Summer Scholar Report

Replicating Prebiotic Astrochemistry Through the Use of a Silicate Grain Surface Analog

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Through the use of a silicate grain surface analogue, it is possible to replicate the prebiotic astrochemical processes that occur in dark interstellar clouds for terrestrial examination. Silicon dioxide was chosen as a substrate not only due to its abundance in these clouds but also because it is generally inert. SiO2 nano- and microparticles were subjected to water under controlled conditions, and monitored using diffuse reflectance Fourier transform spectroscopy, allowing for a comparative study of how reactions occur at their surfaces. It was determined that undiluted nanoparticles are a favorable surface
analog.

I. Introduction

Astrochemistry is the study of the formation, interaction, and destruction of elements and molecules in space. One main area of astrochemistry is the study of reactions that occur in the interstellar medium where gas clouds are cold, diffuse, and rich in simple gas phase species. When dust grains (mineral in nature such as silicon, carbon, etc.) travel through these clouds, gas molecules attach to the surface of the dust grains and through either radical or thermal activation, react on the surface of the dust grains which are acting as catalytic surfaces. These reactions are theorized to eventually produce the simple sugars or even amino acids that could then attach to passing meteors or asteroids and react further to produce simple but biologically relevant molecules.

Herbst discusses the molecular nature of the interstellar medium and its contribution to observable astrochemical processes as well as the surface assisted formation of molecular hydrogen.[1] Spectroscopic data suggests molecular hydrogen exists in the interstellar medium in concentrations 10^4 times greater than that of atomic hydrogen. There must be some other plausible pathway of formation for H_2 other than three-body collision given that the densities and temperatures in the interstellar medium are so low. The formation of molecular hydrogen and other small molecules is thought to follow the Langmuir-Hinshelwood surface mechanism where physisorbed hydrogen atoms move from lattice site to lattice site on the grain surface until they collide with another hydrogen atom, reacting to create molecular hydrogen. As chemists, we can mimic and observe these surface processes in an attempt to better understand the chemical transformations that occur in the interstellar medium.

Silicon dioxide has been chosen as a substrate due to not only its inertness but also its abundance in the interstellar medium. Other possible substrates include solid NH_3, solid

H$_2$O, and amorphous carbonaceous compounds.[2] Exposing SiO$_2$ micro- and nanoparticles to simple but abundant molecules such as water under controlled conditions allows for the observation of the reactions as they would occur in interstellar space. Particle size (5 nm-250 nm) and shape (amorphous) has been chosen based on interstellar spectroscopic data outlined by Draine.[3] Similar studies using SiO$_2$ nanoparticles and Fourier transform infrared (FTIR) spectroscopy were performed by Dawley *et al*. to mimic processes that occur in the atmosphere of Saturn's largest moon, Titan.[4, 5]

Because it is surfaces that are being studied, it is necessary to choose a surface-sensitive technique for analysis. FTIR spectroscopy, or more specifically, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), is often used in surface studies because each infrared absorption band is characterized by three independent parameters: frequency, intensity, and width.[6] Most other commonly used techniques measure average properties but infrared techniques can be used to measure specific functionalities directly. Qualitative changes in intensity correspond to the behavior of physisorbed molecules, which may change the frequency at which a feature appears in the spectrum. The width of a peak corresponds to the homogeneity of surface groups; a narrow band indicates a more homogenous environment and a broad band indicates a wide array of geometric arrangement.

Water was chosen as the main adsorbate in this study given that the hydrogen bonds are largely electrostatic and are therefore driven by Coulombic attractions.[7] Water is also known to exist in all of its phases in space but largely as an ice mantle, either on its own or at the surface of a grain like the ones mentioned here. This study aims to characterize an acceptable grain analog for DRIFTS studies that replicate prebiotic astrochemical processes that occur in cold interstellar clouds as a result of small gas phase molecules and amorphous dust grains as outlined by Herbst.[1]

II. Methods

Two SiO2 samples were analyzed: microparticles (Acros Organics, 150-420 mm, 50 m^2/g) and nanoparticles (Sigma Aldrich, 7 nm-14 nm, 175-420 m^2/g). The microparticles were diluted to 0.025% in spectral grade KBr (Sigma Aldrich) and the nanoparticles were diluted to 1% in spectral grade KBr. The nanoparticles were also analyzed undiluted. The mixtures were heated in a tube furnace to 450° C in a dry environment before being cooled and ground with a pre-dried mortar and pestle. The samples were put into a Nicolet iS50 FTIR (Thermo Scientific) equipped with a Praying Mantis DRIFTS accessory and coupled with an in situ high temperature reaction chamber (Harrick). The reaction chamber was connected to a gas-handling manifold and recirculating water bath capable of not only introducing known pressures of gases but also evacuating the chamber to 10^{-5} torr and heating and cooling the sample in situ before and after exposure. The particles were exposed to deionized H^{2}O that had undergone five freeze-pump-thaw cycles at room temperature, and spectra were collected

as a function of exposure. The pressures were monitored using baratron pressure gauges coupled to a PR 4000 display (MKS). The spectrometer has a liquid N_2 cooled mercury cadmium telluride (MCT) detector and the system is purged with gaseous N_2 to ensure an inert environment. All spectra reported were collected and analyzed using OMNIC version 7 software with 4 cm^{-1} resolution and 128 scans per spectrum.

III. Results and Discussion

Figure 1 shows the DRIFTS spectra, using a gold foil background, for the OH bending region of SiO_2 for both the nano and microparticles after the samples had been evacuated overnight. The broad peak centered at 3150 cm^{-1} present in both samples indicates that native water is molecularly adsorbed, likely to the KBr that was used to dilute the silica. The nanoparticles show an additional sharp feature at 3745 cm^{-1}, which is indicative of free hydroxyls, or Si-OH bonds. This means that the nanoparticles provide a more advantageous catalytic surface than the microparticles would be able to provide and thereby a more favorable surface for this study.
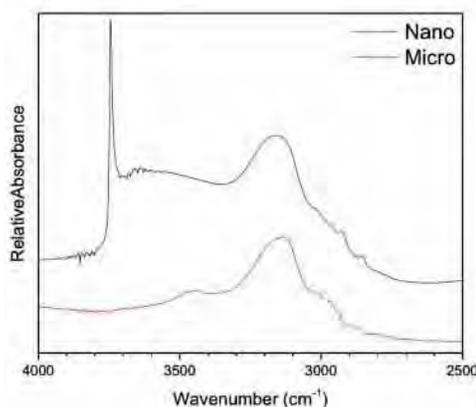

Figure 1: DRIFTS of the OH stretching region of SiO_2 for both the nanoand microparticles. The spectra show similar broad OH stretching features but the nanoparticles exhibit a sharp Si-OH feature 3745 cm^{-1}.

Figure 2 shows the spectra for both 1% nanoparticles in spectral grade KBr and undiluted nanoparticles. The spectrum of pure SiO_2 nanoparticles shows they are strong absorbers of infrared light below 2250 cm^{-1} and therefore must be diluted with an ionic salt to examine lower energy transitions such as the bending mode of adsorbed water at ~1630 cm^{-1}. The downside to using an ionic salt diluent is its hygroscopic nature, as shown by the OH stretching feature in the red spectrum, and in all the diluted samples, at 3150 cm^{-1}, indicative of water adsorbed to KBr. This water is on the substrate even after the substrate has been heated to 750° C. The silanol feature in the diluted sample is also much less intense with respect to the low energy Si-O band.
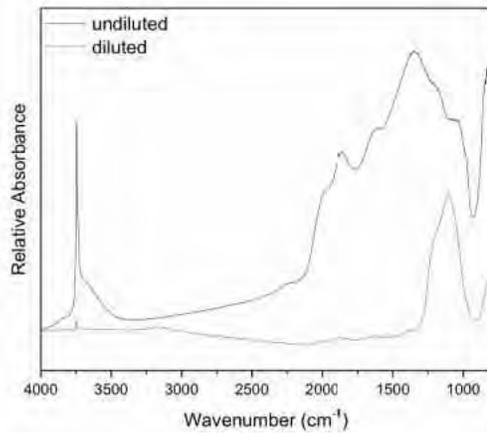
Figure 2: DRIFTS of SiO_2 nanoparticles in both pure, undiluted form
(black) and diluted in KBr (red). The sample was diluted to examine the
water bending features around 1630 cm^{-1}, but the silanol became less intense and
adsorbed water is present even after heat treatment, as shown
by the bump around 3150 cm^{-1}.

To further prove the adverse effect of the ionic salt diluent, Figure 3 shows the DRIFTS of OH
stretching region for diluted SiO_2 nanoparticles when exposed to increasing amounts of water
vapor and the associated adsorption isotherm. The sample was exposed to water in 1 torr
increments with spectra taken immediately after exposure at a pressure
slightly lower than the stated pressure due to the equilibration of the gas line with the reaction
chamber. Likely due to the presense of molecular water on the surface of the
sample, features grow in at 3444 cm^{-1} , 3230 cm^{-1} , and 3113 cm^{-1}. The isolated silanol at 3744
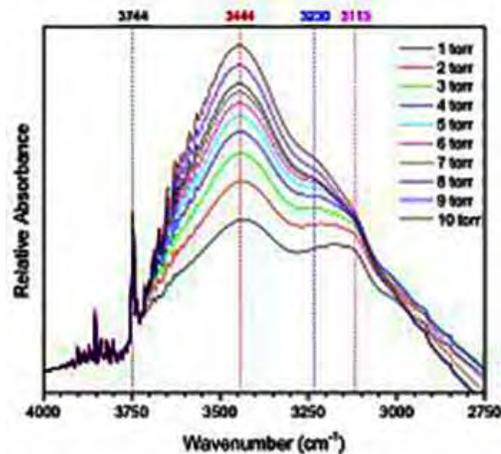cm^{-1} appears to decrease with increased exposure.

Figure 3: DRIFTS of OH stretching region for diluted nanoparticles as a
function of exposure to water. Features grow in at 3444 cm-1, 3230 cm-1,
and 3113 cm-1 while the silanol at 3744 cm-1 appears to shrink.

In order to quantify these observations, adsorption isotherms were constructed using the normalized peak heights, which were plotted as a function of water pressure for each of the four features as shown in Figure 4. The isotherms confirm that the Si-OH peak does decrease, which could be due to the physisorbed water masking the silanol groups at the surface. The feature at 3444 cm^{-1} is due to water adsorbing to the SiO_2 and the peak at 3113 cm^{-1} is due to water adsorbing to KBr. The feature at 3230 cm^{-1} follows a similar trend to the 3444 cm^{-1} (H_2O/SiO_2) feature, indicating it is probably due to water on silica and not KBr.
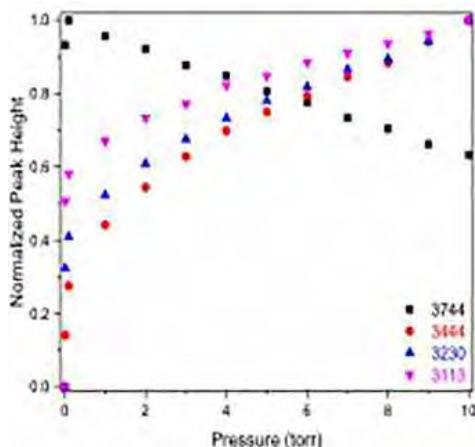

Figure 4: Adsorption isotherms for 1% nanoparticles in KBr as a function of exposure to gas phase water. The isotherms confirm that the peaks at 3444 cm^{-1}, 3230 cm^{-1}, and 3113 cm^{-1} increase while the isolated silanol at 3744 cm^{-1} decreases.

The same experiment was repeated for the undiluted nanoparticles and Figure 5 shows the DRIFTS of the OH stretching region as a function of exposure to water. The stretching features for water grow in at 3683 cm^{-1}, 3604 cm^{-1}, and 3497 cm^{-1}. The isolated silanol at 3744 cm^{-1} appears to decrease with the increase in water pressure, as it had with the diluted particles, but it is much larger with respect to the water stretching features than seen on the dilute sample. An intriguing result is that the features of interest for the undiluted nanoparticles appear at a higher energy in the spectra than the features of the diluted nanoparticles.
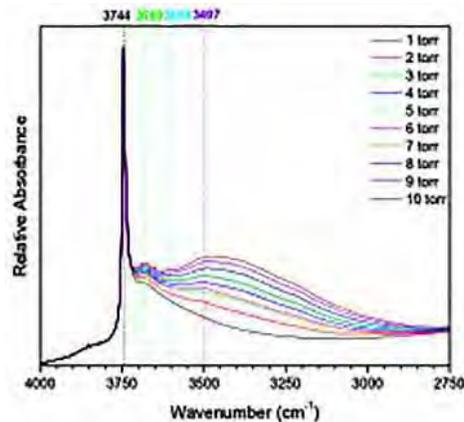
Figure 5: DRIFTS of OH stretching region for undiluted nanoparticles as a function of exposure to water. As had been seen with the diluted particles, the isolated silanol decreases with exposure while the other peaks at 3683 cm^{-1}, 3604 cm^{-1}, and 3497 cm^{-1} all increase.

In order to quantify the behavior of water on the undiluted nanoparticles, the normalized peak height was again plotted as a function of exposure to water, as shown in Figure 6. The features at 3604 cm^{-1} and 3497 cm^{-1} follow near identical trends, indicating that they are due to the same water-SiO_2 interactions. The feature at 3683 cm^{-1} follows a different trend. This coupled with its high energy suggests it is a different type of Si-OH interaction than the silanol, perhaps reaction between water and a defective SiO_2 surface. It may also be due to the shift in the silanol peak due to H-bonding with adsorbed water molecules.[6]
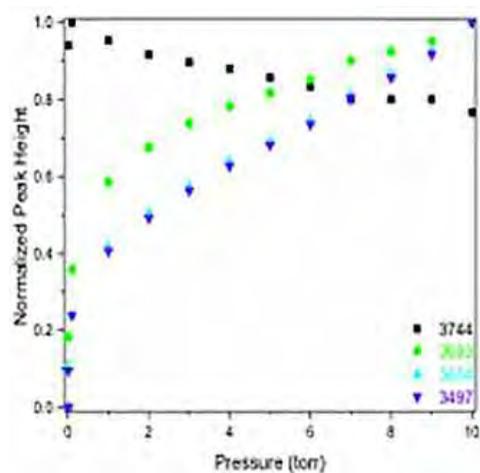

Figure 6: Adsorption isotherms for water on undiluted nanoparticles. The isotherms confirm that the peaks at 3683 cm^{-1}, 3604 cm^{-1}, and 3497 cm^{-1} increase while the isolated silanol at 3744 cm^{-1} decreases.

The shifts of the main features to higher energies in the spectra suggests that interactions are more energetic than they would be in the presence of KBr diluent, which shows that the undiluted nanoparticles are a better model for interstellar reactions using this type of methodology. One possible reason for this shift could be that there are more ways for the silanol groups to stretch or bend at the surface of the sample. As suggested above, it could also be due to hydrogen bonding with molecular water at the surface. Given the spacing of isolated silanols (>30 pm),[8] it is not likely that the groups are hydrogen bonding with each other, but are capable of hydrogen bonding with water to form some sort of water network on the surface of the nanoparticles, which agrees with previous data that suggests that the reactions do not occur on the surface of the particle itself but rather in the icy mantle that likely forms there in the presence of gas phase water at low temperatures.[1]

IV. Conclusion

In conclusion, nanoparticles are favorable silicate grain surface analogs to study reactions in the interstellar medium. Using an ionic salt diluent, like KBr, to investigate the surface reactions on SiO^2 can be quite useful when studying the regions of strong absorption below 2750 cm^{-1}. However, KBr can also serve as a substrate for physisorption of polar molecules, and thus must be used with care in those types of investigations. The slight shift and reduction of intensity of the Si-OH stretching features at ~3750 cm^{-1} indicate that they may interact with the water thin film forming on the substrate as the water vapor pressure increases, probably via hydrogen-bonding. Undiluted nanoparticles are most desirable due to the ability of water and presumably other molecules to physisorb to the surface at even room temperature, thus it is able to serve as a model for space reactions, especially under conditions comparable to those of deep space.

V. Acknowledgements

VI. References

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