

Measurements of Formaldehyde Using Broadband Cavity Enhanced Spectroscopy at 315 - 360 nm

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Formaldehyde is the simplest aldehyde, and the most abundant in the atmosphere. Its sources include primary emissions and secondary photochemical production from anthropogenic and biogenic organic compounds. In many parts of the atmosphere, formaldehyde photolysis makes an important contribution to oxidation by providing a large source of HO_x (=OH + HO₂) radicals. We describe a laboratory instrument for simultaneous measurements of formaldehyde and nitrogen dioxide using broadband cavity enhanced spectroscopy. The output from a laser-driven Xenon arc lamp is coupled into a 1-m optical cavity, and the light exiting the cavity is recorded by a grating spectrometer with a charge-coupled device (CCD) array detector. Using cavity mirrors with 595 ppm loss at 330 nm, we obtain absorption spectra across the 315 - 360 nm spectral region. Mirror reflectivity as a function of wavelength is determined from the known Rayleigh scattering cross sections of He and dry zero air (N₂ + O₂). We use least-squares fitting with published reference spectra to simultaneously retrieve formaldehyde and nitrogen dioxide concentrations. For 1-min sampling at ambient conditions, the precision ($\pm 1\sigma$) on signal is better than 2 ppbv formaldehyde. We will discuss instrument improvements that would be required to reach sub-ppbv levels for atmospheric measurements.