

*Supplementary Information:*

## **Reduction of N<sub>2</sub> to Ammonia by Phosphate Molten Salt and Li electrode: Proof of Concept using Quantum Mechanics**

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### **S1: Computational Methods**

All quantum mechanics molecular dynamics (QM-MD or AIMD) were performed using Density Functional Theory (DFT) in the Vienna Ab initio Simulation Package (VASP) version 5.4.4. The exchange-correlation effects were described using the PBE generalized gradient approximation (GGA) functional. Van der Waals forces were taken into account using the Grimme-Becke-Johnson D3 correction for dispersion. The energy cutoff for the planewave basis set was set to 500 eV. Interactions between core and valence electrons were modeled by projector augmented wave pseudopotentials.

A canonical (NVT) ensemble used for temperature-dependent QM-MD, where the simulation was coupled to a thermal bath via a Nose-Hoover thermostat with damping constant 0.1 ns. All periodic calculations used gamma-centered K point grids. The density of the K points varied from calculation to calculation depending on the size of the system. The minimal stoichiometric cell and its derivatives used a 1x1x1 K point mesh. The electrode-electrolyte interface calculations used 2x2x2 K point meshes.

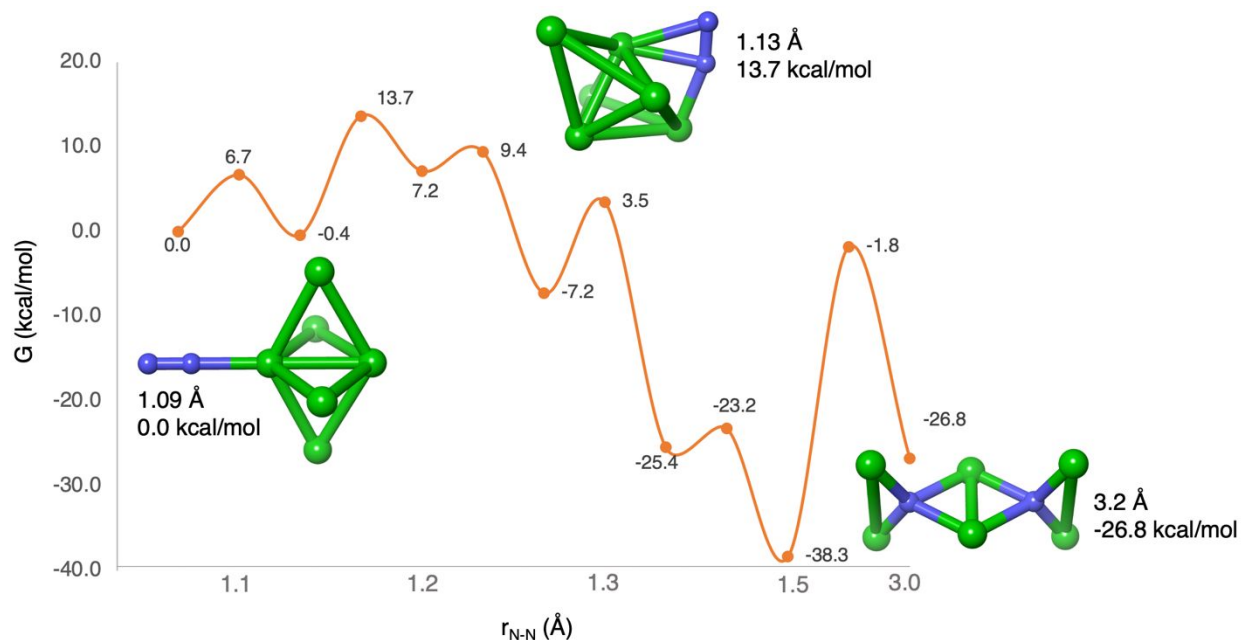
All non-periodic (finite) quantum chemical calculations were performed using the Jaguar software package version 10.9 by Schrodinger Inc. All finite structures were optimized using the M06-2X hybrid GGA functional with the Grimme-Becke-Johnson D3 empirical correction for London Dispersion. All elements were treated with the triple- $\zeta$  6-311G\*\*++ basis set (or 6-311G\*+ for systems without hydrogen). Vibrational frequency calculations were used to predict zero-point energies, enthalpies, and entropies at various temperatures ranging from 298 to 1100 K on all structures. These frequency calculations were also used to confirm local minima for stationary geometries and saddle points for transition states.

### **S2: Relaxed Coordinate Scans of N<sub>2</sub> in Li Clusters**

We demonstrated the reduction of dinitrogen by lithium to form  $\text{Li}_3\text{N}$  using QM-MD for periodic cells.

To confirm the energy and time period required to break the nitrogen-nitrogen triple, double, and single bond, we also performed a non-periodic relaxed coordinate scan of the dinitrogen bond with the minimal system of a single  $\text{N}_2$  with six surrounding lithium, leading toward two  $\text{Li}_3\text{N}$ .

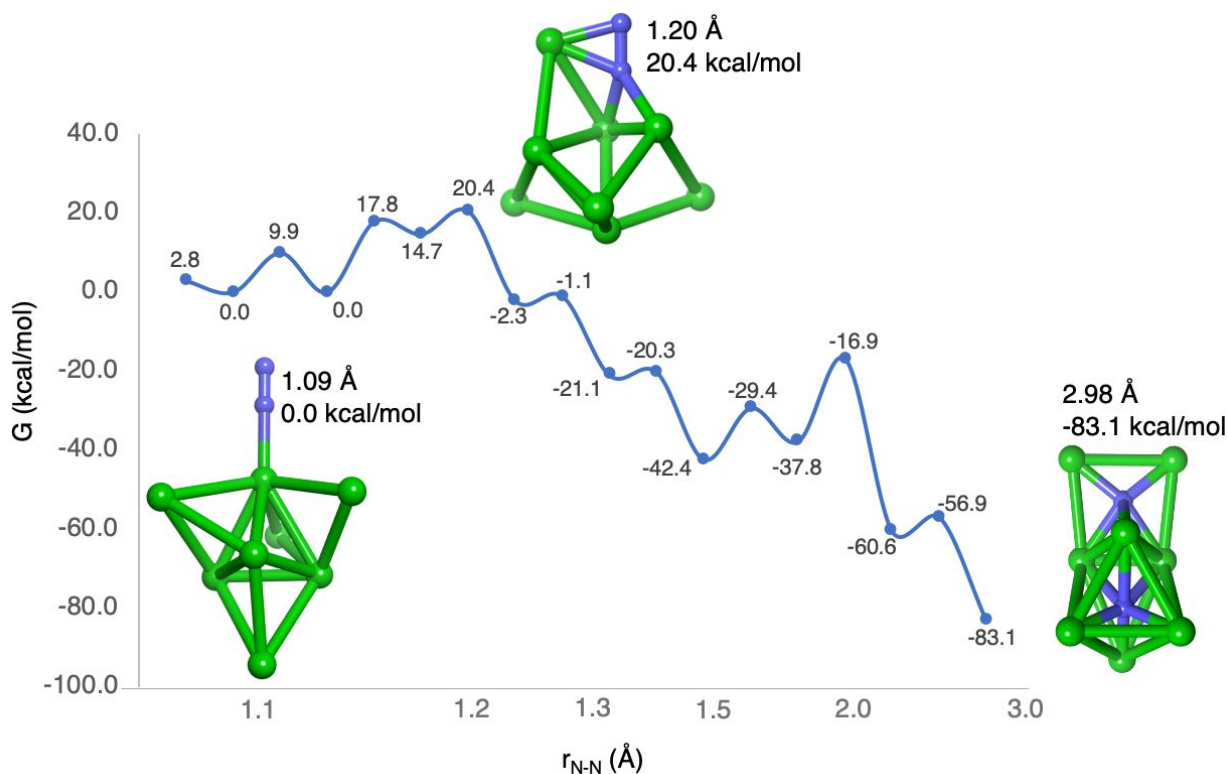
We begin with the dinitrogen at its nominal triple bond length of 1.09 Å end-on coordinated to a six-atom lithium cluster. We then stretched the nitrogen-nitrogen bond in steps, allowing the lithium cluster to engulf the dinitrogen until the dinitrogen was completely dissociated at 3.2 Å.



**Scheme S1:** M06-2X-D3 free energy profile for  $\text{N}_2$  activation by six lithium at 298 K. The data points are spaced evenly along the  $r_{\text{N-N}}$  axis for visual purposes. The three structures correspond to the 0.0 kcal/mol starting state with an N-N distance of 1.09 Å (left), the 13.7 kcal/mol highest-energy transition state with an N-N distance of 1.13 Å (middle), and the -26.8 kcal/mol product state with an N-N distance of 3.2 Å (right).

While scanning the nitrogen-nitrogen bond distance, we observe numerous minima and maxima corresponding to dissociation and association of various N-N, Li-N, and Li-Li couplings. We find the overall dissociation barrier to be 13.7 kcal/mol above the starting state, while the reaction overall is exergonic by -26.8 kcal/mol. The free energy plot reveals that complete dissociation of dinitrogen is impeded by an even lower lying state in which the dinitrogen has a single bond length at 1.48 Å. Additionally, this global minima at 1.48 Å is followed by a relatively high transition state of 36.5 kcal/mol above the global minima, making it slow to break this single bond. This is consistent with the QMMD in which the dinitrogen spent the majority of dynamics at the single bond length.

To remedy this issue, we added additional lithium to the calculation. Coordination of lithium to the nitrogens is clearly favorable, so addition of sufficient lithium might make full dinitrogen dissociation the global minima, as opposed to having a premature global minimum at the dinitrogen single bond.



**Scheme S2:** M06-2X-D3 free energy profile for N<sub>2</sub> activation by eight lithium at 298K. The data points are spaced evenly along the  $r_{N-N}$  axis for visual purposes. The three structures correspond to the 0.0 kcal/mol starting state with an N-N distance of 1.09 Å (left), the 20.4 kcal/mol highest-energy transition state with an N-N distance of 1.20 Å (middle), and the -83.1 kcal/mol product state with an N-N distance of 2.98 Å (right).

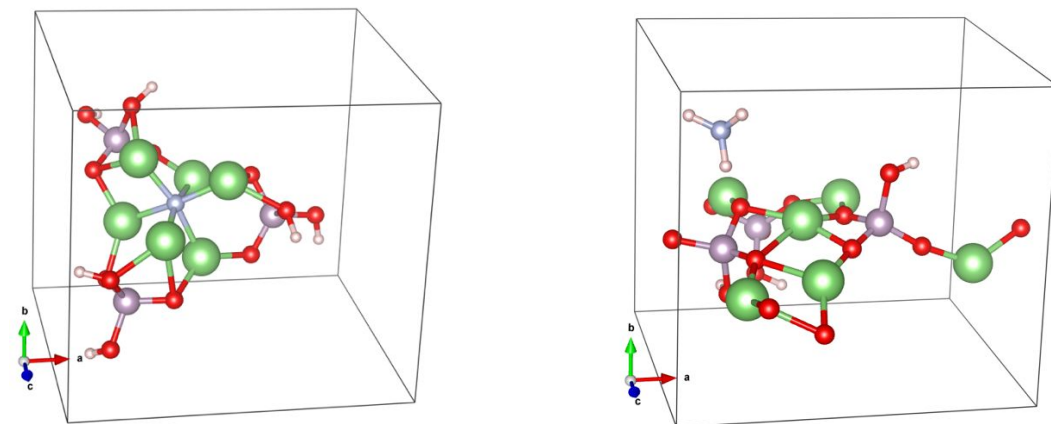
Thus we added 2 additional Li to the 6 Li + N<sub>2</sub> system for a total of eight Li. This increases the overall barrier of dinitrogen dissociation to 20.4 kcal/mol. This barrier corresponds to the breaking of the nitrogen-nitrogen triple bond, although breaking of Li-Li coupling also occurs in this transition state. While the overall barrier is larger, the fully reduced nitride product with a 2.98 Å nitrogen-nitrogen distance is now the global minimum at -83.1 kcal/mol. This fully dissociated state is 40.7 kcal/mol lower than the singly bonded “hydrazido” (N<sup>2-</sup>) state at -42.4 kcal/mol ( $r_{N-N}$  = 1.48 Å). Again, numerous minima and maxima exist between the triply bonded dinitrogen and the fully dissociated nitride product, corresponding to breaking of Li-Li couplings and formation of Li-N couplings.

With excess lithium, dinitrogen takes the minimum energy pathway to dissociate towards nitride anions. Therefore, the dinitrogen would coordinate only 6 lithium to overcome the 13.7 kcal/mol barrier as opposed to the 20.4 kcal/mol. Then the dinitrogen would coordinate 2 additional lithium (8 total) and fully dissociate to -83.1 kcal/mol. Therefore, the minimum energy pathway for dinitrogen reduction by lithium has a max barrier of 13.7 kcal/mol and is exergonic by 83.1 kcal/mol.

### S3: NH<sub>3</sub> Formation from LiH<sub>2</sub>PO<sub>4</sub>

The minimal stoichiometric cell contains a single Li<sub>3</sub>N and three LiH<sub>2</sub>PO<sub>4</sub>s. This minimal system allows us to focus on whether the phosphate molten salt is capable of forming ammonia. From

**reaction S1**, three proton transfers from the phosphates to the nitride anion results in formation of one NH<sub>3</sub>. It is also possible for one of the phosphates to become doubly deprotonated as in **reaction S2**.



**Figure S1:** The minimal stoichiometric cell starting with a single Li<sub>3</sub>N and 3 LiH<sub>2</sub>PO<sub>4</sub> after minimization (**left**) and proceeding to formation of ammonia (**right**).

We placed the Li<sub>3</sub>N and three surrounding LiH<sub>2</sub>PO<sub>4</sub>s into a periodic cell and minimized the energy. The nitride anion adopts a pseudo-octahedral geometry coordinated to six lithium atoms, which is consistent with crystal structures where nitride anions are observed to coordinate up to eight lithium atoms in alpha-Li<sub>3</sub>N. Furthermore, all lithium atoms were found to bridge two phosphate oxygen atoms, making the lithium atoms three-coordinate.

After minimization, we heated the cell to temperatures ranging from 600 to 900 K in 100 K increments with a system pressure of 0 atm and carried out reactive dynamics using forces from quantum mechanics (QM-MD or AIMD) for 50 ps at the various temperatures. Here we used the canonical ensemble (NVT) with fixed volume and a Nose-Hoover thermostat. Even without an applied potential, the formation of N-H bonds to produce NH<sub>3</sub> is very favorable. For all temperatures, the first N-H bond forms during heating, following which the two additional N-H bonds form sequentially.

- At 600 K, the second N-H formed at 14 ps, while the third bond did not form within 50 ps.
- At 700 K, the second N-H bond formed at 11 ps, and the final N-H bond formed at 32 ps.
- At 800 K, the second N-H bond formed at 7 ps, and the final N-H bond formed at 15 ps.
- At 900 K the second N-H bond formed at 2 ps, and the final N-H bond formed at 9 ps.

(these results are summarized in **Table S1**).

These proton transfers always occurred through breaking the first O-H bond of the phosphates, never the second (**reaction 1** and never **reaction 2**). This is consistent with the phosphate second O-H bond being far stronger than the first.

**Table S1:** Time for NH, NH<sub>2</sub>, and NH<sub>3</sub> formation at various temperatures from doubly protonated phosphates. NVT dynamics were performed at the PBE-D3 level with a Nose-Hoover thermostat.

Temperature (K)	NH formation	NH <sub>2</sub> formation (ps)	NH <sub>3</sub> formation (ps)
600	during heating	14	>50
700	during heating	11	32
800	during heating	7	15
900	during heating	2	9

This minimal stoichiometric cell shows promising results for ammonia synthesis through a molten salt electrolyte. NH<sub>3</sub> formation within 9 ps indicates an overall barrier no higher than 10 kcal/mol at 900 K to convert the nitride anion to ammonia.

Reaction barriers can be extracted from reactive molecular dynamics using the Eyring kinetics equation (**equation S1**). Using kinetic rate constants at varying temperatures, the enthalpic, entropic, and free energy barriers can be extracted from the linear relationship between  $\ln \frac{k}{T}$  and  $\frac{1}{T}$  according to **equation S2**.

$$k = \frac{K_B T}{h} e^{\frac{S^\ddagger}{R}} e^{\frac{-H^\ddagger}{RT}} \quad (\text{equation S1})$$

$$\ln \frac{k}{T} = -\frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T} + \ln \frac{K_B}{h} + \frac{\Delta S^\ddagger}{R} \quad (\text{equation S2})$$

Using the formation times for NH<sub>x</sub> species along with their respective temperatures, we compute reaction barriers as follows, where  $\Delta G^\ddagger$  is calculated at 900 K from  $G = H - TS$ :

$$\text{Li}_2\text{NH} + \text{LiH}_2\text{PO}_4 \rightarrow \text{LiNH}_2 + \text{Li}_2\text{HPO}_4 \quad \Delta G^\ddagger = 6.5 \frac{\text{kcal}}{\text{mol}} \quad \Delta H^\ddagger = 16.2 \frac{\text{kcal}}{\text{mol}} \quad \Delta S^\ddagger = 10.8 \frac{\text{cal}}{\text{mol} \cdot \text{K}}$$

$$\text{LiNH}_2 + \text{LiH}_2\text{PO}_4 \rightarrow \text{NH}_3 + \text{Li}_2\text{HPO}_4 \quad \Delta G^\ddagger = 9.2 \frac{\text{kcal}}{\text{mol}} \quad \Delta H^\ddagger = 5.6 \frac{\text{kcal}}{\text{mol}} \quad \Delta S^\ddagger = -3.9 \frac{\text{cal}}{\text{mol} \cdot \text{K}}$$

These reaction barriers show that ammonia formation is extremely rapid, with  $\Delta G^\ddagger = 9.2$  kcal/mol at 900 K. In this system, both reactions involve breaking a phosphate O-H bond and forming an N-H bond. However, the opposite signs of the entropic barriers (10.8 versus -3.9 cal/mol/K) indicates that the lithium plays an associative role in the first reaction and a dissociative role in the second reaction.

We also investigated the effect of excess lithium in the minimal stoichiometric cell by doubling the number of lithium from six to twelve, forming a mini-Li electrode. We re-minimized and heated the system to 900 K. Before reaching 900 K, two PO-H bonds break to form one H<sub>2</sub>. Then a third PO-H bond breaks to form LiH, where hydrogen bridges two lithium particles with Li-H distances hovering around 2.0 Å. Thus before the system reaches 900 K we have one H<sub>2</sub> and one LiH. The first N-H bond is made at the end of heating with the hydrogen coming directly from a doubly protonated phosphate. The second N-H bond forms 7 ps into dynamics, where the hydrogen came from a broken H<sub>2</sub>. Finally, the third N-H bond to form ammonia is made at 19 ps in the dynamics, with the hydrogen again coming from an H<sub>2</sub>. With the additional lithium, ammonia

formation took 19 ps which is 10 ps longer than with half the lithium (9 ps). Although unwanted  $H_2$  formed, the  $H_2$  dissociated in favor of N-H bond formation, ultimately forming ammonia.  $H_2$  dissociation in favor of N-H bond formation was activated by coupling lithium to  $H_2$ . The coupling lithium induces a dipole in  $H_2$ , making the adjacent hydrogen partially negative and the opposite hydrogen partially positive. The partially positive hydrogen is then attacked by the hydrazido ( $N^2$ )/nitride ( $N^{3-}$ ) ion to form an N-H bond.

#### S4: Pressure dependence of Minimal Stoichiometric Cell

To capture the effects of pressure on the formation of ammonia, we took the minimal stoichiometric system that was heated to 900K and switched to the microcanonical ensemble (NVE) and applied an external pressure ranging from 0 to 10,000 atm *via* a Pulay correction to the stress tensor. Because we started with a preheated system, the first N-H bond had already formed as we saw previously.

At 0 atm in which no external pressure was applied, the second N-H bond formed at 0.9 ps and the third formed at 5.3 ps to produce ammonia. We see at 900K and 0 atm, ammonia forms faster in NVE than in NVT. This is because of the exothermic nature of ammonia formation that increased the temperature in NVE, leading to a self-accelerating reaction. In contrast for NVT MD the temperature is held constant, which inhibits self-acceleration by the thermostat. When the external pressure is increased to 1 atm, the second N-H bond forms at 0.8 ps and the third forms at 3.1 ps.

At 10,000 atm, the second N-H bond forms at 0.8 atm and the third at 2.1 ps (these results are summarized in table X). Clearly, increased pressure leads to increased rate of ammonia formation.

**Table S1:** Formation of N-H bonds during PBE-D3 NVE dynamics at 900K various external pressures.

External Pressure	NH formation	$NH_2$ formation	$NH_3$ formation
0 atm	during heating	0.9 ps	5.3 ps
1 atm	during heating	0.8 ps	3.1 ps
100 atm	during heating	0.8 ps	2.1 ps

Simulation of the minimal stoichiometric cell using both NVT and NVE ensembles hints towards rapid synthesis of ammonia at reasonable temperatures and pressures. As we expected, increased temperature and pressure lead to increased speed of N-H bond formation. We also saw NVE results in quicker ammonia formation due to exothermic self-acceleration.

#### S5: Use of Other Alkali Metals

To further improve the rate of ammonia formation, we examined the effect of the counterion on the reaction. So far we have considered just Li to balance the charge of the nitride and phosphate anions. In principle, we could replace Li with a different alkali metal to modify the nitride and phosphate charge distributions, which might in turn increase the speed of ammonia formation. Taking our optimized minimal cell, we replaced the Li atoms with Na or K and re-minimized. In the Li system the Li-N distances ranged from 1.9 to 2.0 Å. With the system re-minimized for Na, the Na-N distances range from 2.3 to 2.4 Å, and for the K system the K-N distances range from 2.7 to 2.9 Å. Because there is greater separation between the nitride anion and its nearest neighbors, it is possible that proton transfer will be more facile due to decreased shielding in these Na and K



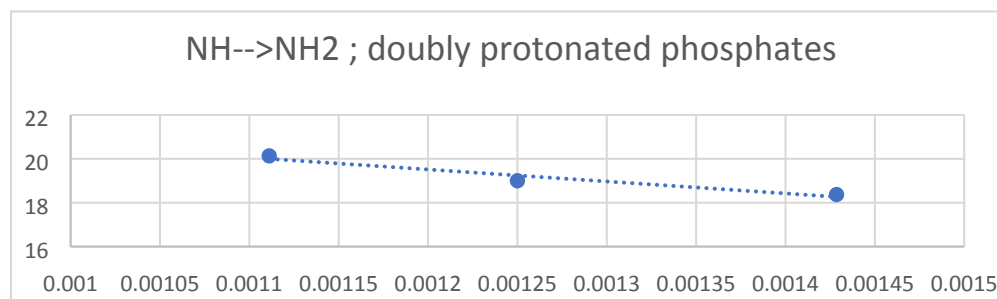
minimum systems, even though Na and K are larger in size. Indeed, switching from Li to Na we observe increased speed for the formation of ammonia. Similar to with Li, the first N-H bond forms during heating in the Na system; the second and third N-H bonds are then formed at 1.8 and 2.5 ps into NVE dynamics at 0 atm. Recall that with Li the final N-H bond to produce ammonia formed at 5.3 ps, the Na system is 53% faster than the Li for ammonia synthesis. When we replace Li with K we find the opposite effect: synthesis of ammonia is slower in the K system by 30%. The first, second, and third N-H bonds were formed at 6.9, 7.1, and 7.4 picoseconds into NVE dynamics at 900K and 0 atm. This can be explained by the fact that the binding energy for K to substrates is typically higher than that of Na and Li, meaning coupling between K and the nitride is stronger. Analogously, binding energy of Na to substrates is typically lower, resulting in weaker coordination of Na to the nitride anion and subsequently easier displacement of Na by a proton. Ultimately, we find that replacement of Li with Na in the minimal stoichiometric cell leads to 53% faster formation of ammonia, while replacement with K leads to 30% slower formation of ammonia.

### S6: Arrhenius-Eyring Linear Regressions

Simulations were carried out multiple times at various temperatures to arrive at average statistics. Using the average formation times for NH<sub>2</sub> and NH<sub>3</sub> and the corresponding temperatures, we can calculate pseudo-rate constants ( $k$ ). From here, we can arrive at reaction barriers by applying the Arrhenius relation to Eyring's kinetic equation (**equation S2**), where  $\ln(k/T)$  depends linearly on  $1/T$ . A linear regression is performed on the data points to arrive at the fitted coefficients. The enthalpic barrier ( $\Delta H^\ddagger$ ) is extracted from the first order term (the slope) and the entropic barrier ( $\Delta S^\ddagger$ ) is extracted from the zeroth order term (the intercept). We can then calculate temperature-dependent free energy barriers from  $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ . In the plots below, the X axes are  $1/T$  and the Y axes are  $\ln(k/T)$ .

#### NH → NH<sub>2</sub> from doubly protonated phosphates

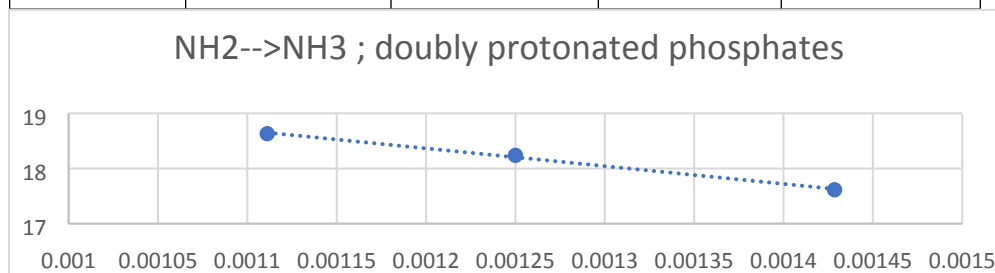
T (K)	time (fs)	$k$	$1/T$	$\ln(k/T)$
700	15000	66666666667	0.00142857	18.37189058
800	7000	1.42857E+11	0.00125	19.00049924
900	2000	5E+11	0.00111111	20.13547917



-H/R	H		lnKb/h + S/R	S		G (900K)
-5460.400	10.858		26.067	4.588		6.729

### NH<sub>2</sub> → NH<sub>3</sub> from doubly protonated phosphates

T (K)	time (ps)	k	1/T	ln(k/T)
700	32000	31250000000	0.00142857	17.61420488
800	15000	66666666667	0.00125	18.23835919
900	9000	1.11111E+11	0.00111111	18.63140178

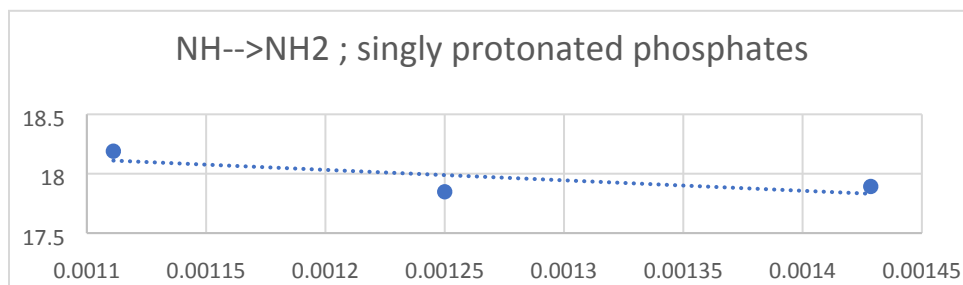


-H/R	H		lnKb/h + S/R	S		G (900K)
-3217.700	6.398		22.226	-3.050		9.144

### NH → NH<sub>2</sub> from singly protonated phosphates

T (K)	time_avg (ps)	k	1/T	ln(k/T)
700	24.225	41279669763	0.00142857	17.8925556
800	22.1666667	45112781955	0.00125	17.8478197
900	14	71428571429	0.00111111	18.189569

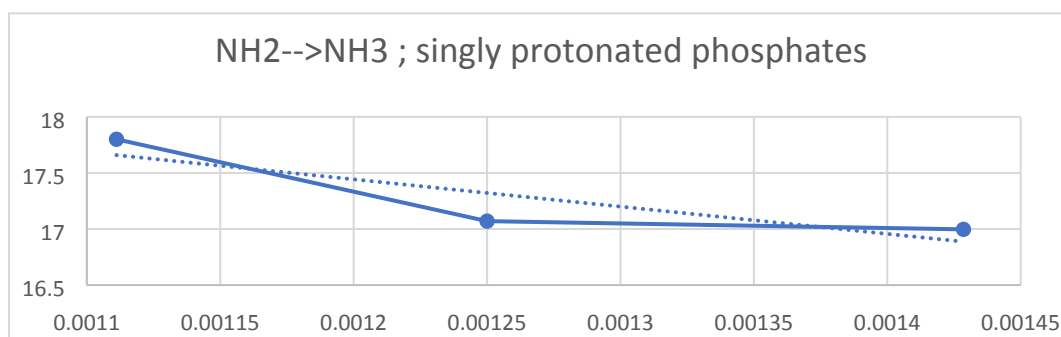




-H/R	H		lnKb/h + S/R	S		G (900K)
-880.280	1.750		19.089	-9.286		10.108

### NH<sub>2</sub> → NH<sub>3</sub> from singly protonated phosphates

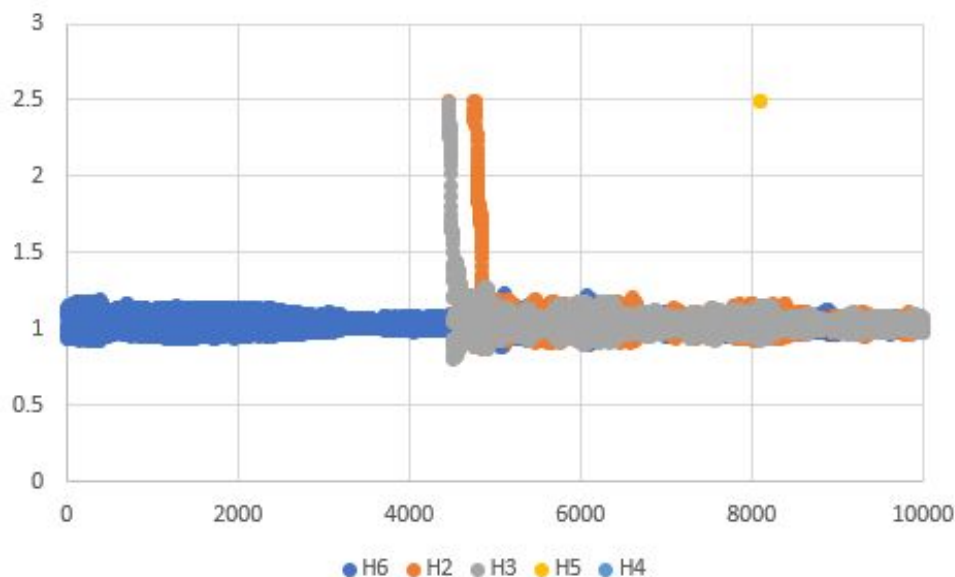
T (K)	time_avg (ps)	k	1/T	ln(k/T)
700	59.33333333	16853932584	0.00142857	16.9967695
800	48.25	20725388601	0.00125	17.0700136
900	20.66666667	48387096774	0.00111111	17.8001043



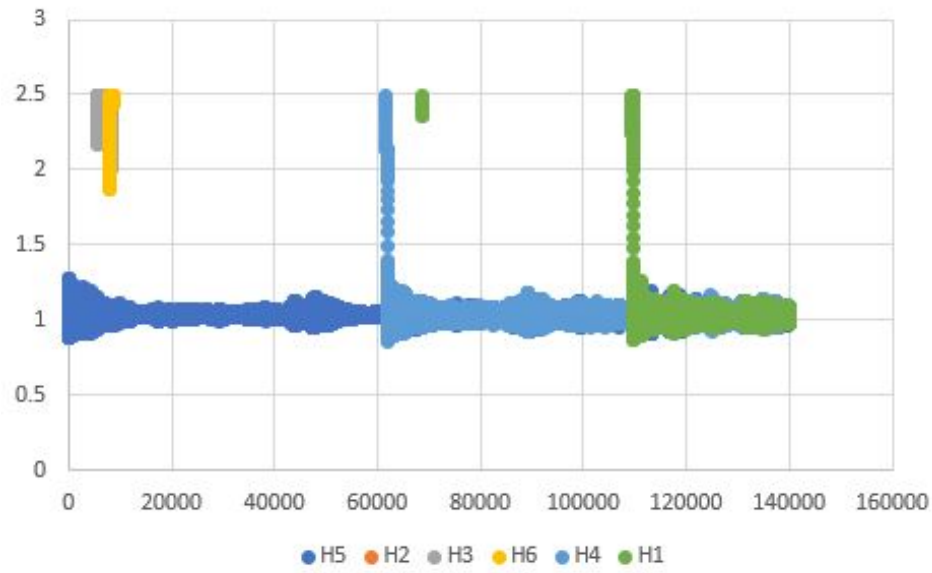
-H/R	H		lnKb/h + S/R	S		G (900K)
-2431.600	4.835		20.361	-6.761		10.920

### S7: Radial Distribution Functions for Singly Protonated Phosphates

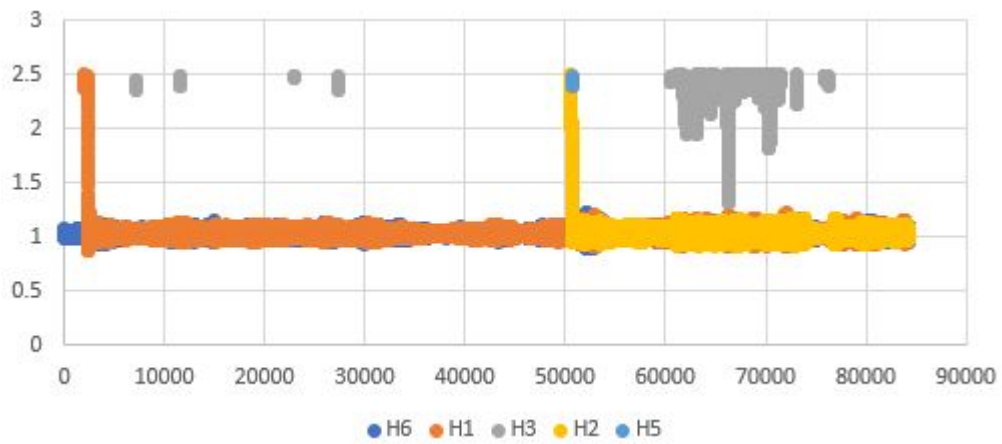
The following time-dependent radial distribution functions represent the distances of relevant hydrogens relative to the nitride ion centers throughout the duration of dynamics. Specifically, these are time-evolving N-H distances during ammonia formation from singly protonated phosphates. In the following plots, the X axes are times in femtoseconds and the Y axes are nitrogen-hydrogen distances in angstroms. When the function falls to  $\sim 1.01$ , this represents an N-H bond being formed. The formation of ammonia is represented by three functions falling to  $\sim 1.01$ , corresponding to three hydrogens being bonded to the nitrogen center. In all radial distribution functions, one function is already at  $\sim 1.01$  at time = 0, meaning that an N-H bond was present at the beginning of the dynamics. As we stated in the manuscript, this is because all nitride centers formed single N-H bonds during heating to desired temperatures, which then carried over to the constant temperature dynamics shown here. Each plot is labeled with the following notation: X-Y-Z. X is temperature (ranging from 700-900 K), Y is the specific run at that temperature (ranging from 1-3), and Z is the nitrogen index (ranging from 1-2). The hydrogen index in the plots is arbitrary.



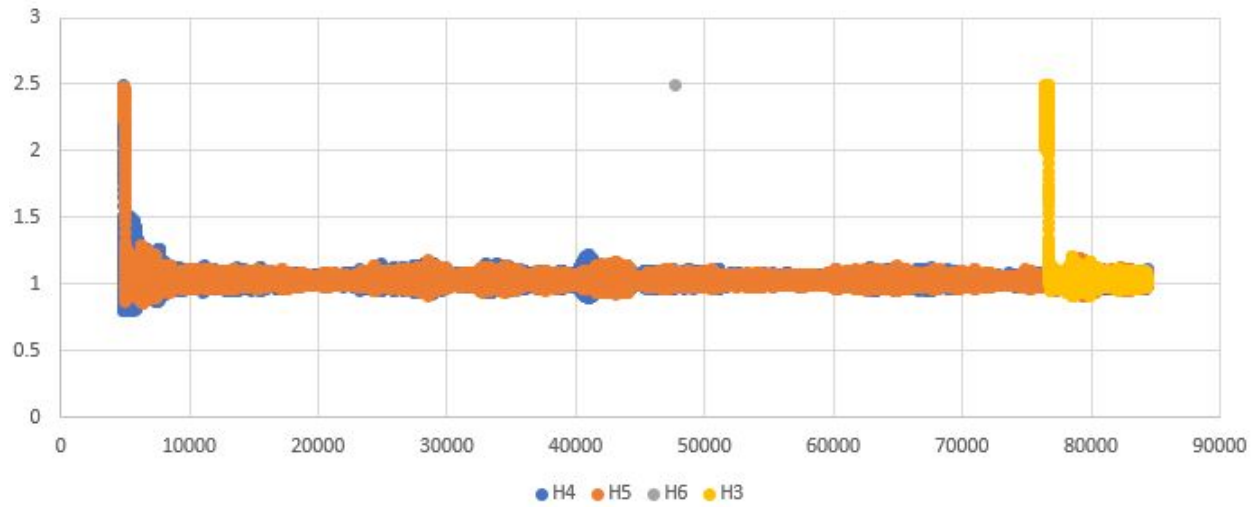
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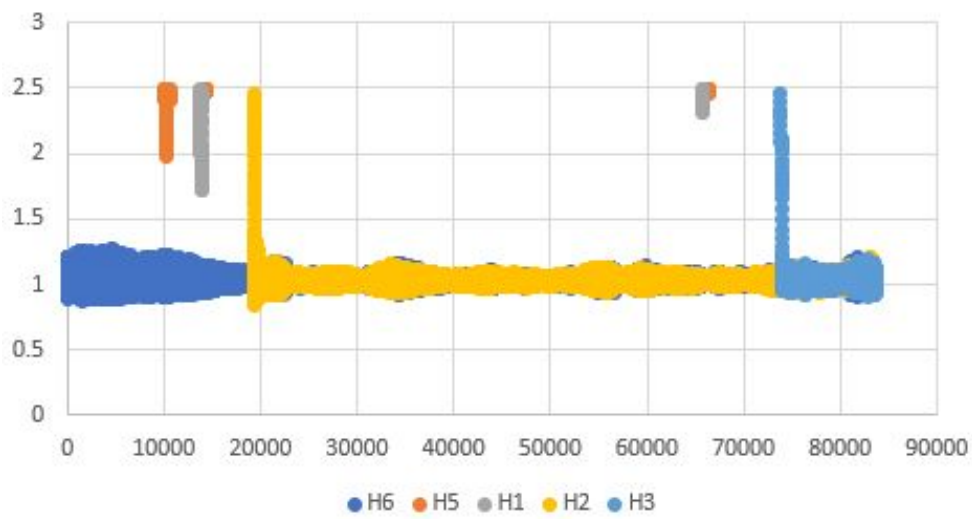
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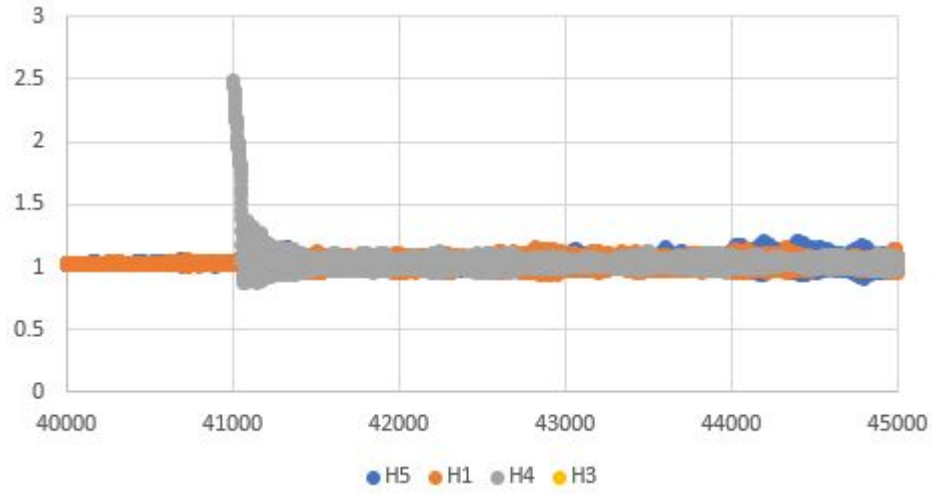
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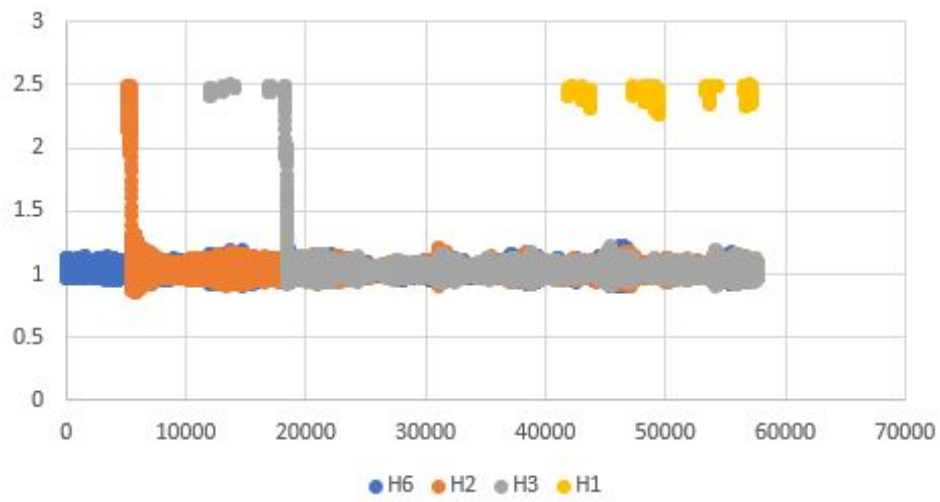
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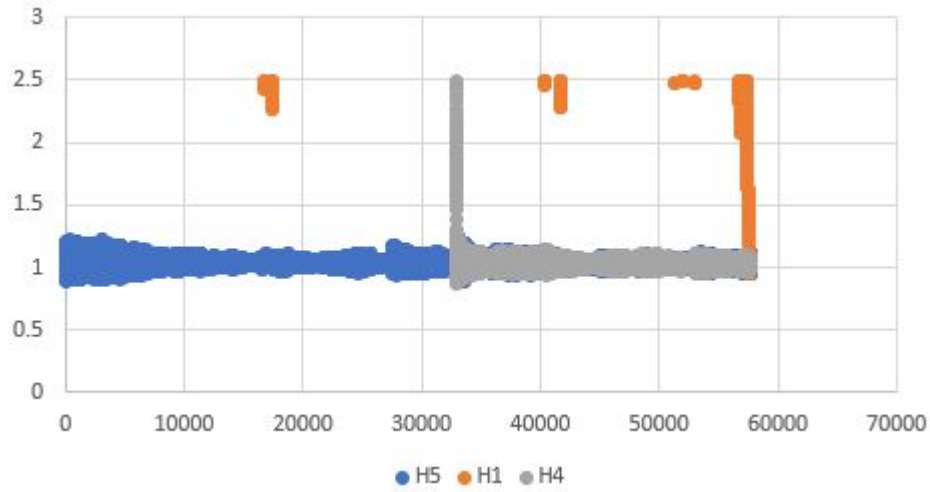
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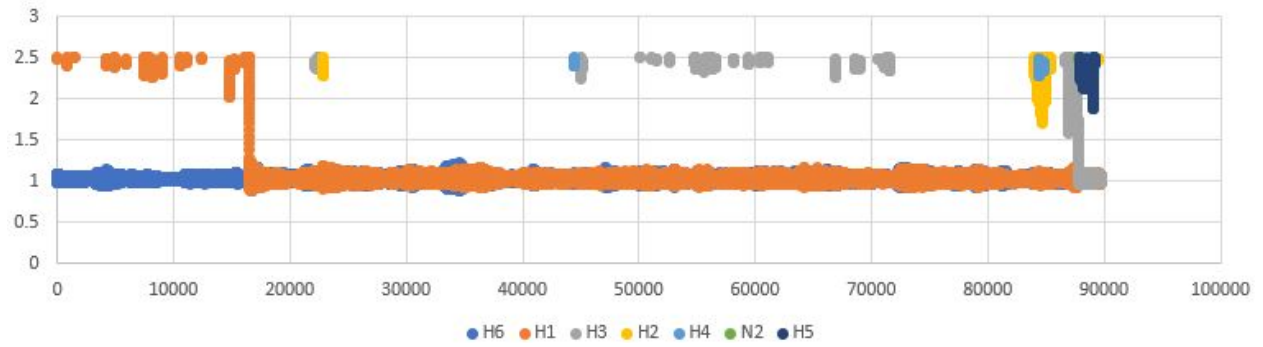
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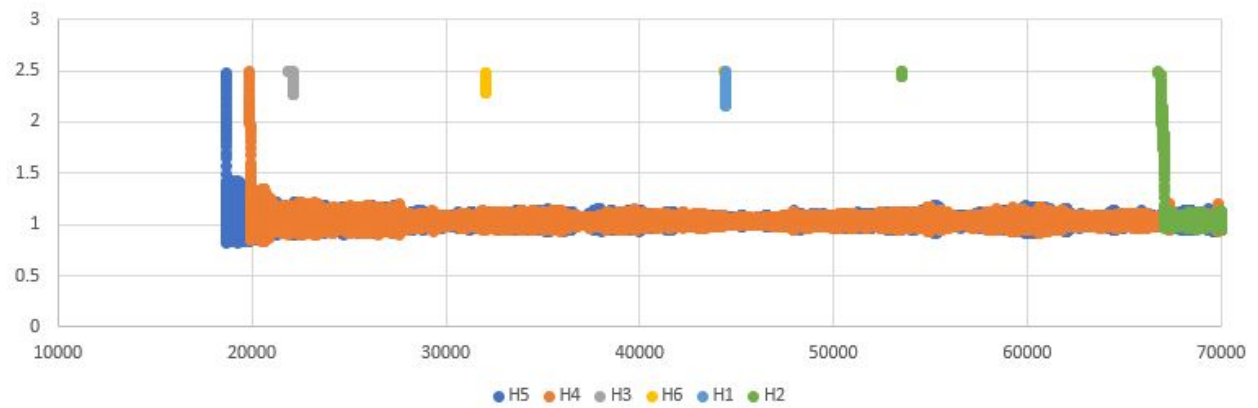
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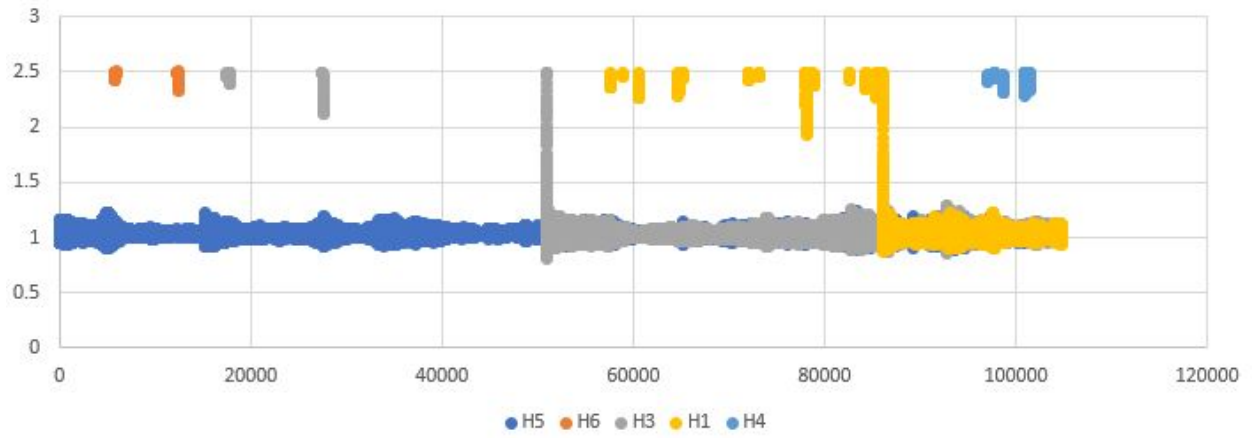
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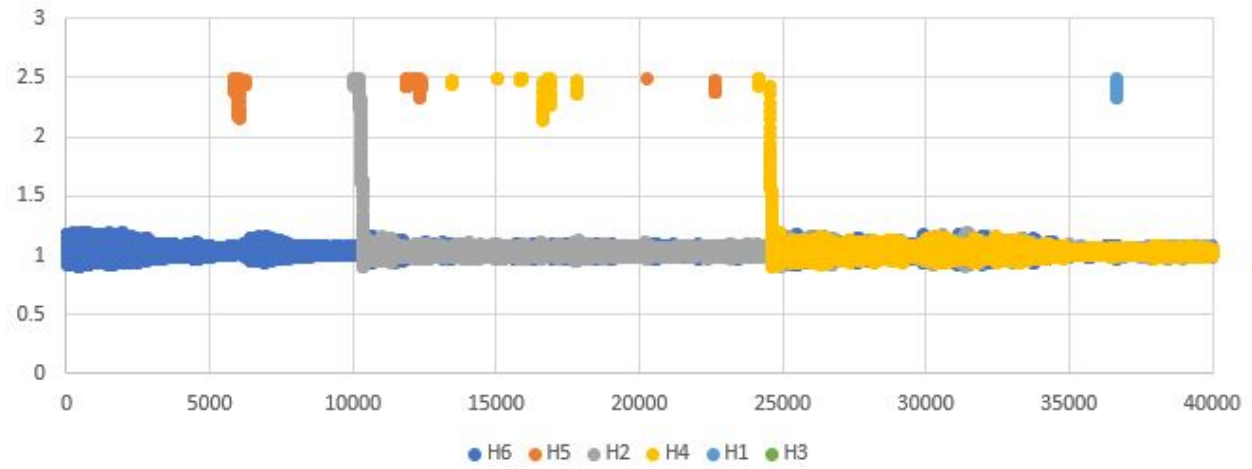
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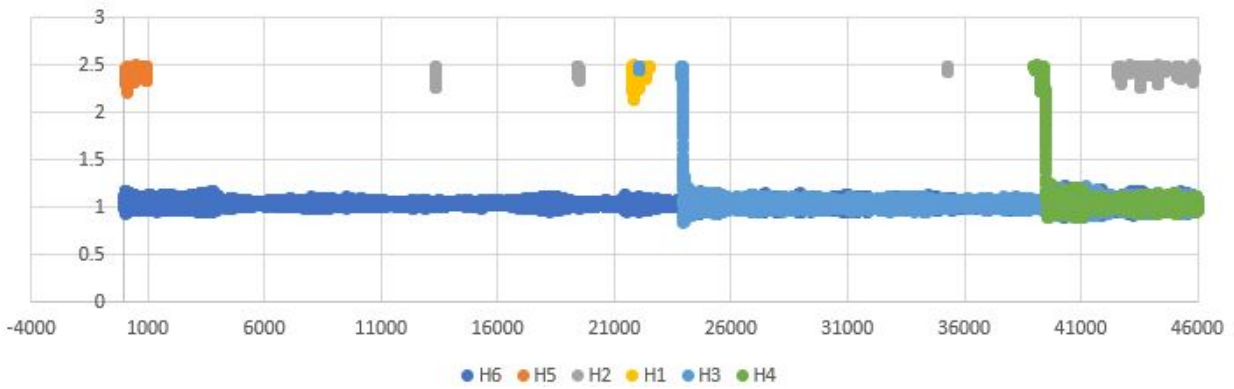
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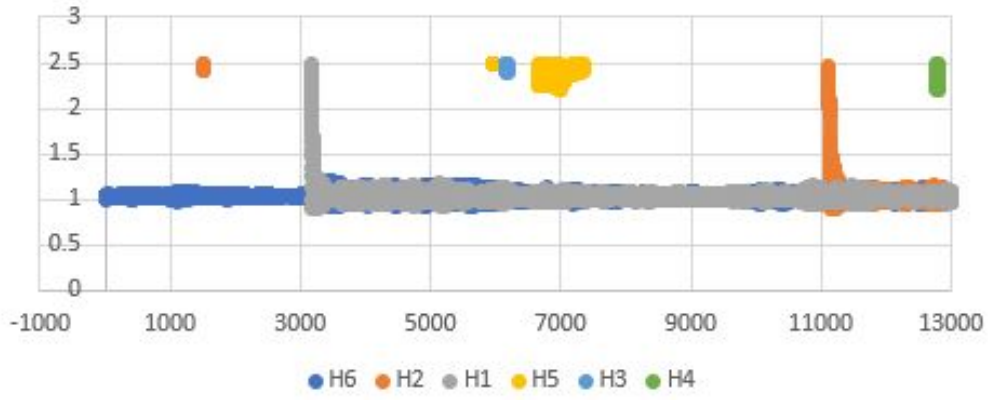


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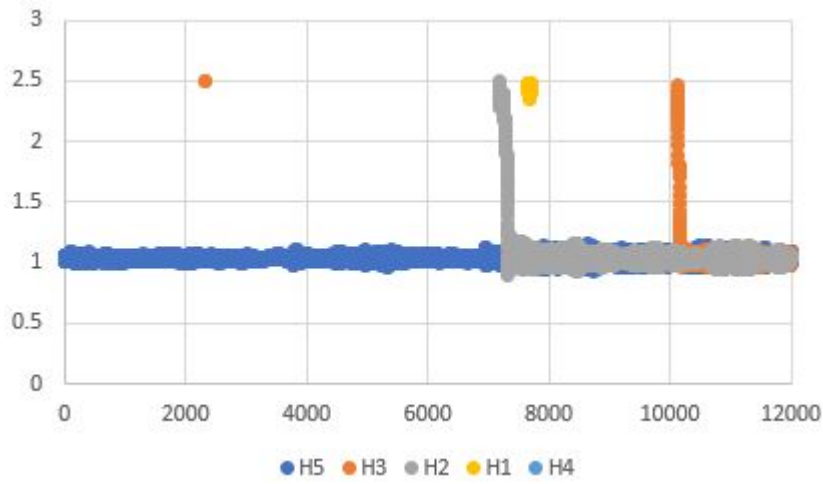


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900-2-1



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