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Atmospheric photochemistry at a fatty acid coated air/water interface

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Over the past 20 years, interfacial processes have become increasingly of interest in the field of atmospheric chemistry, with many studies showing that environmental surfaces display specific chemistry and photochemistry, enhancing certain reactions and acting as reactive sinks or sources for various atmospherically relevant species. Many molecules display a free energy minimum at the air-water interface, making it a favored venue for compound accumulation and reaction. Indeed, surface active molecules have been shown to undergo specific photochemistry at the air-water interface.

This presentation will address some recent surprises.

Indeed, while fatty acids are believed to be photochemically inert in the actinic region, complex volatile organic compounds (VOCs) are produced during illumination of an air-water interface coated solely with a monolayer of carboxylic acid. When aqueous solutions containing nonanoic acid (NA) at bulk concentrations that give rise to just over monolayer NA coverage are illuminated with actinic radiation, saturated and unsaturated aldehydes are seen in the gas phase and more highly oxygenated products appear in the aqueous phase. This chemistry is probably initiated by triplet state NA molecules excited by direct absorption of actinic light at the water surface. As fatty acids covered interfaces are ubiquitous in the environment, such photochemical processing will have a significant impact on local ozone and particle formation.

In addition, it was shown recently that a heterogeneous reaction between SO_2 and oleic acid (OA; an unsaturated fatty acid) takes place and leads efficiently to the formation of organosulfur products. Here, we demonstrate that this reaction proceeds photochemically on various unsaturated fatty acids compounds, and may therefore have a general environmental impact. This is probably due to the chromophoric nature of the SO_2 adduct with C=C bonds, and means that the contribution of this direct addition of SO_2 could be in excess of 5%.