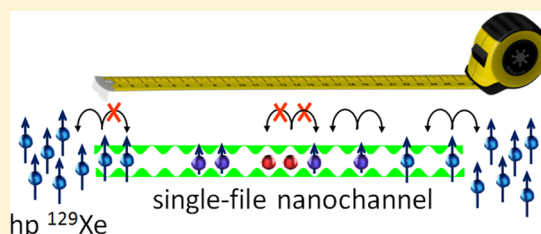


Single-File Nanochannel Persistence Lengths from NMR

Muslim Dvoyashkin,[†] Hrishi Bhase,[†] Navid Mirnazari,[†] Sergey Vasenkov,[‡] and Clifford R. Bowers^{*,†}[†]Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States[‡]Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611, United States

ABSTRACT: Crystalline solids composed of one-dimensional channels with cross-sectional dimensions below 1 nm represent an intriguing class of materials with important potential applications. A key characteristic for certain applications is the average open channel persistence length, i.e., the ensemble average distance from a channel opening to the first obstruction. This paper introduces an NMR-based methodology to measure this quantity. The protocol is applied to polycrystalline specimens of two different dipeptide nanotubes: L-Ala-L-Val and its retro-analog L-Val-L-Ala. Persistence lengths derived from the NMR measurements are found to be comparable to the typical crystallite dimensions seen in scanning electron microscopy (SEM) images, indicating that the crystals of these AV and VA specimens are essentially hollow with practically no blockages. Applications of the method to an AV sample that has been pulverized in a mortar and pestle showed that the open channel persistence length was reduced from 50 to 6.6 μm , consistent with the crystallite sizes observed in SEM images.



Crystalline solids composed of one-dimensional channels with cross-sectional dimensions below 1 nm represent a unique class of materials. Within the confined spaces, chemical or photochemical transformations may be constrained by guest–host interactions,¹ and the one-dimensional topology may also yield anomalous transport properties with potential applications to gas storage, separations, catalysis, and drug delivery. Representatives include the crystalline dipeptides,^{2,3} transition metal molecular wheels,⁴ and bis-urea macrocycles.⁵ In all of these materials, microscopy reveals needle-shaped single crystals in which the channel axis is aligned parallel to the long dimension of the crystal. A key property resulting from self-assembly is the perfect monodispersity in the cross-sectional geometry. Channel lengths resulting from spontaneous crystallization, on the other hand, usually exhibit a very broad distribution, as exemplified in the scanning electron microscopy (SEM) images of the polycrystalline specimens of the dipeptides L-Ala-L-Val (AV) and its retro-analog L-Val-L-Ala (VA) shown in Figure 1a and 1b. Individual crystals extending into the hundreds of micrometers in length and a few micrometers in width can be seen. On the basis of the crystal structure, we know that these crystallites are spanned by millions of parallel nanochannels. But are these channels open at both ends? Are they hollow and unobstructed all the way through from one end of the crystal to the other? How could this be investigated? The answers to these questions are critically important to applications.

As noted in ref 6, defects may or may not alter sorption characteristics. Pore architecture may be altered without changing the total capacity or diffusion properties, or channels may be blocked, reducing the accessible pore volume and sorption capacity. The specific sorption capacity in solids with one-dimensional pores depends on both the average crystallite length and the blockage density. Hence the open channel

persistence length, defined here as the average distance between a channel opening and the first obstruction, is not available from sorption measurements alone. Here we demonstrate how this quantity can be determined by combining information from several different types of NMR measurements.

Diffusion of Xe in L-Ala-L-Val (AV) nanochannels exhibits single-file dynamics.^{7,8} The hallmark of single-file diffusion (SFD) is the $t^{1/2}$ time-scaling of the mean-squared displacement, i.e., $\sigma^2 = 2Ft^{1/2}$, where F is the single-file mobility.⁹ The open channel persistence length, as defined above, can be estimated by combining hyperpolarized spin tracer exchange (HSTE) NMR data with single-file mobility data measured on the same specimens at the same temperature and Xe pressures.⁷ Average open channel persistence lengths $\bar{l}$ were thus obtained for VA, AV, and a sample of AV that was pulverized in a mortar and pestle (pAV). Comparison of these values to the crystallite lengths seen in the SEM will afford an estimation of the blockage densities in these materials.

■ MATERIALS AND METHODS

Crystalline AV and VA consist of helical channel structures with mean channel diameters of 0.51 and 0.49 nm, respectively.^{3,10,11} The spacing of the windings is nearly the same in the two materials – about 1 nm.¹¹ Xe satisfies the single-file criterion in AV and VA, as evidenced by the loading dependence of the ¹²⁹Xe chemical shift tensors.^{8,12} The as-received specimens of VA and AV show a broad distribution of channel lengths with a mean of roughly 50–100 μm , whereas the pAV specimen consists of particles roughly 5 μm in average length (see Figure 1).

Received: November 27, 2013

Accepted: January 16, 2014

Published: January 16, 2014



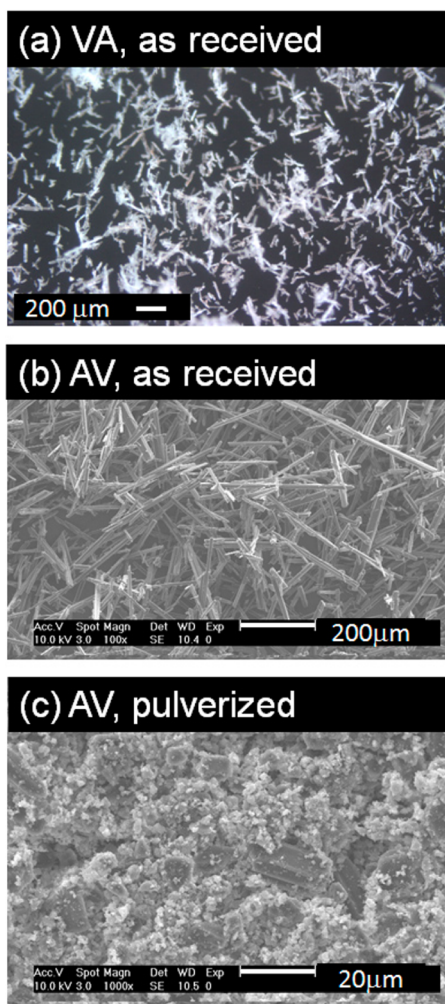


Figure 1. SEM images of three dipeptide specimens: (a) VA, as received from Bachem Americas, LLC; (b) AV, as received from Bachem Americas, LLC; (c) AV after pulverizing in a mortar and pestle.

NMR spin hyperpolarization methods such as ^{129}Xe spin exchange optical pumping (SEOP)^{13,14} can produce signal enhancements of more than 4 orders of magnitude, making it possible to follow diffusion in AV and VA in real time in the 10 ms–200 s time-window.^{8,15,16} Xenon-129 typically exhibits a large chemical shift in physisorbed environments relative to the gas. In VA and AV, the adsorbed and gas phase peaks are well-resolved, allowing exchange between the adsorbed and gas phases to be studied by applying the selective-saturation recovery pulse sequence.^{8,15}

The HSTE NMR technique is illustrated in Figure 2. Utilization of the nuclear spin as a particle tag is advantageous for tracer exchange studies^{17–19} because the system is conveniently reinitialized using chemical shift-selective radio-frequency pulse excitation. Hyperpolarized ^{129}Xe gas produced by SEOP is continuously pumped through the NMR sample holder containing the porous solid sample.^{14,20} Hyperpolarized atoms of the bulk gas enter the channel openings and undergo spin–lattice relaxation as they propagate into the channel spaces, while unpolarized atoms desorb from the channels and are purged from the sample space by the continuous flow of gas. In one-dimensional channels with diffusion-limited exchange kinetics, the recovery of the adsorbed phase ^{129}Xe

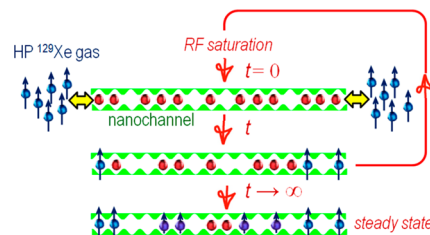


Figure 2. Schematic illustration of the hyperpolarized spin tracer exchange experiment. The NMR spectrum is recorded at a series of time delays following frequency selective RF saturation of the nanochannel-adsorbed ^{129}Xe polarization.

spin signal contains information about the diffusion time-scaling. A steady-state gradient in the ^{129}Xe spin hyperpolarization along the channel axis is ultimately established.

Single-file systems such as Xe in AV or VA can potentially exhibit up to four distinct diffusion time regimes (not including ballistic transport at very short t).^{17,21} The initial period (regime *i*) of ordinary Fickian Diffusion (FD), where $\sigma^2 = 2D_0t$, is followed by the onset of SFD (regime *ii*). In finite, doubly open-ended channels devoid of obstructions, particle displacements correlated to diffusion of the center-of-mass lead to a crossover to a center-of-mass (CM) diffusion (regime *iii*).^{17,21} CM diffusion is characterized by Fickian time-scaling, $\sigma^2 = 2D_{\text{CM}}t$, but with reduced diffusivity $D_{\text{CM}} = D_0(1 - \theta)/(\theta L)$,^{21,22} where L is the number of sorption sites in the channel and θ is the fractional occupancy. A fourth regime, restricted diffusion, occurs in singly open ended channels. For particles located initially at the center of the channels, the crossover between regimes *ii* and *iii* in doubly open-ended channels can be estimated analytically:²¹

$$\sigma^2(t_c) = (2\lambda l/\pi)(1 - \theta)/\theta \quad (1)$$

where λ is the elementary random walk displacement. For other initial locations, deviations from the $t^{1/2}$ time-scaling of the MSD will occur at shorter diffusion times, depending on proximity to the file boundary and boundary conditions.

In sufficiently long channels, where the minimum channel length in the distribution fulfills the criteria

$$l_{\text{min}}/2 \gg \sqrt{2F\sqrt{T_{1c}}} \quad \text{or} \quad l_{\text{min}}/2 \gg \sqrt{2DT_{1c}} \quad (2)$$

for SFD and FD, respectively, the spin hyperpolarization on the sorbate molecule relaxes with a time constant T_{1c} before the sorbate reaches the midpoint of the channel. When this “long channel” criterion is fulfilled, the signal arising from the hyperpolarized sorbates within the channels can be estimated analytically in the two limiting cases of pure SFD and pure FD:⁸

$$S_c(t) \propto \langle I_{zc}(t) \rangle = I_{zc} \frac{\bar{n}\pi}{2\Gamma(1/4)} \frac{\sqrt{F}}{\bar{l}} \int_0^t \tau^{-3/4} e^{-\tau/T_{1c}} d\tau \quad \text{SFD} \quad (3)$$

$$= I_{zc} \frac{\bar{n}\sqrt{4\pi D}}{\bar{l}} \int_0^t \tau^{-1/2} e^{-\tau/T_{1c}} d\tau \quad \text{FD} \quad (4)$$

The total signal depends on $\bar{n}$, the ensemble average number of channel openings per channel (ranging from 0 to 2), and $\bar{l}$, the average open channel persistence length. A time-scaling of $\sigma^2(t)$ intermediate between the limiting cases of pure SFD and pure FD may result if the data is acquired in a time window spanning the crossover between different diffusion regimes. Effects of intermolecular interactions, adsorption barriers, and transport impedances may also produce such deviations. Deviations may

be analyzed by fitting the normalized HSTE-NMR data to the following function:^{16,23}

$$\gamma_{\text{NMR}}(t) = \frac{S_c(t)}{S_c(t \rightarrow \infty)} = \frac{\int_0^t \tau^{a-1} e^{-\tau/T_{1c}} d\tau}{\int_0^\infty \tau^{a-1} e^{-\tau/T_{1c}} d\tau} \quad (5)$$

where $a = 0.25$ in the case of pure SFD to $a = 0.5$ for FD. In sufficiently long channels, T_{1c} can be measured independently by thermally polarized NMR (sensitivity permitting). This leaves a as the single remaining fitting parameter.

In cases when fitting of the HSTE-NMR data to 5 indicates purely single-file or purely Fickian diffusion, the prefactors in eq 3 or 4 can be obtained by referencing the adsorbed phase NMR signal to the signal of the hyperpolarized gas:

$$\frac{S_c(t)}{S_g} = \frac{n_c}{n_g} \langle I_{zc}(t) \rangle \quad (6)$$

$$= C_F \int_0^t \tau^{-3/4} e^{-\tau/T_{1c}} d\tau \quad \text{SFD} \quad (7)$$

$$= C_D \int_0^t \tau^{-1/2} e^{-\tau/T_{1c}} d\tau \quad \text{FD} \quad (8)$$

where

$$C_F = \frac{\bar{n}}{\bar{l}} \frac{\pi \sqrt{F}}{2\Gamma(1/4)} \left(\frac{n_c}{n_g} \right) \quad (9)$$

and

$$C_D = \frac{\bar{n}}{\bar{l}} \sqrt{\frac{\pi D}{2}} \left(\frac{n_c}{n_g} \right) \quad (10)$$

Here, Γ is the complete gamma function and n_c/n_g is the ratio of the number of channel-adsorbed to gas phase atoms within the detected region of the coil. The integral forms (eqs 7 and 8) first appeared in the seminar paper of Meersmann et al.,¹⁵ but the constants of proportionality, C_F and C_D , were not specified in that work. The explicit analytical forms, given in eqs 9 and 10, were derived in a subsequent paper.⁸ These equations provide practical relationships for estimating $\bar{l}$ from the measured quantities n_c/n_g , F and C_F or D and C_D .

$$\bar{l} = \frac{\bar{n}\pi}{2\Gamma(1/4)} \left(\frac{\sqrt{F}}{C_F} \right) \left(\frac{n_c}{n_g} \right) \quad (\text{SFD, 2-site exchange model}) \quad (11)$$

$$\bar{l} = \bar{n} \sqrt{\frac{\pi}{2}} \frac{\sqrt{D}}{C_D} \left(\frac{n_c}{n_g} \right) \quad (\text{FD, 2-site exchange model}) \quad (12)$$

Similar expressions but with slightly different numerical factors can be derived using an alternate approach involving integration of the spin-relaxation weighted residence time distribution.^{17,24}

RESULTS AND DISCUSSION

Figure 3a–c presents the fully relaxed, thermally polarized ^{129}Xe spectra in VA, AV, and pAV at 9.4 T, 297 K, and 3 bar Xe in the gas phase. About 200 mbar of O_2 gas was mixed with the Xe and a recycle delay of 30 min was used to ensure complete relaxation in the signal averaging of 32 transients. The adsorbed phase ^{129}Xe NMR peaks in both polycrystalline dipeptide

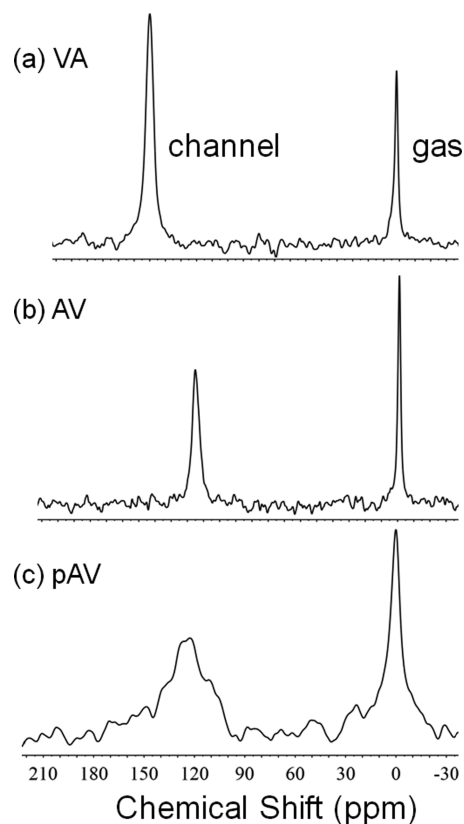


Figure 3. Fully relaxed, thermally polarized ^{129}Xe NMR spectra of the three polycrystalline dipeptide specimens at a Xe pressure of 3 bar and O_2 pressure of 200 mbar and a sample temperature of 298 K. Spectra were acquired at 9.4 T using a single $3.5 \mu\text{s}$ pulse. The free gas peak is observed near 0 ppm whereas the channel adsorbed peaks occur at 150 and 120 ppm for VA and AV, respectively. The ratio of the signal integrals measured from each spectrum are reported in Table 1.

specimens exhibit a symmetric line shape with a fwhm ≈ 7 ppm. The ratio of the channel-adsorbed and gas phase NMR signal integrals provides a quantitative measure of the ratio of the number of adsorbed and gas phase atoms, n_c/n_g . For as-received VA, $n_c/n_g = 2.7 \pm 0.1$. For AV and pAV, $n_c/n_g = 1.43 \pm 0.07$ and 1.4 ± 0.1 , respectively. The relative signal ratios are consistent with the relative loadings of VA and AV. Grinding significantly altered the ^{129}Xe spectrum. The bulk gas peak and channel-adsorbed peaks are both broader in the pAV, presumably due to increased exchange effects in shorter channels.

Figures 4 and 5 present the experimentally measured $\gamma_{\text{NMR}}(t)$ data for VA, AV, and pAV, together with nonlinear least-squares best fits to eq 5. Fitting yielded $a = 0.3 \pm 0.01$, 0.25 ± 0.01 , and 0.24 ± 0.01 , respectively.

For VA, the data at short t increasingly deviate from the SFD model in the direction toward higher values of a . It has the appearance of a crossover from FD to SFD. The deviation could be due to depolarization of the gas phase as a result of mixing with unpolarized gas desorbing from the channels. The bulk gas phase signal integrals, normalized to the signal integrals obtained in the steady-state, are included in Figures 4 and 5. Notice that the signal of the bulk phase is initially depressed by about 15% with respect to the steady-state value, and increases over the first 100 s of the experiment.

For both AV and pAV, nearly perfect agreement with the pure SFD model is obtained at all t . Equation 1 predicts a

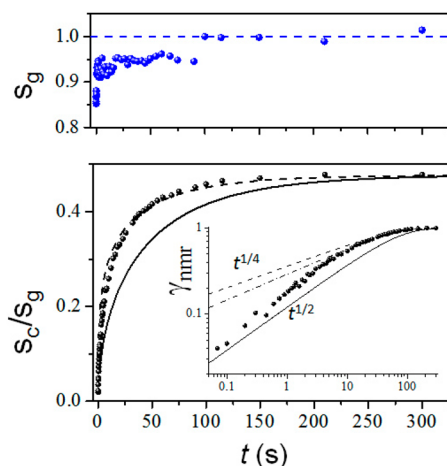


Figure 4. Hyperpolarized ^{129}Xe spin tracer exchange NMR signal integrals (referenced to the gas phase) acquired in VA at 298 K using 3 bar Xe at ~ 100 mL/min. The black dashed curves show the best fits to eq 7 taking C_F as the fitting parameter. The blue symbols in the upper panel represent the integrals of the free gas signal. Inset: log–log representation of the normalized tracer exchange data (black spheres) together with best fits (dashed curves) to eq 5 taking a as the single fitting parameter (results given in Table 1). The functions $\gamma_{\text{NMR}}(t)$ with $a = 0.25$ and $a = 0.50$ are represented by the black dot-dashed and solid curves, respectively.

crossover to CM diffusion under PFG NMR conditions.²¹ Taking $\lambda \approx c/3 \approx 0.33$ nm (corresponding to a capacity of ~ 3 Xe atoms per c-translation of the unit cell), $\bar{l} = 6.2$ μm and $\theta = 0.35$, the crossover is estimated to occur at $\sigma(t_c) \approx 50$ nm for hollow, doubly open-ended AV channels. The HSTE-NMR experiments probes displacements up to ~ 3.5 μm , yet no indication whatsoever of any transition $\gamma_{\text{NMR}} \propto t^{1/4} \rightarrow t^{1/2}$ stemming either from mutual passages within the nanochannels or as a consequence of CM diffusion is detected. CM diffusion is fully suppressed in channels with single openings. The coefficients C_F were extracted from the HSTE data with the aid of eq 7. Three different methods were utilized as follows: (1) Linear least-squares fit of $\log(s_c(t)/s_g)$ vs $\log t$ to the data at short t yields an intercept $\log(4C_F)$. This approach does not require measurement of T_{1c} . (2) Acquisition of the steady-state (SS) signal ratio, which is related to C_F by $s_c(\infty)/s_g = C_F T_{1c}^{1/4} \Gamma(1/4)$. (3) Nonlinear least-squares fitting of $s_c(t)/s_g$ to the data over the full range of t with C_F as a fitting parameter.

Table 1 summarizes all of the parameters used in the estimation of $\bar{l}$ for all three samples, including F values obtained by PFG-NMR.⁷ The mean channel lengths $\bar{l}$ reported in the last column of Table 1 assume $\bar{n} = 1$. The values are comparable to the physical crystallite lengths seen in the SEM images of each specimen. However, because $\bar{n}$ is an unknown quantity, $\bar{l}$ could conceivably be greater by up to a factor of 2 (i.e., if all channels are doubly open ended).

To summarize, an improved two-step protocol for the analysis of hyperpolarized xenon-129 spin tracer exchange NMR data has been demonstrated. In the first step, the time-scaling of the mean-squared displacement is extracted from the hyperpolarized spin tracer exchange data using eq 5. In VA, fitting yielded $\sigma^2 \propto t^{0.60 \pm 0.02}$, which shows significant deviation from pure SFD, whereas in AV and pAV $\sigma^2 \propto t^{0.50 \pm 0.02}$ is obtained, which further validates previous claims of pure SFD of Xe in this material.^{7,8} In the second step, fitting of the HSTE-NMR data to the analytical model referenced to the gas phase

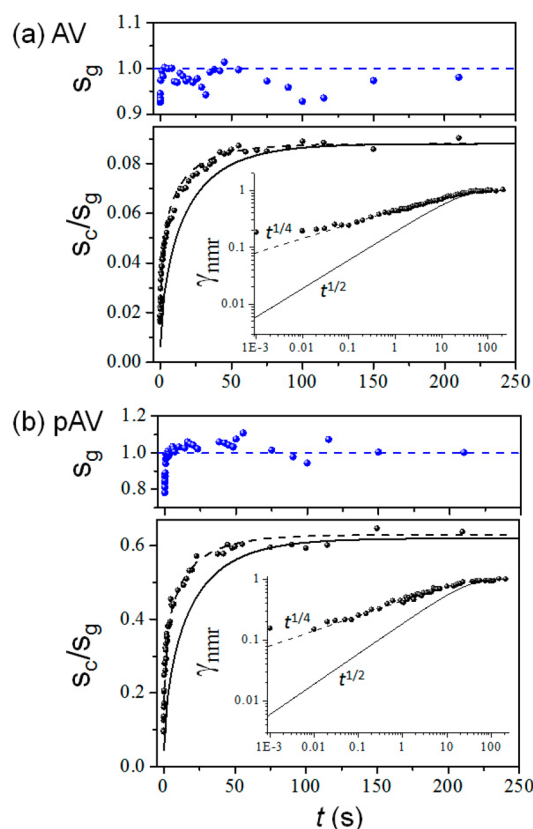


Figure 5. Hyperpolarized ^{129}Xe spin tracer exchange NMR signal integrals (referenced to the gas phase signal) acquired in (a) AV and (b) pAV at 298 K using 3 bar Xe at ~ 100 mL/min. The dashed black curves show the best fits to eq 7 taking C_F as the fitting parameter. The blue symbols in the upper panels have the same meaning as in Figure 4. Insets: log–log representation of the normalized tracer exchange data (black spheres) together with best fits (dashed curves) to eq 5 taking a as the single fitting parameter (results given in Table 1). The solid black curves represents $\gamma_{\text{NMR}}(t)$ with $a = 0.50$.

signal facilitated estimation of the average open channel persistence lengths, as reported in Table 1. In the case of VA, the reported $\bar{l}$ -value should be considered to be good only at a qualitative level.

CONCLUSIONS

The open channel persistence lengths in VA, AV, and p-AV are found to be comparable to the typical crystallite dimension seen in the SEM images. This indicates that the crystals are effectively hollow all the way through with defect densities per unit channel length estimated to be less than 10 ppm. Our methodology is validated by experiments performed on a sample of pulverized AV, which resulted in a reduction of the open channel length from 50 to 6.6 μm . The particles seen in the pulverized sample appear to be at most 5 μm in size, suggesting most of the channels are blocked at one end. Whether this is due to grinding-induced damage to the channel openings or defects intrinsic to the material remains unclear.

The HSTE-NMR data show no indication of an incipient transition to CM diffusion. In addition to channel blockages, particle–particle interactions,²⁵ particle clustering,²⁶ and/or the occurrence of molecular desorption barriers, may also play a role.^{19,27} Further theoretical work is clearly needed to elucidate and assess the relative importance of these factors.

Table 1

	<i>a</i>	<i>n_c/n_g</i>	<i>s_c/s_g</i>	<i>C_F</i> (by method)			<i>T_{1c}/s</i>	<i>F/m² s^{-1/2}</i> (ref 7)	$\bar{\Gamma}/\mu\text{m eq 11}$
				1	2	3			
VA	0.3 ± 0.01	2.70 ± 0.10	0.48		0.054	0.040	87	4.4 ± 0.2 × 10 ⁻¹³	20 ± 2
AV	0.25 ± 0.01	1.43 ± 0.07	0.088	0.0095	0.0099	0.0097	36	6 ± 0.7 × 10 ⁻¹³	50 ± 10
pAV	0.24 ± 0.01	1.40 ± 0.10	0.64	0.072	0.072	0.071	36	6 ± 0.7 × 10 ⁻¹³	6.6 ± 0.3

AUTHOR INFORMATION

Corresponding Author

*C. R. Bowers. E-mail: russ@ufl.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under Grant No. CHE-0957641. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

REFERENCES

- (1) Geer, M. F.; Walla, M. D.; Solntsev, K. M.; Strassert, C. A.; Shimizu, L. S. *J. Org. Chem.* **2013**, *78*, 5568–5578. Dawn, S.; Shimizu, L. S. *Abstr. Pap. Am. Chem. Soc.*, 2011, 242. Roy, K.; Wang, C.; Smith, M. D.; Dewal, M. B.; Wibowo, A. C.; Brown, J. C.; Ma, S. G.; Shimizu, L. S. *Chem. Commun.* **2011**, 47, 277–279. Xu, Y. W.; Smith, M. D.; Krause, J. A.; Shimizu, L. S. *J. Org. Chem.* **2009**, *74*, 4874–4877. Yang, J.; Dewal, M. B.; Profeta, S.; Smith, M. D.; Li, Y. Y.; Shimizu, L. S. *J. Am. Chem. Soc.* **2008**, *130*, 612–621.
- (2) Gorbitz, C. H. *Chem. Commun.* **2006**, 2332–2334. Gorbitz, C. H.; Nilsen, M.; Szeto, K.; Tangen, L. W. *Chem. Commun.* **2005**, 4288–4290. Gorbitz, C. H. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2004**, *60*, O626–O628.
- (3) Gorbitz, C. H. *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 849–854.
- (4) King, P.; Stamatatos, T. C.; Abboud, K. A.; Christou, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 7379–7383. Tasiopoulos, A. J.; Vinslava, A.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 2117–2121.
- (5) Roy, K.; Shimizu, L. S. *Abstr. Pap. Am. Chem. Soc.*, 2011, 242. Yang, J.; Shimizu, L. S. *Abstr. Pap. Am. Chem. Soc.*, 2007, 233. Dewal, M. B.; Lufaso, M. W.; Hughes, A. D.; Samuel, S. A.; Pellechia, P.; Shimizu, L. S. *Chem. Mater.* **2006**, *18*, 4855–4864.
- (6) Newsam, J. M.; Deem, M. W. *J. Phys. Chem.* **1995**, *99*, 8379–8381.
- (7) Dvoyashkin, M.; Wang, A.; Vasenkov, S.; Bowers, C. R. *J. Phys. Chem. Lett.* **2013**, *4*, 3263–3267.
- (8) Cheng, C. Y.; Bowers, C. R. *ChemPhysChem* **2007**, *8*, 2077–2081.
- (9) Kärger, J. *Phys. Rev. A: At., Mol., Opt. Phys.* **1992**, *45*, 4173–4174.
- (10) Gorbitz, C. H.; Gundersen, E. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1996**, *52*, 1764–1767.
- (11) Soldatov, D. V.; Moudrakovski, I. L.; Ripmeester, J. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 6308–6311.
- (12) Moudrakovski, I.; Soldatov, D. V.; Ripmeester, J. A.; Sears, D. N.; Jameson, C. J. *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101*, 17924–17929. Anedda, R.; Soldatov, D. V.; Moudrakovski, I. L.; Casu, M.; Ripmeester, J. A. *Chem. Mater.* **2008**, *20*, 2908–2920.
- (13) Raftery, D.; Long, H.; Meersmann, T.; Grandinetti, P. J.; Reven, L.; Pines, A. *Phys. Rev. Lett.* **1991**, *66*, 584–587. Cates, G. D.; Benton, D. R.; Gatzke, M.; Happer, W.; Hasson, K. C.; Newbury, N. R. *Phys. Rev. Lett.* **1990**, *65*, 2591–2594. Driehuys, B.; Cates, G. D.; Miron, E.; Sauer, K.; Walter, D. K.; Happer, W. *Appl. Phys. Lett.* **1996**, *69*, 1668–1670.
- (14) Zook, A. L.; Adhyaru, B. B.; Bowers, C. R. *J. Magn. Reson.* **2002**, *159*, 175–182.
- (15) Meersmann, T.; Logan, J. W.; Simonutti, R.; Caldarelli, S.; Comotti, A.; Sozzani, P.; Kaiser, L. G.; Pines, A. *J. Phys. Chem. A* **2000**, *104*, 11665–11670.
- (16) Cheng, C.-Y.; Stamatatos, T. C.; Christou, G.; Bowers, C. R. *J. Am. Chem. Soc.* **2010**, *132*, 5387–5393.
- (17) Vasenkov, S.; Kärger, J. *Phys. Rev. E* **2002**, *66*, 052601.
- (18) Ackerman, D. M.; Wang, J.; Wendel, J. H.; Liu, D. J.; Pruski, M.; Evans, J. W. *J. Chem. Phys.* **2011**, *134*, 114107. Brauer, P.; Brzank, A.; Karger, J. *J. Phys. Chem. B* **2003**, *107*, 1821–1831. Heinke, L.; Tzoulaki, D.; Chmelik, C.; Hibbe, F.; van Baten, J. M.; Lim, H.; Li, J.; Krishna, R.; Karger, J. *Phys. Rev. Lett.* **2009**, *102*, 65901. Ilyas, A.; Eic, M.; Zahedi-Niaki, M. H.; Vasenkov, S. *J. Phys. Chem. B* **2008**, *112*, 3821–3825. Karger, J. *Adsorption* **2003**, *9*, 29–35. Liu, D. J.; Wang, J.; Ackerman, D. M.; Slowing, I. L.; Pruski, M.; Chen, H. T.; Lin, V. S. Y.; Evans, J. W. *ACS Catal.* **2011**, *1*, 751–763. Rodenbeck, C.; Karger, J.; Hahn, K. J. *Catal.* **1995**, *157*, 656–664. Rodenbeck, C.; Karger, J.; Hahn, K. *Collect. Czech. Chem. Commun.* **1997**, *62*, 995–1014. Rodenbeck, C.; Karger, J.; Hahn, K. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **1997**, *55*, S697–S712.
- (19) Gulín-González, J.; Schuring, A.; Fritzsche, S.; Karger, J.; Vasenkov, S. *Chem. Phys. Lett.* **2006**, *430*, 60–66.
- (20) Brunner, E.; Haake, M.; Kaiser, L.; Pines, A.; Reimer, J. A. *J. Magn. Reson.* **1999**, *138*, 155–159. Seydoux, R.; Pines, A.; Haake, M.; Reimer, J. A. *J. Phys. Chem. B* **1999**, *103*, 4629–4637.
- (21) Hahn, K.; Kärger, J. *J. Phys. Chem. B* **1998**, *102*, S766–S771. Nelson, P. H.; Auerbach, S. M. *J. Chem. Phys.* **1999**, *110*, 9235–9243.
- (22) Vanbeijeren, H.; Kehr, K. W.; Kutner, R. *Phys. Rev. B* **1983**, *28*, S711–S723.
- (23) Bowers, C. R.; Cheng, C.-Y.; Stamatatos, T. C.; Christou, G. *AIP Conf. Proc.* **2011**, 1330; Cheng, C. Y.; Bowers, C. R. *J. Am. Chem. Soc.* **2007**, *129*, 13997–14002.
- (24) Rodenbeck, C.; Kärger, J.; Schmidt, H.; Rother, T.; Rodenbeck, M. *Phys. Rev. E* **1999**, *60*, 2737–2740.
- (25) Delfau, J. B.; Coste, C.; Saint Jean, M. *Phys. Rev. E* **2011**, *84*, 011101.
- (26) Sholl, D. S.; Lee, C. K. *J. Chem. Phys.* **2000**, *112*, 817–824. Sholl, D. S.; Fichthorn, K. A. *Phys. Rev. Lett.* **1997**, *79*, 3569–3572.
- (27) Schuring, A.; Vasenkov, S.; Fritzsche, S. *J. Phys. Chem. B* **2005**, *109*, 16711–16717.

NOTE ADDED AFTER ASAP PUBLICATION

After this paper was published ASAP January 27, 2014, a correction was made to the first sentence of the Materials and Methods section. The corrected version was reposted January 28, 2014.