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***Interactive comment on* “Molecular hydrogen (H₂) emissions and their isotopic signatures (H/D) from a motor vehicle: implications on atmospheric H₂” by M. K. Vollmer et al.**

Anonymous Referee #1

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General Comments: This is a useful contribution. It presents - for the first time - a systematic study of the D-content of molecular H₂ in car exhaust with and without catalytic converter. The authors' interpretation of the observations suggests that two mechanisms dominate the isotopic signature in H₂: Equilibration between H₂ and H₂O possibly driven by the water-gas shift reaction, and superimposed an enrichment due to the catalytic removal of H₂ from the exhaust. The implications of the results on the use of isotope analysis for local and global H₂ source strengths from car traffic are also addressed.

Specific comments: page 3030, line 6: The comparison of the present results to those

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of Bottinga (1969) are not hampered by the fact that he and the present authors use different delta-scales, but rather by the fact that the D-content of H₂O in the exhaust was not measured in the present study. The latter has therefore to be derived. Stating the assumed D-content of H₂O in exhaust and making the conversion to a common scale at the beginning of this paragraph would probably simplify this paragraph, and make it more readable. There is, however, another point which needs to be addressed in this context. Fuel is not the only source of hydrogen to the system. At 50% relative humidity and 295 K temperature the combustion air contains about 1.3% of water vapour. This amounts to about 10% of the hydrogen added by the fuel. If its D-content differs substantially from that of the fuel this added water could make a significant difference in the delta-value of the water vapour in the exhaust. Since the delta-value of the CH₄ employed differs substantially from that of the gasoline, at least in one case a correction is needed.

p 3032, l 14: The definition of eq.(1) and its symbols are somewhat confusing when applied to Fig.3. This Figure plots $\ln(1 + \text{deltaDf})$ against $\ln(f)$. Extrapolation of the lines in Fig.3 to $\ln(f) = 0$ should yield $\ln(1 + \text{deltaDo})$. The so obtained deltaDo, however, differs markedly from the pre-TWC deltaD used as definition for deltaDo in line 14. Please make the definitions consistent. Also, it seems to me that the deltaDo extrapolated from Fig.3 could very well be the actual equilibrium delta-values undisturbed by the superimposed fractionation from H₂ removal.

Technical comments: p 3022, l 22:Change "enhanced deltaD-values by >50%o" to "deltaD-values enhanced by >50%o"

p3029, l 6: "cocking". Is this a misprint? What does it mean?

p 3029, l 26: Refer to the paper by Bottinga (1969) at the end of the sentence.

p 3030, l 1: I propose to change the first sentence to: "To explore the above hypothesis, we first investigate whether the post-TWC samples at the different TWC temperatures of the 4 operating modes show this equilibration effect."

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 3021, 2010.

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