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Pressure dependent deuterium fractionation factors in the production of molecular hydrogen from formaldehyde photolysis

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The pressure dependence of the relative photolysis rates of HCHO and HCDO has been investigated using a new photochemical reactor at the University of Copenhagen. Photolysis lamps were chosen to irradiate the samples at wavelengths longer than the threshold for radical products, H+HCO, thereby producing only molecular hydrogen. The relative rate for the photolytic production of molecular products, H2 and CO, was measured at total pressures from 50 to 1030 mbar, corresponding to altitudes from surface to 22 km. The experiments show that the D of photochemical hydrogen produced in situ will increase substantially with altitude. A box model shows that the variation in the D of photochemical hydrogen with altitude seen in field measurements can be explained completely by the pressure dependent effects in HCHO/HCDO photolysis.