

# Organic compounds as deposition nuclei: compounds representative of biomass burning emissions and oxidation products

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**The main idea:** High molecular weight (i.e. insoluble in water) organic compounds may act as deposition nuclei in the upper troposphere. Here, we present data on the interaction of representative compounds with thin films of water at temperatures below 0 °C.

## Why high molecular weight organic compounds?

A wide spectrum of organic compounds is produced in biomass burning (see e.g. Elias et al, 1999), and biomass burning is frequently associated with deep convection, particularly in the tropics. A significant fraction of the compounds produced are insoluble in water (or very sparingly soluble) and thus could serve as ice nuclei. See box to the right for physical properties and structures.

## Why does oxidation matter?

Oxidants in the upper troposphere (e.g. O<sub>3</sub> and OH radicals) will alter the original compounds, changing the ways in which they interact with water. For instance, the reaction products of oleic acid with ozone include nonanoic acid (Hearn and Smith, 2004). The dipole–dipole interaction between water and polar head groups like those found on long chain alcohols and acids may lead to more water adsorbed at a given relative humidity (see e.g. Asad et al. 2004). However, it is not clear what effect the polar head groups will have on ice nucleation; straight chain alcohols are some of the best heterogeneous ice nucleators, while acids are not particularly effective. The compounds are chosen to test the effect of the presence (absence) of the C=C bond, polar head groups, and kinks in the chains.

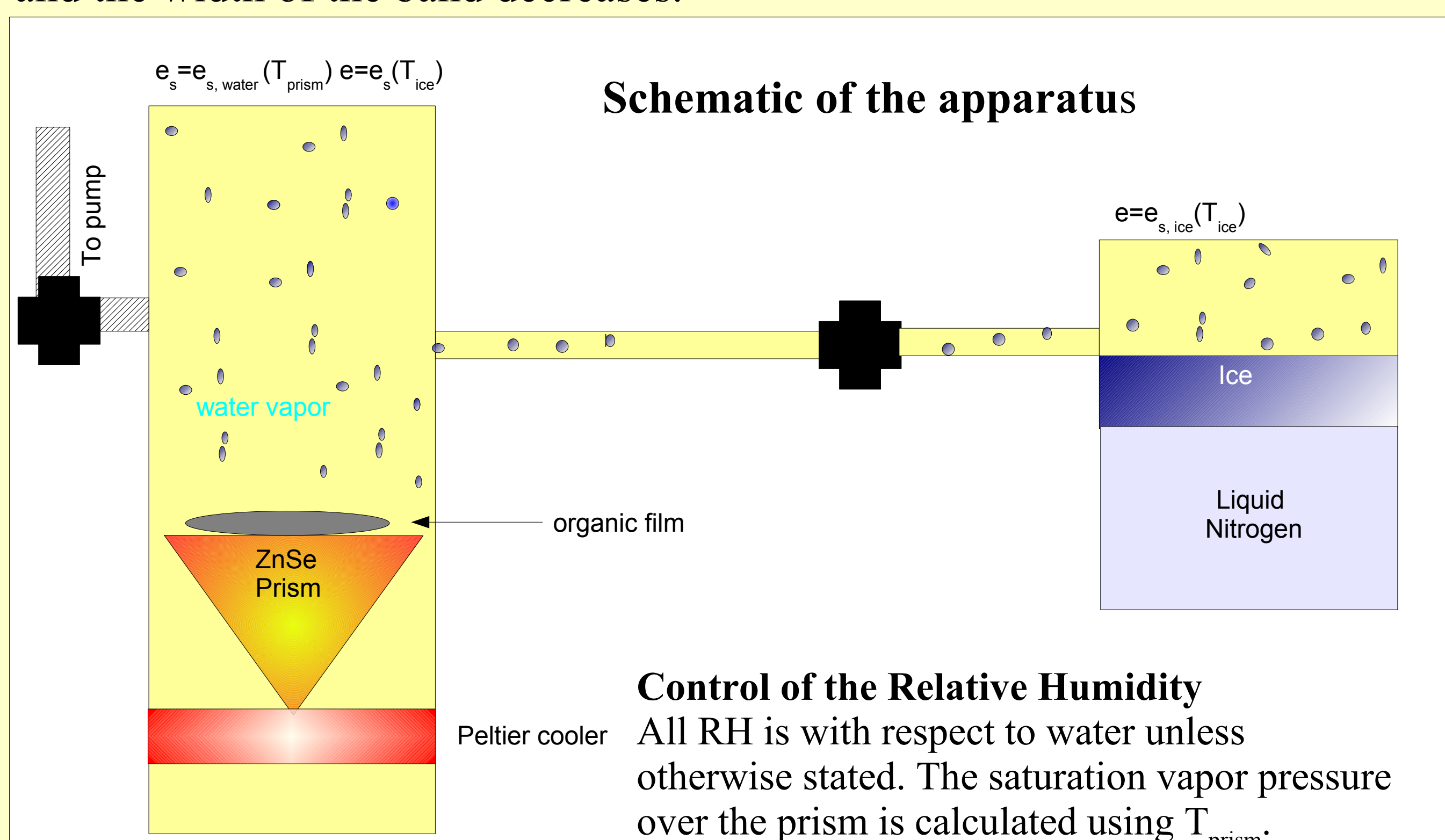
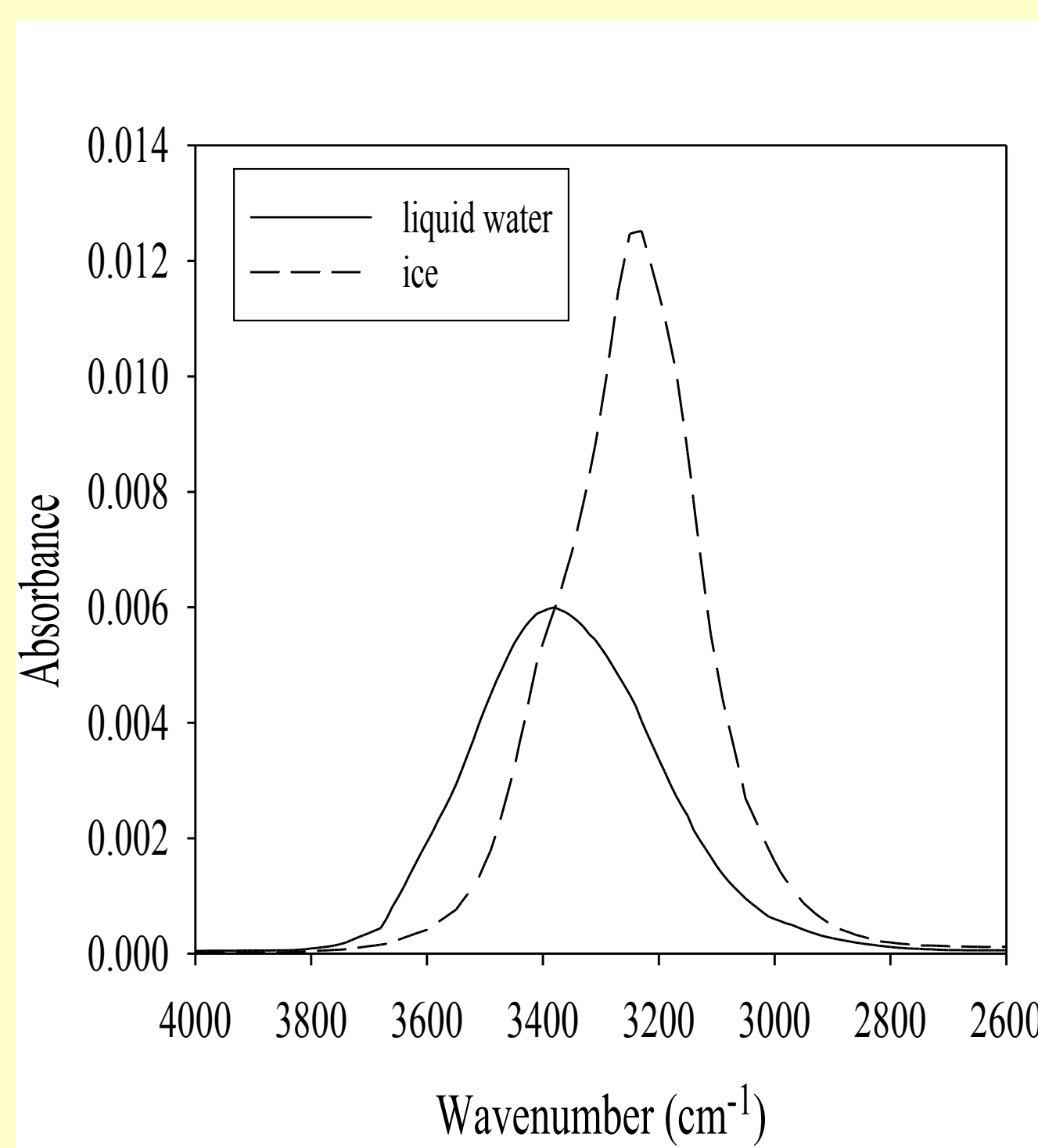
## Heterogeneous nucleation is a thin film phenomenon

By definition, heterogeneous nucleation is freezing catalyzed by the presence of another substance. The formation of the critical nucleus must be dictated by the thin film of water which is interacting with the substrate. Studying the properties of that thin film provides insight into the ice nucleating efficacy of the substrate.

## Information from the infrared spectra

The magnitude of the absorption band of the condensed phase (liquid or ice) indicates the amount of water interacting with the organic, while the band position and shape provide information on the phase (see figure to the right).

The liquid water band is peaked at ~ 3400 cm<sup>-1</sup>. Upon freezing, the peak red shifts to ~ 3200 cm<sup>-1</sup>, the absorbance magnitude increases by a factor of 2, and the width of the band decreases.



The vapor pressure at the prism can then be calculated from the saturation

$$\text{vapor pressure of ice at the temperature } T_{\text{ice}}. \text{ Then: } RH = \frac{e_s(T_{\text{ice}})}{e_s(T_{\text{prism}})}$$

$T_{\text{prism}}$  = constant during a single experiment.  $T_{\text{ice}}$  is varied to control RH.

**Spectra:** Spectra are acquired with a Bruker Tensor 37 at 8 cm<sup>-1</sup> resolution using 100 scan averaging. The attenuated total reflection (ATR) element is a 45 degree ZnSe prism. The film of organic is deposited onto the prism before a background is acquired. Unless the adsorbed water vapor alters the molecular environment of an appreciable fraction of the organic film, the organic's characteristic absorption bands are not seen in the spectrum.

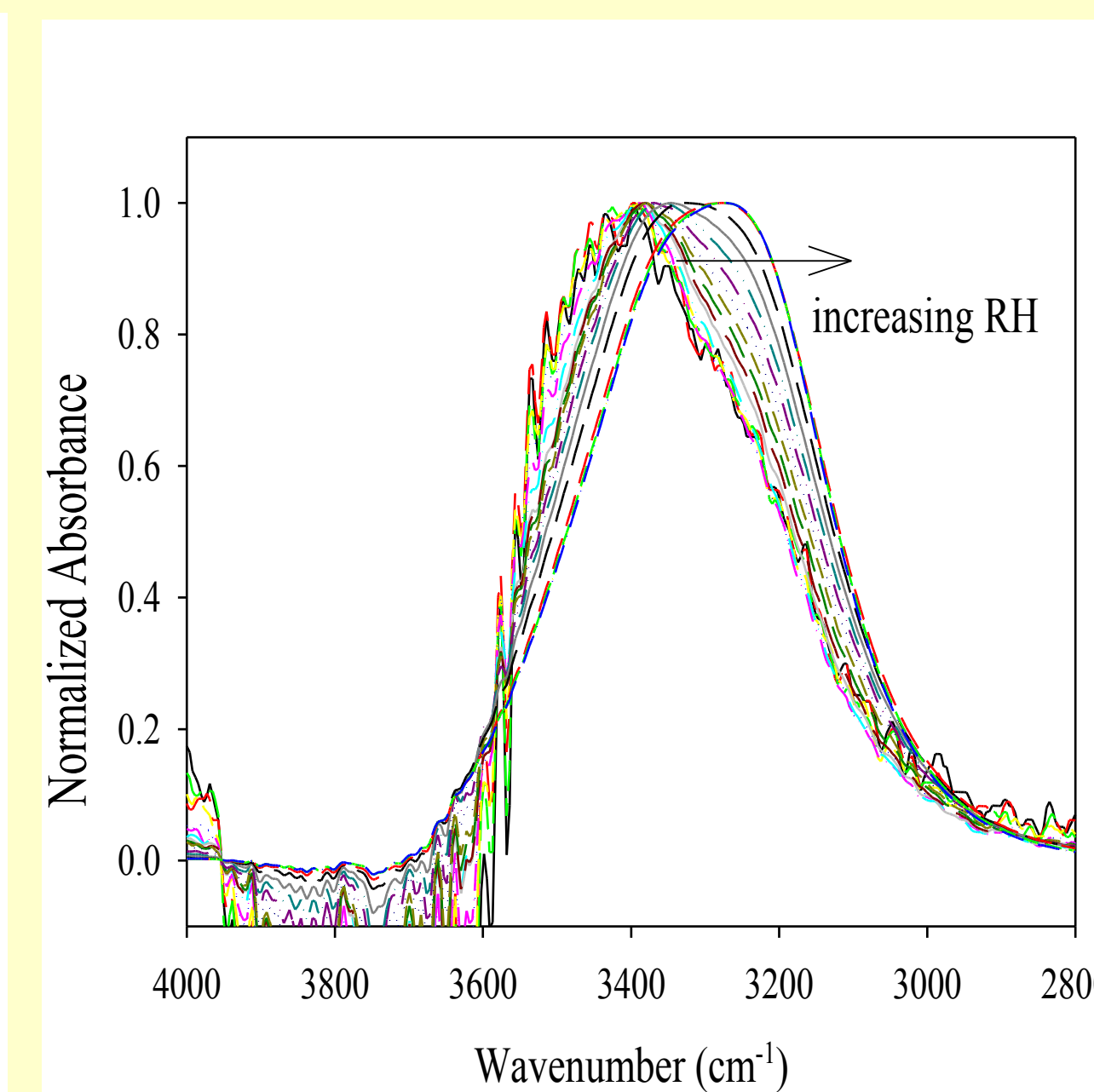
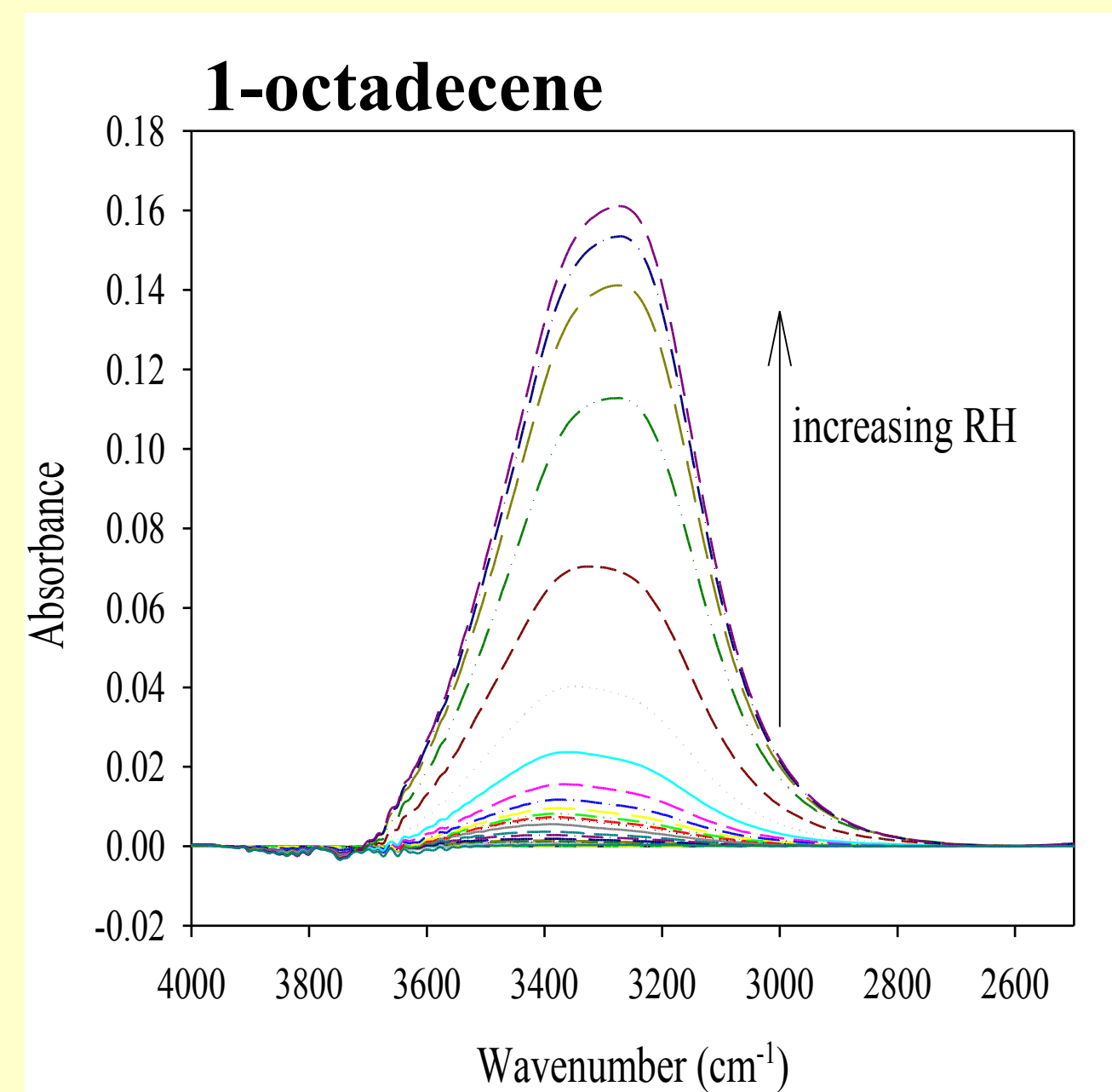
## References

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Elias, V., BRT Simoneit, A.Pereira, J. Cabral, J. Cardoso (1999). Detection of high molecular weight organic tracers in vegetation smoke samples by high-temperature gas chromatography-mass spectrometry. *Environ. Sci. Technol.*, 33, 2369-2376.  
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## Acknowledgments

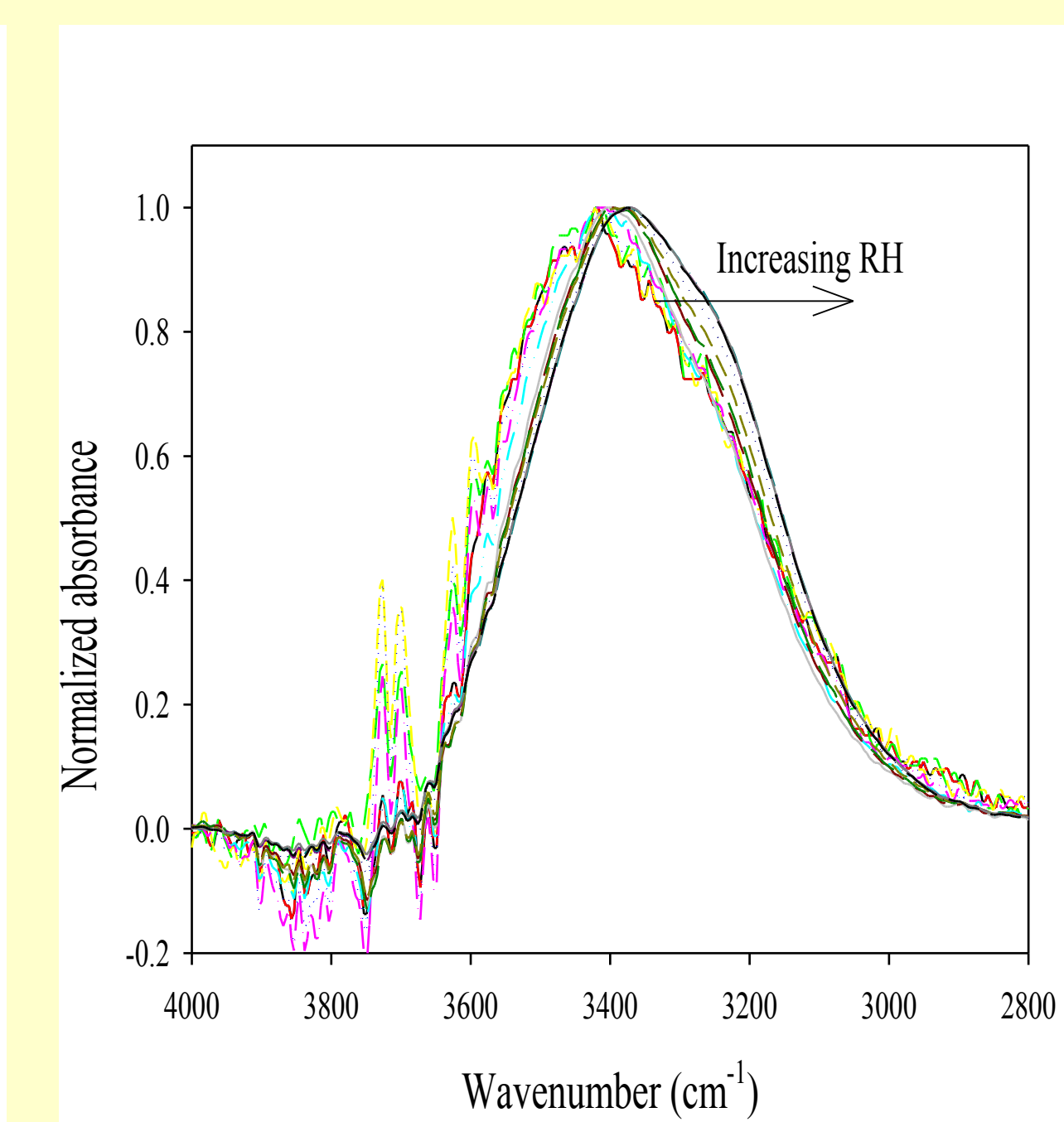
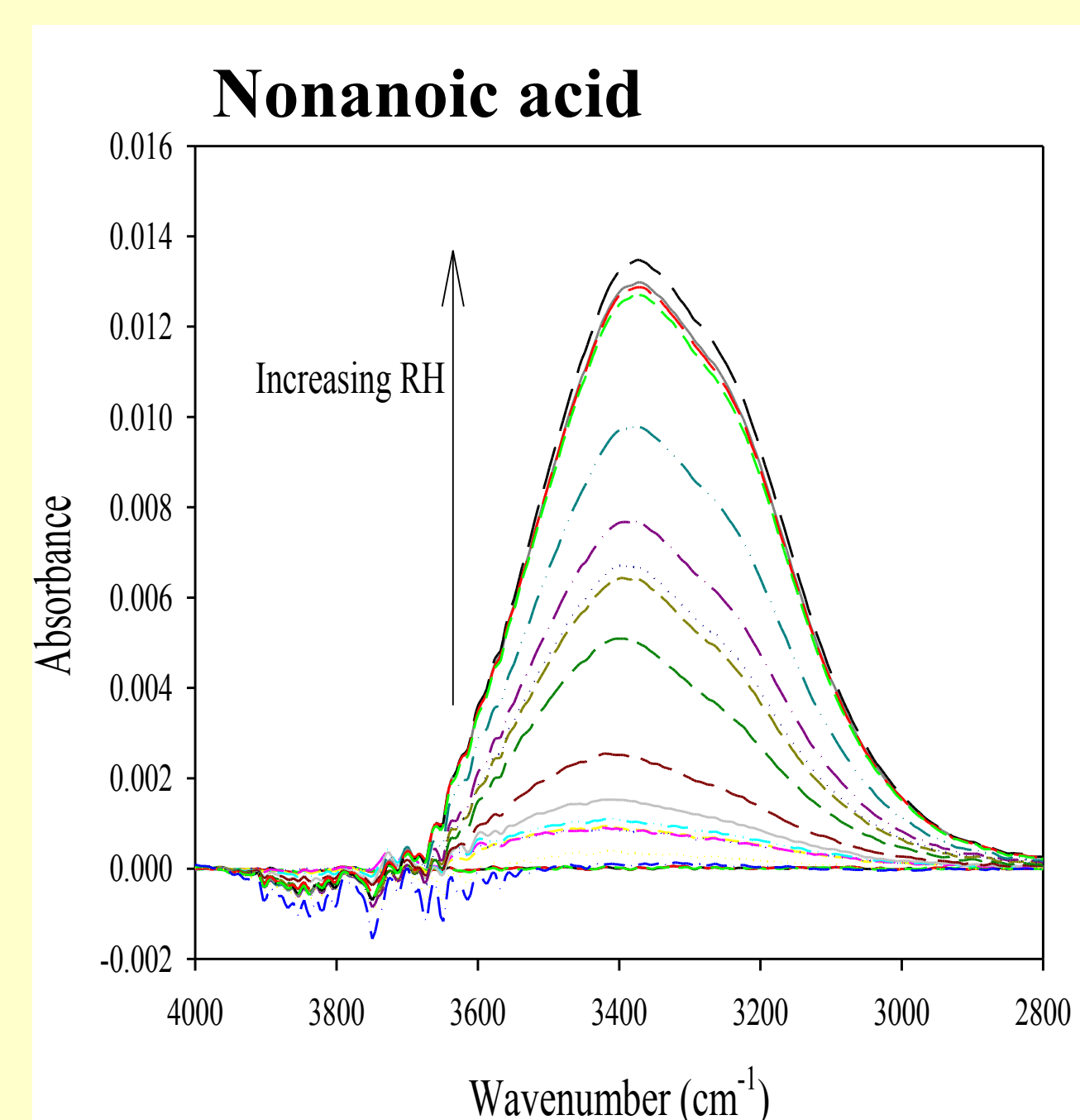
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Compound	Formula (mol weight)	Melting point (°C)
1-octadecene	C <sub>18</sub> H <sub>36</sub> (252.5)	18
oleic acid	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub> (282.5)	13
nonanoic acid	C <sub>9</sub> H <sub>18</sub> O <sub>2</sub> (158.2)	13



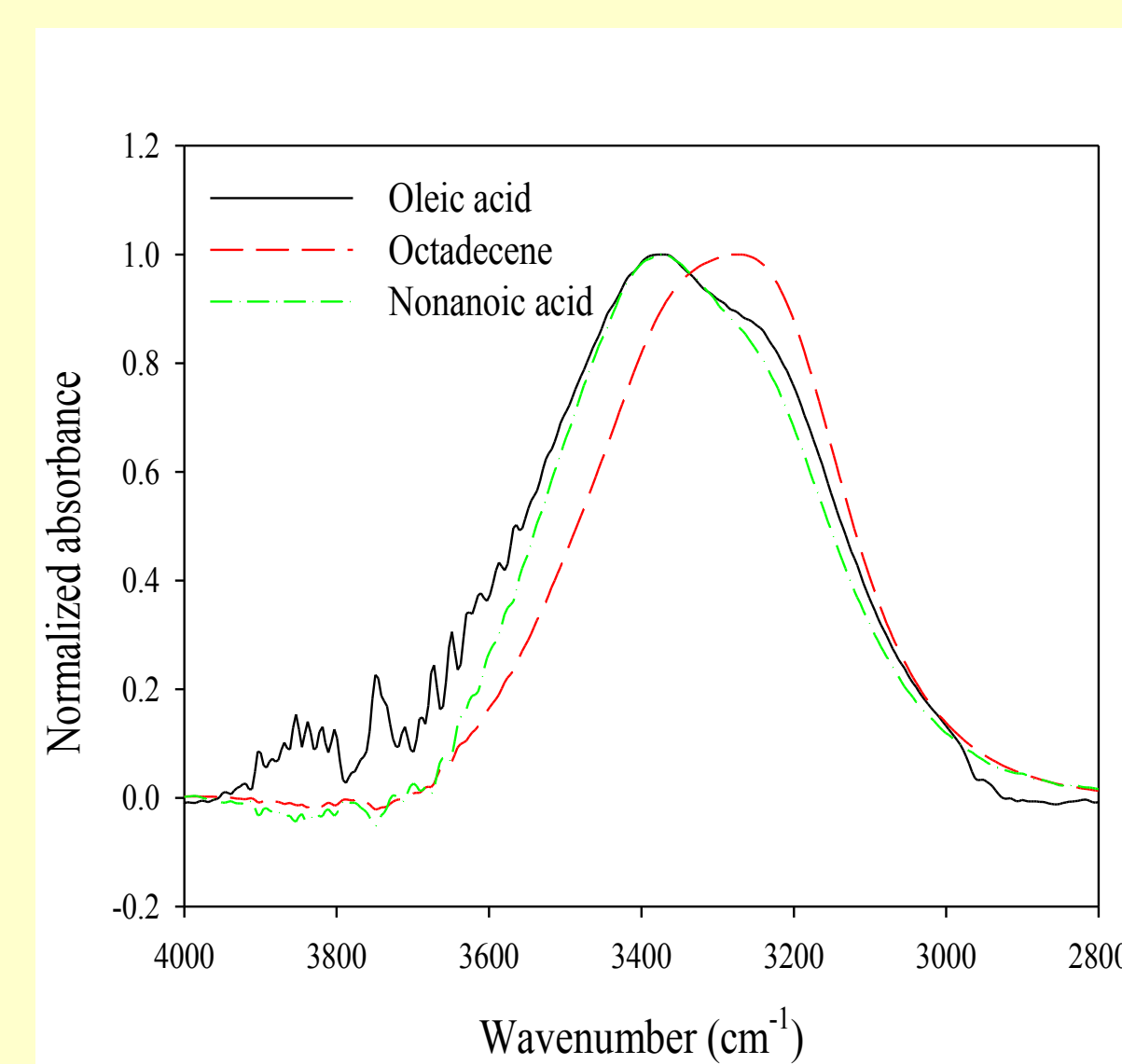
**1-octadecene at -5 °C:** Left panel: Spectra of water adsorbed to the organic as a function of relative humidity. Right panel: Spectra from the left panel, normalized to facilitate comparison. (The spectra taken at lower relative humidities appear noisier because of interference from residual water vapor in the purge box.)

The spectra show that the intermolecular environment that the water molecules are in changes as the thickness of the adsorbed film increases. The growth of the shoulder at ~ 3270 cm<sup>-1</sup> indicates the water is a more structured environment. Note that the relative peak at 3270 cm<sup>-1</sup> becomes more intense than the higher wavenumber peak.



**Nonanoic acid at -2 °C:** Left panel: Spectra of water adsorbed to the organic as a function of relative humidity. Right panel: Spectra from the left panel, normalized to facilitate comparison. (The spectra taken at lower relative humidities appear noisier because of interference from residual water vapor in the purge box.)

Again, the spectra show that the intermolecular environment that the water molecules are in changes as the thickness of the adsorbed film increases. In this case, though the shoulder at 3270 cm<sup>-1</sup> becomes more pronounced, it remains a secondary feature.



## Comparison of normalized spectra for octadecene, nonanoic acid, and oleic acid at ~ 100% RH

Water films on the acids at ~ 100% RH are in similar environments. (Note, however, the presence of the pronounced shoulder at 3270 cm<sup>-1</sup>.) In contrast, the water on the octadecene is significantly red-shifted relative to the acids.

**Concluding remark:** The absorbance profiles of water adsorbed to organic compounds representative of biomass burning suggest that those compounds may be moderately active deposition nuclei at lower temperatures.