

# ORGANIC COMPOUNDS AS DEPOSITION NUCLEI BEFORE AND AFTER OXIDATION

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## 1. INTRODUCTION

Biomass burning contributes to overall atmospheric aerosol and ozone concentrations. Although at times natural, the majority of this activity (such as burning land for clearing) is anthropogenic. Biomass burning, in conjunction with deep convection, has the potential to quickly transport high molecular weight organic compounds into the upper troposphere, which could affect cirrus cloud formation through heterogeneous nucleation processes. Enhancing the concentration of these aerosol, which could increase cirrus cloud development, could affect earth's radiation budget and, thus, temperature distribution.

Not only is the concentration of atmospheric organic aerosol increased during biomass burning, but the properties of the constituent compounds can also be altered through oxidation by (for example) ozone or OH radicals. Frequently such oxidation results in the formation of polar head groups, which interact more strongly with water. The relatively slow dissolution of high molecular weight organics, coupled with the cold temperatures and low water content of the upper troposphere create prime environmental conditions for deposition nucleation.

In order to better understand this process, we initially gather a general understanding of the nucleation rates for various compounds affiliated with biomass burning. Determining the rates at which these compounds act as deposition ice nuclei will enable a better understanding of the contribution that biomass burning has on the formation of cirrus clouds. Following this analysis we expose the system to an oxidizing agent such as ozone or OH radicals and once again analyze the nucleation rates of the compound.

## 2. STUDY OF ICE NUCLEATION IN THE DEPOSITION MODE BY HIGH MOLECULAR WEIGHT ORGANIC COMPOUNDS.

Infrared spectroscopy is the principal tool for the investigation. It is uniquely suited to this topic since both organic compounds and water have characteristic absorption bands in the infrared. The positions of the symmetric and anti-symmetric stretch can be used to gage the degree of order within the organic film (Dluhy and Cornell, 1985). For instance, using the position and integrated absorbance of those two features, Ochshorn and Cantrell (2006) showed that the structure of films of heptadecanol changes in response to the changes in the structure of the water sub-phase as a function of temperature. Infrared spectroscopy not only determines the characteristics of organics, it also enables the presence of water vapor and ice to be quantified.

Careful control and measurement of the relative humidity (with respect to ice) is critical. As noted above, FTIR enables monitoring of

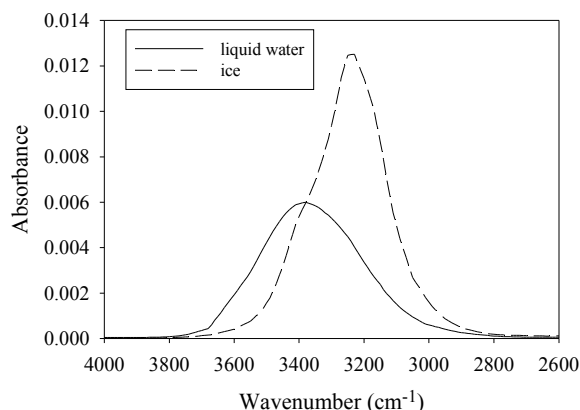


Figure 1: Calculated absorbances for films of water on an attenuated total reflection prism for both liquid (solid line) and ice (dashed line). Notice that the peak in the liquid water absorbance is approximately 3400  $\text{cm}^{-1}$ , while the peak absorbance of ice is approximately 3200  $\text{cm}^{-1}$ . In both cases, the thickness of the film is 15 nm.

the amount of water absorbed to the organic at any point during the study. Figure 1 is an illustration of the sensitivity. 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 provides information on the phase. The peak absorbance for liquid water is  $\sim 3400\text{ cm}^{-1}$  while peak absorbance for ice is  $\sim 3200\text{ cm}^{-1}$ . Because the optical cross sections are known in both phases, the area under the curve can be inverted to determine the amount of water in the condensed phase.

Representative compounds for study include octadecene, octadecanol, and oleic acid (cis-9 octadecenoic acid). The compounds are chosen not only because of their affiliation with biomass burning, but also because they have a wide range of characteristics such as functional groups (alcohols and acids), conformation, linearity, and saturation. Each functional group exemplifies unique characteristics when exposed to water vapor.

The presence of a functional group such as alcohol or acid should affect the way in which an organic compounds interacts with water, which has an intrinsic dipole moment. As a consequence, we expect that, octadecanol (for instance) would be associated with more water than octadecene at a given relative humidity. However, it is not clear whether more water will necessarily lead to a higher nucleation rate.

Once emitted to the atmosphere, organic compounds are oxidized, for example by  $\text{O}_3$  a product of biomass burning, and OH radicals. Hearn and Smith (2004) have predicted that oxidation has the ability to

increase the number of polar head groups in certain organic compounds. This could increase the organics' ability to act as deposition nuclei. For example, when 1-octadecene is oxidized by ozone the products include formaldehyde, formic acid, heptadecanal, and heptadecanoic acid (Hearn and Smith, 2004). In this case, a relatively poor deposition nucleator with a carbon-carbon double bond is cleaved during oxidation to form acid groups and aldehydes, both of which are hydrophilic. The new mixture of compounds will interact with water vapor in a different manner, which may lead to a higher nucleation rate (in the deposition mode).

### 3. REFERENCES

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