Supplementary Material (ESI) for *PCCP*

SUPPORTING INFORMATION

Probing Local Structures of Siliceous Zeolite Frameworks by Solid-State NMR and First-Principles Calculations of ^{29}Si-O-^{29}Si Scalar Couplings

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Simulations of 2D DQ-SQ spectra for extracting *J*-coupling constants.

Equation for calculating the pair of doublets in a 2D INADEQUATE double-quantum–single-quantum correlation NMR spectrum between resonances with isotropic chemical shifts Ω_A and Ω_B, with (tilted) Lorentzian peaks:

$$S(f_{SQ}, f_{DQ}) = \sum_{i=1}^{4} A_i \left(\frac{2}{\pi\, w_{DQ}} \right) \left(\frac{w_{DQ}^2}{w_{DQ}^2 + 4\left[\Omega_A + \Omega_B - f_{DQ}\right]^2} \right) \times \left(\frac{2}{\pi\, w_{SQ}} \right) \left(\frac{w_{SQ}^2}{w_{SQ}^2 + 4\left[\Omega_i - f_{SQ} - \frac{1}{2}\left(\Omega_A + \Omega_B - f_{DQ}\right)\right]^2} \right)$$

$$\Omega_1 = \Omega_A - \tfrac{1}{2} J_{AB}$$
$$\Omega_2 = \Omega_A + \tfrac{1}{2} J_{AB}$$
$$\Omega_3 = \Omega_B - \tfrac{1}{2} J_{AB}$$
$$\Omega_4 = \Omega_B + \tfrac{1}{2} J_{AB}$$
$$A_1 = A_4$$
$$A_2 = A_3$$

Unit cell parameters and fractional coordinates of the structure of siliceous zeolite Sigma-2, as determined from single-crystal XRD analyses.[1]

Space group: *I41*/*AMD* (# 141)

(10.2316 Å, 10.2316 Å, 34.3642 Å)

(90°, 90°, 90°)

Atom	Name	*x*	*y*	*z*	Occupancy
Si	T1	0.28570	0.25000	0.11830	0.50000
Si	T2	0.28170	0.50000	0.00000	0.50000
Si	T4	0.15110	0.25000	0.19550	0.50000
Si	T3	0.15340	0.25000	0.03470	0.50000
O	O1	0.00000	0.25000	0.20670	0.25000
O	O2	0.21930	0.12200	0.21300	1.00000
O	O3	0.22850	0.25000	0.07530	0.50000
O	O4	0.16750	0.25000	0.14910	0.50000
O	O5	0.00000	0.25000	0.04240	0.25000
O	O6	0.19130	0.37750	0.01010	1.00000
O	O7	0.37200	0.37800	0.12500	0.50000

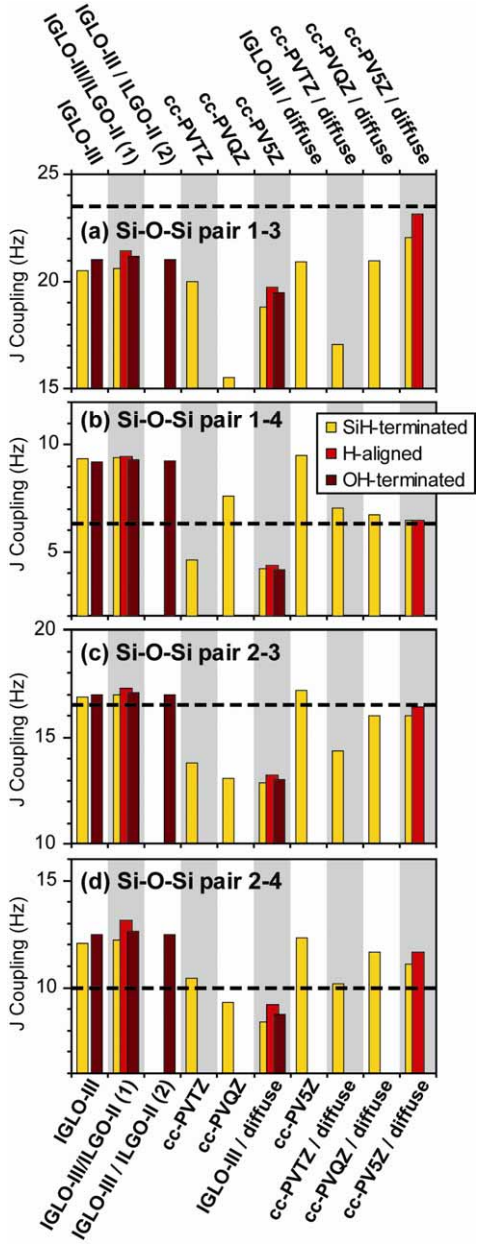

Figure S1. Histograms showing the $^{2}J(^{29}\text{Si-O-}^{29}\text{Si})$ coupling constants calculated by DFT, using different cluster approaches to describe $^{29}\text{Si-O-}^{29}\text{Si}$ site pairs (a) 1-3, (b) 1-4, (c) 2-3, and (d) 2-4 of the siliceous zeolite Sigma-2. Different groups of color bars along the *x*-axes correspond to different levels of descriptions (basis sets) that are referred to using the locally dense basis set (LDBS) labels defined in Table 1. The yellow, red, and brown colors correspond to the so-called "SiH-terminated", "H-aligned", and "OH-terminated" cluster definitions(see text for details), respectively, used for the calculations. The experimental *J*-coupling value is indicated on each histogram by a horizontal dashed line. The same vertical scale is used for all of the plots.

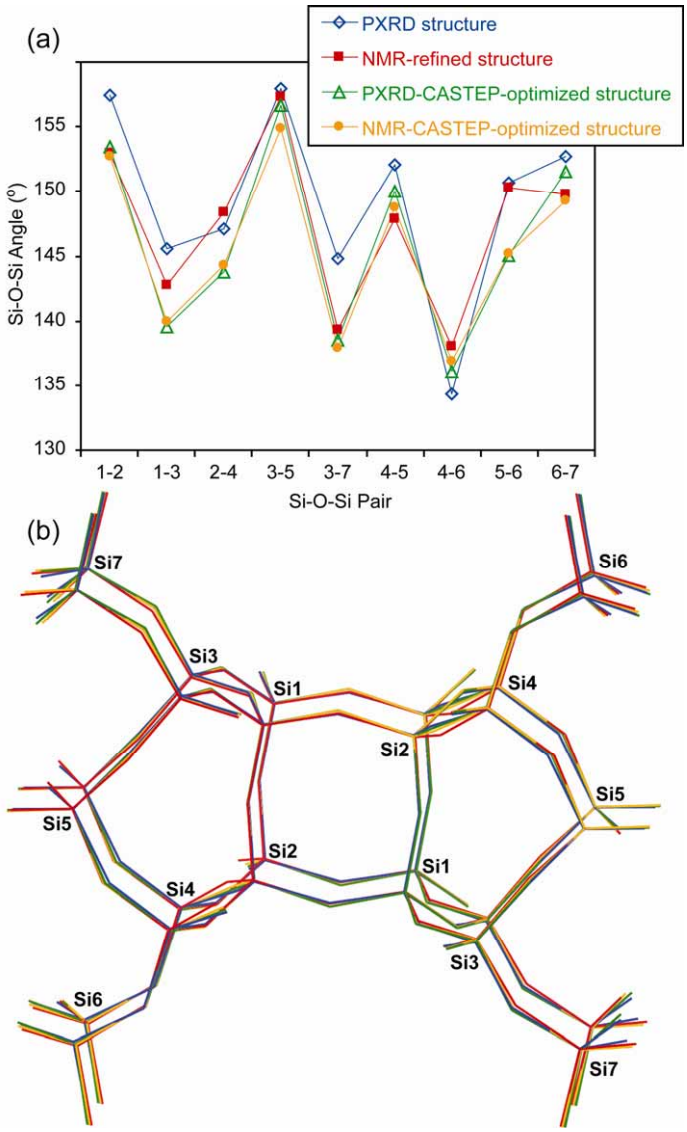

Figure S2. (a) Si-O-Si bond angles measured for zeolite ZSM-12 structures shown in (b) for each pair of ^{29}Si-O-^{29}Si sites for which $^{2}J(^{29}\text{Si-O-}^{29}\text{Si})$-couplings can potentially be measured (*i.e.*, all connected pairs, but identical ^{29}Si sites.) Bond angles extracted from the powder XRD and ^{29}Si-NMR-refined structures are shown as blue open diamonds and red solid squares, respectively, and Si-O-Si angles measured from structures obtained by DFT optimizations of the powder XRD and ^{29}Si-NMR-refined structures are shown as green open triangles and yellow solid circles, respectively. (b) Schematic representations of the zeolite framework structures of siliceous ZSM-12 obtained from powder X-ray diffraction (PXRD) analyses[2] (blue), from structure refinements using ^{29}Si chemical shift anisotropies[3] (red), and their DFT optimizations (green and yellow, respectively). Si atoms are labeled and separated by bridging O atoms.

Unit cell parameters and fractional coordinates of the structure of siliceous zeolite ZSM-12, as determined from powder-XRD analyses.[2]

Space group: *C2/C* (# 15)

(24.8633 Å, 5.0124 Å, 24.3275 Å)

(90°, 107.7215°, 90°)

Atom	Name	*x*	*y*	*z*
Si	T1	0.44020	0.53190	0.41290
Si	T2	0.06780	-0.07080	0.45890
Si	T3	0.37540	0.03200	0.36090
Si	T4	0.13380	0.42180	0.44840
Si	T5	0.28360	0.08220	0.42750
Si	T6	0.21390	0.58530	0.38320
Si	T7	0.28690	0.01000	0.24630
O	O1	0.42800	0.50530	0.47300
O	O2	0.50340	0.47250	0.42250
O	O3	0.42450	0.82200	0.38720
O	O4	0.33010	-0.00450	0.39560
O	O5	0.08410	-0.36240	0.45130
O	O6	0.34520	-0.02180	0.29720
O	O7	0.25040	0.24410	0.26290
O	O8	0.26020	0.37160	0.40780
O	O9	0.15540	0.51010	0.39110
O	O10	0.18530	0.44800	0.50260
O	O11	0.29970	0.09050	0.18860
O	O12	0.39950	0.33700	0.37020
O	O13	0.10690	0.13720	0.43940
O	O14	0.23430	0.88280	0.40930

Unit cell parameters and fractional coordinates of the structure of siliceous zeolite ZSM-12, based on ^{29}Si-NMR-chemical-shift refinement of powder-XRD analyses.[3]

Space group: *C2/C* (# 15)

(24.8633 Å, 5.0124 Å, 24.3275 Å)

(90°, 107.7215°, 90°)

Atom	Name	*x*	*y*	*z*
Si	T1	0.06051	0.01576	0.08681
Si	T2	0.06895	0.06505	0.96065
Si	T3	0.37450	0.01422	0.36276
Si	T4	0.36436	0.07274	0.55175
Si	T5	0.28296	0.07964	0.42726
Si	T6	0.28935	0.08807	0.12110
Si	T7	0.28669	0.03678	0.24686
O	O1	0.07267	-0.01767	0.02569
O	O2	0.00415	0.05663	0.92162
O	O3	0.42549	0.18699	0.88999
O	O4	0.33063	0.01234	0.89952
O	O5	0.40681	0.14010	0.03877
O	O6	0.34189	0.05509	0.79711
O	O7	0.25866	0.29514	0.26707
O	O8	0.24063	0.13213	0.59685
O	O9	0.34554	0.00364	0.10714
O	O10	0.30881	0.08737	0.49589
O	O11	0.30198	0.11274	0.18937
O	O12	0.10188	0.18795	0.63140
O	O13	0.10644	0.14017	0.43782
O	O14	0.23195	0.13366	0.90907

Unit cell parameters and fractional coordinates of the structure of siliceous zeolite ZSM-12, based on DFT optimization of the powder-XRD structure.

Space group: *C2/C* (# 15)

(24.8633 Å, 5.0124 Å, 24.3275 Å)

(90°, 107.7215°, 90°)

Atom	Name	*x*	*y*	*z*
Si	T1	0.43895	0.53807	0.41271
Si	T2	0.06758	-0.07613	0.45931
Si	T3	0.37448	0.03586	0.36166
Si	T4	0.13394	0.41902	0.44677
Si	T5	0.28335	0.08316	0.42777
Si	T6	0.21211	0.59114	0.38094
Si	T7	0.28553	0.01136	0.24533
O	O1	0.42678	0.50924	0.47413
O	O2	0.50345	0.46368	0.41925
O	O3	0.42742	0.83926	0.38859
O	O4	0.32935	-0.00488	0.39671
O	O5	0.08521	-0.38174	0.45328
O	O6	0.34508	-0.03643	0.29462
O	O7	0.25029	0.23703	0.26741
O	O8	0.26282	0.38489	0.41017
O	O9	0.15381	0.49966	0.39168
O	O10	0.18880	0.43376	0.50323
O	O11	0.29837	0.10679	0.18758
O	O12	0.39707	0.33955	0.36692
O	O13	0.10869	0.12013	0.43799
O	O14	0.22986	0.88350	0.40868

Unit cell parameters and fractional coordinates of the structure of siliceous zeolite ZSM-12, based on DFT optimization of the ^{29}Si-NMR-refined structure.

Space group: *C2/C* (# 15)

(24.8633 Å, 5.0124 Å, 24.3275 Å)

(90°, 107.7215°, 90°)

Atom	Name	*x*	*y*	*z*
Si	T1	0.06090	0.02825	0.08697
Si	T2	0.06770	0.07858	0.95936
Si	T3	0.37408	0.02676	0.36242
Si	T4	0.36540	0.08555	0.55281
Si	T5	0.28289	0.08679	0.42764
Si	T6	0.28843	0.09516	0.11969
Si	T7	0.28573	0.02966	0.24569
O	O1	0.07236	0.00137	0.02520
O	O2	0.00338	0.04857	0.91888
O	O3	0.42694	0.17115	0.88861
O	O4	0.32960	0.01151	0.89834
O	O5	0.41271	0.11685	0.04405
O	O6	0.34365	0.04390	0.79539
O	O7	0.25528	0.27179	0.26884
O	O8	0.23760	0.11416	0.59290
O	O9	0.34603	-0.00018	0.10795
O	O10	0.30983	0.08261	0.49688
O	O11	0.30048	0.11887	0.18845
O	O12	0.10303	0.17041	0.63237
O	O13	0.10786	0.11846	0.43684
O	O14	0.22967	0.11508	0.90943

References for Supporting Information section

1. A. Stewart, *Zeolites*, 1989, **9**, 140-145.
2. C. A. Fyfe, H. Gies, G. T. Kokotailo, B. Marler and D. E. Cox, *J. Phys. Chem.*, 1990, **94**, 3718-3721.
3. D. H. Brouwer, *J. Magn. Reson.*, 2008, doi:10.1016/j.jmr.2008.1006.1020.