Low Temperature Mixing of Polar Hydrogen Bond Forming Molecules in Amorphous Solid Water (ASW)

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Understanding the mixing of atoms and molecules in amorphous solid water (ASW) at low temperatures is of interest and relevance to model studies of photochemistry that take place in the interstellar medium (ISM). In this study we explore how the physical properties of guest molecules (polarity, hydrogen bonding capabilities) affect their level of mixing and distribution within thin films of ASW deposited on a Ru(0001) substrate under ultrahigh vacuum (UHV) conditions and at low temperatures of 35 – 100 K[1]. Methanol and ammonia were chosen as guest molecules that interact strongly with water. Both guest molecules have similar gas phase dipole moments to that of water and can form hydrogen bonds with water.

Here, the extent of mixing and distribution of methanol and ammonia in ASW films is investigated by using a Kelvin probe to conduct non-invasive isothermal contact potential difference (ΔCPD) measurements and temperature programmed contact potential difference experiments (TP-ΔCPD). The adsorption temperature affects the extent to which the guest molecules are dispersed throughout the ASW film. Upon adsorption at 35 K, both methanol and ammonia form hydrogen bonds with surrounding water molecules at the guest molecule/ASW interface but do not migrate far from their initial location in the ASW film. This is confirmed by the observation of the "inverse volcano" process for the first time, in which guest molecules migrate towards the substrate upon water crystallization rather than desorb to the vacuum as in a typical "volcano" process. The efficiency of the "inverse volcano" process is affected by the initial location of the guest molecules (close to the substrate, middle layer or on top of the ASW film), which indicates that at this temperature (35 K) the guest molecules form a distinct layer within the ASW film. At increased adsorption temperatures, the methanol and ammonia become more homogenously distributed throughout the ASW film. For methanol, extensive mixing is achieved only upon adsorption at 100 K, while ammonia is already extensively mixed upon adsorption at 70 K. The temperatures at which full mixing is observed are correlated with phase transitions in the guest molecules, namely glass transition and crystallization temperatures. Homogenous (complete) mixing is only obtained when the films are heated above the glass transition temperature of the host molecules, which for water is 136 K.

[1] Michelle Akerman*, Roey Sagi and Micha Asscher, Low Temperature Mixing of Polar Hydrogen Bond Forming Molecules in Amorphous Solid Water (ASW), *J. Phys. Chem. C* **(2022)**, https://doi.org/10.1021/acs.jpcc.2c00877.