

Investigations of Water Uptake On Sodium Acetate Trihydrate And Nonhydrate As Model Aerosol Surfaces Using The DRIFTS And ATR-FTIR Techniques

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Abstract

Research primarily pertains to *in situ* monitoring of water uptake on sodium acetate trihydrate and sodium acetate nonhydrate. Thin water films provide an environment, which has the ability to host atmospherically important aqueous chemical reactions. Aqueous reactions in thin water films are facilitated through properties of bulk water adsorption. Therefore, a model compound was used to investigate the properties of hydration, on the molecular and bulk scale. The selected model compound, sodium acetate trihydrate, exhibits both hydrophobic and hydrophilic character, along with three molecularly bound water molecules. The aforementioned moieties of sodium acetate trihydrate allowed the compound to be used as a model for both organics as well as salts. The trihydrate moiety provides an infrared spectroscopic signal distinguishable from that characteristic of bulk water absorption. The nonhydrate form of sodium acetate was synthesized in our research laboratory. Both the trihydrate and the nonhydrate forms of sodium acetate were investigated via Fourier transform infrared spectroscopy (FT-IR). The experimental system includes an arid environmental box surrounding the spectrometer to remove interference from atmospheric gases. The flow of gases in the system is regulated by four mass flow controllers that allow for mixing of different gases and dilution of reagents prior to introduction to the reaction cell. After exposure to humid nitrogen gas, sodium acetate trihydrate was formed from sodium acetate nonhydrate via the DRIFTS technique, which is atmospherically and chemically interesting.

Keywords: Aerosol, Water-uptake, DRIFTS

1. Introduction

Aerosols are small particles aloft in the atmosphere, and can exist in either the liquid or solid phase. Solid and liquid aerosols behave differently; solid phase aerosols are able to host adsorbed organic and inorganic molecules, whereas liquid phase aerosols tend to solvate organic and inorganic molecules. The aforementioned differences are rooted in the thermodynamics that govern each phase. However, the interactions that both liquid and solid phase aerosols have with suspended gas phase molecules are primarily catalytic.^{1,2} Aerosols may absorb species or host adsorbed species that facilitate atmospherically relevant chemical reactions, via preferential orientation and photo-catalytic activity.³

Under atmospheric conditions, the majority of the solid aerosols surfaces have water vapor adsorbed. Adsorption of water vapor to the surface of an aerosol interferes with adsorption of other gas phase molecules, by limiting the amount of catalytic step edges exposed to the atmosphere. At step edges or lattice defects, elimination of electric fields of nearby ions is less complete, which facilitates physical adsorptions and chemical interactions.⁴ Additionally, adsorption of water vapor influences the optical properties of the aerosol, which ultimately affects the Earth's radiative

budget.⁵ NaCl has been studied for use as a model inorganic salt whose behavior can be loosely applied as a generalized behavior for all suspended inorganic salts.^{6,7}

Molecularly thin films of water vapor have been studied on many salts, where it has been shown that water uptake is a function of increasing relative humidity (RH). The morphology of a surface changes with exposure to humidity; catalytic step edges on the surface of NaCl have been shown to undergo rearrangements with exposure to water vapor at a relative humidity above 47%. For NaCl, a relative humidity of 47% is considered pre-deliqescence conditions, however there is sufficient water vapor that restructuring of the surface has been observed.⁸ Deliquescence is the point at which a solid phase aerosol is solvated by bulk water that was adsorbed to the surface. It follows that since water uptake is a function of relative humidity, deliquescence is also dependent upon relative humidity; therefore, deliquescence relative humidity (DRH), is the relative humidity at which a solid spontaneously dissolves. Hydrophobic and hydrophilic moieties on a molecule, affect the hygroscopic character. However, these moieties alone do not dictate the DRH of the molecule, other factors such as crystal packing structure, size of the aerosol, and purity of the compound also influence the observed DRH. The opposite to that of deliquescence is efflorescence; where a post-deliqescence sample gives up its bulk water, multilayer, and monolayer of adsorbed water. Efflorescence is dependent upon relative humidity and spontaneously occurs at the efflorescence relative humidity (ERH). Interestingly, for the same sample, the DRH and the ERH do not have to coincide.⁶ The DRH for NaCl has been previously determined as a range of 70-75 percent relative humidity,^{6,8} whereas the ERH for NaCl has been reported as occurring at approximately 45 percent relative humidity.⁹ Additionally, the DRH for sodium acetate (NaOAc) nonhydrate has been reported as between the range of 38- 42 % RH.¹⁰

Thin films of water adhere to the surface of a salt through electrostatic, dispersion, induction, repulsion, and hydrogen bonding interactions. Water has electric dipoles, electric quadrupoles, and higher moments, which promote electrostatic interactions. The electric field created from an ionic substrate falls off exponentially with increasing distance (z). Additionally, the magnitude of the electrostatic binding energy between a water molecule and the surface also decreases with increasing distance and therefore only directly affects the water molecules in the first monolayer. The net attractive energy decays as a function of distance as z^{-3} as well, and results in dispersion energies between water molecules and the surface that are only significant for water molecules in the first monolayer. Likewise, induction and repulsion are also inversely proportional with distance, and will only directly affect the energetics of the water molecule- substrate interactions in the first monolayer. For water molecules in the first monolayer, hydrogen bonding within the thin film is comparable to the bonding between the monolayer and substrate. Whereas, additional monolayers are not directly affected by interactions with the substrate, instead hydrogen bonding occurs amongst neighboring water molecules.⁴ There has been at least two types of adsorbed water identified, a highly ordered type which is like ice, a less ordered type which is reminiscent of bulk water, as well as the states that lie between these two extremes.⁵

Electromagnetic radiation with a frequency characteristic of infrared energy matches the energy of molecular vibrations. Since the electronic component of the electromagnetic radiation is sinusoidal, the amplitude of the wave is periodic. When the energy of the incident electromagnetic radiation matches the energy of a molecular vibration, the electric-dipole of a molecule interacts with the oscillating electric field, and induces a molecular vibration. Infrared spectroscopy uses these concepts to extract chemical information from characteristic absorptions. As the energy of the incident beam matches a vibrational mode in the sample, the intensity of the incident beam is absorbed, and the signal arriving at the detector is respectively weaker. After the signal has been transformed with a Fourier Transform, a plot of Absorbance vs. Wavenumber, or Transmittance vs. Wavenumber can be plotted.¹¹

Two methods of Infrared Fourier Transform Spectroscopy (FTIR) are utilized in this article, attenuated total reflectance (ATR) FTIR and diffuse reflectance FTIR. The ATR technique is an infrared spectroscopic technique that measures specular reflection of a sample. At an angle greater than the critical angle (θ_c) an infrared beam is focused on an ATR crystal to induce total internal reflectance (TIR). The beam bounces at the crystal/sample interface due to the higher refractive index of the ATR crystal compared to that of the sample.¹² Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is a technique used to observe interfacial or surface interactions and is shown with Figure 1. The DRIFTS technique records infrared spectra *in situ*, which allows for dynamic interaction or reaction conditions of choice to be investigated inside the sample compartment of the spectrometer. The incident beam undergoes both specular and diffuse reflectance as it interacts with the surface of a powder sample. However the unique design of the DRIFTS technique eliminates the specular component from ever reaching the detector.^{13,14} The aforementioned DRIFTS technique can be used to investigate surface dynamics, through the acquisition of difference spectra. Under static conditions, a single beam of the sample is collected as the background file. Exposed to the same static conditions a subsequent single beam of the sample is collected and ratioed to the aforementioned background file. It follows that since there was no difference between the conditions of the aforementioned single beams, the ratio of the two leads to the procurement of a baseline measurement. As changes occur on the surface of the powder, through

molecular interactions or chemical reactions, the resultant spectra will change accordingly. The presence of a negative peak indicates a species or feature that was there during the procurement of the baseline is no longer present. Likewise, the presence of a positive peak indicates the apparition of a species or feature that was not there during the procurement of the baseline. Difference spectra can be used to investigate the chemical history of a reaction or interaction between an analyte of choice and the surface. Kubelka- Munk, the units applicable to surface reflectance of a scattering medium,¹⁵ are used with the DRIFTS technique. ATR can analyze solid and liquid samples and serve to confirm results obtained from DRIFTS techniques because ATR and DRIFTS techniques respectively provide chemical information obtained from specular and diffuse components of reflection.

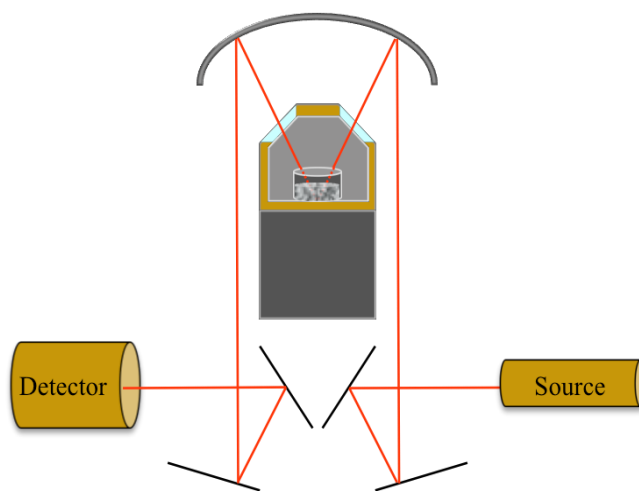


Figure 1. A simplified schematic of the DRIFTS technique that illustrates the infrared beam (red line) passing through the sample contained within the DRIFTS cell

The energetics of an adsorbed molecule is dependent upon the types of interactions the molecule experiences. Spectroscopically distinguishable via infrared spectroscopy are the types of hydrogen bonding networks observed as the amount of water vapor above the sample increases. Pertaining to water uptake by crystalline NaCl, a spectroscopic signal located at approximately 3700 cm^{-1} , can be assigned to a population of gas phase water molecules, a population of water molecules at the vapor interface, or a superposition of each of the aforementioned populations, all of which do not partake in hydrogen bonding.⁴ The spectroscopic signal located near 3500 cm^{-1} , is attributed to a population of adsorbed liquid water, which form small islands. These islands of water molecules allow for interactions with the surface of the NaCl, as well as among adsorbed water molecules on the interior.¹⁶⁻¹⁹ A broad spectroscopic signal located near 3400 cm^{-1} , is attributed to a population of bulk water, which has a high level of disorder.²⁰ The spectroscopic signal located near 3200 cm^{-1} can be attributed to the highly ordered ice-like monolayer of adsorbed water molecules.⁴

Although water adsorption onto NaCl has been studied extensively, the primary goal of this research was to recreate literature observations for water adsorption onto crystalline NaCl in order to validate our DRIFTS methodology. The secondary goal of this research was to investigate adsorption of water vapor onto both hydrated and nonhydrated forms of crystalline NaOAc. Switching the anion from chloride to acetate is fundamentally interesting since chloride is an inorganic atom that packs very well into a crystal structure, whereas acetate is an organic molecule that has both hydrophilic and hydrophobic moieties, and also exists as trihydrated and nonhydrated forms. Investigation of the uptake of water vapor by NaOAc was conducted to see how the DRH and ERH are manipulated when a chloride ion is replaced with an acetate ion.

2. Methods

Infrared spectroscopy (Thermo-Nicolet Avatar 370 FT-IR) was used to study salt samples under humid conditions. The sample cell is part of a DRIFTS accessory, which has temperature control as well as pressure control down to vacuum conditions (SpectraTech 6106640). Heterogeneous interactions of a solid-powder sample and gases flowed at a measurable flow rate in the DRIFTS cell. IR radiation reflects off the surface of the sample, through the headspace above the sample, and the interface of the sample between phases.²¹ This provides fundamental information on the interactions and reactions that occur between phases and during phase transitions.^{4-7, 22}

The flow system to the cell is shown with Figure 2, where dry ultra high purity (UHP) nitrogen (N_2) is fed into two of four mass flow controllers (MFC – MKS Mass-Flo Controller). Other gases such as oxygen (O_2), or UHP helium (He) can be used with the MFC. The four MFC are controlled manually via a four-channel readout (MKS Type 247). The flow ranges of the four MFC are in units of cubic centimeters per minute (ccm) and have tolerances of 0-50 ccm, 0-500 ccm, 0-1,000 ccm, and 0-10,000 ccm, respectively. For the two later MFC a loss of accuracy occurs at lower flow rates. For the purposes of this deliquescence experiment only the 50 ccm and 500 ccm MFCs were used. Before introduced to the sample chamber, dry UHP nitrogen moves from the MFC to either a 250 mL volume bubbler (Ace Glass) to collect humidity or directly to a mixing junction. The bubbler as seen in Figure 2 was used to introduce water to the UHP nitrogen. At the bubbler, arid UHP nitrogen was saturated with water and then subsequently flowed to a mixing junction, where humid UHP nitrogen was diluted to obtain a desired relative humidity. The ratio of humid UHP nitrogen flow to the arid UHP nitrogen flow, provided a facile way to control the relative humidity flowed to the DRIFTS cell.

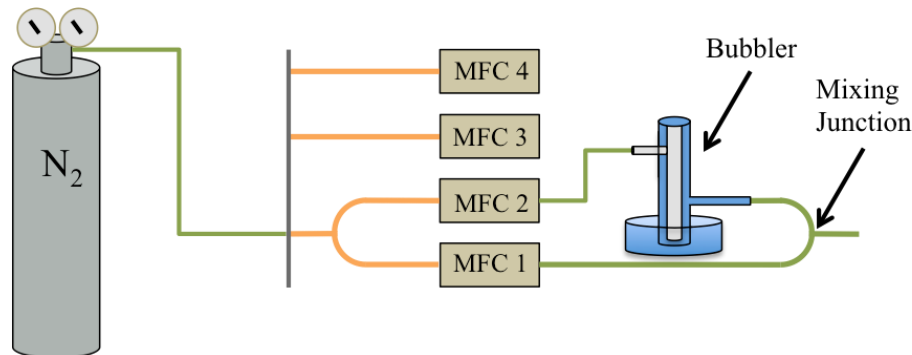


Figure 2. A schematic of the gas introduction system used to create desired humid conditions used to investigate water uptake on various surfaces. MFC = mass flow controller

The infrared spectrometer has been housed in an environmental box made of Plexiglas and purged by the system seen in Figure 3. House air was used as the purge gas for the environmental box. The purge system consists of a 50-psi pressure restriction valve, followed by the air-drying system. To remove water vapor in the line, the air is passed through a large desiccant filled tube (the desiccant was changed as it became saturated with water). After the drying process the air is scrubbed of oxygen, and subsequently scrubbed of carbon dioxide with activated charcoal. Due to the heat generated from the instrument in the environmental box the purge air was cooled to maintain optimal instrument operating conditions. The air was cooled by passing copper tubing placed in a refrigerator (LAUDA IC-60) at -40°C , as a result the environmental box housing the DRIFTS apparatus was maintained between $25\text{-}27^{\circ}\text{C}$.

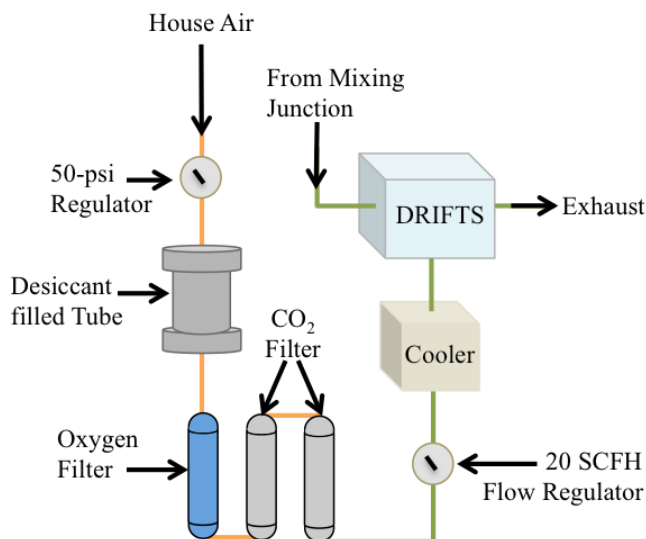


Figure 3. A schematic of the environmental box purge system, which shows the drying, scrubbing, regulating, and cooling of house air used to maintain an inert environment surrounding the spectrometer

To obtain accurate relative humidity measurements gravimetric analysis of water vapor present in the flow through the DRIFTS cell was carried out. An aluminum U-tube, immersed in liquid nitrogen, was placed adjacently downstream from the mixing junction. The ideal gas law was used to determine the mass of H_2O , which was flowed through the U-tube. The U-tube was weighed multiple times to ensure accuracy and precision. Analysis allowed for the determination of the real relative humidity of the system. Measured relative humidity was plotted against expected relative humidity and a linear regression was overlaid on top of the plot as to determine the average percent of expected relative humidity.

The deliquescence of powdered NaCl and NaOAc were studied *in situ* with the DRIFTS technique. Samples of NaCl and NaOAc trihydrate (Fisher Scientific) were kept under heat, to ensure a dry conditioned salt surface. Laboratory grade NaOAc trihydrate was used in preliminary studies and was found to not effloresce the hydrate to produce the nonhydrated form of NaOAc in the drying oven at modest temperatures (~ 100 °C). The nonhydrated NaOAc sample was synthesized in our laboratory via titration of 0.1 M acetic acid (HOAc) with 0.1 M sodium hydroxide (NaOH) and subsequent recrystallization of NaOAc . The equivalence point represents the point in the reaction where all of the HOAc has been converted to NaOAc via reaction with NaOH . Therefore the pH of the equivalence point for the conditions above was calculated as 8.74,²³ and a calibrated pH meter was used to monitor the progress of the titration. During the titration UHP nitrogen gas was bubbled through the beaker of HOAc as to reduce undesired pH fluctuations, which otherwise would have been expected from spontaneous dissolution of carbon dioxide (CO_2). The 0.05 M NaOAc solution was heated on a hotplate to evaporate the water and recrystallize the NaOAc ; all while UHP nitrogen gas was bubbled through the solution.

One at a time, samples of NaCl , NaOAc trihydrate, and NaOAc nonhydrate were placed in the sample cup and leveled with a spatula (Fuller, et al.). After the sample cup was placed in DRIFTS cell, the environmental box and the DRIFTS cell were respectively purged overnight with dry house air and UHP nitrogen. Under static conditions both a background spectra and a subsequent spectra were collected to create a baseline. The aforementioned background spectrum was then used to collect active, or *in situ*, spectra of the salts under increasingly humid conditions. To confirm hydration experiments the hydrated salts were analyzed with an IR instrument (Thermo Nicolet Avatar 360 FT-IR) fitted with an ATR attachment (Thermo Nicolet Smart Miracle ATR). All spectra were recorded via EZ-Omic with 200 scans and a resolution of 2 cm^{-1} . To eliminate the possibility of false results, the samples were isolated from atmospheric conditions when transferred between instruments.

3. Results and Discussion

The relative humidity generated in the gas introduction system was gravimetrically measured with an aluminum U-tube, which was partially submerged in liquid nitrogen. Humid nitrogen was flowed through the aluminum U-tube, where deposition of water vapor occurred. Relative humidities of 0.0, 56.0, 59.3, 63.9, 69.7, 71.7, 80.2, 80.7, and 84.4 % were respectively measured for the expected relative humidities of 0.0, 65.0, 70.0, 75.0, 80.0, 85.0, 90.0, 95.0, and 100.0 %. A plot of expected relative humidity against actual relative humidity is shown with Figure 4.

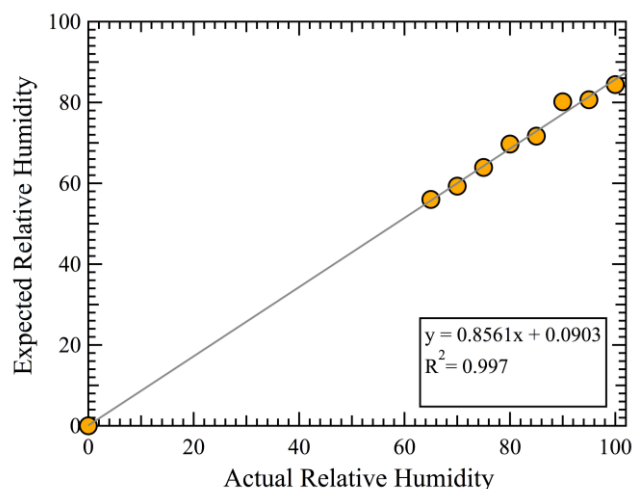


Figure 4. A plot of expected RH vs. actual RH (yellow circles). The text box shows the values of the best-fit line

A linear regression was applied to the data and produced an equation for the best-fit line that had a slope of 0.8561 and an R^2 value of 0.997. The slope of the best-fit line indicates the humidity the flow system produces, on average, is 85.61 % of the expected value based on the dilution ratios of the MFC. Additionally, the intercept of the best-fit line, 0.0903, indicates a lack of sensitivity to measurements of humidity under semi-arid conditions.

Successful preparation of a 0.05 M solution of NaOAc occurred with drop wise reaction of 0.1 M NaOH with 0.1 M HOAc. While nitrogen was bubbled through the 0.05 M solution of NaOAc, the volume of the 0.05 M solution was reduced on a hotplate to promote recrystallization. As the volume was reduced, NaOAc crashed out of solution, however recrystallization happened when there was hardly any solution left. An infrared spectrum of the NaOAc nonhydrate sample and of the NaOAc trihydrate were obtained with a Thermo-Nicolet Avatar 370 FT-IR and is shown with Figure 5. NaOAc trihydrate displayed three OH vibrational modes located at approximately 3412 cm^{-1} , 3270 cm^{-1} , and 3165 cm^{-1} , whereas over this region the prepared NaOAc sample was absent of any spectroscopic signals and indicated that the nonhydrated form of NaOAc was synthesized.

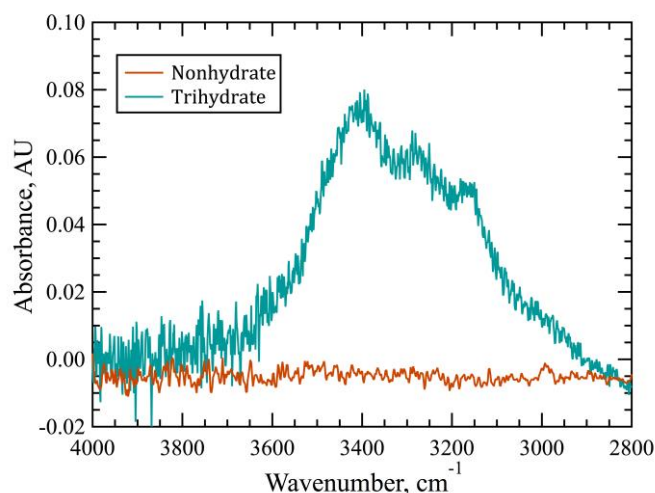


Figure 5. ATR spectra of NaOAc non-hydrate (orange) and NaOAc trihydrate (green)

Adsorption of water vapor onto the surface of powdered NaCl was investigated with the DRIFTS technique as to verify the ability to adsorb molecularly thin films of water onto a salt surface. Additionally, adsorption of water on NaCl has been studied extensively;^{4, 6-8, 16-20, 24} therefore, obtained spectroscopic signals can be compared with reported literature values as a way to validate the quality of our system. The spectroscopic signals obtained from adsorption of water vapor onto the surface of NaCl via the DRIFTS technique is shown with Figure 6.

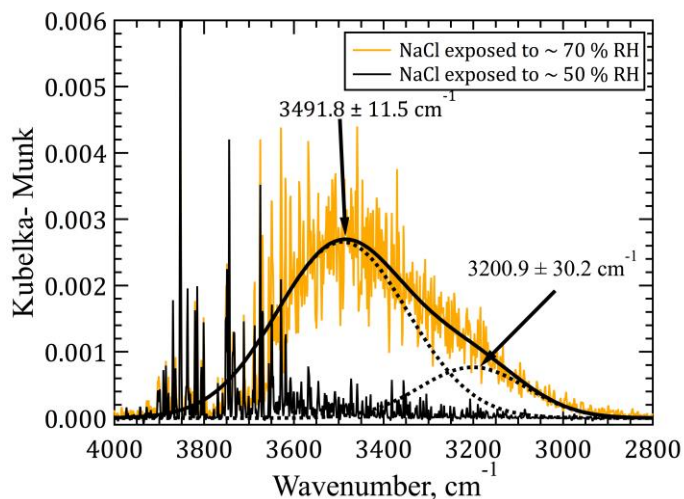


Figure 6. DRIFTS spectra of NaCl water uptake, black showing NaCl exposed to ~50% RH and orange ~70% RH. A curve-fit was applied to deconvolute the spectra

The spectra obtained in Figure 6 is in excellent agreement with reported spectroscopic literature values for water uptake on NaCl.^{4, 8, 20} A curve-fit function composed of a summation of two Gaussian functions was applied to the spectroscopic data in Figure 6. Excellent agreement between the curve-fit and the spectroscopic signal was obtained when the two Gaussian functions were positioned at $3491.8 \pm 11.5 \text{ cm}^{-1}$ and $3200.9 \pm 30.2 \text{ cm}^{-1}$, respectively. The

reasonably broad Gaussian peak located at $3491.8 \pm 11.5 \text{ cm}^{-1}$ represents a surface where small islands of adsorbed water have some character of bulk adsorption.²⁰ The relatively shallow Gaussian peak located at $3200.9 \pm 30.2 \text{ cm}^{-1}$ is indicative of ice like adhesion of water onto a NaCl surface.^{4,20,23} The aforementioned agreement between positions of the Gaussian peaks and positions of reported spectroscopic signals provided an affirmation to the sensitivity of the DRIFTS technique.

NaOAc trihydrate was exposed to humid nitrogen gas and was investigated *in situ* with DRIFTS. As shown by Figure 7, adsorption of water onto NaOAc trihydrate was observed when the sample was exposed to 75 % relative humidity. The complexity of the spectroscopic signal is of current interest, and a curve-fit composed of a summation of four or more Gaussian functions may be used to approximate the signal. The more Gaussian functions summed together, the better the superposition of those functions matches the spectroscopic signal; however, to be a valid function for spectroscopic signals, each Gaussian function needs to correspond to a real vibrational mode.

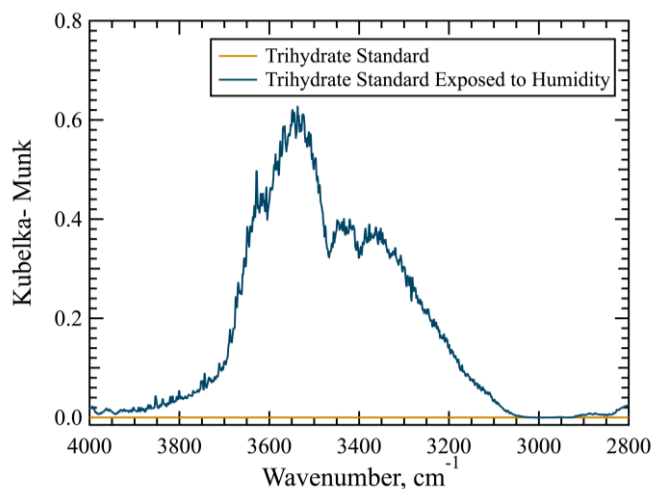


Figure 7. Difference DRIFTS spectra of NaOAc trihydrate water uptake. The standard was normalized to itself prior to water uptake (yellow spectra). After exposure to RH the blue spectra resulted

The prepared nonhydrate sample of NaOAc was exposed to humid nitrogen gas and was investigated *in situ* and confirmed with DRIFTS and ATR, respectively. Successful adsorption of water onto the surface of powdered NaOAc nonhydrate was spectroscopically determined with the DRIFTS technique and is shown with Figure 8. The order that the spectroscopic signals are listed in the legend is the order in which the spectroscopic signals were obtained. The blue signal was collected approximately 10 minutes after the baseline was established, while the gold and orange signals were respectively collected approximately 120 and 140 minutes after the procurement of the baseline. Even though the relative humidity decreased from the blue signal to the gold signal, the intensity of the signal gained an order of magnitude. This was attributed to the duration in which the surface of NaOAc nonhydrate was exposed to humid nitrogen gas as well as being a post deliquescence relative humidity. The spectroscopic signal subsequently diminished in size with exposure to arid nitrogen gas, however efflorescence of the adsorbed water did not occur, which indicated that NaOAc nonhydrate had been irreversibly modified through *in situ* hydration in the DRIFTS cell. Although, efflorescence of NaCl has been reported,⁹ the prepared nonhydrate sample of NaOAc did not effloresce under arid conditions, this indicates that exchanging the chloride anion for the acetate anion does indeed modify interactions at the surface.

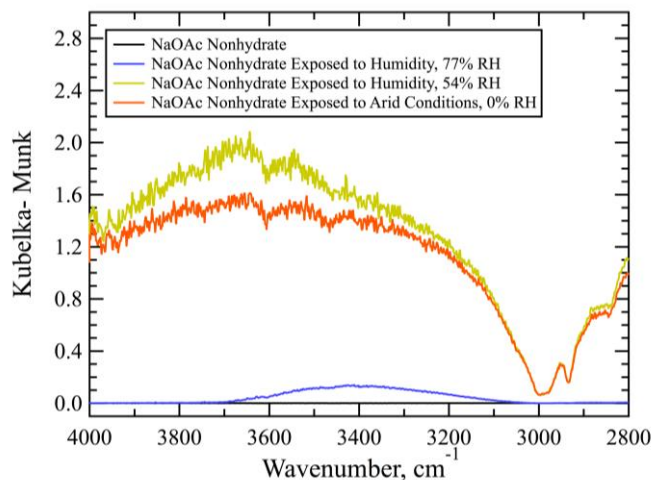


Figure 8. Difference DRIFTS spectra for NaOAc nonhydrate water uptake

A spatula was used to transfer the NaOAc nonhydrate sample exposed to humidity from the DRIFTS cell to the ATR. The instant the spatula made contact with the sample, the entire sample crystallized. The tip of the spatula was used to gently chisel out and place the center of the sample onto the ATR crystal. The NaOAc nonhydrate sample exposed to humidity clearly deliquesced in the DRIFTS cell. Infrared spectrums of NaOAc nonhydrate exposed to humidity and the NaOAc trihydrate were obtained with the ATR and is shown by Figure 9. Both of the spectroscopic signals had three distinct vibrational modes associated with them. Curve-fit functions, composed of a summation of three Gaussian functions were applied to each of the two spectroscopic signals in Figure 9. Excellent agreement between the NaOAc trihydrate sample and the respective curve-fit function was obtained when the three Gaussian functions were positioned at 3412 cm^{-1} , 3270 cm^{-1} , and 3165 cm^{-1} , respectively. Likewise, excellent agreement between the NaOAc nonhydrate sample exposed to humidity and the respective curve-fit function was obtained when the three Gaussian functions were positioned at 3410 cm^{-1} , 3263 cm^{-1} , and 3162 cm^{-1} , respectively. The agreement between peak positions indicated that NaOAc trihydrate was synthesized after the NaOAc nonhydrate sample was exposed to humid nitrogen gas and subsequently exposed to arid nitrogen gas.

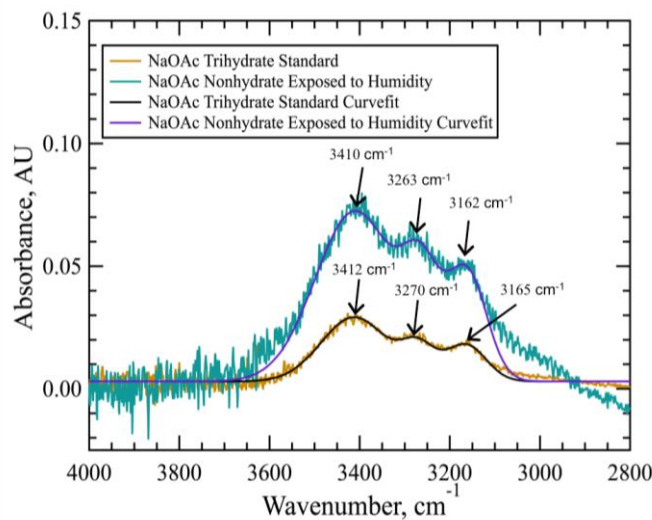


Figure 9. ATR spectra that confirms the formation of NaOAc trihydrate from the synthesized NaOAc nonhydrate sample after being exposed to humidity above the reported DRH for NaOAc

Interestingly, the water taken up by the nonhydrated sample appears to be non-reversible (ie. does not display efflorescence). Placement of the nonhydrate sample that was exposed to humidity in an oven in excess of 100 °C did not remove the adsorbed water. This was confirmed by recording ATR spectra of the sample after sitting in the oven for well over 24 hours. The spectra were extremely similar to that seen in Figure 9. This indicates that efflorescence might not occur in hygroscopic samples that can form stable hydrates. Current investigations involve examining other model aerosol surfaces that might be more atmospherically relevant, such as organic salts containing longer hydrocarbon chains, to examine if this effect is exclusive to NaOAc. *Ab initio* computations are also being investigated to further deconvolute the spectra presented herein.

4. Conclusions

In situ analysis of atmospherically relevant compounds are difficult experiments to design and provide a wealth of information about the processes that may take place in the real atmospheric conditions. Having the ability to control humidity, temperature, gas phase composition, solid phase composition, and pressure in the small reaction chamber has led to *in situ* measurement of water uptake by three salts and opens up opportunities for different systems to be studied. The system is set up to use two gases at this time but can be adjusted so that four gases can be used at a time. Since the environmental box is made of a material that does not transmit UV light the box is also ideal for photochemical studies. Further analysis of the sodium acetate trihydrate salt will be carried out via computational analysis in hope that these computational endeavors will provide thermodynamic information about the hydrate, provide information about the three water peaks that show up in our spectra, and provide some insight to the formation of the hydrate.

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