Heterogeneous nucleation of ice from supercooled solutions by films of high molecular weight organic compounds

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High molecular weight organic compounds and heterogeneous nucleation?

The best catalyst for freezing water isn't mineral dust or silver iodide – It's an organic compound. Both testosterone and hentriacontanol ($C_{31}H_{63}OH$) catalyze freezing of pure water at a supercoooling of only 1 ºC. (Silver iodide requires -4 ºC.)

What makes these organic compounds such efficient ice nucleators?

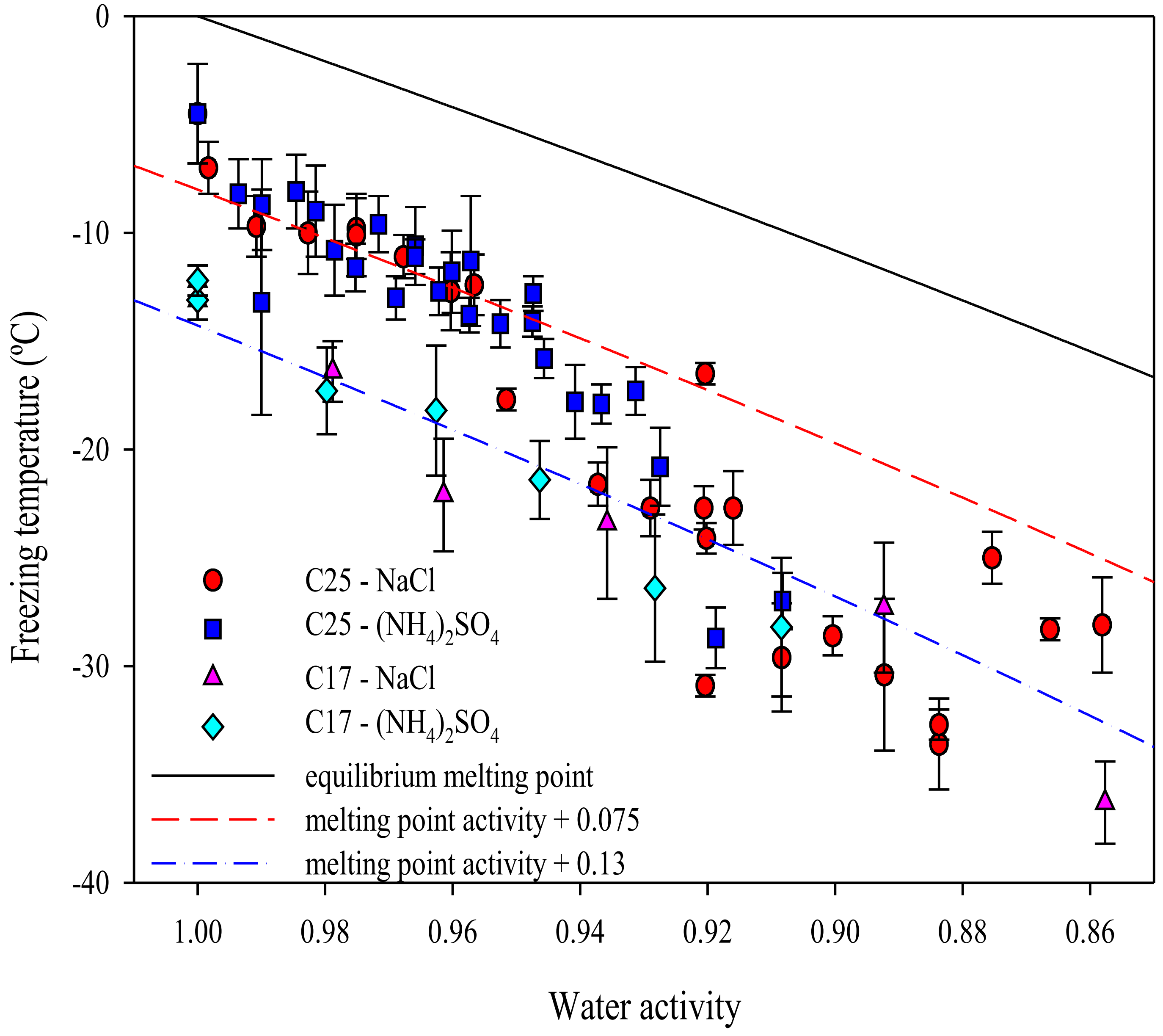
High molecular weight organic compounds are emitted to the atmosphere, most notably through biomass burning. When coupled with deep convection, organic compounds could affect ice processes in the original convective clouds and in clouds that form in the de-trained air at higher altitudes. Testing the properties of all compounds and combinations of compounds is neither feasible nor warranted. Progress should be possible with judicious choices of model compounds and mixtures.

Can freezing due to these organic compounds be predicted or paramaterized?

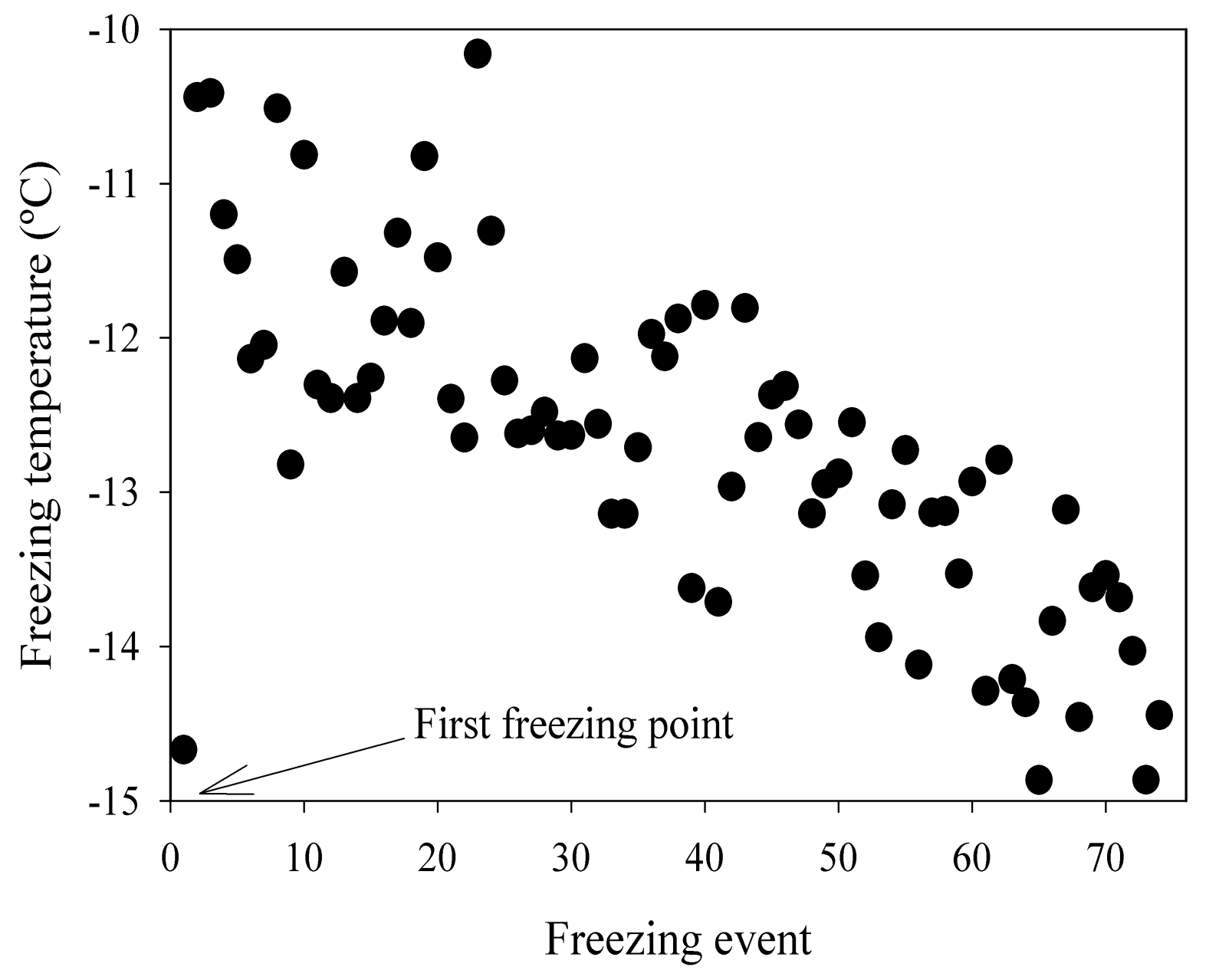
Oxidation may change the way that the compounds interact with solutions. For example, oxidation can create polar headgroups, making the compound amphiphilic.

How does oxidation change the nucleating efficiency of high molecular weight organic compounds?

Heterogeneous freezing of solutions as a function of water activity $C_{25}H_{51}OH$ and $C_{17}H_{35}OH$ as catalysts



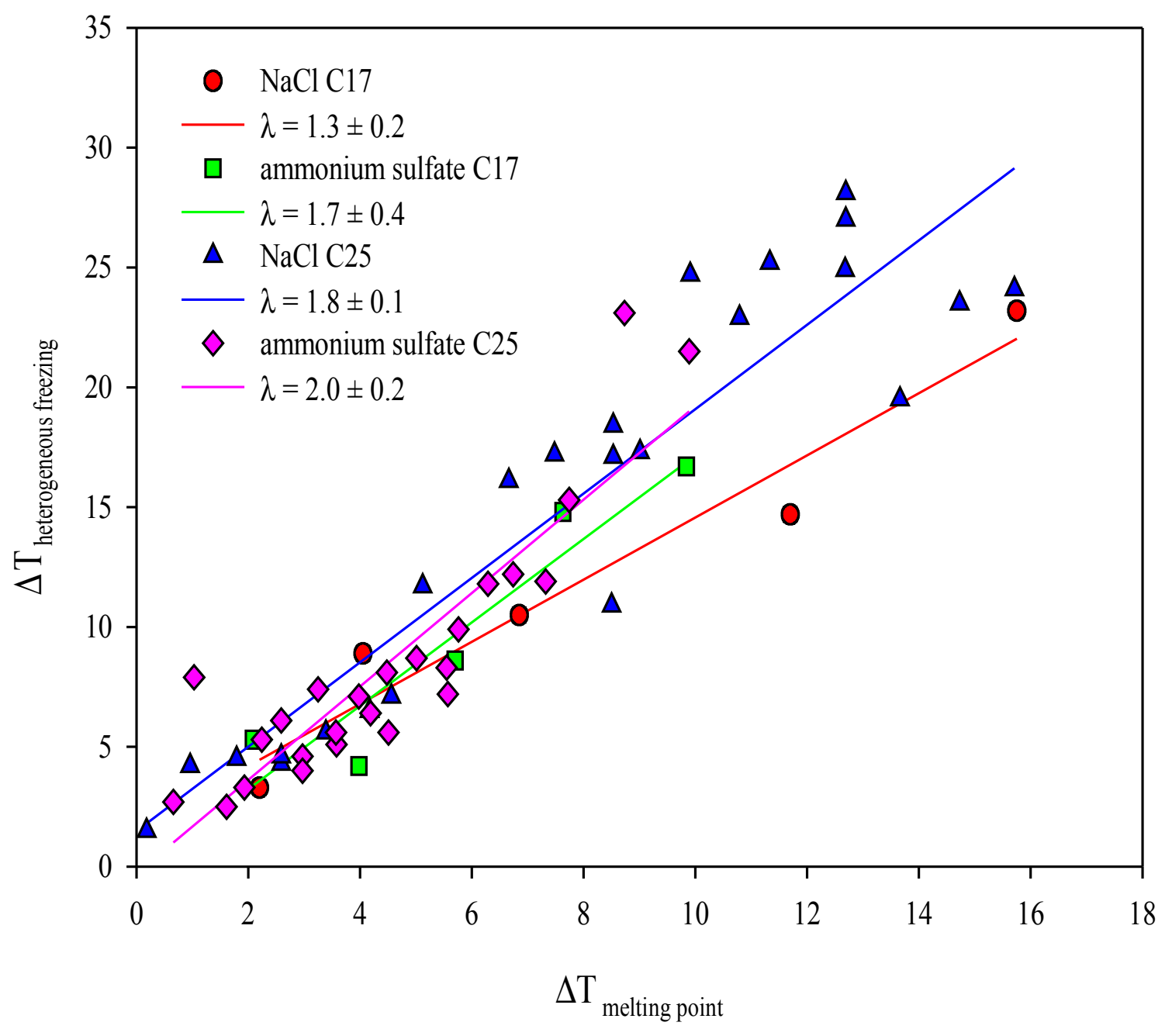
The structure of the alcohol films is not constant; we conclude this based on a trend in the freezing temperature (figure to the right) and changes in the CH_2 absorption bands (see below). The low first freezing point is a consequence of a form of pre-activation. (Ask me for details.)



An alternative view of heterogeneous freezing can be written as:

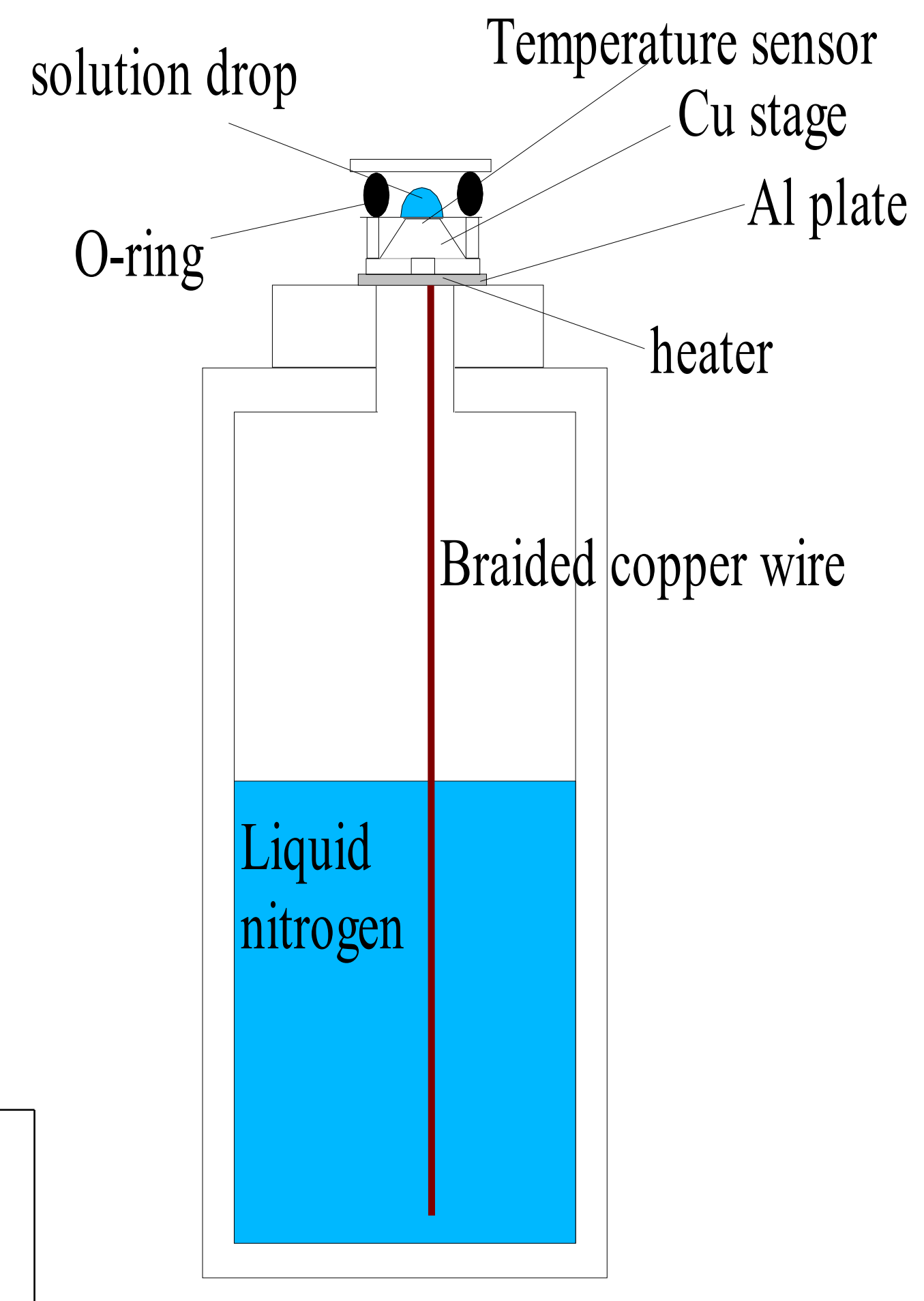
$$\Delta T_{het.\ freeze} = \lambda \Delta T_m,$$

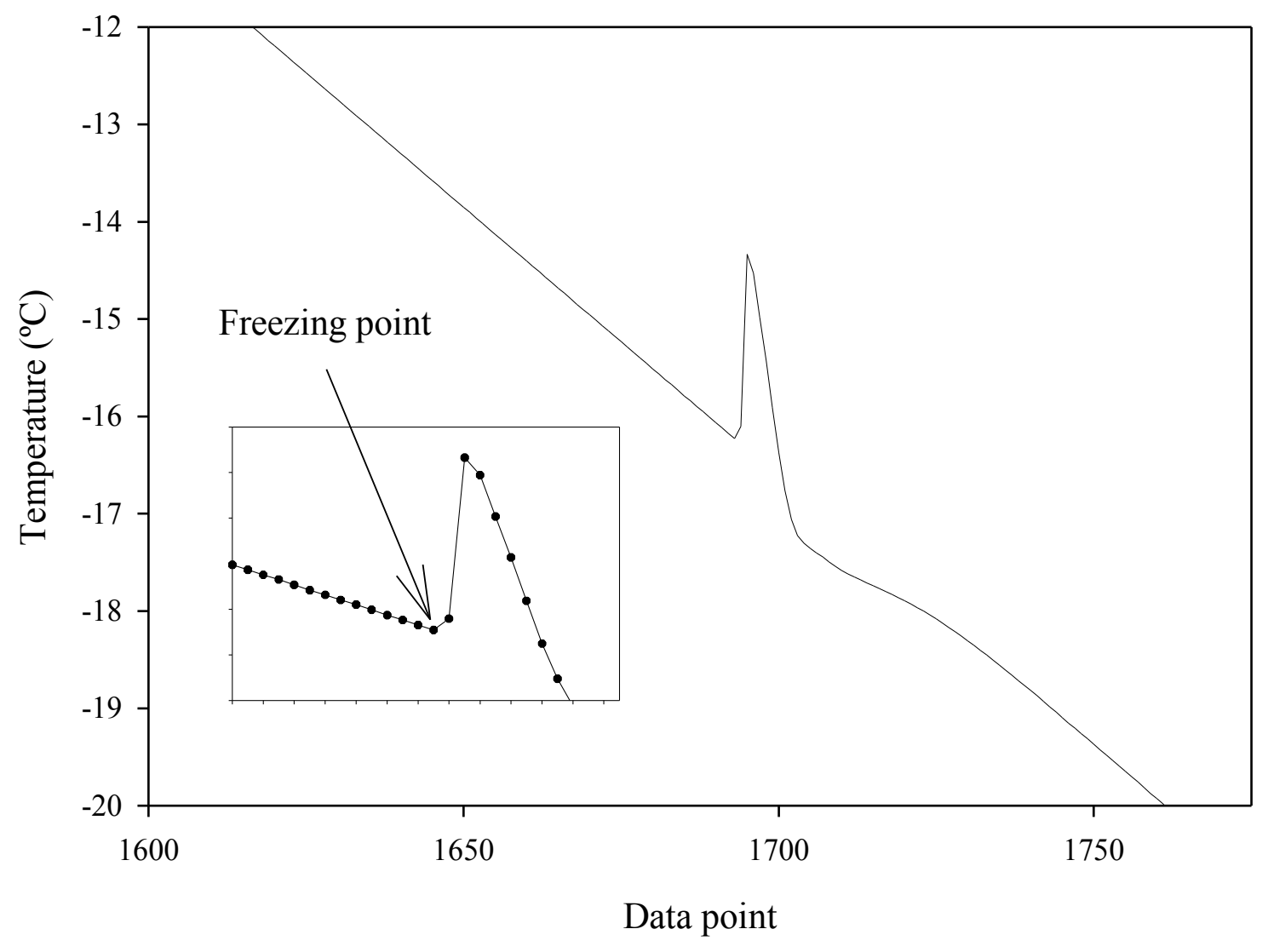
where $\Delta T_{het.\ freeze}$ is the difference between the catalyzed freezing temperature of pure water and the catalyzed freezing temperature of the solution and ΔT_m is the freezing point depression. λ is generally in the range 1.1 to 1.9 for homogeneous and heterogeneous freezing (Archuleta et al., 2005).



Technical details

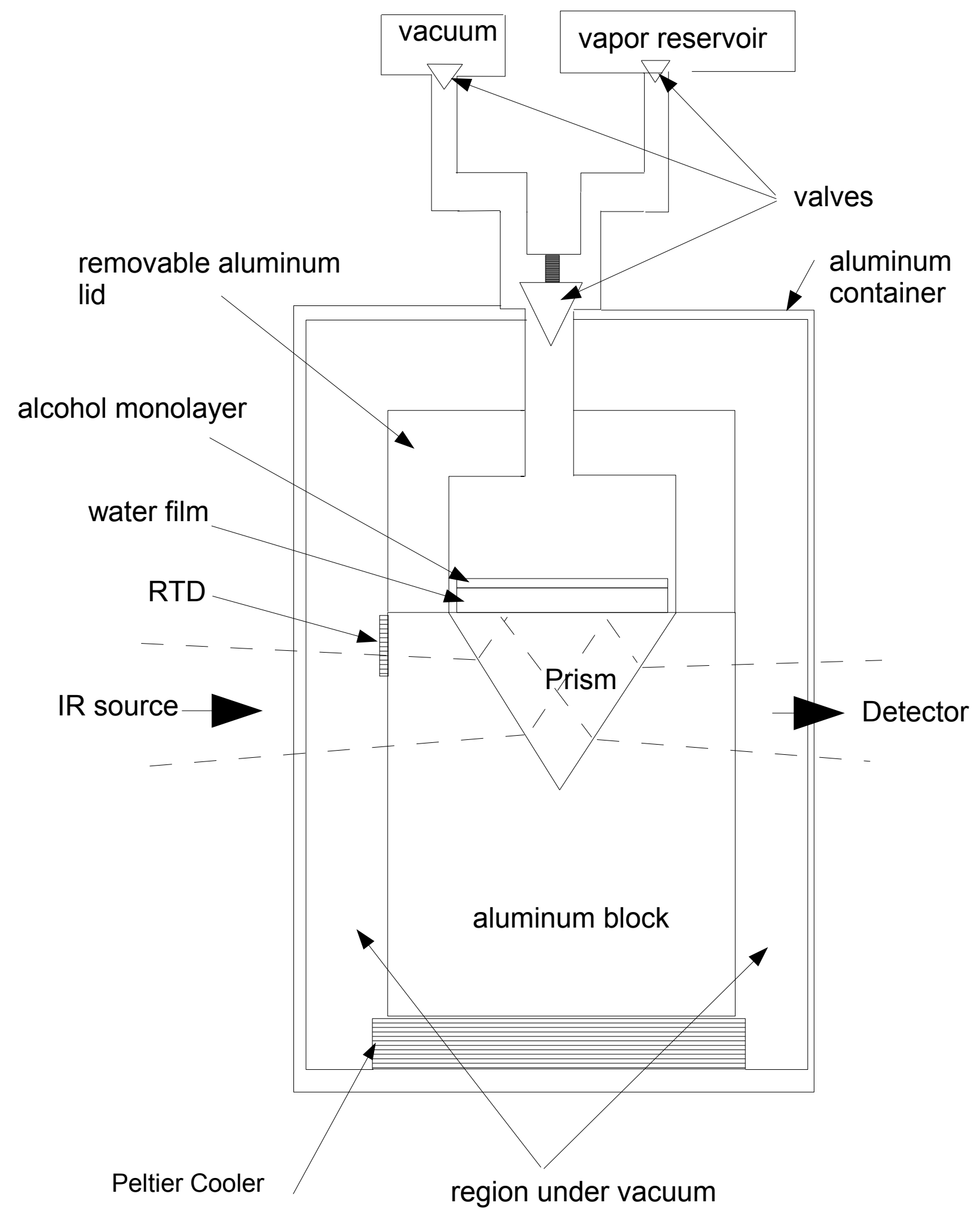
To capture the stochastic nature of nucleation, we freeze the same droplet repeatedly, detecting the temperature at which it freezes from the rise in temperature due to the release of latent heat. Our system is designed to isolate the droplet from the environment and control and record the temperature down to ~ -50 ºC over 8 to 10 hours. This is accomplished with a Lakeshore Model 330 T controller interfaced with LabView. A Plexiglass collar (not shown) over the stage minimizes condensation onto the apparatus. A portion of a typical temperature trace is shown below.





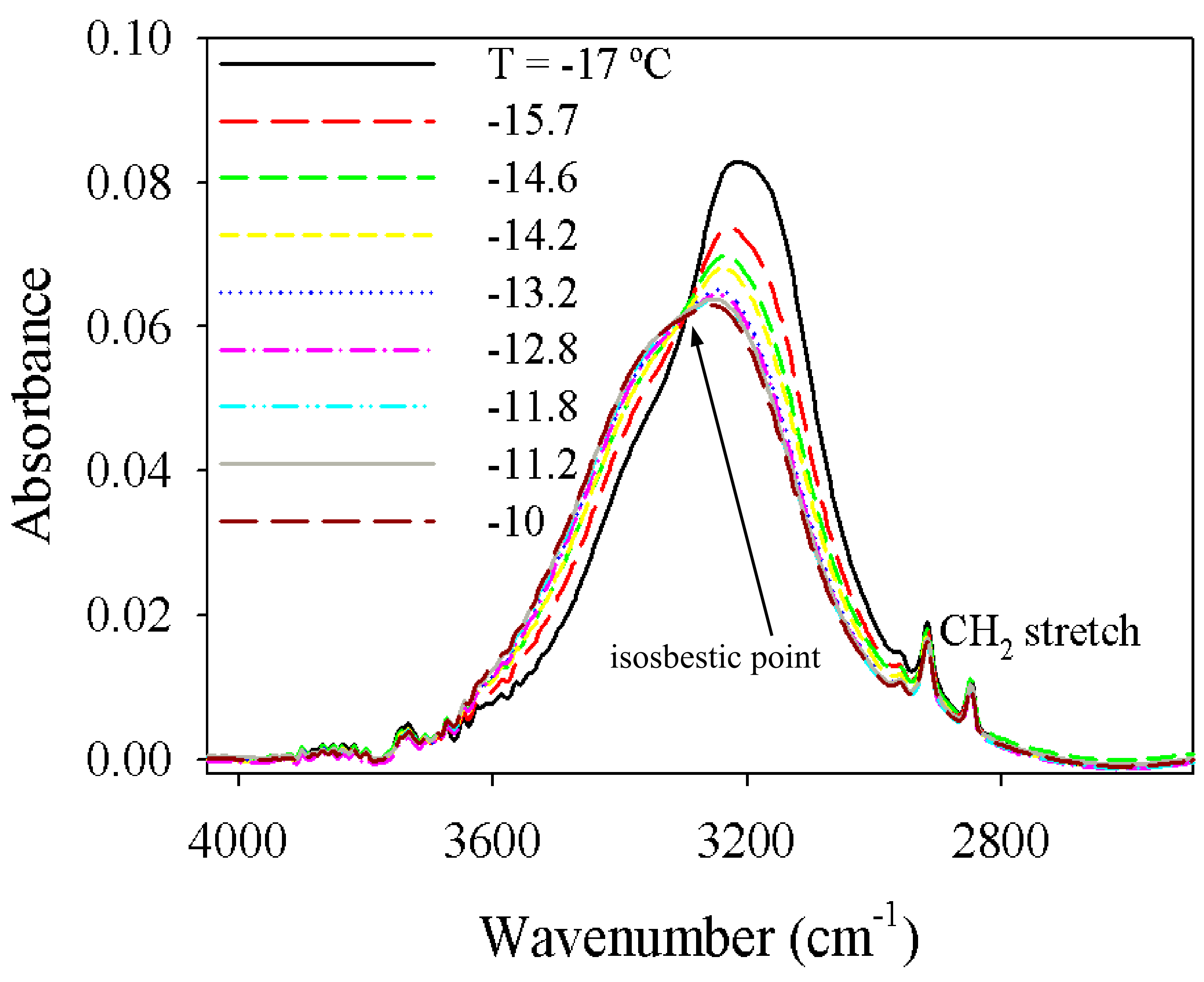
We interrogate thin (~ 50 nm) films of water topped by a film of an organic compound using attenuated total reflection spectroscopy. Water films are deposited from the vapor, alcohol films via a chloroform spreading solution. The evanescent wave penetrates the combined thickness of the water/organic film.

The OH stretching frequency in water is sensitive to the local environment, specifically hydrogen bonding. Following that region of the spectrum is an indication of changes in the local structure. The CH_2 stretch is also sensitive to conformation, providing information on changes in the structure of the organic film as well.



Water activity is a good predictor of homogeneous freezing in many solutions (Koop et al., 2000). Heterogeneous freezing may follow a similar pattern. Our results indicate that the freezing point for pentacosanol (C25) does not follow a constant offset from the equilibrium melting point, but that heptadecanol (C17) does. Temperature dependent water activities for ammonium sulfate solutions were calculated from the known molarity of the solution and the freezing temperature using the formalism in Clegg et al. (1995). The water activities for the sodium chloride solutions are calculated from Clegg et al. (1998), which is for T = 298.15. Water activity in solution is not a strong function of temperature, so we have not attempted to account for the temperature dependence in the NaCl solutions.

Infrared spectra of water and $C_{25}H_{51}OH$ as a function of temperature

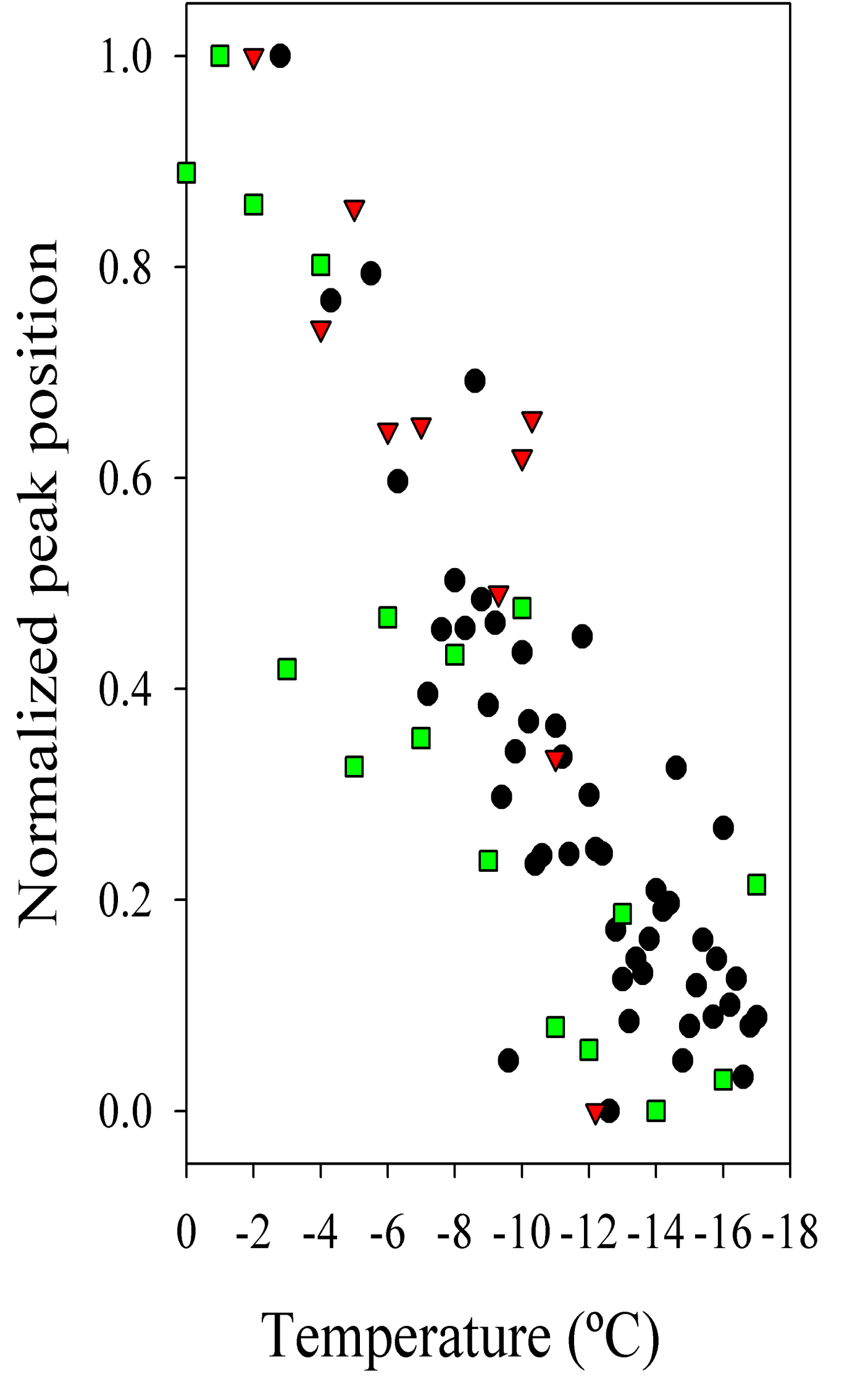


The clear, continuous shift in the spectrum of water is due to the influence of the alcohol film at the surface. We see no such shift with pure water or water with a film of the corresponding alkane. The shift is a function of temperature, not time. (i.e. if temperature were held constant at -14.2, the spectrum would not continue to shift.) Note the isosbestic point at ~ 3300 cm^{-1}. This suggests that a liquid-like component is converting to an ice-like component as a function of temperature.

Changes in the peak position of the CH_2 antisymmetric stretch indicate that the structure of the alcohol film changes with temperature. We hypothesize that this is in response to changes in the structure of water at the alcohol-water interface. (There is a similar trend in the symmetric stretch.)

Our conjecture is that the alcohols may be such effective ice nucleators because the film can take up some of the strain induced at the interface as an ice crystal begins to form. Inorganic substrates are unlikely to "help out" in this way. (This conjecture was put forward in another form by Fukuta and Mason in the 60s.)

Normalized peak position of the CH_2 antisymmetric stretch for three different tests of $C_{17}H_{35}OH$

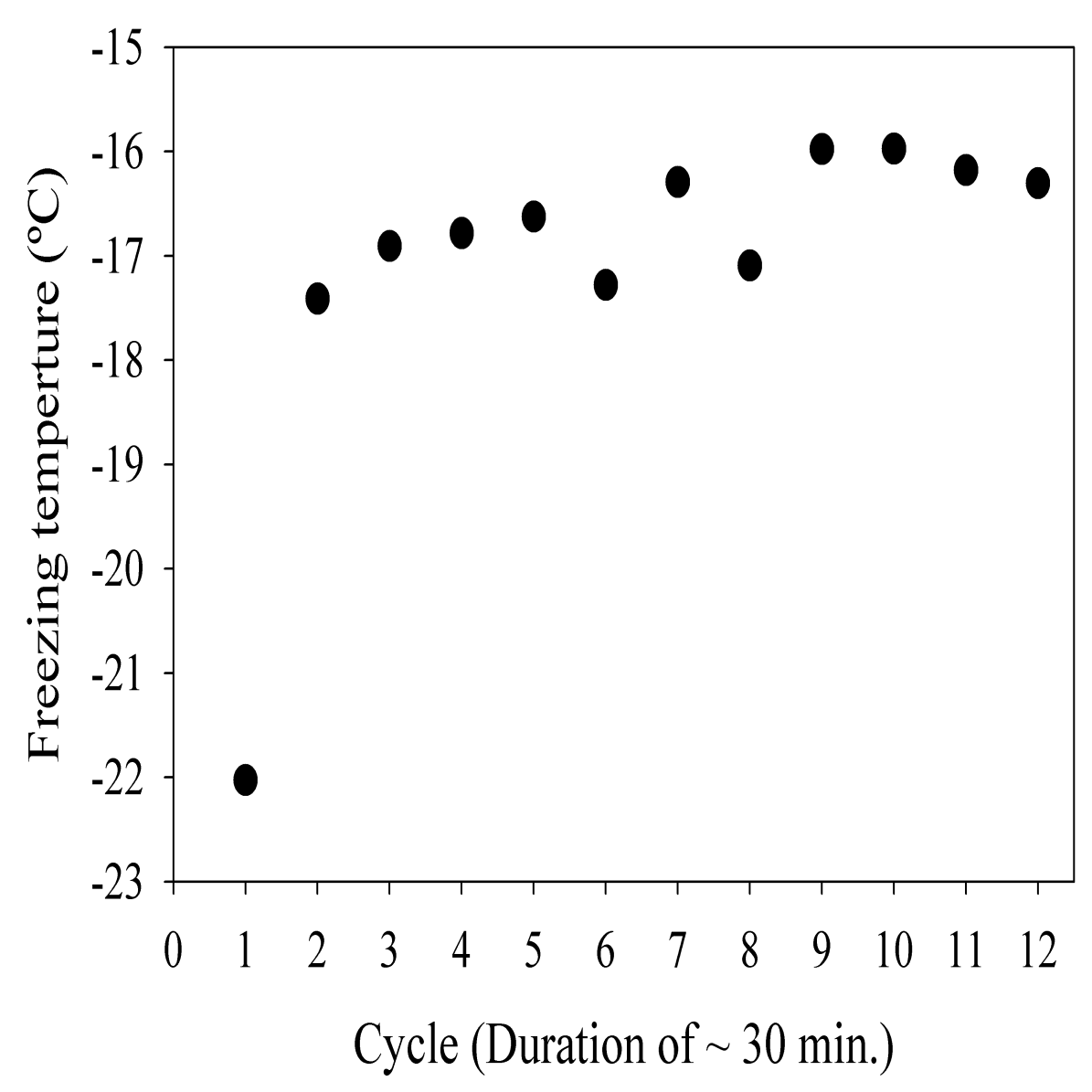


What happens as these compounds are oxidized?

The plot to the right shows the change in freezing temperature of a 0.25 M aqueous NaCl solution droplet with a film of oleyl alcohol as a function of exposure to O_3.

cis-$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OH$

Ozone attacks the double bond, which may change the structure of the film and therefore its effectiveness as a nucleator.



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Acknowledgments

Funding from NSF (CHE-0410007) and NASA's New Investigator Program (NNG04GR41G) is appreciated. Carly Robinson's summer research (2005) was funded in part by the Michigan Space Grant Consortium.

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