Molecular Hydrophobicity of Hydroxylated MgO Surfaces

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Abstract

Interfaces between minerals and water play a vital role in many geochemical and industrial processes such as dissolution and growth, sorption of heavy metals and organic contaminants, heterogeneous catalysis, corrosion, and many more. Due in part to its simple geometric structure, MgO (periclase) is a useful model system for understanding how the interaction between specific surface structure and water yield macroscopic observables such as wettability. Here we report the first vibrational sum frequency generation (vSFG) spectroscopy study of MgO (100) and (111) single crystal surfaces, using hydrated conditions both in the ambient atmosphere and in contact with a bulk aqueous fluid. Although most metal oxide surfaces are hydroxylated and strongly interacting with water, for MgO crystal surfaces in air or water vibrational sum frequency generation (vSFG) spectra show the presence of strong non-H-bonded OH stretching vibrations ($\sim 3700\text{ cm}^{-1}$), suggesting an unusual molecularly hydrophobicity.

Introduction

Advancing molecular-level understanding of the structure and dynamics at metal oxide-water interfaces is important across a wide range of natural and industrial systems because of its influence over processes such as ion adsorption, nutrient transport, wastewater management, electrode chemistry, corrosion, and heterogeneous catalysis. Particularly crucial is understanding the interactions of oxide surfaces with water molecules which, by hydroxylation, can strongly impact the resulting surface structure and reactivity. In particular, the hydrated surface structure within the first few monolayers dictates how bulk water molecules interact with the material, including setting important properties such as the extent of hydrophilic or hydrophobic character. However, relationships between interfacial structure, hydroxylation, and bulk water wettability remain poorly predictable.

Due to its simple cubic (rocksalt) structure, MgO is an ideal model system to explore this relationship, which must begin with understanding the hydroxylation behavior of its major low-index surfaces of (100) and (111) orientations. Many theoretical and experimental studies have been carried out to understand how these surfaces interact with water¹⁻⁸, yet the molecular-level picture of the surface structure of the MgO-water interface is not clear. This is particularly true for MgO(111), for which all parting planes of the bulk crystal structure are nominally Tasker type III and thus electrostatically unstable (polar) terminations highly prone to reconstruction.⁹ For the more well studied and simpler case of electrostatically stable MgO(100), it is generally agreed that water molecules physisorb on the defect-free surface while the presence of the under-coordinated defect sites such as step edges, corners, kinks, divacancies, valleys, etc. favors dissociative chemisorption of the water.^{1,2} However, such concepts do not necessarily enable direct prediction of the net interaction of the surface with water that controls wettability and other macroscopic observables, which is based in part on molecular orientations of surface hydroxyls and their capacity to form H-bonding networks with sorbed water.

It has been reported that anhydrous MgO is very hydrophilic.^{8,10} Using MD simulations, Kerisit and De Yoreo⁸ recently demonstrated that the simple cubic termination of MgO(100) should be more

hydrophilic than the basal surface of both muscovite ($\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$) and pyrophyllite ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$). Tuan et. al.¹⁰, by using the CLAYFF force field showed that for the surface with a top atomic layer composed of MgO, the water-surface contact angle is approximately 47° , likewise indicating a rather moderately hydrophilic surface. An experimentally determined water contact angle of 58.1° remains higher than the theoretical prediction, albeit measured using pressed pellets of MgO powder^{10,11}. However, it is noteworthy that both simulation studies relied upon non-dissociable water models, thus hydroxylation was either evaluated by approximation or ignored. Given that in most settings metal oxide surfaces tend to be hydroxylated, it is the interaction of water with the hydroxylated surface that is more relevant to understanding the reactivity of the hydrated surface.

Second-order non-linear vSFG spectroscopy is an ideal approach to understand hydroxylation properties of various metal oxide surfaces and their relationship to overlying hydration water layers. vSFG has excellent surface sensitivity and is particularly useful in structural characterization of the nature and extent of H-bonding of the surface molecular groups.¹²⁻¹⁶ Surprisingly, vSFG spectroscopy has not yet been applied to this important archetypal interface of hydrated MgO surfaces. Systematic vSFG spectroscopic study not only provides interface-specific structural information at the molecular level but also allows direct interrogation of surface hydroxyl group orientations. In this study, we exploit vSFG spectroscopy to probe the hydroxylation and hydration of single crystal MgO(100) and (111) surfaces under ambient laboratory conditions both in the air (relative humidity $\sim 25\%$) and in contact with bulk water. Results show that both as-prepared terminations are strongly hydroxylated, with prominent vSFG spectral features from interfacial non-H-bonded hydroxyl groups appearing both in ambient air and while in contact with bulk water. The hydroxylation structure of MgO single crystals at ambient conditions gives rise to negligible interaction with hydration waters, a property at the molecular scale that could lead to macroscopically observable hydrophobic character.

Results And Discussion

The single crystal MgO substrates for the vSFG experiment were cleaned to ensure the complete removal of the adsorbed hydrocarbons from the surfaces (see **SI** for details). The vSFG spectra were recorded from both the MgO(100) and MgO(111) single crystal substrates using the SSP polarization combination, where each letter in the polarization combination nomenclature signifies the polarization state of the sum frequency signal, visible, and IR beam, respectively. S-polarized beam has the incident electric field perpendicular to the incident plane, whereas, P-polarized beam has the optical field parallel to the incident plane.

Figure 1 shows vSFG spectra in the SSP polarization combination along with the corresponding fit for the MgO(100) and MgO(111) single crystal substrates at the interface with air. The fitting parameters are available in tables S1-S2 in the **SI**. In both cases, the presence of the strong bands in the OH stretching region shows that the as-prepared MgO surfaces are hydroxylated. This property is not unexpected given prior work showing both the tendency for clean MgO surfaces in vacuum to react with water vapor near

ambient conditions^{17,18} and the near-equilibrium between MgO and Mg(OH)₂ (brucite) in low temperature hydrous environments.¹⁹ Furthermore, Carrasco et. al. by using X-ray photoelectron spectroscopy, infrared reflection absorption spectroscopy, and density functional theory calculations showed that the extensive hydroxylation of thick bulklike MgO films occurs above the threshold water pressure of 10⁻⁴ mbar.²⁰

Despite the absence of detailed knowledge about the exact arrangement of surface atoms present on our (100) and (111) samples, it is nonetheless reasonable to presume two main categories of surface hydroxyl groups arising from dissociative adsorption of water molecules on the under-coordinated (UC) ions namely Mg²⁺_{UC} or O²⁻_{UC} based on the following scheme:³

Scheme 1: Hydroxylation of the MgO surface

The OH groups on the surface cations Mg²⁺_{UC}, usually are monocoordinated OH groups and O_{UC}H groups generated by protonation of surface oxide anions are multi-coordinated. Beyond terrace sites, the degree of coordination further depends on the position of the hydroxyl groups on the surface with respect to defects (corners, edges, kinks, etc.).

Peak assignments for our vSFG spectra can be done similarly as proposed in the literature for bulk hydroxylated MgO.^{2,3} For example, the comprehensive model proposed by Knozinger et al.² for the IR spectra of hydroxylated MgO powders synthesized by chemical vapor deposition can be adopted. Each spectrum is fitted with three component peaks as shown in Figure 1. The details of the fitting and fitting parameters are available in the SI. The three main components in ambient air are i) strong and relatively narrow high frequency band (>3680 cm⁻¹), ii) the relatively broad shoulder band centered around ~3660 cm⁻¹, and iii) the broad weak band in the low frequency region (<3600 cm⁻¹). It is well known that the vibrational frequency of the OH stretch is dependent primarily on the nature of the H-bonding and the actual coordination number of the hydroxyl oxygen. The OH stretching frequency generally follows the order of isolated non-H-bonding > H-bond acceptors > H-bond donors. Following this model, the narrow band in the high frequency region (>3680 cm⁻¹) can be attributed to the isolated and under-coordinated (UC) OH groups attached to Mg²⁺ which are not involved in the hydrogen bonding. The shoulder around ~3660 cm⁻¹ is due to the under-coordinated (U'C) OH groups. On the other hand, the weak band in the lower frequency region (<3600 cm⁻¹) can be assigned to the multi-coordinated OH groups as well as the H-bonded OH of the adsorbed molecular water molecules which are involved in H-bonding interactions. Even though the overall vibrational band structure of the MgO(100) and MgO(111) surfaces is similar, there are two important differences in the spectra. First, there is a peak shift in the high frequency band in MgO(100) (3685 cm⁻¹) compared to that for MgO(111) (~3720 cm⁻¹). This could be explained by the difference in the net orientation of the hydroxyl groups due to differences expected in the surface terminations. The blue shifted peak at 3720 cm⁻¹ suggests a more inert nature of the surface hydroxyl groups on MgO(111) relative to MgO(100). It is interesting to note here that the peak at 3720 cm⁻¹ for the

MgO(111) surface is also blue shifted by about 20 cm^{-1} compared to nominally “free” OH stretching ($\sim 3700\text{ cm}^{-1}$) of the water molecule at the air/water interface.^{21,22} Secondly, the intensity of the lower frequency bands for MgO(100) is stronger compared to that of MgO(111), as shown in Figure 1C. Given the bulk crystal structure, and prior studies, the MgO(100) surface is likely terminated with alternating Mg and O atoms. Less certain is the termination for MgO(111) but, in principle, this surface could be terminated predominantly with either Mg or O atoms of the MgO lattice. The shift in the peak position of the narrowband peak of MgO(111) to higher frequency likely indicates that the UC hydroxyl groups on the MgO(111) surface are less influenced by nearby U'C hydroxyl groups, relative to that on MgO(100). In addition, the vSFG intensity of the lower frequency bands of MgO(111) is weaker than that for MgO(100). These observations suggest that the MgO(111) termination may be Mg-dominant, although further verification is needed. It is also possible that the intensity differences arise from orientational differences of the H-bonded OH groups on the two surfaces.

The air/MgO results clearly show that both MgO surfaces are strongly hydroxylated, and it is expected that the surface hydroxyls exert a great influence on MgO reactivity. To explore this, we collected vSFG spectra of the surfaces in contact with liquid H₂O and liquid D₂O, focusing on the OH and OD stretching regions (see **SI** for detail). The use of D₂O enabled us to distinguish between the surface hydroxyl groups on the air side (OH groups) from the hydroxyl groups on the liquid side (OD groups) of the sample. Hence, we ensure that the vSFG signal recorded is free from that of the air/MgO interface, as shown in **Figure S3** in **SI**. The vSFG spectra were also recorded from the silica/water and alumina/water interfaces in the same experimental geometry as the reference spectra (see **Figure S4**). Also, the time dependent vSFG experiments were performed to ensure the MgO surface does not undergo a significant change in the surface structure during the experimental period due to its solubility in the water (See **Figure S5** in **SI**).

Figure 2 shows the vSFG spectra from MgO(111) and MgO(100) in contact with D₂O including peak-fitting results. The fitting parameters are available in tables S3-S4 in the **SI**. The spectra in the OD stretching region have similar spectral features as in the air-MgO spectra with the OH peaks. The presence of the prominent OD stretches indicates that the surface OH groups on MgO undergo H/D exchange upon contact with the D₂O. The vSFG spectra from MgO/D₂O are mainly dominated by spectral features from the hydroxylated MgO surface with OD groups. The vibrational signature from the molecular D₂O at the interface is minimal. This observation shows that even though the surface hydroxyl groups undergo H/D exchange, there remains minimal to no H-bonding interaction between surface OD groups and D₂O. There could be two possible explanations for the low vSFG signal in the H-bonding region in the MgO/water spectra. One possibility would be that the water molecules at the interface are arranged in a way to minimize the total dipole moment which results in weak vSFG intensity. The possibility of this scenario is less likely as the vSFG intensity in the PPP polarization also is very weak (see **Figure S6** in **SI**).²³ The second possibility is that the water-water H-bonding interactions are much more favored than the surface to water interactions for the MgO/water interface. Also, at the interface hydroxyl groups may possess very little conformational degrees of freedom which restricts them from adopting configurations necessary to form a stable H-bonding network with overlying water molecules.

Hence the overlying water instead is forced to self-H-bond resulting in a 2D network formed amongst the water molecules adjacent to the surface hydroxyl groups.^{24,25} Such species are SFG inactive and hence do not show up in the vSFG spectra.

The vSFG spectra of the MgO/D₂O interface are significantly different than those for the silica/water or alumina/water interfaces as shown in Figure S3 in **SI**. With the same experimental geometry, the vSFG spectra from the silica/water interface are dominated by the vibrational signature of H-bonding OH modes with no non-H-bonding OH stretching mode. The Al₂O₃(0001)/D₂O interface shows a somewhat similar spectral profile as that of the MgO/D₂O with a weaker non-bonding OH stretching mode with very weak H-bonding OH stretching modes. However, spectra of MgO/water interfaces show a very strong non-H-bonding OH stretching mode with relatively weak H-bonding OH stretching modes. This observation shows that even though the MgO surface hydroxyl groups are involved in H/D exchange with D₂O, there is negligible H-bonding interaction between surface hydroxyls and D₂O. The collective findings suggest that the hydroxylation structure of MgO single crystals at ambient conditions gives rise to negligible interaction with hydration waters, a property at the molecular scale that could lead to macroscopically observable hydrophobic character.

Moreover, the air/MgO and MgO/water spectra do not differ significantly in terms of the spectral profile (**Fig. S3**). Collectively this is a strong indicator of the hydrophobic nature of the hydroxylated MgO surface, a somewhat counterintuitive finding given the general assumption that a hydroxylated surface should be predisposed to participate in H-bonding interactions with adjacent water molecules. Both the MgO(111) and MgO(100) substrates show similar characteristic changes when exposed to the bulk of the liquid water. Like that for the air/MgO interface (Fig. 1), there are similar structural differences in the spectra between MgO(100)/D₂O and MgO(111)/D₂O interfaces, as shown in Figure 2. The narrow bands at ~2755 cm⁻¹ of MgO(111) and ~2730 cm⁻¹ of MgO(100) correspond well to the ~3720 cm⁻¹ and 3685 cm⁻¹ OH band counterparts. The peak shift of ~25 cm⁻¹ of the high frequency narrow band from MgO(111)/D₂O to MgO(100)/D₂O is in excellent agreement with that at the air/MgO interface (peak shift of ~35 cm⁻¹) taking into account the frequency rescaling factor of 1.35 for the isotopic exchange spectra of OH and OD stretches for H₂O/vapor and D₂O/vapor interfaces.²⁶ Similarly, the low frequency broadband (<2650 cm⁻¹) also behaves like its OH counterpart (<3600 cm⁻¹). Also, the blue shift in the high frequency narrow band in MgO(111)/D₂O compared to that of MgO(100)/D₂O suggests that the isolated hydroxyl groups on the MgO(111) surface are more stable and, thus, this surface is expected to be more hydrophobic. This observation is also in agreement with the decrease in the amplitude of the low frequency bands in MgO(111)/D₂O spectra as compared to that in MgO/D₂O(100) spectra as shown in Figure 2C.

The presence of a prominent high frequency band at the MgO/water interface indicates that the hydroxyl groups responsible for this band are not affected by the presence of bulk water. Understanding why these hydroxyl groups do not interact with nearby water molecules could be critical in understanding the origin of molecular hydrophobic/hydrophilic character of interfaces and the technological applications of MgO.

The vSFG spectra from hydrophilic solid/water interfaces tend to be dominated by the H-bonded OH stretching modes of the adsorbed water molecules. The presence of weakly H-bonded or dangling OH stretching mode of water molecules in the vSFG spectra is typically considered the main characteristic of hydrophobic interfaces. Dalstein *et al.* showed that the surface modification of the fused silica with the hydrophobic silane monolayer results in strong free OH peaks at the silica/water interface.²³ Cyran *et al.* argued that the presence of the relatively weak shoulder $\sim 3660\text{ cm}^{-1}$ at the silica water interface reflects molecular hydrophobicity of the silica surface.²⁷ Isaenko *et al.* showed that the isolated silanol vSFG signal from the planar amorphous silica surfaces was unchanged up to relative humidity $\sim 95\%$ which was taken as evidence of the hydrophobic character of the silica surface at the molecular level.²⁸ Thus, the presence of the isolated non-H-bonded hydroxyl stretching mode in the vSFG spectra of the MgO/water interface indicates the molecular hydrophobicity of the hydroxylated MgO surfaces.

Although our vSFG results indicate that hydroxylated MgO surfaces are microscopically hydrophobic, it is less clear how this translates into possible macroscopic wettability behavior. Following identical surface preparation procedures, macroscopic water contact angle (WCA) measurements showed our MgO(100) and MgO(111) surfaces are both hydrophilic, with WCAs of $26\pm 1^\circ$ and $33\pm 2^\circ$, respectively (see **SI** for details). However, though lower than those predicted for anhydrous MgO surfaces,^{8,10} such values are still larger than of a typical hydrophilic surface such as silica and $\alpha\text{-Al}_2\text{O}_3$ (see **Figure S7**). Moreover, the slightly larger measured WCA of MgO(111) compared to MgO(100) is also consistent with our vSFG results. However, traditional macroscopic WCA measurements do yet appear capable of fully explaining the molecular hydrophobicity we observe by vSFG for hydroxylated MgO surfaces.

In conclusion, we showed that hydroxylated MgO surfaces at the molecular level act hydrophobically, as indicated by the dominance of strong stretching bands from non-H-bonded OH groups. The hydroxylated MgO(111) surface shows even less intermolecular interactions with water molecules at the interface, compared to that of MgO(100). Key aspects of these trends at the molecular scale appear to persist upscale into water contact angle measurements. MgO/water interfaces could, therefore, provide a useful platform for exploring the basis for metal oxide hydrophobicity in general.

Methods

Materials

MgO(111) >99.95% pure with surface finish $< 15\text{ Å}$ polished on both sides, MgO(100) >99.95% pure with surface finish $< 10\text{ Å}$ polished on both sides and $\text{Al}_2\text{O}_3(0001)$ (both sides EPI polished with $\text{RA} < 5\text{ Å}$ and Purity >99.99%) single crystal substrates were purchased from the MTI corporation (Richmond, CA, USA). The IR grade fused silica substrates (60-40, scratch-dig or better surface quality) were purchased from Esco Optics (Oak Ridge, NJ, USA). The substrates were rinsed with distilled water and then with nanopure deionized water several times and blow-dried with air and treated with UV-ozone for 30 minutes with subsequent plasma cleaning for about 5 minutes using Harrick plasma cleaner (Ithaca, NY USA) before using for the experiment.

D₂O (99.9 atom % D atoms) was purchased for Sigma-Aldrich Corp. St. Louis, MO, USA. The nanopore DI water with a resistivity of 18.1 MΩ × cm was used for the experiments with the water.

vSFG Experiment

The commercial scanning picosecond vSFG spectrometer (EKSPLA, Lithuania) setup with 532.1 nm visible beam and tunable infra-red (IR) beam was used to obtain SFG spectra in the O-H and O-D stretching regions. This setup has a spectral resolution of ~6 cm⁻¹. The angle of incidence is 65° and 55° for the visible and the IR beam, respectively. Both the beams were overlapped spatially and temporally at the sample surface. SFG spectra presented here were collected using the SSP and PPP polarization combination, where each letter signifies the polarization state of the sum frequency signal, visible, and IR beam, respectively. S-polarized beam has the incident electric field perpendicular to the incident plane, whereas, P-polarized beam has the optical field parallel to the incident plane. The vSFG signal is normalized with the visible and IR pulse energy. The arbitrary unit (a.u.) for the normalized vSFG intensity is thus counts/(10⁻³ × mJ²). A homemade sample cell with the inlet and outlet for liquid was used for the vSFG studies at the solid-liquid interface (see SI for more detail). The MgO substrate is at the top and is in contact with the bulk of D₂O.

Fitting of the vSFG data

vSFG data are fitted using multiple peak fitting algorithm in the OriginPro 2017 software with costume peak function for the vSFG intensity as shown in the equation below:

$$I_{SFG} = y_0 + \left| \sum_q \frac{A_q}{x - xc_q - i\omega_q} \right|^2 \quad (1)$$

Here, I_{SFG} is the intensity of the vSFG signal. The y_0 is the non-resonant contribution. A_q , xc_q , and ω_q are the amplitude, peak center, and width of the q^{th} vibrational mode, respectively.

Declarations

Conflicts of interest

The authors declare no competing interests.

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Figures

Figure 1

vSFG spectra in SSP polarization combination along with the fitting results at the air/MgO interface in the OH stretching region. Panel A and panel B shows the spectra collected at the air/MgO interface from the MgO(100) and MgO(111) single crystal substrates, respectively. Panel C shows the amplitude of the fitted peaks at the air/MgO interface for MgO(100) and MgO(111) single crystal substrates.

Figure 2

vSFG spectra in SSP polarization combination along with fitting results at the MgO/D₂O interface in the OD stretching region. Panel A and panel B shows the spectra collected at the MgO/D₂O interface from the MgO(111) and MgO(100) single crystal substrates, respectively. Panel C shows the amplitude of the fitted peaks at the MgO/D₂O interfaces for MgO(111) and MgO(100) single crystal substrates.

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