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UV photochemistry of methyl hydroperoxide trapped in ice

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Organic hydroperoxides are important tropospheric trace gases as they are an important source of OH radicals. The simplest in this class is methyl hydroperoxide (CH₃OOH) which is a product of methane oxidation by OH and HO₂ radicals. Sinks of CH₃OOH are photolysis, reactions with OH radicals or dry and wet deposition. Laboratory studies have shown that CH₃OOH absorbs strongly over the region between 200 and 360 nm resulting in excitation to a dissociative electronic excited state. The pathway with the lowest threshold energy involves single bond cleavage giving rise to the CH₃O + OH radical products. Our recent measurements at Neumayer station in Antarctica have shown that CH₃OOH mixing ratios during the polar day are considerably higher than during the polar night and correlate with UV radiation. In laboratory experiments we have now simulated the UV photochemistry of CH₃OOH trapped in ice (H₂O and D₂O) at 14 K and for comparison in solid argon matrices. The photoproducts (CH₂O, CO, CO₂) formed in the ice have been identified by means of FTIR spectroscopy.