Computational Analysis of Mass Spectra and Growth Patterns of Ammonium Nitrate Nanoparticles

Ubaidullah S. Hassan
Prof. Robert Q. Topper

Department of Chemistry and Department of Chemical Engineering
The Cooper Union for the Advancement of Science and Art

Haze in Beijing, China

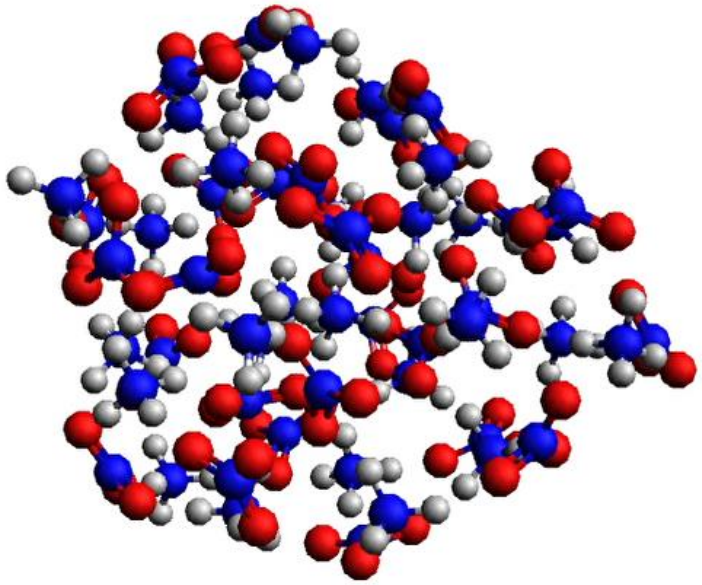
Feng Li—Getty Images **(2015)**

- Aerosols can deposit in the lungs causing asthma, allergies, and cancer
- Ammonium nitrate makes up ~40% by mass of all particulate matter with a width of less than 2.5 µm

Our group's software

Maintained at GitHub: https://github.com/steventopper/Transrot

- Used for predicting the structures of nanoparticles (simulated annealing Monte Carlo geometry optimizations)
- Minimizes energy according to OPLS force field



$$\mathrm{U} = \sum_{i} \sum_{j>i} [\underbrace{\frac{D_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^{6}}}_{\text{Van der Waals}} + \underbrace{\kappa \frac{Q_i Q_j}{r_{ij}}}_{\text{Electrostatic}}]$$

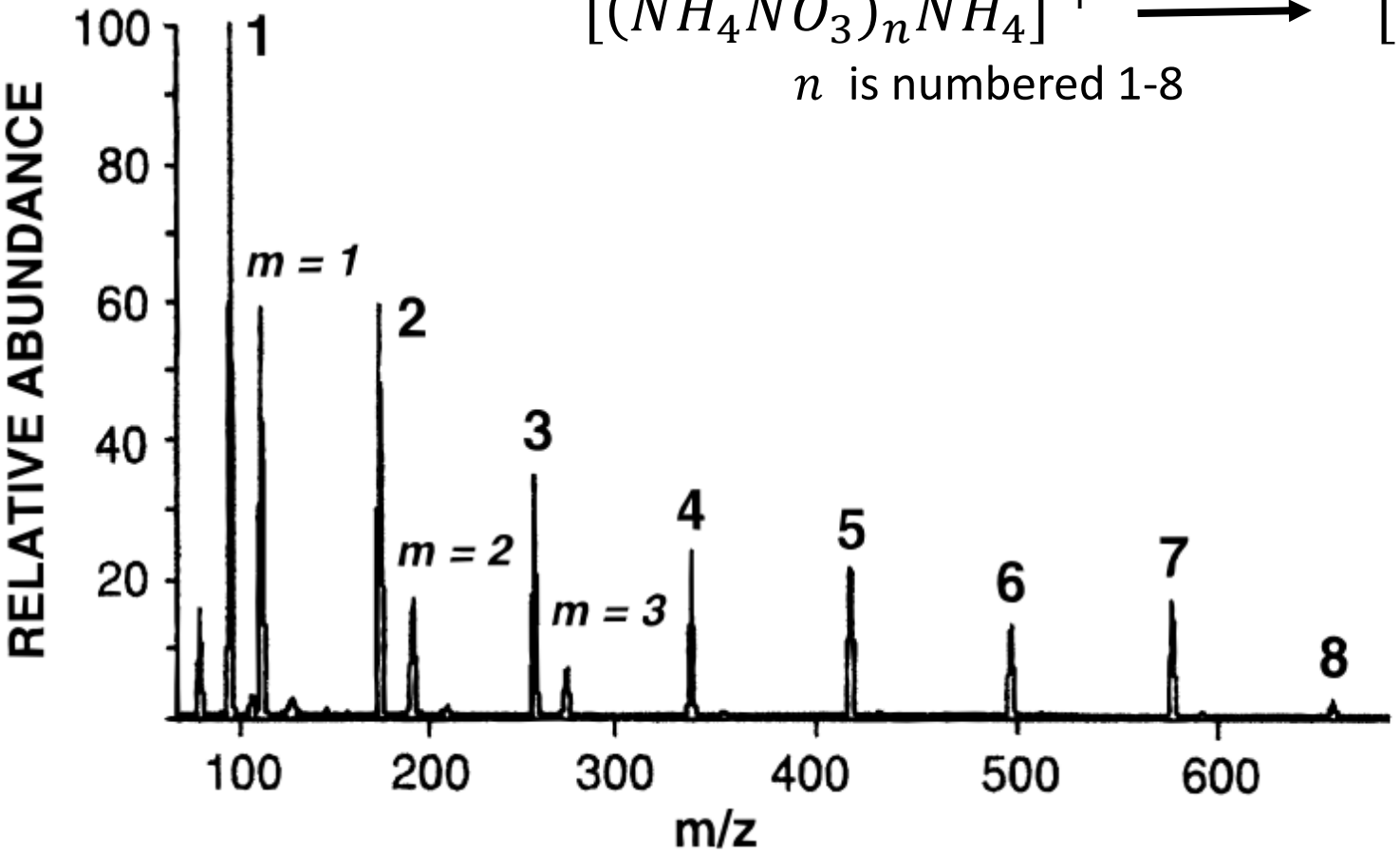
- Followed up by density functional theory calculations (ωB97M-V/6-311+G(2df,2p))

Positive-ion sputtered mass spectrum from the literature

$$[(NH_4NO_3)_nNH_4]^+ \longrightarrow [(NH_4NO_3)_mNH_3NH_4]^+ + HNO_3$$

n is numbered 1-8

$m = n - 1$



Dunlap and Doyle *J. Phys. Chem.* **(1996)**

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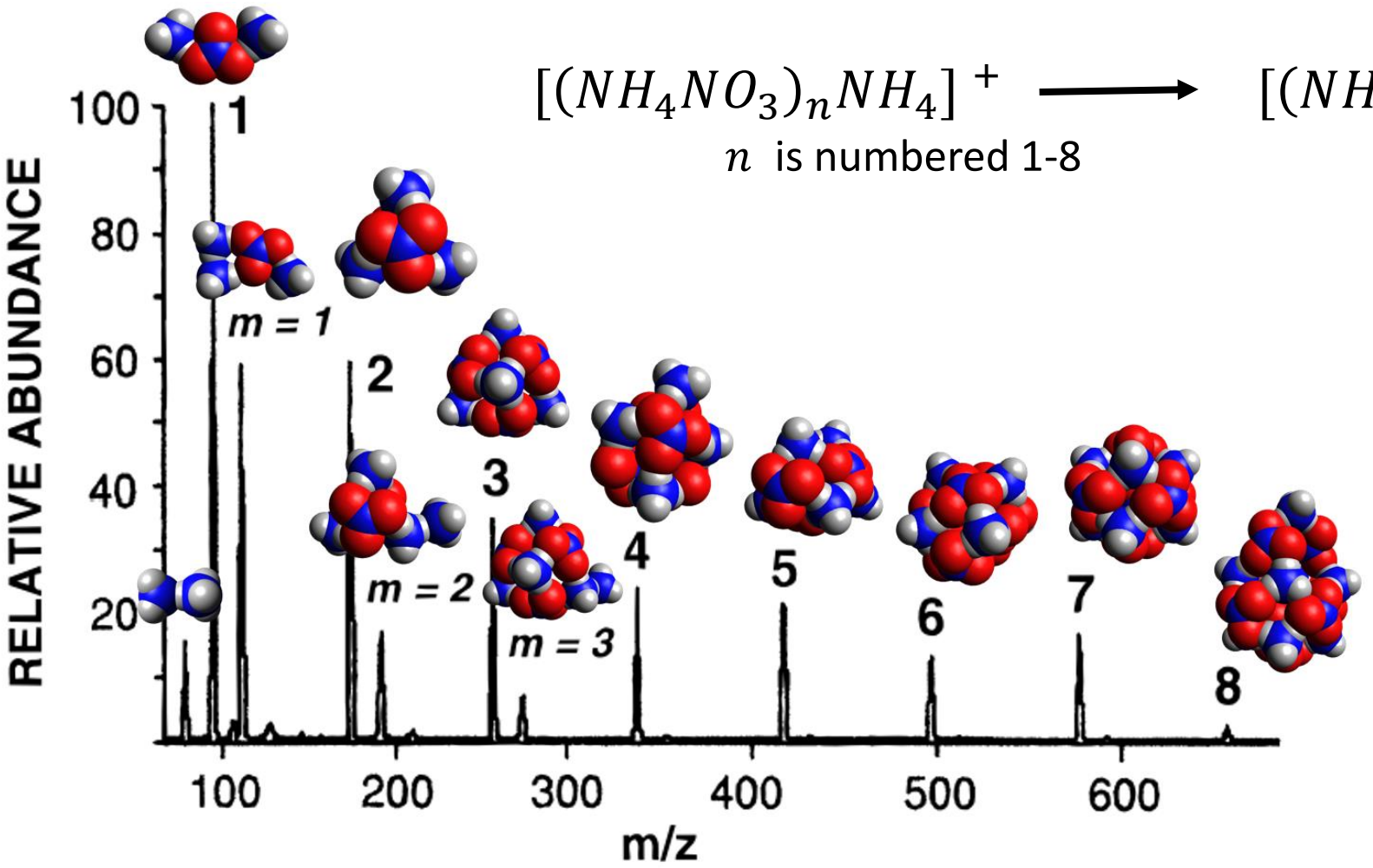
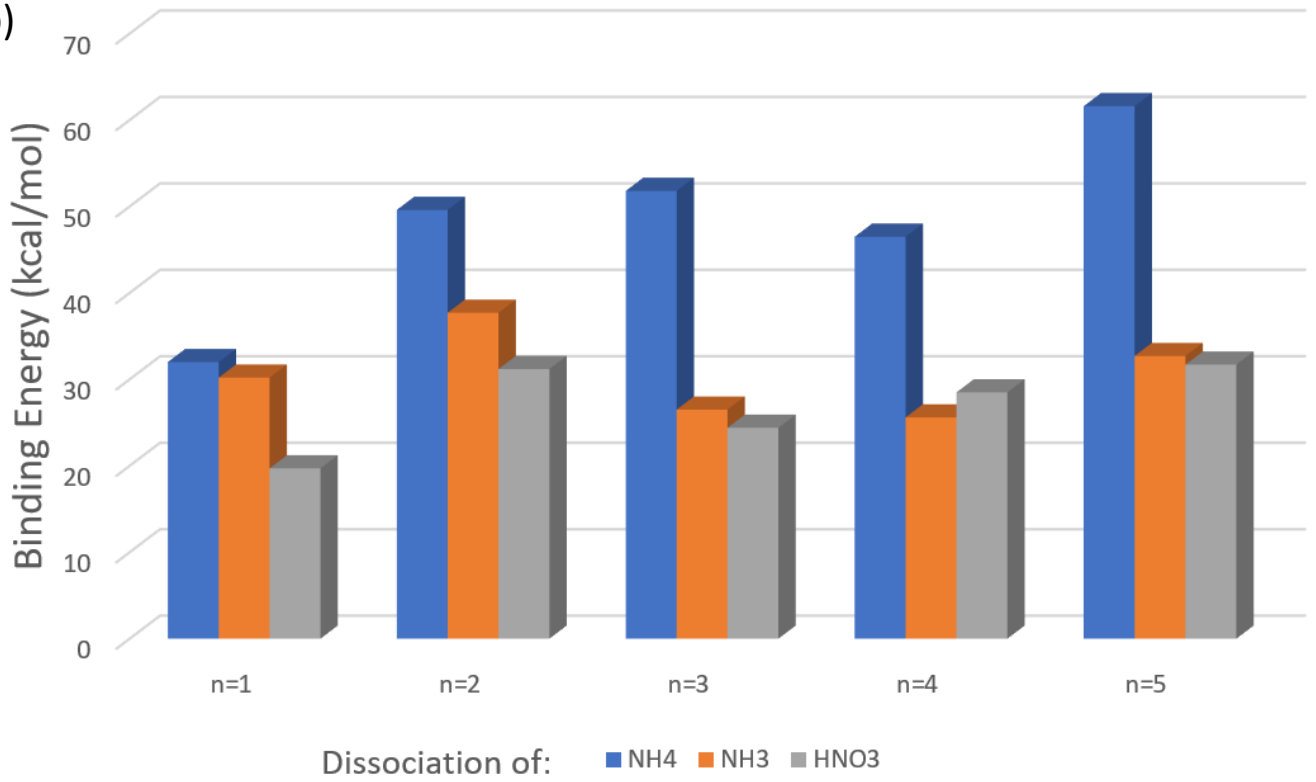


Dunlap and Doyle *J. Phys. Chem.* **(1996)**

Explaining the peaks in the positive-ion sputtered mass spectrum

DFT ωB97M-V/6-311+G(2df,2p)

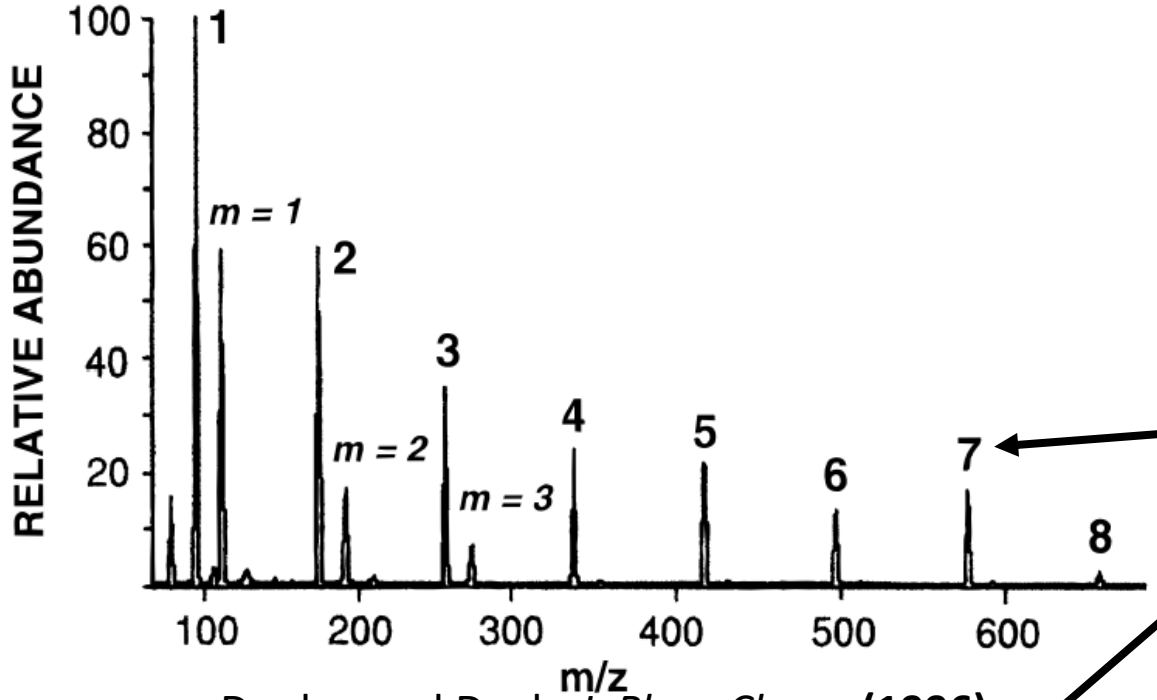


$$NH_4^+ + (NH_4NO_3)_n \longrightarrow [(NH_4NO_3)_nNH_4]^+$$

$$NH_3 + [(NH_4NO_3)_{n-1}NH_4HNO_3]^+ \longrightarrow [(NH_4NO_3)_nNH_4]^+$$

$$HNO_3 + [(NH_4NO_3)_{n-1}NH_3NH_4]^+ \longrightarrow [(NH_4NO_3)_nNH_4]^+$$

$$\Delta V_n^+ = V_{n-1}^+ - V_n^+$$



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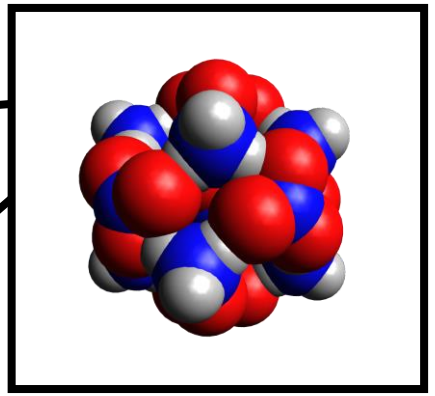
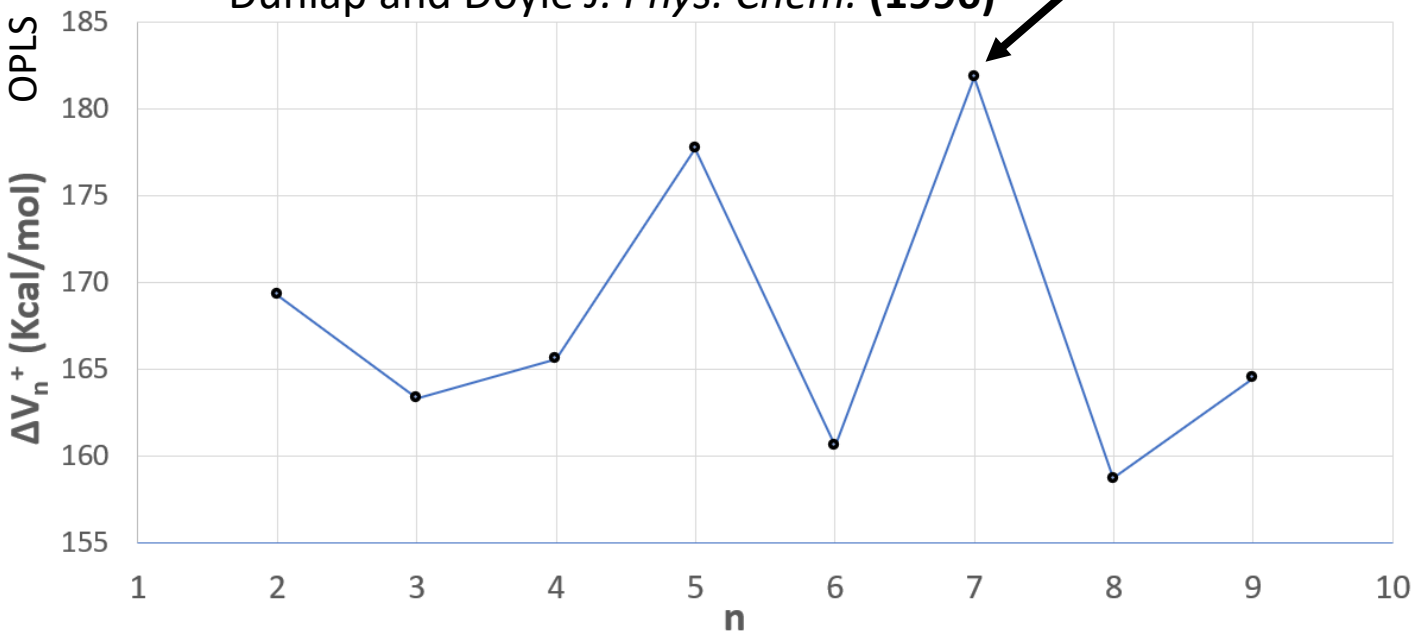
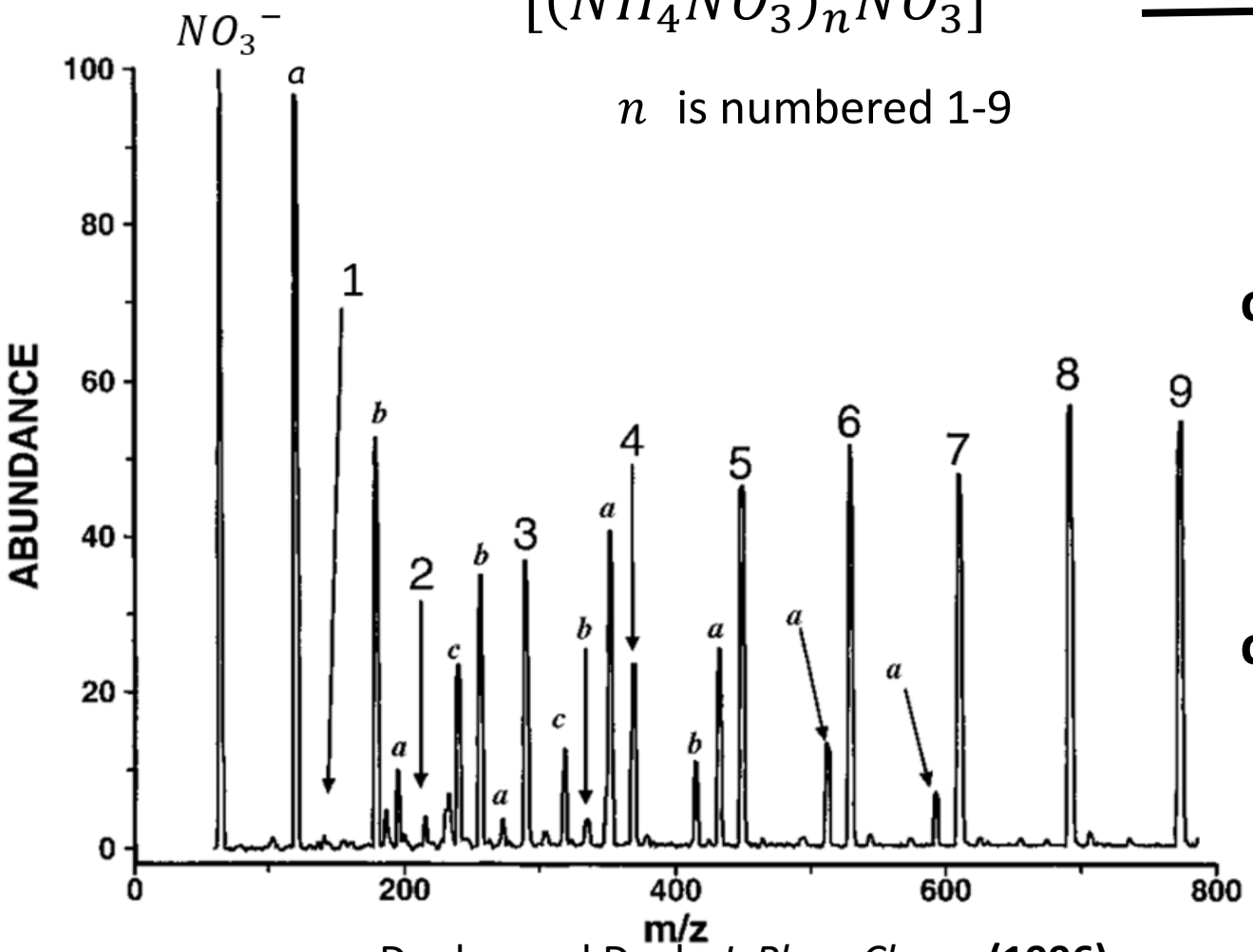




Negative-ion sputtered mass spectrum



Dunlap and Doyle *J. Phys. Chem.* **(1996)**

$[(NH_4NO_3)_nNO_3]^-$ ⟶ $[(NH_4NO_3)_{n-1}HNO_3NO_3]^- + NH_3$

n is numbered 1-9

a

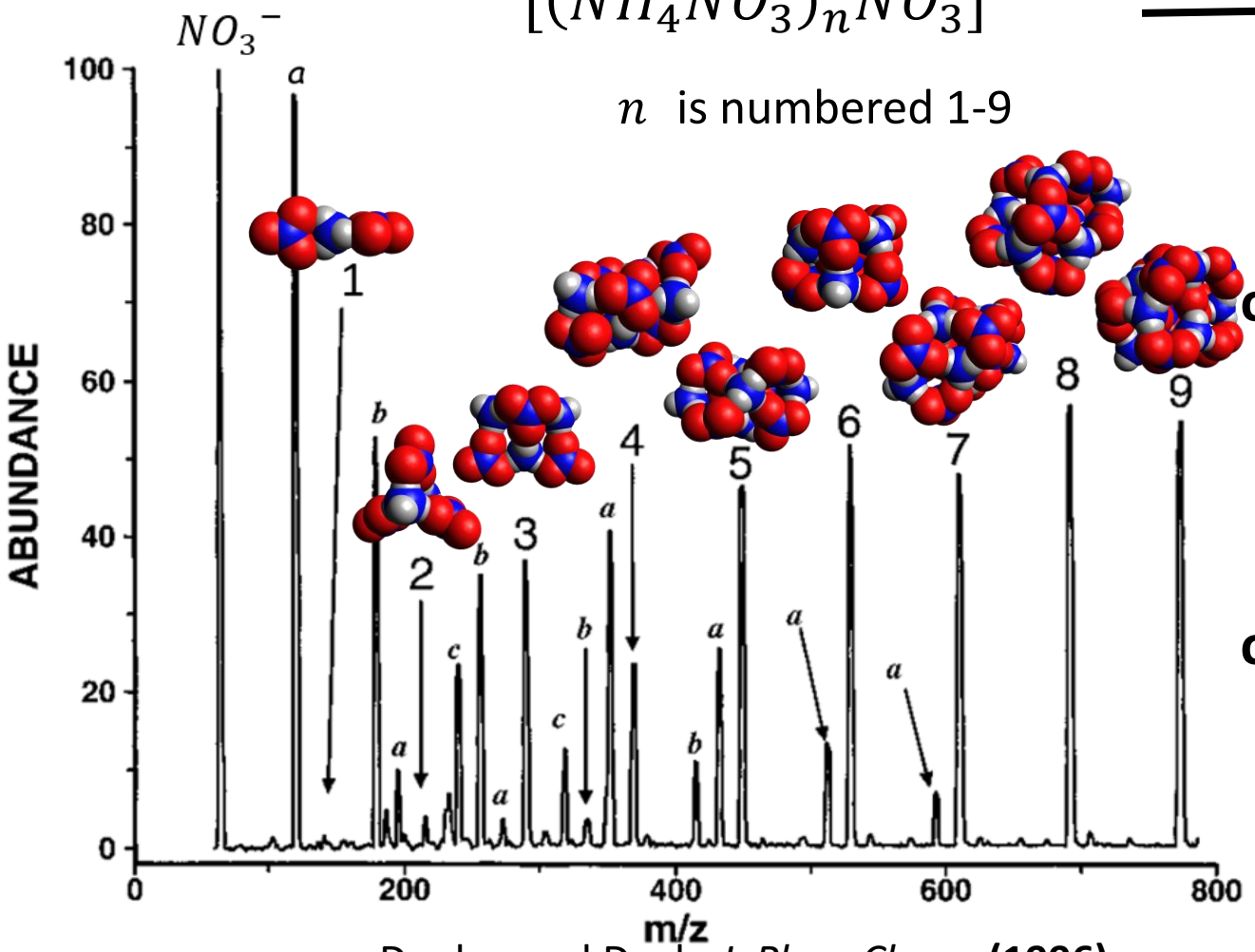
or $[(NH_4NO_3)_{n-2}(HNO_3)_2NO_3]^- + 2NH_3$

b

or $[(NH_4NO_3)_{n-3}(HNO_3)_3NO_3]^- + 3NH_3$

c

Negative-ion sputtered mass spectrum



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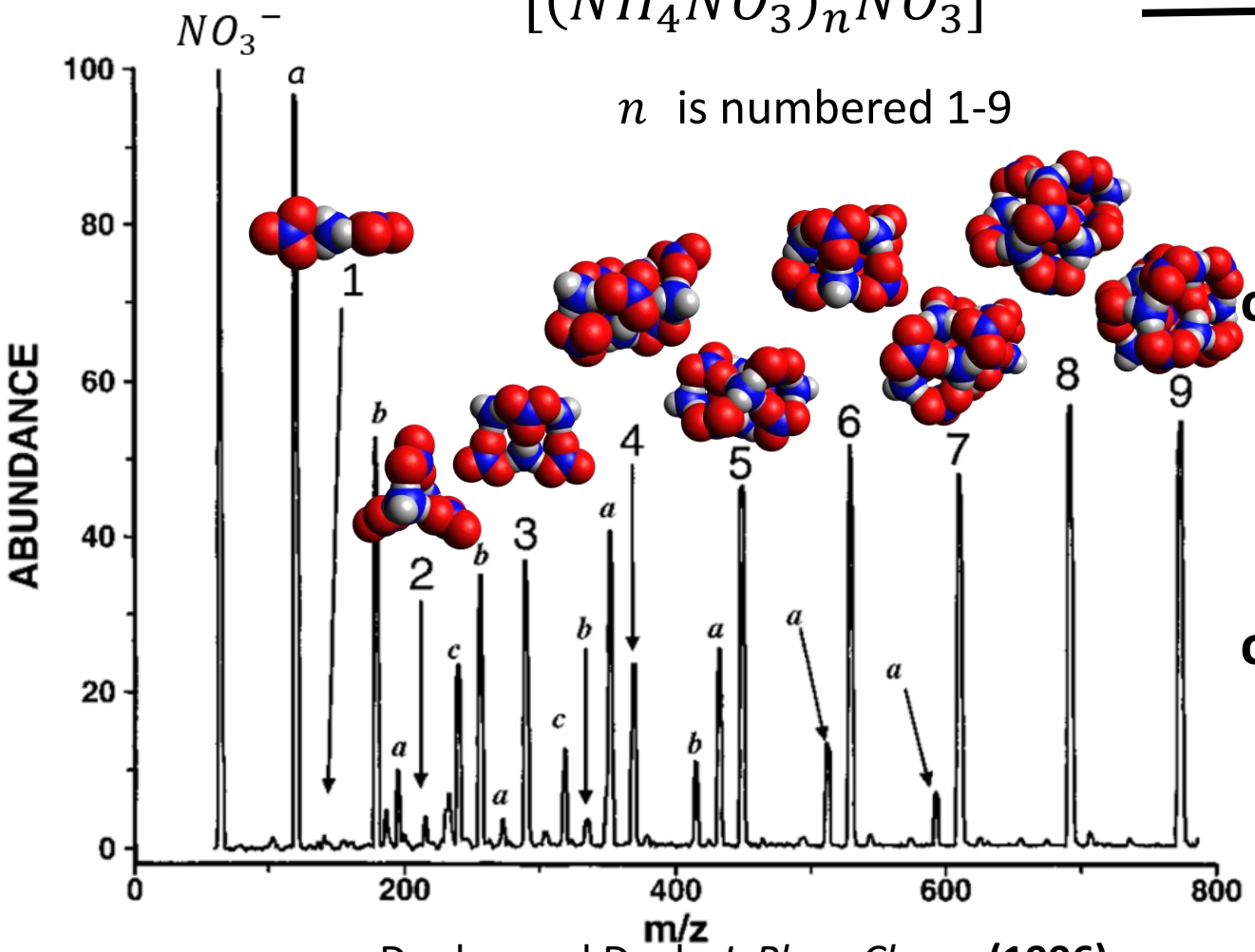

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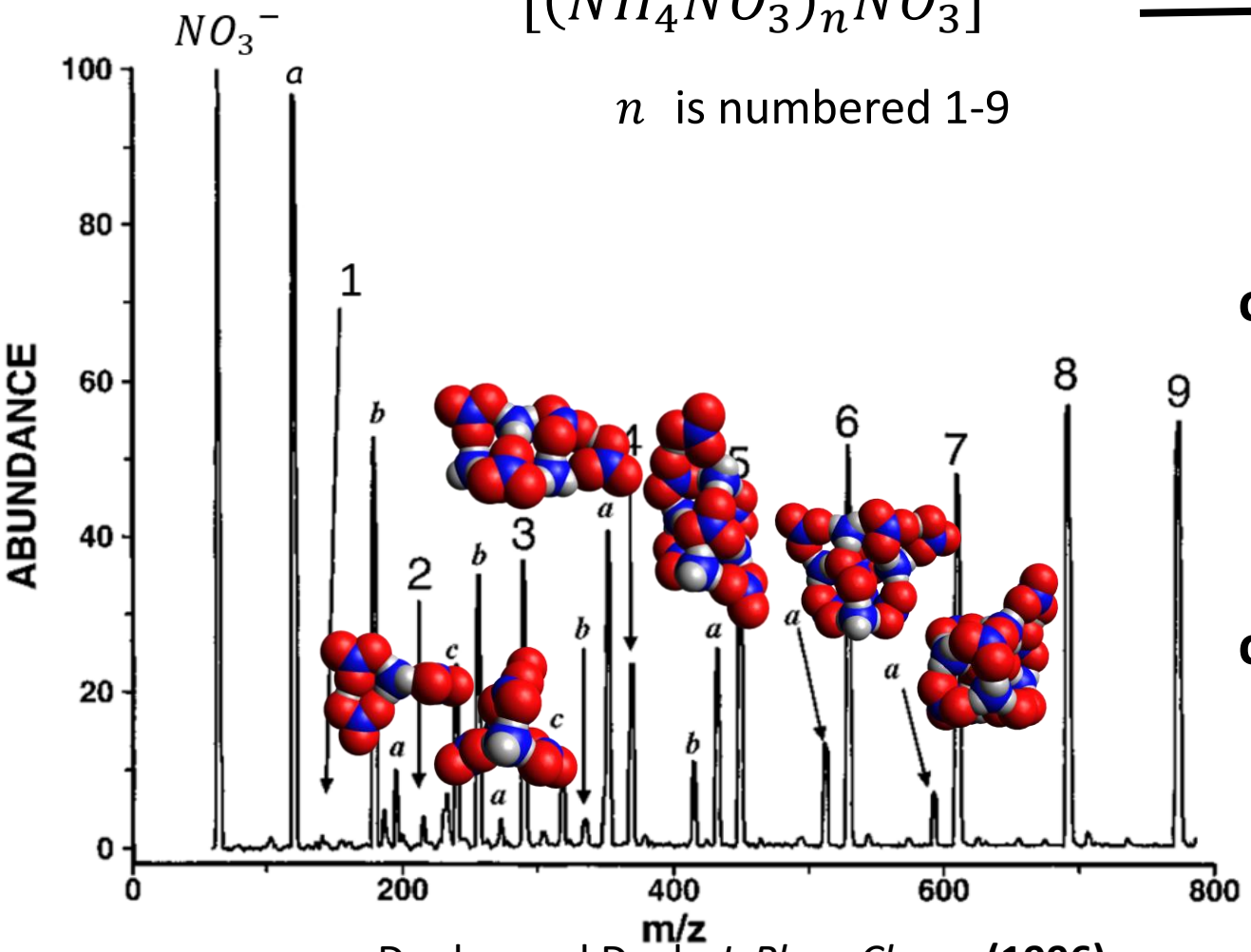

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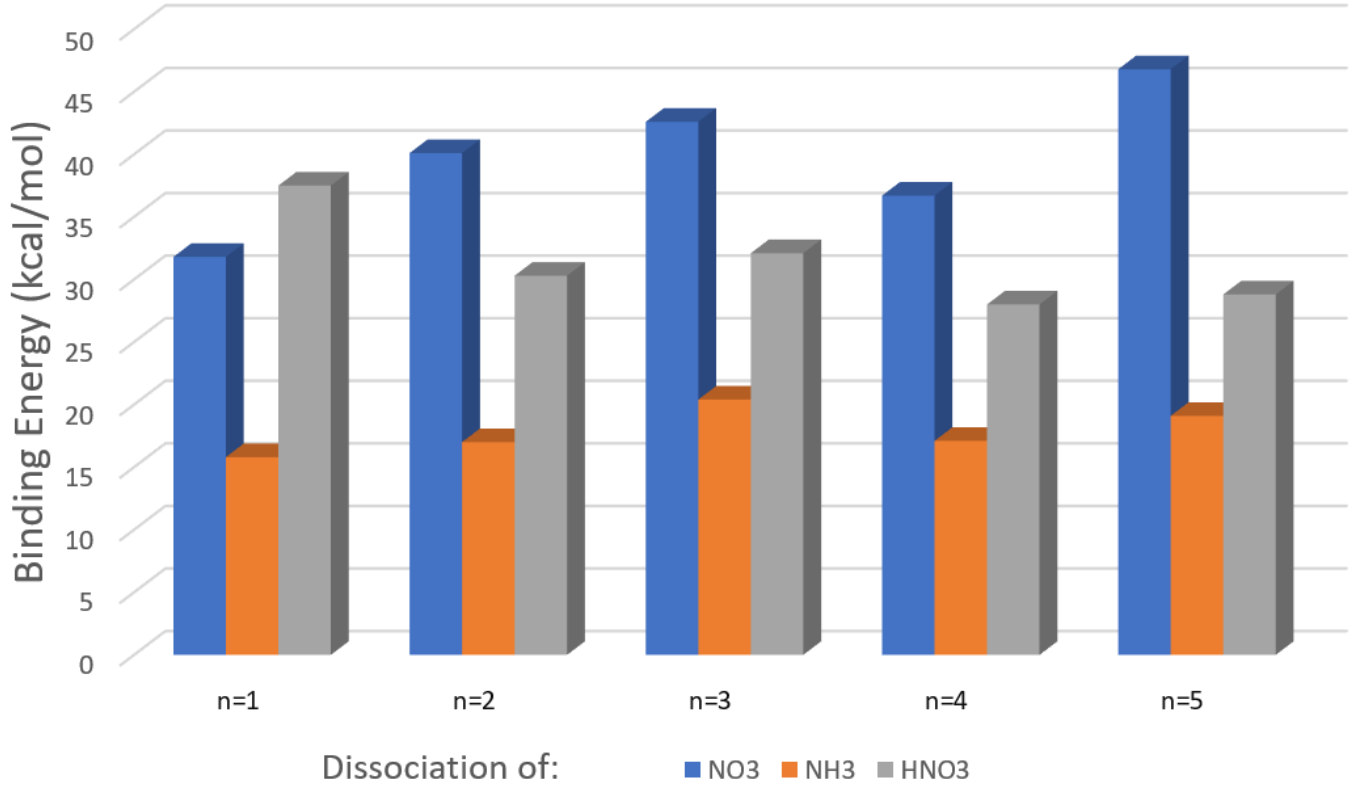
or $\underbrace{[(NH_4NO_3)_{n-2}(HNO_3)_2NO_3]^-}_{b} + 2NH_3$

or $\underbrace{[(NH_4NO_3)_{n-3}(HNO_3)_3NO_3]^-}_{c} + 3NH_3$

Explaining the peaks in the negative-ion sputtered mass spectrum

DFT ωB97M-V/6-311+G(2df,2p)

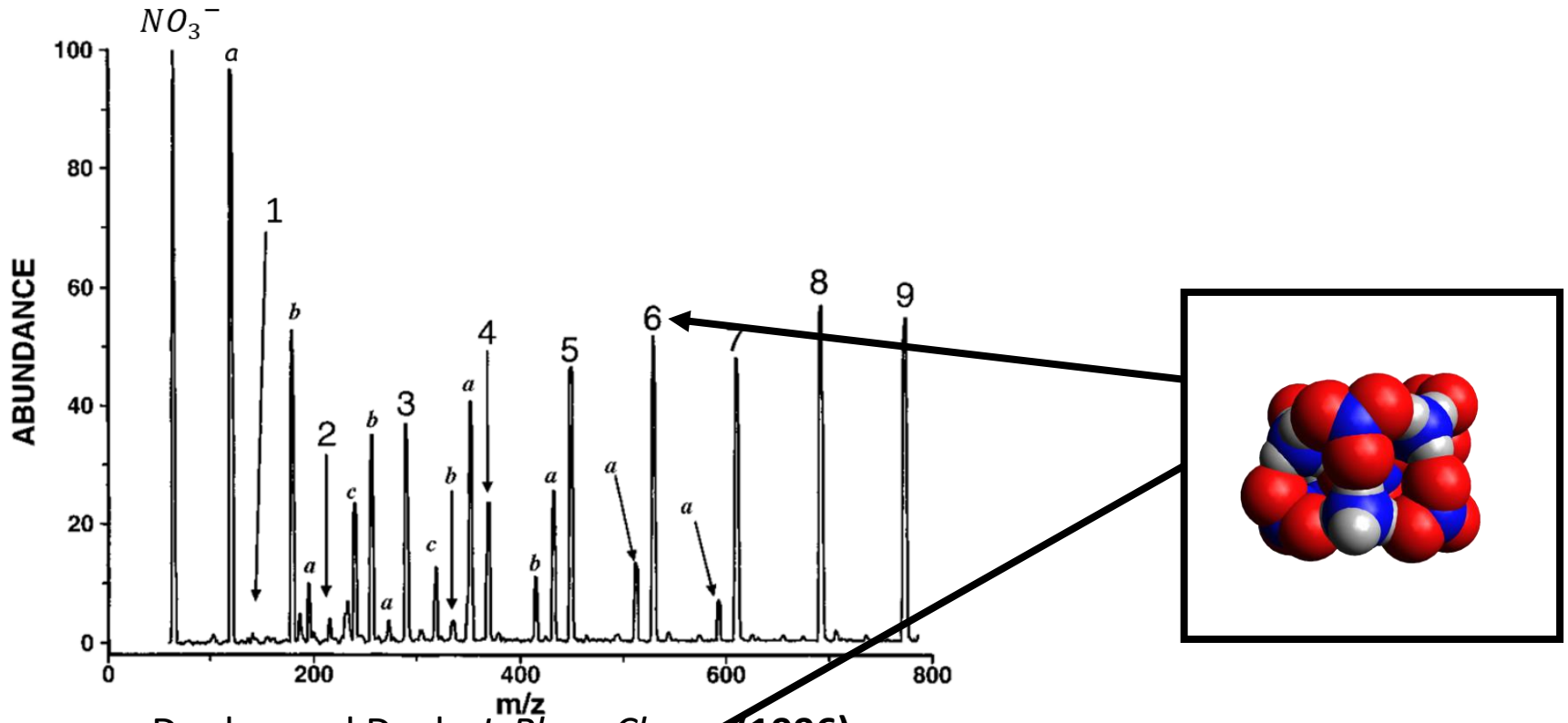


$$NO_3^- + (NH_4NO_3)_n \longrightarrow [(NH_4NO_3)_nNO_3]^-$$

$$NH_3 + [(NH_4NO_3)_{n-1}HNO_3NO_3]^- \longrightarrow [(NH_4NO_3)_nNO_3]^-$$

$$HNO_3 + [(NH_4NO_3)_{n-1}NH_3NO_3]^- \longrightarrow [(NH_4NO_3)_nNO_3]^-$$

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



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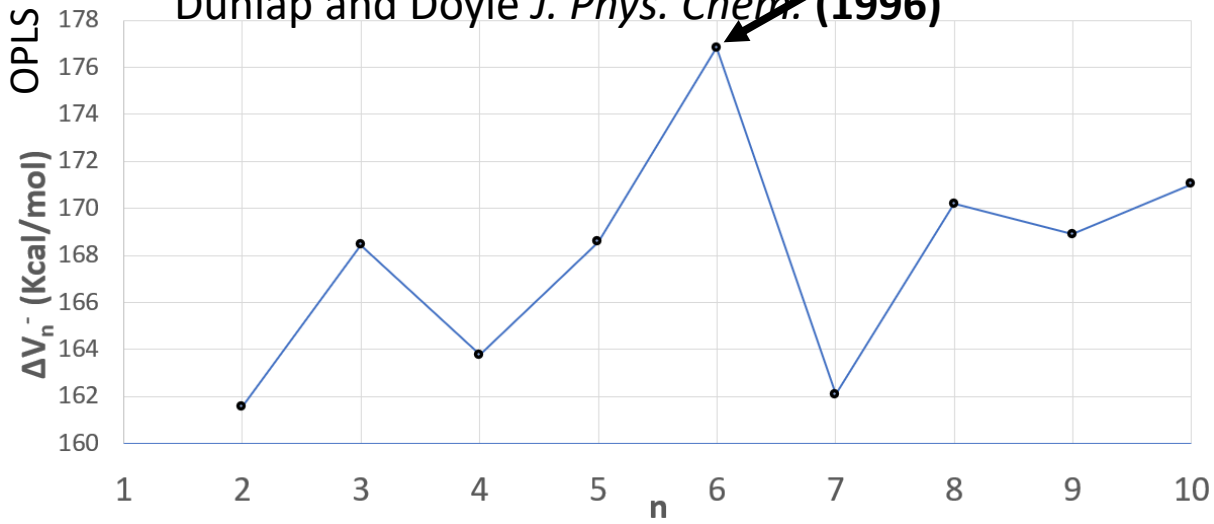
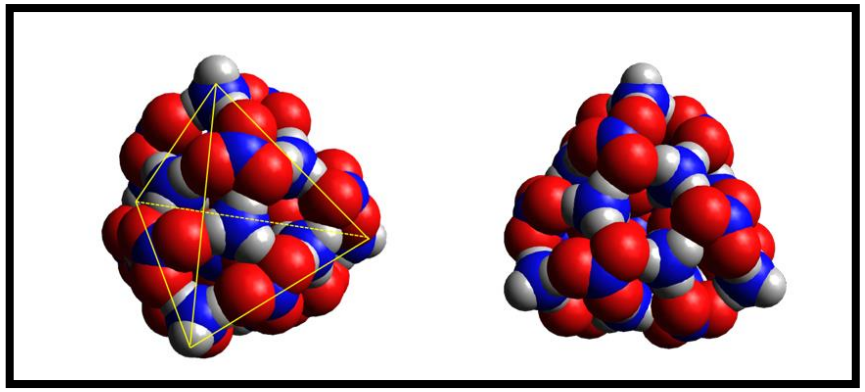


$(NH_4NO_3)_n$

n=16



$(NH_4Cl)_n$

n=13

Topper et al. *J. Phys. Chem. A* **(2011)**

$(NH_4NO_3)_n$

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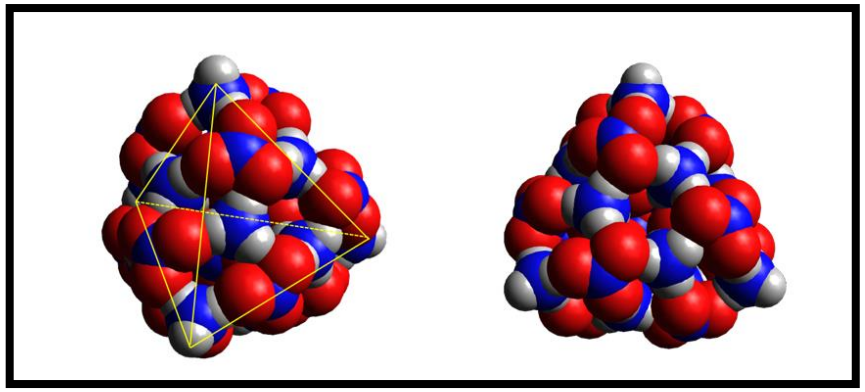

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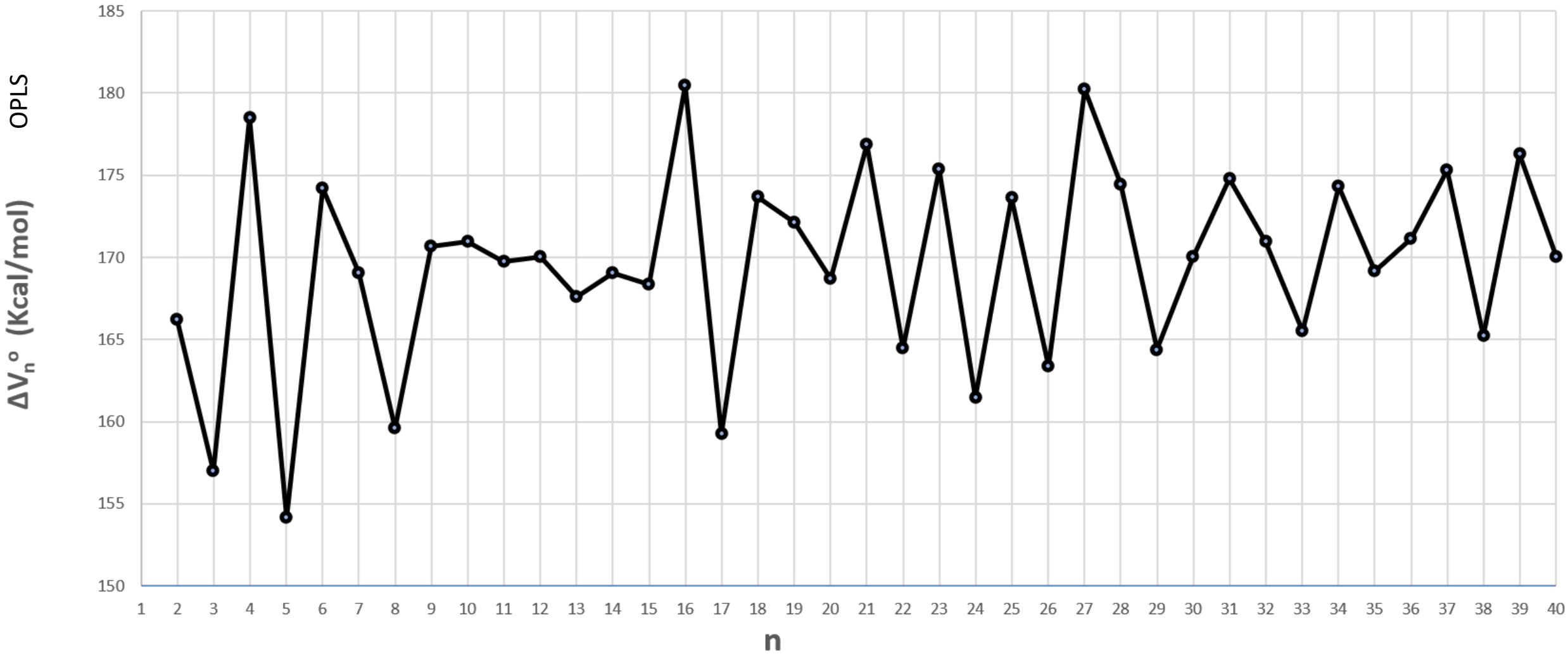
$$\Delta V_n^0 = V_{n-1}^0 - V_n^0$$



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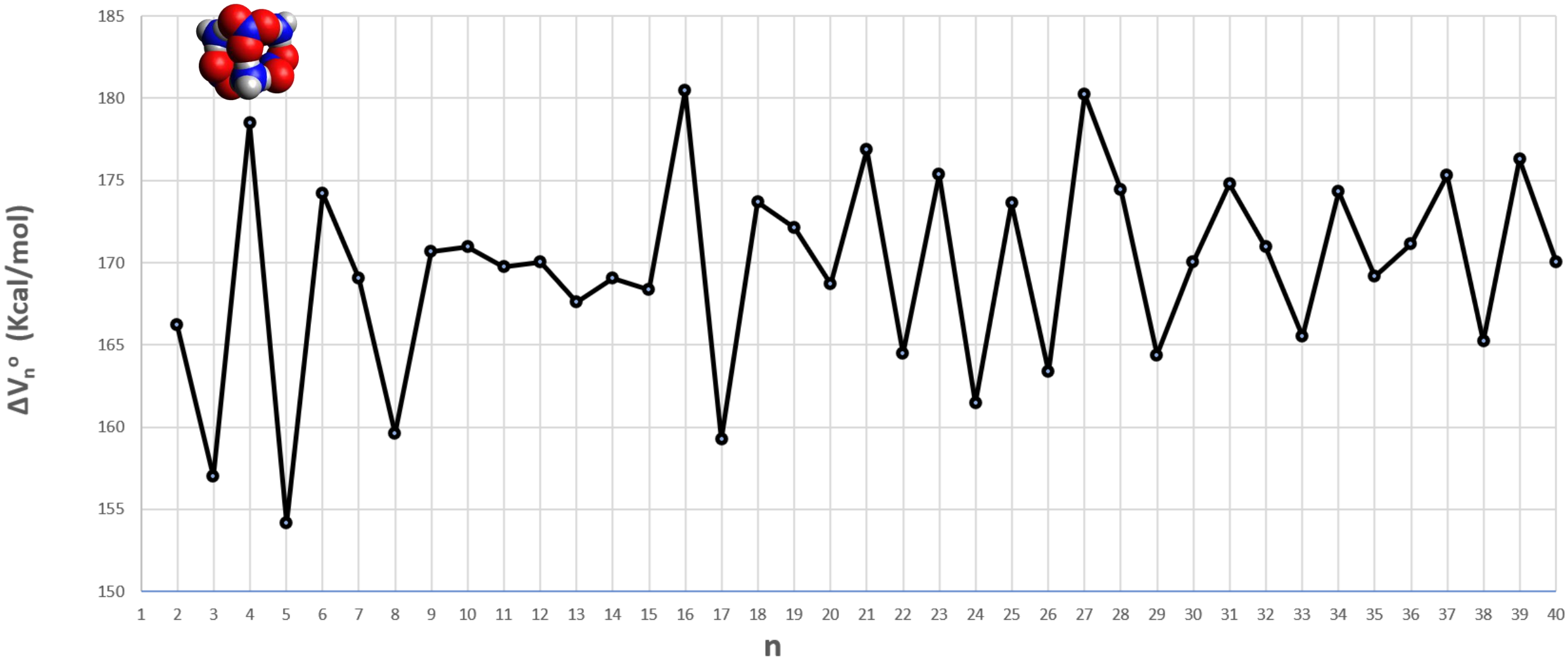

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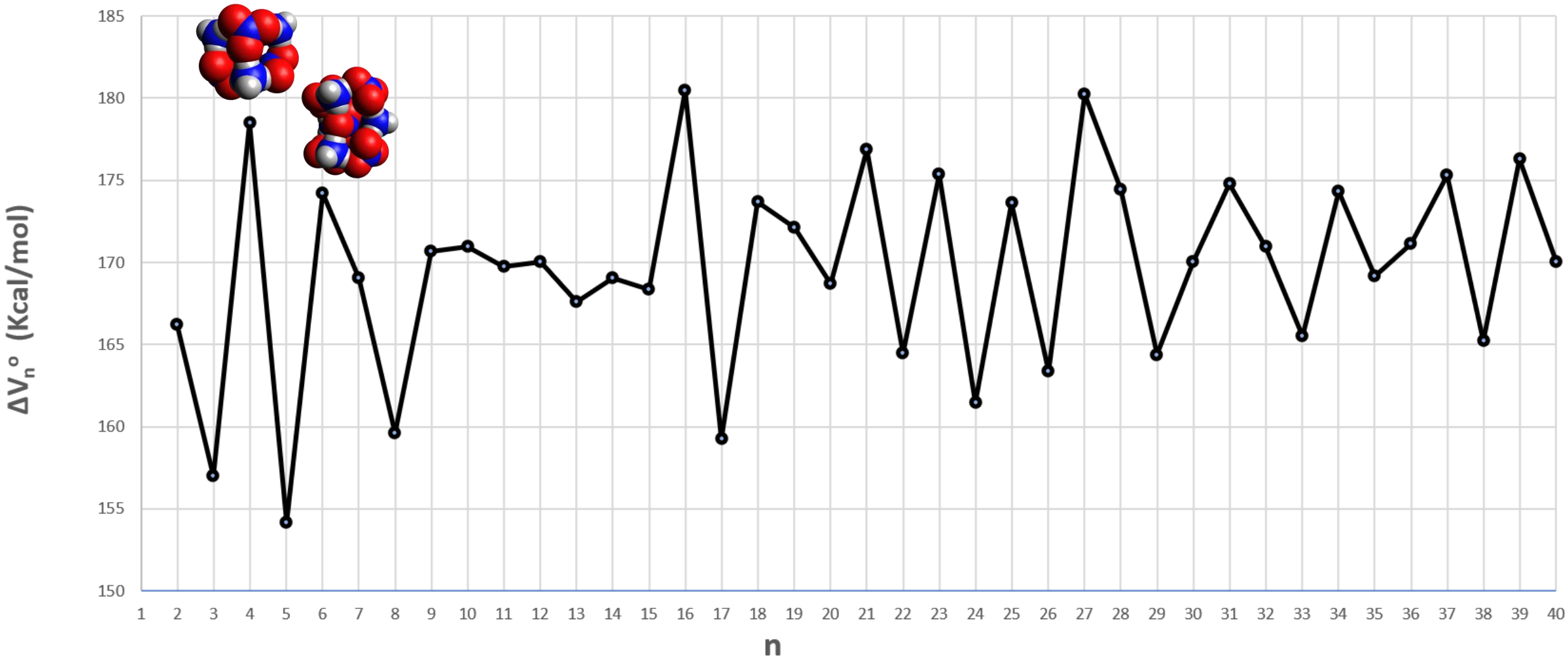

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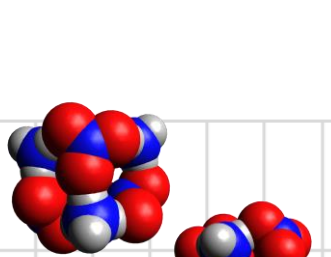

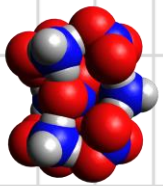

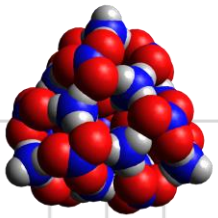

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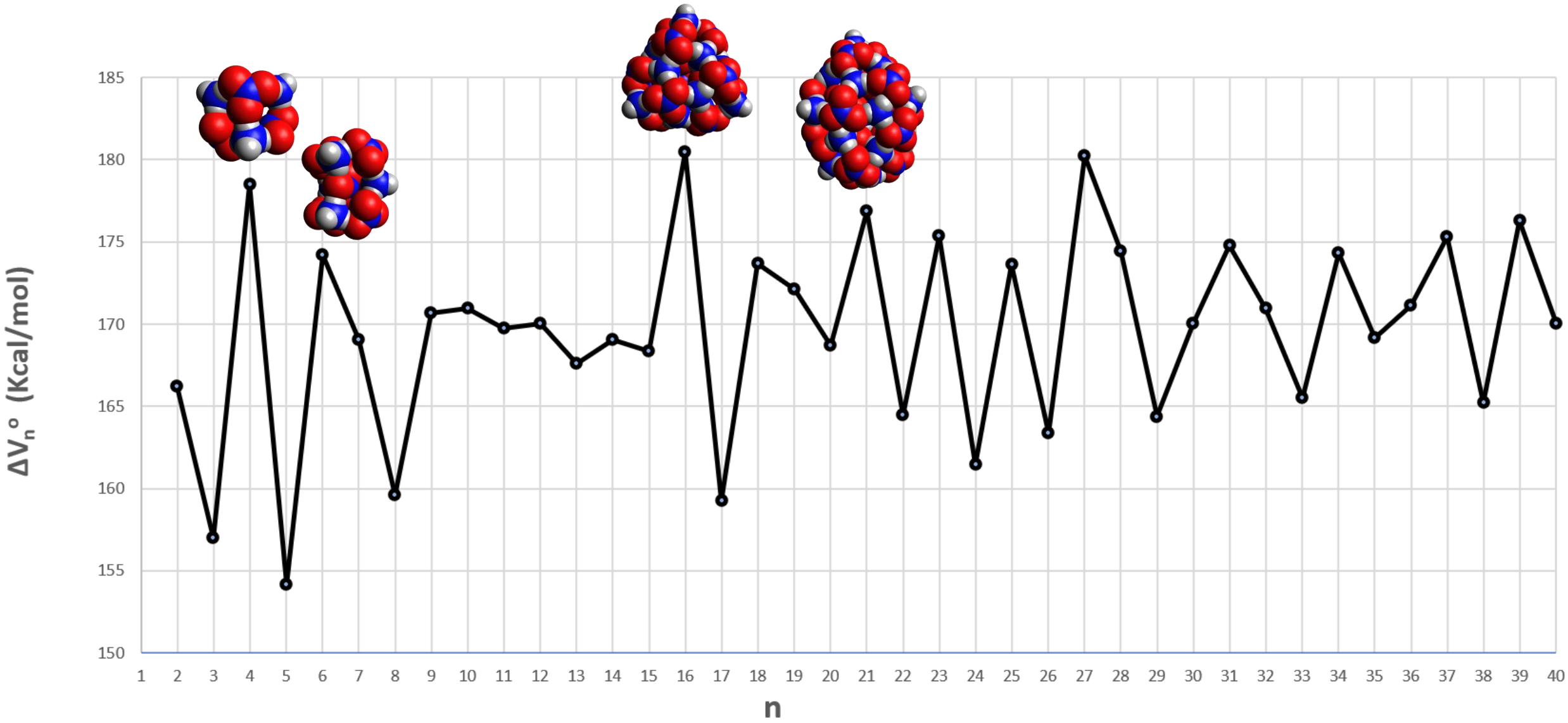

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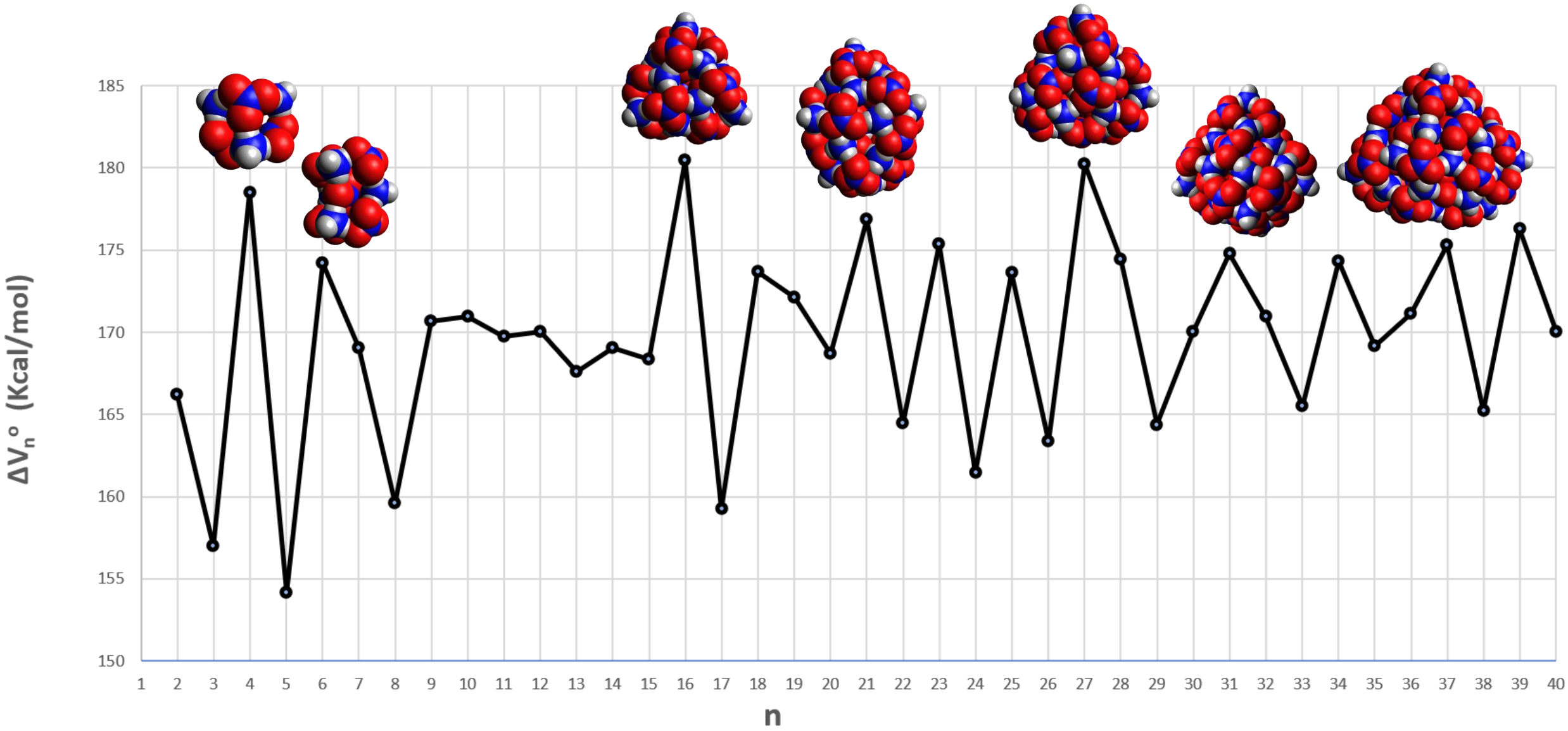

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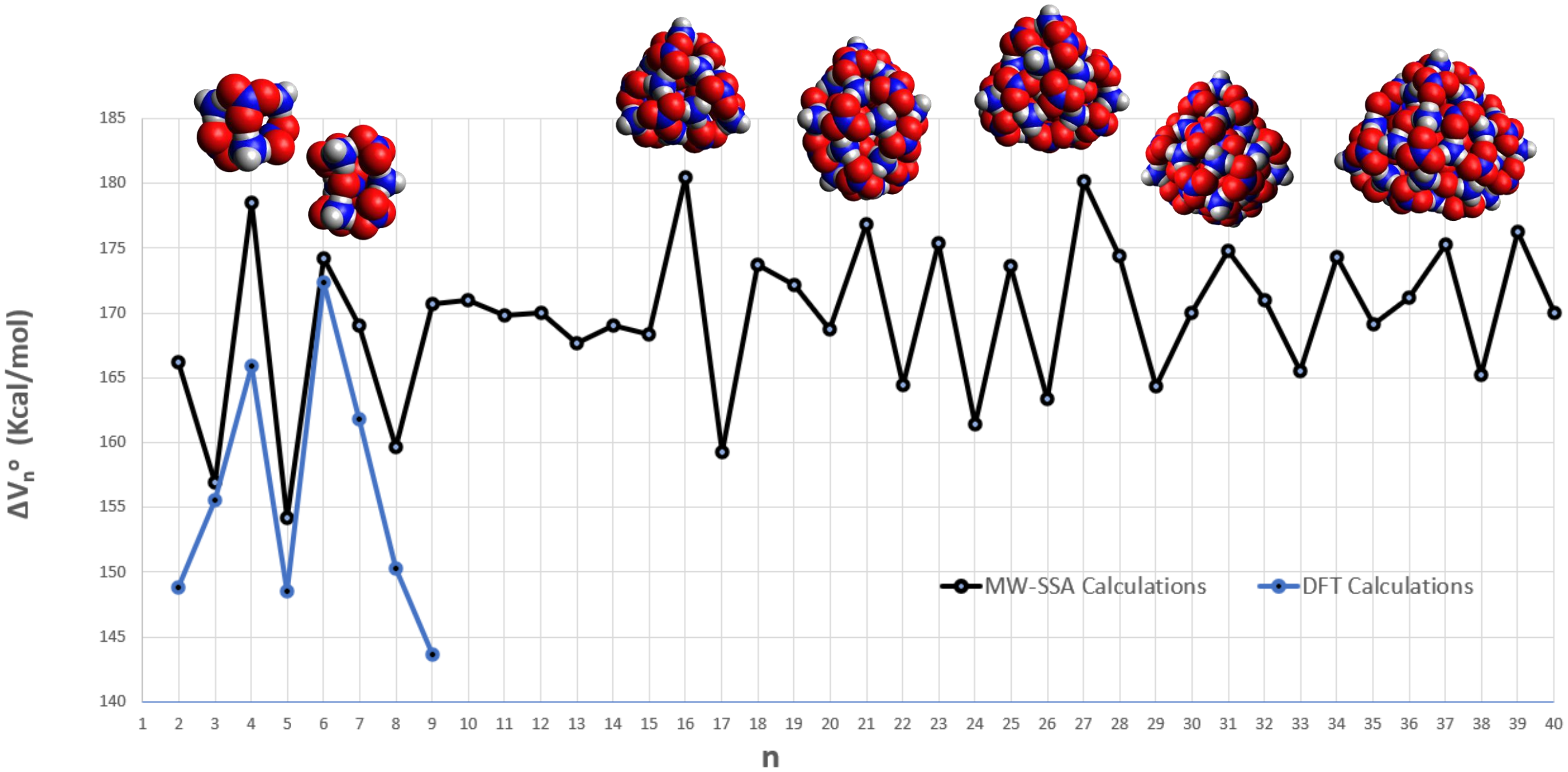

Future Work and Acknowledgments

- Finish DFT calculations on all peaks and explain the "*b*" and "*c*" peaks in the negative-ion mass spectrum
- Would repeated sputtered mass spectra show the same trends?
- Continue predicting the structures of larger nanoparticles
  - When does it start looking like the bulk?
  - What is special about the n=16 peak?

Steven Topper

Sangjoon (Bob) Lee