**Atmospheric
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# *Interactive comment on* "Pressure dependent deuterium fractionation in the formation of molecular hydrogen in formaldehyde photolysis" *by* E. J. K. Nilsson et al.

**E. J. K. Nilsson et al.**

msj@kiku.dk

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Reply to Referee Comments Pressure dependent deuterium fractionation in the formation of molecular hydrogen in formaldehyde photolysis. E.J.K. Nilsson et al.

Dear ACP,

The authors would like to thank the reviewers for their careful reading of the text and for providing some very useful comments. As detailed below, we have made an effort to address all of the comments in the revised manuscript. The goal of the study is to demonstrate that there is a significant pressure effect in the fractionation occuring in the molecular channel, and this result does not depend on the specific choices of

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photolysis quantum yield parameterization or the radical channel quantum yield. This work does not present any new information about the radical channel quantum yield. In addition, the results for the molecular channel are not necessarily in conflict with previously published values. The most likely reason is that this study used a UVA lamp as the light source, whereas the other determinations used sunlight. We have added discussion and more detail to the text.

On behalf of the authors, M. S. Johnson

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Referee #1

This paper describes photolysis of formaldehyde, using an artificial light source, by FTIR detection of the rate of removal of HCHO relative to that of HCDO at varying bath gas pressures. Isotopic information may help to better understand certain aspects of the important oxidation pathway from CH4 to H2 and CO, and the fate of HCHO in general. Therefore these experiments are important, but after reading the manuscript, the reader is left with many questions. The extensive modelling of the isotopic chain of atmospheric HCHO by e.g. Mar et al. 2007 had shown that the fractionation for deuterium must be different in the stratosphere, but no parameter (pressure, light spectrum, temperature) could be identified. It now is likely that pressure plays a major role. Thus the fact that H2 shows a nearly flat vertical profile, and stratospheric enrichment of D in H2 can be better understood now. An important question is however why the present experiments are not compatible with results from other studies. Importantly the study by Feilberg et al.(2007) is from the same group. At the outset the reader is puzzled why there is no explanation given why this is the case. If comparison with other laboratories is difficult, one would expect a discrepancy or inconsistency of this sort to be given scrutiny. The manuscript shows that several issues/statements need consideration or changes. The experiments are not as conclusive and uncertainties/confusions still remain.

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Reply. The authors thank the referee for the thorough review of both content and structure of the manuscript. We have made significant changes to the manuscript in order to clarify our analysis and highlight the important results. The experiments presented here are not necessarily inconsistent with previous results.

The title should, if maintained in this form, at least be "Pressure dependence of.." because it now suggests that there is a pressure independent fractionation and a pressure dependent fractionation. The authors have not measured the hydrogen formed for its D/H ratio. To be clear, the title should state that it is the fractionation of deuterium in formaldehyde due to photolysis using lamp light.

Reply. Title has been changed to "Pressure dependence of the deuterium isotope effect in the photolysis of formaldehyde by ultraviolet light"

Abstract. Why is the rate for HCHO given relative to that of HCDO (only _0.03% of natural H2CO)? The isotopic ratio is wisely given as the D/H ratio; that is the rare over the abundant isotope. Why then relate the reaction rate of the abundant isotopologue to that of the rare one? In this way, the isotope community makes it harder for non specialists to work with their data.'

Reply. The definition of Kinetic Isotope Effect is, according to IUPAC (http://goldbook.iupac.org/K03405.html); "The effect of isotopic substitution on a rate constant [...] the effect of isotopic substitution in reactant A is expressed as the ratio of rate constants kl/kh, where the superscripts l and h represent reactions in which the molecules A contain the light and heavy isotopes, respectively." This is the convention used by the isotope community and is used to enable comparison of the present data with that from previous studies.

Is the measurement uncertainty at 50 and 1030 mbar 0.1 in both cases?

Reply. The authors thank the referee for making us aware of an error in the abstract; using the upper and lower limits of the errors in column 2 of Table 2, the correct number

with error limit at 50 mbar should read 1.1 +0.15/-0.1.

How accurate is an uncertainty estimate that the authors give 2 significant digits at 1030 mbar?

Reply. We discuss the determination of error in Section 3. We have added information concerning the accuracy of the pressure gauges.

The "extrapolation" of the lamp results to the stratosphere at 50 km seems premature.

Reply. Text has been changed and is now referring to pressures instead of the corresponding altitudes.

Written is that the ratio between the channels depends on actinic flux. Is this a result of this study?

Reply. No, it is not a result of this study; the text has been changed to clarify this.

The introduction requires work. P24030, L22. Does the statement by Forster et al. pertain to the reaction of H2 with OH, or also including the soil sink? The lifetime of CO is about 1 month and its concentration is about 80 ppb. H2 has about 500 ppb, but its lifetime against OH is several years. The reviewer is not certain here, please check this. If the removal by soils is involved the statement has no value in the context of this paper.

Reply. We have rewritten the introduction to remove possible misunderstanding regarding the relative roles of the OH and soil sinks.

P24030, L24. "the rest is removed by soil bacteria". Because this is the larger fraction, one should state it the other way around, namely, "the rest is removed by OH" It also is an insult to the soil bacteria involved. Moreover, is it the bacteria, fungi, or perhaps mostly certain soil enzymes? Unless one is well informed it is safer to use the concept "soil sink".

Reply. The text is changed according to the comments of the referee.

P24030, L25. The statement is badly formulated and hence useless, also because it is superfluous. I suggest to delete it.

Reply. The text now reads: "There is an interest in the fate of molecular hydrogen in the atmosphere, in order to determine the effect of a proposed hydrogen economy"

P24031.L6. The quantifier "dramatic" is not a rational concept. Furthermore, in the same sentence, the meaning of the word "presumed" is no clear.

Reply. The text has been rephrased and now reads: "They estimate that photochemical H2 should have a $\delta$D of +130 $\pm$ 70 ‰ compared to ocean water, a significant enrichment relative to the dominant source, methane, with a $\delta$D of -86 $\pm$ 3 ‰"

P24031.L8. "biogenic VOC is likely to be at least this depleted in deuterium". Even though this is a citation, it raises questions. Atmospheric CH4 is depleted in D because of several reasons, one is that bacterial CH4 (wetlands, ruminants) is depleted. The reason can be understood on the basis of metabolic pathways. But for VOC it is not so clear. Is this statement based on atmospheric measurements? If so, it must be based on certain VOCs, these should then be mentioned. Is it based on isoprene (abundant species) D/H measurements?

Reply. We have added a reference to Smith et al.'s work determining ïĄďD in natural compounds, e.g. isoprenoids.

P24031, L20. CH3D reacts slower, why then are the products enriched in D? Why do the authors write "more slowly" and not (more objectively) slower? Also notice the semantic inconsistency that now results from the statement in the abstract (H relative to D, thus one would logically write "faster", certainly not "more speedily..).

Reply. Text has been changed and now reads: "The C-D bond in methane is less reactive than the C-H bonds and when methane is oxidized this results in methoxy radicals that are enriched in deuterium."

P24031.L23. "great" One may state that there are "great scientists or presidents" but

for isotope fractionation, this qualifier is not appropriate.

Reply. "great" has been replaced by "large".

P24031.L27. "these", which ones exactly are meant?. "a depletion" or better "the depletion"

Reply. "these" is replaced by "the". We have written "a depletion", since this is the first time that the depletion in formaldehyde photolysis is mentioned. When introducing something for the first time it is correct to use the indefinite article "a".

P24032.L6. "Roaming atom". Going into detail, a question that arises is whether water clusters play a role in HCHO photolysis in the troposphere. This potentially is another factor that differs between lab experiments (reactors) and outside air.

Reply. Given the concentration of water and a reasonable estimate of the equilibrium constant, the concentration of the formaldehyde-water complex in the atmosphere or in the photoreactor is going to be a thousandth of the concentration of the formaldehyde monomer. The increase in the absorption cross section for the complex would have to be unusually large for this process to contribute to formaldehyde removal. Even if this were the case, it is likely that when the formaldehyde-water complex absorbs light with an energy above the dissociation threshold, it will simply break the weakest bond in the system, i.e. the intermolecular bond, and this will leave the formaldehyde molecule below the dissociation threshold. For example, this is the mechanistic reason that the photolysis quantum yield for sulfuric acid the $H_2SO_4*H_2O$ complex is zero in the energy range where the lone $H_2SO_4$ molecule dissociates.

P24032.L25. Table 1. The light source used by Rhee should be mentioned. Often in papers, the authors list their result in a table with results from others. Extending Table 1 would help readers to get a clearer impression, certainly because there are discrepancies.

Reply. A column with light sources has been added to Table 1. The result of the present

study (1030 mbar) has been added to the table. The data are further discussed and compared in the results section of the paper.

P24032.L27. "similar ..even though.. statistically distinct" One more grey hair here, this is a sort of statement we read in newspapers.

Reply. Sentence deleted.

P24033.L3. Why this statement? What is the H2 isotope scheme? What about the role of the "great deuterium enrichment".

Reply. We assume the reviewer is referring to the statement by Pieterse . Their model of atmospheric oxidation of methane to molecular hydrogen indicates that the isotope effects in formaldehyde photolysis are critical, which is part of our motivation for doing this work.

P24033.L14. Is the diameter of the reactor 25 cm? Why does it have stainless steel flanges? Stainless steel is a mixture of iron, nickel and more, and these elements are known to exhibit a wide range of catalytic properties. It seems to be an unwise choice, unless the flanges are coated or treated to render their surfaces inert. Is the tube made of quartz or of silica. Quartz is found in nature, often is not so pure, and rarely in the form of a tube.

Reply. The inner surfaces of the stainless steel flanges were electropolished to minimize the surface area available for reaction. While no surface is perfect and it is true that stainless steel is not inert, this design provides a balance between strength (resistance to deformation under vacuum) and a minimal surface area. We have added a description of blank experiments performed to demonstrate the stability of formaldehyde in the cell. For details on the photochemical reactor we refer to the reference given in the manuscript; Nilsson et al. (2009).

P24033.L23. The inlet line was heated. Why this? Is the pressure in the inlet line so high that formaldehyde condenses on its wall? How can one be sure that only

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formaldehyde molecules enter the reaction chamber. When the tubing is heated, why then should the reactor not be heated? Furthermore, when for instance laboratory air enters such a reactor, several layers of water molecules form on its surface. These layers are very persistent. Was the reactor "baked" prior to the experiments? How is this for formaldehyde? Even one monolayer of formaldehyde represents an amount that can be significant. Could it be that HCDO is enriched on the wall of the reactor? How does HCHO stick to silica surfaces with abundant OH groups? Are hydrogen bridges involved? This could give a strong preference for the absorption of HCDO over HCHO. The authors correctly point out that small vessels may have stronger artefacts. However the surface to volume ratio is basically a function of one dimension only, which means that surface effects are not orders of magnitude smaller. In particular in laboratory experiments and using FTIR much could have been verified that now intrinsically remains questionable. Perhaps the authors used a method similar to Gratien et al. (2007), which is a basis for confidence that pure gas phase results free of artefacts haven been obtained. One way to admit formaldehyde would be to expand it from an intermediate known volume, and ascertain that the pressure ratios are as expected for an ideal gas free of absorption problems. But perhaps the absorption problems are related to the amount of water on the walls of the reactor. It remains unsatisfactory, and the discord with other results (of what?) raises doubts. For how long did experiments typically last?

Reply. When samples are introduced into the cell, the inlet line is exposed to higher pressures of formaldehyde than the other regions of the system. In order to avoid potential problems we heated this region. In addition, part of the inlet line was not inside the temperature controlled box, but exposed to the laboratory that held a lower temperature than the photochemical reactor. Prior to experiments the reactor was baked out in order to remove water from the system. Experiments were conducted where formaldehyde was left in the dark chamber for several hours, and the concentration was monitored. From these measurements we could see that initially a few percent of the formaldehyde is removed from the gas phase, most likely by sticking to the walls.

The formaldehyde was expanded into the empty chamber from an intermediate calibrated volume. As mentioned in the text experiments lasted from 6 to 35 h. We have added descriptions to the text.

P24034, L2. Why does Table 2 not give the formaldehyde partial pressures (or ranges)? Why were these pressure selected (0.09 to 4.5 microbar)? How were these pressures measured? The authors write that their reactor is temperature controlled. Have they tried to raise the temperature and observe the change in the (initial) formaldehyde pressure?

Reply. Partial pressures are now given in Table 2 for each experiment. More information about the introduction of formaldehyde to the chamber has been added to the experimental section.

P24034.L5. From Figure 1 it is not visible where the maximum light intensity is. What was the light intensity in the reactor?

Reply. As stated in section 2.2 the emission maximum is at 350 nm. We had unfortunately no means of measuring the absolute intensity inside the reactor.

P24034. Is it possible to use the FTIR spectra to check for the water content of the gas in the reactor? How high was it?

Reply. Yes, it is possible and this information was used as input to the model, which has now been added as supplementary information.

P24035.L25. "After convoluting with the photolysis lamp spectrum, recent work by Troe shows.." This is an interesting statement. Did Troe wait for Copenhagen?

Reply. The sentence has been rephrased to read: Troe's results (2007) can be convoluted with the lamp spectrum to show that [. . .]"

P24035. Given the lamps used, what fraction is actually following the radical channel? There seems to be an (unavoidable) uncertainty here.

Reply. The fraction depends on pressure as discussed in the text. Yes, there is an uncertainty, as described, but it does not affect the conclusion that there is a significant pressure dependent effect in the molecular channel.

P24036.L20. In Figure 5, mistakingly Figure 4 is mentioned. Also note that in the literature we use the full stop as separator and not the comma. The authors can perhaps change the language setting in their Microsoft software, to get correct plots.

Reply. Changes made according to comment.

P24037.L3. Why exactly are such values unacceptable?

Reply. Discussion has been added to the text.

P24037.L23. The fit does appear not to fit. Why is this? Furthermore, Fig 6 and Fig 3 can be combined. To devote a figure to this fit seems unreasonable. Or is Figure 6 meant to be for atmospheric conditions, which cannot be true. Why is there such a large spread (similar but statistically different) in the measurement results displayed in Figure 3. Figure 3 has a very brief caption, that basically tells nothing more than we glean from the figure. What error bars are given, how were they determined? How do the authors explain the deviations?

Reply. Last paragraph of results section and Figure 6 has been removed from the manuscript since the many uncertainties discussed earlier make a parameterization premature.

P24039. It is unfortunate that the work is not convincing in many aspects, also because the reporting is poor. What was the surface to volume ratio here, and by others? Further: : : "including our analysis here" assumes the ratios to be wavelength independent. There is literature on isotope enrichment using laser light. Enrichment is attractive when there is a strong wavelength dependence.

Reply. We agree, strong enrichments are expected for narrow linewidth light sources for molecules with vibrational structure such as $SO_2$ (Danielache et al., JGRA, 2008).

However, in the present study we are only considering broadband photolysis, either by broadband fluorescent lamps, or by sunlight. Further we have discussed in the conclusion that further work is needed to address wavelength dependence. For example the contribution from the roaming atom mechanism will vary with wavelength, and it is likely to have a different fractionation than the 'traditional' molecular channel. Discussion on possible effects of wavelength dependence is extended in the final section of the manuscript.

In the end the authors recommend what has to be done, including using FTIR for checking the products. The biggest question mark is formulated as follows. When the present results are in conflict with earlier work in the same lab, why is this not discussed, and why is FTIR then not used to check product channels to avoid the uncertainty about the results.

Reply. Discussion extended. The results of this study do not necessarily conflict with earlier work.

Whereas both channels produce CO, only the molecular channel produces H2. Even aliquot taken from the reactor could have been analysed for the D/H ratio of the H2 formed.

Reply. Unfortunately our laboratory is not able to analyse H2 or dD(H2) but these would indeed be very useful experiments, given in particular the lack of knowledge about the KIE in the radical channel.

When reading the paper, one gets the impression that the authors believe that the only reaction in the reactor is the photolysis of formaldehyde. What role did other photochemical reactions play, how much OH was formed? In the troposphere OH is formed directly by UV light photolyzing ozone. However, radical formation leads to a great deal of recycling of OH. Given the radical reactions in the reactor, can OH be excluded, H2O2 etc.?

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Reply. We have added a discussion of the effect of reactions with OH and HO2 on formaldehyde to the paper. Because of the dry conditions and lack of O1D, there is very little OH in the system. Neither of the reactions removes a significant amount of formaldehyde compared to photolysis.

The quantum yield of the molecular channel depends on pressure, but there are few data on this. What was the quantum yield under the conditions used? Has it been measured? Neither for the actual lamp conditions, and not at all for sunlight conditions is "c (= kh/kH)" known, and the implications for the real atmosphere bear therefore large uncertainties. Note the disagreements with the various daylight experiments.

Reply. As described in the text we have used the quantum yield parameterization provided by the JPL review. We have also discussed the uncertainties associated with this approach.

Compared to GC analyses, FTIR can do much more (we hope) and it remains strange that actually only 2 variables have been observed. If there would been no disagreements so far, one could justify the experiment, but when there is conflict one has to go further. In particular the presence of chemistry other than photolysis is not treated. Maybe the spectra still hold valuable information for a more complete analysis.

Reply. We have analyzed the infrared spectra for all IR active gases: formaldehyde, water, CO, H2O, CO2. We have looked for, but not seen, formic acid, hydrogen peroxide, ozone, nitrogen oxides. In addition, we have added model results to the paper which demonstrate that the chemistry other than photolysis has a negligible impact on the observed changes in formaldehyde concentrations.

Remaining points. Why is in Table 2 ":" (unusual) used as separator and also "/". Are the nominal ratios based on pressure readings or FTIR measurements? What is the meaning of the classifier "nominal"? The figure captions in general are not precise and informative enough.

Reply. We have revised the tables and figure captions. The nominal values are based on the masses of formaldehyde isotopomers added to the mixture. A mixture was used so that we could obtain a reproducible ratio.

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Reply to referee #2

This study uses a large quartz laboratory chamber, UV lights with wavelengths>300 nm, and an FTIR to measure the relative photolysis rates of HCHO and HCDO at different pressures of synthetic air from 50 to 1030 mbar. They measure pressuredependent differences in the relative photolysis rate coefficients J(HCHO)/J(HCDO) and use these to infer what the pressure dependence of the H/D isotope effect for photolysis of formaldehyde to the molecular channel might look like given different values of the H/D isotope effect for photolysis to the radical channel that have been inferred from other experimental studies in natural sunlight. While I do think that the pressure dependence itself they measure is quite interesting and represents a step forward in ultimately trying to understand (if not quantify) the chemical physics of the large photolysis isotope effects for formaldehyde and their as-yet unquantified contribution to the isotope budget of atmospheric H2 in different regions of the atmosphere (e.g., surface, upper trop, stratosphere), this manuscript is poorly-written throughout (including the motivation, organization, context of previous work, discussion of uncertainties, and comparison of these results with previous work) to the point that it detracts from what is interesting and new. Furthermore, the atmospheric implications are poorly described and likely overreaching without a model to back them up, making their conclusions about the atmosphere weak at best and I suspect wrong at worst. With some considerable work to better organize, motivate, and describe the experiments and their limitations, combined with an improved discussion of discrepancies and atmospheric implications, the work may be acceptable, but not in its present form.

Reply. We have rewritten the manuscript and added material in an effort to increase

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the quality of the presentation. We emphasize that the goal of this paper is to describe the first experimental evidence for the isotope effect in the molecular channel. It is not to also present a full atmospheric chemical model. We have rewritten the manuscript to clarify this. Nonetheless our conclusions regarding the atmosphere are valid: the KIE will change as a function of pressure.

Major issues: 1. The terminology and symbols used are frequently incorrect and at times convoluted in the most esoteric symbols when simply calling them "isotope effects" or "branching ratios" would suffice. For example, kHCHO/kHCDO is frequently referred to as a "relative rate" when in fact, as written, it is a ratio of rate coefficients, not rates, and, indeed, this is how isotope effects are defined. They certainly are not the "relative rates" in the experiment when the ratio of [HCHO]/[HCDO] is not unity in any of the experimental runs given in Table 2. Equation (6) gives the photolysis rate coefficient, j, but then j is never used again, but k's are for the same quantity. Esoteric c's and r's are used, when there is a common language that chemists use (c defined and used here is simply the branching ratio for the molecular vs the radical channel, and r defined and used here is the photolysis isotope effect for the radical channel). Calling them by their correct as well as commonly used names would improve the readability of this manuscript a great deal (in addition to correcting the outright errors in usage and terminology).

Reply. Equation 6 has been revised, and we have added an explanation for the choice of nomenclature. We have used the so-called relative rate method in this study, a method found in textbooks and used in thousands of peer-reviewed articles, to measure the ratio of rate coefficients.

2. More experimental information could be given in the manuscript that is relevant to thinking about this experiment and its comparison with previous relevant experiments and what the differences might be; there is no need to require readers to go to a previous publication for such critical and relevant information. (If space is needed, the rambling, unfocused and sometimes inaccurate introduction could be cut down con-

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siderably, as well as several paragraphs of redundant information in the intro vs the results section that appear almost verbatim in both sections. . .). Details of the UV light source should be given, including its wavelength cut-offs and distribution (more than just the shape of the flux shown in Figure 1 – especially since no secondary y-axis is given there to indicate numbers or units). Furthermore, no mixing ratios for HCHO and HCDO are given in Table 2, and they can't even be calculated by the reader (not even to within 2 orders of magnitude!) because the proper information is not given. When trying to figure out discrepancies between this work and previous ones, mixing ratios may come into play and could potentially play an important role. Yet no one will be able to determine them from the lack of information currently in the manuscript. Finally, what about possible interfering reactions (e.g., water degassing from the chamber walls?) and how they could be checked for or eliminated from consideration or modeled if necessary? This should be discussed, either in the experimental section or the discussion of results.

Reply. Thank you for the useful comments; we have revised the presentation by extending the information in text and by giving the partial pressures of formaldehyde in Table 2. We also present the results of a box model calculation showing that photolysis is the only significant removal process for formaldehyde in the experimental system.

3. Certainly a more coherent discussion of possible reasons why there might be a discrepancy between this and previous work is in order, and it is not that hard to at least speculate. There is also no need to call the Feilberg results (from essentially the same group) as "unacceptable;" in my opinion, they are simply measuring different things! For example, the isotope effects are likely integrated over pressure, temperature, and light flux, and these will certainly not be the same in the quartz cell with UV lights and the natural sunlight in the Euphore chamber in Spain. For example, Orr-Ewing's group has shown a Solar Zenith Angle dependence to the radical channel quantum yield, and, upon a quick reading of the Feilberg et al. 2007 paper, the EUPHORE experiments were started at 6 am and lasted for 2 to 4 hours. While the authors here

do state in one sentence in the penultimate paragraph of the manuscript that they and others "assume that kh/kd and kH/kD are independent of wavelength," a more coherent discussion, albeit speculative, would be useful and productive here.

Reply. Thank you for the ideas. There is not necessarily a conflict between this and previous work. Table 1 has been revised. We have extended the discussion on discrepancies between the different studies, pointing out wavelength dependence and different experimental conditions as possible sources.

4. The atmospheric implications themselves seem too speculative, however. The authors state quite unequivocally that "in the present work we identify the pressure dependence of the photolysis of formaldehyde as the cause for the variation in alpha with altitude" but then follow with "The consequences of this mechanism must be investigated using stratospheric models." I think they have these sentences backwards and that the only defendable statement is: "The consequences of this mechanism (i.e., a pressure dependent isotope effect) must be investigated using atmospheric models, and it may be that this pressure dependence is important enough to be responsible for a large part of the variation in alpha with altitude." There are lots of reasons that alpha can vary with altitude (see, e.g., Mar et al., 2007); this may not be the only one and the authors have not shown otherwise, so to speculate but sound so definite is not warranted. Furthermore, the statements in the abstract are also overreaching from the laboratory data in this manuscript: that kH/kD is 1.8 at the surface to unity at 50 km. Is this what it appears to be, simply stating the pressure in their laboratory experiment and equating that with an altitude in the atmosphere? If so, this also is unwarranted. And, further: "The study concludes that the dD of photochemical hydrogen produced in situ will increase substantially with altitude." This is also speculative, and not even limited to their experiments at hand since many other isotope effects than just those in formaldehyde photolysis, as well as the relative rates (and here I do mean rates, not relative rate coefficients!) of many chemical reactions in the oxidation of CH4, will all contribute to dD of H2 produced photochemically.

Reply. We have extended and tried to clarify the text according to the comments of the referee, in particular we have rephrased the abstract regarding the kH/kD at different altitudes.

A few other minor issues that I feel are important enough to comment on: * The authors could help their readers out by explaining briefly why (previous work) suggests that the radical channel photolysis isotope effect should not be pressure dependent.

Reply. We have added an explanation to Section 3.

* Why do the authors think that isotope effects in the molecular channel of less than 1 are not reasonable at low pressures when using the Rhee radical channel isotope effect? Why not?

Reply. An explanation has been added to text.

* Gerst and Quay used isotopic mass balance to argue (convincingly!) that dDhv is on average large and positive and roughly +130 per mil. However, their "mechanism" was not quantitative and thus could NOT (quantitatively) explain deuterium enrichment in H2 produced from CH4, as stated here; it certainly did get people interested in trying to measure it, however, and their hypothesis was indeed qualitatively correct.

Reply. Text rewritten.

* In my opinion, the H2 isotope budget is the most interesting application; a more focused introduction could be based on that alone, leaving HCHO and even CH4 out of, for example "the carbon cycle," which is quite a stretch.

Reply. Text rewritten.

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 24029, 2009.