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***Interactive comment on* “Hydrogen isotope fractionation in the photolysis of formaldehyde” by T. S. Rhee et al.**

T. S. Rhee et al.

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We thank Matthew Johnson for the comments on our paper. We reply the questions and comments on point-by-point basis as follows:

Q: The terms 'incomplete photolysis' (R1) and 'complete photolysis' (R2) are defined in the introduction, referring to the $\text{H} + \text{HCO}$ and $\text{CO} + \text{H}_2$ product channels in formaldehyde photolysis respectively. This terminology is confusing, because the experimental procedure relies on the complete photolysis of an HCHO sample to products, presumably involving some amount of both the 'complete' and 'incomplete' pathways. These two reactions are usually called the radical channel and the molecular channel. For example, page 12749, caption to Figure 4, it is written '...that the complete photolysis of CH_2O yields H_2 with a dD value that is the same as that of the initial CH_2O .' It is unclear whether this means '100% photolysis of CH_2O via R1 and R2 but leading to

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100% yield of molecular hydrogen' or 'Photolysis only at wavelengths that can produce H₂ via R₂'.

R: We agree with the reviewer's comment and removed the term 'incomplete' and 'complete' for the radical (R₁) and molecular (R₂) channels to the CH₂O photolysis in the revised version. Our intention behind using those terms are what the reviewer pointed out; while the products of the radical channel undergo further reaction with O₂, those for the molecular channel are relatively inert in the atmosphere.

Q: The introduction should contain a reference to J. Troe's recent work on the photolysis of formaldehyde, Troe, J., Analysis of quantum yields for the photolysis of formaldehyde at $\lambda > 310$ nm. Journal of Physical Chemistry A, 2007. 111(19):p. 3868 - 3874.

R: We appreciate the reviewer's comment to draw our attention to J. Troe's recent work. We cited J. Troe's paper in the introduction of the revised version.

Q: There are significant uncertainties in the experimental procedure that are not discussed adequately in the text: 1. What is the role of heterogeneous reactions in the photolysis cell? Many pathways are possible, for example: formation of paraformaldehyde; isotopic fractionation in the photolysis of paraformaldehyde, trimeric formaldehyde or surface-adsorbed formaldehyde; isotopic exchange between hydrogen and water (either surface-adsorbed water present at the beginning of the experiment or water formed by R₃, R₆, R₁₁, R₁₇, R₂₄, R₂₆, R₂₈); isotopic exchange between hydrogen and formic acid or hydrogen peroxide; isotopic fractionation due to diffusion of hydrogen through the glass; isotopic fractionation occurring due to radical recombination reactions on the surface. It is known that isotopic exchange will take place when hydrogen is stored in a flask with water.

R: As replied to the Reviewer #1's comments, the stability test conducted over 2 days shows that it is not likely that heterogeneous reactions play a role in our experiments of CH₂O photolysis. Regarding isotope exchange between H₂ and water, one can recognize its insignificance in view of the experimental periods of the present experiments. It

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is evidenced by tropospheric H₂ enriched in deuterium (D) with respect to ocean water, in stark contrast with the depletion in D of H₂ when thermodynamic equilibrium would reach between them ($dD = \sim -700$ permil). The reason is that the isotopic exchange between H₂ and H₂O is too slow to be detected within the lifetime of H₂ in the atmosphere. By analogy, for a period of less than a month it is hard to expect the isotope exchange between H₂ and water in the reactor. We are of course aware of problems that may arise due to catalytic production of H₂ from or isotopic exchange with H₂O on metal surface and have intentionally used glass reactors and vessels. The isotope exchange rate between H₂ and H₂O in either liquid or gas phase is not influenced by a catalytic reaction on quartz surface (Lecluse and Robert, 1994). In conclusion, the isotope exchange between H₂ and water is expected to be negligible in the present experiments. Due to the lack of information available on the rate constants, it is hard to judge if isotope exchange between H₂ and H-containing compounds other than H₂O was significant in the reactor. However, results from the experiments with the Xe lamp suggest it to be negligible. As shown in Table 1, the dD value of H₂ obtained from the experiments with the Xe arc lamp increased by only 17 permil after 152 hours. Attributing this to the isotope exchange between H₂ and H-containing compounds alone, the maximum possible increment of the dD value would be ~ 30 permil ($277/152 \times 17 = 31$) which is within the uncertainty of the term, 'dD-H₂ of final product' in Table 2. It is very unlikely, however, that the increase of dD value of H₂ is only due to this isotope exchange. Overall, the isotope exchange between H₂ and H-containing compounds including H₂O in the reactor should not significantly change the results from the present experiments. Diffusivities (or permeability) of H₂ in glass and quartz are of the order of $\sim 10^{-14}$ and $\sim 10^{-13}$ cm²/s, respectively, which is too slow to influence the present experiments (He diffuses but H₂ not at any appreciable rate). A rough estimate indicates a diffusion depth of H₂ of few μm for 10 - 15 days. Again, the experiments with the Xe arc lamp shows that the variability of the dD value due to the sum of all possible contamination processes could be ~ 17 permil for 152 hours. This again suggests that H₂ is basically inert to chemical and physical reactions in the reactor.

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Q: 2. The authors have made a significant technical advance in developing a procedure for measuring the absolute concentration of hydrogen gas in a sample and are able to combine this with a measurement of $dD(H_2)$. This is not an easy measurement. The mercury arc lamp will produce H_2 , but also H and HCO, and a complex secondary chemistry will ensue. It is very important that the authors present the raw data concerning the absolute hydrogen concentrations produced in the 'complete photolysis' experiments. For one thing this will document how much if any hydrogen is lost through conversion to H_2O , H_2O_2 , $HCOOH$, etc., which would almost certainly involve isotopic fractionation. In addition the uncertainty in the hydrogen measurement must be combined with the uncertainty in the pressure gauge measurement of HCHO concentration to give the uncertainty in the dD of the original HCHO. Also the accuracy of the hydrogen concentration measurement must be ca. 3%. It is inadequate to simply argue that there is 100% conversion given the number of complicating issues that are present. It is hard to be convinced that the uncertainty in the determination of the dD of the original HCHO is 4 per mil. Also 12728, 11, 'Given that complete photolysis of CH_2O yields H_2 that has the same isotopic ratio as that of the initial CH_2O ...' This topic is fundamental to the paper and should be discussed in more detail. Was there any evidence of H_2O , $HCOOH$ or HO_2H formation (for example, were these measured, could they be seen in the cold trap used to clean the H_2 sample?) Also note 12732, 6-8, '...follows from the fact that the isotopic compositions of the initial CH_2O and of the H_2 that are formed from complete photolysis are identical.' Here the assumption has become a fact. 'Identical' is rather strong given the complexity of the photochemistry and the difficulty of the measurements. It would be better to present a proper error analysis than to assume.

R: Regarding the question of determination of the absolute amount of H_2 and its dD value from the photolysis of pure CH_2O , it is well-known that final products of photolysis of pure CH_2O are H_2 and CO as mentioned on p.12720 (e.g., Horowitz and Calvert, 1978). Opposite to what the reviewer argued, the production of H-containing compounds other than H_2 in the photolysis of pure CH_2O , e.g., H_2O , H_2O_2 , $HCOOH$,

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etc, cannot happen. According to Table A1, H₂O production needs the OH radical in the reactor, which cannot be produced without O₂. Production of H₂O₂ and HCOOH also requires O₂ in the reactor. Opposite to what the reviewer expected, the secondary reactions between the molecules and radicals produced during the photolysis are not so complicated; it is rather simple and H₂ is a unique product containing the hydrogen isotopes from photolysis of pure CH₂O air. Consequently it is not necessary to be concerned about the possibility of loss of H and D isotopes to other than H₂. We do not understand the point why the reviewer argues that the uncertainty of the dD values of original CH₂O should include the uncertainties in the measurement of CH₂O and H₂ mixing ratios. In addition, why must the uncertainty of H₂ measurement be ca. 3 %? According to Rhee et al. (2004), it is about 2 %. Also, we did not simply assume 100% conversion of H₂ from CH₂O photolysis, but it is based on a series of measurement of H₂ mixing ratios after the photolytic breakdown of pure CH₂O. The reviewer doubts the uncertainty (+/-4 permil) of the dD value of CH₂O. As clearly stated in the text, the dD of CH₂O is determined from the isotopic analysis of the H₂ formed from CH₂O photolysis. Thus, the uncertainty is based on the analytical precision and accuracy described in Rhee et al. (2004). Even the paper by Feilberg et al. (2007) stated that the uncertainty of dD of H₂ is +/-3 permil using the same method. We revised the sentences exemplified in the reviewer's comment. As shown in Table 2 and discussed in the text (p.12730), we did carry out error analysis to determine the uncertainty of isotopic fractionation factor for CH₂O photolysis.

Q: The spectral distribution of the actinic flux is a key parameter in this paper, as is the spectral distribution of light from the lamps. Are measurements available of the spectral flux distribution for the solar photolysis experiments? It would be useful to add UV spectra of the glasses used in the experiments as supplementary information to the paper e.g. the Schott duran and quartz glasses used. The UV transmission of quartzes varies and the cutoff is not simply 'ca. 200 nm' for all types.

R: We add in the revision a figure for spectroscopic or optic properties of the materi-

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als used in the experiment. The solar spectral flux during the photolysis experiments were not measured so we have to rely on the TUV radiation model to infer photolysis rates. We did not measure complete UV transmission spectra for all quartz reactors. However, since the CH₂O photolysis to the radical and molecular channels starts at ~240 nm, we believe that the small difference of cut-off wavelength for different types of quartz is not a significant problem in the present experiment.

Q: At the top of page 12723 it is written that 'the unique source of H₂ in the reactor is CH₂O photolysis' but according to the model presented in Table A1, molecular hydrogen is produced by R2, R4, R10 and R16. Please present model results for what fraction of the H₂ is coming from these other sources.

R: The total fraction of the sum of the H₂ from R4, R10, and R16 is less than ~10⁻⁸. This is negligible compared to the fraction of the H₂ from photolysis of CH₂O (R2), which is larger than 0.5, as shown in Figure 3.

Q: On page 12723, line 11, 'there are substantial differences between the measurements and the model predictions at longer photolysis periods.' The model is not able to reproduce the experiments, i.e. the photochemistry in the cell is not captured by the model. Why is this? In addition to differences in the gas phase, there are likely to be reactions occurring on the surface. These uncertainties should be included in the final result. Another indication of problems is that while the solar zenith angle for the experiments was 27 to 48 degrees, the model predicts that the *sza* would need to be 85 degrees to match the results (12723, 20). It appears that too much molecular hydrogen is being produced in the experiment relative to the model, which could be a sign of radical recombination reactions on the surface or other kinds of surface photochemistry.

R: There are several possibilities to cause the difference of $\phi(\text{H}_2)$ between measurements and model prediction: Firstly, in the model we fed a constant photolysis rate although the experimental situation was not, secondly, as mentioned in Section 3.1,

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the period of photolysis is given as number of daylight hours ignoring the conditions under which the experiments were conducted. However, as shown with gray shadings in Figure 1, the model can capture the temporal evolution of the measurement data when either large SZA as shown in Figure 2 or preferential penetration of long wavelength photons during the experiments, i.e., during sunrise or sunset or cloudy sky, are employed. As discussed above, we do not, however, suspect heterogeneous reaction to be responsible for the large value of $\phi(\text{H}_2)$.

Q: 12731, 28, what is not direct about the spectroscopic measurement?

R: 'directly' in that sentence does not refer to spectroscopic method but to inferring $\alpha(\text{h}\nu)$. To make the sentence clear, we improved the sentence.

Q: 12732, 1-4, these factors are accounted for in the error analysis of this paper.

R: Yes, they were.

Q: 12732, 5, what is the relevance of the comment 'performed at the level of natural deuterium abundance'? It is true that Feilberg et al. use enriched samples but this has nothing to do with the veracity of the result.

R: We stated the comment to explain the difference between the two experiments.

Q: 12743, it is great that the authors have done a sensitivity analysis of the model since this is the key to the data analysis. There are a few comments. 1. The uncertainty parameter in the relative photolysis rates of H_2O_2 and CH_2O is 4 percent of the ratio. This seems too low, the absorption cross sections themselves of both of these compounds are likely to be in error by at least this much, not to mention uncertainty/changes in the spectral distribution of the actinic flux.

R: The photolysis rates of CH_2O and H_2O_2 were obtained from TUV model at the range of SZA from 0 to 90° . We did not count on the uncertainty of cross section, yield, and actinic flux of the two compounds because these parameters are not fed into the model but the ratio of the photolysis rate.

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Q: 2. The kinetic isotope effect of $\text{CH}_2\text{O} + \text{OH}$ has been measured, but the KIEs of the $\text{CH}_2\text{O} + \text{H}/\text{HO}_2$ reactions have not been measured. The $\text{CH}_2\text{O} + \text{HO}_2$ reaction is an association reaction (as opposed to abstraction) and a guess of 1 with a large error bar would be better than the current guess.

R: Since no data are available for the isotope fractionation of the reactions $\text{CH}_2\text{O} + \text{H}/\text{HO}_2$, the change in the value of the isotopic fractionation factor does not give us a meaningful information. But, it is important to figure out if these reactions would play a significant role in the determination of $\alpha(r)$. Shown in Table 2 and Figure 4, the reactions $\text{CH}_2\text{O} + \text{H}/\text{HO}_2$ contribute little to the uncertainty of $\alpha(r)$.

Q: 3. The sensitivity analysis has included the uncertainty in the KIEs of the H, OH and HO_2 reactions, as discussed, but it has not included uncertainty in the concentrations of these radicals. This is a serious point. The lifetimes of the radicals will depend on many things including surface reactions, concentrations of reaction partners and other radicals, concentrations of impurities. It would not be unreasonable to assume that the modeled concentrations could vary from the true concentrations by more than 50%. This will clearly have an effect on the uncertainty of αr . (see also Figure 3).

R: The H, OH, and HO_2 radicals are created in the model via a series of the reactions shown in Table A1, but not given. The uncertainties of those radical concentrations are implicitly contained in the initial mixing ratio of CH_2O ($[\text{CH}_2\text{O}]_0$), photolysis rate of CH_2O ($J(\text{CH}_2\text{O})$), the yield of H_2 ($\Phi(\text{H}_2)$), and the ratio of the photolysis rate of H_2O_2 to CH_2O . Therefore, it is not necessary to conduct sensitivity analysis for the uncertainties of H, OH, and HO_2 themselves.

Proofreading: 12716, 24, 'a wide large range' -> 'a large range'

R: Revised.

12721, 26 to 29, unclear sentence, please rewrite.

R: Revised.

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12722, 2, I believe this capital phi should be a low case phi, since only the lower case phi is a measurable quantity

R: Capital phi is correct as lower-case phi is also related to the duration of photolysis. The yield of H₂ (capital phi) depends on the energy of photon.

12722, 27, 'FACIMILE' -> 'FACSIMILE'

R: Revised.

12723, 12, the sentence beginning 'In particular...' cannot be understood, please rewrite. What is the phrase beginning 'that are based on most likely values' referring to?

R: Please refer to the reply above to 'on page 12723, line 11'. The phrase 'that are based on most likely values' refers to the photochemical conditions in Mainz during the experiments as shown in Figure 2 and 3.

12727, 5-6, 'By the same way' -> 'Similarly'; 'results in a same relations' -> 'results in similar expressions'

R: Revised.

12733, 3, subscript '-H₂'

R: Revised.

12738, 13-15, this paper is now published, the full reference is, K. L. Feilberg, M. S. Johnson, A. Bacak, T. Röckmann and C. J. Nielsen, Relative tropospheric photolysis rates of HCHO and HCDO measured at the European Photoreactor Facility, Journal of Physical Chemistry A, 111 (37), 9034 -9046, 2007.

R: Revised.

Feilberg, K.L., Johnson, M.S., Bacak, A., Röckmann, T., and Nielsen, C.J.: Relative tropospheric photolysis rates of HCHO and HCDO measured at the European Photo-

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toreactor facility, *J. Phys. Chem.*, 111 (37), 9034-9046, 2007.

Horowitz, A., and Calvert, J.C.: The quantum efficiency of the primary processes in formaldehyde photolysis at 3130 Å and 25°C, *Int. J. Chem. Kinet.*, 10, 713-732, 1978.

Lecluse, C., and Robert, F.: Hydrogen isotope exchange reaction rates: Origin of Water in the Inner Solar-System, *Geochim. Cosmochim. Acta*, 58 (13), 2927-2939, 1994.

Rhee, T.S., Mak, J., Röckmann, T., and Brenninkmeijer, C.A.M.: Continuous-flow isotope analysis of the deuterium/hydrogen ratio in atmospheric hydrogen, *Rapid Commun. Mass Spectrom.*, 18 (3), 299-306, 2004.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 7, 12715, 2007.

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