

Radical quantum yields from formaldehyde photolysis in the 30400 – 32890 cm⁻¹ (304 – 329 nm) spectral region: Detection of radical photoproducts using Pulsed Laser Photolysis-Pulsed Laser Induced Fluorescence

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Formaldehyde (HCHO) is ubiquitous in the troposphere and is one of the most important carbonyl molecules in the lower atmosphere. It is produced by the oxidation of methane, isoprene, acetone, and other volatile organic compounds (VOCs), fossil fuel combustion, and biomass burning. HCHO has the potential to significantly influence both local and regional scale atmospheric chemistry and is one of the indicators of poor air quality because essentially every organic species in the atmosphere degrades with a reaction pathway that includes HCHO.

The dominant loss mechanism for HCHO is photolysis which occurs via two pathways with threshold energies indicated in parentheses:



In this work the quantum yield for the production of radical products, H+HCO has been measured directly using a Pulsed Laser Photolysis – Pulsed Laser Induced Fluorescence (PLP – PLIF) technique across the 30400 – 32890 cm⁻¹ (304 – 329 nm) spectral region. This is the first study at a resolution approaching the Doppler linewidth of HCHO rotational features and also the first work to report a contiguous action spectrum across the actinic uv region. The H and HCO photofragments reacted with NO₂ and were monitored using LIF of the OH radical as a spectroscopic marker. Using the HCHO absorption cross section previously obtained in this laboratory, the relative quantum yield was determined two different ways. Direct division of the action spectrum by the absorption cross sections produced a high resolution picture of the rotationally resolved quantum yields allowing us to examine the rotational dependence of the yields. These were compared with band specific yields, produced by integrating over vibrational features before division. Yields were normalized to a value of 0.69 at 31750 cm⁻¹ based on the current recommendation of Sander et al. In The first high-resolution absolute radical quantum yield measurements were reported by Gorrotxategi Carbajo et al. using cavity ring down (CRD) detection of HCO with a resolution of 0.5 cm⁻¹. Absolute yields were measured at seven wavelengths and then used to scale relative yields. The resolution of the current study is estimated to be better than 0.09 cm⁻¹, a factor of five higher, and provides data over the entire spectral range whereas Gorrotxategi Carbajo et al. were unable to obtain yield measurements over several wavelength intervals due to limited signal-to-noise ratios over regions where $\sigma_{\text{HCHO}} < 1.8 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$. This included all of the 1₀4₀³, 2₀4₀²6₀¹, and 5₀¹ + 1₀4₀¹ bands and a significant portion of the 2₀5₀¹ band. We find greater structure than prior studies and for the 5₀¹ + 1₀4₀¹ combination band centered at 31125 cm⁻¹ the measured radical quantum yield is significantly less than the values reported in recent studies. The rotational and vibrational dependence of the quantum yield and its atmospheric implications will be discussed.

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References:

Sander, S. P., et al., *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17*, Jet Propulsion Laboratory, Pasadena, 2011.

Gorrotxategi Carbajo, P., Smith, S. C., Holloway, A. L., Smith, C. A., Pope, F. D., Shallcross, D. E. and Orr-Ewing, A. J., *J. Phys. Chem. A*, 2008, **112**, 12437-12448.