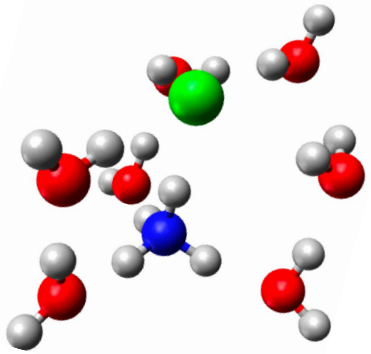

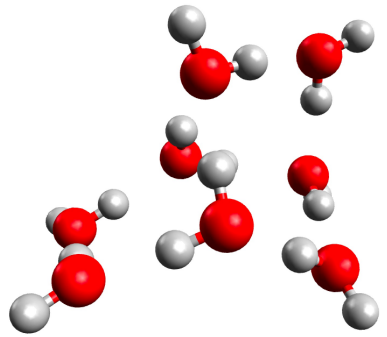

Mag-Walking Simulated Annealing Monte Carlo Study of Nano-solvated Ammonium Chloride

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I. Motivation – Atmospheric Nanoparticles

Research Area:

In Topper's research group, we study atmospheric nanoparticles using theoretical and computational tools.

Today's Focus:

Nano-solvated ammonium chloride (NH_4Cl) in water clusters ($N•H_2O$)

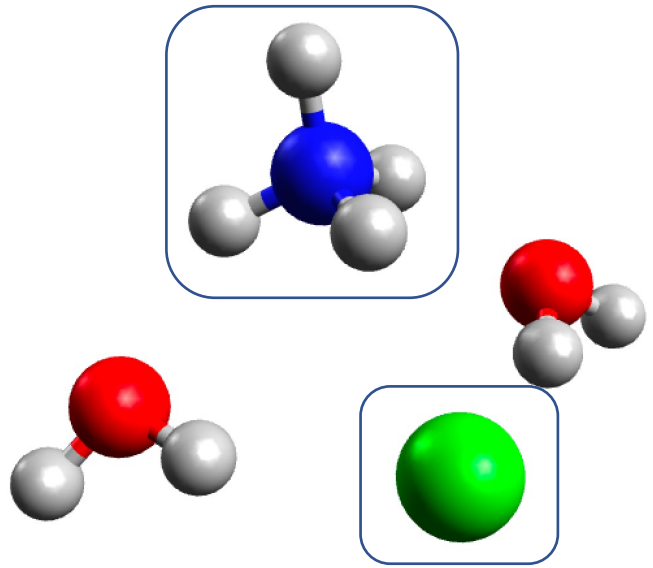


Figure 1. Solvated $NH4^+$ and Cl^- in N = 2 water molecules

I. Motivation – Why Ammonium Chloride?

Ammonium chloride appears to be associated with air pollution and haze.

Ammonium Chloride Associated Aerosol Liquid Water Enhances Haze in Delhi, India

Ying Chen*, Yu Wang, Athanasios Nenes, Oliver Wild, Shaojie Song, Dawei Hu, Dantong Liu, Jianjun He, Lea Hildebrandt Ruiz, Joshua S. Apte, Sachin S. Gunthe*, and Pengfei Liu*

Chen et al. *ACS Environmental Science and Technology* (**2022**)

Chen et al. *ACS Environmental Science and Technology* (**2022**)

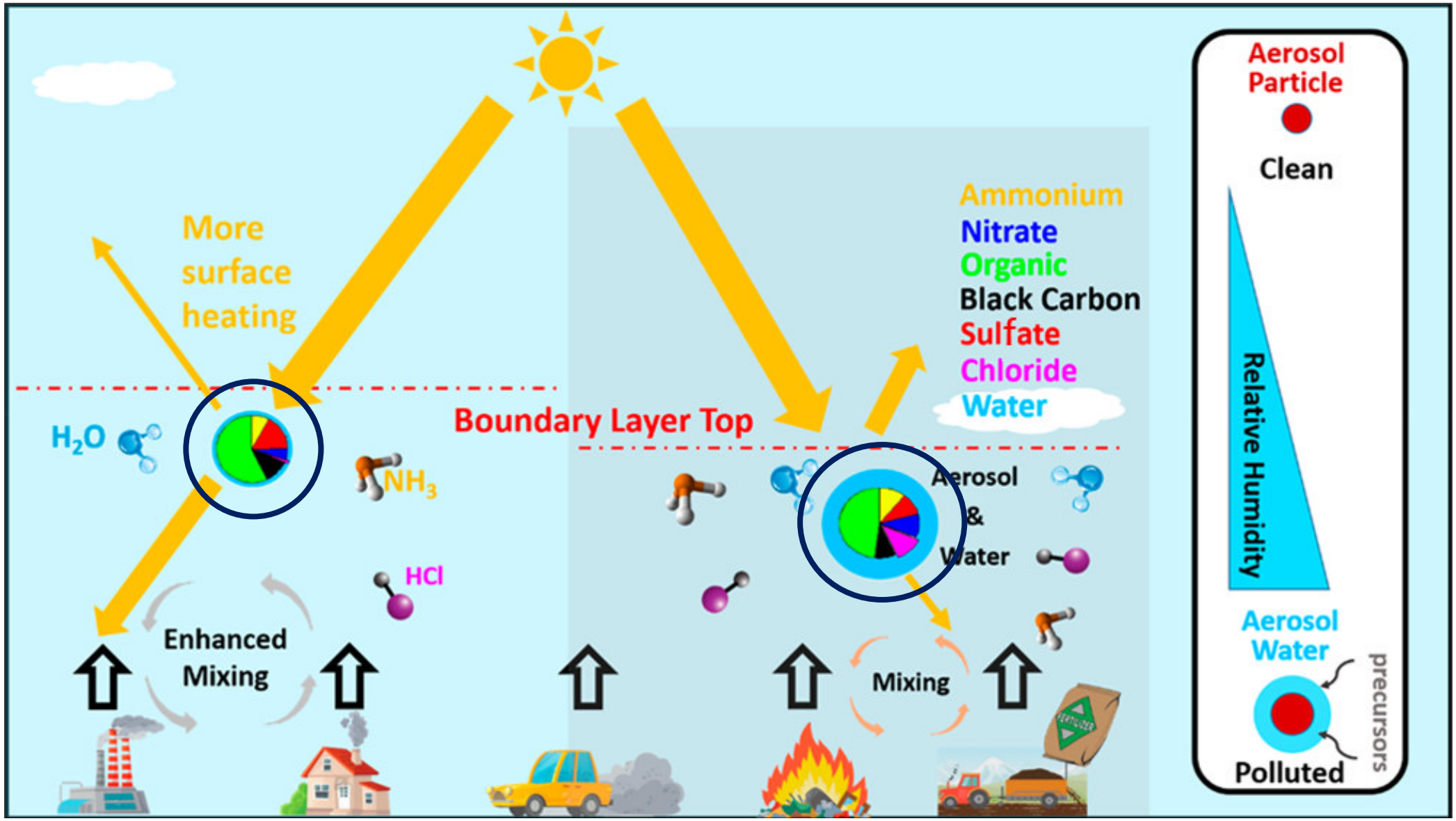


Figure 2. Nano-solvated ammonium chloride and haze production

I. Motivation – Research Goal

Goal: To understand the formation process of ammonium chloride solvated in aerosol (N = 2 to 8) water clusters.

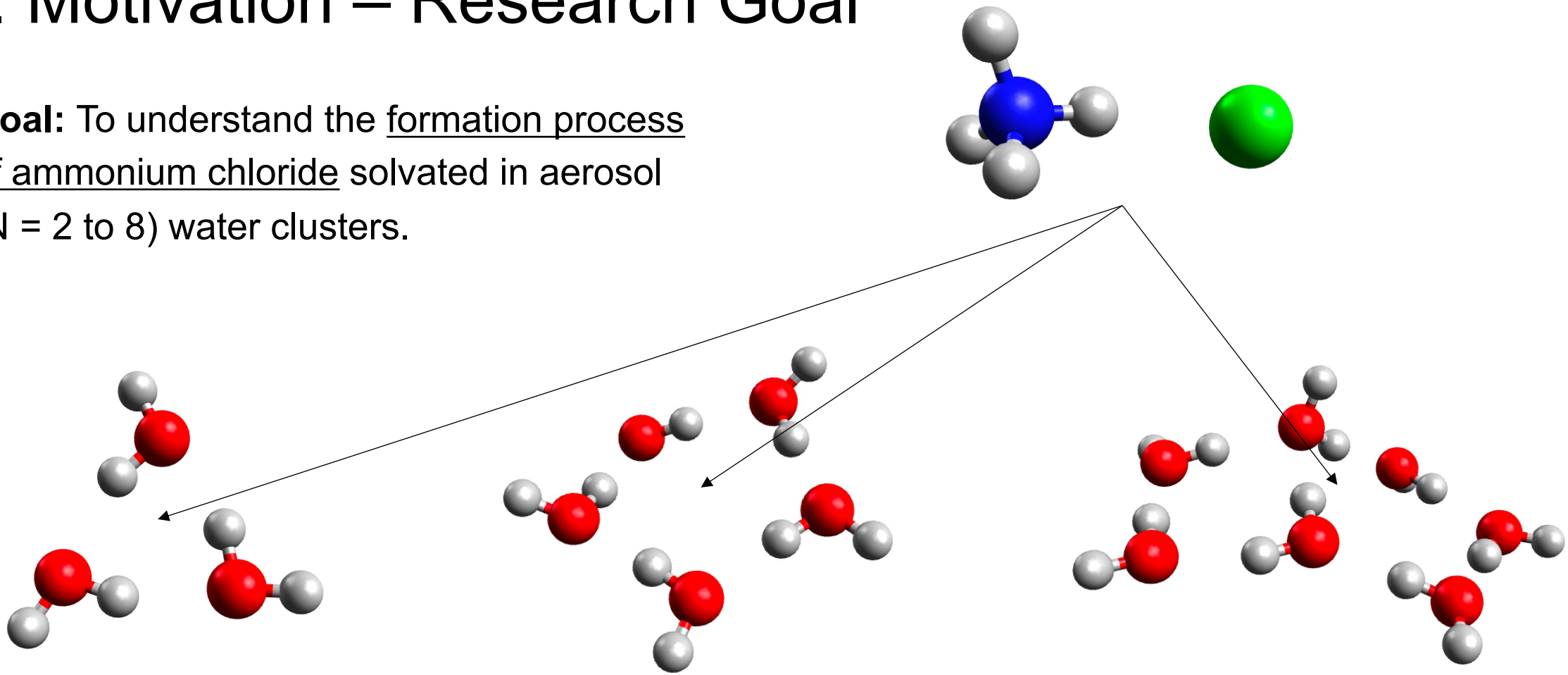


Figure 4. Solvated ammonium chloride and water clusters with N = 3, 5, 7 water molecules (left to right)

II. Method – Challenge

Model:

Interaction Potential to assess molecule structures.

$$V = \sum_i \sum_{j>i} \left[\frac{q_i q_j}{r_{ij}} + A_{ij} \exp(-\alpha_{ij} r_{ij}) + \frac{D_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^{6}} \right]$$

BOSS 4.9 (Jorgensen et al.)

Challenge:

<u>Identifying the global minimum</u> due to the exponentially increasing number of local minima.

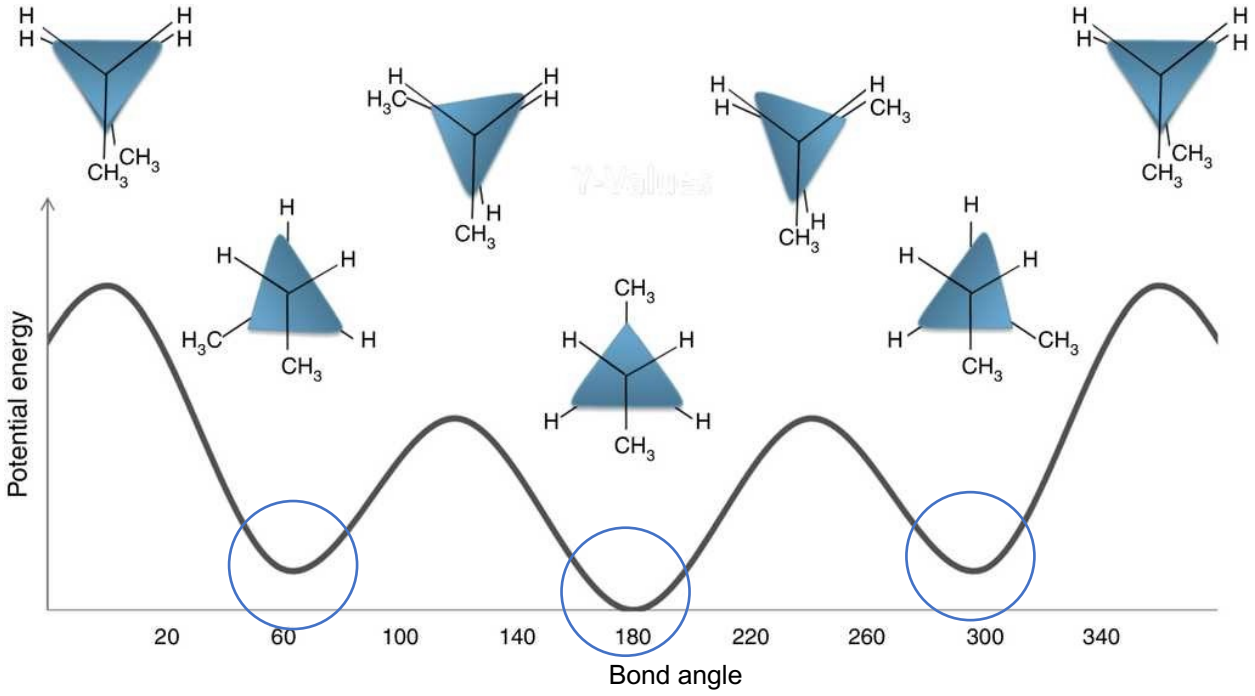


Figure 5. Newman projections and 3 local minima for butane

Khalilian et al. *Educación Química* (**2016**)

II. Method – Strategy

Computational Strategy

Step 1. Mag-Walking Simulated Annealing Monte Carlo Method to find the lowest energy structures. Software) *TransRot*

Step 2. Quantum Mechanical calculations to determine thermodynamic properties and energetics. Software) *SPARTAN*

II. Method – Introducing Monte Carlo

Original Metropolis Monte Carlo

Generate x'
(Make a trial move)

The Original Metropolis Algorithm:

Translate an atom within a small cube by a random amount

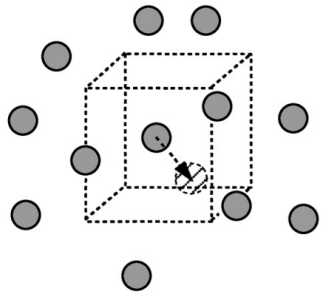


Figure 6. Illustration of Metropolis Monte Carlo

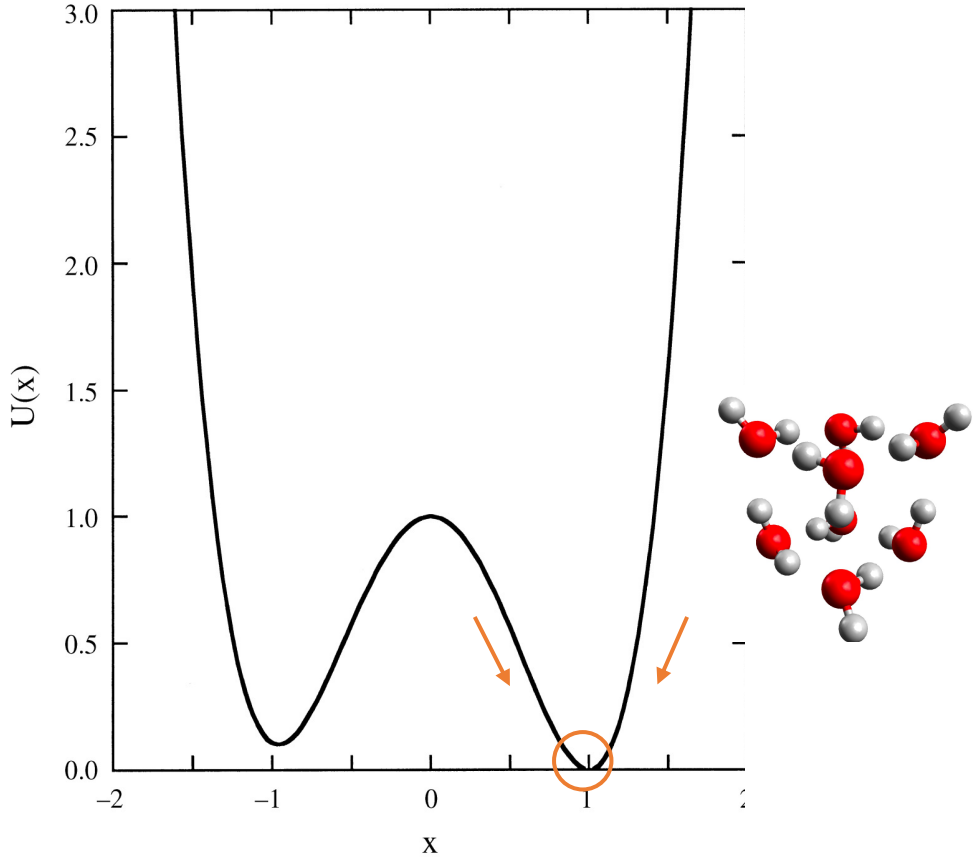


Figure 7. Asymmetric double-well potential

Topper et al. *Reviews in Computational Chemistry* (**2003**)

II. Method – Mag-Walking Simulated Annealing

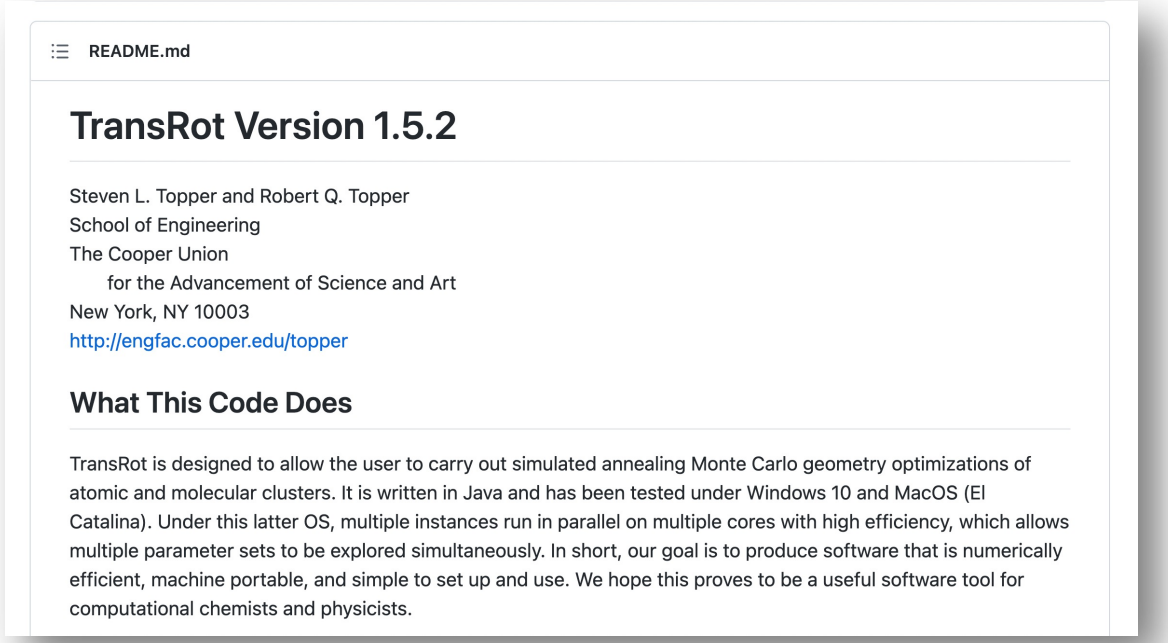
Significant **improvements** were made in locating the global minimum by

1. Varying step size: Optimized random translational and rotational movements.

2. Annealing: System is cooled, reheated and re-cooled.

Frantz, Freeman, Doll JCP (**1990**)
Topper et al. *Reviews in Computational Chemistry* (**2003**)

TransRot is open source!



README.md

TransRot Version 1.5.2

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What This Code Does

TransRot is designed to allow the user to carry out simulated annealing Monte Carlo geometry optimizations of atomic and molecular clusters. It is written in Java and has been tested under Windows 10 and MacOS (El Catalina). Under this latter OS, multiple instances run in parallel on multiple cores with high efficiency, which allows multiple parameter sets to be explored simultaneously. In short, our goal is to produce software that is numerically efficient, machine portable, and simple to set up and use. We hope this proves to be a useful software tool for computational chemists and physicists.

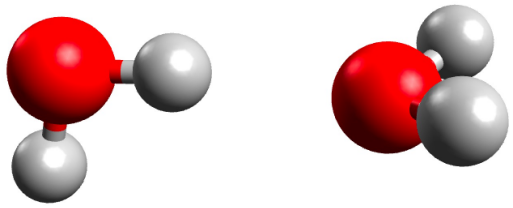
Github link: github.com/steventopper/Transrot

(Developed by Steven. L. Topper)

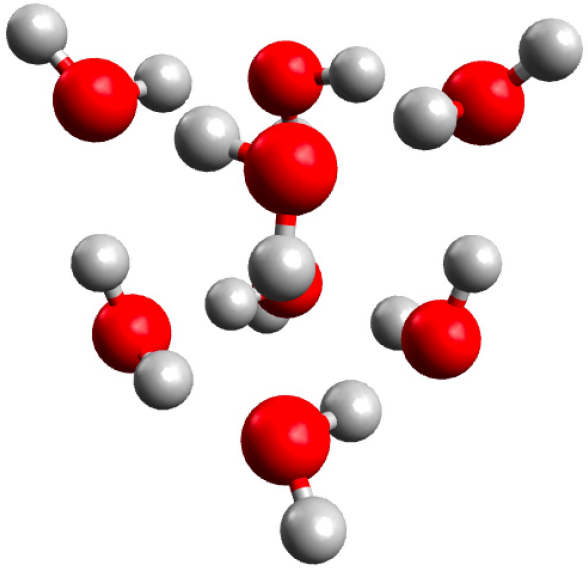
II. Method – Test TransRot

Test Criteria:

Compare TransRot's global minimum of water clusters (N = 2 to 8) with literature values.



N=2



N=8

II. Method – Test TransRot

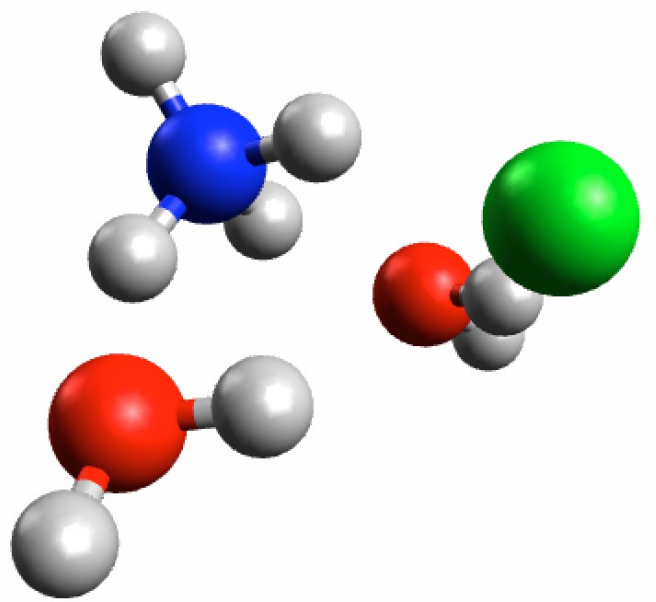
Table 1. Comparison of TIP4P Water Clusters Global Minima Energy Values between TransRot and Literature **(kJ/mol)**

N	TransRot	Cambridge Cluster Database	Difference (Cambridge - TransRot)
2	-26.08713	-26.08757	-0.0004
3	-69.99271	-69.99387	-0.0012
4	-116.58841	-116.59042	-0.0020
5	-152.10631	-152.10900	-0.0027
6	-197.77712	-197.78053	-0.0034
7	-243.56793	-243.57240	-0.0045
8	-305.51275	-305.51832	-0.0056

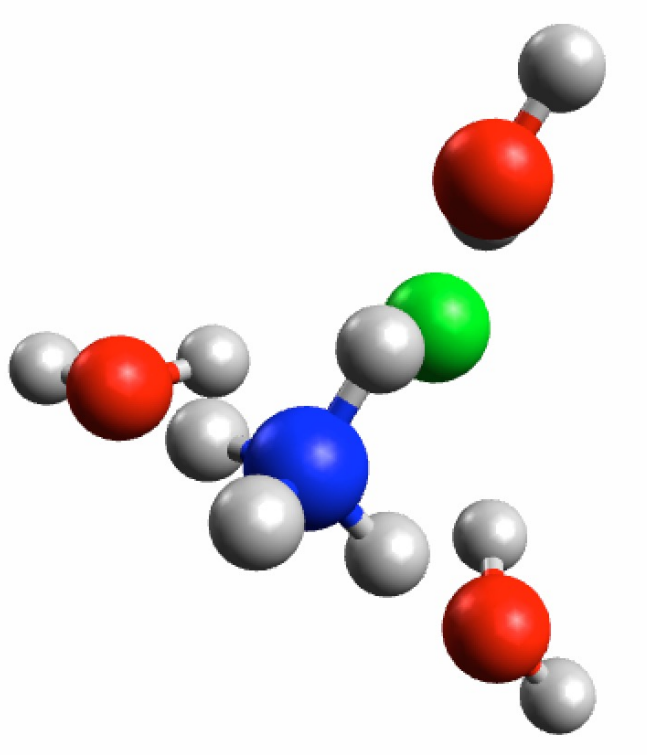
Wales et al. *Chemical Physics Letters* (**1998**)

III. Results – TransRot Calculations

After geometry optimization, one minimum was found for N = 2, 3, 5, 6



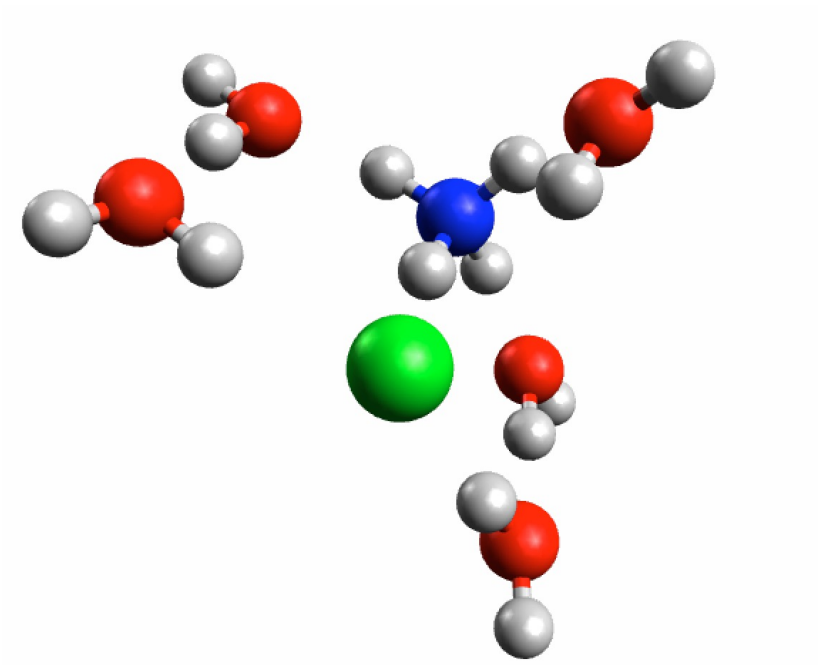
N = 2



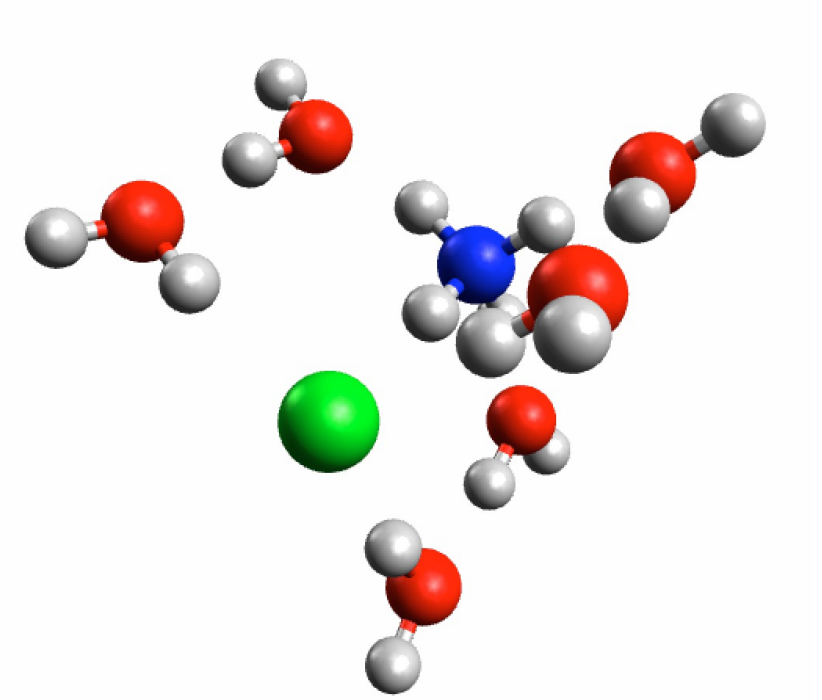
N = 3

III. Results – TransRot Calculations

After geometry optimization, one minimum was found for N = 2, 3, 5, 6



N = 5

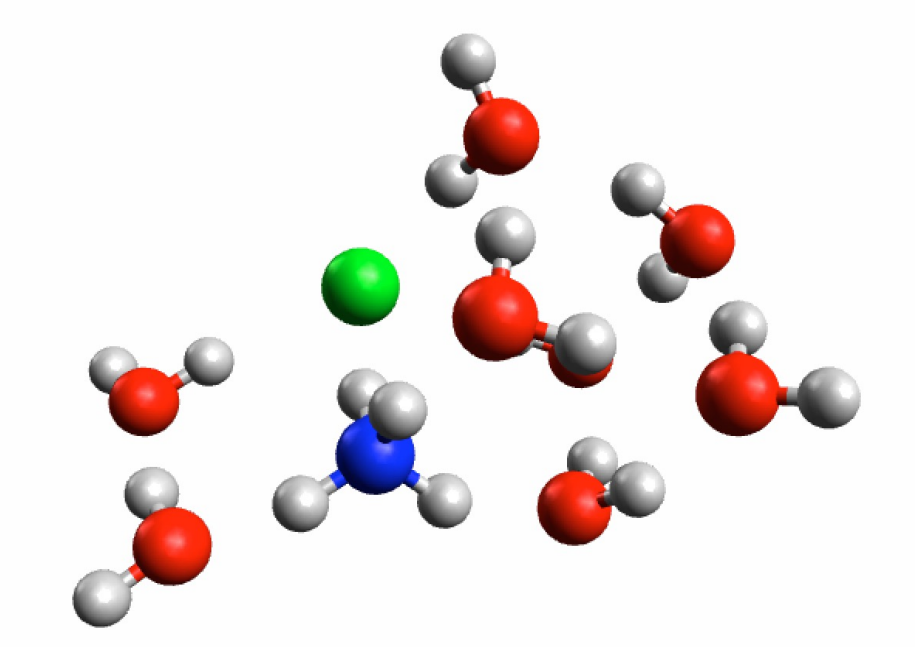


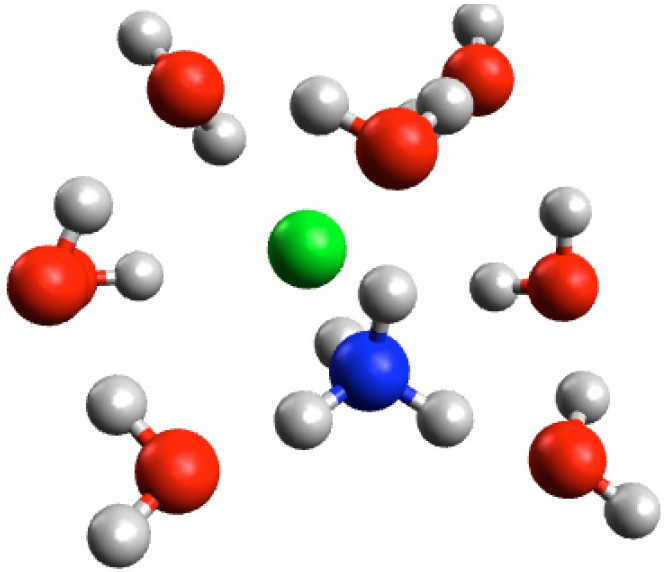
N = 6

III. Results – TransRot Calculations

After geometry optimization, two minima were found for N =7, 8

N = *7*





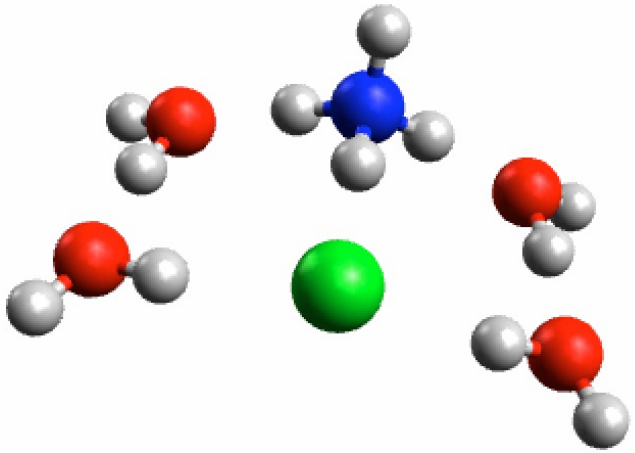
Structure 1
(Lower E)

ΔE₁₂ = 10.6 kJ/mol

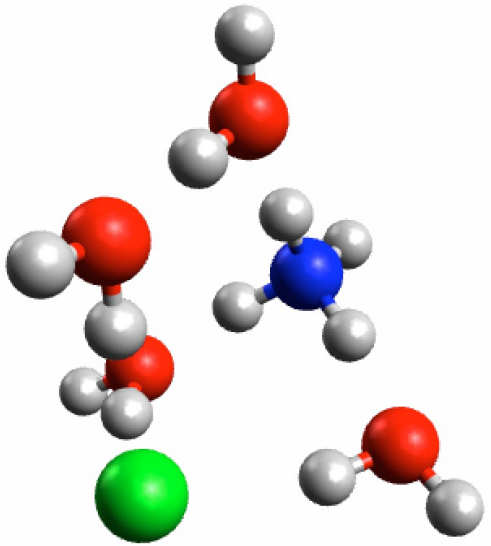
Structure 2
(Higher E)

III. Results – TransRot Calculations

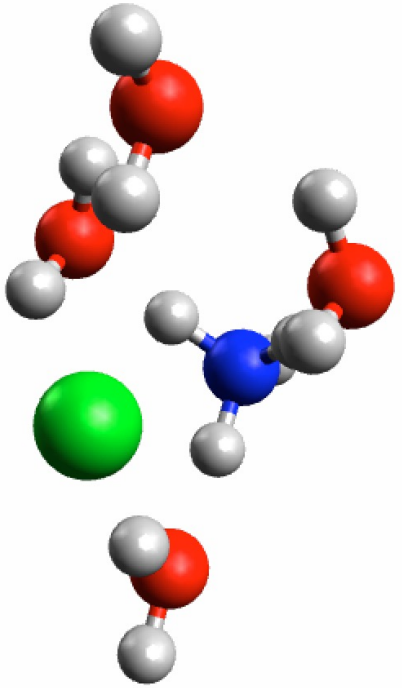
After geometric optimization, three minima were found for N = 4



Structure 1
(Lowest E)



Structure 2



Structure 3
(Highest E)

ΔE_{12} = 9.4 kJ/mol

ΔE_{23} = 8.1 kJ/mol

ΔE_{13} = 17.5 kJ/mol

III. Result – QM Calculations

Two sets of QM calculations method/basis set were used

Set 1:
Møller-Plesset: RI-MP2/6-31+G*

Set 2:
Density Functional Theory: wB97M-V/6-31+G*

Lomboy and Topper. *The Journal of Physical Chemistry A* (**2021**)

III. Result – QM Calculations

IE was calculated for each cluster formation.

Reaction: $NH_4^+ + Cl^- + N \bullet (H_2O) \rightarrow$ Cluster

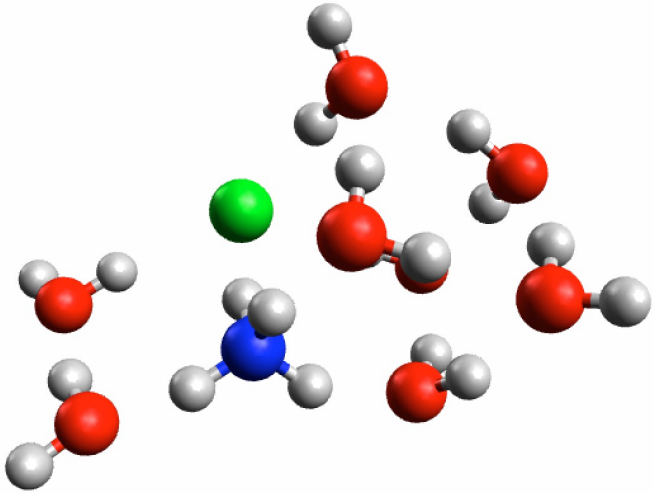
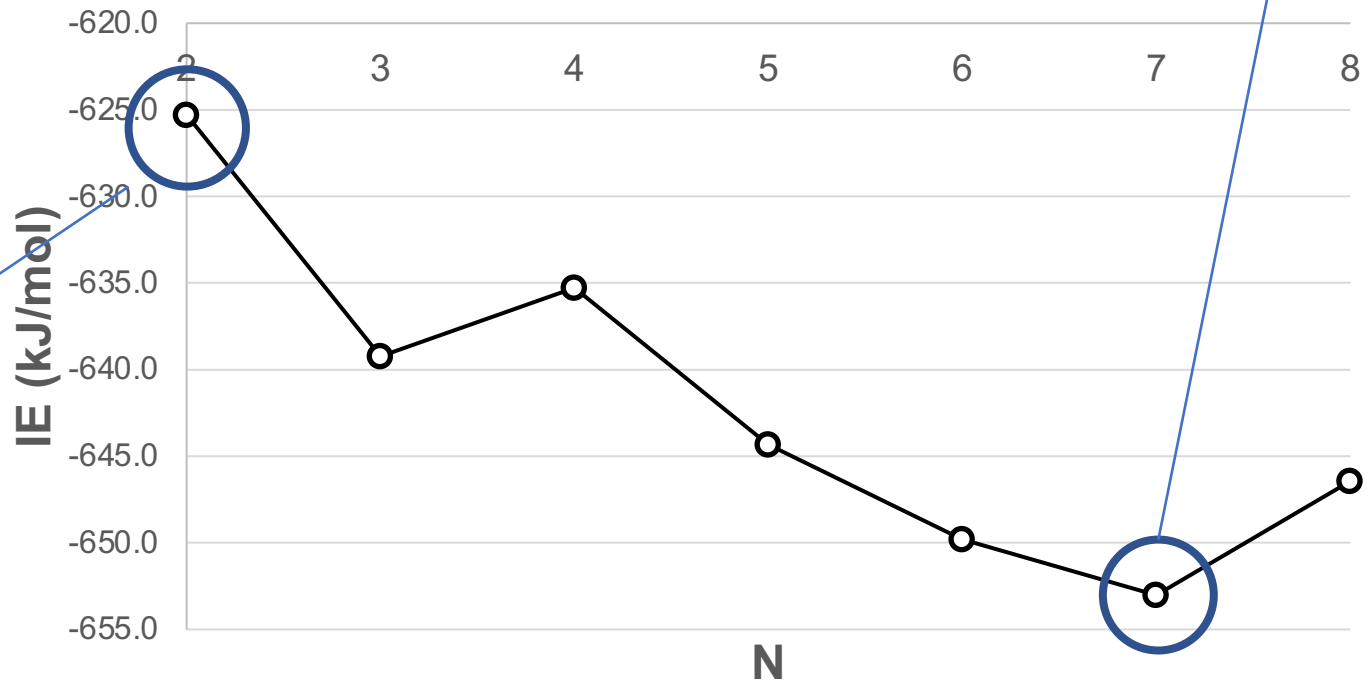
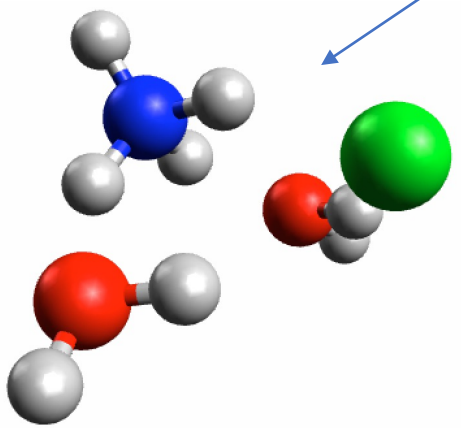
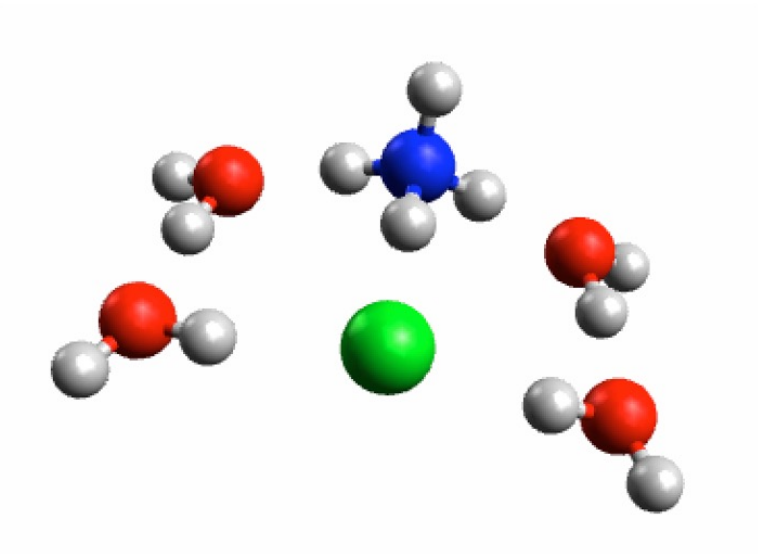


Figure 1. IE with wB97M-V / 6-31+G* (Set 1)

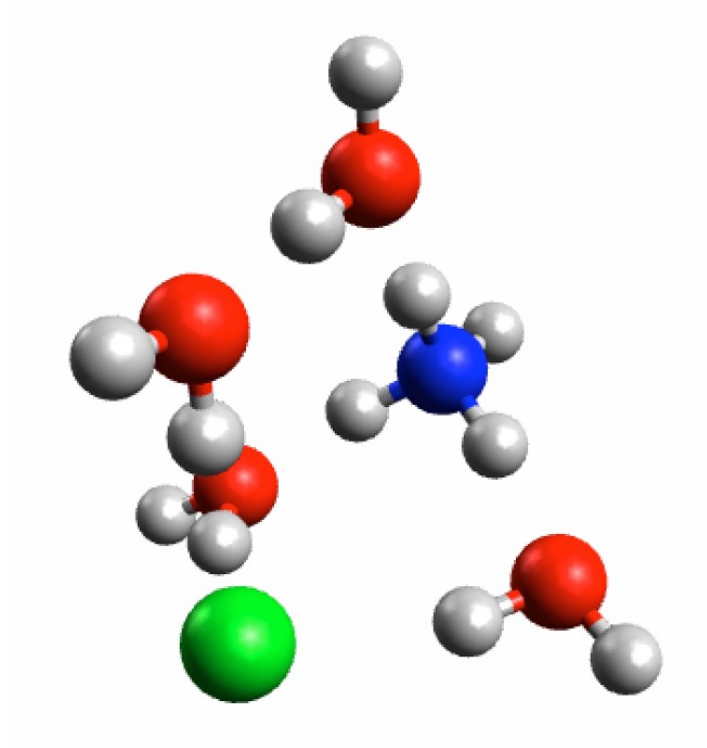




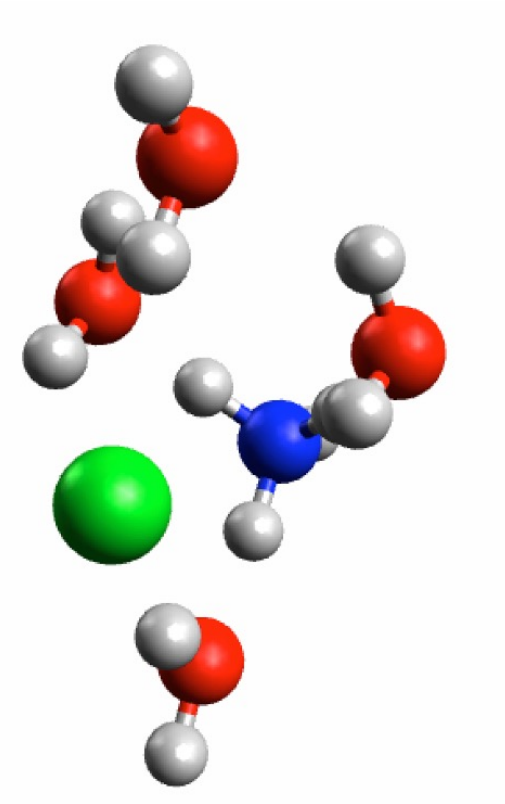
N = 4



Structure 1



Structure 2



Structure 3

IV. Future Work

Next Step:

- Use larger basis sets (aug-cc-pVTZ, etc.)
- Try Coupled Cluster methods (CCSD(T))
- Determine ΔG, ΔH, ΔS, etc., and spectra during formation.

V. Acknowledgements

I would like to express my sincere gratitude towards

Dr. Robert Q. Topper

Professor of Chemistry

Advisor

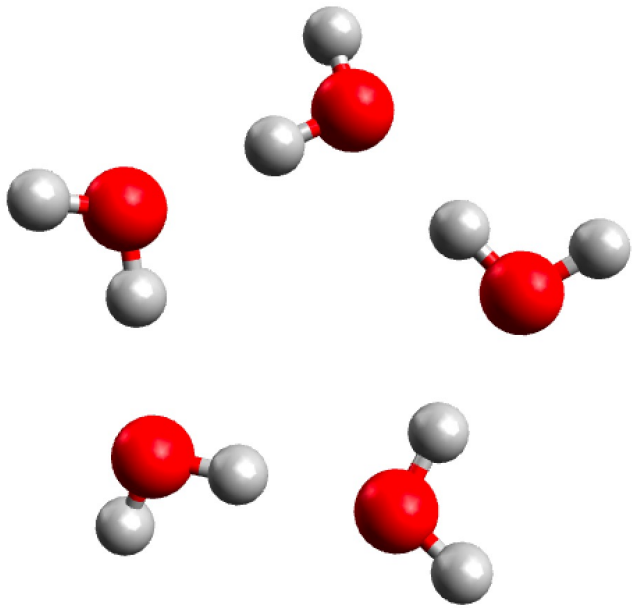
Steven L. Topper

Developer of TransRot

Department of Chemistry

Cooper Union

Thank you!



Thank you

Sangjoon (Bob) Lee