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Cavity enhanced differential optical Absorption Spectroscopy (CE-DOAS) – application and Light-Path Correction.

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Atmospheric trace gas measurements by cavity assisted long-path absorption spectroscopy are an emerging technology. Initial approaches made use of monochromatic cavity ring-down (CRD) devices, while more recently steady state approaches became known as cavity enhanced absorption spectroscopy (CEAS) technologies.
An interesting approach is the combination of CEAS with broad band light sources. Broad-band CEAS (BB-CEAS) has several enormous advantages over CRD. For instance LED's can be used instead of pulsed lasers, significant simplifying the instrumental set-up. Furthermore, BB-CEAS absorption spectra can be analysed using the DOAS technique realising all advantages of DOAS. This cavity enhanced DOAS (CE-DOAS) technique offers e.g. sensitive detection of very small differential absorption structures (usually vibrational molecular bands), quantitative detection of a particular molecule, simultaneous measurement of several molecular species with overlapping spectra and even determination of the aerosol extinction. In contrast to the CRD technique, where the shortening (compared to the "empty" cavity) of the ring-down time is always proportional to the additional absorbance, an important problem associated with BB-CEAS is the reduction of the light path by the trace gas absorption. In extreme, but not unrealistic cases the optical density of an absorption structure can become nearly independent of the trace gas concentration in the cavity, thus the CEAS Method would almost completely loose its sensitivity to trace gas absorptions. In typical applications the optimum sensitivity is reached in situations where the light path reduction effect is neither negligible nor dominating, thus correction of this effect is required.
We present a detailed, theoretical investigation of these relationships, present several methods to correct for the cases between the two above extremes, and demonstrate the usefulness of our new approach with experimental data.