

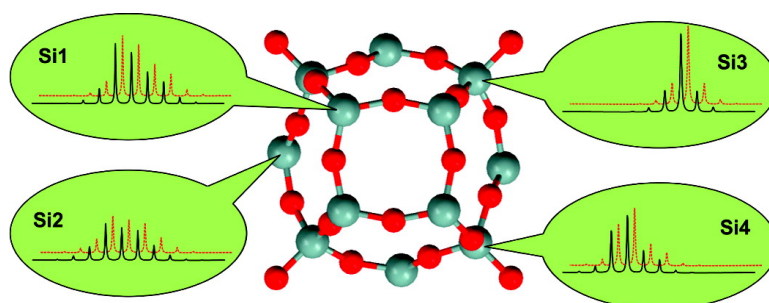
Communication

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NMR Crystallography of Zeolites: Refinement of an NMR-Solved Crystal Structure Using *ab Initio* Calculations of ^{29}Si Chemical Shift Tensors

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The incorporation of solid-state NMR data into the process of crystal structure determination, referred to as *NMR crystallography*, is emerging as an important approach for structural characterization of materials.^{1–7} Structure determination of crystalline solids generally involves three main steps: (1) the unit cell and space group are first established, usually using diffraction methods, (2) an initial structural model is derived or *solved* from the available data, (3) this model structure is *refined* by optimizing it to give the best agreement with the available data. For materials that are difficult to grow as single crystals of suitable dimensions for single-crystal X-ray diffraction (XRD), solid-state NMR can play an important complementary role to powder XRD experiments in these structure determination steps.

The application of NMR crystallography to zeolites has been particularly successful. The structures of zeolites are of interest as their properties are related to structure, yet their characterization is not straightforward because of their structural complexity and the fact that suitably large single crystals cannot usually be obtained. It has recently been shown that, given the unit cell parameters and space group determined from powder XRD, the crucial second step of structure solution can be achieved using ^{29}Si double-quantum (DQ) NMR experiments.¹ These structures are solved in the sense that the topologies of the zeolite frameworks, as defined by the positions and connectivities of the Si atoms, are established. However, these structures remain incomplete since the positions of the bridging oxygen atoms remain unknown. Furthermore, the ^{29}Si DQ NMR data are not sufficiently sensitive to local environments to yield highly accurate structures.

To obtain complete and accurate structures, NMR measurements that are far more sensitive to local structural environments are required. It has recently been shown that the principal components of ^{29}Si chemical shift (CS) tensors in zeolites can be measured and accurately calculated from first principles.⁸ The accuracy of the calculations was shown to be strongly dependent on the quality of the structural coordinates. In this Communication, ultrahigh-field (21.1 T) NMR measurements and *ab initio* calculations of ^{29}Si CS tensors are incorporated into an NMR crystallography structure refinement tool for zeolites. It is shown that the framework structure of Sigma-2 can be solved from ^{29}Si DQ NMR data and subsequently refined against the ^{29}Si CS tensors to give an NMR-determined crystal structure that is in very good agreement with the single-crystal XRD structure.

The ^{29}Si NMR data for Sigma-2 used for structure solution and refinement steps are displayed in Figure 1. The ^{29}Si CP MAS NMR spectrum in Figure 1a indicates there are four unique Si sites with equal occupancies in the crystal structure. Figure 1b presents the slow CP MAS spectrum collected at 21.1 T⁸ from which the principal components of the ^{29}Si CS tensors were determined (see Supporting Information). The DQ curves⁹ in Figure 1c provide information about the Si–O–Si connectivities and distributions of Si–Si distances between the various pairs of Si sites. These DQ curves were combined with the unit cell and space group reported

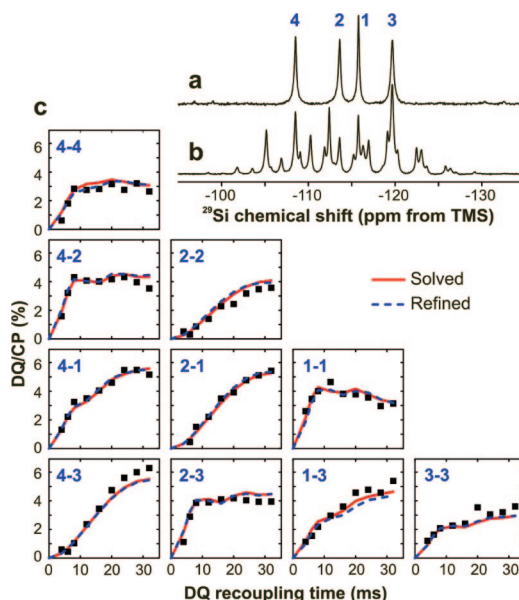


Figure 1. ^{29}Si NMR data used for structure solution and refinement of Sigma-2. (a,b) ^{29}Si CP MAS NMR spectra obtained at 21.1 T using MAS frequencies of (a) 3000 and (b) 600 Hz. (c) ^{29}Si DQ curves obtained at 7.0 T. The solid red and dashed blue lines are the calculated curves using Si coordinates after structure solution and refinement steps, respectively.

in the powder XRD study of Sigma-2¹⁰ to solve the Si coordinates of the structure using the structure solution method described in ref 1 (see Supporting Information). The DQ curves calculated for this NMR-solved structure are shown as solid red lines in Figure 1c.

Oxygen atoms were placed midway between Si atoms known from ^{29}Si DQ NMR to be connected via Si–O–Si linkages, and this structure was subjected to a geometry optimization based on expected distances,¹¹ minimizing the cost function

$$\chi_{\text{dist}}^2 = \sum_{\Lambda} \sum_j \left\{ (r_{\Lambda}^{(j)} - r_{\Lambda}^*) / \sigma_{\Lambda} \right\}^2 \quad \Lambda = \text{Si-O, O-O, Si-Si} \quad (1)$$

where $r_{\Lambda}^{(j)}$ represents the distances calculated from the model structure and r_{Λ}^* and σ_{Λ} are the target distances and standard deviations. The target Si–O, O–O, and Si–Si distances and standard deviations were 1.60 ± 0.01 , 2.61 ± 0.02 , and 3.10 ± 0.05 Å, respectively, derived from the distributions in single-crystal XRD structures of high-silica zeolites (see Supporting Information).

The structure was further refined by optimizing the Si and O atomic coordinates to give the best agreement between experimentally measured and *ab initio* calculated ^{29}Si CS tensor components. *Ab initio* Hartree–Fock (HF) calculations of ^{29}Si shielding tensors were carried out on clusters extracted from a given structure (see Supporting Information). The quality of agreement between ex-

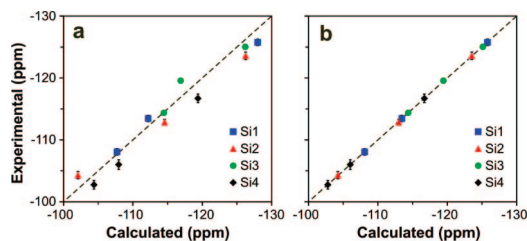


Figure 2. Comparisons of experimental and *ab initio* calculated principal components of the Sigma-2 ^{29}Si CS tensors using Si and O atomic coordinates solved from ^{29}Si DQ curves followed by geometry optimization (a) before and (b) after refinement against ^{29}Si CS tensors.

perimental, $\delta_{ii}^{(s)\text{exp}}$, and *ab initio* calculated, $\delta_{ii}^{(s)\text{calcd}}$, CS tensor components was quantified by

$$\chi_{\text{CS}}^2 = \sum_{s=1}^4 \sum_{i=1}^3 \{(\delta_{ii}^{(s)\text{exp}} - \delta_{ii}^{(s)\text{calcd}})/\sigma_{ii}^{(s)}\}^2 \quad (2)$$

where *s* denotes the Si site, *i* denotes the principal component, and $\sigma_{ii}^{(s)}$ is the estimated uncertainty of the corresponding principal ^{29}Si CS tensor component.

There are 20 parameters describing the crystal structure that were optimized in the structure refinements. All Si and O sites were found by the NMR structure solution method to be located on special positions and the unit cell parameters were fixed. Since a refinement against the 12 measured CS tensor components alone is underdetermined, the minimization of χ_{CS}^2 was carried out with a Gauss–Newton optimization method¹² modified for underdetermined situations^{12b} (see Supporting Information).

Figure 2a shows the quality of agreement between experimental and calculated ^{29}Si CS tensor components after geometry optimization, but prior to refinement against the tensors. The χ_{CS}^2 and χ_{dist}^2 values were 219.1 and 17.6, respectively, at this stage. The subsequent refinement of the structure against the ^{29}Si CS tensors *alone* converged after nine iterations to a χ_{CS}^2 value of 1.0 with an increase in χ_{dist}^2 to 43.8. A combined refinement of $\chi_{\text{CS}}^2 + \chi_{\text{dist}}^2$ in which the 11 Si–O, 16 O–O, and 7 Si–Si unique distances were incorporated as restraints (so that the refinement was overdetermined) converged after nine iterations to χ_{CS}^2 and χ_{dist}^2 values of 0.8 and 25.3 and yielded a very similar structure.

Figure 2b shows the improved correlation between experimental and calculated tensor components after refinement against the CS tensors alone. The ^{29}Si DQ curves calculated from the refined Si coordinates are displayed as dashed blue lines in Figure 1c and remain in excellent agreement with the experimental data.

These NMR-refined structures are in very good agreement with the single-crystal XRD structure of Sigma-2.⁸ The mean and maximum deviations of the atomic positions from the XRD structure are only 0.015 and 0.034 Å for the structure refined against the CS tensors alone, while they improve slightly to 0.011 and 0.026 Å with distance restraints. Figure 3 clearly shows that the agreement with the XRD structure is much improved after refinement. The Si coordinates obtained after solving the structure from the DQ curves deviate by an average of 0.186 Å, while the Si coordinates after refinement improve to mean deviations of only 0.007 and 0.009 Å without and with distance restraints. Furthermore, and very importantly, the refinement procedure yields oxygen coordinates with a mean deviation from the XRD structure of only 0.020 Å (CS tensors alone), which improves to 0.011 Å when distance restraints are included.

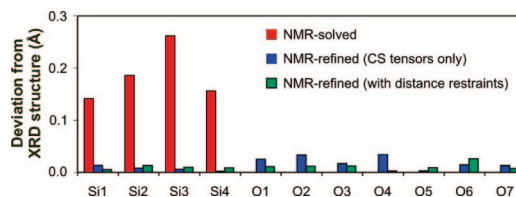


Figure 3. Deviations of the NMR-determined atomic coordinates from the single-crystal XRD structure.⁸

There have been a number of excellent recent examples^{3b,5–7} in which chemical shift calculations have been incorporated into crystal structure determinations, however none involve a direct refinement against CS tensors. This work presents a valuable structure refinement tool for zeolite NMR crystallography that, when combined with structure solution from DQ NMR, provides an approach to yield single-crystal XRD quality structures from solid-state NMR data. It is anticipated that this approach could be extended to other materials, incorporate experimental measurements and *ab initio* calculations of other NMR parameters such as quadrupolar interaction parameters, and utilize the recent advances in *ab initio* calculations of periodic systems.¹³

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Supporting Information Available: Details of NMR experiments and *ab initio* calculations, distance distribution plots derived from single-crystal XRD structures of high silica zeolites, details of the structure solution and refinement procedures, comparison of Sigma-2 crystal structures determined by NMR and XRD. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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