Determining Optical Path Lengths for Aerosol-Free Cavity Enhanced Spectroscopy: Theoretical Calculations Based On Mirror Characterization and Rayleigh Scattering Vs Determination from Measurements of Collision Induced Absorption of Oxygen Molecules

Sean Coburn[1,2], Rainer Volkamer[1,2]
[1]University of Colorado Boulder, Boulder, Colorado, USA
[2]CIRES, Boulder, Colorado, USA

Cavity enhanced absorption spectroscopy (CEAS) presents a powerful analytical method with the demonstrated capability to measure numerous trace gases over a wide range of wavelengths. One critical aspect of this technique is the determination of the optical path length within the cavity. Two methods for determining this parameter are discussed and compared here for a CEAS instrument coupled to a broadband LED light source and utilizing the differential optical absorption spectroscopy (DOAS) retrieval method, which has the capability to simultaneously measure multiple trace gases over a wide wavelength range (>30 nm) and has been demonstrated to be insensitive to broadband processes such as lamp drift (and thus does not require explicit knowledge of lamp intensity). The first method is the through the characterization of the cavity mirrors (measuring reflectivity) and calculating extinction due to Rayleigh scattering within the cavity, and the second uses measurements of oxygen molecule collision induced absorption within the cavity when sampling air (rather than calibration gases such as N_2, He, or Ar). Results of a comparison of these two methods is presented for several laboratory campaigns all representing aerosol free measurements, but with different configurations of the instrument described above (i.e., different mirrors, base cavity lengths, set-up personnel). Overall, these methods show good agreement with percent differences typically (<7%), even under conditions where extinction due to the absorption of other trace gases starts to become relevant.