Water Condensation Kinetics on a Hydrophobic Surface

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Employing thermal desorption spectroscopy, we show that the effective probability of water condensation at low water vapor pressure on an octane film is much below unity at 100–120 K. This unusual finding is related to a small binding energy of H_2O monomers on octane ($\simeq 0.08$ eV), requiring the formation of critical water clusters for condensation to occur. This results in strong temperature and impingement-rate dependencies of the water condensation rate and a nonlinear uptake as a function of dose time. All these features are rationalized quantitatively by a kinetic model of water condensation.

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Understanding the kinetics of formation of thin ice films on solid substrates at low temperatures is of high current interest from different perspectives including meteorology, environmental and cosmic physics, and chemistry [1]. For example, water condensation, e.g., on dust particles, may affect cloud formation [2]. Hitherto, the early nucleation and growth of ice films have been studied almost exclusively on hydrophilic substrates where the binding energy of H_2O monomers to the surface is sufficiently large to result in irreversible adsorption at temperatures ≤ 120 K [3,4]. For such substrates, the H_2O uptake is proportional to dose time, usually with a sticking coefficient at or close to unity. In this Letter, we present the first detailed study of the kinetics of H_2O adsorption on a very *hydrophobic* substrate where the binding energy of the H_2O monomers to the surface is expected to be much less than the water-water interaction. As a model system, we use multilayer octane (C_8H_{18}) films on a Pt(111) surface. In this case, we find the kinetics of the H_2O uptake to be dramatically different compared to that observed on hydrophilic substrates, exhibiting strong temperature and impingement-rate dependencies of the uptake efficiency and a nonlinear uptake as a function of dose time.

The experiments were performed in an ultrahigh vacuum chamber designed to provide a low background pressure during dosing/desorption of water and small organic molecules (see Ref. [5] for a description of the chamber design and sample cleaning procedures). Water/octane molecules were dosed from the vapor over their respective liquid phases, through tubes terminating in front of the sample. The magnitude of the incident molecular flux was adjusted by variable leak valves. The dosing time for water was controlled by turning the dosing tube onto/away from the sample.

In a typical experiment, (i) an octane film was prepared by dosing a certain amount of octane on the Pt(111) surface, (ii) water was dosed onto the as-deposited octane film, and finally (iii) water and octane were desorbed by increasing the sample temperature linearly in time.

The amount of condensed water was evaluated from the integrated area of the $m/e = 18$ mass-spectrometer signal in the temperature-programmed desorption (TPD) trace. For some runs, the intensity at $m/e = 43$, which was the major peak in the octane mass spectrum, was also monitored, allowing determination of the octane-film thickness.

Prior to describing the data for water adsorption on octane films, it is instructive to recall briefly the situation for pure water and octane on Pt(111). The former system, H_2O/Pt(111), was studied extensively in the past [3,6]. The corresponding TPD spectrum (Fig. 1) contains (i) the peak and shoulder at 165–175 K (which saturate with increasing coverage) due to desorption from a water bilayer and (ii) the lower temperature peak (which grows indefinitely with increasing coverage) reflecting desorption from water multilayers. For convenience, we use in Fig. 1 and below the unit of one water bilayer equivalent (WBE) for an integrated intensity corresponding to the
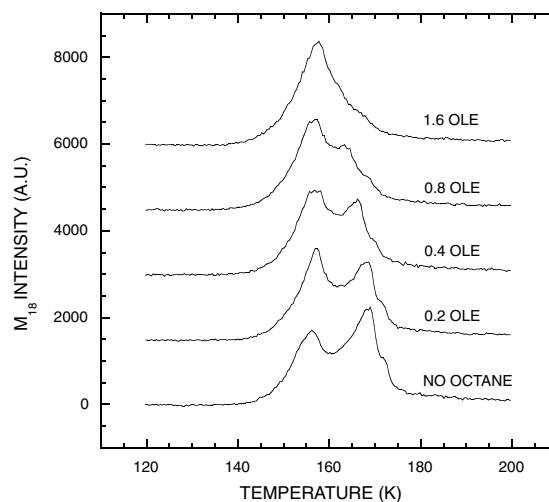

FIG. 1. Water desorption traces from clean Pt(111) and Pt(111) covered by 0.2–1.6 OLE of octane. The adsorbed overlayer was formed at 110 K by dosing 1.8 WBE.

area under the water desorption trace from Pt(111) obtained at a coverage just before the multilayer desorption signal becomes visible. The incident dose of water in the uptake experiments was calibrated from multilayer adsorption experiments on clean Pt(111) at ≈ 110 K where a sticking coefficient of unity can be assumed [3].

Octane is reported to form a commensurate monolayer on Pt(111) desorbing at ≈ 270 K, while octane multilayers desorb at 170 K [7]. (In our TPD traces for octane on Pt(111), we observed an additional peak at 210 K, not discussed previously. These data will be presented elsewhere.) By analogy with the case of water, we calibrate the octane desorption signal by the saturation area under the 270 K monolayer peak and refer to this integrated intensity as one octane layer equivalent (OLE).

Returning to water condensation on octane films, we first show (Fig. 1) water desorption traces obtained after dosing 1.8 WBE onto surfaces that had been precovered by a thin octane film. With increasing octane coverage from 0.2 to 1.6 OLE, the water bilayer peak gradually disappears, indicating reduction of the direct H_2O-Pt interaction. For these thin films, the effective H_2O sticking coefficient stays close to unity as evident from the fairly constant area under the spectra.

The amount of water condensed on mesoscopically thick octane films, at constant incident water dose, is shown in Fig. 2. As the octane-film thickness increases, the condensation efficiency is seen to drop considerably. For sufficiently thick films, the effective sticking coefficient for H_2O adsorption on octane is thus much below unity even at 110 K.

To investigate the uptake kinetics in more detail, we focused on the thick octane-film limit and studied adsorption of water on bulklike octane films with constant thickness estimated to lie in the range 500–1500 OLE. Figure 3 shows the amount of water condensed on such films as a function of total incident water dose (exposure) for five different substrate temperatures in the range 100–120 K (the incident dose, W, is related to the dosing time via $W = Ft$ and the constant value of the incident flux, $F = 0.13$ WBE/s). Here, the H_2O sticking coefficient is again much below unity. Furthermore, (i) the uptake efficiency is seen to be strongly temperature dependent with condensation at lower temperatures being more efficient, and (ii) the dependence of the condensed amount of water on the exposure time is nonlinear, with an increasing condensation efficiency for higher water coverages. (In these experiments, the growth of the octane film was carried out at temperatures identical to those at which water was subsequently dosed. Control experiments where water was dosed at 100 K onto an octane film grown at 120 K demonstrate that the temperature dependence of the uptake efficiency is not a result of different octane-film morphologies caused by different growth temperatures.)

The influence of the incident water flux on the amount of condensed water for constant incident dose and temperature was investigated in separate experiments where it was found [Fig. 4(a)] that the H_2O sticking coefficient increases with increasing incident flux.

The key point to rationalize the observations above appears to be that the binding energy of H_2O monomers on the octane surface is too small to cause their
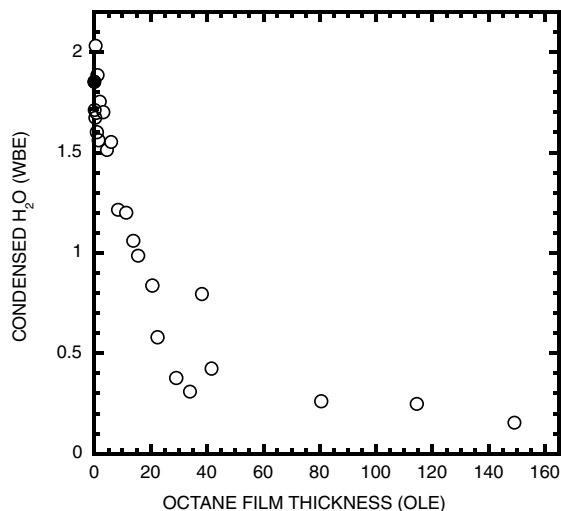
FIG. 2. Amount of water condensed on octane films (open circles) as a function of the film thickness for 1.8 WBE dosed at 110 K. For comparison, the filled circle gives the water uptake for clean Pt(111). The error bar is representative for all the data points.
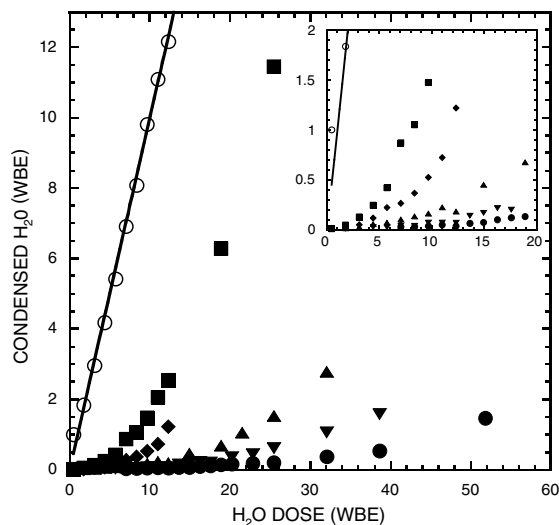
FIG. 3. Amount of condensed water versus total incident dose for thick octane films on Pt(111) at 100 K (squares), 105 K (diamonds), 110 K (upward triangles), 115 K (downward triangles), and 120 K (filled circles). For reference, data for clean Pt(111) at 110 K (open circles) are also presented (in this case, the condensation coefficient is unity). The inset shows the low-dose region in more detail. All data are for a constant incident flux of $F = 0.13$ WBE/s.
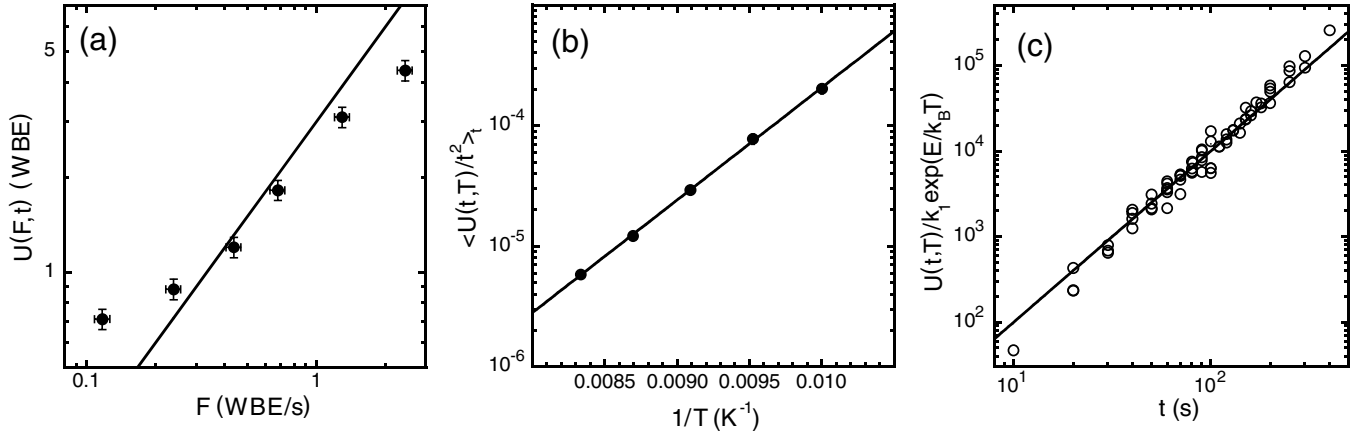
FIG. 4. Water uptake kinetics on thick octane films: (a) amount of condensed water as a function of dose flux, F, at constant temperature (105 K) and constant incident dose ($W = 11$ WBE) (the dose times, t, range from 4 to 109 s). The solid line is the best fit of the data to $y = k_0 F$. (b),(c) The data from Fig. 3 arranged to show the scaling-law dependence on substrate temperature and dosing time, respectively. In (b) and (c), the solid lines are the best fits of the data to $y = k_1 \exp(E/k_B T)$ and $y = k_2 t^2$, respectively. (In all equations here, y is the ordinate of the respective plots.)

irreversible adsorption at the investigated temperatures of 100–120 K. Instead, the water monomers are only temporarily (of order 0.1 ns; see below) adsorbed on the octane film, where they diffuse over the surface until either desorption to the gas phase or trapping by incorporation into clusters of two or more water molecules on the surface occurs. The probability of nucleation of such clusters increases with increasing density (coverage) of temporarily adsorbed monomers. The amount of accumulated ice, at a given dose, therefore increases with decreasing temperature at constant impingement rate or with increasing impingement rate at constant temperature. As more water is accumulated on the surface with increasing dosing time, the likelihood increases that an adsorbed monomer is trapped at existing water clusters before desorption occurs, explaining the nonlinearity of the uptake curves as a function of incident dose. In the lowest temperature experiment (100 K), the slope of the condensation curve eventually approaches that for deposition on clean Pt (Fig. 3), but this complete condensation efficiency is first reached after approximately 10 WBE have condensed, indicating 3D growth of the ice clusters on the octane film.

To quantify our results, we have analyzed various scenarios of water condensation on a hydrophobic surface at submonolayer coverage and found that the most probable one implies that the critical nuclei are H_2O dimers. The conventional mean-field equations for this case are as follows [8]:

$$dN/dt = D\rho^2, \tag{1}$$

$$d\rho/dt = F - k_d\rho - D\rho(2\rho + N). \tag{2}$$

Here ρ is the surface concentration of monomers, N is the surface concentration of crystallites containing two or more H_2O molecules, F is the H_2O impingement rate (per

unit area), D is the H_2O diffusion coefficient, and k_d is the H_2O desorption rate constant. Physically, Eq. (1) describes the diffusion-limited formation of dimers, while Eq. (2) takes into account H_2O adsorption and desorption (the first two terms on the right-hand side) and monomer consumption due to formation and growth of crystallites (the last two terms). In the present case, D and k_d should be thought of as *effective* kinetic parameters for a surface with a possible *weak heterogeneity* (see, e.g., Ref. [9]).

Equations (1) and (2) are usually solved [8] in the limit of slow desorption [$k_d\rho \ll D\rho(2\rho + N)$]. We are, however, interested in the opposite case, $k_d\rho \gg D\rho(2\rho + N)$, when the adsorbate-substrate interaction is weak. Employing in the latter case the steady-state approximation ($d\rho/dt = 0$), we obtain from Eq. (2)

$$F \simeq k_d\rho. \tag{3}$$

Substituting this expression into Eq. (1) and integrating yield

$$N \simeq DF^2 t/k_d^2. \tag{4}$$

The H_2O uptake, $U(t)$, results primarily from crystallite growth, i.e.,

$$dU \simeq D\rho N dt. \tag{5}$$

Using Eqs. (3) and (4), we integrate Eq. (5) as

$$U(t) \simeq D^2 F^3 t^2/2k_d^3. \tag{6}$$

Inserting into this expression the temperature dependencies of the diffusion and desorption rate constants, $D \propto \exp(-E_{\mathrm{dif}}/k_B T)$ and $k_d \propto \exp(-E_{\mathrm{des}}/k_B T)$, we finally obtain a scaling law for water uptake on the hydrophobic surface

$$U(T, F, t) \propto \exp[(3E_{\mathrm{des}} - 2E_{\mathrm{dif}})/k_B T]F^3 t^2. \qquad (7)$$

Guided by the analysis above, we plot in Figs. 4(b) and 4(c) the uptake data from Fig. 3 in coordinates corresponding to the scaling law. The expected Arrhenius dependence on temperature, $U(T) \propto \exp(E/k_B T)$, is clearly confirmed in Fig. 4(b), where the uptake data have been normalized with respect to dosing time (also, an average over the different dosing times has been performed for each temperature). To examine the dependence on dose time, the uptake data are normalized for their temperature dependence by using the Arrhenius parameters derived from Fig. 4(b). The corresponding plot, Fig. 4(c), demonstrates an excellent agreement with the expected t^2 scaling. To finally compare the experimentally observed flux dependence of the uptake with Eq. (7), one has to bear in mind that the data of Fig. 4(a) were obtained for a constant incident dose, W, and the dosing times therefore varied as $t = W/F$. For these data, Eq. (7) predicts $U(F, t) \propto F$ in reasonable agreement with Fig. 4(a). [Normalizing to the varying dose times, we obtain $U(F, t)/t^2 \propto F^{2.8}$ in good agreement with Eq. (7) (plot not shown).]

From the slope of the Arrhenius plot [Fig. 4(b)], we have $3E_{\mathrm{des}} - 2E_{\mathrm{dif}} = 0.19$ eV. This equation does not allow one to disentangle unambiguously the diffusion and desorption activation energies, but since E_{dif} must necessarily lie between zero and E_{des}, it is possible to provide the upper and lower values for E_{des}, 0.2 and 0.07 eV, respectively (the most likely value is in the lower end of this range since E_{dif} is expected to be much smaller than E_{des}, e.g., $E_{\mathrm{des}} = 0.08$ eV for $E_{\mathrm{des}} = 4E_{\mathrm{dif}}$; the residence time of a monomer before desorption at 100 K at this binding energy is only of order 0.1 ns). The monomer binding energy in this range is thus very small compared to the sublimation energy for ice (0.50 eV) [3] but is a fully reasonable value for van der Waals dominated interaction between water and the nonpolar octane film. (Note that our way of obtaining the H_2O binding energy for a *hydrophobic* surface is unique; the conventional Readhead equation does not work here due to the strong tendency of H_2O to form islands.)

Finally, we comment briefly on water condensation on thin octane films. The desorption traces obtained in this limit (Fig. 1) show that direct H_2O-Pt interaction is negligible already for film thicknesses corresponding to 1 ML of octane. For such a film, the water condensation still, however, occurs with nearly unit probability even at a low water dose of 1.8 WBE. This can be because either (i) a small number of empty Pt sites exists between the octane molecules where heterogeneous H_2O nucleation occurs or (ii) van der Waals interaction between H_2O molecules, on top of an octane monolayer, and the underlying Pt substrate adds sufficient strength to the H_2O binding to make the monomers stable or more long-lived than on thick octane, creating an increased probability for homogeneous nucleation of water clusters. In either case, the slow decrease of the uptake efficiency with increasing average octane-film thickness (Fig. 2) seems to indicate that octane first forms a single monolayer and then grows in a 3D-island fashion.

In summary, we have comprehensively investigated the temperature, flux, and time dependence of the efficiency of water condensation on a hydrophobic octane surface. The condensation probability is found to be very low even at 100 K. This is due to a small binding energy of H_2O monomers on octane ($\simeq 0.08$ eV), requiring formation of nuclei with more than one H_2O molecule for sustainable ice condensation to occur. Taking into account these features, we have derived a scaling law which describes quantitatively the observed temperature, time, and flux dependence of the condensation kinetics.

In a more general context, we may note that experiments of the type described make it possible to estimate the H_2O monomer binding energy on hydrophobic substrates, i.e., a molecular scale measure of their wetting ability. This may be useful for technological applications and/or in meteorology where water condensation on hydrophobic particles is one of the processes affecting cloud behavior [2]. Condensation on hydrophobic surfaces can be studied at higher temperatures of direct interest in meteorology by slightly modifying the current experimental procedure and by matching higher temperature with a concomitant pressure increase.

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