

Symmetry-Amplified J Splittings for Quadrupolar Spin Pairs: A Solid-State NMR Probe of Homoatomic Covalent Bonds

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S Supporting Information

ABSTRACT: Chemically informative J couplings between pairs of quadrupolar nuclei in dimetallic and dimetalloid coordination motifs are measured using J -resolved solid-state NMR experiments. It is shown that the application of a double-quantum filter is necessary to observe the J splittings and that, under these conditions, only a simple doublet is expected. Interestingly, the splitting is amplified if the spins are magnetically equivalent, making it possible to measure highly precise J couplings and unambiguously probe the symmetry of the molecule. This is demonstrated experimentally by chemically breaking the symmetry about a pair of boron spins by reaction with an N-heterocyclic carbene to form a β -borylation reagent. The results show that the J coupling is a sensitive probe of bonding in diboron compounds and that the J values quantify the weakening of the B–B bond which occurs when forming an sp^2 – sp^3 diboron compound, which is relevant to their reactivity. Due to the prevalence of quadrupolar nuclei among transition metals, this work also provides a new approach to probe metal–metal bonding; results for $Mn_2(CO)_{10}$ are provided as an example.

Chemical bonds are central to our understanding of chemistry, and large strides are being taken to continue to improve our description of bonding interactions.¹ Applications of J couplings between two nuclear spins measured via NMR spectroscopy to probe and understand structure and bonding in organic molecules, inorganic materials, and biomolecules are widespread and have a long history. Exciting developments which rely on the measurement or understanding of J coupling continue apace and are broad in scope. Impressive recent examples include accessing long-lived nuclear spin order,² zero-field J spectroscopy of aromatic compounds,³ the experimental observation of J coupling in van der Waals complexes,⁴ the development of novel biomolecular structure determination tools,⁵ and the design and application of NMR correlation experiments to probe the structure of solids.⁶

J coupling measurements in condensed phases are challenging for pairs of quadrupolar nuclei ($S > 1/2$).⁷ The NMR properties of such nuclei are affected by the interaction of their electric quadrupole moment with the electric field gradient at the nucleus. For example, in solution, rapid quadrupolar relaxation often obfuscates any fine structure due to J coupling. Given that the majority of spin-active nuclides are quadrupolar (e.g., ^{11}B , ^{17}O , ^{23}Na , ^{27}Al , ^{35}Cl , ^{55}Mn), experimental NMR

methods to probe their chemical and electronic environments are desirable. The case of magnetically equivalent quadrupolar spin pairs poses an additional challenge. In the solid state, pairs of magnetically equivalent nuclei have the same NMR tensor magnitudes and orientations, a situation which has been referred to as “total magnetic equivalence”.⁸ Although the practical definition of magnetic equivalence can differ for spin systems in solution, even casual users of NMR are aware that J couplings vanish from the NMR spectrum for groups of magnetically equivalent spins-1/2 (e.g., the three protons on a methyl group). For the chemist, pairs of magnetically equivalent quadrupolar nuclei are found in a plethora of materials and compounds which are the subjects of current research including, e.g., homometallic organic frameworks with potential catalytic and gas storage applications,⁹ small molecules exhibiting metal–metal multiple bonds,¹⁰ and diboron compounds which are attracting attention as a source of nucleophilic boron.¹¹ We show here how the relevant homonuclear J coupling constants for systems such as these can be measured with unprecedentedly high precision in the solid state and, with the use of a symmetry-breaking reaction, demonstrate the chemical insights available from such measurements.

For non-equivalent nuclei, J coupling may be measured from splittings in the 1D NMR spectra, but more precise measurements are typically made for spin-1/2 nuclei using J -resolved experiments¹² or spin-echo modulation.¹³ Heteronuclear J -resolved experiments have been performed for spin pairs involving a spin-1/2 nucleus and a quadrupolar nucleus;¹⁴ however, attempts to perform such experiments on pairs of quadrupolar nuclei have been met with limited success.¹⁵ In a J -resolved experiment, chemical shifts (and second-order quadrupolar coupling) are refocused with a 180° radio-frequency pulse. However, if both of the coupled spins are inverted by this pulse, the evolution of the J coupling is not perturbed and the spin echo intensity is modulated.⁸ For quadrupolar nuclei with significant quadrupole couplings, typically only the central transition (CT, $m = 1/2 \leftrightarrow -1/2$) can be inverted, and thus only the J coupling involving two spins in the central states would modulate the spin echo intensity, whereas most of the signal would be perfectly refocused. We have recently discussed homonuclear J coupling involving quadrupolar nuclei and showed that J coupling could be measured for pairs of magnetically equivalent spins; however, the multiplets are characterized by unusual line

Received: July 12, 2013

Published: August 7, 2013

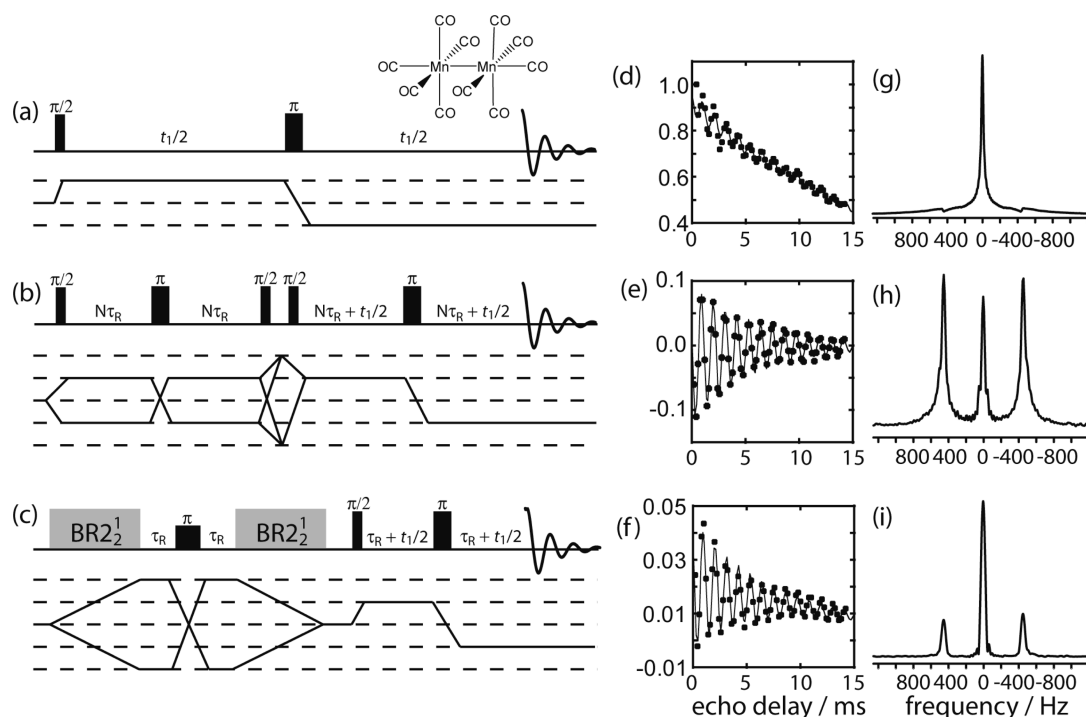


Figure 1. *J*-resolved solid-state NMR experiments for half-integer spin quadrupolar nuclei. Pulse sequences for the regular, *J*-DQF, and dipolar-DQF *J*-resolved experiments are shown in (a), (b), and (c), respectively; coherence transfer pathways are shown below the pulse schemes. The modulations of the echo intensities as a function of the echo delay for ^{55}Mn in dimanganese decacarbonyl subjected to each of the three experiments are shown in (d), (e), and (f), and the Fourier transforms of these signals are shown in (g), (h), and (i). The vertical scales in (d), (e), and (f) show the relative intensities for an equivalent number of scans; however, the data shown here were acquired with differing numbers of scans to ensure good signal-to-noise (see SI).

spacings and intensities.^{7e} In the case of magnetically equivalent spins, only the triplet transitions would become *J*-modulated, whereas all other transitions would be refocused. Triplet transitions are those between the states of the spin pair characterized by a total spin, *I*, of 1 (see Supporting Information (SI) for details).^{7e}

For magnetically equivalent or non-equivalent spin pairs, only a simple doublet is expected in a *J*-resolved experiment involving quadrupolar nuclei since the inversion pulse is CT selective. For non-equivalent pairs, the splitting would simply be equal to the *J* coupling constant, as is familiar from NMR experiments on spin-1/2 nuclei. However, if the spins are magnetically equivalent, the splitting would be $(2S + 3)(2S - 1)/4$. For spin-1/2 nuclei, this term evaluates to zero and explains the lack of *J* splittings for pairs of magnetically equivalent spins;¹⁶ conversely, we notice that the splitting is amplified for quadrupolar nuclei by factors of 3, 8, 15, and 24 for nuclei of spin 3/2, 5/2, 7/2, and 9/2, respectively. These large scaling factors suggest that very precise *J* coupling constants may be measured with this method and that smaller multiple-bond *J* coupling constants may also be accessible.

An experimental demonstration using a ^{55}Mn (*S* = 5/2) *J*-resolved experiment on powdered dimanganese decacarbonyl, which contains a Mn–Mn bond, is presented in Figure 1. The Mn nuclei are related by an inversion center and are totally magnetically equivalent. The most basic *J*-resolved experiment (Figure 1a) shows that most of the signal is not *J* modulated since only $1/(S + 1/2)$ of spins in the triplet states can be used to measure *J* coupling (see SI). The other transitions lead to a strong peak at zero frequency that can completely dominate the weaker *J* doublet (Figure 1g). The time domain signal shows a

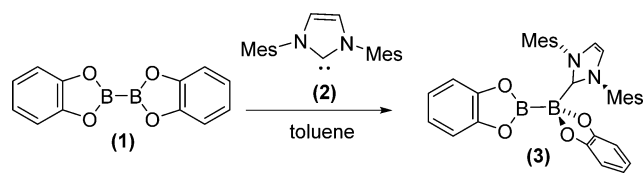
strong exponential decay and only a weak modulation (Figure 1d). This lack of modulation is consistent with previous attempts to perform this experiment reported in the literature. We then employed two double-quantum filtered (DQF) *J*-resolved experiments which use either the *J* coupling (Figure 1b) or the dipolar coupling (Figure 1c) in order to select the triplet states which are *J* modulated. DQF *J*-resolved experiments have also been performed to overcome the low natural abundances of certain isotopes.¹⁷ In the first experiment, an INADEQUATE^{18,19} block is used to excite the DQ transitions prior to performing the spin echo. In the latter, the recently described BR2_2^1 symmetry-based DQ recoupling scheme is used to excite double-quantum transitions²⁰ with COG72-(4,13,4,1,0;35) phase cycling.²¹ The use of dipolar coupling, as opposed to *J* coupling, may be helpful for samples with small *J* coupling constants, as the dipolar coupling may be larger and require shorter DQ excitation times. In principle, the largest DQ excitation efficiency for a pair of equivalent spins in CT-selective methods is $1/(S + 1/2)$. This corresponds to theoretical maximum excitation efficiencies of 50%, 33%, 25%, and 20% for DQ-SQ correlation experiments involving nuclei of spin 3/2, 5/2, 7/2, and 9/2, respectively.

Both DQF experiments perform well in suppressing the central peak to reveal a well-resolved doublet in the frequency domain and strong cosinusoidal oscillations in the time domain. The intensity of the central peak in Figure 1i is larger when compared to that in Figure 1h due to intermolecular DQ dipolar recoupling (see SI). Importantly, the doublet splitting which we measure is 8 times larger than the *J* coupling measured using 1D double-rotation (DOR) NMR;^{7e} this is the expected *J* coupling amplification factor for magnetically

equivalent spin-5/2 nuclei. The much sharper lines measured presently, along with the amplification of the J splitting, make it possible to obtain sub-hertz precision ($^1J(^{55}\text{Mn}, ^{55}\text{Mn}) = 113.0 \pm 0.5$ Hz), nearly 2 orders of magnitude higher precision than is possible with DOR NMR. Another experimental J value for a pair of magnetically equivalent spin-5/2 nuclei is that for molecular iodine in the gas phase.²² The reduced coupling constant, $K = 4\pi^2J/\gamma_1\gamma_2h$, of about $760 \times 10^{20} \text{ N A}^{-2} \text{ m}^{-3}$ for I_2 is much larger than the value of $15.5 \times 10^{20} \text{ N A}^{-2} \text{ m}^{-3}$ for the ^{55}Mn – ^{55}Mn spin pair and can be explained in terms of the orbitals and mechanisms which contribute to the J coupling.^{7e,23} K is useful for assessing the electronic contribution to the coupling for spin pairs consisting of different isotopes because it is independent of the values of the magnetogyric ratios of the coupled nuclei.

The dependence of the observed spectral splitting on the criterion of magnetic equivalence provides a stringent test for the symmetry of molecules, with large, amplified splittings expected for symmetric molecules imparting magnetic equivalence. To test this hypothesis, we have chemically broken the symmetry of bis(catecholato)diboron (**1**) using the popular N-heterocyclic carbene (NHC) IMes (**2**; see Scheme 1). This

Scheme 1. Reaction of 1 with an NHC To Break the Molecular and Magnetic Symmetry



reaction forms an sp^2 – sp^3 diboron compound, an important source of nucleophilic boron for β -borylation reactions.¹¹ As ^{11}B has a spin of 3/2, we expect to observe a spectral splitting that is approximately 3 times larger in compound **1** than in compound **3** (where magnetic equivalence is absent), even though the bonding should remain fairly similar.

The results of ^{11}B DQF- J -resolved solid-state NMR experiments on bis(pinacolato)diboron (**4**), **1**, and its NHC-complexed analogue, **3**, are shown in Figure 2. Results for **4** are shown to provide a direct comparison with **1**; in both cases the boron spin pairs are related by inversion centers and are totally magnetically equivalent. Interestingly, the J coupling is notably smaller in **4** ($J(^{11}\text{B}, ^{11}\text{B}) = 120 \pm 2$ Hz) than in **1** ($J(^{11}\text{B}, ^{11}\text{B}) = 136 \pm 1$ Hz). This is consistent with the longer B–B bond in **4** (1.704 \AA)^{11d} when compared to **1** (1.678 \AA)²⁴ and demonstrates the utility of this method in studying molecular structure in diboron complexes, as these experiments are rapid, are easy to implement, and can be performed on any powdered sample. The J coupling obtained for **1** using the DQF- J -resolved experiment is an order of magnitude more precise than that obtained using DOR NMR^{7e} and does not require specialized hardware.

In the case of **3**, the three- and four-coordinate boron sites are clearly resolved (Figure 2c) and are both split by a common J coupling of 106.8 ± 0.4 Hz. This unequivocally indicates the presence of a bond between the two boron sites. The observed splitting is notably smaller than the 408 ± 3 Hz in **1** and 360 ± 6 Hz in **4**. This is easily understood, as the J splitting is only amplified in the case of magnetically equivalent spin pairs. Upon breaking the symmetry of **1** by coordinating it to an

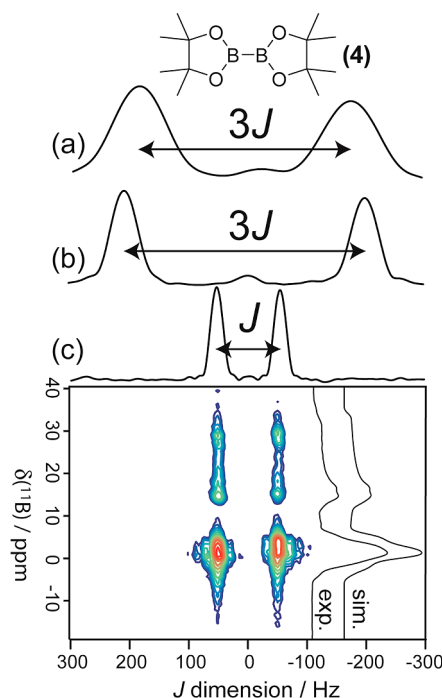


Figure 2. J -DQF J -resolved solid-state NMR spectra for compounds **4** (a), **1** (b), and **3** (c). In (c), the three- and four-coordinate boron peaks are resolved and split by J . MAS NMR spectra (exp, sim) of **3** are also shown in (c).

NHC, the doublet splitting is equal to J as opposed to $3J$. Since the J coupling was found to be smaller in **3** compared to **1**, weakening of the B–B bond when it is complexed to an NHC has been demonstrated, a feature that is important to the reactivity of such compounds.¹¹ In the X-ray crystal structure of an analogous compound of **4** that is coordinated to an NHC,^{11d} it is also clear that the B–B bond is weakened (B–B distance of 1.743 \AA); however, J couplings provide a more rapid approach to characterizing the bond and directly probe the electronic structure of the bond, as opposed to an internuclear distance.

We have performed TPSS/QZ4P DFT calculations (see SI) of the J coupling constants in these complexes to better understand the effects of bonding on their values. All non-relativistic contributions to J are included in these calculations and can be further interpreted using orbital contributions to provide insight into the electronic structure and bonding.^{7e,25} It can be seen in Figure 3a that the trend in J coupling is very well

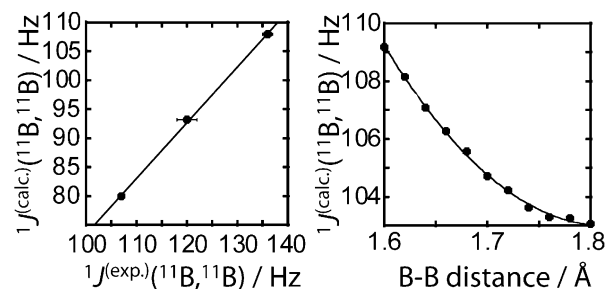


Figure 3. (a) Correlation between DFT-calculated and experimental J coupling constants for diboron compounds ($J^{\text{calc}} = 0.964J^{\text{exp}} - 22.9$ Hz; $R^2 = 0.9993$). (b) Computed bond length dependence of the J coupling constant in **1** ($J^{\text{calc}} = 555.1 \text{ Hz} - 498.8 \text{ Hz/\AA} \cdot d + 137.6 \text{ Hz \AA}^2 \cdot d^2$; $R^2 = 0.9987$).

reproduced using DFT. We have additionally performed a series of calculations as a function of the B–B bond length for 1. The ^{11}B – ^{11}B J coupling constant is highly correlated to the B–B bond length, and a weaker orbital overlap (i.e., longer bond length) corresponds to a smaller J coupling, in agreement with our experimental observations.

In summary, we have developed J -resolved NMR experiments specifically designed for use with half-integer quadrupolar nuclei. The use of a double-quantum filter is necessary to remove non-modulated signals. These experiments provide simple doublets, greatly simplifying the analysis of the NMR data. Interestingly, if the coupled spins are magnetically equivalent (i.e., A_2 spin pairs), the J splittings are amplified according to the spin quantum number. Conversely, amplified splittings are a direct indication of magnetic equivalence of the nuclei involved in a homoatomic covalent bond. These experiments hold promise for studying dimetallic and dimetalloid coordination environments, a common motif in homogeneous and heterogeneous catalysts. More generally, the method provides a rapid and direct approach to probe homonuclear bonding interactions in solids. An open question to be addressed concerns the analysis of intermediate cases where the spins are only chemically equivalent or form tightly coupled AB systems. Preliminary results suggest that amplified splittings are observed only when the spins are totally magnetically equivalent.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental details; theoretical treatment of the J -resolved experiments for quadrupolar nuclei. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to NSERC for funding and thank Carolyn Higman for useful discussions.

■ REFERENCES

- (1) (a) Gagliardi, L.; Roos, B. O. *Nature* **2005**, 433, 848. (b) Roos, B. O.; Borin, A. C.; Gagliardi, L. *Angew. Chem., Int. Ed.* **2007**, 46, 1469. (c) Wagner, F. R.; Noor, A.; Kempe, R. *Nature Chem.* **2009**, 1, 529. (d) Shaik, S.; Danovich, D.; Wu, W.; Su, P.; Rzepa, H. S.; Hiberty, P. C. *Nature Chem.* **2012**, 4, 195.
- (2) Tayler, M. C. D.; Levitt, M. H. *J. Am. Chem. Soc.* **2013**, 135, 2120.
- (3) Blanchard, J. W.; Ledbetter, M. P.; Theis, T.; Butler, M. C.; Budker, D.; Pines, A. *J. Am. Chem. Soc.* **2013**, 135, 3607.
- (4) Ledbetter, M. P.; Saielli, G.; Bagno, A.; Tran, N.; Romalis, M. V. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, 109, 12393.
- (5) (a) Chen, L.; Kaiser, J. M.; Polenova, T.; Yang, J.; Rienstra, C. M.; Mueller, L. J. *J. Am. Chem. Soc.* **2007**, 129, 10650. (b) Bertini, I.; Emsley, L.; Felli, I. C.; Laage, S.; Lesage, A.; Lewandowski, J. R.; Marchetti, A.; Pierattelli, R.; Pintacuda, G. *Chem. Sci.* **2011**, 2, 345.
- (6) (a) Iuga, D.; Morais, C.; Gan, Z.; Neuville, D. R.; Cormier, L.; Massiot, D. *J. Am. Chem. Soc.* **2005**, 127, 11540. (b) Griffin, J. M.; Yates, J. R.; Berry, A. J.; Wimperis, S.; Ashbrook, S. E. *J. Am. Chem. Soc.* **2010**, 132, 15651.
- (7) (a) Wi, S.; Frydman, L. *J. Chem. Phys.* **2000**, 112, 3248. (b) Wi, S.; Frydman, V.; Frydman, L. *J. Chem. Phys.* **2001**, 114, 8511.
- (c) Perras, F. A.; Bryce, D. L. *J. Magn. Reson.* **2011**, 213, 82.
- (d) Jakobsen, H. J.; Bildsøe, H.; Brorson, M.; Gan, Z.; Hung, I. *J. Magn. Reson.* **2013**, 230, 98. (e) Perras, F. A.; Bryce, D. L. *J. Chem. Phys.* **2013**, 138, 174202.
- (8) Duma, L.; Lai, W. C.; Carravetta, M.; Emsley, L.; Brown, S. P.; Levitt, M. H. *ChemPhysChem* **2004**, 5, 815.
- (9) (a) Zheng, S.-T.; Wu, T.; Chou, C.; Fuhr, A.; Feng, P.; Bu, X. *J. Am. Chem. Soc.* **2012**, 134, 4517. (b) Li, Y.-W.; Wang, L.-F.; He, K.-H.; Chen, Q.; Bu, X.-H. *Dalton Trans.* **2011**, 40, 10319. (c) Kramer, M.; Schwarz, U.; Kaskel, S. *J. Mater. Chem.* **2006**, 16, 2245.
- (10) Da Re, R. E.; Eglin, J. L.; Carlson, C. N.; John, K. D.; Morris, D. E.; Woodruff, W. H.; Bailey, J. A.; Batista, E.; Martin, R. L.; Cotton, F. A.; Hillard, E. A.; Murillo, C. A.; Sattelberger, A. P.; Donohoe, R. J. *J. Am. Chem. Soc.* **2010**, 132, 1839.
- (11) (a) Lee, K.-s.; Zhugralin, A. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, 131, 7253. (b) Bonet, A.; Gulyás, H.; Fernández, E. *Angew. Chem., Int. Ed.* **2010**, 49, 5130. (c) Bonet, A.; Pubill-Ulldemolins, C.; Bo, C.; Gulyás, H.; Fernández, E. *Angew. Chem., Int. Ed.* **2011**, 50, 7158. (d) Kleeberg, C.; Crawford, A. G.; Batsanov, A. S.; Hodgkinson, P.; Apperley, D. C.; Cheung, M. S.; Lin, Z.; Marder, T. B. *J. Org. Chem.* **2012**, 77, 785. (e) Wu, H.; Radomkit, S.; O'Brien, J. M.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2012**, 134, 8277.
- (12) Aue, W. P.; Karhan, J.; Ernst, R. R. *J. Chem. Phys.* **1976**, 64, 4226.
- (13) (a) Hahn, E. L. *Phys. Rev.* **1950**, 80, 580. (b) Hahn, E. L.; Maxwell, D. E. *Phys. Rev.* **1951**, 84, 1246.
- (14) Massiot, D.; Fayon, F.; Deschamps, M.; Cadars, S.; Florian, P.; Montouillout, V.; Pellerin, N.; Hiet, J.; Rakhmatullin, A.; Bessada, C. *C.R. Chimie* **2010**, 13, 117.
- (15) (a) Hung, I.; Uldry, A.-C.; Becker-Baldus, J.; Webber, A. L.; Wong, A.; Smith, M. E.; Joyce, S. A.; Yates, J. R.; Pickard, C. J.; Dupree, R.; Brown, S. P. *J. Am. Chem. Soc.* **2009**, 131, 1820. (b) Barrow, N. S.; Yates, J. R.; Feller, S. A.; Holland, D.; Ashbrook, S. E.; Hodgkinson, P.; Brown, S. P. *Phys. Chem. Chem. Phys.* **2011**, 13, 5778.
- (16) Musher, J. I. *J. Chem. Phys.* **1967**, 46, 1537.
- (17) (a) Lai, W. C.; McLean, N.; Gansmüller, A.; Verhoeven, M. A.; Antonioli, G. C.; Carravetta, M.; Duma, L.; Bovee-Geurts, P. H. M.; Johannessen, O. G.; de Groot, H. J. M.; Lugtenburg, J.; Emsley, L.; Brown, S. P.; Brown, R. C. D.; DeGrip, W. J.; Levitt, M. H. *J. Am. Chem. Soc.* **2006**, 128, 3878. (b) Martineau, C.; Fayon, F.; Legein, C.; Buzaré, J.-Y.; Silly, G.; Massiot, D. *Chem. Commun.* **2007**, 2720.
- (18) Bax, A.; Freeman, R.; Frenkiel, T. A. *J. Am. Chem. Soc.* **1981**, 103, 2102.
- (19) Lesage, A.; Bardet, M.; Emsley, L. *J. Am. Chem. Soc.* **1999**, 121, 10987.
- (20) Wang, Q.; Hu, B.; Lafon, O.; Trébosc, J.; Deng, F.; Amoureux, J. P. *J. Magn. Reson.* **2009**, 200, 251.
- (21) (a) Levitt, M. H.; Madhu, P. K.; Hughes, C. E. *J. Magn. Reson.* **2002**, 155, 300. (b) Jerschow, A.; Kumar, R. *J. Magn. Reson.* **2003**, 160, 59.
- (22) Wallerand, J.-P.; du Burck, F.; Mercier, B.; Goncharov, A. N.; Himbert, M.; Bordé, Ch. *J. Eur. Phys. J. D* **1999**, 6, 63.
- (23) Bryce, D. L.; Wasylshen, R. E.; Autschbach, J.; Ziegler, T. *J. Am. Chem. Soc.* **2002**, 124, 4894.
- (24) Clegg, W.; Elsegood, M. R. J.; Lawlor, F. J.; Norman, N. C.; Pickett, N. L.; Robins, E. G.; Scott, A. J.; Nguyen, P.; Taylor, N. J.; Marder, T. B. *Inorg. Chem.* **1998**, 37, 5289.
- (25) (a) Autschbach, J. *J. Chem. Phys.* **2007**, 127, 124106. (b) Perras, F. A.; Bryce, D. L. *Can. J. Chem.* **2011**, 89, 789.