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A consistent molecular hydrogen isotope chemistry scheme based on an independent bond approximation

G. Pieterse, M. C. Krol, and T. Röckmann
Institute for Marine and Atmospheric Research Utrecht, Utrecht, The Netherlands

Abstract. The isotopic composition of molecular hydrogen (H_2) produced by photochemical oxidation of methane (CH_4) and Volatile Organic Compounds (VOCs) is a key quantity in the global isotope budget of (H_2). The many individual reaction steps involved complicate its investigation. Here we present a simplified structure-activity approach to assign isotope effects to the individual elementary reaction steps in the oxidation sequence of CH_4 and some other VOCs. The approach builds on and extends the work by Gerst and Quay (2001) and Feilberg et al. (2007b). The description is generalized and allows the application, in principle, also to other compounds. The idea is that the C-H and C-D bonds – seen as reactive sites – have similar relative reaction probabilities in isotopically substituted, but otherwise identical molecules. The limitations of this approach are discussed for the reaction CH_4+Cl. The same approach is applied to VOCs, which are important precursors of H_2 that need to be included into models. Unfortunately, quantitative information on VOC isotope effects and source isotope signatures is very limited and the isotope scheme at this time is limited to a strongly parameterized statistical approach, which neglects kinetic isotope effects. Using these concepts we implement a full hydrogen isotope scheme in a chemical box model and carry out a sensitivity study to identify those reaction steps and conditions that are most critical for the isotope composition of the final H_2 product. The reaction scheme is directly applicable in global chemistry models, which can thus include the isotope pathway of H_2 produced from CH_4 and VOCs in a consistent way.

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