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Comparing quantum-chemical calculation methods for structural investigation of zeolite crystal structures by solid-state NMR spectroscopy[†]

Darren H. Brouwer,^{a*} Igor L. Moudrakovski,^b Richard J. Darton^c and Russell E. Morris^d

Combining quantum-chemical calculations and ultrahigh-field NMR measurements of ²⁹Si chemical shielding (CS) tensors has provided a powerful approach for probing the fine details of zeolite crystal structures. In previous work, the quantum-chemical calculations have been performed on 'molecular fragments' extracted from the zeolite crystal structure using Hartree–Fock methods (as implemented in Gaussian). Using recently acquired ultrahigh-field ²⁹Si NMR data for the pure silica zeolite ITQ-4, we report the results of calculations using recently developed quantum-chemical calculation methods for periodic crystalline solids (as implemented in Cambridge Serial Total Energy Package (CASTEP)) and compare these calculations to those calculated with Gaussian. Furthermore, in the context of NMR crystallography of zeolites, we report the completion of the NMR crystallography of the zeolite ITQ-4, which was previously solved from NMR data. We compare three options for the 'refinement' of zeolite crystal structures from 'NMR-solved' structures: (i) a simple target-distance based geometry optimization, (ii) refinement of atomic coordinates in which the differences between experimental and calculated ²⁹Si CS tensors are minimized, and (iii) refinement of atomic coordinates to minimize the total energy of the lattice using CASTEP quantum-chemical calculations. All three refinement approaches give structures that are in remarkably good agreement with the single-crystal X-ray diffraction structure of ITQ-4. Copyright © 2010 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: NMR; ²⁹Si; solid-state NMR; zeolites; NMR crystallography; chemical shielding tensors; quantum-chemical calculations

Introduction

Solid-state NMR spectroscopy has emerged as an important technique for structure determination of crystalline solids.^[1] Innovative approaches have been developed that connect advances in NMR pulse sequence design, quantum-chemical calculations of NMR parameters, magic-angle spinning (MAS) technology, and higher magnetic fields with modeling, computational chemistry, and the crystallography that is traditionally carried out with diffraction methods. The general philosophy behind 'NMR crystallography'^[1] is to incorporate the wide variety of information available in solid-state NMR experiments into the process of crystal structure determination, typically in combination with other structural characterization methods and computational chemistry, and particularly for those materials for which it is difficult to obtain suitably large single crystals for single-crystal diffraction experiments.

The process of structure determination of crystalline solids generally involves three main steps. First, the long-range periodicity of the crystal structure, as defined by the unit cell parameters and the space group, is established. Second, an initial structural model is derived or *solved* from the available data. Lastly, the structural model is typically *refined* or optimized to give the best agreement with the available data. For each of these steps, NMR researchers are finding creative ways to incorporate the information available from solid-state NMR experiments into the structure determination process.

The application of NMR crystallography to zeolites has been particularly successful.^[2–6] The crystal structures of zeolites are of interest, as their unique properties are intimately related to their structural architecture, yet their characterization is not straightforward due to their structural complexity and the fact that suitably large single crystals cannot usually be obtained for analysis by single-crystal X-ray diffraction (XRD). It has been demonstrated that, given the unit cell parameters and space group determined from powder XRD, a zeolite crystal structure can be

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solved using ^{29}Si double-quantum (DQ) NMR experiments.^[2,5] The structure is solved in the sense that the general structure of the zeolite framework is established. With the positions and connectivities of the Si atoms established, a full initial structural model can be constructed by placing bridging oxygen atoms midway between connected Si atoms. However, such a solved structure is in need of further refinement since the exact positions of the bridging oxygen atoms need to be located and the ^{29}Si DQ NMR data are not sufficiently sensitive to local environments to yield highly accurate structures.

By means of ultrahigh-field measurements and quantum-chemical calculations, it has been shown that the ^{29}Si chemical shielding (CS) tensors of the Si sites in zeolites are very sensitive to the local environments^[4] (it should also be noted that measurement and calculation of ^{29}Si –O– ^{29}Si J -couplings has been developed as another tool for investigating local structural features in zeolites^[7]). This combination of experiment and quantum-chemical calculations provides a very sensitive probe of the quality of a given crystal structure, as ^{29}Si CS tensors calculated using higher quality crystal structures from single-crystal XRD data are in much better agreement with experimental values than those calculated using poorer quality crystal structures determined from powder XRD data. This sensitivity of ^{29}Si CS tensors to structure has been incorporated into an NMR structure refinement method by which Si and O coordinates are refined in order to minimize the differences between experimentally measured and quantum-chemical-calculated principal components of ^{29}Si CS tensors.^[5,6]

In all previous work involving quantum-chemical calculations of ^{29}Si CS tensors in zeolites, the calculations were performed using Hartree–Fock methods (as implemented in the Gaussian program^[8]) on ‘clusters’ or ‘molecular fragments’ that were extracted from the crystal structure. Although these calculations were deemed to be quite successful, a significant approximation is being made of what the three-dimensional periodic crystal structure actually is. Recently, quantum-chemical calculation methods have become available that incorporate the full periodicity of crystal structures using plane-wave density functional theory (DFT) methods, facilitating more realistic calculations on the actual crystal structure, rather than approximate fragments or clusters. One of the aims of this work is to compare calculations of ^{29}Si tensors on clusters extracted from a zeolite crystal structure (using the Gaussian program) to calculations on the full crystal structure [using the Cambridge Serial Total Energy Package (CASTEP) program^[9–11]]. Plane-wave DFT calculations of ^{17}O and ^{29}Si NMR parameters using CASTEP have been reported for the zeolite ferrierite; however, only isotropic ^{29}Si chemical shifts were reported.^[12] A second aim of this work is to compare the NMR structure refinement strategy^[5,6] to performing a geometry optimization of an initial structure with CASTEP in which the total lattice energy is minimized. These are two of the structure refinement options available for zeolite NMR crystallography.

The structure that is investigated in this work is the pure silica zeolite ITQ-4.^[13,14] The structure for this zeolite was first determined from synchrotron powder XRD^[14] and was later determined in a variable temperature single-crystal XRD study of its negative thermal expansion properties.^[15] Using ultrahigh-field measurements, we report the ^{29}Si CS tensors of this material for the first time. With quantum-chemical calculations of the ^{29}Si CS tensors, it is possible to evaluate the accuracy of these two structures. Also, a structure for this molecule was successfully solved from ^{29}Si DQ NMR data^[2] in a ‘blind test’. In this work, we aim to complete the NMR crystallography of this structure

by performing a refinement of this NMR-solved structure. Having the single-crystal XRD structure available is useful for evaluating whether the NMR refinement or CASTEP geometry optimization strategies are successful.

Experimental

Synthesis of the pure ITQ-4 zeolite sample was carried out according to the method in Refs [13,14.] The sample was subsequently calcined to remove the organic structure-directing agent, leaving behind a pure silica zeolite framework.

Solid-state NMR experiments were carried out on a Bruker AVANCE-II 900 MHz NMR spectrometer operating at a magnetic field of 21.1 T (178.831 MHz ^{29}Si Larmor frequency) using a standard-bore, double-resonance, 4-mm MAS NMR probe. The ^{29}Si chemical shifts were referenced by setting the ^{29}Si resonance for a sample of neat liquid tetramethylsilane (TMS) sealed in a 3-mm glass tube to 0 ppm.

Spectrum-fitting of the slow spinning ^{29}Si MAS NMR spectrum, in order to estimate the span Ω and skew κ values of the ^{29}Si CS tensors and their uncertainties, was carried out according to the protocol previously described.^[4,6] The principal components $\delta_{11} \geq \delta_{22} \geq \delta_{33}$ were calculated using the relations $\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, $\Omega = \delta_{11} - \delta_{33}$, and $\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$, while their uncertainties were determined from the widest possible ranges of their values given the uncertainties in δ_{iso} , Ω , and κ .

Ab initio Hartree–Fock calculations were performed with Gaussian09 (revision A.02)^[8] using the gauge including atomic orbital (GIAO) method for NMR shielding calculations. The calculations were carried out on clusters extracted from the crystal structures with the Si site of interest at the core of each cluster. Each central Si atom was surrounded by at least three coordination spheres with the outer atoms terminated with hydrogen atoms placed 0.96 Å from the oxygen atom along the O–Si bond vector to the Si in the next coordination sphere (that is not included in the cluster). In the case of some clusters in which the atoms in the outer coordination spheres close in on one another to form four rings, an additional Si atom was included to close the ring and was terminated with hydrogen atoms placed 1.48 Å from the Si atom along the Si–O bond vector to the O atom in the next coordination sphere (that is not included in the cluster). This is the same general strategy for extracting clusters from crystal structures employed in previous work.^[4–6,16–18] The calculations employed 6-311G(2df) basis sets for the central Si atom, nearest neighbor O atoms, and next-nearest neighbor Si atoms, while the outer Si, O, and H atoms employed 6-31G basis sets. This cluster size and basis set have been shown to have reached convergence.^[4] To facilitate comparison of calculated and experimental chemical shifts, the calculated shielding tensor values were converted into chemical shift values using α -quartz as a secondary chemical shift standard. The calculated absolute shielding values σ were converted to relative chemical shifts δ with respect to TMS using

$$\delta^{\text{TMS}}(\text{cluster}) = \sigma_{\text{iso}}(\alpha\text{-quartz}) + \delta_{\text{iso}}^{\text{TMS}}(\alpha\text{-quartz}) - \sigma(\text{cluster}) \quad (1)$$

where $\sigma_{\text{iso}}(\alpha\text{-quartz})$ and $\sigma(\text{cluster})$ were calculated using the same basis sets and cluster size. The experimentally observed isotropic chemical shift for α -quartz was $\delta_{\text{iso}}^{\text{TMS}}(\alpha\text{-quartz}) = -107.28$ ppm^[4] and the calculated absolute isotropic shielding (using the coordinates from a single-crystal XRD structure^[19]) value

was σ_{iso} (α -quartz) = 491.19 ppm. The Gaussian09 calculations were carried out on the Shared Hierarchical Academic Research Computing Network, while other calculations were carried out with notebooks written for *Mathematica* 7.0.^[20] Each cluster calculation of shielding tensors took approximately 2 h, and calculations for the various clusters were run in parallel. The NMR refinement procedures took several days to complete.

NMR structure refinements were carried out according to the protocol described in Ref. [5] and outlined in detail in Ref. [6.] The structure refinement procedure finds the set of Si and O atomic coordinates giving the best agreement between experimentally measured and *ab initio* calculated ^{29}Si CS tensor components, with restraints on the closest Si–O, O–O, and Si–Si distances. The distance least-squares (DLS) method^[21] was also applied to optimize the structure by refining the Si and O atomic coordinates to minimize differences between closest Si–O, O–O, and Si–Si distances and specified target distances. The NMR structure refinement procedure expands upon the DLS method with the incorporation of additional observations of ^{29}Si CS tensors. In all cases, 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, which are representative of the distance distributions found in single-crystal XRD structures of zeolites.^[6] In this work, the NMR structure refinement strategy has been extended to include the unit cell parameters as variables in the refinement. Uncertainties in the optimized parameters for the DLS optimization and NMR refinement were estimated according to the method described in Ref. [6.]

Plane-wave DFT calculations of nuclear magnetic shielding tensors were performed using the NMR module of the CASTEP code^[9,11] which employs the Gauge Including Projector Augmented Wave algorithm^[10] and is a part of the Accelrys Materials Studio simulation and modeling package.^[22] The Perdew–Burke–Ernzerhof (PBE) functional was used with the generalized gradient approximation for all calculations.^[23] The convergence of calculated NMR parameters on the size of a Monkhorst–Pack *k*-point grid and a basis set cut-off energy were tested for all systems. The sufficient basis set cut-off energies were 550 eV and the *k*-point spacing was always less than $0.05 \text{ \AA}^{-1}$. On-the-fly pseudopotentials were used as supplied in Materials Studio. All calculations were performed on primitive cells using the cell parameters and atomic coordinates as indicated further in the text. The geometry optimization was performed using the PBE functional and the same Monkhorst–Pack *k*-point grid spacings and cut-off energies as in corresponding single point energy calculations. Convergence tolerance parameters in geometry optimization have been set as follows: energy, 10^{-5} eV/atom; maximum force, 0.03 eV/Å; maximum stress, 0.05 GPa; maximum displacement, 10^{-3} Å. Computations were performed using an Intel 2.6-GHz dual core processor with 8 MB RAM. Lattice energy calculations took approximately 5 h, CS calculations took about 2 days, while geometry optimizations took 1 day with fixed unit cell parameters and 2 days for a full geometry optimization. The absolute shielding constants obtained in the calculations were converted into the chemical shift scale according to Eqn (1) with σ_{iso} (α -quartz) = 430.59 ppm, calculated from the single-crystal structure of α -quartz^[19] under identical conditions.

Results

The crystal structure of ITQ-4 is displayed in Fig. 1(a). The structure was first determined from synchrotron powder XRD data^[14]

Figure 1. (a) Crystal structure of the ITQ-4 pure silica zeolite viewed down the *c*-axis. (b) Representative Si-centered and H-terminated clusters extracted from the crystal structure for Gaussian calculations of ^{29}Si CS tensors.

and was subsequently redetermined in a variable temperature synchrotron single microcrystal study of the negative thermal expansion properties of ITQ-4.^[15] The structure shown here is the single-crystal structure determined at 290 K. The structure consists of one-dimensional channels oriented along the crystallographic *c* axis. These channels are made up of 12-membered rings and have an elliptical opening of about 6.2×7.2 Å after taking into account the van der Waals radii of oxygen atoms. The structure consists of four crystallographically unique Si sites with equal occupancies and ten unique O sites.

The ^{29}Si MAS NMR spectrum corresponds nicely to the crystal structure, having four clearly separated peaks with equal peak areas (Fig. 2(a)). The assignments of the peaks to the crystallographic Si sites are based on previously reported two-dimensional (2D) ^{29}Si NMR experiments.^[2] As shown in Fig. 2(b), with a slow MAS frequency (670 Hz) and ultrahigh magnetic field (21.1 T), it is possible to observe the four individual spinning sideband profiles with a sufficient number of spinning sidebands for reliable estimations of the ^{29}Si shielding tensors. Figure 2(c) shows the best fit spectrum made up of the sum of the four individual spinning sideband profiles shown in Fig. 2(d).

Figure 2. (a and b) Experimental ^{29}Si MAS NMR spectra of ITQ-4 obtained at 21.1 T and MAS spinning frequencies of (a) 3000 Hz (40 scans) and (b) 670 Hz (1000 scans) with recycle delays of 8 s. (c) Simulated 670 Hz MAS spectrum composed of (d) individual simulated spinning sideband patterns for each Si site. The arrows indicate the isotropic peaks.

From these individual spinning sideband profiles, it was possible to estimate the principal components of the ^{29}Si CS tensors. A series of spinning sideband profiles were calculated for a range of span (Ω) and skew (κ) values and then compared with the experimental spinning sideband profiles. The spinning sideband profiles for the values of Ω and κ giving the best agreement are compared with the experimental profiles in Fig. 3(a). Contour plots of the agreement between experimental and calculated spinning sideband profiles (χ^2_{ssb}) were constructed (Fig. 3(b)) in order to estimate the best fit values for the span and skew and their uncertainties. The determined ^{29}Si CS tensor components are listed in Table 1. The spans of the tensors range from about 21 to 32 ppm, while the skews indicate that none of the tensors is axially symmetric.

Figure 3. (a) Plots of spinning sideband intensities extracted from slow MAS spectrum (black) and calculated from best fit values of Ω and κ (gray). (b) Contour plots of χ^2_{ssb} from which the best fit values of Ω and κ and their uncertainties were estimated. The quantum-chemical-calculated values of Ω and κ for the single-crystal XRD structure using Gaussian (blue squares) and CASTEP (red circles) are also indicated. The experimental values are listed in Table 1, while the calculated values are listed in Table S1.

With good estimates of the ^{29}Si CS tensor principal components, it is now possible to test the quality of the powder and single-crystal XRD crystal structures as well as the different quantum-chemical methods available for calculating ^{29}Si CS tensors. First, the ^{29}Si CS tensors calculated with Gaussian09 are considered. These calculations require a 'molecular fragment' or 'cluster' that has been extracted from the crystal structure. For each of the four types of Si atoms, a cluster was extracted from the crystal lattice with at least three coordination spheres surrounding the Si atom of interest and the outer Si or O atoms terminated with H atoms. Figure 1(b) shows representative clusters of each of the four Si sites, with the central Si atom highlighted in purple.

Table 1. Experimental principal components of the ^{29}Si chemical shift tensors of ITQ-4

Si site	δ_{iso} (ppm)	Ω (ppm)	κ	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)
Si1	-110.4 ± 0.1	31.7 ± 1.2	0.05 ± 0.06	-94.9 ± 1.0	-109.8 ± 0.7	-126.5 ± 1.0
Si2	-112.1 ± 0.1	27.9 ± 1.5	0.10 ± 0.06	-98.6 ± 1.1	-111.2 ± 0.7	-126.5 ± 1.1
Si3	-109.2 ± 0.1	26.1 ± 1.7	0.06 ± 0.07	-96.4 ± 1.3	-108.7 ± 0.8	-122.5 ± 1.3
Si4	-107.5 ± 0.1	21.5 ± 1.1	-0.39 ± 0.09	-95.4 ± 1.0	-110.3 ± 0.6	-116.9 ± 1.0

Figure 4. Quality of agreement between experimental and quantum-chemical-calculated principal components of ^{29}Si CS tensors: (a and b) calculated with Gaussian and (c and d) calculated with CASTEP using the ITQ-4 crystal structure determined from (a and c) powder XRD diffraction and (b and d) single-crystal XRD diffraction. The experimental values are listed in Table 1, while the calculated values are listed in Table S1.

Gaussian09 calculations were first performed on clusters extracted from the synchrotron powder XRD structure.^[14] Once calculated, the values were converted from the absolute CS scale to relative chemical shift values (using α -quartz as a reference) to facilitate comparisons with experimental data. The calculated values are listed in Table S1 and are compared with the experimental ^{29}Si CS tensor principal components in Fig. 4(a). The overall agreement, quantified by the root-mean-square (rms) difference between calculated and experimental ^{29}Si CS tensor principal components, is 8.1 ppm. The agreement is quite good for Si1 and Si2, but poor for Si3 and Si4, suggesting that the atomic positions for Si3 and Si4 and their surrounding oxygens may not be entirely accurate.

Similar Gaussian09 calculations were then carried out on clusters extracted from the single-crystal XRD structure.^[15] The calculated values are listed in Table S1 and are compared with the experimental ^{29}Si CS tensor principal components in Fig. 4(b). The agreement between experimental and calculated values is dramatically improved (rms = 2.3 ppm) indicating that the crystal structure derived from single-crystal data is superior to the structure derived from powder data. This improvement is consistent with previous comparisons of calculations from powder and single-crystal XRD zeolite structures.^[4]

A comparison of the atomic coordinates of the single-crystal and powder XRD structures reveals quite small differences, with average deviations of the Si and O coordinates of only 0.03 Å. It seems remarkable that these two structures that are so similar give such differences in the agreement of the quantum-chemical-calculated ^{29}Si CS tensors with experimental data. Using CASTEP, the total lattice energies of both structures were calculated and, as shown in Fig. 5, the single-crystal XRD structure is more than 1 eV lower in energy than the powder XRD structure. Plots of

the distributions of the closest Si–O, O–O, and Si–Si distances (Fig. 6) reveal that the likely cause of the higher energy and poorer agreement between calculated and experimental ^{29}Si CS tensors is the much wider distribution of these distances for the powder XRD structure. There are several distances that fall well outside of the range of distances expected for zeolite crystal structures. Presumably, the ^{29}Si CS tensors and lattice energy are extremely sensitive to small changes in these closest distances. Recall that the poorest agreement between experimental and calculated ^{29}Si CS tensors for the powder XRD structure was observed for Si3 and Si4 (Fig. 4). The closest Si–O distances around Si3 are 1.575, 1.561, 1.618, and 1.651 Å, while the closest Si–O distances around Si4 are 1.548, 1.611, 1.658, and 1.666 Å. This large scatter in Si–O distances suggests significant distortion of the local geometry around these Si atoms, which probably accounts for the poor agreement of the calculated ^{29}Si CS tensors. The corresponding distances for Si1 and Si2 do not deviate nearly so much from the expected value of 1.60 Å, and thus these local environments are not as distorted, and the calculated and experimental ^{29}Si CS tensor components are in decent agreement.

Quantum-chemical calculations of the ^{29}Si CS tensors using both the powder and single-crystal XRD structures of ITQ-4 were also carried out using CASTEP. In these calculations, the entire crystal structure is used, rather than extracted molecular fragments. The results of these calculations are presented in Table S1 and in Fig. 4. As shown in Fig. 4(c), the calculated values for the powder XRD structure are in quite poor agreement (rms = 9.7 ppm) with the experimental values. However, as shown in Fig. 4(d), the agreement of the values calculated from the single-crystal XRD structure with the experimental values is excellent (rms = 1.3 ppm). The similar improvement from powder to single-crystal XRD structure for both Gaussian and CASTEP calculations indicates that it is the superior quality of the single-crystal structure that is mostly leading to the improvement.

A comparison of Fig. 4(b) and (d) reveals a slight improvement in the quality of agreement for the CASTEP calculations compared to Gaussian calculations using the single-crystal structure. This improvement, also illustrated in Fig. 3(b), likely arises from the fact that the entire crystal structure is being used in the calculation, rather than some extracted molecular fragment such as is used as an approximation in the Gaussian calculations. Given that the improvement is slight, Gaussian calculations remain a viable method for calculating ^{29}Si CS tensors in zeolites. The main advantage of performing Gaussian calculations with smaller extracted clusters is that the calculations are significantly less computationally demanding than CASTEP calculations on the full crystal structure.

One of the aims of making experimental measurements and performing quantum-chemical calculations of ^{29}Si CS tensors is to incorporate these methods into 'NMR crystallography' of zeolites, an approach by which solid-state NMR and quantum-chemical calculations play an integral role in the determination of zeolite crystal structures. The general strategy consists of using powder XRD data to establish the unit cell parameters and space group, while advanced multidimensional dipolar recoupling NMR methods are used to solve the crystal structure by deriving an initial structural model. The final step is to then perform some sort of structure refinement procedure to find the best structure that is in highest agreement with all available data, a step in which quantum-chemical calculations can be very useful.

For the ITQ-4 zeolite, it has previously been demonstrated in a 'blind test' that its crystal structure can be solved from a

Figure 5. Comparisons of the various ITQ-4 structures: (a) average deviation of Si (dark gray) and O (medium gray) coordinates from those of the single-crystal XRD structure of ITQ-4. The light gray bars indicate the average magnitudes of the estimated uncertainties for the Si and O coordinates. (b) Root-mean-square differences between experimental ^{29}Si CS tensor components and those calculated using Gaussian (dark gray) and CASTEP (medium gray). (c) Total lattice energies calculated using CASTEP. The asterisks (*) indicate structures for which the unit cell parameters were refined.

combination of powder diffraction (from which unit cell and space group are derived) and ^{29}Si DQ NMR methods.^[2] In this work here, we have explored a number of options available for further refining this 'NMR-solved' crystal structure in order to improve upon its quality. By doing so, we are demonstrating the feasibility of the full NMR crystallography structure determination process for zeolites. Furthermore, since a single-crystal XRD structure is available for this material, we have a reliable structure by which we can judge the overall success of the NMR crystallography process. By demonstrating its success, we can develop confidence of this approach for structures for which high-quality crystal structures do not exist or are not achievable, for example the partially ordered layered silicate materials that Chmelka has reported.^[24]

The three options we have explored are (i) a relatively simple geometry optimization based on the DLS method^[21] in which the nearest Si–O, O–O, and Si–Si distances are optimized to specified target distances; (ii) an 'NMR-refinement'^[5,6] of the structure in which the agreement between experimental and calculated ^{29}Si CS tensors is optimized in addition to the distances being optimized in the DLS method; and (iii) a full quantum-chemical geometry optimization using CASTEP in which the lattice energy is minimized.

The starting structure is the NMR-solved structure, as reported in the supporting information of Ref. [2] solved from ^{29}Si DQ NMR

data. Since only Si coordinates are found by this method, the first step was to add O atoms midway between Si atoms that are known to be connected via Si–O–Si linkages (established from 2D NMR spectra). Comparing this structure to the single-crystal XRD structure reveals that the Si and O atoms do not have unsurprisingly large average deviations from the corresponding Si atoms in the single-crystal structure of 0.34 and 0.49 Å, respectively. When this structure is used to calculate the ^{29}Si CS tensors with Gaussian, there is extremely poor agreement with the experimental data (rms = 29.2 ppm). This is not surprising since the O atoms have simply been placed midway between Si atoms, which may a good starting point but gives very unrealistic local geometries which are highly distorted. These large deviations from ideal geometry can be seen in the mean and standard deviations of the nearest Si–O and O–O distances of 1.55 ± 0.02 and 2.48 ± 0.29 Å, respectively, which are both very far off from what is typical for zeolites (1.60 ± 0.01 and 2.61 ± 0.02 Å). Another indication that this is a poor structure is that the calculated lattice energy of -16800 eV is over 40 eV higher compared to that of the single-crystal structure. This structure is clearly in need of further refinement and improvement.

This NMR-solved structure was then optimized using the DLS method, with the unit cell parameters held fixed to those used in the NMR structure solution. As shown in Fig. 5(b), both Gaussian and CASTEP calculations of the ^{29}Si CS tensors for this structure give

Figure 6. Distributions of the closest (a) Si–O, (b) O–O, and (c) Si–Si distances for the various ITQ-4 structures. The points with error bars represent the mean and standard deviation of each set of distances. The asterisks (*) indicate structures for which the unit cell parameters were refined.

values that are in good overall agreement with experimental data ($\text{rms} = 2.3$ ppm), indicating that this is a much improved structure. The total lattice energy, as calculated by CASTEP, for this structure is significantly lowered to be very comparable to that of the single-crystal XRD structure (Fig. 5(c)), further suggesting a much improved structure. Indeed, as shown in Fig. 5(a), the average deviations of the Si and O atoms from the single-crystal XRD were reduced dramatically, down to 0.02 and 0.04 Å, respectively. Interestingly, an analysis of the estimated uncertainties of the atomic coordinates reveals that the average uncertainties of the Si and O positions are quite large at 0.08 and 0.16 Å. So, while this DLS-optimized structure might be quite accurate, it is not very precise.

This NMR-solved and DLS-optimized structure was then used as the starting structure for the remaining two structure refinement options. By including the additional structural information contained in the ^{29}Si CS tensors, it was hoped that the accuracy and precision of the ‘NMR-refined’ structure would be improved. The first refinement involved keeping the unit cell parameters fixed. The differences between the experimental and calculated ^{29}Si CS tensors were successfully minimized down to an rms of 0.8 ppm and the closest interatomic distances were well matched to expected distributions (Fig. 6). While the average uncertainties of the Si and O positions decreased to 0.04 and 0.09 Å with the incorporation of more observations, the NMR-refined structure had larger deviations from the single-crystal XRD structure (0.07 and 0.13 Å for Si and O atoms, respectively). A second refinement with the unit cell parameters free to refine resulted in a structure with only slightly smaller deviations from the single-crystal structure but with larger uncertainties (Fig. 5(a)).

In both cases, the lattice energies were only very slightly increased over the starting DLS-optimized structure. The CASTEP calculated ^{29}Si CS tensors did not show the same improvement in agreement with experimental tensors that the Gaussian calculations did, with the agreement remaining at around $\text{rms} = 1.8$ ppm in each case.

Starting from the NMR-solved and DLS-optimized structure, CASTEP geometry optimizations to give minimum lattice energies were performed with and without the unit cell parameters fixed. The geometry optimization with the unit cell parameters fixed gave a structure with a slightly lower overall energy compared to all other structures (Fig. 5(c)). Calculations of the ^{29}Si CS tensors remained in good agreement with the experimental values (Fig. 5(b)). This structure is quite close to the single-crystal XRD structure, having average deviations of Si and O coordinates from the single-crystal XRD structure of 0.04 and 0.06 Å, respectively (Fig. 5(a)). When the unit cell parameters are free to refine in addition to the atom coordinates, a structure with slightly increased lattice energy results, but the agreement between experimental and calculated ^{29}Si CS tensors becomes worse (Fig. 5b). The increase in energy with this less restrained optimization may suggest that the true minimum has not been found. Interestingly, all of the closest Si–O, O–O, and Si–Si distances seem to have increased systematically (Fig. 6) as have the unit cell parameters (Table S2). Upon comparison to the single-crystal XRD structure, we see that the average deviations of Si and O coordinates from the single-crystal structure have increased nearly twofold to 0.08 and 0.11 Å, respectively (Fig. 5(a)).

Discussion

These results seem to indicate that the simplest geometry optimization with the DLS procedure gives a structure that is very close to the single-crystal XRD structure. For comparison purposes, the single-crystal XRD structure is considered to be the closest to the 'true' structure, as we have done in previous work.^[5] This DLS-optimized structure has a low overall lattice energy and gives good agreement between experimental and calculated ²⁹Si CS tensors for both Gaussian and CASTEP calculations. Further efforts to improve upon this structure with more sophisticated methods, either by incorporating ²⁹Si CS tensors into the refinement procedure or by performing a quantum-chemical geometry optimization, actually led to structures that had slightly larger deviations from the single-crystal XRD structure, albeit still with relatively small deviations (on the order of 0.1 Å). It remains to be seen whether this will be a general conclusion for pure silica zeolites or it only applies in this one case.

In the NMR refinement, it appears that the ²⁹Si CS tensor data may be being overinterpreted. If we consider that the single-crystal structure is closest to the 'true' crystal structure, then any improvement in the agreement between calculated and experimental ²⁹Si CS tensor components beyond about rms = 2 ppm may not be very meaningful. Indeed, the gains in the agreement in the ²⁹Si CS tensors (calculated using Gaussian) for the two NMR-refined structures do not lead to increased agreement of the coordinates with the single-crystal structure. In fact, the agreement gets slightly worse compared to the DLS-optimized structure. However, the average deviations of the coordinates are similar in magnitude to the estimated uncertainties, suggesting that the 'correct' structure is still being found, within the uncertainties of the method.

The CASTEP optimization with the unit cell parameters fixed led to quite a good structure that is in good agreement with the single-crystal structure, has low lattice energy, and shows good agreement between calculated and experimental ²⁹Si CS tensors. However, there seems to be a tendency for CASTEP to overestimate the interatomic distances. While it is only slight for the optimization with unit cell parameters fixed, it is quite noticeable with the optimization with the unit cell parameters free to refine (Fig. 6). This is an effect that has been reported elsewhere for zeolites.^[12]

CASTEP geometry optimizations of powder XRD structures have been shown in numerous cases to improve the quality of agreement between experimental and calculated NMR parameters. One example is the calculation of ¹⁷O NMR parameters and isotropic ²⁹Si chemical shifts for the zeolite ferrierite which shows significant improvement in the quantum-chemical-calculated NMR parameters once the powder XRD structure was geometry-optimized with CASTEP.^[12] For aluminophosphate microporous materials, related to silica zeolites in many regards, Ashbrook and co-workers have shown that CASTEP geometry optimizations of powder XRD structures led to significant improvements in the agreement between calculated and experimental ³¹P and ²⁷Al NMR parameters.^[25,26] Although the results are not presented here, a CASTEP geometry optimization of the powder XRD structure of ITQ-4 gave rise to a structure with much improved agreement between calculated and experimental ²⁹Si CS tensors and a lattice energy comparable to the CASTEP optimization starting with the NMR-solved and DLS-optimized structure.

Interestingly, these two CASTEP-optimized structures of ITQ-4 are not identical, which leads to an important issue: it is likely that, for any of the optimization procedures, there may exist multiple

local minima and that it is difficult to ensure that the global minimum has been found. It is not unreasonable to assume that the multidimensional hypersurfaces involved in these optimizations are very complex. This issue is evident in the fact that, with the exception of the powder XRD structure, the remaining six structures are clearly different, yet their lattice energies all fall within a small range of only 0.5 eV. However, it is important to be mindful that we are dealing with small differences in the structures, on the order of only 0.1 Å.

Conclusions

The combination of experimental measurements and quantum-chemical calculations of ²⁹Si CS tensors is a powerful approach for investigating the detailed local structures of zeolites. We have shown here again that obtaining the best agreement between experimental and quantum-chemical-calculated NMR parameters requires the highest possible quality of the crystal structure, with single-crystal structures being superior to those determined by powder XRD, even though a comparison of the structures may show only small deviations. Furthermore, we have shown that the Gaussian calculations on clusters extracted from the crystal structure give quite good results even though a significant approximation is being made by using a cluster. CASTEP calculations on the full crystal structure show slightly improved agreement between experimental and calculated ²⁹Si CS tensors, which is consistent with CASTEP being a more thorough and realistic calculation, not having to approximate a periodic crystal structure with a molecular fragment cluster.

We have now completed the NMR crystallography of the zeolite ITQ-4 by demonstrating that the NMR-solved structure reported earlier^[2] can successfully be refined by a variety of methods *independent of diffraction methods* to give a crystal structure that is in remarkably good agreement with the single-crystal XRD structure. All three approaches – a simple DLS geometry optimization, NMR refinement against ²⁹Si CS tensors, and plane-wave DFT geometry optimizations – give optimized structures that are within about 0.1 Å of the single-crystal structure. The first two approaches are more specific to zeolites, while the latter, using CASTEP (or other programs that perform plane-wave DFT calculations) to optimize the geometry by minimizing the lattice energy, has the important advantage that it can be much more broadly applied to a wide variety of materials.

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Supporting information

Supporting information may be found in the online version of this article.

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