The Structure of Nanoclusters and Thin-Films of Water Ice: Implications for Icy Grains in Cold Molecular Clouds

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Abstract

The cubic to hexagonal phase transformation in water ice ($I_c \rightarrow I_h$) is used to measure the extent to which surface structure and impurities control bulk properties. In *pure* crystalline (I_c) water ice nanoclusters and in thin-films of *impure* water ice, $I_c \rightarrow I_h$ occurs at lower temperatures than in thin-films of *pure* water ice. The disordered surface of the 20 nm diameter nanoclusters promotes transformations or reactions which would otherwise be kinetically hindered. Likewise, impurities such as methanol introduce defects into the ice network, thereby allowing sluggish structural transitions to proceed. Such surface-related phenomena play an important role in promoting chemical reactions on interstellar ice grains within cold molecular clouds, where the first organic compounds are formed.

In cold interstellar molecular clouds, gaseous species such as H_2O, CH_3OH, CO, CO_2, H_2CO and NH_3, condense onto sub-micron silicate and carbon grains to form water-rich icy mantles.[1,2] By a combination of processes that includes gas-grain chemical reactions, ultraviolet photolysis and cosmic ray bombardment, these components can react further to produce complex organic compounds.[3,4,5,6,7] Icy planetesimals of the early outer solar system, that probably formed through successive aggregation and agglomeration of such ice-coated grains may have carried significant amounts of pre-biotic organic material to the primitive Earth [8] thereby seeding it with the starting materials for life.

It is often difficult to study surface-influenced natural systems using laboratory analogs due to the low ratio of surface to bulk in the ice typically used in such experiments. Likewise, amorphous water ice cannot be made in bulk quantities via vapor deposition because the heat of fusion of the condensing molecules is sufficient to cause the ice to crystallize into the I_c polymorph. Water ice nanoclusters, having a large surface area relative to the bulk ice, allow the study of surface-mediated phenomena over laboratory timescales.

Water ice nanoclusters are useful analogs for studying a variety of processes that occur within icy grains in the extraterrestrial environment. The surface of ice nanoclusters prepared in the laboratory is similar to the surface of interstellar ice grains. In cold molecular clouds, the silicate cores of interstellar grains are typically ~100 nm in diameter and have a coating of impure amorphous water ice. Depositional, thermal and radiolytic processes leave the surface and subsurface molecules in a disordered state. In this state, structural defects become mobile and reactions of trapped gases and small molecules can occur. The large surface area of nanocluster deposits relative to their bulk allows for routine observation of such surface-mediated processes.

Transmission electron microscopy (TEM) has been used to investigate nanocluster and thin-film deposits of pure water and water:methanol mixtures. The clusters are prepared by a novel technique of rapidly cooling a mixture of water vapor in an inert carrier gas.[9] This rapid cooling causes the clusters to nucleate and grow as liquid droplets. As the droplets grow, crystallization occurs. Crystallization continues within the liquid droplet until the water vapor is depleted from the gas phase and the entire droplet is crystallized. The clusters formed by this process (Fig. 1a) have a modal diameter which varies from 16 to 28 nm as the percentage of water vapor in the carrier gas is varied from 0.5 to 2%. These distributions are nearly symmetrical around the modal value with only a small tail extending to larger cluster diameters.

It has been determined from the breadth of the electron diffraction peaks (Fig. 1b) that the average diameter of crystalline domains within the clusters is >11 nm (due to broadening of the peak by instrumental factors, this value constitutes only a lower limit). Because the lower limit of the average domain size is 11 nm while the average cluster size as determined from electron micrographs is 16 nm, one can conclude that the clusters are single crystals. This conclusion is supported by the direct observation of clusters in bright- and dark-field mode TEM.

It has previously been reported that crystalline ice nanoclusters have, in addition to an disordered surface bilayer, a disordered region called the subsurface.[10] The thickness of this layer, as determined by Fourier Transform – Infra Red (FT-IR) spectroscopy is approximately 2 bilayers.[10] For a 16 nm diameter cluster containing a >11 nm crystalline core, this leaves a <2.5 nm (<25 Å) surface layer which is non-crystalline. Since a bilayer is approximately 4Å thick this would suggest that there are <6 bilayers at the surface of the clusters with an amorphous structure. One of the layers constitutes the surface, leaving <5 bilayers in the subsurface.

Electron diffraction patterns also reveal the crystalline phase of the nanoclusters. When initially formed, the clusters are in the I_c polymorph with a very small I_h component (Fig. 1b). This I_h component is attributable to crystalline defects in which the normal abcabc... stacking sequence of the I_c polymorph is interrupted by abab... domains typical of the I_h polymorph. The I_c structure of as-deposited nanoclusters slowly converts to the I_h polymorph when the clusters are annealed at higher temperatures. This conversion can be observed at temperatures as low as 130K on the time scale of many hours, 30-70 K below the normally observed $I_c \rightarrow I_h$ transition temperature .

Pure water deposited as a thin film at cryogenic temperatures is deposited as amorphous ice. If this deposit is then warmed, it converts into I_c around 140K[11]. Annealing to temperatures as high as 160K still does not lead to the conversion of the I_c into I_h (Fig. 2a). However, if a mixture of water and methanol is deposited as a thin film and then warmed, it forms I_c and the clathrate[12][13][14]

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and monohydrate[1516] of methanol between 140 and 160K, depending upon the mixture (Fig 2b). When further warmed, the I_c component converts to I_h between 150 and 160K. This conversion, which occurs 40-50 K below the normally observed $I_c \rightarrow I_h$ transition temperature is due to the presence of methanol increasing the number of orientational defects[17] within the ice.

From these data one can see that the bulk behavior of ice can be greatly affected by the presence of a significant component of disordered surface structure relative to the bulk, or of modest numbers of polar guest molecules within its structure. In the presence of methanol, I_c can be converted into I_h at a temperature lower than the expected $I_c \rightarrow I_h$ transformation. Pure ice nanoclusters have an I_c structure that converts to I_h in a temperature region in which pure thin-film deposits will remain in the I_c phase. This conversion of the ice nanoclusters is due to the increased number of defects injected into the bulk of the ice by the large surface area. This phenomenon, which does not manifest itself readily in laboratory studies of bulk ice analogs, is not confined to structural changes alone, but rather would affect any bulk property – volatilization, water/guest molecule reactions, radical recombination within the ice matrix, and the like. Such changes are fundamentally important in the study of ices in interstellar space.

Figure 1. (a). TEM image of a cluster deposit made from a mixture of 0.5% H_2O vapor in N_2. This image shows an example of the relative distribution of the clusters formed. The length of the scale bar is 110nm, while its thickness is 16nm. (b). diffraction pattern of a cluster deposit formed from a mixture containing 5% water vapor in N_2 carrier gas.

Figure 2. Electron diffraction patterns of (a) a thin-film of pure H_2O annealed to 160K and b) a thin-film mixture of H_2O and methanol annealed to 155K. A pure H_2O deposit converts to the kinetically favored I_c structure while in the presence of methanol the H_2O converts into the thermodynamically stable I_h.form.

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