

\*\* Answer to the comments of Referee #2

The photolysis of formaldehyde is a major source of hydrogen throughout the atmosphere. Since the photolysis rates of formaldehyde and its deuterated analogues, primarily CHDO, in their molecular channels are altitude dependent, there is an isotopic enrichment of HD relative to H<sub>2</sub> in the stratosphere. Quantification of this enrichment is a long standing issue in atmospheric science. Based on previous experimental data on the fluorescence as well on the photo-decomposition of formaldehyde and its deuterated analogues, together with detailed molecular kinetic modelling, the present paper provides an improved understanding of the wavelength dependence of molecular and radical channels of the photolysis of formaldehyde which goes beyond previous interpretations. The paper therefore is valuable and hence publishable provided that a number of aspects are taken into account:

In the summary stronger emphasis of the present findings with respect to their atmospheric relevance should be made in order to attract stronger interest of the average readership of this journal.

*The emphasis on the atmospheric relevance of the photolysis of formaldehyde is expressed by adding the sentence 'The importance of the photolysis of formaldehyde in the atmosphere is exhibited by presenting the altitudinal dependence of the isotopic fractionation through the yield of the HD channel' to the abstract.*

The organisation of the manuscript has a number of deficits which should be rectified. The first one is the presentation of the overall mechanism to include both radiative as well as collisional deactivation steps. For instance: There is energy transfer (quenching) allowed in both S<sub>0</sub> and S<sub>1</sub> electronic states. But why is no fractionation of CHDO\* – either via a molecular or radical channels - from the electronically excited S<sub>1</sub> state included? Is the initial energy insufficient?

*Most of the photolysis energy was used to reach the S<sub>1</sub> state. The dissociation of the S<sub>1</sub> state itself needs additional energy (see e.g. the energy diagram in Chuang et al, Fig 1)*

The fact that the radical channels are pressure independent, as stated later in the manuscript, should be indicated in the mechanism. In the form of the mechanism presented here, reactions (2a), (3a) and (6a) imply that this is not the case.

*That there is no pressure dependence at atmospheric conditions is now stated explicitly: 'At atmospheric pressures, as considered in this paper, the contributions of the individual quenching processes are insignificant with respect to the overall radical quantum yield'.*

The inclusion of a schematic energy diagram of both electronic states involved and their threshold energies for decomposition together with arrows for the different pathways of excitation and de-excitation via the cascade would significantly improve the understanding of the mechanism.

*As we are not working with explicit energy levels, but rather with grouping based on an above/below dissociation threshold criterium, we refrain from showing the energy diagram and refer instead to the literature.*

In such mechanisms with energy dependent channels the fundamental molecular rate coefficients are principally  $k(E)$ s as delineated in detail in the paper by Troe. These become thermal rate coefficients  $k$  only with the underlying assumption that the system is thermalized at all energies. Very likely this is the case under atmospheric conditions, but it should be mentioned.

*It is now mentioned explicitly that the system is thermalized under atmospheric conditions.*

In the form presented in the manuscript, all quenching reactions are not mass conserving because the collider  $M$  does not show up on the product side of the equations. Please correct.

*$M$  is added to the product side where necessary. (Table 1)*

It should also be mentioned that due to this mechanism and the consecutive reactions of the products only the molecular channel contributes to isotopic fractionation. The products of the radical channel ( $H+CHO$ ) never end up as  $H_2$ .

*The sentence 'Due to consecutive reactions only the molecular channel contributes to the HD production.' is added to the text. The HD channel is also mentioned in the abstract.*

On line 262 it is stated that the bond strength of C-H and C-D are almost the same. In the view of the reviewer this is not consistent with the notion that the zero point energy for C-D is lower than that of C-H. It also contradicts the statement in this paper that the „threshold energies for the radical channels in  $CH_2O$  and  $CHDO$  are different (lines 271-273)“

*Our original formulation can indeed be misunderstood. To avoid this confusion, the sentence is rephrased to 'This in turn implies that the C-H bond strengths are similar in the isotopologues, and the same is true for the C-D bond strengths.'*

The correspondence between text, figure captions and figures needs much better organisation in order to improve the readability of the manuscript. For instance, Fig. 4 should never be the first figure to be cited in the text. Moreover, the figure captions should be more self-explanatory and more comprehensible even without recurrence to the text

*The main text, as well as the figure and table captions, have been modified to provide a more readable and self-contained text, with consistent use of symbols and cross-referencing to the equations where needed. Fig. 4 is now no longer cited first (at that point it the content of Fig 4 was not explained yet), in favor of a "see below" reference.*

In line 266 is a „neither“ missing

*'neither' is added.*

In line 275 replace „1-term“ by „one-term“

*'1-term' and '3-term' are replaced by 'one-term' and 'three-term' everywhere. The words have also been inserted in text and figure captions to help differentiate between the various functions.*

The chapter headline „Isotopic fractionation during the photolysis of CH<sub>2</sub>O“ should be extended to include CHDO

*In the chapter headline 'CH<sub>2</sub>O' is replaced by the more general term 'formaldehyde'.*

Line 606-608 figure caption of Fig. 11 needs rephrasing.

*The figure caption of Fig.11 is rephrased, re-arranging the text and explicitly providing the necessary symbols to link to the main text.*