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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.

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General comments: A very nice contribution that adds significantly to our knowledge of H₂ production from internal combustion engines and the isotopic effects associated with engine operating conditions and air/fuel ratio. The paper also contributes to the body of literature related to exhaust emission ratios.

Specific comments: Regarding the adjustment factor for comparing the measured results to Bottinga, 1969 – since D of H₂O was not measured, the assumption that H₂O is the dominant hydrogen pool results in the shift of ~100 per mil; however, since it is reported on p. 3026 line 23 that [H₂O] was measured along with a full suite of other

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exhaust gases, the $[H_2O]/[H_2]$ ratio could be used to lend some insight into the validity of this assumption. In addition, this ratio would lend insight into the importance of the role of the water-gas-shift as well as the relative strength of the various other proposed controlling mechanisms. It would also, perhaps, alleviate the concerns of reviewer 1 regarding the role of H_2O vapor introduced at the engine intake.

Regarding the suggestion of two separate isotope effects during the loss of H_2 in the TWC – It may be that the same process, i.e. oxidation of H_2 to H_2O , is responsible for both observed effects. Not only are H_2 and H_2O attempting to reach thermodynamic equilibrium on a catalytic surface in a brief period of time but a fraction of the H_2 is being converted to H_2O , a reaction which may have a kinetic fractionation associated with it. Again, knowing the concentration of both species both entering and leaving the TWC would help determine if it is strictly the H_2/H_2O system that is driving the observed isotopic effects or if additional species are involved.

P 3029, line 26-28: Rahn et al., 2002 in their conclusions also suggested $H_2O:H_2$ temperature dependent equilibrium processes for the observed range of deuterium in terrestrial H_2 .

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