

# Probing the interaction of amorphous solid water on a hydrophobic surface: dewetting and crystallization kinetics of ASW on carbon tetrachloride

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# Introduction:

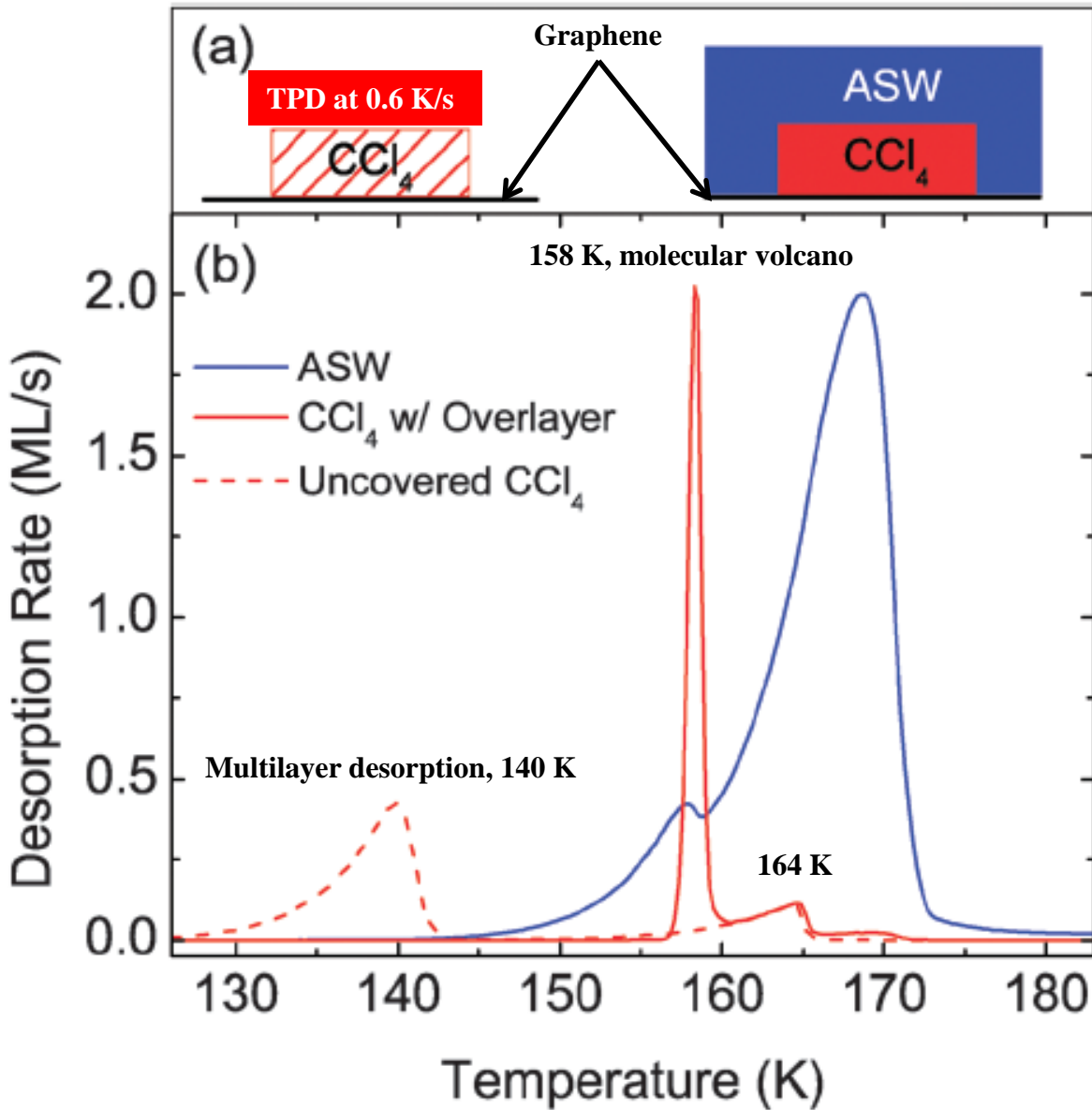
- Water is fundamental to a staggering array of processes ranging across various disciplines.
- Interest in water stems from its ubiquity and numerous, often anomalous, properties such as the apparent oxymoron of hydrophobic ice.
- Amorphous solid water (ASW) which forms when water is vapor deposited below 130 K in vacuum, is kinetically metastable and transforms to a thermodynamically stable crystalline phase upon heating.
- The interaction of water with a hydrophobic surface is important for understanding many industrial and biological processes.
- The canonical wisdom is that water on a hydrophobic surface clusters to form structures that maximize the number of hydrogen bonds, thus lowering the overall energy of the system.
- While exact determination of the energetics of ASW interaction with  $\text{CCl}_4$  is difficult, the formation of water clusters is expected because bulk water has a surface energy approximately three times that of  $\text{CCl}_4$ .
- Temperature programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS) are used to probe the structure and crystallization kinetics of water deposited on  $\text{CCl}_4$  layers.
- Water deposited at low temperatures appears to “wet” the hydrophobic surface whereas at higher temperatures the deposited water clearly dewets from  $\text{CCl}_4$ .
- The “molecular volcano” arises from the sudden episodic release of an immiscible underlayer,  $\text{CCl}_4$ , due to the formation of cracks through a crystallizing amorphous solid water overlayer.

# Experimental section:

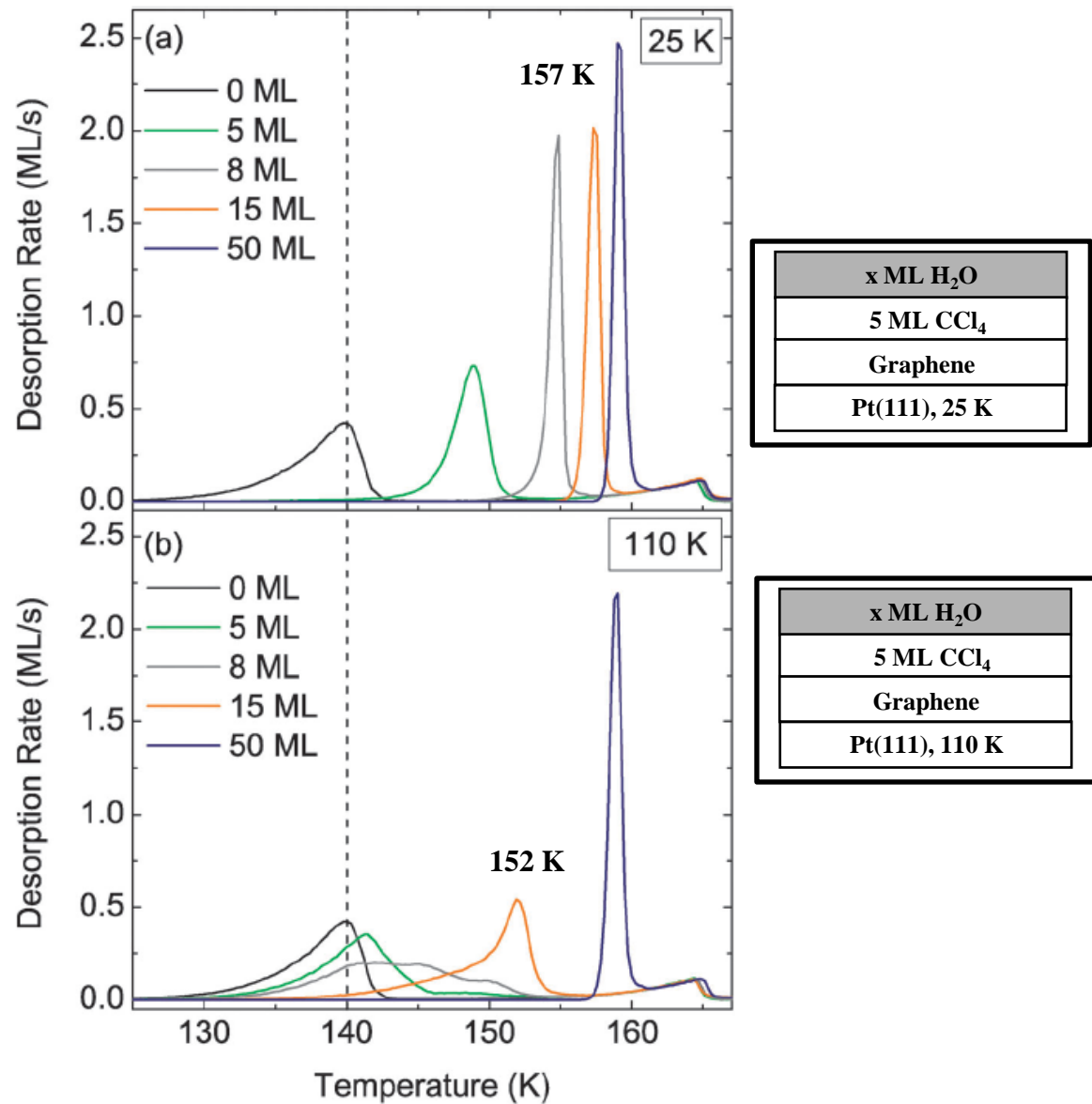
- Experiments were performed in an ultra high vacuum system (UHV) with a base pressure of  $1 \times 10^{-10}$  Torr and the base temperature is 25 K.
- The substrate is Pt(111).
- The Pt(111) substrate was cleaned by Ne<sup>+</sup> ion sputtering at 1.5 keV followed by O<sub>2</sub> exposure and subsequent UHV annealing at 1000 K.
- After cleaning and annealing, graphene was deposited by heating the Pt(111) substrate to 1100 K in the presence of decane, resulting in a single layer of carbon with graphene structure.

# Results:

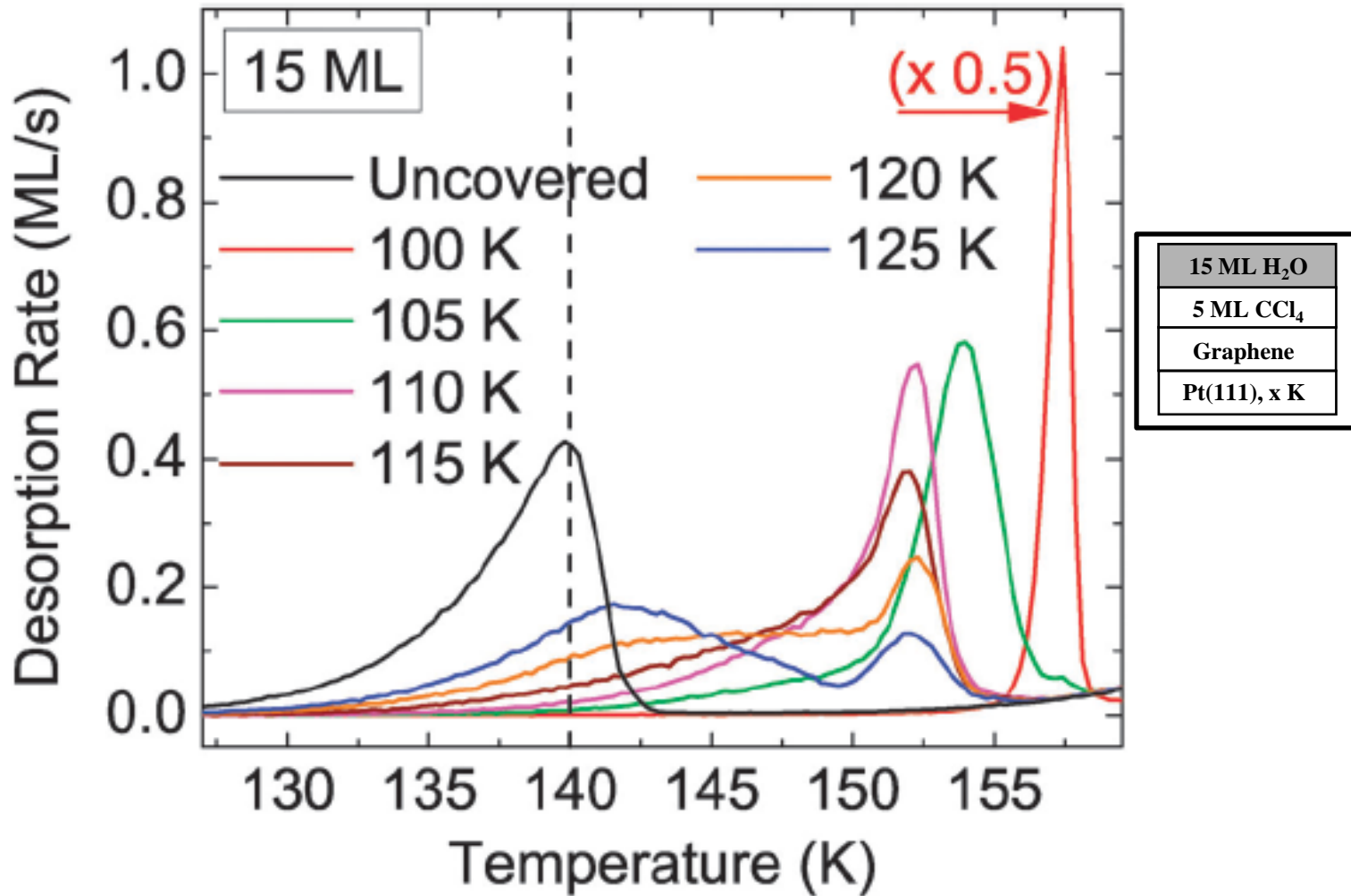
Origin of molecular volcano



(a) Schematic of two desorption experiments shown below. (b) Temperature programmed desorption of 5 ML CCl<sub>4</sub> (dashed red line) deposited on graphene and 5 ML CCl<sub>4</sub> (solid red line) with a 30 ML ASW overlayer (solid blue line).

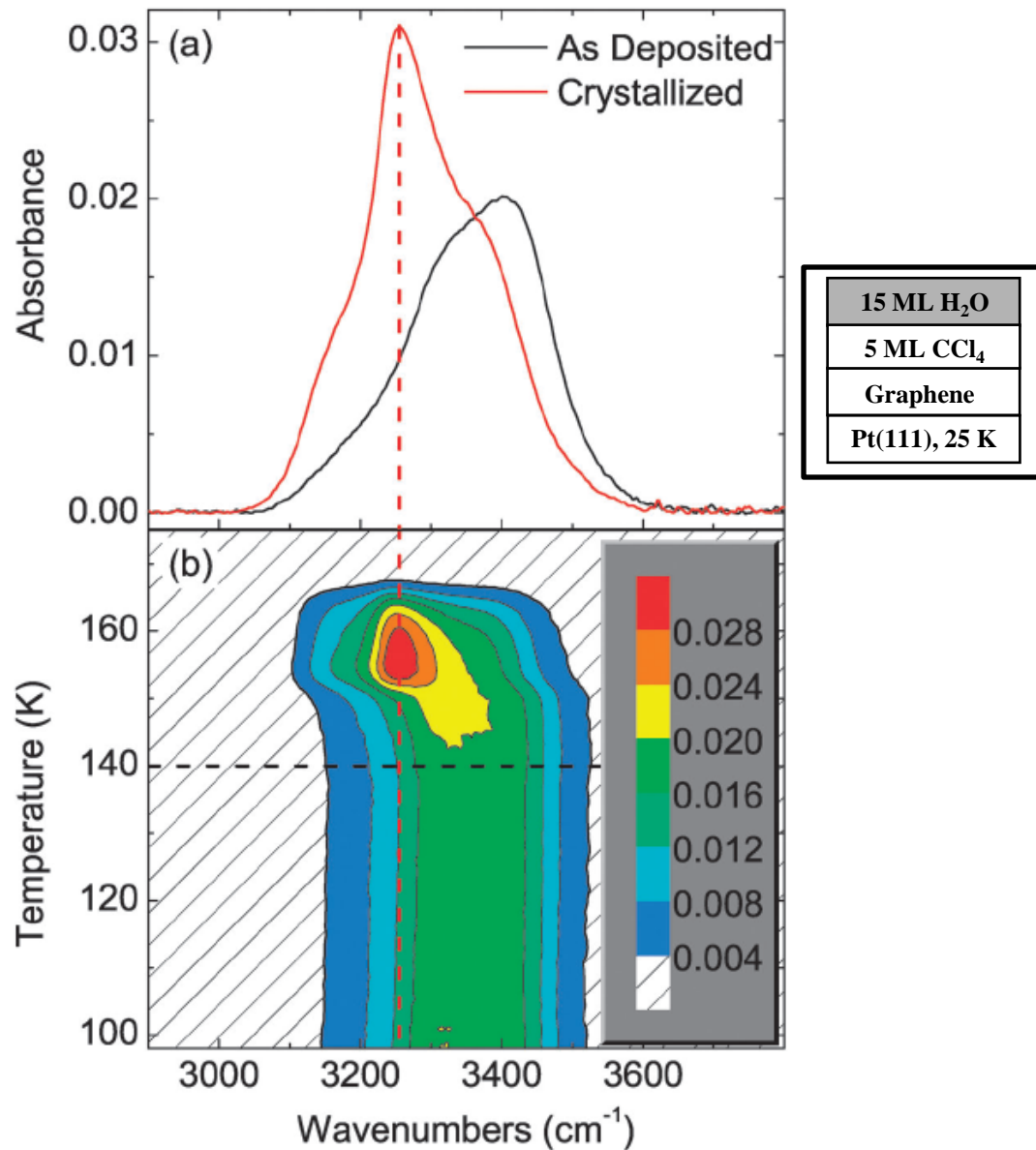


TPD spectra of 5 ML CCl<sub>4</sub> desorption from a graphene surface as a function of ASW overlayer thickness at an ASW deposition temperature of (a) 25 K and (b) 110 K.



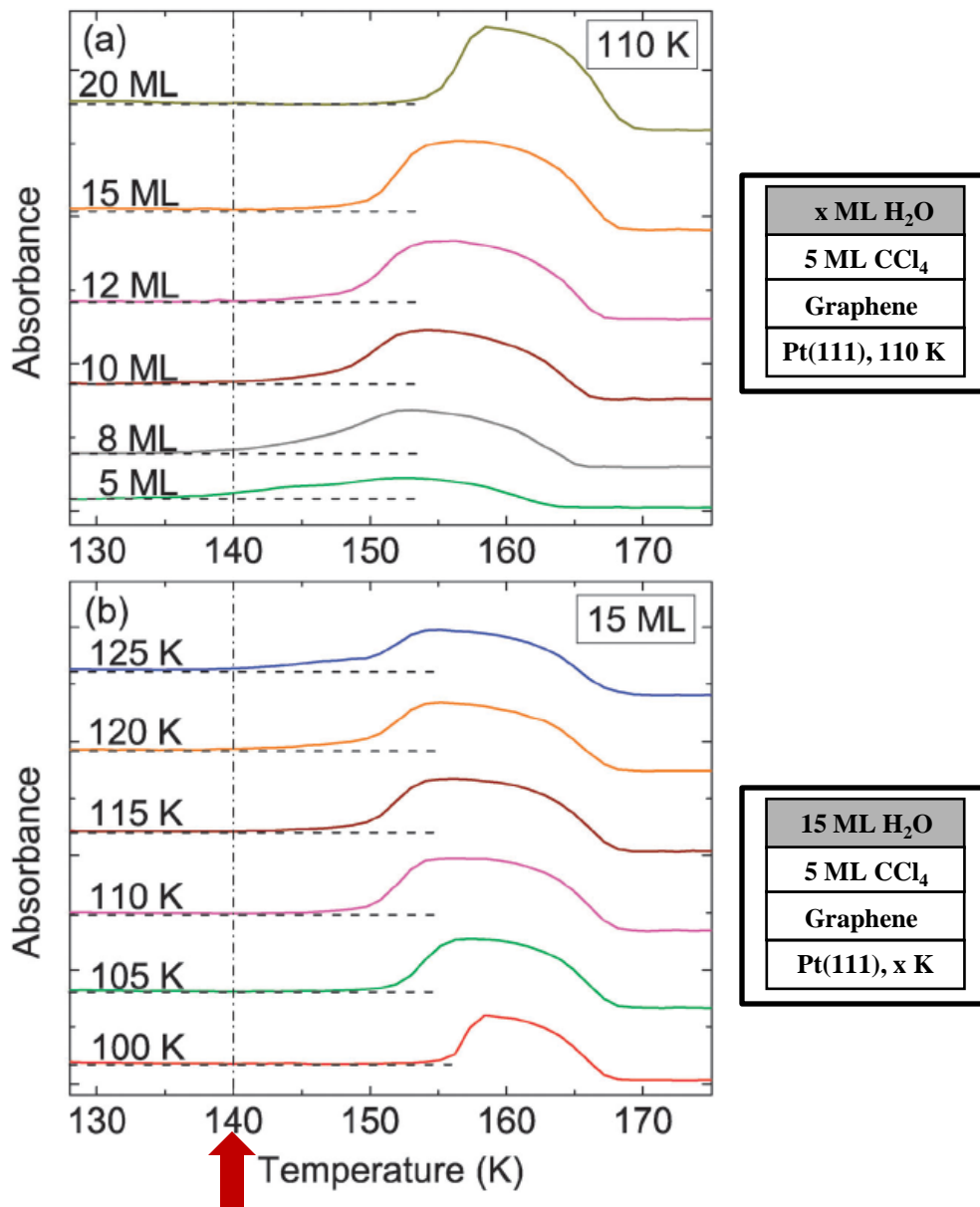
Desorption spectra of 5 ML of  $\text{CCl}_4$  covered with 15 ML of ASW at various ASW deposition temperatures.

# Infrared studies of ASW crystallization



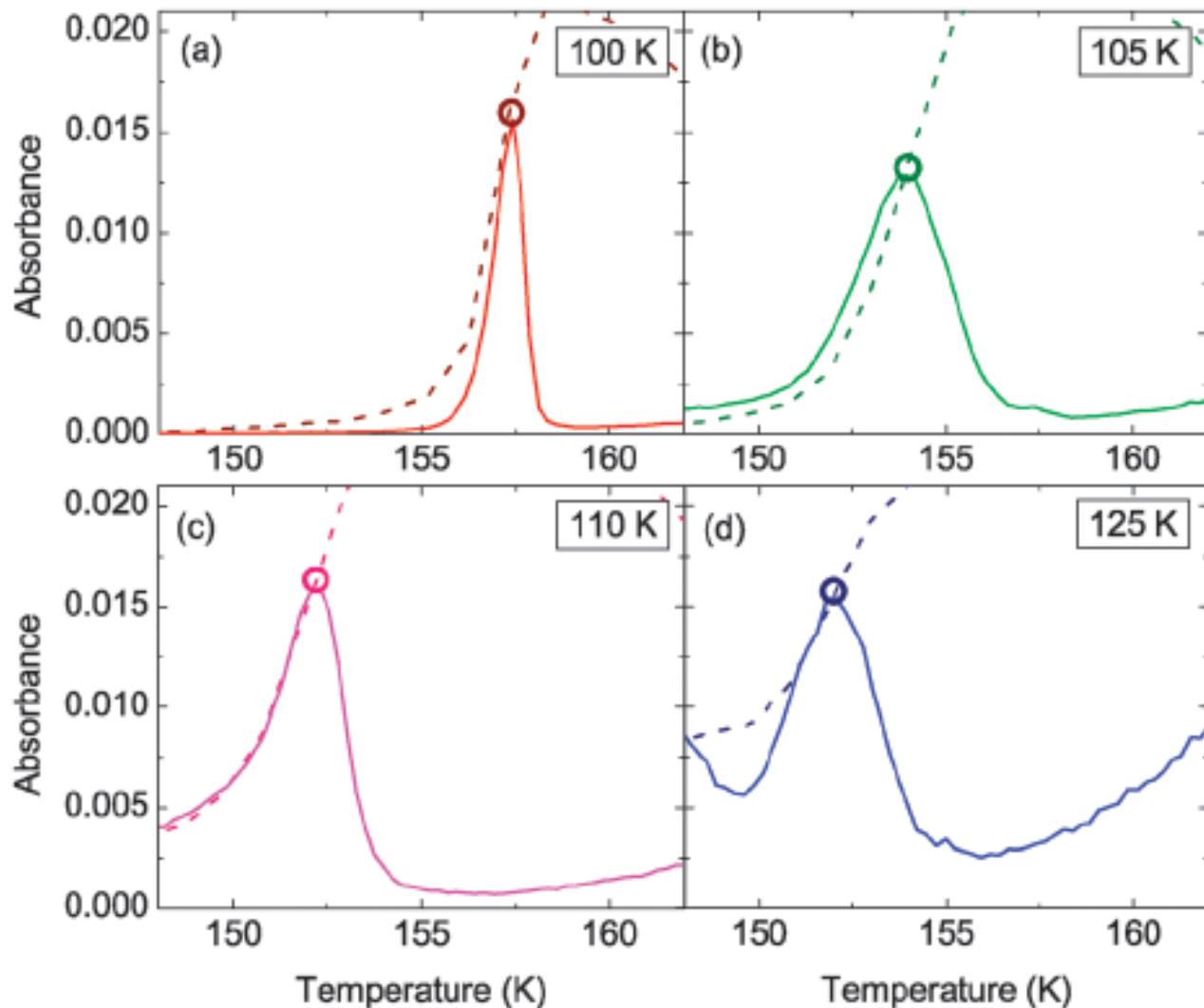
(a) IR spectra of a 15 ML ASW film deposited at 25 K (black line) and after heating (red line) to 160 K. The growth of a peak at  $3247 \text{ cm}^{-1}$  indicates water crystallization. (b) Contour plot of infrared spectra taken during TPD at  $0.6 \text{ K/s}$  of a 15 ML water overlayer deposited at 110 K.

**The formation of crystalline nuclei at higher deposition temperatures, so called pre-seeding, which leads to the earlier onset of crystallization.**



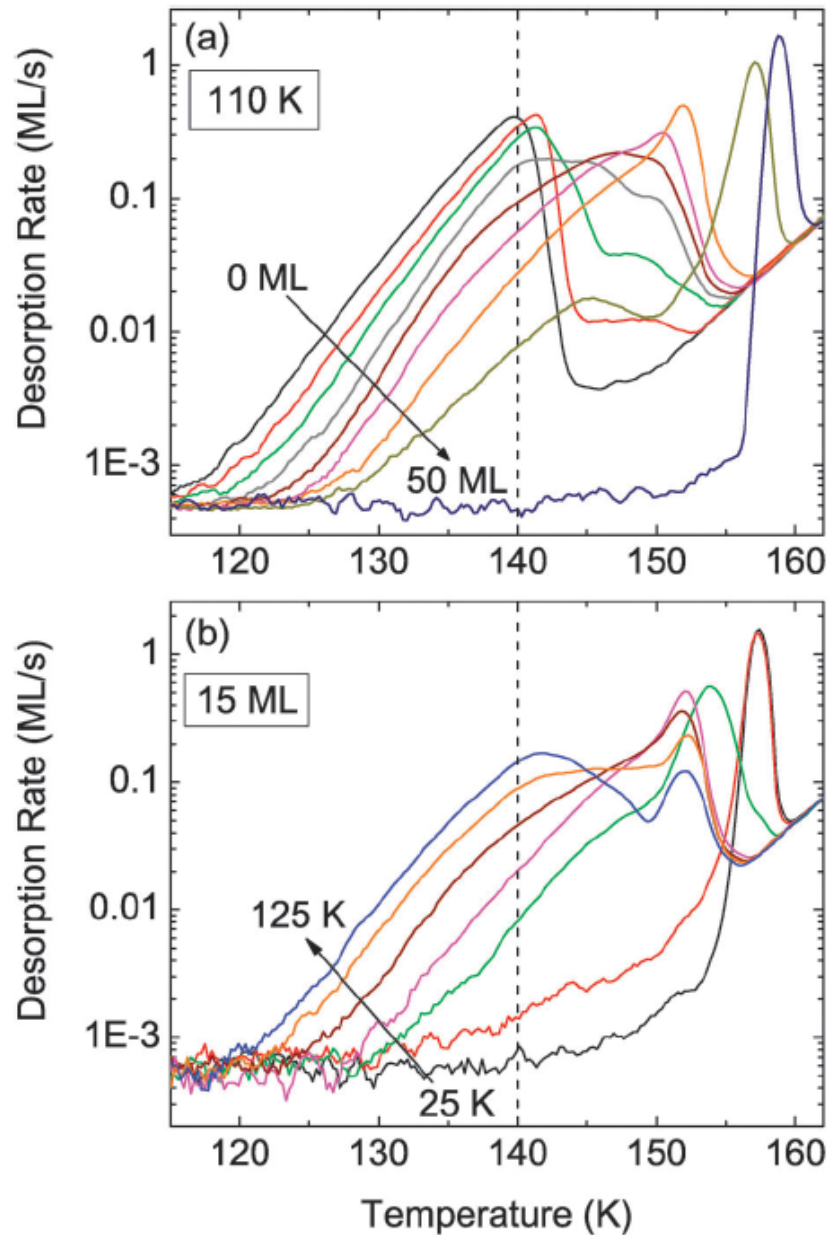
Cuts through FTIR spectra at  $3247\text{ cm}^{-1}$  during TPD at a rate of  $0.6\text{ K/s}$  for (a) H<sub>2</sub>O overlayers from 5 ML to 20 ML deposited at 110 K and (b) 15 ML ASW overlayer deposited at temperatures ranging from 100 K to 125 K.



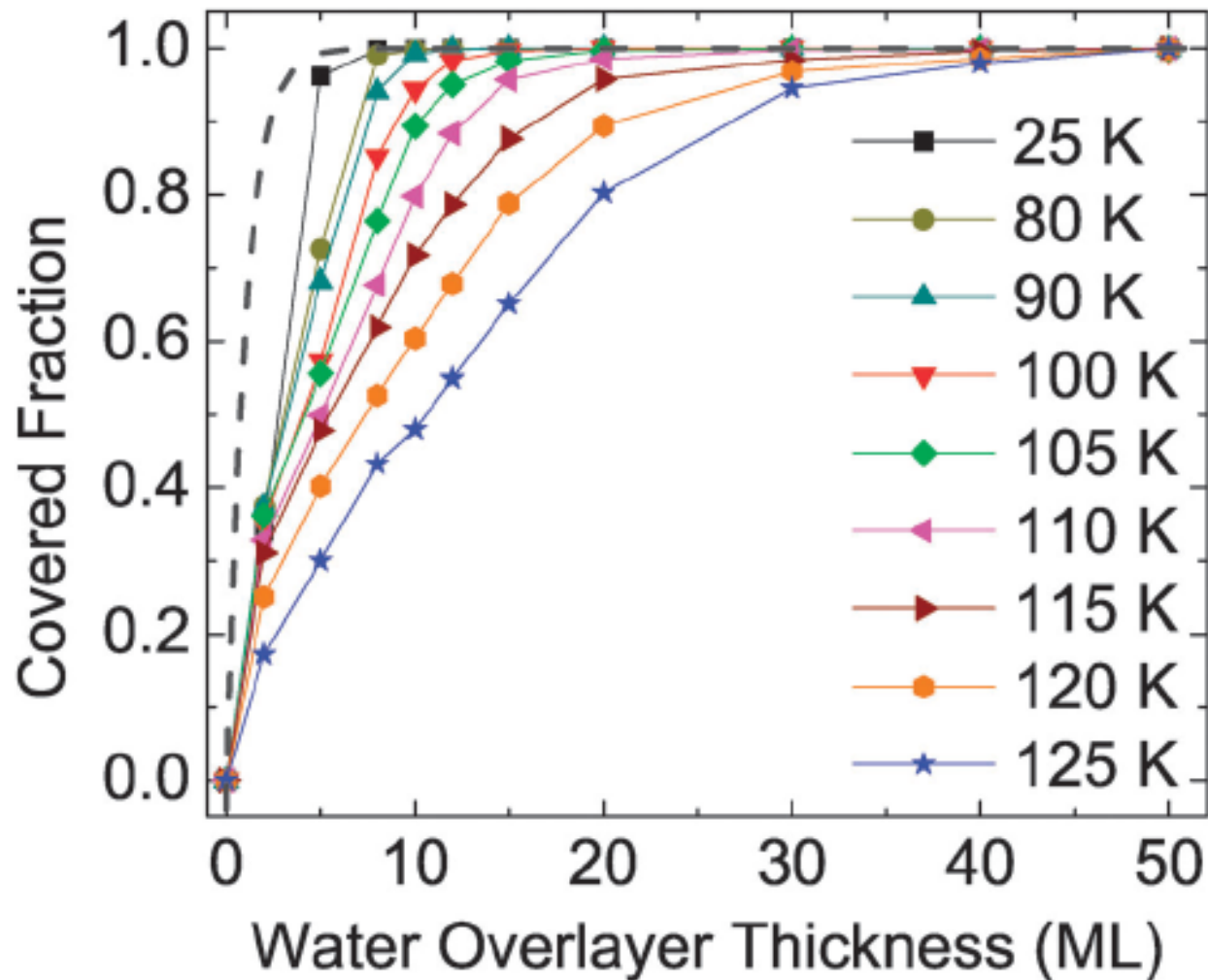


RAIRS traces at  $3247\text{ cm}^{-1}$  (dashed lines) and TPD spectra (solid lines) of 15 ML ASW overlayers crystallizing during TPD at  $0.6\text{ K/s}$ . Circles indicate the peak of the molecular volcano, for each temperature the volcano release occurs after the infrared absorbance has increased to  $0.015 \pm 0.001$ .

# Dewetting of ASW on a hydrophobic $\text{CCl}_4$ substrate



Log plots of  $\text{CCl}_4$  desorption in the dewetting region during TPD at 0.6 K/s for 5 ML  $\text{CCl}_4$  on graphene with (a) ASW overlayers of 0, 2, 5, 8, 10, 12, 15, 20, and 50 ML deposited at 110 K and (b) 15 ML ASW overlayer with deposition temperatures of 25, 100, 105, 110, 115, 120, and 125 K.



Relative amount of  $\text{CCl}_4$  covered by ASW as a function of water overlayer thickness and deposition temperature as derived from desorption of  $\text{CCl}_4$  at 135 K during TPD at a ramp of 0.6 K/s. The dashed black line corresponds to random deposition of the ASW overlayer.

## Summary & conclusion:

- ASW with the hydrophobic  $\text{CCl}_4$  surface depends on both the amount of ASW deposited and the deposition temperature.
- At low deposition temperatures ASW can kinetically “wet” the hydrophobic  $\text{CCl}_4$  layer.
- However, as the deposition temperature is increased adsorbing water molecules become more mobile and are able to adopt a lower-energy dewetted structure.
- Two distinct desorption regimes of  $\text{CCl}_4$  covered by an ASW overlayer have been determined through a combination of TPD and RAIRS.
- Dewetting occurs at various combinations of low  $\text{H}_2\text{O}$  coverage and high deposition temperatures resulting in a mixture of free and overlayer restricted  $\text{CCl}_4$  desorption.
- Eruption of the volcano is directly correlated to the crystallization of the ASW overlayer and crystallization is dependent upon the ASW thickness and deposition temperature.

**Thank you**