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The Tropospheric Photochemistry of Formaldehyde

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Photolysis of HCHO (formaldehyde) in the troposphere, which is important for HO_x and O_3 production, occurs *via* two major pathways known as the molecular (1) and radical (2) channels:

$$HCHO + h\nu \xrightarrow{\lambda < 361\,nm} H_2 + CO \quad (1)$$

$$HCHO + h\nu \xrightarrow{\lambda < 330\,nm} H + HCO \quad (2)$$

To date, wavelength dependent radical quantum yields for HCHO photodissociation have not been measured directly. We are using a Cavity Ring-Down Spectroscopy (CRDS) set up which enables direct HCO photoproduct detection to determine absolute HCO quantum yields. The calibration method is based on the UV photolysis of Cl_2 in the presence of HCHO. Briefly, this method consists of simultaneous addition of Cl_2 and HCHO to the ring down cavity, both of which are photolysed by a UV laser beam. The Cl atoms formed from Cl_2 photolysis react with HCHO forming HCO. Formyl radical absorption coefficients, which are taken as proxy for HCO concentrations, are determined for both photolysis of HCHO and the reaction of HCHO with Cl atoms. Varying the concentrations of Cl_2 added to the ring down cavity results in a proportional change in HCO production, from which absolute quantum yields for the radical channel can be obtained. The validity of this calibration method has been tested by measuring time dependent decays of HCO radicals and comparing the experimental results to those simulated using an ACUCHEM model. The model uses

published rate constants and initial reactant concentrations calculated from measured absorption coefficients.