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Supporting Information

## **Beyond Beer's Law: Why the Index of Refraction Depends (Almost) Linearly on Concentration**

Thomas G. Mayerhöfer,\* Alicja Dabrowska, Andreas Schwaighofer, Bernhard Lendl, and Jürgen Popp © 2020 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

# Beyond Beer's law – why the index of refraction depends (almost) linearly on concentration – Supporting Information

Thomas G. Mayerhöfer <sup>\*[a]</sup>, Alicja Dabrowska <sup>[b]</sup>, Andreas Schwaighofer <sup>[b]</sup>, Bernhard Lendl <sup>[b]</sup>, Jürgen Popp <sup>[c]</sup>

## Materials and methods.

**Reagents and samples.** Chloroform (water free, ≥99%) and ε-caprolactam (≥98%) were purchased from Sigma-Aldrich. ε-Caprolactam stock solution was prepared and diluted to concentrations ranging between 10 and 70 mmol L<sup>-1</sup>.

**Experimental Setup.** The experimental setup consists of a Mach-Zehnder type interferometer with a temperature-stabilized transmission flow cell integrated in each of the beam paths. The laser beam emitted by a thermoelectrically-cooled external cavity-quantum cascade laser (Daylight Solutions Inc., San Diego, USA; tuning range: 1729.94 and 1565.06 cm<sup>-1</sup>, laser Driver 1001-TLC) was split at a ratio of R:T = 50:50 by a CaF<sub>2</sub>-beam splitter (Thorlabs BSW510). Both, the reflected and transmitted beam, pass 270 μm liquid flow cells (1" CaF<sub>2</sub> wedged windows with PTFE-spacer), and are recombined with another beam splitter (identical to first beam splitter) and mirror before getting focused on two pyroelectric detectors (Infratec LME-336, detectivity  $4.0 \cdot 10^8 \text{ cm}\sqrt{\text{Hz}}/W$  at 500 K, aperture size 5 mm diameter) by two parabolic gold

mirrors (Thorlabs MPD229M01). To minimize fringing, the detectors were mounted in an angle of approximately 30 degrees to the beam. One of the mirrors in the interferometer is attached to a piezo actuator (3.6 μm maximum displacement) connected to a commercial piezo controller (Thorlabs MDT694A). The laser was operated at a repetition rate of 100 kHz with a duty cycle of 4.4% and an over modulated square wave with a frequency of 100 Hz (train of pulses). The recorded detector signals were

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[a] PD Dr., T.G. Mayerhöfer  
Spectroscopy/Imaging  
Leibniz Institute of Photonic Technology  
Albert-Einstein-Str. 9, Jena, Germany  
And Institute of Physical Chemistry and Abbe Center of Photonics  
Friedrich Schiller University, Jena  
D-07743, Helmholtzweg 4, Germany  
E-mail: [Thomas.Mayerhoefer@ipht-jena.de](mailto:Thomas.Mayerhoefer@ipht-jena.de)

[b] A. Dabrowska, Dr. A. Schwaighofer, Prof. Dr., B. Lendl  
Institute of Chemical Technologies and Analytics,  
Technische Universität Wien, Getreidemarkt 9/164,  
1060 Vienna, Austria  
E-mail: [bernhard.lendl@tuwien.ac.at](mailto:bernhard.lendl@tuwien.ac.at)

[c] Prof. Dr., J. Popp  
Spectroscopy/Imaging  
Leibniz Institute of Photonic Technology  
Albert-Einstein-Str. 9, Jena, Germany  
And Institute of Physical Chemistry and Abbe Center of Photonics  
Friedrich Schiller University, Jena  
D-07743, Helmholtzweg 4, Germany  
E-mail: [Juergen.Popp@ipht-jena.de](mailto:Juergen.Popp@ipht-jena.de)

amplified and filtered with a custom-built lock-in amplifier synchronized to the 100 Hz modulation of the laser before being digitized by a NI DAQ-ADC (Model 9205, National Instruments Corp., Austin, TX, USA).

**Recording of spectra.** The experimental setup provides the possibility to record absorption and dispersion spectra of samples in the desired spectral region defined by the tuning range of the laser. Dispersion spectra were recorded based on the analysis of the differential detector signal  $\Delta I_{rel}(\tilde{\nu})$  throughout the spectral scanning. Prior to the measurement, when both flow cells were filled with reference solution (solvent), the differential signal was adjusted to 0. The relation  $\Delta I_{rel}(\tilde{\nu}) = 0$  means that there is an equal distribution of the intensity on the detectors. The adjustment to the zero-point was made by the manual change of voltage on the piezo-controller, which drives the piezo-actuator and thus displaces the mirror mounted on the piezo element. After adjustment, background (Cell 1: solvent, Cell 2: solvent) and sample (Cell 1: solvent, Cell 2: sample) spectra were recorded. Introduction of the sample solution in one of the arms causes a phase shift and thus variations of the  $\Delta I_{rel}(\tilde{\nu})$ , proportional to the refractive index of the sample.

Absorption spectra were obtained by blocking the beam in one of the arms of the Mach-Zehnder interferometer. Accordingly, the beam passed through one flow cell filled with solution and the total amount of transmitted light was measured by summing up the intensity recorded by the two detectors. Measurements were made for solvent and analyte and the absorbance spectrum was calculated as follows:

$$A(\tilde{\nu}) = -\log_{10} \left( \frac{I_{D1sample} + I_{D2sample}}{I_{D1solvent} + I_{D2solvent}} \right) \quad (1)$$

Four dispersion and four absorbance spectra were recorded per concentration, collecting 151 points per spectrum.

**Data Analysis.** During post-processing, 16 data-points at wavenumbers coinciding with water vapor absorption bands were excluded from each data set. For dispersion spectra, a Savitzky-Golay filter (order: 3, frame length: 25) was applied to reduce instrumental noise.

To obtain a dispersion spectrum of the sample, the background measurement was subtracted from the sample measurement, resulting in the analyte spectrum of the relative intensity  $\Delta I_{rel}(\tilde{\nu})$ . To derive the values of the relative change of the refractive index  $\Delta n(\tilde{\nu})$  from the measurement data, formulas (2) and (3) were applied. First, the spectrum of displacement is calculated  $\delta(\tilde{\nu})$  and then a spectrum of the sample's

refractive index is derived.

$$\delta(\tilde{\nu}) = \frac{\lambda}{2\pi} \sin^{-1} \Delta I_{rel}(\tilde{\nu}) \quad (2)$$

$$\Delta n(\tilde{\nu}) = n - n_0 = \frac{\delta(\tilde{\nu}) \cdot \sqrt{2}}{d} \quad (3)$$

Quantitative analysis of the absorbance spectra was carried out by evaluating the band maximum at 1659  $\text{cm}^{-1}$  and calculating the band area from 1610 to 1700  $\text{cm}^{-1}$ .

For obtaining calibration curves of the dispersion spectra, the slopes of the dispersion spectra in the points of inflection were used. These points coincide with the band maxima in the corresponding absorption spectra. The evaluation of the slopes was performed by calculating a tangent using three data points prior and after the known wavenumber values of the corresponding absorption band maximum. Data processing was performed in MATLAB R2017a (Mathworks Inc., Natick, USA).

For more detailed information, please refer to:

S. Lindner, J. Hayden, A. Schwaighofer, T. Wolflehner, C. Kristament, M. Gonzalez-Cabrera, S. Zlabinger, and B.Lendl, "External Cavity Quantum Cascade Laser based Mid-Infrared External Cavity Quantum Cascade Laser based Mid-Infrared Dispersion Spectroscopy for Qualitative and Quantitative Analysis of Liquid-Phase Samples" Applied Spectroscopy, 2019. DOI: 10.1177/0003702819892646.

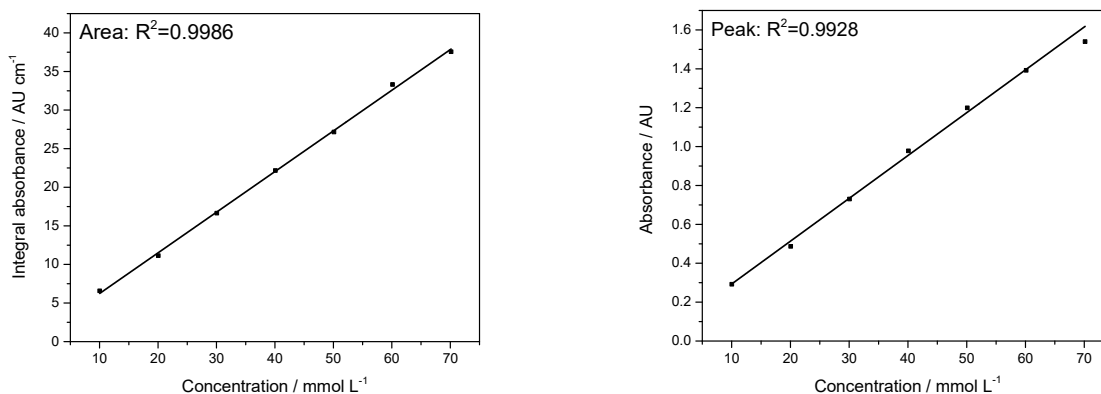


Figure S1. Calibration curves of the absorbance spectra obtained by height evaluation at 1659  $\text{cm}^{-1}$  and by integration of the absorbance band from 1610 to 1700  $\text{cm}^{-1}$ .

Units of the quantities:

Quantity	Symbol	Unit
Absorbance	$A(\tilde{\nu})$	-
Molar attenuation coefficient	$\varepsilon^*(\tilde{\nu})$	$\left[ \frac{\text{mol}}{\text{L} \cdot \text{cm}} \right]$
Concentration	$c$	$\left[ \frac{\text{mol}}{\text{L}} \right]$
Thickness	$d$	[cm]
Polarisation	$\vec{P}$	$\left[ \frac{\text{A} \cdot \text{s}}{\text{m}^2} \right]$
Number of dipole moments per unit volume	$N$	$\left[ \frac{1}{\text{m}^3} \right]$
Dipole moment	$\vec{p}$	[A · m · s]
Vacuum permittivity	$\varepsilon_0$	$\left[ \frac{\text{A} \cdot \text{s}}{\text{V} \cdot \text{m}} \right]$
Electric field	$\vec{E}$	$\left[ \frac{\text{V}}{\text{m}} \right]$
Polarizability	$\alpha$	$\left[ \frac{\text{A} \cdot \text{s} \cdot \text{m}^2}{\text{V}} \right]$
Electric susceptibility	$\chi$	-
Relative dielectric function	$\varepsilon_r$	-
Index of refraction	$n$	-
Index of absorption	$k$	-
Wavenumber	$\tilde{\nu}$	[cm <sup>-1</sup> ]
Oscillator strength	$S$	[cm]
Molar oscillator strength	$S^*$	$\left[ \frac{\text{cm} \cdot \sqrt{\text{L}}}{\sqrt{\text{mol}}} \right]$
Damping constant	$\gamma$	[cm]
Charge	$q$	[A · s]
Reduced mass	$\mu$	[kg]