Probing local structures of siliceous zeolite frameworks by solid-state NMR and first-principles calculations of ²⁹Si–O–²⁹Si scalar couplings[†]

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Subtle structural details of siliceous zeolites are probed by using two-bond scalar (J) coupling constants to characterize covalently bonded ²⁹Si-O-²⁹Si site pairs and local framework order. Solid-state two-dimensional (2D) ²⁹Si{²⁹Si} NMR measurements and first-principles calculations of ${}^{2}J({}^{29}Si-O-{}^{29}Si)$ couplings shed insights on both the local structures of siliceous zeolites Sigma-2 and ZSM-12, as well as the sensitivity of J couplings for detailed characterization analyses. DFT calculations on a model linear silicate dimer show that ${}^{2}J$ (Si–O–Si) couplings have complicated multiple angular dependencies that make semi-empirical treatments impractical, but which are amenable to cluster approaches for accurate J-coupling calculations in zeolites. DFT calculations of ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings of the siliceous zeolite Sigma-2, whose framework structure is known to high accuracy from single-crystal X-ray diffraction studies, yield excellent agreement between calculated and experimentally measured ${}^{2}J(Si-O-Si)$ couplings. For the siliceous zeolite ZSM-12, calculated ${}^{2}J({}^{29}Si-O-{}^{29}Si)$ couplings based on less-certain powder X-ray diffraction analyses deviate significantly from experimental values, while a refined structure based on ²⁹Si chemical-shift-tensor analyses shows substantially improved agreement. ²⁹Si J-coupling interactions can be used as sensitive probes of local structures of zeolitic frameworks and offer new opportunities for refining and solving complicated structures, in combination with complementary scattering, modeling, and other nuclear spin interactions.

1. Introduction

The determination of zeolite crystal structures is often challenging, because most zeolites are difficult to prepare as single crystals and therefore must typically be characterized by using samples comprised of micrometre-scale polycrystalline powders. In such cases, zeolite crystal structures can be determined by using sophisticated analyses of powder X-ray diffraction (XRD) data,¹ or more recently, by using solid-state ²⁹Si nuclear magnetic resonance (NMR) spectroscopy.^{2–6} However, whereas single-crystal diffraction data generally yield detailed and confident structure solutions even for complicated morphologies, powder samples are more difficult to characterize. In the absence of high-quality single-crystal XRD data, uncertainties or ambiguities often persist in fine details of local bonding geometries, which can have important effects on the molecularlevel understanding of a material's structure and corresponding properties. Similarly, layered silicates, including clays and surfactant-templated layered silicates, ^{7,8} have often presented major challenges to determinations of their framework structures, due to the presence of stacking disorders or other defects that reduce or complicate the 3D periodicity required for detailed characterization by diffraction techniques. As a consequence, the structures of only a small number of these layered systems have been solved,⁹ despite extensive efforts to characterize their local and long-range ordering to understand or modify their molecular or macroscopic properties.

NMR spectroscopy provides valuable and complementary information to XRD data that can be used to propose, validate, and/or refine candidate silicate framework structures, including in the case of non-crystalline solids with short-range molecular order.⁸ These possibilities derive from the large set of nuclear spin interactions to which solid-state NMR measurements are sensitive and that are intrinsically related to the local structural features of silicate frameworks. These interactions include the ²⁹Si isotropic chemical shift and chemical shift anisotropy (CSA),4 i7O chemical shift and quadrupolar effects,^{10,11,29}Si-²⁹Si dipole-dipole couplings,^{2,3} and the usually much smaller (5-20 Hz) two-bond isotropic indirect spin-spin scalar ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings between covalently bonded ²⁹Si-O-²⁹Si species, which have been used in 2D NMR correlation analyses of zeolite and layered silicate structures.^{3,7,8,12–16} The accurate measurement of scalar (J)

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[†] Electronic supplementary information (ESI) available: Histogram plots of ${}^{2}J({}^{29}\text{Si-O}-{}^{29}\text{Si})$ coupling calculations carried out on clusters extracted from the zeolite Sigma-2 framework structure (Fig. S1). Equations for the simulation of 2D J-mediated ²⁹Si{²⁹Si} NMR spectra with tilted lineshapes and extraction of experimental J-coupling constants. Plots of Si-O-Si angles associated with J-coupled pairs in the different ZSM-12 structures [Fig. S2(a)]. Schematic representations and comparison of the framework structures of zeolite ZSM-12 obtained from powder-XRD analyses, Si-chemical-shift-NMR-refinement, and DFT optimizations [Fig. S2(b)]. Unit cell parameters and fractional coordinates of the single-crystal XRD structure of Sigma-2, and of the powder-XRD and ²⁹Si-NMR-refined structures of ZSM-12, along with their DFT-optimized variants. See DOI: 10.1039/b815361b

couplings using solid-state NMR has recently been the focus of much methodological attention, $^{15,17-19}$ although the structural insights obtained from these measurements have so far remained generally limited, except for a few recent examples. 15,20 This is mainly because, in spite of much effort, 21,22 it has remained difficult in most cases to establish clear dependencies (empirical or otherwise) between the *J* couplings and simple structural parameters. 23 This is attributed to the complexity of scalar interactions, which can involve several distinct contributions, such as the so-called Fermi-contact, spin–dipole, and spin–orbit interactions. 24

Nevertheless, new links between the fine structural features of solids and associated scalar couplings are expected to be enabled by recent advancements in capabilities to calculate predictively NMR scalar couplings at the *ab initio* or density functional levels of theory. Here, the efficacy of density functional theory (DFT) calculations for predicting $^{2}J(^{29}\text{Si}-\text{O}-^{29}\text{Si})$ couplings in zeolitic frameworks is demonstrated, along with the sensitivity of these couplings to the fine details of the local framework structure. Comparisons are made between calculated and experimentally measured $^{2}J(^{29}\text{Si}-\text{O}-^{29}\text{Si})$ couplings, which in combination, yield new insights on zeolite framework structures. Taking first the siliceous zeolite Sigma-2, whose structure is known to great accuracy from single-crystal XRD analyses,⁴ through-bond ²J(²⁹Si–O–²⁹Si) couplings are computed by using DFT and separately measured by using solid-state two-dimensional (2D) J-mediated ²⁹Si{²⁹Si} NMR spectroscopy. The DFT calculations are implemented by applying a cluster approach in which different cluster definitions and description levels are compared with respect to their respective abilities to reproduce the experimentally measured J-coupling trends and quantitative values. The local character of the indirect ²⁹Si-²⁹Si spin-spin interaction requires great care in the description of the coupled atoms, with the result that small molecular clusters are sufficient to provide accurate J-coupling calculations. Using these insights, ${}^{2}J({}^{29}Si-O-{}^{29}Si)$ couplings are then calculated, measured, and compared for the more structurally challenging siliceous zeolite ZSM-12, for which single-crystal XRD data are not available. The combined DFT and experimental J-coupling analyses demonstrate the sensitivity of such couplings to subtle details of the local bonding geometries, within the uncertainties of the atomic coordinates obtained from powder X-ray diffraction results. J couplings correlate sensitively to local zeolite framework features and can be used as criteria against which the qualities of proposed structures can be assessed.

2. Experiments and methods

2.a Materials

The sample of powdered polycrystalline siliceous zeolite Sigma-2 was synthesized and characterized by wide-angle X-ray scattering (WAXS), as described in ref. 25, and used as-made. The sample of powdered polycrystalline siliceous zeolite ZSM-12 was prepared and characterized by WAXS, as described in ref. 26, and used after removal of the structuredirecting agent by calcination. The siliceous Sigma-2 and ZSM-12 zeolite samples are the same as used and reported in ref. 4–6.

2.b NMR experiments

Solid-state two-dimensional (2D) refocused-INADEQUATE ²⁹Si{²⁹Si} experiments²⁷ for the measurement of ²J(²⁹Si–O–²⁹Si) couplings were conducted on Sigma-2 and ZSM-12 zeolite samples with ²⁹Si in natural abundance (4.7%) on a Bruker AVANCE-200 spectrometer (4.7 Tesla) operating at 200.50 and 39.83 MHz for ¹H and ²⁹Si, respectively. The measurements were conducted at room temperature under magic-angle-spinning (MAS) conditions at 5 kHz using a 7 mm Bruker doubleresonance CP-MAS probehead. The experiment conducted on the Sigma-2 sample was recorded with 32 t_1 increments, each with 192 scans. The cross-polarization (CP) contact time between the weakly-coupled protons of the organic structure-directing agent located in the zeolite cages and the ²⁹Si nuclei of the Sigma-2 framework was 20 ms, and the half-echo time τ was 15 ms. Continuous-wave ¹H decoupling was applied at a ¹H nutation frequency of approximately 30 kHz during the DQ excitation, evolution, reconversion, and acquisition periods. The recycle delay was 4.5 s, for a total experiment time of approximately 16 h. The experiment conducted on zeolite ZSM-12 was collected with 32 t_1 increments, each increment consisting of two experiments (each with 2304 transients) having a 45° phase difference between all pulses prior to the evolution period for quadrature detection in the indirect dimension (i.e. the so-called States method²⁸), and using a half-echo time τ of 20 ms. A recycle delay of 12 s was employed with direct excitation of the ²⁹Si nuclei, yielding a total experiment time of approximately 26 days. Such a long measurement time was required to obtain acceptable signal sensitivity, because of the relatively broad ²⁹Si peak widths, the low magnetic field strength, and the long spin-lattice ²⁹Si relaxation times.

2.c Deconvolution of NMR spectra

To estimate the ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings for Sigma-2, the 1D ²⁹Si CP-MAS spectrum was first fitted to obtain isotropic ²⁹Si chemical shifts for each of the four well-resolved peaks. These shifts were used to calculate the slices in the double-quantum (DQ) dimension and were fixed for subsequent estimations of the J couplings. For each of the slices, the ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings were estimated by performing a least-squares fit with the following free parameters: the respective J-coupling value (doublets at a fixed isotropic shift $\pm J/2$), ²⁹Si peak widths (kept equal for each peak in a given doublet), integrated peak areas (outer two peaks in a slice kept equal and inner two peaks in a slice kept equal), and the relative Lorentzian-Gaussian lineshape contributions (fixed to be same for all four peaks in a slice). Similarly for ZSM-12, the 1D ²⁹Si MAS spectrum was first fit to obtain isotropic ²⁹Si chemical shifts for the peaks, which were then used to calculate the frequencies in the DQ dimension and then fixed in the 2D deconvolution procedure. For each pair of correlated doublets, the peaks were calculated at the fixed isotropic shifts $\pm J/2$, and the *J*-coupling value was adjusted to give the best fit. Again, the integrated peak areas of the outer two peaks in a correlation were kept equal, along with those of the inner two peaks, which were also kept equal. All

peaks were (tilted) Lorentzian in shape in both dimensions with half-height widths of 6 Hz (0.15 ppm) and 28 Hz (0.71 ppm) in the single-quantum and double-quantum ²⁹Si dimensions, respectively. The explicit equations describing the calculation of the fitted 2D spectrum are included in the ESI.†

2.d DFT calculations

Calculations of ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ coupling constants were carried out at the density-functional level of theory, using Gaussian 03,²⁹ and the B3 hybrid (Hartree-Fock exchange with DFT exchange-correlation) functional,³⁰ combined with the LYP correlation functional,³¹ unless mentioned otherwise. Locally dense basis sets were used for accurate J-coupling calculations. Calculations on the protonated silicate linear dimer, whose structure was initially optimized using 6-31G* basis sets on all atoms, were then carried out using an IGLO-III basis set on the coupled ²⁹Si atoms, and IGLO-II on the oxygen atoms, while the 6-31G basis was kept for the hydrogen atoms. The different locally dense basis sets used for the cluster calculations from the zeolite structures are detailed in Table 1. Parameters for the IGLO-II and IGLO-III basis sets were obtained from the Basis Set Order Form of the Environmental and Molecular Sciences Laboratory at the Pacific Northwest National Laboratory (US).³² Integrations were computed within a so-called "fine" grid, having 75 radial shells and 302 angular points per shell (resulting in about 7000 points per atom). All Gaussian calculations were submitted through the GridChem³³ cyber-infrastructure for computational chemistry.34

Optimizations of the zeolite ZSM-12 framework structure were conducted with periodic boundary conditions using the CASTEP code,³⁵ which relies on a plane-wave-based DFT approach. The electron correlation effects were modeled using the PBE generalized-gradient approximation³⁶ with "ultrasoft" pseudo-potentials³⁷ and a plane-wave cut-off energy of 600 eV. The primitive unit-cell parameters, namely (12.6818 Å, 12.6818 Å, 24.3275 Å) and (107.361°, 107.361°, 22.796°) were taken from the powder XRD structure²⁶ and kept fixed during the optimization. A $5 \times 5 \times 1$ Monkhorst–Pack³⁸ grid was used to sample the Brillouin zone, and so-called "fine" convergence electronic and ionic optimization criteria were used.

3. Results and discussion

3.a ${}^{2}J({}^{29}Si-O-{}^{29}Si)$ couplings in siliceous Sigma-2

In most cases, scalar (or synonymously, J) couplings are not or are only barely resolved in solid-state NMR spectra. Typically, scalar couplings are measured indirectly using spin echoes, where the inhomogeneous broadening is refocused, potentially leading to much longer dephasing, and thus improved resolution in a so-called 'J-resolved' dimension.³⁹ In some highly ordered systems, however, the linewidths can be small enough for even small couplings to be resolved and thus potentially measurable without using spin echoes. This is the case in a few siliceous zeolite systems, in particular.^{12,13} For example, siliceous zeolite Sigma-2 (having an SGT-type framework) can be prepared with large enough single crystals for the atomic coordinates to be determined with high accuracy by using single-crystal X-ray diffraction.²⁵ Consequently, zeolite Sigma-2 represents an excellent system to probe the accuracy of DFT calculations of experimentally measured ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings. Fig. 1(a) shows a schematic representation of the zeolite framework of zeolite Sigma-2, with two distinct types of cages and the four crystallographically distinct Si sites indicated.²⁵ The unit cell parameters and fractional coordinates, as reported in ref. 25, are provided in the ESI.[†]

The two-dimensional (2D) refocused-INADEQUATE ²⁹Si{²⁹Si} NMR spectrum of zeolite Sigma-2 in Fig. 1(b) yields highly resolved intensity correlations, from which throughbond ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings can be extracted. Well-defined double-quantum-correlated peaks are observed between the four inequivalent four-coordinated (so-called 'tetrahedral' or 'T') ²⁹Si sites, all of which correspond to fully condensed Q^4 ²⁹Si moieties at -108.8, -114.9, -116.0, and -119.9 ppm and are labeled as sites 4, 2, 1, and 3, respectively. (' Q^{n} ' refers to four-coordinate ²⁹Si atoms with n other silicon next-nearest neighbors that are covalently bonded through bridging oxygen atoms.) For these measurements, correlated ²⁹Si{²⁹Si} signals that appear at the sum of their individual frequencies in the indirect (vertical) double-quantum dimension establish unambiguously the existence of J-coupling-mediated interactions between pairs of ²⁹Si-O-²⁹Si sites within the Sigma-2 framework. The high degree of crystallinity of the Sigma-2 sample, combined with the weak interactions between the ²⁹Si

Table 1	Locally dense basis se	ts (LDBS) used	to calculate ² J(²⁹ Si-	-O-29Si)-coupling	constants for differen	t cluster definitions	(see text
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LDBS label ^a	Coupled Si	Central O	Next-nearest O	Other Si	Other O	Н
IGLO-III	IGLO-III	6-31G*	6-31G*	6-31G*	6-31G*	6-31G
IGLO-III/IGLO-II $(1)^b$	IGLO-III	IGLO-II	6-31G*	6-31G*	6-31G*	6-31G
IGLO-III/IGLO-II (2) ^b	IGLO-III	IGLO-II	IGLO-II	6-31G*	6-31G*	6-31G
cc-PVTZ	cc-PVTZ	6-31G*	6-31G*	6-31G*	6-31G*	6-31G
cc-PVOZ	cc-PVOZ	6-31G*	6-31G*	6-31G*	6-31G*	6-31G
cc-PV5Z	cc-PV5Z	6-31G*	6-31G*	6-31G*	6-31G*	6-31G
IGLO-III/diffuse ^c	IGLO-III	6-31++G*	6-31++G*	6-31++G*	6-31++G*	6-31++G
cc-PVTZ/diffuse ^c	cc-PVTZ	6-31++G*	6-31++G*	6-31++G*	6-31++G*	6-31++G
cc-PVOZ/diffuse ^c	cc-PVOZ	6-31++G*	6-31++G*	6-31++G*	6-31++G*	6-31++G
cc-PV5Z/diffuse ^c	cc-PV5Z	6-31++G*	6-31++G*	6-31++G*	6-31++G*	6-31++G

^{*a*} LDBS labels refer to the basis set used to describe the coupled ²⁹Si nuclei, and then (after "/") to information related to surrounding atoms. ^{*b*} Labels (1) and (2) distinguish cases in which (1) only the central bridging O atom or (2) all of the oxygen atoms of the first coordination sphere of the coupled ²⁹Si nuclei are described with an IGLO-II basis set. ^{*c*} diffuse functions, indicated by "++" in the basis set definition, are of the form (3df, 3pd).



Fig. 1 (a) Schematic representation of the structure of siliceous zeolite Sigma-2, showing Si atoms at the vertices of the polygonal shapes and oxygen atoms bridging between adjacent Si T-sites as straight lines. (b) Solid-state 2D refocused INADEQUATE ²⁹Si $\{^{29}Si\}$ NMR spectrum of siliceous zeolite Sigma-2, which possesses a SGT-type crystalline framework. (c) Experimental 1D slices (in black) extracted at the double-quantum frequencies corresponding to the different ²⁹Si $-O^{-29}Si$ pairs of inequivalent silicon T-sites. The red solid lines are 1D spectral deconvolutions of the respective experimental slices from which the ² $J(^{29}Si-O^{-29}Si)$ (scalar) couplings have been obtained with ±1 Hz accuracy.

nuclei within the silicate framework and the protons of the structure-directing species, provide extremely narrow $^{29}\mathrm{Si}$ lineshapes in the 2D $^{29}\mathrm{Si}\{^{29}\mathrm{Si}\}$ NMR spectrum. This is illustrated in Fig. 1(c) for slices extracted at DO frequencies that correspond to pairs of interconnected ²⁹Si-O-²⁹Si sites in the framework, namely site pairs 1-3, 2-3, 4-1, and 4-2 at -236.0, -233.6, -224.8, and -222.5 ppm, respectively, which exhibit narrow lines with full-widths at half-maximum (fwhm) of 0.2 to 0.4 ppm (*i.e.* 8 to 16 Hz at a field strength of 4.7 T). The 2D ²⁹Si{²⁹Si} DQ-correlated peaks are each clearly split into doublets due to their ${}^{2}J({}^{29}Si-O-{}^{29}Si)$ couplings, which can subsequently be measured with good accuracy (estimated to ± 1 Hz) by deconvoluting the different slices, as shown in red in Fig. 1(c), even for couplings as small as 6.3 Hz. The scalar coupling constants thus measured provide a reliable target for their calculation by DFT, using the accurate framework structure for Sigma-2 obtained from single-crystal XRD.

Scalar ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings have complicated dependences on local bond-angle geometries, with a major contribution from ²⁹Si–O–²⁹Si bond angles, along with non-negligible contributions from several bond and dihedral angles involving the J-coupled ²⁹Si nuclei and their first and second coordination spheres. This is evidenced in Fig. 2(a) by the clear deviations of the measured $^{2}J(^{29}\text{Si-O-}^{29}\text{Si})$ couplings in zeolite Sigma-2 from a strictly linear correlation to the associated ²⁹Si-O-²⁹Si bond angles. The contributions that are responsible for these deviations have been explored semi-quantitatively in Fig. 2(b-e) for a simple model system, (OH)₃²⁹Si-O-²⁹Si(OH)₃, *i.e.* the protonated linear silicate $Q^1 - Q^1$ dimer, where the effect of the distortions of various bond and dihedral angles on ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings can be predicted by DFT calculations. As shown in Fig. 2(b), distortions of ²⁹Si-O-²⁹Si bond angles from the DFT-optimized angle (i.e. 122.7°) are associated with the largest variation range of the ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ coupling (±5 Hz for distortions of ±30°). exhibiting monotonic, though not strictly linear, behavior. These

results are in good agreement with the trend observed for the experimentally measured ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings for zeolite Sigma-2 [Fig. 2(a)] and consistent with similar results recently reported by Massiot and co-workers.⁴⁰

In addition, however, significant though smaller contributions are predicted from distortions of the O-29Si-O bond angles, six of which simultaneously contribute to each J-coupling constant associated with the respective ²⁹Si T-site pairs. As shown in Fig. 2(c), distortions of one of the $O^{-29}Si(1)$ -O angles by -10 to $+40^{\circ}$ can introduce ± 3 Hz variations in the $^{2}J(^{29}\text{Si}-\text{O}-^{29}\text{Si})$ values. Because of the combined (and presumably partially additive) effects of variations of the six different O-²⁹Si-O angles, it is clear that diverse values of ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings with relatively large apparent "scatter" can result. Furthermore, other local bonding parameters also have non-negligible contributions to the net J couplings, such as $O^{-29}Si - O^{-29}Si$ torsion angles. H–O–²⁹Si–O dihedral angles, or bond lengths (not shown). For example, Fig. 2(d) shows that rotations (indicated by a blue arrow) around the covalent bond between a T-site Si(1) and the central oxygen atom induce variations of ± 1.5 Hz (which are similar for rotations around the adjacent O-Si(2) covalent bond). Finally, a smaller variation range of the order of 1 Hz was obtained for rotations around the terminal O-H bonds of the linear dimer [Fig. 2(e)], which should likely be taken into account for calculations involving ²⁹Si Q^3 sites, which are often present, for example, in layered silicates. Based on these calculations, distributions of the four ²⁹Si-O-²⁹Si angles are expected to exert the largest influences on ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings, due to their effects on the local bonding geometries within the first coordination spheres of the coupled ²⁹Si nuclei, but other contributions, notably from the O-²⁹Si-O bond angles, are likely not negligible.

Thus, the diversity of local bonding geometries within the first coordination spheres of the coupled ²⁹Si nuclei can have large effects on the ²J(²⁹Si–O–²⁹Si) couplings measured. Unfortunately, the dependence of the ²J(²⁹Si–O–²⁹Si)



Fig. 2 (a) Experimental ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings measured for zeolite Sigma-2 and plotted as a function of their respective ²⁹Si–O–²⁹Si bond angles between pairs of Si T-sites, as extracted from the single-crystal XRD structure.²⁵ A clear monotonic, though not strictly linear, correlation is observed, with larger J couplings observed for pairs of sites with larger bond angles. (b-e) Effects on calculated $^{2}J(^{29}\text{Si}-\text{O}-^{29}\text{Si})$ coupling of the distortions of local (b,c) bond angles and (d.e) dihedral angles from their DFT-optimized value for the (gas-phase optimized) protonated linear silicate dimer: (b) calculated ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings as a function of the ${}^{29}\text{Si}(1)-\text{O}-{}^{29}\text{Si}(2)$ bond angle (initial value from DFT optimization: 122.7°); (c) effect of the variation of one of the O-²⁹Si(1)–O bond angles (initial value: 104.0°); partial geometry optimizations of the hydrogen atoms and of the two other oxygen atoms bonded to the Si(1) atom were carried out at each step; (d) calculated ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings as a function of one of the O–Si(1)–O–Si(2) torsion angles (initial value: -30.2°); (e) effect of the variation of one of the H-O-Si(1)-O dihedral angles (initial value from DFT optimization: 165.9°). Calculated J couplings are all plotted to the same vertical scale for direct comparison of the predicted ranges of variation associated with the different local angular distortions.

couplings on the local covalent bond geometry is sufficiently complicated that, till now, no models (empirical or otherwise) have been available to predict the value of these interactions in zeolitic frameworks with a reasonable accuracy. By comparison, *ab initio* or DFT calculations‡ typically describe the complete physics of the *J*-coupling interaction (at least in theory), and thus intrinsically account for the effects of every feature of the local geometry, independent of the atoms (and/or nuclei) involved. As a result, DFT calculations in combination with experimentally measured *J*-coupling correlations are expected to be particularly useful and may provide new insights on the local structures of zeolites and other molecularly-ordered silicate materials.

Calculating indirect spin–spin couplings using *ab initio* or DFT approaches, however, is challenging for several reasons. First, determination of the exact value of the Fermi contact term, which is generally the dominant contribution of the isotropic part of this interaction (at least in systems that do not involve multiple bonds), requires knowledge about all of the excited electronic states of the system. Moreover, as for chemical shift interactions, the prediction of indirect spin–spin couplings requires accurate descriptions of the electronic densities at the exact positions of the *J*-coupled nuclei. Because of these complications, DFT calculations of *J* couplings are expected to reproduce experimental trends, rather than necessarily provide quantitatively accurate values.

The siliceous zeolite Sigma-2, for which a single-crystal XRD-derived structure is available, represents an excellent system to probe the degrees of accuracy of calculated ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings, based on different cluster definitions and levels of description (i.e. basis set density). Oxygen-centered clusters have previously been extracted from several zeolite structures to calculate ¹⁷O NMR parameters, using different cluster definitions.^{10,11} Here, these cluster definitions, along with a new type of definition, are briefly described and then evaluated with respect to the accuracies of the ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings that they predict, as assessed by their comparisons to the experimental values. For example, Fig. 3 shows three distinct types of clusters centered on the ²⁹Si(1)–O–²⁹Si(4) (site pair 1–4) fragment of zeolite Sigma-2. These clusters are used without further geometry optimization to keep the local structure as close as possible to that of the crystal structure from which they are extracted and, thus, correspond to non-equilibrium geometries when considered in isolation.

The smallest type of cluster used here, the Si–H-terminated two-T-shell clusters (where 'T' refers to four-coordinated, so-called 'tetrahedral' silicon sites), is illustrated in Fig. 3(a). In these clusters, the oxygen atoms in the third coordination sphere of the coupled ²⁹Si nuclei have each been replaced by hydrogen atoms to form 0.148 nm Si–H bonds, each of which is directed along a former Si–O bond.¹⁰ Such clusters have a typical composition of Si₈O₇H₁₈, or Si₈O₈H₁₆ if both coupled ²⁹Si atoms are in a four-membered ring. This cluster definition is typically too small for accurate calculations of ¹⁷O NMR parameters,¹⁰ in which case larger clusters such as the OH-terminated two-T-shell clusters shown in Fig. 3(b) need to be considered. In this second type of cluster, the terminal

[‡] In DFT calculations, empirical parameters may be used for the calculation of the electronic density through exchange–correlation functionals, whereas "*ab initio*" refers to methods, such as Hartree–Fock, or computationally demanding post-Hartree–Fock approaches, that do not involve the use of empirical parameters.



Fig. 3 Different O-centered clusters extracted from the structure of zeolite Sigma-2 (as determined by single-crystal XRD analyses²⁵) and centered on the 29 Si(1)–O– 29 Si(4) fragment with different bond terminations. Si, O, and H atoms are displayed in blue, red, and white, respectively. (a) SiH-terminated two-T-shell cluster, with 0.148 nm Si–H bonds replacing and aligned along each putative Si–O bond. (b) OH-terminated two-T-shell cluster, with H atoms replacing and aligned along each putative Si–O bond and 0.096 nm from the replaced Si atoms (fourth nearest T-site neighbors). Four- and five-membered rings that respectively include one or both coupled 29 Si atoms are included in the cluster. (c) "H-aligned" cluster, with H atoms added and aligned with respect to each Si–O bond in the second or third coordination sphere of the coupled 29 Si atoms at distances of 0.097 nm.

hydrogen atoms are each located in the direction of the respective Si-O bond that is being replaced (in the third to fourth coordination spheres of the coupled ²⁹Si atoms), with an Si-H bond length of 0.096 nm.10 Four-membered silicate rings involving (at least) one of the ²⁹Si coupled atoms and five-membered rings involving both ²⁹Si coupled atoms (as for site pair 1-4 in zeolite Sigma-2) are entirely included within the cluster, and H atoms are placed at 0.148 nm from the Si atoms of the fourth coordination sphere of the coupled ²⁹Si atoms, along the Si-O bonds that they replace. This cluster definition has been previously used to calculate ¹⁷O NMR parameters for zeolites that are in agreement with experimental measurements.^{10,11} However, it involves a significantly larger number of atoms, with compositions such as $Si_{10}O_{24}H_{16}$ or $Si_{12}O_{25}H_{18}$, according to whether four- or five-membered silicate rings containing the coupled ²⁹Si sites are present. Finally, a third alternative cluster definition of intermediate size can be defined [Fig. 3(c)], in which all of the Si atoms in the fourthcoordination sphere are each replaced by H atoms at distances of 0.097 nm along the respective Si-O bonds that they extend (in the second to third coordination spheres of the coupled ²⁹Si atoms.) This cluster definition has the advantage that it uses a smaller coordination sphere for calculations involving coupled ²⁹Si nuclei in four- or five-membered silicate rings, resulting in clusters with typical compositions Si₈O₂₄H₁₆ or Si₈O₂₅H₁₈. The fixed value of 180° for the terminal ²⁹Si–O–H bond angles used in this case is physically unrealistic, but eliminates the degree of freedom associated with the O-29Si-O-H torsion angle, thereby reducing the calculation time with a modest anticipated effect on overall accuracy. In the following, the illustrated cluster definitions for the J-coupled

²⁹Si(1)–O–²⁹Si(4) site pair of zeolite Sigma-2 in Fig. 3(a–c) will be referred to as "SiH-terminated", "OH-terminated", and "H-aligned" clusters, respectively.

The fundamental requirements of *J*-coupling calculations, and in particular the dominant Fermi contact contribution, require the use of particularly large basis sets on the coupled atoms and potentially also on the surrounding atoms. Therefore, several levels of description have been compared by using Gaussian 03 (ref. 29) to assess their effectiveness for reproducing experimental ${}^{2}J({}^{29}Si-O-{}^{29}Si)$ coupling trends and quantitative values. The different locally-dense basis sets (LDBS's) used for the calculations described are tabulated in the "Experiments and Methods" section, in Table 1, with the details of the basis set used for each type of atom in the different clusters.

Calculations of ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings have been systematically carried out using these LDBS's, for the three distinct types of clusters shown in Fig. 2. The results are reported in Table 2, and in Fig. S1 in the ESI,[†] which shows the same information as in Table 2 in the form of histograms. The coupled ²⁹Si atoms have been described using dense basis sets such as the IGLO-III basis set,41 whose accuracy for the prediction of NMR parameters has been demonstrated for different nuclei (see, for example, ref. 42 and 43), or Dunning's correlation-consistent basis sets cc-PVXZ,⁴⁴ whose densities increase from X = T to Q to 5, corresponding to the splitting of each valence atomic orbital into three, four, or five basis functions that are, respectively, referred to as "triple-", "quadruple-", or "quintuple-zeta" (i.e. "Z") basis sets. In most cases, surrounding atoms have been described by using standard 6-31G* basis sets (6-31G for H atoms), with the addition in some cases of diffuse functions of the type (3df, 3pd), which are expected to affect the electronic densities at the positions of nearby nuclei, including the coupled ²⁹Si atoms of principal interest (see Table 1 for details). A different exchangecorrelation functional, namely the B3-PW91 functional,⁴⁵ has also been tested (results not shown), with no significant differences being found, compared to calculations carried out with the B3-LYP functional³¹ used for all of the results presented here. A first observation that can be made from the results shown in Table 2 is that all of the combinations of LDBS and cluster definitions examined are able to reproduce the experimental ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ -coupling trends very well. This is reflected in the linear regression coefficients R^2 between calculated and experimental J-coupling constants, which are all above 0.96 (see Table 2). However, with respect to the individual quantitative values of the calculated couplings, the agreement with the experimental values is in most cases mixed [see ESI,† Fig. S1(a-d)].

A few general observations can be made and conclusions drawn from detailed examination of ${}^{2}J({}^{29}\text{Si}-\text{O}{}^{29}\text{Si})$ couplings calculated for zeolite Sigma-2 and their comparisons with the experimental values. First, for a given level of description, the small amplitudes of the variations observed between the coupling values obtained using the different cluster definitions is note-worthy. In particular, the small SiH-terminated two-T-shell clusters appear to be a reasonable compromise between structural accuracy and computational requirements. Approximate computational requirements are listed for comparison in Table 2 (last column), which were taken into account when selecting the most

Cluster definition	LDBS label	J_{13}/Hz	J_{14}/Hz	J_{23}/Hz	J_{24}/Hz	u^a	v/Hz^a	R^2	χ^{2b}	CPU/h ^c
SiH-terminated	IGLO-III	20.53	9.31	16.85	12.09	1.51	-8.2	0.993	22.4	2
	IGLO-III/IGLO-II (1)	20.63	9.41	16.96	12.22	1.51	-8.3	0.993	23.0	2
	cc-PVTZ	15.49	7.59	13.08	9.31	2.10	-9.8	0.988	77.9	2
	cc-PVQZ	20.02	4.63	13.80	10.42	1.16	-0.1	0.968	22.4	3
	cc-PV5Z	18.80	4.22	12.86	8.42	1.21	0.7	0.994	42.2	11
	IGLO-III/diffuse	20.93	9.50	17.20	12.35	1.49	-8.2	0.993	22.8	5
	cc-PVTZ/diffuse	17.06	7.02	14.36	10.17	1.68	-6.4	0.975	46.6	5
	cc-PVQZ/diffuse	20.99	6.71	15.99	11.65	1.23	-2.9	0.981	9.4	6
	cc-PV5Z/diffuse	22.07	6.48	16.00	11.09	1.13	-1.6	0.993	3.5	90
H-aligned	IGLO-III/IGLO-II (1)	21.47	9.44	17.28	13.13	1.45	-8.1	0.990	24.4	12
-	cc-PV5Z	19.75	4.34	13.22	9.21	1.15	0.7	0.986	29.3	34
	cc-PV5Z/diffuse	23.16	6.47	16.39	11.67	1.06	-1.2	0.989	3.0	960
OH-terminated	IGLO-III	21.05	9.17	16.96	12.47	1.45	-7.6	0.993	20.5	17
	IGLO-III/IGLO-II (1)	21.16	9.28	17.07	12.61	1.45	-7.8	0.993	21.5	20
	IGLO-III/IGLO-II (2)	21.02	9.24	16.95	12.47	1.46	-7.8	0.994	21.1	23
	cc-PV5Z	19.50	4.18	13.03	8.78	1.16	0.9	0.990	34.0	50
Experimental		23.5	6.3	16.5	10.0					

 Table 2
 Calculated ${}^2J({}^{29}Si-O-{}^{29}Si)$ -couplings constants for siliceous zeolite Sigma-2 and linear regression coefficients relative to experimentally measured coupling constants

^{*a*} From best fits to the expression: $J_{exp} = u_*J_{calc} + v$. ^{*b*} Calculated using eqn (1). ^{*c*} Computational times are only estimates, as not all calculations were conducted on similar processors.

appropriate levels of description. They show in particular that calculations involving the SiH-terminated clusters are much less demanding computationally (typically by 5–10 times) than the much larger H-aligned or OH-terminated clusters. Nevertheless, the SiH-terminated clusters provide *J*-coupling values that are in each case close (within <5%) to those obtained with the larger clusters. This observation confirms the highly local character of the indirect spin–spin coupling interaction, compared to the chemical shift or quadrupolar interactions, since the SiH-terminated clusters have been shown to be too small for the accurate prediction of ¹⁷O NMR parameters in zeolites.^{10,11}

Second, the density of the basis sets used to describe noncoupled nuclei appears to have little influence on the calculated ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings. Indeed, results obtained with the IGLO-III basis set on *J*-coupled ${}^{29}\text{Si}$ atoms do not change significantly upon replacement of the standard 6-31G* basis set used to describe the central oxygen atom and/or the next-nearest oxygen neighbors of the coupled ${}^{29}\text{Si}$ nuclei with the heavier IGLO-II basis set. In contrast, the quality of the basis set used to describe the coupled ${}^{29}\text{Si}$ nuclei has a dramatic effect on the magnitude of the calculated ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings. The general agreement between calculated $J_{\text{calc}}{}^{(i)}$ and experimental $J_{\text{exp}}{}^{(i)}$ coupling constants, where *i* corresponds to a given ${}^{29}\text{Si}-\text{O}-{}^{29}\text{Si}$ site pair, is reflected in Table 2 by the χ^{2} coefficients defined as:

$$\chi^{2} = \sum_{i=1}^{N} \left(\frac{J_{\exp}^{(i)} - J_{calc}^{(i)}}{\sigma^{(i)}} \right)^{2},$$
(1)

where $\sigma^{(i)}$ is the experimental uncertainty associated with the measured $J_{\exp}^{(i)}$ coupling constant (here, 1 Hz for every ²⁹Si–O–²⁹Si site pair). We note that rigorous definitions of the χ^2 values use standard deviations of the experimental values as the $\sigma^{(i)}$ coefficients, instead of the estimates used here based on the uncertainties of the measurements. Thus, the

 χ^2 coefficients as defined in eqn (1) serve as internal bases of comparisons of the results obtained in the analyses of the Sigma-2 or the ZSM-12 zeolite structures. In the absence of diffuse functions on the surrounding atoms, the cc-PVTZ basis sets yield calculated ${}^2J({}^{29}\text{Si}\text{-O}-{}^{29}\text{Si})$ couplings that are in poor agreement with the experimental values, as reflected by a high χ^2 value of 77.9.

Increasing the basis set density on coupled ²⁹Si nuclei using the IGLO-III, cc-PVQZ, or cc-PV5Z bases provides improved agreement ($\gamma^2 = 22.4$, 22.4, and 42.2, respectively) between calculated and experimental couplings. These different levels of description show distinct trends, as expressed by the best fits of the experimental data and calculated values to the linear relation $J_{exp} = u_*J_{calc} + v$. For example, as shown in Table 2, different slopes u = 1.51, 1.16, and 1.21 (compared to the ideal value of 1) and intercepts v = -8.2, -0.1, and 0.7 Hz(compared to the ideal value of 0 Hz) are obtained by using the IGLO-III, cc-PVQZ, or cc-PV5Z basis sets, respectively. It is interesting that the cc-PVOZ basis set exhibits better agreement than the denser cc-PV5Z basis. In both cases, $^{2}J(^{29}\text{Si}-\text{O}-^{29}\text{Si})$ -coupling constants calculated using correlation-consistent basis sets cc-PVXZ with sufficient density (e.g. X = Q or 5) show superior agreement with the experimentally measured values, compared to the IGLO-III basis sets.

The agreement between the experimental ${}^{2}J({}^{29}\text{Si}-\text{O}{}^{29}\text{Si})$ values and those calculated by using the different correlationconsistent basis sets appears to be further improved by adding diffuse functions on the surrounding atoms that account for long-range through-bond contributions. Augmentation of the basis sets used to describe the non-coupled atoms with such diffuse functions leads to improved convergence of the ${}^{2}J({}^{29}\text{Si}-\text{O}{}^{-29}\text{Si})$ couplings calculated using cc-PVXZ basis sets of increasing density (from X = T to Q to 5) towards the experimental coupling values. This is indicated by the convergence of the slopes u = 1.68, 1.23, and 1.16 toward the ideal value of 1, of the intercepts v = -6.4, -2.9, and -1.6 Hztoward zero, and by the systematic decrease of γ^2 values from 46.6 to 9.4, and 3.5, respectively (Table 2). By comparison, the IGLO-III calculations remain little affected by the addition of diffuse functions on the surrounding atoms. Fig. 4 shows the correlation plot obtained with the SiH-terminated clusters, using the cc-PV5Z basis set on coupled ²⁹Si atoms and 6-31G* basis sets with added (3df, 3pd) diffuse functions on the other atoms. A satisfyingly linear correlation between the experimental and calculated J-coupling constants is obtained at this level of description (u = 1.16, v = -1.6 Hz, $R^2 = 0.993$, and $\chi^2 = 3.0$). This consequently allows ${}^2J({}^{29}\text{Si-O}{}^{-29}\text{Si})$ couplings to be calculated with good accuracy within an acceptable, albeit long, computational time (typically of the order of 90 CPU-hours with current microprocessors, see Table 2). By comparison, calculations carried out at the same level of description with the larger H-aligned cluster, although slightly more accurate, are more than an order of magnitude longer in duration, which reduces significantly their practicality. The results obtained with the structurally well-characterized zeolite Sigma-2 thus demonstrate that it is possible to calculate $^{2}J(^{29}\text{Si}-\text{O}-^{29}\text{Si})$ couplings in zeolitic frameworks with good accuracy using the cluster approaches discussed, provided an appropriate level of description is used.

3.b ${}^{2}J({}^{29}Si-O-{}^{29}Si)$ couplings in siliceous zeolite ZSM-12

For more challenging systems, such as siliceous zeolite ZSM-12, the same DFT protocol can be used to explore the sensitivity of *J*-coupling calculations to fine details of the local silicate framework structure. Compared to Sigma-2, ZSM-12 presents additional complications, due to its richer structure which has been characterized by powder (as opposed to single-crystal) XRD.²⁶ The structure of zeolite ZSM-12, as determined from powder XRD data and analyses in ref. 26 is shown



Fig. 4 Correlation plot that compares calculated and experimental ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ -coupling constants for the four distinct pairs of interconnected ${}^{29}\text{Si}-\text{O}-{}^{29}\text{Si}$ is its in zeolite Sigma-2. DFT calculations of the ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings were conducted using locally dense basis sets with cc-PV5Z on the coupled ${}^{29}\text{Si}$ atoms and 6-31G* basis sets augmented with (3df, 3pd) diffuse functions on other atoms. The dashed line indicates the ideal 1:1 correlation axis between the experimental and calculated values. The solid line corresponds to the best linear regression of the ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ data points.

schematically in Fig. 5(a), and the unit cell parameters and fractional coordinates are provided in the ESI.† At the molecular level, all seven of the distinct ²⁹Si T-sites in siliceous ZSM-12 are resolved in the 1D ²⁹Si MAS NMR spectrum shown in Fig. 5(b), although their respective J doublets are not. The larger number of inequivalent ²⁹Si T-sites (seven as compared to four in the case of Sigma-2) and apparently lower overall degree of crystallinity lead to generally lower spectral resolution and sensitivity, compared to Sigma-2 [(Fig. 1(b)]. Nevertheless, the solid-state 2D ²⁹Si{²⁹Si} J-coupling-mediated spectrum (Fig. 5(b), black contours) shows well resolved DQ-correlated peaks from which the covalent interconnectivities between the various T-sites in siliceous ZSM-12 can be directly determined. Specifically, as indicated by the horizontal lines in Fig. 5(b), the correlated DO intensities establish connectivities via bridging oxygen atoms between ²⁹Si-O-²⁹Si site pairs 1-2, 1-3, 2-4, 3-5, 3-7, 4-5, 4-6, 5-6, and 6-7,²⁶ consistent with the powder-XRD structure of ZSM-12 shown in Fig. 5(a) and previous NMR measurements.¹³

Importantly, by using the refocused-INADEQUATE technique, as opposed to conventional INADEQUATE as employed in ref. 13, significantly enhanced spectral resolution is achieved in the J-mediated 2D ²⁹Si{²⁹Si} NMR spectrum of siliceous zeolite ZSM-12. As a consequence, narrow ridge patterns are resolved in Fig. 5(b) in the 2D ²⁹Si{²⁹Si} NMR contour spectrum, which reflect a much higher extent of local ordering in the ZSM-12 sample than is apparent in the 1D ²⁹Si MAS spectrum. Similar observations have recently been made for several other solids with complicated crystallinities.^{8,16,46,47} By comparison, the intensity ridges observed in the 2D refocused INADEQUATE ²⁹Si{²⁹Si} spectrum of Fig. 5(b) are significantly and remarkably narrower, such that weak J doublets are observed. In this case, 1D slices extracted from the 2D spectrum at the DQ frequencies of every ²⁹Si-O-²⁹Si pair (Fig. 5(c), in black) show ²⁹Si peaks that are sufficiently narrow (<0.2 ppm fwhm, *i.e.* < 8 Hz at 4.7 T) for most of the J doublets to be resolved. This is in spite of the low magnitude of these couplings relative to the inhomogeneous broadening (ca. 0.5 ppm fwhm, corresponding to 20 Hz at 4.7 T) of the 1D ²⁹Si MAS NMR peaks.

An interesting feature of the elongated cross-peaks observed in the 2D ²⁹Si{²⁹Si} NMR spectrum of zeolite ZSM-12 in Fig. 5(b) is that the J-coupling doublets $[e.g., the J_{12} doublet at$ ca. (-224, -111 ppm)] are all tilted parallel to the spectrum diagonal (*i.e.* the 2:1 axis in a DO-SO experiment.) Such parallel ridges may be due to (i) structural disorder on a length scale larger than the distances between the covalently bonded ²⁹Si-O-²⁹Si pairs probed here⁴⁸ or to macroscopic effects, such as (ii) anisotropic bulk magnetic susceptibility^{46,49} or (iii) variations of the static magnetic field during the 26-day-long experiment.§ There have been several recent reports^{18,50} of distributions of ${}^{2}J({}^{31}P-O-{}^{31}P)$, ${}^{2}J({}^{31}P-N-{}^{31}P)$, and $^{2}J(^{29}\text{Si-O-}^{29}\text{Si})$ couplings with strong linear correlations to ³¹P or ²⁹Si chemical shifts in disordered solids. However, unlike those studies, the uniform tilts of all of the J-doublets

[§] For example, a line broadening of the order of 0.5 ppm in a 26-day experiment could be caused by a (monotonic) drift of the static 4.7 T magnetic field by less than 0.3 Hz h^{-1} for ¹H, which is within specifications that are typical of current superconducting magnets.



Fig. 5 (a) Schematic representation of the structure of ZSM-12, showing Si atoms at the vertices of the polygonal shapes and oxygen atoms bridging between adjacent Si T-sites as straight lines. (b) Solid-state 2D refocused-INADEQUATE ²⁹Si{²⁹Si} NMR spectrum of siliceous zeolite ZSM-12 (black contour plots). Superimposed is a colored plot of the 2D spectral deconvolution from which ${}^{2}J({}^{29}Si-O-{}^{29}Si)$ values have been extracted for each ${}^{29}Si-O-{}^{29}Si$ site pair with estimated accuracies of ± 2 Hz. A single-pulse 1D ${}^{29}Si$ MAS spectrum is shown along the top axis, revealing that all seven distinct ${}^{29}Si$ T-sites are resolved. (c) 1D ${}^{29}Si$ NMR slices extracted from the experimental spectrum (in black) and from the 2D deconvolution (in red) at the DQ frequencies associated with the different ${}^{29}Si-O-{}^{29}Si$ site pairs. The *J* doublets associated with each site pair are indicated by the horizontal bars above each pair of peaks.

parallel to the 2D spectrum diagonal in Fig. 5(b) indicate that ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings are not correlated with ${}^{29}\text{Si}$ chemical shifts, as would likely be the case if long-range structural disorder (*i*) were the principal cause of the peak broadening. Thus, anisotropic bulk magnetic susceptibility and/or variations of the static magnetic field during the experiment appear more likely to account for the broadening observed in the 2D ${}^{29}\text{Si}\{{}^{29}\text{Si}\}$ refocused INADEQUATE spectrum of zeolite ZSM-12.

Overlap among several of the different 2D 29 Si 29 intensity correlations was overcome by using a 2D deconvolution procedure (see "Experiments and Methods") to obtain ²J(²⁹Si–O–²⁹Si)-coupling constants for covalently bonded ²⁹Si-O-²⁹Si site pairs. The resulting simulated 2D refocused-INADEQUATE²⁹Si{²⁹Si} spectrum is shown as the colored plot, superimposed on the black contours of the experimental spectrum, in Fig. 5(b). In addition, the corresponding 1D slices extracted from the 2D simulated spectrum are displayed in red in Fig. 5(c), below those extracted from the experimental 2D spectrum in black. The resulting ${}^{2}J({}^{29}Si-O-{}^{29}Si)$ coupling constants, measured with estimated accuracies of $ca. \pm 2$ Hz, are reported in Table 3 and fall within the range of 10-19 Hz. An exception is that associated with site pair 4-6 for which the DQ-correlated signal intensities are weak, making accurate identification of the J doublets and corresponding measurement of coupling values difficult. The weak DQ-correlated signal intensities most likely result from relatively low efficiency of the J-mediated transfer for this site pair, suggesting that the associated coupling constant is small, presumably substantially less than 10 Hz. This is consistent with the substantially smaller ²⁹Si(4)–O–²⁹Si(6) bond angle (134.4° in the powder-XRD structure) between sites 4 and 6, than for all other ²⁹Si-O-²⁹Si site pairs (144.8 to 158.6° in the

powder-XRD structure). The *J*-coupling constants measured here by using the refocused-INADEQUATE ²⁹Si{²⁹Si} technique are expected to be significantly more accurate than could have otherwise been obtained by using the conventional INADEQUATE experiment.

As for zeolite Sigma-2, DFT calculations of ${}^{2}J({}^{29}Si-O-{}^{29}Si)$ couplings were conducted on SiH-terminated bridging O-centered clusters extracted from the powder XRD structure of ZSM-12,²⁶ using the so-called "cc-PV5Z/diffuse" LDBS definition (see Table 1), and compared to the experimental values. The results are reported as a correlation plot between experimental and calculated J-coupling constants, shown in Table 3 and as open blue diamonds in Fig. 6, along with u, v, R^2 , and χ^2 coefficients calculated as above. Based on the generally accepted powder XRD structure of ZSM-12, poor agreement is found between experimental and calculated couplings, in marked contrast to the case of Sigma-2 (see Fig. 4). The weakness of the observed correlation ($R^2 = 0.21$) is likely a consequence of the relatively high uncertainties associated with atom positions in the ZMS-12 crystal structure derived from powder X-ray diffraction data, despite the high degree of local ordering indicated by the very narrow 2D NMR lineshapes. These J-coupling measurements and calculations complement previous work in which it was demonstrated that ²⁹Si chemical shift tensors calculated for this powder-XRD structure of ZSM-12 are, similarly, in poor agreement with the experimentally measured tensors.⁴ These results point to the high sensitivity of the ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings to the fine details of the local framework structure, separate to and consistent with ²⁹Si chemical shift tensors.

The sensitivity of ²⁹Si chemical shifts tensors to local structures in zeolite frameworks has recently been incorporated into a crystal-structure-refinement procedure in which Si and O

Table 3Experimental ${}^{2}J({}^{29}\text{Si}\text{-O}{}^{-29}\text{Si})$ coupling constants measuredfor siliceous zeolite ZSM-12

		$J_{ m calc}/{ m Hz}^b$						
Site Pair	$J_{\rm exp}/{ m Hz}^a$	PXRD	NMR-refined	DFT-opt from PXRD	DFT-opt from NMR-refined			
3-1	10	11.4	9.2	12.0	11.7			
3–7	10	14.8	9.3	6.8	6.9			
3–5	14	13.1	14.1	9.5	9.7			
6–7	19	14.8	13.6	11.8	11.2			
4–5	15	13.0	11.9	8.5	7.9			
4-2	12	12.5	12.7	11.1	10.6			
6-5	11	14.5	13.0	9.3	9.4			
1–2	16	15.3	13.2	13.6	12.3			
	u^c	1.05	1.13	1.38	1.58			
	$v (Hz)^c$	-1.1	-0.4	-0.9	-2.5			
	R^2	0.25	0.45	0.90	0.84			
	$\chi^{2 d}$	14.6	13.0	21.4	27.5			

^{*a*} *J*-coupling values are estimated from the 2D deconvolution of the refocused-INADEQUATE ²⁹Si{²⁹Si} spectrum shown in Fig. 5, with estimated uncertainties of \pm 2 Hz. ^{*b*} Values calculated for SiH-terminated clusters extracted from the powder-XRD and CSA-refined structures (3rd and 4th columns, respectively), using the cc-PV5Z basis set on coupled ²⁹Si atoms and 6-31G* basis sets with added (3df, 3pd) diffuse functions on other atoms (so-called "cc-PV5Z/diffuse" LDBS). ^{*c*} From best fits to the expression: $J_{exp} = u_*J_{cale} + v$. ^{*d*} Calculated using eqn (1).

atomic coordinates are optimized to minimize the differences between the experimental and *ab initio* calculated principal components of the ²⁹Si chemical shifts tensors.^{5,6} For Sigma-2, it was demonstrated that the mean deviation of the Si and O coordinates for the chemical-shift-refined structure from the single-crystal XRD structure was only 0.01 Å.⁶ This NMR crystal-structure-refinement strategy was subsequently applied to ZSM-12,⁵ yielding an improved crystal structure (unit cell parameters and fractional coordinates given in the ESI⁺) that yields excellent agreement between the experimental and calculated ²⁹Si chemical shift tensors. Differences between the powder-XRD and ²⁹Si-NMR-refined structures are reflected, for example, by $0^{\circ}-6^{\circ}$ variations of the Si–O–Si angles observed upon refinement of the structure based on ²⁹Si CSA interactions, as shown in the ESI,† Fig. S2. Unfortunately, a highquality single-crystal XRD structure for ZSM-12, to which direct comparisons might be made, does not exist.

Nevertheless, the ${}^{2}J({}^{29}\text{Si}\text{-O}-{}^{29}\text{Si})$ couplings can be used to provide another important means to probe the quality of the ZSM-12 crystal structures, as determined from the analyses of the powder-XRD and ${}^{29}\text{Si}\text{-NMR}$ -refined structures. A new set of ${}^{2}J({}^{29}\text{Si}\text{-O}-{}^{29}\text{Si})$ coupling constants was calculated using SiH-terminated clusters extracted from the ${}^{29}\text{Si}\text{-chemical-shift}\text{-refined crystal structure}^{5}$ of zeolite ZSM-12 to assess whether this structure provides better agreement with the experimentally measured couplings. The resulting ${}^{2}J({}^{29}\text{Si}\text{-O}-{}^{29}\text{Si})\text{-coupling constants are reported as red solid$ squares in Fig. 6. Significantly improved agreement betweenthe experimental and calculated J couplings is observed, as $expressed by the larger linear regression coefficient, <math>R^{2} = 0.45$, than is obtained ($R^{2} = 0.21$) for the powder-XRD ZSM-12 structure. This result independently establishes that the ${}^{29}\text{Si}$ chemical-shift-refinement of the ZSM-12 structure leads to a revised framework with improved and self-consistent molecular-level descriptions. Still, the agreement between the experimental and calculated ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings remains relatively poor, which indicates that the ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings might be more sensitive than ${}^{29}\text{Si}$ chemical shifts (and far more so than powder XRD) to local structural features. This, consequently, suggests that ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ coupling interactions could be used to further refine the framework structure of ZSM-12, and of other zeolites for which single-crystal XRD structures cannot be obtained or are otherwise unavailable.

In particular, least-square minimizations using calculated and experimental CSA parameters alone could lead to a local minimum that may not correspond to the 'real' structure, although it may better reproduce most details of local covalent bonding than powder-XRD analyses alone. For example, the refined structures that account for the CSA interactions may



Fig. 6 Correlation plots that compare the experimental and calculated ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ -coupling constants for the different pairs of interconnected ²⁹Si-O-²⁹Si sites in siliceous zeolite ZSM-12. Blue open diamonds correspond to J-coupling calculations conducted on SiH-terminated clusters extracted from the structure determined from powder-XRD analyses²⁶ and using the cc-PV5Z basis set on ²⁹Si-coupled atoms and 6-31G* basis sets with added (3df, 3pd) diffuse functions on other atoms (so-called "cc-PV5Z/diffuse" LDBS). The best regression of these points (blue dash-dotted line) displays poor linearity, $R^2 = 0.21$. Red solid squares represent J-coupling calculations conducted on clusters extracted from a ZSM-12 structure refined by using the ²⁹Si chemical shift tensors of each site.⁵ The best associated linear regression (red dotted line) yields an improved correlation ($R^2 = 0.45$), indicating that the overall quality of the local framework structure is improved by the ²⁹Si-chemical-shift-NMRrefinement procedure. Green open triangles and yellow solid circles correspond to J-coupling calculations performed on clusters extracted from structures fully optimized with DFT, starting from the powder-XRD and NMR-refined structures, respectively, both of which yield improved linearity (green dashed line, $R^2 = 0.90$, and solid vellow line, $R^2 = 0.84$).

be energetically slightly unfavorable in terms of local bonding configurations to which the ${}^{2}J({}^{29}\text{Si}-\text{O}{}^{-29}\text{Si})$ couplings are highly sensitive. Thus, it is expected that *J*-coupling measurements and calculations on structures that are known to relatively low precision could become powerful new probes and optimization criteria for siliceous zeolite framework structures. This is especially the case if such *J*-coupling analyses are used in conjunction with optimizations based on first-principles calculations with periodic boundary conditions, which would impose tight bond angle and bond length constraints (presumably to *ca.* 10^{-3} nm).

To further explore the sensitivity and accuracy of ²J(²⁹Si–O–²⁹Si) couplings calculated from cluster approaches (within the limits of the description level used here), DFT optimizations of the ZSM-12 zeolite framework structure were conducted by using the code CASTEP,³⁵ which allows a full solid-state treatment of the system using a plane-wave-based approach with periodic boundary conditions. Such local geometry optimizations do not rely on experimental constraints other than the unit cell parameters (from the powder-XRD data²⁶), and are only subject to the intrinsic approximations of DFT. Two separate optimizations were conducted independently, using the powder-XRD and the ²⁹Si-NMR-refined structures as starting points, and the resulting Si-O-Si bond angles associated with J-coupled ²⁹Si–O–²⁹Si pairs are shown in the ESI,[†] Fig. S2(a). Si–O–Si bond angles obtained for the powder-XRD-CASTEPoptimized and the NMR-CASTEP-optimized structures are very similar (less than 2° differences for each pair), indicating that similar energy minima were found from the two different starting points (consistent with calculated final energies that are only 0.01 eV apart.) Interestingly, for Si-O-Si pairs that showed larger differences in their associated Si-O-Si angles between the powder-XRD and the ²⁹Si-NMR-refined structures, namely pairs 1–2, 3–7, 4–5, and 4–6 (differences $>4^{\circ}$), the DFT-optimizations leads to Si-O-Si angles that are much closer to those of the ²⁹Si-NMR-refined structure. This observation adds to the level of confidence for the results obtained from the independent ²⁹Si-NMR-based and DFT-optimization methods.

 $^{2}J(^{29}\text{Si}-\text{O}-^{29}\text{Si})$ coupling calculations potentially offer a new means of evaluating the DFT-refined structures, based on their comparisons with experimental values. For example, for Si-O-Si site pairs 2-4 or 5-6 in zeolite ZSM-12, the DFT optimizations lead to bond angles that are different from both the powder-XRD and ²⁹Si-NMR-refined structures (Table 3). As previously done for the respective initial structures, SiH-terminated clusters were extracted from each of the DFT-optimized frameworks (referred to henceforth as "PXRD-CASTEP-optimized" and "NMR-CASTEPoptimized" structures), and ²J(²⁹Si-O-²⁹Si) couplings were subsequently calculated with Gaussian 03. The results are shown in Fig. 6 as green open triangles and yellow solid circles for the PXRD-CASTEP-optimized and NMR-CASTEPoptimized structures, respectively, alongside the previously discussed results for the initial powder-XRD (blue open diamonds) and ²⁹Si-NMR-refined (red solid squares) structures. The DFT optimizations result in improved linearity of the calculated versus experimental correlations

 $(R^2$ coefficients of 0.90 and 0.84, respectively), compared to the initial structures $(R^2 = 0.21 \text{ and } 0.45)$. However, the corresponding best fits to straight lines (green dashed line and yellow solid line) deviate substantially from the ideal 1:1 correlation axis, probably as a result of systematic errors of either the DFT geometry optimization or the *J*-coupling calculations using cluster approaches. The different ZSM-12 structures are overlaid in the ESI,† Fig. S2(b), revealing discrepancies that lead to the large differences in their calculated ²⁹Si chemical shift anisotropies⁵ and ² $J(^{29}Si-O^{29}Si)$ couplings. These observations again suggest that ² $J(^{29}Si-O^{-29}Si)$ couplings, in combination with DFT optimizations, may enable increased accuracy and reliability of zeolite framework structure refinements.

In summary, the accuracy and precision of structure solutions will likely be improved by incorporating $^{2}J(^{29}\text{Si}-\text{O}-^{29}\text{Si})$ couplings into structure-refinement protocols, in combination with DFT optimizations, X-ray scattering results, and chemical shift and dipolar interactions. These various techniques and interactions are sensitive to a complementary set of length scales and parameters, such as bond and dihedral angles and distances. Currently, the heavy computational requirements for accurate J-coupling calculations using cluster approaches make it challenging to integrate these interactions into iterative structure-refinement approaches that combine multiple constraints. However, investigations are under way for improving the accuracy and the efficiency of J-coupling calculations (e.g. the development of specifically-optimized basis sets⁵¹), which, along with progress in microprocessor technology, should allow these limitations to be overcome in the near future. Furthermore, indirect spin-spin couplings have very recently been calculated for the first time from plane-wave-based approaches using periodic boundary conditions.⁵² This novel approach offers an attractive alternative that is complementary to cluster calculations. Indeed, plane-wave-based calculations intrinsically account for long-range solid-state environments and avoid the tedious and generally highly system-specific basis set explorations. By comparison, cluster approaches are particularly suitable for exploring the dependence of calculated interactions on local structural parameters, such as bond lengths, and bond and torsion angles (see Fig. 2).²² In this context, the results presented here are expected to provide an important basis of comparison to probe the reliability of these new plane-wave-based computational approaches for the calculation of ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ coupling constants.

4. Conclusions

Two-bond indirect ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ spin–spin couplings between ${}^{29}\text{Si}$ atoms connected *via* bridging oxygen atoms have been calculated with high accuracies for zeolitic frameworks. Such calculations are extremely sensitive to the local framework structure, showing promise for the use of ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings to probe, establish, and refine the local structures of zeolites and layered silicates, including ones that remain unsolved. Measurement of ${}^{2}J({}^{29}\text{Si}-\text{O}-{}^{29}\text{Si})$ couplings with high accuracies in siliceous zeolitic frameworks using state-of-the-art solid-state NMR methodologies enables new opportunities for developing iterative procedures that integrate these new and sensitive local constraints into structure-determination or -refinement protocols. Furthermore, *J* couplings are expected to have strong general potential for use as sensitive probes of local features in a large range of solids with complicated extents of structural order. These include molecularly ordered polymers, organic crystals, biomolecules, and inorganic or hybrid materials with both spin-1/2 and quadrupolar (I > 1/2) nuclei, between which *J* couplings can now also be accurately measured.^{19,53}

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