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Incoherent broadband cavity-enhanced total internal reflection spectroscopy of surface-adsorbed metallo-porphyrins

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An improvement of conventional attenuated total reflection (ATR) spectroscopy is demonstrated by applying an incoherent broadband light source (short-arc Xe-lamp) in a cavity-enhanced evanescent-wave absorption method. With this novel approach the absorption spectra of several metallo-octaethyl porphyrins (Palladium (PdOEP), Platinum (PtOEP) and Zinc- (ZnOEP)) in thin acetone solution layers and on a fused silica (FS) surface were studied between 390 and 625 nm. The time dependence of the evaporation process of the solution on the FS surface is described. The maximum sensitivity of the setup is estimated at approximately 2×10^{-5} per pass, which translates into a minimal detectable surface density of less than 2×10^{-3} monolayers for the porphyrins studied (based on absorption in the strong Soret bands). Changes of surface and solution spectra are characterised and discussed on basis of observed band broadenings and spectral shifts.

This new approach is of relevance for investigations in atmopsheric and planetary sciences involving absorbers on surfaces and heterogeneous chemistry.