Interactive comment on “A simple formulation of the CH$_2$O photolysis quantum yields” by E.-P. Röth and D. H. Ehhalt

Anonymous Referee #3

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This paper presents a new formulation of the molecular, radical and total quantum yields of the photolysis of formaldehyde at atmospheric conditions, intended to be used in atmospheric modelling. The authors provide alternative expressions, using combinations of energy-dependent functions, to fit the experimentally measured quantum yield data at various wavelengths. The resulting parameters in these expressions have a more physical meaning than the empirical polynomial formulation used by the JPL-2011 evaluation to fit the quantum yields. The authors demonstrate that the present formulation compares well with the currently recommended JPL-2011 parameterisation. This article is well written and should be published after consideration of the following comments.

General comments
Page 7242, lines 12-16 and page 7243, lines 3-14. The authors base their analysis on the measured quantum yields data set filed by JPL-2011 and IUPAC (2006), but omit all measurements with an “obvious bias”. They do not include recommended data of IUPAC (2013), which include QY data by Pope et al (2005) and Tatum Ernest et al. (2012). It has to be noted that not all studies report absolute QYs. The data of Smith et al. 2002, and Pope et al. 2005 were normalized to the JPL-value $\Phi_{\text{rad}} = 0.753$ at 303.75 nm, whereas the QY data of Tatum Ernest et al. were normalized to the JPL-value $\Phi_{\text{rad}} = 0.69$ at 314.95 nm. Those normalized values fall right on the JPL fit. 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.

Page 7243, lines 10-17, and Figure 1 It is not clear from the text if the fit shown in Fig 1 represents Eq (3) or Eq (11) of Table 4. Moreover, the tail of the fit in Fig 1 at $\lambda > 330$ nm does not well represents the experimental data. This pronounced tail could affect the j-value. Also the difference between the QY plateau value at 300-310 nm and the JPL fit is quite pronounced. Is it possible to improve the fitting at the plateau and tail of the QY curve?

Page 7245, line 10 What is the correlation coefficient for IUPAC (2013)?

Figures 1 to 3: Specify in the figure captions the Equations that were used for the specific fit.

Page 7248, lines 6-11; and Page 7249, lines 18- 22 In order to better evaluate the effect of the fit parameters, 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 fits of Eqs (11)-(13). Also a graphically comparison of the Eqs (7) and (8) would be useful.

Moreover, for comparison reasons with the JPL and IUPAC evaluations, it would be advantageous to list the recommended QY from Eqs (11) to (13) for the molecular, radical and total quantum yields channels in tabular form (at 1 nm interval).
Page 7250, line 14 The reference Gratien et al. (2007) relates an intercomparison between measured absorption spectra in the range 300-360 nm. Preferably another reference should be used: Gratien, A., Nilsson, E., Doussin, J.-F., Johnson, M.S., Nielsen, C.J. Stenstrøm, Y., and Picquet-Varrault, B.;: UV and IR absorption cross-sections of HCHO, HCDO, and DCDO, J. Phys. Chem. A, 111, 11506-11513, 2007. In their paper, the cross sections were measured in the range 240-370 nm at 296 K.

Page 7251, line 5. What is the resolution of the formaldehyde absorption cross sections used to calculate the j-values. Have the authors considered using other available absorption spectra at higher resolution? Such spectra are listed in the spectral Atlas. (http://www.uv-vis-spectral-atlas-mainz.org)

Page 7252, lines 9-24 and Figure 6 It would be useful to include the calculation of the j values in Fig 6 using the QY data of IUPAC 2013.

Typos and corrections

Page 7243, line 12 correct “wavelength”

Page 7243, lines 25-26; page 7247, line 13; and page 7250, line 9: replace “heat of formation” by “heat of reaction”

Page 7264: correct Gratien (not Gratian) in the figure caption. What is the resolution of spectrum shown?

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