Thermal and Nonthermal Physiochemical Processes in Nanoscale Films of Amorphous Solid Water

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Introduction:

- Amorphous solid water (ASW) is a disordered form of ice created by vapor deposition onto a cold substrate (< 130 K).

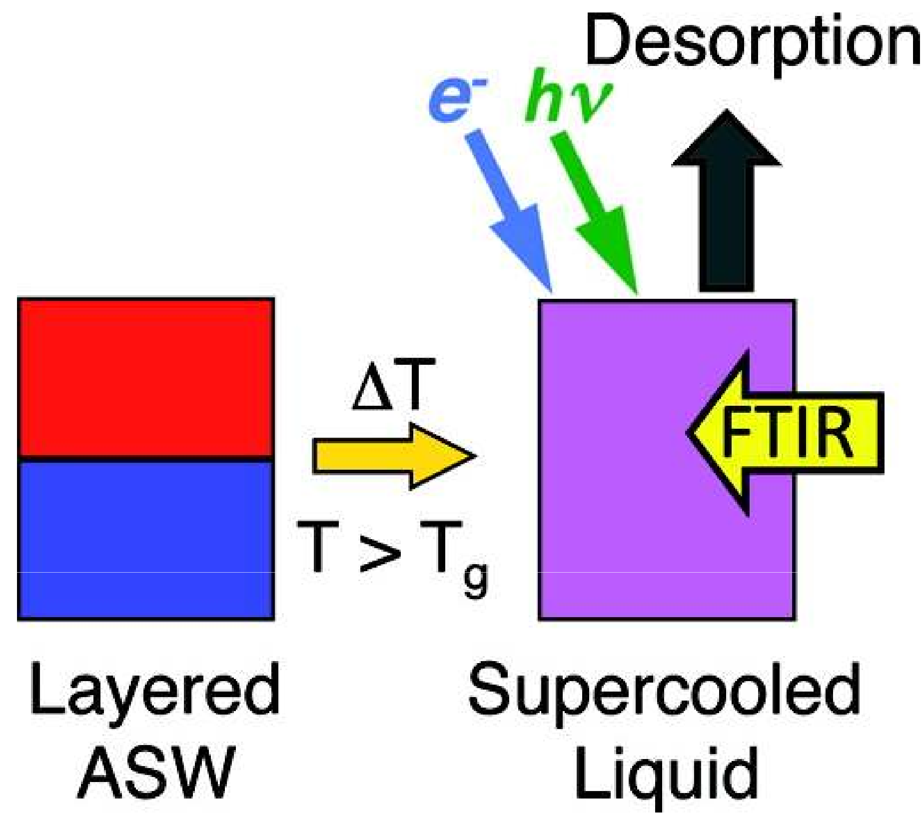
- ASW is a convenient model system for studying the stability of amorphous and glassy materials as well as the properties of highly porous materials.

- By using molecular beam technique it is possible to control the deposition conditions to create compositionally tailored, nanoscale films of ASW at low temperature.

- The use of nanoscale films allows to probe the physical and chemical properties of ASW films at temperatures near where they transform into deeply supercooled liquids prior to crystallization.

❖ In this account properties of ASW (thermal properties of ASW and non thermal reactions in ASW films) have been presented by using molecular beams and surface science technique.

❖ Experiments were conducted in UHV chamber.



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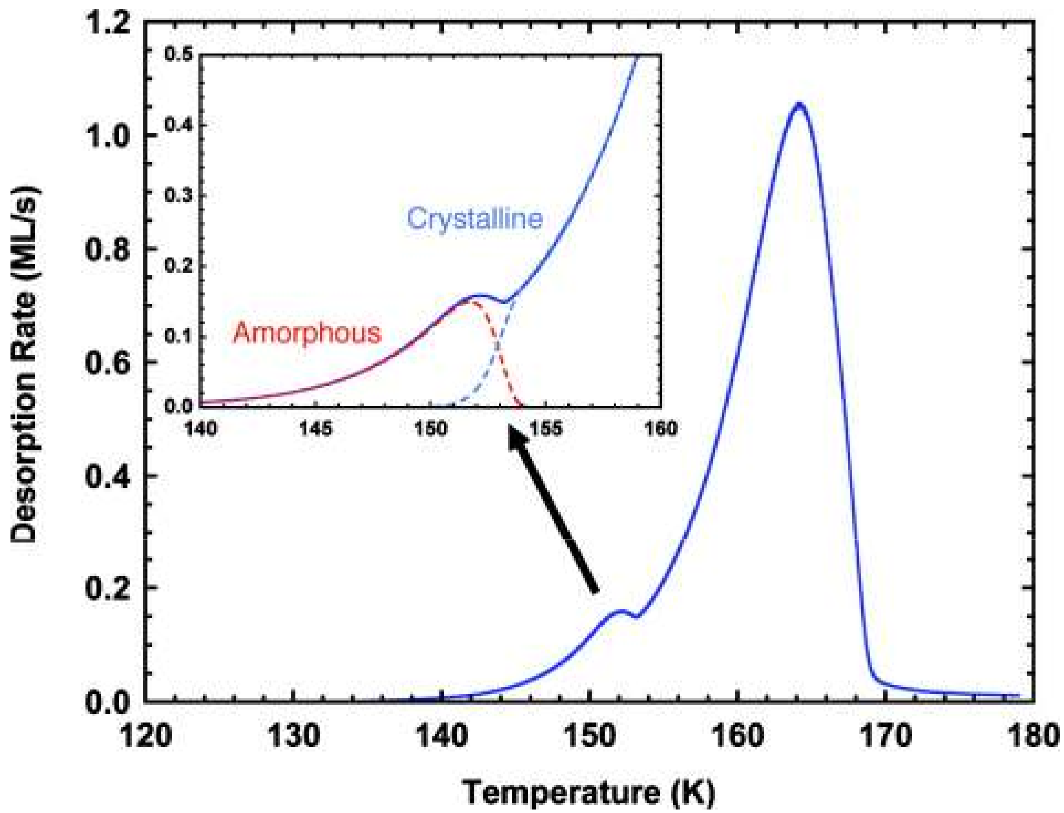
Thermal Properties of ASW:

A. Desorption and crystallization.



TPD spectrum from a 100 ML ASW film of H_2O deposited at normal incidence at 20 K on a Pt(111) substrate. The film was heated at 0.1 K/s.

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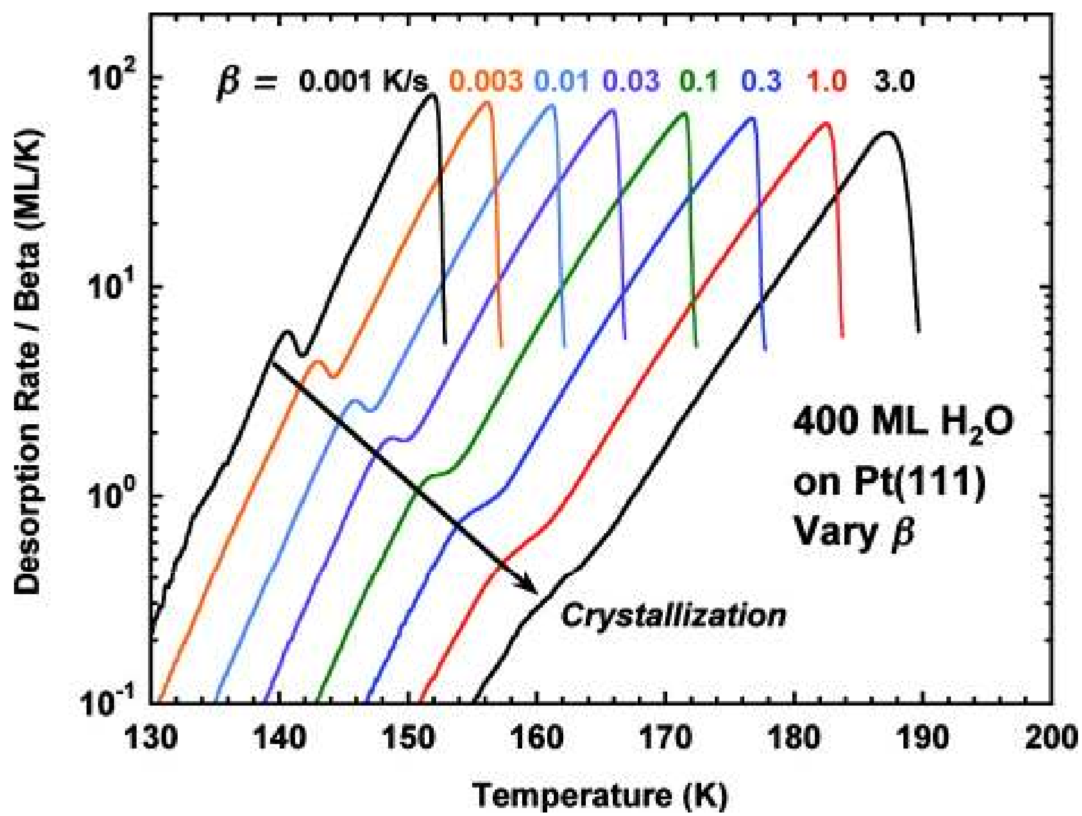

TPD spectra from 400 ML ASW films deposited at normal incidence and 20 K and then heated at various ramp rates. The spectra are plotted as the desorption rate (ML/s) divided by the ramp rate (K/s).

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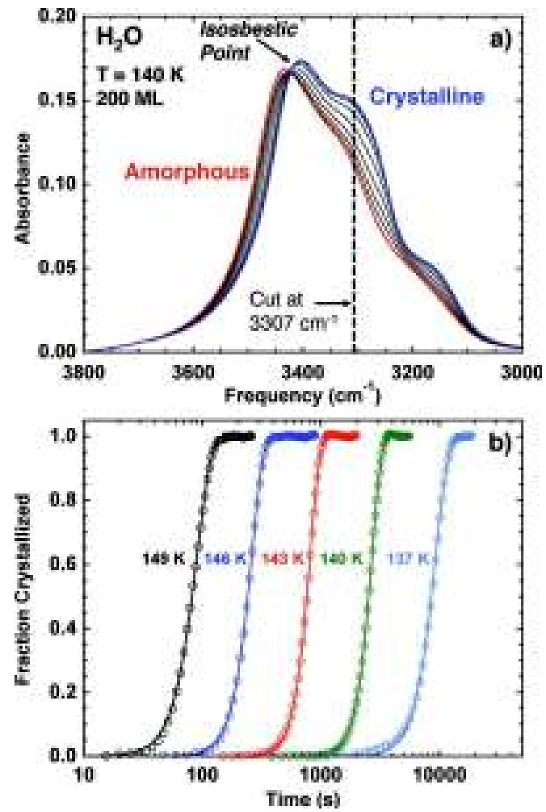
Avrami equation, $x(t) = 1 - \exp(-(kt)^n)$, where t is time, k is the phenomenological rate constant, and n is related to the crystallization mechanism. For all temperatures, the fit values of n were near 4.



(a) Time-resolved infrared spectra of the OH stretch region of a 200 ML film. The first spectrum (red) is from a completely amorphous film, and the last spectrum (blue) is from a crystallized film. (b) The fraction crystallized versus time for a series of 200 ML films (symbols) held at several isothermal temperatures.

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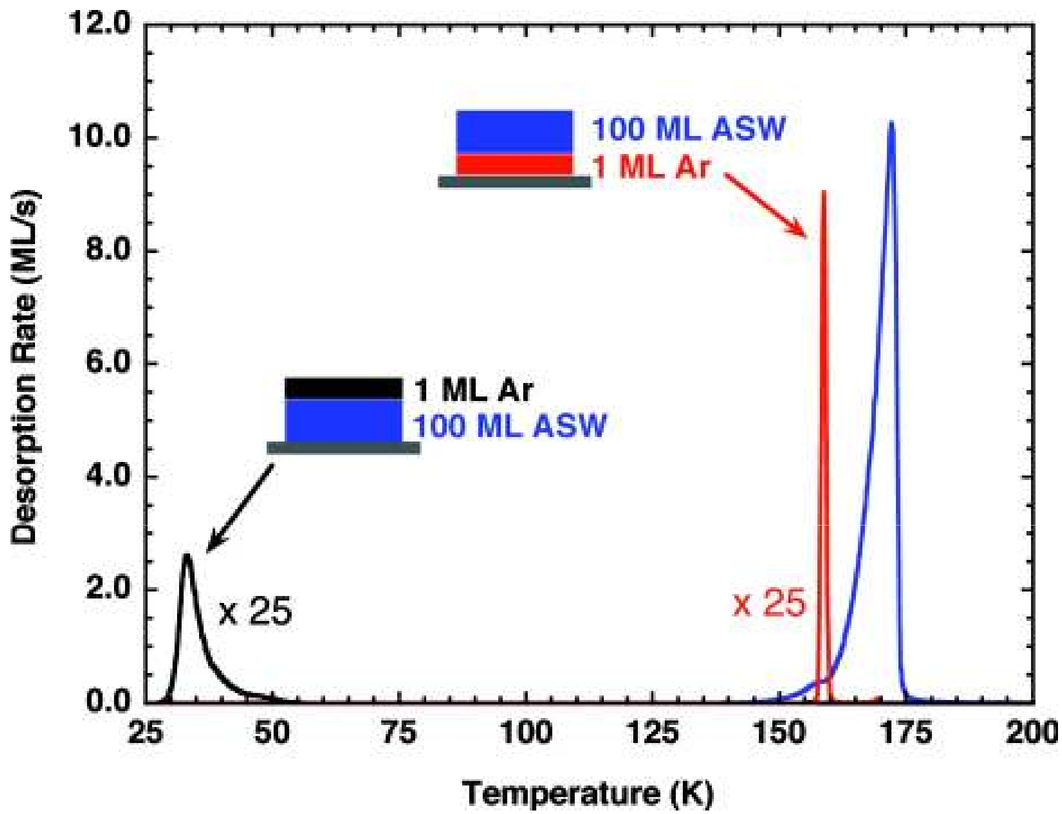
Crystallization of ASW can result in structural changes in the film…



TPD spectra for 1 ML of Ar deposited on top (black) and underneath (red) of 100 ML ASW (blue) films.

❖ The extent to which ices can trap and retain gases can be important in determining the chemical composition of astrophysical bodies.

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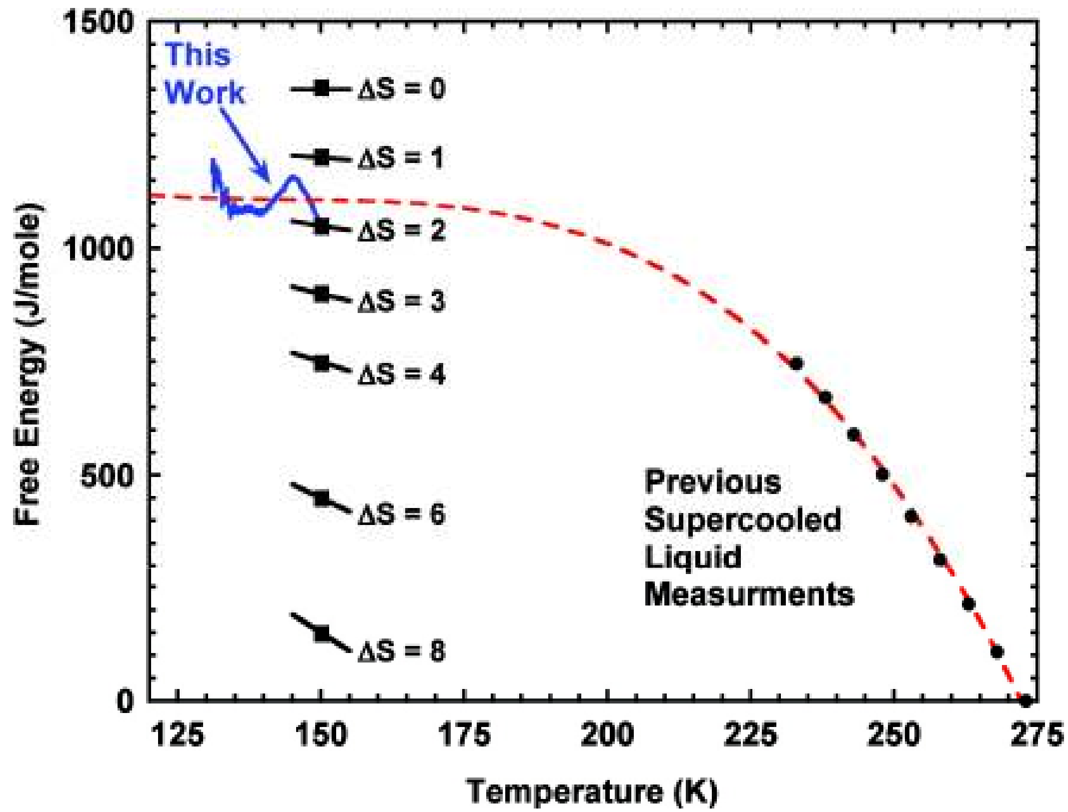
B. Free energy.

The free-energy difference between the amorphous and crystalline phases is given by $\Delta G = RT\ ln(rate_{amorphous}/rate_{crystalline})$.

Estimated free energy = 1100 ± 50 kJ/mol and the entropy = 1.6 ± 1 J/(mol K) at temperatures near 150 K.



The experimental excess free energy for ASW (blue line) calculated from the ASW and crystalline desorption rates and for supercooled liquid H_2O (circles) from the literature.

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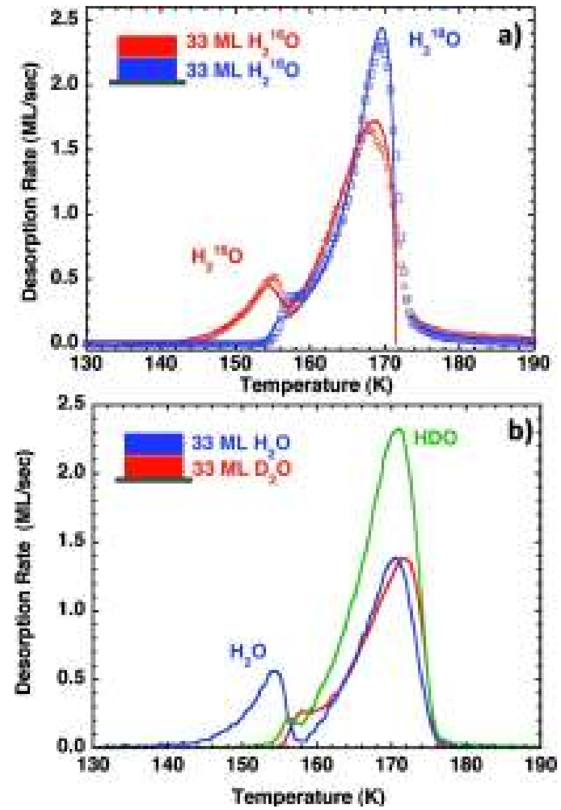
C. Diffusivity.

The extracted diffusivities range from ~1 × 10^{-15} cm2/s at 150 K to ~1 × 10^{-12} cm2/s near 160 K.



(a) TPD spectra from a composite film with 33 ML of $H_2{}^{16}O$ (○) on top of 33 ML of $H_2{}^{18}O$ (□). The lines are simulations using a one-dimensional diffusive transport model. (b) TPD spectra from a composite film of 33 ML of H_2O on top of 33 ML of D_2O.

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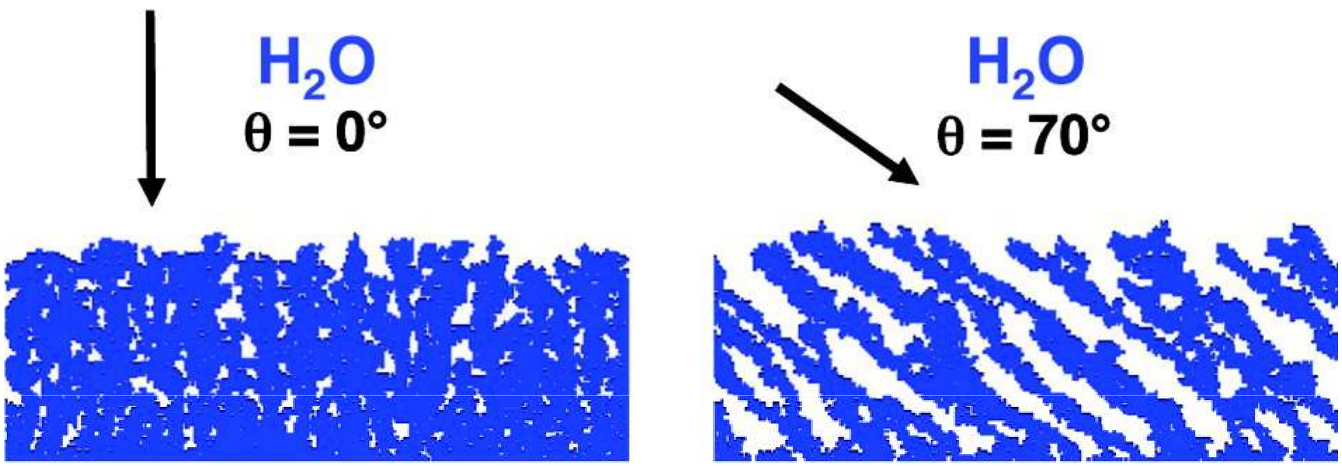
D. Morphology of ASW.



Ballistic deposition model simulations for the growth of ASW films at incident growth angles of 0°(left) and 70° (right).

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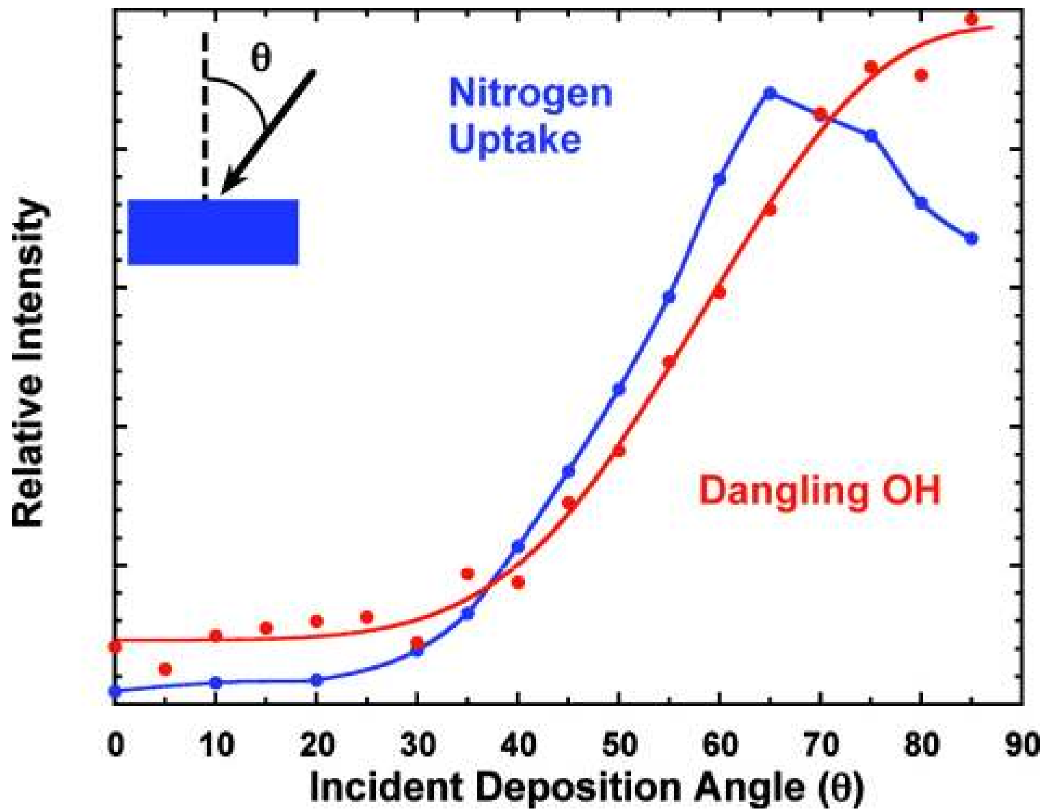

Nitrogen uptake (blue) and dangling OH bond intensity (red) for 100 ML ASW films deposited at various deposition angles.

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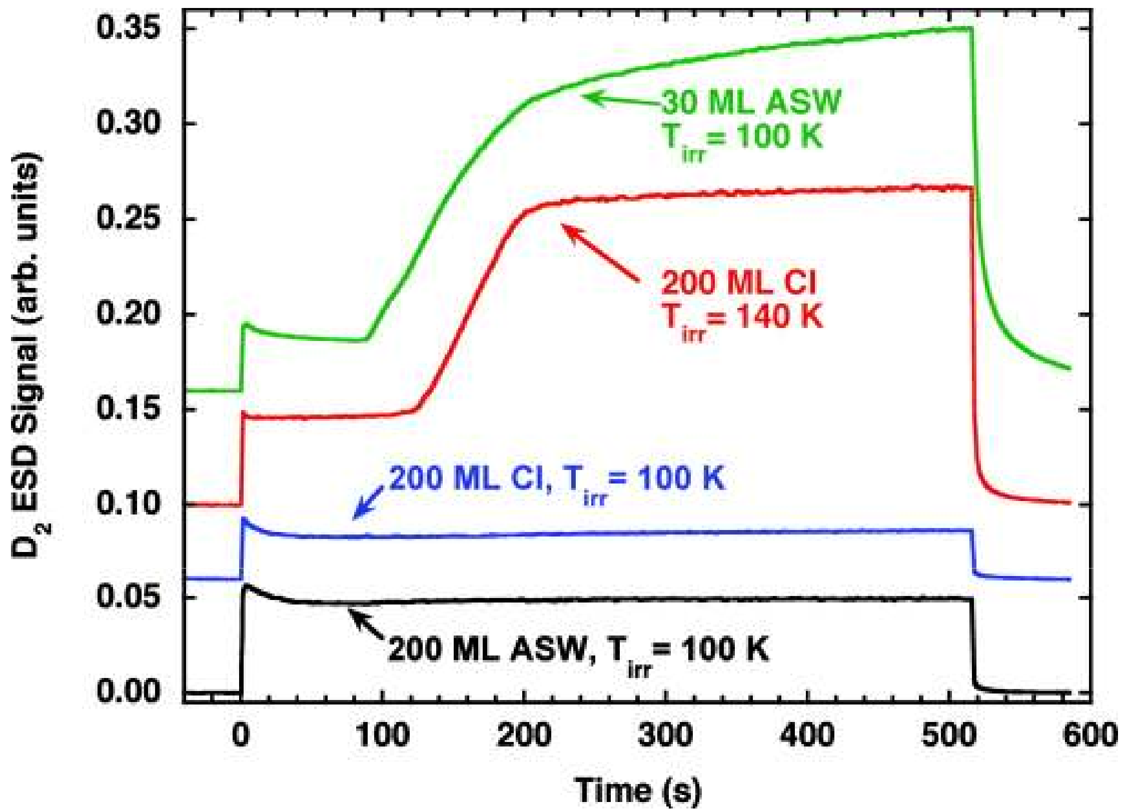
Nonthermal Reactions in ASW Films.



D_2 electron-stimulated desorption (ESD) signals at 100 or 140 K vs time from CI and ASW D_2O films adsorbed on Pt(111). Incident electron energy is 87 eV. The electron beam is turned on at *t* = 0 s and turned off at *t* = 520 s.

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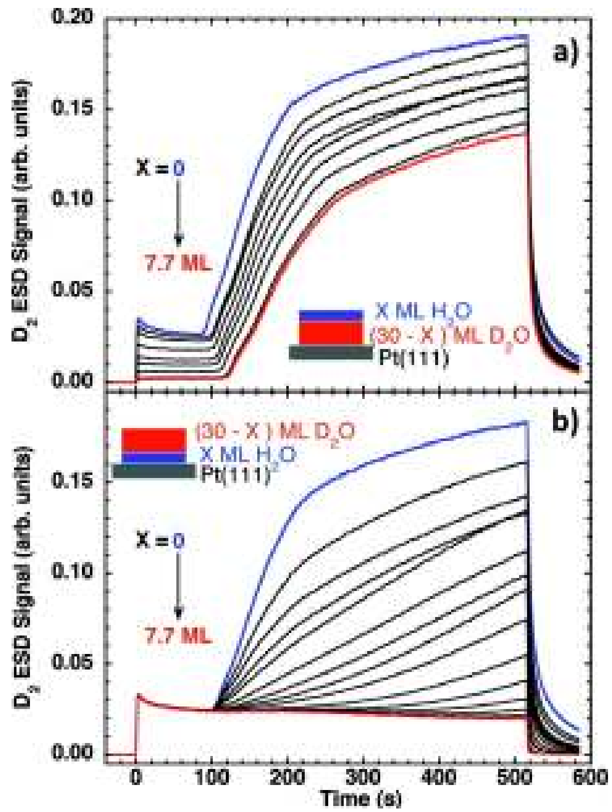

D_2 ESD signals vs time from isotopically layered ASW films of D_2O and H_2O. The films were deposited at 120 K and irradiated at 100 K with 87 eV electrons: (a) (30 – *X*) ML D_2O capped with *X* ML of H_2O, Incident electron energy is 87 eV. (b) (30 – *X*) ML D_2O deposited on top of an *X* ML H_2O spacer.

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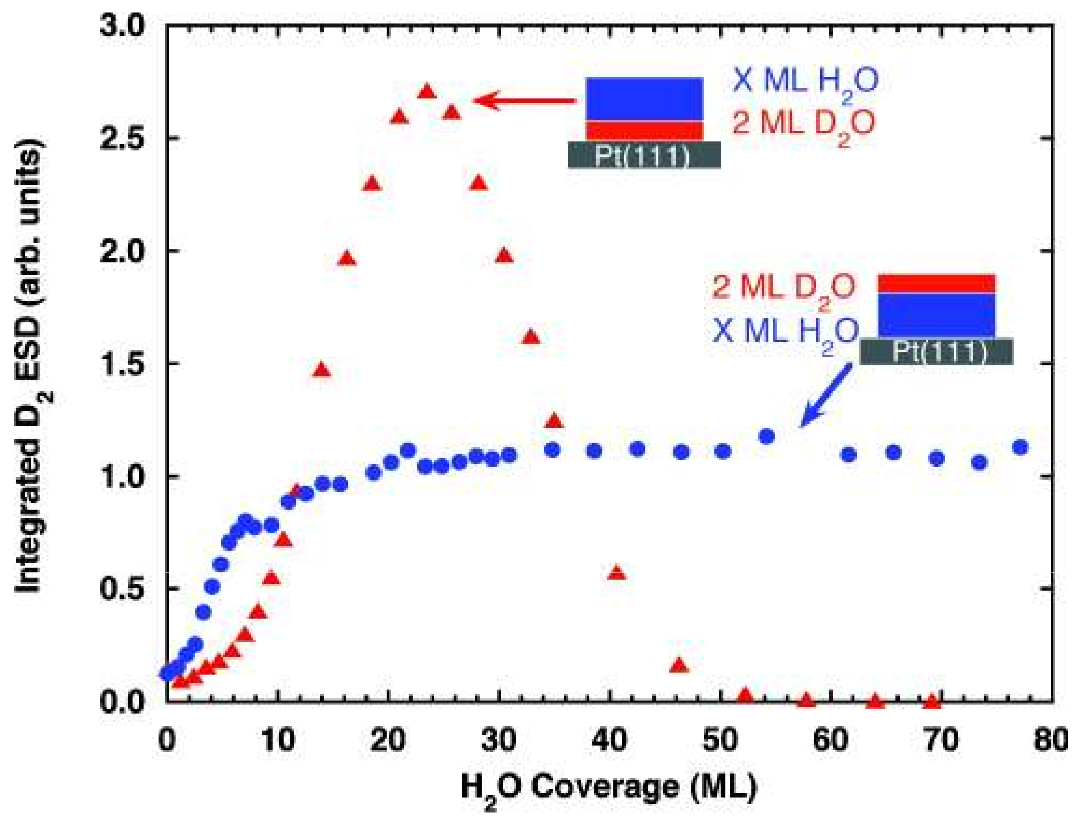

Integrated D_2 ESD yields vs H_2O coverage from isotopically layered ASW films of 2 ML D_2O and various coverages of H_2O. Incident electron energy is 87 eV.

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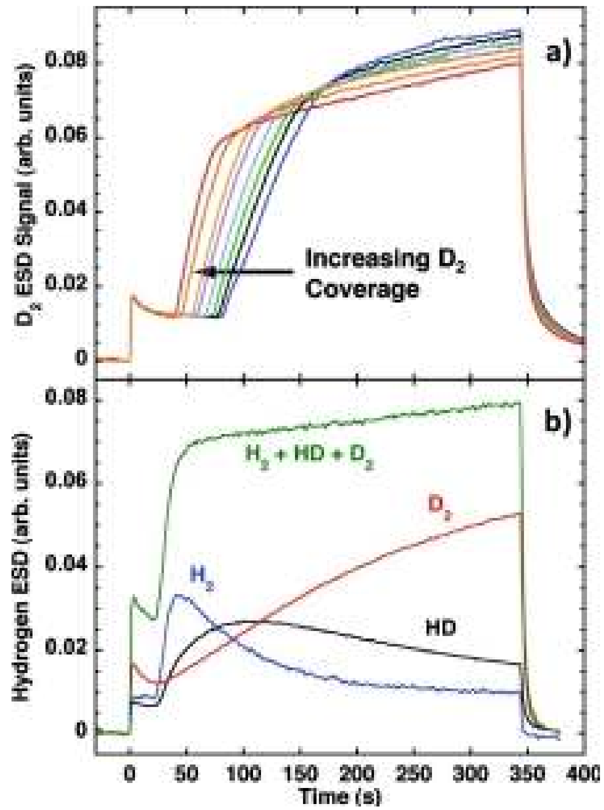

D_2, HD, and H_2 ESD yields versus time for 30 ML D_2O films adsorbed on Pt(111) predosed with (a) deuterium atoms or (b) hydrogen atoms.

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Conclusion:

❖ Thermal and nonthermal properties of water and amorphous meterials can be studies by using ASW as a model.

❖ Future work will use ASW films as a model “solvent” to explore the physical and reaction properties of aqueous supercooled liquid solutions.

❖ The experiments suggest that mobile electronic excitations are responsible for the reactions at the interfaces of thin ASW films. Protonic defects (e.g., $H3O^+$), delocalized electrons, holes, and excitons are potential candidates for the mobile excitations.

THANKS