Crystal Structure of Xenon Encapsulate within Na-A Zeolite

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The positions of Xe atoms encapsulated in the molecular-dimensioned cavities of fully dehydrated Na-A have been determined. Na-A was exposed to 1050 atm of xenon gas at 400 °C for seven days, followed by cooling at pressure to encapsulate Xe atoms. The resulting crystal structure of Na-A(7Xe) ($a = 12.249(1)$ Å, $R_1 = 0.065$, and $R_2 = 0.066$) were determined by single-crystal X-ray diffraction techniques in the cubic space group $Pm\overline{3}m$ at 21(1) °C and 1 atm. In the crystal structure of Na-A(7Xe), seven Xe atoms per unit cell are distributed over four crystallographically distinct positions: one Xe atom at Xe(1) lies at the center of the sodalite unit, two Xe atoms at Xe(4) are found opposite four-rings in the large cavity, and four Xe atoms, two at Xe(2) and others at Xe(3), respectively, occupy positions opposite and between eight- and six-rings in the large cavity. Relatively strong interactions of Xe atoms at Xe(2) and Xe(3) with Na$^+$ ions of four-, eight-, and six-rings are observed: Na(1)-Xe(2) = 3.09(6), Na(2)-Xe(3) = 3.11(2), and Na(3)-Xe(2) = 3.37(8) Å. In each sodalite unit, one Xe atom is located at its center. In each large cavity, six Xe atoms are found, forming a distorted octahedral arrangement with four Xe atoms, at equatorial positions (each two at Xe(2) and Xe(3)) and the other two at axial positions (at Xe(4)). With various reasonable distances and angles, the existence of (Xe)$_6$ cluster is proposed (Xe(2)-Xe(3) = 4.78(6) and 4.94(7), Xe(2)-Xe(4) = 4.71(6) and 5.06(6), Xe(3)-Xe(4) = 4.11(3) and 5.32(4) Å. Xe(2)-Xe(3)-Xe(2) = 93(1), Xe(3)-Xe(2)-Xe(3) = 87(1), Xe(2)-Xe(4)-Xe(2) = 91(4), Xe(2)-Xe(4)-Xe(3) = 55(2), 59(1), 61(1), and 68(1), and Xe(3)-Xe(4)-Xe(3) = 89(1)°). These arrangements of the encapsulated Xe atoms in the large cavity are stabilized by alternating dipoles induced on Xe(2), Xe(3), and Xe(4) by eight- and six-ring Na$^+$ ions as well as four-ring oxygens, respectively.

Introduction

The zeolite provides an ordered matrix that can trap various gas molecules such as neon,[1] argon,[1-3] krypton,[1] xenon,[4-18] dinitrogen,[2] carbon dioxide,[2] methane,[19,20] and dihydrogen.[21-23] in its void space when the diameters of guest molecules somewhat exceed the window size of the zeolite at room temperature.[24,25] Among those, xenon has been extensively utilized as a probe for studying the pore structures and other properties of various zeolites by using ^{129}Xe NMR spectroscopy.[4-18] That is because xenon atoms are particularly sensitive to their environment due to their chemical inertness and high polarizability. Such occlusion of xenon atoms in zeolites has also been studied by using various other scientific methods such as molecular dynamics simulations,[13,14] Grand Canonical Monte Carlo simulation,[14-16] and single-crystal X-ray diffraction method,[25] and so on. These techniques, together with the ^{129}Xe NMR spectroscopy,[4-18] were extensively used in order to elucidate physico-chemical properties, the distribution and the size of supported metal particles, the location of cations, the effect of electric fields, the migraion processes of cations and the occluded species like metal clusters or the clusters of rare-gas atoms in various zeolites.[4-25]

After pioneering work of Fraissard,[4] ^{129}Xe NMR technique was used by Samant *et al.*[24] to monitor the process of the encapsulation of xenon atoms and to provide information on the distribution of xenon in Na-A zeolite. They forced xenon atoms into the Na-A zeolite at 40 bar and 525 K and took the ^{129}Xe NMR spectrum, showing five peaks assigned to various Xe clusters in the α-cages. Chmelka *et al.*[18] also used the ^{129}Xe NMR spectroscopy to probe directly the distribution of xenon atoms confined in Na-A zeolite. These separate theoretical studies and adsorption experiments suggested that xenon packing arrangements were almost certainly dominated by local surface effects and geometric constraints even at low loadings. Based on an idealized geometric model,[18] a pentagonal bipyramidal arrangement of xenon atoms tangent to the interior walls of the α-cages appeared feasible near the saturation occupancy with 7 Xe atoms per cavity. Assemblies of 6 xenon atoms were expected to posses cubic symmetry, while a lower symmetry configuration was anticipated with 7 Xe atoms.

Jameson *et al.*[14-16] studied on the equilibrium distribution of the Xe atoms among the α-cages of Na-A ranging from very low xenon loading up to saturation by ^{129}Xe NMR and also simulated by using a Grand Canonical Monte Carlo (GCMC) method in order to compare results with those of NMR study. They observed trapped Xe atoms in the α-cages of Na-A in ^{129}Xe spectrum. Their GCMC, hypergeometric distribution, and continuum model provided quantitative agreement with the experimental equilibrium distribution of Xe atoms among the cavities of the zeolite. They actually found 11 local minima for a single Xe atom in the α-cage to show some of the minimum energy configurations (Xe$_1$-Xe$_8$). No Xe atoms was found in the middle of the α-cage

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either when it is alone in the cage or when there are 8 Xe atoms in the α-cage.

Even though there are no direct evidences, most scientists working on xenon occlusion into zeolites by ^{129}Xe NMR, Grand Canonical Monte Carlo Simulation (GCMC), and Molecular Dynamics Simulation have suggested that Xe atoms (kinetic diameter = 3.96 Å)[26] could not gain access to the sodalite cavities with the windows of free diameter *ca.* 2.2 Å.[4,15,24,27] However, recently in the crystal structures of Cs₃-A(*x*Ar), *x* = 5 and 6,[3] Cs₃-A(5Kr),[28] and Cs₃-A(*y*Xe), *y* = 2.5, 4.5, and 5.25,[25] one Ar (kinetic diameter = 3.40 Å),[26] Kr (3.60 Å),[26] or Xe atom (3.96 Å)[26] was always and unambiguously found near the center or at the center of each sodalite unit. These results indicated the existence of dynamic processes for the passages of those atoms through a six-ring whose aperture is formally considered to be too small (*vide supra*).

Interestingly, it was generally considered that Na-A zeolite may not be suitable for the storage of Xe atoms due to its larger window size. Xe atoms with 3.96 Å of kinetic diameter could not be efficiently entrapped within α-cage having window size of 4.2 Å. However, Chmelka *et al.*[18] identified the saturation occupancy with 7 Xe atoms per cavity of Na-A by ^{129}Xe NMR spectroscopy. This result could not be explained by the simple kinetic diameter relationships between guest molecules and window size of zeolites. Therefore, the blocking effect of Na⁺ ions on 8-rings with known free kinetic diameter of 4.2 Å for Xe atoms of the large cavity has not been well understood. Furthermore, the stability of Xe atoms in Na-A and their interaction with zeolite framework will be different from those of Xe atoms in Cs₃-A in which the blocking effects of Cs⁺ ions on eight-rings of the large cavity were proven in various early works published.[3,25-28] The existence of encapsulated Xe atom in the sodalite unit without such Cs⁺ blocking cations on eight-rings has not been suggested by any other techniques like ^{129}Xe NMR, Grand Canonical Monte Carlo simulation (GCMC), Molecular Dynamics Simulation, and X-ray crystallographic method.

In this work, xenon atoms were encapsulated at high pressure in the cavities of fully dehydrated Na-A zeolite, the native zeolite A, in order to observe their position and to further characterize the confinement effect crystallographically. Together with the blocking effect of Na⁺ ions on the eight-rings of Na-A, the precise coordinates of encapsulated Xe atoms, sensitive to the electrostatic field in an unperturbed zeolite, would be seen. Perhaps interesting clusters of Xe atoms formed by induced dipole attractions (London forces) in the large cavity and Xe atom trapped in the sodalite unit at high pressure would be characterized.[3,25-28]

Experimental Section

Colorless single crystals of the native zeolite 4A, Na₁₂Si₁₂-Al₁₂O₄₈ · 27H₂O (Na₁₂-A · 27H₂O or Na-A·27H₂O),[29] were synthesized by Kokotailo and Charnell.[30] A single crystal of hydrated Na-A, a cube 80 μm on an edge, was lodged in a

fine Pyrex capillary with both ends open. This capillary was transferred to a high-pressure line connected to the vacuum line. After cautious increases in temperature of 25 °C/h under vacuum, followed by complete dehydration at 400 °C and 1 × 10⁻⁴ Torr for two days, forced sorption of Xe into the crystal was carried out at 400 °C for seven days with 1050 atm of Xe (Matheson, 99.996%). High pressure of xenon gas was produced by condensing the gas in the high pressure chamber (immersed in a liquid-nitrogen bath), which contains the capillary with Na-A crystal, followed by reheating up to appropriate temperature after isolating the chamber from the vacuum line. Encapsulation was accomplished by cooling the chamber at pressure to room temperature with an electric fan. Following the release of Xe gas from the chamber, both tips of the capillary were presealed with vacuum grease under nitrogen before being completely sealed with a small torch. No changes were noted in the appearance of the crystal upon examination under the microscope.

The cubic space group *Pm3m* (no systematic absences) was used in this work for the reasons discussed previously.[31,32] The cell constants, *a* = 12.249(1) Å at 21(1) °C, was determined by a least-squares treatment of 15 intense reflections for which 20° < 2θ < 30°. Each reflection was scanned at a constant scan speed of 0.5°/min in 2θ with a scan width of (0.60 + 0.67tanθ)°. Background intensity was counted at each end of a scan range for a time equal to half the scan time. The intensities of all lattice points for which 2θ < 70° were recorded. Absorption correction (μR *ca.* 0.27)[33] was judged to be negligible for this crystal, since semi-empirical Ψ-scans showed only negligible fluctuations for several reflections. Only those reflections in final data set for which the net count exceeded three times its standard deviation were used in structure solution and refinement. This amounted to 185 reflections. Other crystallographic details are the same as previously reported.[3,25-28]

Structure Determination

Full-matrix least-squares refinement was initiated with the atomic parameters of all framework atoms [(Si,Al), O(1), O(2), and O(3)] and Na⁺ at Na(2) in Cs₃Na₈H-A.[3,25-28] A refinement with anisotropic thermal parameters for all framework atoms and isotropic thermal parameter for Na⁺ at Na(2) converged quickly to the error indices $R_1 = \Sigma|F_o-|F_c||/\Sigma F_o = 0.251$ and $R_2 = (\Sigma w(F_o-|F_c|)^2/\Sigma w F_o^2)^{1/2} = 0.369$ with occupancies of 7.0(9) for Na⁺ at Na(2). A difference Fourier function based on this model revealed several peaks deep in the sodalite and large cavity. A subsequent refinement with inclusion of a peak at the center of the sodalite unit as Xe(1) and another one slightly off 3-fold axis opposite a six-ring in large cavity as Xe(3) (see Table 1) converged to the error indices $R_1 = 0.124$ and $R_2 = 0.151$ and resulting occupancies of 8.2(4), 1.32(5), and 8.1(2) at Na(2), Xe(1), and Xe(3), respectively. With fixed occupancy of 8.0 (its maximum value by symmetry) at Na(2), including peaks Na⁺ on the eight-ring as Na(1) and opposite eight-ring in the large cavity as Xe(2) further reduced the error indices to 0.076 and

Table 1. Positional, Thermal, and Occupancy Parameters[a]

	Wyckoff position	x	y	z	U_{11} or U_{iso}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Occupancy[c]	
											fixed	varied
(Si,Al)	24(k)	0	1834(3)	3714(3)	24(2)	15(1)	6(1)	0	0	3(2)	24[d]	
O(1)	12(h)	0	2288(10)	5000[e]	41(8)	20(8)	24(7)	0	0	0	12	
O(2)	12(i)	0	2913(7)	2913(7)	54(9)	19(5)	19(5)	0	0	3(7)	12	
O(3)	24(m)	1131(6)	1131(6)	3417(7)	28(3)	28(3)	30(5)	16(5)	1(4)	1(4)	24	
Na(1)	12(i)	0	4345(26)	4345(26)	178(54)	60(18)	60(18)	0	0	5(25)	3	2.9(3)
Na(2)	8(g)	2042(6)	2042(6)	2042(6)	46(3)	46(3)	46(3)	20(4)	20(4)	20(4)	8	8.2(4)
Xe(1)	1(a)	0	0	0	21(1)						1	0.97(2)
Xe(2)	48(n)	2439(35)	3765(33)	4559(37)	19(2)						2	2.14(6)
Xe(3)	24(m)	2981(22)	3709(16)	3709(16)	15(1)						2	1.93(6)
Xe(4)	24(m)	3071(11)	3071(11)	4625(11)	11(1)						2	1.85(5)
Na(3)	12(j)	2127(100)	2127(100)	5000[e]	10(5)						1	0.420(3)

[a]Positional parameters $\times 10^4$ and thermal parameters $\times 10^3$ are given. Numbers in parentheses are the estimated standard deviations in the units of the least significant figure given for the corresponding parameter. The anisotropic temperature factor is $\exp[-2\pi^2 a^{-2}(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{12}hk + 2U_{13}hl + 2U_{23}kl)]$. [b]Isotropic thermal parameters in units of Å^2. Xe(1) is isotropic by symmetry. [c]Occupancy factors are given as the number of atoms or ions per unit cell. [d]Occupancy for (Si) = 12, occupancy for (Al) = 12. [e]Exactly 0.5 by symmetry.

0.072 with resulting occupancies of 2.9(3), 0.97(2), 3.33(6), and 2.39(6) at Na(1), Xe(1), Xe(2), and Xe(3), respectively. When this model was refined with fixed occupancies of 3.0 and 1.0 (their maximum values by symmetry) at Na(1) and Xe(1), respectively, another peak was found in the large cavity. Further inclusion of this peak opposite a four-ring in the large cavity as Xe(4) reduced the error indices to 0.065 and 0.066 with resulting occupancies of 2.14(6), 1.93(6), and 1.85(5) at Xe(2), Xe(3), and Xe(4), respectively. The refinement with anisotropic thermal parameters for all atoms except for isotropic thermally refined with all occupancies fixed at 3.0, 8.0, 1.0, 2.0, 2.0, and 2.0 for Na(i) and Xe(j), $i = $ 1 to 2 and $j = 1$ to 4, respectively, and converged to $R_1 = $ 0.066 and $R_2 = 0.067$. Finally, another peak was found on the opposite a four-ring in the large cavity, Na(3), (0.21272, 0.21272,0.5) position. The final cycles of refinement with a occupancy fixed at 1.0 for Na(3) converged to $R_1 = 0.065$ and $R_2 = 0.066$. The final structural parameters for this crystal are given in Table 1. Selected interatomic distances and angles are given in Table 2.

The values of the goodness-of-fit, $(\Sigma w(F_o-|F_c|)^2/(m-s))^{1/2}$, are 1.94; the number of observations, m, is 185 and the number of parameters, s, is 40. All shifts in the final cycles of refinement were less than 0.1% of their corresponding estimated standard deviations. The quantity minimized in least-squares is $\Sigma w(F_o-|F_c|)^2$, where the weights (w) are the reciprocal squares of $\sigma(F_o)$, the standard deviation of each observed structure factor. Atomic scattering factors for Xe, Na^{+}, O[-], and (Si,Al)[1.75+] were used. The function describing (Si,Al)[1.75+] is the mean of the Si[4+], Si[0], Al^{3+}, and Al[0] functions. All scattering factors were modified to account for anomalous dispersion.[34,35]

Results and Discussion

Zeolite A Framework and Cations. In the crystal structure of fully dehydrated Na-A ($Na_{12}Si_{12}Al_{12}O_{48}$ or Na_{12}-A), each unit cell contained three Na^{+} ions at Na(1) all located at one crystallographically distinct position. Wyckoff position of 12(i) with point symmetry of *mm*, on the eight-rings. These Na ions are about 0.85 Å away from the centers of the eight-rings. Each Na^{+} ions at Na(1) is 2.49(3) Å from one O(2) oxygen and 2.65(2) Å from two O(1) oxygens. Although these distances are somewhat longer than the sum, 2.29 Å, of the conventional ionic radii of Na^{+} and O[2-], these positions are well defined by the results of crystallographic refinements (*vide supra*). Such somewhat longer approach distances of 8-ring cations are also observed in many monopositive cationic forms of zeolite A.[36-42]

Eight six-rings per unit cell are fully occupied by eight Na ions at Na(2) as seen in the crystal structure of Na_{12}-A.[37] These Na^{+} ions at Na(2) have 2.31(1) Å distance from three O(3) oxygens. They are extended in the distance of 0.32 Å into the large cavity from the (111) planes at O(3) (see Table 3). The O(3)-Na-O(3) angles are close to 120° (118.2(1)°), so the Na ions are nearly trigonal-planar.

The presence of twelfth Na ion for the electric neutrality of negative charge accompanied with framework ($Si_{12}Al_{12}O_{48}$) was expected opposite four-ring in the large cavity, as found in the crystal structures of many monopositive cation exchanged zeolite A.[36-38] This twelfth Na^{+} ion was found with rather smaller occupancy (0.420(3) per unit cell) as Na(3) and introduced for the neutralization of the anionic charge of the framework.[36-38] The Na^{+} ion at Na(3) is 2.62(1) and 2.60(9) Å away from O(1) and O(3) oxygens of the four-ring, respectively, and these distances are relatively longer than other Na-O distances because of averaging effect with low occupancy at this position.

Xenon Atom in the Sodalite Unit. One xenon atom per unit cell is unambiguously found at Xe(1), at the center of the every sodalite unit with a full occupancy at this special position (see Table 2 and Figure 1). It is impossible for some sodalite unit to have zero Xe(1) atom and other to have more than one, to average to one, because only one equivalent position should exist in the 1(a), Wyckoff position. Therefore, every sodalite unit contains one (0.97(2)) Xe(1)

Table 2. Selected Interatomic Distances (Å) and Angles (deg)[a]

Distances		Angles	
(Si,Al)-O(1)	1.674(7)	O(1)-(Si,Al)-O(2)	107.2(6)
(Si,Al)-O(2)	1.650(8)	O(1)-(Si,Al)-O(3)	113.4(5)
(Si,Al)-O(3)	1.675(9)	O(2)-(Si,Al)-O(3)	106.4(4)
Na(1)-O(1)	2.65(2)	O(3)-(Si,Al)-O(3)	111.6(5)
Na(1)-O(2)	2.49(3)	(Si,Al)-O(1)-(Si,Al)	141.1(10)
Na(2)-O(3)	2.31(1)	(Si,Al)-O(2)-(Si,Al)	161.1(5)
Na(2)-O(2)	2.927(9)	(Si,Al)-O(3)-(Si,Al)	143.8(3)
Na(3)-O(1)	2.62(1)	O(1)-Na(1)-O(2)	63(1)
Na(3)-O(3)	2.60(9)	O(1)-Na(1)-O(1)	125(1)
Xe(3)-Na(2)	3.11(2)	O(3)-Na(2)-O(3)	118.2(1)
Xe(2)-Na(1)	3.09(6)	O(1)-Na(3)-O(1)	99(4)
Xe(2)-Na(3)	3.37(8)	O(3)-Na(3)-O(3)	97(4)
Xe(1)-Na(2)	4.341(6)	O(1)-Na(3)-Xe(2)	96(5), 151(2)
Xe(1)-O(3)	4.63(1)	O(3)-Na(3)-Xe(2)	98(3), 144(3)
Xe(1)-O(2)	5.056(8)	Xe(1)-Na(2)-O(3)	82.1(3)
Xe(4)-O(1)	3.92(2)	Xe(3)-Na(2)-O(3)	91.0(5), 111.4(7)
Xe(4)-O(3)	3.68(2)	Xe(1)-Na(2)-Xe(3)	166.5(7)
Xe(4)-O(2)	4.32(2)	Na(1)-Xe(2)-Na(3)	71(2)
Xe(3)-O(3)	3.91(3)	Na(1)-Xe(2)-Xe(4)	147(2)
Xe(3)-O(2)	3.91(3), 4.66(3)	Na(1)-Xe(2)-Xe(3)	96(2), 168(2)
Xe(3)-O(1)	4.35(3)	Xe(3)-Xe(2)-Xe(3)	87(1)
Xe(2)-O(1)	3.54(7)	Xe(4)-Xe(2)-Xe(4)	87(1)
Xe(2)-O(2)	3.76(6)	Xe(3)-Xe(2)-Xe(4)	49.3(7), 50.4(7), 64(2), 70(1)
Xe(2)-O(3)	3.87(6)	Xe(2)-Xe(3)-Xe(2)	93(1)
Xe(2)-Xe(3)	4.78(6), 4.94(7)	Xe(4)-Xe(3)-Xe(2)	91(1)
Xe(2)-Xe(4)	4.71(6), 5.06(6)	Xe(4)-Xe(3)-Xe(4)	90.7(6)
Xe(3)-Xe(4)	4.11(3), 5.32(4)	Xe(3)-Xe(4)-Xe(3)	89(1)
		Xe(2)-Xe(4)-Xe(2)	91(4)
		Xe(2)-Xe(4)-Xe(3)	55(2), 59(1), 61(1), 68(1)

[a]The numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

Table 3. Deviations of Atoms (Å) from the (111) plane at O(3)[a]

	Na-A(7Xe)
Na(2)	0.32
Xe(1)	-4.02
Xe(3)	3.42[b]

[a]A negative deviation indicates that the atom lies on the same side of the plane as the origin, *i.e.,* inside the sodalite unit. [b]Deviation of Xe atoms from the center of (111) plane.
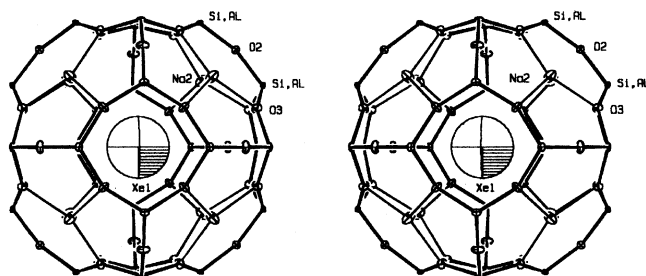

Figure 1. Stereoview of a sodalite unit in the unit cell, showing an encapsulated Xe atom located at the center. The zeolite A framework is drawn with solid line between oxygens and tetrahedrally coordinated (Si,Al) atoms. Ellipsoids of 20% probability are shown.

atom. A dynamic process for the passage of a Xe atom through a six-ring, whose aperture is formally too small (2.2 Å), must exist at 400 °C. The xenon atom at Xe(1) have distances of 4.341(6) and 4.63(1) Å from the nearest Na$^+$ ions and six-ring oxygens, respectively. These long distances indicate an absence of appreciate bonding characters at its average position.

A theoretical calculation indicated that a xenon atom in a sodalite unit containing Na$^+$ ions should find an energy minimum at its center, at Xe(1).[1] It should be considered, however, because Xe(1) is at a crystallographic inversion center, that the electrostatic field gradient must be zero and that the xenon atom can be polarized only when it vibrates away from this position. This possible movement is probably suggested by its rather larger thermal parameter (see Table 1).

Xenon Atoms in the Large Cavity. Six atoms of xenon in the large cavity of Na$_{12}$-A(7Xe) are found at three crystallographically distinct positions. This indicates that the xenon atoms are not arranging themselves by simple packing within the highly symmetric zeolite framework to form a octahedral. Their geometry is affected by interactions among the sorbed atoms (*vide infra*) whose locations are, in turn, related with interactions between atoms of zeolite host and
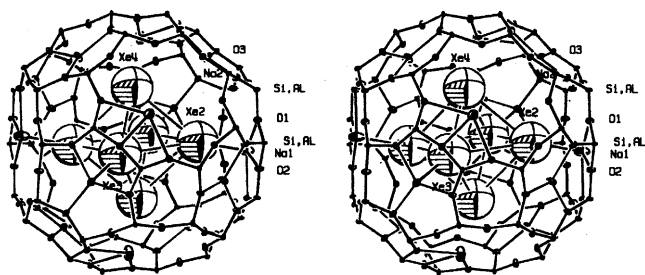
Figure 2. Stereoview of the large cavity with six Xe atoms at Xe(2), Xe(3), and Xe(4). The six xenon atoms have a hexagonal arrangement. The most significant interactions among Xe atoms, and those between Xe and Na⁺ ions and framework oxygens, are indicated by fine solid lines. A Na⁺ ion at site III (opposite four-ring) is removed for clarity. See the caption to Figure 1 for other details.

Xe atoms. Two Xe atoms at Xe(2) lie on a slightly deviated from 3-fold axis opposite six-ring, two Xe atoms at Xe(3) lie on opposite eight-ring, and the other two Xe atoms at Xe(4) lie opposite four-ring (see Figures 2 and 3).

The closest approach of these xenon atoms to nonframework cations is 3.09(6) Å for Xe(2)-Na(1), 3.11(2) Å for Xe(3)-Na(2), and 3.37(8) Å for Xe(2)-Na(3), while those to framework oxygens are 3.68(2) and 3.92(2) Å for Xe(4)-O(3) and Xe(4)-O(1), respectively (see Table 2). Considering the radii of the cations (r_{Na^+} – 0.97 Å),[43,44] framework oxygens (1.32 Å),[43,44] and xenon atoms (2.18 Å as $r_{min}/2$[26] and as found in the solid[45]), some of the xenon atoms are sufficiently close to their neighbors to be considered as having relatively strong interactions. In particular, when the distances are compared to the sum of the above radii for Na⁺ and Xe, 0.97 + 2.18 – 3.15 Å, the approach distances of the

Four-ring

Four-ring

Figure 3. Schematic diagram of the hexagonal of six xenon atoms and five Na⁺ ions at Na(1), Na(2), and Na(3) in the large cavity. The immediate environment of each Xe atom and the dipole moment it induces on each Xe are shown. The favorable interactions between the polarized Xe atoms are indicated by line lines and the unfavorable ones by dashed. See the caption to Figure 1 for other details.

xenon atoms at Xe(2) and Xe(3) to the eight- and six-ring Na⁺ ions (3.09(6) and 3.11(2) Å, respectively) indicate strong Na⁺-Xe interactions, probably reinforced and arose from the forced packing with high occupancies of xenon atoms. And the approach distance of the xenon atom at Xe(2) to the Na ion at Na(3), also, indicate a relatively strong Na⁺-Xe interaction (3.37(8) Å).

In contrast, as shown in Figure 2 and 3, inter-xenon distances of 4.78(6) and 4.94(7) Å for Xe(2)-Xe(3), 4.71(6) and 5.06(6) Å for Xe(2)-Xe(4), and 4.11(3) and 5.32(4) Å for Xe(3)-Xe(4), respectively, in the corresponding large cavities (*vide infra*) are nearly an angstrom larger than those in solid Xe,[45] except for 4.11(3) Å for the distance of the Xe(3)-Xe(4)'s (*vide infra*). It should be considered that this short distance of the Xe(3)-Xe(4) is inevitable because the xenon atoms at Xe(4) have to occupy on the opposite four-rings in order to have a favorable orientation by induced dipoles after the four xenon atoms are distributed over the Na⁺ ions at Na(1) and Na(2) of the six- and eight-rings.

The xenon atoms at Xe(3) in the large cavities appear to interact much more strongly with six-ring Na⁺ ions than do those at Xe(1). This Xe(3)-Na⁺ interaction (3.11(2) Å) is shorter than the corresponding Xe(1)-Na⁺ distance (4.341(6) Å). Similarly, the Ar, Kr, and Xe atoms of large-cavity in Cs₃-A(xAr), x – 5 and 6,³ Cs₃-A(5Kr),[28] and Cs₃-A(yXe), y – 2.5, 4.5, and 5.25,[25] respectively, interacted more strongly with Na⁺ ions than do the small-cavity Ar, Kr, and Xe's. The Xe(3)-O(3) distance (3.91(3) Å) is also generally shorter than the Xe(1)-O(3) distance (4.63(1) Å).

Xenon Cluster. Each two xenon atoms at Xe(*i*), *i* – 2 to 4, on the inner surface of the large cavity may be placed within their partially occupied equipoints in various ways. Possible distances between two xenon atoms such as, 1.24(7), 2.23(7), 3.34(6), and 3.40(7) Å for Xe(2)-Xe(3), 1.53(6), 2.25(7), 3.19(7), and 3.35(7) Å for Xe(2)-Xe(4), and 1.37(3), 2.19(3), 2.30(3), and 3.14(4) Å for Xe(3)-Xe(4), respectively, are impossibly short and dismissed. Some inter-xenon distances found among the equipoints of Xe(2), Xe(3), and Xe(4), 4.5(1) and 5.4(1) Å for Xe(2)-Xe(2), 4.48(4), 4.96(7), and 5.23(4) Å for Xe(3)-Xe(3), and 4.74(4), 4.82(4), and 5.45(3) Å for Xe(4)-Xe(4), are possible. However, these are also dismissed because the dipoles induced on these pair of Xe(2), Xe(3), and Xe(4) atoms are oriented unfavorably. The next possible set of distances between Xe atoms, 4.78(6) and 4.94(7) Å, 4.71(6) and 5.06(6) Å, and 4.11(3) and 5.32(4) Å for Xe(2)-Xe(3), Xe(2)-Xe(4), and Xe(3)-Xe(4), respectively, are most plausible. However, various arrangements remain possible. A distorted octahedral arrangement is selected as most plausible because of its higher symmetry and by considerations regarding alternating polarizations of xenon atoms (see Figure 3), as previously discussed in the structures of Cs₃-A(xAr), x – 5 and 6,³ Cs₃-A(5Kr),[28] and Cs₃-A(yXe), y – 2.5, 4.5, and 5.25.[25] Each two Xe(*i*), *i* – 2 and 3, atoms on the opposite eight- and six-rings in the large cavity occupy equatorial positions and two Xe(4) atoms on the opposite four-rings are at axial positions (see Figure 3). In this arrangement, ε polarizations from all
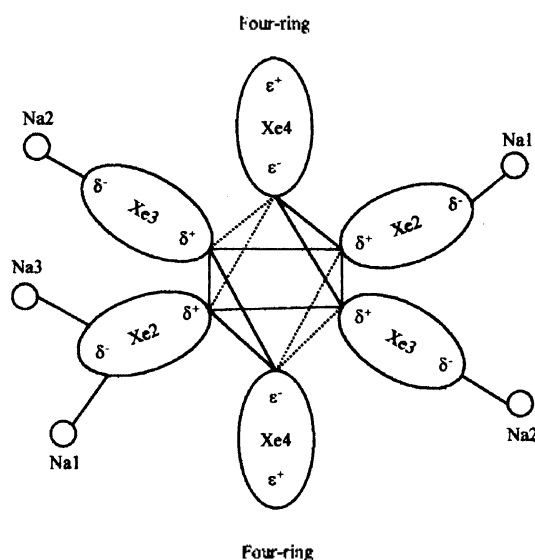
two Xe(4) atoms point toward the center of the large cavity where each can interact with each of the four δ' polarizations from the Xe(*i*). *i* = 2 and 3, atoms.

Supplementary Material Available. Observed and calculated structure factors for Na-A(7Xe) are available upon your request to the correspondence author.

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