

# Structure-reactivity trend for the ozonolysis of fatty acid monolayers with shifted double bond position

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Monomolecular films of surface active substances such as fatty acids and lipids are model systems for organic-covered environmental water interfaces as well as biomembranes. These monolayers of nanoscale thickness change the physical and chemical properties of the surfaces of aqueous aerosols and natural water bodies and are subject to ageing processes: The change of the viscoelastic properties of the seawater surface considerably influences turbulent air-sea gas exchange and surface oxidation processes alter the ability of aerosols to act as cloud condensation nuclei. Both aspects have implications for climate models.

One approach to gain molecular insight into the variable structure and reactivity of surface films is the combination of the Langmuir-Wilhelmy method with the nonlinear surface-sensitive vibrational sum frequency generation (VSFG) spectroscopy.<sup>1</sup> Relying on intensity-concentration calibration curves, we are able to accurately link VSFG intensity with surface concentrations. Consequently, ozone oxidation experiments conducted in a small reactor under controlled conditions could be performed to yield surface concentration-time profiles for direct rate constant measurements.

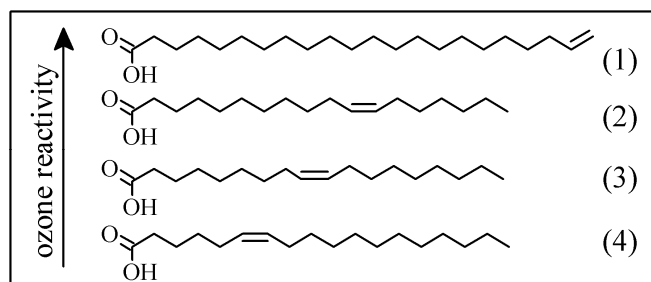


Fig. 1: Structure-reactivity trend for the ozonolysis of fatty acid monolayers.

In this contribution, we will illustrate the application of the surface-sensitive VSFG spectroscopy as a quantitative tool to identify structure-reactivity relationships for heterogeneous O<sub>3</sub> oxidation. Distinct reactivity differences have been found depending on the position of the double bond in the alkyl chain of monomolecular fatty acid films of 21-Docosenoic acid (1), Vaccenic acid (2), Oleic acid (3), and Petroselinic acid (4) (Fig. 1).

The observed trends are discussed in terms of surface accommodation resulting in ozone adsorption layers, ozone solubilities, and different ozone permeabilities through monolayers with variable surface densities.

## References

- (1) Kleber, J.; Laß, K.; Friedrichs, G. *J. Phys. Chem. A* **2013**, 117, 7863-7875, doi: 10.1021/jp404087s.