

# Effect of humidity on lubricated carbon overcoats

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An apparatus has been designed and built to measure the adsorption of contaminants on the surfaces of lubricated carbon overcoats such as those used on magnetic data storage media. The device is based on a quartz crystal microbalance housed in a high vacuum chamber and can be used to make rapid measurements of both the amounts and the rates of contaminant adsorption from the gas phase during exposure. Initial measurements of the adsorption of water during exposure to water vapor indicate that at room temperature and moderate humidity levels (~50% RH) the amount of water on a surface is of the order of one adsorbed monolayer. Adsorption and desorption is remarkably rapid indicating that equilibrium with ambient humidity is reached on timescales of minutes. Finally, the comparison of H<sub>2</sub>O and D<sub>2</sub>O adsorption indicates that the adsorbed water either forms a hydrogen bonded network on the surface or is hydrogen bonded to some species exposed at the surface of the carbon overcoat.

**KEY WORDS:** magnetic hard disks; carbon overcoats; quartz crystal microbalance; water absorption; heat of absorption

## 1. Introduction

The surfaces of magnetic data storage media are commonly coated with a thin film (~20–50 Å) of amorphous hydrogenated carbon (a-CH<sub>x</sub>) that is then covered with an even thinner film (~10 Å) of lubricants such as perfluoropolyalkyl ethers. This lubricant/overcoat combination must protect the surface of a magnetic hard disk in a wide range of environmental conditions. The media surface must be protected from damage due to intermittent contacts with the read-write head as it flies over the disk and from damage such as corrosion due to the environment. The read-write head flies over the spinning disk at a height of ~50–70 Å above the lubricant surface. Given the very small margins for error in the dimension of the head–disk interface it is not surprising that contamination of the disk surface can play a major role in causing failure of disk drives [1–4]. One of the goals of the research reported in this paper is to develop and apply a device for measurement of contaminant adsorption on the surfaces of magnetic data storage media.

Humidity is one of the most widely variable environmental conditions to which a disk surface is exposed during normal operation. Drives must operate in environments ranging from desert-like to tropical. There are a number of reports of the effects of humidity on the properties of the lubricant films used to protect the disk surface [5–7]. These suggest that humidity can affect lubricant mobility, and ultimately disk lifetime. Humidity is also likely to be an important factor in media corrosion. In addition to humidity the disk surface is exposed to other contaminants that are outgassed by various components of the drive. These can lead to phenomena such as corrosion and head smear both of which are detrimental to the operation of the drive [8]. One of the roles of the lubricant/overcoat is to protect the media from con-

tamination. In order to better understand these phenomena there is a need for the measurement of contaminant adsorption rates and adsorption isotherms on lubricated overcoats.

This paper describes an apparatus that has been designed to provide fast (~10 s) and quantitative (< 1 ng/cm<sup>2</sup>) measurements of the adsorption of contaminants on lubricated carbon overcoats. This is accomplished through the use of a standard quartz crystal microbalance (QCM) housed in a vacuum chamber that allows controlled exposure to contaminants with partial pressures in the range 10<sup>-7</sup>–10<sup>3</sup> Torr. Initial measurements have been made using exposures to H<sub>2</sub>O vapor in order to simulate environments of varying humidity. Smallen *et al.* [9] measured water adsorption on thin film magnetic media using an ellipsometer with a humidity chamber mounted on a sample stage. Water adsorption was measured on lubricated and unlubricated carbon overcoats with hydrogen contents varying from 0 to 30%. The lubricants used were Fomblin Z-25, AM2001 and Fomblin Zdol. Water adsorption was observed to be dependent on the hydrogen content for both lubricated and unlubricated carbon overcoats. They have also measured water adsorption on three different types of read-write heads with different compositions. They have concluded that water adsorption on magnetic recording heads depends both on the head composition and surface roughness.

Using the QCM based system developed for this work we have measured the amount of H<sub>2</sub>O and D<sub>2</sub>O adsorbed on an a-CH<sub>x</sub> overcoat (100 Å) lubricated with 20 Å of Fomblin Z03. We find that the amount of water adsorbed at room temperature and vapor pressures equivalent to roughly 50% humidity is on the order of one molecular monolayer. One of the most interesting things is that the rates of adsorption and desorption are quite rapid. In fact steady state or equilibrium adsorption is probably established on timescales of less than 1 min or, in other words, much faster than the timescale

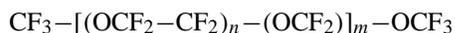
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for normal fluctuations in ambient humidity. This suggests that on a real disk the coverage of H<sub>2</sub>O is always in equilibrium with the vapor pressure of water or humidity within the drive. Finally, the comparison of H<sub>2</sub>O and D<sub>2</sub>O adsorption indicates that the adsorbed water is hydrogen bonded either to the surface or in an intermolecular network.

## 2. Experimental

The apparatus designed and constructed for measurement of contaminant adsorption on lubricated overcoats is based on a small high vacuum chamber pumped with a turbomolecular pump. Although it can reach pressures in the 10<sup>-10</sup> Torr range after baking this was not necessary for the work described here and the usual base pressure after introducing a sample and pumping overnight was 10<sup>-8</sup> Torr. The chamber has an ion gauge for high vacuum pressure measurement and a capacitance manometer gauge for pressure measurements in the range 0.1–1000 Torr. Adsorption was measured on the surface of a quartz crystal microbalance by controlling the pressure of gasses in the chamber. Vapors and gasses were introduced into the chamber through a needle valve. The QCM is a commercially available unit (Maxtek Inc.) that is mounted on a linear motion device. It is equipped with two quartz crystals to allow comparisons of adsorption on two sample surfaces exposed to identical conditions. The quartz crystals are of the AT cut with resonant frequencies of ~5 MHz. The temperature of the QCM is measured by a K-type thermocouple spotwelded to the quartz crystal housing. The QCM is water-cooled and the temperature of water can be controlled using a recirculating water chiller. This apparatus will allow measurements of contaminant adsorption on the quartz crystal surface with a time resolution on the order of 10 s and an accuracy of ~1 ng/cm<sup>2</sup>. This can be accomplished using partial pressures of contaminants in the range 10<sup>-7</sup>–100 Torr.

As supplied the surfaces of the quartz crystals are coated with gold films used as electrodes. The gold surfaces have been modified in this work by sputter deposition of 100 Å of a-CH<sub>x</sub> followed by dip-coating to apply a thin (20 Å) film of Fomblin Z03 lubricant (Mol. Wt. = 2500 amu). The carbon-coated quartz crystal was dip-coated by submersion into a solution of Fomblin Z03 in Vertel XF and then withdrawn at a rate of 4 mm/s. This procedure has previously been calibrated and is known to produce a lubricant film of 20 Å thickness on the surfaces of hard disks. Fomblin Z03 is long chain fluoroether polymer with no functional end groups,



For the measurements described in this paper the quartz crystals with overcoat and lubricant were introduced into the vacuum chamber which was then evacuated with the turbopump for a period of ~12 h prior to measurements. The lubricant/overcoat was then exposed to gasses and vapors (H<sub>2</sub>O, D<sub>2</sub>O, and Ar) introduced into the chamber through

the needle valve. The H<sub>2</sub>O and D<sub>2</sub>O were kept in a small glass sample vial attached to the needle valve. Prior to introduction into the chamber they were purified by freeze–pump–thaw cycles to remove any dissolved gasses. Once purified the vapor was then introduced into the chamber to reach a fixed pressure measured by the capacitance manometer. During introduction of the water vapor into the chamber the quartz crystal frequency was monitored in order to measure the amount of material adsorbing on the surface as a function of time during exposure. Once the desired pressure of water vapor was achieved it was held constant for a period of ~30 min following which it was pumped from the system. The frequency of the QCM was monitored throughout the introduction and removal of vapor from the chamber.

## 3. Results and discussion

### 3.1. H<sub>2</sub>O adsorption

In order to test the system for measurements of contaminant adsorption on media surfaces we have first compared the uptake of H<sub>2</sub>O on quartz crystals with and without lubricated overcoats. One quartz crystal was introduced into the chamber with its surface modified by Fomblin Z03/a-CH<sub>x</sub> while the second quartz crystal simply had the gold overcoat provided by the manufacturer. Figure 1 shows the adsorption and desorption of H<sub>2</sub>O from the surface during exposure of the surfaces to H<sub>2</sub>O vapor. Initially the chamber was under vacuum. At 15 min H<sub>2</sub>O vapor was introduced into the chamber through the needle valve and the pressure was allowed to increase steadily to a final pressure of 10 Torr. At room temperature a vapor pressure of 10 Torr corresponds to a relative humidity of ~50%. From 20 to 55 min the pressure was kept constant and then the H<sub>2</sub>O vapor was rapidly pumped from the chamber by opening the valve to a mechanical pump and then turning on the turbopump. Clearly, figure 1 reveals both adsorption and desorption of H<sub>2</sub>O on the lubricated overcoat during the exposure and evacuation of H<sub>2</sub>O vapor.

There are several important features to be observed in the H<sub>2</sub>O uptake and desorption profiles of figure 1. The first is the differences in the uptake of H<sub>2</sub>O on the lubricated *versus* gold surfaces. It is quite apparent that there is H<sub>2</sub>O adsorption on the quartz crystal that has been coated with Fomblin Z03/a-CH<sub>x</sub> while there is negligible adsorption on the gold-coated surface. One would expect that the adsorption on gold might be less than on the lubricated overcoat since the gold surface is probably quite inert. It should be pointed out that H<sub>2</sub>O adsorption on various gold surfaces has been measured many times and is not very reproducible although it always adsorbs substantially less H<sub>2</sub>O than the lubricated overcoat. Typically, at a pressure of 10 Torr the amount of water adsorbed on the gold surface is 10 ± 5 ng/cm<sup>2</sup>. By comparison the amount of H<sub>2</sub>O adsorbed on the lubricated overcoat is 40 ± 5 ng/cm<sup>2</sup> at a vapor pressure of 10 Torr. The irreproducibility in the measurement of water uptake on the

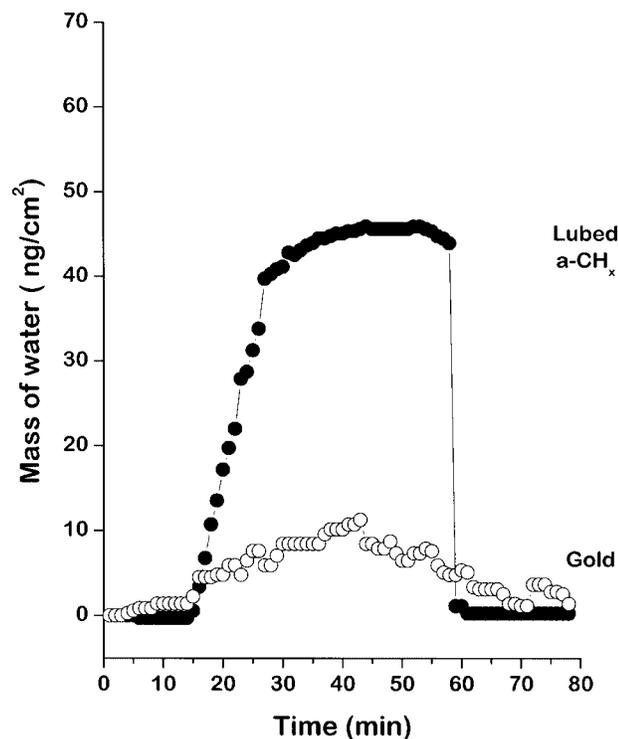


Figure 1. The mass of H<sub>2</sub>O adsorbed on the surface of quartz crystals covered with gold and with a lubricated a-CH<sub>x</sub> film during exposure to H<sub>2</sub>O vapor. The modified quartz crystal surface was coated with 100 Å of a-CH<sub>x</sub> and 20 Å of Fomblin Z03. Water adsorption on the lubricated surface begins as soon as the pressure of H<sub>2</sub>O vapor increases and then plateaus once the pressure of H<sub>2</sub>O is held constant at 10 Torr. The desorption of the H<sub>2</sub>O from the surface begins as soon as the H<sub>2</sub>O is pumped from the chamber. There is almost no adsorption of H<sub>2</sub>O on the gold surface.

gold surfaces is probably due to the fact that we have made no special effort to clean or prepare those surfaces and they are probably contaminated to varying extents.

It is important to determine the coverage of water on the surface of the carbon overcoat in the presence of humidity. The amount of H<sub>2</sub>O adsorbed on the lubricated overcoat for an exposure to 10 Torr of H<sub>2</sub>O vapor is  $\sim 40$  ng/cm<sup>2</sup>. If one takes the volume of a water molecule from the density of bulk water to be 30 Å<sup>3</sup> then the area per molecule is roughly 10<sup>-15</sup> cm<sup>2</sup> and an adsorbed mass of 40 ng/cm<sup>2</sup> corresponds to coverage of about 1.3 monolayers. There are several assumptions that go into this estimate. One is that the packing of water in an adsorbed layer on the lubricated overcoat is similar to its packing in condensed water. The second is that the surface area of the lubricated overcoat is roughly its apparent surface area. In other words we assume that the surface is not extremely rough or porous. This is borne out by previous measurements which suggest that the real surface area of such overcoats is on the order of twice the apparent area [10]. In any case, using liberal error bars the measurement suggests that the coverage of H<sub>2</sub>O is probably  $1.3 \pm 0.3$  monolayer at room temperature and a relative humidity of 50%. Preliminary measurements in the humidity range 0–50% indicate that the amount of adsorbed H<sub>2</sub>O is roughly linear in the relative humidity. It is worth pointing

out that we do not learn anything about the distribution of adsorbed water on the surface. It may be adsorbed in the pores of the a-CH<sub>x</sub> film, on the lubricant itself, or in the form of islands interspersed between regions of adsorbed lubricant. Our results indicate that under high humidity conditions the amount of adsorbed water on data storage media would be in excess of a monolayer if it were uniformly distributed over the surface.

There have been other measurements of the adsorption of water on a-CH<sub>x</sub> films that have yield coverages in the same range as observed in our experiments. Karis has measured the adsorption of water on a nitrogenated carbon overcoat lubricated with Fomblin Zdol 4000 that was 43% chemisorbed to the surface [2]. According to his estimate Zdol adsorbs  $\sim 0.3$  monolayers of water at 50% humidity. His study however does not involve water adsorption on Fomblin Z03. In another study by Smallen [9], it has been reported that water adsorption on both lubricated and unlubricated disks is independent of the lubricant type or lubricant thickness but primarily depends on the hydrogen content of carbon overcoats. Smallen has reported that at 25% relative humidity 2 monolayers of water are adsorbed on an unlubricated carbon overcoat with 30% hydrogen. In other words these studies are indicative of the fact that adsorption of water is dependent on the type of the carbon overcoat.

A final point to be made concerning the adsorption/desorption of H<sub>2</sub>O from the surface of the lubricated overcoat comes from examining the rates of uptake and loss during introduction and pumping of H<sub>2</sub>O vapor from the chamber. During introduction of the H<sub>2</sub>O vapor into the chamber the amount of adsorbed H<sub>2</sub>O increases roughly linearly in time, as does the H<sub>2</sub>O pressure. Once the pressure reaches 10 Torr and ceases to rise the coverage of H<sub>2</sub>O reaches a plateau. During evacuation the amount of adsorbed H<sub>2</sub>O drops almost to zero in under 1 min. Although we have not yet made accurate measurements of H<sub>2</sub>O adsorption or desorption rates it is quite clear that the adsorption and desorption processes are reaching completion on a timescale of the order of minutes. This indicates that adsorbed water is in equilibrium with humidity in the environment. Certainly on the timescales on which the humidity within a drive changes it can be assumed that the coverage of adsorbed H<sub>2</sub>O on the media surface is in equilibrium with the humidity in the drive.

### 3.2. Argon adsorption

The two control measurements that have been performed to test the use of the QCM as a means for measuring the adsorption of contaminants on lubricated overcoats are comparison with adsorption on a gold surface shown above and exposure to Ar gas. The heat of adsorption of Ar on either gold or a lubricated overcoat should be extremely small and thus there should be little or no adsorption at room temperature. Figure 2 shows the response of the QCM during an exposure to 10 Torr of Ar at room temperature. The Ar is introduced into the chamber between 10 and 15 min, held at

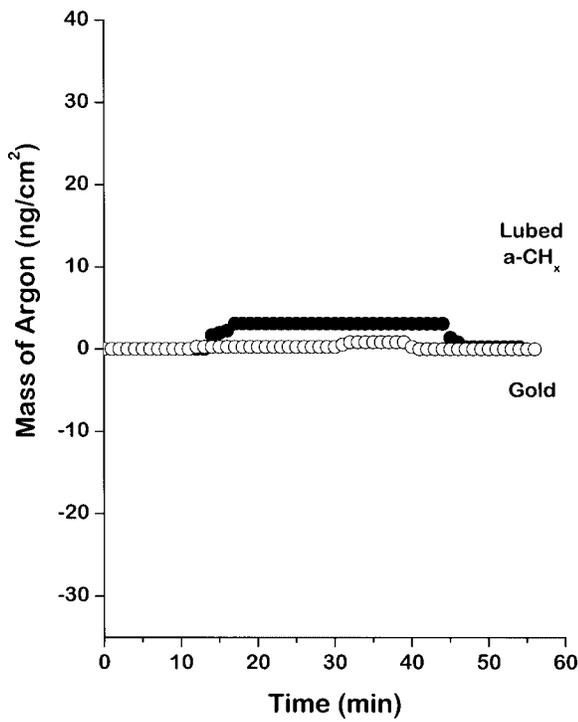


Figure 2. The mass of Ar adsorbed on the surface of quartz crystals covered with gold and with a lubricated a-CH<sub>x</sub> film during exposure to Ar gas at room temperature. The total amount adsorbed at an Ar pressure of 10 Torr is negligible when compared to the amount of H<sub>2</sub>O adsorbed during exposure to H<sub>2</sub>O vapor at 10 Torr.

10 Torr and then pumped out at 45 min. It is quite apparent that there is little adsorption on either the lubricated overcoat or on the gold surface. The point of this is to illustrate clearly that the response of the QCM during exposure to H<sub>2</sub>O vapor is due to adsorption rather than to changes in either the pressure or perhaps the temperature during introduction of gas into the chamber.

### 3.3. D<sub>2</sub>O adsorption

The adsorption of D<sub>2</sub>O on the lubricated overcoat has been studied in order to show clearly that the response of the QCM is due to water adsorption. All things being equal the adsorption of D<sub>2</sub>O (20 amu) on the lubricated overcoat ought to result in an increase in mass that is ~10% higher than that observed with H<sub>2</sub>O (18 amu) simply because of the isotopic mass difference between deuterium and hydrogen. Figure 3 shows the response of the QCM to an exposure to 5 Torr of D<sub>2</sub>O at room temperature. In this case roughly 35 ng/cm<sup>2</sup> of D<sub>2</sub>O are adsorbed on the surface or 1.75 ± 0.14 times the mass of H<sub>2</sub>O adsorbed under the same conditions. Roughly the same ratio of D<sub>2</sub>O to H<sub>2</sub>O adsorption has been observed at other pressures. This is more than can be accounted for simply on the basis of the molar mass difference of D<sub>2</sub>O and H<sub>2</sub>O. The reason can be appreciated from the fact that the heat of adsorption of the D<sub>2</sub>O may be higher than that of H<sub>2</sub>O. The heat of vaporization of D<sub>2</sub>O (45.38 kJ/mol at 25 °C) is higher than that of H<sub>2</sub>O (43.99 kJ/mol at 20 °C) and is reflected in the fact that the boiling point of D<sub>2</sub>O is

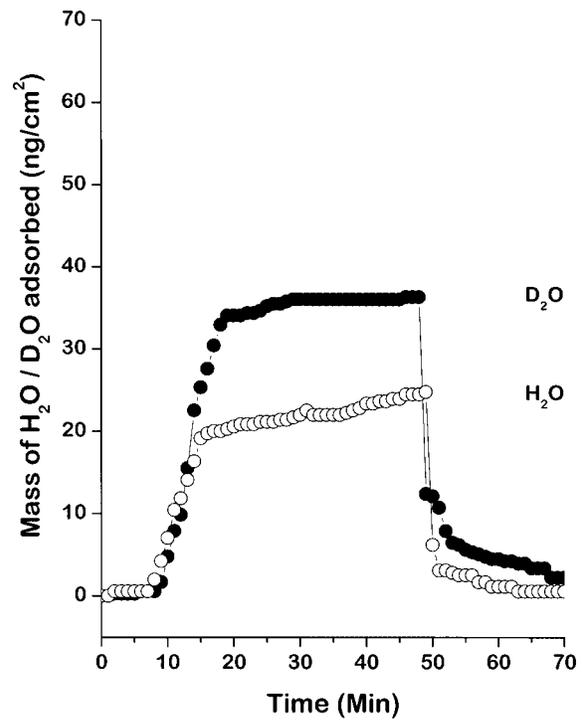


Figure 3. The masses of D<sub>2</sub>O and H<sub>2</sub>O adsorbed on the surfaces of quartz crystals covered with a lubricated a-CH<sub>x</sub> film during exposure to 5 Torr of D<sub>2</sub>O or H<sub>2</sub>O vapor at room temperature. The mass of adsorbed D<sub>2</sub>O is roughly 75% greater than the amount of adsorbed H<sub>2</sub>O under identical conditions in spite of the fact that the mass of D<sub>2</sub>O is only 10% greater than that of H<sub>2</sub>O. This implies that the heat of adsorption of D<sub>2</sub>O is greater than that of H<sub>2</sub>O. This is consistent with a hydrogen bonding interaction of water with the surface.

101.4 °C as opposed to 100.0 °C for H<sub>2</sub>O [11]. The difference in the heats of vaporization is due to the fact that water molecules in the condensed phase interact through hydrogen bonding. These hydrogen bonds are, of course, broken during vaporization. The higher mass of the deuterium atom results in a lower zero-point vibrational energy of the O–D ··· O hydrogen bond and thus a higher heat of vaporization needed to disrupt the deuterium bonding network in condensed D<sub>2</sub>O.

We can estimate the difference in the heats of adsorption of H<sub>2</sub>O and D<sub>2</sub>O based on the amounts adsorbed at a pressure of 5 Torr at room temperature. The ratio of the adsorbed masses is:

$$\frac{m_{\text{D}_2\text{O}}}{m_{\text{H}_2\text{O}}} = 1.75 \pm 0.14,$$

which gives a ratio of molar coverages of

$$\frac{\theta_{\text{D}_2\text{O}}}{\theta_{\text{H}_2\text{O}}} = 1.58.$$

The coverages are dictated by equilibrium constants of the form

$$\frac{\theta}{P} \propto \exp\left(-\frac{\Delta H_{\text{ads}}}{RT}\right),$$

where  $P$  is the vapor pressure of water and  $\Delta H_{\text{ads}}$  is the heat of adsorption on the a-CH<sub>x</sub> surface. Finally the ratio of the molar coverages of H<sub>2</sub>O and D<sub>2</sub>O is

$$\frac{\theta_{\text{D}_2\text{O}}}{\theta_{\text{H}_2\text{O}}} = \exp\left(\frac{\Delta\Delta H_{\text{ads}}}{RT}\right).$$

This yields a value of  $\Delta\Delta H_{\text{ads}} = 1.1$  kJ/mol for the difference in the heat of adsorption of H<sub>2</sub>O and D<sub>2</sub>O on the a-CH<sub>x</sub> at room temperature. This number is very close to the difference in the heats of vaporization of D<sub>2</sub>O and H<sub>2</sub>O which is  $\Delta\Delta H_{\text{vap}} = 1.4$  kJ/mol. The fact that the heat of adsorption of D<sub>2</sub>O is greater than that of H<sub>2</sub>O suggests that the interaction with the surface involves hydrogen bonding. While it is possible that there is some direct hydrogen bonding interaction between the adsorbed water and various functional groups on either the a-CH<sub>x</sub> or the lubricant it is also quite possible that the adsorbed water simply exists as a network of intermolecular hydrogen bonds.

#### 4. Conclusions

The use of the QCM and its potential for measurement of contaminant adsorption on lubricated carbon overcoats has been demonstrated. The initial results reported in this paper on the adsorption of water from humid environments already indicate that at moderate relative humidity water is adsorbed on the lubricated overcoat at coverages approaching a monolayer. The fact that the QCM can measure water uptake and desorption on timescales of the order of seconds has enabled us to show that under the normal operating conditions of a drive the water adsorbed on the disk surface is in equilibrium with the ambient humidity and that changes in ambient

humidity can cause significant changes in the coverage of adsorbed water on a timescale of minutes. Finally, the comparison of the coverages of adsorbed H<sub>2</sub>O and D<sub>2</sub>O indicate that the water interacts with the surface through a hydrogen-bonding interaction.

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