Response to Reviewers

We thank the reviewers for their detailed comments and helpful suggestions. We have addressed each comment below, with the Referee comment in **bold italicized text**, our response in plain text, and any manuscript changes noted in <u>blue text</u>. In addition, the revised manuscript with changes marked up has been attached to the end of our response to the Referee.

Reviewer # 1

Comments:

My major criticism of the paper was that only two components were used to show the feasibility of the method. The authors have now measured three additional substances showing quite reasonable agreement with data available in the literature. It is interesting to note that DSC measurements of Glycerol and DOP agrees quite well, while citric acid shows a stronger deviation.

I recommend publishing the revised version after the correction of some technical issues.

In the updated Table 1: Nakanashi and Nozaki report as Tg for the hexanetriol (200+-2) K and not 196 K!

There are two additional data for this compound in the literature: (206.4+-0.5) K from Dorfmüller et al. (1979) and 202 K from Böhmer et al. (1993).

The citation of Beirnes and Burns in J. Appl. Polym. Sci. paper has a wrong publication date: it is 1986 and not 2003.

References:

Dorfmüller et al.: The Journal of Chemical Physics 71, 366 (1979); doi: 10.1063/1.438079

Böhmer et al. : The Journal of Chemical Physics 99, 4201 (1993); doi: 10.1063/1.466117.

We thank the reviewer for reading and reviewing our manuscript carefully, as well as his/her feedback. We have updated the Tg value of hexanetriol from Nakanishi and Nozaki to 200 ± 2 K. (The 196 K was extracted from Figure 6 of the original paper and it was not as accurate as 200 K).

We also changed the citation year of Beirnes and Bruns to 1986.

We have added the two references of Tg of 1,2,6-hexanetriol to Table 1.

Chemical Compound Tg (K)-Measured T_g (K)-Literature Formula <189 K (2 K/min) 190 K (Zondervan et al., 2007) 192 ± 2 K (5 K/min) 191 K (Chen et al., 2012) Glycerol $C_3H_8O_3$ 196 K (Amann-Winkel et al., 2013) $194 \pm 2 \text{ K} (10 \text{ K/min})$ 191.7 ± 0.9 K (Lienhard et al., 2012) 200 ± 2 K (Nakanishi and Nozaki, 2010) 1,2,6- $C_6H_{14}O_3$ 206.4 ± 0.5 K (Dorfmüller et al., 192 ± 2 K (5 K/min) Hexanetriol 1979) 202 K (Böhmer et al., 1993) Di-n-butyl $C_{16}H_{22}O_{4}$ 174 K (Dufour et al., 1994) 180 ± 2 K (5 K/min) Phthalate Dioctyl 190 K (Beirnes Kimberley and $C_{24}H_{38}O_{4}$ 194 ± 2 K (5 K/min) Phthalate Burns Charles, 1986) 281 ± 5 K (Bodsworth et al., 2010)^{*} 285 ± 0.2 K (Lu and Zografi, 1997) Citric Acid $C_6H_8O_7$ 281.9 ± 0.9 K (Lienhard et al., 2012) $307 \pm 5 \text{ K} (5 \text{ K/min})$ 283-286 K (Dette et al., 2014) 260 ± 10 K (Murray, 2008)^{**}

"Table 1. Glass transition temperatures for selected organic species measured by broadband

dielectric spectroscopy with a thin-film interdigitated electrode array

* The data was based on modeling result. **The data was based on extrapolation of a fit to the

data."

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Kinetically Controlled Glass Transition Measurement of Organic Aerosol Thin Films Using Broadband Dielectric Spectroscopy

3

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23

24 Abstract

25 Glass transitions from liquid to semi-solid and solid phase states have important implications for 26 reactivity, growth, and cloud forming (cloud condensation nuclei and ice nucleation) capabilities 27 of secondary organic aerosols (SOA). The small size and relatively low mass concentration of 28 SOA in the atmosphere make it difficult to measure atmospheric SOA glass transitions using 29 conventional methods. To circumvent these difficulties, we have adapted a new technique for 30 measuring glass forming properties of atmospherically relevant organic aerosols. Aerosol 31 particles to be studied are deposited in the form of a thin film onto an interdigitated electrode (IDE) using electrostatic precipitation. Dielectric spectroscopy provides dipole relaxation rates 32 33 for organic aerosols as a function of temperature (373 to 233K) that are used to calculate the 34 glass transition temperatures for several cooling or heating rates. IDE-enabled broadband 35 dielectric spectroscopy (BDS) was successfully used to measure the kinetically controlled glass 36 transition temperatures of aerosols consisting of glycerol and four other compounds with selected 37 cooling/heating rates. The glass transition results agree well with available literature data for 38 these five compounds. The results indicate that the IDE-BDS method can provide accurate glass 39 transition data for organic aerosols under atmospheric conditions. The BDS data obtained with 40 the IDE-BDS technique can be used to characterize glass transitions for both simulated and 41 ambient organic aerosols and to model their climate effects.

42

43 Keywords

44	Broadband Dielectric Spectroscopy	Glass Trans	ition	Organic Aerosols
45	Interdigitated Electrodes	Thin Films	Aerosol	Climate Effects

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46 **1 Introduction**

47 Aerosol particles have important climate and health effects because they can scatter 48 sunlight, form clouds by acting as cloud condensation nuclei (CCN), alter visibility, and affect 49 human health (Hallquist et al., 2009; Jimenez et al., 2009). Recent studies have confirmed that 50 organic aerosols, which comprise approximately half of the total submicron aerosol mass in the 51 atmosphere, can change from liquid to glassy state at ambient humidity levels and temperatures 52 (Zobrist et al., 2008; Virtanen et al., 2010; Shrestha et al., 2014; Zhang et al., 2015). The effect 53 of temperature may be especially important when aerosol particles are lifted into the free 54 troposphere, where the temperature change can rapidly alter their phase from liquid to glass 55 (Koop et al., 2011). The physical state of the aerosol strongly influences air quality and aerosol 56 climate effects. Evidence suggests that secondary organic aerosols, formed through oxidation of 57 gas phase organic compounds, have much lower vaporization rates than previously assumed, 58 which changes the reactivity of the gas phase species as well as their fate in the atmosphere. The 59 phase state of aerosol particles also influences the diffusion of the gas phase species into the 60 atmosphere, affecting the oxidation extent and multiphase reactions of the particles. For 61 example, Shiraiwa and Seinfeld (2012) used models to predict that when aerosol particles are in 62 certain semi-solid and glassy phase states, the reactive uptake of gas phase species will be 63 kinetically limited. Kuwata and Martin (2012) showed that the phase state of secondary organic 64 aerosols (SOA) affects the uptake of ammonia into the particles. Zhang et al. (2018) provided 65 experimental and modeling evidence that the reactive uptake of isoprene-derived epoxydiols (IEPOX) into acidic sulfate particles is influenced by the phase state, which can contribute to at 66 67 least a 30% reduction of isoprene-derived SOA in the Southeast U.S.

68

The phase state of the aerosols also affects their climate properties. For example, in the

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69 glassy state, the water vapor uptake by the SOA is greatly reduced, limiting the ability of 70 particles to have liquid water condense on them and thus hampering the formation of liquid 71 cloud droplets (Shiraiwa et al., 2011; Zobrist et al., 2011; Price et al., 2015). However, there is 72 evidence that glassy SOAs are effective ice nucleation agents. Their ability to nucleate ice 73 crystals to form Cirrus clouds in the upper troposphere may be particularly important given the 74 key role of these clouds in global warming (Wilson et al., 2012; Berkemeier et al., 2014). Lack 75 of adequate data describing these processes contributes to the high uncertainty of atmospheric 76 aerosol impact on climate change (Shiraiwa et al., 2017).

77 The importance of the phase state of organic aerosols in the evaluation of their climate 78 effects has motivated several studies in this field. However, these studies are difficult to perform 79 and the data obtained so far are limited. Renbaum-Wolff et al. (2013) studied the phase state and 80 viscosity of the water-soluble part of α -pinene SOA at several humidity levels and phase 81 separation effects. Zhang et al. (2015) characterized the viscosity of α -pinene SOA across a wide 82 range of relative humidity levels. Rothfuss and Petters (2017) studied the viscosities of sucrose particles with sodium dodecyl sulfate (SDS) particles up to 10⁷ Pa under sub-freezing 83 84 temperature regimes. There have also been a few studies exploring the glass transition 85 temperature of atmospherically relevant organic compounds by using differential scanning 86 calorimetry (DSC) (Koop et al., 2011; Lienhard et al., 2012; Dette et al., 2014; Dette and Koop, 2015). 87

Despite past studies, very little information is available on how organic aerosols become glass as temperature, and the rate of cooling/heating changes. Such information is required to model the aerosol phase when aerosols are transported from one region of the atmosphere to another (Murray et al., 2010; Wilson et al., 2012). In an early 2011 study Koop and co-workers

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92 performed experiments that led them to estimate glass transition temperature (T_g) values of 268-93 290K for a range of surrogate biogenic SOA compounds by utilizing the DSC method. The 94 results show that oxidation and/or oligomerization reactions leading to higher oxygen to carbon 95 ratios (O:C) yield higher T_g values. Dette et al. (2014) used the "metastable aerosol by the low 96 temperature evaporation of solvent" (MARBLES) technique to provide information on the glass-97 to liquid transition temperatures of pure organic compounds and organic-inorganic binary 98 mixtures. Their results show that the glass transition temperatures of these mixtures can be 99 accurately described by the Gordon-Taylor equation that describes the glass transition of binary 100 mixtures. However, to evaluate the impact of SOA and its possible phase transitions on climate 101 and air quality issues, the current techniques need to be improved in order to adapt to the 102 atmospheric aerosol sampling requirements.

103 The small particle size and relatively low concentration of SOA in the atmosphere make 104 it difficult to measure atmospheric SOA glass transitions using conventional methods. First, a 105 reliable measurement of glass transitions with currently used techniques requires a relatively 106 large mass, typically milligram levels of the compound, while reasonable field collection 107 methods yield organic aerosols in the femtogram mass range (Dette et al., 2014; Dette and Koop, 108 2015). Second, it is difficult to collect suspended aerosols and transfer them to the analysis 109 apparatus without contaminating the sample with trace water. Trace amounts of water absorbed 110 by SOA can substantially alter glass transition properties (Bateman et al., 2015; Price et al., 111 2015; Rothfuss and Petters, 2017; Shiraiwa et al., 2017). To circumvent these difficulties, we 112 have adopted a new technique for measuring glass forming properties of atmospherically 113 relevant organic compounds. The technique combines broadband dielectric spectroscopy (BDS) 114 utilizing interdigitated electrodes (IDE) (Chen et al., 2012) with organic aerosol sample

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115 deposition using electrostatic precipitation (Liu et al., 2013).

116 BDS is one of the most widely used techniques for measuring the dynamics and glass 117 transition of liquid and semi-solids (Richert, 2014). In the usual arrangement, dielectric 118 spectroscopy instruments consist of two parallel metallic plates with the sample filling the space 119 between the plates. As was stated, the traditional dielectric method usually requires mass in the 120 milligram range to perform the measurement (Richert, 2014). Such high mass loading cannot be 121 reasonably attained with aerosol collected under normal atmospheric conditions. A relatively 122 new technique, using interdigitated electrodes (IDE), which requires only one surface for 123 samples and requires mass only in the femtogram range (Chen et al., 2012), is suitable for 124 atmospheric aerosol phase studies. A thin film is deposited on the IDE first, then the dielectric 125 spectra are recorded to characterize the glass transition of aerosol particles at variable cooling or 126 heating rates.

The purpose of this study is to demonstrate the new IDE-BDS analysis technique by presenting results of the glass transition of SOA surrogates using this technique. In section 2 below, we first describe the experimental setup including aerosol generation, thin film deposition on the IDE, temperature conditioning chamber, and the BDS measurement system. Then data analysis, including glass transition determination, is discussed in section 3. Section 4 includes discussion of the advantages of the IDE-BDS method, as well as caveats associated with its current implementation.

134 **2. Experimental Setup**

A schematic diagram of the experimental setup is shown in Figure 1. The setup is
conveniently divided into four parts:1. Aerosol sample generation, 2. Thin film formation via
electrostatic precipitation on the Interdigitated electrodes (IDE) with associated humidity control

138 3. Temperature conditioning chamber and 4. Broadband Dielectric Spectroscopy measurement139 system.

140 **2.1 Aerosol generation.**

141 Two types of aerosol generation systems are used in our experiments. The first is a home-142 made self-nucleation generation device used for producing liquid organic aerosol samples 143 including glycerol, 1,2,6-hexanetriol, di-n-butyl phthalate, and dioctyl phthalate. About 0.5 gram 144 of the glycerol is placed at the bottom of a round flask and the temperature of the flask is heated 145 to 20°C below the boiling temperature of the organic liquid. A condenser is connected to the top 146 of the flask to cool the temperature of that region. A flow of 2 liters per minute (Lpm) of dry air 147 passes through the condenser and brings the aerosol particles to the region where the aerosols are 148 precipitated onto the IDE.

The second method utilizes a commercial unit (TSI, 3076) to generate atomized citric acid aerosols. About 0.5 gram of citric acid is dissolved in 100 mL of high purity water to form the atomizing solution. About 30 psi pressure of dry air is applied on one end of the atomizer to generate a constant 3 Lpm aerosol-containing flow to the second part of the system, which is the thin film generation system that will be described below.

154 **2.2 Interdigitated electrode (IDE) and thin film formation.**

An IDE (NIB003744, MS-01/60, NETZSCH Instrument North America) is used in this study as a substrate for measuring the dielectric constants of organic materials. The IDE consists of two thin electrodes that are interdigitated together like entwined finger tips, as shown in Figure 2. Each interdigitated pair serves as a small capacitor for dielectric analysis. The thin electrodes are made from platinum (Pt) and are arrayed on a quartz substrate. The electrodes utilized in this study are spaced 1 µm apart and are able to withstand temperatures up to 200 °C.

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161 The combination of multiple interdigitated pairs of electrodes greatly enhances the sensitivity of

162 the technique compared to a single pair of electrodes that would have been used in the

163 conventional technique.

164 An electrostatic deposition method is used to deposit organic films on the IDE (Liu et al., 165 2013). The electrostatic precipitator has one inlet and one outlet. A stream of aerosolized 166 oxygenated organic liquid droplets to be studied is passed through an inlet with a high voltage 167 corona discharger (-5000V) so that all the droplets are negatively charged to varying degrees. The 168 flow is directed above the substrate held at +3000 V within the precipitator. Due to opposite 169 charges, the charged particles are electrostatically deposited onto the substrate, gradually merging 170 together to form thin films. The remaining flow is then withdrawn from the precipitator and flows 171 through a HEPA filter connected to a pump. The flow rate through the precipitator is maintained 172 between 1.7-1.9 Lpm. Depending on the amount of aerosol material being deposited onto the 173 surface, the deposition can remain either remain as discrete aerosol droplets, or at higher droplet 174 depositions, can form a uniform thin film, as shown in Figure 2. For this study thin films are 175 formed. The volume concentration of the aerosol particles at the inlet of the precipitator was 4.5×10^{11} nm³ cm⁻³. After collecting for 5 hours, the film thickness is estimated to be 1-2 μ m on a 176 177 $1 \text{ mm} \times 8 \text{ mm}$ substrate based on the difference of volume concentration between the inlet and the 178 outlets of the precipitator, the flow rate, the collection time, and assuming 50% collection 179 efficiency.

180

0 **2.3 Temperature conditioning chamber.**

181 The IDE substrate coated with organic material is then transported to the temperature 182 conditioning chamber using tweezers. The temperature conditioning chamber consists of a 183 stainless steel cap and a heating/cooling surface using either a liquid nitrogen cooler or a heating 184 furnace. The sample temperature can be controlled from ~-150°C to +200°C. Details of the 185 chamber are shown in Figure 1. The cooling/heating rate can be varied from 1 K/min to 25 186 K/min. The chamber is flushed with dry nitrogen gas to reduce the relative humidity (RH) prior 187 to temperature conditioning. A K type thermocouple is located on top of a reference cell inside 188 the conditioning chamber, to monitor sample temperature. The typical cooling cycle starts 189 around 20 °C and ends at about -140 °C, while the heating cycle starts at -140 °C and ends at 30 190 °C. The cooling and heating cycle are adjusted to the desired cooling/heating rates between 2 191 K/min and 10 K/min.

192 2.4 Broadband Dielectric Spectroscopy (BDS) measurement system.

193 The BDS instrument used in this study is manufactured by NETZSCH Inc. (DEA 288 194 model). A periodic signal from the instrument is applied to the IDE electrodes. The frequency of the signal ranges from 10⁻³ Hz to 1 MHz. The data acquisition part of the instrument then 195 196 measures the impedance, Z_{sample} , of the sample as a function of the applied frequency. The 197 impedance measurement yields the capacitance of the sample on top of the IDE. By measuring 198 the impedance of the uncoated and organic-coated IDE, three IDE capacitances can be obtained, 199 i.e., when the IDE is uncoated, Z_{empty} , when it is coated with organic compounds, Z_{coated} , and the 200 geometric capacitance of the IDE without any substrate, Z_{geo} . Approximate values of the real and 201 imaginary part of the sample permittivity, $\varepsilon_{\text{sample}}$, can be obtained using Eq. (1) (Chen et al., 202 2012)

203

$$\varepsilon_{sample} = 1 + \frac{Z_{loaded} - Z_{empty}}{Z_{geo}} \tag{1}$$

204 For demonstration and data comparison purposes, we have used glycerol, 1,2,6-205 hexanetriol, di-n-butyl phthalate, and dioctyl phthalate (99%, Sigma Aldrich, St. Louis, MO, 206 USA) as the test compounds for homogeneous nucleation and citric acid (99%, Sigma Aldrich, Zhang et al.

St. Louis, MO, USA) as the surrogate organic aerosol generated by atomizing solutions. For
atomizing solutions, the surrogate compound is mixed with high purity water. All reagents were
used as provided without further purification.

210 **3. Data Analysis**

211 **3.1 Calculating Relaxation Time** τ

212 The thin film on the IDE is usually cooled at a selected cooling rate and then heated back to 30°C. 213 After a cooling-heating cycle, the dielectric constant at each temperature measured, ε (ω), is 214 recorded by instrument. The relaxation time, τ , can be obtained by curve fitting the Havriliak-215 Negami equation of the real and imaginary parts ($\varepsilon'(\omega)$) and $\varepsilon''(\omega)$, respectively) with the 216 frequency ω , as shown in Figure 3 (Chen et al., 2012). The detailed equation for $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ 217 is shown in Eqns. (S1) and (2). At each temperature, the dielectric spectra often show peaks at 218 specific frequencies, designated as dielectric relaxation peaks. Different peaks give different τ 219 values after fitting Eq. (2) with the data points.

220
$$\varepsilon''(\omega) = \Delta\varepsilon (1 + 2(\omega\tau)^{\alpha} \cos\left(\frac{\pi\alpha}{2}\right) + (\omega\tau)^{2\alpha})^{-\beta/2} \sin(\beta\varphi)$$
(2)

221 with
$$\Delta \varepsilon = \varepsilon_s - \varepsilon_{\infty}$$
, $\varphi = \arctan\left(\frac{(\omega\tau)^{\alpha} \sin\left(\frac{\pi\alpha}{2}\right)}{1 + (\omega\tau)^{\alpha} \cos\left(\frac{\pi\alpha}{2}\right)}\right)$

222 where ε_s is the permittivity at lower frequency, ε_{∞} is the permittivity at the high frequency limit,

223 α , β are fitting parameters, and τ is the characteristic relaxation time of the medium

224 (Adrjanowicz et al., 2009; Chen et al., 2012).

Log τ is then plotted as a function of the inverse of the temperature to further examine how relaxation time changes as a function of temperature. The error bar represents twice the standard deviation of the fitting result. The resulting curve can be used to calculate the glass transition temperature of the compound, as described in section 3.2.

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229 **3.2 Glass Transition Determination**

230 The glass transition temperature is defined as the temperature where a compound changes 231 from liquid to glass. Several methods have been used to indirectly determine the glass transition 232 temperatures. A common way to calculate the glass transition temperature using BDS is to measure 233 relevant parameters and to calculate the dielectric relaxation τ described in section 3.1 at several 234 equilibrium temperatures T, and then plot $\log \tau$ as a function of 1000/T. The data points are fitted 235 using the Vogel-Fulcher-Tammann (VFT) formula (Vogel, 1921; Fulcher, 1925; Tammann and 236 Hesse, 1926). The glass transition is customarily defined as the temperature where $\tau = 100$ s in the 237 fitted curve (Chen et al., 2012; Richert, 2014). The result usually agrees with the DSC 238 measurement within a few degrees (Richert, 2014). However the method is limited, because not 239 all compounds become glass as $\tau=100$ s (Saiter et al., 2007; Bahous et al., 2014). Furthermore, this 240 method does not take into account kinetic effects on glass transition, specifically the effect of 241 cooling and heating rates (Elmatad et al., 2009, 2010; Keys et al., 2013; Limmer and Chandler, 242 2014; Hudson and Mandadapu, 2018), as glass transition temperature changes with cooling and 243 heating rates.

The method used in our studies is based on dynamical facilitation theory (Elmatad et al., 2009; Chandler and Garrahan, 2010; Keys et al., 2011; Keys et al., 2013; Hudson, 2015, Hudson and Mandadapu, 2018), which also takes into account the effect of cooling rate on the glass transition. According to this theory, as a compound is cooled and transitions from a liquid to a supercooled liquid it exhibits super-Arrhenius behavior given by the following equation:

249

$$\log \tau / \tau_0 = J^2 (1/T - 1/T_0)^2$$
(3)

where J is an energy scale intrinsic to each material related to the rate of motion of
 individual molecules, T_o is termed the "onset temperature" and refers to the temperature at which

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a liquid showing Arrhenius relaxation becomes a supercooled liquid showing super-Arrhenius relaxation, and τ_0 is a temperature-independent reference time scale of the order of the time taken for molecules to locally rearrange (Keys et al., 2011).

255 As temperature further decreases, the supercooled liquid becomes glass-like, exhibiting 256 Arrhenius behavior. The temperature where the supercooled liquid changes to glass is the glass 257 transition temperature of the compound at the specific cooling rate studied. As the sample is 258 continuously cooled at a specific cooling rate, the dielectric relaxation peaks can be generated as 259 a function of the sample temperature. The experimentally obtained data are plotted in the form 260 $\log \tau$ vs 1/T. The data obtained at the higher temperature range are fitted to the super-Arrhenius 261 function and the data obtained at the lower temperature range are fitted to the Arrhenius function. 262 Figure 4 shows a typical relationship between the dielectric relaxation timescale and the 263 temperature, as a compound is cooled down or warmed up between the liquid state and glassy 264 state. As illustrated in Figure 4, the kinetically controlled glass transition temperature (or the true 265 glass transition temperature) is the temperature at the intersection of the two functions. The 266 traditional method determines the glass transition temperature as shown in dashed lines where τ 267 =100 s. Depending on the compound, the true glass transition temperature may not be the same 268 as the glass transition temperature determined by using $\tau = 100$ s, as shown in section 4 below. 269 The uncertainty of the glass transition temperature is estimated based on varying the fitting 270 parameters of the super-Arrhenius curve and Arrhenius line within a one-sigma range. 271 For glycerol, measurements of glass transitions were performed at three cooling rates: 2 272 K/min, 5 K/min, and 10 K/min. At each cooling rate the compound is cooled from approximately 273 300 K to 125 K, while the dielectric peaks are measured simultaneously as a function of 274 temperature. The organic film is thin enough so that its temperature reaches equilibrium with the

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cooling/heating medium, reducing the errors caused by heat transfer within the sample itself.

276 Such measurements are difficult to perform with conventional techniques due to slow heat

transfer in large mass samples, which often leads to inaccurate results. The effect of cooling rates

278 on glass transition measurements will be discussed in the following section.

279 **4 Results and Discussion**

280 4.1 Glass transition temperature of selected organic compounds

Aerosols are generated by two methods in this study, and in each method, we measured the glass transition of a compound that has been studied in the literature. Glycerol, 1,2,6hexanetriol, di-n-butyl phthalate, dioctyl phthalate, and citric acid particles were generated through the homogeneous nucleation method or the atomizer method, respectively. The measured dielectric spectra of each compound show distinct relationships of their dielectric relaxation timescales with a 5 K/min cooling rate, as shown in Figure 5. This is a confirmation of the expected behavior.

288 By calculating the corresponding temperature when the super-Arrhenius curve intersects 289 with the Arrhenius curve, the glass transition of each compound can be derived. As is shown in 290 Table 1, the kinetically controlled glass transition data agree well with previously measured 291 literature values of glycerol (Zondervan et al., 2007; Chen et al., 2012; Amann-Winkel et al., 292 2013), 1,2,6-hexanetriol (Dorfmüller et al., 1979; Böhmer et al., 1993; Nakanishi and Nozaki, 293 2010), di-n-butyl phthalate (Dufour et al., 1994), dioctyl phthalate (Beirnes Kimberley et al., 294 1986), and measured values are mostly within 4% of the cited literature value, except for one 295 study by Dorfmüller et al. (1979). The comparison of the dielectric relaxation timescale of 296 glycerol measured in this study with literature values is shown in Figure S1, for several different 297 temperatures. The results show that our measurements match the previously published results in

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the super-Arrhenius region when the compound is in equilibrium at a given temperature, with almost identical values. As the temperature continues to drop, glycerol and other compounds we tested fall out of equilibrium and become glass, which exhibits Arrhenius behavior. The transition from super-Arrhenius to Arrhenius behavior in this study provides the kinetically controlled glass transition as the compounds change from liquid to glassy state.

303 For citric acid, there is no dielectric measurement available. The kinetically controlled 304 dielectric spectra fitted using Eq. (S2) are shown in Figure 6. From the fitting results in Figure 6, 305 the dielectric relaxation timescales τ are derived as a function of temperature, as shown in Figure 306 7. The kinetically controlled glass transition temperature derived from Figure 7 agrees 307 reasonably well (within 10% error) with four literature results (Lu and Zografi, 1997; Bodsworth 308 et al., 2010; Dette et al., 2014; Lienhard et al., 2014). The fifth set of literature data (Murray, 309 2008) is based on extrapolation of a fit to experimental data and is about 20K lower than other 310 values reported by the literature. The differences can be explained by the following reasons: (1) 311 To date there have been no measurements of the dielectric spectra for citric acid to our 312 knowledge. The citric acid references in Table 1 are based on DSC measurements, which may 313 not be in exact agreement with the dielectric measurement. Angell (2012) pointed out that there 314 are at least three different definitions of the glass transition and the Tg determined by each can 315 be 50 K different from each other. DSC uses heat capacity changes to measure the glass 316 transition while dielectric relaxation uses molecular movements to define the glass transition. 317 Due to the difference in measurement parameters and the definition of the glass transition, these 318 two measurements can provide different Tg values of the same compound by up to 10 K 319 (Shinyashiki et al., 2008). (2) This study focuses on the kinetically controlled glass transition 320 temperature at a given cooling rate, i.e., the transition between the Arrhenius and super-

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321 Arrhenius relaxation regimes to determine the glass transition temperature. If the more 322 conventional method, i.e. fitting the super-Arrhenius curve to obtain the glass transition 323 temperature when $\tau = 100$ s, is applied to the data, as shown in Figure 7, the obtained glass 324 transition temperature would be 281 ± 3 K, which is within 1% difference compared with the 325 two nearest literature values. However, as previous publications have pointed out (Keys et al., 326 2013; Bahous et al., 2014; Limmer and Chandler, 2014; Hudson, 2018), using the transition from 327 super-Arrhenius to Arrhenius region is likely to reflect the true glass transition when taking 328 kinetic factors, such as cooling/heating rates, into consideration. (3) Moreover, glass transition 329 data of citric acid are rather limited and there are differences between each study. For instance, 330 from the literature data, the differences between three reported glass transition temperatures are 331 up to 10%, which is about the same difference obtained by comparing our data to the other two 332 nearest literature results. (4) The heating and cooling rates may also contribute to the difference 333 of the T_g of citric acid between the literature and this study, as this study uses a lower cooling 334 rate than the ones reported by the literature. Moynihan et al. (1974) reported that a change of 2 335 K/min to 10 K/min cooling rate could alter the glass transition temperature of borosilicate by 15 336 K. It is possible that citric acid is a less fragile liquid, similar to borosilicate, i.e., the glass 337 transition temperature depends strongly on cooling or heating rates. Therefore, the difference 338 herein is likely due to including kinetic considerations such as heating/cooling rates in the 339 measurement of the glass transition. We report the citric acid glass transition temperature as 307 340 \pm 5 K at 5 K/min warming rate, which is likely a more accurate way of reflecting the glass 341 transition, as the kinetic process is considered, as shown in Figure 7.

Even though the issues listed above are likely to be the primary reasons leading to ~10% difference of the glass transition temperature of citric acid between our results and the literature,

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344 the following factors may play a role: (1) Atomizing the citric acid solution and re-depositing 345 citric acid particles via electrostatic precipitation could introduce impurities during the 346 atomization process that may affect the glass transition temperatures; (2) The glass transition of 347 citric acid was measured during a warming cycle. A fast non-recordable cooling cycle at 348 20K/min was performed prior to warming in order to inhibit the citric acid crystal formation. The 349 hysteresis effect will lead to an increase of the glass transition temperature from the warming 350 cycle compared with data obtained from the cooling cycle (Wang et al., 2011); (3) Lu and 351 Zografi (1997) have shown that different ways of preparing the citric acid can lead to differences 352 in glass transition measurements. The thicknesses of the thin films are equal to or less than one 353 micrometer, leading to confinement effects and differences in glass transition temperature 354 measured from bulk compounds (Park and McKenna, 2000). The results show that the thin film 355 IDE-BDS method can accurately measure the glass transition temperatures of various organic 356 compounds that are comparable to the composition of organic aerosols.

4.2 The influence of cooling rates on glass transition temperatures

358 One advantage of this study is the introduction of cooling and heating rates as variables for 359 glass transition temperature measurement for organic compounds. For BDS studies, the glass 360 transition temperature of a compound is often deduced by measuring the sample at a few 361 isothermal temperatures and fitting the curve of temperature and relaxation time in order to identify 362 the temperature when relaxation time corresponds to 100 s. This traditional approach makes it 363 difficult to directly compare the result with glass transition temperatures deduced from DSC 364 studies with variable cooling rates. One of the advantages of our technique is that variable cooling rate measurements are performed on the thin film and the cooling rate dependent glass transition 365 366 temperature of target species is determined.

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367 The influence of cooling rate on glass transition temperature was carefully examined by 368 repeating the glycerol experiment at two additional cooling rates. The resulting super-Arrhenius 369 curve for each cooling rate is plotted against the Arrhenius lines of that cooling rate, as shown in 370 Figure 8. As a compound remains in the supercooled liquid stage, the relaxation time is short 371 enough that it is constantly in equilibrium with external perturbations, leading the super-Arrhenius 372 region totally reversible so it should behave the same for all cooling rates. The super Arrhenius 373 part of the data from all three different cooling rates all collapse into one single trend, indicating 374 the data collected agree well with the theory. The super-Arrhenius curve in Equation (3) from 375 Elmatad et al. (2009) is also plotted as the black dashed line and it also agrees well with our 376 experimental results. As the cooling continues, the relaxation time gets longer until it cannot keep 377 up with the external temperature change, leading to the compound falling out equilibrium and 378 forming a glass. Therefore, a faster cooling rate often leads to a quick falling out of equilibrium 379 and a higher glass transition temperature for the compounds studied, as demonstrated in Figure 8. 380 Based on the intercept of the super-Arrhenius curve and the Arrhenius line, the glass transition 381 temperatures for 5 K/min and 10 K/min cooling are determined to be 192 ± 2 K and 194 ± 2 K. 382 For 2 K/min cooling, because an Arrhenius line does not appear within our range of measurement, 383 the glass transition temperature will likely be lower than 189 K. This study reports an increase of 384 5 K or more in the glass transition of glycerol as the cooling rate changes from 2 K/min to 10 385 K/min. The reported increase in glass transition temperature during these cooling rates agrees with 386 the behavior of sorbitol and fructose in another study performed by Simatos et al. (1996), which 387 also measured the dependence of glass transition temperature on cooling rate with small organic 388 molecules.

389 Our results agree reasonably well with other studies for the glass transition temperatures 390 of the five compounds chosen. However, there are a couple possible caveats for this study. One 391 is the influence of humidity during the cooling process. Even though dry nitrogen is used to flush 392 through the cooling chamber to remove any extra water vapor present prior to cooling, there is still 393 the possibility that the chamber wall surface can degas and release water vapor to the system during 394 the cooling process. The effect of water vapor on the testing materials is likely to be small, but 395 should be considered when the organic compound tested can readily absorb water at low RH 396 conditions. The other potential caveat is the influence of non-equilibrium heat transfer within the 397 thin film on the measurement of the glass transition temperature. Because the sample is being 398 cooled from underneath, the heat transfer between the upper and lower boundaries of the film can 399 lead to uncertainties in measuring the glass transition temperature. The organic thin films made 400 during the experiments are within the micrometer range, therefore the thermal gradient across the 401 film is small enough to be likely insignificant compared with other systematic errors. Moreover, 402 theoretical models to predict the glass transition of compounds with variable cooling rates are 403 needed in further studies to verify and explain these experimental measurements.

404 **5** Summary

In this work, we have demonstrated a novel method using interdigitated electrodes, broadband dielectric spectroscopy, and electrostatic precipitation together as an efficient and powerful approach studying the phase and glass transitions of organic particles under various cooling rates. The method is particularly suitable for studying the glass transition of submicron organic particles whose mass loading is generally too small for other kinds of glass transition measurement techniques. The results from this technique agree well with published studies using

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411 other methods. Future publications will report glass transition measurements for simulated SOA
412 mixtures as well as laboratory produced SOA particles.

413 The dielectric relaxation peaks of glycerol and four other compounds were recorded, and 414 the logarithm of characteristic relaxation time were calculated and plotted as a function of inverse 415 temperature. The transition between the super-Arrhenius and Arrhenius curves were used to 416 determine the temperature where the super-cooled liquid fell out of equilibrium to become glass, 417 which is defined as the true experimental glass transition temperature. Furthermore, cooling rates 418 are demonstrated to have an effect on the glass transition temperature. By changing the cooling 419 rate from 2 K/min to 10 K/min, the glass transition temperature increases by at least 5 K for 420 glycerol.

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Table 1. Glass transition temperatures for selected organic species measured by broadband

Compound	Chemical Formula	Tg (K)-Measured	T _g (K)-Literature
	C ₃ H ₈ O ₃	<189 K (2 K/min)	190 K (Zondervan et al., 2007)
Glycerol		192 ± 2 K (5 K/min)	191 K (Chen et al., 2012)
Giyeeloi		194 ± 2 K (10 K/min)	196 K (Amann-Winkel et al., 2013)
			191.7 ± 0.9 K (Lienhard et al., 2012)
	C ₆ H ₁₄ O ₃		200 ± 2 K (Nakanishi and Nozaki, 2010)
1,2,6- Hovenstrial		192 ± 2 K (5 K/min)	206.4 ± 0.5 K (Dorfmüller et al.,
TTEXAILEUTOI			1979)
			202 K (Böhmer et al., 1993)
Di-n-butyl Phthalate	$C_{16}H_{22}O_4$	180 ± 2 K (5 K/min)	174 K (Dufour et al., 1994)
Dioctyl Phthalate	$C_{24}H_{38}O_4$	194 ± 2 K (5 K/min)	190 K (Beirnes Kimberley et al., 1986)
	C ₆ H ₈ O ₇	307 ± 5 K (5 K/min)	281 + 5 K (Bodsworth et al 2010)*
			285 ± 0.2 K (Lu and Zografi, 1997)
Citric Acid			281.9 ± 0.9 K (Lienhard et al., 2012)
			283-286 K (Dette et al., 2014)
			260 ± 10 K (Murray, 2008) ^{**}

dielectric spectroscopy with a thin-film interdigitated electrode array

* The data was based on modeling result. **The data was based on extrapolation of a fit to the

data.

List of Figures



Figure 1. A schematic diagram of the experimental setup and procedure. The experimental approach consists of four parts: aerosol generation, thin film deposition using an electrostatic precipitator, the temperature control system, and the broadband dielectric spectroscopy measurement system.



Figure 2. A schematic diagram of the key experimental setup. The upper panel shows the formation of organic thin films though electrostatic deposition. The lower panel shows the working principle of broadband dielectric spectroscopy (BDS) with an interdigitated electrode sensor. A compound is placed on an array of interdigitated electrodes with a periodic voltage, and the compound's impedance is recorded.



Figure 3. The dielectric relaxation spectrum of glycerol at different temperatures. The open circles are measured experimental data and the solid lines are literature data from Chen et al. (2012). As temperature decreases, the dielectric peaks shift towards lower frequencies, indicating that the relaxation timescale increases.



Figure 4. An illustrated plot of the relationship between dielectric relaxation time scale and temperature. The logarithm of the relaxation is plotted against inverse T, i.e., $\log \tau$ vs 1000/T. By linking the data points together, one can plot the super-Arrhenius curve (red) and the Arrhenius line (green). Using a consistent cooling rate, the intersection of the two regions identifies the compound's glass transition temperature, as indicated by the shaded blue region. The intersection of the two black lines represents the glass transition point. The intersection of the two black dashed lines shows the glass transition temperature determined using the traditional method of identifying the temperature when τ =100 s.



Figure 5. A plot of superimposed data points and curves constructed for glycerol, 1,2,6hexanetriol, di-n-butyl phthalate, and dioctyl phthalate cooled at 5K/min. The solid color lines represent the fitted curves for the super-Arrhenius and Arrhenius region. The intersection between the two lines indicates the kinetically controlled glass transition region for each compound. The glass transition at a 5K/min cooling rate for each compound is shown in the plot.



Figure 6. The dielectric relaxation spectrum of citric acid at different temperatures. The solid circles are measured experimental data and the solid lines are fitted curves parameterized from Eq. (S2) and Adrjanowicz et al. (2009).



Figure 7. A plot of superimposed data-points and curves constructed for citric acid warmed at 5K/min. The solid color lines represent the fitted curves for the super-Arrhenius and Arrhenius region. The blue shaded area shows the glass transition region. The two vertical black lines associated with the blue shaded area indicate the corresponding temperature range where the super-Arrhenius curve intersects with the Arrhenius line. The traditional glass transition temperature, i.e., the temperature when τ =100 s, is also marked.



Figure 8. A plot of superimposed data-points and curves constructed for glycerol cooled at 2K/min, 5K/min, and 10K/min. The black dashed line represents literature data of the super-Arrhenius region from Elmatad et al. The open circles are experimental data and the solid lines are fitting results. The inset shows the glass transition temperature of glycerol as a function of cooling rates. At 2 K/min cooling, the glass transition temperature has a higher bound of 189 K.

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