

# Bridging Gaps between Clusters in Molecular-Beam Experiments and Aerosol Nanoclusters

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Cite This: *J. Phys. Chem. Lett.* 2023, 14, 287–294



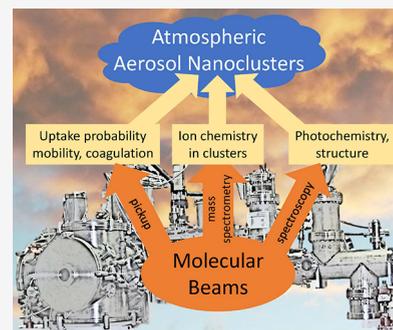
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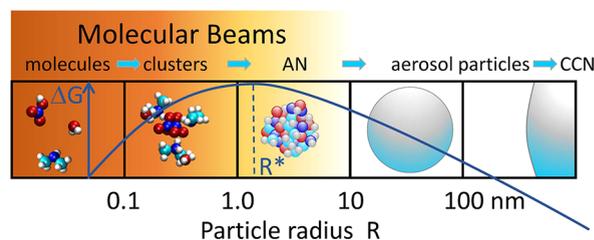
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**ABSTRACT:** Clusters in molecular beam experiments can mimic aerosol nanoclusters and provide molecular-level details for various processes relevant to atmospheric aerosol research. Aerosol nanoclusters, particles of sizes below 10 nm, are difficult to investigate in ambient atmosphere and thus represent a gap in our understanding of the new particle formation process. Recent field measurements and laboratory experiments are closing this gap; however, experiments with clusters in molecular beams are rarely involved. Yet, they can offer an unprecedented detailed insight into the processes including particles in this size range. In this Perspective, we discuss several up-to-date molecular beam experiments with clusters and demonstrate that the investigated clusters approach aerosol nanoclusters in terms of their complexity and chemistry. We examine remaining gaps between atmospheric aerosols and clusters in molecular beams and speculate about future experiments bridging these gaps.



The importance of atmospheric aerosols has been outlined in many reviews<sup>1–5</sup> and textbooks.<sup>6,7</sup> Briefly, they absorb and scatter solar and terrestrial radiation and form the seeds on which clouds develop, thus determining the Earth's albedo and radiation budget, playing a key role in the greenhouse effect and global warming. They alter the chemical composition of the atmosphere by providing surfaces and condensed phases for heterogeneous chemistry. In polluted areas, aerosol particles can severely impact human health. Due to all these effects, the research focused on atmospheric aerosols has recently grown also in the field of physical chemistry. A substantial part of atmospheric aerosols is generated in processes called *new particle formation* (NPF) by nucleation and condensation of gaseous precursors in the atmosphere.<sup>7–9</sup> The evolution of atmospheric aerosol particle starts with the formation of molecular clusters that can be stabilized, e.g., by acid–base reactions, and further grow by adding molecules from the gas phase into particles exceeding tens of nanometers in diameter, which become condensation nuclei for clouds, **Figure 1**. In aerosol literature, particles composed of a few to hundred(s) of molecules are usually called *clusters*. These clusters correspond in size to sub-nanometer up to about 2 nm in diameter. Larger particles up to about 10 nm are often called *aerosol nanoclusters* (AN).<sup>10</sup> The range of particle sizes below 10 nm is difficult to cover with instruments detecting and analyzing aerosols in ambient atmosphere. Thus, it represents a gap in our understanding of atmospheric aerosols.<sup>10</sup> At the same time, this is the size range crucial in NPF processes.<sup>8–11</sup> Often size distributions of aerosol particles peak in this size range, and the small aerosol particles provide a huge surface for heterogeneous chemistry.<sup>7</sup> An overview of different experimental techniques used in aerosol



**Figure 1.** Schematic illustration of aerosol nucleation and growth from gas-phase molecules over clusters and aerosol nanoclusters (AN) to aerosol particles which can serve as cloud condensation nuclei (CCN). The overlaid blue line illustrates the free Gibbs energy  $\Delta G$  that reaches its maximum at a critical radius  $R^*$  from which the particles grow spontaneously. The colored (brown-yellow) area indicates the region covered by the molecular beam experiments discussed in this Perspective. The  $R$ -scale is only approximate.

nucleation experiments can be found elsewhere.<sup>3,10,12–14</sup> In particular, mass spectrometry is widely used to measure the composition of atmospheric aerosols,<sup>10,15–20</sup> and progress in mass spectrometry and other particle detection techniques is closing the above-mentioned gap.<sup>10</sup> Time-of-flight mass spectrometry (TOF-MS) techniques have been implemented

**Received:** November 10, 2022

**Accepted:** December 20, 2022

**Published:** January 4, 2023



in field measurements as well as in laboratory experiments, namely in various condensation flow tube-based reactors and aerosol chambers, e.g., the CLOUD experiment in CERN.<sup>13,21–23</sup>

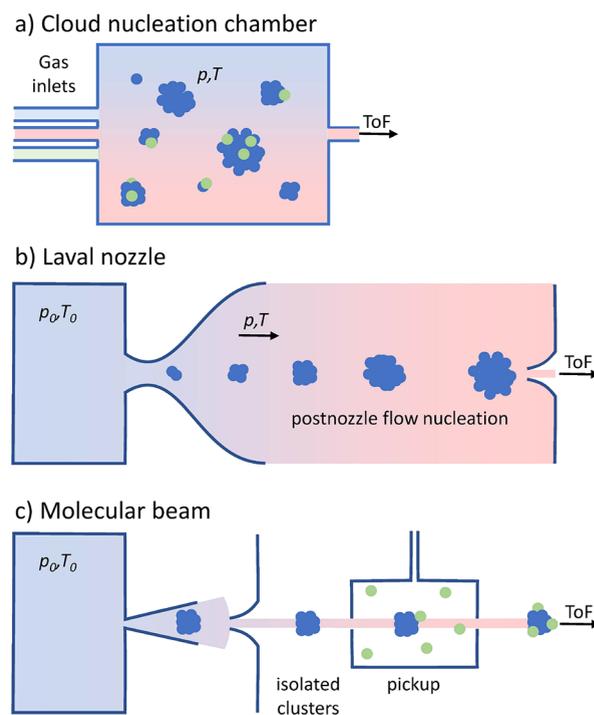
From another perspective, molecular beam (MB) experiments with clusters can provide useful information about AN in the sub-nanometer to 10 nm size range. It ought to be mentioned that aerodyne aerosol mass spectrometers (AMS) widely used in aerosol research<sup>3,15,16</sup> are essentially based on MB techniques. In AMS, aerosol particles are sampled through an aerodynamic lens and transferred into a vacuum, where they can be ionized directly or after deposition on a surface and vaporization using lasers or electrons. Aerodyne AMS are mainly used for mass spectrometric analysis of larger aerosol particles from  $\sim 50$  nm to  $\mu\text{m}$  scale.<sup>16</sup> However, here we focus on smaller particles, and especially on different experiments than pure mass spectrometry that can be performed with aerosol nanoclusters in MB. Earlier cluster studies claimed the relevance to atmospheric aerosol processes, e.g., the work in Castleman's group<sup>24–26</sup> and others<sup>27,28</sup> reviewed recently.<sup>29,30</sup> Here, we argue that up-to-date MB experiments with clusters can provide relevant information for atmospheric nanoaerosols and processes related to NPF. We examine the gaps between AN and clusters in MB in the light of recent cluster experiments. We further speculate about experiments which have the potential to bridge the gaps and bring cluster beam investigations even closer to field and laboratory studies of atmospheric AN.

**Nucleation and Pickup Experiments.** A widely used theoretical approach to atmospheric aerosol nucleation is the phenomenological classical nucleation theory (CNT).<sup>9,14,31</sup> The CNT treats the clusters within the classical liquid drop model as spherical bulk-liquid droplets that start to grow spontaneously when their size increases over the threshold where the Gibbs free energy reaches its maximum and decreases with further increase in the droplet radius, see Figure 1. Since this approach relies on bulk-liquid characteristics, it neglects the properties of individual molecules important for nanometer-size clusters. To understand the vapor nucleation at a molecular level, a kinetic approach is applied: clusters grow and shrink by collisions with individual molecules that stick to them as well as cause fragmentation and evaporation. These processes can be described by a set of general dynamic equations.<sup>14,31,32</sup> They require association and evaporation rates, which can be calculated theoretically<sup>32</sup> but are difficult to obtain experimentally.<sup>33</sup>

Recently, the association rate constants for monomer–cluster collisions were extracted from water nucleation measured in Laval nozzle expansions.<sup>33</sup> Cluster nucleation in Laval nozzles relevant to atmospheric aerosols was investigated in many studies previously; see refs 14 and 34 and references cited therein. Such experiments can offer many advantages and analogies to real atmospheric processes: e.g., the generated clusters are probed under a collisional regime, where sticking collisions with gas-phase molecules as well as evaporation from clusters occur. Due to the collisions, an equilibrium temperature of the cluster can be established in a Laval nozzle, and macroscopic terms such as temperature, pressure, and relative humidity are well defined.

On the other hand, clusters in MB are isolated in a vacuum. They are initially produced in supersonic expansions similar to Laval nozzle expansions, yet due to a gas rarefaction in high vacuum the collisions quickly cease, typically at a distance of about 20 nozzle diameters<sup>35</sup> (i.e., for a typical nozzle of 100  $\mu\text{m}$  diameter, there are essentially no collisions after about 2 mm

downstream from the nozzle throat). Due to the limited number of collisions, equilibrium conditions often cannot be established (i.e., temperatures corresponding to translational, rotational, and vibrational degrees of freedom are different). In a typical experiment, generated clusters further pass through a skimmer into an ultrahigh vacuum, where they fly without any interactions with gas-phase molecules. A schematic drawing of the different aerosol nucleation experiments is shown in Figure 2.



**Figure 2.** A schematic drawing of different aerosol nucleation experiments. In cloud nucleation chambers and flow reactors (a), different gases are mixed under equilibrium conditions, and nucleation is driven by pressure and temperature (assisted by other nucleation agents such as radiation). In Laval nozzles (b), the gas mixture is expanded through a nozzle, and collisions and nucleation continue in the postnozzle flow. In molecular beams (c), clusters are generated in the nozzle expansion, which ceases shortly after the nozzle, and fly isolated in a vacuum, and uptake of individual molecules by the clusters can be investigated in a pickup experiment. In all these experiments, clusters can be probed by mass spectrometry and other means.

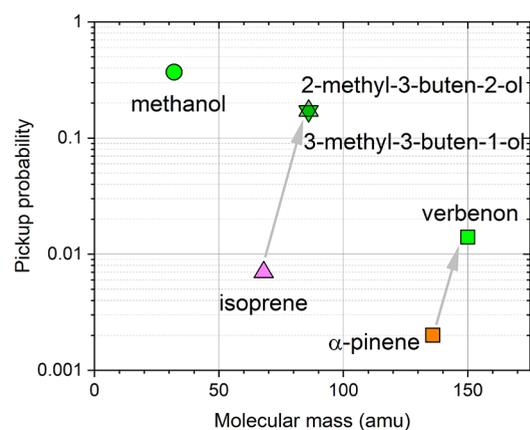
Molecular beam experiments provided some information about cluster nucleation in the nozzle: e.g., in the case of mixed nitric acid and water vapor expansions, the acid molecules served as a nucleation center generating mainly hydrated clusters containing at least one nitric acid molecule.<sup>36</sup> Even though the conditions under which the clusters are generated in MB are far from realistic atmospheric conditions, the formed clusters can resemble atmospheric particles in some stage of the nucleation process, and control over the particle composition and their isolation in vacuum enable unique experiments. Particularly, *pickup experiments* can provide useful information for aerosol nucleation: a cluster beam enters a pickup cell filled with a diluted gas, and the uptake of individual gas molecules by the cluster is investigated.<sup>30</sup> Such experiments allow for isolation of the uptake process from other processes (e.g., evaporation) taking place when the vapor is in contact and in equilibrium with the particle. Thus, in MB, pickup/uptake probability can be measured, and in special cases also sticking coefficients of

individual molecules to clusters can be derived.<sup>37,38</sup> Besides, such MB experiments allow observation of the behavior of the adsorbed molecules on the clusters, e.g., their mobility and coagulation into smaller clusters on/in the host cluster.<sup>39,40</sup>

Early pickup experiments with atmospheric relevance in the 1990s investigated the uptake of methanol<sup>41</sup> and other organic molecules<sup>42</sup> and  $N_xO_y$  molecules<sup>27</sup> by large water clusters. Methods based on the pickup of molecules by clusters were also used to determine neutral cluster sizes<sup>43,44</sup> and pickup cross sections.<sup>45,46</sup> The pickup cross sections of large water clusters (mean size  $\bar{N} \approx 260$  corresponding to a radius of  $\bar{R} \approx 1.2$  nm) for several atmospherically relevant molecules were measured.<sup>47,48</sup> The cross section of these clusters for the pickup of  $H_2O$  molecules was more than twice as large as their calculated geometrical cross section due to attractive interactions between the clusters and polar water molecules.<sup>47,48</sup> These experiments have recently been confirmed by measurement of the monomer–cluster association rate constants from water nucleation measurements in a Laval nozzle, as mentioned above.<sup>33</sup> The association rate constants obtained by Li et al.<sup>33</sup> were 4–5 times larger than the collision rates obtained assuming geometrical cross sections of spherical water clusters. This is qualitatively consistent with the larger cross sections derived from the MB experiments.<sup>47</sup>

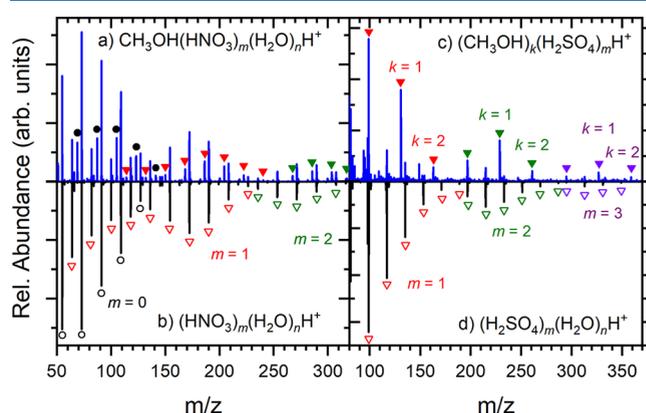
Different molecular components have been added to approach the chemical composition of AN. Sulfuric acid is the most relevant compound in NPF; however, nitric acid and ammonia condensation has been recently suggested as an important source of NPF in urban areas as well as in cold upper troposphere.<sup>49</sup> A recent computational study suggested that nitric acid can drive early stages of particle formation as efficiently as sulfuric acid.<sup>50</sup> In addition, nitric acid–water clusters can be used as a model systems for hydrated acid aerosol particles in MB.<sup>51,52</sup> Organic molecules represent a key component in NPF as well.<sup>13,53–55</sup> Volatile organic compounds (VOCs) are emitted into the atmosphere from a variety of biogenic and anthropogenic sources, and they are efficiently oxidized in the atmosphere, yielding derivatives with a lower volatility, which facilitates their condensation onto pre-existing atmospheric particles.<sup>8,12,56</sup> Therefore, uptake of VOCs and their oxidized derivatives on hydrated nitric acid clusters was investigated.<sup>38</sup> Kinetic pickup probabilities were determined in a MB experiment, where single molecules were adsorbed on the clusters. Figure 3 shows the measured pickup probabilities for atmospheric VOCs isoprene and  $\alpha$ -pinene compared to their oxidized derivatives, represented by 2-methyl-3-buten-2-ol and 3-methyl-3-buten-1-ol for isoprene, and by verbenon for  $\alpha$ -pinene. Pickup of methanol was measured as a benchmark.<sup>37</sup> The pickup probabilities are plotted as a function of molecular mass, since they depend on a molecule–cluster collision energy, and subsequently on the molecular mass (see ref 38 for a detailed discussion). The pickup probabilities for the oxidized molecules are significantly larger than the ones for the corresponding VOCs, as indicated by the gray arrows. The increase is due to the formation of hydrogen bonds between the oxidized molecules and cluster, whereas the interactions of the parent VOCs are weaker and nonspecific.<sup>38</sup> New experiments are currently ongoing in our laboratory exploring the effect of molecular structure on the pickup probability.

Although nitric acid represents a suitable model system, the majority of atmospheric aerosols are better approximated by hydrated sulfuric acid clusters. Therefore, we also investigated the uptake of different molecules by  $(H_2SO_4)_M(H_2O)_N$  clusters.



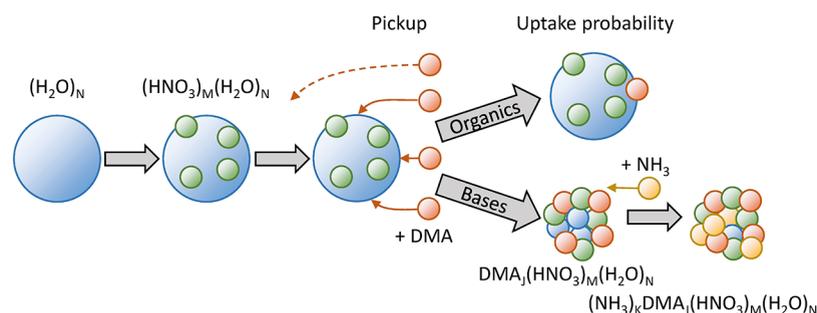
**Figure 3.** Pickup probabilities for methanol (green circle), isoprene (pink triangle) and its oxidized derivatives 2-methyl-3-buten-2-ol and 3-methyl-3-buten-1-ol (overlapping green triangles), and  $\alpha$ -pinene (orange square) and its derivative verbenon (green square). Gray arrows indicate the pickup probability increase with the oxidation of the corresponding VOC.

Figure 4 shows preliminary results for the uptake of methanol by these clusters. Panel (a) shows the mass spectrum of



**Figure 4.** Comparison of mass spectra for the pickup of methanol on hydrated nitric and sulfuric acid clusters. (a) Methanol pickup on nitric acid with  $CH_3OH(HNO_3)_m(H_2O)_nH^+$  series labeled by closed symbols for  $m = 0$  (black), 1 (red), and 2 (green triangles). (b) Corresponding spectrum without pickup; open symbols indicate  $(HNO_3)_m(H_2O)_nH^+$  series with the same color coding. (c) Sulfuric acid spectrum after methanol pickup;  $(CH_3OH)_k(H_2SO_4)_m(H_2O)_nH^+$  series labeled  $m = 1$  (red), 2 (green), and 3 (purple triangles). (d) Corresponding spectrum without pickup; open symbols indicate  $(H_2SO_4)_m(H_2O)_nH^+$  series with the same color coding. Bottom spectra are plotted upside down for better comparison of peak positions.

$(HNO_3)_M(H_2O)_N$  clusters after the pickup of  $CH_3OH$  molecules. Protonated  $CH_3OH(HNO_3)_m(H_2O)_nH^+$  series,  $m = 0, 1, \text{ and } 2$ , are labeled by closed symbols. They correspond to the analogous  $(HNO_3)_m(H_2O)_nH^+$  series in pure clusters without pickup, indicated in panel (b) by open symbols. The series with methanol is remarkably similar to the one without; the peaks are shifted by methanol mass  $\Delta m/z = 32$  and have lower intensities. Only the series with a single methanol molecule could be identified. These observations justified our evaluation of the above-mentioned uptake probabilities—we integrate the mass peaks series with and without the adsorbed molecules, and an appropriate ratio of these integrals corresponds to the uptake probability (see ref 38 for details).



**Figure 5.** Schematic illustration of the increasing complexity of clusters investigated in the present MB experiments: from pure ice nanoparticles to hydrated acid clusters, which were doped by further molecules in pickup experiments. Uptake probabilities were evaluated for the pickup of organic molecules. Doping with base molecules DMA and  $\text{NH}_3$  led to acid–base chemistry, and complex  $\text{NH}_3/\text{DMA}/\text{HNO}_3/\text{H}_2\text{O}$  clusters were prepared in a double-pickup experiment.

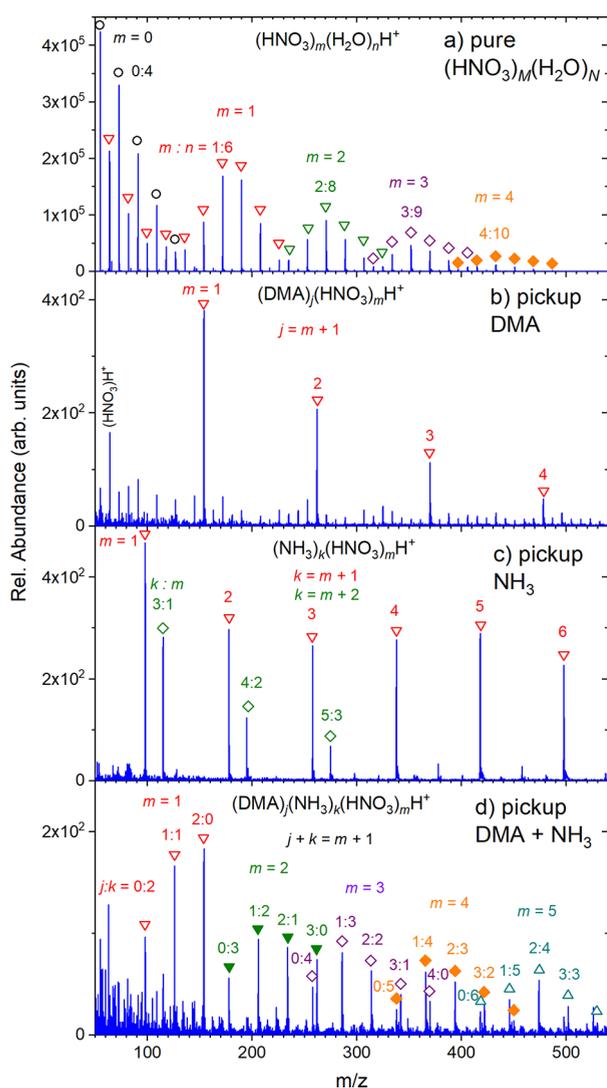
However, the spectrum after the methanol pickup by sulfuric acid clusters in Figure 4c has a different character. Figure 4d shows the spectrum of pure  $(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n$  clusters without pickup. It is similar to the nitric acid spectrum in Figure 4b: protonated  $(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n\text{H}^+$  cluster ion series with  $m = 1-3$  and up to  $n = 6$  water molecules are observed. On the other hand, after the methanol pickup, the completely dehydrated series  $(\text{CH}_3\text{OH})_k(\text{H}_2\text{SO}_4)_m\text{H}^+$ ,  $m = 1-3$ , with up to  $k = 2$  methanol molecules dominate the spectrum. Reasonable spectra with pickup of only a single methanol molecule could not be obtained with sulfuric acid. From this spectrum, we cannot derive the pickup probability, since the different character of the spectra precludes the application of our procedure outlined in ref 38. Nevertheless, some qualitative conclusions can be made: First, the differences in the spectra point to a larger pickup probability for methanol by sulfuric acid than by nitric acid. Second, a complete dehydration of sulfuric acid clusters upon methanol uptake is observed, while the nitric acid clusters with adsorbed methanol are still substantially hydrated. This can have interesting implications for aerosol chemistry, which calls for further MB and theory investigations.

**Chemical Composition of Clusters and Atmospheric Aerosols.** One of the major gaps between clusters in MB and atmospheric AN exists in their chemical composition. Aerosol particles in the atmosphere are complex multicomponent species, and their composition can often only be determined approximately. For aerosols generated in laboratory experiments, the input gas components are known exactly, and the composition of clusters generated in MB can be determined relatively well by mass spectrometry, although fragmentation upon ionization, intracluster ion–molecule reactions, and other processes have to be cautiously considered.<sup>28,29,36,57–61</sup> Figure 5 illustrates the increasing complexity of clusters investigated in MB experiments discussed in this Perspective. They converge toward the composition of atmospheric AN. Mixed nitric acid–water<sup>24,25,36,51,52</sup> and sulfuric acid–water<sup>62</sup> clusters already represented a small step toward atmospheric AN. Other acids are detected in atmospheric aerosols, too; e.g., methanesulfonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ ) was observed in substantial amounts in field measurements of the coastal marine boundary layer.<sup>63</sup> Recent MB experiments with hydrated methanesulfonic acid clusters revealed their chemistry upon gradual hydration and interaction with electrons.<sup>64</sup>

The uptake of different molecules on hydrated nitric acid clusters discussed above represented a further step toward multicomponent atmospheric AN.<sup>37,38</sup> In atmospheric aerosols, reactions between acid and base molecules lead to cluster

stabilization and growth. In this respect, uptake of dimethylamine  $(\text{CH}_3)_2\text{NH}$  (DMA) on hydrated nitric acid clusters has recently been investigated in a MB experiment.<sup>65</sup> Figure 6 shows examples of hydrated nitric acid cluster mass spectra after the pickup of DMA molecules. The ions were produced by 70 eV electron impact ionization. The ionization of pure  $(\text{HNO}_3)_m(\text{H}_2\text{O})_n$  clusters without any pickup yielded the protonated cluster ion fragment series  $(\text{HNO}_3)_m(\text{H}_2\text{O})_n\text{H}^+$ , Figure 6a. The shape of these series was previously explained by  $\text{HNO}_3$  acid dissociation in water.<sup>24,36</sup> Clearly, the spectrum exhibits substantially hydrated clusters. When DMA molecules are picked up by these clusters prior to their ionization, the spectrum is dominated by the  $(\text{DMA})_j(\text{HNO}_3)_m\text{H}^+$  series with  $j = m + 1$ , Figure 6b, and water essentially evaporates from these clusters. The same dehydration trend was observed upon a slow electron attachment, generating negatively charged clusters  $(\text{DMA})_j(\text{HNO}_3)_m\text{NO}_3^-$  with  $j \leq m$ .<sup>65</sup> Thus, the water molecules partly evaporate from the neutral clusters due to the energy released upon the acid–base reaction. It substantiates findings from chamber nucleation experiments, where anhydrous aerosol particles are detected despite the fact that water vapor strongly enhances the aerosol nucleation.<sup>21–23</sup> The mass spectra exhibit an intriguing difference in the cluster ion composition, suggesting clusters with the number of DMA exceeding the number of  $\text{HNO}_3$  molecules in the positive ion spectrum, while the negative one indicates more  $\text{HNO}_3$  than DMA molecules in the clusters. The experiments were accompanied by *ab initio* calculations, which explained this puzzle by the tendency to maximize the number of  $\text{DMA}\cdot\text{H}^+\cdots\text{NO}_3^-$  ion pairs. This condition was fulfilled for the observed cluster ions, and for the corresponding neutral clusters it implicated an equal number of DMA and  $\text{HNO}_3$  molecules for the minimum energy structure.

Dimethylamine together with ammonia are among the most studied bases involved in NPF in the atmosphere. Here, we also show our preliminary results for the pickup of ammonia in Figure 6c. The spectrum is dominated by  $(\text{NH}_3)_k(\text{HNO}_3)_m\text{H}^+$  series with  $k = m + 1$  analogous to Figure 6b. There is also a weaker  $k = m + 2$  series (green diamonds), which could be alternatively assigned to a non-protonated  $(\text{NH}_3)_{k-1}(\text{HNO}_3)_m\text{H}_2\text{O}^+$  clusters. Experiments with deuterated  $\text{ND}_3$  can provide unambiguous assignment in future. At the moment, we focus on the synergistic effect between ammonia and dimethylamine. In laboratory investigations of atmospheric aerosols combining amines and ammonia together with sulfuric acid, an increase in NPF rates by orders of magnitude was observed in comparison with two-component acid–amine or



**Figure 6.** Examples of hydrated nitric acid cluster mass spectra after pickup of DMA and  $\text{NH}_3$  molecules and 70 eV electron ionization. (a) Pure  $(\text{HNO}_3)_M(\text{H}_2\text{O})_N$  clusters without any pickup. Protonated cluster ion fragment series  $(\text{HNO}_3)_m(\text{H}_2\text{O})_n\text{H}^+$  are indicated by symbols for different  $m$ , and pronounced peaks in the series are labeled by  $m:n$ . (b) The spectrum after the pickup of DMA molecules is dominated by a single series  $(\text{DMA})_j(\text{HNO}_3)_m\text{H}^+$  with  $j = m + 1$ . (c) The spectrum after the pickup of ammonia exhibits an analogous series  $(\text{NH}_3)_k(\text{HNO}_3)_m\text{H}^+$  with  $k = m + 1$  and a weaker  $k = m + 2$  series (green diamonds). (d) Subsequent pickup of DMA and  $\text{NH}_3$  exhibits  $(\text{DMA})_j(\text{NH}_3)_k(\text{HNO}_3)_m\text{H}^+$  series with  $j + k = m + 1$ . Different colors (and symbols) indicate these series for different  $m$ , and individual peaks are labeled by  $j:k$ .

acid–ammonia mixtures.<sup>66,67</sup> The measurements suggested that atmospheric nucleation rates were significantly increased by synergistic interactions between ammonia and amines.<sup>67</sup> This effect has recently been investigated theoretically in sulfuric acid/dimethylamine/ammonia clusters.<sup>68</sup> Ammonia forms bridges in sulfuric acid–dimethylamine clusters since it can generate more intermolecular interactions than dimethylamine. We can pick up different molecules in successive pickup cells in our MB experiment. Thus, we have investigated the subsequent uptake of DMA and  $\text{NH}_3$  molecules by the  $(\text{HNO}_3)_M(\text{H}_2\text{O})_N$  clusters shown in Figure 6d. The spectrum exhibits a  $(\text{DMA})_j(\text{NH}_3)_k(\text{HNO}_3)_m\text{H}^+$  series with  $j + k = m + 1$ , as

indicated by different colors and symbols. Here, DMA molecules were first picked up by the clusters, followed by the pickup of  $\text{NH}_3$ . Switching the order in which the molecules were picked up resulted in no qualitative change in the spectrum. Thus, the composition and presumably also the structure of the detected cluster ions do not depend on the order in which the molecules are deposited on the neutral clusters. In other words, the clusters will converge to the same structures, independent of whether DMA or  $\text{NH}_3$  molecules were picked up by the cluster first and had time to react with the acid in the cluster before the other kind of molecules were added. This is an interesting result on which further experiments and theoretical calculations will concentrate. This example illustrates MB experiments, where the cluster complexity approaches real atmospheric AN. At the same time, MB experiments provide a deeper insight into the processes in the cluster after the uptake of DMA and  $\text{NH}_3$  separately compared to experiments with co-nucleating mixtures of DMA,  $\text{NH}_3$ , acids, and water all at the same time.

**Interaction with Radiation.** Various types of radiation play important roles in NPF and atmospheric aerosol chemistry and physics.<sup>21,22</sup> Interactions of aerosol particles with photons, free electrons, ions, and other energetic particles result in the generation of ions and radicals that often undergo immediate secondary reactions and further processes in ambient atmosphere. If radiation effects on aerosols are investigated in cloud-chamber type experiments, the underlying elementary processes are masked by following reactions and can be revealed only indirectly. On the other hand, clusters in MB represent ideal objects to mimic the interaction of isolated atmospheric aerosol particles with various types of radiation and particles, and at the same time the products of primary processes can be detected directly.

Just to mention one example relevant to photochemistry in the stratosphere, large pure water clusters (ice nanoparticles) were implemented as laboratory analogues of polar stratospheric cloud (PSC) particles. PSCs provide ice surfaces in the stratosphere to catalyze reactions of reservoir species (e.g.,  $\text{HCl}$ ,  $\text{ClONO}_2$ ) to active species (e.g.,  $\text{Cl}_2$ ,  $\text{HOCl}$ ), yielding  $\text{Cl}$  radicals upon photolysis with solar UV radiation, leading to ozone depletion.<sup>69,70</sup> With this motivation, the pickup and photodissociation of hydrogen halides ( $\text{HX}$ ,  $\text{X} = \text{Br}$ ,  $\text{Cl}$ ,  $\text{I}$ )<sup>71–73</sup> and Freon ( $\text{CF}_2\text{Cl}_2$ )<sup>74</sup> on ice nanoparticles were investigated in MB. For hydrogen halides, a detailed molecular-level mechanism of their excitation was revealed by MB experiments combined with *ab initio* calculations:<sup>71,72</sup> an ion pair  $\text{H}_3\text{O}^+\cdots\text{X}^-$  was formed in the ground state, and the UV excitation yielded a neutral hydronium radical ( $\text{H}_3\text{O}$ ) and halogen radical ( $\text{X}$ ) within a charge-transfer-to-solvent excitation process.<sup>75</sup> The hydronium radicals ultimately decayed into water molecules, and  $\text{H}$  fragments were detected; see refs 71 and 72 and references cited therein for more details. Theoretical calculations suggested that in the case of  $\text{HCl}$  the acidic dissociation can lead to an enhancement of the  $\text{HCl}$  photolysis rate by orders of magnitude, which could be relevant for the halogen budget in the atmosphere.<sup>71</sup> The pickup of Freon  $\text{CF}_2\text{Cl}_2$  on clusters led to a caging of  $\text{Cl}$  atoms after UV photodissociation,<sup>74</sup> in contrast to the photodissociation of free gas-phase molecules.<sup>76</sup> These experiments demonstrate the importance of the cluster environment in UV photodissociation in atmospherically relevant systems, which can be investigated in detail in MB. They can be extended by combination with pickup experiments depositing hydrogen halides and other atmospheric molecules on hydrated nitric acid clusters, which represent better proxies to

PSC particles, and investigating their UV photochemistry. It ought to also be mentioned that the interactions of atmospherically relevant clusters with electrons<sup>51,52,59,77</sup> and ions<sup>78,79</sup> have been explored in different MB experiments.

**Future Directions.** A few examples above have demonstrated that MB experiments can successfully model processes in atmospheric aerosol nanoparticles and provide a useful molecular-level insight. Further developments of MB experiments can bring clusters in MB even closer to atmospheric AN. Co-expansion and pickup MB methods discussed above can already produce multicomponent clusters mimicking complex aerosols. However, species which are not easy to evaporate are difficult to incorporate into clusters in MB, yet they are indispensable components of many aerosol particles, e.g., salts in sea-spray aerosols.<sup>1,3,6,7,80</sup> Aerosol particles can be generated directly from liquid salt solutions using an atomizer and transferred into a MB with an aerodynamics lens;<sup>81</sup> however, the sizes of such particles are typically in the 10<sup>2</sup> nm range. Electrospray ionization (ESI) is ideally suited for the generation of salt–solution clusters, yet it produces charged clusters while the majority of atmospheric aerosol particles are neutral. Nevertheless, charged clusters can be neutralized by a charge transfer for positive ions<sup>82,83</sup> or electron detachment for negative ones. Thus, using an ESI source with a mass selection of ionic clusters and their subsequent neutralization might enable unique experiments with *size-selected neutral clusters*, which are atmospherically relevant.

Many processes relevant to NPF and aerosol particle growth and their chemistry happen upon particle–particle collisions. The dawn of MB in chemistry was marked in the 1960s by investigations of molecule–molecule collision dynamics in crossed molecular beams.<sup>35,84</sup> Similar crossed beam experiments with clusters can reveal details of cluster–cluster collisions relevant to atmospheric AN collisions. Aerosol particles can grow by cluster coalescence mimicked in cluster collisions. However, other interesting atmospheric phenomena can be investigated in crossed beams as well. For example, particle collisions were implemented in the charging of thunderstorm clouds via a charge transfer between colliding particles.<sup>85,86</sup> While the collisional mechanism of thundercloud charging is well established, the details of the charge transfer between colliding particles is still not completely understood at a molecular level, and crossed cluster beam experiments could elucidate such processes.

One of the major factors determining chemistry in atmospheric aerosols is their temperature. This represents one of the biggest challenges for MB experiments, since the cluster temperature cannot be easily controlled nor measured.<sup>29</sup> Although limited control can be achieved in special cases by changing cluster source conditions,<sup>87</sup> in this respect, the cloud-chamber, flow-tube, and Laval-nozzle type experiments are superior, offering a precise control over the range of atmospherically relevant temperatures. Reaction time also represents an important factor in chemistry; however, the level of control and possibilities to extend the reaction time in MB experiments are limited by the physical distance which the clusters fly in a MB apparatus (usually milliseconds or shorter). Despite these deficiencies, clusters in MB represent a viable approach to provide detailed molecular-level insight relevant to atmospheric AN, and future MB experiments and developments of MB techniques will prove instrumental for understanding of atmospheric aerosols.

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### Notes

The author declares no competing financial interest.

### Biography

Michal Fárník obtained his Ph.D. at the Faculty of Mathematics and Physics, Charles University, Prague, in 1995. He completed three postdoctoral stays: 1995–1998 Alexander von Humboldt Fellowship in Göttingen, Germany; 1998–2001 at JILA in Boulder, Colorado, USA; and 2002–2004 back in Göttingen. In 2005, he received a prestigious return fellowship of the Czech Science Academy to start new research at the J. Heyrovský Institute in Prague, where he founded his new laboratory focused on experiments with clusters in molecular beams. His group investigates dynamics of processes in molecules interacting with photons and electron in cluster environments. The main emphasis is on clusters of atmospheric and astrochemical relevance.

## ACKNOWLEDGMENTS

The author acknowledges the support of the Czech Science Foundation GAČR project number 21-07062S, and the Praemium Academiae of the Czech Academy of Sciences. The results from the author's group reviewed in this Perspective were obtained thanks to Jozef Lengyel, Andriy Pysanenko, Viktoryia Poterya, Jaroslav Kočíšek, Juraj Fedor, and Eva Pluhařová.

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