# The Molecular Volcano Revisited: Determination of Crack Propagation and Distribution During the Crystallization of Nanoscal Amorphous Solid Water Films


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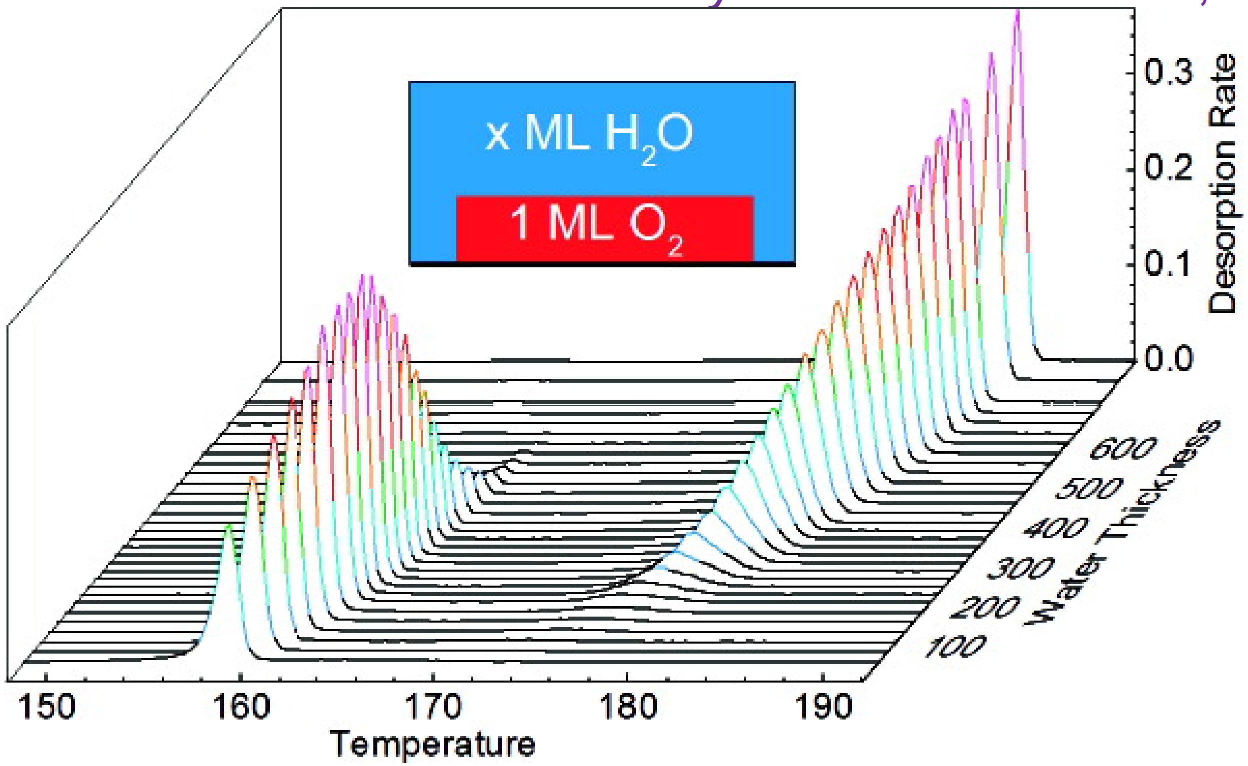


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# Introduction

❖ Amorphous solid water (ASW) is a kinetically metastable form of water formed when $H_2O$ impinges on a surface cooled below 130 K, and is the most abundant form of $H_2O$ in the universe.

❖ ASW forming on grains of dust in the interstellar medium (ISM) may play an important role in the formation and collection of molecules that are essential to an array of astrophysical processes.

❖ The trapping of $O_2$ by ASW may be of paramount importance to explaining the low abundance of molecular oxygen detected in the ISM and why significant quantities have been detected only in relatively warm regions of the Orion nebula.

❖ Temperature programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS) are utilized to understand how the crystallization of ASW leads to the release of O2.

# Experimental section

❖ Experiments were performed on a 1-cm diameter Pt(111) substrate cooled to a base temperature of ∼20 K in an ultrahigh vacuum system (UHV), with a base pressure of <1 × $10^{-10}$ Torr.

❖Graphene was deposited by heating the Pt(111) substrate to 1100 K in the presence of decane.

❖The species $O_2$ and $H_2O$ were deposited at normal incidence via quasi-effusive molecular beams.

❖ TPD spectra were collected at a ramp rate of 1 K/s utilizing an Extrel quadrapole mass spectrometer monitoring at m/z = 18 for $H_2O$ and m/z = 32 for $O_2$.

❖ Infrared spectra were acquired with a Bruker Equinox 55 at an 82° ± 1° angle of incidence utilizing a mercury cadmium telluride (MCT) detector.

# Result and Discussion

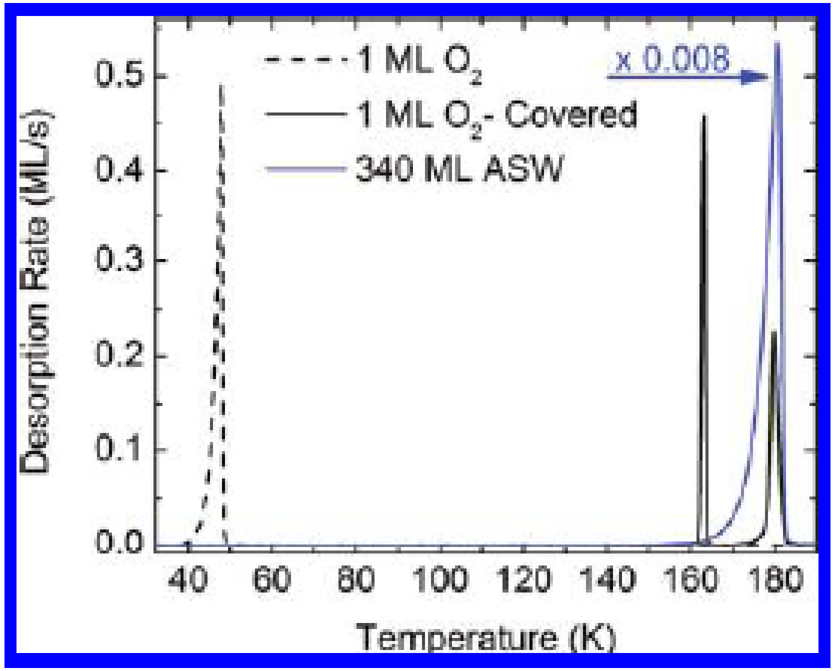
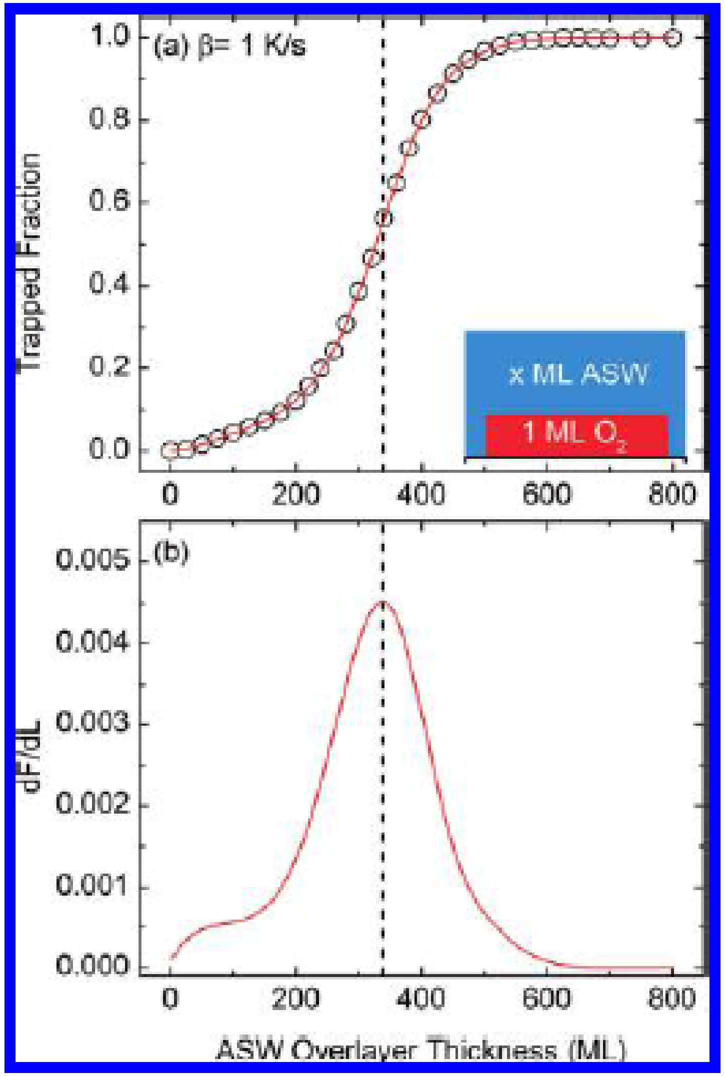



**Figure 1.** (a) TPD of 1 ML $O_2$ from graphene (dashed line) and 1 ML of $O_2$ covered by 340 ML ASW (black line). Also shown is the water TPD (blue line).




$$F(L) = 1 - \Sigma A_i e^{-(L/\Lambda_i)^{n_i}}$$

**Figure 2.** (a) Fraction of 1 ML $O_2$ trapped (○) versus increasing ASW coverage for a series of TPD. (b) The derivative of the sigmoid (-) in (a) gives the distribution of vertical crack lengths formed during the crystallization of ASW.

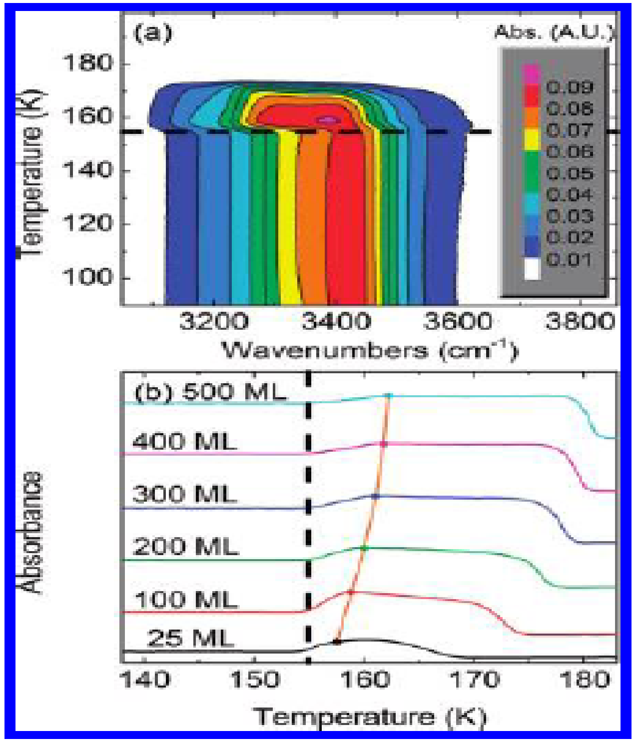



Figure 3. (a) Contour plot of the OH stretch region for 100 ML ASW ramped to 200 K at 1 K/s. (b) Frequency cuts through RAIRS spectra at different ASW overlayer thicknesses, peak of volcano eruption marked by a dot.

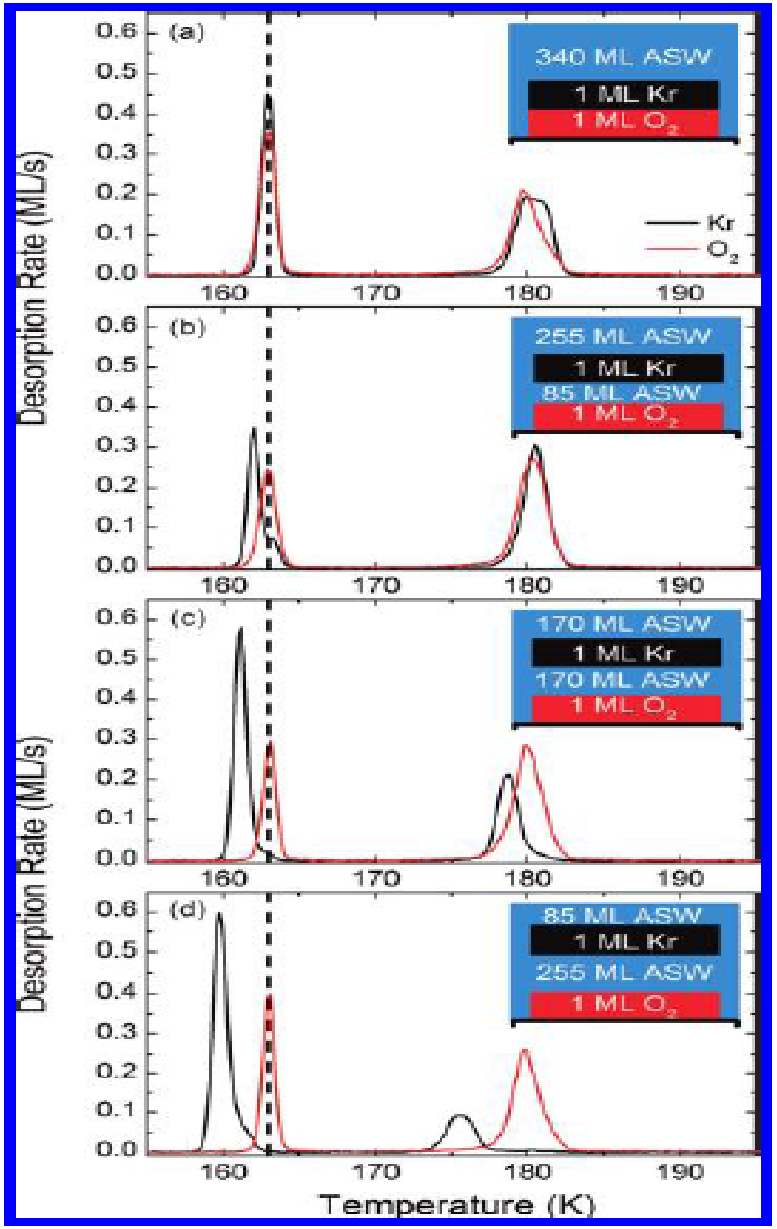



Figure 4. Series of TPD spectra for 1 ML $O_2$ covered by 340 ML of ASW and 1 ML of Kr placed at various locations in the overlayer. In (a) the Kr and $O_2$ are below 340 ML of ASW, while the layers are separated by 85 ML ASW in (b), 170 ML in (c), and 255 ML in (d).

# Conclusion

❖ Two distinct desorption regimes of $O_2$ covered by ASW have been defined, one corresponding to crystallization-induced cracking known as the "molecular volcano", and a second higher temperature peak that corresponds to $O_2$ trapped beneath the $H_2O$ layer after crystallization.

❖ Monitoring the degree of trapping as a function of ASW overlayer thickness allowed to determine the vertical length distribution of cracks formed through ASW during crystallization.

❖ Additionally, utilizing a combination of RAIRS and TPD measurements, cracks were shown to originate at the ASW/vacuum interface.

❖ Understanding the mechanism for the release of trapped gases from ASW is crucial to modelling outgasing from various ices of current astrophysical interest.

# Future possibilities

- ❖ How the crack length distribution depends on factors such as the heating rate, underlayer composition, and underlayer thickness can be studied?

# THANK YOU