence of \( \Phi_{\text{rad}} \). We therefore assume all these data to be comparable and their variance attributable to experimental error. Thus all these data are combined in Fig. 1. Smith et al. (2002) attributed some of the variance in their data to a line structure in \( \Phi_{\text{rad}} \). The possibility of a line structure is corroborated by the data of Tatum Ernest et al. (2012), which show a strong feature in \( \Phi_{\text{rad}} \) at 321 nm. For comparison, the data of Tatum Ernest et al. are also shown in Fig. 1, but they are not used for the fit.

To fit the experimentally observed wavelength dependence of \( \Phi_{\text{rad}} \) we use a combination of two functions of the type mentioned above, one for the decay of \( \Phi_{\text{rad}} \) to longer wavelengths at about 328 nm, the other for the decay towards shorter wavelengths at 277 nm. To obtain the fit parameters and their errors, a simplex algorithm (Nelder and Mead, 1965) is used in combination with a bootstrapping method with 2000 arbitrary removals of 20% of the data. The result is given by Eq. (3), with \( \lambda \) in nm:

\[
\Phi_{\text{rad}} = \frac{0.72 \pm 0.01}{1 + \exp\left(-\frac{(1/\lambda - 1/328.0\pm0.6)}{(5.2\pm0.6)\times10^{-5}}\right)} - \frac{0.38 \pm 0.03}{1 + \exp\left(-\frac{(1/\lambda - 1/278.4\pm0.8)}{(4.7\pm1.1)\times10^{-5}}\right)}.
\]

Equation (3) is also shown in Fig. 1.

Equation (3) holds primarily for room temperature. The respective parameters will be labeled by the subscripts \( l, s \). They stand for the short and long wavelength region. The index \( m \), introduced below in Sect. 5, stands for the intermediate wavelength. The \( \lambda_0 \) mark the inflection points in the
In principle, another weak on the altitude profile of the respective photolysis frequency. will investigate the impact of this scaled) to 1 lowing Troe (2007) one can add a term 3

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$_2$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. 6 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 easily be 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) have already indicated, even the strong feature in $\Phi_{\text{rad}}$ at 321 nm produces only a small change in the photolysis frequencies in the atmosphere. In fact, superposition of this feature on Eq. (3) would increase $j_{\text{mol}}$ by less than 2% at all altitudes and decrease $j_{\text{rad}}$ by less than 4%, because it coincides with a small value in the absorption coefficient of CH$_2$O. Thus the error possibly introduced by the neglect of the line structure is comparatively small (see discussion below). (2) The measurements of $\Phi_{\text{rad}}$ by Smith et al. (2002) and Gorrotxategi Carbajo 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).

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, 2013). The reason for the inclusion of IUPAC (2006) is that these data, which were first published in 2002 and remained on the internet until 2012, had many users in the past and possibly still have users at present. Also 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 add here the coefficient of determination $c_d$.

In the present case this is identical to the correlation coefficient between fitted and measured data. These correlation coefficients are: $c_d = 0.821$ (IUPAC, 2006); $c_d = 0.840$ (Troe, 2007); $c_d = 0.898$ (JPL: Sander et al., 2011); $c_d = 0.876$ (IUPAC, 2013), and $c_d = 0.905$ (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 and Warneck (1979) and Moortgat et al. (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 ± 0.09 – not significantly different from 1 – the maximum possible value. Therefore, in the fit we fixed 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.

The measurements in Fig. 1 indicate that $\Phi_{\text{rad}}$ vanishes at $\lambda > 340$ nm; at these wavelengths, $\Phi_{\text{tot}}$ becomes identical to $\Phi_{\text{mol}}$. Moreover, tunneling processes extend the photolysis of CH$_2$O to H$_2$ and CO well beyond the threshold energy of about 350 nm (Troe, 2007). In this energy regime the rate of decay into the molecular channel decreases to values where collisional quenching of the excited formaldehyde molecule (R5) begins to compete. Consequently, $\Phi_{\text{mol}}$ and $\Phi_{\text{eq}}$ become pressure-dependent. Based on theoretical modeling and comparison with the data of Moortgat et al. (1978, 1983), Troe (2007) proposed a Stern–Volmer formulation for $\Phi_{\text{mol}}$ for $\lambda > 340$ nm:

$$
\Phi_{\text{mol}} = \frac{1}{1 + 1.4 \exp(c (\lambda - \lambda_0)) (M/M_0)},
$$

with $\lambda_0 = 349$ nm; $c = 0.225$ nm$^{-1}$ for $\lambda > \lambda_0$ and $c = 0.205$ nm$^{-1}$ for $\lambda < \lambda_0$ and $M$ the number density of the bath.
gas. \( M_0 = 2.46 \times 10^{19} \) cm\(^{-3}\), the number density at 1013 hPa pressure and 300 K temperature. Troe (2007) also pointed out that on theoretical grounds, the temperature dependence of \( \Phi_{\text{mol}} \) should be small compared to the experimental uncertainties and thus negligible at this stage. This is somewhat at variance to the measurements by Moortgat et al. (1983) which seem to indicate such a dependency, albeit with large uncertainties and thus negligible at this stage. This is somewhat

\[
\Phi_{\text{tot}} = \frac{1}{1 + \exp \left( \frac{-(1/\lambda - 1/\lambda_{0,l})}{b_l} \right)} (M/M_0), \tag{6}
\]

with \( \lambda \) given in nm.

We have not been able to find a complete explanation for the experimentally observed weak decrease of \( \Phi_{\text{tot}} \) at shorter wavelengths in literature. We note, however, that \( \lambda_{0,l} = 284.3 \) corresponds closely to the heat of reaction for R4 (see Sect. 2).

Following the arguments by Troe (2007), we assume the temperature dependence of \( \Phi_{\text{tot}}(\lambda) \) to be negligible. But again here, 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 (2013, 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 the \( \Phi_{\text{tot}}(\lambda) \) 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 nm < \( \lambda < \) 350 nm. The consequence of this deviation on the coefficient of determination is relatively small: \( c_d = 0.913 \), whereas the others are: JPL, \( c_d = 0.959 \); Troe, \( c_d = 0.944 \); this work, \( c_d = 0.956 \). In IUPAC (2013) this deviation is removed; the corresponding \( c_d \) 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). 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

\[
\Phi_{\text{mol}} = \frac{1}{1 + \exp \left( \frac{-(1/\lambda - 1/\lambda_{0,l})}{b_l} \right)} (M/M_0) - 0.75 \pm 0.03 - \frac{1}{1 + \exp \left( \frac{-(1/\lambda - 1/352.5 \pm 0.6)}{3.9 \pm 0.5} \right)} (M/M_0) + 0.24 \pm 0.05 + \frac{1}{1 + \exp \left( \frac{-(1/\lambda - 1/274.2 \pm 3.3)}{2.3 \pm 2.1} \right)} (M/M_0). \tag{7}
\]

Eq. (7) makes the implicit assumption that the short-wave decreases in \( \Phi_{\text{tot}} \) and \( \Phi_{\text{rad}} \) have the same \( \lambda_{0,l} \) and \( b_l \). The estimated 1\( \sigma \) errors of the fit parameters are entered in Eq. (7).
Table 1. Recommended quantum yield functions for use in atmospheric chemistry models (wavelength $\lambda$ in nm).

<table>
<thead>
<tr>
<th>Function</th>
<th>Formula</th>
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<tbody>
<tr>
<td>$\Phi_{\text{rad}}$</td>
<td>$\frac{0.74 \pm 0.01}{1 + \exp \left(\frac{-(1/\lambda - 0.32744 \pm 0.51) \times 10^{-4}}{(5.4 \pm 0.3) \times 10^{-5}}\right)} - \frac{0.40 \pm 0.04}{1 + \exp \left(\frac{-(1/\lambda - 0.27908 \pm 0.13) \times 10^{-4}}{(5.2 \pm 2.4) \times 10^{-5}}\right)}$</td>
</tr>
<tr>
<td>$\Phi_{\text{tot}}$</td>
<td>$\frac{1}{1 + \exp \left(\frac{-(1/\lambda - 0.32744 \pm 0.51) \times 10^{-4}}{(5.4 \pm 0.3) \times 10^{-5}}\right)} (M/M_0) - \frac{0.27 \pm 0.02}{1 + \exp \left(\frac{-(1/\lambda - 0.27908 \pm 0.13) \times 10^{-4}}{(5.2 \pm 2.4) \times 10^{-5}}\right)}$</td>
</tr>
<tr>
<td>$\Phi_{\text{mol}}$</td>
<td>$\frac{1}{1 + \exp \left(\frac{-(1/\lambda - 0.32744 \pm 0.51) \times 10^{-4}}{(5.4 \pm 0.3) \times 10^{-5}}\right)} (M/M_0) - \frac{0.74 \pm 0.01}{1 + \exp \left(\frac{-(1/\lambda - 0.32744 \pm 0.51) \times 10^{-4}}{(5.4 \pm 0.3) \times 10^{-5}}\right)} + \frac{0.18 \pm 0.02}{1 + \exp \left(\frac{-(1/\lambda - 0.27908 \pm 0.13) \times 10^{-4}}{(5.2 \pm 2.4) \times 10^{-5}}\right)}$</td>
</tr>
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</table>

In Fig. 3, $\Phi_{\text{mol}}(\lambda)$ from Eq. (7) is compared to the measured data on $\Phi_{\text{mol}}(\lambda)$. The latter consist of direct measurements of $\Phi_{\text{mol}}$ by Moortgat and Warneck (1979) and Moortgat et al. (1983), and data based on measured $\Phi_{\text{tot}}$ and $\Phi_{\text{rad}}$ by Horowitz and Calvert (1978). The agreement of Eq. (7) with the measurements is quite reasonable. For further comparison, Fig. 3 also includes the recommendations by JPL (Sander et al., 2011), and IUPAC (2006, 2013), as well as a fit based on $\Phi_{\text{tot}}$ and $\Phi_{\text{rad}}$ derived from Troe (2007). The respective coefficients of determination are: $c_d = 0.822$ (IUPAC, 2006); $c_d = 0.838$ (Troe, 2007); $c_d = 0.947$ (JPL; Sander et al., 2011) $c_d = 0.843$ (IUPAC, 2013); $c_d = 0.958$ (this work).

5 Simultaneous fit of $\Phi_{\text{rad}}$, $\Phi_{\text{mol}}$, and $\Phi_{\text{tot}}$

A comparison of the parameters and their errors obtained from the individual fits of the various $\Phi$ suggests that the $\lambda_{0,s}$, $\lambda_{0,m}$, $\lambda_{0,t}$ and $b_s$, $b_m$, $b_l$ in a given fit equation do not differ significantly from the corresponding parameters in the others. We therefore felt justified to attempt a simultaneous fit of all $\Phi$. In this attempt we assume that the corresponding $\lambda_0$ and $b$ parameters in the various equations for $\Phi$ are indeed identical. We further assume that $\Phi_{\text{tot}}$ reaches a maximum value of 1 and that Eq. (1) holds. With these assumptions, the total number of fit parameters for all three $\Phi$ together reduces to nine. The simultaneous calculation of the nine unknown parameters results in the Eqs. (8) to (10) for the $\Phi_i$ listed in Table 1, their estimated $1\sigma$ errors are also entered in the equations.

The functions of Table 1 differ somewhat, but hardly significantly from those given by Eqs. (3), (6), and (7) considering the experimental uncertainties. The coefficients of determination are comparable to those from the individual fits: $c = 0.904$ for $\Phi_{\text{rad}}$, 0.951 for $\Phi_{\text{tot}}$, and 0.934 for $\Phi_{\text{mol}}$. Because of their simplicity, Eqs. (8)–(10) represent our preferred formulation of the CH$_2$O quantum yields and will be used in the discussion below.

6 Discussion

In the foregoing sections we presented new formulations of $\Phi_{\text{tot}}$, $\Phi_{\text{rad}}$, and $\Phi_{\text{mol}}$ for CH$_2$O. The presentation also made it clear that there is room for improvement. One improvement concerns the temperature dependence of $\Phi$. Given the experimental uncertainties we have refrained from providing $T$ dependences for the $\Phi_i$. But there are temperature dependences in 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 CH$_2$O to the vertical temperature profile.

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

The impact of this new formulation of $\Phi$ on the atmospheric photolysis frequencies of CH$_2$O is of major interest to atmospheric chemists; photolysis frequency $j$ is given by

$$j = \int_0^\infty \Phi(\lambda) \sigma(\lambda) F_\lambda(\lambda) \, d\lambda,$$

i.e., it also depends on the absorption cross section, $\sigma(\lambda)$, of CH$_2$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). Its effect on the \( j_i \) is quite small – e.g., less than 0.3 % for \( j_{\text{rad}} \) – and included in the calculations. The atmospheric actinic photon flux density consists of downwelling and upwelling 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 \( \sigma(\lambda) \), \( F_2(\lambda) \), and \( \Phi_{\text{mol}}(\lambda) \), together with the wavelength-dependent integrand of Eq. (11) at 30 km altitude and 33° solar zenith angle. We particularly notice the sharp cutoff in \( F_2(\lambda) \) around \( \lambda = 320 \text{ nm} \) 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 \( \lambda < 300 \text{ nm} \) 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 long-wave cutoff of \( \sigma(\lambda) \) makes only a minor contribution. \( j_{\text{mol}} \) is shifted 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. The curve for \( \sigma \cdot F_j \) in Fig. 4 nicely illustrates why the line structure observed by Tatum Ernest et al. (2012) at 321 nm has so little impact on \( j_{\text{mol}} \); it would increase the quite small feature at 321 nm in that product by only a factor of 1.5.

Given the \( \Phi_i \) from the Eqs. (8) to (10) in Table 1, \( \sigma(\lambda) \) 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. The calculations were made with 1 nm spectral resolution and are shown in Fig. 5. The shaded areas mark the 1σ error bounds of the \( j_i \) profiles based on the errors of the fitting parameters for \( \Phi_i \) given in Sect. 5. As expected, all \( j_i \) increase with altitude. In the case of \( j_{\text{rad}} \), that increase is essentially due to the vertical change in \( F_2(\lambda) \), 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 only a minor contribution. \( j_{\text{tot}} \) 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).

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

(12)

This means that 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 $\Phi_{i\text{mol}} = \Phi_{i\text{tot}} - \Phi_{i\text{rad}}$ also on $j_{\text{mol}}$. The effect is largest at around 15 km, the height of the temperature minimum, and about $-9\%$ for $j_{\text{rad}}$ and 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 of the $T$ dependence of $\Phi_{i\text{rad}}$ could lead to a significant change in the predicted vertical profiles of $j_{\text{rad}}$ and $j_{\text{mol}}$.

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, 2013), and JPL (Sander et al., 2011). The JPL recommendation includes an explicit temperature dependence for $\Phi_{i\text{rad}}$. In addition both, JPL and IUPAC (2006, 2013) treat the density dependence of $\Phi_{i\text{mol}}$ 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 $\Phi_{i\text{mol}} (\lambda)$ 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 below our values 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 to 3) based on the JPL recommendation and on the present work appear reasonably equivalent, we feel our formalism is 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 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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