Composition-Dependent Clathrate Hydrate Formation of Trimethylene Oxide and Consequences of Dissociation

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The influence of molecular ice composition on the structure of clathrate hydrate (CH) in ultrahigh vacuum (UHV) conditions is unprecedented. This study investigates the formation of structure I (sI) and structure II (sII) CH of Trimethylene oxide (TMO) by changing the concentrations of TMO within a water ice matrix, maintaining consistent temperature and pressure conditions. TMO and water ice mixtures, with ratios of 1:1 and 1:5 is co-deposited on Ru(0001) substrate at 10 K then thermally anneal to 135 K.

At elevated temperatures, the $5^{12}6^2$ cage of sI CH is predominantly occupied by TMO in the 1:1 mixture, whereas the $5^{12}6^4$ cage of sII CH is favored in the 1:5 mixture (see Figure 1).[1] SI CH exhibits greater stability at higher temperatures compared to sII CH. Notably, the dissociation of CH has differing effects on amorphous solid water (ASW) depending on the CH structure. Dissociation of structure II CH facilitates the conversion of ASW to hexagonal ice, a phenomenon not observed in structure I CH, where ASW remains amorphous even after CH dissociation.This distinct behavior is attributed to the composition of ice. The ability of host TMO molecule to form hydrogen bond with water within the $5^{12}6^2$ cage, an interaction absent within the relatively larger $5^{12}6^4$ cage. The nonplanar conformation of hydrogen-bonded TMO becomes planar after cage dissociation and does not desorb completely, as evidenced by RAIRS studies. The presence of this small amount of TMO inhibits the hexagonal ice formation. This study demonstrates that CH can both inhibit and induce the crystallization of water ice, with sI CH inhibiting crystallization while sII CH represents dissociation-induced crystallization.

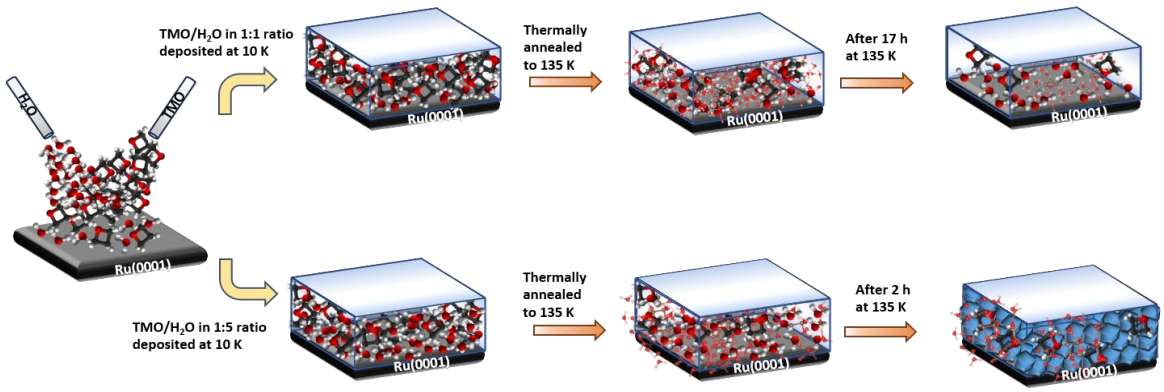

Figure 1: Schematic diagram of the formation and dissociation of TMO CHs.

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[1] Buch, V.; Devlin, J. P.; Monreal, I. A.; Jagoda-Cwiklik, B.; Uras-Aytemiz, N.; Cwiklik, L. Clathrate Hydrates with Hydrogen-Bonding Guests. *Phys. Chem. Chem. Phys.* **2009**, *11* (44), 10245– 10265.