



# Water on MgO(100)—An infrared study at ambient temperatures

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## Abstract

Transmission Fourier transform infrared spectroscopy (FTIR) is used to investigate water adsorbed on the (100) face of MgO under ambient conditions. From these measurements, we find that water reversibly adsorbs to MgO(100) creating liquid-like layers at temperatures ranging from  $-10\text{ }^{\circ}\text{C}$  to  $40\text{ }^{\circ}\text{C}$  with slight hysteresis seen during a complete adsorption/desorption cycle. The adsorption isotherms of water on MgO(100), throughout the entire temperature range sampled, resemble a typical BET plot, which coupled with the fact that IR absorption due to the OH stretch of the adsorbed water does not change as a function of coverage, suggests that the layer grows in via three-dimensional island formation. Thermodynamic analysis indicates three distinct regions of water adlayer growth.

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## 1. Introduction

Mineral or metal oxide dust produced from windblown soils is an important component of the earth–atmosphere system [1–5]. It is estimated that 1000–3000 teragram ( $1\text{ }T_g = 10^{12}\text{ g}$ ) of such aerosols are emitted annually into the atmosphere [6,7]. In comparison, the global estimate of second-

ary aerosols (carbonaceous substances, organics, sulfate and nitrate for example) is  $\sim 400\text{ }T_g$  per year [8,9]. These dust particles have, until recently, been regarded as essentially non-reactive, hydrophobic chemical substrates. Only their alkalinity was considered for its neutralizing effect on rain-water acidity [10]. However, there is a growing body of data that suggests that metal oxides offer important reactive surfaces [11–19]; thus, an understanding of the mechanisms by which mineral aerosols contribute to heterogeneous tropospheric processes is now timely.

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The presence of thin water films, or adlayers, on dust particles within the atmosphere opens up the possibility of reactions occurring on the water surface, via condensation onto the water film; within the water layer, via dissolution of reactive gases into the condensed phase; and at the water/oxide interface. Thus, the presence of water can greatly influence the reactivity at the surface of the dust particle and the extent to which it is able to participate in heterogeneous atmospheric reactions. Recent studies indicate that even small amounts of strongly adsorbed water may play a critical role in the interaction of gases with surfaces traditionally presumed to be solids [20].

Magnesium oxide is often described as a model basic oxide, having a simple rock-salt structure, a single valence state, only one stable low-index surface orientation—the (100) face, and most importantly, it is transparent in the infrared. In addition, magnesium is the eighth most abundant element in the Earth's crust and the third most plentiful element dissolved in seawater [21]. So while MgO is not one of the more common minerals found in the tropospheric aerosol, it can serve as a model substrate for studies of adsorption and reactions on tropospheric dust particles. Magnesium oxide has the additional benefit of having a similar lattice constant to that of hydrogen bonded water. MgO has a rock-salt crystalline structure with a cation interatomic distance of 3.0 Å [22], very similar to the hydrogen-bonding oxygen interatomic distance of water at 2.8 Å [23] and exactly the same as in the water dimer [24]. This could allow for more relaxed hydrogen bonding between water molecules adsorbed on MgO(100).

As a model substrate, MgO has been one of the most widely studied metal oxide surfaces [22]. Yet there continues to be much ambiguity surrounding the interactions between water and the MgO surface [25]. Theoretical studies traditionally indicate that water physisorbs onto the terraces and reacts with defect sites [26–31], yet there are a growing number of reports stating that at a critical coverage, the dissociation of water is stabilized by the presence of the lateral interactions of neighboring waters on this surface [32–35] creating a mixed monolayer of water and hydroxyl groups. The experimental results are equally mixed, with both

molecular [36–40] and dissociative [41–48] adsorption being reported. For the most part, the experimental work has been performed in the low temperature/low pressure regime necessary for typical surface analytical techniques.

Some preliminary infrared studies of water adsorption to well defined MgO(100) surfaces have been published by our group [49,50]. There we used transmission Fourier transform infrared (FTIR) spectroscopy to study water on MgO(100) at room temperature. We continue our investigation of the adsorption of water on MgO(100) under tropospherically relevant conditions, namely within a temperature range of  $-10$  to  $+40^{\circ}\text{C}$  and relative humidities up to 95%. The FTIR data are analyzed to determine the surface interactions of adsorbed water in dynamic equilibrium with the gas phase on the MgO surface.

## 2. Experimental section

Vibrational spectra were recorded using a Nicolet Nexus 670 FTIR, equipped with a liquid nitrogen cooled InSb (indium antimonide) detector. The resolution was set at  $8\text{ cm}^{-1}$  and the monitored frequency region was  $4500\text{--}1850\text{ cm}^{-1}$ . Both the background and sample interferograms were collected with 100 scans ( $\sim 1$  min) and were transformed with a Happ–Genzel apodization function. Absorbance,  $A = \log\left(\frac{I_0}{I}\right)$ , was plotted as a function of wavenumber,  $\bar{\nu}$ , using a single-beam sample spectrum intensity,  $I$ , and the appropriate background intensity,  $I_0$ . Water vapor features, which can obscure absorbance by the adlayer, were reduced by purging the spectrometer and subtracting out a reference spectrum of water vapor that had been appropriately scaled. The subtraction process can cause anomalous absorption errors. A complete investigation of this problem and ways to circumvent it has been discussed in detail by Weis and Ewing [51]. Besides subtraction of the water vapor features, which is necessary to obtain accurate values for the integrated absorbance, no other corrective procedures were performed on the resulting spectra. The integrated absorbance was obtained by a numerical integration procedure available through Omnic 6.0, the software pro-

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