Demonstration of Three-dimensional Lattice Connectivities in Zeolites by Two-dimensional High Resolution Solid State N.M.R. Spectroscopy

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It is demonstrated that the three-dimensional connectivities in zeolite ZSM-39 may be determined by two-dimensional ^{29}Si magic angle spinning (MAS) solid state n.m.r. spectroscopic experiments.

Zeolites are open framework structures, constructed from SiO_4^{4-} and AlO_4^{5-} tetrahedra which usually contain channels and cavities, and are of widespread interest because of their unique sorptive and catalytic properties.[1,2]

Although zeolites are highly crystalline, they are usually microcrystalline with dimensions of only a few microns, precluding the use of routine single crystal diffraction techniques and structural refinements must usually be attempted from more limited powder diffraction data. In recent years high resolution solid state n.m.r. spectroscopy has emerged as a complementary technique to diffraction measurements on these systems[3] the former probing local environments and the latter long-range orderings and periodicities. In the case of highly siliceous analogues, sharp resonances are observed whose numbers and relative intensities reflect the number and relative occupanices of the crystallographically inequivalent lattice sites in the unit cell, establishing a direct link to diffraction measurements.[4] The potential of solution n.m.r. spectroscopy for structure determinations has been greatly expanded in recent years by the development of two-dimensional experiments such as COSY (COrrelation SpectroscopY) which establish the bonding connectivities between atoms within a molecular structure. In principle, it should be possible to perform similar experiments in the solid state where, in the case of three dimensional lattices such as zeolites (in contrast to the case of molecular crystals), the three dimensional connectivities should be obtained. In the present work we demonstrate for the first time that such experiments can indeed be successful and that they yield the correct connectivities for the (known) lattice structure of zeolite ZSM-39.

A completely siliceous sample of zeolite ZSM-39 was synthesised hydrothermally in 8 days at 200 °C with piperidine as template. To increase the number of ^{29}Si–O–^{29}Si interactions the silicon source was enriched to 80% ^{29}Si.

The ZSM-39 high temperature structure (space group *Fd*3) contains three crystallographically inequivalent sites T_1, T_2, and T_3 with relative proportions 8:32:96 and is shown schematically in Figure 1.[7] At room temperature, the symmetry is lower and the degeneracy of the T_3 site is lifted, giving three resonances of intensities 32:32:32. The solid-state ^{29}Si magic angle spinning (MAS) n.m.r. spectrum shown at the top of Figure 2 clearly reflects the asymmetric unit in the lattice, the assignments of the resonances being unambiguous from the known site occupancies. The T_3 site gives rise to three resonances of which two are resolved.[8] In the present work we will interpret the interactions as being, to a first approximation between the three sites T_1, T_2, and T_3. From

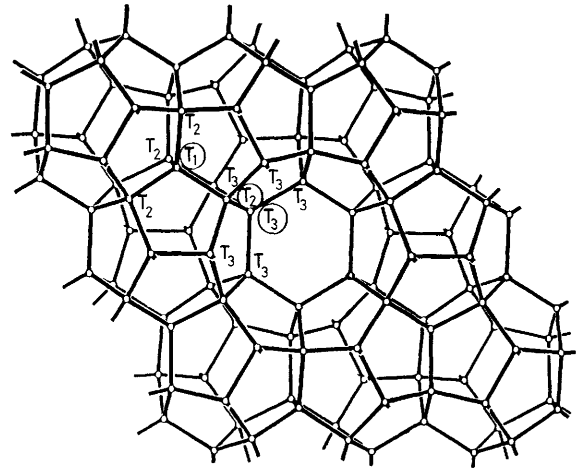

Figure 1. Schematic representation of the lattice framework of zeolite ZSM-39. The three inequivalent lattice sites are represented by T_1, T_2, and T_3 (circled) and in each case the four nearest neighbours are indicated.

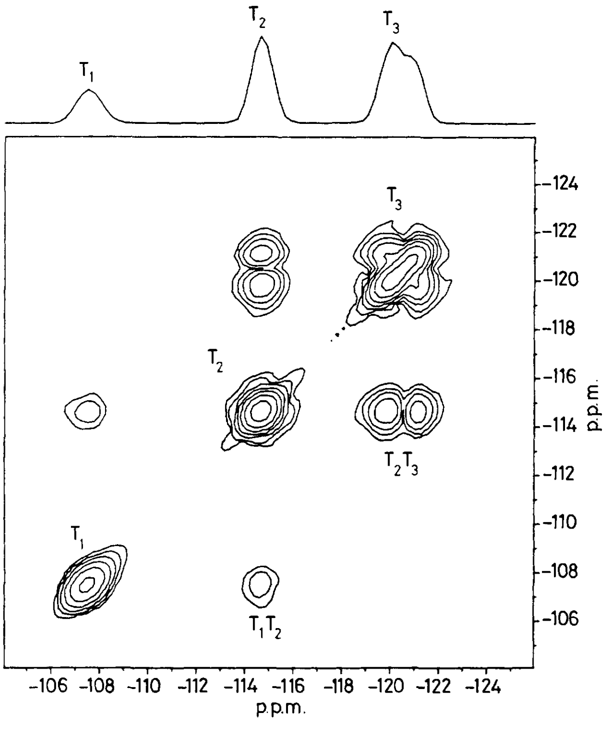

Figure 2. Two dimensional contour plot of a 2D$^-$ spin-diffusion experiment on zeolite ZSM-39 carried out at 298 K using a (CP) (t_1) $[-\pi/2_{(x)}]$ (fixed delay) $[\pi/2_{(x)}]$ (t_2 aquire) pulse sequence. A Bruker MSL 400 spectrometer was used operating at 79.6 MHz, 128 experiments were performed with 8 scans each, a sweep width of 5KHz was used and the number of data points collected during acquisition was 256. In each case, the fixed delay during which spin diffusion occurs, was 10 s and the time between successive scans was 10 s. Proton decoupling was not used and the total experimental time was approximately 6 h. Sine bell squared apodization was used in the data treatment and the final plot has been symmetrized. Shown at the top of the plot is the projection of the data onto the F_2 axis which indicates the resolution of the ^{29}Si spectrum.

the structure, it can be seen that there are direct Si–O–Si connections between T_1 and T_2 and also between T_2 and T_3 but none between T_1 and T_3.

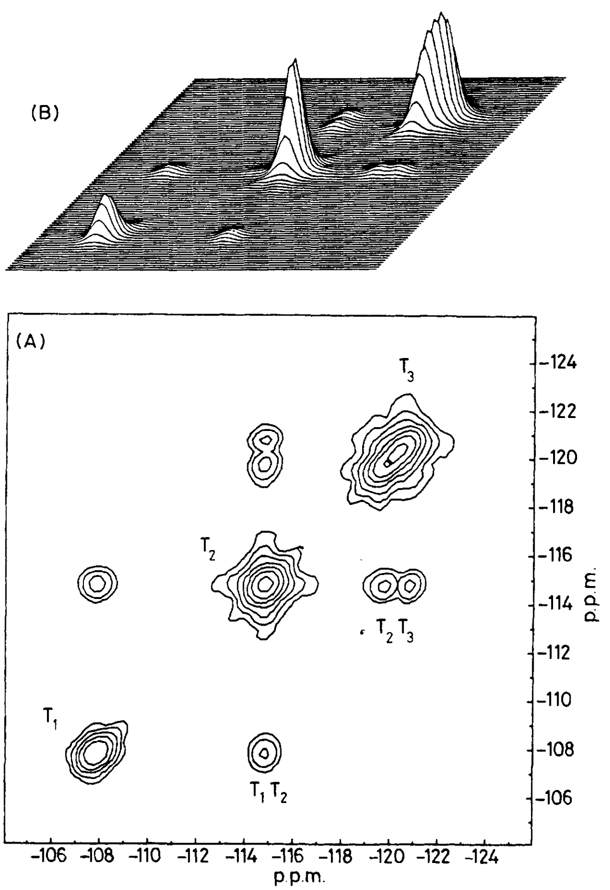

Figure 3. Results of a ^{29}Si COSY experiment on zeolite ZSM-39 carried out at 373 K using a (CP) (t_1) (fixed delay) $[\pi/2_{(x)}]$ (fixed delay) (t_2 aquire) sequence. The higher temperature induces a narrowing of the resonances, 128 experiments were performed with 64 scans each, a sweep width of 5kHz was used and the number of data points collected during aquisition was 256. In each case, the fixed delay was 5 ms and the time between successive scans 10 s. Proton decoupling was not used and samples were spun at *ca.* 3 kHz. Sine bell apodization was applied in the data treatment and the total experimental time was 23 h. The data are not symmetrized. (A); presentation in the format of a contour plot. (B); presentation as a stacked plot giving a better indication of the S/N of the experiment.

Figure 2 shows the results of a ^{29}Si 2D n.m.r. spectroscopic spin-diffusion experiment carried out using the parameters given in the figure caption. The attraction of this experiment, analogous to the two-dimensional Nuclear Overhauser Effect SpectroscopY (NOESY) technique in solution and introduced in solid-state n.m.r. spectroscopic studies by Szeverini *et al.*[10] lies in the strong dependence of the interaction on the through-space internuclear distance ($1/r^6$ if there is a motion and $1/r^3$ if there is not) and it has previously been proposed as a probe of interactions between nuclei on different molecules in molecular crystals.[11] Because of the large differences in internuclear distance between directly connected silicons and others further removed (~3 Å for ^{29}Si–O–^{29}Si *vs.* ~5.5 Å for ^{29}Si–O–Si–O–^{29}Si) it was hoped that they would be clearly differentiated. Figure 2 shows that the expected connectivities T_1T_2 and T_2T_3 are clearly observed while that between T_1 and T_3 is not seen. Although this result is encouraging and certainly merits further investigation, we feel that some caution should be used in the interpretation of data of this type as the theoretical description of the interactions[12,13] involves additional contributions from the chemical shift anisotropies and the isotropic shift differences of the interacting nuclei whose importance is difficult to estimate. Further experiments on systems of known structure will be needed to properly establish whether experiments of this type are reliable probes of lattice connectivities in these systems, although it would seem that in this case, since the atoms involved all have tetrahedral co-ordinations and the shift ranges involved are small, the non-distance dependent effects could well be minimal.

An alternative and more reliable and unambiguous method is the COSY technique which in solution relies on the scalar couplings between the interacting nuclei which operate through the bonding electrons.[13] ^{29}Si–O–^{29}Si connectivities within the reference molecule Q8M8 in the solid state have recently been demonstrated by Benn and co-workers.[14] The results of a 2D COSY experiment on the ZSM-39 sample discussed above are presented in Figure 3. The sequence used was identical to that used in solution studies except that the initial preparation step was a $^{1}H/^{29}Si$ cross-polarization sequence[15] and the experiment was carried out using the conditions given in the figure caption. Again, the connectivities T_1T_2 and T_2T_3 are exactly those expected from the known lattice structure.

The data presented in Figures 2 and 3 thus clearly demonstrate the potential of solid-state n.m.r. spectroscopic techniques in establishing three-dimensional lattic connectivities in framework structures. Using the results of the present study, which indicate the importance of the t_2 values of the resonances in these experiments, the optimum experimental parameters may be chosen and natural abundance samples investigated, making the method quite generally applicable. Preliminary results from experiments in natural abundance have been obtained for zeolites ZSM-5, ZSM-12, and KZ-2 and these are currently being interpreted. These studies thus complement present techniques for investigation of zeolite lattices but will be equally useful for many other systems, for example in phosphate structures based on ^{31}P–O–^{31}P interactions.

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