Sticking Probability of High-Energy Methane on Crystalline, Amorphous, and Porous Amorphous Ice Films

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Rebecca S. Thompson, Michelle R. Brann, and S. J. Sibener

The James Franck Institute and Department of Chemistry, The University of Chicago, 929 East 57th Street, Chicago, Illinois 60637, United States

ABSTRACT: We present research detailing the sticking probability of CH₄ on various D₂O ices of terrestrial and astrophysical interest using a combination of time-resolved, in situ reflection absorption infrared spectroscopy (RAIRS) and King and Wells mass spectrometry techniques. As the incident translational energy of CH₄ increases (up to 1.8 eV), the sticking probability decreases for all ice films studied, which include high-density, non-porous amorphous (np-ASW), and crystalline (CI) films as well as porous amorphous (p-ASW) films with various pore morphologies. Importantly, sticking probabilities for all p-ASW films diverge and remain higher than either np-ASW or CI films at the highest translational energies studied. This trend is consistent across all porous morphologies studied and does not depend on pore size or orientation relative to the substrate. It is proposed that in addition to offering slightly higher binding energies the porous network in the D₂O film is very efficient at dissipating the energy of the incident CH₄ molecule. These results offer a clear picture of the initial adsorption of small molecules on various icy interfaces; a quantitative understanding of these mechanisms is essential for the accurate modeling of many astrophysical processes occurring on the surface of icy dust particles.

INTRODUCTION

Examining molecular and atomic adsorption onto frozen water ices is necessary to create accurate models of the chemical and physical processes occurring in atmospheric and terrestrial environments. Furthermore, understanding the interactions between gas molecules and different molecular ices can help to classify the composition and the history of complex multi-component ices. Adsorption on icy surfaces, in astrophysical environments for instance, is a critical first step in a variety of recombination and addition reactions, some resulting in the formation of small organic molecules.

Ice can exist in a variety of crystalline and amorphous forms. Crystalline (CI) water ice with its hexagonal lattice is the most common form of snow and ice on Earth and can also be found in warmer astrophysical environments. Amorphous solid water (ASW), on the other hand, is the most abundant form of water in astrophysical environments and is present in comets, planetary rings, and interstellar clouds. ASW can be classified into two types: high-density non-porous (np-ASW) and low-density porous (p-ASW) based on its pore structure. In general, ASW morphology plays a significant role in the adsorption of volatile gas species within astrophysical ices. Although not yet found in such environments, p-ASW can exist as the result of heterogeneous molecular synthesis occurring on dust grains in the interstellar medium (ISM). Exposure to ultraviolet light, X-rays, cosmic radiation, or thermal processing can also induce morphological changes in astrophysical ices. Over time and as a result of these processes, ASW ices can become CI and vice versa. Because of this, there is an interest in understanding the precise role of surface morphology in gaseous adsorption.

This work uses high-energy projectiles to examine adsorption mechanisms on various astrophysical ices. A particular focus is on porous amorphous water ices and how the pore structure influences the energy accommodation and uptake of incident molecules. In general, a molecule impacting a surface adsorbs if it loses enough of its kinetic energy to the lattice upon impact. Accurate measurements of sticking probabilities are essential because a higher sticking probability can lead to greater observed reactivity as has been shown for a variety of molecules on amorphous ices.

We present the first study examining the sticking probability of CH₄ as a function of translational beam energy on p-ASW of varying porosities, np-ASW, and CI D₂O ice films under ultrahigh vacuum (UHV) using the King and Wells method and molecular beam techniques. Molecular beams enable tunable control of incident energy and thus precise knowledge of the sticking process. CH₄ was chosen primarily due to its known presence in many astrophysical environments, including its potential incorporation in icy clathrates found in outer solar

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system bodies such as Titan. Within those environments, reactions involving CH$_4$ can be a significant contributor to the formation of complex organic molecules. Additionally, CH$_4$ allows us to exclusively probe adsorption phenomena because its light mass and lower momenta may preclude direct embedding underneath the surface. We demonstrate that for the highest energy beam (1.6 eV) the sticking probability is higher for p-ASW than np-ASW and CI ices. For the p-ASW ices, we also determine that there is no difference in sticking probability as a result of increased porosity.

Our results build upon previous work in our group focused on the sticking probability of D$_2$O and H$_2$O on CI for incident translation energies ranging from 0.3 to 0.7 eV. The sticking probability was near unity for those measurements and did not change as a function of water ice morphology or surface temperatures ranging from 140 to 155 K. By using CH$_4$ and expanding the water ice morphology to include amorphous water ices with and without pores as well as higher incident translational energies, our measurements provide a more complete understanding of the dynamics of sticking between projectiles and water ices. Such work is critical to creating an average growth rate of 0.5 ML/min. The ice thickness was determined by backfilling the UHV chamber to a pressure of 1.0 × 10$^{-7}$ Torr D$_2$O, which corresponds to a growth rate of 0.1 ML/s. RAIR spectra were collected at regular time intervals during exposure, which allowed for direct quantification of film thickness from integrated intensity of the large O–D stretch between 3600 and 2800 cm$^{-1}$.

Figure 1 shows a typical normalized O–D stretch for the three different ice films used in this study. Following literature precedent and as a result of D$_2$O molecule coordination differences among these films, this region can be used to distinguish p-ASW, np-ASW, and CI films. In particular, the interface of p-ASW films contains a significant fraction of three- and two-coordinated surface D$_2$O molecules (“dangling bonds”) that can be clearly resolved spectroscopically at 2725 and 2740 cm$^{-1}$, respectively. Though also present in the np-ASW film, this dangling bond region is much lower intensity, reflecting the large difference in surface areas between porous and nonporous films. The temperature of the substrate during dosing dictates the water ice morphology; the substrate temperatures used for ice growth were 150 K for CI, 107 K for np-ASW, and 25 K for p-ASW.

ASW films with increased porosity were produced by changing the angle of the directed doser relative to surface normal. The films used in this study were produced at 30°, 60°, or 70° as well as via background deposition. As characterized by Stevenson et al., porosity increases with deposition angle, so the D$_2$O films dosed at 30° are less porous than those grown at 60° or 70°. The pores also grow with an orientation that matches deposition angle. Although films produced via background deposition (backfilling the chamber with water vapor) are as porous as those grown at 70°, the water molecules approach the surface with a thermal energy distribution and random angular orientation resulting in nonuniform pore orientation and size. The intensities of the dangling bond spectroscopic signals are known to roughly scale with porosity, so RAIR spectra can be used to qualitatively confirm that ices with different porosities have been formed. Unless otherwise specified in this work, “p-ASW” refers to our default porous film grown at 30°, and porous films grown at other deposition angles (60, 70, and background) will be identified as such.

**Figure 1.** Normalized infrared spectra of the O–D stretch distinguish porous amorphous (p-ASW, green), non-porous amorphous (np-ASW, red), and crystalline (CI, blue) D$_2$O ices on Au(111) dosed at 25, 107, and 150 K, respectively. The inset demonstrates that while dangling O–D modes are observed for both ASW films they are significantly more intense in the p-ASW films.

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**EXPERIMENTAL SECTION**

All experiments were conducted in a molecular beam scattering instrument previously discussed in full detail. Generally, this instrument consists of a UHV chamber with base pressures of 10$^{-10}$ Torr connected to a triply differentially pumped molecular beamline. Inside the chamber, a state-of-the-art helium-cooled sample manipulator (Advanced Research Systems) enables precise and accurate temperature control of the Au(111) sample substrate between 20 and 800 K. The crystal is exposed to the beam and monitored in real time with optics for in situ reflection absorption infrared spectroscopy (RAIRS). Gas scattering and incident flux are also monitored with a residual gas analyzer (RGA).

All RAIR spectra are analyzed with Gaussian peaks atop either linear or cubic baselines, depending on the region. Spectra were acquired with a Nicolet 6700 infrared spectrophotometer (Thermo Fisher) using incident p-polarized IR radiation at an angle of 75° to the Au(111) crystal and a liquid-nitrogen-cooled mercury cadmium telluride (MCT/A) detector. Each RAIR spectrum is an average of 70–200 scans taken using 4 cm$^{-1}$ resolution with a clean Au(111) sample for the background. For ice preparation, D$_2$O was chosen (rather than H$_2$O) due to its preferable O–D stretch frequency that avoids overlap with the $\nu_3$ methanol mode.

D$_2$O films were produced via a directed doser at a 30° angle and approximately 4 cm from the Au(111) crystal. D$_2$O was typically leaked in at a pressure of 2.0 × 10$^{-9}$ Torr, leading to an average growth rate of 0.5 ML/min. The ice films used in this study were between 150 and 300 layers thick.
CH$_4$ beams were produced by expanding 1% CH$_4$ in H$_2$ or neat CH$_4$ at stagnation pressures of 200–400 psi through a 10 μM molybdenum pinhole. Resistively heating the beam nozzle from room temperature to 970 K resulted in CH$_4$ translational energies of up to 0.3 eV for the neat CH$_4$ beam and up to 1.8 eV for the CH$_4$ beam seeded in H$_2$. The translational energy distribution widths ($\Delta E/E$) ranged from 12% to 21%. Translational energies were measured by time-of-flight (TOF) using a mechanical chopper (a rotating slotted disk) to modulate the beam prior to detection with an in-line quadrupole mass spectrophotometer (QMS). For one experiment (investigating the impact of embedding phenomena), CF$_4$ beams were produced by expanding 1% CF$_4$ in H$_2$ at stagnation pressures of 300–500 psi through a 20 μM molybdenum pinhole. Resistively heating the beam nozzle temperature to over 950 K resulted in a CF$_4$ translational energy of 5.3 eV with a $\Delta E/E \approx 40\%$.

The CH$_4$ or CF$_4$ flux was determined by first measuring the pressure rise with a nude Bayard–Alpert ion gauge calibrated to N$_2$ for a neat CH$_4$ or CF$_4$ beam open to the chamber. The flux was then calculated by taking into account the relative gauge sensitivity to CH$_4$ and N$_2$ along with the chamber pumping speed, and the spot size of the beam on the Au(111) crystal. Using neat beams at varied stagnation pressures, the calculated fluxes were correlated to a pressure rise for $m/z = 15$ (CH$_4$) or for $m/z = 69$ (CF$_4$) measured by a RGA not in line with the beam. A linear regression then enabled a conversion between measured RGA fluxes and total CH$_4$ and CF$_4$ flux. Typical beam fluxes for the CH$_4$ and CF$_4$ beams were $2.21 \times 10^{13}$ atoms cm$^{-2}$ s$^{-1}$ and $1.27 \times 10^{14}$ atoms cm$^{-2}$ s$^{-1}$, respectively. All beam exposures in this study were performed at normal incidence.

Sticking probability was determined using the King and Wells technique. In order to conduct multiple trials with a given film, the ice was first annealed to 70 K for 30 min. While this reduced porosity slightly, it ensured that repeated King and Wells cycles did not further alter the film morphology throughout the day. A typical King and Wells experiment conducted at a surface temperature of 33.5 K is shown in Figure 2 where $m/z = 15$ for CH$_4$ is monitored as a function of time using an RGA out of line with the beam. The experiment begins with monitoring the background signal prior to introducing any CH$_4$ into the chamber ($P_1$). Next, the CH$_4$ beam is introduced into the chamber, but with a flag in front of the substrate. This pressure rise is the full indirect CH$_4$ flux ($P_2$). Then the flag is removed, at which point CH$_4$ molecules begin sticking to the surface ($P_3$). The initial sticking probability ($S$) is thus calculated as

$$S = \frac{(P_3 - P_1)}{(P_2 - P_1)}$$

(1)

Over time, the CH$_4$ signal rises back up to the blocked value as the available surface sites become filled and CH$_4$ can no longer adsorb onto the surface. The specific challenges with performing King and Wells measurements on the CH$_4$/ice system are fully addressed in the Discussion section below.

To explore the generalizability of our results, the sticking probabilities for CH$_4$ on np-ASW, p-ASW, and CI H$_2$O films were also examined. We note that for all the CH$_4$ translational energies studied the sticking probability values were the same as those observed for D$_2$O ices; we did not observe any significant isotopic effect at our experimental resolution, as has been previously detected between D$_2$O impinging on H$_2$O and D$_2$O ices.

## RESULTS

### King and Wells

King and Wells measurements of initial sticking probabilities were performed on a prepared ice substrate held at 33.5 K for all results presented in this study. This temperature choice reflects a number of important considerations related to both the nature of the CH$_4$/D$_2$O interaction and the King and Wells method itself. As discussed by He et al., there are three potential challenges with performing King and Wells measurements for this ice system. First, the liquid helium cooling of the sample manipulator may impact the pumping speed of the chamber, thereby altering the reflected portion of the beam at different sample temperatures. We avoid this by taking all measurements at a single sample temperature, where the unknown improvement in chamber pumping speed is consistent across experiments. Second, because CH$_4$ interacts with the ice surface via weak dispersion forces rather than direct chemisorption, these experiments require low surface temperatures. Furthermore, ice surfaces have a wide range of binding sites and binding energies. These two factors present a second challenge; a well-defined saturation of the CH$_4$-reflected signal might be difficult to observe over short exposure time scales. Although full reflection may ultimately be observed with long exposures, CH$_4$ desorption as well as finite adsorption of background H$_2$O and D$_2$O at these low temperatures over long time scales compete to prevent signal saturation. As such, all initial sticking probability measurements referenced herein are calculated using the initial CH$_4$ indirect flux rather than the value at saturation. These considerations, therefore, are mitigated by our experimental setup.

Beyond the aforementioned considerations, we are also specifically interested in quantifying the initial sticking probabilities in the low-coverage, submonolayer regime. This is desirable because the concentrations of small molecules in the ISM are typically quite low. Moreover, we want to eliminate any contribution from multilayer sticking, which occurs more readily in porous films, even at higher surface temperatures. As such, the desired temperature regime should be high enough to restrict all sticking to the submonolayer. In light of these considerations, 33.5 K was selected as the surface temperature of interest. At this temperature, however, the monolayer is not perfectly stable.

![Figure 2. CH$_4$ signal ($m/z = 15$) monitored with the RGA during a representative King and Wells experiment conducted at a surface temperature of 33.5 K. $P_1$ (orange) is the background CH$_4$ signal; $P_2$ (blue) is the full CH$_4$ flux with flag blocking the substrate; $P_3$ (pink) is CH$_4$ adsorption with flag removed.](image-url)
Figure 3. Isothermal desorption of CH₄ from crystalline (CI, a), non-porous amorphous (np-ASW, b), and porous amorphous (185 layers, c) ice films (top) allows for quantitative estimation of monolayer thickness, as measured via the integrated absorbance of the ν₄ mode. Growth of the same peak area during exposure at 33.5 K (bottom) confirms that the amount of adsorbed CH₄ is significantly less than a full monolayer for each type of ice. This is also demonstrated in the corresponding RAIR spectra for desorption a 25 K (blue, d) and 33.5 K (pink, d).

on the surface. While this does not impact the measurements of initial sticking probabilities, CH₄ surface coverage at long exposure time scales will reflect contributions from both adsorption and desorption. By explicitly quantifying and accounting for the rates of desorption, we also account for the third concern with King and Wells measurements, which is that they typically do not have the time resolution to distinguish between molecules that are directly reflected from the surface and those that adsorb for a short time and then desorb again.

As shown in the top panels of Figure 3a–c, quantification of the monolayer was established via isothermal desorption experiments for each ice film. After dosing a multilayer film of CH₄ at 20 K, the integrated area of the ν₄ mode was tracked over time at an elevated temperature. 32.54–56 A distinct slope change is observed when multilayer desorption changes to monolayer, thereby allowing for an approximate quantification of monolayer thickness. The bottom panels of Figure 3a–c show that when the surface is held at 33.5 K (as during a King and Wells experiment) the total amount of adsorbed CH₄ reaches a maximum far below the respective monolayer thickness for each type of ice film. Measured desorption rates for all films at 33.5 K are similar in magnitude to the incident CH₄ flux, so this steady-state maximum indicates that only a small fraction of the monolayer is stable on the surface over long time scales (as shown in Figure 3c in pink).

Figure 3 highlights another important feature of this system, which is that the monolayer thickness (and uptake at 33.5 K) on the porous film is significantly higher than uptake on either CI or np-ASW films (likely due to the increased surface area). 37 This effect has been well-documented previously—Kimmel et al. demonstrated, for example, that a 50 layer film of p-ASW deposited at 30° sees a total CH₄ adsorption of ~2 monolayer equivalents. 40 On this basis one might expect, therefore, that a 185 layer film (as used in Figure 3c) would likewise adsorb roughly 7–8 monolayers of CH₄. Indeed, the data show that the p-ASW monolayer adsorption is almost exactly 8 times that of the CI and np-ASW films. Similarly, steady-state adsorptions at 33.5 K are on the order of 10¹⁴ CH₄ cm⁻² on the porous films and 10¹³ CH₄ cm⁻² on crystalline and non-porous films.

Sticking Probabilities for CI, np-ASW, and p-ASW.
Measured sticking probabilities for CH₄ on crystalline (CI), non-porous (np-ASW), and porous (p-ASW) D₂O films are displayed in Figure 4. Clearly, as the CH₄ incident energy increases, the observed trend on the porous film diverges from both CI and np-ASW; sticking probabilities remain significantly higher for the porous film. This divergence will be discussed in further detail below. First, however, it is important to note that crystalline and non-porous films display nearly identical sticking probability trends throughout the range of incident energies studied. This insensitivity to morphology (CI versus np-ASW) has been observed in other experimental and theoretical systems, including D₂O sticking on H₂O and D₂O₃. H₂O sticking on H₂O,17 and CO sticking on H₂O.6,58 The theoretical work of Al-Halabi et al., for example, shows not only that the sticking of CO is nearly equal between np-ASW and CI H₂O films but also an exponential decay of sticking probability with incident translational energy that is roughly comparable to that measured in this study. 38

It is important, when discussing adsorption to both porous and non-porous films, to elucidate the contribution of any
penetration of the incident CH₄ into the bulk ice. Previous work in this lab has identified a significant activated uptake channel for incident projectiles in the ice bulk (term “embedding”). After investigating this process for a range of molecules in np-ASW H₂O, a clear momentum barrier for this channel was established (embedding probabilities in CI films were significantly lower than those observed for np-ASW). In general, the momenta reached in the current study (using the relatively light CH₄) are well below this barrier, so no embedding is expected in either np-ASW or CI films. There is, however, the question of whether the use of D₂O (rather than H₂O) or a more porous ice morphology will effectively lower this barrier, making direct comparisons of sticking probabilities across more challenging films. To examine this, both porous and non-porous D₂O ice films were exposed to beams of 5.3 eV CF₄. CF₄ was selected because it has a higher mass and has proven a significant signal growth at 1276 and 1257 cm⁻¹ during exposure. Upon exposure to CH₄ (Figure 6a), there is a slight red shift in intensity of the dangling O–D stretching mode is slightly red-shifted (b). Annealing to 70 K removes all CH₄ and leaves the original D₂O film unchanged.

Figure 6. RAIR spectra of D₂O films are unchanged by CH₄ exposure and subsequent anneal. During exposure, some CH₄ adsorbs to the surface (a), and the dangling O–D stretching mode is slightly red-shifted (b). Annealing to 70 K removes all CH₄ and leaves the original D₂O film unchanged.

RAIR spectra of the film before, during, and following CH₄ exposure. Upon exposure to CH₄ (Figure 6a), there is a slight red shift in intensity of the dangling O–D mode (Figure 6b). This shift is well documented in FTIR studies of sequential CH₄/H₂O deposits and indicates that some of the surface D₂O molecules are coordinating with the adsorbed CH₄. After annealing the sample back to 70 K following the experiment, however, all CH₄ desorbs, and there are no lasting changes in the O–D stretch or the dangling O–D peaks. This indicates that the water film height, morphology, and porosity are not impacted by CH₄ sticking experiments, even at the highest energies studied (1.8 eV).

Amorphous Films, Varied Porosity. In the previous section, we established that sticking probabilities of CH₄ are higher for p-ASW films than either np-ASW or CI films at high incident energies. This comparison, however, only includes porous films deposited at 30° relative to surface normal. Figure 7 depicts the sticking probabilities for CH₄ on a variety of porous films, including those deposited via directed doser (at 30°, 60°, and 70° from surface normal) as well as via background deposition. Surprisingly, there is no strong variation in sticking probabilities for CH₄ on any of these films, despite the expected differences in pore orientation and film density.

To further understand these results, it is possible to quantify CH₄ coverage on a given surface during a period of exposure...
and compare it across films. We can estimate the amount of adsorbed CH₄ at a given time t₁ using the following equation

\[ N_{\text{CH}_4} = \left( P_2 - P_0 \right)(t_1 - t_0) - \int_{t_0}^{t_1} P(t) \, dt \]  

(2)

In eq 2, \( P_2 \) is the indirect CH₄ flux when the beam is blocked from the substrate; \( P_0 \) is the background CH₄ pressure when the beam is closed; and \( t_0 \) is the time at which the flag is removed; and the film is fully exposed to CH₄. The last term is a simple numerical integration of the raw King and Wells pressure reading between those two time values. In doing this analysis for high translational energy CH₄ beams (1.8 eV), we find that in the first seconds of exposure (corresponding to a total exposure of \( (5.0 \pm 0.4) \times 10^{14} \text{CH}_4 \text{cm}^{-2} \)) CI and np-ASW films have adsorbed \( (1.0 \pm 0.1) \times 10^{14} \text{CH}_4 \text{cm}^{-2} \) while 200 ML porous films (at all deposition angles) have accumulated \( (1.8 \pm 0.3) \times 10^{14} \text{CH}_4 \text{cm}^{-2} \). This increase is the result of both increased surface area and higher initial sticking probabilities on porous films at these beam energies, and the difference only widens as exposure continues. The difference in uptake is illustrated qualitatively in Figure 8a, which depicts normalized King and Wells data for representative trials on np-ASW, CI, and p-ASW films. To aid in visual comparison, the data have been normalized in both axes by incident flux. Clearly, the porous film adsors more CH₄ before desorption takes over.

In Figure 8b the results of a similar coverage analysis are displayed for all porous ices. In this depiction, total coverage is scaled further by surface area to give an approximate “fractional coverage”. Relative surface area is defined via the integrated intensity of the dangling O−D feature. As discussed in Figure 1, this feature provides a reasonable measure of porosity and is related to the total surface area of the film. 41,68 Though the initial sticking probability is consistent across porous films, the relative accumulation of CH₄ is 1–2 times higher for films deposited at 30° and via background deposition than those deposited at 60° or 70°. The roots of this behavior will be addressed further in the Discussion section below.

## DISCUSSION

There are two new, significant findings to come out of this work. The first is that the sticking probability of CH₄ on p-

![Figure 7](image1.png)

**Figure 7.** Sticking probabilities are shown for CH₄ impinging on porous D₂O films held at 33.5 K, deposited via directed doser at 30° (red), 60° (green), and 70° (gray) relative to surface normal as well as via background deposition (purple). For the incident energies studied, there are no clear differences in sticking probabilities for these films. Error bars represent the standard deviation of at least three measurements on at least two different days.

![Figure 8](image2.png)

**Figure 8.** Representative, normalized King and Wells data for all films studied show a clear increase in CH₄ uptake on porous films relative to CI and np-ASW. (a) Total uptake on a porous film (p-ASW, red) is nearly an order of magnitude higher than on either crystalline (CI, yellow) or non-porous (np-ASW, blue). Time and intensity axes are normalized to the incident flux. (b) Fractional CH₄ coverage is higher for porous films deposited at 30° or via background deposition (red, purple) than for those deposited at 60° or 70° (green, gray). Fractional coverage is defined as the total adsorbed CH₄ scaled by the integrated areas of the dangling bond feature. All data were selected from trials using 1.8 eV and CH₄ beams.

ASW D₂O films do not decay as fast as it does on CI and np-ASW D₂O films. The second is that under our energetic conditions the sticking probability trend does not depend on the type of porous ice film used. What follows is a qualitative discussion of why these trends occur and how future studies might further refine the proposed conclusions.

Sticking probabilities for a particular system are known to depend on both the binding energy between the surface and the adsorbate as well as the surface conditions (morphology, temperature, etc.).44,66 Binding energies for a variety of molecules on different ices of astrochemical interest have been widely reported. As discussed, the low-coverage binding energy for CH₄ on np-ASW ice has been reported in the range of 0.06−0.14 eV.5 Additionally, differences in binding energy for CO (CH₄ and CO are expected to have similar binding interactions on ice) 39,49,53,69 between CI and np-ASW are small and on the order of 0.01 eV at most.49 This suggests a partial explanation for the similarity in sticking probabilities between these two ica films. Binding energies on porous films, on the other hand, may be higher than those for either np-ASW or CI ice interfaces. Many studies assert that the binding energy distribution for molecules on porous films is wider and peaks at higher values.42 This idea is refined by Zubkov et al., who concluded that while the distribution of binding sites on the surface is independent of film thickness and porosity the lower fractional coverages of adsorbates on porous films (due to their increased surface area) lead to adsorbrates interacting with more higher-energy binding sites.45,47,72 In short, it is likely that at the low coverages investigated here CH₄ binds somewhat more strongly to the porous films.
Binding energy, however, is not a sufficient explanation on its own. Whatever the variation may be for the different ice films, all available reported binding energies for CO and CH$_4$ are less than 0.2 eV. This is significantly lower than most of the incident energies studied here, suggesting that there must be an additional mechanism for energy accommodation by the surface. Indeed, theoretical work has been done to show that energy dissipation into ice films is incredibly facile under similar conditions.29 We suggest, therefore, that it is the distinct morphology of the porous films that is largely responsible for the observed divergence in sticking probabilities at high incident energies. Desorption studies from a variety of porous substrates have found that desorption kinetics are governed by diffusive motion within pores and multiple collisions with pore walls.57,71 Indeed, the energy-dissipating effects of these pore wall collisions have been previously cited in studies of molecular or atomic interactions with ice.74,75 Zubkho et al. also found that prior to desorption molecules on porous ice experience hundreds of desorption–readesorption attempts (as compared to just one attempt on non-porous).76 Perhaps the most significant evidence of this energy accommodation by pore walls was demonstrated in a study of HD recombination. Hornekaer et al. found that on porous ice a significant fraction of newly formed HD remained adsorbed to the surface, indicating that the porous network was extremely efficient at dissipating the 4.5 eV recombination energy.29 This is in contrast to a non-porous film, which saw almost zero retention of the HD molecules following recombination. In summary, the higher sticking probabilities for CH$_4$ on p-ASW relative to np-ASW and CI likely result from diffusion on and multiple collisions with pore walls, leading to a more efficient dissipation of incident translational energy. It is possible, then, that the sticking probability as discussed here on porous films is more of an uptake coefficient, a measure of advantageous deceleration induced by the physical pore structure, rather than a higher capacity for site-specific energy accommodation on different types of icy surfaces.

In order to discuss CH$_4$ coverage, it is important to mention the impact of desorption. As mentioned previously, only a fraction of a CH$_4$ monolayer can remain stably adsorbed on the surface at 33.5 K. Therefore, we expect the increase in reflected signal after the first few seconds (after initial sticking is measured) to be a result of both directly reflected CH$_4$ and steadily desorbing CH$_4$. Ultimately, when the reflected signal levels off at long exposure time scales, adsorption and desorption are occurring at equal rates. Measured isothermal, low-coverage desorption rates for all porous films studied here are roughly equivalent and comparable in magnitude to the incident flux, making it possible to compare coverages across these films despite the competing rates of adsorption and desorption.

At normal incidence, this study showed that porous films of any orientation are equally efficient at dissipating the energy of impinging CH$_4$, but these films adsorb relatively different amounts of CH$_4$, depending on deposition conditions. The invariance in sticking probability across films of different porosities suggests that the D$_2$O pore surface is equally efficient at accommodating the incident energy of the CH$_4$ molecules, regardless of how that pore is oriented relative to the incident beam. These results also suggest, however, that incident CH$_4$ is not sampling the full surface area of the pore network of 60° and 70° films before beginning to desorb. This can perhaps be understood in terms of pore geometry and size.

Films deposited at 30° have lower total surface areas, but they also have pores that are closer to perpendicular to the substrate.9,77 Relatively more of the pore surface area, therefore, is accessible to the incident beam. Likewise background deposited films have a distribution of pore sizes and orientations, some fraction of which will be perpendicular or near-perpendicular to the substrate. On the other hand, the more tilted, wider pores of the 60° and 70° films present fewer surface sites for the incident beam. So while CH$_4$ may undergo multiple collisions with the pore structure before sticking, these coverage results indicate that adsorbed CH$_4$ is not necessarily diffusing fully into the pore structure and filling up all available surface sites, particularly on the more angled porous film structures. A future experiment that explores the angular dependence of sticking and uptake on these porous films would be a significant step toward identifying the relative importance of factors such as pore orientation and size.

## CONCLUSION

In this work we present detailed sticking probability measurements for high translational energy CH$_4$ impinging on a variety of D$_2$O ice films at 33.5 K. We confirm that at the energies studied CH$_4$ is unable to either embed in the bulk or significantly impact the morphology of any ice, including low-density porous films. As incident translational energy increases, the sticking probability decreases for all films. However, CH$_4$ sticks with greater probability to p-ASW films than it does to either CI or np-ASW films at the same energies. Furthermore, we observe no substantial changes in sticking probability when changing the exact morphology (pore orientation and size) of the porous film used. Even though there may be slight changes in binding energies between CH$_4$ and the different films, we propose that the porous morphology is largely responsible for this observed divergence. Multiple collisions with pore walls are likely efficient at dissipating the incident energy of the CH$_4$ projectile. This conclusion is supported by the fact that porous films with more beam-accessible pore surfaces (films deposited at 30° and via background deposition) accumulate relatively more CH$_4$ during exposure than do films with fewer accessible pore surfaces (deposited at 60° and 70°).

These results are further evidence that the morphology of ice films (and other industrial substrates) critically influences the adsorption and subsequent reactivity of incident molecules. Even if not universally porous, small cracks, fissures, and other morphological deformities in the surface of astrophysical ices may lead to an increased uptake of gaseous molecules, thereby impacting phenomena including the outgassing of comets, chemical reactions in the ISM, and thermal and electrical processing of icy dust grains.9,68

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: s-sibener@uchicago.edu.

### ORCID

S. J. Sibener: 0000-0002-5298-5484

### Notes

The authors declare no competing financial interest.

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REFERENCES


(55) Grundy, W. M.; Schmitt, B.; Quirico, E. The Temperature-Dependent Spectrum of Methane Ice 1 between 0.7 and 5 Mn and Opportunities for Near-Infrared Remote Thermometry. Icarus 2002, 155, 486−496.


