The Effective Surface Area of Amorphous Solid Water Measured by the Infrared Absorption of Carbon Monoxide

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Abstract

The need to characterize ices coating dust grains in dense interstellar clouds arises from the importance of ice morphology in facilitating the diffusion and storage of radicals and reaction products in ices, a well-known place for the formation of complex molecules. Yet, there is considerable uncertainty about the structure of interstellar medium ices, their ability to store volatiles, and under what conditions. We measured the infrared absorption spectra of CO on the pore surface of porous amorphous solid water (ASW), and quantified the effective pore surface area of ASW. Additionally, we present results obtained from a Monte Carlo model of ASW in which the morphology of the ice is directly visualized and quantified. We found that 200 ML of ASW annealed to 20 K has a total pore surface area that is equivalent to 46 ML. This surface area decreases linearly with temperature to about 120 K. We also found that (1) dangling OH bonds only exist on the surface of pores; (2) almost all of the pores in the ASW are connected to the vacuum–ice interface, and are accessible for adsorption of volatiles from the gas phase; there are few closed cavities inside ASW at least up to a thickness of 200 ML; (3) the total pore surface area is proportional to the total three-coordinated water molecules in the ASW in the temperature range 60–120 K. We also discuss the implications on the structure of ASW and surface reactions in the ice mantle in dense clouds.

Key words: astrochemistry – ISM: molecules – methods: laboratory: molecular – methods: laboratory: solid state

1. Introduction

In dense clouds in the interstellar medium (ISM), dust grains are covered by frozen molecules, mostly water ice in amorphous form (Hagen et al. 1981). The ice provides a catalytic surface where atoms and molecules are stored and where reactions leading to the formation of many molecular species take place (Herbst & van Dishoeck 2009; Vastel et al. 2014). Thus, they are important molecular factories, together with gas-phase reactions. Laboratory measurement of the surface area available for catalysis is therefore important for understanding the chemistry on and in the ice mantle.

In typical laboratory experiments under zero pressure, two recognized forms of amorphous solid water (ASW) can be formed from water vapor deposition—porous and non-porous (compact). Whether the structure of ASW is porous or compact depends on the deposition methods (Stevenson et al. 1999; Kimmel et al. 2001b; Dohnálek et al. 2003; Raut et al. 2007a). Generally, a lower deposition temperature and a higher deposition angle with respect to the surface normal favor a higher porosity. If ASW is grown from water vapor deposition onto a substrate at 130 K or above, the ice is compact. It was also reported that ASW grown from a collimated beam of water vapor at normal incidence forms a compact structure even at lower temperatures (Kimmel et al. 2001b). Omnidirectional deposition of water vapor when the substrate is at lower than 130 K forms porous ASW. Upon heating, porous ice gradually transforms into non-porous ice. Pore collapse during thermal annealing (Bossa et al. 2012) and as a result of irradiation with ions or UV light (Palumbo 2006) has been previously studied in the laboratory. However, the question still remains whether the ice mantle covering dust grains is porous or compact.

One useful signature of porous ASW is the presence of OH dangling bonds (dOH). It is established that there are two types, for doubly and triply coordinated water molecules at the ice surface (Buch & Devlin 1991; Devlin & Buch 1995). Their presence is uncovered in the IR tail of the OH stretch, at 3720 and 3696 cm⁻¹ for doubly and triply coordinated water molecules, respectively. It is conceivable to link the presence and strength of the dOH to the porosity of ice; however, this linkage has been proven difficult to establish unambiguously. Experimental studies (Palumbo 2006; Raut et al. 2007b; Isokoski et al. 2014; Mitterdorfer et al. 2014) show that the total number of dangling bonds is not proportional to the porosity, and some porosity is retained when the signature of dangling bonds disappears. This is an important point, as dOH IR signatures have not been seen in observations so far (Keane et al. 2001). It is also known that the position and strength of dOH bonds are affected by the presence of other atoms or molecules (see He et al. 2018b for a recent investigation of change in the IR bands of the dangling bonds due to adsorption of H₂, D₂, Ar, CO, N₂, CH₄, and O₂). Furthermore, the thermal treatment of ASW irreversibly changes the network of pores: as the temperature is increased, the ice morphology changes and pore collapse occurs. In this work, we investigate again the relation between dOH bands and porosity, and hope to find new insights into this decades-old problem.

Compared to the studies mentioned above, which mostly focused on measuring the porosity (or equivalently the density) of the ASW, fewer details are available about the link between the morphology and catalytic properties of ices. Raut et al. (2007b) performed energetic ion bombardment of ASW and found that the surface area of porous ice decreases at a faster rate than the pore volume during ion-induced compaction. The
underlying reason for this difference is still not well understood, but several mechanisms have been proposed, including coalescence of micropores, preferential destruction of smaller pores, and smoothing of pore wall topology (Raut et al. 2007b). Prior laboratory measurements of porosity based on density (Bossa et al. 2014; Cazaux et al. 2015) do not reflect the true catalytic potential of the ASW surface. It is important to measure the pore surface area that is accessible for the adsorption of volatiles from the gas phase. Palumbo (2006) studied the accessible pore surface area after compaction of the ASW by energetic ions. However, in highly shielded clouds, thermal processes should dominate over energetic processing, and the temperature dependence of the pore surface area is the most important factor. One of the main goals of this study is to fill this gap and use the infrared absorption spectrum of CO as a tool to quantify the temperature dependence of the catalytic surface area that is accessible to volatile molecules condensed from the gas phase.

ASW is also the main component of comets. Although it is widely accepted that comets are among the most pristine ice objects in the solar system, little is known about the structure of the ASW in the cometary core. As the structure of the ice changes when the comet is exposed to solar irradiation, molecules can be trapped in the ice well beyond the temperature at which they would desorb if they were adsorbed on the surface (Bar-nun et al. 1985; Smith et al. 1997; Alan May et al. 2013). Recently, the Rosetta mission has detected a number of molecules from comet 67P/Churyumov–Gerasimenko. Notably, molecular oxygen has been detected at an abundance of 4% with respect to water (Bieler et al. 2015). A satisfactory explanation is still lacking. To quantify the release of volatiles from the comet, it is important to understand the link between the trapping of volatiles and the ice structure. In this study we also look into the trapping of CO in ASW under different temperature conditions.

2. Experimental Setup

A detailed description of the apparatus can be found in previous publications (He & Vidali 2018; He et al. 2018b), so here only the main features that are relevant to this study are summarized. Experiments in this study were carried out using an ultra-high vacuum apparatus with a base pressure of $4 \times 10^{-10}$ Torr. A gold coated copper disk attached to the cold head of a closed-cycle helium cryostat was used as the sample disk onto which ices were grown. The temperature of the sample can be controlled between 5 and 350 K to an accuracy of better than 50 mK. Ices are grown by vapor deposition from the chamber background. CO gas and water vapor entered the chamber via two separate precision leak valves, which are automated by stepper motors controlled with LabVIEW programs. Ice thickness in units of monolayer (ML) is calculated from the impingement rate based on an integration of the chamber pressure (He et al. 2018b). One monolayer is defined as $10^{15}$ molecule cm$^{-2}$ on a flat surface. The ion gauge correction factor and velocity of both water and CO were taken into account in the calculation. The relative uncertainty in the CO dose and water dose are less than 0.1% and 1%, respectively. The main source of uncertainty is from the hot cathode ion gauge, which has an absolute uncertainty up to 30%. More details on the deposition control are reported in He et al. (2018b). Ice on the sample is measured using a Fourier Transform InfraRed (FTIR) spectrometer in the Reflection Absorption InfraRed Spectroscopy (RAIRS) configuration.

In the experiments, we first deposited 200 ML of porous ASW when the surface was at 10 K, then heated the ice at a ramp rate of 3 K minute$^{-1}$ from 10 to 200 K. The RAIR spectra were measured continuously during the heating and we monitored how the two dOH bands change with temperature. Next, we carried out a whole set of experiments of CO deposition on top of 200 ML of ASW annealed at different temperatures. The ASW samples were grown when the sample was at 10 K, and then annealed at 20, 40, 60, 80, 100, 120, and 140 K for 30 minutes. Afterward, the ice sample was cooled down to 20 K (except for the 20 K annealing) before depositing CO continuously until the ASW pore surface was fully covered by CO, as indicated by the emergence of the longitudinal optical (LO) mode of CO at $\sim 2143$ cm$^{-1}$. The CO deposition rate was chosen so that there are enough data points during the deposition, and it varies between experiments. The CO deposition temperature was chosen to be 20 K, because at this temperature, CO has enough mobility on the surface of p-ASW (He et al. 2018b).

3. Modeling

Ice simulations are conducted using the off-lattice microscopic kinetic Monte Carlo model MIMICK (Model for Interstellar Monte Carlo Ice Chemical Kinetics), adapted from the works of Garrod (2013) and Clements et al. (2018), with flat geometry and periodic boundary conditions. The model allows the diffusion of individual molecules to be traced over time, at various temperatures. As well as thermal diffusion (hopping) between surface potential minima, non-thermal diffusion is also allowed, immediately following the deposition of each water molecule onto the surface; the gas-phase translational energy of the molecule and the energy it gains as it enters the surface potential allow it to diffuse if its energy is sufficient to overcome the local diffusion barrier(s). The model uses isotropic Lennard-Jones potentials, which were parameterized within the model by Clements et al. (2018) using experimental density data from the literature for amorphous water formed through background deposition at various temperatures (Brown et al. 1996).

In the present models, water is deposited at interstellar temperatures (10–20 K) and then heated at laboratory rates (1–3 K minute$^{-1}$) up to a temperature of 150 K. First, the water molecules are deposited using background deposition onto a square surface of length 650 Å, significantly smaller than a surface used in the experiments for computation time. A deposition rate of 10$^{13}$ cm$^{-2}$ s$^{-1}$ and temperature of 10 K were used and two thicknesses were tested (25 ML and 200 ML). Surface area and density are calculated for each ice and measured during heating.

The ice surface area (including pore surfaces) is calculated by counting the number of surface molecules. This value is then divided by the total number of water molecules in the ice. This ratio corresponds to the coverage of the surface to the total ice thickness in monolayers. With the microscopic model the surface coverage can be directly measured. An average of the thin ice (25 ML) and the thick ice (200 ML) was used to calculate the pore surface; as we later discuss, the surface area is dependent on thickness between 10 and 200 ML. Images were created using the freeware POV-Ray to visualize all of ice, or using cross sections, the connectedness of the pores.
4. Results and Analysis

4.1. Infrared Characterization of Pure ASW

ASW has three main absorptions in the mid-infrared region: OH stretching at ∼3300 cm⁻¹, bending mode at 1640 cm⁻¹, and libration mode at ∼700 cm⁻¹. On the blue shoulder of the OH stretch band, there are two small absorption features at ∼3696 and ∼3720 cm⁻¹, generally attributed to three-coordinated and two-coordinated water molecules, respectively (Buch & Devlin 1991). The dOH bands contain important information regarding the structure of the ASW, and are the focus of this subsection.

The dOH region of the RAIR spectra of the 200 ML ASW during heating is shown in Figure 1. As the ice temperature is raised, both dOH bands decrease. By 60 K, the 3720 cm⁻¹ band is almost gone, while the 3696 cm⁻¹ band persists until above 140 K. To quantify the temperature dependence of both bands, we use two Gaussian functions to fit the two dOH bands. Because the two dOH bands lie on the tail of the main OH stretching band, it is important to find a function that fits the baseline. In previous studies, spline interpolation or polynomial functions were typically employed to fit the baseline (Dartois et al. 2013; Bu et al. 2016; Mitchell et al. 2017). We find that for the work presented here they are not good enough for an accurate description of the baseline, and lead to inaccuracies in dOH band area calculations. Gaussian and Lorentzian functions are very often used to fit solid state infrared absorption features. Typically, disordered ices have relatively broad Gaussian line shapes, while crystalline ices have narrower Lorentzian line shapes. We tried (1) one Gaussian; (2) one Lorentzian; (3) two Gaussians; and (4) one Gaussian and one Lorentzian functions to fit the blue side of the OH stretch peak; the two dOH bands are also included in the fitting. Figures 2 and 3 show the fitting and the residuals, respectively. It can be seen that the fitting using one Gaussian and one Lorentzian, in addition to two Gaussians for the dOH bands, achieves the best results. For analyses that do not require high accuracy, one Gaussian function also fits the blue half of the OH stretch well. In the remainder of this work, we use one Gaussian and one Lorentzian to fit the blue side of the OH stretch band. Based on the above fitting scheme, the band areas of both dOH bands during warming of the 200 ML ASW are calculated and presented in Figure 4. At ∼60 K, the 3720 cm⁻¹ band becomes negligible, which suggests the disappearance of two-coordinated dangling bonds. This is consistent with previous experimental studies (Raut et al. 2007b; Smith et al. 2009; Bu et al. 2015). The 3696 cm⁻¹ band drops linearly with temperature from 60 K to above 140 K. The residual 3696 cm⁻¹ band at above 140 K is largely due to the dangling bonds located on the outer surface (Smith et al. 2009).

4.2. CO on ASW

In the next set of experiments, we use the infrared bands of CO to probe the pore surface area of ASW annealed at different temperatures. It is well-established that the infrared absorption feature of CO interacting with water ice is different from that of pure CO ice. The RAIRS of pure CO shows the longitudinal optical (LO) mode at 2143 cm⁻¹ (which is the typical one that is excited in the grazing mode geometry), while CO interacting with water shows two bands at ∼2140 and ∼2152 cm⁻¹.
According to our previous laboratory measurement of the diffusion of CO on the surface of porous amorphous solid water (p-ASW, He et al. 2018b), diffusion of CO becomes significant at about 15 K. At 20 K, the diffusion is very efficient. If CO is deposited on top of ASW at 20 K, CO should diffuse into the pores and occupy the pore surface of the ASW. Once the whole surface area is covered by CO, and CO begins to build up as “pure” CO ice, the LO mode emerges. By examining the amount of CO deposited at which the LO peak emerges, the accessible surface area of p-ASW can be obtained. In the following, we first present a detailed analysis of the results of CO deposition on ASW annealed at 60 K and cooled to 20 K, and then show the results at other annealing temperatures.

Figure 5 shows the RAIR spectra of C–O stretching mode during deposition of CO on ASW annealed at 60 K and cooled to 20 K. At low CO deposition doses, there are two broad components centered at ∼2140 and 2152 cm⁻¹. When the CO dose is over ∼30 ML, the LO mode at 2143 cm⁻¹ emerges, which we take as a sign of full coverage of the pore surface.

There have been several experimental studies of the interaction between CO and ASW surface (e.g., Fraser et al. 2004; Collings et al. 2005). Although it is generally accepted that the ∼2152 cm⁻¹ component is due to the adsorption of CO on the dOH sites of ASW, there is no direct experimental evidence, as far as we know, that demonstrates the correlation between dOH bands and the 2152 cm⁻¹ component. We used two Gaussian functions to fit the 2140 and 2152 cm⁻¹ components, and one Lorentzian function to fit the 2143 cm⁻¹ component, and then we studied how these three components change with CO deposition dose. An example fitting is shown in Figure 6. We apply a similar fitting to all of the spectra in this experiment. The resulting band areas for the three components are shown in Figure 7.

As was discussed in He et al. (2018b), introducing CO in ASW shifts the dOH bands. In Figure 8, the dOH region of the RAIR spectra before and after the CO deposition is shown. Before CO deposition, the dOH band is at 3694–3696 cm⁻¹ (the peak position varies between 3694 and 3696 cm⁻¹, depending on the annealing temperature; hereafter, we refer to this peak as the 3696 cm⁻¹ peak), while after CO deposition, the area of the 3696 cm⁻¹ peak decreases to zero and the dOH induced by CO shows up at ∼3636 cm⁻¹. We used one Gaussian function to fit the 3696 cm⁻¹ peak and one Gaussian function to fit the 3636 cm⁻¹ peak, and obtained how the two peaks change with increasing CO deposition. The area of the 3696 cm⁻¹ peak is shown in Figure 7, together with the peak areas of the three components of C–O stretching mode. Between 0 and 12 ML, the 3696 cm⁻¹ band area decreases to zero. At the same time, the band area of 2152 cm⁻¹ components increases from 0 to the saturation level. The anti-correlation between these two bands is evident. This is direct evidence that the 2152 cm⁻¹ component is associated with CO binding to the dOH bonds.

At about 27 ML of CO deposition, the 2140 cm⁻¹ band begins to saturate, while at the same time the 2143 cm⁻¹ LO band emerges. This demonstrates that at about 27 ML of CO deposition, all the pore surface area is occupied, and “pure” CO starts to build up. This happens at a higher CO dose than the full covering of the dOH bonds, likely because CO molecules...
preferentially occupy the dOH sites than non-dOH sites. In a prior study by Zubkov et al. (2007), it is reported that the full coverage of pore surface by nitrogen adsorption happens simultaneously with the saturation of the shifted dangling bond intensity. They suggested that N2 does not preferentially bind to dangling OH groups. The difference between that work and this one is possibly due to the relative interaction energies of the two adsorbates. While nitrogen adsorption shifts the 3-coordinated dOH peak to 3668 cm\(^{-1}\), CO adsorption shifts it by a larger amount, to 3635 cm\(^{-1}\) (He et al. 2018b). We take the CO dose at which the 2143 cm\(^{-1}\) component just starts to show up, 27 ML in this case, to be the pore surface area. The fact that the 3696 cm\(^{-1}\) band disappears after CO deposition indicates that all of the pore surface area is accessible for CO adsorption, and there is insignificant number of closed cavities inside the ASW (which would have been detected by residual dOH band at 3696 cm\(^{-1}\)). Therefore, 27 ML is the accessible area and is also the total pore surface area of the 200 ML ASW annealed to 60 K.

Similar CO depositions were carried out on 200 ML ASW samples that were annealed at 20, 40, 80, 100, 120, and 140 K, and cooled down to 20 K. RAIR spectra were recorded during CO depositions at 20 K and are shown in Figure 9. We determine the pore surface areas for the ASW annealed at different temperatures by visually examining the CO deposition dose at which the 2143 cm\(^{-1}\) component emerges. The ASW surface area versus annealing temperature is shown in Figure 10. The pore surface area decreases linearly with annealing temperature almost up to 120 K, above which the surface area becomes about 2 ML. Considering that the surface of ASW is rough, 2 ML covers probably the very top of the surface, i.e., the ice–vacuum interface. The ice becomes fully compact at 140 K. The almost linear decrease in pore surface area with annealing temperature in the range 20–120 K is also seen in the neutron scattering experiments by another group (S. Gärtner 2019, private communication).

In the previous section, we focused on the infrared spectra during CO depositions. Here in this section, we focus on the TPD stage of the same set of experiments. After the deposition of CO on ASW at 20 K, the ice was heated up from 20 to 200 K at a ramp rate of 0.1 K s\(^{-1}\) while RAIR spectra were measured continuously. The band area of the C–O stretching mode was calculated for each spectrum during warming up (see Figure 11). For ices that are annealed at 60 K and above, the C–O stretch band area becomes zero after the temperature goes past 60 K (for clarity purpose, curves for 80 K and above are not shown in the figure). This is in agreement with the study by Horimoto et al. (2002), who carried out similar experiments using methane instead of CO. In the figure, the desorption of CO from the ice can be separated into three regions. The first region is below about 55 K, which is the temperature at which CO on ASW surface (including the surface of pores) desorbs. The second region is from about 55 K to about 150 K, during which the CO band area drops linearly with temperature. These
are the CO molecules that are trapped in the ASW matrix and released back into the gas phase gradually. Here, we do not exclude the possibility that the band strength of CO buried inside bulk ASW can change with temperature. Indeed, experimental measurements by Schmitt et al. (1989) have found that the band strength of C–O stretching for CO buried in water ice has a reversible component that decreases almost linearly with the temperature between 50 and 120 K. The irreversible component corresponds to the gradual releasing of CO from the bulk ASW. The third desorption happens when the ASW crystallizes, and all of the remaining CO molecules are forced out of the ice. This is sometimes referred to as the “molecular volcano” (Smith et al. 1997). The amount of CO that is in the ice at about 60 K represents the CO that is trapped inside the ASW matrix, and we define it as the trapping amount. When the ASW is annealed to 60 K or above, the ASW does not trap any CO. The lower the annealing temperature, the higher the number of CO molecules that can be trapped. The linear decrease of the C–O stretching band area during heating is similar to that of CO$_2$ (see Figure 4 of He et al. 2018a). This suggests that the linearity may be a general phenomenon that occurs to all volatiles that are trapped in ASW. In a forthcoming paper, we will present a detailed study on the trapping of volatiles in ASW.

4.4. Dangling OH Bonds during CO Deposition

During CO deposition on ASW, as the pore surface is gradually covered by CO, the dOH band at 3696 cm$^{-1}$ decreases, and the band at 3636 cm$^{-1}$ increases. We applied the fitting scheme as discussed above to obtain the area of the dOH band during CO deposition. Figure 12 shows the area of the 3696 cm$^{-1}$ dOH band during CO deposited on ASW that has been annealed at different temperatures. For the ASW that was annealed at 140 K, the dOH band area is too small, and is not presented in the figure. For an annealing temperature of 20 and 40 K, there are two dOH bands after annealing, and the fittings of the peaks is more complicated and are not considered here. The main finding from Figure 12 is that the dOH always drop to zero at high enough CO doses, regardless of the annealing temperature. This suggests that almost all the pore surface inside the ASW is accessible to CO, and the pores throughout the ice are interconnected. This agrees with the previous results by Raut et al. (2007a), who demonstrated that all of the pores are interconnected and are accessible to CH$_4$ adsorption.

4.5. Modeling of ASW Ice Porosity

Figure 13 shows the structure of simulated water ice; the column-like structure becomes smoother with increasing temperatures, until eventually an entirely smooth structure is obtained at 140–150 K. In the model, the initial ice was deposited at 10 K and then heated to $\sim 150$ K, where the ice starts to desorb into the gas phase. The first two images of the model (at 10 and 70 K) have essentially the same structure. The model indicates there is little to no rearrangement of the ice until a temperature of 60 K is reached. At 60–80 K, diffusion of water becomes efficient enough to play a role in the surface area and porosity, and increases at higher temperatures. The structure begins to smooth, by eliminating first the smaller pores until gradually all the pores are removed. Through this process, the ice reaches its maximum density at 150 K. It is important to note the model does not include the phase change from amorphous to crystalline ice, which would occur at $\sim 140$ K; this does not alter the results of the model, as the main focus is between temperatures of 10 and 140 K.

In the laboratory results shown in Figure 10, we see that the accessible surface area decreases steadily up to 140 K. As stated above, the three-coordinate dOH absorption band (3696 cm$^{-1}$) linearly decreases from 60 to 140 K, likely corresponding to the decrease in the surface area; this matches the decrease of the exposed surface in the model. As seen in Figure 14, the coverage steadily decreases after 80 K is reached. Until that temperature is reached, very little rearrangement and pore collapse occur; this is probably due to the fact that the model uses isotropic potentials, and is not sensitive to defects (OH dangling bonds), which the experiment is sensitive to. However, within the model we see a reasonable match at lower temperatures given that CO is a proxy for the extent of the accessible exposed H$_2$O network.

Figure 15 shows the modeling results of the ratio of the number of surface molecules to the total number of molecules during the deposition of 200 ML water onto a 10 K surface. In the first few monolayers, there is a large fraction of surface molecules. After the thickness reaches more than $\sim 10$ ML, the fraction of surface molecules is no longer dependent on the thickness. This suggests that the structure of the ASW film is homogeneous and the conclusions in this work based on measurements of 200 ML ASW can be generalized to other thicknesses as well, as long as the ice is thicker than a threshold, which in this study is, $\sim 10$ ML. This is more or less in agreement with previous studies by Stevenson et al. (1999),
Kimmel et al. (2001a, 2001b), and Smith et al. (2009), although the threshold thickness in those studies differ from this study.

Previously, Kimmel et al. (2001a, 2001b) used a kinetic model where a hit and stick method was used. Each individual molecule sticks to the surface depending on the trajectory angle selected. That model does not include kinetic energy, but has a parameter that designates how many times each incoming particle is allowed to hop before being permanently sticking. The images in Kimmel et al. show that the pores are also interconnected at the temperature of deposition, but their work does not include a linear warm-up of the ice. The model presented here is a kinetic model and hopping is set by the temperature, which in this case is essential as we linearly increase the temperature to replicate the experimental results.

We show that the pores are interconnected and maintain this structure for high temperatures.

Unlike the experiments, within the model no rearrangement occurs below 60 K, because of the isotropic treatment used. Essentially, the model does not show the small-scale rearrangement due to re-alignment of water molecules within their original potential. While the model cannot achieve these changes, it can provide a direct way to measure the surface coverage of water ice. The surface area can be monitored during heating instead of requiring CO adsorption experiments where the water ice must be cooled down to 20 K to measure the amount of CO adsorbed on the ASW. Furthermore, the determination of surface area using CO adsorption as in the laboratory experiments may not be exactly the same as that from counting the number of water molecules on pore surfaces as in the modeling. A small difference between these two methods is possible.

Figure 16 shows the interconnectedness of the pores. A portion of ice was imaged to show the inner structure and not the total structure. Visually it shows that most pores are connected within the shown plane. As the ice is heated the pores collapse until eventually empty cavities within the water ice are left. The cavities appear to be the remnants of the initial column-like structure, which minimizes its energy by forming approximately spherical structures. The encapsulated pores are fairly small in size, with widths around 2–3 nanometers. These cavities may allow entrapment of some volatile species such as CO until a later temperature. By 150 K all cavities have collapsed and the volatiles have either been desorbed or are stuck within a water matrix.

5. Discussion and Astrophysical Implications

One of the main spectroscopic pieces of evidence of porous ASW is the presence of dOH bonds, which have been seen in numerous laboratory experiments. Whether the infrared signature of dOH bonds at 3696 and 3720 cm⁻¹ is a good measurement of porosity has been debated. Palumbo (2006)
performed energetic ion bombardment on ASW and found that the decrease of pore surface area is four times less than the decrease in dOH absorption. From this experiment, one might conclude that the dOH band area is not proportional to the pore surface area. However, ion bombardment also induces chemistry that produces molecules such as O_2, O_3, H_2O_2, which may interact with the dOH bonds and shift or shield the dOH bands (He et al. 2018b). It is unclear from their experiments what is the relation between dOH band area and pore surface area for pure ASW. In this regard, thermal processing of ASW is a more appropriate experiment. There have been experiments that focused on thermal processing of ASW (Bossa et al. 2012, 2014; Isokoski et al. 2014). However, those studies quantified the density of the ice instead of the pore surface area. In this study, we measured the pore surface area of ASW that is annealed at different temperatures, and also quantified the temperature dependence of the dOH band area during heating of ASW. Additionally, we used a kinetic Monte Carlo model to determine the pore surface area of ASW during heating, by computing directly the total number of surface molecules. We have shown in Figure 4 that the two-coordinated dOH (3720 cm\(^{-1}\)) decreases sharply between 10 and 60 K, and disappears almost completely by \(\sim\)60 K. There is possibly a smoothing of the pore surface or merger of smaller pores to form larger ones. The three-coordinated dOH absorption band (3696 cm\(^{-1}\)) decreases almost linearly between 60 and 140 K. This linear decrease with temperature can be compared with the linear decrease of pore surface area shown in Figure 10. Both seem to decrease linearly with temperature, although the curve in Figure 10 drops to the minimum at a slightly lower temperature than that in Figure 4. This small difference can be explained by the fact that in measuring the pore surface area using CO adsorption, ASW was annealed for 30 minutes, while when measuring the dOH bands shown in Figure 4, the temperature was ramped up continuously without the annealing step. The comparison between these two figures suggests that at least under our experimental conditions, the infrared absorption band of 3696 cm\(^{-1}\) seems to be a good measurement of the pore surface area in the temperature range from 40 to 140 K.

The presence of cavities inside ASW has been reported in several prior studies (Eldrup et al. 1985; Horimoto et al. 2002; Zheng et al. 2007). However, it is unclear whether these cavities are closed inside the bulk ASW or interconnected and accessible from the vacuum–ice interface. In Figure 3 of Raut et al. (2007b) and Figure 8 of Cazaux et al. (2015), it was hinted that there are closed cavities, but there was no discussion of the connectivity of the cavities. In Figure 12, it is evident that after CO adsorption, the 3696 cm\(^{-1}\) band always drops to zero, regardless of the annealing temperature. This suggests that there is an insignificant number of closed cavities inside the bulk ASW, and almost all of the cavities (pores) are connected to the vacuum–ice interface. This is verified by the modeling, which shows that volatile species should indeed be able to access almost all of the pore surface inside the ice. This is also in agreement with the experimental results of Raut et al. (2007a), who found that the number of closed pores is insignificant in a 1000 ML ASW. However, we have to point out that this conclusion may not be applicable to an ASW much thicker than 1000 ML. Bu et al. (2016) reported that a thick ASW may crack spontaneously during growth or during warming up. It remains a question how the spontaneous cracking affects the connectivity of the cavities/pores inside ASW.

From Figure 12, we can reach the conclusion that all of the dOH bonds are located on a pore surface accessible from the vacuum–ice interface instead of inside the bulk ASW. On the surfaces of pores, a water molecule can form two, three, or four bonds with neighboring water molecules, and they are called two-, three-, or four-coordinated, respectively. Figure 4 shows that as long as the ASW is heated to \(\sim\)60 K, two-coordinated water molecules disappear, leaving three- and four-coordinated molecules. Based on the comparison of Figure 10 with Figure 4, we can see that between 60 and 140 K, the number of three- and four-coordinated water molecules is roughly proportional to the total pore surface area. This indicates that the ratio between three- and four-coordinated water molecules is more or less a constant. As the properties of ASW surface are determined by the relative ratio between two-, three-, and four-coordinated water molecules, this would indicate that other than differing in the total pore surface area, the properties of the pore surface remain the same between 60 and 140 K. Previously, Zubkov et al. (2007) performed TPD measurements of N\(_2\) adsorbed on both compact and porous ASW, and found that if a correction for surface area is taken into account, the desorption energy distribution on porous ASW is nearly identical to that of compact ASW. Our results based on a different method agree with their conclusion. From a laboratory perspective, the independence of surface property on porosity suggests that in some scenarios, one may be able to carry out experiments on a porous ASW that is annealed to 60 K, and the result would be the same—aside from a scaling factor—as that on an ASW that is annealed to 140 K, which has a compact structure. Since experiments on a porous ASW would in general have a much higher sensitivity than on the very top surface of a compact ASW, this conclusion is very useful in laboratory studies of ASW. One example of its application is presented in He et al. (2018b), who measured the diffusion of volatile molecules on the surface of porous ASW. Conclusions in that study would be applicable to the surface of any ASW (porous or compact) that is annealed to 60 K and above.

The surface of ASW is known to catalyze the formation of molecular species on dust grains in the ISM. Porous ASW possess a specific surface area up to a few hundred m\(^2\) g\(^{-1}\) and therefore may account for most of the catalytic surface on the dust grains. Even if ASW undergoes thermal processing, significant residual porosity may be retained (Isokoski et al. 2014). However, it was unclear how much of the residual porosity can actually contribute to the catalysis of chemical reactions. The key question here is whether these remaining pores are closed cavities buried inside the bulk ice, or they are accessible to volatiles from gas adsorption. Our experimental results in Figure 12 show that all of the dOH in the ASW can be covered by CO molecules, which suggests that all of the pore surface area is accessible for reactive species condensed from the gas phase. The large pore surface actually contributes to the catalysis of the formation of complex species in the ice. The fact that all pores are connected all the way to the vacuum–ice interface suggests the possibility that volatile molecules that are formed on the pore surface can diffuse and desorb from the ice before the desorption of water. The desorption of molecules before water desorption has the potential to explain the observations that found complex organic molecules in regions
with high-extinction (Vasyunin & Herbst 2013; Agúndez et al. 2015) and regions outside the water snow line in protoplanetary disks (Oberg et al. 2015).

6. Conclusions

In this study we used the infrared absorption spectrum of carbon monoxide as a tool to measure the pore surface area of ASW grown by vapor deposition and annealed at different temperatures. A kinetic Monte Carlo model was used to visualize the porosity and measure the surface area directly. Below are the findings from this study:

1. Experimental results show that the total pore surface area in 200 ML of ASW at 20 K is equivalent to 46 ML, and decreases linearly with annealing temperature to $\sim$120 K.
2. Almost all pores are connected to the vacuum–ice interface and accessible for volatile adsorption.
3. All dangling OH bonds, as inferred by the 3696 and 1 dOH bands, which is due to three-coordinated water molecules, disappears when the ASW is heated to 60 K.
4. The 3720 cm$^{-1}$ OH band, which is due to three-coordinated water molecules, decreases more or less linearly between $\sim$60 and 140 K.
5. The 3696 cm$^{-1}$ OH band, which is due to three-coordinated water molecules, decreases more or less linearly between $\sim$60 and 140 K.
6. The ratio between three- and four-coordinated water molecules on the surface of pores remains constant between 60 and 140 K; this indicates that the surface properties, as far as adsorption of volatiles is concerned, do not change significantly in this temperature range, except for the change in the total surface area.
7. The 2152 cm$^{-1}$ OH band, which is due to three-coordinated water molecules, disappears when the ASW is heated to 60 K.
8. ASW annealed to 60 K or above loses the capability to trap CO molecules from the gas phase.
9. After the first $\sim$10 ML, the fraction of surface molecules to the total number water molecules does not change with thickness.

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