A Model for $^{12}CH_2D_2$ and $^{13}CH_3D$ as Complementary Tracers for the Budget of Atmospheric CH_4

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Methane is an important greenhouse gas with a potential significance in both current and past climate change. We present a theoretical model to investigate the potential of $^{13}CH_3D$ and $^{12}CH_2D_2$, the doubly substituted mass-18 isotopologues of methane, as tools for tracking atmospheric methane sources and sinks. We use electronic structure methods to estimate kinetic isotope fractionations associated with the major sink reactions of methane in air (reactions with OH and Cl radicals), and combine literature data with reconnaissance measurements of $^{13}CH_3D$ and $^{12}CH_2D_2$ to estimate the compositions of the largest atmospheric sources. This model atmospheric budget is investigated both at steady state and in a simplified box model, applying different dynamic (non-steady state) conditions to it by inducing changes in the emission or sink fluxes. The steady-state model predicts that sink reactions will generate a marked (>100‰) clumped isotope excess in atmospheric $\Delta^{12}CH_2D_2$ relative to the net source composition. $^{12}CH_2D_2$ measurements may thus be useful for tracing both atmospheric source and sink fluxes. The effect of sinks on $\Delta^{13}CH_3D$ is much less pronounced, indicating that $^{13}CH_3D$ in air will give a more focused picture of the source composition.