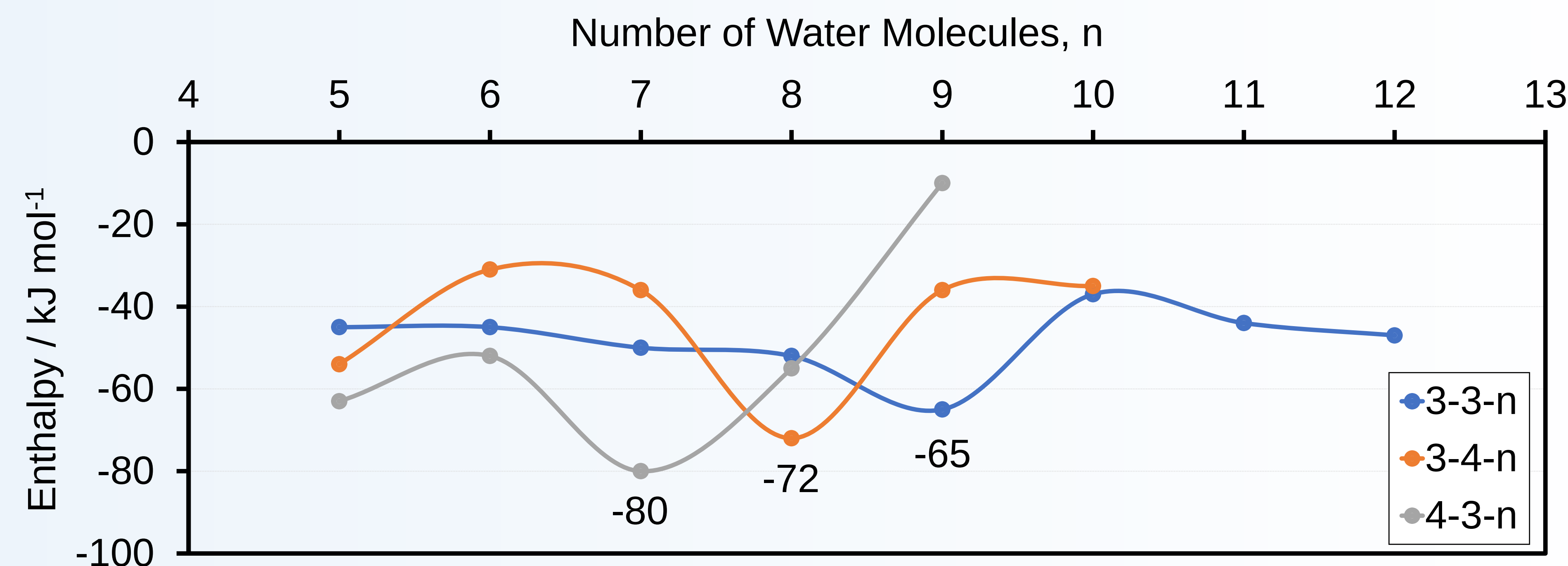
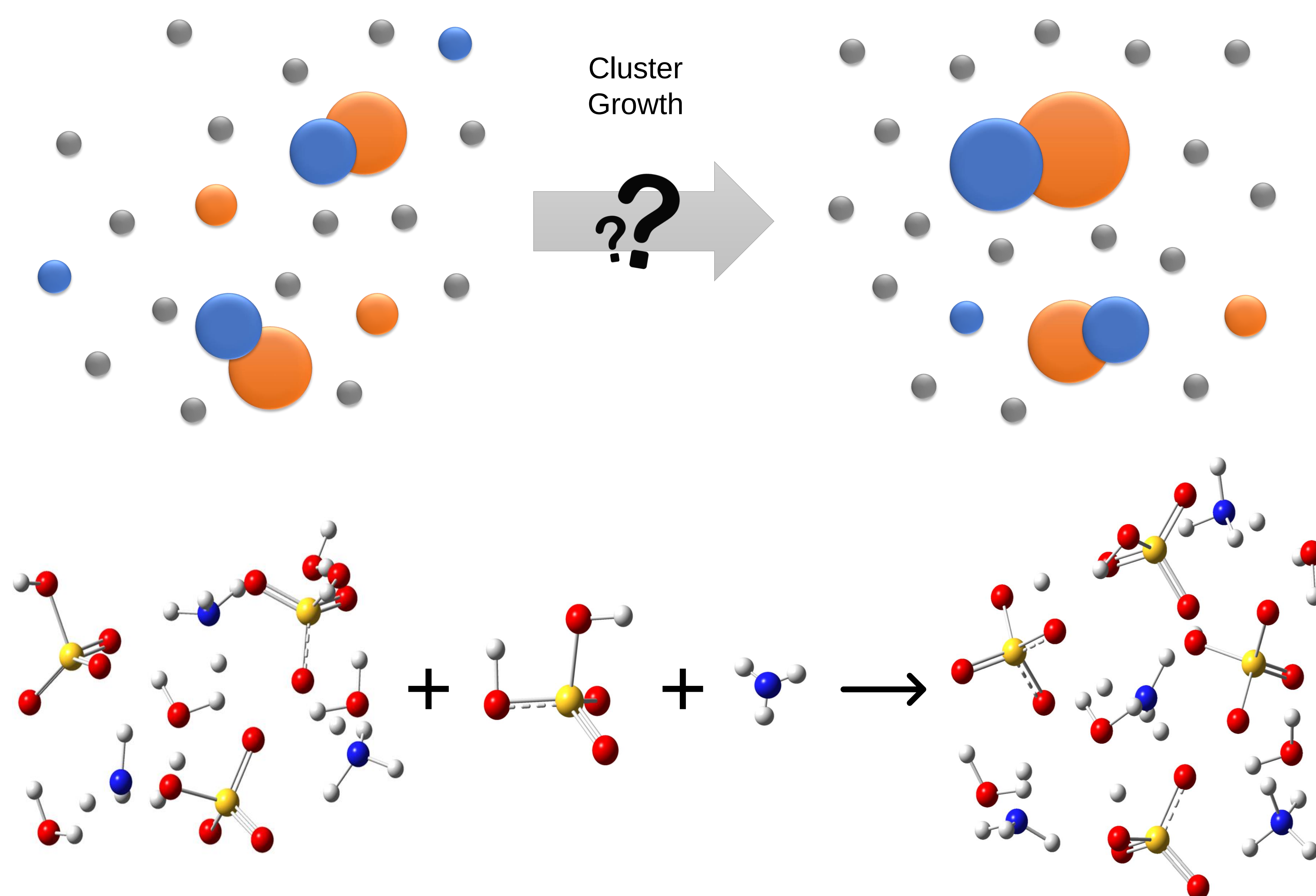


# Computational Study on Hydration Motifs of Atmospheric Sulphuric Acid-Ammonia Clusters

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## Introduction

- ✓ Understanding the formation of cloud condensation nuclei (CCN) is essential for predicting cloud precipitation pathway.<sup>1</sup>
- ✓ CNN originates from cluster of sulphuric acid-ammonia pair.<sup>2</sup> The role of water toward the growing cluster remains elusive.
- ✓ Stepwise hydration of (H<sub>2</sub>SO<sub>4</sub>)<sub>3</sub>(NH<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>n</sub> (abbreviated as 3-3-n) shows minima in enthalpy profile. Hydration of cluster has a saturation point. Simultaneous addition of one H<sub>2</sub>SO<sub>4</sub> and one NH<sub>3</sub> into 3-3-n induces large exothermicity and further trigger rapid water evaporation.

## Methods

Energetic stability of stepwise hydration in (H<sub>2</sub>SO<sub>4</sub>)<sub>x</sub>(NH<sub>3</sub>)<sub>y</sub>(H<sub>2</sub>O)<sub>n</sub> clusters was evaluated using density functional theory based molecular dynamics (DFT-MD). The stepwise hydration begins with 3-3-4 which is obtained from the Atmospheric Cluster Database (ACDB).<sup>3</sup> Input of hydrated structures (3-3-n) from n=4 to n=12 are generated by ABCluster using force field method. MD simulations were performed at 200K canonical ensemble for 5 ps.

## Cluster Growth via Stepwise Hydration

1. Successive hydration of cluster shows **favourable water binding**. Average hydration energy liberated upon binding heats up the cluster and triggers evaporation of at least 1 water molecule.
2. Both homogeneous (3-3-n) and heterogeneous (3-4-n & 4-3-n) clusters show **minima which indicates saturation of hydration**.

3-3-n averages -48 kJ/mol (minimum -65 kJ/mol at n=9)

3-4-n averages -47 kJ/mol (minimum -80 kJ/mol at n=7)

4-3-n averages -53 kJ/mol (minimum -72 kJ/mol at n=8)

## Cluster Growth via Acid-Base Pair

1. Acid-base cluster growth liberates large amount of heat.
 
$$3-3-4 + 1 \text{ acid} + 1 \text{ base} \rightarrow 4-4-4 \quad \Delta H_1 = -208 \text{ kJ mol}^{-1}$$

$$3-3-16 + 1 \text{ acid} + 1 \text{ base} \rightarrow 4-4-16 \quad \Delta H_3 = -201 \text{ kJ mol}^{-1}$$
2. Heat liberated induces evaporation of water.
 
$$4-4-0 + 1 \text{ water} \rightarrow 4-4-1 \quad \Delta H_a = -79 \text{ kJ mol}^{-1}$$

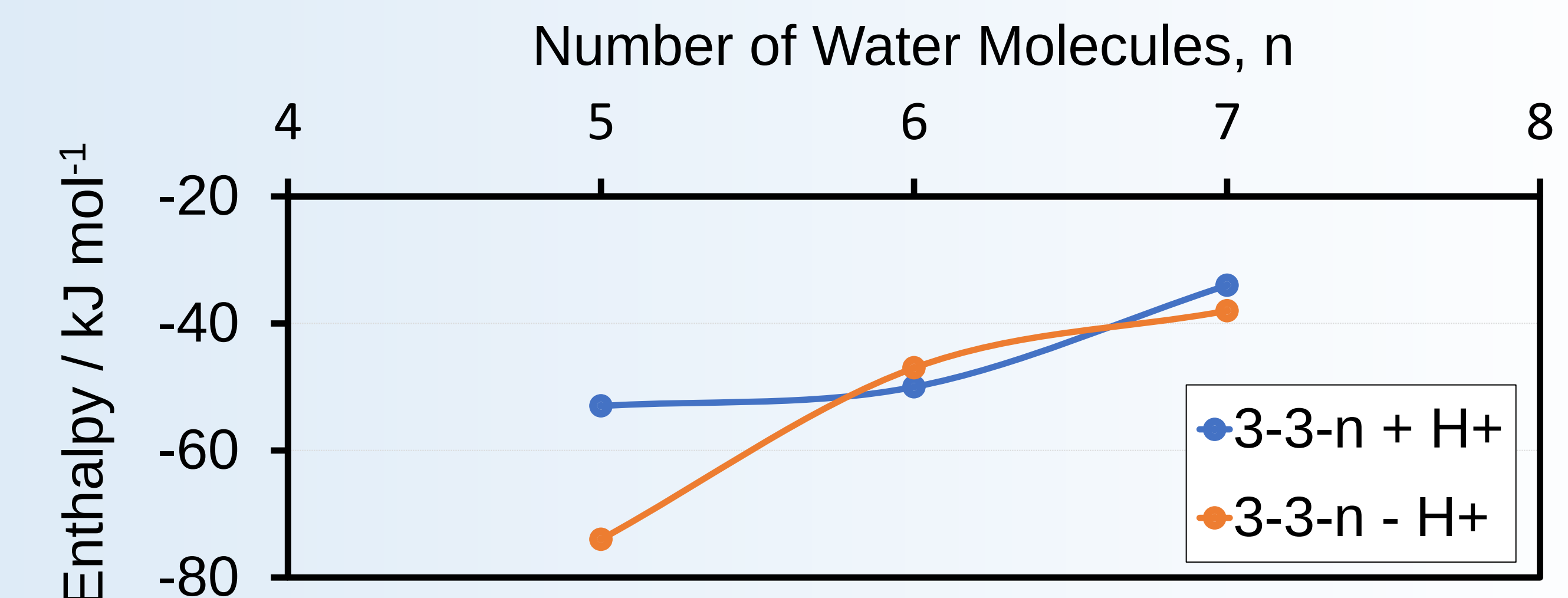
$$4-4-1 + 1 \text{ water} \rightarrow 4-4-2 \quad \Delta H_b = -18 \text{ kJ mol}^{-1}$$

$$4-4-2 + 1 \text{ water} \rightarrow 4-4-3 \quad \Delta H_c = -50 \text{ kJ mol}^{-1}$$

$$4-4-3 + 1 \text{ water} \rightarrow 4-4-4 \quad \Delta H_d = -53 \text{ kJ mol}^{-1}$$
3. Addition of 1 acid and 1 base induces evaporation of 4 water molecules from the cluster.
 
$$3-3-4 : \Delta H_1 \approx \Delta H_a + \Delta H_b + \Delta H_c + \Delta H_d$$

$$3-3-16 : \Delta H_3 \approx \Delta H_a + \Delta H_b + \Delta H_c + \Delta H_d$$

## Cluster Growth of Charged 3-3-n



## References

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### Acknowledgement:

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