A Novel NIR ew-cw-CRD Spectrometer for Investigating Heterogeneous Processes at the Quartz-Air/Water Interface: Characterization and First Measurements

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Many cavity designs utilizing the evanescent wave (ew) have been developed such as monolithic resonators, fiber loop schemes and setups with an additional prism inside the cavity. Common to all implementations is that the attenuation of the ew resulting from total internal reflections (TIR) yield information about absorbing species adsorbed on the TIR surface. A novel ew-cw-CRD spectrometer has been built allowing us to observe vibrational overtone absorption bands in the near-infrared (NIR) region between 1600-1700 nm. A tunable external cavity diode laser served as a narrowband light source. The spectrometer was designed for this wavelength region due to 1.) the possibility to detect organic compounds based on their C-H overtone vibrations, 2.) the availability of high-quality mirrors and quartz prisms with low absorption and scattering losses and 3.) low disturbances caused by interfering water absorption bands, hence enabling the investigation of liquid water systems. A further advantage of our reactor is a modular design providing the possibility of both gas phase and interfacial measurements including photolysis. The performance of the spectrometer has been characterized by measuring empty cavity signals and by using Trichloroethylene (TCE) as a test substance. Spectra and adsorption isotherms are presented. As expected for single mode excitation of the ringdown cavity using narrow bandwidth radiation, measured spectra are affected by resonance effects stemming from the additional etalons arising from the configuration of the mirrors and the prism. Beating frequencies can be clearly related to the different intrinsic cavities. Several cavity modulation schemes and special fitting and averaging procedures have been tested to overcome the overlaying beating structure and therefore to increase the quality of the spectra. Nevertheless, despite long ringdown times (up to 3.7 µs in a 0.5 m cavity), minimum detectable absorbance is limited to $A_{min,10} = 2.7\times10^{-6}$.