SUPPLEMENTAL INFORMATION

Energetics and Kinetics of Alkali Ion Exchange in Analcime

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Analcime Framework

Analcime has a complex framework, making it a challenge to show all features in 2D figures. Additional views of the cage, 8-member ring and 6-member ring from different angles are presented in Figure S1.

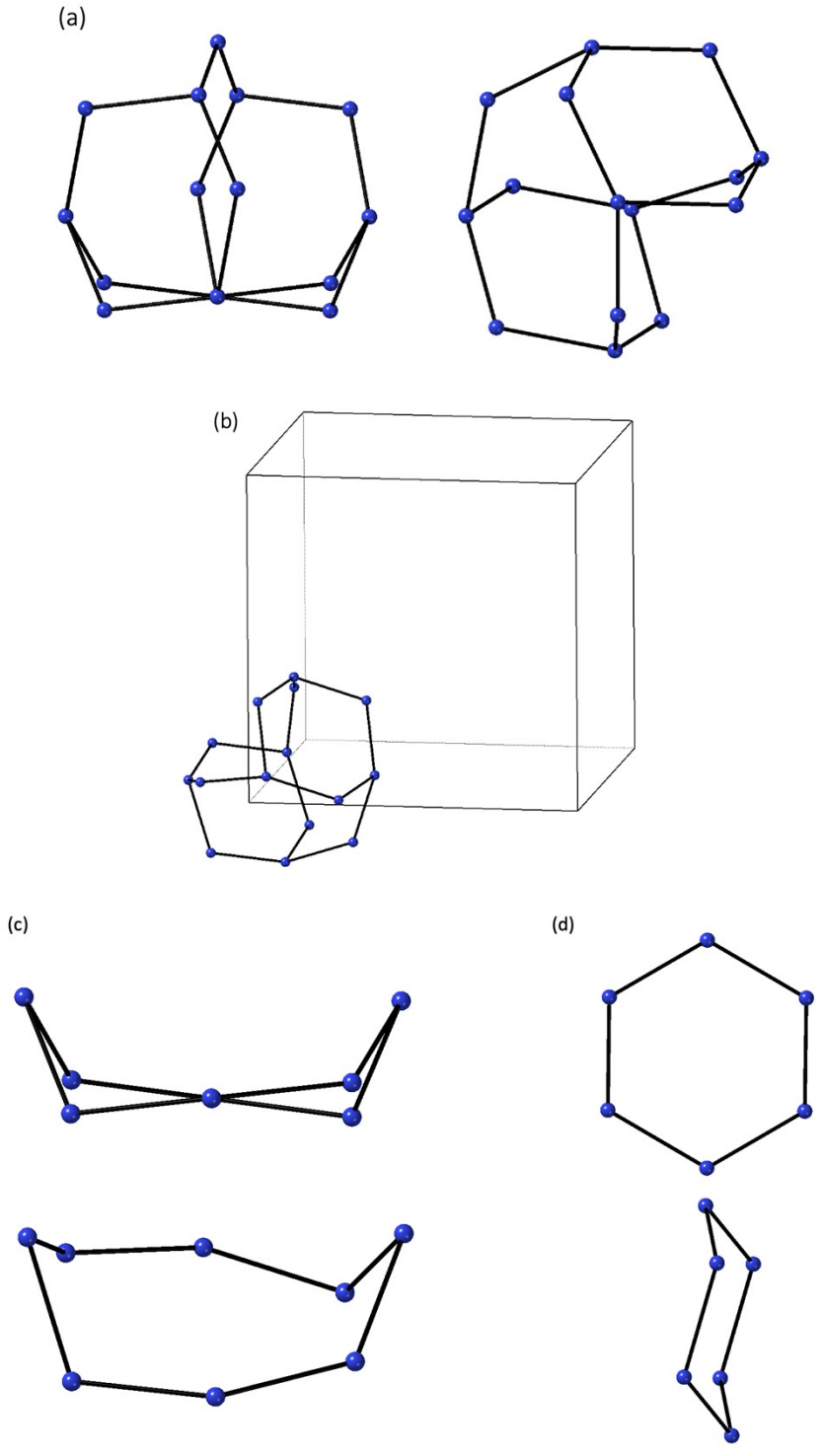

Figure S1:(a) two views of a single cage of 3 eight-member rings and 2 six-member rings, (b) a cage at left corner shared by four unit cells, Two views of (c) a single 8-member ring and (d) a 6-member ring.

The Energetics Associated with Ion Exchange

All Na^+ and Cs^+ sites in Analcime Framework

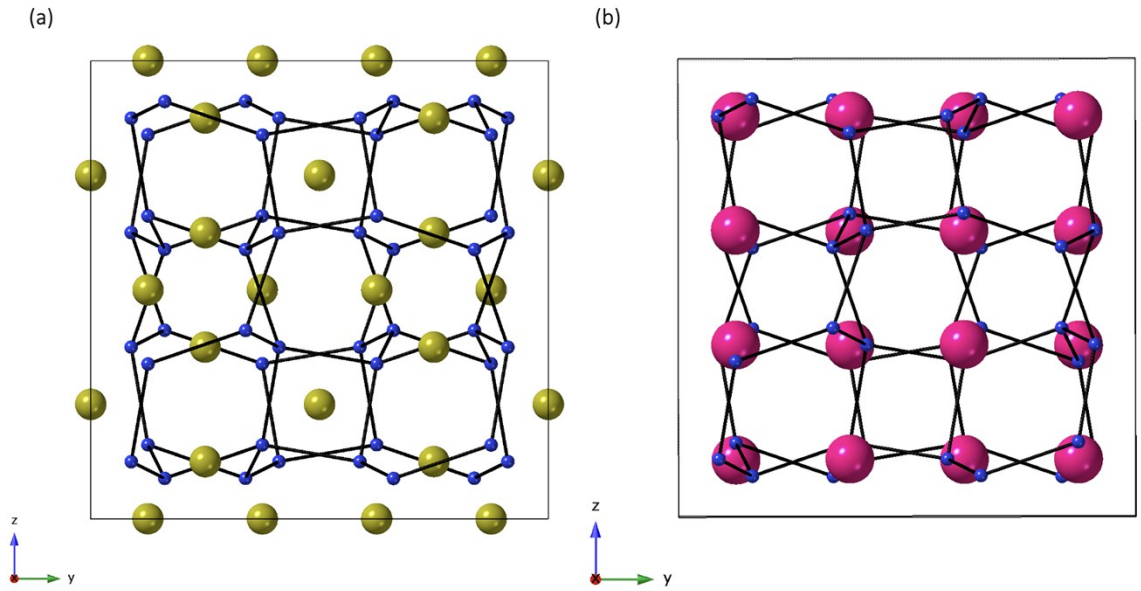

Figure S2: (a)24 8-member ring sites(Na^+) in analcime framework, (b)16 cage sites(Cs^+) in analcime framework.

Reference State of Hydration Ions

Figure S3 illustrates the hydration states of Na^+ and Cs^+ adopted in calculation, where Na^+ is hydrated by 4 water molecules and Cs^+ by 10 water molecules. Table S1 shows the total energy of hydrated Na^+ and Cs^+.

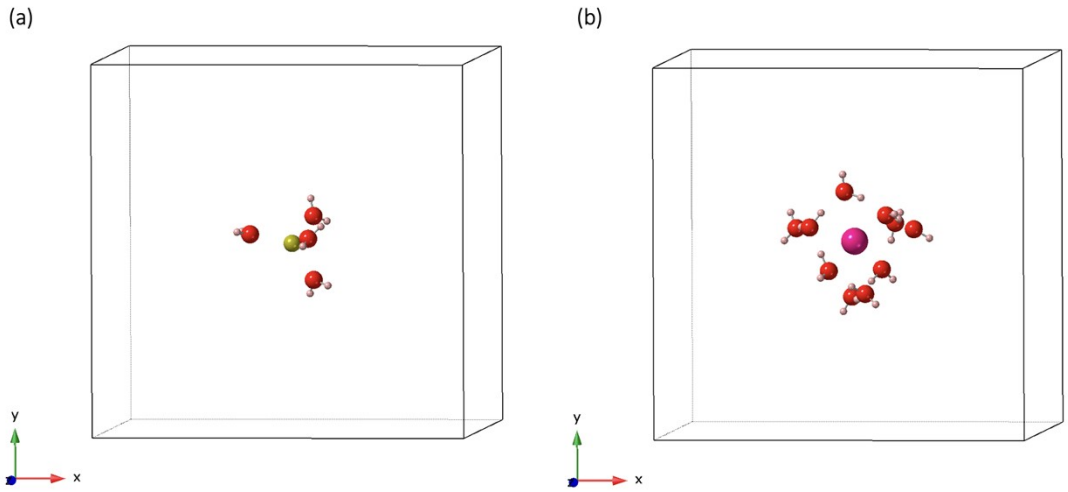

Figure S3: in a 20x20x20 Å vacuum box (a) a Cs^+ coordinated with 10 water molecules, (b) a Na^+ coordinated with 4 water molecules.

For hydrated Li^+, Rb^+ and K^+, the total energy is obtained from the previous group member An, Ta[1], where the water molecule coordination for Li and K is 4[2][3], for larger Rb is 8[4].

Table S1: Total Energy of Hydrated Ions

Ion species	Total Energy(eV)
$(H_2O)_{17}$	-251.81
Li^+	5.30
Na^+	5.13
K^+	4.29
Rb^+	4.13
Cs^+	3.85
$Li^+.(H2O)_4$	-56.36
$Na^+.(H2O)_4$	-55.27
$K^+.(H2O)_4$	-55.26
$Rb^+.(H2O)_8$	-114.44
$Cs^+.(H2O)_{10}$	-144.93

Reference State of the Water Molecule

Seventeen water molecules are placed disorderly in an 8×8×8 Å vacuum box. The calculated total energy of this water cluster is -251.81eV, averaged to one molecule is -14.85eV.

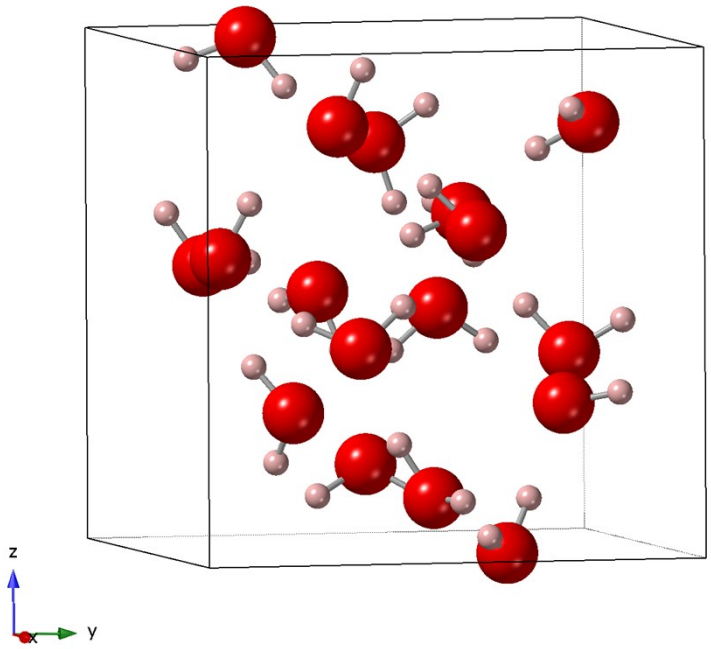

Figure S4: Disordered H_2O cluster in an 8×8×8 Å vacuum box.

Total Energy of analcime system incorporating one ion

Table S2 and S3 are calculated total energy of analcime containing one Al and one ion by DFT.

Table S2: Total Energy of NaAlANA containing 1 Al and 1 Na^+

Ion species	Total Energy(eV)
A1	-1150.44
A2	-1150.44
B1	-1150.61
B2	-1150.61
C1	-1150.62
C2	-1150.62
C3	-1150.62
C4	-1150.62

Table S3: Total Energy of CsAlANA containing 1Al and 1 Cs^+

Al position	Total Energy(eV)
Type I	-1152.60
	-1152.60
	-1152.60
	-1152.60
	-1152.60
	-1152.60
Type II	-1152.67
	-1152.67
	-1152.67
Type III	-1152.75
	-1152.75
	-1152.75
	-1152.75
	-1152.75
	-1152.75

The calculated total energy of charged system $AlANA^-$ is -1144.66eV. Introducing an Al will also bring a negative charge defect, and to compensate the charge state, the background charge is reduced by one in DFT calculation.

Total Energy and Exchange Energy of Li^+, K^+ and Rb^+

Since Na^+ and Cs^+ relative energies reflect the symmetry of 8-member rings and cavities. For other species Li^+, K^+ and Rb^+, only one site for each type of Al site is calculated. Tables S4 and S5 gives total energy and exchange energy of Li^+, K^+ and Rb^+, where K^+ and Rb^+ follow same order of energy with Cs+, but for Li^+, different from Na^+, Al at B site has more negative value than Al at C site. The exchange energy of Li^+ and K^+ with Na has positive values, which means the exchange process is not thermodynamically feasible.

Table S4: Total energy for ions at different Al positions

Ion species	Al position	Total Energy(eV)
Li	A	-1151.45
	B	-1151.88
	C	-1151.73
K	I	-1150.66
	II	-1150.78
	III	-1150.85
Rb	I	-1150.86
	II	-1151.99
	III	-1150.04

Table S5: Exchange energy of ions with Na^+ at different Al positions

Al position		Exchange Energy(eV)
LiAlANA(A)	NaAlANA(A)	0.56
LiAlANA(B)	NaAlANA(B)	0.30
LiAlANA(C)	NaAlANA(C)	0.46
KAlANA(I)	NaAlANA(C)	0.43
KAlANA(II)	NaAlANA(C)	0.31
KAlANA(III)	NaAlANA(A)	0.06
KAlANA(III)	NaAlANA(B)	0.23
RbAlANA(I)	NaAlANA(C)	0.01
RbAlANA(II)	NaAlANA(C)	-0.11
RbAlANA(III)	NaAlANA(A)	-0.34
RbAlANA(III)	NaAlANA(B)	-0.17

Migration Energy

Depending on Al position, the NEB profile maybe unsymmetrical. Here, more migration paths are presented.

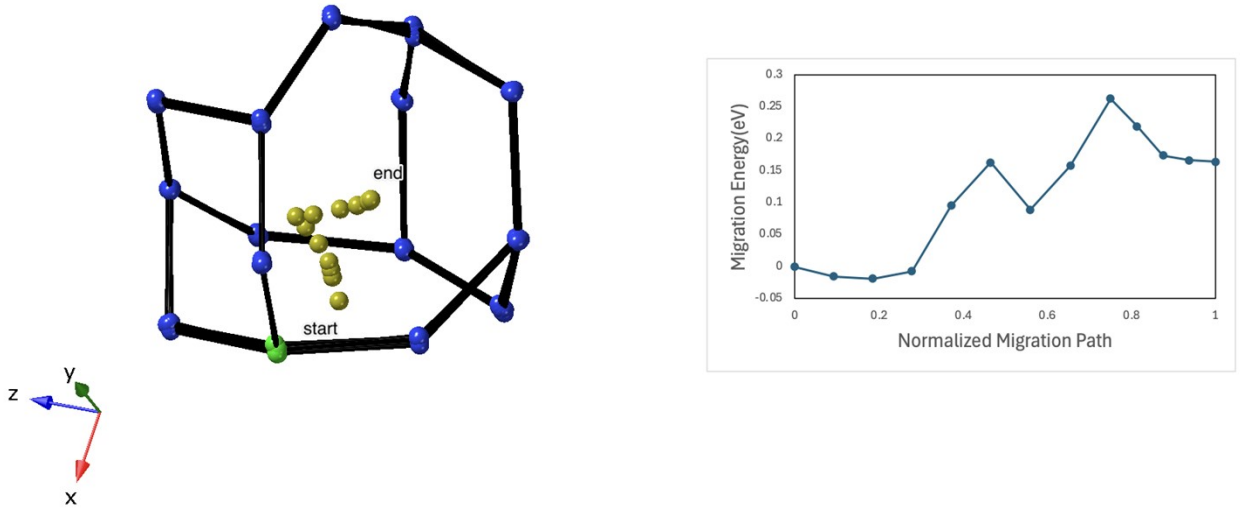

Figure S5: Migration energy profile for Na^+, where Al is at B site for initial 8-member ring and A site for ending 8-member ring.

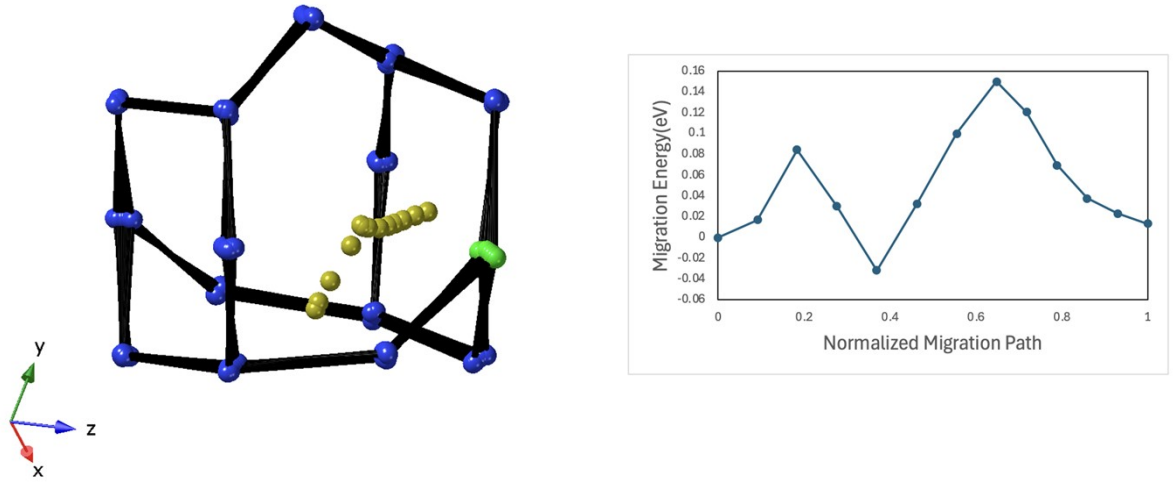

Figure S6: Migration energy profile for Na^+, where Al is at A site for initial 8-member ring and ends at 6-member ring.

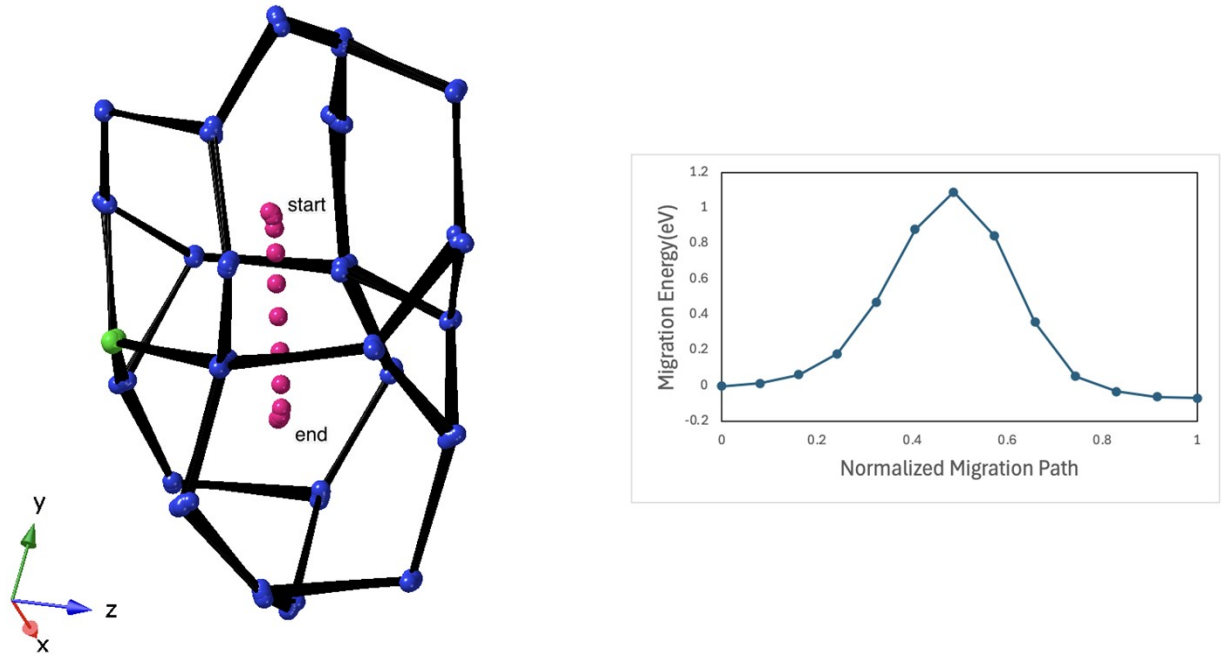

Figure S7: Migration energy profile for Cs^+ through 8-member ring channel, where Al is at I site for initial cage and III site for ending ring.

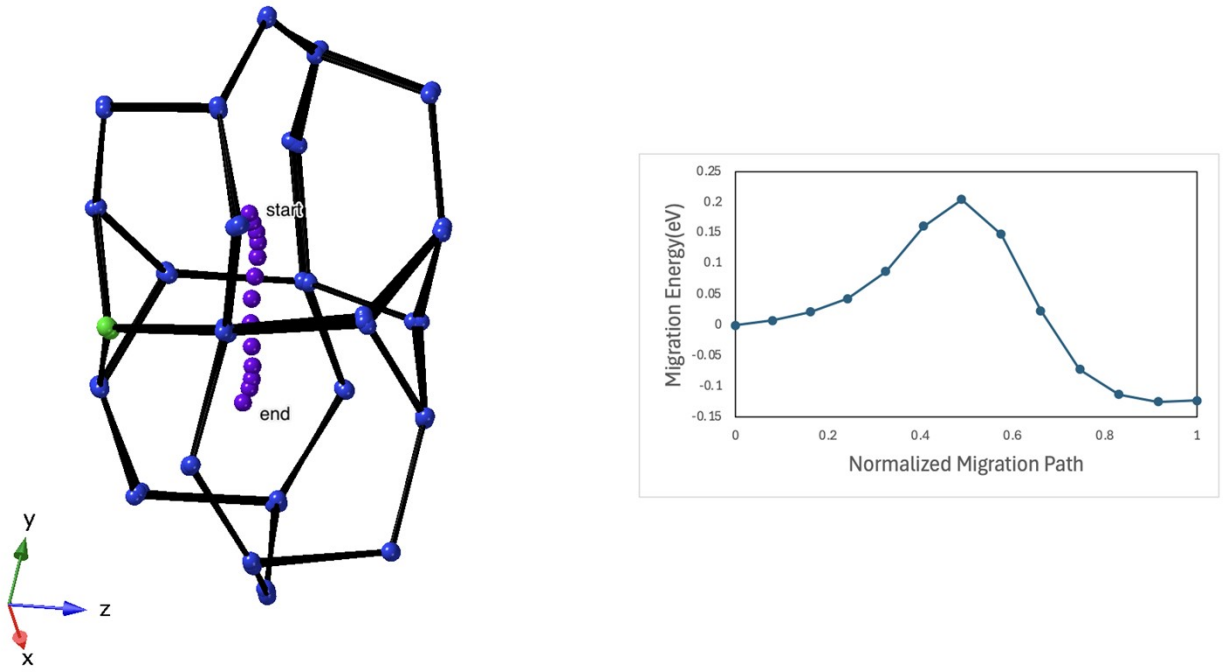

Figure S8: Migration energy profile for K^+ through 8-member ring channel, where Al is at I site for initial cage and III site for ending ring.

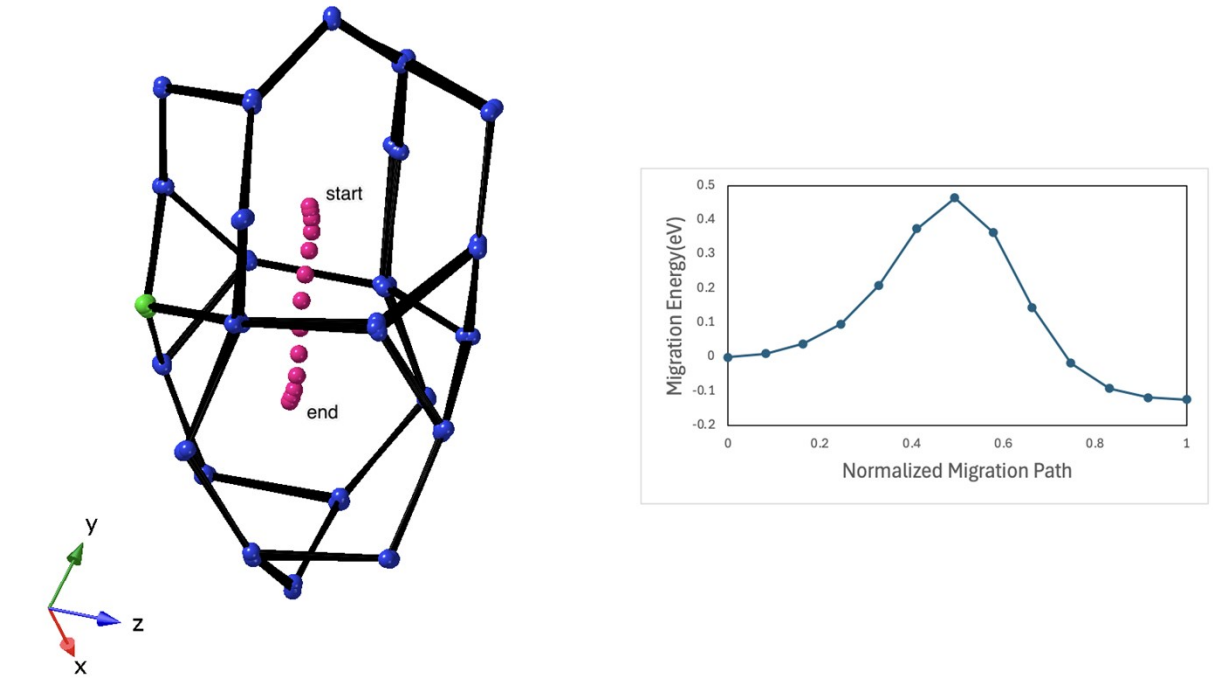

Figure S9: Migration energy profile for Rb^+ through 8-member ring channel, where Al is at I site for initial cage and III site for ending ring.

References

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[4] Caralampio, D. Z.; Martínez, J. M.; Pappalardo, R. R.; Marcos, E. S. The Hydration Structure of the Heavy-Alkalines Rb^+ and Cs^+ through Molecular Dynamics and X-Ray Absorption Spectroscopy: Surface Clusters and Eccentricity. Phys. Chem. Chem. Phys. 2017, 19, 28993–29004. DOI: 10.1039/c7cp05346k.