

^{129}Xe Magic-angle spinning spectra of xenon in zeolite NaA Direct observation of mixed clusters of co-adsorbed species

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Abstract

We present the first demonstration that the individual ^{129}Xe resonances corresponding to Xe_n ($n = 1-8$) clusters inside the α -cages of zeolite NaA can be narrowed under magic-angle spinning (MAS). Under these high-resolution conditions we also observe upon addition of Kr the individual peaks corresponding to mixed clusters, Xe_nKr_m , inside the α -cages, which will allow the first direct determination of the distribution of co-adsorbates in a microporous solid. Under MAS the chemical shifts of the Xe_n clusters are shown to be highly sensitive to “disorder” in the zeolite and provides new, quantitative information about the presence of α -cages of several types.

Keywords: Xenon; Zeolite NaA; Magic-angle spinning; Adsorption; Clusters

1. Introduction

In our studies of molecular interactions and dynamics of sorbates in microporous solids using nuclear magnetic resonance (NMR) observables together with computer simulations, we have focused on xenon clusters trapped in the regular array of cages in the NaA zeolite [1–4]. We have directly observed the fractions of α -cages in zeo-

lite NaA that have trapped from one to eight Xe atoms [1] and measured the equivalent of state-to-state rate constants for migration of xenon atoms from one α -cage to another [3], as have others [5,6]. These direct determinations of adsorbate distribution as a function of loading and temperature provide detailed tests of computer simulations of Xe distributions in zeolites [2–4]. Furthermore, the chemical shifts of the individual clusters measured as a function of temperature provide a test of the averaging amongst the large numbers of configurations of a particular cluster within an α -cage [2,4]. Thus, we have elicited information on the structure of the Xe_n clusters through the computer simulations.

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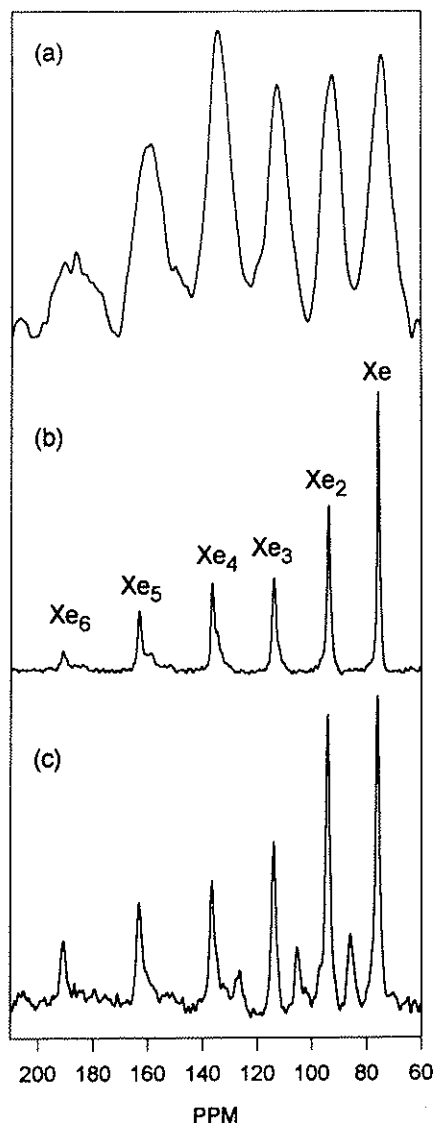


Fig. 1. (a) Static ^{129}Xe NMR spectrum of a sealed sample of xenon in dehydrated zeolite NaA at equilibrium at 300 K, showing the peaks corresponding to Xe, Xe₂, Xe₃, ..., Xe₆ inside the α -cages. This spectrum was taken on a Bruker AM400 spectrometer. The zeolite (sample I) was obtained from Union Carbide (courtesy of E. Flanigen). (b) ^{129}Xe NMR spectrum of the same sealed sample of xenon in dehydrated zeolite NaA under MAS at 2 kHz obtained on an 8.45-T home-built spectrometer (see text for details). (c) ^{129}Xe MAS NMR spectrum of a sealed sample of xenon and krypton in the same dehydrated zeolite NaA from the same source. The resonances corresponding to the mixed clusters XeKr, Xe₂Kr, and Xe₃Kr are readily assignable as described in the text. Chemical shifts are in ppm in the IUPAC convention, relative to isolated xenon atom.

A typical ^{129}Xe NMR spectrum is shown in Fig. 1a in which individual peaks of Xe_{*n*} (*n* = 1, 2, ..., 6) clusters may be seen. However, the

origins of the linewidths observed (about 10 ppm) has been a puzzle, since ~ 1 -ppm-wide lines are rather commonplace in ^{129}Xe NMR studies of other zeolites [7,8]. We have previously found that it is possible to "burn" a hole as narrow as 1 ppm in one of the broad lines in a spectrum such as that shown in Fig. 1a by using a selective DANTE [9] pulse sequence. Furthermore, T_2 (Carr–Purcell–Meiboom–Gill, CPMG) experiments on several different samples of Xe in zeolite NaA have yielded relaxation times of 15–40 ms, indicating limiting linewidths in the range of ~ 10 –20 Hz. This evidence suggests that the broad lines are a superposition of a large number of narrow resonances with a range of chemical shifts, and that they might be narrowed by MAS. Of course, these T_2 and hole-burning experiments do not differentiate between what might be regarded as a continuous or "glassy" spread of isotropic chemical shifts, which would not narrow under MAS, and a "powder average" distribution, which would be expected to average under MAS. Fortunately, we have found that the latter case pertains for our Xe and Xe–Kr in zeolite samples, with even slow (~ 2 kHz) sample spinning causing a remarkable narrowing of the ~ 1 -kHz experimental linewidths. This has enabled us to resolve peaks from Xe–Kr clusters and to detect the effects of cation binding on Xe_{*n*} chemical shifts, as well as detect a range of cage types in different Xe–NaA samples. Thus, Xe MAS NMR of zeolites appears to be a potentially powerful new approach to investigating zeolite structure, as well as probing distributions of Xe and co-adsorbates in NaA zeolites. Based on these results, it also seems likely that Xe MAS NMR may also be of use in probing structure in other complex solid materials, such as polymers [10], and even protein (e.g. myoglobin) crystals [11].

2. Experimental

2.1. Sample preparation

For MAS NMR, we used a Gay probe design [12] with a small pressurized sample cell located

inside a conventional 5-mm NMR tube. The sample tube is made from ordinary borosilicate glass tubing of nominal 4 mm O.D. and about 2.5 cm from the test-tube bottom to a slightly necked-down portion. For safety reasons it is essential to anneal the tubes in a commercial annealing oven at this juncture to remove stresses. The tube volume is then calibrated with mercury, previously dried zeolite is introduced, a small glass wool plug is introduced to keep the zeolite in place, and the tube is carefully flame-narrowed above the center of the necked-down region to provide for a minimal area of stress in the final sample tube. The resulting assembly is then dried at 350°C under vacuum for at least 16 h under “thin-bed” conditions (a bed thickness of about 1–1.5 mm) to remove residual water which may have been introduced in handling the zeolite. Use of a Young-type stopcock allows easy transfer from the drying vacuum line to a standard line in which a measured amount of xenon (99.9% ^{129}Xe from ICON, Mount Marion, NY, USA) can be introduced, without loss of vacuum at any previous time. The final sample is flame-sealed under liquid nitrogen, has an accurately known volume of about 0.1 ml, contains a known mass of NaA zeolite (about 25 mg) and a known number of moles of xenon. Our experience indicates that these samples will routinely withstand internal pressures of at least 50 atm, although extreme caution must always be exercised when handling any such samples. Equilibration of samples at 300 K is very slow since the xenon atoms diffuse slowly to the empty centers of the crystallites. To accelerate the approach to an equilibrium distribution of the xenon throughout the α -cages of NaA, the samples are kept in an oven at 350°C for 12 h, then temperature-programmed down to 60°C for a few days, then left at room temperature at which equilibration takes place over about a week. In this work, some spectra were taken before equilibrium was achieved and are so indicated. The zeolites used in this work were obtained from the following sources: sample I, an ultra-high-purity NaA from E. Flanigen, Union Carbide; sample II, a commercial Linde sieve (4A, Lot No. 941084060045, Union Carbide Linde Division, South Plainfield, NJ, USA); sample III,

Table 1

Summary of the characteristics of xenon in Linde 4A

Type of cage	$\delta (\text{Xe}_n)$	Number of cages	$\langle n \rangle_{\text{Xe}}$
A	Standard	Most numerous	Higher
B	Lower by ca. 4 ppm	Somewhat fewer	Lower by about 1+

a second commercial Linde 4A drying sieve, courtesy of B. Calvert at Mobil.

2.2. NMR spectroscopy

^{129}Xe MAS NMR spectra were obtained at 99.5676 MHz (8.7 T) on a home-built spectrometer which consists of an 89-mm-bore superconducting solenoid magnet (Oxford Instruments, Osney Mead, Oxford, UK), a Nicolet 1180/Explorer 2090-IIIC data system (Nicolet, Madison, WI, USA) and a variety of digital and radiofrequency circuitries. A probe of Gay design [12] manufactured by Probe Systems (Champaign, IL, USA) was used for data acquisition. The 4-mm sealed sample was placed inside a standard (cutoff) Wilmad 5 mm O.D. NMR sample tube with a layer of PTFE tape between the two tubes to keep the smaller one in place. Samples were spun at about 2 kHz using 40-p.s.i. air. We have encountered only minimal difficulty in spinning the hand-made sample tubes (which always showed some minimal irregularities). Data were obtained using a 90° pulse (4.5–5 μs) excitation and a recycle delay between 5 and 10 s. 4K complex (2 $\times$ 2K) data points were collected for all spectra with 10 000–40 000 transients being averaged in each case. All spectra were recorded by using a 50-kHz ($\sim$ 500 ppm) sweep width. Line broadening due to exponential multiplication of 5 Hz was routinely applied prior to Fourier transformation. Conventional static spectra were obtained at 110.697 MHz on a Bruker AM400 using a recycle delay of 10 s and a sweep width of 42 kHz. Typically, 1K data points were zero-filled to 4K. Temperature control with the Bruker VT unit was within ± 0.2 K. The spinning air varied from 24 to 26°C for the MAS NMR experiments and was not regulated.

2.3. Line shape analysis

The relative intensities of each peak in the Xe spectra were obtained by fitting the line shapes with GRAMS software (Galactic Industries, Salem, NH, USA). From these simulations we determine the distribution, the fractions of the α -cages containing n Xe atoms (and m Kr atoms).

3. Results

Using the Gay probe, we have found that Xe MAS NMR linewidths of Xe_n clusters in Linde NaA zeolites can be as little as 1–1.2 ppm as opposed to ~ 8 –10 ppm in a typical static spectrum, almost an order of magnitude line-narrowing on MAS. Fig. 1a and b show a comparison between a static ^{129}Xe NMR spectrum and the MAS NMR spectrum of the same sample of pure xenon in NaA (sample I). Fig. 1c shows the MAS NMR spectrum of a sample containing a mixture of xenon and krypton in the same zeolite and prepared in the same way. (Xenon had not reached its equilibrium distributions in these samples when these spectra were taken, and the static spectrum in Fig. 1a was taken some time after the MAS spectrum in Fig. 1b.) It is quite clear that MAS narrows down the Xe_n peaks in a dramatic way and provides a means to observe details under MAS that would not otherwise be observed.

The xenon clusters provide a means of discriminating between several zeolites, all of which are nominally NaA. Shown in Fig. 2 is a comparison of zeolites from three sources, all of which have chemical shifts of Xe_n clusters which are indistinguishable from each other in static spectra (data not shown). In sharp contrast, the MAS NMR spectra show Xe_n peak shapes which are quite distinct from each other. The ultrapure NaA zeolite (sample I) provides the cleanest MAS NMR spectrum with only one set of peaks for Xe_n ($n = 1$ –4). Xe_5 and Xe_6 appear single also, when observed immediately upon cooling the sample from 350 to 25°C without temperature programming. As the sample equilibrates at room temperature, additional peaks begin to appear over time

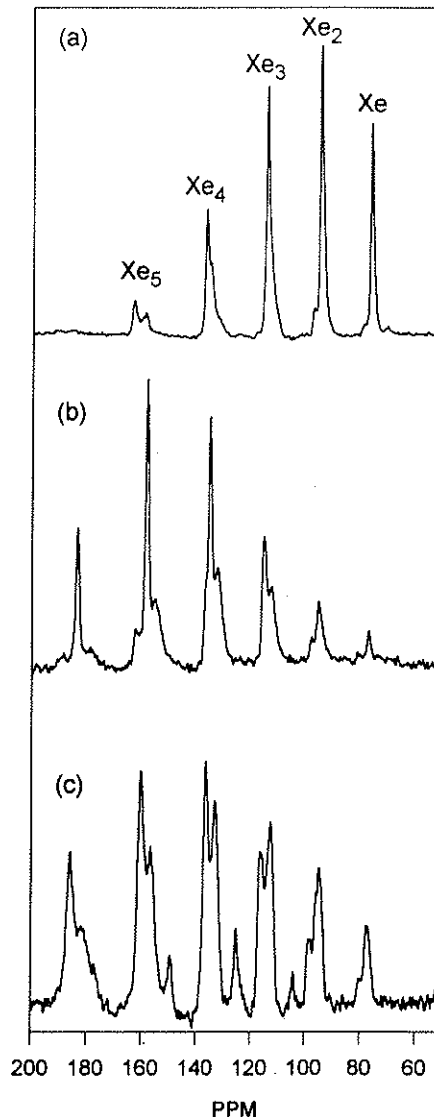


Fig. 2. 99.57-MHz ^{129}Xe MAS NMR spectra of xenon in NaA zeolite from three different sources: (a) sample I; (b) sample II; (c) sample III.

at lower chemical shifts, close to the original Xe_5 and Xe_6 , and a shoulder appears on the original Xe_4 , as indeed can already be seen in Fig. 2a. We discuss these changes further below. Xenon in zeolite sample II (Fig. 2b) shows two sets of Xe_n peaks, while sample III (Fig. 2c) shows an additional set of peaks, also in progressions of Xe_n and whose overall intensities give a measure of the relative fractions of what we believe are different types of cages present. The immediate conclusion here then is that ^{129}Xe appears to be a sensitive probe of ultra-structure in A-type zeolites.

The very interesting question now arises as to the nature of the differences seen between the distinct types of cages observed in the three different NaA zeolite samples. In order to establish the nature of the differences between the two main types of cages, we compared several samples of xenon adsorbed in sample II with increasing values of overall $\langle n \rangle_{\text{Xe}}$, as shown in Fig. 3. $\langle n \rangle_{\text{Xe}}$ is the average number of Xe atoms per α -cage in the sample. The MAS NMR spectra clearly show the presence of two sets of peaks, suggesting two different types of cage structure, which we will refer to as A- and B-type cages, characterized by the different chemical shifts of the Xe_n clusters. The *chemical shift increments are the same*, or very nearly so, with the largest B–A shift for Xe_1 and the smallest for Xe_5 , indicating that the internal volumes of the A and B cages are nearly the same. The Xe–Xe contributions to the chemical shifts are measured by the increments, and these in turn are dependent on the nature of the averaging among the inter-Xe distances within the cage, the ranges of these distances being determined to a large extent by the internal volume of the cavity. The total intensity of each set is determined mainly by the number of cages of each type and secondly, by the affinity of the xenon for the cages. On the other hand, the $\langle n \rangle_{\text{Xe}}$ is determined entirely by the affinity of the xenon for these cages. In Fig. 3 the relative total intensities of A and B indicate that A cages represent the dominant type of structure present. Comparison of the envelopes of peaks in the two sets as the overall $\langle n \rangle_{\text{Xe}}$ changes in Fig. 3a–d provides a visual estimate of $\langle n \rangle_{\text{Xe}}$ for each type of cage since $\langle n \rangle_{\text{Xe}} = \Sigma \text{area}(\text{Xe}_n) / \Sigma (1/n) \text{area}(\text{Xe}_n)$, when there are no empty cages. The shaded B peaks obviously have a lower $\langle n \rangle_{\text{Xe}}$ than the A set. The much larger $\langle n \rangle_{\text{Xe}}$ for the type A peaks is consistent with type A cages being preferred by the xenon atoms over the B cages (see Table 1).

Fig. 4 demonstrates an attempt to discover the possible nature of the disorder exhibited by xenon in NaA zeolites. Our initial idea was that there might be sodium deficits, or possibly Ca^{2+} could have been taken up during production, since the effects noted above all appeared quite repro-

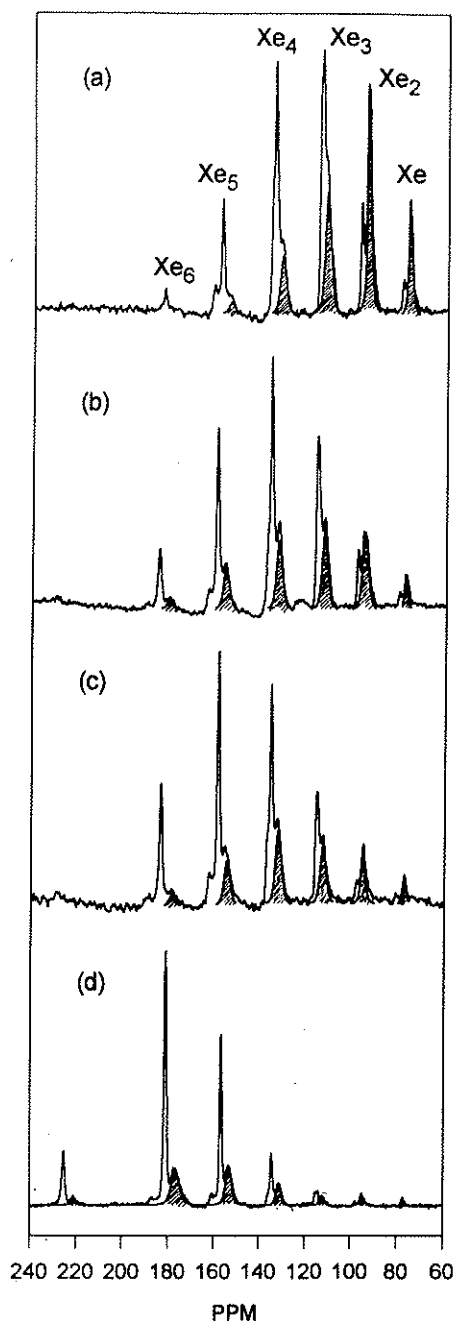


Fig. 3. 99.57-MHz ^{129}Xe MAS NMR spectra of xenon in zeolite NaA (sample II) at various loadings (increasing from top to bottom). The two sets of cluster peaks clearly show two types of cages. One set is shaded for contrast so that the different $\langle n \rangle_{\text{Xe}}$ for the two types of cages becomes clearly evident.

ducible. Samples of NaA (sample II) were therefore placed in three solutions each containing small amounts of Ca^{2+} . After periodic shaking for three days, the supernatant was decanted, and the zeolite washed several times with deionized

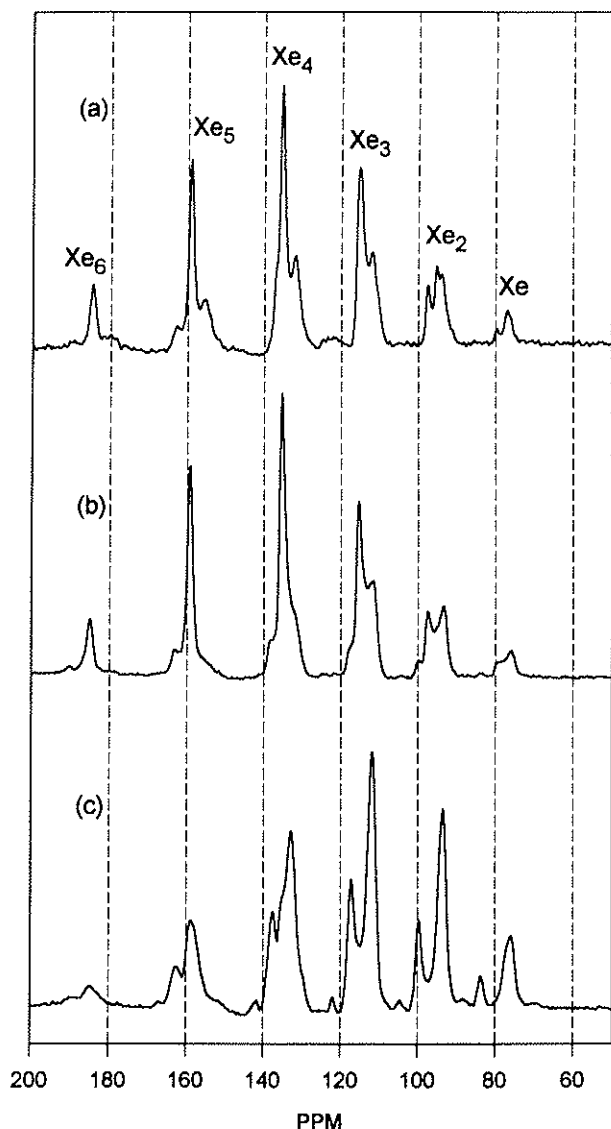


Fig. 4. 99.57-MHz ^{129}Xe MAS NMR spectra of xenon in the following zeolites: (a) NaA (sample II), untreated; (b) after exchange with a small amount of Ca^{2+} ; (c) after exchange with a greater amount of Ca^{2+} .

water (to eliminate dissolved salts). The zeolite is dried at less than 100°C to remove bulk water and then at 350°C overnight before introducing into the sample tube. Analysis of the supernatant

solution and the dried NaA was consistent with $\text{Ca}_x\text{Na}_y\text{Si}_{12}\text{Al}_{12}\text{O}_{48}$ with $x = 0.175, 0.31$ and 0.58 , and $2x + y = 10.7\text{--}11.0$ ($2x + y$ less than 12 has also been found by others [13]). These Ca^{2+} -exchanged zeolite samples were then treated in exactly the same manner as the others (as described in the Experimental section) in preparing adsorbed xenon samples. The MAS NMR spectra of ^{129}Xe in the zeolite with the lowest and highest levels of Ca^{2+} exchange are shown in Fig. 4b and 4c respectively, and are compared with the untreated sample II in Fig. 4a. Incidentally, the overall $\langle n \rangle_{\text{Xe}}$ in these samples decrease in the order $a > b > c$. The results are as follows. Using the zeolite prepared with the smaller amount of Ca^{2+} exchange, the MAS NMR spectrum exhibits the following features: the size of each Xe_n peak in set B increased relative to the respective Xe_n peak in set A, certainly for low n , less so for high n ; Ca^{2+} exchange increased the number of B-type cages at the expense of A-type cages, especially at low n , but not so much at high n ; finally, an additional set (type C) of Xe_n peaks appear ($n = 1\text{--}5$) with higher chemical shifts than the A peaks, but the Xe_n chemical shift increments are the same to the extent that they can be determined (see Table 2).

Further information is obtained with a larger amount of Ca^{2+} exchange. Using the zeolite which has been treated to obtain a larger amount of Ca^{2+} exchange (an average of 0.58 Ca^{2+} per cage), we find the following. There are increased intensities of type B peaks. Type A peaks become greatly diminished in intensity, especially at low n but there is a less pronounced depletion for high n . There is also an overall diminished intensity for Xe_n clusters in type A cages and the type C peaks greatly increased in intensity. Finally, another new set of peaks (type D) appear at yet higher ^{129}Xe chemical shifts, maintaining nearly

Table 2

Results of a small amount of Ca^{2+} ion exchange (average of 0.17 Ca^{2+} per cage)

Type of cage	$\delta (\text{Xe}_n)$	Number of cages	$\langle n \rangle_{\text{Xe}}$
A	Standard	Still dominant	Higher
B	Lower by ca. 4 ppm	Somewhat fewer but increased	Lower by about 1 +
C	Higher by 4 ppm	Few	Too few to determine $\langle n \rangle_{\text{Xe}}$

the same chemical shift increments between clusters. The further growth of type B and type C peaks, and the appearance of type D peaks, indicates that Ca^{2+} exchange created new types of cages containing Ca^{2+} which are distinguishable from each other and which involve increasing numbers of Ca^{2+} ions per cage. The direction of the ^{129}Xe chemical shift of the set of peaks C–D with increasing number of Ca^{2+} ions is consistent with the change in ^{129}Xe chemical shifts at the zero-loading limit in NaCaA upon increasing the Ca/Na ratio [13]. The magnitude of the incremental shift upon increasing Ca^{2+} in the latter case was roughly 4 ppm per added Ca^{2+} ion, which is in the same direction and the same magnitude as the change in the ^{129}Xe chemical shifts that is observed here in going from set C to set D. Since the B peaks increased in intensity relative to the A peaks upon Ca^{2+} exchange, type B peaks in the NaA zeolite (sample II) may be due to an ultrastructural change similar or identical to that caused by Ca^{2+} exchange (see Table 3).

The next experiments involve our ultimate goal of elucidating the physics of co-adsorption phenomena. Towards this end the determination of distributions of the co-adsorbed species provides much detailed information. For example, using xenon to probe the structure and dynamics of mixed adsorbates, we directly observe the distributions of xenon atoms in the presence of co-adsorbed molecules such as argon, as a function of the average occupancy numbers $\langle n \rangle_{\text{Xe}}$ and the $\langle m \rangle_{\text{Ar}}$, Ar being in fast exchange, moving freely from cage to cage during the observations [14]. There are, however, other species that, like Xe, have long mean residence times in the α -cages. Because the chemical shift of ^{129}Xe in the presence of another molecule is quite distinct from that in the presence of another Xe, as we have

determined from the second virial coefficients of nuclear shielding in the gas phase [15–17], we expect the distinct ^{129}Xe chemical shifts for those clusters corresponding to one Xe atom and various numbers of other X molecules in the α -cage to provide separate signals. If individually resolved, the peaks should be directly assignable on the basis of the known relative magnitudes of the shielding virial coefficients for Xe–Xe versus Xe–X [15–17]. In the same way, it should be possible to individually assign every mixed cluster Xe_nKr_m peak, so that both intensity and chemical shift can provide interesting information about co-adsorption.

The first indications that mixed clusters have reasonably long residence times in the α -cages of NaA were evident in static spectra taken under the same conditions as the pure xenon in NaA. Unlike the (fast-exchange) mixture of Xe and Ar in NaA, ^{129}Xe spectra of mixtures of Xe and Kr in NaA showed peaks that are definitely broader than those of Xe_n observed for pure xenon in the same zeolite. For example, Fig. 5a and b hinted at the possibility that additional heteroatom cluster peaks were present. The static ^{129}Xe spectrum of pure xenon in NaA (sample II) at high loading ($\langle n \rangle_{\text{Xe}} = 5.80$) in Fig. 5a shows an essentially featureless 45-ppm region between the Xe_6 and Xe_7 . In contrast, the same 45-ppm region between the Xe_6 and Xe_7 peaks exhibits a discernible extra feature when observed in a sample containing a mixture of xenon and krypton at similar Xe loading ($\langle n \rangle_{\text{Xe}} = 5.85$) in Fig. 5b. Upon MAS, the spectrum of the same sample, Fig. 5c shows the extra peaks with much better resolution, and we can clearly identify Xe_8 , Xe_7 , Xe_6Kr , Xe_6 , Xe_5Kr , and Xe_5 .

Much clearer examples are shown in Fig. 6 where the ^{129}Xe MAS NMR spectra of samples each containing a mixture of xenon with krypton

Table 3
Results of greater Ca^{2+} ion exchange (average of 0.58 Ca^{2+} per cage)

Type of cage	$\delta (\text{Xe}_n)$	Number of cages	$\langle n \rangle_{\text{Xe}}$
A	Standard	Only third largest now	Highest still
B	Lower by ca. 4 ppm	Dominant	Lower than A
C	Higher by 4 ppm	Second highest	Comparable to B
D	Higher by 8 ppm	Fewest	Too few to determine $\langle n \rangle_{\text{Xe}}$

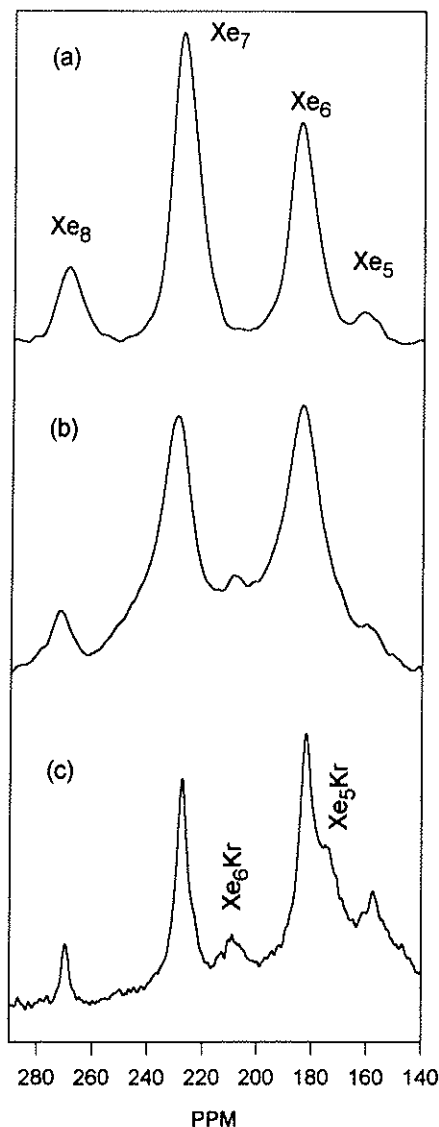


Fig. 5. Comparison of the ^{129}Xe spectra of xenon at high loading ($\langle n \rangle_{\text{Xe}}$ ca. 5.85) in zeolite NaA (sample II): (a) with pure xenon; (b) with Xe and Kr. Both static spectra in a and b were taken at 110.697 MHz on a Bruker AM400 spectrometer; (c) 99.57-MHz ^{129}Xe MAS NMR spectrum of the same sample as in b.

in NaA zeolite (sample I) are displayed. In Fig. 6a the multitude of 1-ppm-wide lines are shown and are readily assigned to specific mixed clusters of Xe_nKr_m ($n = 1-6$, $m = 0-1$). The MAS NMR spectra in Fig. 6a–c clearly show the first observation of individual resonance peaks of mixed clusters up to Xe_5Kr . In particular, we report here the first observation of the mixed clusters XeKr , Xe_2Kr , Xe_3Kr , Xe_4Kr , Xe_5Kr , and Xe_6Kr in the α -cages of the zeolite NaA. The chemical shifts of the mixed clusters given in Table 4 differ

from Xe , $\text{Xe}_2, \dots, \text{Xe}_5$ by amounts that are consistent with the gas-phase chemical shifts of Xe in mixtures of Xe and Kr and with the chemical shift increments between the Xe_n . The mixed clusters are unequivocally identified in the NaA

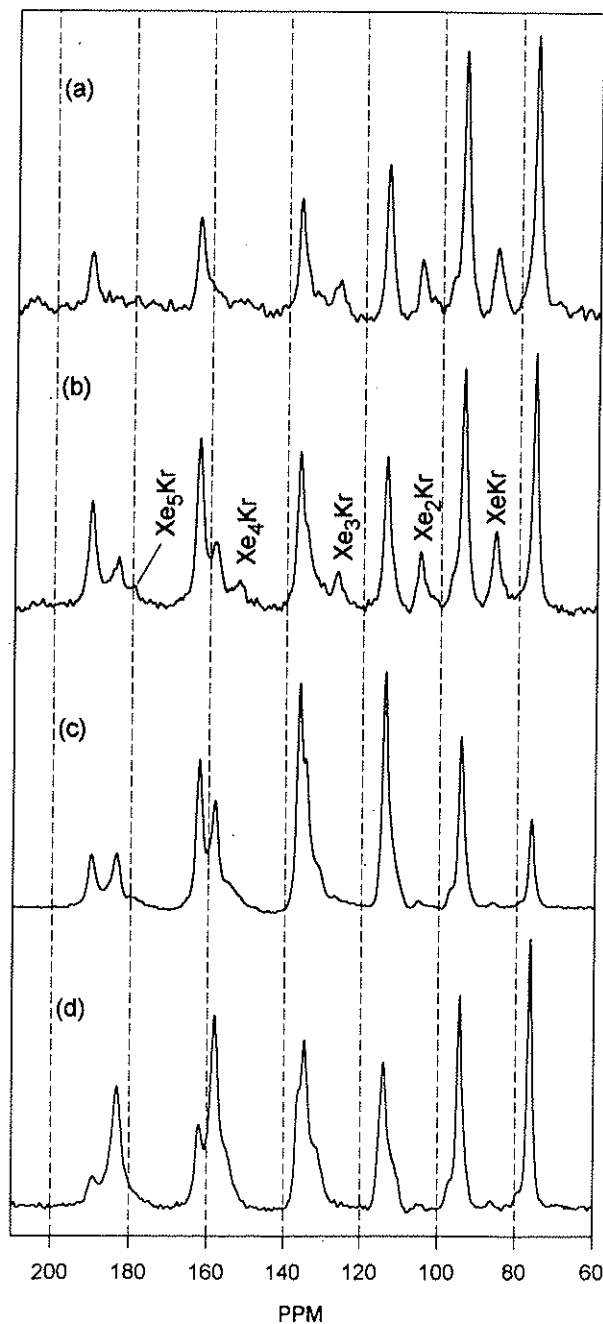


Fig. 6. Study of the time development of the 99.57-MHz ^{129}Xe MAS NMR spectra of samples containing xenon and krypton in zeolite NaA (sample I). (a, b) Spectra taken of the same sample. The spectra have been taken in chronological order a–d. The small peaks are the mixed clusters Xe_nKr . Both the Xe – Kr distribution and the zeolite are approaching thermal equilibrium in the sequence (see text for details).

Table 4

¹²⁹Xe Chemical shifts of the mixed clusters Xe_nKr in the α -cages of zeolite NaA in ppm relative to the Xe_n cluster

Cluster	$\delta(\text{Xe}_n\text{Kr}) - \delta(\text{Xe}_n)$
XeKr	9.9
Xe ₂ Kr	11.0
Xe ₃ Kr	12.8
Xe ₄ Kr	15.7
Xe ₅ Kr	16.3
Xe ₆ Kr	26.5

from E. Flanigen. The same mixed clusters are also observed in zeolite sample II and the chemical shifts from the corresponding Xe_nKr₀ are the same within experimental error. For this demonstration, the krypton concentrations have been chosen so as to make the Xe_nKr₀ peaks the most prominent ones and also to drastically limit the number of mixed cluster peaks in each progression so as to make the assignments less ambiguous.

All of the spectra shown in Fig. 6 were taken on samples which have not been fully equilibrated. The samples were prepared as described in the Experimental section and then kept in an oven at 350°C overnight. For these preliminary explorations, the temperature-programmed equilibration down to room temperature was omitted. The spectra shown in Fig. 6 were taken in chronological order from a to d. In these samples the changes in the sample I zeolite as it approaches thermal equilibrium (at 25°C) after having been in equilibrium at 350°C are well documented by the Xe₅ and the Xe₆ clusters, although there are also systematic changes in the chemical shifts of the smaller clusters as well. Fig. 6a and b are spectra of the same sample. Over time, the single peak for Xe₅ (and Xe₆) in the zeolite at equilibrium at 350°C each generate a second resonance at lower chemical shift which begins to grow until it dominates. These larger clusters are more sensitive to the details of the cage geometry than are Xe₁ or Xe₂. Fig. 6c and d are of samples prepared at the same time with nearly the same amounts of Xe and Kr as Fig. 6a and b, but the MAS NMR spectra were taken at later times, thus providing further glimpses into further evolution in the approach to equilibrium

of zeolite structure and xenon and krypton distribution. The monotonic changes that are observed with time as the zeolite approaches thermal equilibrium from 350 to 25°C are, we believe, consistent with the known existence of two forms of dehydrated NaA. The low-temperature form has been shown to have rhombohedral symmetry ($r\bar{3}c$) at 4.5 and 296 K by neutron powder diffraction [18,19], and there is a well known transition to cubic symmetry at about 335 K [18]. Above this transition, the results of neutron powder diffraction [18] are in good agreement with the single-crystal X-ray structure refinements by Pluth and Smith [20] which established the $Fm\bar{3}c$ structure [20]. The change from $Fm\bar{3}c$ to $r\bar{3}c$ has been documented by neutron diffraction, and structural analysis has revealed that the rhombohedral symmetry is a consequence of the ordering of the Na(II) ions in eight-rings. This has been characterized as a change in the occupancies of the four equivalent (in $Fm\bar{3}c$) Na(II) positions in the eight-ring windows from 1/4 all (at room temperature and below) to two 1/2 and two 0 with otherwise no relaxation of $Fm\bar{3}c$ positional constraints on any of the framework atoms [18]. The MAS spectra shown here appear to be consistent with the presence of this transition, with the lower chemical shifts for the Xe₅ and the Xe₆ clusters being associated with the α -cage form stable at room temperature and below ($r\bar{3}c$). Another alternative is that the change in the α -cages is driven by the Xe atoms. This demonstrates the great sensitivity of the Xe_n cluster shifts to small changes in the α -cages.

Another point of interest in these spectra is that at the beginning (in Fig. 6a) the Xe distribution is that appropriate to 350°C while the Kr distribution is that appropriate to 25°C. With time, the Xe comes into the α -cages from the gas phase, with the outer cages of each crystallite being highly occupied at the outset, while the innermost cages still retain the distributions appropriate to the higher temperature. Fig. 6b is a spectrum of the same sample as Fig. 6a, showing a clearly non-equilibrium Xe distribution whereas the Kr distribution is at equilibrium. The preferential adsorption of xenon drives the Kr out into the gas phase, until the equilibrium Kr distribu-

tion at the much higher $\langle n \rangle_{\text{Xe}}$ appropriate to room temperature is achieved. The spectra in Fig. 6c and d are of two samples with very nearly the same composition as the sample of Fig. 6a and b and show that after a longer period of time the final $\langle m \rangle_{\text{Kr}}$ will be much smaller than at the beginning. (In contrast to the sample in Fig. 6d, the sample in Fig. 6c was temperature-programmed down to 60°C, and thus shows a xenon distribution appropriate to 60°C.) The dynamics of this competitive Xe–Kr adsorption phenomenon will be considered in a later paper.

Higher Kr concentrations allow large numbers of mixed clusters Xe_nKr_m to form in the cages. Why have we not observed the higher mixed clusters? Based on the observed chemical shifts for Xe_nKr we predict that the Xe_nKr_m (fixed n , increasing m) progressions run into each other and overlap, making it more difficult to observe individual mixed rare gas clusters (e.g. Xe_nKr_2 , Xe_nKr_3 runs into $\text{Xe}_{n+1}\text{Kr}_0$, $\text{Xe}_{n+1}\text{Kr}_1$). Furthermore, in bigger clusters containing larger numbers of Kr atoms, the cage-to-cage migration rate constants are expected to be much higher, i.e. the rate constants for leaving the bigger clusters with n Xe atoms and m Kr atoms are greater than for leaving the smaller ones (as is well known from magnetization transfer and two-dimensional EXSY experiments in the pure xenon work) [3,6]. This leads to higher exchange rates for Kr, thus shorter residence times for the mixed clusters with m higher than 1 in samples with higher average Kr occupancies $\langle m \rangle_{\text{Kr}}$ than the ones shown here.

4. Discussion

Several experimental results in our laboratory have indicated that the broad peaks observed in the ^{129}Xe NMR spectra of the Xe_n clusters in NaA were inhomogeneously broadened, arising from either a chemical shift dispersion or from a distribution of local magnetic field environments [21]. In the hole-burning experiment, the narrowest region that could be perturbed by selectively irradiating a narrow region in the center of the 1000-Hz-wide Xe_7 peak was 50–100 Hz. The

results of the CPMG experiment on a high-loading sample led to a natural linewidth of less than 40 Hz, and on samples of lower loading, the CPMG experiments yield even longer coherence life times, corresponding to even narrower natural linewidths. Furthermore, the magnetization transfer experiments reported previously [3] revealed a systematic dependence of the peak widths on the delay times, suggesting that the individual broad peaks might be composed of several narrower peaks. The combined evidence suggested that intrinsically narrow lines might be associated with Xe_n clusters in crystallites of NaA but that the width of the observed peaks arose from a dispersion in resonance position due to a distribution of crystallite orientations. The broad peaks for the Xe_n clusters in the static spectra of xenon in NaA were assumed to be a manifestation of the non-isotropic averaging of the ^{129}Xe shielding inside the α -cage. The ten-fold reduction of the peak width achieved with MAS validates the idea of a dispersion in the resonance frequencies of the Xe_n clusters. A possible explanation for the dispersion is that the resonance frequencies appropriate to the average chemical shift in an α -cage depend on the orientation of the cage with respect to the external magnetic field. The presence of the Na(III), which is coordinated across a four-oxygen ring and partly filling the internal volume of the α -cage, could be sufficient to result in a non-isotropic averaging of the shielding in a Xe_n cluster. A typical zeolite sample contains crystallites randomly oriented in the magnetic field, resulting in different resonance frequencies, which average on MAS. The peak widths observed in the MAS NMR spectra do depend somewhat on cluster size, as might be expected if the natural linewidths are largely determined by the loss of coherence associated with the Xe spins leaving a cage. Previous work [3,6] has established that the Xe atom has a demonstrably larger rate constant for leaving a cage containing the larger Xe_n clusters ($n = 5$ –8), consistent with the MAS results we have obtained.

The nature of the apparent disorder which occurs with Ca^{2+} exchange is not yet fully understood. What is clear is that a distribution of Ca^{2+} over the α -cages occurs. Further Ca^{2+} substitu-

tion gives rise not to a simple conversion of all α -cages to uniformly single Ca^{2+} -substituted cages but to the simultaneous existence of cages with differing numbers of Ca^{2+} ions. The changes in ^{129}Xe chemical shift of Xe_n clusters upon Ca^{2+} for Na^+ substitution are only slightly dependent on the cluster size. The first Ca^{2+} substitution leads to a different direction of the Xe_n chemical shift than subsequent substitutions. That is, the first extra set of peaks that may be attributed to Ca^{2+} substitution have a uniform shift of all Xe_n clusters to a lower ^{129}Xe chemical shift (more shielded), whereas further Ca^{2+} substitution creates cages with Xe_n clusters to higher chemical shifts (deshielded). This observation suggests that the nature of the first Ca^{2+} substitution into an α -cage is qualitatively different from subsequent substitutions. This is consistent with the first Ca^{2+} ion taking the place of one Na(III) and one Na(I) in an α -cage. At low Ca numbers, Ca^{2+} substitution does not appear to lead to the opening up of a window (which would result from substitution of Ca^{2+} for a Na(II) ion in an eight-ring window and one other Na^+ ion). This would lead to formation of two cages interconnected by an open window, which would have led to chemical shifts appropriate to a much larger cavity. For example, in addition to Xe_5 clusters in normal-sized α -cages there would be some Xe_5 clusters found in the double-sized cavity produced from averaging of Xe_n and Xe_{5-n} clusters in adjacent connected α -cages. These double cages would lead to chemical shifts that are fairly predictable from what we know from Grand Canonical Monte Carlo (GCMC) simulations of xenon in A-type zeolites [2]. There is no sign of such double cages in the spectra of Ca^{2+} -exchanged NaA at the low Ca^{2+} substitutions used in this work (up to an average of 0.58 Ca per cage). When the average number of Ca^{2+} substitutions reaches $x = 2$ in $\text{Ca}_x\text{Na}_{12-2x}\text{Si}_{12}\text{Al}_{12}\text{O}_{48}$, it is clear from the NaCaA studies of Tsiao et al. [13] that many interconnected cages can however exist.

5. Conclusions

The results we have presented above show for the first time that the ^{129}Xe NMR spectra of Xe_n

clusters in A zeolites can be narrowed under MAS. Our results indicate that the xenon atom is a very sensitive probe of cation disorder in A zeolites. In the ^{129}Xe MAS NMR spectrum, each type of cage gives a separate set of Xe_n peaks with its own overall intensity (a direct measure of the fraction of cages of that type), its own $\langle n \rangle_{\text{Xe}}$, and its own detailed distribution of Xe_n clusters among the cages. From the intensities we have been able to measure the distributions of two to three distinct types of cages in zeolites, all of which are nominally NaA. With the Ca^{2+} -exchange experiment we have begun to investigate the possible nature of the type of disorder seen in the NaA zeolites used. The very highly resolved spectra obtained under MAS provide detailed information about the nature of Ca^{2+} ion replacement. The chemical shifts of the various Xe_1 peaks in the four types of cages obtained upon Ca^{2+} replacement of Na^+ in NaA are in excellent agreement with the known dependence of the zero-loading ^{129}Xe chemical shift in NaCaA with Na/Ca ratio. From the observed coexistence of cages with differing numbers of Ca^{2+} ions we can determine the distribution of cage types from the overall intensities. These distributions provide equilibrium concentrations for Ca^{2+} replacement, i.e. free energy differences between cage types in the same zeolite sample. Since the chemical potential for xenon in the different cage types are identical (since all are at equilibrium with the same xenon gas in the sample), the different $\langle n \rangle_{\text{Xe}}$ observed for the various cage types in the same sample provide differences in adsorption isotherms or Henry's law constants for each of the various cage types. The highest $\langle n \rangle_{\text{Xe}}$ observed for the type A cages clearly indicates a higher affinity of a xenon for type A cages than for type B, C, or D.

Under the high-resolution conditions afforded by even slow (~ 2 kHz) MAS we have also observed the individual peaks corresponding to mixed clusters Xe_nKr_m inside the α -cages, which has allowed the first direct determination of the distribution of co-adsorbates in a microporous solid. These distributions will provide important detailed tests of computer simulations of co-adsorption phenomena. Furthermore, we have made

the first observations of ^{129}Xe chemical shifts in such mixed clusters. With a known Xe–Kr shielding function [22], these chemical shifts will provide direct tests of Monte Carlo simulations of averaging over large numbers of possible configurations of the mixed rare gas clusters Xe_nKr_m inside an α -cage. [23]. Such results will therefore provide additional detailed tests of computer simulations of co-adsorption phenomena.

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