Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information for "The influence of the local structure on proton transport in a solid oxide proton conductor $La_{0.8}Ba_{1.2}GaO_{3.9}$"

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KEYWORDS: Disordered oxides, proton transport, inelastic neutron scattering, density functional theory, ab initio molecular dynamics.

METHODS

1.1 Sample Preparation

The LBGO sample preparation and hydration are explained elsewhere [1].

1.2 Inelastic Neutron Scattering

Neutron vibrational spectra of the dehydrated (dry) and hydrated (wet) LBGO samples were measured using the VISION (BL-16B) instrument at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL) [2]. Approximately 10 g of each sample was loaded into vanadium sample holders. INS spectra were collected at 5 K for close to 8 hours. The empty vanadium sample holder was also measured and the background was subtracted from the total INS spectra.

1.3 Ab-initio modeling

Density function theory (DFT) calculations were performed using CASTEP for phonon analysis [3]. The starting structure (Fig. S1a) was a $LaBaGaO_4$ unit cell containing 112 atoms (16 La, 16 Ba, 16 Ga, 64 O), with lattice constants (a=10.0665 Å, b=14.6834 Å, c=11.8866 Å) [1]. The dry sample with a composition of $La_{1-x}Ba_{1+x}GaO_{4-x/2}$ (x=0.25) was created by randomly removing two oxygen atoms, and replacing four La atoms with four Ba atoms (Fig. S1b). The wet sample with a composition of $La_{1-x}Ba_{1+x}GaO_{4-x/2}(H_2O)_y$ (x=0.25, y=0.0625) was then produced by refilling one of the O vacancies, and adding two H atoms to form O-H bonds with O at various non-equivalent locations (Fig. S1c). All initial configurations were relaxed before further analysis. The Generalized Gradient Approximation (GGA), as implemented by Perdew-Burke-Ernzerhof [4], was used to describe the exchange-correlation interactions. Ultrasoft pseudopotentials [5] were

employed to account for the effects of core electrons. The force constants were obtained using the finite displacement method. Both the electronic structure calculation and the phonon calculation were performed on the gamma-point only (a 2×2×2 Monkhorst-Pack k-mesh was also tested and the results are consistent). The aClimax software [6] was used to convert the DFT calculated phonon modes to the simulated INS spectra.

The ab initio molecular dynamics (AIMD) simulations were performed using CASTEP [3] and VASP [7,8]. The main results were obtained using the generalized gradient approximation (GGA) according to Perdew, Burke, and Ernzerhof [4] and the projector augmented-wave method [9,10] at VASP. An NVT ensemble was simulated at 800K using a Nose-Hoover thermostat with a time step of 0.5 fs. Simulations were conducted to study the proton migration pathways for two different systems namely the (i) Ba-rich scenario, and (ii) La-rich scenario. The system was first equilibrated for ~2 ps, and then run for another ~5 ps to collect the atomic trajectories. The data provided in the manuscript corresponds to the simulation after equilibration. All AIMD simulations employed a single **k**-point, the Γ – point. Atomic relaxation calculations to analyze the local structure employed a 2x2x2 **k**-point mesh and the residual forces were minimized to lower than 0.01eV/ Å.

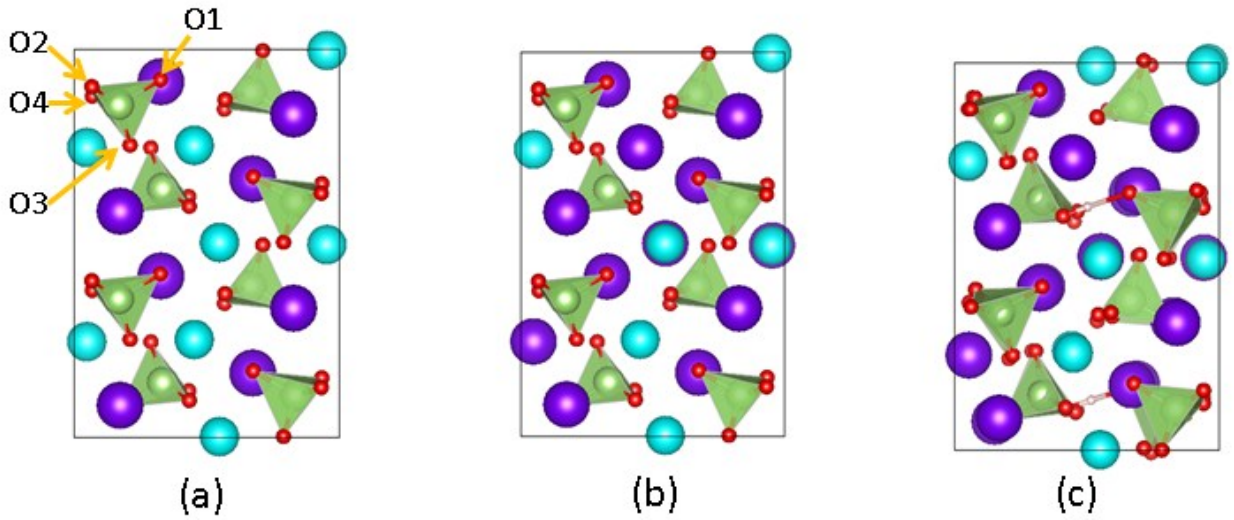

Figure S1. *Structure models for ab initio simulations. (a) Stoichiometric configuration of* $LaBaGaO_4$ *(La: cyan, Ba: purple, Ga: green, O: red); the four non-equivalent O sites are labelled as O1, O2, O3, and O4. (b)* $La_{1-x}Ba_{1+x}GaO_{4-x/2}$ *with x=0.25, for the dry sample; additional Ba atoms and oxygen vacancies are present in the unit cell relative to the parent x=0. (c)* $La_{1-x}Ba_{1+x}GaO_{4-x/2}(H_2O)_y$ *with x=0.25, y=0.0625, for the wet sample; the coordination of* OH^- *is shown.*

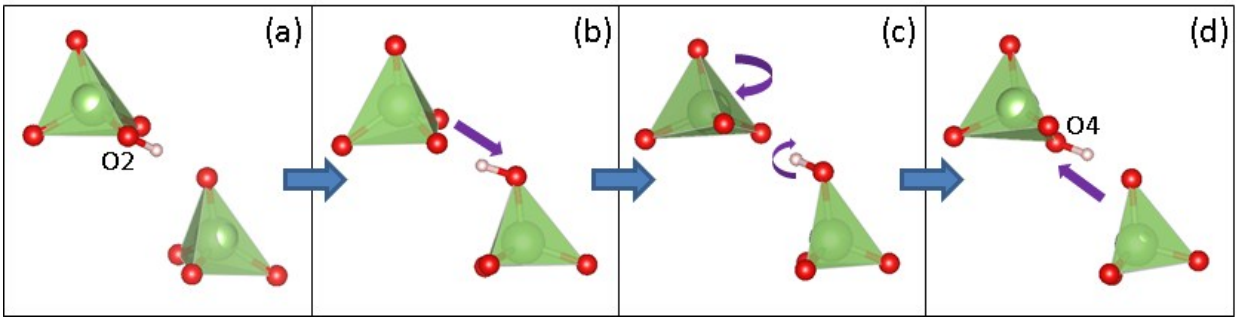

Figure S2. *Inter- and intra-tetrahedron hopping as revealed by CASTEP AIMD simulation. From left to right, the proton first goes from O2 site to the neighboring tetrahedron, then the two tetrahedra reorient relative to each other, and in this case the proton hops back to the original tetrahedron, to the O4 site. In this process, the intra-tetrahedron hopping is realized by a two-step inter-tetrahedron hopping, which has a much lower energy barrier [1]. The proton can also hop to a third tetrahedron, as illustrated in Fig. 2(a), in which the long-range diffusion is realized through such a relay process.*

2. AIMD Results

2.1 Ba-rich Scenario (H1)

The AIMD analysis data corresponding to the Ba-rich scenario (H1) is provided in Figures S2-S4.

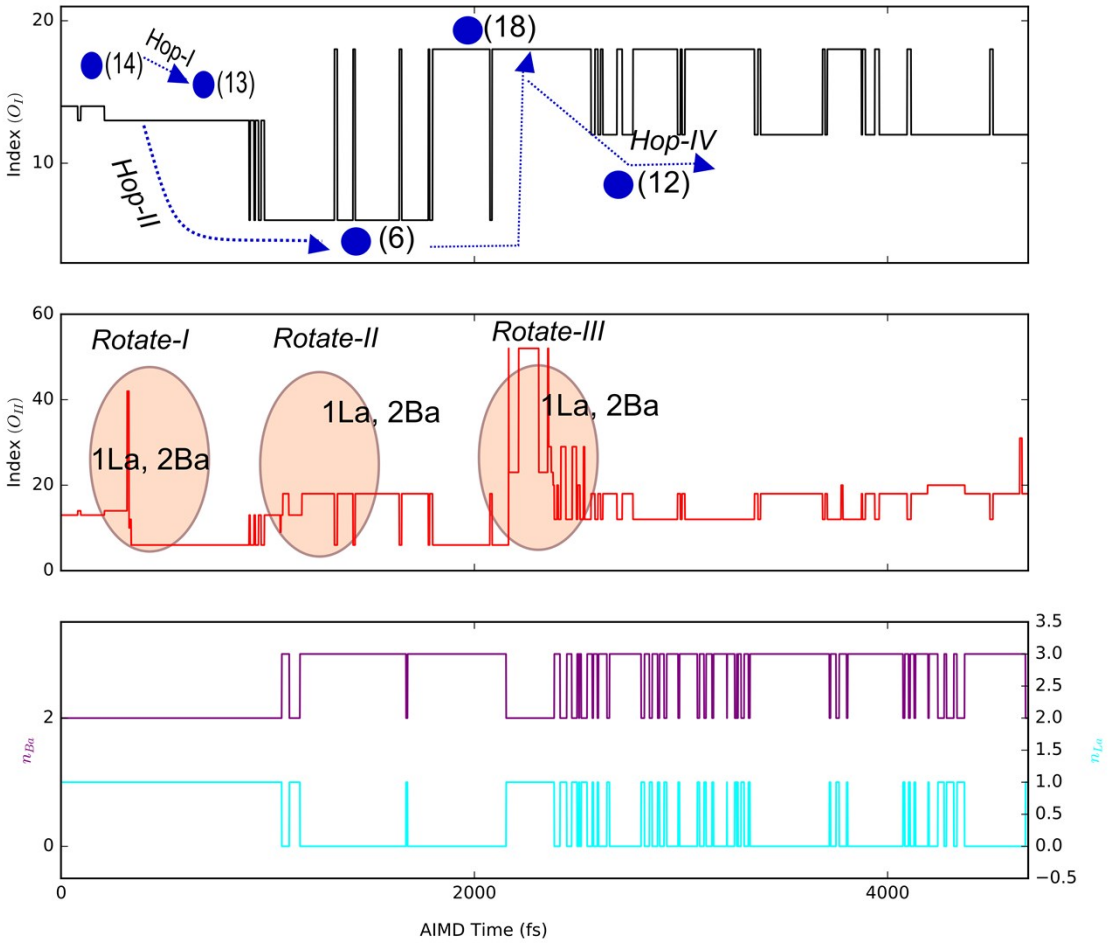

Figure S3. *Analysis of oxygen first* (O_I)*, second* (O_{II})*nearest neighbors and the local Ba (*^{n}*Ba-purple) and La (*^{n}*La - cyan) concentrations near H as a function of AIMD time in Ba rich scenario (H1). As observed from the figure, the local environment near the H remains Ba rich throughout the simulation. The H undergoes 3 rotations and 4 hops demonstrating long range diffusion.*

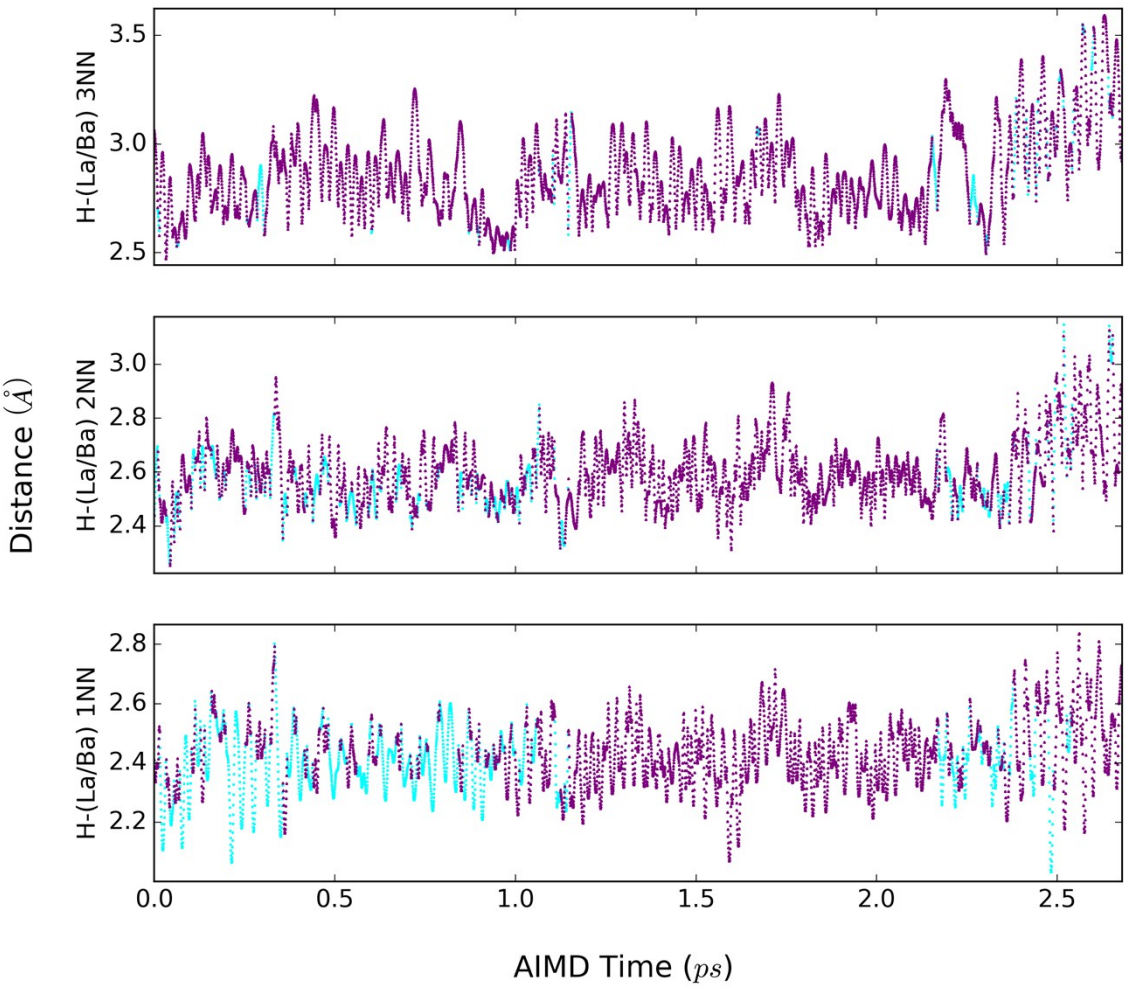

Figure S4. *Analysis of the H distance from the three nearest La/Ba atoms (called 1NN, 2NN and 3NN) in the Ba rich scenario (H1) as a function of time. The Ba and La atoms are color coded with purple and cyan respectively.*

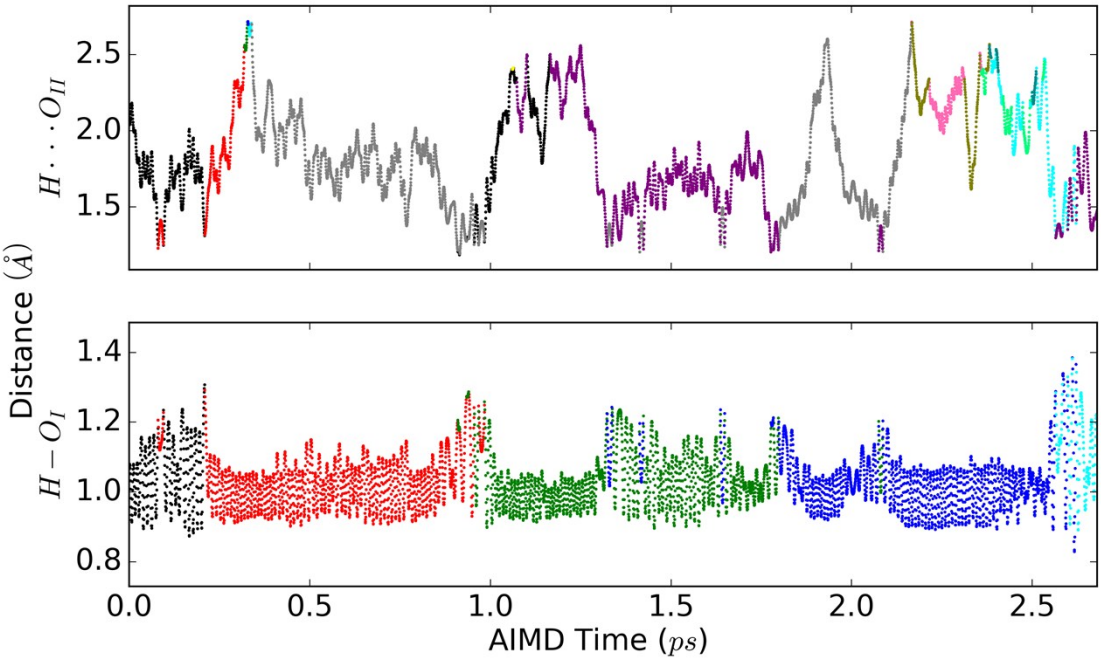

Figure S5. *Analysis of the H distance from the oxygen first (O_I) and second (O_{II}) nearest neighbors for Ba rich scenario (H1) as a function of time. The various colors represent the different oxygen atoms that are in the H neighborhood during the course of the AIMD simulation.*

2.2 La Rich Scenario (H2)

The AIMD analysis data corresponding to the La rich scenario (H2) is provided in Figures S5-S7.

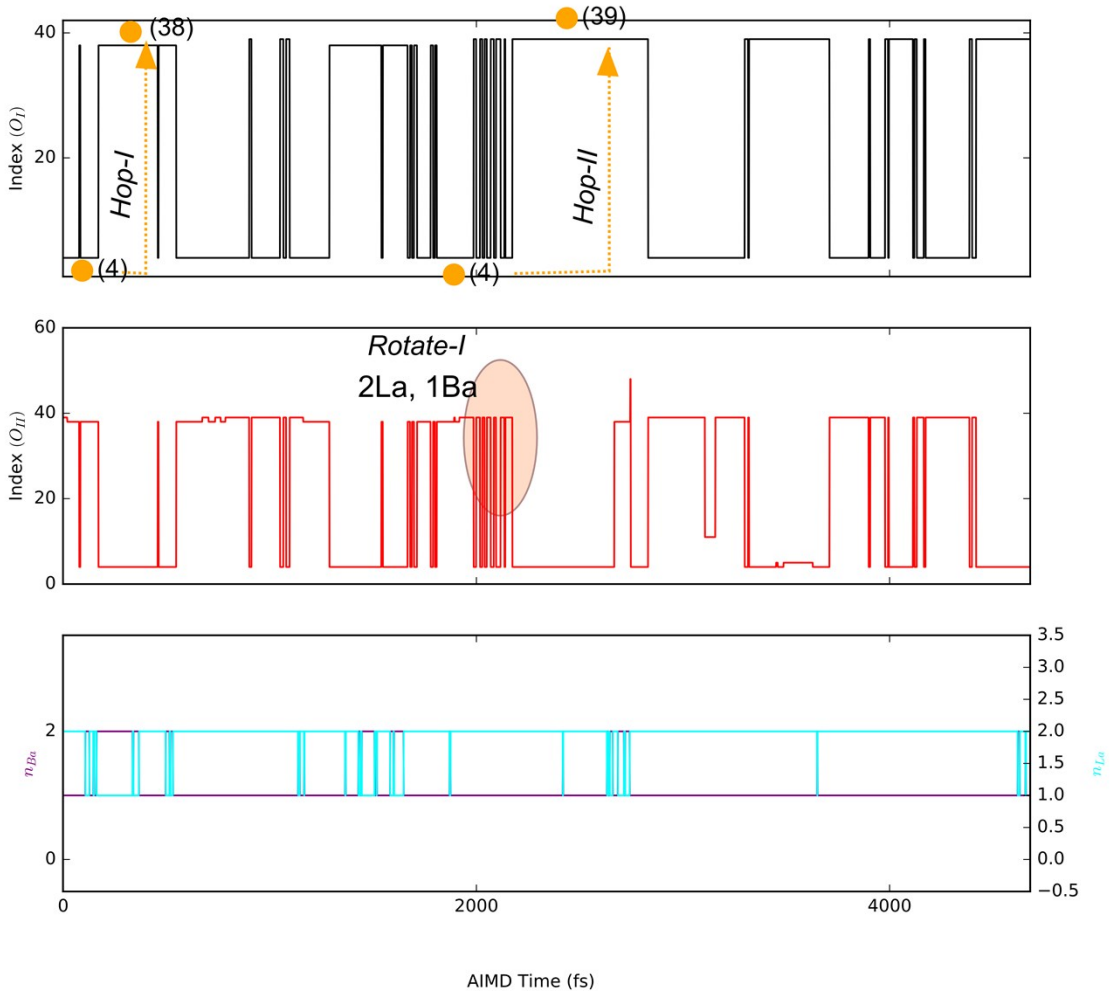

***Figure S6**. Analysis of oxygen first (O_I), second (O_{II}) nearest neighbors and the local Ba (n_{Ba}- purple) and La (n_{La} - cyan) concentrations near H as a function of AIMD time in La rich scenario (H2). As observed from the figure, the local environment near the H remains La rich for most of the simulation time. The H undergoes one rotation and two hops indicating suppression of H rotational modes and in turn long range transport.*

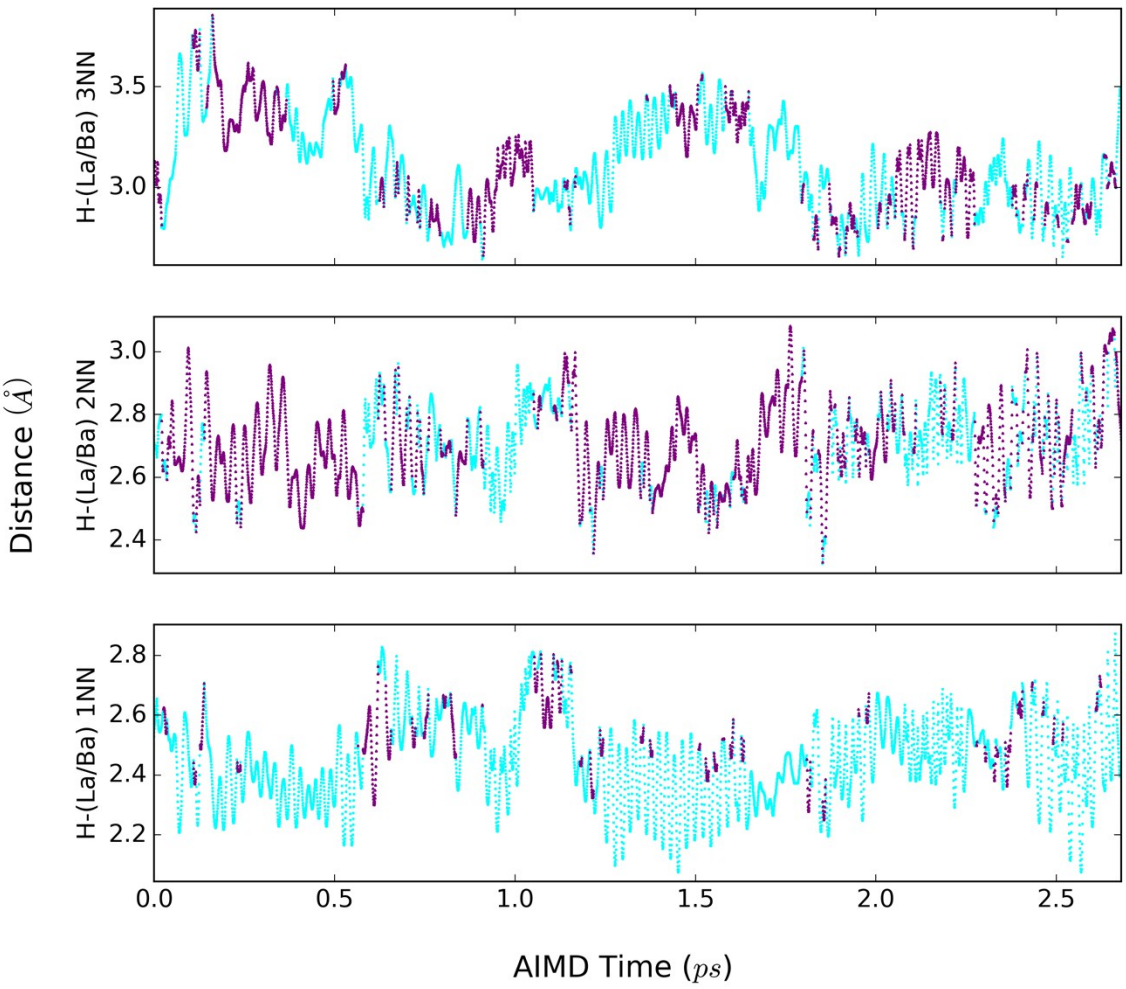

Figure S7. *Analysis of the H distance from the three nearest La/Ba atoms (called 1NN, 2NN and 3NN) in the La rich scenario (H2) as a function of time. The Ba and La atoms are color coded with purple and cyan respectively.*

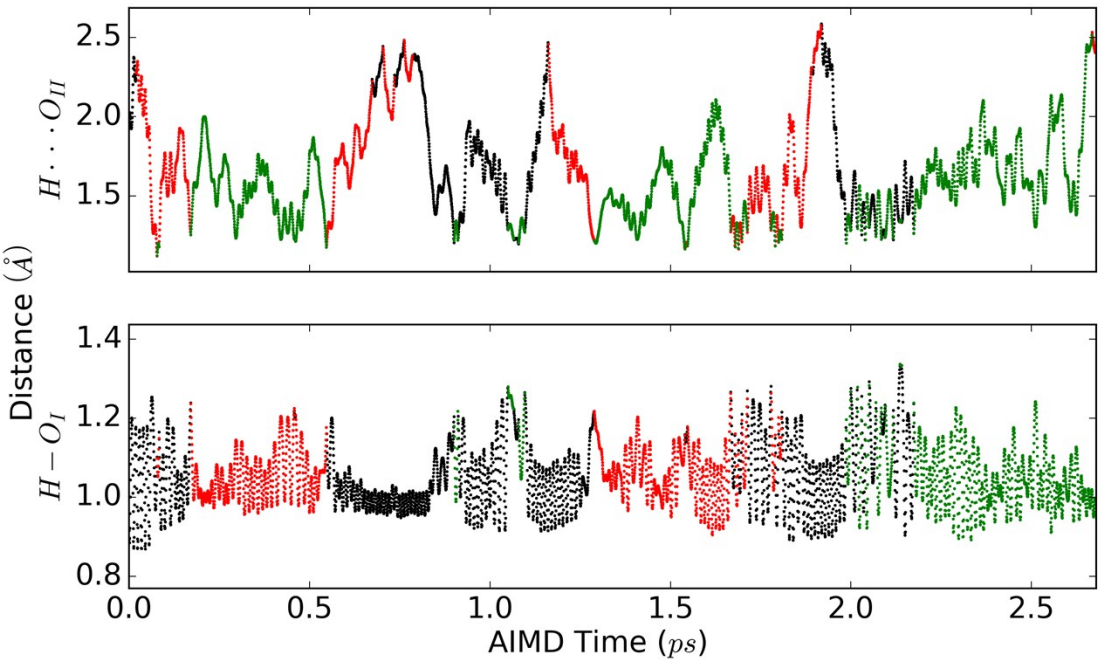

Figure S8. *Analysis of the H distance from the oxygen first (O_I) and second (O_{II}) nearest neighbors for La rich scenario (H2) as a function of time. The various colors represent the different oxygen atoms that are in the H neighborhood during the course of the AIMD simulation.*

Reference:

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