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STEPS TOWARD UNDERSTANDING HETEROGENEOUS CHEMISTRY IN THE TROPOSPHERE: WATER UPTAKE ON ENVIRONMENTALLY RELEVANT SURFACES

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1. INTRODUCTION

Heterogeneous processes in the troposphere have a recognized impact on trace gas concentrations. For example, recent reports of HONO emission from vegetation and other surfaces suggest that there is a heterogeneous chemical source (Calvert *et al.*, 1994; Harrison *et al.*, 1996; Lammel and Cape, 1996; Lammel, 1999; Stutz *et al.*, 2002; Civerolo *et al.*, 2002; Zhou *et al.*, 2002). A number of heterogeneous reactions studied in this laboratory, including NO_2 hydrolysis (1) and the reaction of adsorbed HNO_3 with gaseous NO (2),

$$2\,NO_2 + H_2O \rightarrow HONO + HNO_3 \quad (1)$$
$$NO + HNO_{3(surf)} \rightarrow HONO + NO_2 \quad (2)$$

are known to be dependent on relative humidity (RH) and thus are likely to be dependent on the amount of water present on the reaction surface (Saliba *et al.*, 2001; Finlayson-Pitts *et al.*, 2002; Wingen *et al.*, 2002 (Paper P1.8)). To fully understand these reactions, the amount of water on the surfaces and how it behaves chemically must be understood.

Heterogeneous reactions have largely been studied in laboratory reaction chambers that are composed of glass, quartz, or Teflon, with halocarbon wax-coated components. Therefore, knowledge of the water uptake characteristics of these surfaces is critical for understanding the role of surface water. It is believed that water at the solid/water interface is “structured” and may have properties different from bulk water; the structured orientation of surface water may extend anywhere from three monolayers to many molecular diameters (Drost-Hansen, 1971; Parks, 1984).

There are few reports of water uptake measurements on common laboratory surfaces in the literature. Reports of water uptake on Teflon surfaces at room temperature vary greatly. Svensson *et al.* (1987) reported an uptake of 2 monolayers of water at 5% relative humidity. In contrast, Lammel (1999) reported significant uptake only at relative humidities greater than 80%. Awakuni and Calderwood (1972) measured an uptake of 3 monolayers at 100% RH. Clearly, the water uptake properties of Teflon are not well understood. Lammel (1999) also reported uptake of water on glass, which is in relatively good agreement with measurements of Saliba *et al.* (2001), who report coverages of 1 monolayer at 20% RH and 12 monolayers at 100% RH.

Here, we report the uptake of water on halocarbon wax, PFA and FEP Teflon film, and, for comparison to earlier studies, on smooth borosilicate glass. The implications for understanding heterogeneous reactions in/on surface water films in laboratory systems as well as extrapolation to atmospheric surfaces will be discussed.

2. EXPERIMENTAL METHODS

The amount of liquid water adsorbed on smooth glass, halocarbon wax, and Teflon film was determined as a function of relative humidity by transmission Fourier transform infrared spectroscopy (FTIR). The surfaces of interest were positioned in the infrared beam within a glass cell enclosed with ZnSe windows, as shown in Figure 1. The cell was 3.2 cm in diameter with an 11 cm pathlength. Five surfaces (e.g. glass discs) were placed into thin slots cut in a glass holder that sits on the bottom of the cell, allowing for measurement of water uptake on a total of 10 surfaces. All gas flows through the cell were set using calibrated flow meters (Matheson TF 1050). The relative humidity in the cell was set by mixing flows of dry and 100% RH nitrogen, obtained by passing N_2 through Nanopure water (Barnstead, 18.1 MΩ cm) in two borosilicate glass fritted bubblers, in series. The water bubblers were kept in a room temperature water bath (22 ± 1 °C) to reduce the effects of evaporative cooling. The temperature of the cell in FTIR sample compartment was ~3 °C warmer than the humidified nitrogen. Relative humidities were corrected for this temperature difference and experiments are underway to repeat the measurements under more controlled conditions. All measurements were conducted at atmospheric pressure under dynamic conditions with a total flow rate through the cell of 200 mL min^{-1}.

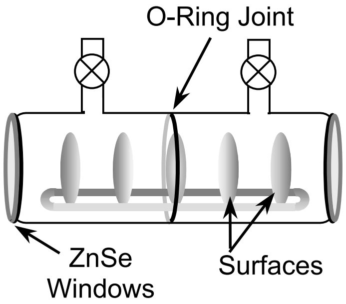

Figure 1. FTIR cell used for measurements of water uptake on glass and other surfaces.

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For measurement of water uptake on glass, thin borosilicate glass discs (number 1 Micro Cover Glasses, VWR Scientific, Inc.) were used. Each glass disc is 0.13 to 0.17 mm thick and 25 mm in diameter. The same discs were used for the halocarbon wax experiments by dipping them into melted halocarbon wax (Halocarbon Products Corp., Series 1500) and inserting them into the glass holder to cool. FEP and PFA Teflon films (2 mil, Livingstone Coating Corp.) were supported by thin halocarbon wax-coated aluminum washers. The Teflon film was pressed onto the warm halocarbon wax coating, which held the film firmly in place. After cutting away the excess film, the Telfon film discs and washers were inserted into the glass holder.

Spectra were obtained as interferograms at 1 cm^{-1} resolution on a FTIR spectrometer (Mattson, Galaxy) equipped with a liquid nitrogen cooled mercury cadmium telluride detector. The KBr window separating the spectrometer's sample and interferometer compartments was removed, as variable amounts of liquid water were spectroscopically observed on the window itself. Surfaces were dried by flowing warmed dry nitrogen (~60 °C) through the cell overnight at high flow rates (>2 L min^{-1}). Background spectra of 2048 scans were obtained each day for the surfaces under dry nitrogen flow. Sample spectra of 1024 scans were obtained at each relative humidity after an equilibration time of 1 hour. The infrared beam was blocked during this time, to reduce the potential of heating of the adsorbed surface water. Water vapor spectra for subtraction were also measured with the surfaces removed from the glass cell.

3. RESULTS AND DISCUSSION

3.1 *Spectroscopic Treatment*

A problem that often arises with the use of thin parallel surfaces in infrared spectrometry, such as the glass and Teflon surfaces used here, is multiple reflection of the infrared beam within each surface (Griffiths and de Haseth, 1986). The multiple reflections cause interference fringes on either side of the centerburst in the interferograms and result in sinusoidal noise peaks in the single beam and absorbance spectra. Replacing these fringes in the interferogram with zeros before the Fourier transform is performed has the effect of removing the interference pattern from the single beam spectrum (Griffiths and de Haseth, 1986). While this zero-filling procedure adds small amounts of noise to the spectrum, the final result is much more useful. Figure 2 shows typical interferograms with and without the zero-filling correction (A) and the corresponding single beam spectra (B). The raw data (red) show interference fringes in the interferogram (A), and sinusoidal noise in the single beam spectrum (B). When the fringes are replaced by zeros (black traces), the resulting single beam spectrum has a significantly improved signal to noise ratio. This type of data analysis was required for measurements on glass and Teflon film; the uneven surface of halocarbon wax-coated glass did not produce interference fringes.

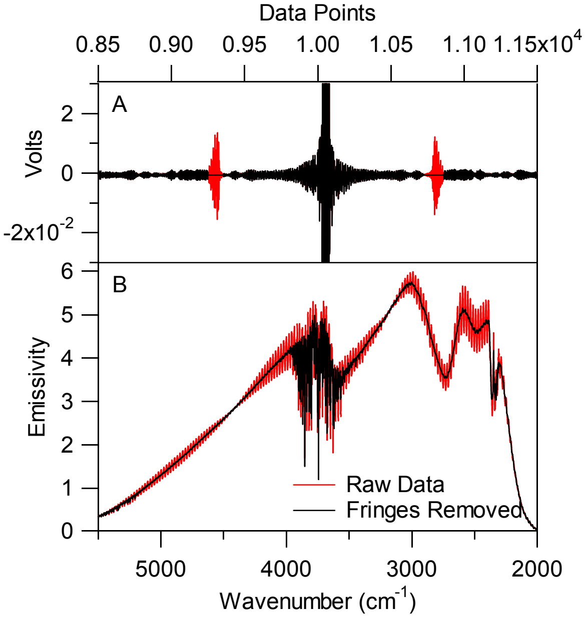

Figure 2. Typical interferogram (A) and single beam spectra (B) for water uptake on smooth glass.

3.2 *Properties of Surface Water*

Absorbance spectra were calculated from the single beam sample and background spectra, after removal of interference fringes, as necessary. A typical absorbance spectrum is shown in Figure 3 for liquid water on glass at 80% RH (red trace). The broad feature from 2800-3800 cm^{-1} is from the OH stretching vibration in liquid water. However, the sharp water vapor peaks from 3500-3900 cm^{-1} interfere with the integration of the liquid water peak, which is quantified from 2800-3800 cm^{-1} for these experiments. After subtracting water vapor, the resulting spectrum, shown in black, has sharp positive and negative peaks in the water vapor absorption region. It has been shown that small instabilities in the wavenumber scale of the spectrometer produce changes in the laser wavenumber of up to ± 0.034 cm^{-1} (Weis and Ewing, 1998). Even such a small shift can lead to the spurious peaks observed here. Fortunately, the peaks do not contribute significantly to the liquid water peak area since they are roughly equally positive and negative.

Information about the nature of the surface water film can be obtained from the infrared spectra themselves. Figure 4 shows a series of spectra of water adsorbed on halocarbon wax at various relative humidities. Also shown is a spectrum measured for bulk water. The bulk water peak is centered at 3400 cm^{-1}, while that of water on the halocarbon wax surface is blue-shifted from this value by up to 100 cm^{-1}, depending on the surface water coverage. This shift indicates reduced hydrogen bonding relative to liquid water. This suggests that the water is interacting more strongly with the surface and thus has a more two-dimensional structure (Drost-Hansen, 1971). The same results were observed for water on silica glass. Similar

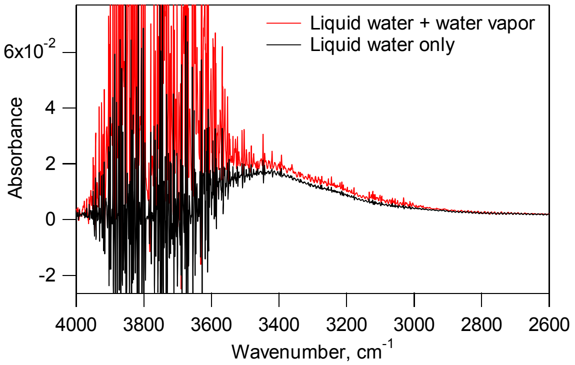

Figure 3. Liquid water spectra on a glass surface at 80% RH. The raw absorbance spectrum is shown in red. The black trace is the same spectrum after subtraction of water vapor.

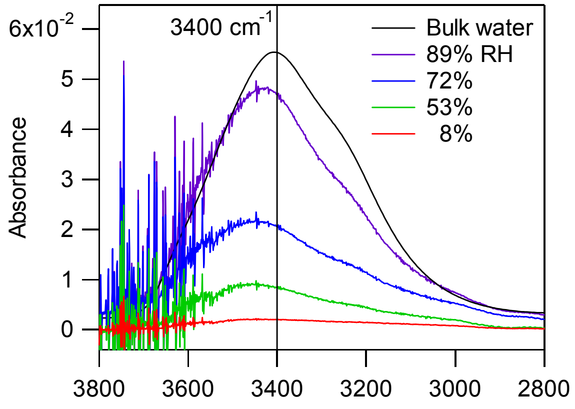

Figure 4. Liquid water spectra on halocarbon wax. Also shown is a bulk water spectrum, for comparison purposes.

shifts were also observed by Ewing and coworkers (Foster and Ewing, 1999; Foster and Ewing 2000; Cantrell and Ewing, 2001) on NaCl and mica surfaces. It is important to note that, even at high relative humidities, water on glass and halocarbon wax does not spectroscopically behave like bulk water. Thus, it may not be appropriate to treat these thin water films and the chemistry occurring in them as if they were bulk aqueous solutions.

3.3 *Water Uptake Isotherms*

The water coverage, Θ, in number of layers, is calculated from the absorbance spectra using Equation I, a modified form of Beer's law (Foster and Ewing, 2000),

$$\Theta = \frac{\tilde{A}\cdot 2.303}{N\cdot S_{H_2O}\cdot \bar{\sigma}} \qquad \text{(I)}$$

where N is the number of surfaces in the infrared beam and S_{H_2O} is the surface density of one water monolayer (10^{15} molec cm^{-2}). The base-10 integrated absorbance, $\tilde{A}$, of the liquid water peak (from 2800 to 3800 cm^{-1}) is calculated from the absorbance spectra. The base-*e* integrated cross section, $\bar{\sigma}$, was calculated in the same range from optical constants reported by Downing and Williams (1975) to equal 1.36×10^{-16} cm molec^{-1}. The true value of the integrated cross section is likely to vary with coverage and so may be different from the bulk water value. Thus, the water coverage values reported here are estimates.

The number of water monolayers adsorbed on each type of surface was calculated for each spectrum and plotted as a function of relative humidity. These values are reported based on the assumption that water molecules are evenly dispersed across the surface. This, however, may not be the case as formation of clusters or islands is likely (Papirer, 2000). The results for water on glass, halocarbon wax, and FEP Teflon film are shown in Figure 5. Water uptake on PFA Teflon, like FEP film, was not above the detection limit. These results indicate greater water uptake on glass than previously reported by this laboratory (Saliba *et al.*, 2001), but are believed to be more accurate in light of improvements in the experimental method.

Although glass and halocarbon wax are chemically very different, their water uptake isotherms are quite similar. This is contrary to what we expected given the hydrophobic nature of halocarbon wax, which is based on polychlorotrifluoroethylene. Halocarbon wax is chemically similar to Teflon (polytetrafluroethylene). However, for both Teflon films, we observed no measurable water uptake, even at 100% RH. It is likely that the surface of Teflon film is smoother than halocarbon wax, and it is known that, on single crystal surfaces, surface water tends to condense at surface defects (e.g. Dai *et al.*, 1995). Thus, the uptake of water may be quite dependent on the roughness of the surface, in addition to its chemical properties. Rudich *et al.* (2000) showed that the corrugation of hydrophobic surfaces impacted the interaction with water and that more corrugated surfaces did, in fact, hold more water.

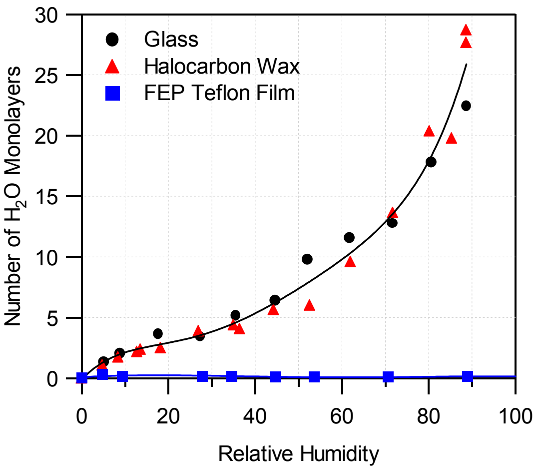

Figure 5. Water uptake isotherms for glass and halocarbon wax surfaces at 25 ± 1 °C. The solid black line is a polynomial fit to the data for glass and halocarbon wax.

That interference fringes were not observed in the interferograms of halocarbon wax coated surfaces is additional evidence that these surfaces are rough compared to Teflon film. It may be that Teflon coatings, which are visibly rougher than Teflon film, will also hold significant quantities of water under laboratory conditions.

4. ATMOSPHERIC IMPLICATIONS

A number of heterogeneous reactions that are relevant in the troposphere require the presence of surface water. Thus, knowledge of the water uptake characteristics of the surfaces in contact with the atmosphere is important for evaluating the importance of heterogeneous chemistry. To extrapolate data obtained in laboratory studies of heterogeneous reactions to the atmosphere, it is necessary to determine how the nature of the surfaces in laboratory reaction systems compares to those in contact with the atmosphere. Silica is an important component of many building materials, including concrete, asphalt, and window glass (Lujan and Ary, 1992) and is known to promote heterogeneous chemistry in laboratory systems (e.g. Saliba *et al.*, 2001; Wingen *et al.*, 2002 (Paper P1.8)). In addition, silica has been identified as a major component of soil and soil derived dust (Gillette, 1997). Therefore, our measurements of water uptake on silica glass are relevant and useful for understanding chemistry on these surfaces. Since halocarbon wax, a hydrophobic material, shows significant water uptake, other hydrophobic materials, such as vegetation, may also hold water in quantities sufficient to support heterogeneous chemistry.

5. ACKNOWLEDGEMENTS

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