^{129}Xe NMR: Dynamic Behavior of Xenon in NaY Zeolite at 77 K[†]

C. I. Ratcliffe* and J. A. Ripmeester

Molecular Structures and Dynamics Group
Steacie Institute for Molecular Sciences
National Research Council of Canada
Ottawa, Ontario, Canada K1A 0R6

Received August 30, 1994

Since the first experiments on atomic xenon in solids other than pure xenon,[1,2] ^{129}Xe NMR has seen extremely wide use in studies of porous media,[3−7] particularly zeolites. Beginning with the work of Ito and Fraissard,[8] numerous studies have focused on ^{129}Xe in zeolites X and Y. The open-pore framework of zeolite Y[9] has large cavities of diameter $\sim$11 Å interconnected tetrahedrally via shared 12-ring windows of diameter $\sim$7.2 Å, taking into account oxygen van der Waals radii. Xe, diameter $\sim$4.3−4.4 Å, can readily pass through the 12-ring windows but cannot gain access to the smaller cavities.

The ^{129}Xe NMR spectra of xenon adsorbed on zeolite Y and its cation-exchanged forms invariably show isotropic lines at room temperature. This observation in itself is very informative. Since a xenon localized on a surface or adsorbed in an anisotropic site should have a sizable chemical shift anisotropy, a truly isotropic line shape can arise only if there is rapid reorientation of the chemical shift tensor by dynamic exchange among sites related by spherical or pseudospherical (e.g., cubic or tetrahedral) symmetry, or by rapid exchange between the gas phase and many randomly oriented particles. (Alternatively an apparently isotropic chemical shift could arise if the exchange-averaged anisotropy is so small that it is hidden by broadening from other interactions; this might occur in a system where the lifetime in the gas phase with zero anistropy is considerably greater than the lifetime on or near the surface with large anisotropy.) It has become clear that at room temperature the observed Xe chemical shift (δ) in zeolite Y is a dynamic average of δ within the zeolite pores (itself a dynamic average over the available pore space) and δ in the "gas" phase between particles. Pulsed field gradient work[10−13] has shown that, on the NMR time scale, xenon exchange can occur over thousands of zeolite cages and, by implication, even between particles below a certain size. Xe chemical shift studies have also demonstrated internal/external and interparticle exchange.[14−22] However, as the temperature is lowered there comes a point at which the bulk of the xenon has condensed into the zeolite, and here we address the behaviour of this xenon at very low temperatures. Several low-temperature studies of xenon adsorbed on Y zeolites have been reported.[22−28] Cheung et al.[24,25] in studies at 144 K observed a jump in δ at loadings higher than about 6 Xe/cage, which was interpreted as a gas to liquid-like transition. Recently we studied a series of powdered Na−Y samples loaded with Xe to different levels as a function of temperature down to 120 K.[22] On cooling there is an initial rapid increase in δ as the Xe condenses into the zeolite pores, followed by a temperature region where the increase either is much slower (low loadings) or even levels off (intermediate and high loadings). At lower temperature still, for all loadings, δ increases more rapidly again.

Here we describe observations on a number of samples after they were quenched to 77 K from 295 K. The samples contained no helium, which is usually added to provide a good thermal bath. Thus the quenched samples were initially in a state far from equilibrium. Loadings, given as *n*Xe/cage, represent the *average* number of Xe atoms per cage. The samples, in sealed 10 mm o.d. Pyrex tubes, were quenched in liquid nitrogen and ^{129}Xe NMR spectra immediately recorded using a probe in which the coil can be immersed in liquid nitrogen. The samples were maintained from then on at liquid nitrogen temperature, and spectra were recorded periodically.

In all cases the initial spectra were complex, with several broad lines and irregular features, and sometimes a trace of solid Xe was detected. With time, however, all irregularities, including the solid Xe line, disappeared, leaving a single, relatively sharp, isotropic line. The higher the Xe loading, the further downfield was δ for these single lines, in accordance with the well-known correlation between δ and space available to the Xe.[4,29] Samples with high or low loading annealed to equilibrium much faster than intermediate loadings; 12 Xe/cage took 1−3 days, and 1 Xe/cage took about 20 h. Furthermore, the bulk density had a quite dramatic effect on the annealing time; e.g., at 6 Xe/cage, equilibrium was reached between 10 and 18 months for the loose powder but only 2−5 weeks for the compacted sample. During the equilibration period the spectra of some samples passed through many different patterns, Figure 1. We have observed similar behavior for Xe in Ca−A zeolite quenched to 77 K. (Samples also containing a small amount of helium gave the equilibrium isotropic lines immediately after quenching.)

These results show several important things, the most significant of which is that within any particle of the Na−Y zeolite the Xe atoms must still be undergoing fast exchange, even at 77 K, 84 deg below the freezing point of bulk Xe. The isotropic lines show that all Xe are equivalent and therefore that the Xe atoms sample all available site types. Since the zeolite lattice is cubic, such motion must produce an isotropic average shift. Incidentally one would predict that, for Xe in a noncubic framework with large pores of size equivalent to those

---

[†] Published as NRCC No. 37298.

(1) Ito, T.; Fraissard, J. *Proceedings of the 5th International Conference on Zeolites, Naples 1980*; Rees, L. V. C., Ed.; Heyden: London, 1980; p 150.

(2) Ripmeester, J. A.; Davidson, D. W. *Bull. Magn. Reson.* **1981**, *2*, 139.

(3) Fraissard, J.; Ito, T. *Zeolites* **1988**, *8*, 350.

(4) Chen, Q. J.; Springel-Huet, M. A.; Fraissard, J. *Stud. Surf. Sci. Catal.* **1991**, *65*, 219.

(5) Dybowski, C.; Bansal, N.; Duncan, T. M. *Annu. Rev. Phys. Chem.* **1991**, *42*, 433.

(6) Barrie, P. J.; Klinowski, J. *Prog. Nucl. Magn. Reson. Spectrosc.* **1992**, *24*, 91.

(7) Raftery, D.; Chmelka, B. F. *NMR: Basic Princ. Prog.* **1994**, *30*, 11.

(8) Ito, T.; Fraissard, J. *J. Chem. Phys.* **1982**, *76*, 5225.

(9) Eulenberger, G. R.; Shoemaker, D. P.; Keil, J. G. *J. Phys. Chem.* **1967**, *71*, 1812.

(10) Heink, W.; Karger, J.; Pfeifer, H.; Stallmach, F. *J. Am. Chem. Soc.* **1990**, *112*, 2175.

(11) Karger, J.; Pfeifer, H.; Stallmach, F.; Spindler, H. *Zeolites* **1990**, *10*, 288.

(12) Karger, J.; Pfeifer, H. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1989.

(13) Karger, J.; Pfeifer, H.; Stallmach, F.; Feoktistova, N. N.; Zhdanov, S. P. *Zeolites* **1993**, *13*, 50.

(14) Shoemaker, R.; Apple, T. *J. Phys. Chem.* **1987**, *91*, 4024.

(15) Conner, W. C.; Weist, E. L.; Ito, T.; Fraissard, J. *J. Phys. Chem.* **1989**, *93*, 4138.

(16) De Menorval, L. C.; Raftery, D.; Liu, S. B.; Takegoshi, K.; Ryoo, R.; Pines, A. *J. Phys. Chem.* **1990**, *94*, 27.

(17) Chen, Q. J.; Fraissard, J. *Chem. Phys. Letts.* **1990**, *169*, 595.

(18) Ryoo, R.; Pak, C.; Chmelka, B. F. *Zeolites* **1990**, *10*, 790.

(19) Chmelka, B. F.; Pearson, J. G.; Liu, S. B.; de Menorval, L. C.; Pines, A. *J. Phys. Chem.* **1991**, *95*, 303.

(20) Ripmeester, J. A.; Ratcliffe, C. I. *Mater. Res. Soc. Symp. Proc.* **1991**, *233*, 281.

(21) Chen, Q. J.; Fraissard, J. *J. Phys. Chem.* **1992**, *96*, 1814.

(22) Ripmeester, J. A.; Ratcliffe, C. I. *Anal. Chim. Acta* **1993**, *283*, 1103.

(23) Ripmeester, J. A.; Ratcliffe, C. I. *J. Phys. Chem.* **1990**, *94*, 7652.

(24) Cheung, T. T. P.; Fu, C. M.; Wharry, S. *J. Phys. Chem.* **1988**, *92*, 5170.

(25) Cheung, T. T. P.; Fu, C. M. *J. Phys. Chem.* **1989**, *93*, 3740.

(26) Cheung, T. T. P. *J. Phys. Chem.* **1992**, *96*, 5505.

(27) Chen, Q. J.; Fraissard, J. *J. Phys. Chem.* **1992**, *96*, 1809.

(28) Pires, J.; Brotas de Carvalho, M.; Ribeiro, F. R.; Nagy, J. B.; Derouane, E. G. *Appl. Catal. A* **1993**, *95*, 75.

(29) Ripmeester, J. A.; Ratcliffe, C. I.; Tse, J. S. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 3731.

0002-7863/95/1517-1445$09.00/0

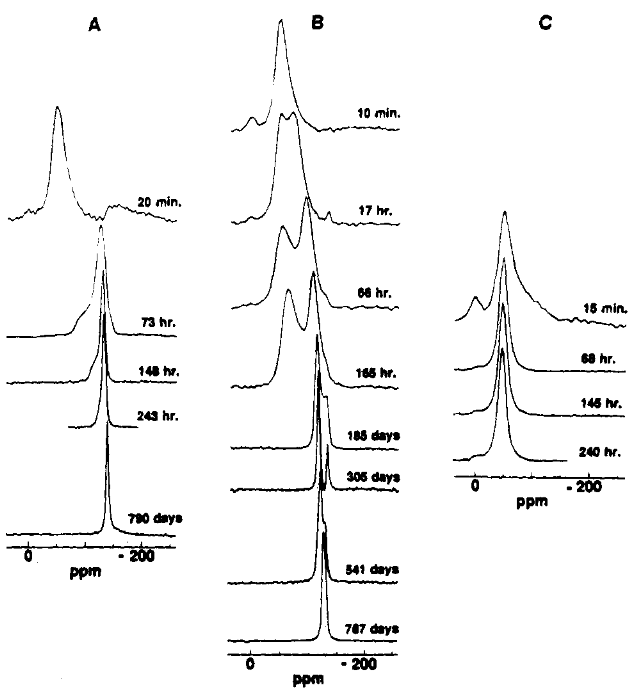

Figure 1. ^{129}Xe NMR spectra at 77 K of powder samples of Xe/NaY as a function of time: (A) 6 Xe/cage (packed powder), (B) 8 Xe/cage (loose powder), (C) 12 Xe/cage (loose powder). The spectra were obtained at 49.79 MHz using a Bruker CXP 180 spectrometer. A recycle time of 40 s was used in order to detect any solid Xe. Shifts are given relative to solid Xe at 77 K, which occurs at ~317 ppm relative to the shift of Xe gas extrapolated to zero pressure.

of Na−Y, the equilibrium 77 K spectrum would be a single but anisotropic line. Clearly the magnitude of the chemical shift anisotropies for the sites involved in the exchange averaging are not known, but if they are assumed to be in the range 10−100 ppm, then the observed lines indicate time scales for the exchange on the order of 3×10^{-4} to 3×10^{-5} s. The next important finding is that while motion within a zeolite particle is rapid at 77 K, exchange between the particles must be slow but finite for there to be any annealing at all. Xe transport most likely occurs through surface contacts between particles. Without He gas to provide good thermal contact in these samples, the rapid quenching produces large thermal gradients and hence Xe density gradients across the bulk sample. Different particles will initially have different average numbers of Xe/cage and, thus, give rise to a distribution of isotropic shifts. Such a distribution has already been suggested by Cheung for samples which he rapidly cooled to 144 K.[24] Equilibrium is eventually established when all particles have the same Xe density. Any bulk Xe formed from the gas phase during quenching must also be able to migrate slowly through surface contact into the zeolite. More densely packed samples have more surface contacts and hence equilibrate faster than loosely packed samples. The sharp lines observed in some of the loosely packed samples at intermediate times, e.g., Figure 1B, probably reflect regions of different bulk density (or clumps of powder) which have equilibrated within themselves but not over the whole sample. We postulate that the shorter annealing times observed for the low and high loadings reflect the ease of migration of a single Xe at low loading or of a "hole" at high loading.

What picture do we have of the state of the Xe at 77 K? It is still definitely very mobile and probably closely associated with the inner surfaces of the zeolite framework. Referring to our earlier temperature-variation studies,[22] we suggested that the initial sharp rise in Xe chemical shift on cooling was due to increasing adsorption of gaseous Xe into the pores until there was very little Xe gas remaining. At this point the Xe density and shift remain relatively constant over a short temperature range. We suspect that in this region the xenon phase in the pores is similar to but not exactly like a gas, in that the Xe rapidly samples the entire void space, though it must spend more time in the potential well associated with the cavity walls,[23] which is also expected from molecular dynamics (MD) simulations.[30−33] Then as the temperature decreases further, condensation of the xenon onto the pore surface and/or clustering of the xenon to produce a liquid- or solid-like phase results in increases in local density and δ. This appears to be the state still present at 77 K. (It is not clear whether Xe−surface or Xe−Xe condensation occurs first or whether they are concurrent.) Note that samples with 12 Xe/cage show less effect since they are already quite dense. At this point we cannot tell whether the isotropic averaging is due to the dynamics of a true fluid or to exchange between a well-defined set of sites in a solid phase. In this regard, however, recent Monte Carlo calculations on the behavior of xenon clusters in Na−A zeolite cages at room temperature[34,35] suggest that in this cage at least there are a very large number of possible sites and the clusters are best described as "fluid". From synchrotron X-ray diffraction studies of Xe at 1 and 1.75 atm in Na−X zeolite at 31 °C it has been suggested that the predominant site for Xe is in association with the S_{II} site Na^+ over the 6-rings of the α-cage.[36] On the other hand, MD simulations of Xe at 188 K in a static Na−Y framework suggest that the principal site at low loading (1 Xe/cage) is over the central 4-rings.[32] Although not in agreement, these two latter findings point to specific sites for Xe, though at this point we must express a desire for stronger physical evidence. MD simulations incorporating a flexible framework (e.g., as in ref 37) for the temperature and Xe loading ranges studied in the present work would be much more informative.

Our next task is to find the temperature at which the Xe finally becomes immobile and if possible determine the number of site types and their associated chemical shift anisotropies.

JA942898W

---

(30) Yashonath, S. *Chem. Phys. Lett.* **1991**, *177*, 54.

(31) Yashonath, S. *J. Phys. Chem.* **1991**, *95*, 5877.

(32) Santikary, P.; Yashonath, S.; Ananthakrishna, G. *J. Phys. Chem.* **1992**, *96*, 10469.

(33) Vigne-Maeder, F. *J. Phys. Chem.* **1994**, *98*, 4666.

(34) Jameson, C. J.; Jameson, A. K.; Baello, B. I.; Lim, H.-M. *J. Chem. Phys.* **1994**, *100*, 5965.

(35) Jameson, C. J.; Jameson, A. K.; Lim, H.-M.; Baello, B. I. *J. Chem. Phys.* **1994**, *100*, 5977.

(36) Dooryhee, E.; Greaves, G. N.; Steel, A. T.; Townsend, R. P.; Carr, S. W.; Thomas, J. M.; Catlow, C. R. A. *Faraday Discuss. Chem. Soc.* **1990**, *89*, 119.

(37) Schrimpf, G.; Schlenkrich, M.; Brickmann, J.; Bopp, P. *J. Phys. Chem.* **1992**, *96*, 7404.