

Comments by referees are in blue.

Our replies are in black.

Changes to the manuscript are highlighted in red both in here and in the revised manuscript.

The work is important and of relevance to the readership. The authors present a review of hygroscopicity measurements as it pertains to the atmosphere and also orthogonal scientific fields (surface science, heterogeneous catalysis, geochemistry/astrochemistry, pharmaceutical and food science, etc). Thus the publication will be of interest to the ACP readership and other fields. The authors have done a good job to describe “non-conventional atmospheric” hygroscopicity measurements. That is they provide an overview of comprehensive laboratory techniques that due to time or spatial resolution is not necessarily applied to field studies. For instance, the spectroscopy section is quite thorough and provides information on the numerous spectroscopy techniques that have been applied in controlled laboratory settings. The review is useful in that it provides a current overview of the current state of technology for hygroscopicity. However, the paper does not include a review of the theoretical hygroscopicity equations (although, I do not think that this is the purpose of the manuscript). Furthermore, I was quite disappointed to find that CCN and IN techniques were not discussed at all and perhaps this omission should be reflected in the title. E.g. "A review of experimental techniques for unsaturated aerosol hygroscopicity studies". Regardless of this disappointment, I highly recommend the work for publication in ACP. The work will be cited heavily in the future. The following are a few concepts and ideas that may strengthen and or clarify ideas in the manuscript. I sincerely encourage the authors to consider addressing these comments before eventual publication.

**Reply:** We would like to thank Ref #1 for his/her insightful comments as well as recommending our manuscript for final publication. We do not review theories related to aerosol hygroscopicity because our manuscript is focused on techniques for aerosol hygroscopicity measurements; similarly, we do not review techniques used for CCN and IN measurements. However, in the original manuscript we have referred readers to literature where aerosol hygroscopicity theories and techniques for CCN and IN measurements are reviewed. We feel that the title we use is proper, although we understand what the referee means. This is because hygroscopicity usually means interaction of water vapor with particles at <100% RH. We have also addressed all the other comments adequately in the revised manuscript, as detailed below.

## Comments.

1. The fluorescence spectroscopy section seems tangential to the hygroscopicity discussion. Much of this sections suggest that EDB is the actual technique and then fluorescence is used to measures the particle properties.

**Reply:** It is true that fluorescence spectroscopy does not measure aerosol hygroscopicity; however, it provides information (for example, the ratio of solvated water to free water) closely related to hygroscopicity. Therefore, we chose to discuss this technique using two paragraphs.

2. Time resolution of hygroscopicity measurements should also be discussed as a recommendation to improve measurements. The DASH-SP and HFIMS are the only fast resolution hygroscopicity measurements techniques currently used. Recent work by Wang et al (HFIM) should also be discussed.

**Reply:** Indeed time resolution is an important aspect, and this has been discussed in the original manuscript (future direction #1, page 92). We would like to thank the referee for bringing the work by Wang et al. (2019) to our attention, and in the revised manuscript (page 95) the work have been cited in addition to that by Langridge et al. (2011) and Pinterich et al. (2017b) as examples of high time resolution instruments for aerosol hygroscopicity measurements.

3. The authors may consider discussing how advances in orthogonal fields may be of future importance to atmospheric measurements. For example, although not currently relevant to aerosol, the production of highly sensitive humidity sensors should be considered (e.g., Liang et al, 2018). The Dash-P and HFIMS, use faster sizing instrumentation however faster RH technology may also advance studies.

**Reply:** The advancement in RH measurements will definitely be very valuable. In the revised manuscript (page 95, future direction #2) we have added the following sentences to discuss this aspect: “Furthermore, currently RH measurements typically have an absolute uncertainty of 1% or larger, and uncertainties in RH measurement would affect hygroscopic growth factors reported at a given RH, especially for high RH at which growth factors are more sensitive to RH; therefore, advancement in RH measurements (Liang et al., 2018) will contribute to the improvement in aerosol hygroscopicity measurement techniques.”

## Minor Corrections

**Reply:** We would like to thank the referee for carefully reading our manuscript and pointing out those typos, as detailed below.

L83, aqueous particle becomes supersaturated?

**Reply:** It means that the aqueous particle becomes a supersaturated solution. In the revised manuscript (page 4) we have expanded this sentence to provide further clarification: “the aqueous particle would become supersaturated (i.e. the aqueous particle becomes a supersaturated solution).”

L85. efflorescence is also kinetically controlled? How? Not clear how this statement is made.

**Reply:** Here we mean that efflorescence not only depends on thermodynamics but also is kinetically controlled. In the revised manuscript (page 4) we have expanded this sentence to provide further explanation: “Therefore, efflorescence is also kinetically controlled (in addition to being thermodynamically controlled) and...”

L70 – Remove or define “and etc”

**Reply:** As suggested, in the revised manuscript we have deleted “and etc”.

L81 – spelling “dehumification”

**Reply:** In the revised manuscript this typo has been corrected.

L95 - , insert word - leading to the formation OF two coexisting liquid”

**Reply:** Corrected.

L95 – change to : in one particle”

**Reply:** Corrected.

L120 – Remove “in specific,”

**Reply:** Removed.

L189 – Change recently to recent

**Reply:** We have checked the manuscript and here “recently” should be used.

L385 – Change isotherm to isothermal

**Reply:** Corrected.

L1480 – “aerosol size is measured as” to “aerosol size is measured AT”

**Reply:** Corrected.

Additional References to consider

Wang, Yang, et al. "Retrieval of High Time Resolution Growth Factor Probability Density Function from a Humidity-controlled Fast Integrated Mobility Spectrometer." *Aerosol Science and Technology* just-accepted (2019): 1-18.

Liang, Jun-Ge, et al. "Thickness effects of aerosol deposited hygroscopic films on ultrasensitive

humidity sensors." *Sensors and Actuators B: Chemical* 265 (2018): 632-643.

**Reply:** As suggested, in the revised manuscript we have discussed these two studies.

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The manuscript “A review of experimental techniques for aerosol hygroscopicity studies” presents a comprehensive and systematic review of the techniques used to study hygroscopicity of aerosols. The experimental techniques are classified into four types, according to how samples are prepared. For each method, besides experimental techniques, typical applications of this method to aerosol hygroscopicity study are provided. Finally, the future direction to improve these techniques are suggested, including improving these methods to use in more variable ambient environment (high RH, low pressure, low T), conducting more instrument inter-comparisons and investigating other physicochemical properties of aerosol together with hygroscopicity. A comprehensive review of the techniques used to study aerosol hygroscopicity is lacking up to now, to the best of my knowledge, although previous papers well summarizes some techniques, especially the HTDMA techniques (Duplissy et al., 2009) and techniques to study physicochemical properties in general (Ault and Axson, 2017). Therefore, this manuscript would be beneficial to ACP readers. The manuscript is well written and clearly organized. I recommend publication of this manuscript in ACP after a few minor comments are addressed.

**Reply:** We would like to thank ref #2 for his/her insightful comments as well as recommending our manuscript for final publication. We have addressed all the comments adequately in the revised manuscript, as detailed below.

1. The authors discussed the advantages and disadvantages/problem of each technique. In the summary part, I suggest authors to add a table to summarize these features so that readers can get an overview and this could somehow work as a guideline when one reads a paper on aerosol hygroscopicity studied using a certain method and choose a suitable technique in their research.

**Reply:** We fully agree with the referee. In the revised manuscript (page 90-94), we have added one table and a few paragraphs to summarize key futures of major techniques for aerosol hygroscopicity measurements.

2. Some studies on other physicochemical properties are discussed this manuscript. While most of them are relevant to the topic of study, some may not be the focus of this manuscript, such as line 1102-1105, 1232-1236, 1380-1383, 1400-1403. Condensing these texts might be desirable.

**Reply:** We agree that these contents are not directly related to aerosol hygroscopicity; however, they are intentionally included because we want to show that these techniques can also be used to investigate other physicochemical properties besides aerosol hygroscopicity. Therefore, we would like to keep them in the manuscript.

Also the lines 1042-1051 (and Fig 15, 16) discussed the application of Raman spectroscopy to study heterogeneous reaction. Since the application of Raman spectroscopy to hygroscopicity has been demonstrated earlier in the manuscript, I suggest omitting this part, especially considering the figures are not considered to be officially published yet.

**Reply:** As requested, in the revised manuscript we have removed Figs. 15-16 and related text, since this part has not yet been officially published.

3. Line 1575, it might be worth noting that “Aerosol Time-of-Flight mass spectrometer” is a single particle mass spectrometer, e.g. specify it by adding the abbreviation.

**Reply:** In the revised manuscript (page 75) we have modified this sentence to make it clear that this instrument is a single particle spectrometer: “as revealed by measurements using a single particle mass spectrometer (Aerosol Time-of –Flight mass spectrometer).” Since this term only appears once in our manuscript, it is not necessary to add its abbreviation.

4. Some texts are underlined (such as line 620 and other part). Is this a typeset problem?

**Reply:** Because there are ~30 figures in our manuscript, we underline the text when a figure is mentioned in the text (such as “As shown in Fig. 1,”). Underlines will be removed when we upload the document required by final publication after the manuscript is accepted.

# 1 **A review of experimental techniques for aerosol hygroscopicity studies**

2

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31

## 32 **Abstract**

33 Hygroscopicity is one of the most important physicochemical properties of aerosol  
34 particles, and also plays indispensable roles in many other scientific and technical fields. A  
35 myriad of experimental techniques, which differ in principles, configurations and cost, are  
36 available for investigating aerosol hygroscopicity under subsaturated conditions (i.e., relative  
37 humidity below 100%). A comprehensive review of these techniques is provided in this paper,  
38 in which experimental techniques are broadly classified into four categories, according to the  
39 way samples under investigation are prepared. For each technique, we describe its operation  
40 principle and typical configuration, use representative examples reported in previous work to  
41 illustrate how this technique can help better understand aerosol hygroscopicity, and discuss its  
42 advantages and disadvantages. In addition, future directions are outlined and discussed for  
43 further technical improvement and instrumental development.

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## 46 **1 Introduction**

47       Aerosol particles are airborne solid or liquid particles in the size range of a few nanometers  
48 to tens of micrometers. They can be emitted directly into the atmosphere (primary particles),  
49 and can also be formed in the atmosphere (secondary particles) by chemical transformation of  
50 gaseous precursors such as SO<sub>2</sub>, NO<sub>x</sub>, and volatile organic compounds (Pöschl, 2005; Seinfeld  
51 and Pandis, 2016). Aerosol particles are of great concerns due to their environmental, health,  
52 climatic and biogeochemical impacts (Finlayson-Pitts and Pitts, 2000; Jickells et al., 2005;  
53 Mahowald, 2011; Mahowald et al., 2011; IPCC, 2013; Pöschl and Shiraiwa, 2015; Seinfeld  
54 and Pandis, 2016; Shiraiwa et al., 2017b).

55       Water, which can exist in gas, liquid and solid states, is ubiquitous in the troposphere.  
56 Interactions of water vapor with aerosol particles largely affect the roles that aerosol particles  
57 play in the Earth system. When water vapor is supersaturated (i.e. when relative humidity, RH,  
58 is >100%), aerosol particles can act as cloud condensation nuclei (CCN) to form cloud droplets  
59 and as ice-nucleating particles (INPs) to form ice crystals (Pruppacher and Klett, 1997;  
60 Lohmann and Feichter, 2005; Vali et al., 2015; Lohmann et al., 2016; Tang et al., 2016a; Knopf  
61 et al., 2018; Tang et al., 2018). Cloud condensation nucleation and ice nucleation activities of  
62 aerosol particles, as well as relevant experimental techniques, have been recently reviewed in  
63 several books and review papers (Pruppacher and Klett, 1997; Hoose and Moehler, 2012;  
64 Murray et al., 2012; Kreidenweis and Asa-Awuku, 2014; Farmer et al., 2015; Lohmann et al.,  
65 2016; Tang et al., 2016a; Kanji et al., 2017), and are thus not further discussed in this paper.

66       When water vapor is unsaturated (i.e. RH <100%), an aerosol particle in equilibrium with  
67 the surrounding environment would contain some amount of absorbed or adsorbed water  
68 (Martin, 2000; Kreidenweis and Asa-Awuku, 2014; Cheng et al., 2015; Farmer et al., 2015;  
69 Seinfeld and Pandis, 2016; Tang et al., 2016a; Freedman, 2017). The amount of water that a  
70 particle contains depends on RH, temperature, its chemical composition and size. The ability

71 of a substance to absorb/adsorb water as a function of RH is typically termed as hygroscopicity  
72 (Adams and Merz, 1929; Su et al., 2010; Kreidenweis and Asa-Awuku, 2014; Tang et al.,  
73 2016a), and the underlying thermodynamic principles can be found elsewhere (Martin, 2000;  
74 Seinfeld and Pandis, 2016). A single-component particle which contains one of water soluble  
75 inorganic salts, such as  $(\text{NH}_4)_2\text{SO}_4$  and NaCl, is solid at low RH. When RH is increased to the  
76 deliquescence relative humidity (DRH), the solid particle will undergo deliquescence to form  
77 an aqueous particle, and the aqueous particle at DRH is composed of a saturated solution  
78 (Cheng et al., 2015). Further increase in RH would increase the water content of the aqueous  
79 droplet, i.e. the aqueous particle would become more diluted as RH increases. During  
80 humidification thermodynamics determines phase transition and hygroscopic growth of the  
81 particle. During **dehumidification**, an aqueous particle would not undergo efflorescence to form  
82 a solid particle when RH is decreased to below DRH; instead, the aqueous particle would  
83 become supersaturated (**i.e. the aqueous particle becomes a supersaturated solution**). Only  
84 when RH is further decreased to efflorescence relative humidity (ERH), the aqueous particle  
85 would undergo crystallization, leading to the formation of a solid particle. Therefore,  
86 efflorescence is also kinetically controlled (**in addition to being thermodynamically controlled**)  
87 and there is a hysteresis between deliquescence and efflorescence. Deliquescence and  
88 efflorescence of multicomponent particles can be more complicated (Seinfeld and Pandis,  
89 2016).

90 It should be pointed out that not all the single-component particles exhibit distinctive  
91 deliquescence and efflorescence. Instead, continuous uptake or loss of liquid water is observed  
92 during humidification and dehumidification processes for many inorganic and organic particles  
93 (Mikhailov et al., 2009; Koop et al., 2011; Shiraiwa et al., 2011). Particles with extremely low  
94 hygroscopicity (e.g., mineral dust) will not be deliquesced even at very high RH; instead,  
95 adsorbed water will be formed on the particle surface (Tang et al., 2016a). Furthermore, a

96 multicomponent particle which contains some types of organic materials may undergo liquid-  
97 liquid phase separation, leading to the formation of two coexisting liquid phases in one **particle**  
98 (Mikhailov et al., 2009; You et al., 2012; You et al., 2014; Freedman, 2017; Song et al., 2017;  
99 Song et al., 2018). It is conventionally assumed that hygroscopic equilibrium of aerosol  
100 particles can be quickly reached. Nevertheless, recent laboratory, field and modeling studies  
101 suggested that atmospherically relevant particles can be semi-solid or amorphous solid  
102 (Virtanen et al., 2010; Zobrist et al., 2011; Renbaum-Wolff et al., 2013; Shiraiwa et al., 2017a;  
103 Reid et al., 2018). The viscosity of these particles can be high enough such that uptake or  
104 release of water is largely limited by diffusion of water molecules in the bulk phase of these  
105 particles.

106 Hygroscopicity determines the amount of water that a particle contains under a given  
107 condition and thereby has several important implications. It affects the size and refractive  
108 indices of aerosol particles, affecting their optical properties and consequently their impacts on  
109 visibility and direct radiative forcing (Malm and Day, 2001; Chin et al., 2002; Quinn et al.,  
110 2005; Hand and Malm, 2007; Cheng et al., 2008; Eichler et al., 2008; Liu et al., 2012; Liu et  
111 al., 2013b; Brock et al., 2016b; Titos et al., 2016; Haarig et al., 2017). Hygroscopicity is also  
112 closely related to the CCN activity of aerosol particles, affecting their impacts on formation  
113 and properties of clouds and thus their indirect radiative forcing (McFiggans et al., 2006;  
114 Petters and Kreidenweis, 2007; Reutter et al., 2009; Kreidenweis and Asa-Awuku, 2014;  
115 Farmer et al., 2015). Aerosol liquid water and/or surface-adsorbed water, largely controlled by  
116 hygroscopicity, determines heterogeneous and multiphase reactions of aerosol particles via  
117 several mechanisms, as revealed by recent studies (Bertram and Thornton, 2009; Shiraiwa et  
118 al., 2011; Rubasinghege and Grassian, 2013; Cheng et al., 2016; Wang et al., 2016; Tang et al.,  
119 2017; Mu et al., 2018; Wu et al., 2018). In addition, hygroscopicity significantly impacts dry  
120 and wet deposition rates of aerosol particles and thus their lifetimes, spatiotemporal distribution

121 and environmental and health effects (Fan et al., 2004; Wang et al., 2014a). For primary  
122 biological aerosols in specific, changes in their atmospheric transport behavior have important  
123 implications for the spread of plants and microbes and therefore the evolution of ecosystems  
124 (Brown and Hovmoller, 2002; Després et al., 2012; Fisher et al., 2012; Fröhlich-Nowoisky et  
125 al., 2016).

126 Atmospheric aerosol is only one of many fields in which hygroscopicity is of great interest.  
127 Hygroscopicity is closely linked to water activities and thermodynamics of solutions (Atkins,  
128 1998). It also determines the amount of surface-adsorbed water and surface reactivity of  
129 various solid materials, and has been widely investigated in surface science and heterogeneous  
130 catalysis (Miranda et al., 1998; Ewing, 2006; Yamamoto et al., 2010b; Chen et al., 2012;  
131 Rubasinghege and Grassian, 2013; Liu et al., 2017). Hygroscopicity is related to the possible  
132 existence of liquid water in some hyperarid environments (such as Mars and the Atacama  
133 Desert on earth) (Martin-Torres et al., 2015): while pure liquid water is not stable in these  
134 environments, the deliquescence of some salts, such as chlorides and perchlorates, can occur  
135 at RH significantly below 100% and lead to the formation of aqueous solutions (Gough et al.,  
136 2011; Gough et al., 2016; Gu et al., 2017a; Jia et al., 2018). Hygroscopic properties  
137 significantly affect transport and deposition of inhaled aerosol particles in the respiratory tract,  
138 therefore playing an important role in the health impact of ambient aerosols as well as efficacy  
139 and side effects of aerosolized pharmaceuticals (Hickey and Martonen, 1993; Robinson and  
140 Yu, 1998; Carvalho et al., 2011; Hofmann, 2011; Haddrell et al., 2014; Winkler-Heil et al.,  
141 2014; Darquenne et al., 2016; Davidson et al., 2017; Winkler-Heil et al., 2017). Impacts of  
142 moisture and implications of hygroscopicity have been well documented for physical and  
143 chemical stability of pharmaceuticals (Ahlneck and Zografis, 1990; Chan et al., 1997; Peng et  
144 al., 2000; Newman et al., 2008; Mauer and Taylor, 2010a; Tong et al., 2010a; Feth et al., 2011)  
145 as well as food ingredients and blends (Mauer and Taylor, 2010b; Allan and Mauer, 2016), and

146 large efforts have been made in pharmaceutical and food industry to prevent relevant products  
147 from deliquescence. Corrosion and degradation of various constructions and buildings depend  
148 largely on RH, and as a result both chemical inertness and hygroscopicity of materials used  
149 should be taken into account (Schindelholz et al., 2014b; Schindelholz et al., 2014a; Vainio et  
150 al., 2016); in addition, deposition of particles of different compositions has also been shown to  
151 affect the extent of corrosion of mild steel (Lau et al., 2008).

152 As summarized in this paper, a number of experimental techniques, which differ largely  
153 in principles, configurations and cost, have been developed to investigate hygroscopic  
154 properties of atmospherically relevant particles. Hygroscopic properties investigated at <100%  
155 RH typically include the amount of water absorbed/adsorbed by particles as a function of RH,  
156 as well as DRH and ERH if they exist. Techniques employed to investigate aerosol  
157 hygroscopicity under supersaturation, commonly termed as CCN activity, are relatively less  
158 diverse, and interested readers are referred to relevant literature (Nenes et al., 2001; Roberts  
159 and Nenes, 2005; Kreidenweis and Asa-Awuku, 2014) for further information. In addition,  
160 technique used to study ice nucleation have been discussed in a number of recent papers  
161 (DeMott et al., 2011; Murray et al., 2012; Ladino et al., 2013; DeMott et al., 2018) and as a  
162 result are not further discussed here.

163 Several review papers and book chapters have discussed some of these techniques used to  
164 investigate aerosol hygroscopicity. For example, Kreidenweis and Asa-Awuku (2014)  
165 discussed a few widely used techniques for aerosol hygroscopicity measurements, and Tang et  
166 al. (2016) summarized in brief experimental techniques used to investigate water adsorption  
167 and hygroscopicity of mineral dust particles. There are also a few review papers focused on a  
168 specific technique or a specific category of techniques. For example, Swietlicki et al. (2008)  
169 reviewed aerosol hygroscopicity measured in various environments using humidity-tandem  
170 differential mobility analysers, and provided a nice overview of this technique; application of

171 single particle levitation techniques to investigate properties and processes of aerosol particles,  
172 including aerosol hygroscopicity, was reviewed by Krieger et al. (2012); Titos et al. (2016)  
173 reviewed techniques used to investigate the effect of hygroscopic growth on aerosol light  
174 scattering, and Ault and Axson (2017) summarized and discussed recent advancements in  
175 spectroscopic and microscopic methods for characterization of aerosol composition and  
176 physicochemical properties.

177       Nevertheless, to our knowledge there is hitherto no paper or book which covers most of  
178 (if not all) experimental techniques used for hygroscopicity measurements. This paper aims at  
179 providing the first comprehensive review in this field. For each technique, we first introduce  
180 its operation principle and typical configurations, and then use exemplary results to illustrate  
181 how this technique can help better understand hygroscopic properties. According to the way  
182 samples under investigation are prepared, experimental techniques covered in this paper are  
183 classified into four categories, which are discussed in Sections 2-5. In Section 2, we discuss  
184 experimental techniques applied to bulk solutions. Experimental techniques for particles  
185 deposited on substrates, levitated single particles and aerosol particles are reviewed in Sections  
186 3-5, respectively. Remote sensing techniques can also be employed to retrieve aerosol  
187 hygroscopicity (Ferrare et al., 1998; Feingold and Morley, 2003; Pahlow et al., 2006; Schuster  
188 et al., 2009; Li et al., 2013; Lv et al., 2017; Bedoya-Velasquez et al., 2018; Fernandez et al.,  
189 2018); however, they are not covered in this paper because we intend to focus on in-situ  
190 techniques and application of remote sensing to investigate aerosol hygroscopicity has been  
191 discussed very recently in a book chapter (Kreidenweis and Asa-Awuku, 2014). In addition,  
192 techniques for measuring CCN and IN activities of aerosol particles are not covered in the  
193 present paper, and interested readers are referred to relevant literature (Roberts and Nenes,  
194 2005; Lance et al., 2006; Petters et al., 2007; Good et al., 2010a; DeMott et al., 2011; Latham  
195 and Nenes, 2011; Hiranuma et al., 2015; Wex et al., 2015).

## 196 **2 Bulk solution-based techniques**

197 In principle, the hygroscopicity of a compound can be determined by measuring the water  
198 vapor pressure of air over (i.e. in equilibrium with) the aqueous solution at a given  
199 concentration (Pitzer, 1991; Rard and Clegg, 1997). Experimental data can then be used to  
200 derive water-to-solute ratios as a function of RH for aqueous solutions, and the RH over the  
201 saturated solution can generally be regarded as the DRH. Experimental methods based on this  
202 principle have been widely used since the early 20<sup>th</sup> century (or probably even earlier) (Adams  
203 and Merz, 1929; Hepburn, 1932) and are still being used (Königsberger et al., 2007; Sadeghi  
204 and Shahebrahimi, 2011; Golabiazar and Sadeghi, 2014) to investigate thermodynamic  
205 properties of aqueous solutions. In general, these methods can be further classified to two  
206 categories, i.e. isopiestic and nonisopiestic methods (Rard and Clegg, 1997).

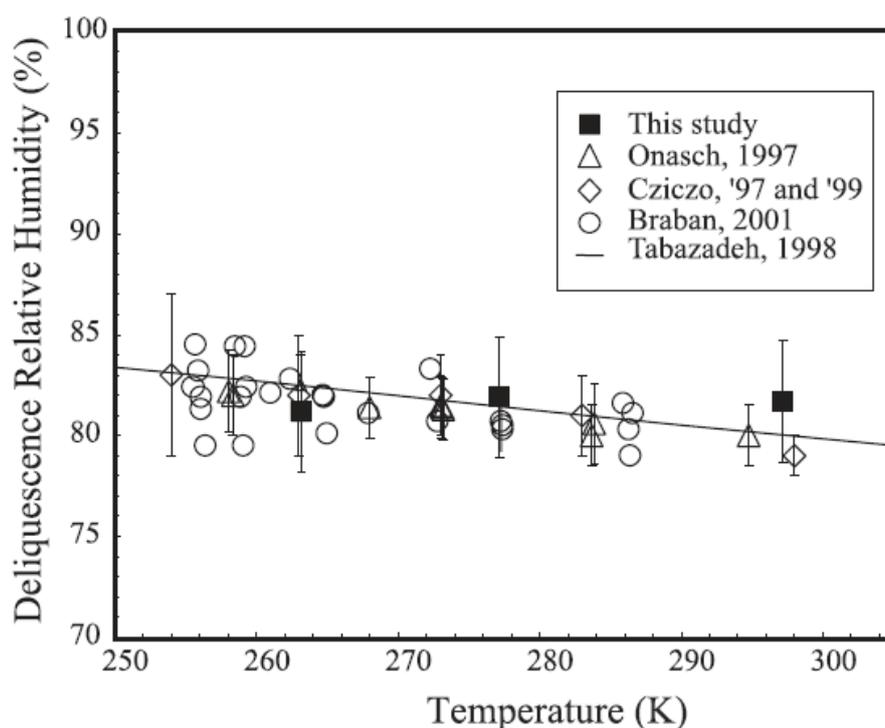
### 207 **2.1 The isopiestic method**

208 The isopiestic method was described in a number of previous studies (Spedding et al., 1976;  
209 Rard and Miller, 1981; Pitzer, 1991; Hefter et al., 1997; Rard and Clegg, 1997; Königsberger  
210 et al., 2007), and a brief introduction is provided herein. For a typical experiment, two open  
211 vessels which contain a reference solution and a sample solution are housed in a sealed chamber  
212 with temperature being well controlled, and water vapor will be transferred between the two  
213 solutions until an equilibrium is reached. For the reference solution, its water activity should  
214 be well documented as a function of concentration. When the equilibrium is reached, the water  
215 activity of the sample solution is equal to that of the reference solution. If we measure the  
216 concentrations of the two solutions in equilibrium, the water activity of the sample solution at  
217 a given concentration can then be determined.

### 218 **2.2 Nonisopiestic techniques**

219 The water vapor pressure over (or the water activity of) an aqueous solution can be  
220 determined using a number of methods (Rard and Clegg, 1997), including but not limited to (i)

221 the static vapor pressure method, i.e. direct measurement of the vapor pressure over a solution  
222 after being degassed (Adams and Merz, 1929; Jakli and Vanhook, 1972; Apelblat, 1992); (ii)  
223 the dynamic vapor pressure method, i.e. measurements of the amount of water vapor from an  
224 aqueous solution required to saturate a given volume of air (Bechtold and Newton, 1940); (iii)  
225 measurements of the boiling temperature of an aqueous solution; (iv) measurements of the dew  
226 point or RH of the air over an aqueous solution (Hepburn, 1932); and (v) the vapor pressure  
227 osmometry (Amdur, 1974; Sadeghi and Shahebrahimi, 2011). These techniques are described  
228 elsewhere (Pitzer, 1991; Rard and Clegg, 1997), and interested readers are referred to the two  
229 papers (and references therein) for more information. A few recent studies are discussed below  
230 to illustrate how nonisopiestic techniques could be used to investigate hygroscopic properties  
231 of compounds relevant for atmospheric aerosols.



232  
233 **Figure 1.** Comparison of DRH values as a function of temperature (250-300 K) measured by  
234 different studies. Reprint with permission by Brook et al. (2002). Copyright 2002 John Wiley  
235 & Sons, Inc.

236

237 The RH of air over 10 mL aqueous solutions which were contained in sealed test tubes  
238 kept at constant temperatures were measured by Tolbert and coworkers (Brooks et al., 2002;  
239 Wise et al., 2003) to investigate water activities as a function of solution concentration. In the  
240 first study (Brooks et al., 2002), RH over saturated solutions were measured for  $(\text{NH}_4)_2\text{SO}_4$ ,  
241 several dicarboxylic acids, as well as mixtures of  $(\text{NH}_4)_2\text{SO}_4$  with individual dicarboxylic acids  
242 to determine their DRH. As shown in [Fig. 1](#), the DRH values of  $(\text{NH}_4)_2\text{SO}_4$  measured by  
243 Brooks et al. (2002) agreed well with those reported in previous studies (Cziczo et al., 1997;  
244 Tabazadeh and Toon, 1998; Cziczo and Abbatt, 1999; Onasch et al., 1999; Braban et al., 2001)  
245 for temperature ranging from ~250 to ~300 K, confirming that the simple technique could  
246 determine DRH in a reliable manner. It was further found that the presence of water soluble  
247 dicarboxylic acids would reduce the DRH of  $(\text{NH}_4)_2\text{SO}_4$ , whereas the presence of less soluble  
248 dicarboxylic acids had no measurable effects (Brooks et al., 2002). In a following study (Wise  
249 et al., 2003), RH of air over eutonic mixtures of  $(\text{NH}_4)_2\text{SO}_4$ /dicarboxylic acids were measured  
250 at 25 °C to investigate the effect of organic acids on hygroscopic growth of  $(\text{NH}_4)_2\text{SO}_4$ . The  
251 presence of water soluble dicarboxylic acids reduced hygroscopic growth of  $(\text{NH}_4)_2\text{SO}_4$ , while  
252 the effect of less soluble dicarboxylic acids were found to be negligible (Wise et al., 2003).

253 Water activity meters, which measure the dew point temperature of the air in equilibrium  
254 with an aqueous sample, are commercially available (Maffia and Meirelles, 2001; Marcolli et  
255 al., 2004; Salcedo, 2006). For example, water activities meters were employed by Salcedo  
256 (2006) and Maffia and Meirelles (2001) to study hygroscopic properties of organic acids and  
257 their mixtures with  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$  at 25 °C.

### 258 **2.3 Discussion**

259 Bulk solution-based techniques have the advantage of being inherently accurate and very  
260 simple, while one major drawback is that these measurement cycles can be very time-  
261 consuming, typically taking days up to months to reach the equilibrium (Königsberger et al.,

262 2007). Particle water content can be quantitatively determined for unsaturated solutions,  
263 whereas no information can be provided for supersaturated solutions. Bulk solution-based  
264 methods do not require particle sphericity assumption to derive particle water content, but  
265 cannot be used to study water adsorption. Generally speaking, while these techniques are useful  
266 for understanding properties of deliquesced particles, they are not applicable for direct  
267 measurements of ambient aerosol particles.

### 268 **3 Particles deposited on substrates**

269 In this section we review and discuss techniques which can be used to investigate  
270 hygroscopic properties of particles (either particle ensembles or individual particles) deposited  
271 on substrates. This section is further divided to five parts: techniques for which changes in  
272 water vapor and particle mass are measured to investigate particle hygroscopicity are reviewed  
273 in Sections 3.1 and 3.2, and microscopic and spectroscopic tools employed to investigate  
274 particle hygroscopicity are reviewed in Sections 3.3 and 3.4. Measurements of change in  
275 electrical conductivity for understanding hygroscopic properties of particles are briefly  
276 discussed in Section 3.5.

#### 277 **3.1 Measurement of water vapor**

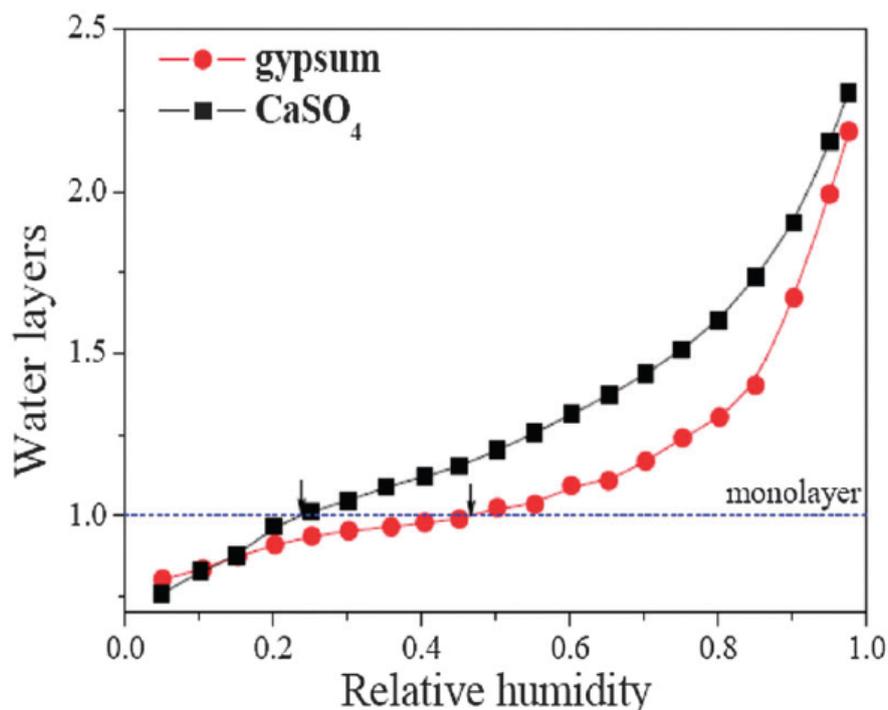
278 Particles would absorb/adsorb water vapor from the gas phase to reach a new equilibrium  
279 as RH increases, while water vapor will be released if RH decreases. Measurement of change  
280 in water vapor can be used to investigate hygroscopic properties. Exposure of water vapor to  
281 particles can be achieved either in a static cell or in a flow cell.

##### 282 **3.1.1 Physisorption analyser**

283 When exposed to water vapor, particles will absorb/adsorb water vapor, leading to  
284 depletion of water vapor in the system. The amount of water absorbed/adsorbed by particles  
285 can be determined from the measured change in water vapor pressure (if the volume remains  
286 constant), and the RH can be calculated from the final water vapor pressure when the

287 equilibrium is reached. The amount of water associated with particles can be determined as a  
288 function of RH by varying the initial water vapor pressure.

289 Commercial instruments, usually designed to measure the Brunauer-Emmett-Teller (BET)  
290 surface areas using nitrogen or helium (Torrent et al., 1990), have been utilized to investigate  
291 hygroscopic properties of atmospherically relevant particles (Ma et al., 2010b; Ma et al., 2012b;  
292 Hung et al., 2015). For example, Ma et al. (2010b) integrated an AUTOSORB-1-C instrument  
293 (Quantachrome, US) with a water vapor generator, and employed this apparatus to investigate  
294 hygroscopic properties of NaCl,  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ . The measured DRH values and mass  
295 hygroscopic factors were found to agree very well with those reported in literature (Ma et al.,  
296 2010b). This method has proved to be very sensitive; as shown in Fig. 2, change in adsorbed  
297 water as small as  $<0.5$  monolayer can be reliably quantified (Ma et al., 2013a). In addition to  
298  $\text{CaSO}_4$  and gypsum, this instrument was also employed to investigate hygroscopic properties  
299 of fresh and aged  $\text{Al}_2\text{O}_3$ , MgO and  $\text{CaCO}_3$  particles (Ma et al., 2012a).



300

301 **Figure 2.** Water adsorption isotherms of  $\text{CaSO}_4$  (black square) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , red  
302 circle) at 278 K. Reprinted with permission by Ma et al. (2013a). Copyright 2013 the PCCP  
303 Owner Societies.

304

305 A similar instrument (Micromeritics ASAP 2020) was employed by Hung et al. (2015) to  
306 examine the hygroscopicity of black carbon, kaolinite and montmorillonite particles at 301 K,  
307 and a sensitivity of sub-monolayers of adsorbed water could be achieved. Assuming a dry  
308 particle diameter of 200 nm, the single hygroscopicity parameters,  $\kappa$ , were determined to be  
309  $\sim 0.002$  for montmorillonite and  $< 0.001$  for both black carbon and kaolinite (Hung et al., 2015).

310 This technique is able to quantify particle water content for unsaturated samples, and is  
311 sensitive enough to measure adsorbed water; however, it cannot be (at least has not been) used  
312 to examine supersaturated samples. This technique, which is independent on particle size and  
313 morphology, can also been used to investigate hygroscopic properties of ambient aerosol  
314 particles in an offline manner. For example, a physisorption analyser was used to study  
315 hygroscopic properties of ambient aerosol particles collected in Beijing during an Asian dust  
316 storm, and one monolayer of adsorbed water was formed on these particles at 46% RH (Ma et  
317 al., 2012b).

### 318 **3.1.2 Katharometer**

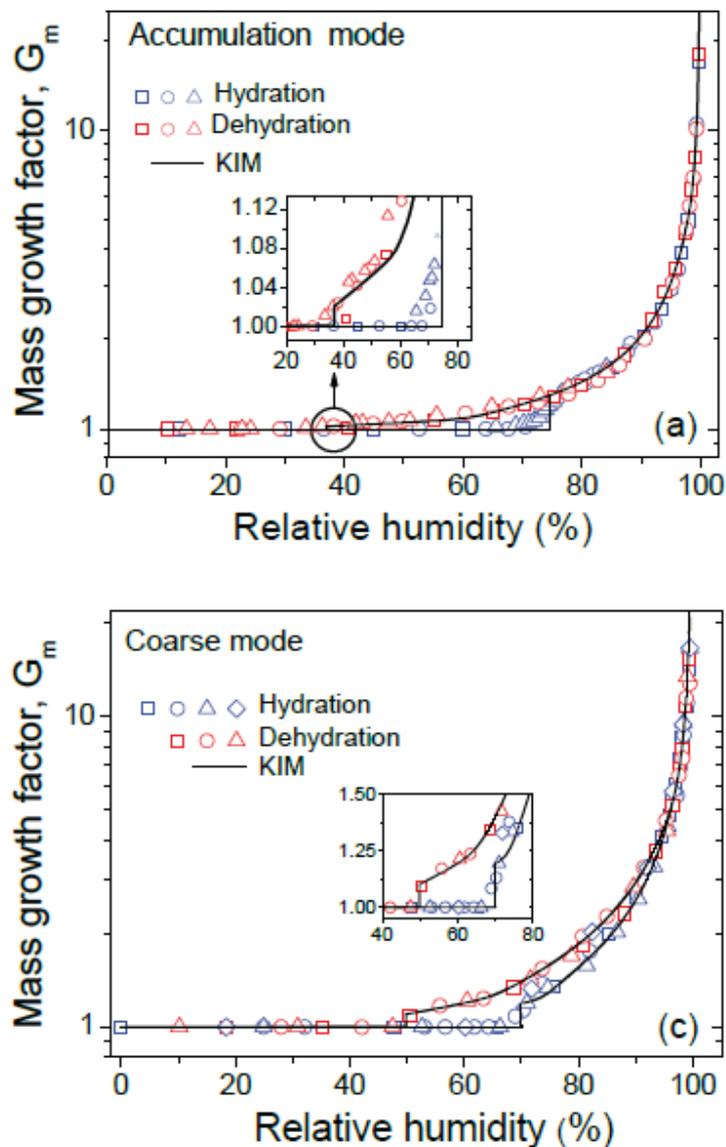
319 The katharometer, also known as the thermal conductivity detector, can be used to measure  
320 water vapor concentration. Lee and co-workers employed a katharometer to investigate liquid  
321 water content of aerosol particles collected on filters (Lee and Hsu, 1998; Lee and Hsu, 2000;  
322 Lee and Chang, 2002). In this setup (Lee and Chang, 2002), aerosol particles were collected  
323 on a Teflon filter and then equilibrated with a helium flow at a given RH; after the equilibrium  
324 was reached, the particle-loaded filter was purged with a dry helium flow, which was  
325 subsequently directed to a katharometer to measure the water vapor concentration. As a result,

326 the liquid water content associated with particles at a given RH could be quantified. The  
327 performance of this new method was systematically examined (Lee and Hsu, 1998; Lee and  
328 Hsu, 2000; Lee and Chang, 2002), and the measured water-to-solute ratios at different RH  
329 during both humidification and dehumidification processes were found to agree well with those  
330 reported in literature for several compounds, including NaCl, NH<sub>4</sub>Cl, Na<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and  
331 NH<sub>4</sub>NO<sub>3</sub>.

332 Mikhailov et al. (2011, 2013) also developed a katharometer-based method to investigate  
333 aerosol hygroscopicity. The instrument, called filter-based differential hygroscopicity analyser  
334 (FDHA), are described elsewhere (Mikhailov et al., 2011), and a brief introduction is provided  
335 here. In this apparatus, a humidified helium flow was split to two identical flows which were  
336 then passed through a pair of differential measurement cells: the reference cell contained a  
337 blank filter, and the sample cell contained a filter laden with particles (typically less than 0.1  
338 mg). The difference in water vapor concentrations in these two cells, caused by  
339 absorption/adsorption of water by particles loaded on the filter, was measured using a  
340 differential katharometer, and the amount of water taken up by particles could be quantified by  
341 integration of the katharometer signals over time. This instrument could measure hygroscopic  
342 growth at very high RH (up to 99%).

343 Hygroscopic properties of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NaCl, levoglucosan, malonic acid, and mixed  
344 (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>/malonic acid particles were examined using FDHA at different RH during  
345 humidification and dehumidification (Mikhailov et al., 2013), and the measured mass growth  
346 factors agreed well with those reported in literature. This instrument was further employed to  
347 investigate hygroscopic properties of particles collected from a pristine tropical rainforest (near  
348 Manaus, Brazil) (Mikhailov et al., 2013), a suburban boreal forest site (near the city of St.  
349 Petersburg, Russia) (Mikhailov et al., 2013) and a remote boreal site (the Zotino Tall Tower  
350 Observatory, ZOTTO) in Siberia (Mikhailov et al., 2015). Fig. 3 displays the measured

351 hygroscopic properties of aerosol particles collected at the ZOTTO site. As shown in Fig. 3,  
352 both supermicrometer and submicrometer particles started to uptake substantial amount of  
353 water at ~70% RH; nevertheless, efflorescence took place at different RH, with ERH being  
354 ~35% RH for submicrometer particles and ~50% RH for supermicrometer particles (Mikhailov  
355 et al., 2015). It was suggested that the observed difference in ERH could be explained by the  
356 difference in organic contents in submicrometer and supermicrometer particles (Mikhailov et  
357 al., 2015): submicrometer particles contained larger fractions of organic materials,  
358 consequently leading to the reduction of ERH.



359

360 **Figure 3.** Mass growth factors of particles collected at the ZOTTO site in Serbia in June 2013:  
361 (upper panel) accumulation mode; (lower panel) coarse mode. The solid curves represents  
362 simulations using the  $\kappa_m$ -interaction model (KIM). Reprinted with permission by Mikhailov et  
363 al. (2015). Copyright 2015 Copernicus Publications.

364

365 The katharometer-based technique can be used to determine particle water content for  
366 unsaturated and supersaturated samples, independent of particle size and morphology (Lee and  
367 Chang, 2002; Mikhailov et al., 2013). It has also been successfully used as an offline method  
368 to investigate hygroscopic properties of ambient aerosol particles (Mikhailov et al., 2013;  
369 Mikhailov et al., 2015). It remains to be tested whether this technique is sensitive enough to  
370 investigate water adsorption of a few monolayers or less.

### 371 **3.1.3 Knudsen cell reactor**

372 Knudsen cell reactors are low-pressure reactors widely used to investigate heterogeneous  
373 uptake of trace gases (Al-Abadleh and Grassian, 2000; Karagulian and Rossi, 2005; Karagulian  
374 et al., 2006; Wagner et al., 2008; Liu et al., 2009; Zhou et al., 2012). This technique was also  
375 employed in several studies to explore water adsorption by particles with atmospheric  
376 relevance (Rogaski et al., 1997; Seisel et al., 2004; Seisel et al., 2005). For example, the initial  
377 uptake coefficient was reported to be  $0.042 \pm 0.007$  for uptake of water vapor by Saharan dust  
378 at 298 K (Seisel et al., 2004). Another study (Rogaski et al., 1997) found that pretreatment with  
379  $\text{SO}_2$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  could significantly increase water uptake by amorphous carbon.  
380 Knudsen cell reactors are normally operated in the molecular flow regime, and thus water vapor  
381 pressure used in these experiments is extremely low. As a result, although these measurements  
382 can provide mechanistic insights into the interaction of water vapor with particles at the  
383 molecular level, limited information on aerosol hygroscopicity under atmospheric conditions  
384 can be provided.

## 385 **3.2 Measurement of sample mass**

386 Aerosol hygroscopicity can be quantitatively determined by measuring the mass of  
387 particles as a function of RH under **isothermal** conditions. This can be achieved by several  
388 types of experimental techniques, as introduced below.

### 389 **3.2.1 Analytical balance**

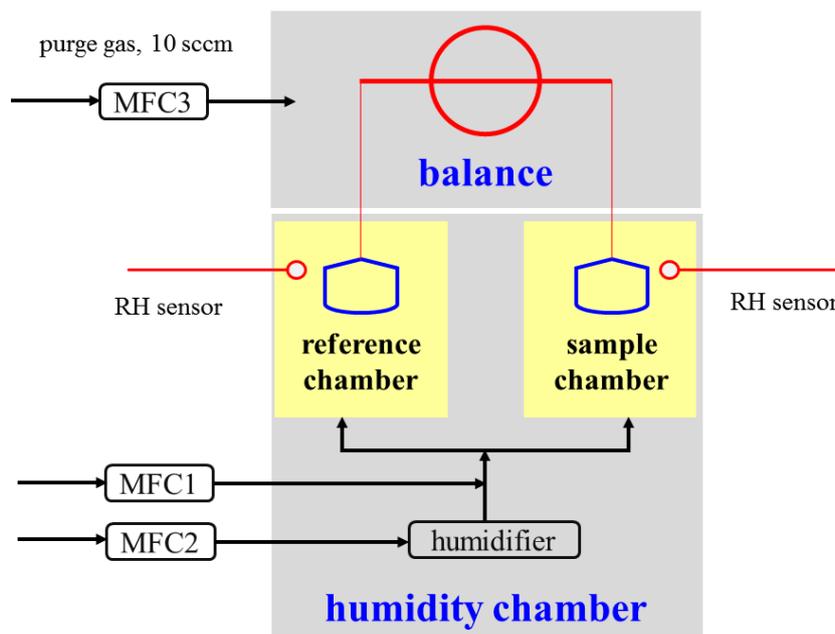
390 In a simple manner, the change in particle mass due to water uptake can be measured using  
391 an analytical balance under well controlled conditions (Hänel, 1976; McInnes et al., 1996;  
392 Hitzenberger et al., 1997; Diehl et al., 2001). For example, Diehl et al. (2001) investigated  
393 hygroscopic properties of ten pollen species at room temperature, using an analytical balance  
394 housed in a humidification chamber. The mass of pollen samples were measured at 0, (73±4)  
395 and (95±2)% RH. The average ratios of the mass of adsorbed water to dry mass increased from  
396 around 0.1 at 73% RH to ~3 at 95% RH (Diehl et al., 2001), suggesting that pollen samples  
397 can adsorb substantial amount of water at elevated RH.

398 Analytical balance was also employed to investigate hygroscopic properties of ambient  
399 aerosol particles. McInnes et al. (1996) employed an analytical balance to explore the  
400 hygroscopic properties of submicrometer marine aerosol particles collected on filters, and  
401 found that liquid water accounted for up to 9% of the dry particle mass at 35% RH and up to  
402 29% of the dry particle mass at 47% RH. In another study (Hitzenberger et al., 1997), size-  
403 segregated aerosol particles were collected on aluminum foils using a nine-stage cascade  
404 impactor in downtown Vienna, and their hygroscopic properties were examined using an  
405 analytic balance. Aerosol hygroscopicity was found to be strongly size dependent  
406 (Hitzenberger et al., 1997), and the mass ratios of particles at 90% RH to that at dry condition  
407 were found to be 2.35-2.6 for particles in the accumulation mode and 1.16-1.33 for those in the  
408 coarse mode.

### 409 3.2.2 Thermogravimetric analysis

410 Similar to humidity-controlled analytical balance, thermogravimetric analysers (TGA) can  
411 directly measure the mass change of particle samples at different temperature to investigate  
412 aerosol hygroscopicity. Commercial TGA instruments are typically integrated with automated  
413 systems for humidity generation and control. They can control temperature and RH very  
414 precisely, and are very sensitive in mass measurement (typically down to 1  $\mu\text{g}$  or even better).

415 Thermogravimetric analysers, sometimes also called vapor sorption analysers (VSA), have  
416 been employed by several groups to investigate hygroscopic properties of atmospherically  
417 relevant particles. For example, water uptake by  $\text{CaCO}_3$  and Arizona test dust was measured at  
418 room temperature using a Mettler-Toledo TGA with an accuracy of 1  $\mu\text{g}$  in mass measurement  
419 (Gustafsson et al., 2005), and about 4 monolayers of adsorbed water were formed at 80% RH  
420 for both mineral dust samples. A similar instrument was utilized to determine the DRH of  
421 dicarboxylic acids and their sodium salts at different temperatures (Beyer et al., 2014;  
422 Schroeder and Beyer, 2016), and the DRH was found to decrease with temperature for malonic  
423 acid, from 80.2% at 277 K to 69.5% at 303 K (Beyer et al., 2014). This method was also used  
424 to probe water adsorption by different soot particles (Popovitcheva et al., 2001; Popovicheva  
425 et al., 2008a; Popovicheva et al., 2008b), although no details of the instrument used were  
426 provided. It is worth noting that TGA and/or VSA have been widely used to investigate  
427 hygroscopic properties of pharmaceutical materials. For example, at room temperature  
428 anhydrous theophylline was observed to transform to hydrate at 62% RH, and its DRH was  
429 determined to be 99% (Chen et al., 2010).



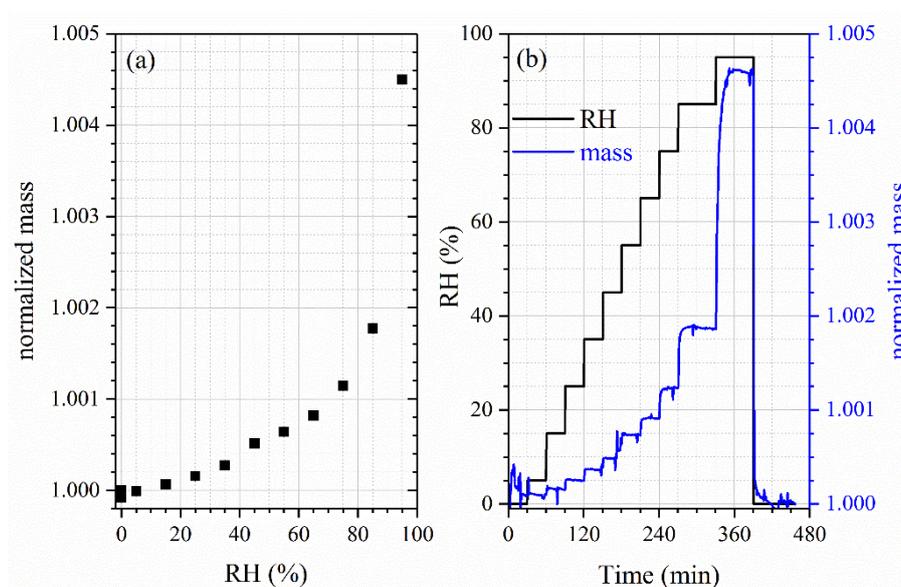
430

431 **Figure 4.** Schematic diagram of a vapor sorption analyser (Q5000SA, TA Instruments, New  
 432 Castle, DE, USA). Three mass flow controllers were used (MFC1: the dry flow; MFC2: the  
 433 humidified flow; MFC3: the dry flow to purge the balance). Reprint with permission by Gu et  
 434 al. (2017b). Copyright 2017 Copernicus Publications.

435

436 Very recently, Tang and coworkers systematically evaluated the performance of a vapor  
 437 sorption analyser to investigate hygroscopic properties of particles of atmospheric relevance  
 438 (Gu et al., 2017b). The instrument, with its schematic diagram shown in [Fig. 4](#), has two sample  
 439 crucibles housed in a temperature- and humidity-regulated chamber, and one crucible is empty  
 440 so that the background is simultaneously measured and subtracted. DRH values of six  
 441 compounds, including  $(\text{NH}_4)_2\text{SO}_4$  and NaCl, were determined at different temperatures (5-30  
 442 °C) and found to agree well with literature values. In addition, the mass change as a function  
 443 of RH (up to 90%), relative to that at 0% RH, was also found to agree well with those calculated  
 444 using the E-AIM model (Clegg et al., 1998) for  $(\text{NH}_4)_2\text{SO}_4$  and NaCl at 5 and 25 °C. Therefore,  
 445 it can be concluded that the vapor sorption analyser is a reliable technique to study hygroscopic  
 446 properties of atmospherically relevant particles.

447 The vapor sorption analyzer was used to examine hygroscopicity of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at 25 °C  
448 (Gu et al., 2017b), and the results are displayed in [Fig. 5](#). The hygroscopicity of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$   
449 was found to be very low, and the sample mass was only increased by <0.5% when RH was  
450 increased from 0 to 95%. This instrument was very sensitive to the change in sample mass due  
451 to water uptake; for example, as shown in [Fig. 5b](#), a relative mass change of <0.025% within 6  
452 h could be accurately determined. This instrument was further employed to investigate  
453 hygroscopic properties of perchlorates (Gu et al., 2017a; Jia et al., 2018), Ca- and Mg-  
454 containing salts (Guo et al., 2019), and primary biological particles (Tang et al., 2019), which  
455 play significant roles in the environments of the earth and the Mars. To our knowledge, the  
456 VSA technique has not yet been used to explore hygroscopic properties of ambient aerosol  
457 particles.



458  
459 **Figure 5.** Sample mass of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (relative to that of 0% RH) as a function of RH at 25  
460 °C, measured using a vapor sorption analyzer. (a) Change of sample mass with RH up to 95%;  
461 (b) change of sample mass and RH with experimental time. Reprint with permission by Gu et  
462 al. (2017b). Copyright 2017 Copernicus Publications.

### 463 3.2.3 Quartz crystal microbalance

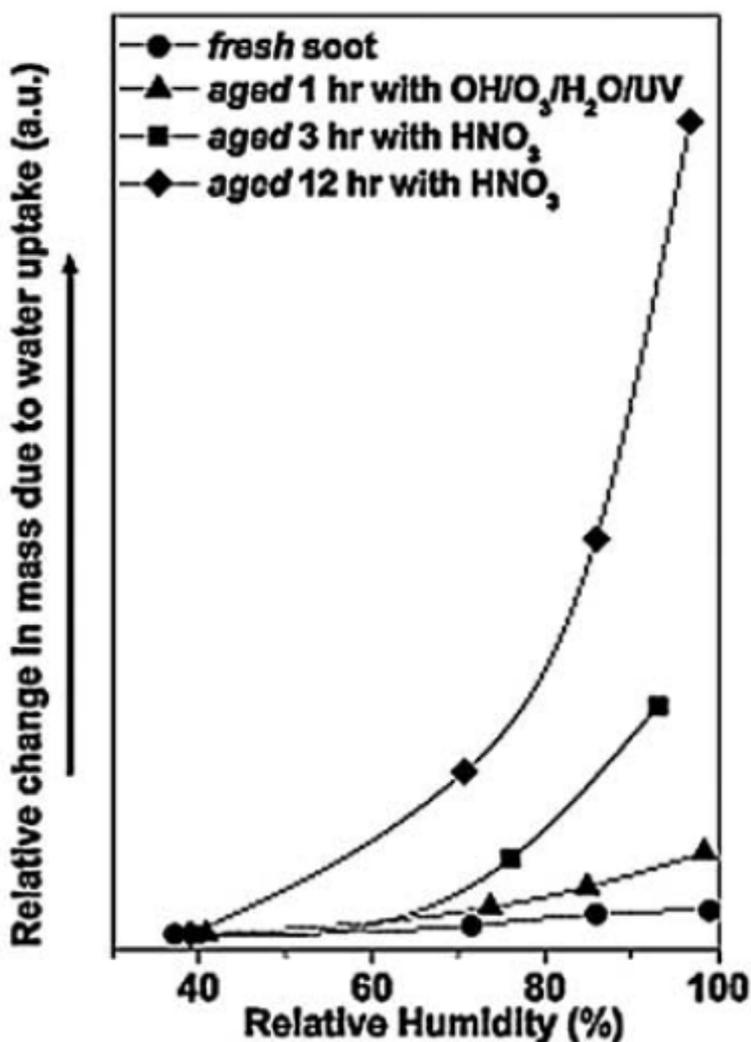
464 It was proposed in 1959 (Sauerbrey, 1959) that a film attached to the electrodes of a  
465 piezoelectric quartz resonator would cause a decrease in the resonance frequency, given by Eq.  
466 (1):

$$467 \Delta f = -C_f \cdot \Delta m \quad (1)$$

468 where  $\Delta f$  is the change in resonance frequency,  $\Delta m$  is the mass of the film, and  $C_f$  is a constant  
469 specific for the quartz resonator and can be experimentally calibrated. Eq. (1), known as the  
470 Sauerbrey equation, forms the basis for using the piezoelectric quartz resonator as a  
471 microbalance, which is usually called quartz crystal microbalance (QCM). QCM is a highly  
472 sensitive technique for particle mass measurement, and could be extended to investigate aerosol  
473 hygroscopicity. In a typical experiment, a particle film is first coupled to the quartz crystal, and  
474 RH is then varied with the resonance frequency being simultaneously recorded. According to  
475 Eq. (1), change in the mass of the particle film, due to change in RH, is proportional to the  
476 change in resonance frequency. Hygroscopicity measurements only need the information of  
477 relative mass change (relative to that under dry conditions), and as a result, knowledge of  $C_f$  is  
478 not required. QCM has a very high sensitivity in mass measurement, and it has been reported  
479 that the change in mass on the order of a few percent of a monolayer can be reliably determined  
480 (Tsionsky and Gileadi, 1994).

481 A QCM was used to measure the DRH of a number of inorganic and organic salts,  
482 including NaCl,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{CH}_3\text{COONa}$  and  $\text{CH}_3\text{COOK}$  (Arenas et al., 2012), and the  
483 measured values agreed very well with those reported in previous work. Several studies  
484 (Thomas et al., 1999; Demou et al., 2003; Asad et al., 2004b; Liu et al., 2016) have utilized  
485 QCM to explore hygroscopic properties of organic compounds of atmospheric interest. For  
486 example, Demou et al. (2003) quantitatively determined the amount of water taken up by  
487 dodecane, 1-octanol, octanoic acid, 1,5-pentanediol, 1,8-octanediol and malonic acid at room

488 temperature. The DRH was measured to be ~72% for malonic acid and ~95% for 1,8-octanediol,  
489 and in general compounds with higher oxidation state showed higher hygroscopicity (Demou  
490 et al., 2003). Another study (Asad et al., 2004b) found that exposure to O<sub>3</sub> would substantially  
491 increase the hygroscopicity of oleic acid. Using a QCM, Zuberi et al. (2005) explored the effect  
492 of heterogeneous reactions on hygroscopic properties of soot particles. As shown in Fig. 6,  
493 while water adsorption was very limited for fresh soot particles, hygroscopicity of soot particles  
494 was significantly increased after heterogeneous reactions with OH/O<sub>3</sub> and HNO<sub>3</sub> (Zuberi et al.,  
495 2005).



496

497 **Figure 6.** Water uptake (quantified as the ratio of mass of water taken up to that of dry particle  
498 mass) of fresh and aged soot particles. Reprinted with permission by Zuberi et al. (2005).  
499 Copyright 2005 John Wiley & Son, Inc.

500

501 QCM has also been applied to study hygroscopic properties of mineral dust particles,  
502 including oxides (Schuttlefield et al., 2007a), clay minerals (Schuttlefield et al., 2007b;  
503 Yeşilbaş and Boily, 2016) and authentic dust samples (Navea et al., 2010; Yeşilbaş and Boily,  
504 2016). For example, Yeşilbaş and Boily (2016) measured the amount of water taken up by 21  
505 different types of mineral particles up to 70% RH at 25 °C, and found that particle size played  
506 a critical role in water adsorption by these minerals. At 70% RH, submicrometer-sized particles  
507 could adsorb up to ~5 monolayers of water, while the amount of water adsorbed by micrometer-  
508 sized particles can reach several thousand monolayers (Yeşilbaş and Boily, 2016). Another  
509 study (Hatch et al., 2008) suggested that ~3 monolayers of adsorbed water was formed on  
510 CaCO<sub>3</sub> particles at 78% RH, and internal mixing with humic and fulvic acids could  
511 substantially increase the hygroscopicity of CaCO<sub>3</sub>.

512 It should be pointed out (as often not fully considered) that a few assumptions are required  
513 for the Sauerbrey equation to be valid (Rodahl and Kasemo, 1996), including: (i) the film  
514 deposited on the quartz crystal is rigid, i.e. internal friction is negligible; (ii) the film is perfectly  
515 coupled to the quartz crystal, i.e. there is no slip between the film and the crystal. The Sauerbrey  
516 equation may not hold if these conditions are not fulfilled, and the stiffness of the particle film  
517 would significantly affect the quartz resonator response (Dybwad, 1985; Pomorska et al., 2010;  
518 Vittorias et al., 2010; Arenas et al., 2012). Rodal and Kasemo (1996) suggested that the  
519 Sauerbrey equation can offer reliable mass change measurement only if the film is thin enough  
520 and does not slide on the QCM electrode. In addition, as supersaturated films formed on the

521 quartz crystal are unstable, QCM may not be able to explore hygroscopic properties of  
522 supersaturated samples.

523 Piezoelectric bulk wave resonators, which work in a way similar to the QCM, have been  
524 used for monitoring aerosol mass concentrations (Thomas et al., 2016; Wasisto et al., 2016).  
525 When particles are deposited onto the resonator surface, the resonance frequency will be  
526 linearly reduced with the particle mass. Very recently a new method based on piezoelectric  
527 bulk wave resonators was developed to investigate aerosol hygroscopicity (Zielinski et al.,  
528 2018). Aerosol particles were first collected on the resonator surface and then exposed to  
529 changing RH. Measured DRH and ERH values were found to agree with literature for NaCl  
530 and  $(\text{NH}_4)_2\text{SO}_4$ ; in addition, good consistency between experimentally measured and E-AIM  
531 predicted hygroscopic growth curves was found for NaCl,  $(\text{NH}_4)_2\text{SO}_4$  and NaCl/malonic acid  
532 mixture (Zielinski et al., 2018). Therefore, this technique appears to be a very promising  
533 method for aerosol hygroscopicity measurements.

### 534 **3.2.4 Beta gauge and TEOM**

535 In addition to the gravimetric method, the beta gauge method is widely used to measure  
536 aerosol mass concentrations in a semi-continuous way (Courtney et al., 1982; Chow, 1995;  
537 McMurry, 2000; Solomon and Sioutas, 2008; Kulkarni et al., 2011). A beta gauge measures  
538 the attenuation of beta particles emitted from a radioactive source through a particle-loaded  
539 filter, and if properly calibrated, attenuation of beta particles through the filter can be used to  
540 quantify the mass of particles loaded on the filter (McMurry, 2000). The mass of aerosol  
541 particles, after being collected on a filter, was measured at different RH in a closed chamber  
542 using a beta gauge to determine the aerosol liquid water content (Speer et al., 1997). Laboratory  
543 evaluation showed that the liquid water content of  $(\text{NH}_4)_2\text{SO}_4$  determined using this method  
544 agreed well with those measured gravimetrically (Speer et al., 1997), and when compared to  
545 humidification, a hysteresis was found during dehumidification for  $(\text{NH}_4)_2\text{SO}_4$ . The ability to

546 observe hysteresis is related to the use of hydrophobic substrate (for example, Teflon is usually  
547 a good option) in particle sampling. In addition, the beta gauge method was preliminarily  
548 employed to explore hygroscopic properties of submicrometer ambient aerosol particles (Speer  
549 et al., 1997). Further tests with other compounds, in addition to  $(\text{NH}_4)_2\text{SO}_4$ , are required to  
550 validate the robustness and reliability of this method.

551 Another widely-employed semi-continuous technique for aerosol mass measurement is  
552 tapered-element oscillating microbalance (TEOM) (Patashnick and Rupprecht, 1991; Chow et  
553 al., 2008; Solomon and Sioutas, 2008; Kulkarni et al., 2011). In a typical TEOM instrument,  
554 the wide end of a tapered hollow tube is mounted on a base plate, and its narrow end is coupled  
555 to a filter used to collect aerosol particles (Kulkarni et al., 2011). The oscillation frequency  
556 of the tapered hollow tube depends on the mass of particles collected on the filter and can be  
557 used to measure particle mass if properly calibrated (Kulkarni et al., 2011). Rogers et al. (1998)  
558 explored the possibility of using TEOM to measure aerosol liquid water content. Increase in  
559 particle mass was observed when a humid particle-free air flow was passed through a particle-  
560 loaded filter in the TEOM, and the particle mass started to decrease after a dry particle-free air  
561 was introduced (Rogers et al., 1998). This suggested that TEOM had the potential to examine  
562 hygroscopic properties of aerosol particles, though further experimental evaluation is needed  
563 to assess its performance.

### 564 **3.2.5 Discussion**

565 All the techniques discussed in Section 3.2 determine particle water content through direct  
566 measurement of sample mass or properties that are related to the sample mass, and hence there  
567 is no requirement on particle shape. Some of these techniques, such as thermogravimetric  
568 analysis (Gustafsson et al., 2005) and quartz crystal microbalance (Schuttlefield et al., 2007a;  
569 Yeşilbaş and Boily, 2016), are sensitive enough to investigate water adsorption down to one or  
570 a few monolayers, while other techniques, such as the analytic balance, may not be sensitive

571 enough for this application. If particles are supported on proper substrates (such as hydrophobic  
572 films), these techniques can be used to investigate hygroscopic properties of supersaturated  
573 samples, as demonstrated for the beta gauge method (Speer et al., 1997) and the piezoelectric  
574 bulk wave resonators (Zielinski et al., 2018). Nevertheless, supersaturated solutions formed in  
575 majority of these applications may not be stable enough for hygroscopic growth measurements,  
576 and as a result measurements have been rarely reported for supersaturated samples. In principle  
577 these techniques can all be used offline to investigate ambient aerosol particles if samples with  
578 enough mass can be collected. Analytical balance (McInnes et al., 1996; Hitzenberger et al.,  
579 1997) and the beta gauge method (Speer et al., 1997) have been used to explore hygroscopic  
580 properties of ambient aerosols; to our knowledge, application of thermogravimetric analysis,  
581 quartz crystal microbalance, TOEM and piezoelectric bulk wave resonators to ambient samples  
582 is yet to be demonstrated.

### 583 **3.3 Microscopic techniques**

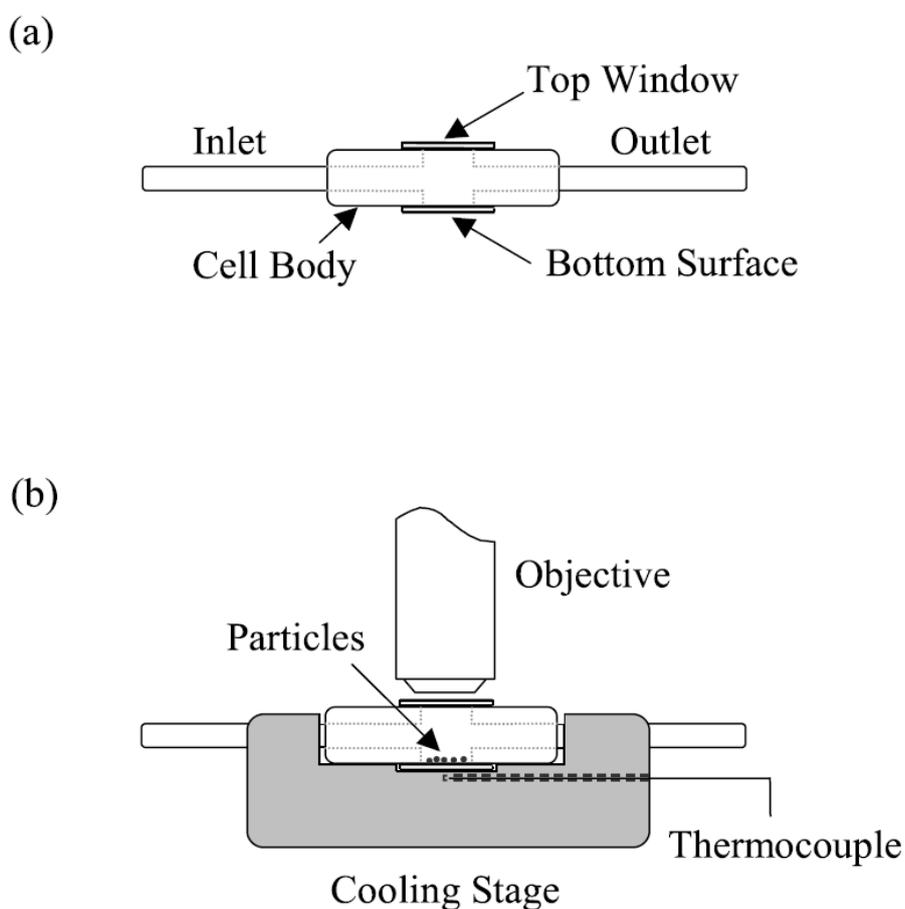
584 Deliquescence and efflorescence can be monitored using a number of microscopic  
585 methods, as discussed in this section. Furthermore, change in particle size at different RH, as  
586 measured microscopically, can be used to determine hygroscopic growth factors.

#### 587 **3.3.1 Optical microscopy**

588 Optical microscopy was employed to investigate phase transition of atmospheric particles  
589 as early as in 1950s (Twomey, 1953; Twomey, 1954). In these two studies (Twomey, 1953;  
590 Twomey, 1954), a large number of aerosol particles collected in Sydney were found to  
591 deliquesce at 71-75% RH, implying that they consisted mainly of sea salt. Since then, optical  
592 microscopy has been widely used to study hygroscopic properties of atmospherically relevant  
593 particles, and herein we only introduce representative studies conducted in the last two decades.

594 Bertram and co-workers (Parsons et al., 2004a; Parsons et al., 2004b; Parsons et al., 2006)  
595 developed a flow cell-optical microscope apparatus to investigate phase transitions of

596 individual particles deposited on glass slides coated with hydrophobic films. As show in Fig.  
597 7, the glass slide was placed in a flow cell mounted on a cooling stage for temperature  
598 regulation. A dry nitrogen flow was mixed with a humidified nitrogen flow and then delivered  
599 into the flow cell through the inlet, and the two flows were regulated using two mass flow  
600 controllers to adjust water vapor pressure (and thus RH) in the flow cell. Phase transitions of  
601 particles deposited on the glass slide were monitored using a microscope, and particle images  
602 were recorded using a CCD camera.



603  
604 **Figure 7.** Schematic diagram of the flow cell-optical microscope apparatus developed by  
605 Bertram and co-workers to investigate particle phase transitions: (a) side view of the flow cell;  
606 (b) side view of the entire apparatus. Particles were deposited on a glass slide placed on the  
607 bottom of the flow cell, which was mounted on a cooling stage. Objective: objective lens of

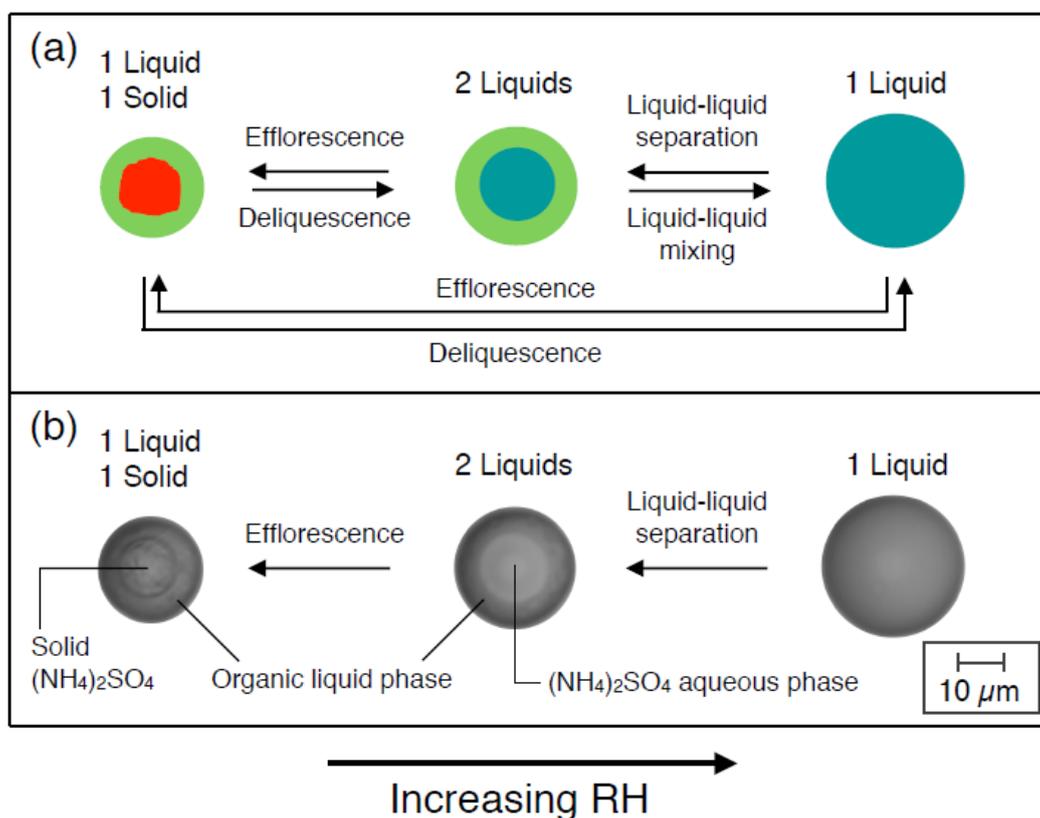
608 the microscope. Reprint with permission by Parsons et al. (2004b). Copyright 2004 John Wiley  
609 & Sons, Inc.

610

611 The performance of this apparatus was evaluated by measuring DRH of  $(\text{NH}_4)_2\text{SO}_4$   
612 particles from ~260 to 300 K (Parsons et al., 2004b), and the measured DRH agreed well with  
613 those reported in literature. This setup was then used to investigate the deliquescence of  
614 malonic, succinic, glutaric and adipic acid particles from 243 to 293 K (Parsons et al., 2004b)  
615 and deliquescence and crystallization of  $(\text{NH}_4)_2\text{SO}_4$  and NaCl particles internally mixed with  
616 organic compounds (Pant et al., 2004; Parsons et al., 2004a). It was found that if  $(\text{NH}_4)_2\text{SO}_4$  or  
617 NaCl particles contained substantial amounts of organic materials, their DRH would be  
618 significantly reduced and these particles were more likely to be aqueous in the troposphere  
619 (Pant et al., 2004). A similar instrument was employed to investigate deliquescence and  
620 efflorescence of  $\text{HIO}_3$  and  $\text{I}_2\text{O}_5$  particles (Kumar et al., 2010), and the DRH at 293 K were  
621 reported to be 81% for  $\text{HIO}_3$  and 85% for  $\text{I}_2\text{O}_5$ . Li and co-workers employed an optical  
622 microscope to investigate hygroscopic properties of individual particles emitted from  
623 residential coal burning (Zhang et al., 2018), collected over the Arctic (Chi et al., 2015), and  
624 collected during haze events at an urban site in northern China (Li et al., 2014a; Sun et al.,  
625 2018). It was found that during hydration urban haze particles typically had core-shell structure  
626 at 60-80% RH and fully deliquesced at >80% RH, while during dehydration most of these  
627 particles remained to be aqueous at >50% RH (Sun et al., 2018).

628 As illustrated by [Fig. 8a](#), besides deliquescence and efflorescence, atmospheric aerosols  
629 can also undergo liquid-liquid phase separation (LLPS), leading to coexistence of two liquid  
630 phases (Bertram et al., 2011; You et al., 2012; You et al., 2014; Freedman, 2017). LLPS can  
631 impact the direct and indirect radiative forcing of atmospheric aerosol particles as well as their  
632 heterogeneous reactivity, and therefore has received increasing attention in the last several

633 years (You et al., 2012; Freedman, 2017). Optical microscopy has played an important role in  
 634 understanding LLPS of atmospherically relevant particles (Bertram et al., 2011; You et al.,  
 635 2012; You et al., 2014). Fig. 8b shows optical microscopic images of an internally mixed  
 636 particle during an experiment in which RH was decreased while temperature was kept at ~291  
 637 K (Bertram et al., 2011), and the particle contained  $(\text{NH}_4)_2\text{SO}_4$  and 1,2,6-trihydroxyhexane  
 638 with a mass ratio of 1:2.1. As shown in Fig. 8b, at high RH the particle existed as an aqueous  
 639 droplet, and LLPS happened when RH was decreased, leading to the formation of two liquid  
 640 phases; efflorescence took place with further decrease in RH, leading to the formation of a solid  
 641  $(\text{NH}_4)_2\text{SO}_4$  core coated with an organic liquid layer.



642  
 643 **Figure 8.** (a) Some of the phase transitions which may occur for internally mixed atmospheric  
 644 particles consisting of  $(\text{NH}_4)_2\text{SO}_4$  and organic materials. Aqua represents an aqueous phase,  
 645 green represents a liquid phase of organic material, and red presents a solid phase of  $(\text{NH}_4)_2\text{SO}_4$ .  
 646 (b) Optical microscopic images of a particle which contained  $(\text{NH}_4)_2\text{SO}_4$  and 1,2,6-  
 647 trihydroxyhexane with a mass ratio of 1:2.1, during an experiment in which temperature was

648 kept at around 291 K while RH was decreased. Reprint with permission by Bertram et al. (2011).  
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650

651 In addition to identification of phase transitions, analysis of optical microscopic images  
652 recorded can also be used to determine particle size change and as a result hygroscopic growth  
653 factors (Ahn et al., 2010; Eom et al., 2014; Gupta et al., 2015). For instance, Ahn et al. (2010)  
654 employed an optical microscope to investigate hygroscopic properties of NaCl, KCl,  
655  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  particles collected on TEM grids, and found that their measured  
656 hygroscopic growth factors agreed well with those reported in literature for all the four types  
657 of particles examined. A following study (Eom et al., 2014) compared the influence of six types  
658 of supporting substrates (including TEM grid, Parafilm-M, aluminum foil, Ag foil, silicon  
659 wafer and cover glass) on hygroscopicity measurements using optical microscopy, and  
660 concluded that TEM grids were the most suitable substrate for this application. Optical  
661 microscopy was also used to study hygroscopic properties of  $\text{MgCl}_2$  and NaCl- $\text{MgCl}_2$  mixed  
662 particles (Gupta et al., 2015), and hygroscopic properties (including DRH and growth factors)  
663 of these particles were found to differ significantly from NaCl. Since  $\text{MgCl}_2$  is an important  
664 component in sea salt aerosol, this work can have significant implications for hygroscopicity  
665 and thus climatic impacts of sea salt aerosol (Zieger et al., 2017).

666 Optical microscopy can be (and has been widely) coupled to suitable spectroscopic  
667 techniques such as FTIR (Liu et al., 2008b), Raman spectroscopy (Liu et al., 2008c) and  
668 fluorescence (Montgomery et al., 2015), and if so chemical information can be simultaneously  
669 provided.

### 670 **3.3.2 Electron microscopy**

671 Electron microscopy has been widely used in laboratory and field studies to examine  
672 composition, mixing state and morphology of atmospheric particles, as summarized by a few

673 excellent review articles (Prather et al., 2008; Posfai and Buseck, 2010; Li et al., 2015; Ault  
674 and Axson, 2017). Herein we discuss exemplary studies to illustrate how electron microscopy  
675 can help improve our knowledge of aerosol hygroscopicity. This section is further divided to  
676 two parts, i.e. scanning electron microscopy (SEM) and transmission electron microscopy  
677 (TEM).

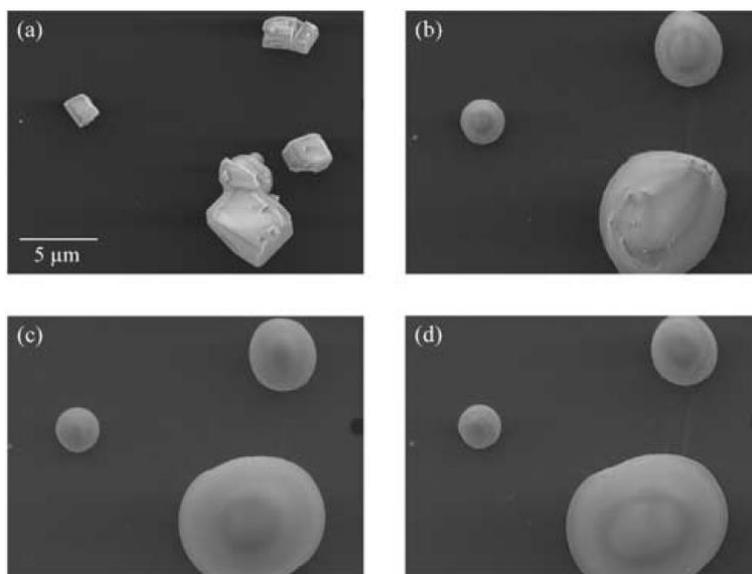
### 678 3.3.2.1 SEM

679 Ebert et al. (2002) developed an environmental scanning electron microscope (ESEM)  
680 technique to explore hygroscopic properties of individual particles, and the instrument they  
681 used had a spatial resolution of 8-15 nm. Changes in particle morphology could be used to  
682 identify phase transitions (deliquescence and efflorescence), and growth factors could be  
683 derived from observed change in particles size at different RH. Their measured DRH and  
684 hygroscopic growth factors (Ebert et al., 2002) were in good agreement with results reported  
685 by previous literature for NaCl,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$ . However, ERH could not  
686 be accurately determined due to the influence of the substrate onto which particles under  
687 investigation were deposited (Ebert et al., 2002).

688 ESEM, coupled to energy disperse X-ray analysis (EDX), was employed to investigate  
689 hygroscopic properties of a wide range of atmospheric particles, including  $(\text{NH}_4)_2\text{SO}_4$   
690 (Matsumura and Hayashi, 2007), sea spray (Hoffman et al., 2004), aerosol particles collected  
691 in nickel refineries (Inerle-Hof et al., 2007), agricultural aerosol (Hiranuma et al., 2008), pollen  
692 (Pope, 2010; Griffiths et al., 2012) and protein (Gomery et al., 2013). For example, Hoffman  
693 et al. (2004) found that both  $\text{NaNO}_3$  and  $\text{NaNO}_3/\text{NaCl}$  particles existed as amorphous solids  
694 even at very low RH and exhibit continuous hygroscopic growth, instead of having clear DRH;  
695 furthermore, EDX analysis showed that Cl was enriched in the core of dried  $\text{NaCl}/\text{NaNO}_3$   
696 particles (Hoffman et al., 2004), implying that during dehumidification NaCl started to  
697 crystalline first because of its lower solubility. This finding may have important implications

698 for chemical and radiative properties of marine aerosol particles (Quinn et al., 2015). In another  
699 study (Pope, 2010), ESEM observations revealed that birch pollen grains swelled internally but  
700 did not take up water on the surface significantly even at 93% RH; however, liquid water could  
701 be observed on the particle surface when RH was >95%. Hiranuma et al. (2008) found that  
702 most of aerosol particles collected at a cattle feedlot in the Texas did not take up significant  
703 amount of water at 96% RH, though a small fraction of coarse particles became deliquesced at  
704 ~75% RH and their sizes were doubled at 96% RH compared to their original sizes.

705 SEM/EDX was utilized by Krueger et al. (2003) to monitor changes in phase, morphology  
706 and composition of individual mineral dust particles after heterogeneous reaction with gaseous  
707 HNO<sub>3</sub>. For the first time, laboratory work showed that solid mineral dust particles could be  
708 transformed to aqueous droplets due to heterogeneous reactions (Krueger et al., 2003). As  
709 displayed in Fig. 9, solid CaCO<sub>3</sub> particles were converted to spherical droplets as  
710 heterogeneous reaction with gaseous HNO<sub>3</sub> proceeded (Krueger et al., 2003), and this was  
711 caused by the formation of Ca(NO<sub>3</sub>)<sub>2</sub> which had very low DRH (Al-Abadleh et al., 2003; Kelly  
712 and Wexler, 2005). A following study (Krueger et al., 2004) examined heterogeneous reactions  
713 of HNO<sub>3</sub> with mineral dust samples collected from four different regions, using SEM/EDX. It  
714 was suggested that calcite and dolomite particles exhibited large reactivity towards HNO<sub>3</sub> and  
715 could be transformed to aqueous droplets, while no morphological change was observed for  
716 gypsum, aluminum silicate clay and quartz particles after exposure to HNO<sub>3</sub> (Krueger et al.,  
717 2004).



718

719 **Figure 9.** SEM images of CaCO<sub>3</sub> particles before and after exposure to 26 ppbv gaseous HNO<sub>3</sub>  
720 at ~41% RH. (a): Before exposure; (b) exposure for 1 h; (c) exposure for 2 h; (d) exposure for  
721 4 h. Reprint with permission by Krueger et al. (2003). Copyright 2003 John Wiley & Sons, Inc.

722

723 The new laboratory discovery by Krueger et al. (2003) has been supported by a number of  
724 field measurements (Li et al., 2015; Tang et al., 2016a), and in some of which SEM was also  
725 utilized. For example, Laskin et al. (Laskin et al., 2005) provided the first evidence  
726 demonstrating that in the ambient air solid nonspherical CaCO<sub>3</sub> particles could be transformed  
727 to aqueous droplets which contained Ca(NO<sub>3</sub>)<sub>2</sub> formed in heterogeneous reaction with nitrogen  
728 oxides. ESEM was also applied to examine mineral dust particles collected in Beijing (Matsuki  
729 et al., 2005) and southwestern Japan (Shi et al., 2008), and both studies found that some Ca-  
730 containing particles existed in aqueous state even at RH as low as 15% because heterogeneous  
731 reactions with nitrogen oxides converted CaCO<sub>3</sub> to Ca(NO<sub>3</sub>)<sub>2</sub>. Similarly, it was shown by  
732 SEM/EDX measurements (Tobo et al., 2010; Tobo et al., 2012) that Ca-containing mineral  
733 dust particles in remote marine troposphere were transformed to aqueous droplets, because  
734 CaCl<sub>2</sub> was formed in heterogeneous reaction of CaCO<sub>3</sub> with HCl.

### 735 3.3.2.2 TEM

736 Compared to SEM, transmission electron microscopy (TEM) has better spatial resolution  
737 and can resolve features down to one nanometer or even smaller. TEM and AFM (atomic force  
738 microscopy) were employed by Buseck and colleagues (Posfai et al., 1998) to examine ambient  
739 particles collected on TEM grids under vacuum and ambient conditions. It was found that  
740 particle volumes were up to four times larger under ambient conditions, compared to vacuum  
741 conditions. Several years later Buseck and co-workers (Wise et al., 2005) developed an  
742 environmental transmission electron microscope (ETEM) which enabled individual particles  
743 to be characterized under environmental conditions. The performance of this instrument was  
744 validated by measuring DRH and ERH of NaBr, CsCl, NaCl, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and KBr particles in  
745 the size range of 0.1-1 μm, and good agreement was found between their measured values and  
746 these reported by previous work for all the five compounds investigated (Wise et al., 2005).

747 The ETEM technique was further employed to investigate hygroscopic properties of a  
748 wide range of atmospheric particles, including NaCl-containing particles (Semeniuk et al.,  
749 2007b; Wise et al., 2007), biomass burning particles (Semeniuk et al., 2007a) and potassium  
750 salts (Freney et al., 2009). The DRH of NaCl particles internally mixed with insoluble materials  
751 was determined to be ~76% (equal to that for pure NaCl), while internal mixing with other  
752 soluble compounds (e.g., NaNO<sub>3</sub>) would reduce the DRH (Wise et al., 2007). DRH and ERH  
753 were reported to be 85 and 56% for KCl and 96 and 60% for K<sub>2</sub>SO<sub>4</sub>, while KNO<sub>3</sub> displayed  
754 continuous hygroscopic growth (Freney et al., 2009); in addition, deliquescence and  
755 efflorescence of internally mixed KCl/KNO<sub>3</sub> and KCl/K<sub>2</sub>SO<sub>4</sub> were also examined (Freney et  
756 al., 2009). In another study (Adachi et al., 2011), aerosol particles, mainly being sulfate  
757 internally mixed with weakly hygroscopic organic materials, were collected at Mexico City  
758 and their hygroscopic properties were investigated using ETEM. It was found that only the  
759 sulfate part was deliquesced at elevated RH, while the entire particles containing deliquesced

760 sulfate did not necessarily become spherical. It was further suggested that the actual light  
761 scattering ability was 50% larger than that estimated by Mie theory which assumes particle  
762 sphericity (Adachi et al., 2011).

763 Recently cryogenic TEM has been deployed to explore morphology, hygroscopic  
764 properties and chemical composition of atmospheric particles (Veghte et al., 2014; Patterson  
765 et al., 2016). For example, it was observed that most nascent sea spray aerosol particles were  
766 homogeneous aqueous droplets, and upon exposure to low RH they would be quickly  
767 reorganized and undergo phase separation (Patterson et al., 2016).

### 768 **3.3.3 Atomic force microscopy**

769 Atomic force microscopy (AFM) is a widely used technique in surface chemistry and  
770 surface science. Compared to other microscopic techniques (e.g., optical microscopy, FTIR  
771 microscopy, TEM and SEM), AFM has several unique advantages. It does not require vacuum  
772 condition, and thus can be operated under environmental conditions; in addition, it has a high  
773 spatial resolution down to the nanometer level, and offers three-dimensional imaging (Morris  
774 et al., 2016).

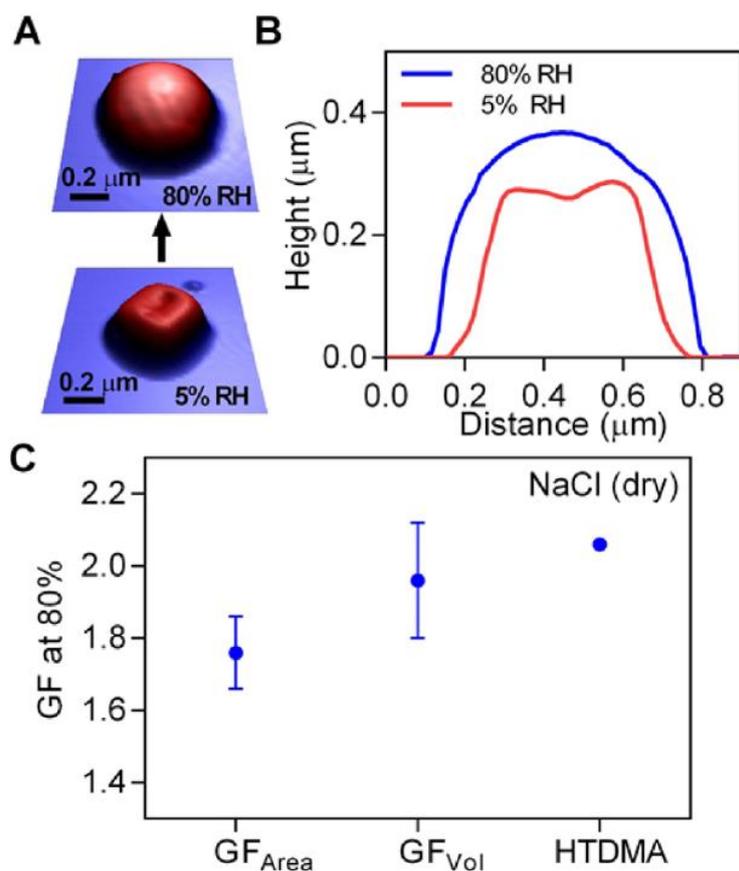
775 In the past two decades, AFM has been gradually utilized in atmospheric chemistry to  
776 observe three-dimensional morphology of aerosol particles, and its application in atmospheric  
777 chemistry started with observation of surfaces of single crystals with atmospheric relevance.  
778 For example, AFM was employed to study the (100) cleavage surface of NaCl during exposure  
779 to water vapor (Dai et al., 1997). A uniform layer of water was formed on the surface and  
780 surface steps started to evolve slowly at ~35% RH; when RH increased to ~73%  
781 (approximately the DRH of NaCl), the step structure disappeared abruptly due to deliquescence  
782 of the surface (Dai et al., 1997). This pioneering work demonstrated that AFM had the potential  
783 to be used to determine DRH of hygroscopic salts, in addition to providing rich information of  
784 surface structure change during exposure to water vapor. AFM was later used to observe

785 MgO(100) and CaCO<sub>3</sub>(1014) surface during exposure to water vapor and gaseous nitric acid  
786 (Krueger et al., 2005). Instabilities of oscillations in AFM images were observed, indicating  
787 that deliquescence of nitrate salts, which were formed in to heterogeneous reaction with nitric  
788 acid, occurred at elevated RH (Krueger et al., 2005).

789 To our knowledge, AFM was successfully used in 1995 to characterize aerosol particles  
790 collected using a low-pressure impactor (Friedbacher et al., 1995). Three years later, Posfai et  
791 al. (1998) used AFM to examine individual particles collected above the North Atlantic Ocean  
792 at different RH. The particle volume was observed to be four times larger under ambient  
793 conditions (measured by AFM) compared to that in the vacuum (measured by TEM) (Posfai et  
794 al., 1998). Another study (Wittmaack and Strigl, 2005) used AFM to measure height-to-  
795 diameter ratios of ambient particles, and concluded that some particles may exist in the  
796 supersaturated metastable state at around 50% RH. Non-contact environmental AFM was used  
797 to examine uptake of water vapor by NaCl nanoparticles at RH below DRH (Bruzewicz et al.,  
798 2011). NaCl nanoparticles started to adsorb water at RH well below its DRH (75%), and a  
799 liquid-like surface layer with thickness of 2-5 nm was formed at 70% RH, suggesting that  
800 deliquescence of NaCl nanoparticles was much more complicated than an abrupt first-order  
801 phase transition.

802 Very recently Tivanski and co-workers (Ghorai et al., 2014; Laskina et al., 2015b; Morris  
803 et al., 2015; Morris et al., 2016) developed an AFM-based method to investigate hygroscopicity  
804 of particles deposited on substrates, and systematically evaluated its performance by measuring  
805 hygroscopic growth factors of NaCl, malonic acid and binary mixture of NaCl with malonic or  
806 nonanoic acid. It was found that hygroscopic growth factors derived from 3D volume  
807 equivalent diameters always agreed well with H-TDMA results; however, hygroscopic growth  
808 factors derived from 2D area equivalent diameters showed significant deviation from H-TDMA  
809 results for some types of particles (Morris et al., 2016). An example is displayed in [Fig. 10](#),

810 suggesting that at 80% RH, the hygroscopic growth factor of NaCl particles derived from the  
811 volume-equivalent diameter was equal to that determined using H-TDMA, significantly larger  
812 than that derived from area-equivalent diameter. Such deviation was caused by anisotropic  
813 growth of particles (Morris et al., 2016), and the extent of deviation depended on the particle  
814 composition and their hydrate state at the time when they were collected on the substrate.



815  
816 **Figure 10.** AFM measurements of hygroscopicity of NaCl particles. (A) 3D AFM images of a  
817 NaCl particle at 5 and 80% RH; (B) Cross section of the particles at 5% (red) and 80% (blue)  
818 RH; (C) Comparison of hygroscopic growth factors derived from changes in mobility diameter  
819 (measured using H-TDMA), area equivalent diameter (measured using AFM) and volume  
820 equivalent diameter (measured using AFM). Reprint with permission by Morris et al. (2016).  
821 Copyright 2016 American Chemical Society.

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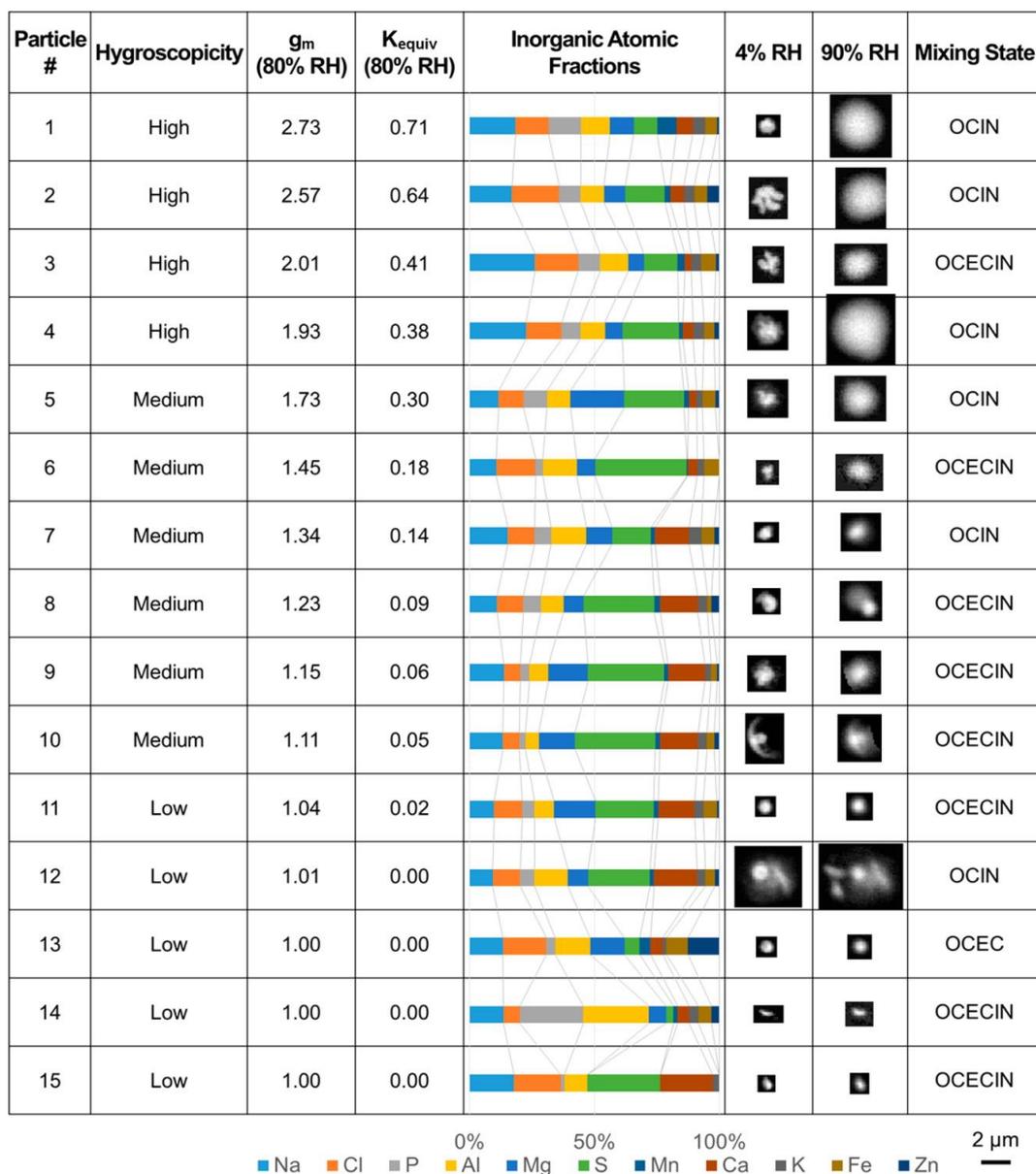
823 In addition to hygroscopicity measurement, AFM were used in several studies to  
824 characterize morphology, structure and other physicochemical properties of atmospheric  
825 particles (Lehmpuhl et al., 1999; Freedman et al., 2010; Laskina et al., 2015a). For example,  
826 AFM measurements found that organic and soot particles would shrink after interactions with  
827 O<sub>3</sub> while inorganic particles remained unchanged (Lehmpuhl et al., 1999). Freedman et al.  
828 (2010) employed AFM coupled to Raman microscopy to characterize atmospheric particles  
829 under ambient conditions, and observed core-shell structure for some organic particles. A  
830 recent study (Laskina et al., 2015a) characterized particles collected on substrates using AFM,  
831 Raman microscopy and SEM, and suggested that microscopy techniques operated under  
832 ambient conditions would offer the most relevant and robust information on particle size and  
833 morphology. Conventional AFM offers no chemical information; however, it can be (and has  
834 already been) coupled to spectroscopic techniques (such as FTIR) (Dazzi et al., 2012; Ault and  
835 Axson, 2017; Dazzi and Prater, 2017), enabling detailed physical and chemical properties to  
836 be provided with high spatial resolution. Very recently, the peak force infrared microscopy, a  
837 type of scanning probe microscopy, was developed to investigate IR absorption and mechanical  
838 properties of ambient aerosol particles (Wang et al., 2017b), and a spatial resolution of 10 nm  
839 could be achieved.

#### 840 **3.3.4 X-ray microscopy**

841 Scanning transmission X-ray microscopy (STXM) is a novel technique which can provide  
842 spatial distribution of physical, chemical and morphological information of individual particles  
843 (de Smit et al., 2008), and has been recently employed to investigate atmospheric particles  
844 (Ault and Axson, 2017). For example, Ghorai and Tivanski (2010) developed a STXM-based  
845 method to study hygroscopic growth of individual submicrometer particles, and proposed a  
846 method to quantify the mass of water associated with individual particles at a given RH. DRH  
847 and ERH values of NaCl, NaBr, and NaNO<sub>3</sub>, determined using STXM (Ghorai and Tivanski,

848 2010), agreed very well with previous results, and mass hygroscopic growth factors were also  
849 reported for these particles. In a following study (Ghorai et al., 2011), STXM was used to  
850 investigate hygroscopic growth of individual malonic acid; in addition to measured mass  
851 hygroscopic growth factors, near-edge X-ray absorption fine structure spectroscopy (NEXAFS)  
852 acquired using STXM suggested that keto-enol tautomerism occurred for deliquesced malonic  
853 acid particles (Ghorai et al., 2011). The keto-enol equilibrium constants were found to vary  
854 with RH, with enol formation favored at high RH (Ghorai et al., 2011).

855 Hygroscopic growth of submicrometer  $(\text{NH}_4)_2\text{SO}_4$ , measured using STXM/NEXAFS  
856 (Zelenay et al., 2011a), agreed well with previous studies; furthermore, analysis of STXM  
857 images and NEXAFS spectra suggested that phase separation occurred for internally mixed  
858  $(\text{NH}_4)_2\text{SO}_4$ -adipic acid particles, and adipic acid was partially enclosed by  $(\text{NH}_4)_2\text{SO}_4$  at high  
859 RH (Zelenay et al., 2011a). An environmental chamber was constructed to be directly coupled  
860 to a STXM instrument (Kelly et al., 2013), and this set-up was utilized to explore hygroscopic  
861 properties of NaCl, NaBr, KCl,  $(\text{NH}_4)_2\text{SO}_4$ , levoglucosan and fructose (Piens et al., 2016).  
862 Measured mass hygroscopic growth factors were compared with those predicted by a  
863 thermodynamic model (AIOMFAC) (Zuend et al., 2011), and good agreement between  
864 measurement and prediction was found for all the compounds investigated (Piens et al., 2016).  
865 In another study, Zelenay et al. (2010b) utilized STXM/NEXAFS to investigate hygroscopic  
866 properties of submicrometer tannic acid and Suwannee River Fulvic acid used as proxies for  
867 humic-like substance found in atmospheric aerosol. Both compounds exhibited continuous  
868 water uptake, and at 90% RH around one water molecule was associated with each oxygen  
869 atoms contained by tannic acid while approximately two water molecules were associated with  
870 each oxygen atoms contained by Suwannee River Fulvic acid (Zelenay et al., 2011b).



871

872 **Figure 11.** Hygroscopicity, mass growth factors at 80% RH ( $g_m$ ), single hygroscopicity  
873 parameters ( $K_{equiv}$ ), inorganic atomic fractions, STXM images (acquired at 4 and 90% RH) and  
874 mixing state for 15 aerosol particles examined. Reprint with permission by Piens et al. (2016).  
875 Copyright 2016 American Chemical Society.

876

877 STXM/NEXAFS has already been applied to explore hygroscopicity of ambient particles.  
878 For example, Pöhlker et al. (2014) collected aerosol particles from the Amazonian forest during  
879 periods with anthropogenic impacts, and then analyzed these particles using STXM-NEXAFS

880 at different RH. Substantial changes in particle microstructure were observed upon dehydration,  
881 very likely caused by efflorescence and crystallization of sulfate salts (Pöhlker et al., 2014).  
882 Piens et al. (2016) employed STXM-NEXAFS to examine hygroscopicity of atmospheric  
883 particles collected from the Department of Energy's Atmospheric Radiation Monitoring site in  
884 the Southern Great Plains. As shown in [Fig. 11](#), compared to particles with medium and low  
885 hygroscopicity, particles with high hygroscopicity always contained larger fractions of Na and  
886 Cl (Piens et al., 2016).

### 887 **3.3.5 Discussion**

888 Hygroscopicity measurements using microscopic techniques typically rely on changes in  
889 particle diameter measured microscopically. Therefore, it would be non-trivial for these  
890 techniques to quantify hygroscopic growth factors for non-spherical particles. In addition, these  
891 techniques may not be sensitive enough to investigate water adsorption. Since single particles  
892 deposited on supporting substances are usually examined, these techniques can be employed  
893 to investigate supersaturated samples if proper supporting substances are used. They have also  
894 been widely used to explore hygroscopic properties of ambient aerosol particles which were  
895 collected on proper substances. As discussed in Section 3.4, microscopic techniques can be and  
896 have widely been coupled to spectroscopic tools, and if so chemical information could be  
897 simultaneously provided;

### 898 **3.4 Spectroscopic techniques**

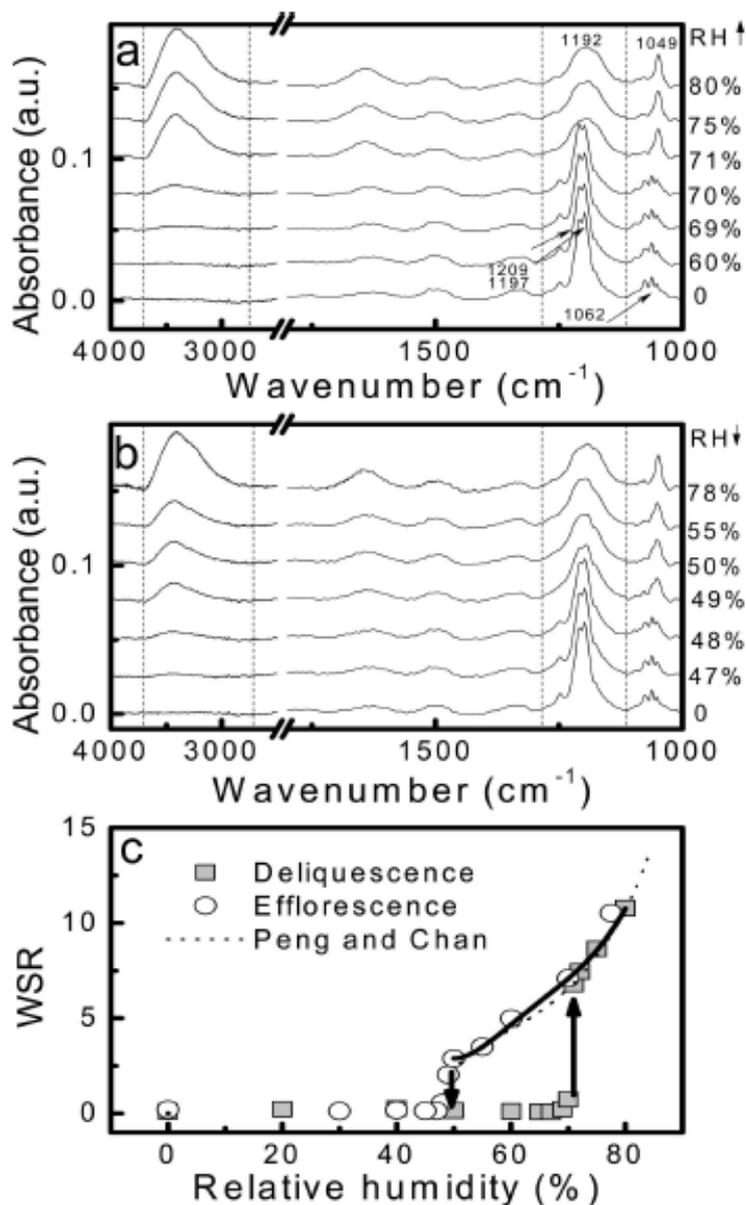
899 Interaction with water vapor would lead to changes in composition and chemical  
900 environment of particles under examination, and these changes can be monitored using  
901 spectroscopic techniques to understand hygroscopic properties of atmospherically relevant  
902 particles.

### 903 **3.4.1 Fourier transform infrared spectroscopy**

904 Fourier transform infrared spectroscopy (FTIR), a vibrational absorption spectroscopy, has  
905 been widely employed in laboratory (Goodman et al., 2000; Eliason et al., 2003; Asad et al.,  
906 2004a; Hung et al., 2005; Najera et al., 2009; Li et al., 2010; Tan et al., 2016; Tang et al., 2016b)  
907 and field work (Maria et al., 2002; Russell et al., 2011; Takahama et al., 2013; Kuzmiakova et  
908 al., 2016; Takahama et al., 2016; Takahama et al., 2019) to characterize chemical composition  
909 of aerosol particles. It can also be used in aerosol hygroscopicity studies. When water is  
910 adsorbed or absorbed by particles, change in IR absorption of particles under investigation due  
911 to water uptake can be recorded as a function of RH, and therefore hygroscopic properties of  
912 these particles can be characterized. One advantage of FTIR is that it can be coupled with a  
913 range of accessories to form different experimental configurations, including transmission  
914 FTIR (Cziczo et al., 1997; Braban et al., 2001; Goodman et al., 2001; Zhao et al., 2006; Song  
915 and Boily, 2013; Leng et al., 2015; Zawadowicz et al., 2015), attenuated total reflection-FTIR  
916 (ATR-FTIR) (Schuttlefield et al., 2007a; Navea et al., 2010; Hatch et al., 2011; Zeng et al.,  
917 2014; Zhang et al., 2014a; Yeşilbaş and Boily, 2016; Navea et al., 2017; Gao et al., 2018),  
918 diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) (Gustafsson et al., 2005;  
919 Ma et al., 2010a; Joshi et al., 2017; Ibrahim et al., 2018) and micro-FTIR for which FTIR is  
920 coupled with a microscope (Liu et al., 2008a; Liu and Laskin, 2009). Particles under  
921 investigation are typically deposited on proper substrates, though aerosol particles can also be  
922 studied using transmission FTIR (Cziczo et al., 1997; Cziczo and Abbatt, 2000; Zhao et al.,  
923 2006; Zawadowicz et al., 2015). FTIR has been used in a large number of studies to investigate  
924 hygroscopic properties of atmospherically relevant particles, and herein we only introduce and  
925 highlight a few representative examples.

926 Micro-FTIR was employed to investigate hygroscopic properties of  $\text{CH}_3\text{SO}_3\text{Na}$  particles  
927 (Liu and Laskin, 2009) and  $\text{NH}_4\text{NO}_3$  (Wu et al., 2007). Fig. 12a shows IR spectra of  $\text{CH}_3\text{SO}_3\text{Na}$

928 particles during humidification, and no significant change in IR spectra was observed when  
929 RH was increased from 0 to 70%; however, when RH was increased to 71%, IR absorption  
930 attributed to the  $\nu(\text{H}_2\text{O})$  band (at  $\sim 3400\text{ cm}^{-1}$ ) became very evident and its intensity increased  
931 with further increase in RH, indicating that the deliquescence of  $\text{CH}_3\text{SO}_3\text{Na}$  particles occurred  
932 at 71% RH. In addition, at  $<71\%$  RH two groups of narrow and structured bands, typically  
933 observed for crystalline samples, were observed for  $\text{CH}_3\text{SO}_3\text{Na}$  particles. The first one,  
934 centered at  $\sim 1197$  and  $1209\text{ cm}^{-1}$ , was attributed to asymmetrical stretching of  $\nu_8(-\text{SO}_3^-)$ , and  
935 the other one, centered at  $1062\text{ cm}^{-1}$ , was attributed to symmetrical stretching of  $\nu_3(-\text{SO}_3^-)$ .  
936 When RH was increased to 71%, both bands were significantly broaden and shifted to lower  
937 wavelengths, further confirming that DRH of  $\text{CH}_3\text{SO}_3\text{Na}$  particles was  $\sim 71\%$ . IR spectra of  
938  $\text{CH}_3\text{SO}_3\text{Na}$  particles during dehumidification are displayed in [Fig. 12b](#). Complete  
939 disappearance of IR absorption at  $\sim 3400\text{ cm}^{-1}$  and significant change in shape and position of  
940 IR peaks of  $\nu_8(-\text{SO}_3^-)$  and  $\nu_3(-\text{SO}_3^-)$  were observed when RH was decreased from 49 to 48%,  
941 suggesting that the ERH of  $\text{CH}_3\text{SO}_3\text{Na}$  was around 48%.



942

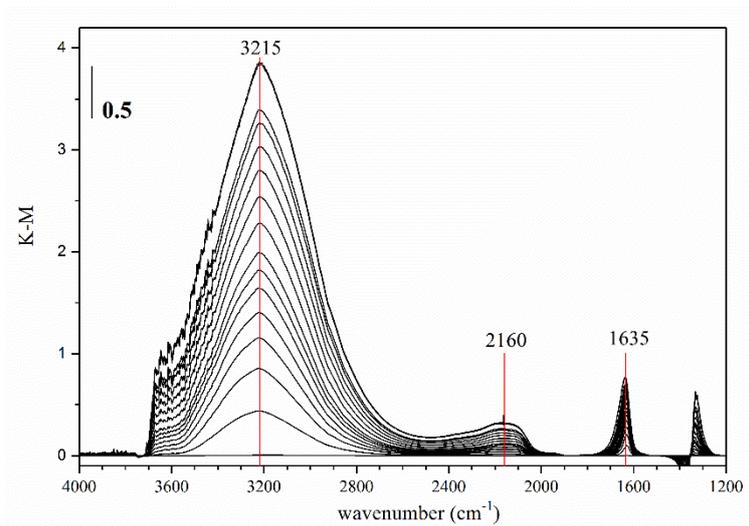
943 **Figure 12.** (a) FTIR spectra of CH<sub>3</sub>SO<sub>3</sub>Na particles during humidification. (b) FTIR spectra of  
 944 CH<sub>3</sub>SO<sub>3</sub>Na particles during dehumidification. (c) Water-to-solute ratios (WSR) of CH<sub>3</sub>SO<sub>3</sub>Na  
 945 particles as a function of RH: comparison between WSR measured by Liu and Laskin (2009)  
 946 using micro-FTIR to those determined by Peng and Chan (2001b) using electrodynamic  
 947 balance. Reprinted with permission by Liu et al. (2009). Copyright 2009 American Chemical  
 948 Society.

949

950 FTIR spectra can also be used to investigate hygroscopic growth quantitatively if IR  
951 absorbance can be calibrated. In the work by Liu and Laskin (2009), the absorbance ratio of  
952  $\nu(\text{H}_2\text{O})$  (at  $\sim 3400\text{ cm}^{-1}$ ) to  $\nu_8(-\text{SO}_3^-)$  (at  $\sim 1192\text{ cm}^{-1}$ ) was calibrated and then used to calculate  
953 water-to-solute ratios (WSR, defined as mole ratios of  $\text{H}_2\text{O}$  to  $\text{CH}_3\text{SO}_3^-$ ) of aqueous  $\text{CH}_3\text{SO}_3\text{Na}$   
954 particles. As shown in [Fig. 12c](#), WSR values determined using FTIR (Liu and Laskin, 2009)  
955 agreed well with those reported in a previous study (Peng and Chan, 2001b) using the  
956 electrodynamic balance (EDB). In another study (Liu et al., 2008a), DRH, ERH and WSR  
957 measured using micro-FTIR were found to agree well with those reported in literature for NaCl,  
958  $\text{NaNO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  particles. ATR-FTIR can be used in a similar way to micro-FTIR to  
959 investigate phase transitions and WSR of atmospherically relevant particles, and has been  
960 applied to a number of compounds, including NaCl (Schuttlefield et al., 2007a; Zeng et al.,  
961 2014),  $\text{NaNO}_3$  (Tong et al., 2010b; Zhang et al., 2014a),  $\text{Na}_2\text{SO}_4$  (Tong et al., 2010b),  $\text{NH}_4\text{NO}_3$   
962 (Schuttlefield et al., 2007a),  $(\text{NH}_4)_2\text{SO}_4$  (Schuttlefield et al., 2007a),  $\text{CH}_3\text{SO}_3\text{Na}$  (Zeng et al.,  
963 2014), sodium formate (Gao et al., 2018), sodium acetate (Gao et al., 2018), and etc.

964 In addition, ATR-FTIR (Schuttlefield et al., 2007a; Schuttlefield et al., 2007b; Hatch et al.,  
965 2011; Navea et al., 2017), DRIFTS (Ma et al., 2010a; Joshi et al., 2017; Ibrahim et al., 2018)  
966 and transmission FTIR (Goodman et al., 2001) have been employed to investigate water  
967 adsorption by insoluble particles, such as mineral dust. [Fig. 13](#) displays IR spectra of adsorbed  
968 water on  $\text{SiO}_2$  at different RH, as measured using DRIFTS at  $30\text{ }^\circ\text{C}$ . As shown in [Fig. 13](#), two  
969 intensive peaks appeared in IR spectra at elevated RH (Ma et al., 2010a), one at  $2600\text{-}3800$   
970  $\text{cm}^{-1}$  attributed to the O-H stretching mode and the other one at  $\sim 1630\text{-}1650\text{ cm}^{-1}$  attributed to  
971 the bending mode of H-O-H. Both peaks can be used to quantify the amount of adsorbed water,  
972 though surface OH groups may also contribute to the IR absorbance at  $\sim 3400\text{ cm}^{-1}$  (Goodman  
973 et al., 2001; Tang et al., 2016a). The intensity of the third peak at  $2100\text{-}2200\text{ cm}^{-1}$ , attributed  
974 to the association mode of H-O-H, was much smaller (Ma et al., 2010a). It is possible but non-

975 trivial to convert IR absorbance to the amount of adsorbed water, and the procedure used can  
976 be found elsewhere (Goodman et al., 2001; Ma et al., 2010a; Joshi et al., 2017; Ibrahim et al.,  
977 2018). It was found that the three-parameter BET equation (Joyner et al., 1945) could well  
978 describe water adsorption as a function of RH on mineral oxides (such as SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>,  
979 MgO and etc.) (Goodman et al., 2001; Ma et al., 2010a; Joshi et al., 2017), authentic mineral  
980 dust from different sources (Joshi et al., 2017; Ibrahim et al., 2018) and Icelandic volcanic ash  
981 (Joshi et al., 2017). Another study (Hatch et al., 2011) suggested that compared to the two-  
982 parameter BET equation, the Freundlich adsorption isotherm could better approximate the  
983 amount of water adsorbed by kaolinite, illite, and montmorillonite at different RH.



984  
985 **Figure 13.** IR spectra of adsorbed water on SiO<sub>2</sub> at 30 °C, as measured using DRIFTS at  
986 different RH. Reprint (with modification) with permission by Ma et al. (2010a). Copyright  
987 2011 Elsevier.

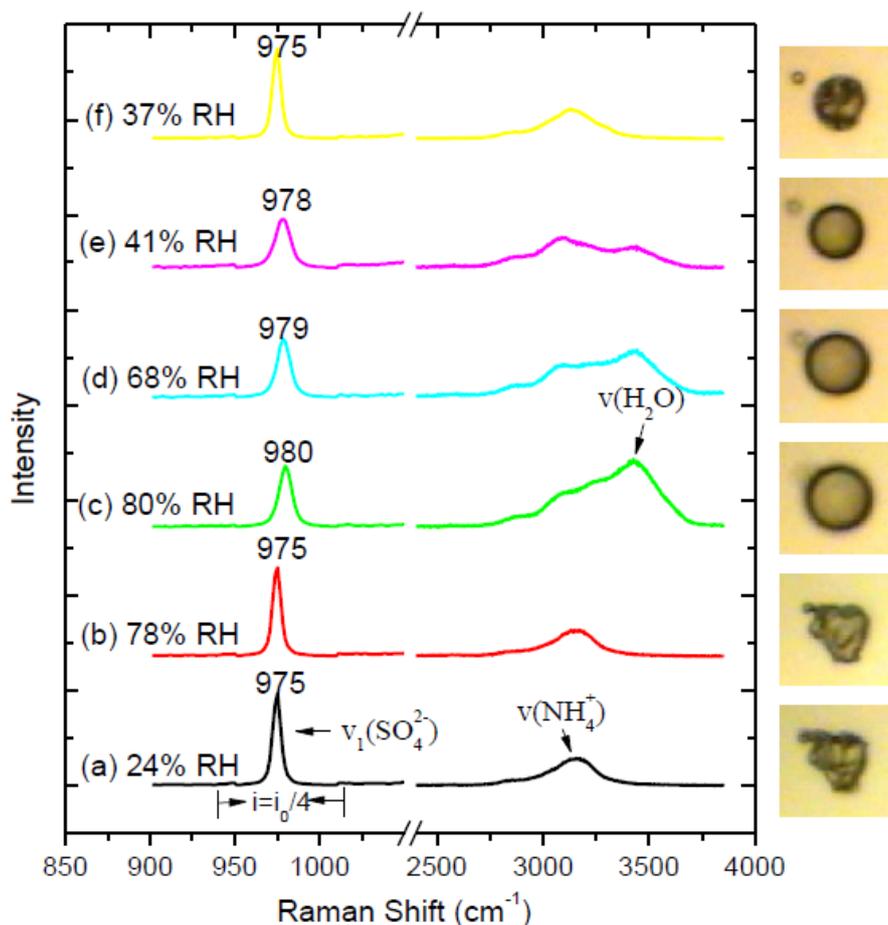
988

### 989 3.4.2 Raman spectroscopy

990 Raman spectroscopy is complementary to infrared spectroscopy. Bands which are weak in  
991 infrared spectroscopy can be strong in Raman spectroscopy, and vice versa. Compared to  
992 infrared spectroscopy, Raman spectroscopy is much less sensitive to H<sub>2</sub>O, despite that  
993 symmetric stretching vibration of H<sub>2</sub>O is Raman active, and this characteristic limits

994 application on Raman spectroscopy in exploring particles with low hygroscopicity. Meanwhile,  
995 Raman spectroscopy is very sensitive to crystalline structures, making it very useful to  
996 investigate particle phase transition. For example, Raman spectroscopy was employed to probe  
997 phase transformation of levitated  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{LiClO}_4$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{KHSO}_4$ ,  $\text{RbHSO}_4$   
998 and  $\text{NH}_4\text{HSO}_4$  microparticles (Tang et al., 1995), and the occurrence of metastable solid states  
999 was observed under ambient conditions for  $\text{Na}_2\text{SO}_4$ ,  $\text{LiClO}_4$ ,  $\text{Sr}(\text{NO}_3)_2$  and bisulfates. Raman  
1000 spectroscopy was also used to investigate hygroscopic properties of supersaturated droplets  
1001 (Zhang and Chan, 2000; Zhang and Chan, 2002b), such as  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{MgSO}_4$ .

1002 For regular spherical droplets, their Raman spectra may overlap with strong morphology-  
1003 dependent resonances (Zhang and Chan, 2002b). Nevertheless, if individual droplets were  
1004 deposited on proper substrates, Raman spectra with high quality (i.e. high signal-to-noise ratios)  
1005 could be obtained using confocal micro-Raman spectroscopy (Wang et al., 2005; Li et al.,  
1006 2006). For example, micro-Raman spectrometry was successfully used to investigate  
1007 hygroscopic properties of  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Ca}(\text{NO}_3)_2$  and  $\text{NO}_2$ -aged  $\text{Ca}(\text{NO}_3)_2$  particles deposited  
1008 on fluorinated ethylene propylene slides (Liu et al., 2008c; Zhao, 2010). Herein we use  
1009  $(\text{NH}_4)_2\text{SO}_4$  as an example to illustrate how Raman spectroscopy can be used to determine  
1010 hygroscopic properties of atmospherically relevant particles. [Fig. 14](#) shows Raman spectra and  
1011 microscopic images of an  $(\text{NH}_4)_2\text{SO}_4$  particle at different RH during humidification and  
1012 dehumidification processes (Liu, 2008). When RH was increased to 80% during humidification,  
1013 the Raman peak centered at  $\sim 3450 \text{ cm}^{-1}$ , attributed to the stretching vibration of  $\text{H}_2\text{O}$ , started  
1014 to become evident; whereas during dehumidification this peak disappeared when RH was  
1015 decreased to 37%. This suggested that deliquescence and efflorescence of  $(\text{NH}_4)_2\text{SO}_4$  took  
1016 place at 80 and 37% RH, respectively.



1017

1018 **Figure 14.** Raman spectra and microscopic images of an  $(\text{NH}_4)_2\text{SO}_4$  particle during  
 1019 humidification (a-c) and dehumidification (c-f). Reprint with permission by Liu (2008).  
 1020 Copyright 2008 Peking University.

1021

1022 As discussed in previous work (Ling and Chan, 2007; Liu et al., 2008c; Zhao, 2010), the  
 1023 occurrence of deliquescence and efflorescence of  $(\text{NH}_4)_2\text{SO}_4$  could also be identified from the  
 1024 change in position and full width at half maxima (FWHM) of the Raman peak at 970-980  $\text{cm}^{-1}$   
 1025 (due to symmetrical stretching of sulfate,  $\nu_1\text{-SO}_4^{2-}$ ). As shown in Fig. 14, during humidification  
 1026  $\nu_1\text{-SO}_4^{2-}$  was shifted from 975 to 980  $\text{cm}^{-1}$  when RH was increased to 80%, and meanwhile its  
 1027 FWHM increased from 6 to 9  $\text{cm}^{-1}$ , implying the occurrence of deliquescence. For comparison,  
 1028 during dehumidification when RH was decreased to 37%,  $\nu_1\text{-SO}_4^{2-}$  was shifted from 978-980  
 1029 to 975  $\text{cm}^{-1}$  and the corresponding FWHM decreased from  $\sim 10$  to 6  $\text{cm}^{-1}$ , suggesting that

1030 efflorescence took place at ~37% RH. Phase transitions could be further inferred from  
1031 microscopic images (Liu et al., 2008c; Zhao, 2010). Fig. 14 shows that the particle under  
1032 investigation became spherical when it was deliquesced (at 80% RH), and became irregular  
1033 when efflorescence occurred (at ~37% RH).

1034 The peak intensity ratio of stretching vibration of H<sub>2</sub>O to symmetrical stretching of sulfate  
1035 is proportional to the molar ratio of H<sub>2</sub>O to sulfate in the solution, and could be used to quantify  
1036 the water-to-solute ratios (WSR) in aqueous (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> droplets if properly calibrated (Liu et  
1037 al., 2008c). WSR values determined using Raman spectroscopy (Liu et al., 2008c) were found  
1038 to agree well with those reported in literature as a function of RH for (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and Ca(NO<sub>3</sub>)<sub>2</sub>  
1039 during humidification and dehumidification processes (Stokes and Robinson, 1948; Tang and  
1040 Munkelwitz, 1994; Clegg et al., 1998; Kelly and Wexler, 2005). In addition, Liu et al. (2008c)  
1041 employed micro-Raman spectroscopy to study heterogeneous reaction of CaCO<sub>3</sub> with NO<sub>2</sub>,  
1042 and revealed that solid CaCO<sub>3</sub> particles were converted to aqueous droplets after heterogeneous  
1043 reaction with NO<sub>2</sub>, due to the formation of Ca(NO<sub>3</sub>)<sub>2</sub>.

1044 Raman spectroscopy has been employed in a number of studies to investigate hygroscopic  
1045 properties of organic aerosols and mixed particles (Ling and Chan, 2007; Ling and Chan, 2008;  
1046 Yeung et al., 2009; Yeung and Chan, 2010; Yeung et al., 2010; Ma and He, 2012; Ma et al.,  
1047 2013a; Ma et al., 2013b). During humidification-dehumidification processes, oxalic acid was  
1048 converted to oxalate when mixed with NaCl (Ma et al., 2013b) or Ca(NO<sub>3</sub>)<sub>2</sub> (Ma and He, 2012),  
1049 and such conversion would lead to significant change in hygroscopic properties of mixed  
1050 particles. When a hygroscopic sulfate, such as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> or Na<sub>2</sub>SO<sub>4</sub>, was mixed with a  
1051 hygroscopic calcium salt, such as Ca(NO<sub>3</sub>)<sub>2</sub> or CaCl<sub>2</sub>, gypsum, the hygroscopicity of which  
1052 was very limited, would be formed by humidification. Raman spectroscopy was also used to  
1053 explore hygroscopic properties of NH<sub>4</sub>NO<sub>3</sub>/(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> mixed particles (Ling and Chan, 2007),  
1054 and the formation of double-salts, including 3(NH<sub>4</sub>NO<sub>3</sub>)·(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and

1055  $2(\text{NH}_4\text{NO}_3)\cdot(\text{NH}_4)_2\text{SO}_4$ , was observed for the first time during crystallization. The effect of  
1056 malonic, glutaric and succinic acids on the hygroscopic properties of  $(\text{NH}_4)_2\text{SO}_4$  particles were  
1057 explored using Raman spectroscopy (Ling and Chan, 2008). Partial crystallization of  
1058  $(\text{NH}_4)_2\text{SO}_4$ /malonic acid droplets took place at 16% RH, while  $(\text{NH}_4)_2\text{SO}_4$ /glutaric acid and  
1059  $(\text{NH}_4)_2\text{SO}_4$ /succinic acid particles became completely effloresced at ~30% RH. In addition,  
1060 partial deliquescence with solid inclusions was observed at 10-79% RH for  $(\text{NH}_4)_2\text{SO}_4$ /malonic  
1061 acid, 70-80% for  $(\text{NH}_4)_2\text{SO}_4$ /glutaric acid, and 80-90% RH for  $(\text{NH}_4)_2\text{SO}_4$ /succinic acid  
1062 particles.

### 1063 **3.4.3 Fluorescence spectroscopy**

1064 Water molecules in aqueous solutions can exist in two states, i.e. solvated water which  
1065 interacts directly with ions, and free water which interacts with other water molecules. Chan  
1066 and co-workers (Choi et al., 2004; Choi and Chan, 2005) developed a method to explore the  
1067 state of water molecules in single droplets levitated in an EDB. Pyranine, a water soluble dye,  
1068 was added into the droplets. When excited by radiation at ~345 nm, Pyranine would emit  
1069 fluorescence, and the spectra peaked at ~440 nm (attributed to the presence of solvated water)  
1070 and ~510 nm (attributed to the presence of free water). The amounts of solvated and free water  
1071 can be derived by combining mass hygroscopic growth factors (determined using the EDB)  
1072 and the ratio of fluorescence intensity at 440 nm to that at 510 nm (Choi et al., 2004). It was  
1073 found that for NaCl,  $\text{Na}_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$ , efflorescence of supersaturated droplets occurred  
1074 when the amount of solvated water was equal to that of free water (Choi et al., 2004; Choi and  
1075 Chan, 2005). Imaging analysis further revealed that solvated and free water were  
1076 homogeneously distributed in the droplets for some types of droplets, e.g.,  $\text{MgSO}_4$ , but  
1077 heterogeneously distributed for other types of droplets, such as NaCl and  $\text{Na}_2\text{SO}_4$  (Choi and  
1078 Chan, 2005).

1079 In another study (Montgomery et al., 2015), fluorescence microscopy was used to monitor  
1080 structural change of particle aggregates with RH. In this work NaCl particle aggregates were  
1081 collected on wire meshes and then coated with Rhodamine which would generate fluorescence.  
1082 Particle aggregates collapsed and became more compact when RH was increased from 0 to 52%  
1083 (Montgomery et al., 2015), lower than the DRH of NaCl (~75%). Hosny et al. (2013) developed  
1084 fluorescence lifetime imaging microscopy (FLIM) to determine viscosity of individual  
1085 particles via measuring viscosity dependent fluorescence lifetime of fluorescent molecular  
1086 rotors. The viscosity of a particles is of interest because it is closely related to the phase state  
1087 of the particle and largely determines diffusion in the particle (Koop et al., 2011; Reid et al.,  
1088 2018). FLIM was used to investigate the viscosity of ozonated oleic acid particles and  
1089 secondary organic particles formed by myrcene ozonolysis, and their viscosity was observed  
1090 to increase largely with decreasing RH and increasing extent in oxidative aging (Hosny et al.,  
1091 2016).

#### 1092 **3.4.4 Other surface characterization techniques**

1093 In addition to spectroscopic and microscopic methods discussed in Sections 3.3 and 3.4,  
1094 there are a number of other surface characterization techniques which can be used to explore  
1095 water adsorption on surfaces, e.g., sum frequency generation spectroscopy (Ma et al., 2004;  
1096 Liu et al., 2005; Jubb et al., 2012; Ault et al., 2013), atmospheric pressure X-ray photoelectron  
1097 spectroscopy (Ketteler et al., 2007; Salmeron and Schlogl, 2008; Yamamoto et al., 2010a),  
1098 scanning tunneling microscopy (Wendt et al., 2006; He et al., 2009), and etc. These techniques,  
1099 which are able to provide fundamental and mechanistic insights into water-surface interactions,  
1100 have mainly been applied to surfaces of single crystals, and their usefulness for particles with  
1101 direct atmospheric relevance is yet to be demonstrated. As a result, these techniques are not  
1102 further discussed here, and readers are referred to aforementioned literature and references  
1103 therein for more details.

### 1104 **3.4.5 Discussion**

1105 Infrared and Raman spectroscopy can be used to quantify particle water content for  
1106 unsaturated and supersaturated samples, with no restriction imposed by particle shape or  
1107 morphology. Infrared spectroscopy is very sensitive to adsorbed water and has been widely  
1108 used to investigate water adsorption (Tang et al., 2016a), as discussed in Section 3.3.1. In  
1109 contrast, Raman spectroscopy is not sensitive enough to detect adsorbed water; nevertheless,  
1110 recent work (Gen and Chan, 2017) showed that electrospray surface enhanced Raman  
1111 spectroscopy was able to detect surface adsorbed water. One important advantage for infrared  
1112 and Raman spectroscopy is that simultaneous measurement of chemical composition can be  
1113 provided; therefore, they have been coupled to other techniques (such as optical microscope,  
1114 electrodynamic balance, and etc.) to further understand hygroscopic properties of  
1115 atmospherically relevant particles, as discussed in Sections 3.3, 3.4, 4.1 and 4.2. Infrared and  
1116 Raman spectroscopy have been widely employed to characterize ambient aerosol particles  
1117 collected on proper substrates, and therefore they can be used to explore hygroscopic properties  
1118 of ambient particles in an offline manner.

### 1119 **3.5 Measurement of electrical properties**

1120 Deliquescence of ionic solids would lead to significant increase in electrical conductivity  
1121 and vice versa efflorescence of electrolyte solutions to ionic solids would cause large decrease  
1122 in electrical conductivity. Therefore, relative changes in electrical conductivity/impedance can  
1123 be used to identify the occurrence of deliquescence and efflorescence (Yang et al., 2006; He et  
1124 al., 2008; Schindelholz et al., 2014b; Schindelholz et al., 2014c). For example, in one study  
1125 (Schindelholz et al., 2014c) micrometer-sized particles were deposited on an interdigitated  
1126 microelectrode sensor housed in an environmental chamber, and the electrical impedance was  
1127 detected online while RH in the chamber was varied. The measured DRH and ERH using this  
1128 method were found to agree well with literature values for several compounds, e.g., NaCl,

1129 NaBr and KCl (Schindelholz et al., 2014c). In another study (He et al., 2008), the electrical  
1130 conductivity and capacitance of a single droplet were measured as different RH to investigate  
1131 hygroscopic properties of NaClO<sub>4</sub> particles. Overall, this method has not been widely applied  
1132 to study atmospherically relevant particles and thus is not further discussed herein.

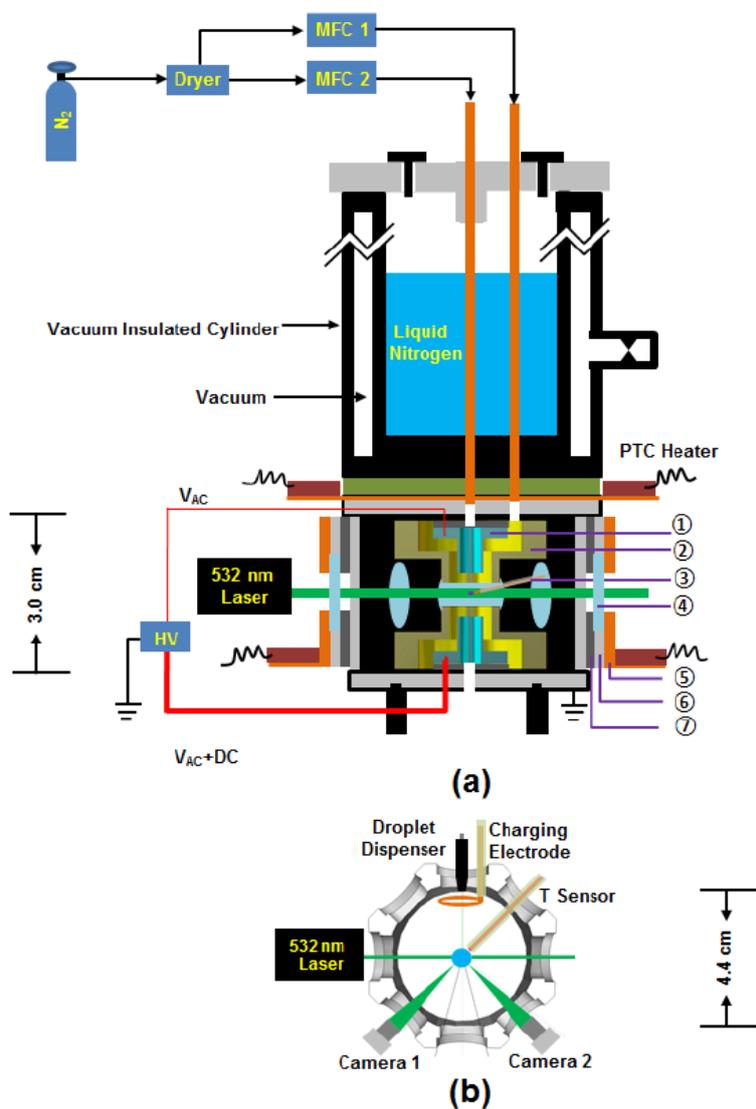
## 1133 **4 Levitated single particles**

1134 Single particle levitation techniques can be broadly classified into three groups (Krieger et  
1135 al., 2012), including electrodynamic balance, optical levitation and acoustic levitation. These  
1136 techniques have been widely used to investigate chemical and physical transformation of  
1137 atmospherically relevant particles (Lee et al., 2008; Krieger et al., 2012). Herein we introduce  
1138 basic principles of each techniques and illustrate how they can help understand aerosol  
1139 hygroscopicity via discussing representative studies.

### 1140 **4.1 Electrodynamic balance**

1141 The electrodynamic balance (EDB) technique has been widely used in the last several  
1142 decades, and diameters of particles which can be levitated by EDB are typically in the range of  
1143 1-100 μm (Davis, 1997; Davis, 2011). The principle, configuration and operation of EDB have  
1144 been extensively documented elsewhere (Reid and Sayer, 2003; Lee et al., 2008; Davis, 2011;  
1145 Krieger et al., 2012), and hence are not described in detail here. In brief, a particle can be  
1146 levitated and trapped at the null point of the EBD chamber when the AC and DC electric fields  
1147 surrounding the particle are properly adjusted. The schematic diagram of a low-temperature  
1148 EDB (Tong et al., 2015) is shown in [Fig. 15](#). The main body of the EDB was an octagonal  
1149 aluminum chamber with an optical window on each side. Two cold nitrogen flows, which were  
1150 first passed through copper tubes immersed in a liquid nitrogen Dewar, were fed into the  
1151 chamber to cool the EDB. Temperature at the null point where a particle was trapped was  
1152 further regulated using a PTC heater, and temperature and RH inside the chamber were

1153 monitored online. A continuous-wave laser at 532 nm was used to illuminate the trapped  
 1154 particle, and the scattered light was measured at an angle of  $21^\circ$  to determine the particle size.



1155  
 1156 **Figure 15.** Schematic diagram of a cold electrodynamic balance. (a) Side view of this set-up:  
 1157 1) inner electrode; 2) outer electrode; 3) temperature and RH sensors; 4) glass optical window;  
 1158 5) heating jacket; 6) optical window holder; 7) rubber insulator. (b) Top view of this set-up:  
 1159 droplets were generated using a droplet dispenser and charged using a charging electrode, and  
 1160 one of them may be trapped at the null point. A 532 nm laser was used to illuminate the trapped  
 1161 particle, and two cameras were used to observe the particle and record the scattered light.  
 1162 Reprint with permission by Tong et al. (2015). Copyright 2015 Copernicus Publications.

1163

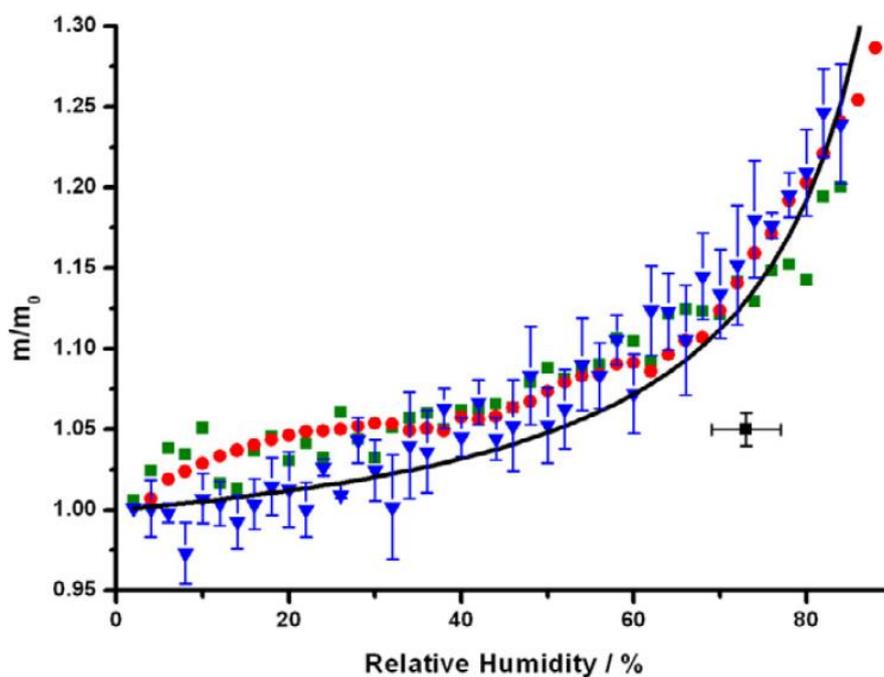
1164 In the absence of other forces, the gravitational force of the particle trapped in the EDB is  
1165 equal to the balancing electrostatic force, given by Eq. (2) (Pope et al., 2010a; Davis, 2011):

1166 
$$mg = nqC \frac{V_{DC}}{z} \quad (2)$$

1167 where  $m$  is the particles mass,  $g$  is the gravitational constant,  $n$  is the number of elementary  
1168 charges present on the particles,  $q$  is the elementary charge,  $z$  is the distance between the two  
1169 electrodes,  $C$  is a constant dependent on the geometrical configuration of the EDB, and  $V_{DC}$  is  
1170 the DC voltage required to levitate the particle. Eq. (2) suggests that as long as the charge  
1171 present on the trapped particle remains constant, the mass of the particle is proportional to the  
1172 DC voltage required to balance its gravitational force. Therefore, the relative mass change of  
1173 the particle due to any physical or chemical processing can be quantified by measurement of  
1174 the DC voltage. Haddrell et al. (Haddrell et al., 2012) discussed conditions when the  
1175 assumption of constant charge may fail and proposed experimental strategies to minimize its  
1176 occurrence.

1177 In hygroscopicity studies, the relative mass change of the trapped particle (typically  
1178 relative to that under dry condition) during humidification and dehumidification can be  
1179 determined to obtain mass hygroscopic growth factors (Peng et al., 2001; Pope et al., 2010a;  
1180 Haddrell et al., 2014; Steimer et al., 2015). For example, EDB has been used to measure DRH,  
1181 ERH and mass hygroscopic growth factors for a number of inorganic (Tang and Munkelwitz,  
1182 1994; Tang and Fung, 1997; Tang et al., 1997; Zhang and Chan, 2002a; Zhang and Chan, 2003;  
1183 Hargreaves et al., 2010b), organic (Peng and Chan, 2001a; Peng et al., 2001; Choi and Chan,  
1184 2002b; Pope et al., 2010a; Steimer et al., 2015) and mixed inorganic/organic particles (Choi  
1185 and Chan, 2002a; Zardini et al., 2008; Pope et al., 2010a) of atmospheric relevance. In addition,  
1186 water uptake by different types of pollen was measured as a function of RH using an EDB  
1187 (Pope, 2010; Griffiths et al., 2012). As displayed in [Fig. 16](#), pollen grains were found to be  
1188 moderately hygroscopic, and the mass of water taken up at 90% RH was around 30% of the

1189 dry mass (Pope, 2010). It was further found that hygroscopic growth of pollen species could  
1190 be described by the  $\kappa$ -Kohler theory, with  $\kappa$  values falling in the range of 0.05-0.1 (Pope, 2010).  
1191 In another two studies (Haddrell et al., 2013; Haddrell et al., 2014), EDB was utilized to explore  
1192 hygroscopic growth of several pharmaceutically relevant formulations, and the results can help  
1193 better understand where medical aerosol particles would deposit in our inhalation system.



1194  
1195 **Figure 16.** Mass hygroscopic growth factors (defined as the ratio of the particle mass at a given  
1196 RH to the dry particle mass) of *Salix caprea* (red circle), *Betula occidentalis* (blue triangle),  
1197 and *Narcissus* sp. (green square). For clarity only the error bars ( $\pm 1 \sigma$ ) are shown for *Betula*  
1198 *occidentalis*, and the mass hygroscopic growth factors have similar uncertainties for the other  
1199 two pollen species. The black square represents water uptake reported by Diehl et al. (2001),  
1200 and the black curve represents the fitted mass hygroscopic growth curve using the  $\kappa$ -Kohler  
1201 theory. Reprint with permission by Pope (2010). Copyright 2010 IOP Publishing Ltd.

1202  
1203 Light scattering techniques can be used to measure optical properties of single particles  
1204 levitated in an EDB. For example, Tang and co-workers (Tang and Munkelwitz, 1994; Tang,  
1205 1997; Tang and Fung, 1997; Tang et al., 1997) measured the intensity of elastically scattered

1206 light from a levitated particle which was illuminated by a He-Ne laser beam, and managed to  
1207 retrieve its diameter and refractive index as a function of RH using the Mie theory. Since the  
1208 relative mass change was also determined at the same time, change in particle density with RH  
1209 could also be determined (Tang and Munkelwitz, 1994; Tang et al., 1997). In addition,  
1210 spectroscopic techniques have been frequently coupled to EDB in order that chemical  
1211 information could be simultaneously provided. For example, Chan and colleagues (Zhang and  
1212 Chan, 2002a; Zhang and Chan, 2003; Lee et al., 2008) directed a laser beam with a wavelength  
1213 of 514.5 nm to the trapped particle in the EDB and measured the resulting Raman signals with  
1214 a CCD detector. This configuration enabled change in particle composition and hygroscopicity  
1215 due to heterogeneous reactions to be monitored online in a simultaneous manner (Lee and Chan,  
1216 2007; Lee et al., 2008). Experimental work in which EDB was coupled to fluorescence  
1217 spectroscopy has also been reported (Choi et al., 2004; Choi and Chan, 2005).

1218 In addition to hygroscopicity research, EDB have also been used in a number of studies  
1219 (Reid and Sayer, 2003; Lee et al., 2008; Pope et al., 2010b; Davis, 2011; Krieger et al., 2012;  
1220 Bilde et al., 2015b) to investigate other physicochemical properties (including vapor pressure,  
1221 mass accommodation coefficients, evaporation coefficients, gas phase diffusion coefficients,  
1222 and etc.) and chemical reactions of atmospheric particles.

## 1223 **4.2 Optical levitation**

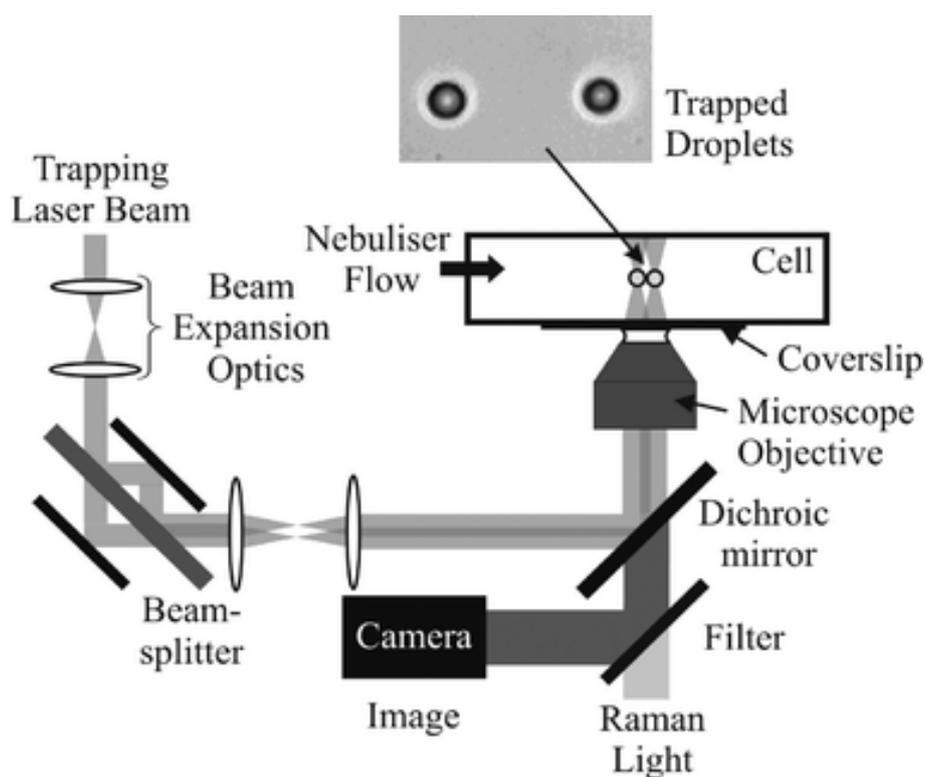
1224 Trapping and manipulation of atoms, molecules, nanostructures and particles have been  
1225 widely used in a number of scientific fields (Ashkin, 2000; McGloin, 2006; Mitchem and Reid,  
1226 2008; Krieger et al., 2012; Lehmuskero et al., 2015; Spesyvtseva and Dholakia, 2016; Gong et  
1227 al., 2018). The effects of radiation pressure on microscopic particles were first demonstrated  
1228 in 1970 (Ashkin, 1970). After that, levitation of solid particles and liquid droplets in air using  
1229 a vertically propagating weakly focused laser beam was achieved (Ashkin and Dziedzic, 1971;  
1230 Ashkin and Dziedzic, 1975). Applications of optical levitation to particles of atmospheric

1231 relevance have been previously reviewed (Mitchem and Reid, 2008; Wills et al., 2009; Krieger  
1232 et al., 2012), and very recently general applications related to trapping single particles in air  
1233 have also been summarized (Gong et al., 2018).

1234       Interaction of an incident laser beam with a particle consists of two forces: (i) a scattering  
1235 force that results from the transfer of momentum to the dielectric particle from backscattered  
1236 photons, and (ii) a gradient force that depends on the gradient of the electromagnetic field  
1237 associated with the optical beam. The first type of force exerts a push on the particle, while the  
1238 second type exerts a pull (Krieger et al., 2012). Utilization of either of these two forces as the  
1239 primary force to trap particles leads to two types of optical levitation techniques, i.e. optical  
1240 levitation trap and optical tweezers. In an optical levitation trap, the laser beam is mildly  
1241 focused and the particle adopts a stable position within the divergent beam above the focus,  
1242 where the downward gravitational force is exactly balanced by the upward scattering force  
1243 (Wills et al., 2009). Droplets of 20-100  $\mu\text{m}$  in diameter can be trapped with active  
1244 compensating adjustment of light intensity with respect to changes in droplet size (Krieger et  
1245 al., 2012); nevertheless, optical levitation traps are intrinsically delicate and unstable (Wills et  
1246 al., 2009). Optical tweezers effectively create a strong intensity gradient in three dimensions,  
1247 by amplifying the gradient force using a microscope objective lens to tightly focus the trapping  
1248 laser beam. The gradient force leads to strong transverse and axial restoring forces that are  
1249 many orders of magnitude larger than the gravitational force of the particle (Wills et al., 2009),  
1250 restoring the particle to the region with the highest light intensity (Krieger et al., 2012).  
1251 Therefore, particles can be captured and held tightly against the scattering and gravitational  
1252 forces, allowing true 3-dimensional confinement of particles with diameters of 1-10  $\mu\text{m}$   
1253 (Krieger et al., 2012).

1254       Different laser beams have been used as incident light sources. In optical levitation traps,  
1255 mildly focused Gaussian beams (Ashkin and Dziedzic, 1975), counter-propagating Gaussian

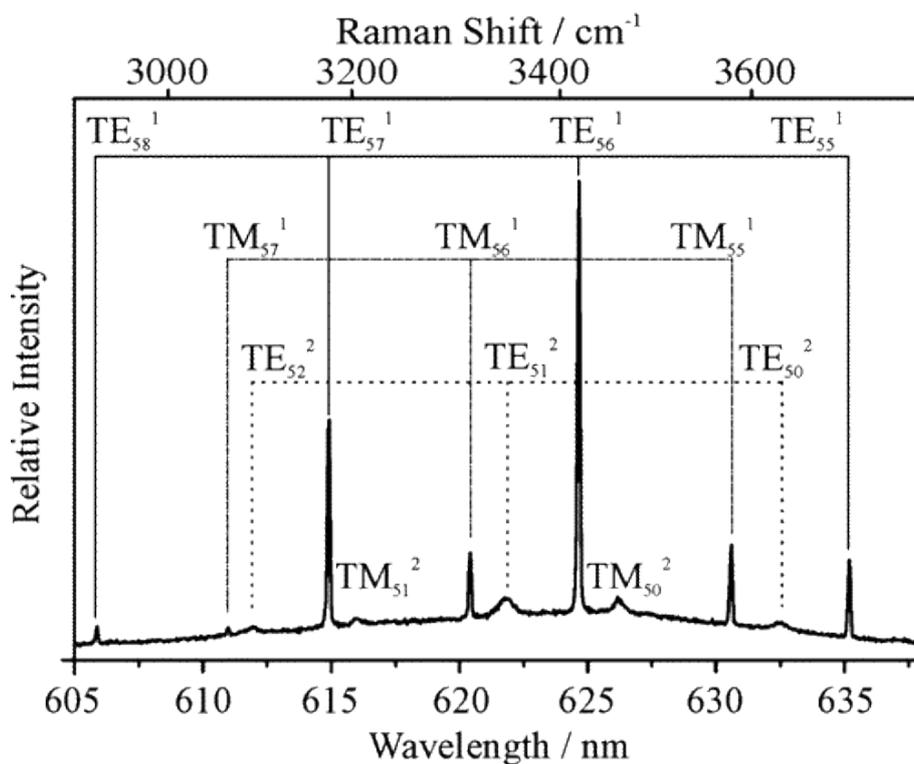
1256 beams (Ashkin, 2000) and a Gaussian beam plus a Bessel beam (Davis et al., 2015a) can be  
1257 used to trap single particles. In optical tweezers, particles can be trapped with a single laser  
1258 beam (Magome et al., 2003; Mitchem et al., 2006a) or in a dual-trap configuration with two (or  
1259 split) laser beams (Fallman and Axner, 1997; Buajarern et al., 2006; Butler et al., 2008), and  
1260 counter-propagating Bessel beams have also been used (Lu et al., 2014). Fig. 17 shows a typical  
1261 experimental setup for a dual-trap configuration of optical tweezers in which droplets were  
1262 generated using a nebulizer and then introduced into the trapping cell (Butler et al., 2008). A  
1263 laser beam at 532 nm was used as the trapping light and focused by an oil immersion objective  
1264 to create a working distance of  $\sim 130 \mu\text{m}$ . A beam splitter was then used to create two parallel  
1265 trapping beams that could be translated independently over distances of  $>50 \mu\text{m}$ , allowing  
1266 individual manipulation or probing of two separate particles in close range.



1267  
1268 **Figure 17.** Schematic diagram of the dual trap configuration of the optical tweezers. Reprint  
1269 with permission by Butler et al. (2008). Copyright 2008 Royal Society of Chemistry.

1270

1271       When a single particle is optically trapped, it can be characterized by a number of  
1272 techniques. Direct imaging is the most straightforward one, and bright field imaging can be  
1273 used to determine particle size with an accuracy of  $\pm 0.2 \mu\text{m}$  (Burnham and McGloin, 2009).  
1274 However, this method suffers from low accuracy in size measurement due to the dependence  
1275 of the axial position on laser power (Knox et al., 2007). Spectroscopy, especially Raman  
1276 spectroscopy, is more accurate in particle size measurement (Wills et al., 2009) and can also  
1277 offer compositional information (Reid et al., 2007). Known as cavity-enhanced Raman  
1278 spectroscopy, spectra recorded from optically trapped particles comprise of spontaneous and  
1279 stimulated Raman scattering (Mitchem et al., 2006a; Wills et al., 2009). Spontaneous Raman  
1280 scattering can be used to investigate changes in OH stretching vibrations ( $2900\text{-}3700 \text{ cm}^{-1}$ ) of  
1281 particulate water during hygroscopic growth as well as hydrogen bonding environments within  
1282 the particle. On the other hand, stimulated Raman scattering can be strongly amplified (by a  
1283 factor of  $>10$ ) (Mitchem et al., 2006a), but it occurs only at distinct wavelengths that are  
1284 commensurate with whispering gallery modes (WGMs). This stimulated Raman scattering  
1285 under WGMs, as shown in [Fig. 18](#), is also commonly referred to as morphology-dependent  
1286 resonances or cavity resonances (Mitchem et al., 2006a). Using the stimulated Raman spectra,  
1287 one can achieve a sizing accuracy of  $\pm 2 \text{ nm}$  that is only limited by spectral dispersion of the  
1288 spectrograph (Mitchem et al., 2006a; Mitchem and Reid, 2008). Other techniques have also  
1289 been coupled with optical levitation, including elastic (Mie) scattering (Ward et al., 2008), light  
1290 absorption (Knox and Reid, 2008), and so on.



1291

1292 **Figure 18.** An example of Raman scattering from a trapped water droplet, illuminated at 514.5  
 1293 nm. Stimulated Raman scattering is observed at wavelengths commensurate with whispering  
 1294 gallery modes. The resonant modes can be assigned by comparison with Mie scattering  
 1295 calculations, and the droplet radius can then be derived. Reprint with permission by Mitchem  
 1296 et al. (2006a). Copyright 2006 American Chemical Society.

1297

1298 There are a number of studies in which optical levitation techniques were employed to  
 1299 investigate hygroscopic properties of atmospheric particles. Based on an early design (Hopkins  
 1300 et al., 2004), Mitchem et al. (2006a) investigated hygroscopic growth of a NaCl particle trapped  
 1301 by optical tweezers for RH >80% by characterizing spontaneous and stimulated Raman  
 1302 scattering. Changes in the OH stretching band of the particle were observed as RH increased,  
 1303 and size measurement was achieved with an accuracy of a few nanometre and a time resolution  
 1304 of 1 s. The measured equilibrium sizes agreed well with these predicted using the Köhler theory,  
 1305 and the largest uncertainties came from the error in RH measurement with a capacitive sensor  
 1306 ( $\pm 2\%$  for RH below 90%) (Mitchem et al., 2006a). The change in the OH stretching band was

1307 also used to probe the formation and destruction of hydrogen bonding in a trapped NaCl particle  
1308 at different RH (Treuel et al., 2010).

1309 A dual-trap configuration of optical tweezers, in which two particles could be levitated  
1310 simultaneously (as shown in [Fig. 17](#)), was employed to investigate hygroscopic properties of  
1311 individual particles (Butler et al., 2008). In this setup, the first particle with well-known  
1312 hygroscopicity (in this case, NaCl) served as an accurate RH probe ( $\pm 0.09\%$  even for  
1313  $RH > 90\%$ ), while the second particle (NaCl/glutaric acid, for example) was interrogated for its  
1314 hygroscopic properties as an “unknown” particle. Excellent agreement between experimental  
1315 measurement and prediction using the Köhler theory was achieved (Butler et al., 2008).  
1316 Hygroscopic properties of inorganic/organic mixed particles, including NaCl/glutaric acid and  
1317  $(\text{NH}_4)_2\text{SO}_4$ /glutaric acid mixtures with different mass ratios, were further studied using this  
1318 comparative approach (Hanford et al., 2008). Measured equilibrium sizes of those  
1319 inorganic/organic mixed particles were found to agree well with theoretical predictions,  
1320 demonstrating the robustness of this approach for hygroscopicity study at the high RH ( $> 97\%$ ).

1321 Using the dual-trap configuration, hygroscopic properties of NaCl and  $(\text{NH}_4)_2\text{SO}_4$  were  
1322 measured at low RH (down to 80%) (Walker et al., 2010). The usage of NaCl as a reference  
1323 particle could reduce the errors associated with the measured equilibrium wet size of  
1324  $(\text{NH}_4)_2\text{SO}_4$  to  $< 0.2\%$ ; for comparison, the errors could be as large as  $\pm 5\%$  when a capacitance  
1325 RH probe was used. The difference between the measured and modelled growth factors was  
1326 found to be in the range of 0.1-0.3% for  $(\text{NH}_4)_2\text{SO}_4$  in the medium RH region (84 – 96% RH)  
1327 (Walker et al., 2010). In a following study (Hargreaves et al., 2010a), the dual-trap  
1328 configuration was utilized to investigate hygroscopic properties of NaCl at 45-75% RH, and  
1329 growth factors of NaCl measured by this (Hargreaves et al., 2010a) and previous studies (Butler  
1330 et al., 2008; Hanford et al., 2008) were found to be in excellent agreement with those predicted  
1331 (Clegg and Wexler, 2011) for RH in the range of 45-99%.

1332       Optical levitation can also be used to explore phase transitions and surface hydration. For  
1333 example, liquid to solid phase transitions were observed for the  $(\text{NH}_4)_2\text{SO}_4$ /glycerol/ $\text{H}_2\text{O}$   
1334 system via morphology-dependent resonances and Raman spectroscopy (Trunk et al., 1997),  
1335 and Raman spectroscopy revealed the presence of adsorbed water on the surface of optically  
1336 levitated mineral oxide particles at different RH (Rkiouak et al., 2014). In addition, optical  
1337 tweezers were utilized to investigate efflorescence and deliquescence of a number of inorganic  
1338 salts (Davis et al., 2015a). Compared to deliquescence, efflorescence usually occurs for a lower  
1339 RH (Martin, 2000). Immersion of solid particles (e.g., mineral dust) in aqueous droplets would  
1340 cause efflorescence to take place at higher RH, as observed in previous work (Han et al., 2002;  
1341 Pant et al., 2006). Recently optical levitation was employed to explore efflorescence of  
1342 supersaturated aqueous droplets induced by collision with solid particles (Davis et al., 2015a;  
1343 Davis et al., 2015b). It was found that upon collision with several different types of solid  
1344 particles, including NaCl, KCl,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ , and etc., aqueous  $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$   
1345 and NaCl droplets would effloresce at RH significantly higher than those for homogeneous  
1346 efflorescence (Davis et al., 2015b).

1347       Kinetics of water uptake by aerosol particles can also be studied using optical levitation  
1348 techniques. For example, hygroscopic properties of NaCl particles coated with oleic acid was  
1349 examined using optical tweezers (Dennis-Smith et al., 2012). It was observed that  
1350 efflorescence and deliquescence behavior of the NaCl particle and the timescales to reach re-  
1351 equilibrium were not affected by the presence of oleic acid; furthermore, heterogeneous  
1352 oxidation by  $\text{O}_3$  was found to increase the hygroscopicity of oleic acid in the NaCl-oleic acid  
1353 mixed particle (Dennis-Smith et al., 2012). In another study (Tong et al., 2011), optical  
1354 tweezers were employed to explore the timescales for mass transfer of water in glassy aerosol  
1355 particles. It was found that the half-time for re-equilibration after RH change could increase

1356 from tens and hundreds of seconds (RH above glass transition) to >1000 seconds (RH below  
1357 glass transition) for sucrose-water, raffinose-water and sucrose-NaCl-water systems.

1358 Particle viscosity determines diffusion coefficients of water molecules in the particles,  
1359 affecting water uptake kinetics (Reid et al., 2018). A novel microrheological method, which  
1360 employed holographic aerosol optical tweezers, has been developed to measure particle  
1361 viscosity in the range of  $10^{-3}$  to  $10^9$  Pa S (Power et al., 2013). In brief, coalescence between  
1362 two airborne particles, with volumes smaller than 500 femtolitres, was initiated using the  
1363 optical tweezers, and the time required by the coalesced particle to relax to a sphere was  
1364 measured to infer particle viscosity. More details of this method can be found elsewhere (Power  
1365 et al., 2013; Song et al., 2016).

1366 In addition, optical levitation techniques have also been employed to investigate a myriad  
1367 of heterogeneous processes, including evaporation of volatile/semi-volatile species, mixing of  
1368 inorganic/organic particles and heterogeneous reactions (Mitchem et al., 2006b; Buajarern et  
1369 al., 2007; Tang et al., 2014; Jones et al., 2015; Gorkowski et al., 2016; Cai and Zhang, 2017).  
1370 Optical tweezers have recently become commercially available, and commercial instruments  
1371 have been used to investigate physicochemical properties and processes of atmospherically  
1372 relevant particles (Davies and Wilson, 2016; Haddrell et al., 2017).

### 1373 **4.3 Acoustic levitation**

1374 Inside a typical acoustic levitator, high frequency sound wave, generated using a  
1375 piezoelectric oscillator (also called radiator), is reflected by a concave reflector. Standing  
1376 waves can be generated in the space between the radiator and the reflector if the radiator and  
1377 the reflector are properly positioned. Droplets with diameters ranging from tens of micrometers  
1378 to a few millimeters can then be trapped in the vertical position near one of these existing wave  
1379 nodes. Detailed description of this technique can be found elsewhere (Kavouras and Krammer,  
1380 2003a; Ettner et al., 2004; Mason et al., 2008). The size of the levitated particle can be

1381 characterized using a camera, and spectroscopic techniques, such as FTIR and Raman  
1382 spectroscopy, can be coupled to the acoustic levitator so that chemical information can be  
1383 simultaneously provided (Brotton and Kaiser, 2013).

1384 Acoustic levitation has been used in a variety of research fields to investigate interactions  
1385 of single solid/liquid particles with different gases (Kavouras and Krammer, 2003b; Mason et  
1386 al., 2008; Schenk et al., 2012), including water vapor. For example, Schenk et al. (2012) used  
1387 an acoustic levitator to measure hygroscopicity of imidazolium-based ionic liquids, and low  
1388 temperature acoustic levitation was developed to study homogeneous and heterogeneous  
1389 freezing of aqueous droplets (Ettner et al., 2004; Diehl et al., 2009; Diehl et al., 2014). Particles  
1390 which can be acoustically levitated are typically  $>20 \mu\text{m}$  (Mason et al., 2008; Krieger et al.,  
1391 2012), while most of atmospheric aerosol particles are significantly smaller (Seinfeld and  
1392 Pandis, 2016). Therefore, compared to the other two levitation techniques (i.e. EDB and optical  
1393 levitation), acoustic levitation is much less widely utilized in atmospheric chemistry (Krieger  
1394 et al., 2012).

#### 1395 **4.4 Discussion**

1396 Both EDB and optical levitation can measure liquid water content for unsaturated and  
1397 supersaturated samples, as particles used in these experiments are free of contact with other  
1398 substances. EDB measures relative mass change to quantify aerosol liquid water content, and  
1399 thus there is no constrain on particle shape; whereas for optical levitation, particle diameter  
1400 change is usually measured optically, and particles under investigation need to be spherical.  
1401 Both techniques may not be sensitive enough to study water adsorption. To our knowledge,  
1402 they have not been used to investigate hygroscopic properties of ambient aerosol particles,  
1403 though in principle they both have the capacity. One reason is that particles that can be explored  
1404 using these techniques are usually one order of magnitude larger than those typically found in  
1405 the troposphere. Another reason could be that only one particle can be examined in each

1406 experiment, while there are numerous aerosol particles in the ambient air. One unique  
1407 advantage of these two techniques is that size, chemical composition and optical properties of  
1408 levitated particles can be obtained in an online and noninvasive manner, making them very  
1409 valuable to explore aerosol properties and processes at the fundamental level (Lee et al., 2008;  
1410 Krieger et al., 2012).

## 1411 **5 Aerosol particles**

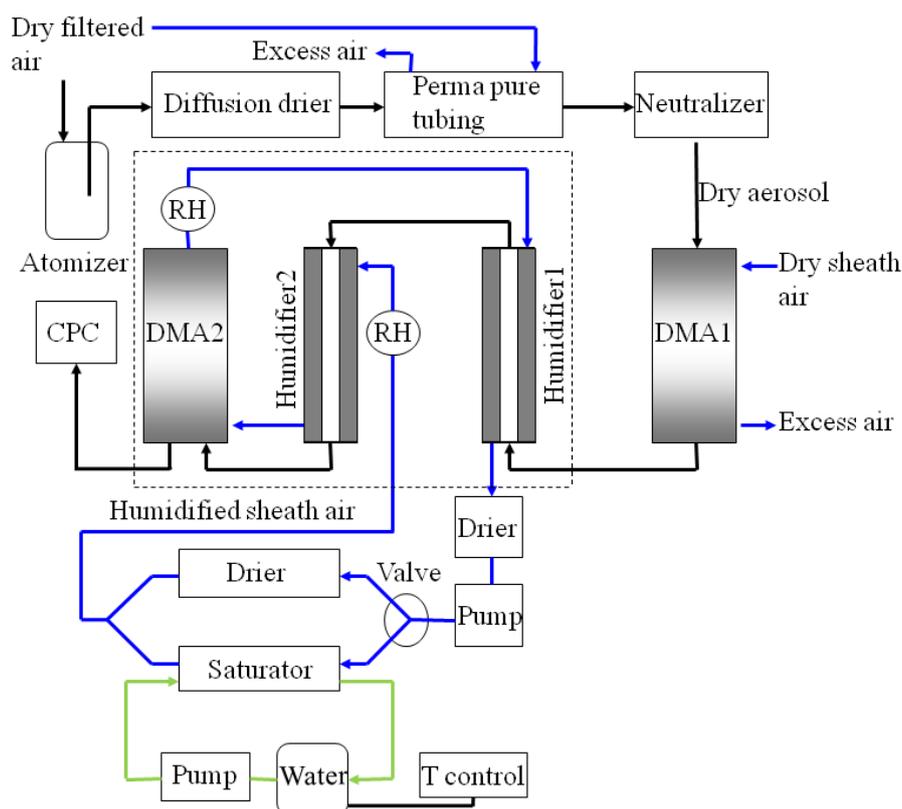
1412 In this section techniques that can be employed to investigate hygroscopic properties of  
1413 airborne aerosol particles and can also be deployed for field measurements are reviewed. We  
1414 discuss in Section 5.1 humidity-tandem differential mobility analysers which measure mobility  
1415 diameter change of aerosol particles upon humidity change. Hygroscopic growth would further  
1416 lead to change in aerosol optical properties, which can be measured to infer aerosol  
1417 hygroscopicity, as reviewed in Section 5.2. In Section 5.3 we discuss in brief a few techniques  
1418 developed to explore hygroscopic properties of black carbon aerosol in specific.

### 1419 **5.1 Humidity-tandem differential mobility analyser (H-TDMA)**

#### 1420 **5.1.1. Basic H-TDMA**

1421 The tandem differential mobility analyser (TDMA) was pioneered in 1978 and called the  
1422 aerosol mobility chromatograph at that time (Liu et al., 1978). The terminology “TDMA” was  
1423 first introduced in 1986 in a study (Rader and McMurry, 1986) which showed that size change  
1424 as small as 1% could be readily measured. In addition to size change due to humidification  
1425 (humidity-TDMA), TDMA can also be used to measure particle size change due to other  
1426 processing such as heating (Bilde et al., 2015a). H-TDMA is probably the most widely used  
1427 technique for aerosol hygroscopicity measurement in both laboratory (Gibson et al., 2006;  
1428 Herich et al., 2009; Koehler et al., 2009; Wex et al., 2009b; Good et al., 2010b; Wu et al., 2011;  
1429 Hu et al., 2014; Lei et al., 2014; Gomez-Hernandez et al., 2016; Jing et al., 2016; Zieger et al.,  
1430 2017) and field studies (McMurry and Stolzenburg, 1989; Swietlicki et al., 2008; Ye et al.,

1431 2011; Ye et al., 2013; Wang et al., 2014b; Yeung et al., 2014b; Atkinson et al., 2015; Cheung  
 1432 et al., 2015; Wu et al., 2016; Sorooshian et al., 2017). There are a number of H-TDMAs  
 1433 developed and used by individual research groups, and all the instruments follow the same  
 1434 principle. Recently these instruments have also become commercially available, e.g., from  
 1435 Brechtel Manufacturing Inc. (Lopez-Yglesias et al., 2014) and MSP Corporation (Sarangi et  
 1436 al., 2019). Swietlicki et al. (2008) provided a good description of the operation principle, and  
 1437 discussed potential error sources for H-TDMA measurements; Duplissy et al. (2009) analyzed  
 1438 the result from an intercomparison of six different H-TDMAs and recommended guidelines for  
 1439 design, calibration, operation and data analysis for H-TDMAs. Below we describe in brief how  
 1440 a typical H-TDMA works.



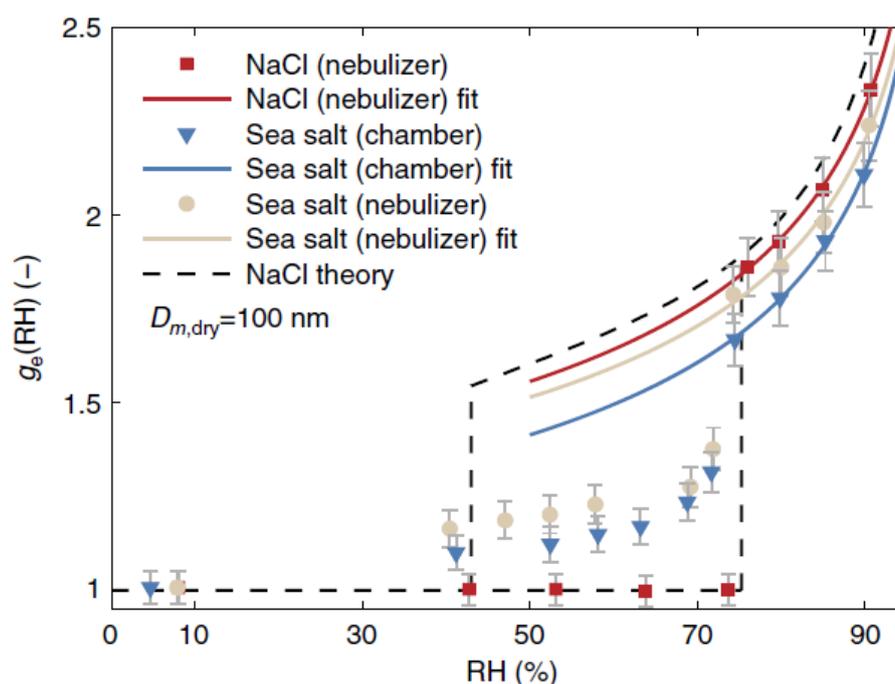
1441  
 1442 **Figure 19.** Schematic diagram of a typical H-TDMA instrument. Reprint with permission by  
 1443 Jing et al. (2016). Copyright 2016 Copernicus Publications.

1444

1445 As illustrated in Fig. 19, polydisperse ambient or laboratory-generated aerosol particles  
1446 were sampled through an aerosol dryer to reduce the RH to <15%, and the dry aerosol flow  
1447 was passed through a neutralizer and then the first DMA (DMA1) to generate quasi-  
1448 monodisperse aerosol particles. After that, the aerosol flow was delivered through a  
1449 humidification section to be humidified to a given RH, and aerosol particles exiting the  
1450 humidification section were monitored using the second DMA (DMA2) coupled with a  
1451 condensation particle counter (CPC) to provide number size distributions. The growth factor  
1452 (GF) is defined as the ratio of aerosol mobility diameter at a given RH to that at dry condition.  
1453 The raw H-TDMA data should be inverted to retrieve the actual growth factor probability  
1454 density function (Rader and McMurry, 1986; Gysel et al., 2009; Good et al., 2010a), and  
1455 currently the inversion algorithm developed by Gysel et al. (2009) is widely used. One major  
1456 uncertainty for H-TDMA measurements stems from the accuracy of RH in the second DMA,  
1457 and considerable efforts are needed to minimize the RH and temperature fluctuation (Swietlicki  
1458 et al., 2008; Duplissy et al., 2009; Massling et al., 2011; Lopez-Yglesias et al., 2014). The  
1459 residence time in the humidification section should exceed 10 s for aerosol particles to reach  
1460 the equilibrium under a given RH, while it should not be more than 40 s due to potential  
1461 evaporation of semi-volatile species (Chan and Chan, 2005; Duplissy et al., 2009). In addition,  
1462 it is important to check the H-TDMA performance via comparing the measured GF with  
1463 theoretical values for reference aerosol particles, such as  $(\text{NH}_4)_2\text{SO}_4$  and NaCl (Swietlicki et  
1464 al., 2008; Duplissy et al., 2009).

1465 In typical laboratory studies (Herich et al., 2009; Koehler et al., 2009; Jing et al., 2016;  
1466 Zieger et al., 2017), aerosol size is measured at different RH using the H-TDMA to get the RH-  
1467 dependent GF. Humidograms, in which GF are plotted as a function of RH, are shown in Fig.  
1468 20 for NaCl and synthetic sea salt aerosol particles, suggesting that at a given RH, GF of sea  
1469 salt aerosol is 8-15% smaller than NaCl aerosol (Zieger et al., 2017). Since both NaCl and

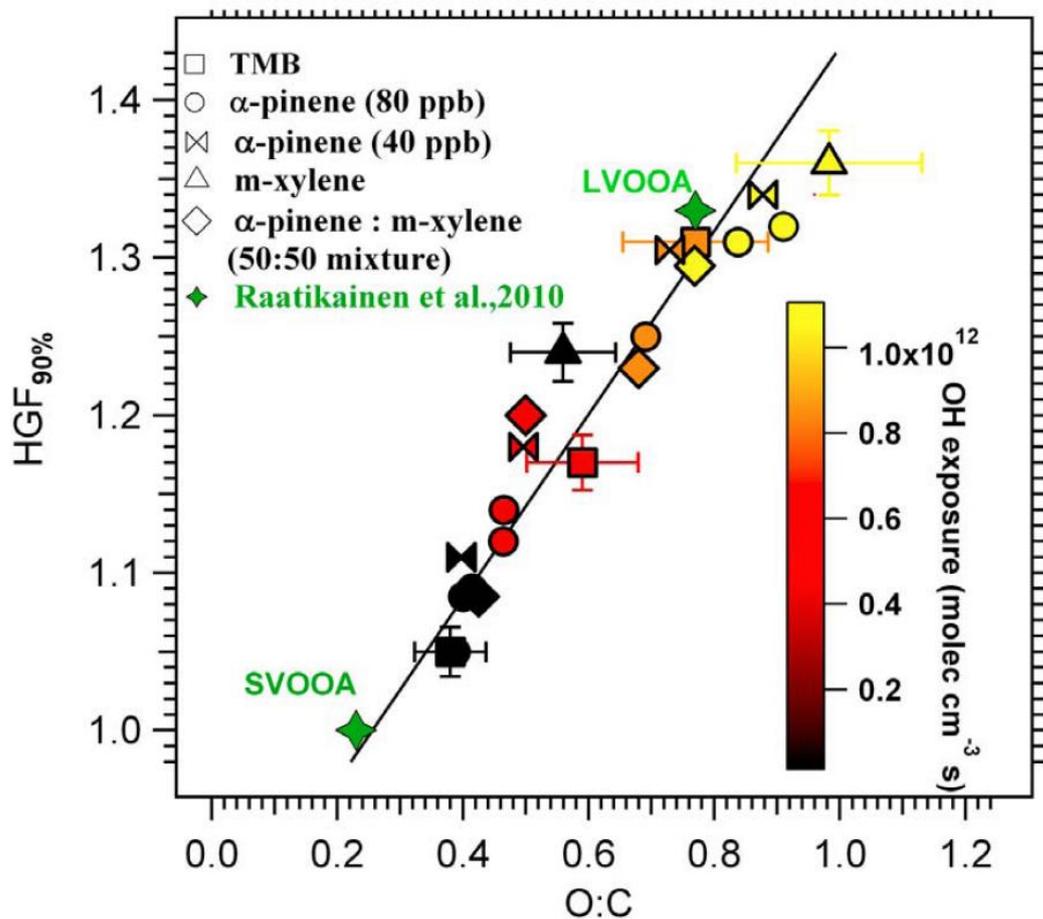
1470 synthetic sea salt aerosol particles are non-spherical under dry conditions, growth factors were  
 1471 reported after shape factor correction. The difference in GF between NaCl and synthetic sea  
 1472 salt aerosols was attributed to the presence of hydrates (such as the hydrates of  $MgCl_2$  and  
 1473  $CaCl_2$ ) with lower hygroscopicity (when compared to NaCl) in synthetic sea salt (Zieger et al.,  
 1474 2017).



1475  
 1476 **Figure 20.** Measured hygroscopic growth factors of NaCl and synthetic sea salt aerosol  
 1477 particles as different RH. NaCl aerosol particles were generated using a nebulizer, and both a  
 1478 nebulizer and a sea spray chamber were used to generate sea salt aerosol particles. Reprint with  
 1479 permission by Zieger et al. (2017). Copyright 2017 The Author(s).

1480  
 1481 H-TDMA has been widely used to investigate hygroscopic growth of secondary organic  
 1482 aerosol (Prenni et al., 2007; Duplissy et al., 2008; Wex et al., 2009a; Good et al., 2010b;  
 1483 Massoli et al., 2010; Duplissy et al., 2011; Alfarra et al., 2013; Zhao et al., 2016), which  
 1484 significantly contributed to submicrometer aerosol particles over the globe (Zhang et al., 2007).  
 1485 Using an aerosol flow tube, Massoli et al. (2010) generated secondary organic aerosols (SOA)

1486 via OH oxidation of  $\alpha$ -pinene, 1,3,5-trimethylbenzenen (TMB), m-xylene and a 50:50 mixture  
1487 of  $\alpha$ -pinene and m-xylene, and measured their hygroscopic growth at 90% RH using a H-  
1488 TDMA. As shown in [Fig. 21](#), measured GF at 90% RH ranged from 1.05 (non-hygroscopic) to  
1489 1.35 (moderately hygroscopic) for SOA systems examined, increasing linearly with O:C ratios  
1490 determined using an Aerodyne High Resolution Time-of-Flight Mass Spectrometer (Massoli  
1491 et al., 2010). In addition, for most SOA systems studied, single hygroscopicity parameters ( $\kappa$ )  
1492 derived from H-TDMA measurements were smaller than these derived from CCN activity  
1493 measurements (Massoli et al., 2010). Gaps between hygroscopic growth and cloud activation  
1494 have also been observed in a number of other studies for SOA (Prenni et al., 2007; Juranyi et  
1495 al., 2009; Petters et al., 2009; Wex et al., 2009a; Good et al., 2010b; Whitehead et al., 2014;  
1496 Zhao et al., 2016). One major reason for such gaps is that SOA usually contain substantial  
1497 amount of slightly soluble materials, which only undergo partial dissolution under water-  
1498 subsaturated conditions but can be dissolved to a significantly larger extent under water  
1499 supersaturated conditions (when more water is available). Further discussion on reconciliation  
1500 between hygroscopic growth and cloud activation can be found elsewhere (Petters et al., 2009;  
1501 Wex et al., 2009a). In another study (Li et al., 2014b), H-TDMA was used to explore  
1502 hygroscopic properties of SOA formed via OH oxidation and direct photolysis of  
1503 methoxyphenol (a model compound for biomass burning aerosol) in the aqueous phase. For  
1504 SOA generated from aqueous phase OH oxidation, GF at 90% RH was observed to increase  
1505 linearly with the O:C ratio, but the slope was around three times smaller than that reported by  
1506 Massoli et al. (2010).



1507

1508 **Figure 21.** Growth factors of SOA measured using a H-TDMA at 90% RH as a function of  
 1509 O:C ratios. Reprint with permission by Massoli et al. (2010). Copyright 2010 American  
 1510 Geophysical Union.

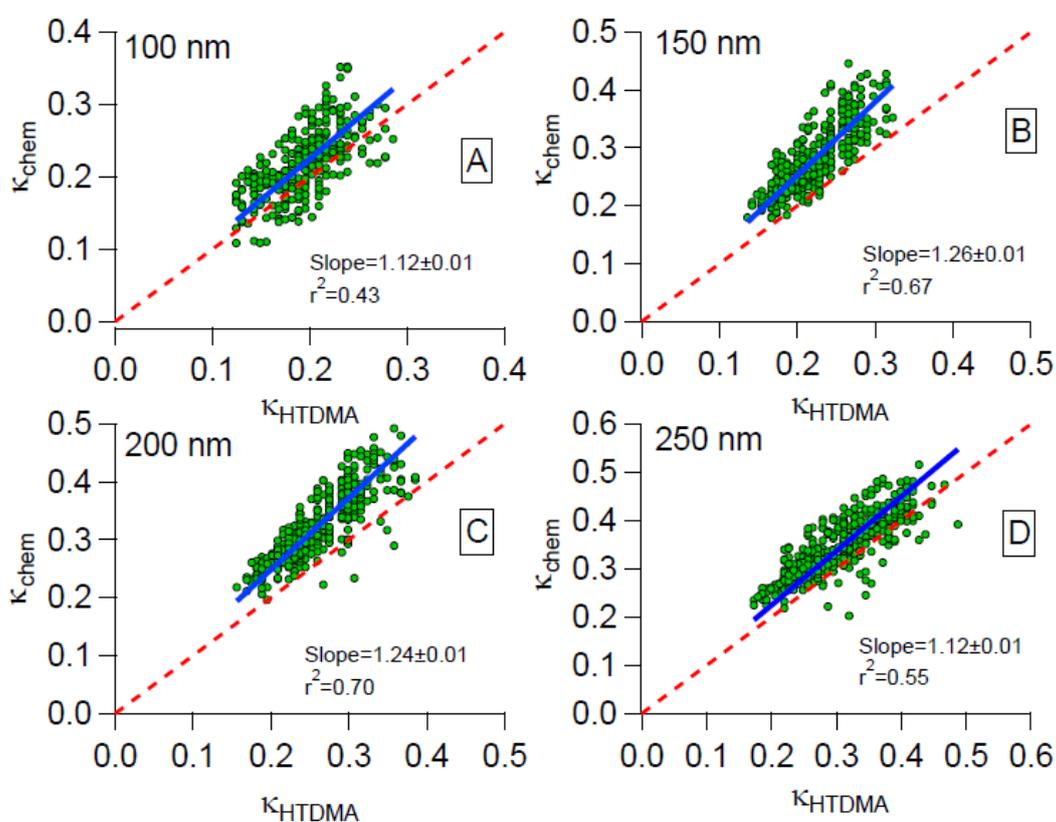
1511

1512 Since RH scanning is time-consuming, in most ambient applications H-TDMA  
 1513 measurements are usually carried out at a fixed RH (mostly 90%, and 85% to a less extent) for  
 1514 one or a few dry particle diameters (Swietlicki et al., 2008; Kreidenweis and Asa-Awuku, 2014;  
 1515 Cheung et al., 2015). Usually at least one diameter in the center of Aitken mode (~50 nm) and  
 1516 one size in the center of the accumulation mode (~150 nm) are selected (Swietlicki et al., 2008).  
 1517 The second DMA is typically scanned over a diameter range to cover a corresponding GF range  
 1518 between 0.9 and 2.0 (sometimes up to 2.5) at 90% RH (Swietlicki et al., 2008). However, there  
 1519 have been a few studies which measured GF of size-selected ambient aerosols as a function of

1520 RH (Santarpia et al., 2004; Cheung et al., 2015). For example, Cheung et al. (2015) measured  
1521 the GF of ambient aerosol particles (100 and 200 nm) as a function of RH (10-93 %) in Hong  
1522 Kong using a H-TDMA, and found that the derived  $\kappa$  values at (or above) 90% RH were  
1523 significantly larger than those derived at 40% RH. Each set of such measurements took ~3 h,  
1524 limiting its application to periods with large fluctuation in aerosol composition (Cheung et al.,  
1525 2015).

1526 To further understand hygroscopic properties of ambient aerosol particles, aerosol  
1527 hygroscopicity closure studies have been widely carried out (Swietlicki et al., 1999; Dick et al.,  
1528 2000; Gysel et al., 2007; Cerully et al., 2011; Wu et al., 2013; Wu et al., 2016; Schurman et al.,  
1529 2017; Hong et al., 2018). In such studies, hygroscopic growth measurements using H-TDMA  
1530 are concurrently performed with aerosol chemical composition measurements, and measured  
1531 growth factors can then be compared to these calculated based measured chemical composition.  
1532 Aerosol chemical compositions were usually measured offline in the early stage (Swietlicki et  
1533 al., 1999; Dick et al., 2000) and have been increasingly determined online with high time  
1534 resolution using aerosol mass spectrometry (Gysel et al., 2007; Wu et al., 2013) and single  
1535 particle mass spectrometry (Wang et al., 2014c; Li et al., 2018a). For example, Wu et al. (2013)  
1536 used a H-TDMA to measure aerosol hygroscopic growth at 90% RH and an Aerodyne High  
1537 Resolution Time-of-Flight Mass Spectrometer (HR-ToF-AMS) to measure size-resolved  
1538 aerosol chemical composition at a middle-level mountain area in central Germany. Single  
1539 hygroscopicity parameters,  $\kappa_{\text{htdma}}$ , derived from growth factors measured using H-TDMA, were  
1540 compared to those derived from aerosol composition ( $\kappa_{\text{chem}}$ ), assuming ideal mixing. If the  
1541 average compositions of submicron particles were used to calculate  $\kappa_{\text{chem}}$ , reasonably good  
1542 agreement between  $\kappa_{\text{htdma}}$  and  $\kappa_{\text{chem}}$  was found for 250 nm particles while no correlation was  
1543 observed for 100 nm particles (Wu et al., 2013). If size-resolved aerosol compositions were  
1544 used to calculate  $\kappa_{\text{chem}}$ , as shown in [Fig. 22](#), good closure between  $\kappa_{\text{chem}}$  and  $\kappa_{\text{htdma}}$  were found

1545 for all the four particle sizes. Fig. 22 also reveals that  $\kappa_{\text{chem}}$  were significantly larger than  $\kappa_{\text{htdma}}$ ,  
 1546 indicating that ideal mixing assumption may overestimate aerosol hygroscopic growth (Wu et  
 1547 al., 2013). Simultaneous H-TDMA and HR-ToF-AMS measurements were also carried out at  
 1548 a coastal suburban site in Hong Kong (Yeung et al., 2014a). Approximations for growth factors  
 1549 of organic aerosols, using the fraction of m/z 44, the oxygen-to-carbon ratio and PMF-resolved  
 1550 organic factors from HR-ToF-AMS measurements, did not yield better closure results, likely  
 1551 because of the overall dominance of sulfate during the whole measurement period.



1552  
 1553 **Figure 22.** Comparison between  $\kappa_{\text{chem}}$  (calculated using size-resolved aerosol compositions)  
 1554 and  $\kappa_{\text{htdma}}$  (derived from H-TDMA measurements) for aerosol particles with dry diameters of  
 1555 (a) 100, (b) 150, (c) 200 and (d) 250 nm. Reprint with permission by Wu et al. (2013).  
 1556 Copyright 2013 Copernicus Publications.

1557

1558 H-TDMA measurements in Shanghai at wintertime showed that aerosol particles (250 nm  
1559 in dry diameter) could be classified into two modes according to their hygroscopicity (Wang  
1560 et al., 2014b). The first mode had growth factors of ~1.05 at 85% RH, mainly containing fresh  
1561 elemental carbon and minerals, as revealed by measurements using a single particle mass  
1562 spectrometer (Aerosol Time-of-Flight mass spectrometer). In contrast, the second mode had  
1563 growth factors of ~1.46 at 85% RH and were enriched with elemental carbon and organic  
1564 carbon particles internally mixed with secondary inorganic materials.

### 1565 **5.1.2 H-TDMAs with extended performance**

1566 While most H-TDMAs only work at around room temperature, Weingartner et al. (2002)  
1567 designed a H-TDMA which could measure hygroscopic growth of aerosol particle below 0 °C  
1568 (temperature: -20 to 30 °C; RH: 10-90 %). Measured hygroscopic growth factors showed good  
1569 agreement with theoretical calculations for (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NaCl and NaNO<sub>3</sub> at both 20 and -10 °C  
1570 (Gysel et al., 2002). This instrument was subsequently deployed at a high-alpine site (3580 m  
1571 above the seal level) to investigate hygroscopic properties of ambient aerosol particles at -10 °C  
1572 (Weingartner et al., 2002), and the average GF at 85% RH were measured to be 1.44, 1.49 and  
1573 1.53 for aerosol particles with dry diameters of 50, 100 and 250 nm.

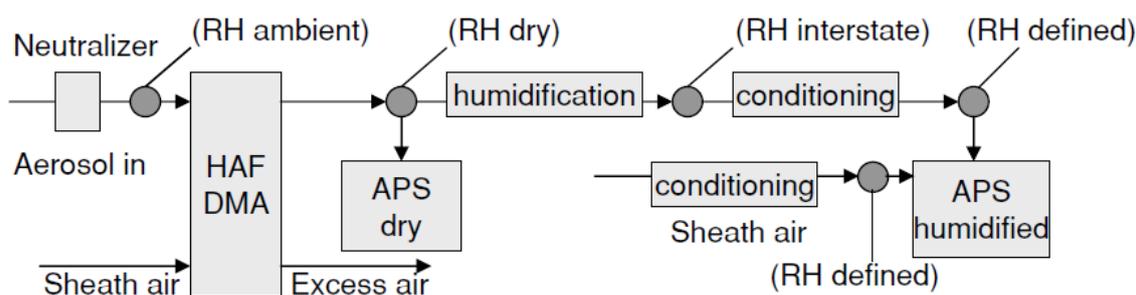
1574 RH in the troposphere frequently exceeds 90%, and it is desirable to investigate  
1575 hygroscopic growth of aerosol particles at >90% RH. Hennig et al. (2005) developed a high  
1576 humidity TDMA which could be operated at 98% RH, and the absolute accuracy of RH at 98%  
1577 was ±1.2%. It was found that within the uncertainties, the measured GF in the RH range of 84-  
1578 98% agreed well with theoretical values (Hennig et al., 2005). The Leipzig Aerosol Cloud  
1579 Interaction Simulator (LACIS), a laminar flow tube designed to study cloud formation and  
1580 growth, could be operated at stable RH ranging from almost 0% up to 99.1% (Stratmann et al.,  
1581 2004), and aerosol particles and/or droplets exiting the flow tube were detected using an optical  
1582 particle sizer especially developed for this instrument. LACIS was employed to study

1583 hygroscopic growth of  $(\text{NH}_4)_2\text{SO}_4$  and NaCl aerosol particles at 85.8-99.1% RH (Wex et al.,  
1584 2005). At 99% RH, measured GF values agreed well with these predicted assuming solution  
1585 ideality for NaCl; whereas for  $(\text{NH}_4)_2\text{SO}_4$ , solution ideality assumption would overestimate GF  
1586 values by up to 20% (Wex et al., 2005). In a following study (Niedermeier et al., 2008), LACIS  
1587 was used to investigate hygroscopic growth of sea salt aerosol up to 99.1% RH.

1588       Long duration is required by the second DMA to measure size distributions of humidified  
1589 aerosol particles, and therefore the H-TDMA technique is usually quite slow. It typically takes  
1590 ~30 min for a traditional H-TDMA to determine GF values at a given RH for five different dry  
1591 diameters (Cerully et al., 2011; Pinterich et al., 2017b). Instruments with fast duty cycles are  
1592 of great interest and have been developed and deployed (Sorooshian et al., 2008; Pinterich et  
1593 al., 2017a; Pinterich et al., 2017b). For example, after replacing the second DMA (used in the  
1594 traditional H-TDMA) with a water-based fast integrated mobility spectrometer which could  
1595 provide 1 Hz size distribution measurements (Pinterich et al., 2017a), the improved instrument,  
1596 called the humidity-controlled fast integrated mobility spectrometer (HFIMS), only took ~3  
1597 min to measure GF of particles with five different dry diameters at a given RH (Pinterich et al.,  
1598 2017b).

1599       Since the upper size limit is <1000 nm for a typical DMA and GF values at 90% RH can  
1600 be >2 for atmospheric particles, most H-TDMAs can only be used for particles with dry  
1601 diameters smaller than 500 nm (McFiggans et al., 2006; Swietlicki et al., 2008). Several  
1602 instruments, which could measure hygroscopic growth of aerosol particles larger than 500 nm  
1603 in dry diameter, have been developed (Kreisberg et al., 2001; Hegg et al., 2007; Massling et  
1604 al., 2007; Snider and Petters, 2008; Kaaden et al., 2009; Kim et al., 2014). One obvious  
1605 approach to overcome the DMA sizing limit is to use optical particle counters for particle sizing,  
1606 as adopted by some previous studies (Kreisberg et al., 2001; Hegg et al., 2007; Snider and  
1607 Petters, 2008). Another approach is to use Aerodynamic Particle Sizers (APS) for particle

1608 sizing (Massling et al., 2007; Kaaden et al., 2009; Schladitz et al., 2011; Kim and Park, 2012).  
 1609 For example, a H-DMA-APS was developed to explore hygroscopic growth of large aerosol  
 1610 particles (Massling et al., 2007; Kaaden et al., 2009). As shown in Fig. 23, the dry aerosol flow  
 1611 was first delivered through a custom-built high aerosol flow-DMA (HAF-DMA) which could  
 1612 select particles with dry mobility diameters over 1000 nm, and the dry aerosol flow exiting the  
 1613 DMA was split into two identical flows; the first flow was directly sampled by the first APS to  
 1614 measure the aerodynamic size distribution under dry conditions, and the second flow was first  
 1615 delivered through a humidifier to be humidified to a given RH (e.g., 90%) and then sampled  
 1616 into the second APS so that the aerodynamic size distribution of the humidified aerosol was  
 1617 measured.



1618  
 1619 **Figure 23.** Schematic diagram of a H-DMA-APS apparatus. Reprint with permission by  
 1620 Kaaden et al. (2009). Copyright 2009 Blackwell Munksgaard.

1621  
 1622 The utilization of H-TDMAs to measure aerosol hygroscopic growth factors assumes  
 1623 particle sphericity. Some particles in the atmosphere, such as mineral dust and soot, are known  
 1624 to be non-spherical, and therefore GF measured using H-TDMA may not correctly reflect the  
 1625 amount of aerosol liquid water (Weingartner et al., 1997; Rissler et al., 2005; Vlasenko et al.,  
 1626 2005; Koehler et al., 2009; Tritscher et al., 2011). Very recently an instrument, called  
 1627 differential mobility analyser-humidified centrifugal particles mass analyser (DMA-HCPMA),  
 1628 was developed to measure mass change of submicron aerosol particles at different RH (10-  
 1629 95 %) (Vlasenko et al., 2017). In this set-up, a dry aerosol flow was delivered through a DMA

1630 to produce quasi-monodisperse particles and then through an aerosol humidifier to be  
1631 humidified to a give RH; after that, the aerosol flow was delivered through a centrifugal particle  
1632 mass analyser (which would classify aerosol particles according to their mass-to-charge ratios)  
1633 (Olfert and Collings, 2005; Rissler et al., 2014; Kuwata, 2015) and then a CPC so that aerosol  
1634 particle mass could be determined as a function of RH (Vlasenko et al., 2017). The measured  
1635 mass growth factors were found to agree well with theoretical values for  $(\text{NH}_4)_2\text{SO}_4$  and NaCl,  
1636 and this newly-developed DMA-HCPMA set-up was successfully deployed to explore  
1637 hygroscopic properties of ambient aerosol particles (Vlasenko et al., 2017). It can be expected  
1638 that DMA-HCPMA would significantly improve our knowledge of hygroscopicity of non-  
1639 spherical aerosol particles.

## 1640 **5.2 Optical properties**

1641 Optical properties of aerosol particles depend on their size and refractive indices, both  
1642 strongly affected by their hygroscopic properties. Measurements of aerosol optical properties  
1643 as a function of RH, indispensable for elucidating the impacts of aerosol particles on visibility  
1644 and radiative balance, can be used to infer aerosol hygroscopicity. Several techniques have  
1645 been developed and deployed, as discussed in this section.

### 1646 **5.2.1 Extinction**

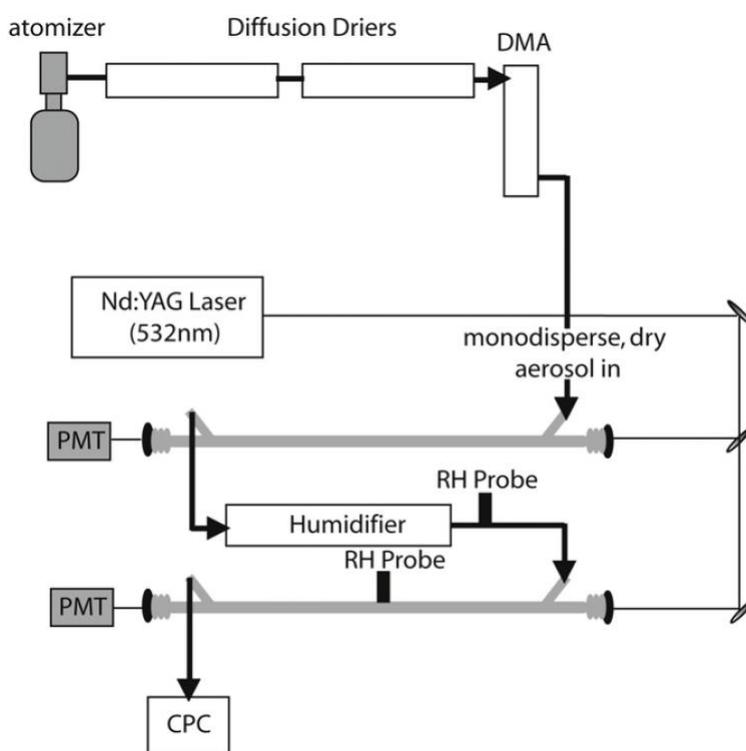
1647 Cavity ring-down spectroscopy (CRDS), a highly sensitive method for optical extinction  
1648 measurement, has been extensively employed for gas and aerosol detection (Brown, 2003;  
1649 Baynard et al., 2006; Baynard et al., 2007; Langridge et al., 2011; Sobanski et al., 2016; Peng  
1650 et al., 2018). For a typical CRDS set-up, a laser beam pulse is coupled into a high-finesse  
1651 optical cavity (which has one high reflectivity mirror on each end) from one end of the cavity,  
1652 and the decay of the intensity of the light transmitted from the other end is monitored. The  
1653 change in decay lifetimes of transmitted light intensity can be related to the extinction  
1654 coefficient,  $\alpha_{\text{ext}}$ , using Eq. (3) (Baynard et al., 2007; Langridge et al., 2011):

1655 
$$\alpha_{ext} = \frac{R_L}{c} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right) \quad (3)$$

1656 where  $R_L$  is the ratio of the distance between the two mirrors to the length of the cavity filled  
 1657 with aerosol particles,  $c$  is the speed of light ( $\text{m s}^{-1}$ ), and  $\tau$  and  $\tau_0$  are the measured decay  
 1658 lifetimes of light intensity with and without aerosol particles present in the cavity. If aerosol  
 1659 particles delivered into the cavity are monodisperse, the extinction coefficient of each  
 1660 individual particles,  $\sigma_{ext}$ , can be calculated using Eq. (4) (Freedman et al., 2009):

1661 
$$\sigma_{ext} = \frac{\alpha_{ext}}{N_p} \quad (4)$$

1662 where  $N_p$  is the aerosol number concentration ( $\text{cm}^{-3}$ ).



1663  
 1664 **Figure 24.** Schematic diagram of the apparatus used by Tolbert and co-workers to measure the  
 1665 dependence of aerosol light extinction on RH. Reprint with permission by Beaver et al. (2008).  
 1666 Copyright 2008 IOP Publishing Ltd.

1667  
 1668 A CRD spectrometer was employed by Tolbert and co-workers to investigate the effects  
 1669 of RH on aerosol optical extinction at 532 nm, and its schematic diagram is depicted in [Fig. 24](#)

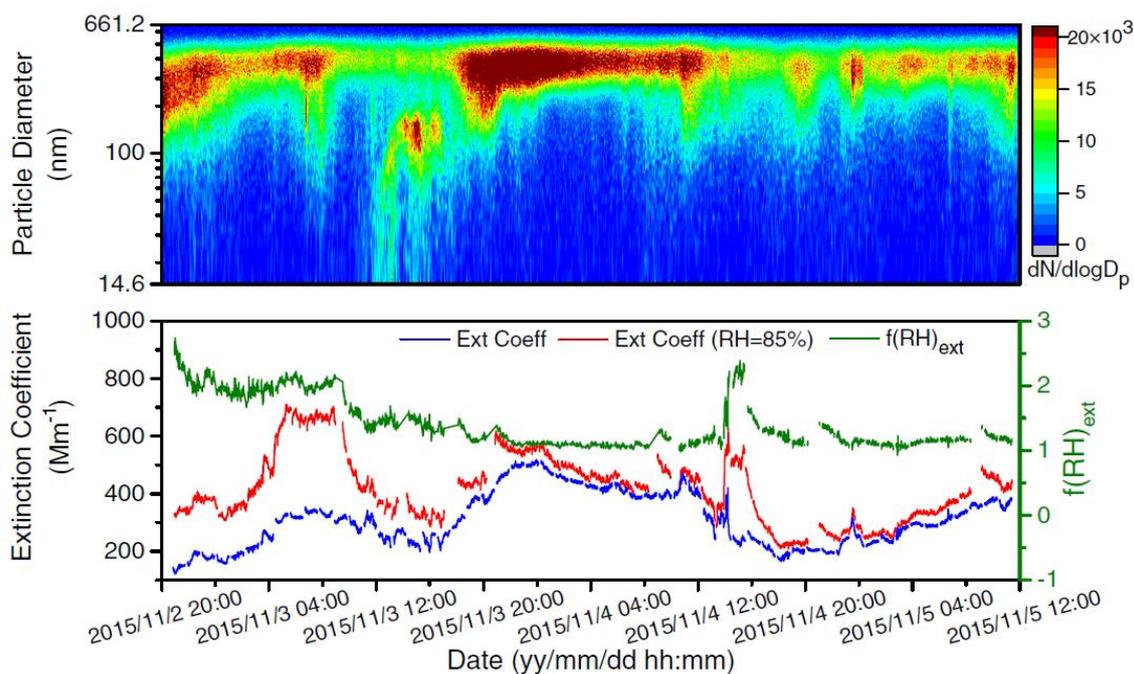
1670 (Beaver et al., 2008). The aerosol flow generated using an atomizer was delivered through  
1671 diffusion dryers to reduce its RH to <10% and passed through a DMA to produce quasi-  
1672 monodisperse aerosol particles. The aerosol flow was then delivered into the first cavity to  
1673 measure the aerosol optical extinction at 532 nm under dry conditions; after that, the aerosol  
1674 flow entered a humidifier to be humidified to a given RH, and was then delivered into the  
1675 second cavity to measure the aerosol optical extinction under the humidified condition. In the  
1676 final, the aerosol flow was sampled by a CPC to measure the number concentration. For  
1677  $(\text{NH}_4)_2\text{SO}_4$  aerosol particles in the size range of 200-700 nm, the measured optical growth  
1678 factors at 80% RH, defined as the ratio of the extinction coefficient at 80% RH to that under  
1679 dry conditions, were found to be in good agreement with those calculated from diameter-based  
1680 growth factors using the Mie theory (Garland et al., 2007).

1681 CRDS was used to examine the effect of RH on aerosol optical extinction for phthalic  
1682 acid, pyromellitic acid and 4-hydroxybenzoic acid aerosol particles in the size range of 150-  
1683 500 nm (Beaver et al., 2008). The optical growth factors were found to be smaller for the three  
1684 organic compounds examined, compared to  $(\text{NH}_4)_2\text{SO}_4$ . For example, for aerosol particles with  
1685 a dry diameter of 335 nm, optical growth factors at 80% RH were measured to be 1.3 and 1.1  
1686 for phthalic and pyromellitic acid (Beaver et al., 2008), compared to 3.0 for  $(\text{NH}_4)_2\text{SO}_4$ . Optical  
1687 extinction coefficients of 4-hydroxybenzoic acid particles at 80% RH were smaller than those  
1688 under dry conditions (Beaver et al., 2008), implying that morphological and structural change  
1689 may occur for these particles during humidification. Similarly, optical growth factors of illite  
1690 and kaolinite aerosol particles were found to be <1 at 50 and 68% RH (Attwood and Greenslade,  
1691 2011), due to structural rearrangement of clay mineral particles after water uptake. Optical  
1692 growth factors of internally mixed aerosol particles, which contained  $(\text{NH}_4)_2\text{SO}_4$  and organic  
1693 materials, were also studied (Garland et al., 2007; Robinson et al., 2013; Robinson et al., 2014).  
1694 Another study (Flores et al., 2012) measured optical growth factors (at wavelengths of 355 and

1695 532 nm) at 80 and 90% RH for aerosol particles with different extent of optical absorption  
1696 ranging from purely scattering (e.g.,  $(\text{NH}_4)_2\text{SO}_4$ ) to highly absorbing (e.g., nigrosine), and  
1697 found good agreement between measured optical growth factors and those calculated using the  
1698 Mie theory.

1699 CRDS has also been widely deployed to investigate optical extinction of ambient aerosol  
1700 particles at different RH (Zhang et al., 2014b; Atkinson et al., 2015; Brock et al., 2016a). For  
1701 example, an eight-channel CRD spectrometer was developed by NOAA Earth System  
1702 Research Laboratory (Langridge et al., 2011). This instrument could measure aerosol optical  
1703 growth factors at three wavelengths (405, 532 and 662 nm) simultaneously, and has been  
1704 successfully deployed for aircraft measurements (Langridge et al., 2011).

1705 In addition to CRDS, broadband cavity enhanced spectroscopy (BBCEAS), also called  
1706 cavity enhanced differential optical absorption spectroscopy (CE-DOAS), is an alternative  
1707 high-finesse cavity based technique with high sensitivity in optical extinction measurements  
1708 (Platt et al., 2009; Washenfelder et al., 2013; Washenfelder et al., 2016). Compared to CRDS,  
1709 one major advantage of BBCEAS is that optical extinction can be measured as a function of  
1710 wavelength. BBCEAS, as described in details elsewhere (Platt et al., 2009; Varma et al., 2013;  
1711 Washenfelder et al., 2013; Zhao et al., 2014; Washenfelder et al., 2016; Wang et al., 2017a; Li  
1712 et al., 2018b), has also been widely used in gas and aerosol measurements. Zhao et al. (2014)  
1713 utilized BBCEAS to measure aerosol optical extinction at 641 nm as a function of RH, and for  
1714 200 nm  $(\text{NH}_4)_2\text{SO}_4$ , the measured optical growth factors agreed well with those calculated  
1715 using the Mie theory. The instrument was further deployed to simultaneously measure optical  
1716 extinction of ambient submicrometer aerosol at <20% and 85% RH at Hefei Radiation  
1717 Observatory. The result is displayed in [Fig. 25](#), suggesting that the optical growth factors at 85%  
1718 RH varied from ~1 to >2.5 during the campaign (Zhao et al., 2017).



1719

1720 **Figure 25.** Aerosol properties measured at Hefei Radiation Observatory. Upper panel: aerosol  
 1721 number size distribution of submicrometer particles; lower panel: extinction coefficient of  
 1722 submicrometer particles under dry conditions (blue curve, left y-axis) and at 85% RH (red curve,  
 1723 left y-axis) and optical growth factors at 85% RH (green curve, right y-axis). Reprint with  
 1724 permission by Zhao et al. (2017). Copyright 2017 Optical Society of America.

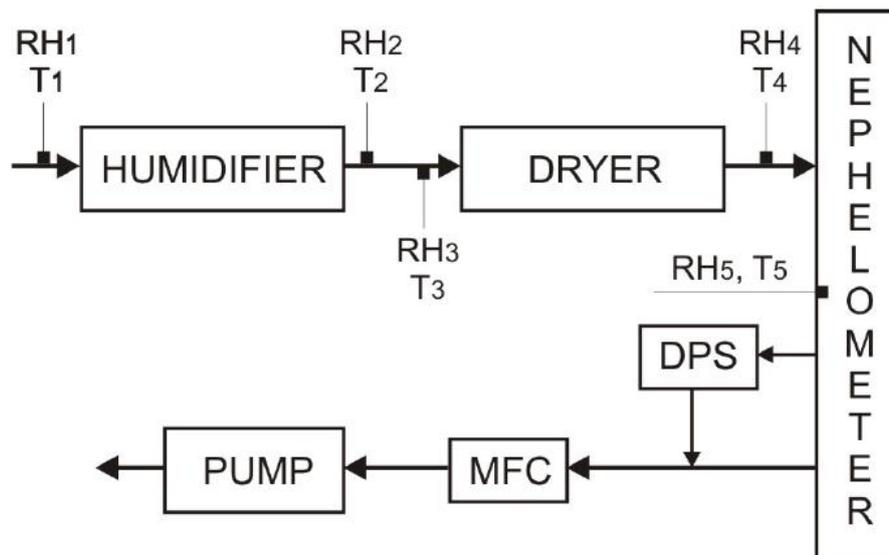
1725

### 1726 5.2.2 Scattering

1727 Humidified nephelometry, which was first developed as early as in the 1960s (Pilat and  
 1728 Charlson, 1966; Covert et al., 1972), has been widely used to measure aerosol light scattering  
 1729 coefficients at different RH (Rood et al., 1985; Carrico et al., 1998; Li-Jones et al., 1998; Day  
 1730 et al., 2000; Malm et al., 2000b; Malm et al., 2000a; Koloutsou-Vakakis et al., 2001; Fierz-  
 1731 Schmidhauser et al., 2010a; Zieger et al., 2010; Zieger et al., 2013; Kreidenweis and Asa-  
 1732 Awuku, 2014; Zhang et al., 2015; Titos et al., 2016). Due to its high time resolution, this  
 1733 technique is very suitable for online measurement of ambient aerosols. A very recent review  
 1734 paper (Titos et al., 2016) summarized and discussed theories, history, measurement  
 1735 uncertainties and ambient applications of this technique in a comprehensive manner. As a result,

1736 herein we only introduce in brief its basic principle, representative instrumental configurations  
1737 and exemplary applications.

1738 The scattering enhancement factor,  $f(\text{RH})$ , defined as the ratio of the aerosol scattering  
1739 coefficient at a given RH to that at dry conditions, is typically reported by humidified  
1740 nephelometry measurements (Kreidenweis and Asa-Awuku, 2014; Titos et al., 2016). Fig. 26  
1741 shows the schematic diagram of a humidified three-wavelength integrating nephelometer (TSI  
1742 3563) at 450, 550 and 700 nm (Fierz-Schmidhauser et al., 2010c). The aerosol flow was first  
1743 delivered through an aerosol humidifier which could increase the RH to 95% and then through  
1744 an aerosol dryer to reduce the RH to below 40%. After that, the aerosol flow was sampled into  
1745 the nephelometer to measure aerosol scattering coefficients at three different wavelengths. The  
1746 flow exiting the nephelometer was pulled through a mass flow controller (to control the sample  
1747 flow rate) by a pump. The performance of the aerosol dryer could be adjusted to vary the RH  
1748 of the flow entering the nephelometer, and thus scattering coefficients could be measured as a  
1749 function of RH (40-90 %); in addition, using such a configuration, light scattering properties  
1750 of supersaturated aerosol particles, i.e. the hysteresis effect, could be examined (Fierz-  
1751 Schmidhauser et al., 2010c). The humidified nephelometer was used to measure light scattering  
1752 properties of monodisperse  $(\text{NH}_4)_2\text{SO}_4$  and NaCl aerosol particles with dry diameters of 100,  
1753 150, 240 and 300 nm, and the measured  $f(\text{RH})$  values agreed with these predicted using Mie  
1754 theory (Fierz-Schmidhauser et al., 2010c). Some instruments could measure aerosol light  
1755 scattering at different RH in a simultaneous manner, via using two or more nephelometers in  
1756 parallel (Carrico et al., 1998).



1757

1758 **Figure 26.** Schematic diagram of a humidified three-wavelength integrating nephelometer  
 1759 (DPS: dew point sensor; MFC: mass flow controller). Reprint with permission by  
 1760 Schmidhauser et al. (2010c). Copyright 2010 Copernicus Publications.

1761

1762 A number of previous studies have carried out field measurements of  $f(\text{RH})$  at various  
 1763 locations over the globe (Zieger et al., 2013; Kreidenweis and Asa-Awuku, 2014; Titos et al.,  
 1764 2016). As summarized by Titos et al. (2016),  $f(\text{RH})$  values (for 80-85% RH) were larger for  
 1765 marine sites (ranging from 1.5 to 3.5), when compared with most continental sites; furthermore,  
 1766  $f(\text{RH})$  values were found to be in the range of 1.1-2.1 for dust particles, and larger  $f(\text{RH})$  values  
 1767 observed for dust may be caused by the co-presence of sea salt aerosol. A field study (Li-Jones  
 1768 et al., 1998) carried out on Barbados (West Indies) found that  $f(\text{RH})$  values (for RH in the range  
 1769 of 67-83%) were very small (1.0-1.1) for mineral dust transported from North Africa,  
 1770 indicating that large variation in ambient RH may not lead to significant change in optical  
 1771 properties of mineral dust aerosol.

1772 Since aerosol light scattering coefficients depend on particle size and refractive index in  
 1773 a complex manner even for spherical particles, it is not straightforward to link  $f(\text{RH})$  with the  
 1774 aerosol liquid water content (Kreidenweis and Asa-Awuku, 2014). A number of studies (Malm

1775 and Day, 2001; Fierz-Schmidhauser et al., 2010b; Zieger et al., 2010; Chen et al., 2014;  
1776 Kreidenweis and Asa-Awuku, 2014; Kuang et al., 2017; Kuang et al., 2018) have discussed  
1777 how measured  $f(\text{RH})$  values could be used to derive single hygroscopicity parameters ( $\kappa$ )  
1778 (Petters and Kreidenweis, 2007) and aerosol liquid water contents. In addition, it should be  
1779 emphasized that humidity-dependent aerosol scattering coefficients (as well as aerosol  
1780 extinction and absorption coefficients) themselves are important parameters to assess the  
1781 impacts of aerosols on visibility and direct radiative forcing.

### 1782 **5.2.3 Absorption**

1783 Photoacoustic spectroscopy has been developed and deployed to measure aerosol optical  
1784 absorption in a direct manner (Arnott et al., 2003; Lack et al., 2009; Lewis et al., 2009;  
1785 Moosmuller et al., 2009; Gyawali et al., 2012; Langridge et al., 2013; Lack et al., 2014). In  
1786 brief, the aerosol flow is continuously sampled into a cell which serves as an acoustic resonator  
1787 section and illuminated by a modulated laser beam. The laser radiation absorbed by aerosol  
1788 particles is transferred to the surrounding air as heat, leading to the generation of acoustic wave  
1789 which is amplified in the resonator and detected using a microphone (Moosmuller et al., 2009;  
1790 Gyawali et al., 2012). The signal intensity measured by the microphone is proportional to  
1791 optical absorption and can be used to derive aerosol optical absorption coefficients after proper  
1792 calibration (Moosmuller et al., 2009; Gyawali et al., 2012). In principle, hygroscopic growth  
1793 of aerosol particles at elevated RH would lead to increase in particle size and thus enhancement  
1794 in aerosol optical absorption due to the lensing effect (Lewis et al., 2009). Nevertheless, several  
1795 studies suggested that photoacoustic spectroscopy measurements at high RH are likely to  
1796 significantly underestimate the actual aerosol optical absorption (Arnott et al., 2003; Lewis et  
1797 al., 2009; Langridge et al., 2013). For example, Langridge et al. (2013) used photoacoustic  
1798 spectroscopy at 532 nm to measure optical absorption of several types of aerosol particles with  
1799 various hygroscopicity, morphology and refractive indices, and found that the measured

1800 absorption exhibited strong low biases at high RH. The underestimation of optical absorption  
1801 is due to that acoustic signals are affected by evaporation of aerosol liquid water when aerosol  
1802 particles absorb radiation and get heated. As a result, Langridge et al. (2013) concluded that  
1803 photoacoustic spectroscopy was not a suitable technique to measure aerosol optical absorption  
1804 at elevated RH. Similarly, other techniques used for direct measurement of aerosol optical  
1805 absorption, such as the filter-based method and photothermal interferometry, did not perform  
1806 well at elevated RH either (Schmid et al., 2006; Sedlacek and Lee, 2007).

1807 An indirect method has been developed (Khalizov et al., 2009; Xue et al., 2009; Brem et  
1808 al., 2012; Chen et al., 2015) to explore the effect of RH on aerosol optical absorption, which  
1809 was calculated as the difference between aerosol light extinction and scattering. In the set-up  
1810 developed by Brem et al. (2012), aerosol light extinction and scattering at three wavelengths  
1811 (467, 530 and 660 nm) were measured at different RH using an optical extinction cell and a  
1812 nephelometer. As RH was increased from 38 to 95%, light absorption of nigrosine aerosol was  
1813 enhanced by a factor of  $\sim 1.24$  for all the three wavelengths (Brem et al., 2012). In some other  
1814 work (Khalizov et al., 2009; Xue et al., 2009; Chen et al., 2015), CRDS, instead of the optical  
1815 extinction cell, was used to measure the aerosol optical extinction.

### 1816 **5.3 Other aerosol-based techniques**

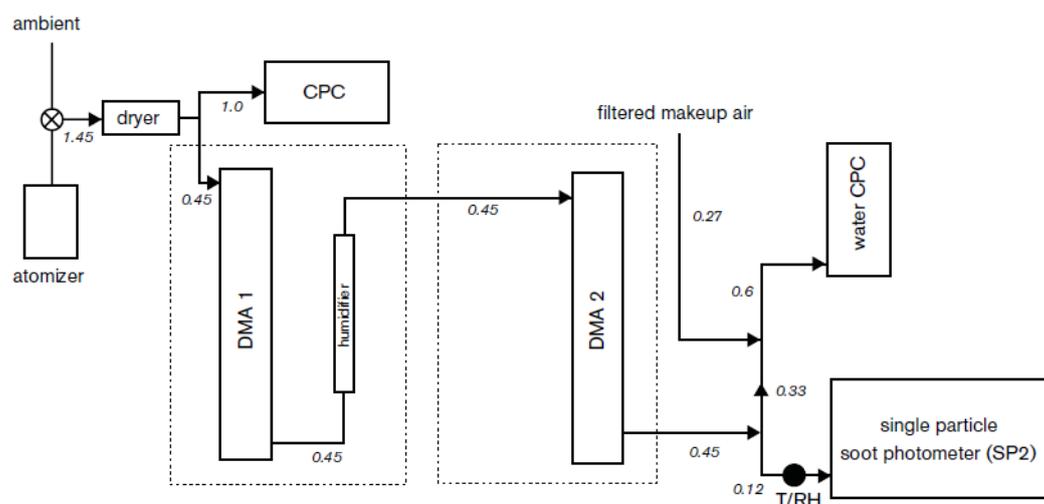
1817 Black carbon (BC) aerosol is of great concern due to its impacts on human health and  
1818 climate (Bond et al., 2013). The hygroscopicity of BC, varying with atmospheric aging  
1819 processes, largely determines its dry and wet deposition rates and thus lifetimes (Schwarz et  
1820 al., 2010; Wang et al., 2014a) and also affects its optical absorption through lensing effects  
1821 (Redemann et al., 2001). Therefore, it is important to understand hygroscopic properties of BC  
1822 aerosol in the troposphere; however, techniques discussed in Sections 5.1-5.2 are not specific  
1823 to BC-containing particles. Since typical BC mass fractions in submicrometer particles are only

1824 a few percentages, in general these techniques cannot provide specific information on ambient  
1825 BC aerosol hygroscopicity.

1826 Single particle soot photometers (SP2), as described in a number of studies (Gao et al.,  
1827 2007; Slowik et al., 2007; Schwarz et al., 2008; Moteki and Kondo, 2010), have been widely  
1828 employed to measure mass and mixing state of individual BC particles in the troposphere. In  
1829 brief, when an aerosol particle which contains a detectable amount of refractory BC enters a  
1830 SP2, it is heated by a laser beam (1064 nm) to the incandescence temperature, leading to the  
1831 emission of thermal radiation. The intensity of the thermal radiation, proportional to the mass  
1832 of refractory BC, is monitored to quantify the amount of BC contained by individual particles.  
1833 In addition, measurement of the light scattered by the particle during its initial interaction with  
1834 the laser beam can be used to derive the optical diameter. Therefore, a SP2 measures both the  
1835 mass of non-refractory BC and the optical diameter of each individual particles. In the last  
1836 several year a few SP2-based instruments have been developed to measure hygroscopic  
1837 properties of BC aerosol in specific (McMeeking et al., 2011; Liu et al., 2013a; Schwarz et al.,  
1838 2015; Ohata et al., 2016), as introduced below.

1839 A SP2 was coupled to a H-TDMA to measure hygroscopic properties of BC aerosol  
1840 (McMeeking et al., 2011), and the experimental diagram is displayed in [Fig. 27](#). The aerosol  
1841 flow was dried to <20% RH and then passed through the first DMA to produce quasi-  
1842 monodisperse aerosol with a specific size; after that, the aerosol flow was humidified to a  
1843 specific RH and then passed through the second DMA. The aerosol flow exiting the second  
1844 DMA was then split to two flows, sampled by a CPC and a SP2, respectively. The usage of  
1845 SP2 enabled identification of BC aerosol particles, and mobility diameter changes of aerosol  
1846 particles identified to be BC could be used to calculate hygroscopic growth factors specific to  
1847 BC aerosol; alternatively, hygroscopic properties of BC aerosol could be obtained from the  
1848 change in optical diameter measured by the SP2 (McMeeking et al., 2011). The H-TDMA-SP2

1849 apparatus was deployed to investigate hygroscopic properties of BC aerosol in June-July 2011  
 1850 at the Weybourne Atmospheric Observatory near the North Norfolk coastline. During this  
 1851 campaign two types of BC aerosol with distinctive hygroscopicity were observed (Liu et al.,  
 1852 2013a). Hygroscopic growth factors at 90% RH were measured to be  $\sim 1.05$  for the first type  
 1853 BC aerosol and ranged from  $\sim 1.25$  to  $\sim 1.6$  for the second type, depending on the composition  
 1854 of soluble materials associated with BC particles (Liu et al., 2013a).



1855  
 1856 **Figure 27.** Schematic diagram of the H-TDMA-SP2 apparatus. Flow rates shown in this figure  
 1857 are in the unit of L/min. Reprint with permission by McMeeking et al. (2011). Copyright 2011  
 1858 Copernicus Publications.

1859  
 1860 Schwarz et al. (2015) developed a humidified-dual SP2 setup (HD-SP2) to measure  
 1861 hygroscopic properties of BC aerosol. In this set-up, one sample flow was dried, and optical  
 1862 diameters of each BC-containing particles were measured under dry conditions using the first  
 1863 SP2; the other sample flow was first humidified to a given RH (e.g., 90%), and optical  
 1864 diameters of individual BC-containing particles were determined using the second SP2. Optical  
 1865 diameters of BC particles measured under dry and humidified conditions could then be used to  
 1866 determine hygroscopic properties specific to BC-containing particles. The HD-SP2 was  
 1867 deployed on the NASA DC-8 aircraft in the summer of 2013 to investigate hygroscopic

1868 properties of BC aerosol in North American wildfire plumes (Perring et al., 2017). An average  
1869  $\kappa$  value of 0.04 was found for the sampled BC aerosol, and was increased by  $\sim 0.06$  after 40 h  
1870 aging in the atmosphere (Perring et al., 2017).

1871 In another study (Ohata et al., 2016), an aerosol particle mass analyser (APM) was coupled  
1872 to a humidified SP2 to investigate hygroscopic properties of BC aerosol. The experimental  
1873 scheme employed can be summarized as below (Ohata et al., 2016): (i) the sample flow, dried  
1874 to  $<10\%$  RH, was delivered through an APM to select particles with a given mass-to-charge  
1875 ratio (with identical mass if multiple charged particles were excluded in data analysis); (ii) the  
1876 aerosol flow exiting the APM was humidified to a given RH and sampled into a SP2 to measure  
1877 optical diameters of BC-containing particles under humidified conditions. Since dry diameters  
1878 of BC-containing particles could be calculated from the mass of particles selected using the  
1879 APM, hygroscopic growth factors of BC aerosol could be consequently determined (Ohata et  
1880 al., 2016).

## 1881 **5.4 Discussion**

1882 All the techniques covered in Section 5 can be (and have been) used in laboratory and field  
1883 measurements. Since airborne particles are examined, aerosol water contents can be quantified  
1884 for unsaturated and supersaturated samples using these techniques. Because these techniques  
1885 rely on measurements of particle diameters to investigate hygroscopic properties, it can be non-  
1886 trivial to determine aerosol liquid water content for nonspherical aerosol particles. In addition,  
1887 they may not be sensitive enough to study water adsorption. Although in general these  
1888 techniques do not measure chemical compositions themselves, a number of offline and online  
1889 instruments, including advanced mass spectroscopic tools (e.g., aerosol mass spectrometers  
1890 and single particle mass spectrometers), are available to provide chemical information in  
1891 parallel, significantly deepening our knowledge of hygroscopic properties of complex aerosols.

## 1892 **6 Summary and final remarks**

1893 Hygroscopicity is one of the most important physiochemical properties of atmospheric  
1894 aerosols, largely determining their environmental and climatic impacts. In addition to  
1895 atmospheric science, it is also of great concern in many other scientific and technical fields,  
1896 such as surface science, heterogeneous catalysis, geochemistry/astrochemistry, pharmaceutical  
1897 and food science, and etc. A myriad of experimental techniques have been developed and  
1898 employed to explore hygroscopic properties of aerosol particles for  $RH < 100\%$ . In this paper  
1899 we have reviewed experimental techniques for investigating aerosol hygroscopicity in a  
1900 comprehensive manner.

1901 Table 1 summarizes key features of major techniques for aerosol hygroscopicity studies  
1902 so that one can get a quick overview of these techniques and understand roughly the advantages  
1903 and disadvantages of each technique. Several techniques discussed in Sections 2-5, such as  
1904 Knudsen cell reactors, Beta-gauge and TEOM, are not included in Table 1, because up to now  
1905 application of these techniques to investigate hygroscopic properties of atmospherically  
1906 relevant particles is still very limited, or because they are only applicable to certain types of  
1907 atmospheric particles. It is difficult to compare a number of techniques in a table, and our  
1908 opinions are arguable; in addition, technical advances may change the picture. For example,  
1909 conventional H-TDMA can only be used for aerosol particles less than 500 nm, and as  
1910 discussed in Section 5.1.2, recent development in long DMA makes it possible to explore  
1911 hygroscopic properties of larger aerosol particles. In total nineteen techniques are included in  
1912 Table 1, and several key features are summarized and compared, including:

1913 1) Working principle: We briefly explain why and/or how each technique can be used to  
1914 investigate aerosol hygroscopicity.

1915 2) Sample status: The sample under investigation is a bulk solution, a sample deposited on  
1916 proper substrates, levitated particles or aerosol particles.

1917           3) Size range: The approximate size range of particles that can be explored using each  
1918 technique. If the sample is a bulk solution or particles deposited on a substrate, the particle size  
1919 range is practically not limited. Therefore, size range is only relevant for techniques which  
1920 examine single particles (either deposited on proper substrates or levitated) and aerosol  
1921 particles. We note that Ault and Axson (2017) provided a nice summary of typical size ranges  
1922 of aerosol particles for a number of techniques used for aerosol characterization.

1923           4) Supersaturated samples: whether a technique can be used to investigate hygroscopic  
1924 properties of supersaturated droplets (when RH is below DRH).

1925           5) Nonspherical particles: whether a technique can be used to measure hygroscopic growth  
1926 factors of nonspherical particles, i.e. whether the measurement of growth factors requires the  
1927 assumption of particle sphericity.

1928           6) Water adsorption: whether a technique is sensitive enough to investigate water  
1929 adsorption down to a few monolayers.

1930           7) Ambient application: whether a technique have been used to explore hygroscopic  
1931 properties of ambient aerosol particles. Furthermore, is the measurement online or offline?

1932

1933 **Table 1.** Summary and comparison of key feature of major techniques for aerosol hygroscopicity measurements. Please refer to text Section 6 for  
 1934 further information.

	isopiestic method	nonisopiestic method	physisorption analyser	katharometer
1) working principle	measure water vapor pressure of a solution	measure water vapor pressure of a solution	measure water vapor change when exposure to a sample	measure water vapor change when exposure to a sample
2) sample status	bulk solution	bulk solution	particles deposited on substrates	particles deposited on substrates
3) size range	not applicable	not applicable	not applicable	not applicable
4) supersaturated samples	No	No	No	Yes
5) nonspherical particles	Yes	Yes	Yes	Yes
6) water adsorption	No	No	Yes	No
7) ambient application	No	No	Yes (offline)	Yes (offline)
	analytical balance	thermogravimetric analysis	QCM	optical microscopy
1) working principle	measure sample mass at different RH	measure sample mass at different RH	measure sample mass at different RH	monitor particle morphology at different RH
2) sample status	particles deposited on substrates	particles deposited on substrates	particles deposited on substrates	particles deposited on substrates
3) size range	not applicable	not applicable	not applicable	>1 $\mu\text{m}$
4) supersaturated samples	No	No	No	Ye
5) nonspherical particles	Yes	Yes	Yes	No
6) water adsorption	No	Yes	Yes	No
7) ambient application	Yes (offline)	Yes (offline)	Yes (offline)	Yes (offline)

	electron microscopy	AFM	X-ray microscopy	FTIR spectroscopy
1) working principle	monitor particle morphology at different RH	monitor particle morphology change at different RH	monitor particle morphology at different RH	monitor IR spectra of the sample at different RH
2) sample status	particles deposited on substrates	particles deposited on substrates	particles deposited on substrates	particles deposited on substrates
3) size range	> 10 nm	> 10 nm	>200 nm	not applicable
4) supersaturated samples	Yes	Yes	Yes	Yes
5) nonspherical particles	No	No	No	Yes
6) water adsorption	No	No	No	Yes
7) ambient application	Yes (offline)	Yes (offline)	Yes (offline)	Yes (offline)
	Raman spectroscopy	EDB	optical levitation	acoustic levitation
1) working principle	monitor Raman spectra of the sample at different RH	measure mass of levitated particles as different RH	measure diameters of levitated particles as different RH	measure diameters of levitated particles as different RH
2) sample status	particles deposited on substrates	levitated particles	levitated particles	levitated particles
3) size range	not applicable	a few to tens $\mu\text{m}$	one to tens $\mu\text{m}$	>20 $\mu\text{m}$
4) supersaturated samples	Yes	Yes	Yes	Yes
5) nonspherical particles	Yes	Yes	No	No
6) water adsorption	No	No	No	No
7) ambient application	Yes (offline)	No	No	No
	H-TDMA	light extinction	light scattering	

---

1) working principle	measure aerosol diameters at different RH	measure aerosol light extinction at different RH	measure aerosol light scattering properties at different RH
2) sample status	aerosol particles	aerosol particles	aerosol particles
3) size range	<1 $\mu\text{m}$	a few nm to a few $\mu\text{m}$	a few nm to a few $\mu\text{m}$
4) RH lower than DRH	Yes	Yes	Yes
5) nonspherical particles	No	No	No
6) water adsorption	No	No	No
7) ambient application	Yes (online)	Yes (online)	Yes (online)

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1935

1936

1937

1938 Future directions are outlined and discussed below in order to improve existing techniques  
1939 and to develop new techniques for a better understanding of aerosol hygroscopicity.

1940 1) The majority of instruments covered in this paper are not applicable to ambient aerosol  
1941 particles. Future directions should focus on the development of aerosol hygroscopicity  
1942 techniques that are field deployable, robust, and automatic. Especially up to now most ambient  
1943 measurements conducted were ground-based, and therefore instruments which have high time  
1944 resolution to be deployed on aircrafts (Langridge et al., 2011; Pinterich et al., 2017b; Wang et  
1945 al., 2019) are highly needed.

1946 2) The maximum RH that many techniques/instruments can currently reach is usually  
1947 around 90%, and recent studies have revealed the importance of hygroscopic growth  
1948 measurements at RH very close to 100% (Wex et al., 2009a). Therefore, efforts should be made  
1949 to improve these instruments so that they can be employed to investigate hygroscopic  
1950 properties at very high RH (e.g., up to 99% RH). Furthermore, currently RH measurements  
1951 typically have an absolute uncertainty of 1% or larger, and uncertainties in RH measurement  
1952 would affect hygroscopic growth factors reported at a given RH, especially for high RH at  
1953 which growth factors are more sensitive to RH; therefore, advancement in RH measurements  
1954 (Liang et al., 2018) will contribute to the improvement in aerosol hygroscopicity measurement  
1955 techniques.

1956 3) Temperatures in the troposphere range from ~200 K to >300 K, and temperature has  
1957 been found to have a profound effect on particle phase state and thus liquid water content.  
1958 Nevertheless, most techniques available currently, especially those which investigate  
1959 hygroscopic properties of aerosol particles, can only be operated at around room temperature.  
1960 Further instrumental development, which would enable hygroscopic growth measurements at  
1961 lower temperatures, is warranted.

1962 4) Most techniques are operated under ambient pressure, while many processes involved  
1963 aerosol particles are often carried out at pressures substantially lower than atmospheric pressure  
1964 (Zhao et al., 2009; Schilling and Winterer, 2014; Rosenberger et al., 2018). As a result, new  
1965 techniques that allow direct measurements of hygroscopic properties at lower pressure are  
1966 needed for better characterization of aerosol hygroscopicity under conditions with reduced  
1967 pressure. Such instruments would also be very valuable for characterizing aerosol particles at  
1968 high altitudes where the pressure is significantly lower than the ground level.

1969 5) Aerosol hygroscopicity is a property that depends on chemical compositions and its  
1970 measurements can be affected by phase state and viscosity of the particles. Application of  
1971 multiple techniques to examine the same type of atmospherically relevant particles will deepen  
1972 our understanding of aerosol hygroscopicity. In addition, simultaneous measurements of  
1973 chemical composition and other physicochemical properties (e.g., particle phase state and  
1974 viscosity) of aerosol particles of different hygroscopicity can be very valuable.

1975 6) As shown in this review paper, many instruments employed to probe aerosol  
1976 hygroscopicity are custom built; furthermore, even for the same type of instruments,  
1977 operational protocols may vary at different groups. Instrumental comparisons, proven to be a  
1978 good approach to validate instrumental performance and identify potential issues, have been  
1979 carried out for H-TDMAs (Duplissy et al., 2009; Massling et al., 2011), and similar  
1980 intercomparison should be performed for other techniques and instruments. Furthermore,  
1981 standardized procedures for calibration, operation, data analysis and quality assurance, if can  
1982 be formulated, would help increase data quality for aerosol hygroscopicity measurements.

1983

#### 1984 **Data availability**

1985 This is a review paper, and all the data used come from literature cited.

1986 **Author contribution**

1987 Mingjin Tang and Chak K Chan conceived and coordinated this paper; Mingjin Tang, Chak K  
1988 Chan, Yong Jie Li, Hang Su, Qingxin Ma and Zhijun Wu wrote the paper with contribution  
1989 from all the other coauthors.

1990 **Competing interests**

1991 The authors declare that they have no conflict of interest.

1992

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2001

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