1 September 2000

Chemical Physics Letters 327 (2000) 85–90

CHEMICAL PHYSICS LETTERS

www.elsevier.nl/locate/cplett

Sensitivity enhancement of the central transition NMR signal of quadrupolar nuclei under magic-angle spinning

Zhi Yao [a], Hyung-Tae Kwak [a], Dimitris Sakellariou [b], Lyndon Emsley [b], Philip J. Grandinetti [a,*]

[a] *Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, OH 43210-1173, USA*
[b] *Laboratoire de Stéréochimie et des Interactions Moléculaires, UMR 5532 ENS-Lyon / CNRS, Ecole Normale Supérieure de Lyon, 69364 Lyon, France*

Received 1 March 2000; in final form 1 June 2000

Abstract

An approach for enhancing the NMR sensitivity of the central transition of spin-3/2 nuclei is presented. Through selective excitation of the satellite transitions using a fast 180° phase alternating pulse train during magic-angle spinning a selectively excited state is prepared where the populations of all eigenstates $|m\rangle$ with the same sign of m are equal, resulting in an enhanced central $m = -1/2 \rightarrow 1/2$ transition polarization. Numerical simulations predict enhancements up to a factor of 2 and values of 1.7 and 1.9 have been obtained experimentally for ^{23}Na in $Na_2C_2O_4$ and ^{87}Rb in $RbClO_4$, respectively. We observe no significant anisotropic lineshape distortion. The conditions for optimum enhancement are discussed. © 2000 Published by Elsevier Science B.V.

1. Introduction

In 1993 Haase and Conradi [1] proposed a method of enhancing the polarization of the central transition of half-integer spin I quadrupolar nuclei by a factor of $2I$ using selective inversion of the outer satellite transitions. This effect was demonstrated on ^{27}Al in a static single crystal of α-Al_2O_3, where the predicted enhancement factor of 5 was obtained. Using frequency swept adiabatic passages Hasse and Conradi demonstrated that a somewhat reduced enhancement of 4.1 could also be obtained in polycrystalline α-Al_2O_3. In a subsequent paper, Haase et al. [2] presented a more detailed theoretical picture to describe such polarization enhancements in static samples. Kentgens and coworkers [3,4] have examined the advantages of employing double frequency (i.e., amplitude modulated) adiabatic sweeps to not only enhance central transition polarization in static samples but also in samples undergoing magic-angle spinning (MAS), and to enhance multiple-quantum to single-quantum coherence transfer in MQ-MAS [5,6]. In the case of polarization enhancement for the central transition of ^{23}Na, where the theoretical maximum enhancement factor is 3, they obtained factors of ~ 2.7 and ~ 1.7 in Na_2SO_4 under static and MAS conditions, respectively. The reduced enhancement during MAS was explained as due to an inter-

* Corresponding author. Fax: +1-614-292-1685; e-mail: grandinetti.1@osu.edu

PII: S0009-2614(00)00805-8

ference between the frequency sweep and the transitions induced by MAS.

More recently, Mahdu et al. [7] employed an X–$\overline{\mathrm{X}}$ pulse train with the goal of enhancing multiple-quantum to single-quantum coherence transfer in MQ-MAS and obtained enhancements similar to those obtained by Kentgens and Verhagen [4]. An interesting difference in the two approaches is that Mahdu et al. maintain a constant cycle time in their X–$\overline{\mathrm{X}}$ pulse train, that is, the frequency is not swept as in the experiments of Kentgens and Verhagen [4]. In a more recent paper, Mahdu et al. [8] explain the mechanism for this enhancement as coherence transfers induced by the adiabatic motion of the rotor [9,10], a mechanism similar to that of RIACT [11], but apparently more efficient.

In light of the success of this approach for MQ-MAS we have investigated the utility of the X–$\overline{\mathrm{X}}$ pulse train in enhancing the central transition polarization in samples undergoing MAS. Such an approach has advantage over double-frequency sweeps that no special hardware is required for implementation and that the enhancements we obtain are similar than those obtained by Kentgens and Verhagen [4].

2. Experimental

All experiments were performed on a 9.4 Tesla Chemagnetics CMX II spectrometer using a Chemagnetics 4 mm MAS probe operating at a ^{23}Na frequency of 105.82652 MHz and a ^{87}Rb frequency of 130.932474 MHz. The samples used for polarization enhancement experiments were polycrystalline $Na_2C_2O_4$ and polycrystalline $RbClO_4$, which have ^{23}Na and ^{87}Rb quadrupolar coupling parameters of $C_q = 2.43$ MHz and $\eta_q = 0.77$, and $C_q = 3.3$ MHz and $\eta_q = 0.20$, respectively. Using the saturation recovery experiment the effective T_1 of 6.4 s was measured for the ^{23}Na central transition in $Na_2C_2O_4$ and 147 ms was measured for the ^{87}Rb central transition in $RbClO_4$. Experiments on $Na_2C_2O_4$ were performed using a 10 s recycle delay and spinning speeds of 6 and 12 kHz. Experiments on $RbClO_4$ were performed using a 1 s recycle delay and a spinning speed of 12 kHz. The radiofrequency (rf) field strength was calibrated using the solid-state ^{23}Na resonance of NaCl and the ^{87}Rb resonance of RbCl. The pulse sequence for enhancing the central transition polarization is shown in Fig. 1. We call this approach rotor assisted population transfer (RAPT). In practice, a 400 ns delay was inserted between each pulse in the X–$\overline{\mathrm{X}}$ pulse train of RAPT to allow time for the transmitter phase to stabilize. The X and $\overline{\mathrm{X}}$ pulse lengths were equal, and the inverse of the total time to complete one X–$\overline{\mathrm{X}}$ interval (including the 400 ns delays) is defined as the RAPT modulation frequency, ν_m.

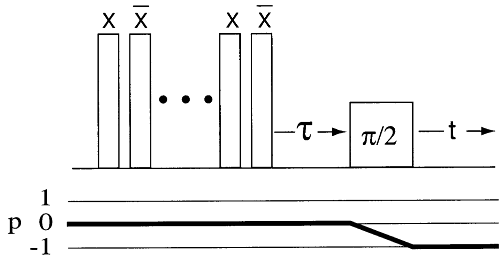

Fig. 1. Pulse sequence for RAPT from the satellites to the central transition for spin $I = 3/2$. For optimum transfer the inverse of the cycle time of the X–$\overline{\mathrm{X}}$ unit is set to $C_q/4$. Experimentally, the optimum duration of the whole pulse train was found to be approximately one rotor period.

3. Results and discussion

Comparisons of central transition spectra of ^{23}Na in polycrystalline $Na_2C_2O_4$ and ^{87}Rb in polycrystalline $RbClO_4$ with and without the RAPT preparation are shown in Fig. 2. A factor of 1.6 and 1.9 sensitivity enhancement is observed in $Na_2C_2O_4$ and $RbClO_4$, respectively. Most importantly, there appears to be no significant lineshape distortions using RAPT, implying that all crystallite orientations experience the same enhancement.

One possible mechanism for the enhancement involves the selective inversion of the satellite transitions, as depicted in Fig. 3a, by the fast amplitude modulated rf pulse, which only irradiates near the satellite transitions, and the motion of the rotor which acts to provide an adiabatic ‘sweep’. In this case, however, we would have expected significant lineshape distortions, since it is impossible, at any given time, for all crystallites to have undergone an odd number of adiabatic passages. Thus, there can-

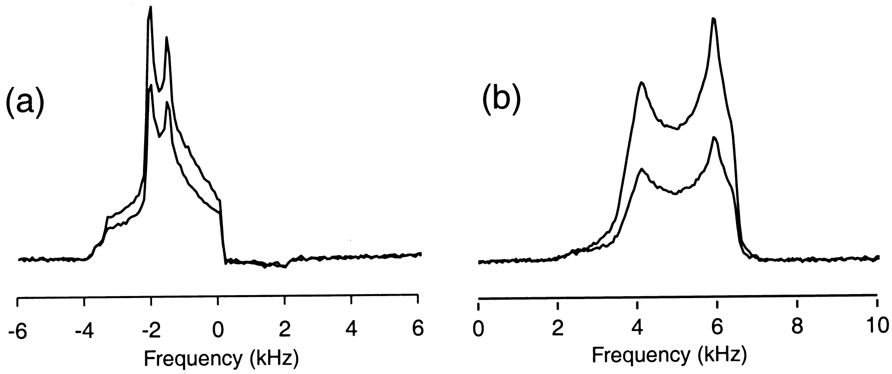

Fig. 2. A comparison of central transition spectra of (a) ^{23}Na in polycrystalline $Na_2C_2O_4$ and (b) ^{87}Rb in polycrystalline $RbClO_4$ with and without the RAPT preparation. In all cases, the spinning speed was 12 kHz, and whole echo acquisition was used to eliminate lineshape distortions due to receiver deadtime. A RAPT modulation frequency and rf amplitude of $\nu_m = 550$ kHz and $\nu_1 = 100$ kHz for $Na_2C_2O_4$ and $\nu_m = 720$ kHz and $\nu_1 = 175$ kHz for $RbClO_4$ were employed. The RAPT duration in both cases was one rotor period.

not be uniform inversion of the satellites for all crystallites using this scheme, and we would predict distortions in the anisotropic lineshapes, as some

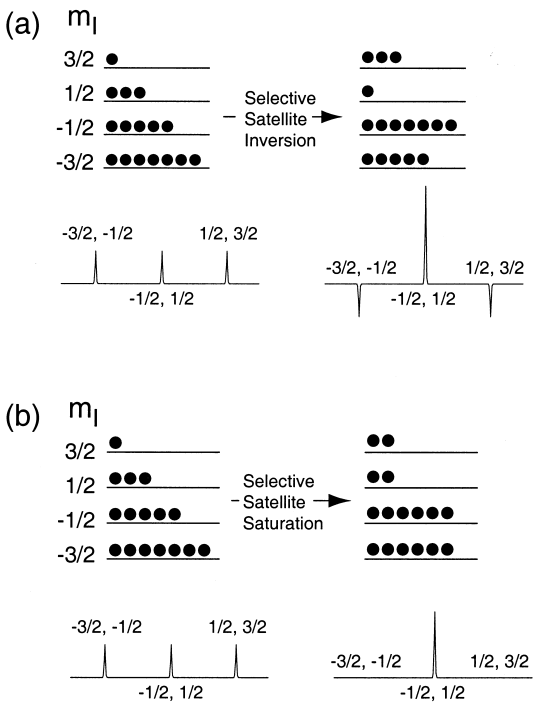

Fig. 3. (a) Selective population inversion of the satellite transitions leads to a sensitivity enhancement of the central transition by a factor of $2I$. (b) Selective excitation or saturation of the satellite transitions leads to a sensitivity enhancement of the central transition by a factor of $I+1/2$.

orientations will be enhanced by a factor of 3 and others will show no enhancement. An alternative mechanism consistent with our observations is that the enhancement is a result of an selective saturation of the satellite populations, as depicted in Fig. 3b, which occurs during the fast 180° phase alternating pulse train with MAS. Although a true selectively saturated state, which in the language of fictitious spin half operators [12,13] corresponds to

$$\langle \mathbf{I}_{x,y,z}^{1-2} \rangle = \langle \mathbf{I}_{x,y,z}^{3-4} \rangle = 0 \qquad (1)$$

in the spin-$3/2$ case, would lead to a factor of two enhancement, it is not necessary to achieve such a state to obtain the enhancement. Any selective deviation of $\langle \mathbf{I}_z^{1-2} \rangle$ and $\langle \mathbf{I}_z^{3-4} \rangle$ from equilibrium will lead to an enhancement, with the goal of RAPT being

$$\langle \mathbf{I}_z^{1-2} \rangle = \langle \mathbf{I}_z^{3-4} \rangle = 0. \qquad (2)$$

Once this condition is satisfied the populations of all eigenstates $|m\rangle$ with the same sign of m will be equal, and an enhanced central $m = -1/2 \rightarrow 1/2$ transition will be observed.

The difference in maximum enhancements between the ^{23}Na and ^{87}Rb RAPT appear to arise from the stronger homonuclear dipolar couplings among the more abundant ^{23}Na nuclei (i.e., 100% for ^{23}Na versus 27.85% for ^{87}Rb), which generate transitions between neighboring ^{23}Na nuclei, thus reducing the efficiency of the selective population equalization of levels having the same sign of m. When enhancing the polarization of the central transition by transferring polarization from the outer transitions it is also important that the outer transitions have re-equilibrated before transferring polarization again [1,14]. We investigated this as a possibility for the lesser enhancement in $Na_2C_2O_4$ by increasing the recycle delay in the RAPT sequence from 10 to 100 s and found no change in the ^{23}Na polarization enhancement.

To determine how sensitive the RAPT enhancement is to the setting of experimental parameters, we investigated its dependence on X–$\overline{\mathrm{X}}$ pulse train duration, the modulation frequency, and rf field strength. Shown in Fig. 4 is the experimental enhancement curve of the central transition spectra of ^{23}Na in $Na_2C_2O_4$ as a function of the X–$\overline{\mathrm{X}}$ pulse train duration and the predicted curves for $\langle \mathbf{I}_z^{1-2} \rangle / \langle \mathbf{I}_z^{1-2} \rangle_{eq}$, $\langle \mathbf{I}_z^{2-3} \rangle / \langle \mathbf{I}_z^{2-3} \rangle_{eq}$, and $\langle \mathbf{I}_z^{3-4} \rangle / \langle \mathbf{I}_z^{3-4} \rangle_{eq}$ based on a full density matrix numerical calculation with the same conditions as the experiment. The shape of the experimental curve for $\langle \mathbf{I}_z^{2-3} \rangle$ agrees qualitatively with the predicted curve, with the experimental enhancement maximum lying below the prediction. The simulated curves verify the selective 'saturation' hypothesis presented above, with the enhancement in $\langle \mathbf{I}_z^{2-3} \rangle$ increasing as the $\langle \mathbf{I}_z^{1-2} \rangle$ and $\langle \mathbf{I}_z^{3-4} \rangle$ expectation values approach zero.

Fig. 5a shows the experimental and theoretical dependence of the RAPT enhancement for ^{23}Na in $Na_2C_2O_4$ on the modulation frequency, ν_m. The modulation frequency was varied over a range of approximately 170–700 kHz. The maximum experimental enhancement factor of 1.67 was found using a modulation frequency of 550 kHz, a value not far from $C_q/4 = 607.5$ kHz. Because of hardware constraints, we were not able to experimentally explore modulation frequencies beyond 700 kHz. Also shown in Fig. 5a, are numerical simulations which predict that the enhancement is diminished at higher modulation frequencies and drops to one for $\nu_m \geqslant C_q/2$, which in the case of $Na_2C_2O_4$ is 1215 kHz.

Finally, we experimentally varied the rf field strength over a range of 10–100 kHz at spinning speeds of $\nu_R = 12$ and $\nu_R = 6$ kHz. These data along with theoretical predictions are shown in Fig. 5b. The enhancement decreases with decreasing rf field strength, and at very low rf field strengths there is no enhancement. Although it would be technically difficult to experimentally explore very high rf field strengths, numerical simulations shown in Fig. 5b predict that the enhancements would eventually di-

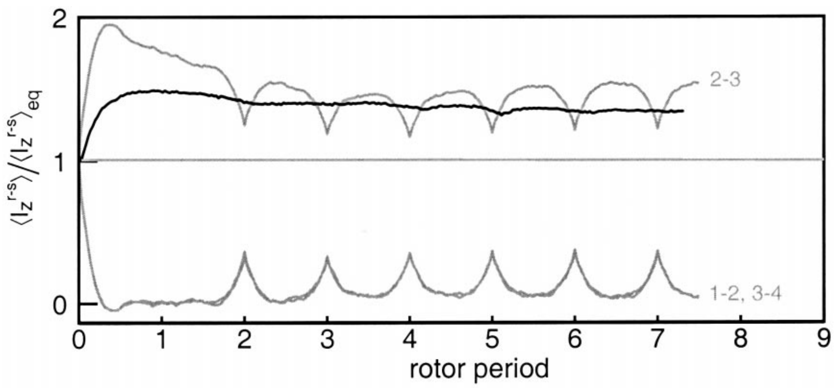

Fig. 4. Dependence of ^{23}Na central transition signal enhancement in $Na_2C_2O_4$ on the duration of the X–$\overline{\mathrm{X}}$ pulse train in the RAPT sequence of Fig. 1 expressed in units of rotor period. The curves in grey are the simulated expectation values of the fictitious spin half operator $\mathbf{I}_z^{r-s}$ scaled by their equilibrium expectation values for the 1–2, 2–3, and 3–4 transitions. The curve in black is the experimental $\langle \mathbf{I}_z^{2-3} \rangle / \langle \mathbf{I}_z^{2-3} \rangle_{eq}$ value measured by a selective $\pi/2$ pulse on the central transition. In both experiment and simulation a rf field strength of $\nu_1 = 101$ KHz was employed during the X–$\overline{\mathrm{X}}$ pulse train, with a modulation frequency of $\nu_m = 427$ KHz, and a spinning frequency of 12 KHz. With this combination there are approximately 35 X–$\overline{\mathrm{X}}$ cycles within about one rotor period. Optimum transfer appears to occur experimentally after one rotor period. The experimental time interval between the pulse train and acquire pulse was $\tau = 50$ ms, and the recycle delay was 10 s. The simulations were based on a full density matrix calculation and were averaged over 3722 crystallite orientations.

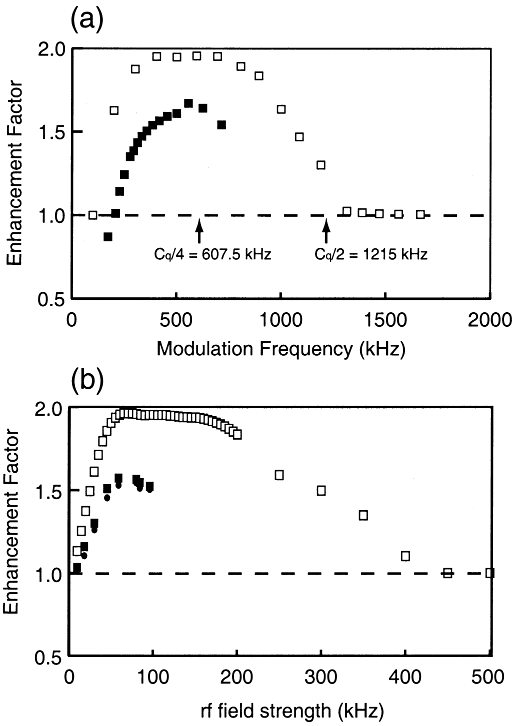

Fig. 5. (a) Dependence of maximum RAPT enhancement on the modulation frequency. Filled squares show the experimental dependence for the ^{23}Na central transition in $Na_2C_2O_4$. For each point a series of experiments were performed with the total number of X–$\overline{\mathrm{X}}$ cycles varied in order to find the maximum enhancement. The modulation frequency, ν_m, is defined as the inverse of the total time to complete one X–$\overline{\mathrm{X}}$ interval. The ν_1 field strength was held constant at 101 kHz. The sample spinning frequency was 12 kHz. Open squares show the predicted dependence of maximum signal enhancement on modulation frequency. Spinning speeds were varied slightly in order to maintain integral relationships between the X–$\overline{\mathrm{X}}$ cycle time and the rotor period. The (ν_m, ν_R) frequency pairs were (100,11.11), (200,11.11) (301.205,10.76), (403.2,10.61), (500,10.42), (595.2,10.26), (694.4,10.21), (806.5,10.21), (892.9,10.15), (1000,10.10), (1087,10.06), (1190,10.00), and (1316,9.97) kHz. (b) Dependence of signal enhancement on rf field strength with a fixed RAPT modulation frequency of $\nu_m = 550$ kHz. Filled squares and circles correspond to experimental data collected for the ^{23}Na central transition in $Na_2C_2O_4$ with $\nu_R = 12$ kHz and $\nu_R = 6$ kHz, respectively. Open squares show the predicted dependence of maximum signal enhancement on the rf field strength with $\nu_m = 550$ kHz and $\nu_R = 12$ kHz. All simulations were averaged over 3722 crystallite orientations.

minish as one approaches the higher rf field strengths where the excitation of the central and satellite transitions are no longer selective.

4. Conclusion

Using a simple X–$\overline{\mathrm{X}}$ pulse train with MAS we have shown that the sensitivity of the NMR signal for the central transition of spin-3/2 nuclei can be enhanced without significant anisotropic lineshape distortions by transferring polarization from the outer transitions via a selective excitation of the satellite transitions. The relevant parameters in optimizing the RAPT enhancement are the rf field strength and modulation frequency. The optimum modulation frequency appears to be on the order of $\nu_m = C_q/4$ for a spin-3/2 nucleus, and may vary slightly depending on the value of η_q. We also found that the enhancement gradually increased with increasing rf field strength, and through numerical simulations we predict that the enhancement will diminish as one approaches the higher rf field strengths where the excitation of the central and satellite transitions are no longer selective. Importantly, the enhancement factors are not critically sensitive to the X–$\overline{\mathrm{X}}$ pulse train modulation frequency or the rf amplitude, yielding a simple experimental protocol. Experimental enhancement factors of 1.7 were obtained in the case of the central transition of ^{23}Na in $Na_2C_2O_4$, and 1.9 in the case of ^{87}Rb in $RbClO_4$. Numerical simulations predict that a maximum enhancement factor of 2 is possible. The less than optimal enhancements observed in $Na_2C_2O_4$ appear to arise from homonuclear dipolar couplings, which act to reduce the efficiency of the selective equalization of populations among levels having the same sign of m. Extension of these ideas to higher spin quadrupolar nuclei with greater enhancements is possible, and in general, a theoretical maximum enhancement factor of $I + 1/2$ can be obtained with selective excitation of the all satellite transitions.

Acknowledgements

This work was supported in part by a grant from the National Science Foundation (No. CHE-9807498). We thank Dr. Joseph Sachleben and Dr. Stefano Caldarelli for helpful discussions. P.J.G. also acknowledges support from the ENS Lyon for a visiting professorship during the early part of this work.

References

[1] J. Haase, M.S. Conradi, Chem. Phys. Lett. 209 (1993) 287.
[2] J. Haase, M.S. Conradi, C.P. Grey, A.J. Vega, J. Magn. Reson. A 109 (1994) 90.
[3] E.V. Veenendaal, B.H. Meier, A.P.M. Kentgens, Mol. Phys. 93 (1998) 195.
[4] A.P.M. Kentgens, R. Verhagen, Chem. Phys. Lett. 300 (1999) 435.
[5] L. Frydman, J.S. Harwood, J. Am. Chem. Soc. 117 (1995) 5367.
[6] A. Medek, J.S. Harwood, L. Frydman, J. Am. Chem. Soc. 117 (1995) 12779.
[7] P.K. Madhu, A. Goldbourt, L. Frydman, S. Vega, Chem. Phys. Lett. 307 (1999) 41.
[8] P.K. Madhu, A. Goldbourt, L. Frydman, S. Vega, J. Chem. Phys. 112 (2000) 2377.
[9] A.J. Vega, J. Magn. Reson. 96 (1992) 50.
[10] J.H. Baltisberger, S.L. Gann, P.J. Grandinetti, A. Pines, Mol. Phys. 81 (1994) 1109.
[11] G. Wu, D. Rovnyak, R.G. Griffin, J. Am. Chem. Soc. 118 (1996) 9326.
[12] S. Vega, J. Chem. Phys. 68 (1978) 5518.
[13] A. Wokaun, R.R. Ernst, J. Chem. Phys. 67 (1977) 1752.
[14] J. Haase, M.S. Conradi, E. Oldfield, J. Magn. Reson. A 109 (1994) 210.