

# Spectroscopy of PAHs to Determine Speciation in Various Environments

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It is well known that polycyclic aromatic hydrocarbons (PAHs) are abundant in the atmosphere (and even in the interstellar space), where they can react and be transported to long distances or deposited on, for example, the surface of water or ice. Some of the PAHs and their metabolites are widely recognized as being among the toxic, carcinogenic, and mutagenic (atmospheric) contaminants; such a fact stresses the importance of defining their fate in the environment.

When the atmospheric temperature drops below 0 °C, water along with other species present in the atmosphere can freeze and, subsequently, melt upon heating. When water freezes, crystals of pure Ih ice are formed, and all other impurities concentrate in the veins between the ice crystals. There, the impurities can be concentrated to interact together. It has been proven that the type of freezing (fast or slow) potentially leads to a different composition of the veins, which naturally affects the behaviour of the impurities therein.

We utilized the known spectroscopies of some of the simplest PAHs (such as benzene, naphthalene, anthracene, and their derivatives) to study the aggregation and speciation of organic impurities on/in ice [1]. The speciation of the impurities in the veins can play a key role in the availability (accessibility) on/in ice [2]. To understand the process of freezing of water with impurities and vein formation, a series of spectroscopic analyses were performed using 1-methylnaphthalene (MeNp) as a model compound.

Freezing of fresh water solution of MeNp enabled the crystallization of MeNp, while freezing of sea water led to the vitrification of MeNp. Furthermore, the role of individual salts of sea water and was examined. Moreover, the freezing method can effect the speciation of MeNp between ice crystals. While spontaneous freezing led to the vitrified form of MeNp, freezing initiated by adding the ice crystals to the undercooled solutions enabled the crystallization of MeNp.

Overall, our results suggest that the various freezing rates can lead to different composition of the veins between the ice crystals, affecting the impurities therein [3]; such an effect exerts an impact on the subsequent behaviour of the impurities during the freezing-melting cycles. Our research has stressed the importance of understanding the freezing process and the formation of the veins, thus elucidating the environmentally relevant freezing and melting processes.

1. Zezula, J., et al., *Distinguishing the glass, crystal, and quasi-liquid layer in 1-methylnaphthalene by using fluorescence signatures*. Journal of Luminescence, 2023. **261**.
2. Zobrist, B., et al., *Ultra-slow water diffusion in aqueous sucrose glasses*. Physical Chemistry Chemical Physics, 2011. **13**(8): p. 3514-3526.
3. Ondrušková, G., et al., *Using Excimeric Fluorescence to Study How the Cooling Rate Determines the Behavior of Naphthalenes in Freeze-Concentrated Solutions: Vitrification and Crystallization*. The Journal of Physical Chemistry B, 2020. **124**(46): p. 10556-10566.