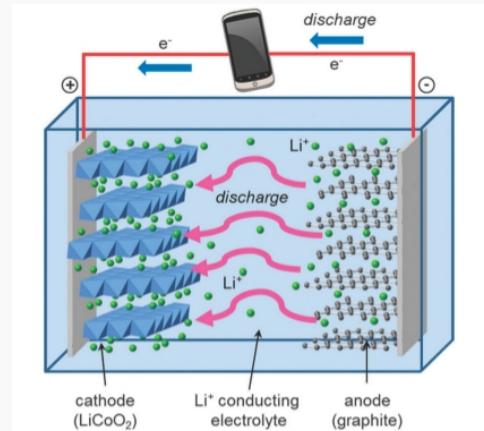


# TUTORIAL SYNOPSIS

## Li-ion diffusion in LiFePO<sub>4</sub> for battery applications

- ❖ Import LiFePO<sub>4</sub> bulk structure
- ❖ Optimize LiFePO<sub>4</sub> lattice parameters
- ❖ Create the Li<sub>6</sub>FePO<sub>4</sub> structures
- ❖ Optimize initial and final configurations
- ❖ Create initial NEB trajectories (IDPP interpolation)
- ❖ Optimize Li diffusion path
- ❖ Calculate the reaction rates using harmonic transition state theory (HTST)



# Import LiFePO<sub>4</sub> bulk structure



Crystallography Open Database

Search results

Result: there are 5 entries in the selection

Switch to the old layout of the page

Download all results as: [list of COD numbers](#) | [list of CIF URLs](#) | [data in CSV format](#) | [archive of CIF files \(ZIP\)](#)

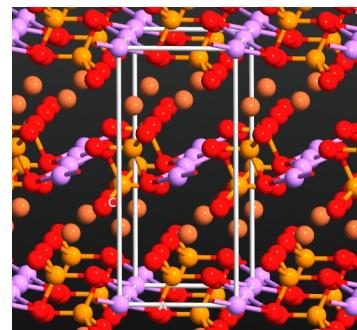
Searching elements including li, fe, P, o number of elements between 4 and 4 text, file, commonname, chemname, mineral contains lifePO4

COD ID	Links	Formula	Space group	Cell parameters	Cell volume	Bibliography
4001845	<a href="#">CIF</a>	Fe Li O4 P	<a href="#">P n m a</a>	10.336; 6.006; 4.6932 90; 90; 90	291.34	Janssen, Yuri; Santhanagopalan, Dhamodaran; Qian, Danna; Chi, Miaofang; Wang, Xiaoping; Hoffmann, Christina; Meng, Ying Shirley; Khalifah, Peter G. Reciprocal Salt Flux Growth of LiFePO4Single Crystals with Controlled Defect Concentrations <i>Chemistry of Materials</i> , <b>2013</b> , <i>25</i> , 4574
4001846	<a href="#">CIF</a>	Fe Li O4 P	<a href="#">P n m a</a>	10.336; 6.006; 4.6932 90; 90; 90	291.34	Janssen, Yuri; Santhanagopalan, Dhamodaran; Qian, Danna; Chi, Miaofang; Wang, Xiaoping; Hoffmann, Christina; Meng, Ying Shirley; Khalifah, Peter G. Reciprocal Salt Flux Growth of LiFePO4Single Crystals with Controlled Defect Concentrations <i>Chemistry of Materials</i> , <b>2013</b> , <i>25</i> , 4574
4001847	<a href="#">CIF</a>	Fe Li O4 P	<a href="#">P n m a</a>	10.3244; 6.0064; 4.6901 90; 90; 90	290.84	Janssen, Yuri; Santhanagopalan, Dhamodaran; Qian, Danna; Chi, Miaofang; Wang, Xiaoping; Hoffmann, Christina; Meng, Ying Shirley; Khalifah, Peter G. Reciprocal Salt Flux Growth of LiFePO4Single Crystals with Controlled Defect Concentrations <i>Chemistry of Materials</i> , <b>2013</b> , <i>25</i> , 4574
4001848	<a href="#">CIF</a>	Fe Li O4 P	<a href="#">P n m a</a>	10.3244; 6.0064; 4.6901 90; 90; 90	290.84	Janssen, Yuri; Santhanagopalan, Dhamodaran; Qian, Danna; Chi, Miaofang; Wang, Xiaoping; Hoffmann, Christina; Meng, Ying Shirley; Khalifah, Peter G. Reciprocal Salt Flux Growth of LiFePO4Single Crystals with Controlled Defect Concentrations <i>Chemistry of Materials</i> , <b>2013</b> , <i>25</i> , 4574
4001849	<a href="#">CIF</a>	Fe Li O4 P	<a href="#">P n m a</a>	10.3165; 6.0095; 4.6988 90; 90; 90	291.31	Janssen, Yuri; Santhanagopalan, Dhamodaran; Qian, Danna; Chi, Miaofang; Wang, Xiaoping; Hoffmann, Christina; Meng, Ying Shirley; Khalifah, Peter G. Reciprocal Salt Flux Growth of LiFePO4Single Crystals with Controlled Defect Concentrations <i>Chemistry of Materials</i> , <b>2013</b> , <i>25</i> , 4574

First | Previous 20 |  of 1 | Next 20 | Last | Display: [5](#) [10](#) [20](#) [50](#) [100](#) [200](#) [300](#) [500](#) [1000](#) entries per page

4001845.cif Show all downloads...

- ❖ Download CIF file
- ❖ Copy it to project folder



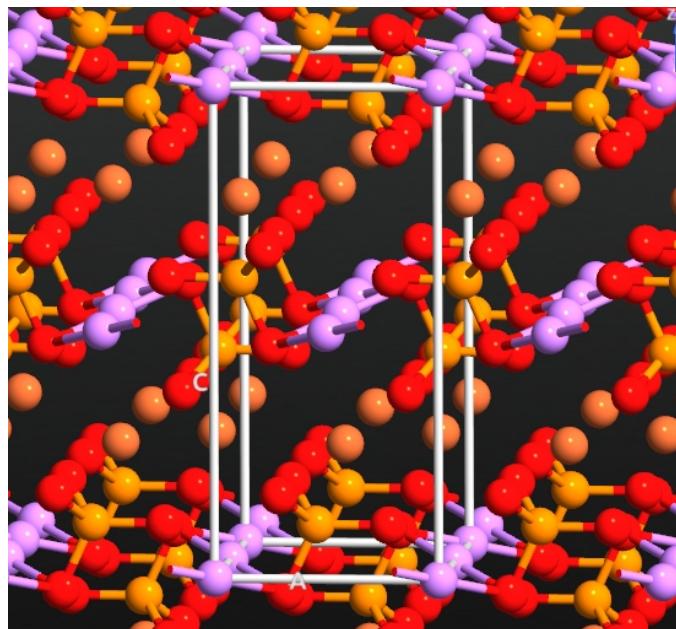
# Optimize LiFePO<sub>4</sub> lattice parameters



## ATK-DFT, ATK 2015.1

- ❖ GGA-PBE exchange correlation potential
- ❖ FHI pseudopotential
- ❖ DZP basis set
- ❖ 7x5x3 k-point sampling
- ❖ 75 Ha density mesh cut-off
  
- ❖ Geometry optimization
- ❖ Max forces 0.05 eV/Å
- ❖ Max stress 0.005 eV/Å<sup>3</sup>

$a = 4.752 \text{ \AA}$	$4.690 \text{ \AA}$ [1]
$b = 6.087 \text{ \AA}$	$6.006 \text{ \AA}$ [1]
$c = 10.451 \text{ \AA}$	$10.336 \text{ \AA}$ [1]

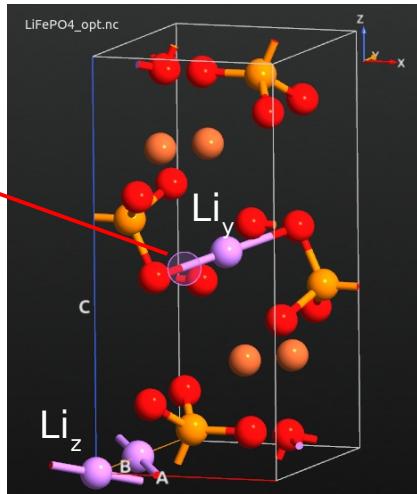


[1] Chemistry of Materials, 2013, 25, 4574

# Create the $\text{Li}_y\text{FePO}_4$ structures

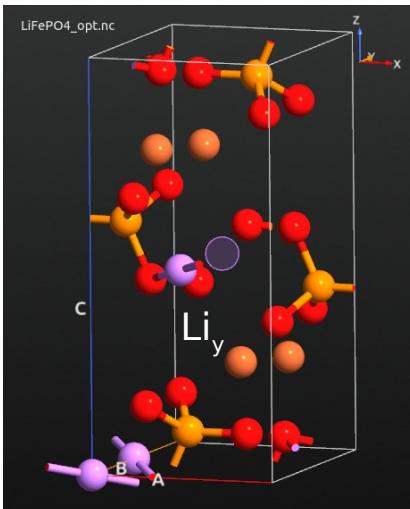


remove one  
Li atom



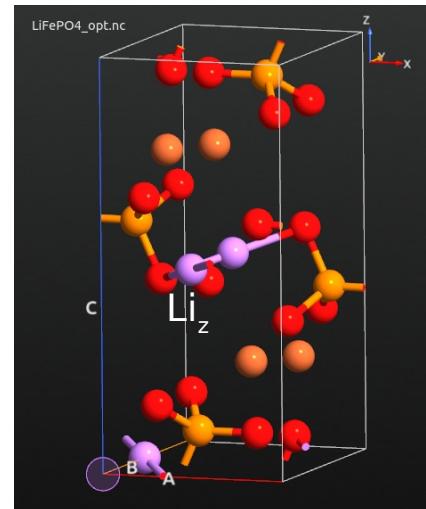
initial configuration

Li diffusion along y axes

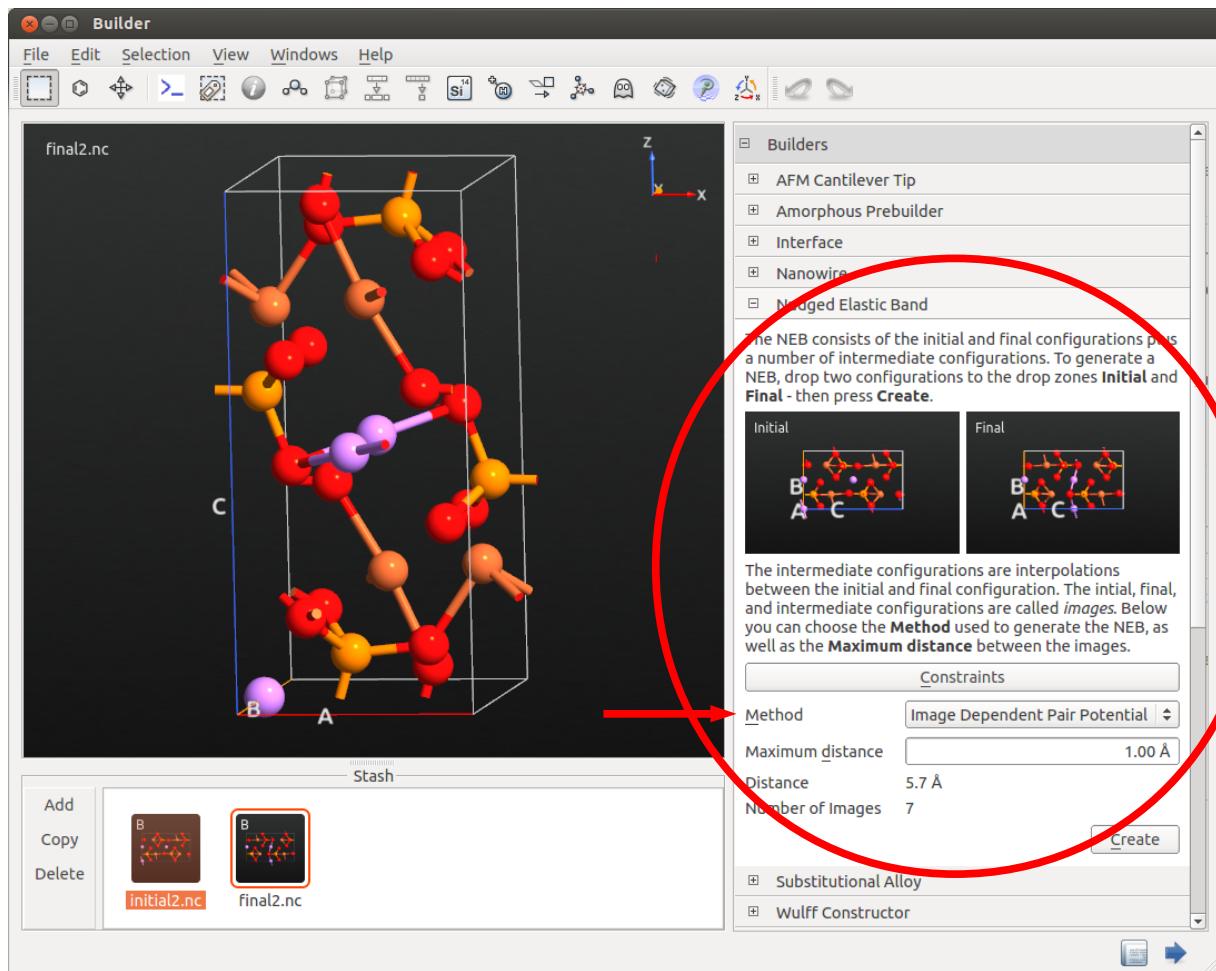


final configurations

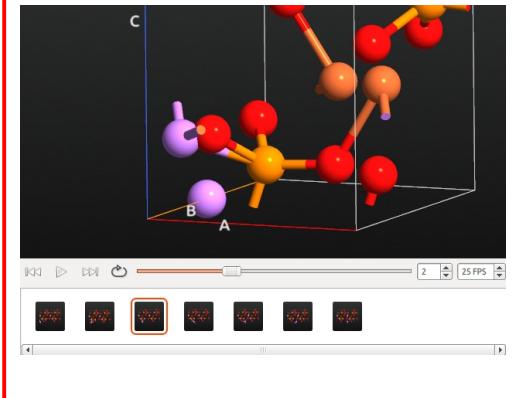
Li diffusion along z axes



# Create initial NEB trajectories (IDPP interpolation)



Linear interpolation - overlapping atoms, bad initial guess



# Optimize Li diffusion path



Script Generator(2) - neb\_22.py\*

File Edit Windows Help

Blocks Script

New Calculator Analysis from File Adjust Configuration Initial State Optimization Analysis

NEB New Calculator OptimizeGeometry HTSTEvent

Global IO

Default output file neb.nc ...

Script detail Minimal

HTST Event

HTST Event

Prefactor

Set Prefactor

Prefactor Value 1e+13 1/s

Calculate Prefactor

Finite Difference Method Central

Minimum Displacement 0.05 Å

IO

Save  Print

File neb.nc ... Label

OK

NEB image level parallelism enabled in ATK 2015  
Controlled by processes\_per\_image in  
ParallelParameters

# Optimize Li diffusion path



```
+-----+
| NEB image level parallelism enabled.
+-----+
| Total number of interior images: 7
| Total number of processes: 16
| Processes per image: 2
| Images calculated in parallel: 8
|
| Process group # 0 will calculate images: 1
| Process group # 1 will calculate images: 2
| Process group # 2 will calculate images: 3
| Process group # 3 will calculate images: 4
| Process group # 4 will calculate images: 5
| Process group # 5 will calculate images: 6
| Process group # 6 will calculate images: 7
| Process group # 7 will be idle!
| WARNING: Load balance problem detected.
|   The number of interior images calculated in parallel is not a
| divisor of the number of interior images. This will greatly
| reduce parallel performance. Either modify the parameter
| "processes_per_image" or the number of MPI processes.
|
| With 2 processes_per_image ideal performance will be obtained
| by using 14 MPI processes.
...
+-----+
```

- ❖ Information about parallelization, a warning will be printed when load balance problem is detected

```
+-----+
| NEB Optimization using the LBFGS optimizer
+-----+
| Iteration Step Length    Max. Force  Max. Energy Image  Max. Energy
+-----+
|      0     0.000e+00    3.062e+01          3    7.653375
|      1     1.448e-01    9.314e+00          4    4.548878
...
|      75    1.659e-02    4.404e-01          4    2.312291
|      76    7.696e-03    4.076e-02          4    2.310350
+-----+
| NEB optimization converged after 76 steps.
+-----+
```

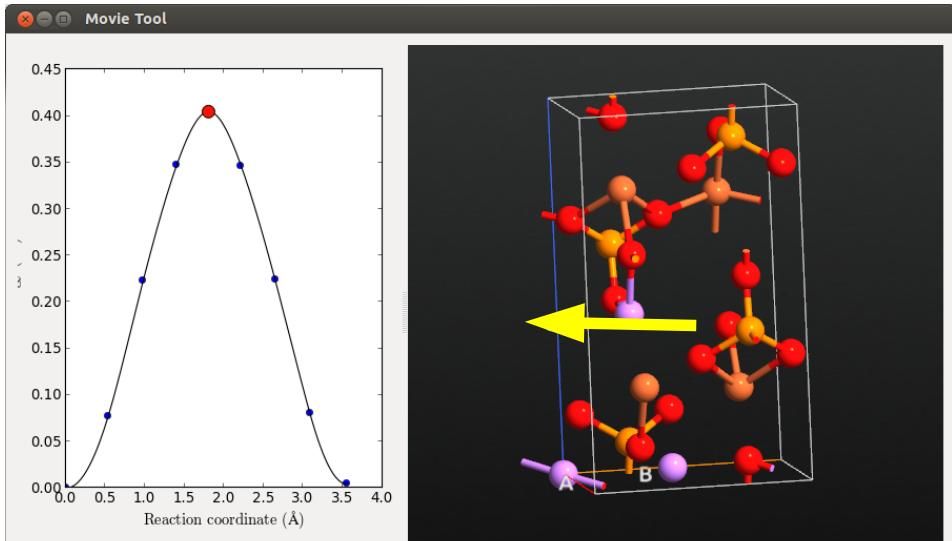
- ❖ Follow the convergence of the NEB trajectory

# Optimize Li diffusion path



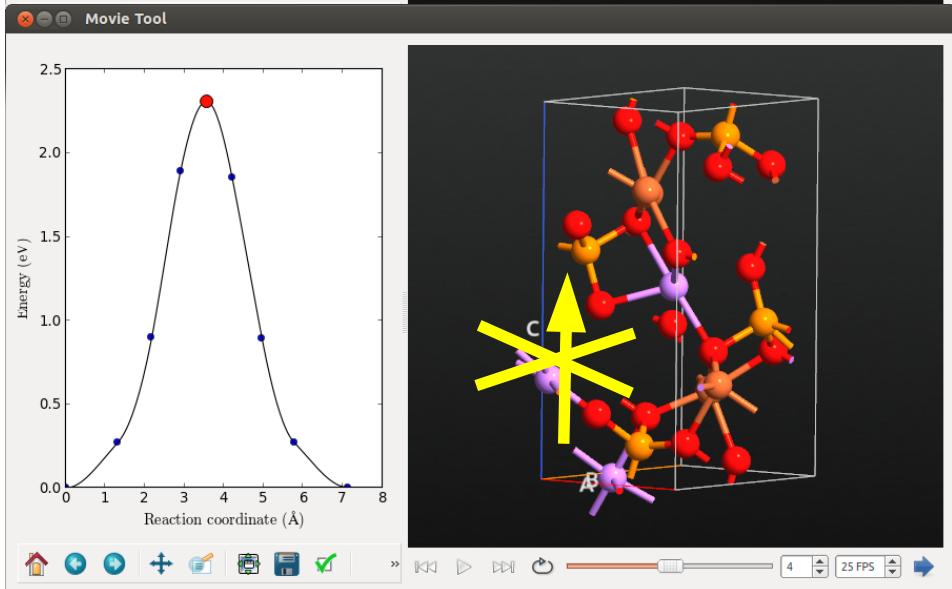
❖ Li diffusion along y axes:

Barrier 0.41 eV

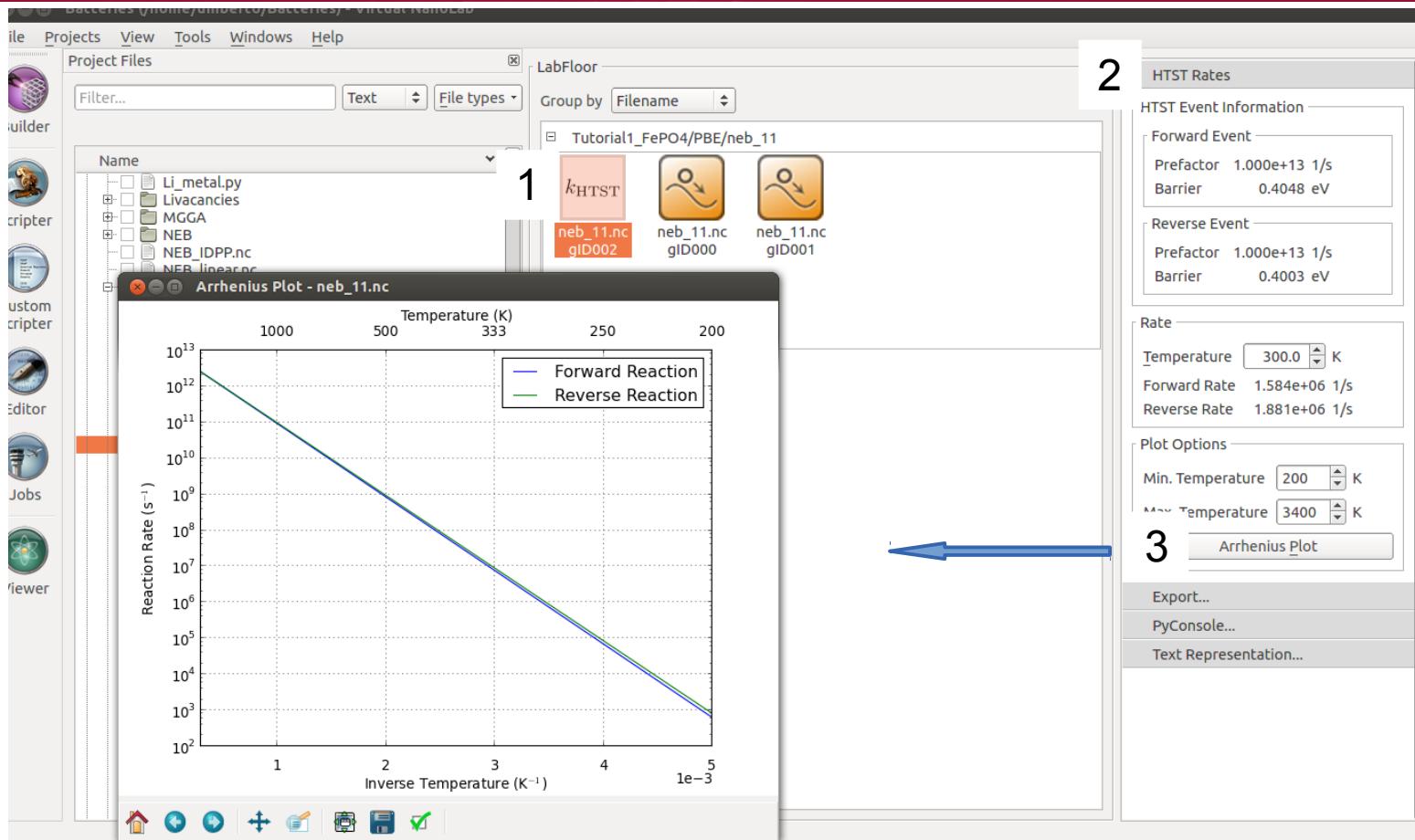


❖ Li diffusion along z axes:

Barrier 2.31 eV



# Calculate the reaction rates using harmonic transition state theory



y direction  
z direction

Barrier  
0.41 eV  
2.31 eV

$k_{\text{HTST}}$  @ 300 K  
 $1.6 \times 10^6 \text{ s}^{-1}$   
 $1.5 \times 10^{-26} \text{ s}^{-1}$

See Tutorial: *Calculating Reaction Rates using Harmonic Transition State Theory*  
[http://docs.quantumwise.com/tutorials/neb\\_htst.html](http://docs.quantumwise.com/tutorials/neb_htst.html)