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Activation energy barriers for Na migration in Na₁₂A zeolite: the main contribution to ionic current via doubly occupied NaII site?

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Abstract.

The activation barriers for Na jumps between the cationic sites NaI, NaII, and NaIII are calculated using VASP in the presence of anions (Cl⁻, Br⁻) or H₂O as well as for the empty Na₁₂A zeolite model. The inter-cage cationic NaIII \rightarrow NaIII' \rightarrow NaIII' path, where NaIII' is located in the neighbor α -cage, was modeled *via* an intermediate state (NaII') corresponding to two NaII cations in one 8R window. This NaII' point can also serve as an intermediate for the second type of intra-cage Na drift, *i.e.*, to a NaIII site in the same cage. Reasonable agreement with experimental activation energy was achieved for NaII' \rightarrow NaIII', NaII \rightarrow NaIII, and NaIII \rightarrow NaIII jumps. The lower activation energy is obtained for the NaII' \rightarrow NaIII' jump than for NaII \rightarrow NaIII, which indicates the possible role of the doubly occupied 8R window as an intermediate state in the Na transfer with high frequency and lower activation energy related to ionic current (intercage transfer) in Na₁₂A.

1. Introduction

The charge transfer by cations in various batteries is one of the important processes, the understanding of which is necessary for the development of a new generation of current sources. This complex task often requires theoretical pre-selection between diffusion profiles in the crystalline media with the spatial symmetry that changes during the cation transfer [1–3]. The best electrode candidate can be selected on the basis of tiny differences of 0.1-0.2 eV in calculated barriers of Na-diffusion [2]. The accuracy of the computational approach has not been profoundly tested. The verification of computational tools can pass through a solution for simpler systems, which are also important for understanding the catalytic activity of alkali cations. Because of the lower cation coordination at the sites with lower binding energies, its reactivity is enhanced at least for some reactions in zeolites. As an example, cationic diffusion was demonstrated as the reason of poisoning effect on cracking reactions [4]. The domination of

alkali cations in the concurrence for framework oxygen atoms (relative to protons) leads to a lower rate at the limiting step of extra framework aluminum formation assigned to the transformation between the $AlOH^{2+}$ and $Al(OH)_2$ in zeolites [4].

Stimulated drift of cations in zeolites was thoroughly studied experimentally [5–22]. In the absence of adsorbed molecules and anions (or when the anions are fixed) it allowed assigning separate dielectric losses in alternating current experiments to cationic transitions between definite sites [5,21]. For these Na jumps two processes with activation energies from 0.46 [16] to 0.61 eV [15] for the high frequency peak and from 0.62±0.02 [21] to 0.90±0.02 eV [5] for the low frequency peak were observed, respectively (more data presented in Table 1). Understanding of the two types of the high and low dielectric spectroscopy frequency processes (HF and LF) with lower and higher activation energies, respectively, is a general problem of cationic conductivity in the zeolites. They were measured in many cationic forms using impedance spectroscopy [10,14,17,21], mono-frequency dielectric measurements [5-9,13,15,16,22,23]. Both transitions are connected with cationic movement, but it is difficult to assign one of the transitions to ionic conductivity [22]. For the case of NaX and NaY zeolites, only analogous LF drift of Na was considered as the main contribution to the ionic current [10,24]. Some possible influences on the processes were already distinguished such as a minor role of the grain boundary effects [12]. Despite of tentative assignment of the cationic SII-SIII-SIII'-SII' movements (as HF peak, with SII and SII' in the same cage) and SII-SIII-SII' movements (as LF peak, with SII and SII' in the neighbor cages) in faujasites, to definite both HF and LF processes, respectively [10,12,13,23], such results were not interpreted at the microscopic level for either NaA, NaX or NaY to our best knowledge. Fundamental importance of respective explanation originates from the correct presentation of the zeolite charge distribution and its reaction on the cationic drift.

Any assignment becomes more complicated in the presence of particles, which can form stable complexes with cations and thus can change the parameters of ionic migration processes. Different influences of neutral molecules were estimated for cation's drift with NH_3 [6,9], SO_2 [9], C_6H_6 [18], $(CH_3)_2CO$ [18], and CO_2 [9] on $Na_{12}A$ (or simply NaA below) [6], Ca_4Na_4A [9] and LiX [18]. Experimental data for the transitions in zeolites allow us to define the role of adsorbed neutral species for the cation's migration.

Vice versa, the distribution of the Na cations is often of prime importance for the passage of adsorbed species [25]. The authors of ref. [25] considered the situation when two types (Na and K) alkali cations populate the cell. The possibility of gas passage is explained by a better K trapping at available SII and SIII sites so that it does not allow the passage of adsorbed molecules in the selected cationic configurations (K cations occupy the 8R window and nearest 4R sites which prevent cationic motion and gas passage through the 8R) [25]. In another work [26], it was concluded that the interaction of cations with CO₂ molecules plays a key role for gas penetration through 8R windows in narrow pore zeolites. Otherwise, some computational attempts to check the diffusion profiles at fixed coordinates of a part of the system were undertaken to estimate the extent of the pore opening in narrow pore zeolites [27]. The use of frozen coordinates makes the obtained data rather arbitrary and less reliable. A stimulation of the pore opening owing to the interaction of a cation with carbonate or hydrocarbonate anions was later shown using both static models [28] and AIMD in the NaKA zeolite [29]. The authors of ref. [29] demonstrated the drift of K^+ cation from the II site in 8R window and hence the ease of cationic jumps. The local minimum for K^+ -CO₃²-complex was previously found outside the 8R plane in narrow pore NaKA by "static" optimizations [28], thus confirming long cationic drifts obtained in narrow pore [28-30] and wide pore [31-34] zeolites. Facilitation of the heavier cation diffusion in wide pore Y zeolites allowed explaining the most intensive IR spectra of CsY together with the specific dependency of the heat of CO₂ adsorption in CsY [32]. But in all these works [25–29,33,34] no diffusion barrier of the alkali cation was calculated to be compared with available experimental data.

Herein, the barriers of Na diffusion will be calculated in sodium form of Linde type A (LTA) or NaA zeolite (Si/Al = 1) in the presence of the anions (Cl⁻, Br⁻) and H₂O molecule. Water remains a candidate for safe and cheap media for electrolyte in future Na-batteries [35,36]. After presenting the computational method and models (part 2), the cationic transitions will be analyzed below (part 3.1), then the barriers will be calculated including the route to new intermediate state which is important for both inter- and intra-cage Na diffusion (part 3.2) considering the addition of NaCl or NaBr salts (part 3.3) and water (part 3.4). The main result of the work is interpreted in the first part of Discussions (part 4).

2. Computational details

Pseudo-unit 2- α -cage cell (Fig. 1a) of fully dehydrated Na₁₂A with the total content Na₂₄Al₂₄Si₂₄O₉₆ (pseudo-NaA) was first induced for KNa₂₃Al₂₄Si₂₄O₉₆ zeolite [28] and later used in some works [27,28,37]. This model allows to replace the full correct Na₉₆Al₉₆Si₉₆O₃₈₄ model containing 8 α -cages [38] (Fig. 1b) and, thus, reduce computational costs¹. But the violation of the periodicity leads to a formation of forbidden Al–O–Al connections at the common sides of its 6R+4R fragments (shown by filled ellipses in Fig. 1b) while the main part of the reduced model is constructed *via* Si–O–Al species. A proper selection permits the calculations in the middle 8R relatively far from the defects. Earlier, the thermodynamic character [39] of the Loewenstein rule, which forbids the Al–O–Al alternation [40], was demonstrated so that these models can be applied for a comparative analysis within one analogous series.

Plane wave computations with the periodic boundary conditions using traditional PBE [41] functional with and without D2 [42] and D3 [43] dispersive corrections within the projector augmented wave (PAW) method [44,45] were performed with VASP [46,47] for non-spin

¹ Respective time evaluation for a smaller MOF model (CuBTC with 624 atoms/unit cell (UC)) showed nearly 2 hours 30 minutes per single point energy calculation using 96 processors of Lomonosov supercomputer [71]. For a full UC of the Na₁₂A (672 atoms) NEB calculations, which require the simultaneous optimization of several configurations, become too computationally expensive.

polarized systems. VASP developers recommend using Na pv pseudopotential (where semi-core states are treated as valence states) for Na but standard (named "Na") pseudopotential was also tested. For calculating the minimum energy path between the initial and final optimized geometries, corresponding to the beginning and end of Na jump, we used the climbing image nudged elastic band (ciNEB) method [48]. In this method, a number of intermediate images (replicas) are simultaneously optimized along the reaction path. Each image finds the lowest energy possible while maintaining equal spacing to neighboring replicas. The search of reaction coordinate corresponds to the determination of atomic coordinates in each replica when the forces applied to their atoms are minimal with required accuracy. The energy cut-off (ENCUT) was set to 500 eV. Precision corresponded to "Normal" level was used which defines the orbital representation in both direct and reciprocal spaces. The Brillouin zone k-sampling was restricted to the Γ -point for the geometry optimization. The diffusion picture was visualized by simultaneous drawing of the initial state, transition states, and final geometries for diffusing the cation (and some closest NaII and NaI cations) in one Figure 2 using MOLDRAW [49]. The application of the NaA model with a single water molecule is justified by the ²³Na NMR data which showed that the remaining water binds to NaII and NaIII cations at low hydration [50] in agreement with the lower binding energies for these cations thus possessing a lower coordination [51] and synchrotron powder diffraction [52]. The highest electric field, which is important for water adsorption, at the directions towards these NaIII or NaII cations were shown by Cohen de Lara and Ngyen Tan [53]. In order to study anion influence a "cation-anion" pair (NaCl or NaBr) was added to keep the neutrality of the system. The starting selection of the anion position was based on the geometry optimization closely to the less coordinated NaII and NaIII cations.

The experimental data about Na jumps in three types of Na-forms (NaA, NaX, NaSOD) are discussed below. The application of the *Fd3* space group for NaX allows to use a reduced unit cell with the Na₂₄Al₂₄Si₂₄O₉₆ formula [54]. Respective unit includes two supercages connected *via* 12R window (Fig. 1e, S1c). Two types of the NaII (near 6R windows) and NaIII

(near 4R windows) cations are of interest for our goal while the NaI and NaI' types in the double prisms are not shown for simplicity (Fig. 1e, S1c). The small size NaSOD zeolite (general view of $3\times3\times3$ fragment is in Fig. S1b) with the Na₆Al₆Si₆O₂₄ formula consists of closely packed βcages with 4 Na cations of one type (Fig. 1d).

3. Results

3.1 Assignment of the transitions

First, we select cationic transitions that should be calculated as the most probable for comparison with the experiment. For this, we address to the dielectric losses in two close Na₁₂A and Ca₁Na₁₀A zeolites [5]. Absence of the NaIII cations in the Ca₁Na₁₀A case led to disappearance of the HF transition with lower activation energy (~48 kJ/mol = 0.5 eV), while the transition with higher activation energy (87 kJ/mol = 0.90 eV) remains in Ca₁Na₁₀A corresponding to the similar bands observed for the LTA and ZK-4 forms with NaII cations (Table 1). Such behavior can be probably explained by the participation of NaIII which possesses lower activation energy. Comparison with the ionic current in alkali MeX and MeY faujasites [10–13,23] leads to the same conclusion that MeIII cations (coordinated to 4R window) participate in the HF transitions with lower activation energy. The similarity between inter-cage jumps in NaX (Fig. 1e, S1c) and NaA (Fig. 2a-b) through 12R and 8R windows, respectively, which separate two supercages in NaX (Fig. 1e, S1c) and two α -cages in NaA (Fig. 1a-b).

Additional tip comes from the molecular dynamics (MD) modeling at 298 K of the binding energies in two different works (-8.3 \pm 0.4, -7.3 \pm 0.4, and -6.5 \pm 0.4 eV/atom [51] or - 1.68 \pm 0.06, -1.21 \pm 0.05, and -1.06 \pm 0.05 eV/atom [55] for NaI, NaII, and NaIII, respectively) which gave two extreme boundaries because of the Na charge +1 [51] and 0.55 e [55], respectively. As the barrier should exceed the heat Δ U, the barriers for the NaI \rightarrow NaIII and

NaII \rightarrow NaIII jumps cannot be smaller than 1.8 and 1.0 eV [51] or 0.62 and 0.15 eV [55], respectively. The extreme character of both estimated heats is confirmed by the fact that neither the major (1.8 eV), nor the minor (0.15 eV) barriers were observed in any experiments with dehydrated NaA (Table 1) (a short discussion is in the part 4). These estimates do not impose any limits on the barriers for the NaIII \rightarrow NaIII transitions. By unifying the data we could first evaluate the Δ U values for the NaI \rightarrow NaIII and NaII \rightarrow NaIII transitions.

The two types of Na jumps were modeled herein from 6R to free 4R site (I \rightarrow III) and from 8R to free 4R site (II \rightarrow III) positions. This attempt to involve the (I \rightarrow III) jumps showed larger barriers between 1.18 and 1.34 eV (the smaller E[#] of 1.18 eV is for a jump in a favorable direction far from the closest NaIII and NaII cations). The latter are close to the barriers observed in β -cage of dehydrated NaSOD zeolites with rather small unit cell (UC) and hence evident spatial restrictions for Na jumps between 6R sites in β -cage (1.16 eV) [17]. These two E[#] values underestimate the $\Delta U = 1.8 \pm 0.4$ eV after modeling of the binding NaI and NaIII energies in NaA using q(Na) = 1 e [51], but nevertheless such large barriers were not measured in dehydrated NaA. The calculated barriers for the (II \rightarrow III) jump of 0.77-0.88 eV possess more realistic values compared to experimental barriers for high energy (II \rightarrow III) transition in NaA (Table 1). As no water relaxation processes happen on dehydrated NaA, we could tentatively assign the low energy experimental transition within the range of 0.46-0.61 eV to the (III \rightarrow III) jumps.

3.2 Intermediate state for inter- and intra-cage Na diffusion

The calculated $E^{\#}$ value for the III-III jump data (0.56-0.66 eV) matches the upper boundary for experimental data (0.46 [16] - 0.61 [15] eV in Table 1) and is in a reasonable agreement (0.77-0.88 eV) with the data for the II-III (0.62-0.90 eV) jumps (both without additional included species or anions in the unit cell). The non-zero ΔU value for the III-III jump (0.35-0.51 eV in Table 1) is a consequence of the removed 8-fold and 12-fold degeneracies of NaII and NaIII positions, respectively (NaII atom shifted from the center of 8R window and NaIII assigned to a unique position SIII in the nearest α -cages), in any NaA group symmetry, either *Pm3m* [56], or *Fm3c* group to differentiate Si and Al atomic positions) [38,57]. As a result of the removed degeneracies, the ΔU value for the III-III jump deviates from zero due to a change of the important cation-cation repulsion emphasized in many works [10,23]. To ascertain this, one could compare the variation of the distances from the NaIII to its two NaII neighbors in the course of the jumps. In the starting geometry of the transfer with two barriers 0.59/0.27 eV (Table 1) the distances from NaIII towards two nearest NaII cations are 5.270 and 5.663 Å, which both shorten to 3.773 and 5.393 Å showing a destabilization of the NaIII at final location. The second reason of the large ΔU for the III-III jump is possibly related to a shifted NaIII position relative to its best equilibrium 4R position. The latter is confirmed by the larger deviation of the Na-O distances in the final geometry (2.395, 2.314, 2.602, 2.718 Å) than in the initial geometry (2.556, 2.409, 2.587, 2.742 Å), geometries relative to the distances obtained for XRD models, *i.e.*, 2×2.47 , 2×2.51 Å with *Pm3m* group [56] or 2×2.59 , 2×2.61 Å for NaIII with more accurate Fm3c group [38]. While two bond lengths for the reagent configuration varied in both directions (-0.181 and 0.132Å relative to those obtained with Fm3c group), three of the distances for the product are distorted stronger (-0.276, -0.195, and 0.108Å), especially regarding the contraction.

All different diffusion profiles for the III \rightarrow III jump showed the two-stage profiles (Fig. 3) which are very important for the charge transfer between the α -cages, providing a contribution to ionic current (Fig. 3). This III \rightarrow III jump passes through an intermediate state while the ciNEB modeling (the 4th or 3rd step in Fig. 3 for closed circles or open circles/squares, respectively, where the number of starting point is 0), when NaIII approaches the 8R plane passing closely above it (NaII' site in Fig. 2h). To distinguish two different ions in one 8R the NaII' notation is assigned to the arriving (former NaIII) cation, while the "old" NaII cation is denoted as NaII"

(both cations are located from different sides of the 8R plane (Fig. 2i). Due to a repulsion from the NaII' or "former NaIII" ([NaII'...NaII"] = 3.631 Å at the PBE/Na_pv level for the case with the barriers of 0.66/0.13 eV in Table 1), the "initial" NaII cation in the same 8R window is transferred to the 3-coordinated intermediate position NaII" ([NaII"-O] = 2.288, 2.307, 2.368Å in Fig. 2h). Two of the three shortest Na"-O distances are shorter than shortest experimental bond of 2.32 Å at the NaI site [38]. (After NaII' passing the 8R window the NaII' returns back to the initial position.). Before getting the NaII' site (Fig. 2h, or point 3 along the diffusion coordinate in Fig. 3) the NaIII overcomes the barrier $E^{\#} = 0.13 - 0.37$ eV (ΔU from -0.10 to 0.22 eV, Table 1). This stable NaII' position is characterized by real frequencies (220, 217, 115 cm⁻¹) which show a slightly more rigid potential (compared to the frequencies of 210, 173, 91 cm⁻¹ for the shifted neighbor NaII'' cation in the same 8R). Finally, it is worth studying which Na of the two NaII' or NaII'' cations is the better candidate for the next jump to a free NaIII' site of the neighbor α-cage.

The next analysis showed similar barriers of 0.33-0.40 eV (Table 1) for both NaII' \rightarrow NaIII' (inter-cage jump through the 8R plane) and NaII' \rightarrow NaIII' jumps (intra-cage jump) which are as much as twice smaller than 0.77-0.88 eV calculated for the conventional NaII \rightarrow NaIII jump (Fig. 2j). It can signify that the NaII' state is the point for cationic jumps in both directions inside or between the cages. The second Na route between the cages is the contribution to ionic current which is thus predicted for low energy (0.40 eV) and high frequency transition. This variety of the cationic motions in Table 1 does not contradict the literature data where three types of Na transfer were recorded in Na₁₂A, whose activation energies were not calculated due to overlapped regions in the spectra of dielectric loss tangent [5].

A possibility of such quasi-stable state (two NaII' and NaII'' cations in one 8R window) was proposed by Ohgushi [58] to develop the kinetic model (see part 4. Discussion). Our optimization shows on the stable intermediate located slightly above (NaII') and below (NaII'') the 8R plane (Fig. 2i) with the distances |NaII'-O|= 2.286, 2.308, 2.435Å (in Fig. 2h for the case

with $E^{\#} = 0.66/0.13$ eV in Table 1). This result confirms the stable model with two Na in one 8R plane [58] while the SI site with two Na nearby [58] was not found by us.

3.3 Influence of the anions

The important question of cationic transport is related to the separate or concert motions of a Na cation and an anion during a cationic jump which is important, for example in sodium batteries with solvent electrolyte [1–3]. The drift of NaIII and both Cl⁻ (Fig. 2e, f) and Br⁻ (Fig. 2c, d) anions is illustrated by three positions per atom at three steps (initial, transition state, final in Fig. 2) as well as three similar points for the NaI and NaII atoms, which are closest to the NaIII trajectory, while other framework atoms are considered as coinciding ones. Due to the fixed cell parameters, disregarding the minor changes of other framework atoms does not corrupt the picture (Figure 2). In one case (Fig. 2g, h) the intermediate position (NaII') of the NaIII is also shown. The distances between the atomic positions in the initial and final geometries are accumulated in Table 2.

This trajectory with the NaII' position close to 8R plane is similarly reproduced in the presence of Cl⁻ anions (Fig. 4a) with the longer NaIII...NaII distance (3.865 Å at the NaII' point with PBE/Na_pv). The decrease of the activation barrier for intra-cage Na diffusion between 6R sites within NaSOD sodalite (Figs.1d, S1b) was estimated experimentally from 1.15 to 0.78 eV (or -32 %) upon Cl⁻ found in the center of the small β -cage (Cl⁻ position is shown by arrow in Fig.1d) [17] compared to larger drop of -52 % from 0.65 to 0.31 eV herein (for one Cl⁻/cell with two α -cages). This simultaneous drift of Na and anion is in agreement with the cationic drift in the zeolites with a carbonate or hydrocarbonate in the cell [28–34]. A smaller amplitude of anionic drift is illustrated compared to Na displacements in Fig. S2a-d. The sum of the distances between the NaIII atomic positions with NaII' intermediate (3.058 + 3.084 = 6.142 Å in Table 2)

even exceeds the length of 5.3 Å used for the computation of conductivity of NaA at the absence of other species [6].

Important differences are observed for the III-III jump trajectories when Br⁻ anion is induced in the cell instead of Cl⁻, or compared to that in the empty cell. The amplitude of the anion motions decreases from Cl⁻ (Fig. 2e, f) to Br⁻ (Fig. 2c, d) being more hindered spatially. While the total cation drift with Br⁻ is slightly shorter (2.652 + 2.928 = 5.580 Å compared to 6.142 Å for Cl⁻), no intermediate NaII⁺ position is obtained (one TS only). A lower activation barrier in the presence of Br⁻ (Fig. 4b) than of Cl⁻ (Fig. 4a) was obtained (Table 1), being in opposite ratio between the electro-conductivity barriers after Br⁻ or Cl⁻ additions to NaSOD zeolite shown by impedance spectroscopy [17]. It can be easily explained due to the steric hindrance for the Na jumps between the NaI⁺ positions at the 6R windows of the smaller β -cage also occupied by bulky Br⁻ in NaSOD (Fig. 1d). With both Na pseudopotentials one obtained the switch of Br⁻ coordination from NaI (3.018 with Na PP or 3.020 Å with Na_pv PP) to NaII nearby (2.872 or 2.865 Å, respectively) at the final state (the NaII – Br⁻ pair is shown by dashed line in Fig. 2d). The Br-NaIII distance varies very little in the course of the Na drift (2.678 or 2.668 Å, respectively).

3.4 Influence of water

The main difference between the drift of an anion (Br⁻, Cl⁻) and of water in the course of a NaIII-NaIII transfer is the minimal barrier (0.27 eV at the PBE-D3/Na level) at the nearly immobile water (Table 1) as compared to the parallel diffusion of H₂O together with NaIII⁺. The heat of the diffusion is nearly the same (0.14 eV compared to 0.09-0.15 eV) because water coordinates tightly to NaI (2.439Å) with rather weak hydrogen bonds (|O...H| = 2.853, 2.972 Å). The parallel Na migration together with one H₂O increases activation energy up to 0.35-0.52 eV depending on the computational level (Fig. 4c). One of the trajectories (PBE-D2/Na, open squares in Fig. 4c) possesses two transition states being close in the energies which relate to the switch of water proton between three framework O atoms belonging to one 6R window, *i.e.*, $|H2...O90|=1.946 \text{ Å} \rightarrow |H1...O43|=1.994 \text{ Å} \rightarrow |H1...O98|=2.023 \text{ Å}$ (similarly to the changes of hydrogen bonds in Fig. 2a, b). The hydrogen bond with the middle O43 atom of the three oxygens results in a lower energy and an intermediate state. Respective water displacement together with the NaIII cation is as large as for Cl⁻ drift, while the shift of the NaIII is shorter being similar to the Br⁻ case (Table 2). Also as for Br⁻, no NaII' geometry was obtained at the 8R window. The data for very low water coverage are rather rare as 1.2 and 2.5 H₂O/cell in NaA [15]. The calculated decrease from 0.65 to 0.35 eV (for one H₂O/cell with two α -cages) is more emphasized than one could evaluate from a known experiment from 0.61 to 0.43 eV (for 1.2 H₂O/cell with one α -cage [15]) (Table 2). However, the data about quantitative changes are contradictive. For example, a weak change of both barriers was shown within the domain of small coverage from 0 to 4 H₂O/cell in NaA [7]. Some discussion is also present in the part 4.

4. Discussion

The stable NaII' state closely to the 8R plane offers us a route for ionic conductivity with Na transfer between neighbor α -cages. The second (larger) barrier of 0.56-0.66 eV (Table 1) at the NaIII-NaIII direction corresponds to the process, when NaIII remains in the same α -cage. It describes local Na motions within one cage which do not contribute to measured ionic current. But its first step could lead to the NaII' intermediate state before passage to a neighbor α -cage. Then the two-step NaIII-NaIII' naIII' process, where NaIII' is in another α -cage, is characterized by the smaller activation $E^{\#} = 0.13-0.37$ eV (Δ U from -0.10 to 0.22eV) at the first step and higher activation (and LF) barriers at the second one (0.33-0.34 eV for NaII'-NaIII', 0.40 eV for NaII' – NaIII', 0.56-0.66eV for NaII' – NaIII in Table 1). Any of the second stages

is nevertheless favored compared to the NaII - NaIII jump with the barrier around 0.85-0.88 eV (Table 1) irrespective of the NaII' or NaII' cation in the doubly occupied 8R site.

An influence of water addition on the activation energy was earlier evaluated by Stamires as a linear function relative to the number of molecules per cell [6]. Similar slopes of the electroconductivity with coverage was observed between 25 and 100°C from 0 to 5-6 water molecules per one unit cell of NaA which includes one α -cage (*Pm3m* group). At the limit of high water coverage the difference between hydrated NaIII and NaII becomes rather small according to modeling [59] so that the observation of only one type of Na jump related to conductivity looks to be very realistic together with two relaxation processes related to water re-orientation [60]. Later, two (high and low frequency) peaks in the dielectric losses spectra were observed in fully hydrated NaA, but the smaller HF barrier value of 0.16 eV [61] could come from the water relaxation processes [60].

A decrease of the barrier and a growth of the conductivity σ with water coverage(Θ) is in agreement with many sources [6,7,16,62]. More complex behavior was demonstrated in ref. [15] even if it was determined simply as a "decrease of the conductivity σ with Θ " (σ grows with Θ for the first step of 1.2 H₂O/cell of NaA and then falls at 2.5 H₂O/cell) [15]. Similar σ -slope towards the H₂O coverage conserves within the wide range of the temperatures (298-373 K) [6]. An important difference of hydrated NaA compared to hydrated NaX is a decrease in the σ (Θ) slope at 6 H₂O/cell of NaA where the cell contains one α -cage (Pm3m group) [6]. The second change of the σ (Θ) slope (from lower to a higher value at 298 K only) corresponds to 16 H₂O/cell [6]. Later work by Morris *et al.* showed instead of a lower slope a nearly constant behavior of the conductivity and, hence, of the activation energy in the range between 7 and 21.2 H₂O/cell in NaA [62]. As a conclusion from these two passages one can believe that the calculated decrease of the activation barrier with water coverage increase is qualitatively correct.

An important result of our study is that nearly immobile water could be more effective at lowering the barrier than water moving together with the cation between the NaIII sites. To describe this case, the analogy of a traveller (Na⁺) without luggage (H₂O) seems to suit perfectly. It would be possible to suggest a possible unified effect of water together with the Cl⁻ and Br⁻ anions. Water can hinder the ionic "Na-anion" attraction in the same way as water weakens the coordination of alkali cations to zeolite anionic framework thus decreasing the bulk and Young moduli of alkali forms [63]. So, water will compete for the cations with the framework oxygens, Cl⁻ or Br⁻ anions. It can moderate the influence of the anion even if the resulting barrier will be nevertheless lower than in dehydrated zeolite (without water or Cl⁻ or Br⁻ anions). The decrease of the barriers for Na drift due to other anions (carbonates) in the zeolites was indirectly confirmed by long displacements of the cations [31,33,64]. We believe that such result is associated with small water coverage, since the shielding of all electrostatic interactions at high coverage will compensate for the addition of halogen anions.

Above (part 3.1) we addressed the MD calculated binding energies, *i.e.*, -8.3 \pm 0.4, -7.3 \pm 0.4, and -6.5 \pm 0.4 eV/atom [51] or -1.68 \pm 0.06, -1.21 \pm 0.05, and -1.06 \pm 0.05 eV/atom [55] for NaI, NaII, and NaIII, respectively. They provide two extreme estimates for the barriers of the Na jumps because of the choice of effective Na charge for modeling from +1 [51] to +0.55 e [55]. Respective Na charge values are extreme boundaries as confirmed by our DFT modeling of the charge distributions in Na-zeolites. The Mulliken Na charges vary within 0.852-0.666 e for NaNAT at the B3LYP level with a series of basis sets [65], while Bader charges are within 0.87-0.88 *e* at NaI positions in CuNaX [66]. The values of 1.0-0.9 *e*, which are closer to the choice of ref. [13], were evaluated fitting the band shifts of fundamental vibrational transitions in adsorbed H₂/Na₁₂A [67] or CO/NaY [68]. Smaller Na charges (0.5 and 0.6 *e*) were applied to model the CO/Na₄Ca₄A spectra [69], but: 1) CO interaction with Ca cation plays the main role in the CO band shift; 2) these small q(Na) values resulted in extremely high Al and Si charges to be in agreement with experimental data. So, our experience shows that the range 0.9-0.7 e is more reliable for the Na charge.

The idea of a two-cation position in one 8R window was adopted herein from the kinetic model elaborated for cationic population by one type of the cations (Na) of the SI, SII, and SIII sites in NaA [58]. The redistribution is realized *via* a series of Na jumps with finite activation barriers. Two types of the processes were recorded experimentally and assigned to Na jumps, *i.e.*, high and low energy peaks in the dielectric losses in dehydrated LTA samples [5,21]. This scheme admitted the possibility of a stable intermediate state of two cations at one site (both 8R or 6R) and considered reciprocal jumps between two neighbor 4R and 8R sites (SIII \leftrightarrow SII') or 4R and 6R sites (SIII \leftrightarrow SI') [58]. The configurations SII' of the respective final transition states for two Na cations at one 8R site (Figure 3b in ref. [58]) were confirmed herein ([NaII'...NaII''] \sim 3.6 Å) and used, while such a possibility of SI' geometry for 6R site (Figure 4b in ref. [58]) requires further verification. Such possibility seems to be less probable because the similar minimal distance \sim 3.6 Å was also observed for the closest NaI...NaIII ions. So, the second Na ion at the 6R window will be probably shifted to another crystallographic Na position.

Important restriction for simplified kinetic modeling for Na exchange [58], which suggests a degeneracy of the Na sites of one type, is determined by the measure of the avoided degeneracy of NaII or NaIII. For NaA it is also one of the reasons why the cation-cation repulsion is important for cationic drift [10,13,14,23]. We mentioned above (part 3.2) one reason, *i.e.*, deleted degeneracy, coming from the asymmetric NaII and NaIII positions. This effect is as important within one α -cage, as within long-range. An unique NaIII cation per each neighboring α -cage occupies one of 12-fold degenerate SIII site thus creating a difference in the electric field and its derivatives at the sites of the central α -cage, so that the difference is essential for the cation stabilization [70]. It was illustrated by the variation of NaIII cationic location in only six nearest α -cages around the central one that resulted in the valuable change of the optimized ionicity of the NaA system increasing with Na charge (Tables 5, 6 in ref. [70]). It also demonstrates that the electric field and its derivatives at the central α -cage produced by NaIII cations in six nearest α -cages possesses the values which are sufficiently large to split the

energies of the degenerated Na states of one type (the respective change of electrostatic potential was not estimated therein).

No one suggests that the absence of NaII' state in the presence of Br⁻ or water definitely forbids the inter-cage Na transport *via* 2-time occupied 8R site. In such a case the minimum of the NaII' intermediate can be located in a shifted position so that careful scanning of the sites, being nearest to the opposite end if diagonal relative to already presented NaII, is required.

5. Conclusions

The route for inter-cage Na transfer is proposed using the stable intermediate site at which two non-equivalent NaII' and NaII' cations occupy one 8R window as was first proposed by Ohgushi. The first stage of two-step NaIII-NaII'-NaIII' process in NaA, where NaIII' is in another α -cage compared to the initial NaIII site, is characterized by a small activation $E^{\#} = 0.13$ -0.37eV. This first step leads to the location of NaII" and NaII' cations in a doubly occupied 8R window being both reciprocally destabilized. The latter is the reason for lower barriers for both the NaII" and NaII' jumps relative to the value of 0.77-0.88 eV computed for the jump between conventional NaII and NaIII sites, *i.e.*, 0.33-0.34 eV for NaII"-NaIII' intra-cage jump, or 0.40 eV for NaII'-NaIII' inter-cage jump. This destabilization is also the reason of non-symmetric NaII' routes for leaving from (0.40 eV for NaII'-NaIII') and remaining in (0.56-0.65 eV for NaII'-NaIII at the second stage) the same cage. The intermediate NaII' position was also found when Cl⁻ is added to the cell but not for Br⁻ or H₂O. Both anions and water led to a decrease of the activation barriers for NaIII transfer. After water addition the maximal decrease of the barrier was achieved for isolated NaIII motion (without a water molecule which coordinates to/at a closest NaI cation). The activation barriers around of 0.40 eV (inter-cage) or 0.33-0.34 eV (intracage) are smaller than measured barriers 0.46-0.61eV for high frequency peaks. The agreement is better for calculated barriers of 0.85-0.88 eV relative to experimental ones between 0.62 and 0.90 eV for low frequency peaks. One should note that the calculated value can vary slightly due to another asymmetric distribution of neighbor NaII and NaIII cations between degenerated positions in the nearest cells. The assignment of the (NaI \rightarrow NaIII) transitions to high energy and LF band in dielectric loss spectra was discriminated comparing to the calculated large barrier. All the steps above were modeled at the PBE-D3, PBE-D2, or PBE/PAW levels using two different pseudopotentials for Na resulting in the close barriers (within 0.02 eV) with the minimal values at the PBE-D3/PAW level.

Supplementary Electronic Materials

The materials contain additional Figures S1a-c with general views of Na, NaSOD, NaX zeolites, Figures S2a-d (copies of the Figs. 2c-f) with the anionic positions along the reaction coordinates, input files in POSCAR format for the reagents, transition states, intermediates (if any), and products (POSCARS.zip).

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Table 1. The activation energy $E^{\#}(eV)$ and heat $\Delta U(eV)$ of the Na jumps between two nearest 4R windows (III \rightarrow III) and from 8R or 6R to 4R windows (II \rightarrow III or I \rightarrow III for conventional Na positions and II' \rightarrow III' or II'' \rightarrow III' from double occupied 8R window, where NaII' and NaII'' types relate to the arriving and initial Na atoms in the 8R window, respectively, to NaIII' site which belongs to the neighboring cage) with or without X = Cl⁻, Br⁻ anions, and water (for III \rightarrow III only) calculated with different DFT methods and Na pseudopotentials (Na_PP = Na or Na pv from VASP library) relative to known experimental data for Na₁₂A.

Jump	Х	DFT/Na_PP	ΔU	E [#]
I→III	-	PBE/Na_pv	1.08	1.18
			1.15	1.34
II→III	-	PBE/Na_pv	0.73	0.88
			0.60	0.77
		PBE-D3/Na	0.68	-
		PBE/Na	0.71	0.85
		Exper.	-	0.90 ± 0.02^{a} [5],
				0.74±0.04 [21],
				0.62±0.02 [22]
II'→III'	-	PBE/Na_pv	0.18	0.40
II"→III'	-	PBE/Na_pv	0.20	0.34
		PBE-D3/Na_pv	0.20	0.33
III→III	-	PBE/Na_pv ^{b)}	0.51/0.06	0.65/0.33
			0.44/-0.10	0.66/0.13
		PBE-D3/Na_pv	0.44/0.06	0.59/0.27
		PBE/Na ^{b)}	0.35/0.22	0.56/0.37
		Exper.	-	0.46 [16], 0.50±0.04 [5,22],
				0.54 [18,19,21],
				0.57 [72],
				0.58 [20], 0.61 [15]
	H_2O	PBE-D3/Na_pv	0.09	0.35°)
		PBE/Na_pv	0.11	0.43
		PBE-D2/Na	0.15	0.52 ^{c)}
		PBE-D3/Na	0.14	0.27 ^{d)}
		Exper.	-	0.43^{e} [15], 0.23^{I} [15]
	Cl	PBE/Na_pv ^{b)}	-0.27/0.04	0.31/0.10
		PBE/Na ^{b)}	-0.32/0.04	0.31/0.13
	Br	PBE/Na_pv	-0.20	0.25
		PBE/Na	-0.35	0.16

^{a)} for Ca₁Na₁₀A and 0.94 eV or 0.92 eV for Na₁₁ZK-4 [5]; ^{b)} second value (after slash) corresponds to the first barrier before NaII' site (Fig. 2g-i); ^{c)} Corresponds to 18/(2*1719) = 0.005 g of H₂O/g of zeolite or 0.6 H₂O/UC (the mass of pseudo-cell unit of two α -cages or 2*1719 carb. mass u.); ^{d)}the case without a parallel water drift (H₂O slightly moves to NaI cation); ^{e)} corresponds to 4.6 % of max. filling (0.01321 µmole of H₂O/g of zeolite with lower formula unit of 1719 carb. mass u. for one unit cell [15]) = 0.011 g of H₂O/g of zeolite or 1.2 H₂O/UC (UC possessing *Pm3m* group with a saturation of 27 H₂O/UC); ^{f)} analogically to the footnote (b) corresponds to 9.3 % of maximal filling or 0.022 g of H₂O/g of zeolite or 2.5H₂O/UC [15].

Table 2. The cationic and atomic ($X = Cl^{-}$, Br^{-} , O atom of water) shifts (Å) in the course of Na diffusion in the presence of incorporated anions/water or in an empty zeolite. The lengths are estimated as the differences between the positions of the species in the "reagent" and "product" configurations (Fig. 2)

Туре	III→III			II→III	
	Br⁻	Cl	H ₂ O	empty	empty
NaIII	4.536	2.652/2.928 ^{a)}	4.598	3.058/3.084 ^{a)}	3.322
NaII	0.813	1.322	0.079	0.126	0.199 ^{b)}
NaI	0.327	0.225	0.154	0.209	0.275
Х	1.057	1.801	1.979	-	-

X1.0571.8011.979--a) Two-step process with an intermediate (the NaII' site is shown in Fig.2g, h and not shown for Cl⁻in Fig.2e, f); ^{b)} the displacement of the closest NaI neighbor atom is shown for this case

Table 3. Na…Na and Na…O_w distances along with the NaIIItrajectory without H_2O_w molecule at the PBE-D3/Na level.

State	NaINaIII	NaIIIO _w	NaIO _w
Initial	3.656	2.309	2.704
TS	3.406	2.301	3.113
Final	3.789	3.827	2.439

Figure captions

Figure 1. Pseudo-NaA (a-b), full NaA (c), NaX (e) unit cells and β -cage of NaSOD (d), used in the discussion. The NaI-NaIII, NaII-NaIII, and NaIII-NaIII jumps are crudely shown by dotted, dashed, and dot-dashed lines, respectively (a, b). The dot-dashed lines (NaIII-NaIII) connect empty (free) sites because of unique NaIII cation per cage (a, b). The regions with the Al–O–Al alternation are shown by shaded ellipses (b). The part of the pseudo-NaA UC (a-b) in full UC of NaA is shown by shaded square (c). In the case of NaSOD (d) all Na positions are equivalent (4 Na inside the β -cage and 4 Na outside the β -cage). A part of them is denoted as NaI due to a similarity with the NaI position in NaA (where such β -cage is present without any internal Na cations), while those inside the β -cage are denoted as NaI'. The transitions between the NaI' sites in NaSOD do not coincide with the other types of the transitions (a, b, e) and are given by dot-dot-dashed lines (d). The position of Cl⁻ anion included in NaSOD [9] is depicted by arrow in (d). The main fragments of NaA (c) and NaX (e) are shown by shaded ellipses (12R, 8R, 6R, 4R). The atomic colors are given in gray (small spheres), red, blue, magenta, and yellow for H, O, Na, Al, and Si, respectively.

Figure 2. The trajectories of the Na jumps (ciNEB modeling) between two nearest 4R sites (III-III sites, a-i) or two nearest 8R and 4R sites (II-III sites, j) in Na₁₂A with water (a, b), Br (c, d), Cl anions (e, f) or without it (g, h, i, j). The atomic colors are given in gray, red (small spheres), magenta, yellow, blue, olive, and red (large spheres)for H, O, Al, Si, Na, Cl, and Br, respectively. Hydrogen bonds are shown by dotted lines (a, b). The arrows show the NaIII motion along with the initial, transition state, and final geometries. The fourth (intermediate or NaII') NaIII position is also shown in (g, h) (see text for the comments). The close positions of nearest Na cations at the initial, transition state, and final steps are shown to demonstrate a measure of their displacement in the course of the jump.

Figure 3. The trajectories of the Na jumps (ciNEB modeling) between two nearest 4R sites (NaIII-NaIII sites) *via* nearest 8R (NaII' sites) in $Na_{12}A$ at different theory levels.

Figure 4. Diffusion profiles of NaIII \rightarrow NaIII path in empty (a) Na₁₂A pseudo-unit cell or in the presence of Cl⁻ (a), Br⁻ (b), and H₂O (b, c) with intermediate state (NaII', a) and without it (b). Different computational approaches PBE (closed circles), PBE-D2(squares), PBE-D3 (open circles) are compared for H₂O (c).



Figure 1c

c)



27









Figure 3



Figure 4a-b



Figure 4c

