

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

Anonymous Referee #2

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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 pressure-dependent differences in the relative photolysis rate coefficients $J(\text{HCHO})/J(\text{HCDO})$ 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 pho-

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tolysis 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.

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, $k_{\text{HCHO}}/k_{\text{HCDO}}$ 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 $[\text{HCHO}]/[\text{HCDO}]$ 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).

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 pre-

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vious publication for such critical and relevant information. (If space is needed, the rambling, unfocused and sometimes inaccurate introduction could be cut down considerably, 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.

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 k_h/k_d and k_H/k_D are independent of wavelength," a more coherent discussion, albeit speculative, would be useful and productive here.

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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 defensible 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 CH_4 , will all contribute to dD of H_2 produced photochemically.

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.

* 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?

* Gerst and Quay used isotopic mass balance to argue (convincingly!) that δD_{H_2} 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 H_2 produced from CH_4 , as stated here; it certainly did get people interested in trying to measure it, however, and their hypothesis was indeed qualitatively correct.

* In my opinion, the H_2 isotope budget is the most interesting application; a more focused introduction could be based on that alone, leaving $HCHO$ and even CH_4 out of, for example "the carbon cycle," which is quite a stretch.

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

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