Investigating Oxygen Diffusion in Solid Oxides by Quasielastic Neutron Scattering and Simulation

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Contents

- Introduction to oxide ion conductors and solid oxide fuel cells
- Introduction to my project
- Introduction to $La_2Mo_2O_9$
- QENS experiment results so far
- Molecular Dynamics Simulation results so far
- Future Work

Oxide Ion Conductors

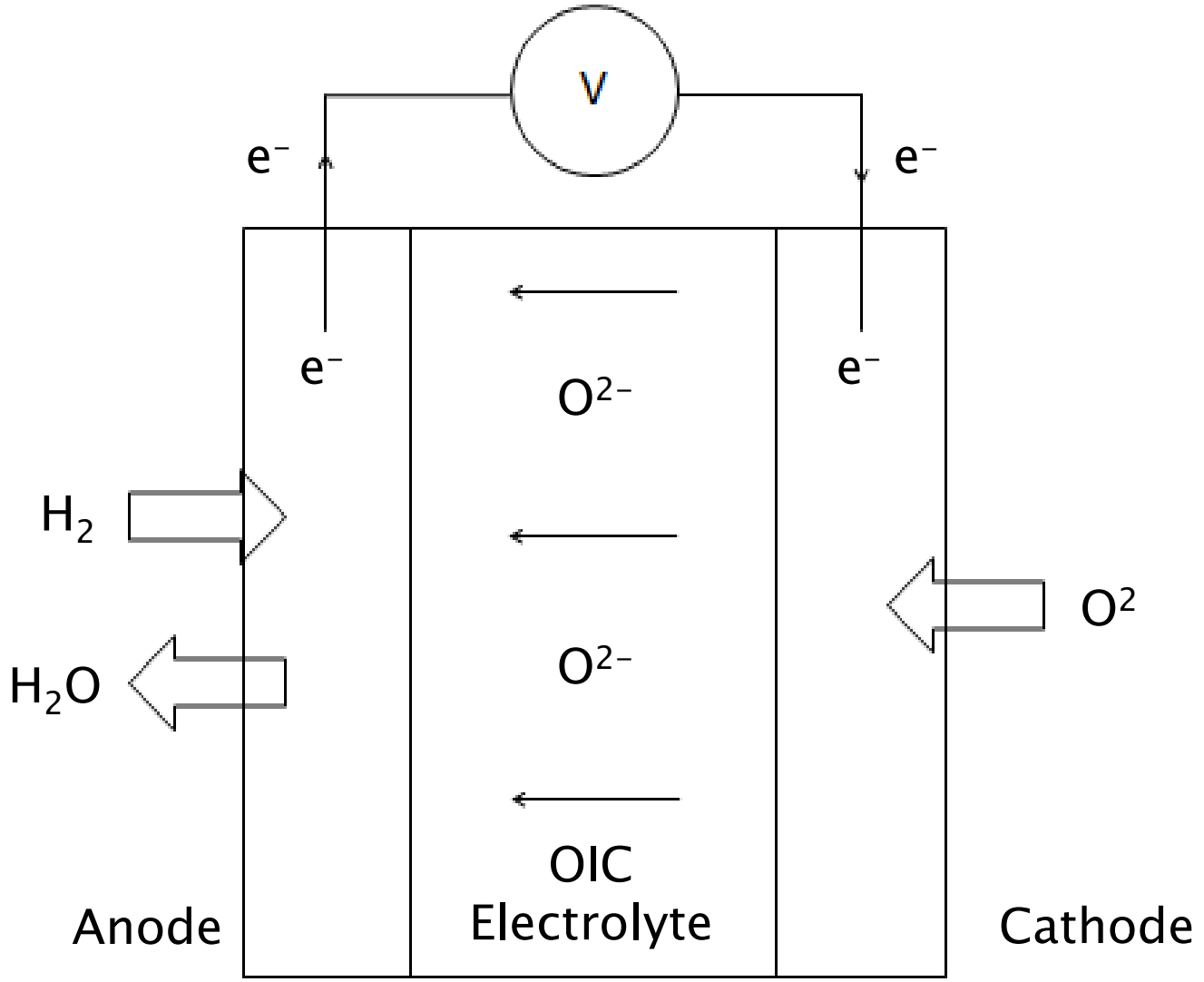
- Solid oxide materials that conduct electricity via diffusion of O^{2-} through their crystal lattice
- In order to be considered useful in applications a conductivity of 0.01 S cm^{-1} is agreed upon as a required minimum
- Current OICs require high temperatures of ~800 °C to reach this limit
- There is great research interest in developing intermediate temperature OICs which can operate in the 500-700 °C range

Solid Oxide Fuels Cells: Operation

One potential application of oxide ion conductors is in solid oxide fuel cells (SOFC)

In a SOFC the oxide ion conductor acts as the electrolyte transporting O^{2-} ions from the cathode to the anode

There the ions oxidise the fuel releasing electrons which enter an external circuit providing power



Solid Oxide Fuel Cells: Applications

- SOFCs can use H_2, natural gas or biogas as a fuel
- The reaction is very efficient with low emissions
- They can act a clean form of distributed power generation
- Can also act as a cleaner replacement for conventional backup generators
- Potential applications as engines on vehicles

Durham University and ILL Collaboration

Durham

Synthesis of materials

↓

Structure (X-rays) – Cell parameters and heavy atoms

↓

Macroscopic Dynamics (Conductivity measurements)

ILL

Structure (Neutrons) – Needed for oxygen

↓

Microscopic Dynamics (QENS and INS)
MD simulations

Understand the relationships between micro and macroscopic dynamics and structure

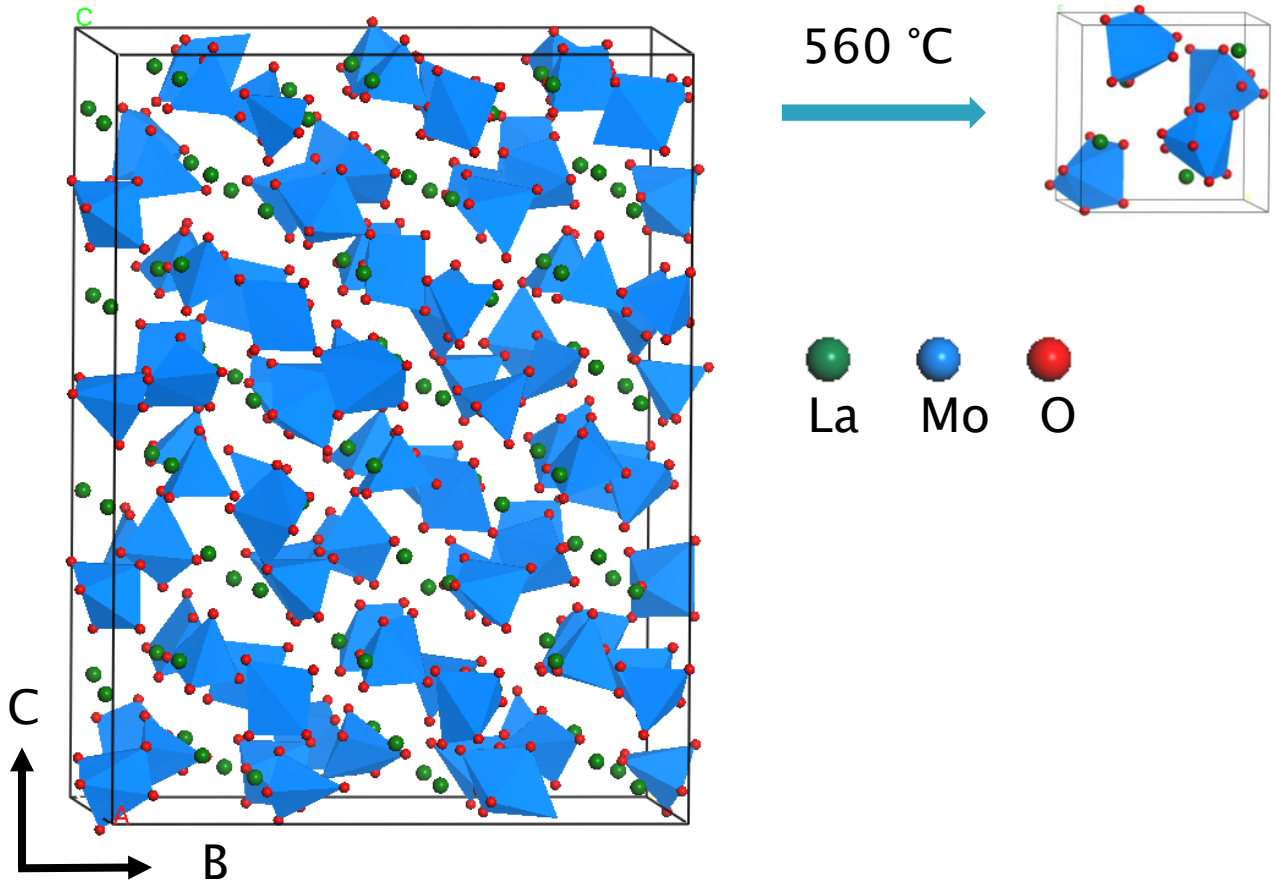
↓

Intelligent Design of New Materials

My Project

- First year at Durham University – Produced samples for neutron experiments at ILL
- Also worked on Na^+ doped $SrSiO_3$ materials and confirmed using SSNMR that although reported as OIC they were in fact Na^+ conductors
- Current work at ILL involves DFT simulations and a QENS experiment
- The main sample under study is $La_2Mo_2O_9$

$La_2Mo_2O_9$: Structure



Low temperature phase $P2_1$:
a = 14.3 Å,
b = 21.5 Å,
c = 28.6 Å
Structure made up of MoO_4, MoO_5 MoO_6 polyhedra

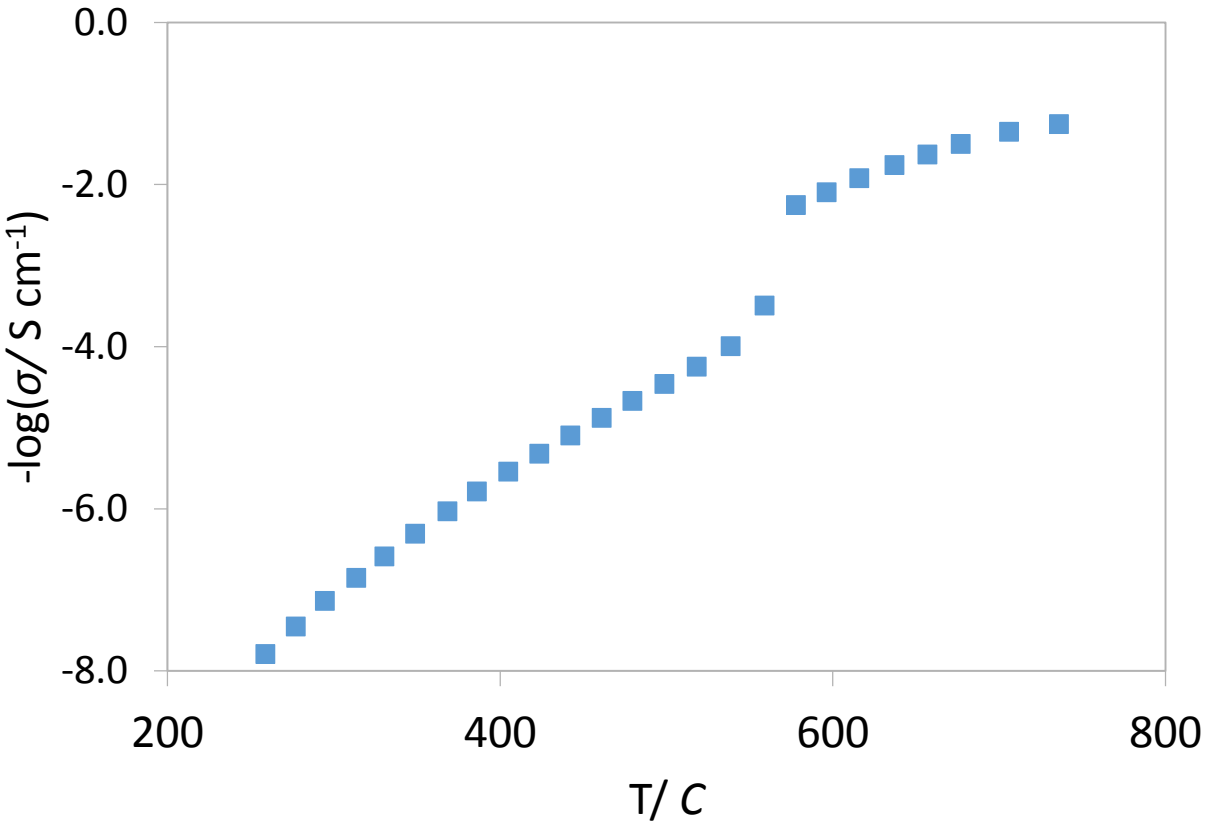
High temperature phase $P2_13$:
a = 7.2 Å
Structure made up of MoO_x polyhedra with partially occupied O sites

$La_2Mo_2O_9$: Conductivity

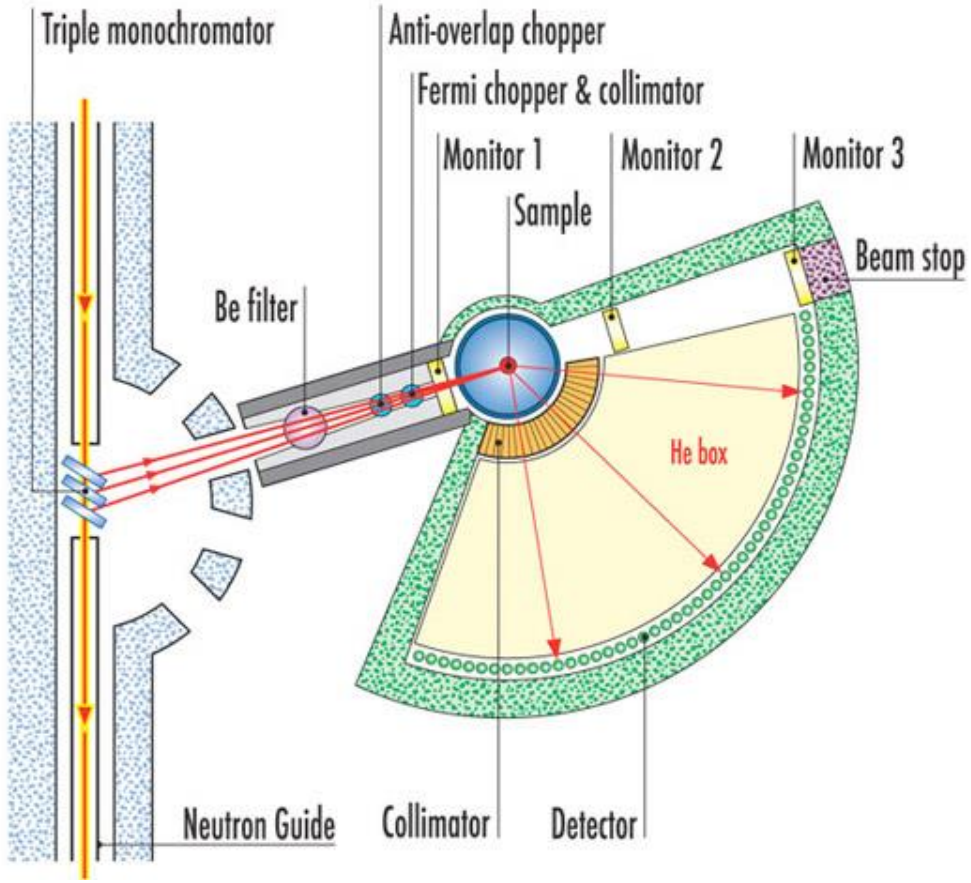
At the phase transition there is an ~10^2x increase in conductivity

Conductivity reaches 0.01 S cm^{-1} goal at ~600 °C

Very good oxide ion conductor



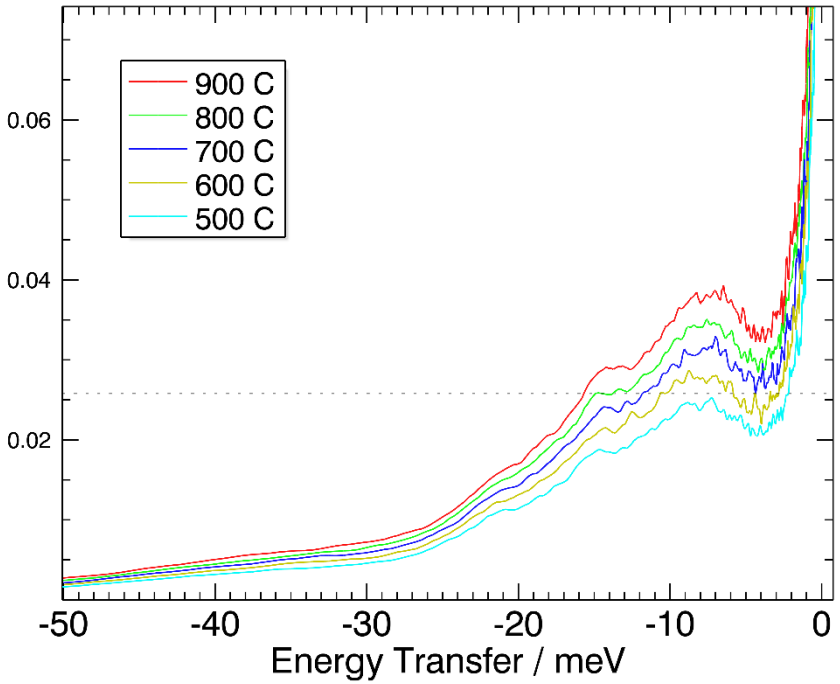
Quasielastic Neutron Scattering: IN6



Time of flight experiments carried out on IN6

No QENS signal was observed => dynamics too slow to be seen on meV / ps energy / time scale

Phonons observed => Could be related to rotations of polyhedra

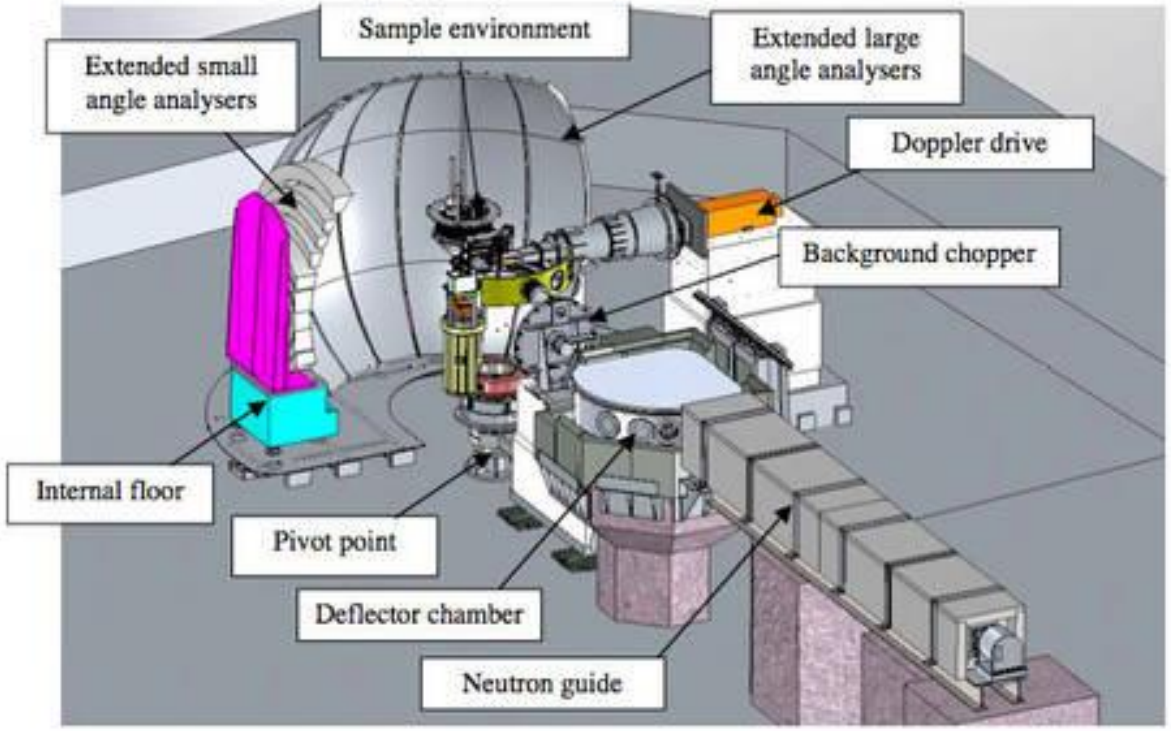


Neutron Scattering IN16b

Timescales probed by IN6 were too fast to see dynamics

Therefore experiments were carried out on IN16b

The μeV energy resolution of IN16b allows nanosecond timescales to be probed which should allow the long range dynamics in $La_2Mo_2O_9$ to be observed



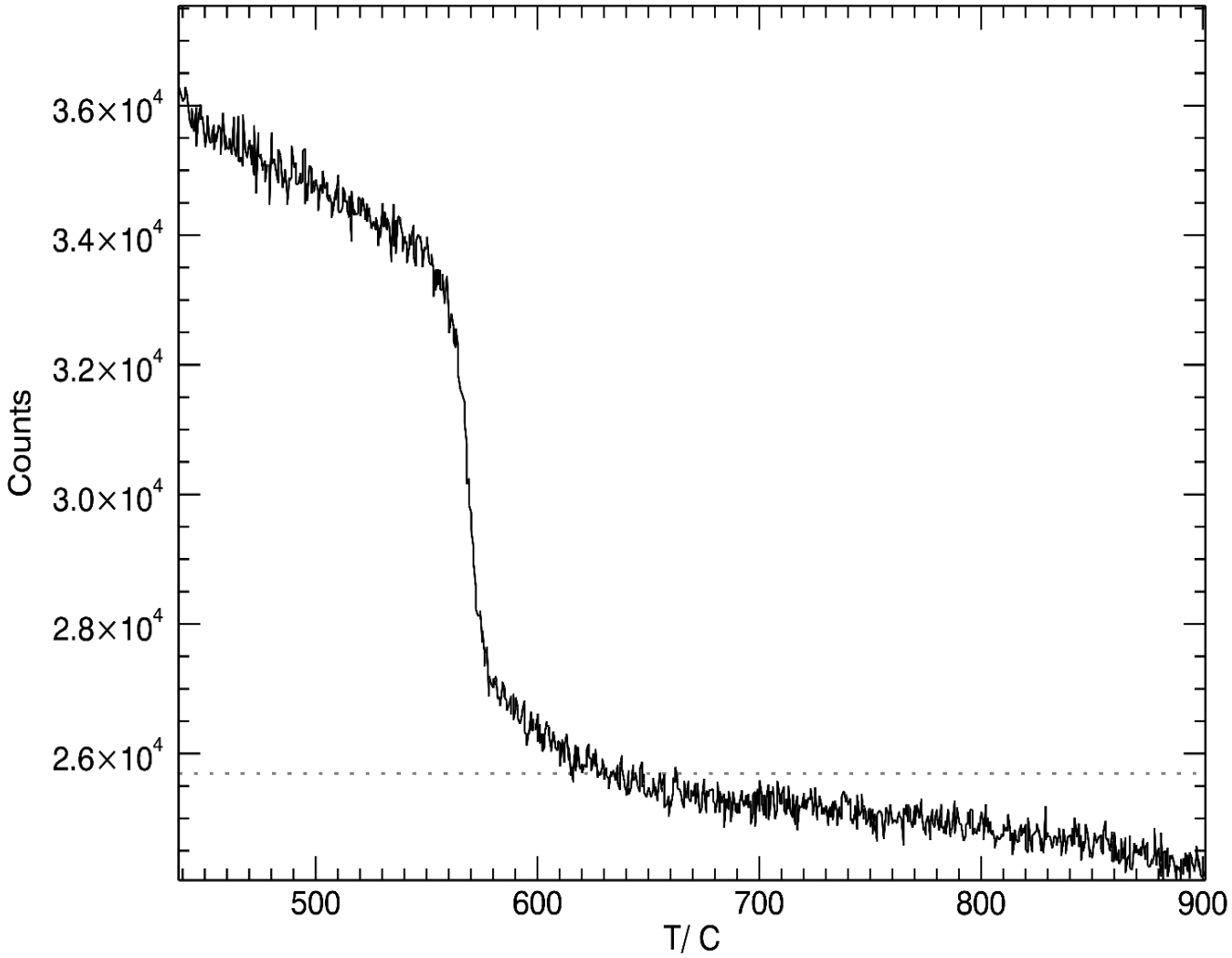
Neutron Scattering: Elastic Scan

An elastic fixed window scan was carried out over a large temperature range

A plot of elastic intensity against temperature shows a large decrease at the phase transition temperature

This indicates that the dynamics have entered the time window of the instrument

This means that these dynamics occur on the nanosecond timescale



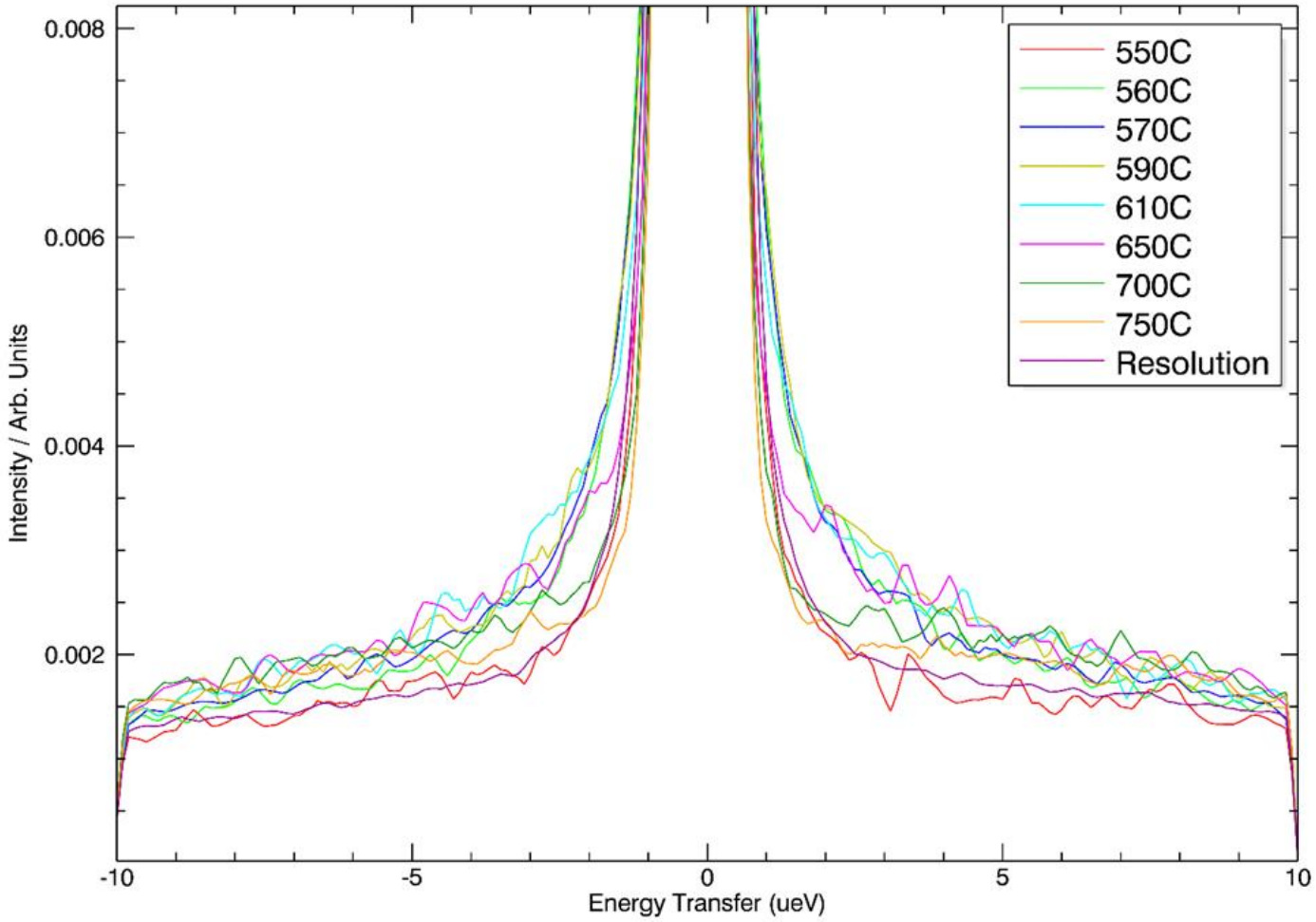
Neutron Scattering: Inelastic Scan

Scans recorded with maximum energy transfer of 10 μeV

A QENS signal is visible for temperatures at the 560° transition temperature and above

At higher temperatures the QENS signal broadens

This broadening can be used to determine the activation energy of the dynamics



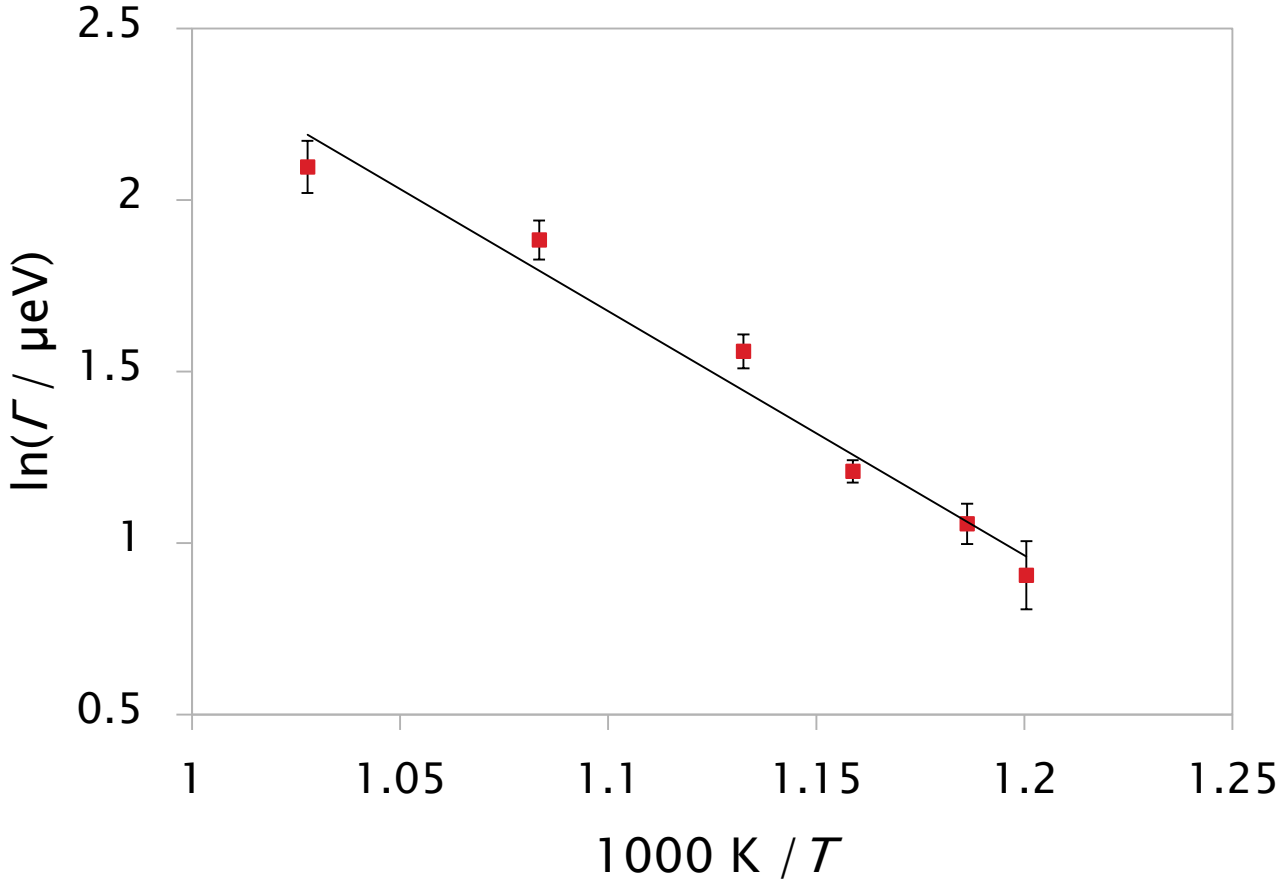
Temperature Dependence of QENS

The QENS linewidth Γ has an Arrhenius relationship with temperature

Plotting this gives an activation energy of 0.61(5) eV

This compares to a value of 0.48 eV found using impedance measurements

This helps confirm that the dynamics probed are the same in both cases



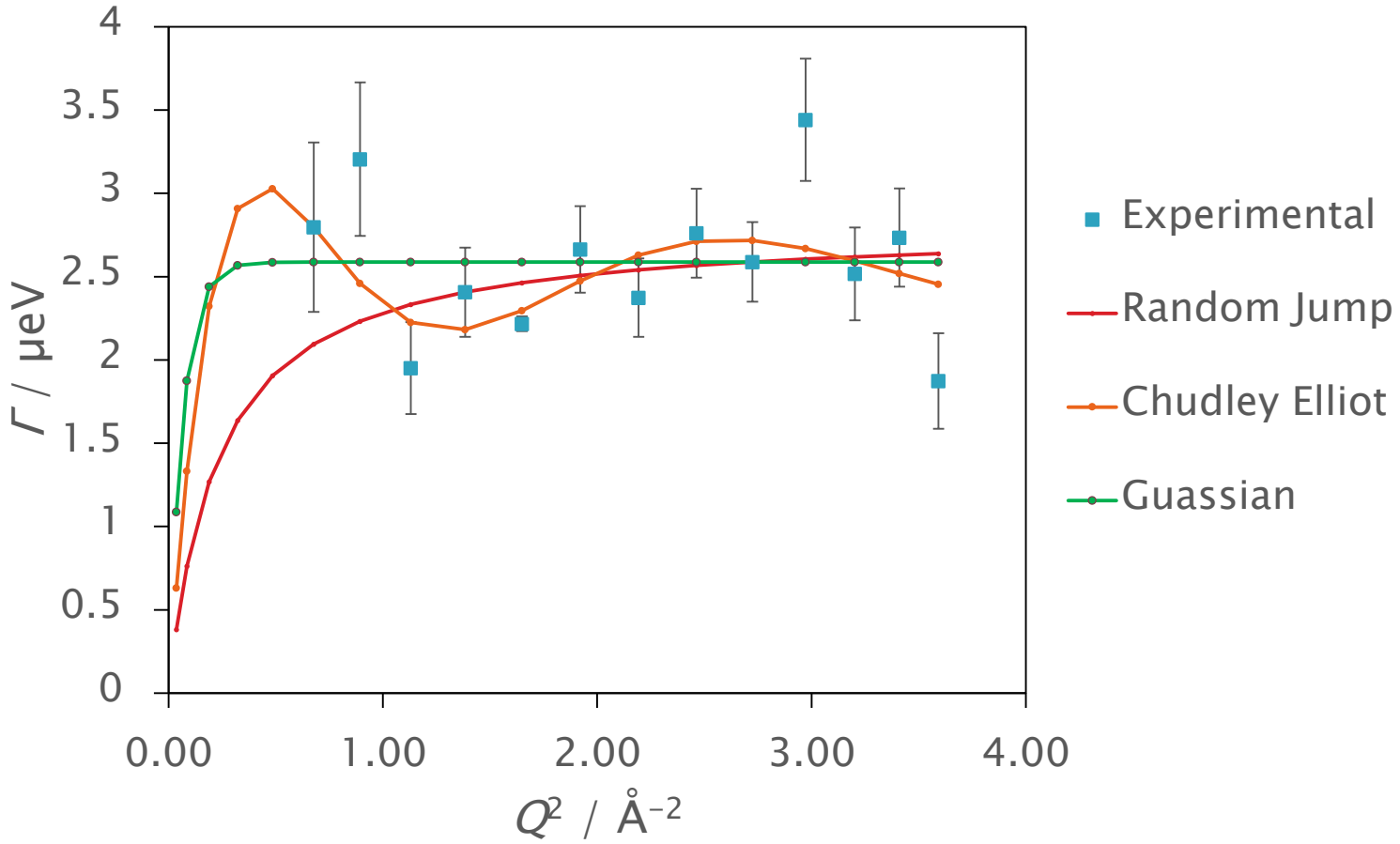
Q Dependence of Γ

The Q dependence of Γ should give information on the diffusion mechanism and provide jump lengths and timescales

Fitting of Γ vs Q^2 for 570 °C data attempted using several models

So far fits have given jump lengths of around 6 Å which is quite long

Data for low Q values needed to get better fits



Ab intio Molecular Dynamics Simulations

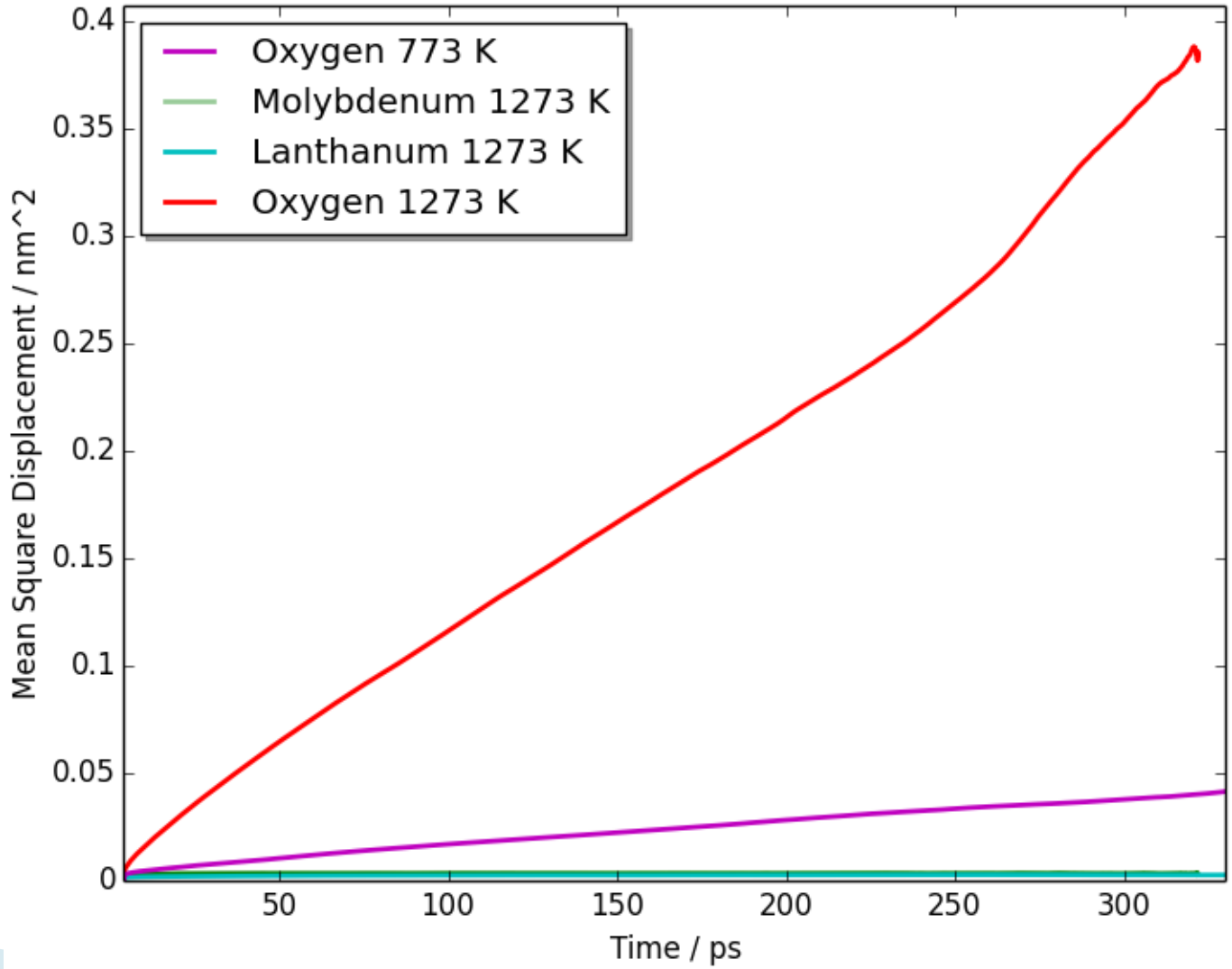
- Density Functional Theory molecular dynamics simulations carried using VASP
- Two temperatures looked at: 773 K and 1273 K
- Simulate positions and velocities in steps of 2 fs
- So far have calculated around 350 ps of simulation time
- These calculations allow the diffusion processes occurring to be visualised in several ways

AIMD: Mean Square Displacement

The figure shows the mean square displacement of specific groups of atoms during the simulation

Simulations show that the metal cations in $La_2Mo_2O_9$ undergo very little motion

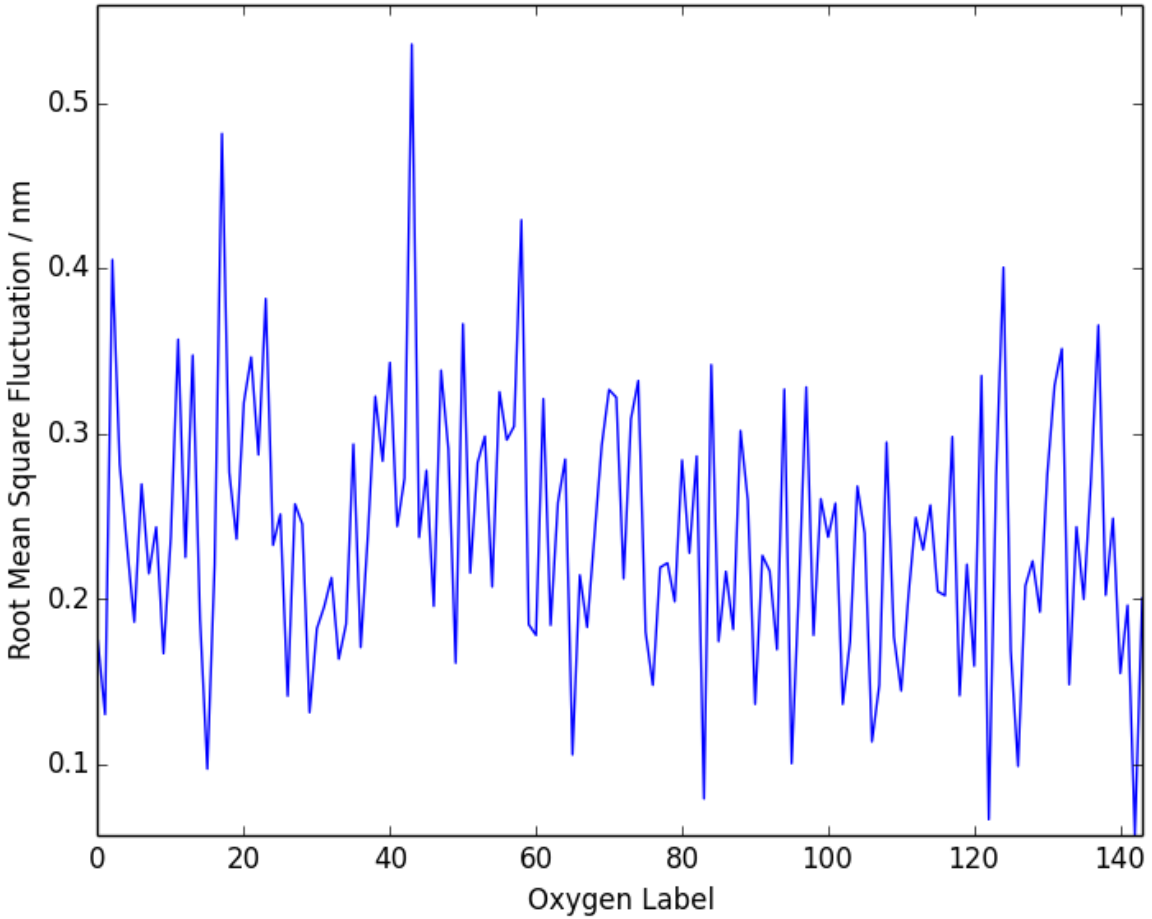
Oxygen atoms move a significant amount ~6 Å on average



AIMD: Root Mean Square Fluctuation

The plot of RMSF shows the difference between the initial and final positions of individual atoms during the simulation

This can be used to identify O atoms that have moved a particularly long distance



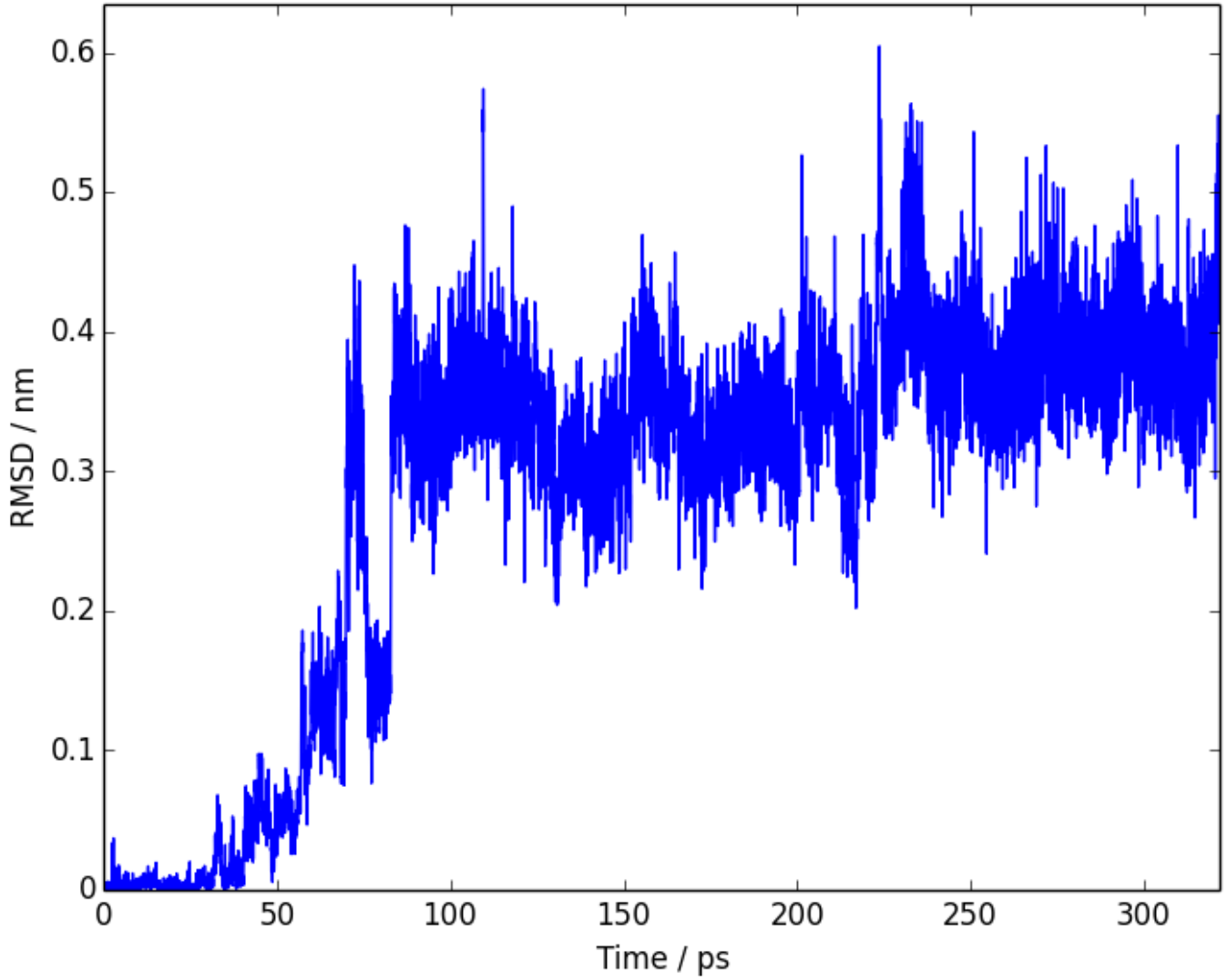
AIMD: Root Mean Square Deviation

The figure shows the RMSD of an individual oxygen atom during the simulation

The can use to determine the time during the simulation at which a diffusion event occurs and how far the O moved

Can separate vibrations and polyhedra rotations from long range translations

This atoms jumps a distance of 2 Å at 80 ps. The corresponds to a jump between Mo polyhedra

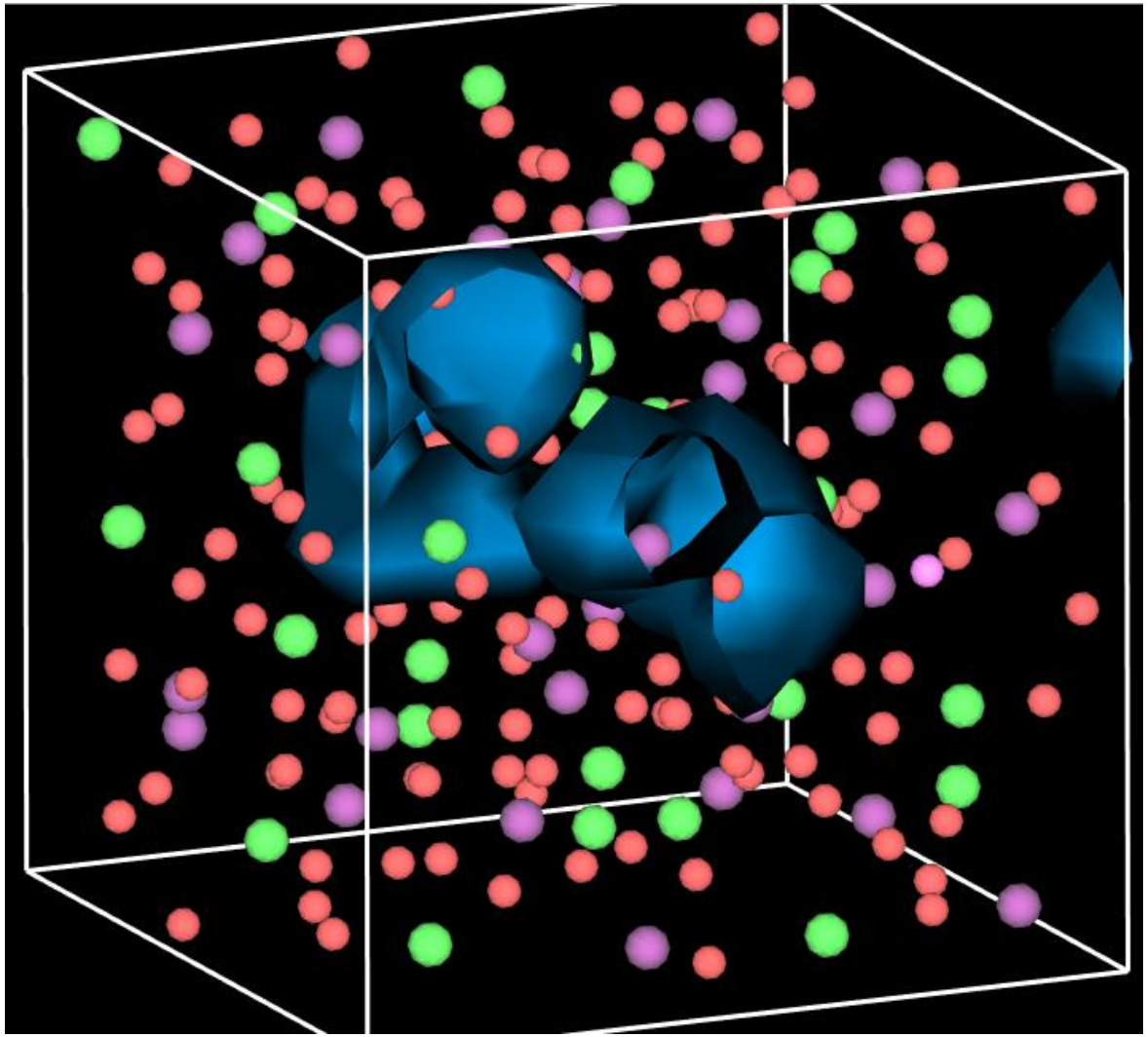


AIMD: Molecular Trace

The figure shows the area visited by a single oxygen atom during the simulation

The atom has undergone several jumps to new polyhedra

This allows the diffusion pathways to be visualised



Future Work

- Conduct a detailed analysis of $La_2Mo_2O_9$ data including QENS results and DFT MD simulations
- Carry out simulations and QENS experiments on other materials eg. $BiVO_x$ and $La_{10}Ge_6O_{27}$
- Develop pair potentials to allow classical MD simulations to be carried out in order to reach simulation times on the order of nanoseconds