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Photolysis of formaldehyde - effects on hydrogen isotopes

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Due to an expected enhanced use of H_2 as an energy carrier in the future it is important to understand the global cycle of H_2 in order to assess the potential impact of increasing H_2 concentrations on the atmosphere. One possibility to obtain further information is to study its isotope composition of H_2 and its precursors. H_2 has two principle source types, combustion sources and photochemical sources. Whereas it is conceptually relatively easy to characterize the isotope content of combustion sources, the complexity of photochemical reaction pathways makes the isotope characterization of this source type more difficult, because many individual reaction steps can be associated with isotope fractionation. Almost all of the hydrogen production proceeds via formaldehyde, the last intermediate species, from which H_2 is produced by photolysis and oxidation. Formaldehyde is the most abundant carbonyl compound in the atmosphere and its photochemical decomposition provides approximately 50% of atmospheric H_2. Previous results have shown that a large isotope fractionation must occur in the photolysis of formaldehyde, but conflicting results have been published. The photolysis rates and the ratios of these rates for the molecular and the radical path-

ways are essential to understand the isotope fractionation, which can provide detailed information about the atmospheric cycle of H_2.

Photolysis experiments were conducted under near-natural tropospheric conditions in the SAPHIR chamber, an atmospheric reaction chamber in Jülich, Germany. Advantages of experiments in reaction chambers are the decoupling of variations due to chemical reactions and dynamic processes and thus the independency of time varying perturbations. Here we present the results of the determination of the H_2 isotope effects in the photolysis of HCHO.