

Enabling investigations of liquids and liquid-solid interfaces with soft X-ray excitation at UHV conditions

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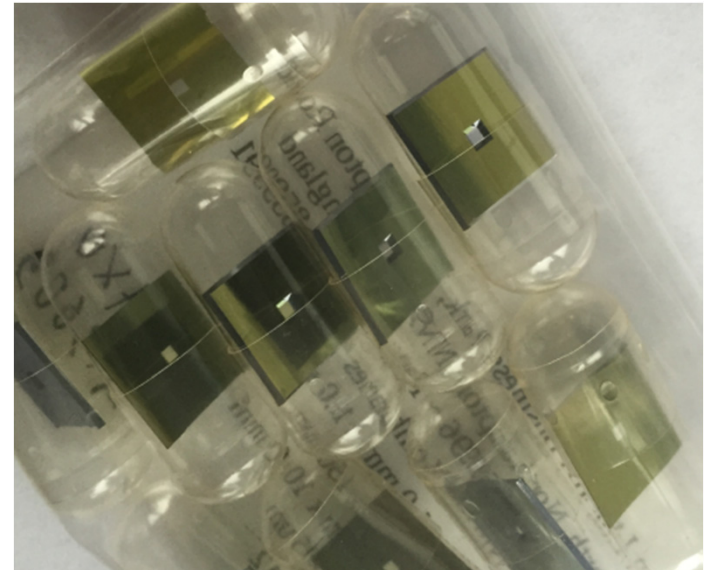
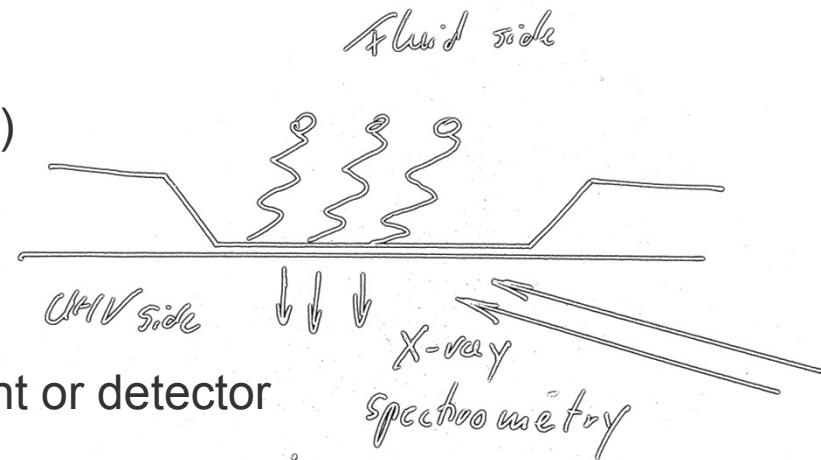
- Motivation for developing a liquid cell
- Challenges for constructing the liquid cell
 - Geometry, thickness and bulging of the window
 - Pressure compensation and degased sample solution
- Construction and design
- First experiments
- Summary
- Perspective

Developing a liquid cell for soft X-ray (< 1 keV) spectroscopy (NEXAFS)

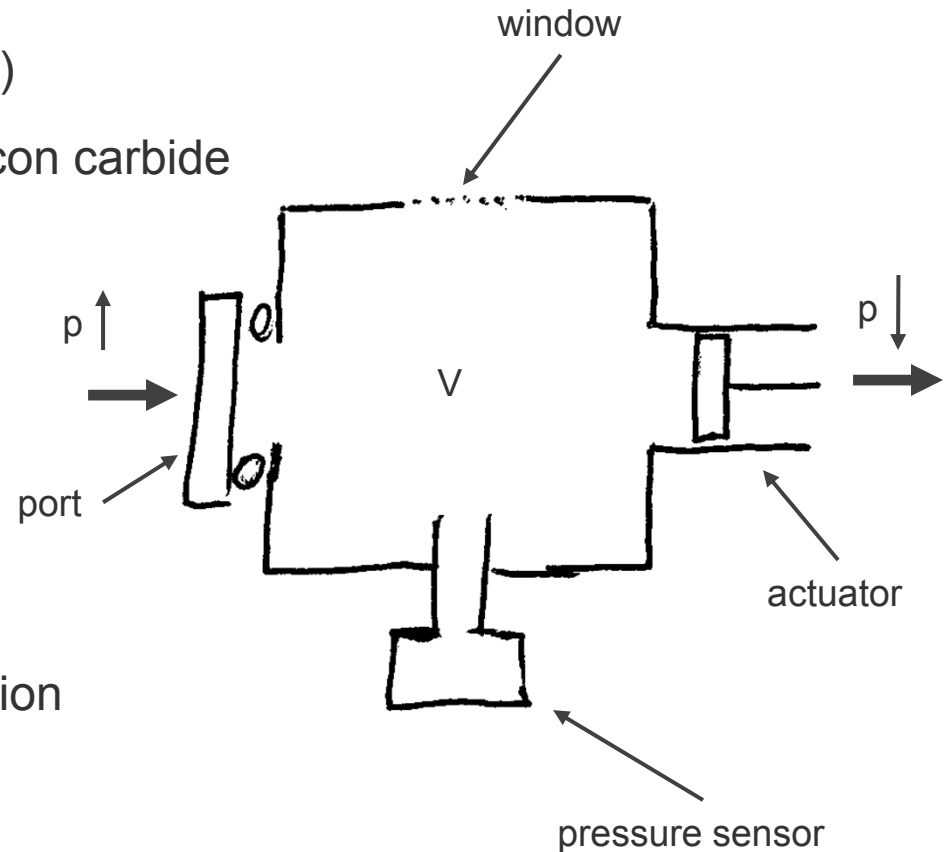
Requirements:

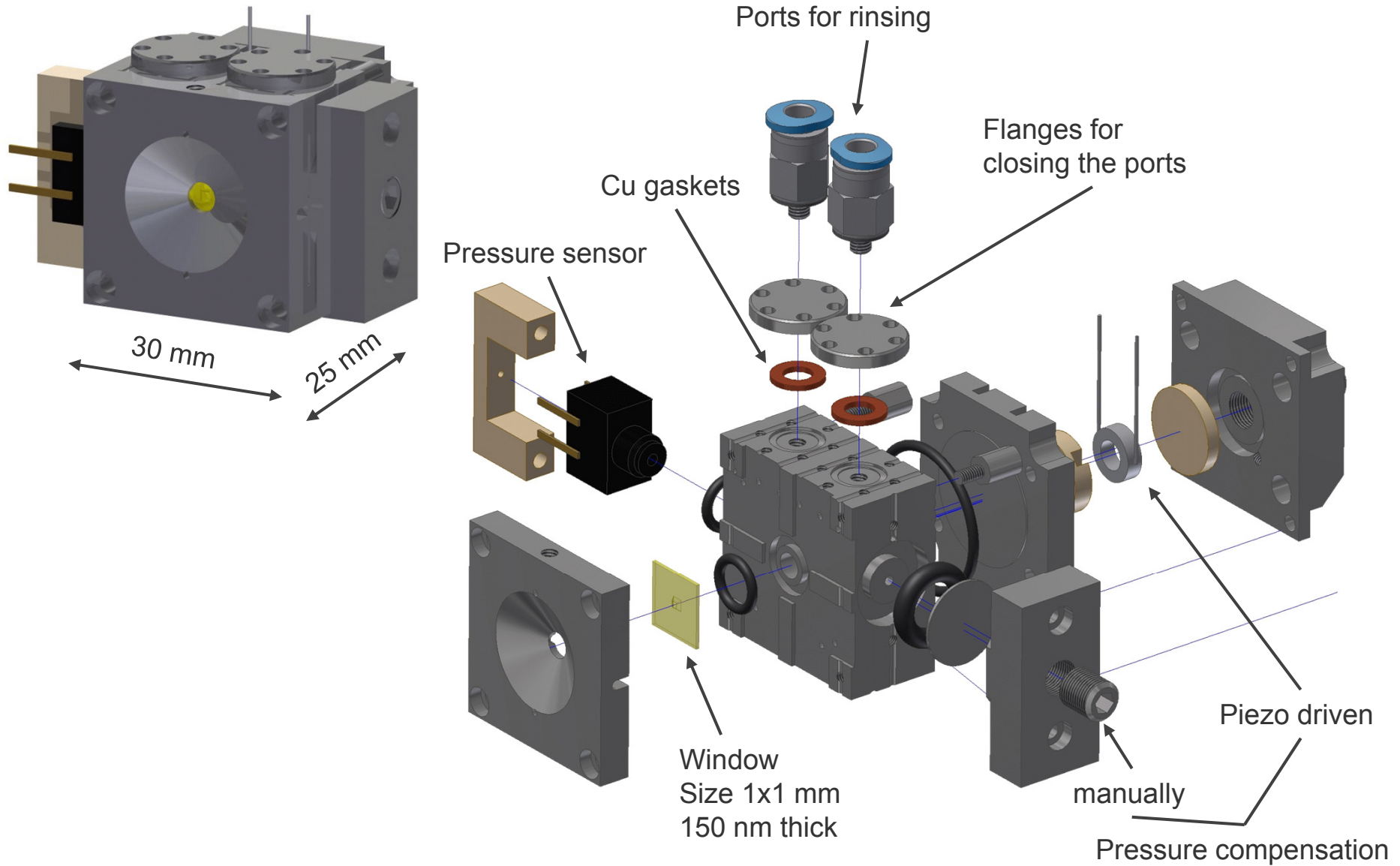
- Investigation of liquids and liquid solid interfaces
- Vacuum-tight but soft X-ray transparent window
- Enabling measurements in emission (reflection) and transmission geometry
- Compact dimensions
- Easy to handle
- Reproduceable measurements

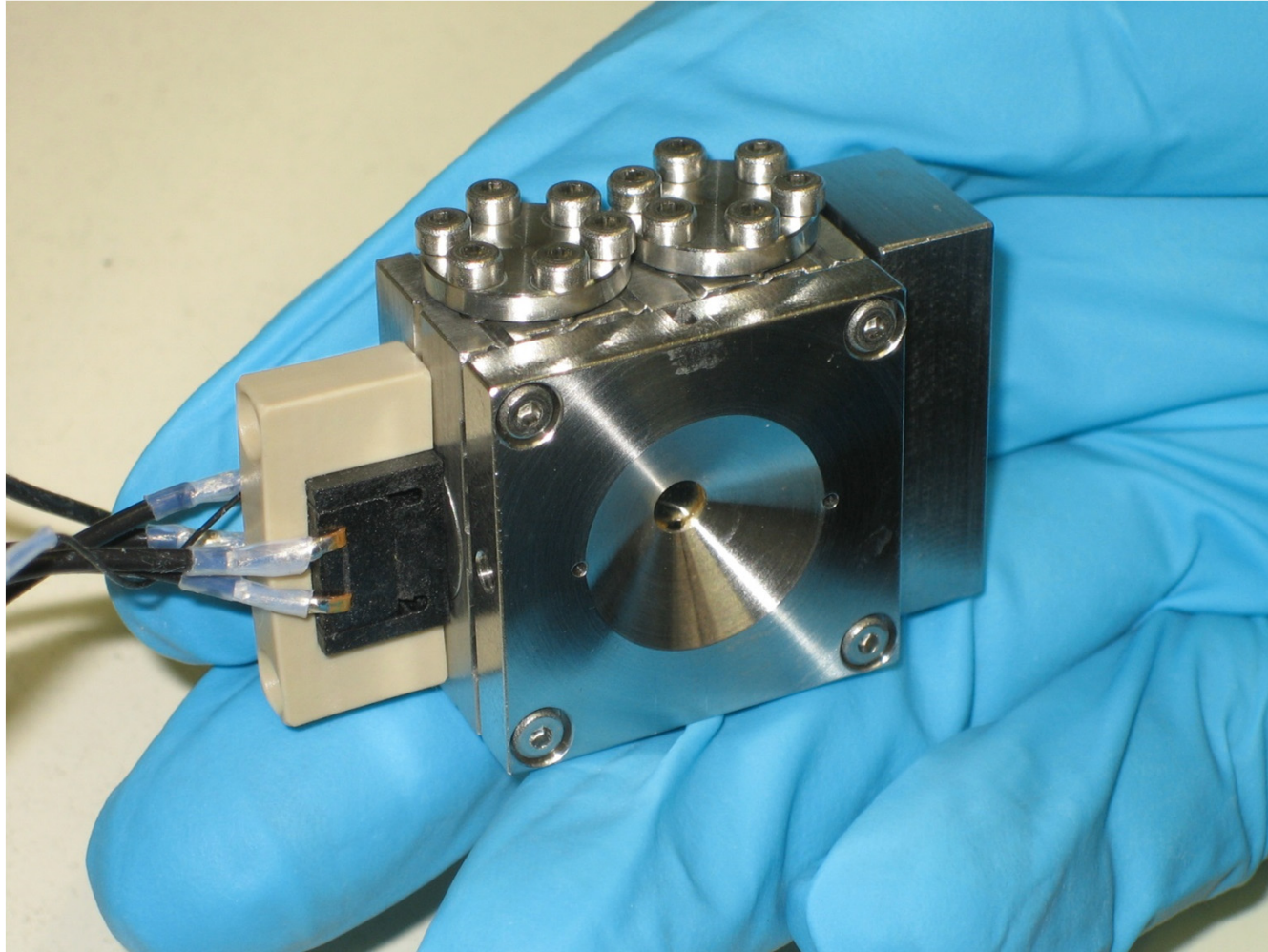
- X-ray analysis in UHV (ultra high vacuum)
 - Reduce absorption
 - Cooled, windowless detector
 - Contamination of sample environment or detector
- Risk of window rupture
- Bulging of window hampers analysis



- Ultrathin window (100...150 nm)
made from silicon nitride or silicon carbide
- Reduce the inner pressure
 - Reduced window bulging
 - Reduced risk of rupture
- Pressure compensation
 - Sensor and actuator
 - Use degased sample solution
 - Filling without bubbles

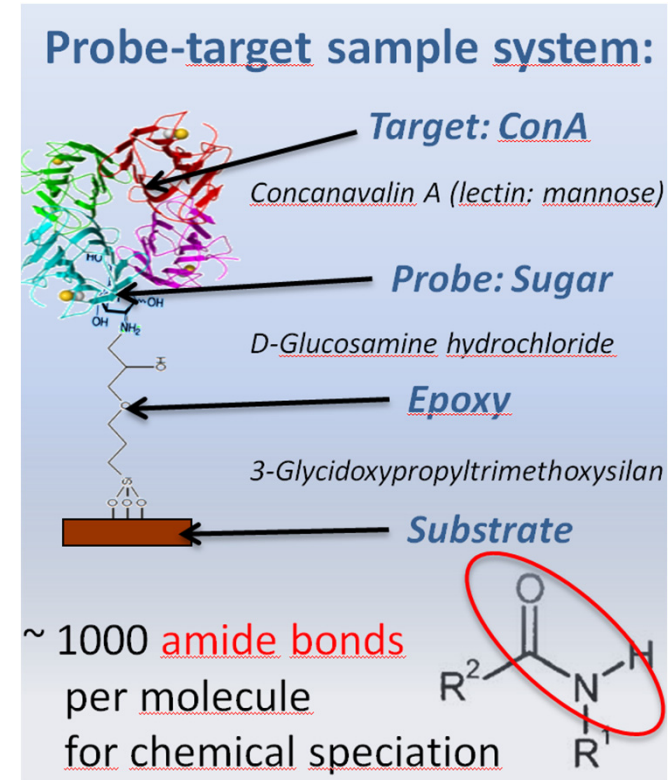






Investigating capture molecule for medical point of care diagnostic sensor

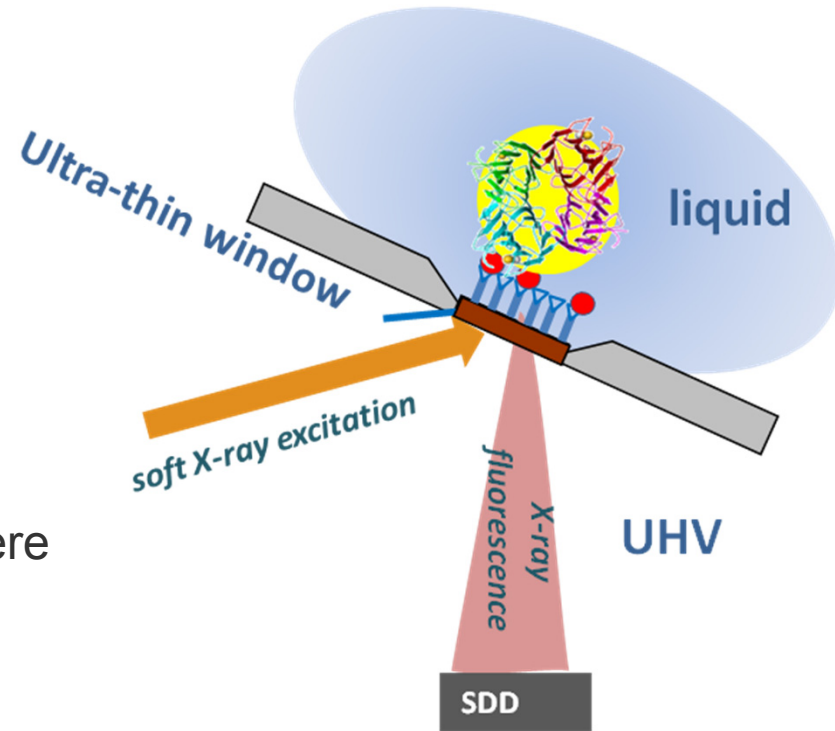
- Capture molecule binds selective and sensitive target molecule to a membrane
- Detection of target molecule by optical method or natural vibration frequency
- Characterization of the probe-target system by X-ray spectroscopy
 - Orientation
 - Chemical state
 - Deposition
- Beamtime BESSY II – PTB Beamline PGM



Paul Dietrich, ECASIA 2013, Sessions Life Science & Biosurface 2

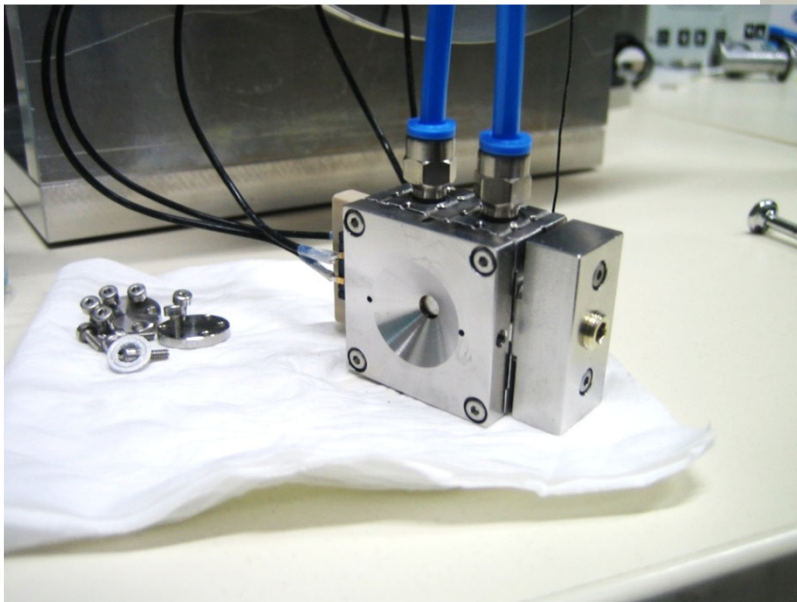
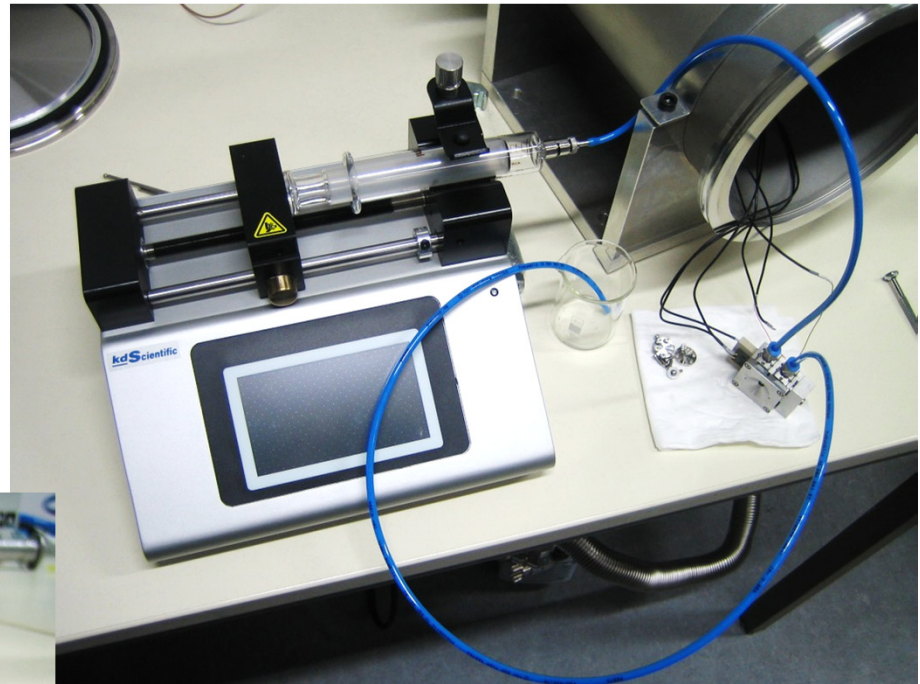
The liquid cell enables investigations of biomolecular films at liquid-solid interfaces

- In situ preparation of probe-target system
- In situ detection of the capture molecule with soft X-ray NEXAFS
- Excitation from different angles
- Measurement under UHV atmosphere
- Reduction of window bulging



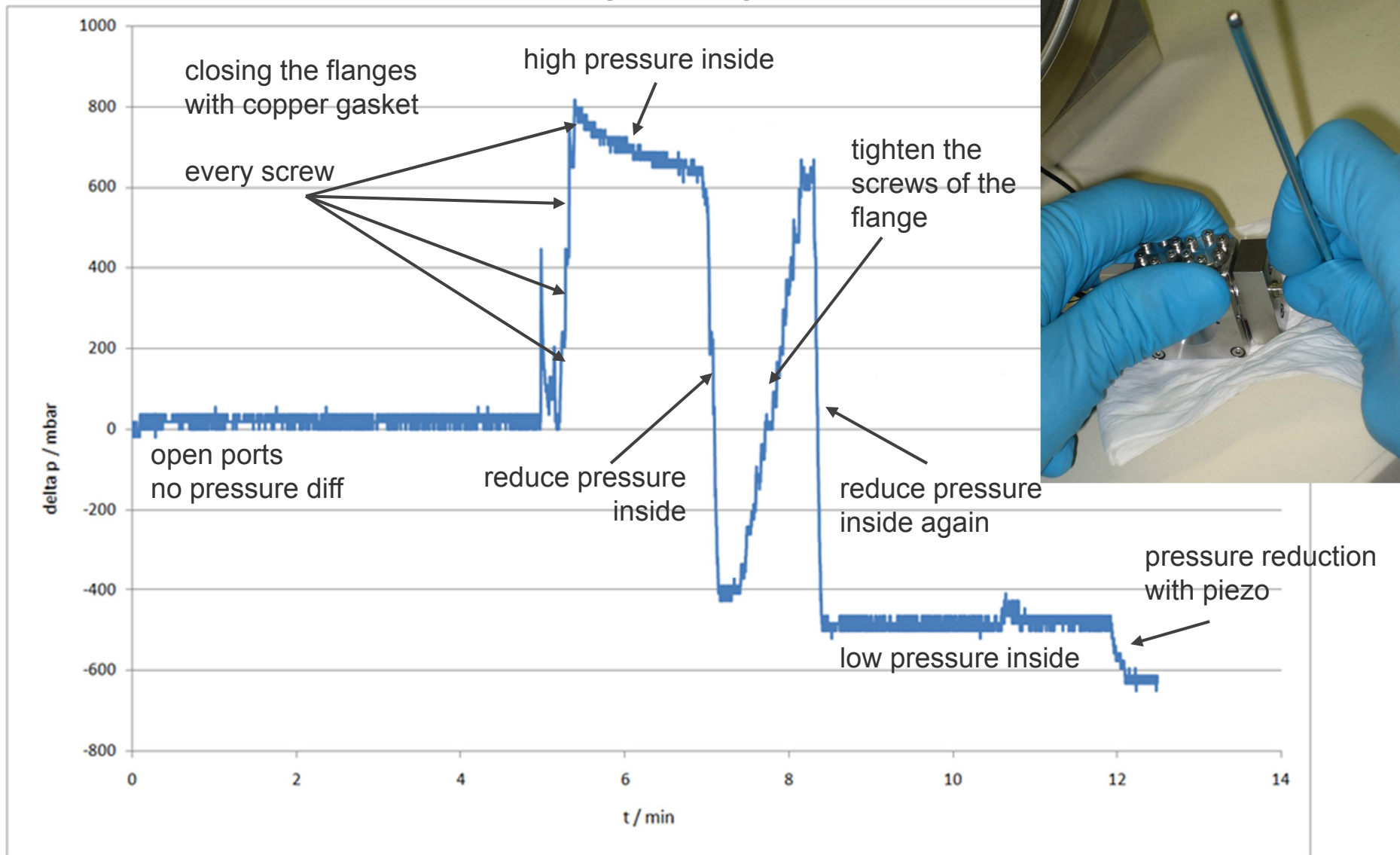
Cornelia Streeck, ECASIA 2013, Session Solid liquid interfaces

- In situ sample preparation
- syringe pump for rinsing the window with sample and flushing solutions

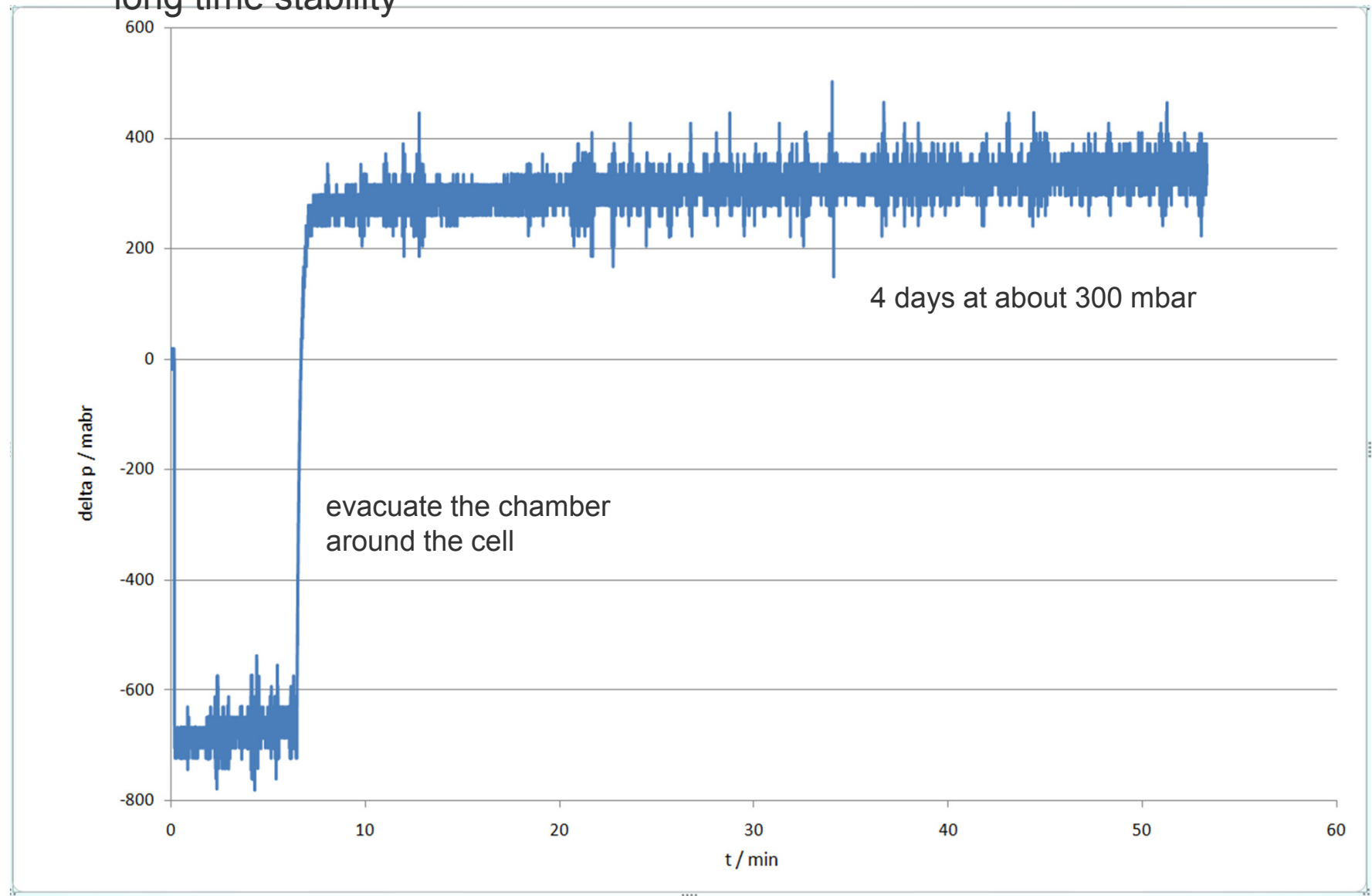


First experiments: installation and commissioning

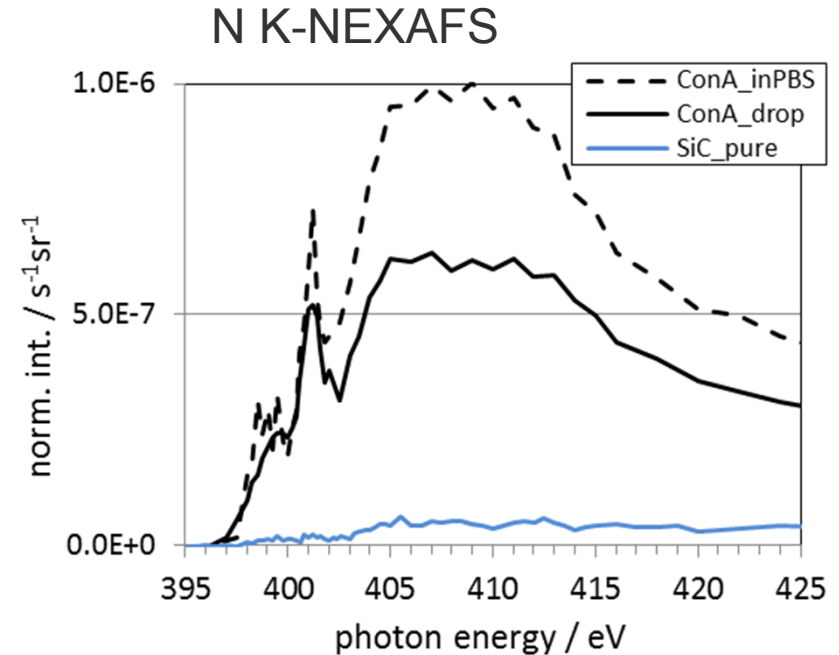
Pressure characteristics during capping the liquid cell



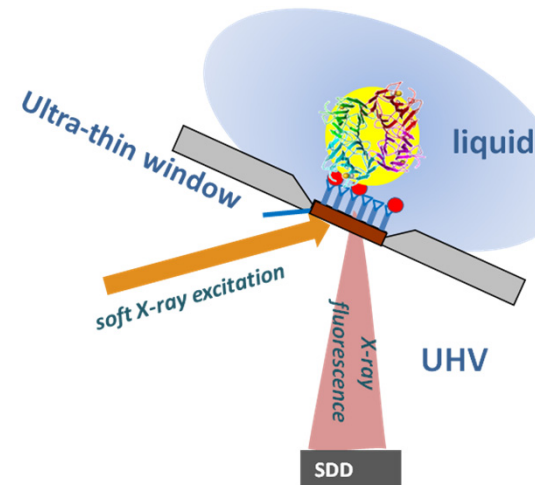
long time stability



NEXAFS investigation of capture molecule (ConA) in liquid environment with the liquid cell

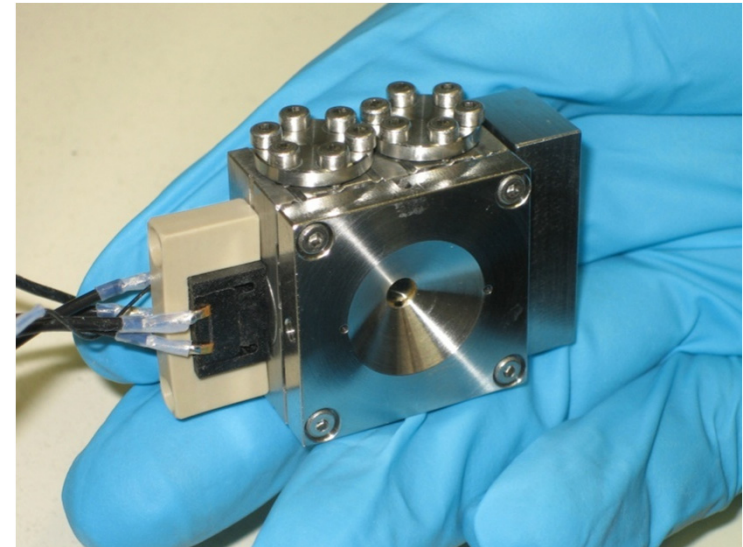


Window material	C K-NEXAFS	N K-NEXAFS
Si ₃ N ₄	 Limited by carbon contaminations	 Limit of detection due to nitrogen in the window
SiC	 Limit of detection due to carbon in the window	 Limited by count rate of nitrogen K α fluorescence line

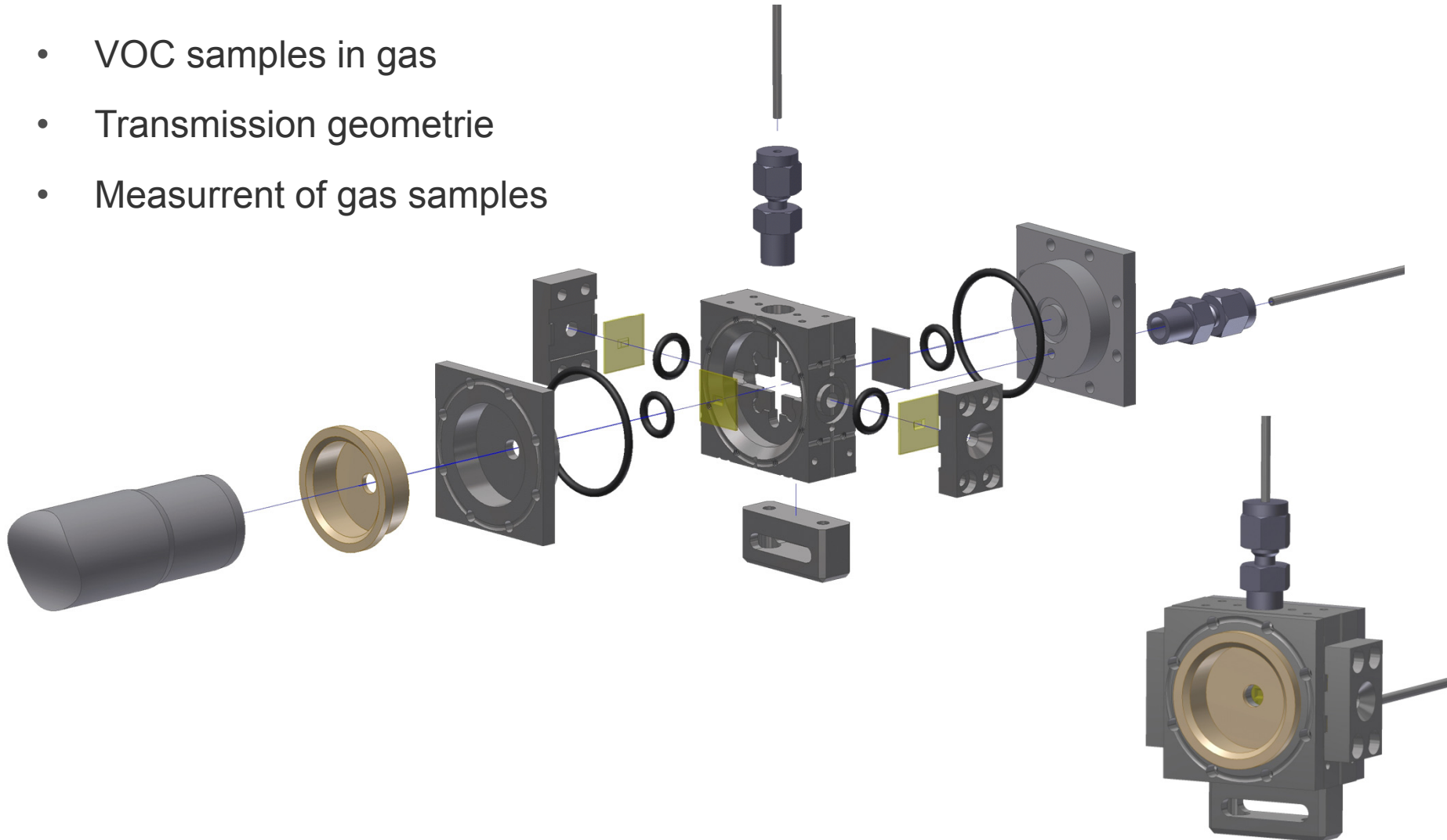


Analysis of liquids and liquid-solid interfaces is now possible with the liquid cell

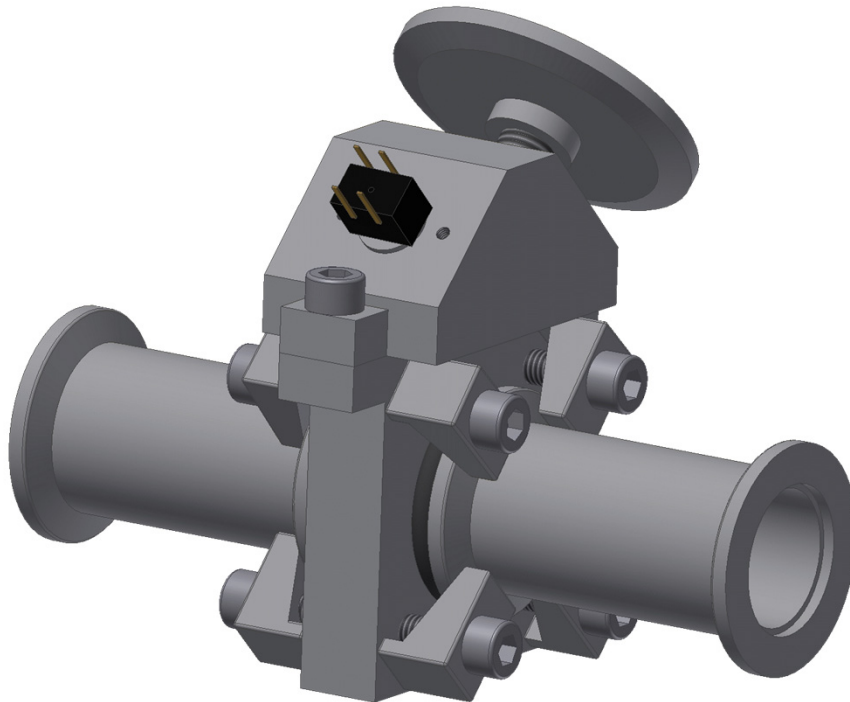
- In situ preparation of molecular films
- Easy and safe handling of liquids in UHV
 - Fast filling
 - Low risk of window rupture
 - Stable over typical period of experiment
- Compact sample holder



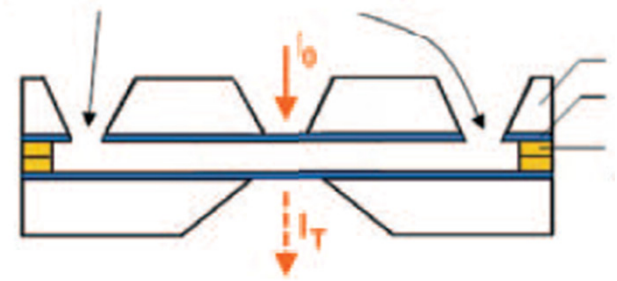
- VOC samples in gas
- Transmission geometrie
- Measurent of gas samples



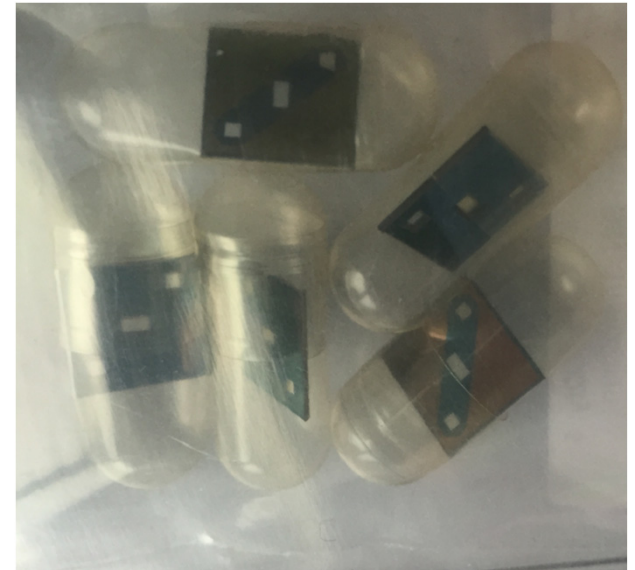
Development of a liquid cell for transmission geometry



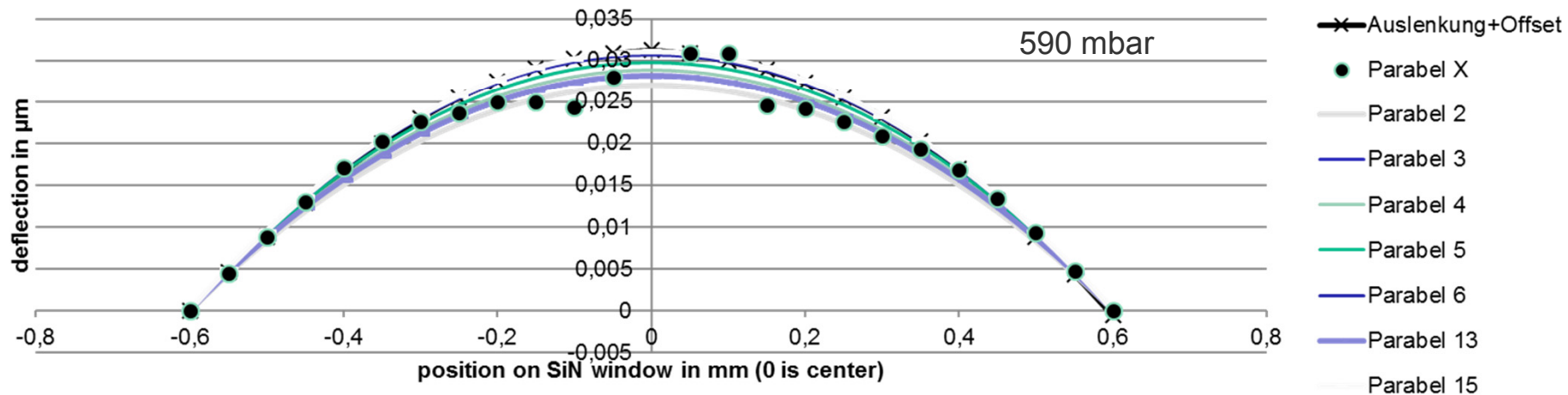
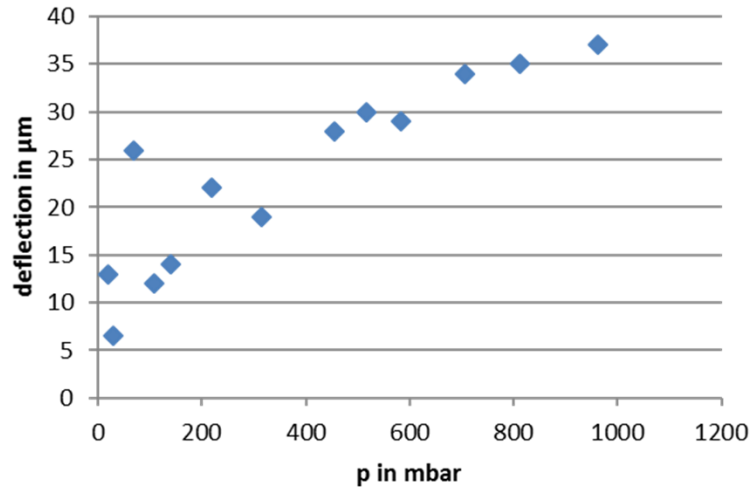
design done by Slava Martyanov



Simon Schreck, Rev. Sci. Instrum. **82**, 103101 (2011)



deflection/ bulging of SiN windows



Further developments:

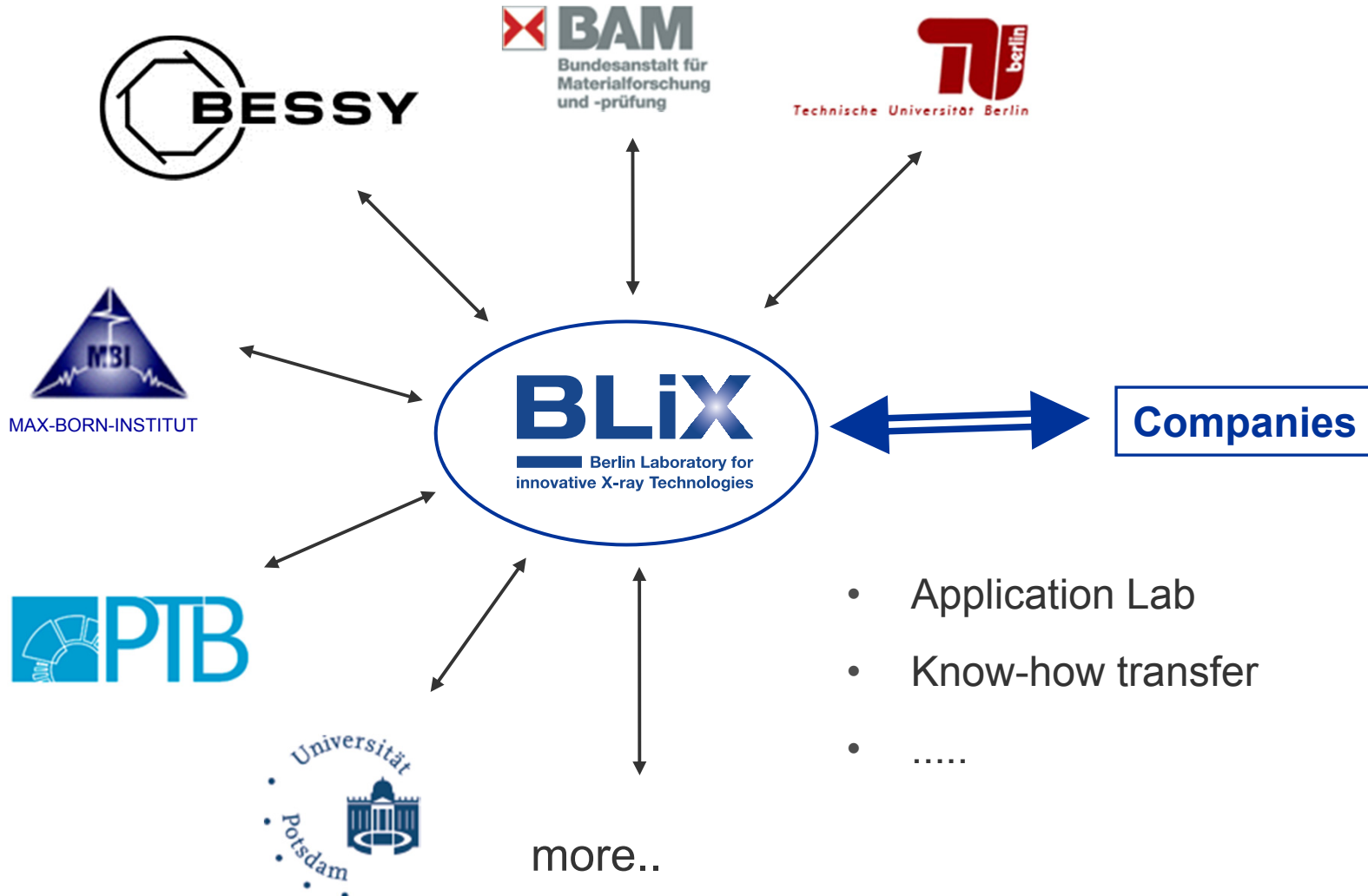
- Enlarged window for excitation and detection under shallow angles
- Advanced pressure compensation
- Implementing Temperature controlling
- Implementing electrical contacts for investigation under exterior voltage
- Investigations of batteries during cycling
- Complementary methods (IR, Raman)

To all colleagues who are involved in this work

- AXP research group: Birgit Kanngießer, Katharina Witte, Wolfgang Malzer, Ioanna Mantouvalou, Slava Martyanov, Janina Lebendig Kula, Adrian Jonas,
- The group of Burkhard Beckhoff (PTB): Cornelia Streeck, Janin Lubeck, Andreas Nutsch, Jan Weser
- Colleagues from BAM: Carolin Nietzold, Wolfgang Unger, Paul Dietrich
- Our mechanical workshop at IOAP: Irene Abendroth, Frank Röhrbein, Jörn Six, Fabian Sielaff
- Max-Planck-Institute for Chemical Energy Conversion: Serena DeBeer

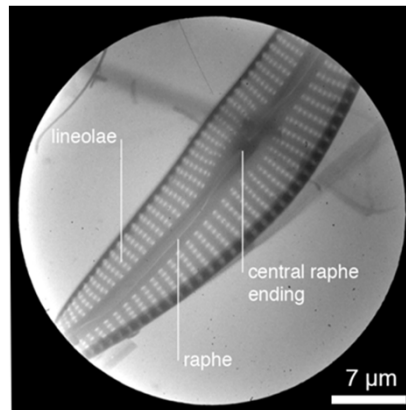


Thank you for your attention

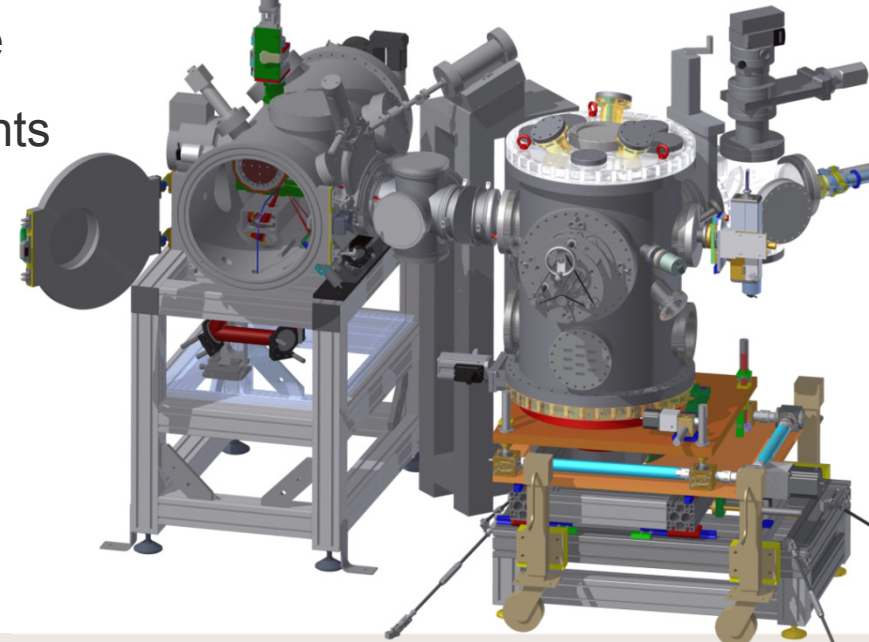


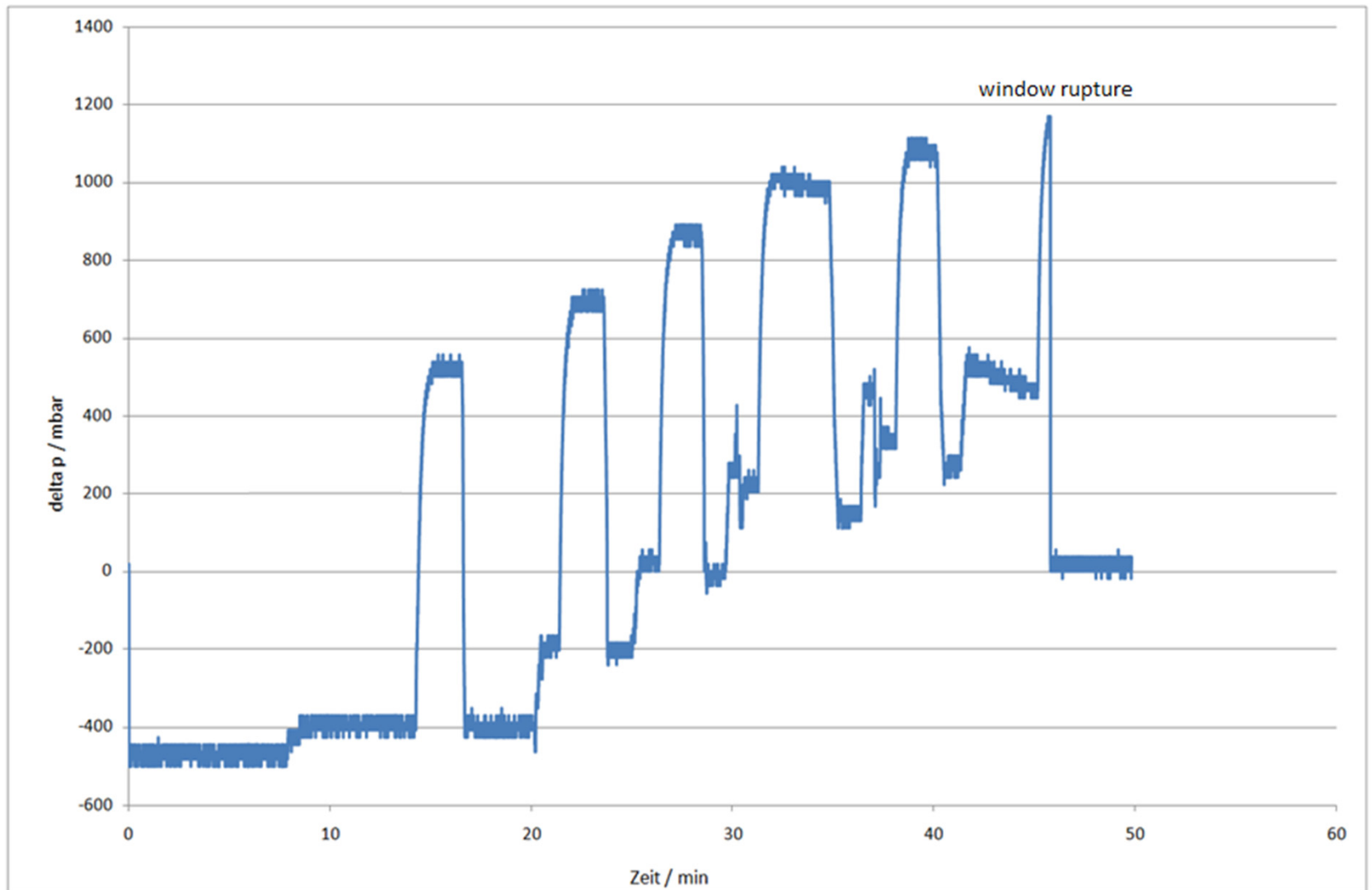
<http://www.blix.tu-berlin.de/>

- X-ray microscopy
 - Soft X-ray: laser produced plasma source on nitrogen jet
 - Hard X-ray: excitation by X-ray tube
- X-ray spectroscopy
 - Soft X-ray: laser produced plasma source on metal target (Cu)
 - Hard X-ray: excitation by X-ray tube
 - Different methods and arrangements

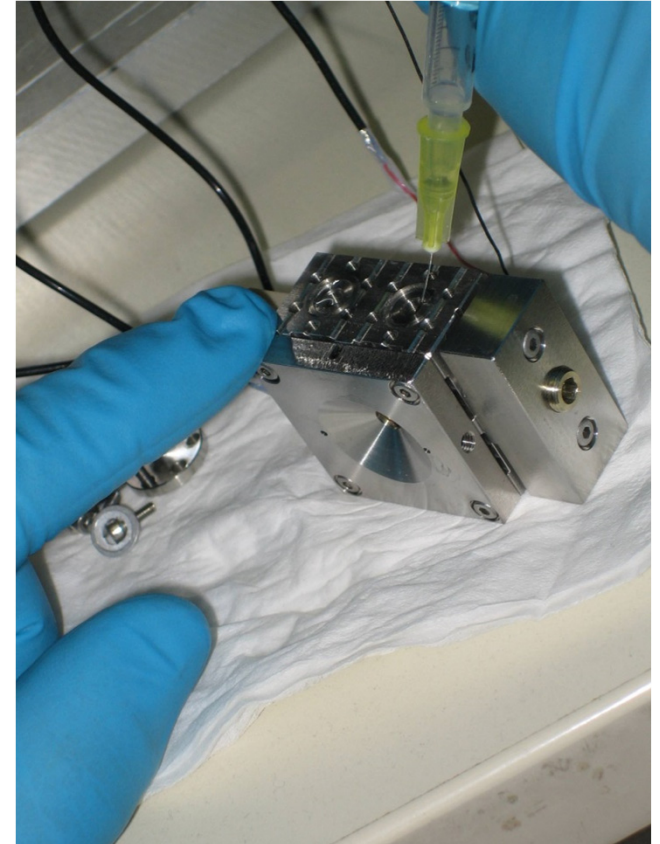
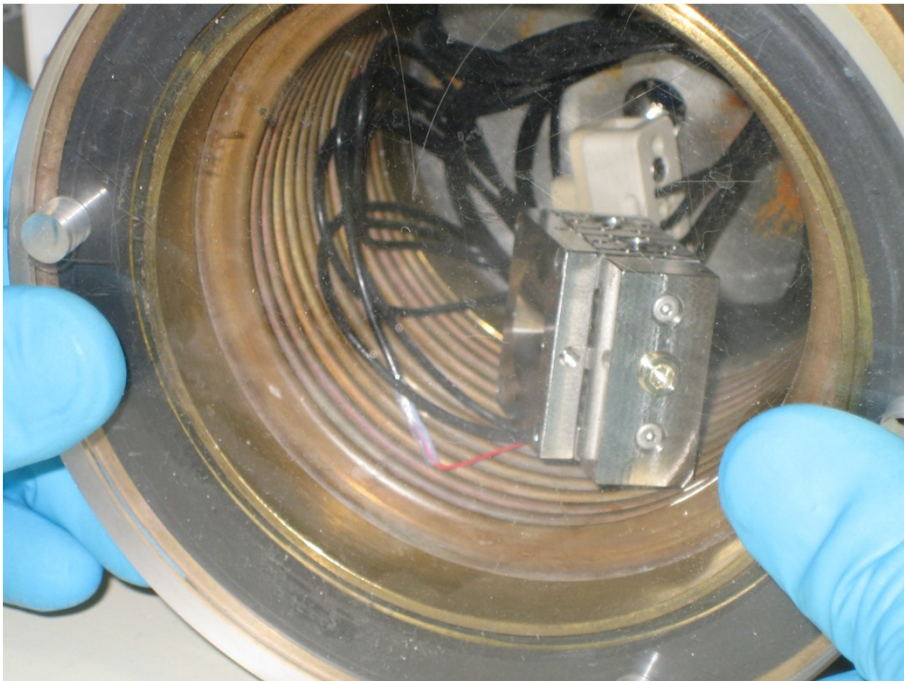


Diatom

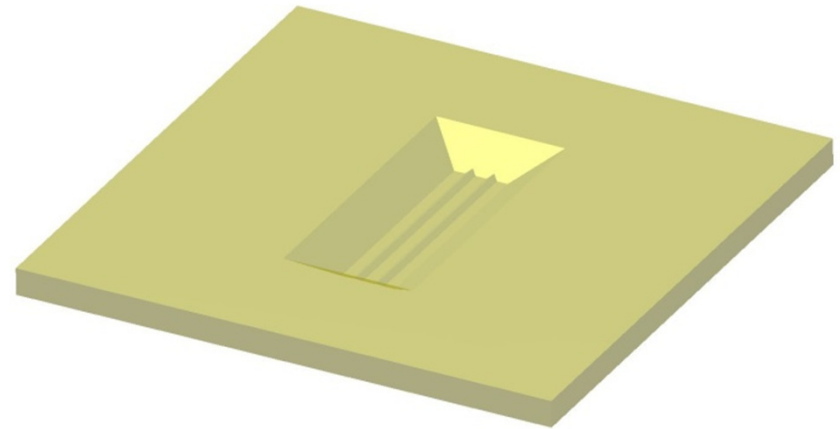
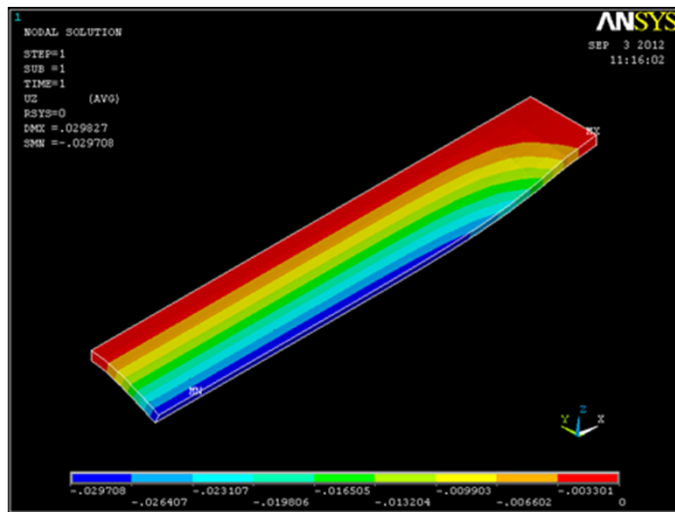




- Evacuate with open connectors
- Refill with degased solution
- Until no further bubbles show up



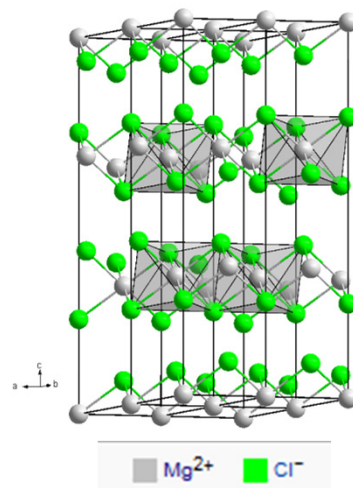
- Size and shape of silicon nitride window
- Finite element method (FEM) simulation
- Rectangular shape for high sensitivity and stability
- Bars for stability of enlarged window



- Silicon nitride window
 - Window size $1 \times 1 \text{ mm}^2$
 - Thickness 150 nm
 - Frame $10 \times 10 \times 0,5 \text{ mm}^3$
- Pressure compensation
- Compact and completely sealed (no pipes)
- Rinsing the window inside the cell
- Measurement in emission geometries
 - 90° XRF
 - small angle excitation

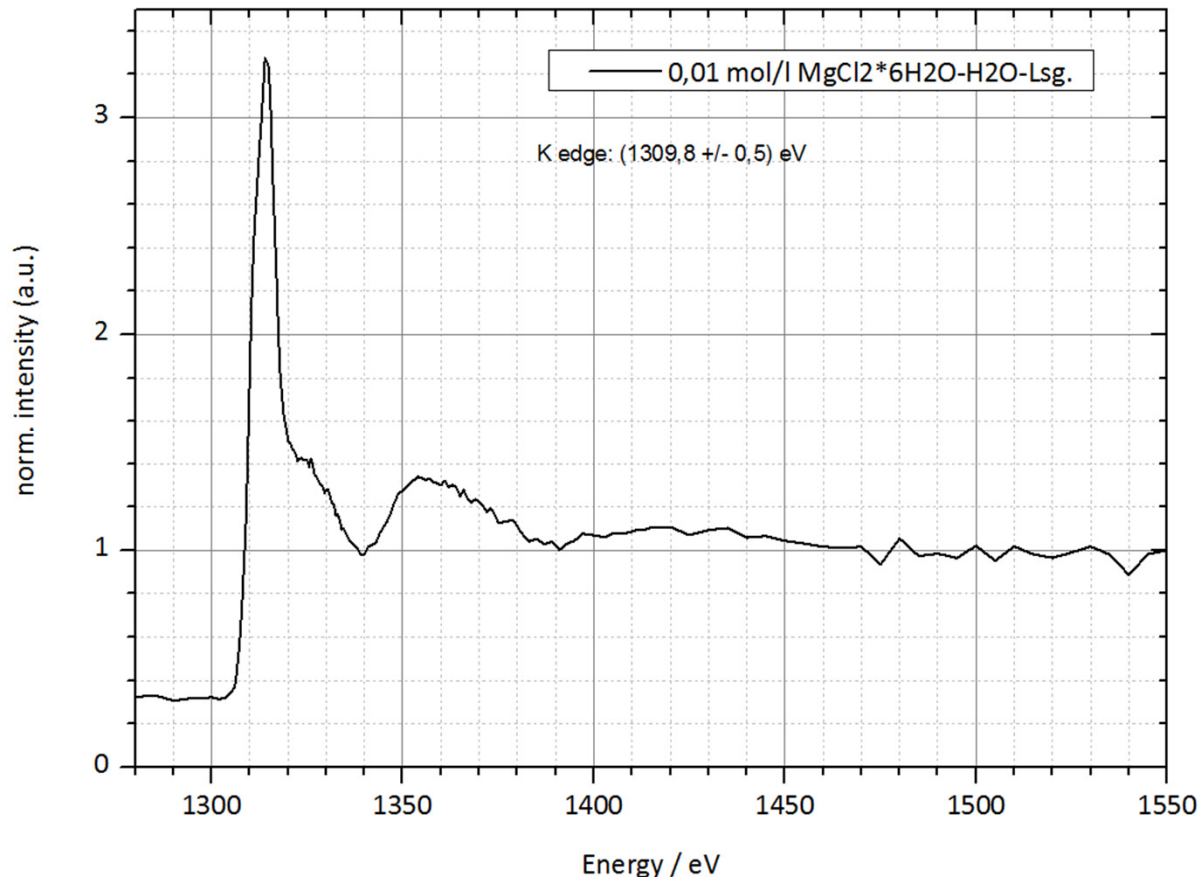


- Beamtime BESSY II – PTB Beamline PGM (20 ... 1900 eV)
 - goal: Mg K-edge NEXAFS of Mg-salt in solution
 - Sample: $\text{MgCl}_2[\text{H}_2\text{O}]_6 - \text{H}_2\text{O} - \text{solution}$
 - concentration: 0,01 mol/l $\rightarrow$ 2,031 g $\text{MgCl}_2[\text{H}_2\text{O}]_6$ auf 1 l H_2O
 - Test system for Mg containing bio-molecules, e.g. Chlorophyll



Measurements done by Katharina Witte and Cornelia Streeck

- $\text{MgCl}_2[\text{H}_2\text{O}]_6 - \text{H}_2\text{O}$ - solution



- success: observable Mg K-edge NEXAFS spectrum of low Mg-concentration solution!

- distinguishable XANES-features at Mg K-edge

- work in progress: interpretation and assignment of characteristic features

- work in progress: comparison to NEXAFS-calculation

Measurements done by Katharina Witte and Cornelia Streeck