# Vacuum FTIR study on the hygroscopicity of magnesium acetate aerosols

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## A R T I C L E   I N F O

## A B S T R A C T

Hygroscopicity and volatility of secondary organic aerosol (SOA) are two important properties, which determine the composition, concentration, size, phase state of SOA and thus chemical and optical properties for SOA. In this work, magnesium acetate ($Mg(Ac)_2$) aerosol was used as a simple SOA model in order to reveal relationship between hygroscopicity and volatility. A novel approach was set up based on a combination of a vacuum FTIR spectrometer and a home-made relative humidity (RH) controlling system. The striking advantage of this approach was that the RH and the compositions of aerosols could be obtained from a same IR spectrum, which guaranteed the synchronism between RH and spectral features on a sub-second scale. At the constant RH of 90% and 80% for 3000 s, the water content within $Mg(Ac)_2$ aerosol particles decreased about 19.0% and 9.4% while there were 13.4% and 6.0% of acetate loss. This was attributed to a cooperation between volatile of acetic acid and $Mg^{2+}$ hydrolysis in $Mg(Ac)_2$ aerosols, which greatly suppressed the hygroscopicity of $Mg(Ac)_2$ aerosols. When the RH changed with pulsed mode between ~70% and ~90%, hygroscopicity relaxation was observed for $Mg(Ac)_2$ aerosols. Diffuse coefficient of water in the relaxation process was estimated to be ~$5 \times 10^{-12}$ m$^2 \cdot$s$^{-1}$ for the $Mg(Ac)_2$ aerosols. Combining the IR spectra analysis, the decrease in the diffuse coefficient of water was due to the formation of magnesium hydroxide accompanying acetic acid evaporation in the aerosols.

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## 1. Introduction

Hygroscopicity, determined by the equilibrium partitioning of water between condensed phase and gas phase, is one of the most important properties of atmospheric aerosol particles [1,2]. Hygroscopic compounds in atmospheric aerosols take up water from ambient environment, lead to phase transformation from solid particles to aqueous droplets at deliquescence relative humidity (RH), and make the droplets growth with increasing RH. Such processes further affect the light scattering, atmospheric lifetime and chemical reactivity of particles [3]. Hygroscopicity decides chemical composition, phase state, and surface properties of aerosols, which have actions on aerosol particles as nuclei for cloud droplets and ice crystals [4,5]. Besides hygroscopicity, volatility is another important property of aerosols, especially for SOA. The equilibrium partitioning of semi-volatile organic components (SVOCs) between the gas and condensed phases governs the size distributions and compositions of SOA, and thus determines the tropospheric particulate mass burden, heterogeneous reaction rates, optical extinction cross-sections and the efficiency of SOA as cloud condensation nuclei (CCN) [6–10]. Hence, it is important to understand hygroscopicity and volatility for acquiring the chemical composition of SOA and for

estimating the indirect and direct effects of SOA on Earth's radiation balance [11].

Previous studies always considered hygroscopicity and volatility separately in gas-particle partitioning of water and SVOCs [12]. In fact, volatilization was often accompanied by hygroscopic change, since dilution by increasing liquid water reduced vapor pressure of SVOCs in condensed phase above the droplet and SVOC continued to condense. Laskin's group found displacement of nitrate acid by weak organic acids during the dehydration process in $NaNO_3$/HA (organic acid) mixtures, which was driven by the evaporation of $HNO_3$ into gas because of its relatively high volatility [13]. Also the particulate phase reaction between $C_2$–$C_4$ dicarboxylic acids and sea salt was reported. Volatilization of HCl and less hygroscopicity of organic salt in the internal mixtures led to decrease in the total water content within the aerosols. Furthermore, it was found that the hygroscopicity of the dicarboxylate played a critical role in determining the aqueous chemistry of dicarboxylic acid — sea salt mixtures during the humidifying and dehumidifying process [14–16].

Though the reactions between inorganic salt and organic acid were investigated, the relationship between hygroscopicity and volatility for SOA was ambiguous. Recent model results showed that CCN could absorb a considerable fraction of the SVOC mass from the atmospheric vapor phase with increasing RH and decreasing temperature [17,18]. Conversely, as RH decreased, mass of liquid phase water diminished to maintain equilibrium between gas and condensed water phases, and

similarly led to adjustments in the equilibrium partitioning of the SVOC. Acetic acid (HAc), which were ubiquitous in atmosphere, had been detected in gas, land and marine aerosol particles [19–21]. Sources of HAc comprised anthropogenic and biogenic emissions and secondary production from gas-phase and aqueous photochemistry [20]. Magnesium was the most prevalent divalent cations in marine and dust aerosol particles [22]. In an experiment performed by Alexander, bidentate-bound carboxylate salts of magnesium formed through the reaction between magnesium and carboxylic acid after exposing to the ambient atmosphere [23]. Even though $Mg(Ac)_2$ was a simple organic salt, hydrolysis of $Mg^{2+}$ in aqueous $Mg(Ac)_2$ solution could facilitate volatile of HAc. Thus $Mg(Ac)_2$ aerosols could be used as a SOA model to make it clear what was the relationship between hygroscopicity and volatility in SOA. In previous work, $Mg(Ac)_2$ aerosols were studied by Raman technique and the chain structure formation was proposed, leading to water transfer limiting at lower RH [24]. In the following studies, a novel approach based on a combination of a home-made RH controlling system and a vacuum FTIR spectrometer was utilized to investigate the hygroscopicity of $Mg(Ac)_2$ dependent upon the volatility of HAc. In this approach, infrared feature bands from water vapor and liquid water were used to determine the RH in sample cell and the hygroscopic property of aerosols with a sub-second time resolution.

## 2. Experimental Section

Magnesium acetate solution (0.1 M) and magnesium sulfate (0.1 M) solution were produced by dissolving $Mg(Ac)_2$ and $MgSO_4$ (AR: analytical grade) directly into triply distilled water, respectively. The monodisperse aerosol droplets were deposited onto $CaF_2$ substrates via atomization and the diameter of resulting droplets were between 1 and 10 μm with average size of 3 μm (see in Fig. S1 in Supporting Information). The optical microscope (XSP - BM, Shanghai) and digital camera (Nikon - 5700) were used to observed the particle size distribution.

The detailed experimental setup was described in previous study, which comprised of vacuum FTIR spectrometer and RH controlling system [25]. The cylindrical cell was made of stainless steel and the two $CaF_2$ windows on which aerosol particles were deposited. The RH controlling system was composed of a water vessel, a vacuum pump and other accessories. The sample cell was connected with the water vessel and the vacuum pump through two solenoid valves.

FTIR spectroscopy was proved as a useful experimental facility to study the reactions and hygroscopic behavior of aerosols [26–32]. In this work, the infrared spectra were collected by the vacuum FTIR spectrometer (Bruker VERTEX 80v), with an actively aligned Ultra-Scan interferometer. In whole experimental process, the pressure in the spectrometer was kept at 0.21 kPa by using a pump (Adixen, ACP 15), thus the signals of ambient water and $CO_2$ almost could not be detected by IR technology and water content estimation and RH calibration were not affected. The mercury cadmium telluride (MCT) detector was utilized to record the FTIR spectra. The slow-scan and rapid-scan modes were achieved by adjusting the scan velocity as 20 kHz and 160 kHz, respectively. In slow-scan mode, 10 spectra were collected in 10 s. While for rapid-scan mode, 10 spectra were gained in 1 s. Spectral resolution of 4 cm$^{-1}$ was selected for enough signal-noise (S/N) ratio. In experimental process, the rapid-scan mode was used to detect the spectra during the pulsed RH process and the slow-scan was for RH changes as steps. All experiments were conducted at ~293 K.

The RH controlling system was applied to control the RH inside the sample cell. Details about the RH controlling system had been described in previous study [25]. As shown in Fig. S1a, the water vapor was injected in the sample cell through two pipes when the precise electromagnetic valve 1 was opened. And vacuum pump exhausted water vapor, when the valve 2 was opened. The desired RH and pressure in the sample cell could be controlled through accurately adjusting the two valves and were monitored by a humidity detector (Dwyer HU1142, ±2%RH) and a differential pressure transmitter (Rosemount

3051, accuracy <0.5%). Often it took about 1 min to establish a gas–liquid exchange equilibrium in the system to gain a RH value by a hygrometer. Therefore, when the IR spectrum was collected with a resolution of 1 min or longer time, the recorder RH by a hygrometer is accurate. As the RH changed rapidly, the spectral time resolution by a rapid scan mode (~0.12 s) was higher than that of the pressure response (~1 s), which resulted in the error between the RH data obtained by the hygrometer and the true RH in a sample cell. In order to avoid these RH differences, water vapor absorbance from IR spectrum was used to determine the RH in the sample cell. The RH derived from IR signals has been validated [25]. In this work, this method was used to study the effect of RH relaxation.

The RH was systematically adjusted by steps and pulses, which were illustrated in Fig. S1b and S1c, respectively. A RH cycle changed by steps was achieved in 6000 s (inset of Fig. S1b) and the changing velocity of RH was about 0.7% at every platform in 274.5 s. In Fig. S1c, several downward pulses were presented and the RH changed at a rate of 19.24% per 0.36 s in every pulse (inset of Fig. S1c).

## 3. Results and Discussion

### 3.1. FTIR Spectra of Mg(Ac)₂ Aerosols

The FTIR spectra of $Mg(Ac)_2$ droplets on dehydration process are recorded and shown in Fig. 1. According to the assignments in literatures, two bands at 1546 and 1411 cm$^{-1}$ at ~90%RH are assigned to the asymmetric ($v_{as}$—$COO^-$) and symmetric ($v_s$—$COO^-$) stretching modes of –$COO^-$, indicating the free $CH_3$—$COO^-$ ions in the $Mg(Ac)_2$ solution [33,34]. As the RH decreases, the bands at 1546 cm$^{-1}$ and 1411 cm$^{-1}$ shift to high wavenumbers gradually and locate at 1558 cm$^{-1}$ and 1417 cm$^{-1}$ at ~65%RH, respectively, together with the appearance of the shoulder at 1448 cm$^{-1}$. In the following dehydration process, the $v_{as}$—$COO^-$ band shifts to 1575 cm$^{-1}$ at 24%RH and then goes to 1587 cm$^{-1}$ at 9.1%RH, and remains unchanged at lower RH at last, while the $v_s$—$COO^-$ band keeps constant despite decrease in RH. Based on the previous report [34], the chain structures connect by the bridging bidentate of $Mg(Ac)_2$ form below 65%RH, which lead to the gel state. At 0.2%RH, the bridging bidentate of $Mg(Ac)_2$ are kept without coordinated water.

### 3.2. Hygroscopicity of Mg(Ac)₂ Aerosols in a Stepwise RH Change Process

In order to understand the hygroscopicity of $Mg(Ac)_2$ droplets, the changes of RH and water content in particles changing with the time are shown in Fig. 2a. The water content is quantified from the normalized integrated absorbance of the OH stretching band in the range of 3660–3000 cm$^{-1}$. The RH changes by a step of RH ~6% and is kept for ~500 s at each step. In the dehydration process, the pronounced water-loss at the RH terrace of 82%, 76% and 69% is observed. Detailed water-losses are from 1.00 to 0.90 at ~82%RH, from 0.78 to 0.73 at ~76%RH, and from 0.58 to 0.52 at ~69%RH, shown in shaded part of Fig. 2a. At lower RH (between ~58% to ~23%), the water content in the aerosols changes slightly as function of the RH owing to adopting gel state.

Fig. 2b illustrates the water content as a function of RH directly. It is obvious that water content in hydration process lags behind that in dehydration process, which is prominent at higher RHs (RH > 60%). In dehydration process, the changes of the three parts (enlarged by color lines) are especially fast, which are corresponding to the shadow of Fig. 2a. After a dehydration-hydration cycle with RH changes by stepwise, the total water content within $Mg(Ac)_2$ aerosols decreases about 23%. For comparison, the similar treatment is performed for $MgSO_4$ particles (Fig. 2c and d). In Fig. 2c, water content remains constant at constant RH in dehydration process at high RH range, which is different from $Mg(Ac)_2$ droplets. When the RH is lower than 40%, there is a continuous water loss at constant RH for $MgSO_4$ particles, which is attributed to water transfer limitation in gel state for $MgSO_4$ particles [35,36].