

Surface Behavior of Malonic Acid Adsorption at the Air/Water Interface

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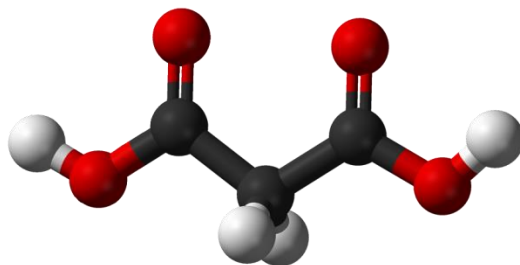
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Malonic Acid

Dicarboxylic acids - the dominant class of water-soluble organics in the environment.

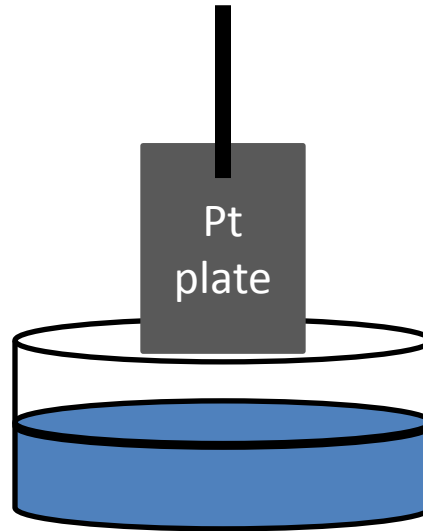
SFG and surface tension measurements: to develop a molecular picture of the behavior of malonic acid at a water surface.

The results provide the basis of the aqueous/organic/inorganic systems that more closely resemble aerosols in the atmosphere.



two carboxylic acid groups
separated by a CH_2 spacer

Measurements



Wilhelmy plate method

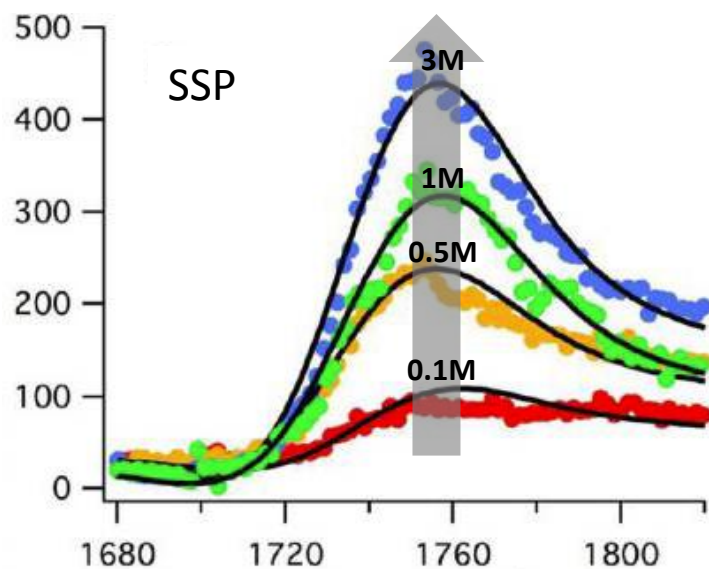
The calculations for this technique are based on the geometry of a fully wetted plate in contact with.

As the surface is brought into contact with the probe instruments will record the height at which this occurs as the 'zero depth of immersion'.

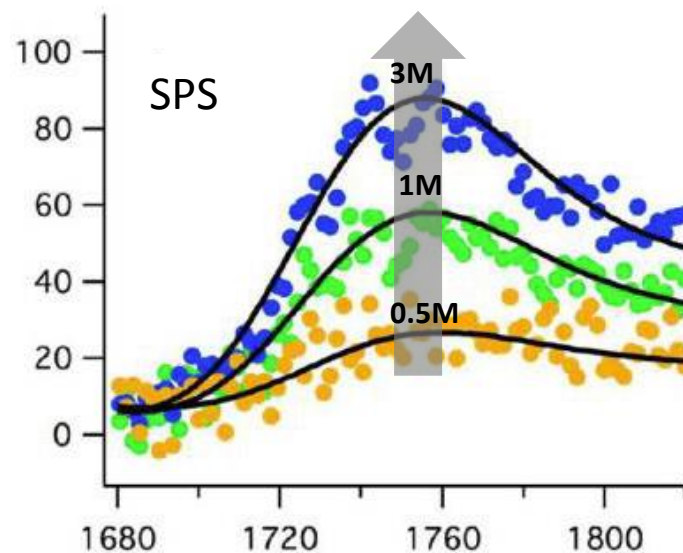
The plate is then completely wetted to a set depth.

When the plate is later returned to the zero depth of immersion, the force it registers can be used to calculate surface tension.

Carboxylic Acid (C=O) Modes



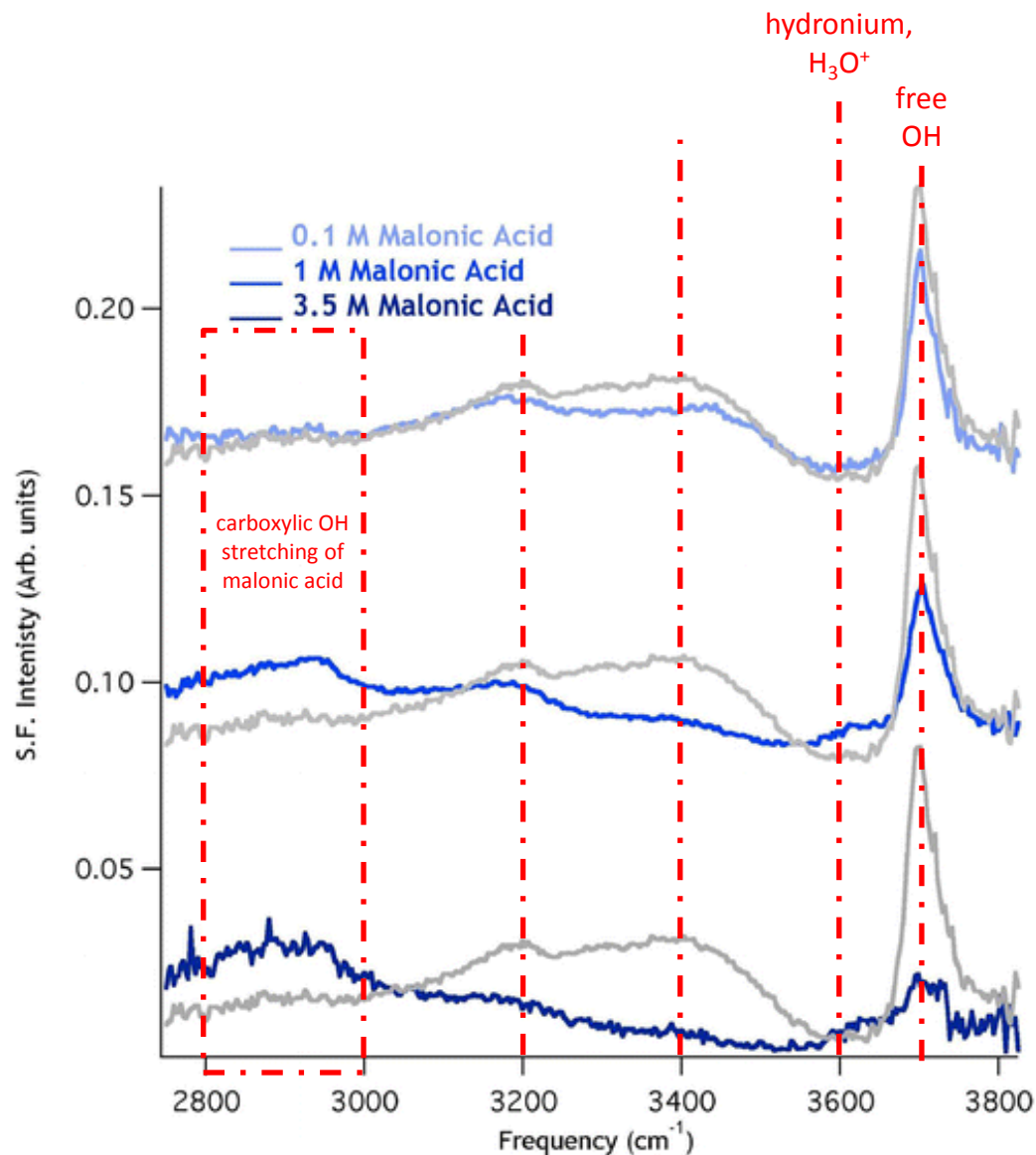
Gaussian width of $28 \pm 1 \text{ cm}^{-1}$



Gaussian width of $37 \pm 1 \text{ cm}^{-1}$

- Malonic acid presents at the water surface with increasing population as the bulk solution concentration increases.

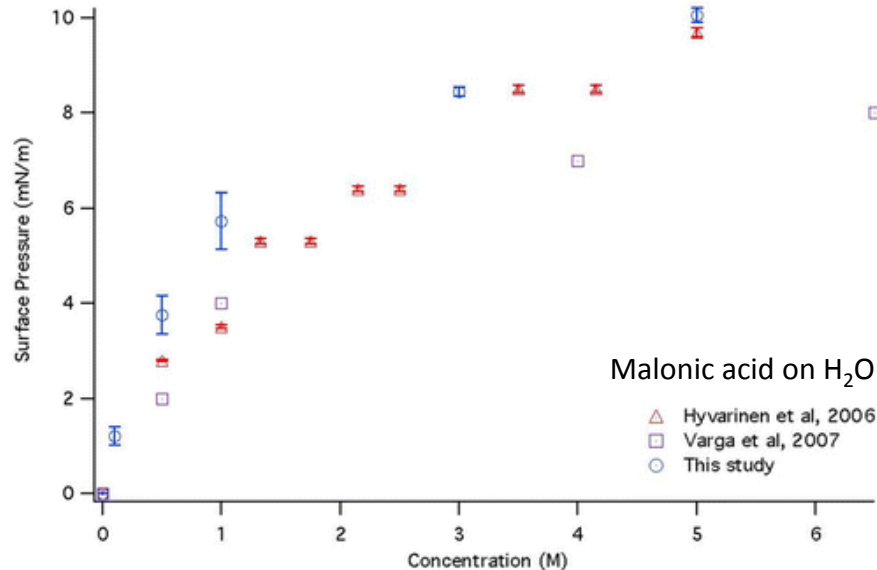
CH and OH Spectral Regions



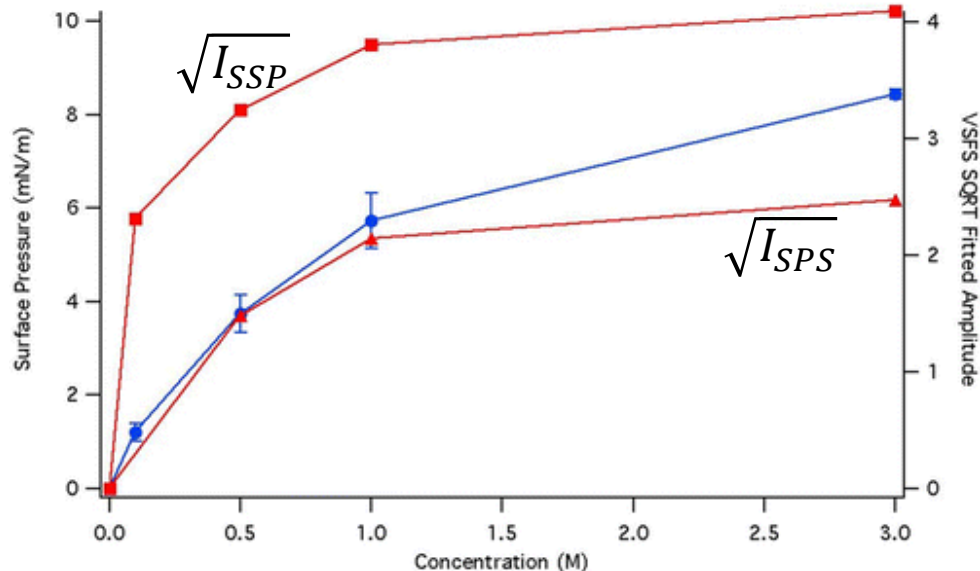
SSP SFG. The gray spectra are of neat water.

- Malonic acid doesn't cover the water surface completely, even at 3.5 M due to large molecular area - $191 \text{ \AA}^2/\text{mol}$.
- Hydronium ions appear due to solvation of ions.

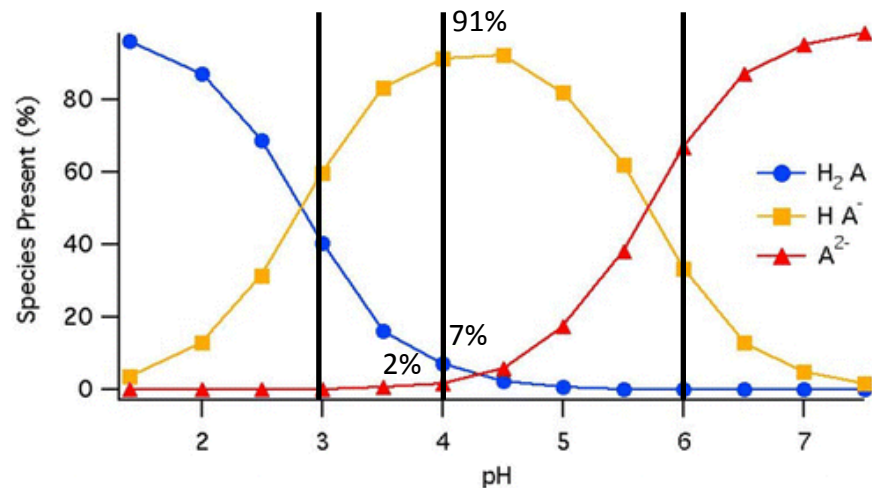
Surface Tension of Malonic Acid and Comparison to VSFS



- Further increases in concentration did not affect the surface pressure.
- Increasing of the concentration of malonic acid in the bulk does not alter the overall orientation of the C=O oscillators.

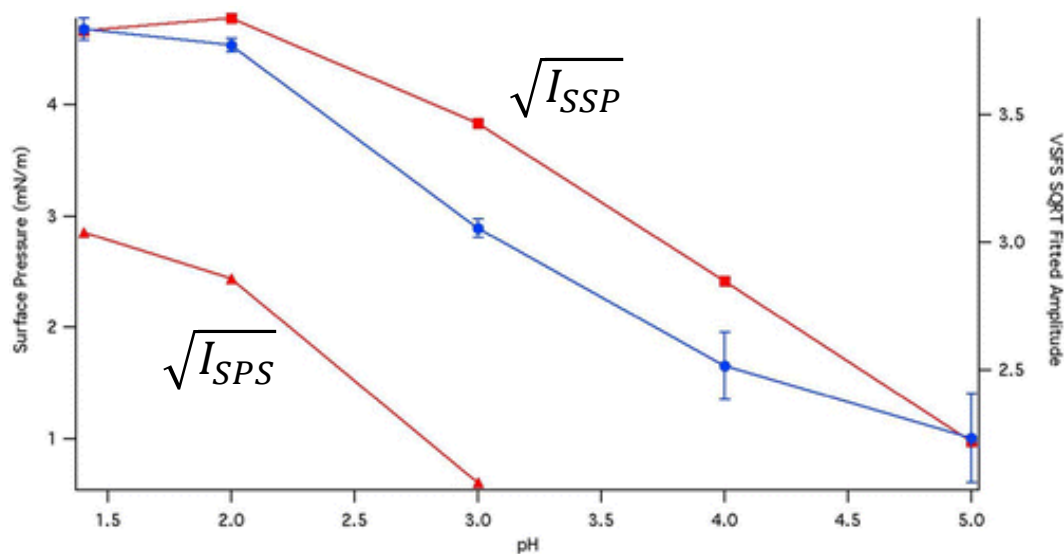
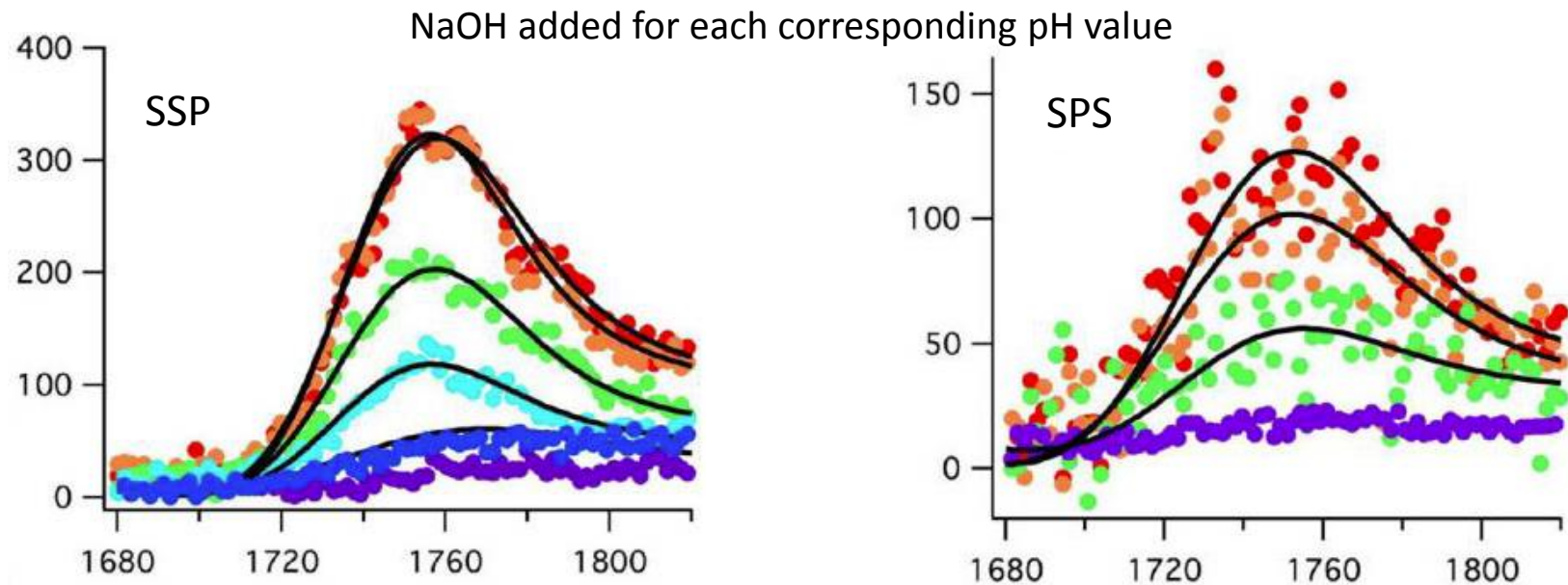


Effect of pH on Malonic Acid Adsorption



- The pKa values for malonic acid are 2.85 and 5.70, because there are two carboxylic moieties.
- Ex) At pH of 4
 - the fully protonated form - 7%
 - the singly protonated form - 91%
 - the completely dissociated form - 2%

C=O mode of aqueous malonic acid at 1 M (adjusted pH)



As the bulk pH was increased, the surface pressure decreased.