DECOMPOSITION AND GROWTH PATHWAYS OF AEROSOLIZED AMMONIUM NITRATE PARTICLES

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MOTIVATION

Improper handling of ammonium nitrate has been responsible for many disasters such as the 2020 Beirut explosion.

→ Better understanding the **decomposition** of ammonium nitrate is important for storing and transporting it safely.

New particle formation causes haze in polluted urban environments and these particles can interact with solar radiation or act as nuclei for cloud condensation.

→ Better understanding the **growth** of ammonium nitrate clusters can lead to better modeling haze formation and the global climate.

METHODS

To explain decomposition pathways observed in sputtered mass spectra from literature, binding energies of various pathways were compared.

↓ OPLS simulated annealing Monte Carlo geometry optimizations using TransRot (OPLS/TR) followed by ωB97X-D3/def2-TZVPD//ωB97X-D3/def2-SVPD calculations

The neutral nanoparticles $(NH_4NO_3)_n$ were studied in hopes to learn about the early stages of particle growth and observe patterns in the structures.

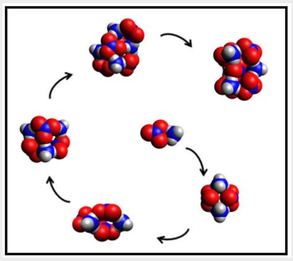

Figure 1. Predicted structures of selected $(NH_4NO_3)_n$ clusters from OPLS/TR calculations followed by ωB97X-D3/def2-SVPD geometry optimization.

RESULTS – DECOMPOSITION

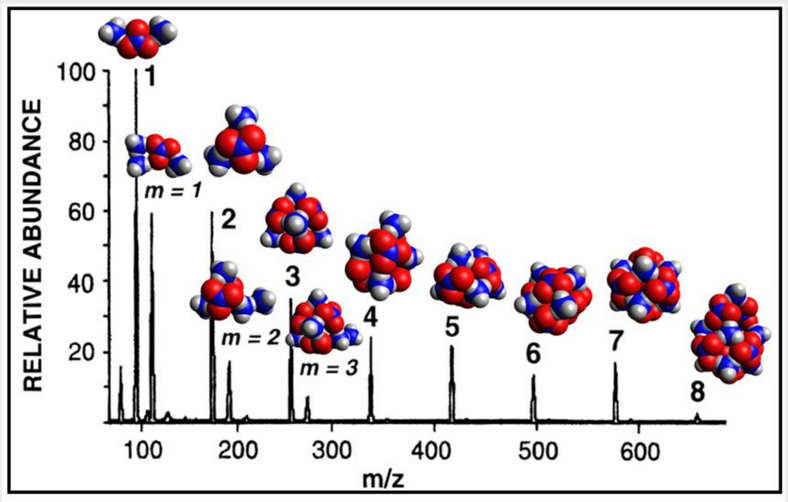

Figure 2. Positive-ion sputtered mass spectrum by Dunlap and Doyle. Predicted structures of parent and daughter cluster ions corresponding to the numbered peaks have been added to the spectrum.

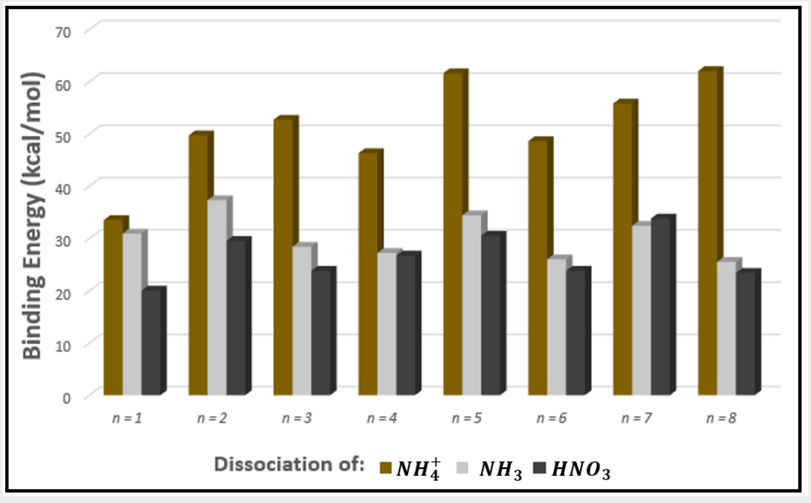

Figure 3. ωB97X-D3 electronic binding energies for different $[(NH_4NO_3)_nNH_4]^+$ fragmentation channels of clusters.

The peaks labeled 1-8 in Figure 2 correspond to the ammonium nitrate cation, $[(NH_4NO_3)_nNH_4]^+$. The "m-series" peaks are related to the n-series through loss of a molecule of nitric acid, shown by R1 where $m = n - 1$. Additionally, decomposition through the loss of ammonia or ammonium were also considered, shown by R2 and R3, respectively.

$$[(NH_4NO_3)_nNH_4]^+ \rightarrow [(NH_4NO_3)_mNH_3NH_4]^+ + HNO_3 \quad \text{(R1)}$$

$$[(NH_4NO_3)_nNH_4]^+ \rightarrow [(NH_4NO_3)_{n-1}HNO_3NH_4]^+ + NH_3 \quad \text{(R2)}$$

$$[(NH_4NO_3)_nNH_4]^+ \rightarrow (NH_4NO_3)_n + NH_4^+ \quad \text{(R3)}$$

From Figure 3 we see that NH_4^+ is generally very difficult to remove, and loss of HNO_3 is much more facile than loss of NH_3 for every case except $n = 7$. This explains the presence of the "m-series" peaks observed in the experimental literature.

The same analysis was done on the mass spectrum for ammonium nitrate anions and our calculations supported the observed decomposition through loss of ammonia.

RESULTS - GROWTH

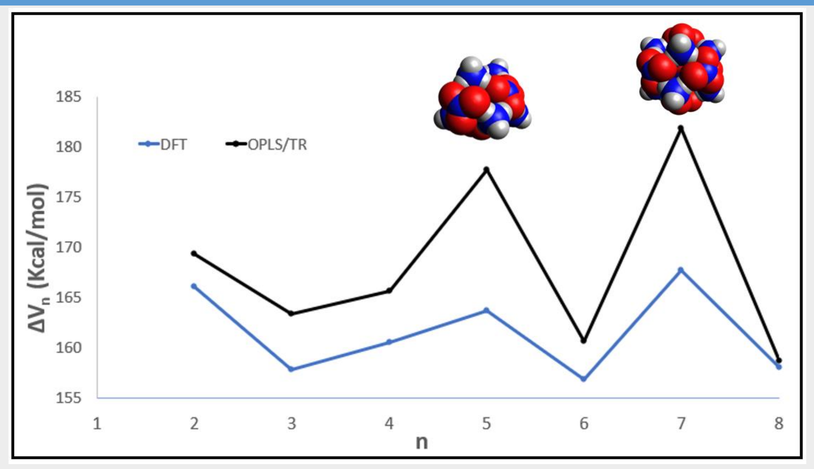

Figure 4. ωB97X-D3 and OPLS/TR differential interaction energies for the $[(NH_4NO_3)_nNH_4]^+$ parent clusters.

The differential interaction energies , ΔV_n, of clusters are calculated according to

$\Delta V_n = V_{n-1} - V_n$.

A high ΔV_n predicts that a structure is relatively stable and energetically disfavored to lose or gain an ion pair.

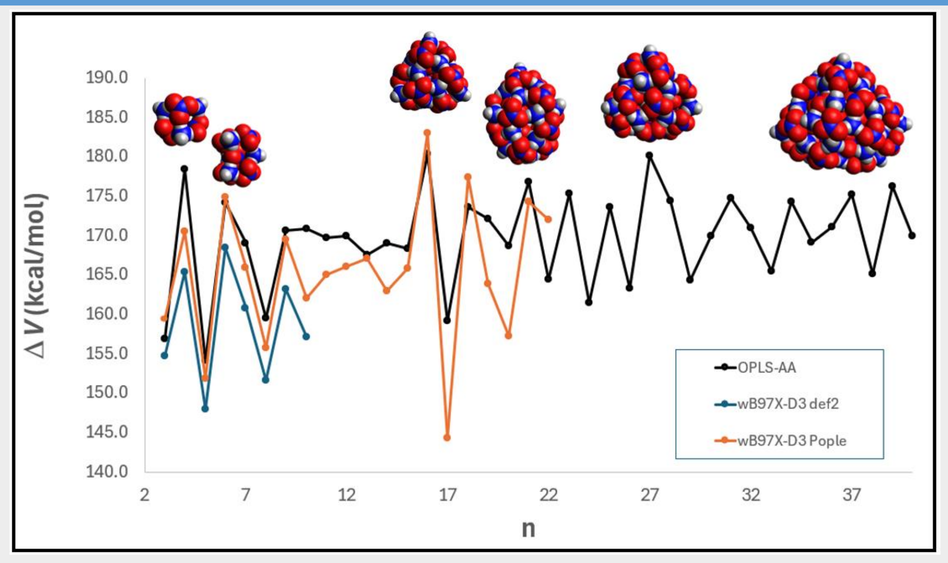

Figure 5. ωB97X-D3 differential interaction energies for $(NH_4NO_3)_n$ from OPLS-AA (black) and ωB97X-D3/def2-TZPD calculations (blue). Also shown: ωB97X-D3/6-311+G(2df,2p)[6-311G*]//wB97X-D3/6-31G(d) calculations (orange). The optimized n = 4, 6, 16, 21, 27, and 37 structures are shown.

Looking back at Figure 2, we see that the $n = 5$ peak in the mass spectrum appears to be slightly taller than the trend in successive peak heights would predict from a uniform decline, and the $n = 7$ peak is slightly taller than its neighbors. Repeated mass spectroscopy experiments with varied sputtering energies would be helpful in revealing whether or not these clusters are unusually stable.

Now looking at the neutral series $(NH_4NO_3)_n$, we see that n = 4 heterocubane structure, butterfly-shaped n = 6 structure, the near-triangular-prism n = 9, and the trigonal pyramidal n = 16 cluster are quite stable.

CONCLUSIONS AND FUTURE WORK

With our computational methods, we were able to fully characterize the presence of the *m*-series in the positive-ion sputtered mass spectrum (corresponding to loss of nitric acid). We also showed preliminary evidence for magic numbers for larger nanoparticles, including larger pyramidal structures. None of these structures seem to resemble the structure of the bulk NH_4NO_3 (s). The question arises of how big the nanoparticle needs to be for its structure to resemble that of the bulk; there should be some critical size when this occurs. Additionally, solvent affects can be considered by adding water molecules to calculations.

ACKNOWLEDGMENTS

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