Authors' Answers to the Referees' Comments

The authors thank the referees for their useful comments and suggestions to improve the clarity and readability of the paper. In the following we reply to their comments:

Referee #1

General Comment :

The authors should make a stronger case earlier in the article.

Reply:

We added a sentence on page 7242, line 11 to indicate that we plan to use the new formalism to obtain the quantum yields for the isotopologue CHDO.

General Comment :

I suggest the authors include both the 2006 and 2013 IUPAC recommendations.

Reply:

The 2013 IUPAC recommendations are included in all relevant figures and in the discussion.

General Comment :

There is a degree of redundancy. Some consolidation would be helpful.

Reply:

All tables except Table 4 are omitted and the 1 σ errors included in the respective equations.

Specific Comment p.7242, l.5 :

Express as summation, with the A parameter a signed quantity?

Reply:

On page 7242, line 4 we replaced 'combination' by 'sums'. This should make clear what is meant.

Specific Comment p.7242, l.13 :

The criteria for rejecting some measurements are unclear

Reply:

We changed that sentence by specifying the criteria for rejecting measurements. We also listed explicitly the measurements not included.

Specific Comment p.7243, l.121 :

    typo – 'wavelength'

Reply:

    corrected

Specific Comments p.7243, l.26 and p.7247, l.13 :

    'heat of formation' should be 'heat of reaction'

Reply:

    changed

Specific Comment p.7242, l.5 :

    Invoking a threshold for three-body dissociation does not help to explain the apparent decrease in the photolysis quantum yield.

Reply:

    We agree, nevertheless we find the coincidence interesting.

Specific Comment p.7248, l.6 :

    Equation (7) seems superfluous.

Reply:

    We agree and omitted the equation.

Specific Comment p.7250, l.9 :

    Replace 'frequencies' with 'rates'.

Reply:

    The term 'photolysis frequency' is generally used in our field. For consistency we prefer to keep it here, too.

Specific Comment p.7251, l.5 :

    Equations 11 – 13 do not appear in the manuscript.

Reply:

    The Table 1 (formerly Tab.4) with these equations (now numbered 8 to 10) is included in the text in due place.

Specific Comment p.7251, l.15-25 :

(1) The effect of the temperature dependence of the absorption cross section should addressed.

(2) The variations of -9% and +6% in j_{rad} and j_{mol} are described as a significant effect. This seems inconsistent with the comment on page 7244, line 19-24. Why is -4% small, but +6% significant?

Reply:

(1) Its effect on the j_i is small, less than 0.3 % for j_{rad} and less than 3% for j_{tot} and included in the calculation. We added a sentence (page.7250, line15) to indicate the size of the effect.

(2) To resolve the apparent inconsistency we have changed the text on page 7244, line23 to indicate that the superposition of the line at 321 nm from Tatum Ernest et al. (2012) on our Φ_{rad} , Eq.(3), would cause an increase in j_{mol} by less than 2 % at all altitudes and a decrease in j_{rad} by less than 4 %. These upper limits are more than a factor of 2 smaller than the changes of +6 % and − 9 % for j_{mol} and j_{rad} at 15 km altitude due to the assumed temperature dependence of Φ_{rad}.

Specific Comment p.7262 :

typo 'Gratien' in figure caption

Reply:

corrected.

Referee #2

General Comment :

The discussion of the quantum yield temperature dependence and its impact on atmospheric photolysis rates seems out of place.

Reply:

The idea is to show the impact of a possible temperature dependence of Φ_{rad} on j_{rad} and j_{mol} to see whether that effect is significant and needs further attention.

Comment p.7264, Figure 4 :

It would be very instructive to include an additional panel that shows the wavelength dependence of the product of the terms shown in this figure.

Reply:

The product is included.

<u>Technical Comment p.7240, l.1:</u>

delete 'various'

Reply:

deleted

<u>Technical Comment p.7240, equations</u> :

It would be useful to provide the photolysis threshold wavelengths (energies) along with the possible photolysis channels.

Reply:

We prefer to introduce the photolysis thresholds in the respective section where they are needed.

<u>Technical Comment p.7241</u> :

Fluorescence is noted here to account for a small yield in the photolysis of CH_2O. I suggest the authors reconsider their decision to neglect fluorescence even if only a minor term.

Reply:

Given the experimental uncertainties in the Φ_i which are on the order of 10 %, our formalism does not include effects which amount to a few % corrections, such as the line structure in Φ_{rad} by Tatum Ernest et al. (2012) or here the fluorescence. But they are mentioned in the text to inform the reader.

<u>Technical Comment p.7242, l.3:</u> :

'a more handy tool …' :The proposed parametrization is more physically based, but not necessarily easier to implement.

Reply:

We changed the sentence on line 2 to make clear that the fourth order polynomial exists only for Φ_{rad}. We are of the opinion that the fit by a functional term is more handy than a look-up table.

<u>Technical Comment p.7243,l.5</u> :

delete 'without any weighing'

Reply:

deleted

Technical Comment p.7243, l.12 :

wavelengths

Reply:

corrected

Technical Comment p.7244, l.9 :

delete 'Discussion'

Reply:

deleted

Technical Comment p.7246, l.1 :

'vanishes' poor wording

Reply:

We prefer to keep 'vanishes'

Technical Comment p.7249 :

equations 11 – 13 do not exist in the paper

Reply:

The Table 1 (formerly Tab.4) with these equations (now numbered 8 to 10) is included in the text in due place.

Referee #3

Comment p.7242, l.12-16 and p.7243,l.3-14

The authors should discuss in more detail their selection criteria and should incorporate the recent high structured QY data of Tatum Ernest et al. (2012) in their analysis.

Reply:

We changed that sentence on page7242, line13 by specifying the criteria for rejecting measurements. We also listed explicitly the measurements not included. We also

added a sentence on page7242, line23 that quantify the effect of a superposition of the line at 321 nm from Tatum Ernest et al. on our Eq.(3) for Φ_{rad} on the photolysis rates in the atmosphere. (see reply to Referee #1)

<u>Comment p.7243,l. 10-17 and Fi.1 to 3</u>

(1) It is not clear from the text if the fit shown in Fig.1 represents Eq.(3) or Eq.(11) of Table 4.
(2) Is it possible to improve the fitting at the plateau and tail of the QY curve of Fig.1 ?

Reply:

(1) The respective equations are now added to the legends.
(2) As we discussed in the text on page7244, line17, there is the possibility to improve the fitting by a wavelength-dependent parameter b, once sufficiently accurate data become available. Another possibility was applied by Troe (2007) who multiplied the QY by a function of the type of Eq.(2). If the tail is cut off at 340 nm, the photolysis frequency is diminished by less than 10 % at all altitudes.

<u>Comment p.7245, l.10</u>

What is the correlation coefficient for IUPAC 2013 ?

Reply:

The coefficient of determination is added to the text, its value is 0.876.

<u>Comment p.7248, l.6-11</u>

It would be interesting to graphically compare the QY curves obtained by the individual Eqs.(3), (4), and (6) with the QY curves obtained by the simultaneous fit of Eqs. (11)-(13). Moreover it would be advantageous to list the recommended QY from Eqs. (11) to (13) in tabular form.

Reply:

We prefer to keep the figures as they are, further addition of curves would make them rather busy.

<u>Comment p.7250, l.14</u>

Preferably another reference should be used for Gratien et al. (2007)

Reply:

We changed the reference.

<u>Comment p.7251, l.5</u>

What is the resolution of the formaldehyde absorption cross section used? Have the authors considered using other available absorption spectra at higher resolution?

Reply:

All calculations were carried out with a resolution of 1 nm, as now mentioned in the text on page7251, line17. To check the influence of the absorption cross section's resolution we used the high resolution formaldehyde spectrum of Meller and Moortgat (2000) with a resolution of 0.01 nm. First, we calculated the photolysis frequencies with original spectrum and then with the cross sections integrated over 1 nm. The differences in the j_i are less than 0.1 %, i.e. in the range of the numerical errors.

<u>Comment p.7252, l.9-24 and Fig.6</u>

It would be useful to include the calculation of the j values in Fig.6 using the QY data of IUPAC 2013.

Reply:

These calculations are added in the text and in Fig.6.

<u>Typos and Corrections</u>

Reply:

Typos are corrected.