Supporting Information

Measuring Aerosol Phase Changes and Hygroscopicity with a Microresonator Mass Sensor

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Author Contributions

†ATZ and PJG contributed equally to this work.

ATZ, PJG and PTG conceived and designed the study. PJG and ATZ performed the experiments and modelling, analyzed the data and wrote the manuscript. All authors assisted with manuscript preparation.

Contents of Supporting Information

Section S1: Additional figures

Figure S-1 shows the resonator collection surface before collecting NaCl and before collecting the mixture of NaCl and MA (*i.e.* after cleaning). A quantitative comparison is presented by Table S-1 showing the difference between the unloaded resonant frequencies before NaCl collection and NaCl/MA collection varying by 20 Hz (6.4 ppm) which is within the minor temperature differences of the measurements.

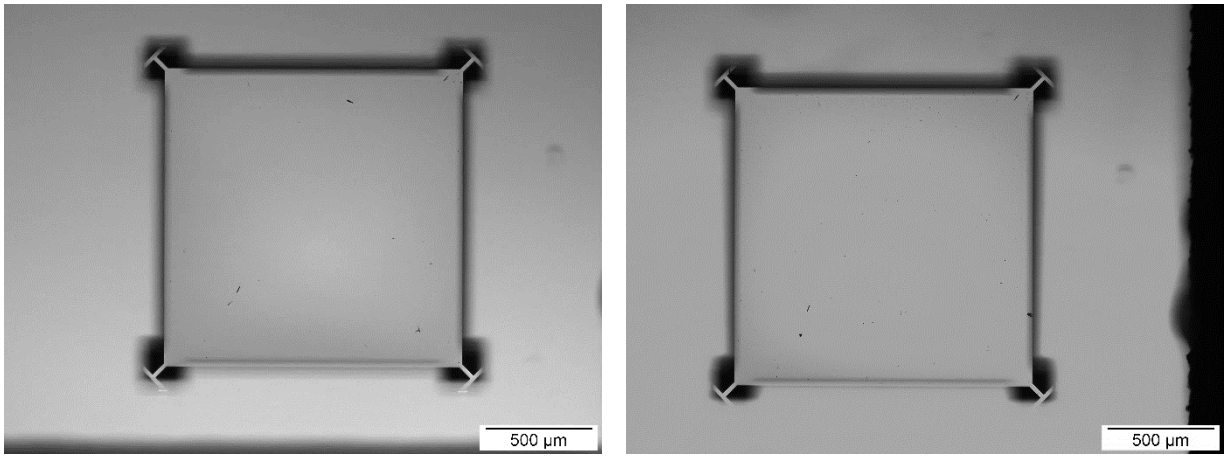

Figure S-1. Collection surface (*i.e.* back) of resonator (left) before collecting NaCl particles and (right) before collecting NaCl/MA particles (after using the cleaning method described by Zielinski *et al.*[1]). Images taken with an optical microscope (BX51, Olympus).

Table S-1. Comparison of resonant frequencies before and after cleaning resonator.

Resonator state	Resonant frequency
Unloaded (before NaCl)[a,b]	3121710 Hz
Loaded with NaCl (prior to humidification)[c]	3120325 Hz
Unloaded (after cleaning, before NaCl/MA)[a,b]	3121690 Hz
Difference between unloaded resonators	-20 Hz (-6.4 ppm)

[a] Frequencies measured without gas flow over resonator.

[b] Temperature of MIS during measurement within 0.5 °C (equivalent to 51 Hz).

[c] Loaded scenario given as a reference to frequency shift from particles (no temperature correction).

Figures S-2 and S-3 show the raw frequency and quality factor data from the AS and NaCl/MA experiments, respectively (as compared to the NaCl data shown in Figure 3).

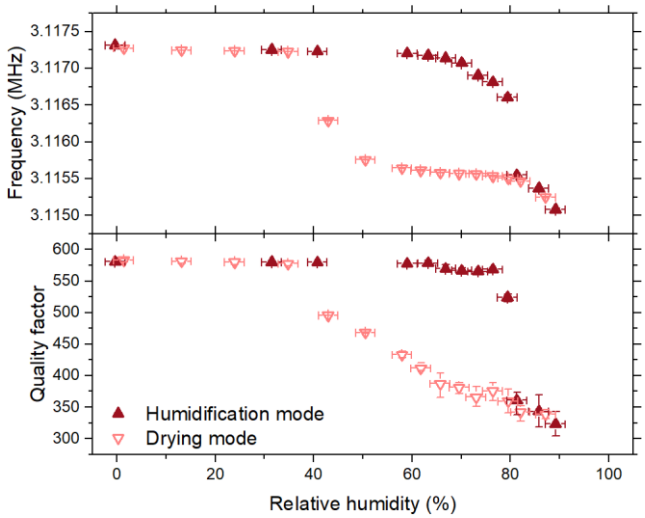

Figure S-2. Resonant frequencies (corrected for temperature) and quality factors for AS at each RH across both the deliquescence mode (darker, filled upwards triangles) and the efflorescence mode (lighter, open downwards triangles). Vertical error bars show the range of the five measurements with the quoted value being the average. Horizontal error bars are based on RH uncertainty (± 2%).

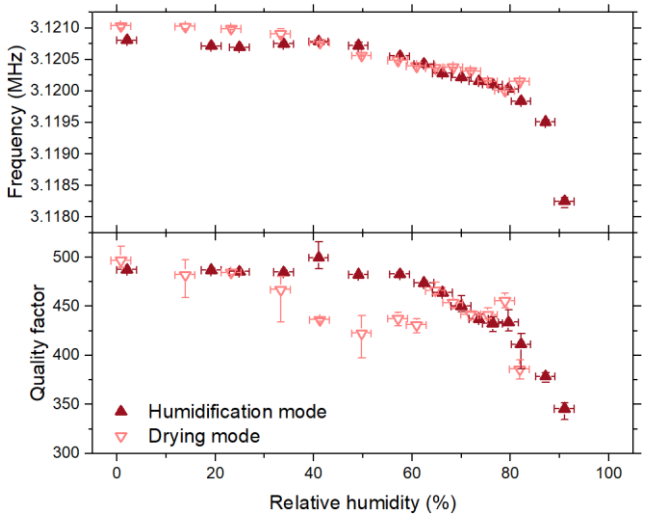

Figure S-3. Resonant frequencies (corrected for temperature) and quality factors for NaCl/MA mixture at each RH across both the deliquescence mode (darker, filled upwards triangles) and the efflorescence mode (lighter, open downwards triangles). Vertical error bars show the range of the five measurements with the quoted value being the average. Horizontal error bars are based on RH uncertainty (± 2%).

Section S2: Conversion of frequency to hygroscopic growth

The following is a brief derivation of how the hygroscopic growth, m/m_0, is calculated from the measured resonant frequencies. The derivation is split into two sections: excluding and including the "stiffness frequency". The derivation assumes frequencies have been corrected for any temperature differences.

Excluding stiffness frequency

For small mass additions the frequency shift recorded by a resonator is related to mass following[2]:

$$\Delta f = \frac{1}{2} f_{\text{unld}} \left(\frac{\Delta k}{k} - \frac{\Delta m}{m} \right) \tag{S-1}$$

where Δf is the frequency shift, f_{unld} is the unloaded frequency, k is the effective stiffness of the unloaded resonator, Δk is the change in stiffness due to the added mass, m is the effective mass of the unloaded resonator, and Δm is the added mass.

The common assumption for particle collection is that $\Delta k \approx 0$ which results in a linear relationship between frequency and mass[3].

$$\Delta f = \frac{-f_{\text{unld}}}{2m} \Delta m$$

or equivalently,

$$\Delta m = \frac{-2m}{f_{\text{unld}}} \Delta f = -S \Delta f$$

where $S \equiv -2m/f_{\text{unld}}$ and is referred to as the mass sensitivity of the resonator.

When looking at particle collection this implies that the collected mass is:

$$\Delta m = -S\left(f - f_{\text{unld}}\right) \tag{S-2}$$

where f is the measured frequency during collection or humidification.

Similarly, when applied to hygroscopic growth this simplifies to:

$$\frac{\Delta m}{\Delta m_{\text{dry}}} = \frac{m}{m_0} = \frac{-S\left(f - f_{\text{unld}}\right)}{-S\left(f_{\text{dry}} - f_{\text{unld}}\right)} = \frac{\left(f - f_{\text{unld}}\right)}{\left(f_{\text{dry}} - f_{\text{unld}}\right)} \tag{S-3}$$

where f_{dry} is the average of frequency measurements at ~0% relative humidity.

This derivation shows the precise mass sensitivity, *S*, is not required as the parameter of interest is a ratio. The value calculated by Equation S-2 is referred to as the "uncorrected" hygroscopic growth value.

Including stiffness frequency

In reality, however, stiffness of the attached particles does play a role in measured frequency shift. Given the difficulty in determining the change in stiffness for a non-uniform, non-metal layer the alternative presented here is to include an additional frequency term. This additional frequency term, that assumes the stiffness effect is constant for a given particle collection and phase, is referred to as the "stiffness frequency" and denoted f_k. Accounting for the stiffness frequency, the collected mass is calculated as follows (in contrast to Equation S-2, above):

$$\Delta m = -S\left(f + f_k - f_{\text{unld}}\right) \tag{S-4}$$

The stiffness frequency can be related to the stiffness change following from Equation S-1. That is,

$$\Delta f = \frac{1}{2} f_{\text{unld}}\left(\frac{\Delta k}{k} - \frac{\Delta m}{m}\right)$$

$$\therefore \Delta m = \Delta k \frac{m}{k} - \frac{2m\Delta f}{f_{\text{unld}}}$$

Using the fact that $\omega = 2\pi f$ and $\omega_{\text{unld}} = \sqrt{\frac{k}{m}}$, where ω is the radial frequency, then Δm can be rewritten:

$$\therefore \Delta m = \frac{-2m}{\omega_{\text{unld}}}\left(\frac{-\Delta k}{2\omega_{\text{unld}}} + \Delta\omega\right) = \frac{-2m}{\omega_{\text{unld}}}\left(\omega - \frac{\Delta k}{2\omega_{\text{unld}}} - \omega_{\text{unld}}\right)$$

Converting back to frequency yields:

$$\therefore \Delta m = \frac{-2m}{f_{\text{unld}}}\left(f - \frac{\Delta k}{2m\, f_{\text{unld}}} - f_{\text{unld}}\right) \tag{S-5}$$

Comparing Equation S-5 to the original definition in Equation S-4 shows that, by inspection, the stiffness frequency is related to the change in stiffness as:

$$f_k = -\frac{\Delta k}{2m\, f_{\text{unld}}}$$

The hygroscopic growth with the stiffness frequency, in comparison to Equation S-3, is given as:

$$\frac{m}{m_0} = \frac{-S\left(f + f_k - f_{\text{unld}}\right)}{-S\left(f_{\text{dry}} + f_k - f_{\text{unld}}\right)} = \frac{\left(f + f_k - f_{\text{unld}}\right)}{\left(f_{\text{dry}} + f_k - f_{\text{unld}}\right)} \tag{S-6}$$

In practice the stiffness frequency is determined from fitting Equation S-6 to a theoretical humidification curve which is then used for the corresponding drying mode. When applicable, the fitting is only applied to the deliquesced particles assuming the change in attachment stiffness is largely due to a phase change. Including the stiffness frequency simply scales the resulting hygroscopic growth curve vertically without changing the determined deliquescence or efflorescence relative humidities. The stiffness frequencies required for fitting each aerosol are given in Table S-2.

Table S-2. Stiffness frequencies calculated for re-scaling NaCl, AS and NaCl/MA based on comparison with theoretical E-AIM results.

Particle type		Stiffness frequency correction (Hz)	Effective m/m_0 rescaling factor
NaCl	Run 1	1143[a]	2.2-3.0
	Run 2	1206[a]	2.3-3.1
AS		139[a]	1.0-1.1
NaCl/MA		333[b]	0.8-1.5

[a] Based on fitting only deliquesced particles
[b] Based on fitting full humidification curve due to lack of clear deliquescence

Section S3: Changes in Q-factor during initial particle collection

Changes in Q-factor during particle collection indicate that the source and extent of damping of the resonator has changed. Table S-2 shows the changes in resonator Q-factor before and after collection of particle samples at <5% RH. While the collection of solid NaCl and AS results in negligible changes in Q-factor, the NaCl/MA mixture shows a substantial decrease, consistent with the hypothesis that mixed particles remain liquid at low RH.

Table S-3. Quality factors before and after initial particle collection at low RH for NaCl, AS and NaCl/MA.

Particle type	Quality factor before collection	Quality factor after collection	% Reduction
NaCl	548	507	7%
AS	603	580	4%
NaCl/MA	600	487	19%

References in Supporting Information

(1) Zielinski, A. T.; Weckman, N. E.; Jones, R. L.; Kalberer, M.; Seshia, A. A. Extending the Lifetime of Resonant Atmospheric Particulate Mass Sensors with Solvent Rinses. *IEEE Sensors Lett.* **2017**, *1*, 1–4.

(2) Prasad, A.; Charmet, J.; Seshia, A. A. Simultaneous Interrogation of High-Q Modes in a Piezoelectric-on-Silicon Micromechanical Resonator. *Sensors Actuators A Phys.* **2016**, *238*, 207–214.

(3) Zielinski, A. T.; Prasad, A.; Seshia, A. A.; Kalberer, M.; Jones, R. L. Effects of Spatial Sensitivity on Mass Sensing with Bulk Acoustic Mode Resonators. *Sensors Actuators A Phys.* **2015**, *236*, 369–379.