Response to Referee #1:

Thanks very much for your comments, suggestions and recommendation with respect to improve this paper. The response to all your comments is listed below.

The manuscript entitled "Identification of Micro-dynamics Phase Transition processes for Ammonium Sulfate aerosols by Two-dimensional Correlation Spectroscopy" investigates the micro-dynamic mechanisms of ammonium sulfate (AS) aerosol phase transitions using two-dimensional correlation infrared spectroscopy (2D-IR), coupled with relative humidity (RH) control. By employing 2D-IR (including generalized 2D-IR and perturbation-correlation moving window 2D (PCMW2D) spectroscopy), the authors successfully elucidate non-equilibrium micro-dynamic processes during AS efflorescence, revealing four distinct sequential steps at the molecular level. This approach advances beyond conventional methods (e.g., ESEM, H-TDMA) that primarily characterize physical parameters (size, shape), offering unprecedented insights into intermolecular interactions (e.g., hydrogen bond dissociation, ion reconfiguration). The manuscript may be suitable for publication after major revisions and addressing the following concerns.

1. The statement “This study could provide critical insight about redefining atmospheric heterogeneous chemistry.” may be not suitable since little information was provided regarding heterogeneous atmospheric chemistry.

Response: We have followed your suggestion and don’t emphasize this point. We have changed some sentences in the introduction. Please check the marked up file for details.

2. How to ensure the accuracy of a 1% RH interval in experiments that is close to the error of a hygrometer?

Response: The FTIR spectrometer starts to take absorption spectra of the samples approximately 1 min after the injection of each designated RH. This time interval is used to stabilize the RH inside the sample cell. We measured the RH at the outlet of the cell and confirmed that the difference from the inlet RH did not exceed 0.5% (RH). Moreover, we use a humidity detector to continuously monitor changes. Here, the 1%(RH) refers to a relative change in reading, not an absolute value. Although the detector has an accuracy of ±0.8%, its systematic error remains consistent between the two humidity points and is largely canceled out when calculating the difference. Therefore, a 1% (RH) change interval is achievable. Please check the marked up file for details.

3. The FTIR measurement is reported to use "a repeat time of 1 scan". This is problematic because FTIR spectroscopy typically requires multiple scans (e.g., 32 or 64) to average out noise and improve SNR. A single scan risks capturing unreliable, noisy spectra, which could distort the identification of subtle spectral changes during phase transitions and may introduce artifacts in the synchronous/asynchronous 2D-IR maps, affecting the precision of transition point determinations.

Response: Multiple scans could average out noise and improve SNR， but it need more time (about 2～3min). A single scan may risk noisy spectra, but the noise is random and high-frequency. And for the AS, the IR absorbance peaks (include the sulfate ion, ammonium ion and liquid water) are low-frequency. A single scan could be smoothed to improve SNR. So the linear baseline corrections and smooth were performed in the regions of 1000～1500cm^{-1} and 2500～3550cm^{-1} for all infrared spectra before calculation and analysis. Then we normalize all pre-processed infrared spectra into 2D-IR spectra. From Fig.1, the pre-processed infrared spectra clearly show the absorption peaks of sulfate, nitrate, and ammonium ions, and allows observation of their peak shifts with changes in relative humidity (RH). And the calculation results in the synchronous/asynchronous 2D-IR maps (Fig.2) were also consistent with the observations reported by Takahama et al. (2007)[1], Yeung et al. (2009) [2]. So a single scan could meet the requirements of the transition point determinations precision. Moreover its precision was not be affected. We have included this interpretation in the revised version. Please check the marked up file for details.

4. How is the sample particle size determined to be 300nm?

Response: In our paper, we used a differential mobility analyzer (DMA) to sort the diameter of the particles. The diameter of 300 nm in the experiment description section should also be electrical mobility diameter. Yan et al. (2020) have compared the D_{ve} and the D_{em} of AS sorted by the identical DMA of this study, which is shown in the figure R1. A good agreement between D_{em} and D_{ve} for ~100 nm AS was observed by Yan et al. (2020). For the AS with an electrical mobility diameter of ~100 nm, its volume equivalent diameter is ~ 94 nm. Please check the marked up file for details.

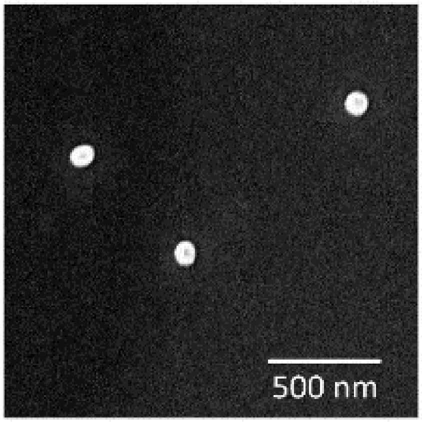

Figure R1 The SEM image of 100 nm AS particles deposited on the silicon wafer.

5. The PCMW2D and generalized 2D-IR analyses are central to identifying transition points and molecular sequences, but their reliability is compromised by incomplete data. For instance, the assignment of positive/negative correlation peaks in Fig. 2, references wavenumbers (e.g., 1084 cm^{-1}, 1417 cm^{-1}) that lack contextual spectral data (e.g., how these peaks evolve with RH). Without clear baseline spectra or RH-dependent intensity curves, the interpretation of "convex/concave variations", remains speculative.

Response: Fig. 1(B) shows the RH-dependent FTIR spectra of AS in 1500-1000 cm^{-1} region upon efflorescence. The blue arrows specifically show the infrared absorption peaks at 1463 cm^{-1} and 1097 cm^{-1}, respectively. The blue downward arrows indicate a decrease in absorption peak intensity with decreasing RH. The red arrows specifically show the infrared absorption peaks at 1417 cm^{-1} and 1084 cm^{-1}, respectively. The red upward arrows indicate an increase in absorption peaks intensity with decreasing RH. It can be observed that as the humidity decreases, the absorption peak intensities at 1463cm^{-1} and 1097 cm^{-1} gradually weaken. At 39% (RH), the 1463 cm^{-1} and 1097 cm^{-1} absorption peaks shift to 1417 cm^{-1} and 1084 cm^{-1}, respectively.

Fig.2(A) gives the synchronous PCMW2D spectra in 1502～1000 cm^{-1} region during the efflorescence process of AS aerosol. As can be seen, (1084 cm^{-1}, 39%) and (1417 cm^{-1}, 39%) show red color, which is a positive correlation peak. While (1097 cm^{-1}, 39%) and (1463 cm^{-1}, 39%) are negative correlation peaks.

So these variations in the peaks (Fig. 1(B)) with RH are consistent with the convex/concave variations (Fig.2(A) and Fig.2(B)). And these variations in the peaks (Fig. 1(A)) with RH are consistent with the convex/concave variations (Fig.2(C) and Fig.2(D)). We have included this interpretation in the revised version. Please check the marked up file for details.

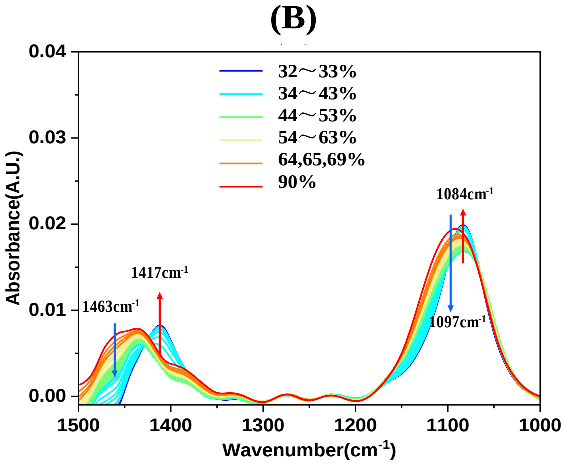

Fig.1 Humidity-dependent FTIR spectra of AS particles upon efflorescence from 65% to 32% at a rate of 1%RH. (B) 1500-1000cm^{-1}. The blue downward arrows indicate a decrease in absorption peak intensity with decreasing RH. And the red upward arrows indicate an increase in absorption peaks intensity with decreasing RH.

6. Is the attribution of infrared peaks based on references? Usually, NH_4^+ exhibits several infrared absorption peaks around 3000 cm^{-1}. Why are the NH_4^+ peaks of the dried sample not obvious around 3000 cm^{-1} in this study?

Response: Fig.R2 the fitted bands for spectra in the region of 2600～3800 cm^{-1} at 90% (RH) which show three infrared absorption peaks for NH_4^+ and one infrared absorption peak for liquid water. Fig.R3 show the fitted bands for spectra in the region of 2600～3400 cm^{-1} at 34% (RH) which show NH_4^+ exhibits three infrared absorption peaks. There are 2887 cm^{-1}, 3036 cm^{-1}, 3209 cm^{-1} for the dried sample at 34% (RH), which is similar with the results of Onasch et (in Fig. R4) [3], Juan et [4] . We have included this interpretation in the revised SI version. Please check the marked up file for details.

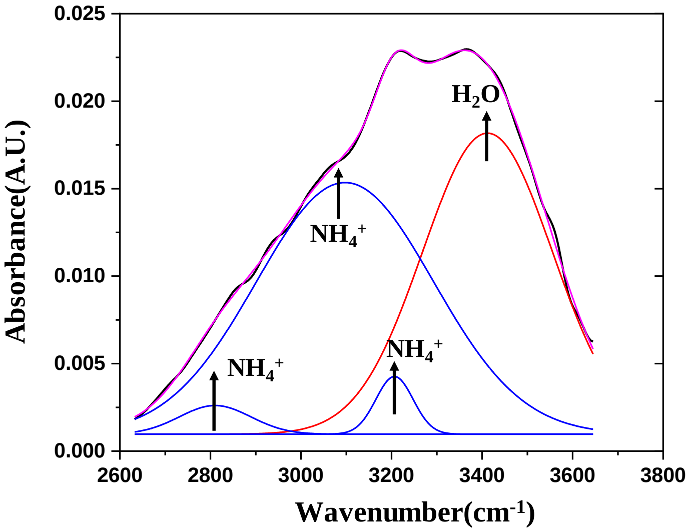

Fig.R2 the fitted bands for spectra in the region of 2600～3800 cm^{-1} at 90% (RH). Dark line: the experimental IR absorbance spectra. Blue and red lines are NH_4^+ and liquid water fitted spectral bands, respectively. Magenta lines: the sum spectra of the fitted spectral components.

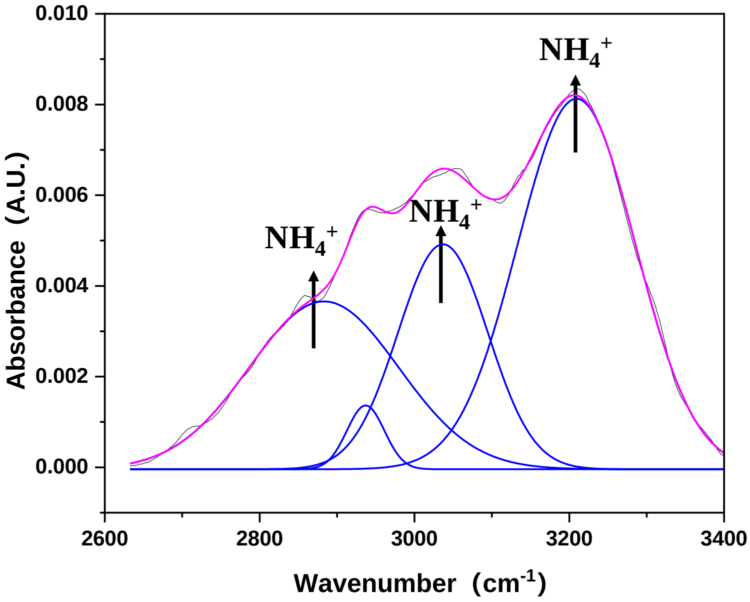

Fig.R3 the fitted bands for spectra in the region of 2600～3400 cm^{-1} at 34% (RH). Dark line: the experimental IR absorbance spectra. Blue lines are NH_4^+ fitted spectral bands, respectively. Magenta lines: the sum spectra of the fitted spectral bands.

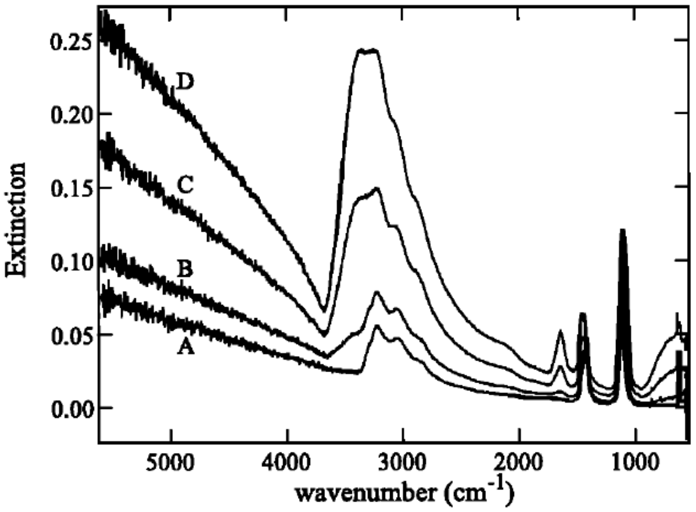

Fig.R4 the IR spectra for AS in different RH[3].（A）the initial dry AS aerosol;(B) the initial uptake of liquid water by AS aerosol; (C) totally deliquesced aerosol sample; (D) aerosol on the water uptake curve above the deliquescence point.

7. How to define complete dryness in experiments? From the infrared spectrum, it appears that there is still a significant amount of H_2O present in the sample.

Response: This effect was caused by background subtraction, and we have reprocessed the background correction. Please check the marked up file for details.

8. There are many spelling and grammar errors. The issue of capitalization of the first letter. For example, Line 53, Line 57, Line 173, these sentences seem not complete.

Response: Done. Please check the marked up file for details.

9. Line 218: DRH

Response: Done. Please check the marked up file for details.

Reference：

1. Takahama, S.; Pathak, R. K.; Pandis, S. N., Efflorescence Transitions of Ammonium Sulfate Particles Coated with Secondary Organic Aerosol. *Environmental Science & Technology* **2007,** *41* (7), 2289-2295.

2. Yeung, M. C.; Lee, A. K. Y.; Chan, C. K., Phase Transition and Hygroscopic Properties of Internally Mixed Ammonium Sulfate and Adipic Acid (AS-AA) Particles by Optical Microscopic Imaging and Raman Spectroscopy. *Aerosol Science and Technology* **2009,** *43* (5), 387-399.

3. Onasch, T. B.; Siefert, R. L.; Brooks, S. D.; Prenni, A. J.; Murray, B.; Wilson, M. A.; Tolbert, M. A., Infrared spectroscopic study of the deliquescence and efflorescence of ammonium sulfate aerosol as a function of temperature. *Journal of Geophysical Research: Atmospheres* **1999,** *104* (D17), 21317-21326.

4. Nájera, J. J.; Horn, A. B., Infrared spectroscopic study of the effect of oleic acid on the deliquescence behaviour of ammonium sulfate aerosol particles. *Physical Chemistry Chemical Physics* **2009,** *11* (3), 483-494.