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Deuterium enrichment in stratospheric H_2: 2D model results and implications for the troposphere

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The isotopic composition of H_2 produced by the photo-oxidation of CH_4, often referred to as "$\delta D_{h\nu}$," is an important yet poorly constrained term in the global isotope budget of atmospheric H_2. Several box model analyses of stratospheric δD-H_2 observations demonstrated empirically that $\delta D_{h\nu}$ is much larger than δD of the CH_4 from which it is derived – a conclusion that qualitatively resolved major discrepancies between the global H_2 concentration and isotope budgets. However, the box model studies necessarily assumed that the overall fractionation factor from CH_4 to H_2 remains constant throughout the stratosphere and, further, that this fractionation factor is valid for the troposphere or can be easily extrapolated from the stratospheric value. Here, we use the Lawrence Livermore 2D chemical-radiative-transport model to investigate these assumptions by determining the sensitivity of stratospheric δD-H_2 and $\delta D_{h\nu}$ and to various known and unknown isotope effects in the elementary steps of the photochemical production and destruction of H_2 and, importantly, their dependence on altitude and latitude. Our results show that (1) kinetic isotope effects (KIEs) for CH_4 oxidation, (2) H vs. D abstraction for several steps between CH_4 and CH_2O, (3) KIEs for CH_2O oxidation, (4) isotope effects for CH_2O photolysis, and (5) KIEs for H_2 destruction all play significant but varying roles in determining δD-H_2 and that calculated values for $\delta D_{h\nu}$ do indeed vary significantly with latitude and altitude, leading to larger uncertainties in $\delta D_{h\nu}$ than previously estimated. Based on these sensitivity studies, we also identify laboratory experiments, theoretical calculations, and atmospheric observations that are most needed to further reduce uncertainties in the magnitude of $\delta D_{h\nu}$ and, hence, the global H_2 isotope budget.