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Isotope effect in the formation of H2 from H2CO studied at the atmospheric simulation chamber SAPHIR

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Formaldehyde of known, near-natural isotopic composition was photolyzed in a large photochemical reactor under ambient conditions. The isotopic composition of the product H2 was used to determine the isotope effects in formaldehyde photolysis. The experiments are sensitive to the molecular photolysis channel, and the radical channel has only a second order effect and can thus not be derived with high precision. The molecular channel kinetic isotope effect, the ratio of photolysis frequencies j(HCHO→CO+H2)/j(HCDO→CO+HD) under tropospheric conditions is determined to be KIEmol=1.63±0.03. Combining this result with the total KIE from a recent relative rate experiment, it is likely that KIEmol and KIErad are not as different as described previously in the literature.