



Freezing of Ethanol Aqueous Solutions Droplets Investigated by *in situ* Raman Spectroscopy and X-Ray Diffraction

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Volatile Organic Compounds (VOCs) and other anthropogenic reduced trace gases may be quickly transported to the upper troposphere in the course of active deep convection [1]. During vertical transport, large amounts of these VOCs may be trapped in supercooled droplets that subsequently freeze. However, whether the organic species are trapped in the bulk or rejected at the gas-ice interface during freezing is still unclear and could lead to different ice particle reactivity in the latter case (compared to pure ice). VOCs are also supposed to be easily released by rapid evaporation once in the UT [2, 3].

The behavior of supercooled droplets of dissolved volatile organic compounds during freezing, the determination of the subsequent crystalline structures formed and the mechanisms by which VOCs are trapped/released in the atmosphere is therefore critical to a better understanding of the creation of new ice particles and the characterization of their surface and reactivity properties.

In this study, two distinct ethanol aqueous solution droplets ($(X_{EtOH})_L = 8.7 \text{ wt } \% \text{ and } 46.5 \text{ wt } \%$) have been investigated by *in situ* Raman spectroscopy and X-ray diffraction between 253 and 188 K. This temperature range has been extended down to 88 K to explore the phase diagram and the behavior below T_g in order to compare with previous work focused on organic compounds of higher molecular weights [4].

Depending on the initial EtOH content, it is proposed that the particle results in a complex structure formed with a supercooled layer of relatively high ethanol content at the liquid/gas interface or with an ethanol hydrate and a supercooled layer of high ethanol content. Each case depends on temperature trajectories and may have the potential to impact several atmospheric processes in comparison to the pure ice case.

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[2] Kerbrat, M. et al., *J. Phys. Chem. A*, **111**, 925 (2007).

[3] Petitjean, M. et al., *J. Phys. Chem. A*, **113**, 5091 (2009).

[4] Zobrist, B. et al., *Atmospheric Chemistry and Physics*, **8**, 5221 (2008).