Weak interactions between water and clathrate-forming gases at low pressures

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ABSTRACT

Using scanning probe microscopy and temperature programed desorption we examined the interaction between water and two common clathrate-forming gases, methane and isobutane, at low temperature and low pressure. Water co-deposited with up to 10^{-1} mbar methane or 10^{-5} mbar isobutane at 140 K onto a Pt(111) substrate yielded pure crystalline ice, i.e., the exposure to up to ~10^7 gas molecules for each deposited water molecule did not have any detectable effect on the growing films. Exposing metastable, less than 2 molecular layers thick, water films to 10^{-5} mbar methane does not alter their morphology, suggesting that the presence of the Pt(111) surface is not a strong driver for hydrate formation. This weak water–gas interaction at low pressures is supported by our thermal desorption measurements from amorphous solid water and crystalline ice where 1 ML of methane desorbs near ~43 K and isobutane desorbs near ~100 K. Similar desorption temperatures were observed for desorption from amorphous solid water.

1. Introduction

Owing to their large natural abundance(s), often at the same location, the interaction between hydrocarbons and water plays an important role in various geochemical and astrochemical settings. Most importantly, some gaseous hydrocarbons like methane combine at low temperatures and elevated pressures with water to form clathrates, i.e., solid hydrates consisting of individual gas molecules surrounded by cages of hydrogen-bonded water molecules [1]. Clathrate deposits have been found in large quantities on the outer continental shelf and in permafrost environments [1–3] and are believed to occur in numerous astrophysical environments [4–7]. The prospect of exploiting them as energy sources but also incidents of pipeline blockages by clathrates and the danger from potential releases of large quantities of methane, a potent greenhouse gas, have fueled extensive research aimed at understanding the interaction between water and hydrate-forming natural gases (henceforth "HFNG"). Various research groups have synthesized natural gas clathrates under laboratory conditions that mimic geological [1,8–11] or astrophysical [5,6,12–14] environments yielding valuable information about thermal properties and bulk phase equilibria.

However, experiments that probe molecular-level amounts of material [15–17] are scarce, and microscopy data are only available down to the micron scale [9,14], Thus, there is little direct experimental support for modeling efforts [18–24] to understand how HFNGs interact with water at the molecular scale. Under conditions at which natural clathrates are typically found on earth, i.e., temperatures between 250 K and 300 K and pressures on the order of 100 bar [1,25], hydrate formation occurs much too fast to be observable with molecular-layer resolution. To achieve such sensitivity, experiments must be conducted at much lower pressure and temperature. In this work we employ an ultrahigh vacuum (UHV) environment to control the amount of examined material with molecular-layer accuracy. We deposit water and HFNGs onto an atomically flat Pt(111) substrate and monitor their interaction using two surface science techniques with sub-molecular layer resolution, scanning tunneling microscopy (STM) and temperature programmed desorption (TPD).

The experimental conditions are chosen with two goals in mind. The first is to increase the likelihood of forming clathrates or precursors thereof, or at least, get as close as possible to clathrate stability, by reducing temperature and increasing gas pressure. The second goal is to adjust the thermal mobility of water molecules such that mass transport involving crystalline ice or clathrates occurs at a rate that permits molecular-layer resolved monitoring. For water molecules, in order to arrange themselves into ordered structures, i.e., the crystal lattice of ice or hydrate cages, they have to be able to break and reform hydrogen bonds at a sufficient rate. Judging from measured rates of bulk diffusion [26] and surface diffusion [27] of ice, the lowest temperature at which formation of crystalline clathrates is expected to occur at a convenient time scale is ≈ 140 K. We thus deposit the films for our STM experiments at ≈ 140 K.

We chose methane for our study because it is by far the most abundant clathrate-forming hydrocarbon. Isobutane was selected because it

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is also rather common, accounting for $\approx 1\%$ of the clathrates found in the Earth's oceans, and because its hydrate requires a significantly lower pressure to be stabilized than methane clathrate [1]. Perhaps due to a recent focus mostly on terrestrial hydrates, there are only few data available for the methane/water system below 230 K, and, apparently none for isobutane/water. Fray et al. [6] compiled an equilibrium–pressure curve of methane clathrate as a function of temperature based on their own measurements and those of Delsemme and Wenger [5], Falabella and Vanpee [12], and others. Extrapolating this curve to T = 140 K suggests that a methane pressure of ≈ 15 mbar is needed to stabilize the bulk phase of methane clathrate. According to Sloan et al.'s compiled data presented in Ref. [1], the hydrate-forming pressure at the lowest temperature for which data are available is ~50 times lower for isobutane (~0.18 bar at 242 K, [1,28]) than for methane (~9 bar at 242 K). If this pressure ratio is similar at T = 140 K, the optimum temperature for our UHV experiments, one would need ≈ 0.3 mbar of isobutane to stabilize the bulk hydrate phase, a pressure that is still excessively high for operating UHV setups.

However, at these low temperatures, clathrates might be able to exist also outside their bulk-stability region as a metastable bulk phase (like amorphous solid water that persists, or cubic ice that persists and even forms at 140 K [29,30]). In addition, clathrates might have an extended stability region near interfaces, the same way as, for example, water pentagon–hexagon–heptagon arrangements represent the equilibrium configuration in the 2D wetting layer of water on Pt(111) [31,32], Ni(111)[33], Pd(111), and Ru(0001) [34], despite not being stable in the bulk at any pressure or temperature. That interfaces could promote the formation of methane clathrates had recently been suggested by Pirzadeh and Kusalik [24] for the case of an ice–solution interface.

Guided by the considerations above we explored various kinetic pathways to promote a strong HFNG–water interaction. Besides co-deposition of water with methane or isobutane, we also grew HFNG and water layers sequentially followed by annealing to ≈ 140 K. Most experiments resulted in ice layers without clear evidence that the presence of the HFNGs had any effect on film structure and morphology. However, when first growing a saturated isobutane monolayer followed by 2–3 molecular layers of water, a film with smooth and clustered regions developed. This morphology, very distinct from that of pure water films, could either indicate formation of a 2D hydrate layer or be the result of water dewetting facilitated by the presence of isobutane.

2. Experimental methods

2.1. Scanning tunneling microscopy experiments

For the STM experiments, we prepared and analyzed the film samples in a UHV chamber with a base pressure of $<3 \times 10^{-11}$ mbar. Water was deposited at a rate of ≈ 1 Å/min by directing water vapor onto an atomically flat Pt(111) surface held at 140 K. For gas exposure the UHV chamber was backfilled using standard UHV leak valves. During most co-deposition experiments the water deposition rate was maintained by monitoring the $m/z = 18$ peak with a mass spectrometer, while gas exposure was controlled with an ion gauge measuring the total chamber pressure. During film growth, the STM tip was retracted far from the sample to exclude tip-induced modifications of the films. STM measurements were performed at T < 110 K using tunnel currents below 1 pA. To image films thicker than 1 nm non-destructively [35,36] we applied a sample bias of ≈ -6 V.

For gas exposures above 10^{-5} mbar all high voltages in the UHV chamber, including ion gauge and mass spectrometer, were turned off. The integrity of the vacuum was maintained by two turbo pumps operating through partially closed valves. The chamber pressure, between 10^{-3} and 1 mbar, was measured with a convectron gauge calibrated for methane, and above 1 mbar, a Heise pressure transducer was used. Condensation of significant amounts of gas onto the coldest parts in the UHV chamber ultimately limited the maximum gas pressures we could apply. In the case of methane, release of condensation heat and possibly increased heat loss via thermal conduction through the methane gas limited the maximum methane pressure to 0.1 mbar. At higher pressures the sample temperature and the methane pressure could not be controlled simultaneously. In the case of isobutane, the maximum pressure for well-controlled experiments was ~10^{-5} mbar. At higher pressures, significant amounts of isobutane desorbed from cold surfaces of the cooling system and re-adsorbed on the sample surface when cooling the sample below 110 K for STM measurements.

2.2. Thermal desorption experiments

The TPD experiments were conducted at PNNL in a UHV chamber with a base pressure of $<1 \times 10^{-10}$ mbar which has been described in detail elsewhere [37,38] Briefly, the substrate was a 1 cm diameter by 1 mm thick Pt(111) single crystal that was spot-welded on the back side to tantalum leads for resistive heating. A K-type thermocouple spot-welded to the back of the Pt(111) substrate was used to measure temperature with a precision of better than ± 0.01 K and an estimated absolute accuracy of ± 2 K. The Pt(111) was cleaned using Ne$^+$ sputtering, oxygen anneal, and temperature annealing previously described [38]. The substrate was cooled using a closed cycle helium cryostat that could achieve a base temperature of ~25 K.

Water films were deposited using a quasi-effusive molecular beam collimated by three stages of differential pumping at normal incidence to the Pt(111) substrate. Water was deposited at a rate of 0.87 ML/s, where 1 ML is defined as the monolayer saturation coverage on the Pt(111) substrate and corresponds to ~1.1×10^{15} molecules/cm^2 [39]. The HFNGs were deposited at normal incidence using a separate quasi-effusive molecular beam collimated by four stages of differential pumping. The coverages of the HFNGs were defined by their monolayer saturation coverages on Pt(111). The ML areal coverage (#/cm^2) can be estimated by converting the liquid density (0.422 g/cm^3 for CH$_4$ and 0.594 g/cm^3 for isobutane) to a number density (molecules/cm^3) and taking the 2/3 root. This procedure yields a ML density of 6.3×10^{14} molecules/cm^2 for methane and 3.4×10^{14} molecules/cm^2 for isobutane. The desorption spectra were obtained with an Extrel quadrupole mass spectrometer in a line-of-sight configuration. Methane desorption was monitored at $m/z = 15$ and $m/z = 43$ was utilized for isobutane desorption. A linear heating rate of 1 K/s was used for all of the TPD experiments.

3. Results and discussion

3.1. The interaction of water and methane

3.1.1. Co-deposition of water and methane

The first experiment to probe water–methane interaction was performed via co-deposition of water and methane onto a well-cleaned Pt(111) single-crystal substrate held at 140 K. The sample surface was simultaneously exposed for 8 min to $p_{water} = 5 \times 10^{-9}$ mbar partial pressure of water and a partial pressure of $p_{meth} = 10^{-5}$ mbar methane. The choice of $p_{Meth} = 10^{-5}$ mbar is dictated by the maximum pressure at which water deposition could be controlled precisely (via mass spectrometer) and the integrity of the ultrahigh vacuum could be fully maintained (via a turbo pump). Except for the added exposure to methane all experimental conditions, i.e., sample temperature, partial pressure of water, and exposure time were chosen to match those that had previously [35,36] been used to grow 2–3 nm high crystallites of ice I$_h$ embedded in a 1-molecule thin wetting layer. Fig. 1(a) shows the unambiguous result: a film evolved that is indistinguishable from ice films grown in the absence of methane. (For comparison see Fig. 3(c) in Ref. [35] and Fig. 1 in [36]). From this close match in morphology we infer that the film grown via co-deposition also consists of pure water ice and not hydrate. This inference is based on the common