Coupled Cation–Anion Dynamics Enhances Cation Mobility in Room-Temperature Superionic Solid-State Electrolytes

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Supporting Information

ABSTRACT: Single-ion conducting solid electrolytes are gaining tremendous attention as essential materials for solid-state batteries, but a comprehensive understanding of the factors that dictate high ion mobility remains elusive. Here, for the first time, we use a combination of the Maximum Entropy Method analysis of room-temperature neutron powder diffraction data, ab initio molecular dynamics, and joint-time correlation analysis to demonstrate that the dynamic response of the anion framework plays a significant role in the new class of fast ion conductors, Na11Sn2PnX12 (Pn = P, Sb; X = S, Se). Facile [PX4]3– anion rotation exists in superionic Na11Sn1PS12 and Na11Sn1PSe12, but greatly hindered [SbX4]3– rotational dynamics are observed in their less conductive analogue, Na11Sn2SbS12. Along with introducing dynamic frustration in the energy landscape, the fluctuation caused by [PX4]3– anion rotation is firmly proved to couple to and facilitate long-range cation mobility, by transiently widening the bottlenecks for Na+ ion diffusion. The combined analysis described here resolves the role of the long-debated paddle-wheel mechanism, and is the first direct evidence that anion rotation significantly enhances cation migration in rotor phases. The joint-time correlation analysis developed in our work can be broadly applied to analyze coupled cation–anion interplay where traditional transition state theory does not apply. These findings deliver important insights into the fundamentals of ion transport in solid electrolytes. Invoking anion rotational dynamics provides a vital strategy to enhance cation conductivity and serves as an additional and universal design principle for fast ion conductors.

■ INTRODUCTION

Fast ion conductors (FICs) are indispensable materials for ubiquitous electrochemical devices such as batteries,1–4 fuel cells,5–7 and sensors.8 The discovery and design of advanced conductive materials largely hinges on understanding the underlying intrinsic nature that dictates their behavior.8,9 In lithium and sodium thiophosphates, which are widely considered to be among the most practical solid electrolytes for solid-state batteries,5,13 much effort has been devoted to developing sophisticated design principles for superionic behavior based on anion packing,14 lattice polarizability,15 activation energy prefactors16,17 cation vacancy concentration,18,19 framework structure,20 and softnesses15,21 among others. However, these and related studies, both experimental and computational, have mostly centered on the relationship of the static structure to the ion-conductive properties,14,22–32 while ab initio molecular dynamics (AIMD) simulations have shown that the fluctuating chemical environment from the polarizable bromide anions in Li3InBr6 contributes to its superionic behavior.33

Although the above factors are very important, by comparison limited attention has been paid to interactions of the cation with the possible dynamics of the anion framework, despite the rotation of anionic tetrahedral moieties (SO42– or PO43–) in high temperature “rotor phases” being proposed to aid in ionic conduction more than 25 years ago. This mechanism was called the paddle-wheel effect.34 It was implicated in seminal studies by Jansen in 1991 on fast ion conduction for a high temperature plastic phase of sodium orthophosphate, Na3PO4.35 Studies of fast ion transport at 850 K in the quintessential plastic crystal, α-Li2SO4, were also proposed to be due to coupling of Li+ cations to the reorientational motion of the [SO4]2– anions.36 Debates...
ensued on whether ion conduction in sulfates was paddle-wheel or percolation. Later, quasi-elastic neutron scattering (QENS) studies confirmed that the PO$_4^{3-}$ anions in Na$_3$PO$_4$ undergo rapid rotational reorientation at 600 K. In solid acids such as CsH$_2$PO$_4$ and CsHSO$_4$ in 1992 it was also reported that proton disordering and fast reorientation modes frequently set on together at high temperature “superprotonic” phase transitions. More recently, partly due to vast improvements in computational capabilities, the possible correlation between ionic conductivity and the rotational freedom of polyanions has received renewed interest. Of late, QENS experiments coupled with AIMD studies have attempted to provide evidence of this effect at lower temperatures (380–530 K) for large closoborane anions CB$_{11}$H$_{12}^-$, demonstrating that anion reorientations lead to fluctuations in the local potential that enhances cation mobility. In the newly discovered superionic antiperovskite, Na$_3$OBH$_4$, the large anisotropic temperature factors of H(D) in diffusion data were implicated as reflecting rotation of the BH$_4^-$ unit, and, coupled with constrained CI-NEB calculations, intriguingly suggest that borohydride rotation can facilitate cation conduction.

While the above studies suggest a connection between ionic conductivity and rotational freedom of the anions, direct evidence for causation (as opposed to association) has been elusive. Exploring complex polyanion-based FICs that have facile anion rotation/reorientation dynamics at room temperature, and verifying the effect of the anion dynamics on cation mobility are of significant importance. The above consid-

Figure 1. Diffusion pathways, jump ratio, diffusion mechanism, and activation energy. (a) The structure of [Na$_{11}$Sn$_2$]PS$_{12}$ determined from single-crystal diffraction in our previous work; ordered SnS$_4$ (cobalt blue) and PS$_4$ (teal) tetrahedra form the 3D framework; Na$^+$-ions fill in the octahedral sites and the formed NaS$_6$ cages are edge-sharing with the PS$_4$/SnS$_4$ tetrahedra; the Na(1)/Na(2)/Na(6) sites (sites with fractional occupancies) are represented by rose ellipsoids and Na(3)/Na(4)/Na(5) sites (almost fully occupied sites) are denoted by red ellipsoids. (b) View of the channels for Na$^+$-ions conduction along the c axis. (c) View of chains that run along the a axis and b axis, as well as the trigonal face bottleneck for Na$^+$-ion transport. (d) Na$^+$-ion jump events extracted from AIMD simulation at 1050 K; note that 1 → 3 represents the jump events from Na(1) to Na(3) site, and so forth. (f) The snapshot for the correlated migration at 15.5–16.5 ps, with the direction of the Na$^+$-ion motion indicated by the arrows. The unit cell contains 88 sodium ions, which are numbered consecutively (for example, Na1–28 refer to Na(1) in the initial configuration; see Methods for details). Na$^+$-ions diffuse in a cooperative manner. Specifically, as Na32 migrates toward a vacancy at the 32g (Na(1)) site, then Na1, Na26, Na53, and Na71 jump toward Na32 along the c axis at the same time. Simultaneously, Na38 and Na87 jump along the a axis toward Na71. The offloading role of the Na(6) site is also evidenced in the right panel; as indicated, Na(2) migrates to Na(1) through the Na(6) site, leaving a vacancy at its original site. (g) Calculated diffusivities at different temperatures. The solid lines are the linear fit to the data (green, pink, and blue circles), yielding an activation energy of 0.18, 0.19, and 0.25 eV for [Na$_{11}$Sn$_2$]PSe$_{12}$, [Na$_{11}$Sn$_2$]PS$_{12}$, and [Na$_{11}$Sn$_2$]SbS$_{12}$, respectively.
erations prompted us to examine the possible role of anion dynamics in alkali thiophosphate and related FICs. These materials are considered to be among those foremost in the choice of solid electrolytes for solid-state batteries due to their combination of high ductility, processability, and conductivity. Although these materials are reported to be subject to probable oxidation at high potential and to reduction at a metallic Li/Na anode, research interest in these materials has increased significantly, because a coating or interface strategy can be applied to resolve or alleviate these reactivity issues. We probed three new structurally analogous fast Na+-ion conductors, [Na\(_{11}\)Sn\(_2\)]PS\(_{12}\), [Na\(_{11}\)Sn\(_2\)]PSe\(_{12}\), and [Na\(_{11}\)Sn\(_2\)]SbS\(_{12}\), that we and others recently reported. While the [Na\(_{11}\)Sn\(_2\)]PS\(_{12}\) and [Na\(_{11}\)Sn\(_2\)]PSe\(_{12}\) materials exhibit high ionic conductivities at room temperature of 1.4−3.7 mS cm\(^{-1}\) and 3.0 mS cm\(^{-1}\) respectively, the conductivity of [Na\(_{11}\)Sn\(_2\)]SbS\(_{12}\) is almost an order of magnitude lower (0.5−0.6 mS cm\(^{-1}\)), despite possessing a larger unit cell volume. Importantly, the almost identical frameworks of these three materials allow us to isolate the dynamics of the anion sublattice in governing Na+-ion mobility.

Here, we use an alternative and more direct approach to QENS to directly prove the coupling between cation and anion dynamics, which employs both theory and experiment. The maximum entropy method (MEM) analysis of powder neutron diffraction data for [Na\(_{11}\)Sn\(_2\)]PS\(_{12}\) visualizes smearing of the sulfur density at room temperature, signifying that the PS\(_4\)\(^{3-}\) polyanionic moieties are undergoing rapid reorientation consistent with a rotor phase. This is not observed for [Na\(_{11}\)Sn\(_2\)]PSe\(_{12}\). In agreement with NPD, AIMD data analysis reveals facile [PS\(_4\)]\(^{3-}\)/[PSe\(_4\)]\(^{3-}\) anion rotation, while no significant [SbS\(_4\)]\(^{3-}\) anion dynamics at any temperature are observed in the much more poorly conductive phase, [Na\(_{11}\)Sn\(_2\)]SbS\(_{12}\). We confirm that anion rotation is directly coupled to cation mobility by tracking the diffusion behavior of the two species and calculating the power spectra, as well as performing time correlation analysis over long time scale AIMD calculations. Importantly, by developing joint-time correlation analysis on data extracted from AIMD, we reveal the existence of dynamic coupling: this is the time-dependent process of the cross term that is the product of Na+-ion migration and PS\(_4\)\(^{3-}\) rotation. That correlation proves the synchronization of the velocity between cation and anion, and also implies momentum transfer between the two, in accord with the power spectrum results.

We further define the origin of the dynamic coupling. As the [PS\(_4\)]\(^{3-}\)/[PSe\(_4\)]\(^{3-}\) anion rotates (along with introducing frustration via intrinsic disorder and flattening the local energy landscape), it transiently opens the triangular Na+-ion bottlenecks along the transport channels as each Na+-ion passes through. That owes to the fact that the chalogenide (i.e., S\(^n\)) ions that form the octahedral Na+ solvation cage are shared with those of the adjoining PS\(_4\) tetrahedron. This defines the paddle-wheel motion. It explains the higher ionic conductivity and lower activation energies of the [Na\(_{11}\)Sn\(_2\)]-PS\(_{12}\) and [Na\(_{11}\)Sn\(_2\)]PSe\(_{12}\) materials as compared to [Na\(_{11}\)Sn\(_2\)]-SbS\(_{12}\). Our work clearly demonstrates that alkali cation mobility is not dictated only by static structural properties, but that coupling of the anion and cation dynamics plays an equally vital role, a concept that generally extends to the design of better superionic conductors.

### RESULTS AND DISCUSSION

Cooperative Cation Diffusion Mechanism from AIMD Simulations. The three cation crystallize in the space group P\(_{4}1/acd\) (No. 142), where ordered SnS\(_4\)/SnSe\(_4\) and P(Sb)S\(_4\)/PSe\(_4\) tetrahedra constitute the 3D framework, and sodium ions are distributed over six sites (Figure 1a). Five of the Na+-ions (Na(1)−Na(5)) form irregular NaS\(_4\) octahedra with partial or high occupancies (79%−98%), and one (Na(6)) sits in a quasi-cubic environment with low occupancy (22% for [Na\(_{11}\)Sn\(_2\)]PS\(_{12}\), 35% for [Na\(_{11}\)Sn\(_2\)]PSe\(_{12}\), and 7% for [Na\(_{11}\)Sn\(_2\)]SbS\(_{12}\)) (Figure 1b). The octahedral sodium cages are edge-bonded to the PnX\(_4\) tetrahedra within the structure (Figure 1c), which is vital for anion−cation coupled motion (see below). We examined the Na+-ion diffusion properties of the [Na\(_{11}\)Sn\(_2\)]PS\(_{12}\), [Na\(_{11}\)Sn\(_2\)]SbS\(_{12}\), and [Na\(_{11}\)Sn\(_2\)]PSe\(_{12}\) compositions at five elevated temperatures (500, 600, 750, 900, and 1050 K) using 220 ps-long AIMD simulations. The much longer trajectory duration (vis a vis ref 18) is necessary to sample all six sodium ion environments and establish the full picture of anion dynamics (see next section). The Na+-ion probability density extracted from the trajectory at 1050 K for [Na\(_{11}\)Sn\(_2\)]PS\(_{12}\) is shown in Figure 1d and Figure S1a.b. The diffusion channels created by face-sharing Na octahedra form a network that spans all three crystallographic directions, due to the strategic partial Na vacancies at the crossover points (Na(1), Na(2), and Na(6) sites) that alternate with the three almost fully occupied Na sites (Na(3), Na(4), and Na(5)). The trigonal faces of the adjoining octahedral NaS\(_4\) cages form the bottleneck to diffusion that the Na+-ions must squeeze through (Figure 1c). We note that the vast majority of the sampling trajectories cluster around the Na(1)−Na(5) sites, while only a few cluster around the Na(6) site in [Na\(_{11}\)Sn\(_2\)]PSe\(_{12}\), showing that it is energetically unstable, i.e., a shallow local minimum. The jump event frequency extracted from the AIMD simulations suggests that the probability of a forward jump between the crossover sites (Na(1) and Na(2)) and Na(6) site is not as high as those along the major pathways, and a backward jump is more likely (Figure 1e). These findings unequivocally rule it out as an important pathway for Na+-ion conduction, in contrast to a previous report.46 We also examined the Na+-ion probability density in [Na\(_{11}\)Sn\(_2\)]SbS\(_{12}\) (Figure S2a−c) and [Na\(_{11}\)Sn\(_2\)]PSe\(_{12}\) (Figure S2d−f), with very similar conclusions.

With so many Na+-ions stuffed in the structure, it is logical that the cations undergo correlated motion. Indeed, examination of AIMD simulations of [Na\(_{11}\)Sn\(_2\)]PS\(_{12}\) as the prototype example reveals that several (2−7) Na+-ions hop in a cooperative fashion. Figure 1f depicts a snapshot of the Na+-ion trajectories in the time frame between 15.5 and 16.5 ps (lattice slice from z = 0.5 to z = 1.5). Simultaneous jump events occur along both the ab plane and the c axis (see figure caption for details). These simultaneous moves occur with the participation of vacancies. The high frequency of multijump events within a relatively short time scale (1 ps) confirms the high mobility of Na+-ions in this structure. Macroscopically, the cooperative migration of Na+-ions is further confirmed by the van Hove function that shows a strong time correlation of Na+-ion hopping with a high probability of a vacated Na site being instantly occupied by another Na+-ion (see Methods and Figure S1c for details).

Figure 1g reveals that [Na\(_{11}\)Sn\(_2\)]PS\(_{12}\) and [Na\(_{11}\)Sn\(_2\)]PSe\(_{12}\) show higher Na+-ion diffusivities than that of [Na\(_{11}\)Sn\(_2\)]SbS\(_{12}\).
at all simulated temperatures. The fitted activation energies of these three compositions are 0.18 eV (for [Na11Sn2]PSe12), 0.19 eV (for [Na11Sn2]PS12), and 0.25 eV (for [Na11Sn2]SbS12), respectively, in reasonable accord with the experimental data (0.28, 0.24, and 0.34 eV, respectively). The lower ion conductivity and higher activation energy of [Na11Sn2]SbS12 as compared to [Na11Sn2]PS12 contradicts expectations based on the larger volume and "softer" and more polarizable lattice of the antimony analogue. Instead, this discrepancy points to the role of other factors, such as the interaction between anions and cations, thus prompting our study.

Facile [PS4] Anion Reorientation but Not [SbS4] via the Maximum Entropy Method. Two representative members of the series, [Na11Sn2]PS12 and [Na11Sn2]SbS12, were investigated by variable-temperature neutron diffraction from cryogenic (3 K) to elevated temperature (450 K). The maximum entropy method (MEM) was employed to probe the nuclear-density distribution extracted from those data. Figure 2a and e shows the three-dimensional (3D) pictures of nuclear density at 450 K through the (001) plane near \( z = 1/8 \), and the (100) plane near \( x = 0 \), respectively. Along with the original lattice positions for the sulfide ions (indicated as S1a, S2a, S3a, and S4a in Figure 2a), another four density maxima (denoted as S1b, S2b, S3b, and S4b) for the sulfide ligands of [PS4] are observed in the slice through (001) (Figure 2a). These are also apparent in the (100) plane (Figure 2e), although the fourth sulfide is obscured in this view. This is very strong evidence for [PS4] anion rotational/reorientational disorder, and it is the first time it has been visualized from experimental data to our knowledge. In sharp contrast, only very mild and localized [SbS4] anion reorientation is indicated in the nuclear density maps of [Na11Sn2]SbS12 (see Figure S3).

The two-dimensional (2D) contour slices of the (001) planes at \( z = 1/8 \) and the (100) plane at \( x = 0 \) are shown in Figure 2b−d and f−h for [Na11Sn2]PS12 and in Figure 2c−d and e−h for [Na11Sn2]SbS12, respectively. Strong [PS4] anion rotational/reorientational disorder is also dominant at room temperature for the [Na11Sn2]PS12 phase. It even persists down to cryogenic temperatures (3 K), suggesting that the [PS4] disorder freezes into a locally disordered state. Conversely, in the nuclear density maps for [Na11Sn2]SbS12, no anion rotational/reorientational disorder can be observed at 3 K.
At room temperature (300 K) and elevated temperature (450 K), \([\text{SbS}_4]\) does begin to show evidence of very mild, distinct, and localized reorientation (see Figure S3g,h). While these time-averaged spatial snapshots demonstrate extreme reorientational disorder in \([\text{Na}_{11}\text{Sn}_2]\)PS\(_{12}\), they also indicate that the anion rotation/reorientation is much more facile and prominent than in the less conductive \([\text{Na}_{11}\text{Sn}_2]\)SbS\(_{12}\), where a much higher temperature is necessary to activate the rotation/reorientation dynamics. Our findings also impact studies of thiophosphate materials by powder diffraction at room temperature, as they reveal that orientational disorder likely adds a degree of complexity that is often overlooked.

### 3D Anion Spatial Distribution and Helmholtz Free Energy Landscape

To obtain a clear picture of the anion reorientational dynamics, we performed a detailed analysis of AIMD results in the reference frame of the crystal lattice (Figure 3). The preferred orientations of the anions were determined by considering the spatial distribution of the P/Sb, Sn, and S/Se atoms. The three-dimensional (3D) spatial distributions of the P/Sb, Sn, S/Se atoms that were extracted from the AIMD simulations for \([\text{Na}_{11}\text{Sn}_2]\)PS\(_{12}\), \([\text{Na}_{11}\text{Sn}_2]\)PSe\(_{12}\), and \([\text{Na}_{11}\text{Sn}_2]\)SbS\(_{12}\) at 1050 K are shown in Figure 3a–c, respectively. The anion rotational dynamics are clearly evident in the density distributions, with the S/Se ligands of \([\text{PS}_4]/[\text{PSe}_4]\) anions exhibiting high density in eight maxima, while those of \([\text{SnS}_4]/[\text{SnSe}_4]\) or \([\text{SbS}_4]\) are localized at their original four maxima. This indicates that very significant rotation occurs for \([\text{PS}_4]\) and \([\text{PSe}_4]\) anions, but not for the \([\text{SbS}_4]\) groups. Anion rotation of the \([\text{PS}_4]/[\text{PSe}_4]\) groups is not random, but preferential, in agreement with the room temperature NPD results. Figure 3d–f exhibits the 2D density distribution of the selected P–S, Sb–S, or P–Se bonds in the spherical coordinates defined in Figure 3a–c. Indeed, eight maxima are observed for the four S/Se atoms bonded to P, with the original four (denoted by A, B, C, and D in Figure 3d,e) having higher probability density and the four

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Figure 3. 2D and 3D probability density distributions and the Helmholtz free energy surface of the chalcogenides (X) of the [PnX\(_4\)] polyanions. Shown for (a) \([\text{Na}_{11}\text{Sn}_2]\)PS\(_{12}\), (b) \([\text{Na}_{11}\text{Sn}_2]\)PSe\(_{12}\), and (c) \([\text{Na}_{11}\text{Sn}_2]\)SbS\(_{12}\) is the probability distribution of P/Sb, Sn, and S/Se, along with the definition of the angles \(\theta\) and \(\varphi\) in the reference frame of the crystal lattice. The angle between the P–S bond and the \(z\) axis is defined as \(\theta\), and the angle \(\varphi\) is the angle between the \(x\) axis and the projection of the P–S vector in the \(xy\) plane. Shown for (d) \([\text{Na}_{11}\text{Sn}_2]\)PS\(_{12}\), (e) \([\text{Na}_{11}\text{Sn}_2]\)PSe\(_{12}\), and (f) \([\text{Na}_{11}\text{Sn}_2]\)SbS\(_{12}\) is the 2D probability of atoms bonded to P/Sb. Shown in (g) \([\text{Na}_{11}\text{Sn}_2]\)PS\(_{12}\), (h) \([\text{Na}_{11}\text{Sn}_2]\)PSe\(_{12}\), and (i) \([\text{Na}_{11}\text{Sn}_2]\)SbS\(_{12}\) is the Helmholtz free energy surface as a function of angle \(\theta\) and \(\varphi\). The Helmholtz free energy \(A\) was computed as \(A(\theta, \varphi) = -k_B T \ln(\rho(\theta, \varphi))\), where \(k_B\) is the Boltzmann constant, \(T\) is temperature, and \(\rho(\theta, \varphi)\) is the probability density distribution of the S/Se ligands of \([\text{PS}_4]/[\text{PSe}_4]\) anions from the AIMD simulations.
additional (indicated by E, F, G, and H in Figure 3d,e) exhibiting slightly lower probability. Only four distinct maxima are shown for the four S atoms bonded to Sb, suggesting that negligible anion reorientation dynamics occur at this temperature within the time scales of AIMD. This is consistent with our NPD results, showing that [SbS4] anions exhibit negligible or much slower orientational dynamics at all of the temperatures studied (see above).

To explore the origin of the different reorientation propensities of [PS4]/[PSe4] and [SbS4] anions, we calculated the Helmholtz free energy for the four S/Se ligands bonded to P5, Sb5, in [Na11Sn2]PS12/[Na11Sn2]PSe12/[Na11Sn2]SbS12 (Figure 3g-i). The Helmholtz free energy surface as a function of the coordinates, angles $\theta$ and $\phi$, contains average properties that correspond to thermodynamic states. The positions and heights of the local minima and transition states represent the rotation paths and barriers, respectively. The Helmholtz free energy surfaces for [Na11Sn2]PS12 and [Na11Sn2]PSe12 (Figure 3g,h) unambiguously demonstrate that the S/Se ligands of the [PS4] and [PSe4] polyanions exhibit a very shallow Helmholtz free energy landscape, while the S ligands of the [SbS4] anion group in Figure 3i show deep potential wells with high Helmholtz free energy barriers of 0.60−0.86 eV. Specifically, the low Helmholtz free energy barriers (0.12−0.24 eV) for the rotation of the S/Se ligands of [PS4]/[PSe4] in [Na11Sn2]PS12/[Na11Sn2]PSe12 permit the S/Se ligands to rotate to their nearby minima in a very short time scale (0.2−3.0 ps), as indicated by the arrows in Figure 3g.h. A more detailed analysis of the trajectory of the S atoms bonded to P or Sb atoms during the AIMD simulations at 1050 K is presented in Figure 4a−f. The P−S and Sb−S bonds are maintained during the simulations (see Figure S4 for details). Both the $\theta$ and $\phi$ angles change with the simulation time in [Na11Sn2]PS12, and very rapid rotation from one configuration to another occurs within a very short time duration (0.2−3.0 ps), in agreement with Figure 3g. A full rotation (360°) was completed in about 10−25 ps. Examination of all of the [PS4]/[SbS4] anion groups shows that all of the eight [PS4] moieties in the unit cell rotate repeatedly over this 220 ps time scale (see Figure S5), while no rotation occurs in the S ligands of three of the [SbS4] tetrahedra over this same time scale. Of the five [SbS4] polyhedra that do exhibit limited dynamic reorientation, rotation is highly hindered. It occurs in sudden cog-like jumps separated by a very long interval (140−165 ps) (see Figure S6 for details), because the Helmholtz free energy wells of the sulfur ligands of [SbS4] vary in depth, as depicted in Figure 3f. In contrast, the sulfur ligands of [PS4] exhibit a smooth and relatively flat Helmholtz free energy surface with shallow wells of uniform energy depth, and therefore rotation is readily activated. Anion reorientation behavior, and the
angular evolution of P–S bonds and Sb–S bonds at other temperatures, are shown in Figures S7 and S8. [PS₄] polyanions rotate at a simulation temperature of 600 K and above, while no [SbS₄] rotation is observed below 1050 K. This again suggests that the motion of the [SbS₄] is still restricted by the local geometry at these temperatures, and can only be activated at higher temperature (1050 K and above). The anion reorientation of [PSe₄] moieties in [Na₁₁Sn₂]PSe₁₂ was also explored (Figure S9). Free rotation of the [PSe₄] polyanions is also observed at 1050 K, which persists down to 750 K, similar to the case of the [PS₄] polyanions in [Na₁₁Sn₂]PS₁₂.

Bader charge analysis of each of the polyanion moieties was carried out to estimate the partial charges on the atoms of the tetrahedral units. The analysis shows that Sb and S share fewer electrons than do P and S/Se, indicative of the more ionic nature of the Sb–S bond (Figure S10). The positive charges on the central atoms follow the trend, P (PSe₄) < P (PS₄) < Sb (SbS₄), and the negative charges on S/Se ligands follow the same order, Se (PSe₄) < S (PS₄) < S (SbS₄). The smaller partial charge difference between the ligands and the
Figure 6. 2D probability density distribution illustrating correlation of polyhedral rotation of PnX4 and the translational motion of the Na+–cation in the [Na11Sn2]PnX12 series within a time frame of 20 ps. The 2D probability density distribution $P_{fl}^{c-c}$ from AIMD simulations of the Pn–X–Na angles ($\gamma$) and the distance ($r$) between X ligands and Na for (a) [Na11Sn2]PS12; (b) [Na11Sn2]PSe12 and (c) [Na11Sn2]SbS12. Distinct correlation is observed for PS4 and PSe4, but not for SbS4; (d) one-dimensional free energy profiles along the distance between the Na cation and the S or Se ligand in [Na11Sn2]PS12, [Na11Sn2]PSe12, and [Na11Sn2]SbS12. Residence time correlation functions for Na+-cations nearest to the polyhedral anion, $\langle b(t) \rangle$ for (e) [Na11Sn2]PS12 and (f) [Na11Sn2]SbS12. The $\langle Pf(t) \rangle$ orientational correlation functions are also shown, along with $\langle bPf(t) \rangle$ orientational correlation function restricted to Na+-cations nearest to the polyhedral anion.

Effects of Anion Rotation: Transiently Opening the Bottleneck for Cation Diffusion. To establish a firm connection between the cation diffusion and anion rotation, analysis of these motions was performed by examining the AIMD snapshots in detail. A duration of 1 ps was randomly picked to study the effects of the anion rotation on the cation diffusion. Figure 5a depicts the snapshot at 21 ps with the embedded trajectories of S between 21 and 22 ps in [Na11Sn2]PS12. Most of the S ligands of the eight [PS4] groups are rotating during this short duration, where the S atoms undergo a move to the adjacent vertex or to the position between two vertices. Meanwhile, significant Na+–ion diffusion events occur cooperatively with the rotation of the anions, as indicated by the green and red arrows (see Figure 5a, right panel). We randomly picked two Na atoms (labeled as Na58 and Na77) in the vicinity of one S ligand (labeled as S78) of the [PS4] anion group and tracked the motions of these three atoms. The results are depicted in movie S1, where the synchronous motion of the two Na+-ions and S is clearly visualized. As the S ligand rotates, fluctuations in the local energy landscape are introduced, which creates viable low-barrier diffusion pathways, and therefore facilitates the escape of the Na+-ion from the local-minimum wells. Specifically, during the 1 ps duration, the [PS4] group containing S78 rotates (Figure 5b), while Na58 migrates $\sim$3.9 Å along the x axis (Figure 5c) (this distance reflects a hop between Na1 and Na5; see Figure 1a, noting that the Na–Na distance is $\sim$3.4 Å in this structure). To confirm the contribution of the [PS4] anion rotation to cation diffusion, we also scrutinized the behavior of the two species in another time frame when [PS4] rotation pauses. The period from S6 to S7 ps was selected randomly to conduct the parallel analysis (see Figure 4 for the full time scale), and the results are shown in Figure S11a–d and movie S2. Both the trajectories (Figure S11a) and the movie explicitly show that Na atoms only liberate at their equilibrium sites when the rotation of the neighboring [PS4] polyanion is suspended. This was further confirmed by the coordinates of the Na atom and the projection of the P–S bond in the ab plane (Figure S11c,d).

We examined the trajectories of Na and S in the [Na11Sn2]SbS12 system in the same time frame as a comparison, and the results are plotted in Figure 5d–f. Notably, the S ligands of [SbS4] anion groups merely linger in the vicinity of their equilibrium positions and no rotation occurs (as illustrated by the combination of trajectories (Figure 5d) and the angular history of the Sb–S bond (Figure 5e)).
Accordingly, the Na cations again linger near their lattice sites (Figure Sd,f), and very few diffusion events occur (see movie S3). This suggests that in [Na11Sn2]SbS12 where no [PnS4] rotation occurs, and in [Na11Sn2]PS12 when the [PnS4] rotation pauses, the Na cations experience a more “fixed” potential due to the absence of anion rotation and are easily trapped in their local minima due to the higher escape barriers.

To explore the origin of this effect, we calculated the size of the trigonal bottleneck that Na+-ions must squeeze through for diffusion to occur (Figure 5g). A significant widening of this dimension is observed when the shared S atom rotates in [Na11Sn2]PS12 (red line in Figure S5h). In accord, the energy barrier for cation hopping is lowered, and diffusion occurs easily and more frequently (Figure 5a and c). When S rotation is paused (in the case of [Na11Sn2]PS12, albeit temporarily) or locked (in [Na11Sn2]SbS12), this bottleneck is much smaller (Figure S11b and Figure S5h). These studies indicate that the [PnS4] anion dynamics affect the Na cation transport by transiently opening the triangular window in the NaS6 octahedral cages (formed by three S2− on either side of the cage) through which the Na cations must diffuse through for transport to occur.

**Direct Evidence of Coupled Anion Rotation and Cation Diffusion.** Having explicitly observed coupled anion rotation and cation diffusion from the AIMD trajectories of S and Na atoms in [Na11Sn2]PS12, we examined the correlation between them by computing the 2D probability distribution (ργ(r)) of the Pn−X−Na angle (γ) and the distance (r) between X ligand and Na atom in the first shell. As shown in Figure 6a and b, ργ(r) is delocalized in two maxima, indicating correlation between S/Se rotation and Na+-ion diffusion in both [Na11Sn2]PS12 and [Na11Sn2]PSe12. Conversely, ργ(r) is localized in only one maxima for [Na11Sn2]SbS12, indicative of the negligible correlation between Na+-ion diffusion and the SbS4 anion libration (Figure 6c). This is reflected quantitatively by the statistical average of the magnitude of the correlation, ⟨P2(X)⟩ of the PnX4 polyanions and the 88 Na+ cations that comprise the supercell in the three materials (Figure S12). A relatively high ⟨P2(X)⟩ of ~0.3 is observed for [Na11Sn2]PS12 and [Na11Sn2]PSe12, but ⟨P2(X)⟩ is only ~0.05 for [Na11Sn2]SbS12.

To obtain a more generic and thorough understanding on the cation–anion correlation, we also examined the power spectrum of cations and anions in the full range of our AIMD simulations. The strong overlap between Na+-ion diffusion and PS4− rotation (Figure S13) indicates that the anion rotation occurs at the same time-scale with the cation motion, further evidence of their linked behavior. The angular velocity autocorrelation function for the PS4 anions in Na11Sn2PS12 is derived from the average angular velocity of individual P and S atoms (ωi). The broad dispersion of the S-derived spectrum is due to the fact that the S atoms bonded to P exhibit positional variance, and hence each gives rise to a slightly different frequency. The Na-derived modes have a strong overlap with the librational/rotational modes of S atoms and the PSE-anion angular spectrum. This is suggestive of momentum transfer between the anion dynamics and cation vibrations at low frequency (<10 THz) prior to diffusion. Further evidence for this is provided below.

The impact of anion rotation on the cation diffusion is also apparent from the Helmholtz free energy barrier of Na+-ions in the three materials (Table 1). In [Na11Sn2]PS12 and [Na11Sn2]PSe12 that exhibit facile anion rotation, Na+-ions exhibit a low one-dimensional Helmholtz free-energy barrier (0.15 eV) as compared to the higher Helmholtz free-energy barrier (0.21 eV) in [Na11Sn2]SbS12 (Figure 6d) in which no significant anion rotation was seen (Figure S14 shows the corresponding 3D Helmholtz free-energy landscapes). The lower free energy barrier for cation diffusion in [Na11Sn2]PS12 and [Na11Sn2]PSe12 confirms that the anion rotational dynamics leads to the frustration of the cation diffusion energy landscape. We performed a comparative NEB study with and without constraints for the S atom positions (Figure S15), similar to previous studies.41,43 One limitation of such an analysis is that it neglects fluctuations in the energy landscape caused by the perturbation of the local potential due to the thermal vibration of the S atoms within the potential well. Nonetheless, our results demonstrate that anion rotation lowers the local energy landscape by as much as 0.10−0.16 eV (Figure S15). These values are of a similar magnitude to the diffusion barrier itself.

![Figure 6](https://example.com/fig6.png)

**Figure 6.** Reveals that for [Na11Sn2]PS12, there is significant coupling between the angular and radial coordinates of the Na+-ion relative to the PS4 group. To confirm this microscopic mechanism and obtain a quantitative measure of the dynamics of the escape of the Na+-ion from local minima, we define a residence time correlation function, ⟨hh(t)⟩ (see Methods for details). This analysis is intended to confirm the dynamical role of anion rotation beyond transition state theory arguments based on barrier heights. We observe that the ⟨hh(t)⟩ correlation function decays faster for [Na11Sn2]PS12 with a characteristic time of 43.7 ps, as compared to [Na11Sn2]SbS12 for which the time is 66.9 ps (Figure 6e,f). These results reveal that cations escape faster from the vicinity of the [PS4] anions than from the [SbS4] anions. Also shown in Figure 6e,f is the ⟨PP(t)⟩ correlation function that probes the decay of anion reorientation. The decay of ⟨PP(t)⟩ is expected to be faster than that of ⟨hP(t)⟩ as observed for both systems. It is, however, important to note that for [Na11Sn2]SbS12, oscillations are observed at short times for both t = 1 and t = 2. This nonexponential behavior is the signature of librational motion and is consistent with the observation of the hindered rotational character of the SbS4 polyhedral anion. Those short time oscillations are not present in the case of [Na11Sn2]PS12 because reorientational motion occurs with faster decay consistent with rotational diffusion behavior.

| Table 1. Helmholtz Free Energy Barrier (Eh) for Na+-Ions and PnX4 Anion Rotation, and Activation Energy (Ea) for Na+-Ion Diffusion in [Na11Sn2]PnX4 (Pn = P, Sb; X = S, Se) from AIMD Simulations |
|---|---|---|---|
| Eh for Na cation diffusion (eV) | 0.15 | 0.15 | 0.21 |
| Eh (experiment, eV) | 0.24, 0.25 | 0.31, 0.60 | 0.28, 0.60 |
| Eh (predicted, eV) | 0.19 | 0.18 | 0.25 |
| Ea for PnX4 anion rotation (eV) | 0.12−0.24 | 0.12−0.20 | 0.60−0.86 |
rotation in water. Figure 6e,f shows that the \( \langle hP_h(t)P(l) \rangle \) correlation function decays much faster for \([Na_{11}Sn_2]PS_{12}\) with values of 8.5 ps for \( l = 1 \) and 3.4 ps for \( l = 2 \). For \([Na_{11}Sn_3]SBSe_{12}\), the decay times are much longer, 26.1 ps for \( l = 1 \) and 11.9 ps for \( l = 2 \). This motion, which is therefore along a collective coordinate, facilitates diffusion of the Na\(^+\)-ion away from the anion. Overall, these observations confirm the dynamical coupling between anion rotation and cation migration. The upshot is that free rotor anions undergo rotational diffusion and facilitate cation migration, while hindered rotor anions can retard cation migration due to longer-lived dynamical correlations.

On the basis of these intriguing observations, we propose an interplay of anions and cations as follows. On one hand, the rotation of these anions moves the cations along in a paddle-wheel-type mechanism by transiently opening the trigonal face (delineated by three \( S^{2-} \) ions) that is the bottleneck for Na\(^+\) transport along the chains in all directions. On the other hand, the motion of the cations drives adjacent cations forward in a cooperative mechanism. The joint contribution of the paddle-wheel (anion–cation interplay) and cooperative transport (cation–cation interaction) enables the high conductivity in \([Na_{11}Sn_3]PS_{12}\) and \([Na_{11}Sn_3]PSe_{12}\). This presents a scenario whereby cations move in an instantaneous fluctuating potential caused by the anion rotation. In turn, anion rotations lower the local potential perceived by the nearby cations and favor a lower activation barrier process. That suggests that there are significant gains to be unlocked in superionic conductors by tuning compositions to invoke such a coupled mechanism.

**CONCLUSIONS**

While the structure of the novel fast ion conductors \([Na_{11}Sn_3]PnX_{12}\) (Pn = P, Sb; X = S, Se) facilitates cation conduction via a cooperative mechanism, the significant improvement of conductivity achieved in the phosphorus analogues reveals the equal importance of the flexibility of the framework in dictating cation diffusion. Dynamic rotation of the [PS\(_4\)]\(^-\) anions at room temperature in the fast Na-ion conductor \([Na_{11}Sn_3]PS_{12}\) directly evidenced using variable-temperature neutron diffraction/MEM analysis, is directly correlated with higher Na\(^+\)-ion conductivity. In contrast, negligible or much slower orientation dynamics are exhibited by [SBSe\(_4\)]\(^-\) anions even at elevated temperature. AIMD simulations consolidate this finding, and further demonstrate [PSe\(_4\)]\(^-\) anion rotation. One conclusion is that soft rotational modes better enable anion rotation. Second, the joint-time correlation analysis developed in this work provides clear evidence of the synchronization of the velocity of the cations and anions (i.e., their “dynamic coupling”). Such coupling is a consequence of the transient widening of the bottleneck for cation migration as the Na\(^+\) ion moves through the window. This shows how effectively the [PX\(_4\)]\(^-\) (X = S, Se) anion rotation facilitates the cation diffusion, in contrast to the hindered anion dynamics of the [SBSe\(_4\)]\(^-\) group. Last, a harmonized mechanism involving the paddle-wheel effect (anion–cation interplay) and correlated diffusion (cation–cation interaction) underlies intrinsic high conductivity in this structure class. The former can be tuned by adjusting the anion groups, and should be a consideration in the future design of fast ion conductors based on polyanions. This concept can be extended to other [PS\(_4\)]\(^-\) or [PSe\(_4\)]\(^-\) polyanion-based solid electrolytes, for example, \( \beta \)-Li\(_3\)PS\(_4\), Na\(_3\)PS\(_4\), Na\(_3\)PSe\(_4\), and others, although [PS\(_4\)]\(^-\)/[PSe\(_4\)]\(^-\) rotation in these materials is activated at a different temperature as our subsequent study will demonstrate.

More generally, the results show that cation mobility is dictated not only by the static framework structure, but that anion dynamics affect the energy landscape perceived by the cations because the cation mobility and anion rotation are strongly correlated. Our findings reveal how the cation–anion interplay can introduce energy barrier frustration and impact fast ion conduction. They highlight the necessity to go beyond simple structural characteristics of the framework. Enhancing anion rotational dynamics constitutes a viable strategy and serves as a complementary and general design principle for emerging fast ion conductors. The concept may be particularly important to the design of divalent ion conductors (or mixed divalent ion/electron conductors), where static anion frameworks rarely support good ion transport. Here, materials with beneficial anion rotational dynamics could play a critical role in enhancing cation diffusion.

**METHODS**

Experimental Methods. \([Na_{11}Sn_3]PS_{12}\) and \([Na_{11}Sn_2]SBSe_{12}\) were synthesized as described in our previous papers.\(^{18,19}\)

Neutron powder diffraction measurements were performed on the high-resolution powder diffractometer ECHIDNA at ANSTO in Australia.\(^{53}\) The NPD data were collected at 3, 300, and 450 K with a wavelength of 1.6220 Å. Data analysis using Maximum Entropy Methods was performed using RIETAN-FP\(^{54}\) and Dynsopor\(^{55}\) codes.

Computational Details. Geometry optimization was performed by DFT calculations using the Vienna ab initio simulation package\(^ {56}\) with the projector augmented-wave (PAW) method.\(^ {57}\) The generalized gradient approximation (GGA) functional parametrized by Perdew–Burke–Ernzerhof (PBE)\(^ {58}\) was employed to describe the exchange correlation potential. Our calculations adopted a plane-wave cutoff of 450 eV. The geometry optimization was performed on the conventional cell containing 208 atoms. The total energy and the force on each atom were converged to within \( 10^{-5} \) eV and 0.01 eV/Å, respectively. A Γ-centered k-point mesh of 2 × 2 × 1 was used for the Brillouin zone integrations. \( N_i \) is the total number for each type of atom in the supercell. In our work, \( N_{Na} = 88, N_{Sn} = 16, N_{P} = 8, \) and \( N_{Se} = 96 \).

AIMD simulations were carried out at a constant temperature within the canonical (NVT) ensemble using a Nose thermostat.\(^ {59}\) The volume of the unit cell was fixed at that of the fully relaxed structure. The samples were heated to the targeted temperature (500, 600, 750, 900, and 1050 K) by velocity scaling over 5 ps, and then equilibrated at the desired temperature. The MD simulations were carried out for 220 ps at each temperature, and a time step of 1 fs was used to integrate the equation of motion. To keep the computational time reasonable for the relatively large unit cell, integration in reciprocal space was only performed at the Γ-point.

Na\(^+\)-ion probability densities were calculated from the atomic trajectories. The diffusion coefficient is defined as

\[
D = \lim_{t \to \infty} \frac{1}{2dt} \left[ \overline{\langle r(t) - r(0) \rangle^2} \right]
\]

where \( d \) is the dimension of the lattice on which the diffusion takes place, and \( t \) is the elapsed time. The average mean square displacement:

\[
\langle \overline{r(t)} - \overline{r(0)} \rangle^2 = \frac{1}{N} \sum_{i=1}^{N} \left( \overline{\langle r(t) - t_i \rangle} - \overline{r(0)} \right)^2
\]

is the averaged displacement of Na atoms over time \( t_i \) and \( t_0 \) is the initial time. \( D \) was obtained by linear fitting to the dependence of the average mean square displacement over 2dt.
Activation energy barriers for cation diffusion were extracted from linear fits to Arrhenius plots of diffusion coefficients derived from AIMD.

The energy landscape of a single Na*-ion along the migration channel was calculated using NEB methods. The defect charge was compensated by a uniform background charge to maintain charge neutrality.

The van Hove correlation function²⁰ (Figure S1c) was calculated from the AIMD simulations. The distinct part $G_{ij}(r,t)$ describes the radial distribution of different ions after time interval $\Delta t$ with respect to the initial reference particle:

$$G_{ij}(r,t) = \frac{1}{4\pi^2 N_j} \left[ \sum_{i=1}^{N_j} \delta(r - |r_i(t_0) - r_j(t + t_0)|) \right]_{t_0} \tag{3}$$

where $\delta$ is the Dirac delta function, $\bar{r}(t)$ is the position of the $i$th particle at time $t$, and $N_j$ and $r$ are the number of diffusing alkali ions in the unit cell and radial distance, respectively.

We also computed the normalized 2D probability density distribution $\rho_{2D}(\gamma, \phi)$ as a function of $\theta$ and $\phi$ for the X ligands of PnX₄ (Pn = P, Sb; X = S, Se) anion from the AIMD simulations in Figure 3 (main text). Here, $\theta$ represents the angle between a selected Pn–X bond and the z axis and $\phi$ corresponds to the angle between the x axis and the projection of the same Pn–X vector in the xy plane. On the basis of this, the Helmholtz free energy surface of the X chalcogenide ligands was computed via

$$A(\theta, \phi) = -k_B T \ln \rho_{2D}(\theta, \phi) \tag{4}$$

where $k_B$ is the Boltzmann constant, and $T$ is temperature.

To study the correlation between the Na*-cation diffusion and the rotation of the chalcogenide ligands (X) quantitatively, the joint probability distribution $\rho_{2D}(\gamma, \phi)$ of the angle between the P–S and S–Na bond vectors ($\gamma$) and distance between S and Na ($r$) were calculated. We define the square root of this 2D distribution as

$$f = \sqrt{\rho_{2D}(\gamma, \phi)} \tag{5}$$

and its uncorrelated counterpart as the product of the 1D distribution for each degree of freedom:

$$g = \sqrt{\rho_{1D}(\gamma) \rho_{1D}(\phi)}$$

To compute the overlap between the correlated and uncorrelated distributions, the inner product is defined as

$$\int dy \, df(y, r)g(y, r) = \langle f | g \rangle \tag{6}$$

If there is a correlation between $\gamma$ and $r$, the following quantity, $\chi_i$, represents the magnitude of that correlation:

$$\int dy \, df(f - g)^2 = \chi_i \quad i = 1, 4 \tag{7}$$

These results are presented in Figure S12. Note that if $\langle f | g \rangle = 1$, $\chi^2$ equals 0, and there is no correlation between $\gamma$ and $r$. Intermediate values of $\langle f | g \rangle$ and $\chi$ indicate some correlation.

The power spectrum was calculated via the Fourier transform of the velocity autocorrelation function ($\sum_{l=1}^{N} \langle \hat{v}_l(t) \hat{v}_l(t+\Delta t) \rangle$), in which $\hat{v}_l$ is the angular velocity of individual S ligand of PS₄ anion groups, which was calculated via

$$\hat{v}_l = \frac{\vec{v}_l \times \vec{r}_l}{|\vec{r}_l|} \tag{8}$$

Here, $\vec{v}_l$ and $\vec{r}_l$ are the position vector and velocity for each S atom relative to the central of mass of PS₄ anion group. Results are shown in Figure S13.

The one-dimensional (1D) Na*-ion probability distribution $\rho_{1D}$ as a function of the distance ($r$) was also calculated from AIMD simulations. The corresponding one-dimensional free energy curve is calculated by

$$A(r) = -k_B T \ln \rho_{1D}(r) \tag{9}$$

Such one-dimensional free energy profiles along the distance between the Na cation and the S or Se ligand in [Na₁₁Sn₂]PS₁₂, [Na₁₁Sn₂]PSe₁₂, and [Na₁₆Sn₂]SbS₁₂ are shown in Figure 6d.

Two-dimensional free energy landscapes were calculated as a function of distance $r$ and angle $\gamma$ using

$$A(r, \gamma) = -k_B T \ln \rho(r, \gamma)_{1D} \tag{10}$$

where $r$ is defined as the distance between the Na and S atoms and the angle $\gamma$ is measured between the P–S and S–Na bond vectors, and the Sb–S and S–Na bond vectors. Results are presented in Figure S14 for [Na₁₁Sn₂]PS₁₂ and [Na₁₆Sn₂]SbS₁₂.

The time scale for the hopping of the Na*-ions to the nearest polyedral anion was calculated by analyzing the decay of the residence time correlation function. This correlation function is defined as $\langle h(t) \rangle \equiv \langle h(R_{\text{cut}}(t) - R(t = 0)) \rangle$, where $h$ is the Heaviside function. This function equals unity when $R < R_{\text{cut}}$ and is zero otherwise ($R_{\text{cut}} = 6.1$ Å for [Na₁₁Sn₂]PS₁₂ and 6.2 Å for [Na₁₆Sn₂]SbS₁₂). The residence time correlation functions are shown in Figure 6e for [Na₁₁Sn₂]PS₁₂ and in Figure 6f for [Na₁₆Sn₂]SbS₁₂. We also calculate the $(PP(\ell))$ correlation function that measures the decay of the orientation between the P–Na (Sb–Na) and P–S (Sb–S) bond vectors. In this correlation function, $P_\ell$ is a Legendre polynomial of degree $\ell = 1, 2$. The argument of $P_\ell$ is the cosine of the angle between the P–Na (Sb–Na) and P–S (Sb–S) bond vectors. We refer to the $l = 1$ case as first order and to the $l = 2$ case as second order. We have also combined the residence time with the rotational dynamics in the $(hP_0h(1)P(1))$ correlation. This correlation function measures the orientational dynamics for the nearest Na*-ions to the polyhedral anion.

## ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b09343.

Additional details on the Na*-ion probability density and van Hove correlation plot for Na₁₁Sn₂PS₁₂, details for Na₁₆Sn₂SbS₁₂ on the Na*-ion probability density and the MEM plots at various temperatures of 3, 300, and 450 K; Pn–X bond length and angle variation during AIMD simulation; Bader charge analysis of Na₁₁Sn₂PnX₁₂; plot showing area of the bottleneck for Na*-ion diffusion with a power spectrum with 2D free energy landscapes for Na*-ions in Na₁₁Sn₂PnX₁₂ with and without constraints on PnS₄ rotation (PDF).

Movie S1 (MP4)
Movie S2 (MP4)
Movie S3 (MP4)

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