

Longitudinal N.M.R. Relaxation of Aluminium-27 in Zeolites is governed by Quadrupole Interactions with Adsorbed Polar Molecules and Exchangeable Cations

Jürgen Haase,^a Harry Pfeifer,^a Wolfgang Oehme,^a and Jacek Klinowski^b

^a *Sektion Physik der Karl-Marx-Universität Leipzig, Linnéstrasse 5, DDR-7010 Leipzig, German Democratic Republic*

^b *Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, U.K.*

Longitudinal relaxation times of ^{27}Al in zeolite frameworks are between *ca.* 0.3 and 70 ms and are governed by quadrupole interactions with polar sorbates and cations; dipolar interactions with guest molecules and paramagnetic impurities are normally insignificant.

The widespread availability of high-field magnets and the routine use of magic-angle spinning (MAS) has led to considerable advances in solid-state ^{27}Al n.m.r. of aluminosilicates, particularly zeolitic catalysts.¹ Such studies are not free from pitfalls and several considerations must be kept in mind. First, in order for the spectra to be quantitatively reliable, they must be acquired using very short and powerful radio-frequency pulses.^{2–4} Secondly, the chemical shifts of signals must include a quadrupole correction.⁵ Finally, in dehydrated zeolites some extra-framework aluminium is 'invisible' to n.m.r. because of very large quadrupolar interactions.⁶ The longitudinal relaxation time T_1 is a fundamental parameter which must be known for efficient design of n.m.r. experiments. It has been established⁷ that T_1 relaxation of ^{29}Si in zeolites is governed by dipole interaction with the paramagnetic oxygen molecule from the atmosphere. We have investigated the relaxation of ^{27}Al , the other major component of zeolitic frameworks.

For half-integer spin nuclei involved in large quadrupole interactions we observe only the central ($+1/2 \leftrightarrow -1/2$) transition of the n.m.r. spectrum. The following mechanisms for T_1 relaxation must be considered:

- (i) dipolar interactions with paramagnetic impurities (such as Fe^{3+} introduced during synthesis);
- (ii) quadrupolar interactions with the crystal electric field gradients modulated by lattice vibrations;
- (iii) dipolar interactions with adsorbed molecules;
- (iv) quadrupolar interactions modulated by the motion of polar sorbate molecules and/or charge-compensating cations.

Our experiments have shown that, except at very low temperatures, the ^{27}Al relaxation is independent of the concentration of paramagnetic species,⁸ which means that mechanism (i) is insignificant. We have also discounted mechanism (ii), which proceeds *via* the two-phonon Raman

process,⁹ by calculating⁸ that it could account for ^{27}Al T_1 times of the order of 100 s, 4–5 orders of magnitude longer than the experimental values. It follows that only mechanisms (iii) and (iv), associated with adsorbed polar molecules and cations, must be considered.

Measurements were carried out on a home-made spectrometer ('UDRIS') operating at 23.5 MHz for ^{27}Al , by using selective saturation of the central transition. The saturating pulse was 50 μs long and the measuring pulse 1.5 μs long. Sample temperature was controlled by flowing nitrogen gas. The amplitude of the free induction decay following the short measuring pulse is proportional to the difference in occupancy ($N_{1/2} - N_{-1/2}$) of the two central levels, and can be approximated by an exponential function⁸ of which T_1 is the time constant.

Figure 1(a) shows the temperature dependence of T_1 in hydrated zeolite NaX with pore filling factor $\theta = 0.9$. The results were completely unaffected by replacing two-thirds of the intracrystalline water with D_2O while keeping the overall filling factor constant. Since ^1H and ^2H have very different gyromagnetic constants, relaxation of ^{27}Al cannot be caused by the *dipole* interaction with ^1H of the water molecules. Furthermore, T_1 dramatically increases upon dehydration of the sample [see Figure 1(b)], which demonstrates that the controlling mechanism in the hydrated samples is the *quadrupole* interaction of ^{27}Al with the crystal electric field gradient produced by the very similar dipole moments of the H_2O and D_2O molecules.

Theoretical considerations¹⁰ indicate that for mechanism (iv), originating from a jumping electrical dipole with the dipolar moment of the water molecule at a distance of 0.5 nm from the ^{27}Al nucleus, T_1 is *ca.* 30 ms; a moving univalent cation at a distance of 0.33 nm gives T_1 *ca.* 1 ms. Both values are typical of those found experimentally. Theory also

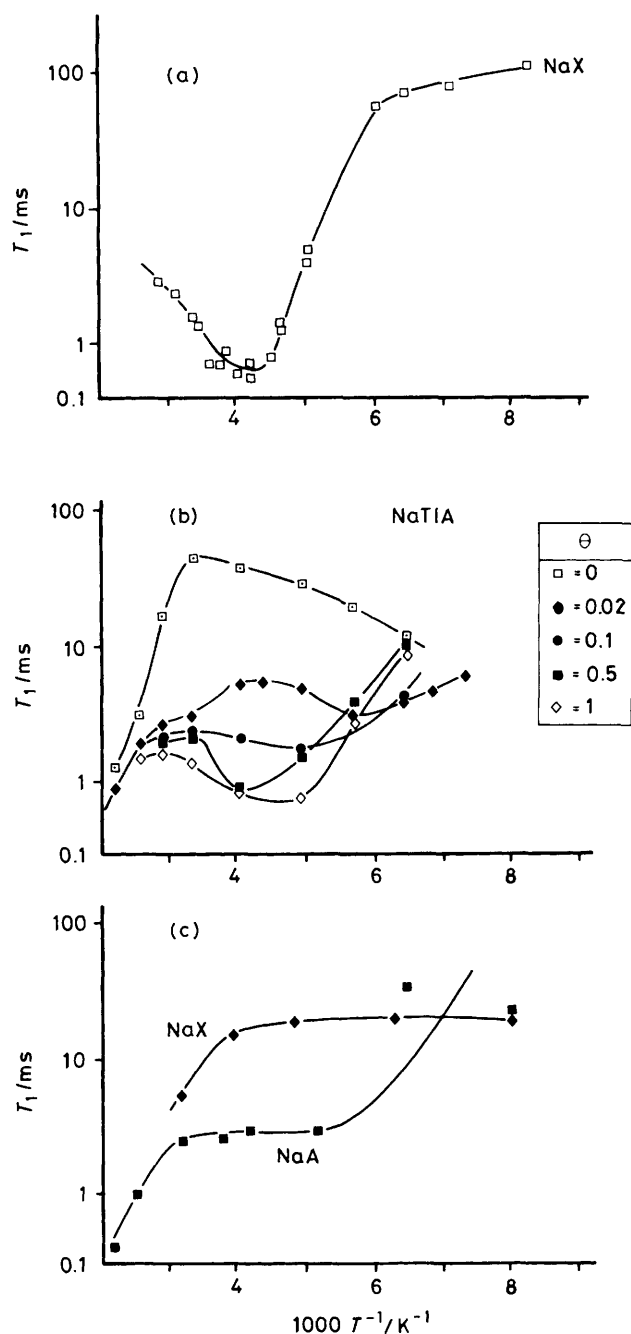


Figure 1. Temperature dependence of the longitudinal relaxation time of ^{27}Al : (a) zeolite NaX loaded with water ($\theta = 0.9$) and with a mixture of H_2O ($\theta = 0.3$) and D_2O ($\theta = 0.6$); (b) zeolite NaTfA at various degrees of hydration; (c) dehydrated zeolites NaX and NaA.

predicts a minimum in T_1 at temperatures at which $\tau_c \omega_{\text{Al}} \approx 0.5-1.0$, where τ_c is the correlation time and ω_{Al} the Larmor frequency. The *proton* T_1 of the intracrystalline water goes through a minimum at the same temperature (Figure 2) provided the measurement is performed in a magnetic field corresponding to the same frequency of 23.5 MHz. Since we know¹¹ that the minimum T_1 for the proton occurs for $\tau_c \omega_{\text{H}} \approx 0.6-1.0$, we conclude that the two correlation times are equal and determined by the mobility of the adsorbed water. Figure 1(b) shows the temperature dependence of T_1 for zeolite

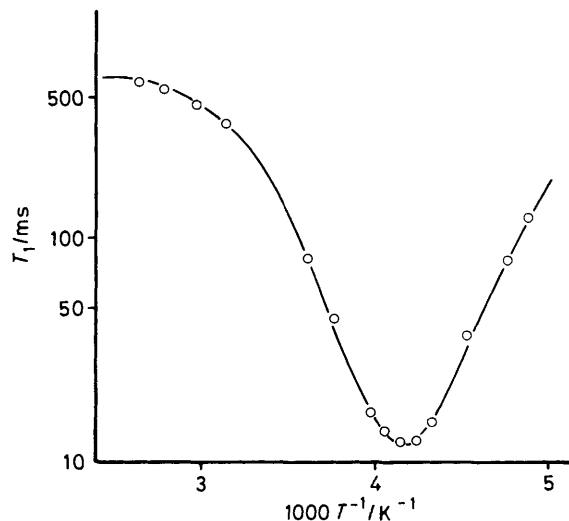


Figure 2. Temperature dependence of longitudinal relaxation time of ^1H n.m.r. for zeolite NaX loaded with water ($\theta = 0.9$) at 23.8 MHz.

$\text{Na}_{2.6}\text{Ti}_{9.4}\text{A}$ at various degrees of hydration. With decreasing water content in the range $1 > \theta > 0.5$ the minimum shifts to higher temperatures (this behaviour is analogous to that of proton T_1); at lower water contents it disappears. Similar behaviour is found in dehydrated zeolite NaX and NaA [Figure 1(c)] but not in $\text{Na}_{3.6}\text{Ca}_{4.2}\text{A}$ or $\text{Na}_{7.4}\text{Mg}_{2.3}\text{A}$. All these results can be explained by assuming that the correlation time τ_c in *dehydrated* zeolites is simply equal to the mean residence time of the cation between successive translational jumps. These residence times have been measured¹²⁻¹⁵ for zeolites NaX and NaA and are entirely consistent with the results in Figure 1(c). The absence of a minimum in dehydrated NaCaA is in agreement with dielectric measurements¹⁴ which indicate that translational cation jumps do not occur at room temperature in the dehydrated sample in the range 30-12 MHz.

Received, 28th January 1988; Com. 8/00305J

References

- 1 J. Klinowski, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1984, **16**, 237.
- 2 A. Samoson and E. Lippmaa, *Chem. Phys. Lett.*, 1983, **100**, 205.
- 3 A. Samoson and E. Lippmaa, *Phys. Rev. B*, 1983, **28**, 6567.
- 4 P. P. Man, Thesis for Docteur d'Etat, Université P. et M. Curie, Paris, 1986.
- 5 D. Freude, J. Haase, J. Klinowski, T. A. Carpenter, and G. Roniker, *Chem. Phys. Lett.*, 1985, **119**, 365.
- 6 D. Freude, E. Brunner, H. Pfeifer, D. Prager, H.-G. Jerschke-witz, U. Lohse, and G. Oehlmann, *Chem. Phys. Lett.*, 1987, **139**, 325.
- 7 J. Klinowski, T. A. Carpenter, and J. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1986, 956.
- 8 J. Haase, Thesis for Dr. rer. nat., KMU Leipzig, 1987.
- 9 A. Abragam, in 'Principles of Nuclear Magnetism,' Clarendon, Oxford, 1961.
- 10 J. Haase, H. Pfeifer, W. Oehme, and J. Klinowski, *Chem. Phys. Lett.*, in the press.
- 11 H. Pfeifer, in 'NMR—Basic Principles and Progress,' vol. 7, Springer, Berlin, 1972.
- 12 U. Lohse, H. Stach, M. Hollnagel, and W. Schirmer, *Monatsh. Deutsch. Akad. der Wiss., Berlin*, 1970, **12**, 814.
- 13 R. Schoonheydt, Thesis, Catholic University of Leuven, 1975.
- 14 U. Lohse, H. Stach, M. Hollnagel, and W. Schirmer, *Z. Phys. Chem. (Leipzig)*, 1971, **246**, 65.
- 15 I. V. Zhilenkov, Proceedings of the 1st All-Union Conference on Theoretical Problems of Adsorption, Moscow, 1967.