

Abstract

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 characterized and discussed on the basis of observed band broadenings and spectral shifts [1]. This new approach is of relevance for investigations in atmospheric and planetary sciences involving absorbers on surfaces and heterogeneous chemistry.

Porphyrins

Porphyrins and their derivatives are common in nature (e.g. chlorophyll, heme, vit. B12). Metallo-porphyrins are created from the fundamental porphyrin, known as porphine or free-base (fb), through substitution of the two core hydrogen atoms with a metal cation - see Figure 3. This substitution determines the absorption and luminescence spectra of the molecule.

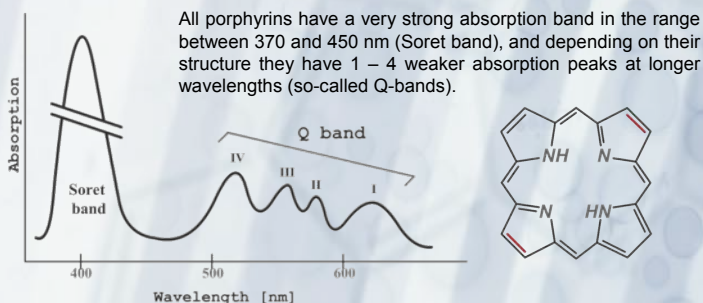


Figure 3: Structure (right) and schematic absorption spectrum (left) of porphine (free-base).

Evaporation of sample solution on prism surface

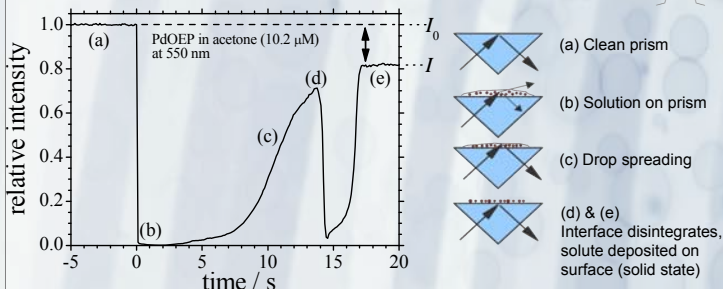


Figure 4: Relative intensity transmitted by the cavity as a function of time: (a) clean prism without solution, (b) sample solution put on the prism surface, (c) solvent evaporation, (d) disintegration of interface, (e) transmission with solute left on prism surface. Meaning of I_0 and I_2 as in Eq. (2).

Incoherent broadband cavity-enhanced absorption spectroscopy

Linear cavity: The intensity of light transmitted by an optically stable cavity is measured with (I) and without (I_0) a sample. The cavity is formed by two highly reflecting mirrors (R) separated by a distance d . Loss, L , of the sample in the cavity is given by [2]:

$$L \approx \left(\frac{I_0}{I} - 1 \right) (1 - R) \quad (1)$$

Folded cavity: The intensity of light transmitted by a folded cavity with an inherent loss, L_p , is measured with (I) and without (I_0) a sample. The cavity is formed by two highly reflecting mirrors (R) and a prism. The loss, L , of the sample on the prism surface is given by [1]:

$$L \approx \left(\frac{I_0}{I} - 1 \right) (L_p + 1 - R) \quad (2)$$

Results

Palladium Octaethyl-Porphyrin (PdOEP)

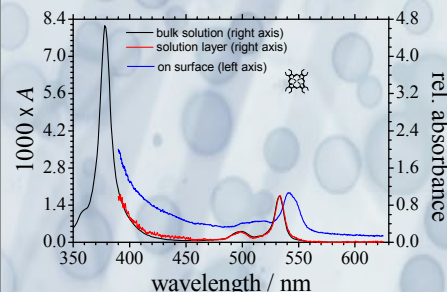


Figure 5: Loss per pass of PdOEP on the quartz prism according to eqn (3). Red line: spectrum of a thin solution layer (10 μ M, PdOEP in acetone). Blue line: spectrum of PdOEP adsorbed on prism surface after solvent evaporation; $(30 \pm 3) \times 10^{12}$ molecule cm^{-2} . Dashed line: spectrum of a ≈ 10 μ M solution of PdOEP in acetone for comparison.

Platinum Octaethyl-Porphyrin (PtOEP)

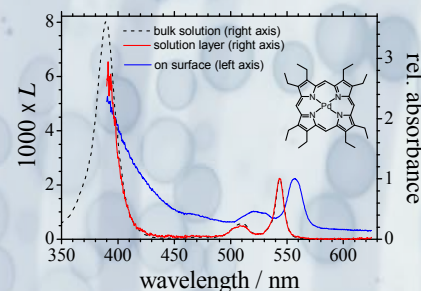


Figure 6: Loss per pass of PtOEP on the quartz prism according to eqn (3). Red line: spectrum of a thin solution layer (PtOEP in acetone). Blue line: spectrum of PdOEP adsorbed on prism surface after solvent evaporation; $(26 \pm 2) \times 10^{12}$ molecule cm^{-2} . Dashed line: spectrum of a ≈ 10 μ M solution of PtOEP in acetone for comparison.

Experimental

A short-arc Xe lamp was used as broadband excitation light source. The collimated beam was coupled into a folded, optically stable cavity consisting of two highly reflecting dielectric mirrors and an internal reflection element (IRE).

The light transmitted through the cavity was focused onto a fibre using an achromatic lens. The fibre was connected to a monochromator/CCD assembly.

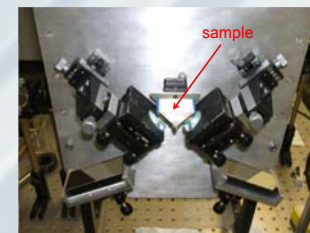


Figure 1: Photograph of setup

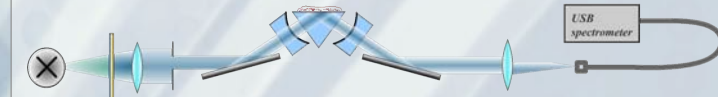


Figure 2: The reflectivity of the dielectric mirrors was 99.5% (25 mm diameter, 2 m radius of curvature). This setup enables the measurement of the absorbance of samples located on the surface of the prism.

Detection limits

The instrument's sensitivity was estimated by taking five measurements of $I_{1,n}$ ($n=1...5$), i.e. without a sample on the IRE. From these five measurements ten "baseline spectra" $A_{0,k}$ ($k=1...10$) were calculated for each combination pair of the five I_1 spectra ($i \leq j, j=2...5$), using $A_{0,k}(\lambda) = \left(\frac{I_{1,i}}{I_{1,j}} - 1 \right) (L_1 + 1 - R)$.

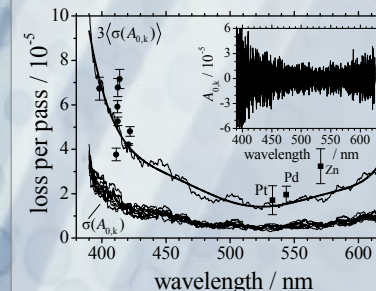


Figure 7: Insert: Ten baseline loss spectra, $A_{0,k}$, measured without sample on the IRE. Lower thin solid lines: Standard deviations, 1σ , calculated within 10 nm intervals and moved across each of the ten $A_{0,k}$ spectra. Upper medium solid line: 3 times the mean standard deviation spectrum. Upper thick solid line (smooth): 7th order polynomial fitted to the curve representing the minimum detectable loss per pass of the instrument. Symbol \blacksquare : detection limits of the three octaethyl porphyrins (Pd-, Pt-, Zn-). Symbol \bullet : detection limits of the seven tetraphenyl porphyrins (Ag-, Cu-, Co-, Ni-, Pd-, Pt-, Zn-) & the free base (see Table).

Minimum detectable surface coverage for various metallo porphyrins used in this study. Column 1: Type of Porphyrin - for OEP the limit is based on detection in the Q-band, for tetraphenyl porphyrins (TPP) and fb the limit is based on absorption in the S-band. Column 2: Wavelength of absorption maximum in the detection band. Column 3: Approximate signal-to-noise ratio (SNR) of the spectrum measured at the lowest sample concentration. Column 4: Minimum detectable coverage in fractions of a monolayer, based on an SNR of 3:1. The error in this column is $\sim 10\%$.

Porphyrin	$\lambda_{\text{max}}/\text{nm}$ at absorption maximum	$\sim \text{SNR}$	Min. detect. coverage/ 10^3 monolayer
PtOEP	544.6 ± 0.2	10	2.10
PtOEP	534.9 ± 0.3	11	1.79
ZnOEP	590.2 ± 0.5	11	1.48
AgTPP	423.4 ± 0.1	40	0.48
CoTPP	430.4 ± 0.3	19	1.16
CuTPP	413.3 ± 0.1	29	0.87
NiTPP	412.8 ± 0.2	19	0.94
PtTPP	413.7 ± 0.2	15	1.06
PtTPP	398.5 ± 0.2	18	1.09
ZnTPP	424.4 ± 0.1	60	0.27
Free base	414.9 ± 0.2	25	0.76

References

- A.A. Ruth and K.T. Lynch, *Incoherent broadband cavity-enhanced total internal reflection spectroscopy of surface-adsorbed metallo-porphyrins*, *Phys. Chem. Chem. Phys.* 10 (2008) 7098-7108.
- S.E. Fiedler, A. Hese and A.A. Ruth, *Incoherent broadband cavity-enhanced absorption spectroscopy*, *Chem. Phys. Lett.* 371 (2003) 284-294.