Kiel University
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Ocean Surface Chemistry & Reaction Kinetics

Surface-Sensitive Methods for Marine Nanolayer Time-Series Studies

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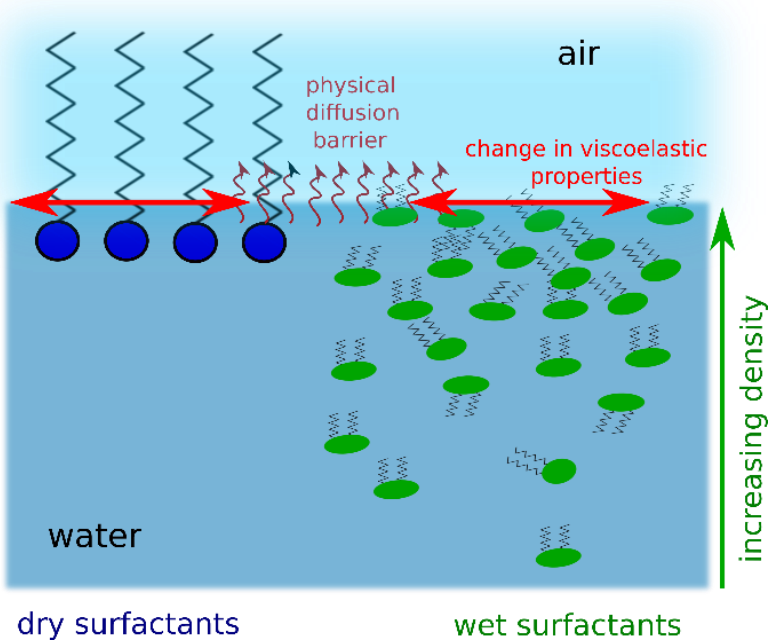
What are surfactants and why are they important?



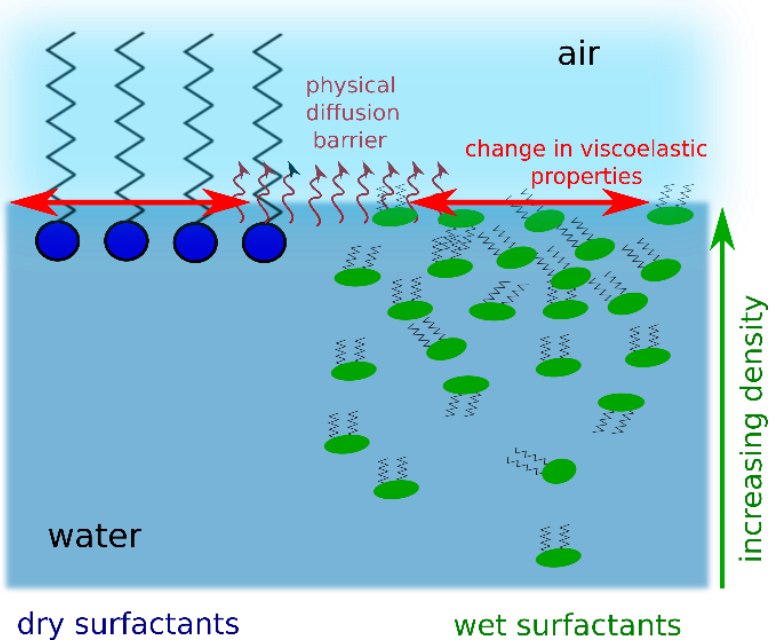
[1] Plot of gas transfer veolcity vs wind speed, with and without surfactant present, indicating that surfactant reduce the transfer

- molecular substances with moieties of different polarity and therefore different solubility
- accumulation at the **interface** of two different phases or solvents, present at the **air-sea interface**

- **alteration** of the physical and chemical properties of the surface → influence on air-gas exchange
- **dry** („insoluble") and **wet** („soluble") surfactants may behave differently

[1] P. S. Liss, R. A. Duce, *The sea surface and global change*, Cambridge University Press, Cambridge, New York **2005**.

Analytical challenges



[1] Plot of gas transfer veolcity vs wind speed, with and without surfactant present, indicating that surfactant reduce the transfer

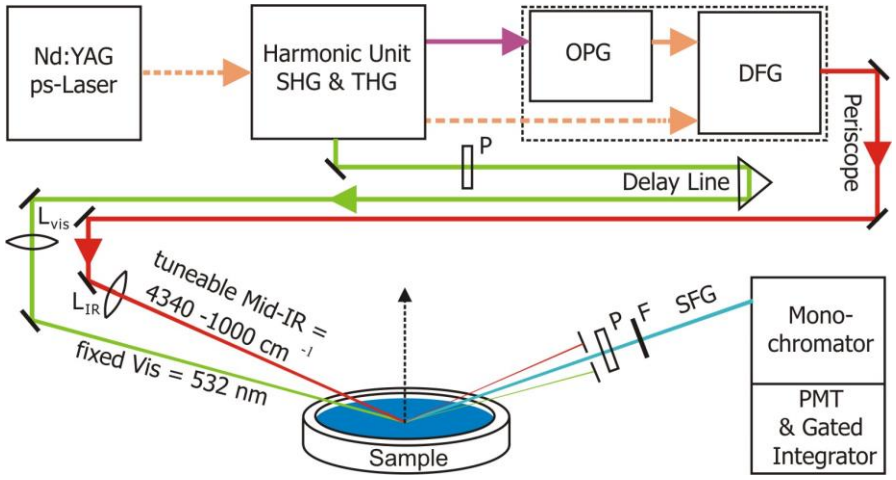
- Special sampling procedure required.
- Hard to distinguish between bulk and surface as the bulk is by far bigger in spatial dimensions and number of molecules.
- Complex analytical techniques required.
- In order to enable efficient interdisciplinary exchange of data, **simple numerical indices** are helpful that are related that are related to the **surfactant abundance**.

[1] P. S. Liss, R. A. Duce, *The sea surface and global change*, Cambridge University Press, Cambridge, New York **2005**.

Sum Frequency Generation Spectroscopy (VSFG)

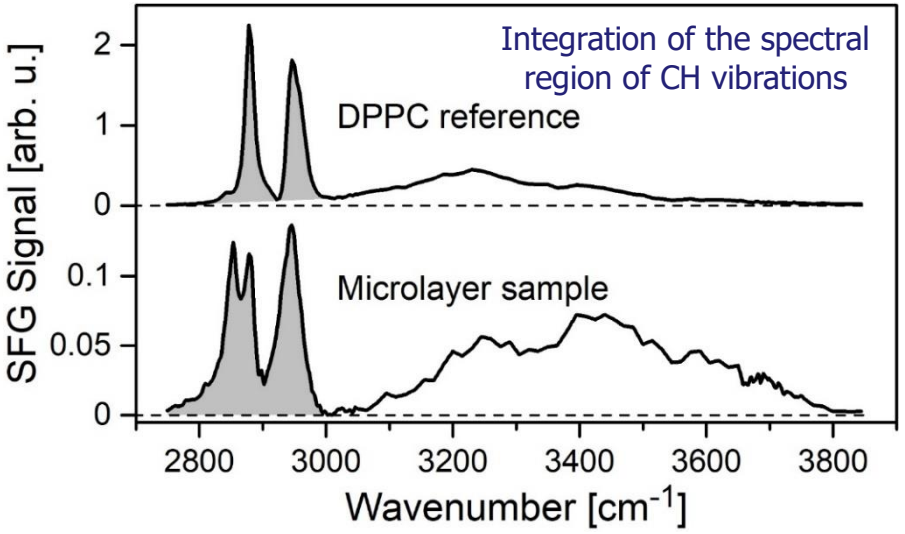
VSFG spectroscopy:

- Nonlinear laser-spectroscopic technique.
- Inherently surface-sensitive due to spectroscopic selection rules
- Sub-monolayer sensitivity.
- Yields vibrational spectrum of the substance → information about chemical composition



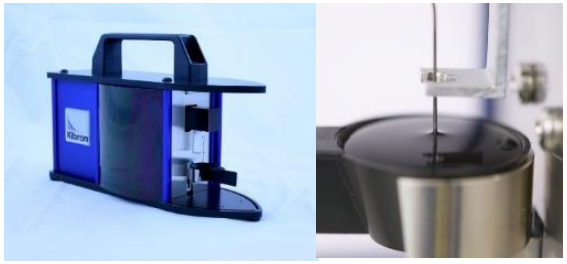
Definition of a **surface coverage index**, referenced to a completely covered surface by a DPPC monolayer:

$$SC_{\mathrm{VSFG}} = \sqrt{\frac{\int_{2750}^{3000}(I(\tilde{\nu}) - I_{\mathrm{H_2O}}(\tilde{\nu}))^{\mathrm{sample}}\mathrm{d}\tilde{\nu}}{\int_{2750}^{3000}(I(\tilde{\nu}) - I_{\mathrm{H_2O}}(\tilde{\nu}))^{\mathrm{DPPC\ reference}}_{20\,\mathrm{\AA}^2}\mathrm{d}\tilde{\nu}}}$$



Surface tension & Langmuir trough (LT)

Static surface tension



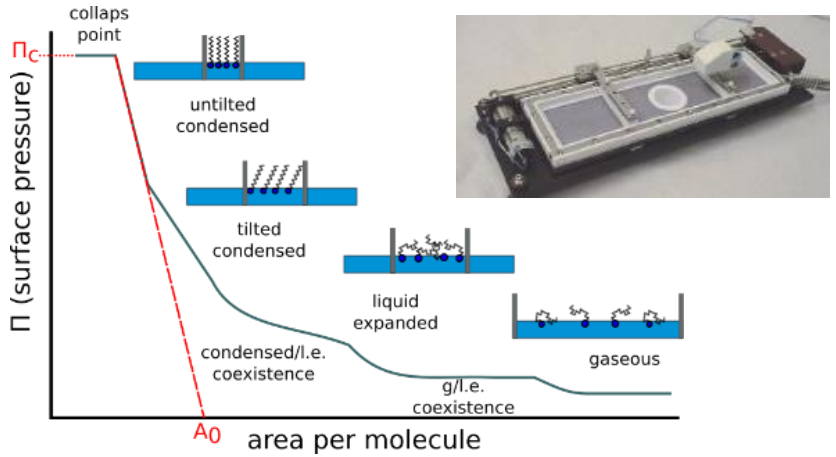
- Surface tension is reduced if surfactants are pesent at the interface.
- A Langmuir isotherm records the decrease of surface tension (i.e., surface pressure) as a function of available area per molecule

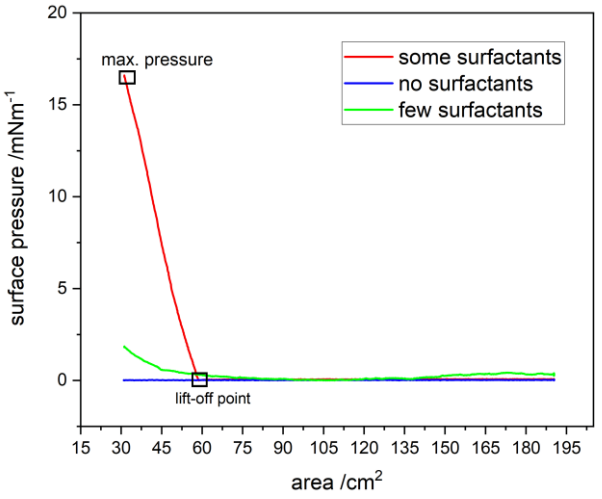
→ **Indices**: surface tension, maximum surface pressure, lift-off compression

Definition of **lift-off compression ratio**:

$$SC_{\mathrm{LT}} = A_{\text{lift-off}}/A_{\text{start}}$$

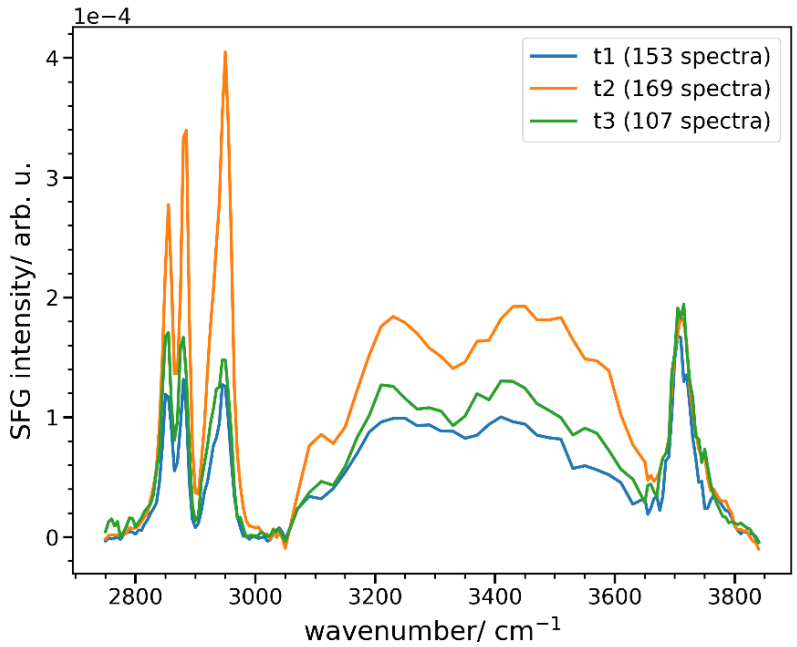
Langmuir trough





Time series study: Boknis Eck (Baltic Sea)

- Monthly microlayer sampling (2008-2018) at Boknis Eck time series station.
- Large amount of spectra, information reduction necessary.
- Both SML and bulk water samples from different depths.
- **Automatic** data analysis: averaging, mapping to distinct time periods, and SC_{VSFG} determination
- Aim: correlation with other physical and biogeochemical parameters

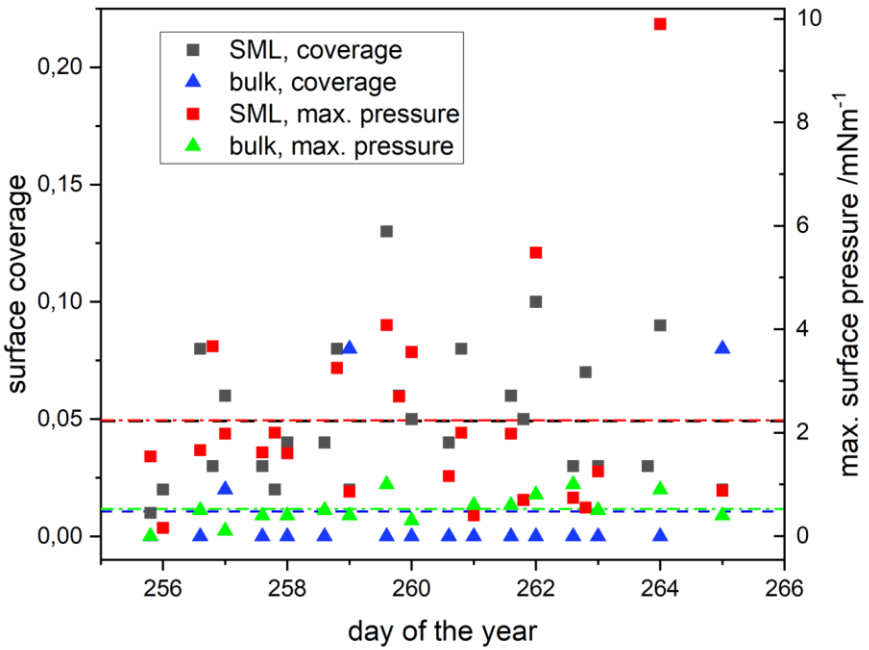


10-year average of surface microlayer samples (total of 430 measurements), grouped into trimesters to highlight the seasonal variation:

$$SC^{\text{Mar-Jun}} < SC^{\text{Nov-Feb}} < SC^{\text{Jul-Oct}}$$
$$0.18 \qquad 0.19 \qquad 0.26$$

Baltic GasEx cruises

- Cruises in June (early trimester 3) and September 2018 (late trimester 3).
- Direct gas exchange measurements (EC, He/SF_6 dual tracer), thorough characterization of surfactant state (polarography, SFG; surface tension, LT isotherms)
- Aim: field-prove of surfactant effect on air-sea gas exchange, directly link gas-exchange data with surfactant indices.



- Significant surfactant enrichment in sea surface microlayer (compared to bulk water)
- Both SC_{VSFG} as well as the maximum surface pressure yield
- Overall low signal (both for LT and VSFG measurements) prohibited exact correlations
- Unfortunately, cruise averages reveal similar surfactant abundances (SC_{VSFG} < 0.1)

Conclusion

- VSFG and LT measurements yield **complementary information on the surfactant state** of the sea-surface microlayer.
- Both VSFG and LT measurements allow for the determination **surface coverage indices**.
- Batch processing in combination with sophisticated software tools allows one to report a **robust and transferable** surface coverage index that can be communicated to the broader community and can be used for easy correlation with other biogeochemical parameters.
- **Further work needed**: cross validation and field-testing in the presence of high surfactant-levels .
- **Perspective**: combine VSFG & LT measurements to enhance sensitivity.