

Supporting Information:

**Modeling the ionization mechanism of
amorphous solid particles without an external
energy source coupled to mass spectrometry**

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S1. Atomic force microscopy images of glutaric acid particles

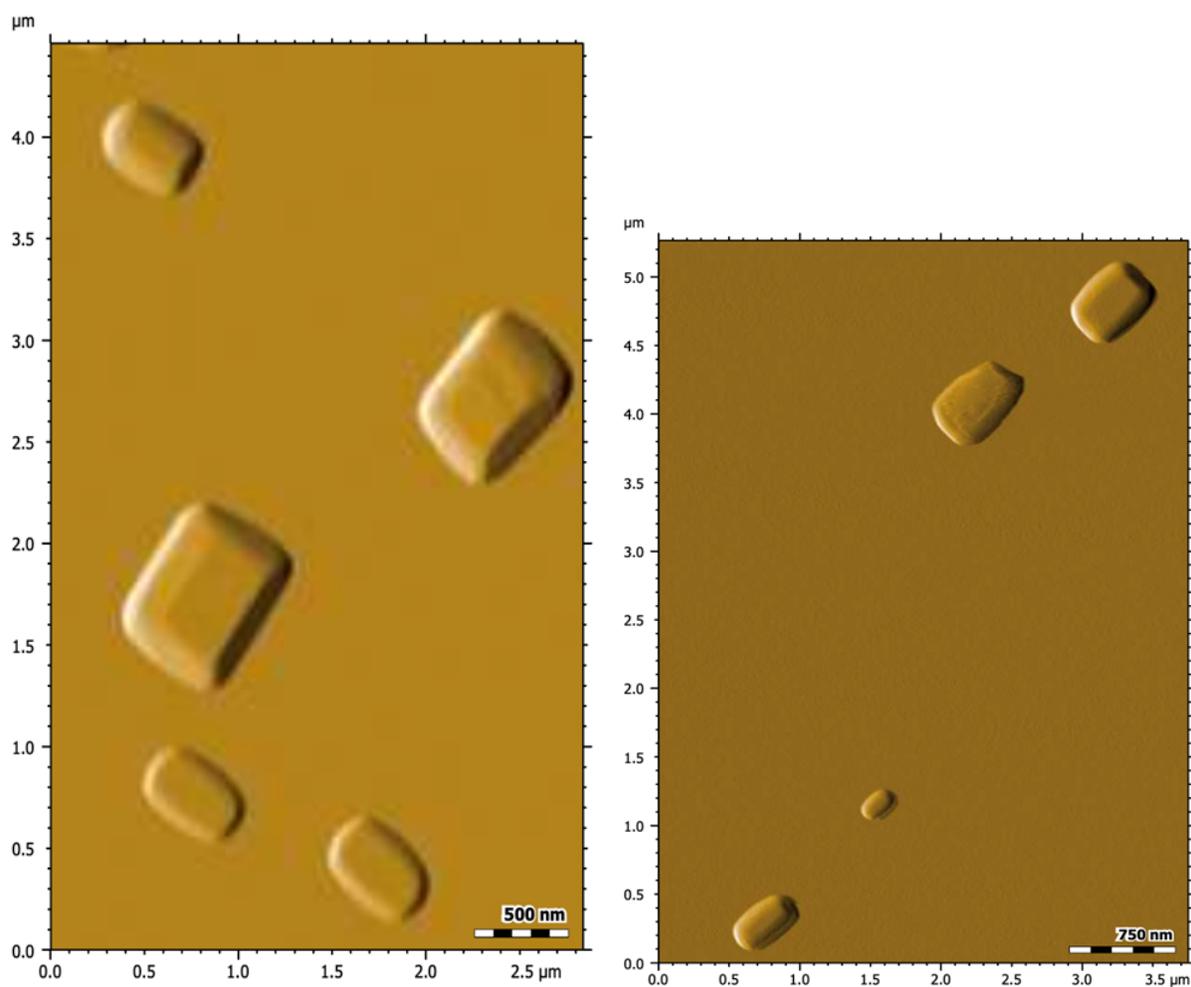


Figure S1: Atomic Force Microscopy (AFM) images of atomized, dried, and impacted glutaric acid particles with diameters of 150 nm to 1 μm acquired using an Anton Paar Tosca 400 atomic force microscope in tapping mode with silicon tips at a resonance frequency of 285 kHz and a force constant of 42 N/m. Particles were impacted on a freshly cleaved mica substrate.

S2. Experimental temperatures

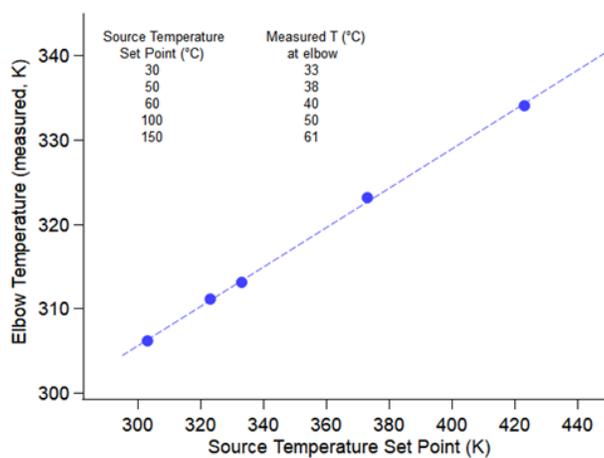


Figure S2: Measured temperatures of the inlet elbow through which particles travel in the mass spectrometer inlet as a function of various source temperature set points. The maximum set point temperature of 150°C (423 K) corresponds to an elbow temperature of 61°C (334 K) that particles are exposed to for ~ 0.1 s.

S3. Radial distribution functions of SA as a function of diacid nano-aggregate size

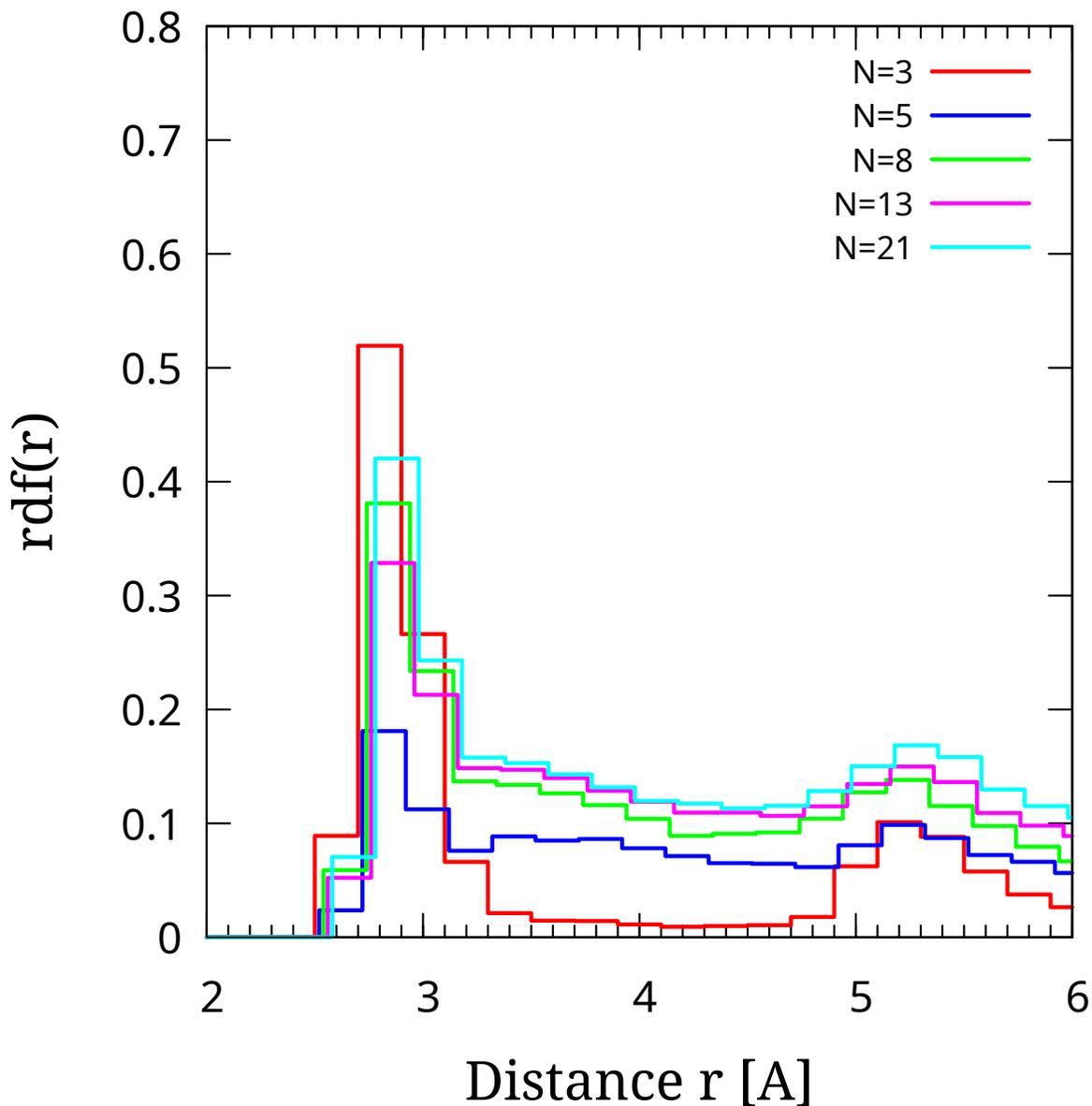


Figure S3: Radial distribution function (rdf) between O1 and O2 in SA nano-aggregates of various sizes $N = 3 - 21$ at $T = 300$ K. The numbering of the oxygen sites is shown in Fig. 1 (a) in the main text. The rdf shows convergence with the increase of N .

S4. Radial distribution functions of diacid nano-aggregates

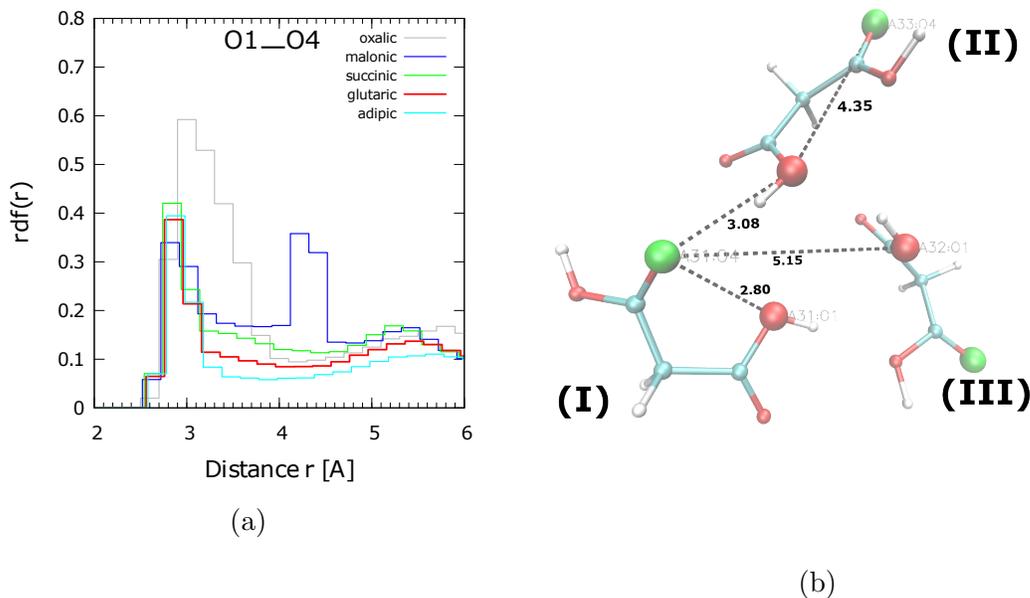


Figure S4: (a) O1-O4 rdf for $N = 21$ of various diacids. The numbering of the atomic sites is as shown in Fig. 1 (a) in the main text. (b) Typical snapshot of a MA trimer that shows some of the MA conformers, indicated as (I), (II), (III). A few oxygen sites in the carboxylic groups have been enlarged for clarity. The enlarged green sphere represents the carbonyl oxygen site and the enlarged red sphere the oxygen site in -OH of the carboxylic group.

Figure S4 (a) shows the rdf between O1 and O4 sites (Fig. 1 (a) in the main text shows the enumeration). We use the example of a MA trimer (Fig. S4 (b)) to show the origin of the peaks in the rdf.

A single diacid molecule in the gaseous phase has several conformers.^{S1} Here we use the example of MA, that due to its small size may more clearly demonstrate the variability in conformers and their signature in the rdfs. The relative energies of three conformers of a single MA molecule have been computed using high level quantum density functional methods by Nguyen et al.^{S1} and of seven conformers by Sheng et al.^{S2} as shown in Fig. 1 in their article. At room temperature the lower energy conformations, (A), (B), and (C) in Sheng et al.^{S2} are accessible by thermal motion at room temperature and may give rise to different peaks in the rdf. In aggregates comprised even a few diacid molecules, higher

energy conformers may also appear at room temperature because they may be stabilized by the interactions with neighboring molecules in the condensed phase.

Figure S4 (b) is a snapshot of a MA trimer from our simulations that shows conformers (I) and (II), which correspond to (B) and (C), respectively, in Fig. 1 of Sheng et al.^{S2} Figure S4 (a) for MA shows that the intramolecular distance depending on the conformer is at ~ 2.80 Å and at ~ 4.35 Å, while the intermolecular distance can vary between ~ 3.08 – 5.15 Å as shown in Fig. S4 (b). The example of MA shows that the peaks in the rdfs arise from a mixture of intermolecular and intramolecular O1-O4 distances.

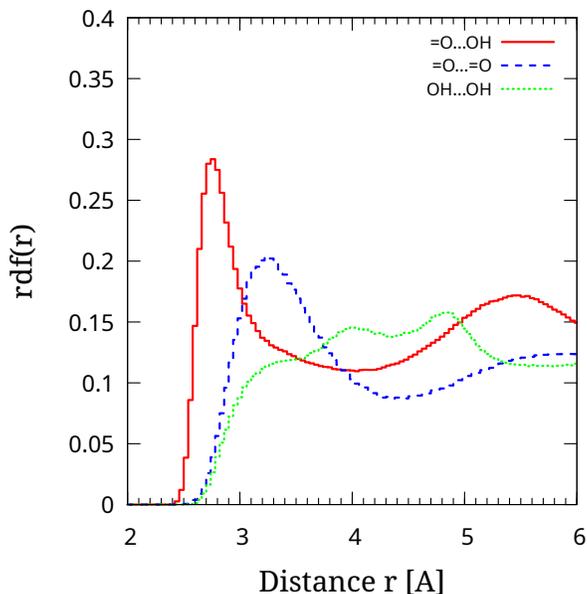


Figure S5: Oxygen-oxygen rdfs of $N = 700$ GA at $T = 360$ K. It is noted that \dots in the legend denotes pairs of O sites examined and not H-bonds.

Figure S5 shows O-O rdfs for $N = 700$ GA at $T = 360$ K.

S5. Typical snapshots of H-bonding patterns in $N = 21$ SA

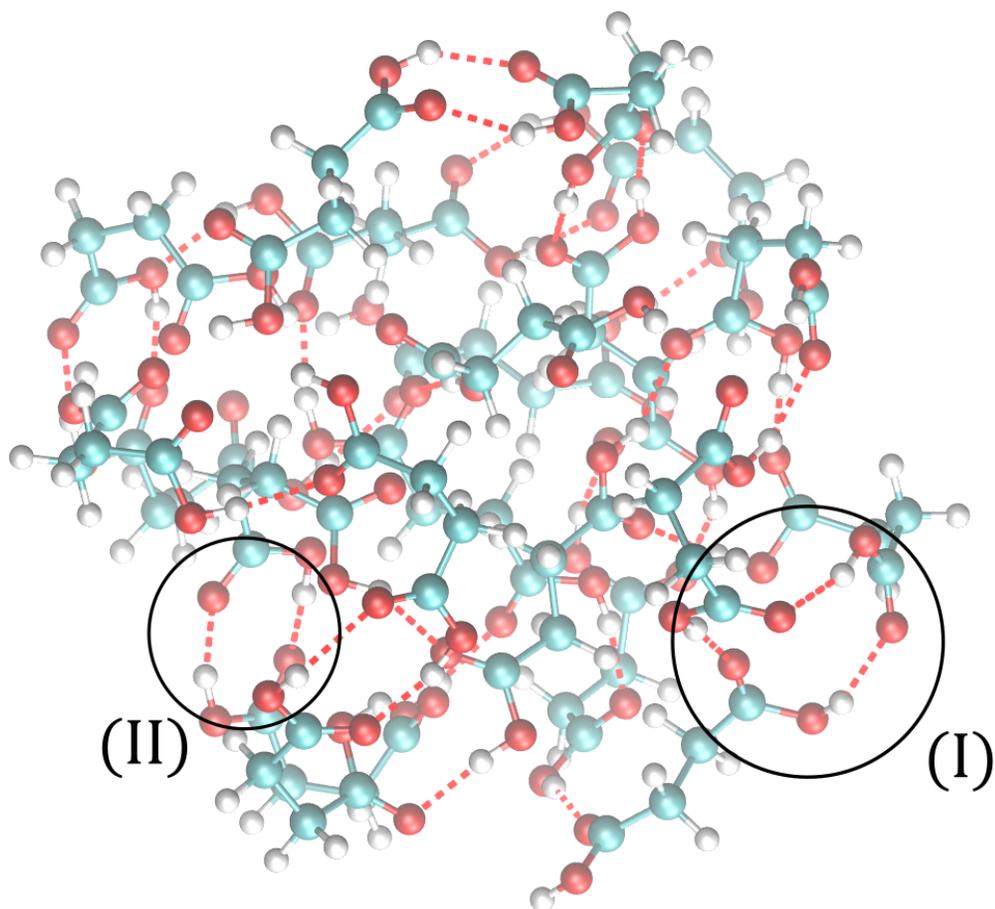


Figure S6: Typical snapshots of dimeric and trimeric ring assemblies formed within the diacid aggregates. $N = 21$ SA. The encircled regions show (I) a trimer, and (II) a dimer formed with two H-bonds between two carboxylic groups belonging to different molecules. The white spheres represent H sites, the red O and the blue C. The red dotted lines indicate the H-bonds. The definition of the H bond is discussed in the main text.

References

- (S1) Nguyen, T. H.; Hibbs, D. E.; Howard, S. T. Conformations, energies, and intramolecular hydrogen bonds in dicarboxylic acids: implications for the design of synthetic dicarboxylic acid receptors. *J. Comput. Chem.* **2005**, *26*, 1233–1241.
- (S2) Sheng, X.; Song, X.; Zhu, H.; Ngwenya, C. A.; Zhao, H. Effects of the inter- and intra-molecular hydrogen bonding interactions in forming atmospheric malonic acid-containing clusters. *Chem. Phys.* **2019**, *524*, 14–20.