

# The vapor pressure of supercooled water measured using infrared spectroscopy

Will Cantrell, Eli Ochshorn and Alexander Kostinski  
Dept. of Physics  
Michigan Technological University

Keith Bozin  
Dept. of Physics  
Lawrence Technological University

## Introduction

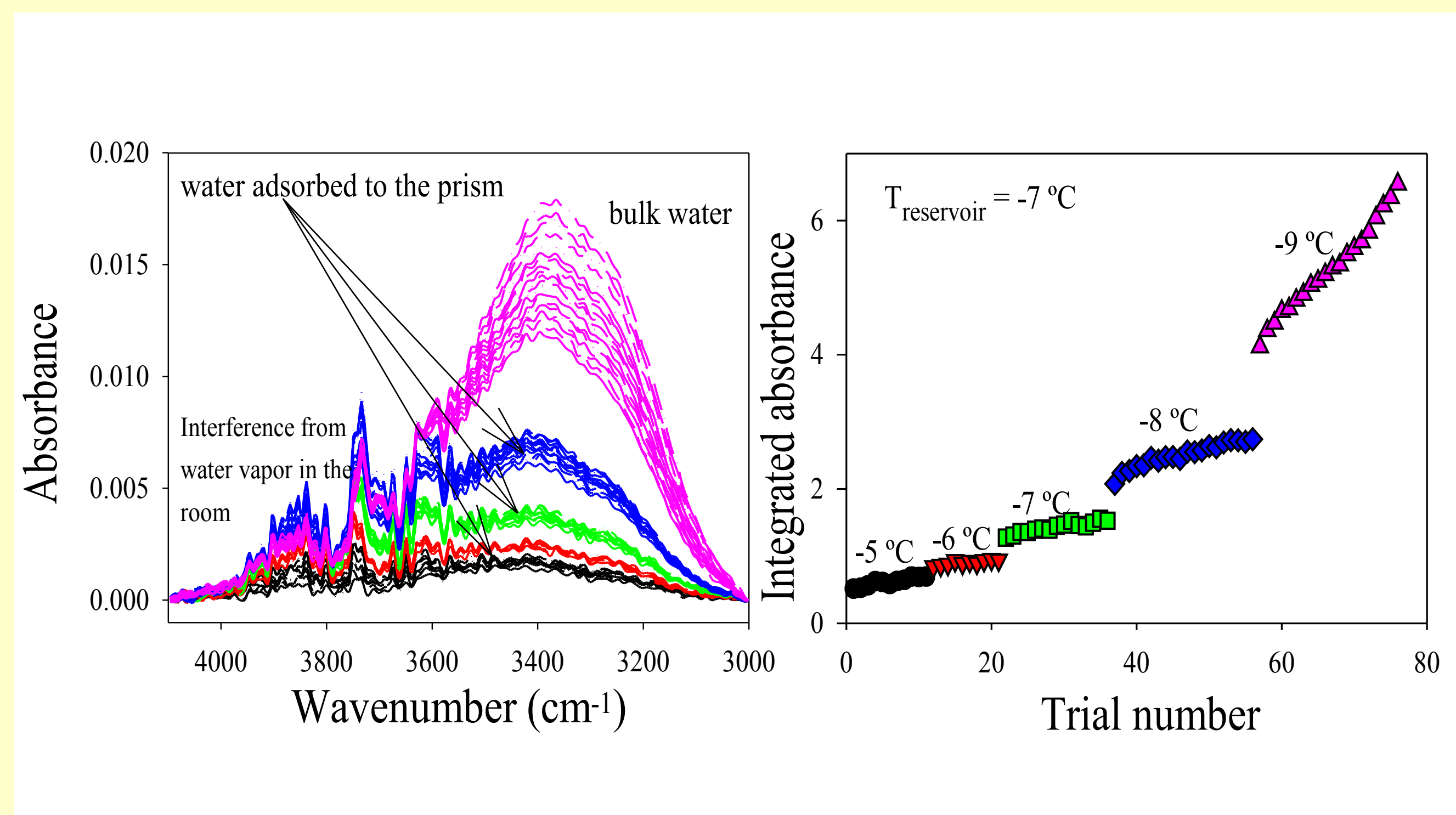
Below the melting point, the vapor pressure of water exceeds that of ice at the same temperature by virtue of the fact that the crystal, not liquid, is the stable state. In clouds, that difference in vapor pressure underlies the Bergeron-Findeison process where ice grows by deposition from the vapor at the expense of surrounding liquid water droplets. To calculate the rate of vapor transport, both the vapor pressure of ice and water must be known since it is the difference (i.e. gradient) in vapor pressure that drives the material transport.

The vapor pressure of ice is well established. The vapor pressure of supercooled water is less certain, primarily because of difficulties inherent in experiments with metastable states.

## The experiment

Use the vapor pressure of ice, which is well known, at one temperature to measure the vapor pressure of water at another, lower temperature. An ice reservoir, held at  $T_{\text{reservoir}}$ , communicates with a silicon surface, held at  $T_{\text{prism}}$ , through the vapor phase. Water only condenses on the prism's surface when  $\mu_{\text{water, prism}} < \mu_{\text{ice, reservoir}}$ , where  $\mu$  is the chemical potential. Monitor the surface of the silicon prism using attenuated total reflection infrared spectroscopy. The experiment proceeds as follows:

- $T_{\text{prism}} > T_{\text{reservoir}}$ ;  $\mu_{\text{water, prism}} > \mu_{\text{ice, reservoir}}$ . Water is only adsorbed to the prism. (See series of integrated absorbances labeled -5 °C along with corresponding spectra.)
- $T_{\text{prism}} = T_{\text{reservoir}}$ ;  $\mu_{\text{water, prism}} > \mu_{\text{ice, reservoir}}$ . Water is still just adsorbed to the prism. (See series of integrated absorbances labeled -7 °C along with corresponding spectra.)
- For some  $T_{\text{prism}} < T_{\text{reservoir}}$ ;  $\mu_{\text{water, prism}} = \mu_{\text{ice, reservoir}}$ ;  $p_{\text{ice}}(T_{\text{reservoir}}) = p_{\text{liquid water}}(T_{\text{prism}})$ . Use the vapor pressure of ice from Murphy and Koop to calculate the vapor pressure of water at  $T_{\text{prism}}$ .
- In practice, we bracket the temperature at which the chemical potentials are equal. In the two panel figure below, the integrated absorbances labeled -8 °C correspond to adsorbed water ( $\mu_{\text{liquid water}}(T_{\text{prism}}) > \mu_{\text{ice}}(T_{\text{reservoir}})$ ) while the steadily increasing integrated absorbances labeled -9 °C correspond to bulk water condensing on the prism. (Note that the infrared spectra show that it is liquid water on the prism, not ice and not a mixture.)
- For  $T_{\text{prism}} < -13$  °C, water de-wets from the prism, precluding us from extending our analysis to lower T.



Infrared spectra (left panel) and corresponding integrated absorbances (right panel) from a typical experiment. The ice reservoir is held at -7 °C. The temperature of the prism is shown with the integrated absorbances. There are five sets of spectra in the left panel, four of which correspond to water adsorbed to the prism. (Adsorbed water is neither ice nor liquid, it is simply water that sticks to a surface; the amount varies with relative humidity.) The fifth set (pink) corresponds to a temperature at which the chemical potential of water at the prism has dropped below that of ice at the reservoir, resulting in a net flux of vapor from reservoir to prism.

## Background: thermodynamics of supercooled water

The slope of a phase coexistence curve on a pressure-temperature diagram is:  $\frac{dp}{dT} = \frac{\Delta S}{\Delta V}$

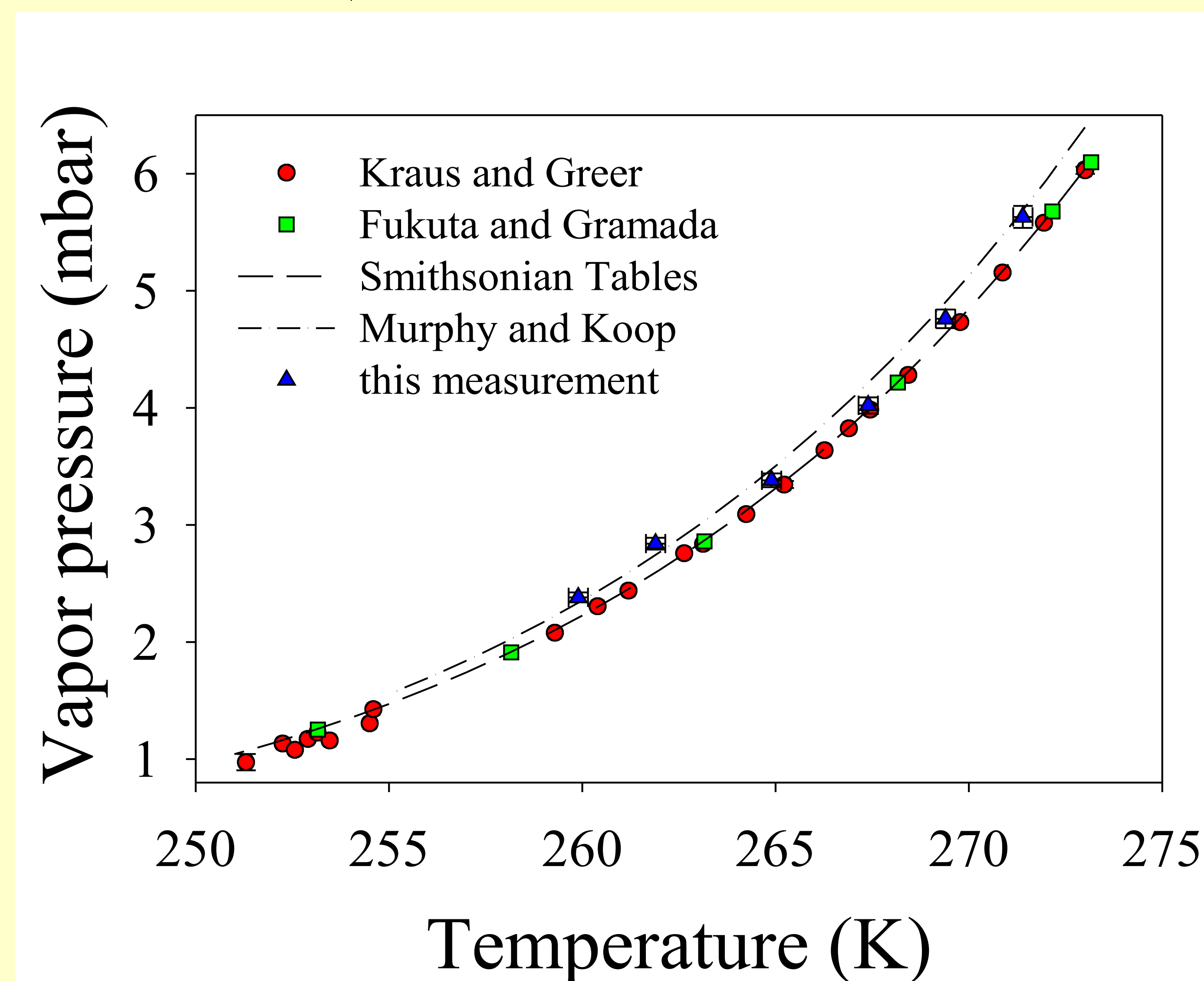
the Clapeyron equation.  $\Delta S$  and  $\Delta V$  are the differences in molar entropies and volumes respectively.

For reversible phase transitions,  $\Delta S$  can be associated with a definite amount of heat through the relationship,  $\Delta S = L/T$ , where  $L$  is the latent heat of the transition and  $T$  is the temperature at which it occurs.

For the liquid-vapor transition, the Clapeyron equation can further be manipulated into a form known as the Clausius-Clapeyron equation:

$$\frac{dp}{dT} = \frac{L_v p}{RT^2}$$

Reversibility is the key to making the transition from the Clapeyron to the Clausius-Clapeyron equation. Only then can the difference in molar entropies be associated with a definite amount of heat,  $L_v$ .

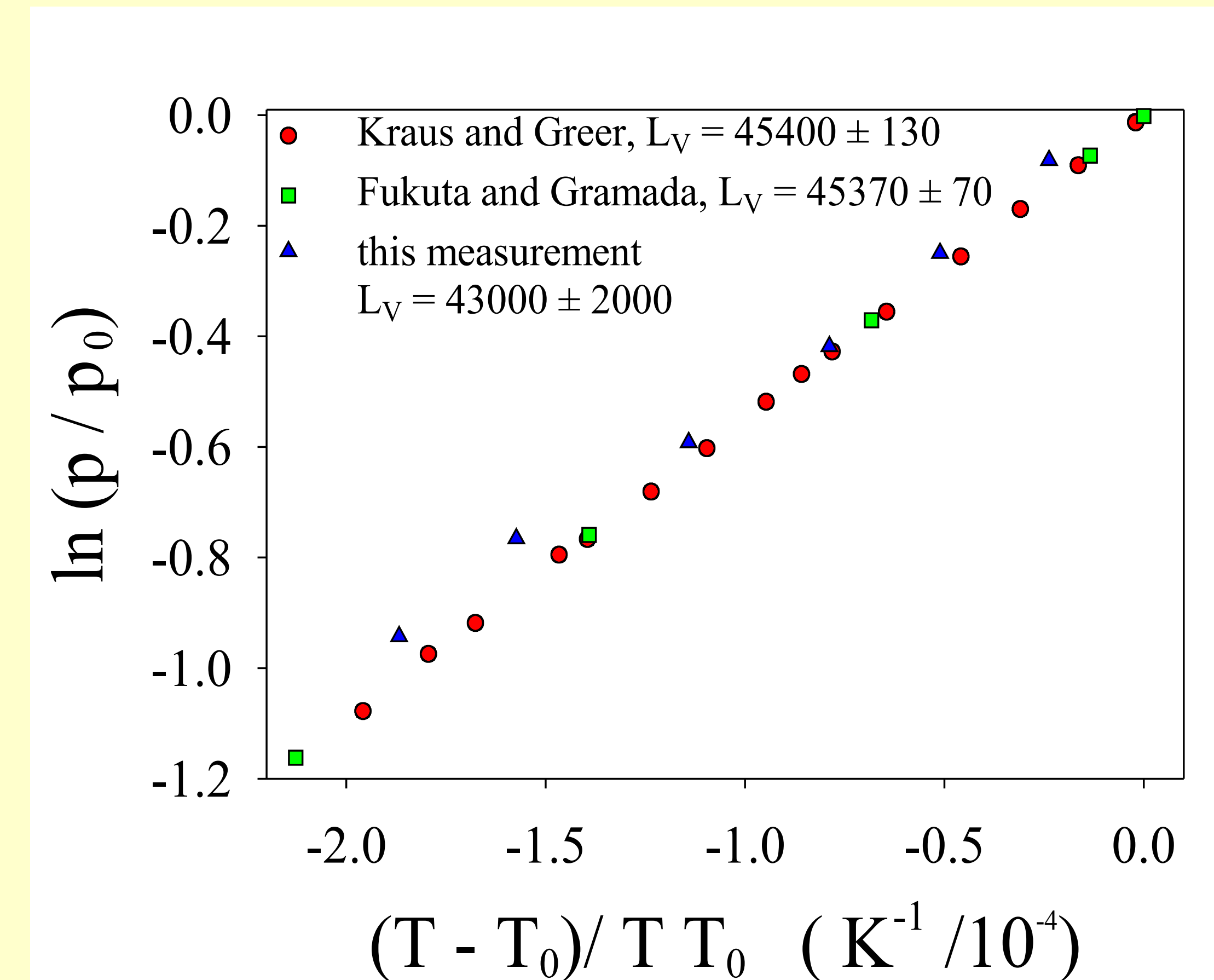


## Vapor pressure of supercooled water

Our measurements of the vapor pressure of supercooled water plotted with data from Kraus and Greer and Fukuta and Gramada along with formulations from Murphy and Koop and the Smithsonian Tables. Our data agrees with previous measurements. (The error bars are from the step size in the temperature of the prism and the uncertainty in the temperature of the reservoir, which translates into an uncertainty in the vapor pressure.)

Our initial goal was to extend the measurement to much lower temperatures, but the water films on the silicon prism de-wet for  $T < -13$  °C. (The water doesn't freeze, but the departure from the plane, parallel geometry makes interpretation of the infrared spectra impossible.)

In particular, we note that Fukuta and Gramada's values for the vapor pressure, which have been criticized as inaccurate, are in accord with ours and other data.



## Vapor pressure → latent heat of vaporization

Given vapor pressure as a function of temperature, the latent heat of vaporization can be derived using the Clausius-Clapeyron equation. The slope of a line fit to the data in the plot shown above is  $L_v / R$ .

Given  $L_v$  and  $L_s$ , the latent heat of sublimation, one might be tempted to use the relation  $L_s = L_f + L_v$  to derive the latent heat of fusion. However, as discussed earlier,  $\Delta S = L/T$  is only true on a phase boundary. The relation between the latent heats is true only at the triple point, where all three phase transitions can be accomplished reversibly. Below the melting point, liquid water is never in equilibrium with ice and freezing is not reversible.

## Conclusions

We have characterized the vapor pressure of supercooled water down to -13 °C. Our measurements are in agreement with previous work. The infrared spectra show unambiguously that the vapor pressure we calculate is that of liquid water, and is not contaminated with ice. We have shown that the latent heat of vaporization can be derived from vapor pressure measurements, but that the latent heat of fusion cannot.

## Further details in:

W. Cantrell, E. Ochshorn, A. Kostinski, and K. Bozin, The vapor pressure of supercooled water measured using infrared spectroscopy. *J. Atmos. Oceanic Technol.*, in review.

See also: A. Kostinski and W. Cantrell, Entropic aspects of supercooled droplet freezing. *J. Atmos. Sci.*, in review.

## Acknowledgments

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## References

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