Journal of Magnetic Resonance **148,** 455–458 (2001)
doi:10.1006/jmre.2000.2270, available online at http://www.idealibrary.com on IDEAL®

NMR Spectra of a Spin-1/2 Nucleus Scalar Coupled to Two Equivalent Spin-1 Nuclei in the Limit of Slow Quadrupolar Relaxation

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Received August 11, 2000; revised November 17, 2000

As was pointed out in our earlier work (*1*), the spectrum of a spin-1/2 nucleus scalar coupled to a group of magnetically equivalent nuclei of spin $> 1/2$ can be dependent on the scalar couplings between such nuclei. Such a disturbance of magnetic equivalence is predicted from the Bloch–Wangsness–Redfield (BWR) theory (*2, 3*) when spin relaxation of the equivalent nuclei is nonnegligible. When the values of the coupling constants between the latter are unknown, effects of such a disturbed magnetic equivalence may be a source of a systematic bias in a quantitative analysis of the spectra. These theoretical predictions were recently confirmed by our experimental studies on the 2,1,3-benzoselenadiazole molecule (*4*). We have found that the cross-correlation quadrupolar spectral density for the equivalent ^{14}N nuclei, obtained from iterative lineshape fits of the experimental spectra, shows a significant dependence on the value of $J(^{14}\text{N}–^{14}\text{N})$ assumed in the calculations (*4*). We therefore had to assess the magnitude of the latter in an independent measurement involving the ^{14}N–^{15}N isotopomer. In a study on quadrupolar cross-correlation in a $^{13}CD_2$ spin system, Werbelow *et al.* (*5*) reported an approximate, closed-form expression for the lineshape of the spin-1/2 nucleus for the limiting case where quadrupolar relaxation rates of the equivalent spin-1 nuclei are small in comparison with the heteronuclear *J*-coupling constant, in which instance the multiplet (pentet) of the spin-1/2 nucleus remains well resolved. However, such a simplification was achieved at the cost of a neglect of the possible effects of disturbed magnetic equivalence on the lineshape. In the present contribution, we specify the range of validity of the above approximation and identify the instances of practical significance where it fails in the description of resolved spectra of a general AX_2 ($I_A = 1/2$, $I_X = 1$) system. Our discussion will involve the case in which relaxation mechanisms other than quadrupolar can be neglected in the description of spin dynamics in the zero-quantum manifold of subsystem X_2. Validity of the extreme narrowing approximation is assumed for the quadrupolar relaxation.

In our formal considerations we will use the same Hilbert space basis as in Refs. (*1, 5*). It comprises 9 vectors $|\alpha)|SM)$ and 9 vectors $|\beta)|SM)$, where $|\alpha)$ and $|\beta)$ are eigenvectors of $\hat{I}_z$, and $|SM)$ are the simultaneous eigenvectors of the squared total *X*-spin, $\hat{\mathbf{S}}^2 = (\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2)^2$, and the total *X*-spin *z*-component, $\hat{S}_z = \hat{S}_{z1} + \hat{S}_{z2}$, operators, concerned with eigenvalues $S(S + 1)$ ($S = 0$, 1, and 2), and $M = -2S, -2S + 1, \ldots, 2S$, respectively. The vectors $|\gamma)|1M)$ are antisymmetric while those $|\gamma)|2M)$ and $|\gamma)|0M)$ are symmetric under permutation of the *X* nuclei. If there were no permutation symmetry (i.e., "macroscopic symmetry" (*6*)) between the *X* nuclei, the manifold relevant to the single-quantum spectra of *A* would include all of the 19 coherences $|I_+\rangle|SMS'M\rangle$, where $|I_+\rangle \equiv |\alpha)(\beta|$, and $|SMS'M\rangle \equiv |SM)(S'M|$, that engage all pairs of *X* states concerned with the same eigenvalue of $\hat{S}_z$. If, as in the instance considered presently, such a symmetry does occur (what, as ought to be emphasized again, does not imply conservation of magnetic equivalence of the *X* nuclei (*1*)), one can discard all of the 8 coherences combining pairs of states that transform differently under permutation of the *X* nuclei. By virtue of macroscopic symmetry invariance obeyed by the BWR relaxation matrix (*6*), such coherences are uncoupled from ones engaging pairs of same-symmetry states and are never observed. Hence, in the system considered, the relevant manifold is spanned by 11 symmetry-allowed coherences. For 9 of the latter, those described by the superkets $|I_+\rangle|SMSM\rangle$, the total spin of the *X* subsystem is a good quantum number. For the remaining two, $|I_+\rangle|2000\rangle$ and $|I_+\rangle|0020\rangle$, the total *X* spin is not conserved. Coherences of the latter type, which involve breaking of magnetic equivalence, were once termed "partly allowed coherences" (*1*) because for negligibly slow relaxation they become irrelevant: when they are effectively uncoupled from the remaining, "fully allowed" coherences, they become undetectable in NMR experiments as being perfectly orthogonal to the magnetization observables, $|I_u\rangle|E_X\rangle$ in the present notation, where $u = x, y, z$, and $\hat{E}_X$ is unit operator for subsystem *X*. However, for finite relaxation rates, including the presently considered limit of slow relaxation,

$$2\pi|J_{AX}| \gg 1/T_{1Q} \geq w, \qquad [1]$$

where $w = 1/T_2^*$ describes an "extraneous" (i.e., caused by

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1090-7807/01 $35.00

factors other than quadrupolar relaxation of the X nuclei) broadening of the A reasonances, these offending coherences can be relevant. This becomes evident when one considers the structure of the 11×11 BWR spectral matrix describing the lineshape of A. Its real part comprises the 0-quantum block of the BWR quadrupolar relaxation matrix, with the diagonal elements augmented by w. The imaginary part is a diagonal matrix. Nine of its elements, those concerned with the superkets $|I_+\rangle|SMSM\rangle$, describe the individual frequencies of the A pentet, $-i(\omega_{0A} + 2\pi MJ_{AX})$; for $|M| = 0$ and 1 these elements are three- and twofold degenerate, respectively. The elements concerned with the superkets $|I_+\rangle|2000\rangle$ and $|I_+\rangle|0020\rangle$ are $-i(\omega_{0A} + 6\pi J_{XX})$ and $-i(\omega_{0A} - 6\pi J_{XX})$, respectively. For slow relaxation, the impact of the coherences with broken magnetic equivalence can be nonnegligible when their frequencies happen to coincide, to within a few quadrupolar relaxation rate constants, with those of the individual pentet components. If there are no such coincidences, in a description of the spectra of A one can retain only the 9×9 block of the spectral matrix, concerned with the magnetic-equivalence-conserving coherences. In view of Eq. [1], this retained part undergoes a further approximate factoring into independent subblocks according to the degeneration pattern of its imaginary (diagonal) elements: each of the two outer components of the pentet will then be described by a 1×1 subblock, each of the two inner components by a 2×2 subblock, and the central component by a 3×3 subblock. Werbelow *et al.* (*5*) found the latter to be further factored into 1×1 and 2×2 sub-subblocks, which allowed these authors to derive closed-form lineshape expressions for each of the individual components of the pentet in the limit of slow quadrupolar relaxation.

Below we give the corresponding limiting lineshape equations, in matrix forms, in the instances where the frequencies of the coherences with broken magnetic equivalence coincide with the frequencies of (i) the outer componets, (ii) the inner components, and (iii) the central component. In writing down the lineshape formulas involved we exploit the fact that the spectra of the system considered are independent of the absolute and relative signs of J_{AX} and J_{XX} (*4, 6*). For the sake of compactness, in the equations presented below the quantities $2\pi|J_{AX}|$ and $2\pi|J_{XX}|$ will be denoted by a and x, respectively, and the quantity $\omega_{0A} - \omega$ by $\Delta\omega$. The quadrupolar auto- and cross-correlation spectral densities, j and k, respectively, expressed in rad s^{-1}, are calibrated according to Ref. (*7*), so that $20j = 1/T_{1Q}$. The relevant spectral submatrices listed below contain explicit expressions for all of the BWR relaxation matrix elements which in the full 11×11 spectral matrix describe couplings between the two coherences with broken magnetic equivalence and the remaining coherences.

Thus, in case (i), each of the outer components will be described by

$$Y_0(\omega) = [1\ 0] \times \begin{bmatrix} i(\Delta\omega \pm 2a) + w + 24j & -8\sqrt{2}(j+k)/3 \\ -8\sqrt{2}(j+k)/3 & i(\Delta\omega \pm 3x) + w + (80j + 44k)/3 \end{bmatrix}^{-1} \times \begin{bmatrix} 1 \\ 0 \end{bmatrix}. \quad [2]$$

In case (ii), the corresponding equation for each of the inner components reads

$$-Y_i(\omega) = [1\ 1\ 0] \times \begin{bmatrix} i(\Delta\omega \pm a) + w + 26j + 2k & -6(j-k) & 4\sqrt{2}(j+k)/3 \\ -6(j-k) & i(\Delta\omega \pm a) + w + 26j - 14k & 0 \\ 4\sqrt{2}(j+k)/3 & 0 & i(\Delta\omega \pm 3x) + w + (80j + 44k)/3 \end{bmatrix}^{-1} \times \begin{bmatrix} 1 \\ 1 \\ 0 \end{bmatrix}. \quad [3]$$

Finally, in case (iii), one of the two subcomponents of the central signal will be described by

$$-Y_{C'}(\omega) = [1\ 1\ 0\ 0] \times \begin{bmatrix} i\Delta\omega + w + 80(j+k)/3 & -16(j+k)/3 & 0 & 0 \\ -16(j+k)/3 & i\Delta\omega + w + 24j & 8\sqrt{2}(j+k)/3 & 8\sqrt{2}(j+k)/3 \\ 0 & 8\sqrt{2}(j+k)/3 & i(\Delta\omega + 3x) + w + (80j + 44k)/3 & -16(j+k)/3 \\ 0 & 8\sqrt{2}(j+k)/3 & -16(j+k)/3 & i(\Delta\omega - 3x) + w + (80j + 44k)/3 \end{bmatrix}^{-1} \times \begin{bmatrix} 1 \\ 1 \\ 0 \\ 0 \end{bmatrix} \quad [4a]$$

while the other will remain unaffected by the coherences with broken magnetic equivalence, and thus (*5*)

$$-Y_{C''}(\omega) = (i\Delta\omega + w + 24j - 16k)^{-1}. \qquad [4b]$$

When the above equations are to be used in practical lineshape calculations, numerical problems may arise when the spectra are calculated using the standard approach of numerical diagonalization of the spectral matrix. This is because, especially for Eq. [4a] when the magnitude of J_{XX} is much smaller than $1/\pi T_{1Q}$, the matrices to be diagonalized are only in a trivial way different from real symmetric matrices. For matrices of such a form, the standard numerical routines designed to handle complex matrices usually calculate correct eigenvalues but incorrect eigenvectors. The numerical calculations to be referred to in the following were performed using a numerically stable method of matrix inversion (*8*). A similar warning pertains to numerical calculations of the resolved spectra using the complete 11×11 matrix.

Note that the relaxation-mediated couplings between the coherences with conserved and broken magnetic equivalence, entering Eqs. [2]–[4], would vanish only in a nonphysical situation where the fluctuating quadrupolar interactions at the *X* nuclei were perfectly anti-correlated, in which instance the corresponding cross-correlation factor $r = k/j$ would be equal to -1. Note also that for a perfect cross-correlation ($r = 1$), impact of the coherences with broken equivalence on the lineshape of *A* will attain a maximum. The latter observation brings out the difference, exposed in detail in Ref. (*1*), between the notion of microscopic conservation of nuclear permutation symmetry (*6*) (which does apply to the system considered when $r = 1$) and that of conservation of magnetic equivalence symmetry. Note at the end that the couplings between the equivalence-conserving and equivalence-breaking coherences do survive even when the two *X* nuclei do not "sense" each other directly, i.e., when both J_{XX} and r happen to vanish.

The situation to which Eq. [4] is referred to is likely to be encountered in practice, especially for $^{13}CD_2$ spin groupings, since the corresponding deuterium–deuterium *J*-coupling constants are generally of the order of a fraction of a hertz and therefore fall in the range of deuterium quadrupolar relaxation rates in liquids of moderate viscosity. Experimental studies on quadrupolar cross-correlations in such a system in perdeuterated ethylene glycol are reported in Ref. (*5*). The observed specta were described in terms of the equivalence-conserving coherences only. Within such a simplified approach, the authors cited could in a unique way relate the ratios of the heights of the central and inner peaks of the pentet to those of the outer peaks, h_c/h_o and h_i/h_o, respectively, to both the cross-correlation factor, r, and the "extraneous" relaxation rate expressed in units of j, $\rho = w/j$. The observed departures of the above lineshape parameters from their respective limiting 3:1 and 2:1 values (attainable in the limit of negligible quadrupolar relaxation) were proposed as quick measures of r in the instances where the magnitude of ρ could be determined independently. Below we show that this generally useful approach may be prone to substantial errors when applied to systems with small or vanishing J_{XX} coupling constants. In Fig. 1 two pairs of h_c/h_o curves as functions of r are displayed. In the calculations, the values of J_{AX} (21.5 Hz) and w/π (0.52 Hz) were assumed according to the findings for deuterated ethylene glycol reported in Ref. (*5*). In each pair, the solid curve was calculated according to Eq. [4] in which the value of J_{XX} was put equal to 0.24 Hz, which is probably the maximum value for the geminal deuterium pair in ethylene glycol (*9*) that could be expected. The dashed curve is calculated from Eq. [17] of Ref. (*5*), which gives the same results as our Eqs. [2] and [4] when a large value (but different from $2J_{AX}/3$) is substituted for J_{XX} in the latter equations. The bottom pair corresponds to the value of $j(T = 323\ \text{K}) = 0.217$ rad s^{-1} reported in Ref. (*5*). The top pair was obtained assuming $j = 0.434$ rad s^{-1}. The display in Fig. 1 is limited to the values of r above -0.75. A consideration of the predictions based on the rotational diffusion model of molecular reorientations (*10*) allows one to conclude that strongly negative values of r are unlikely to be encountered in practice. The corresponding pairs of h_i/h_o curves are not shown because in the case considered (the coherences with broken magnetic equivalnece interfering with the central component) our formalism would merely reproduce the results of (*5*).

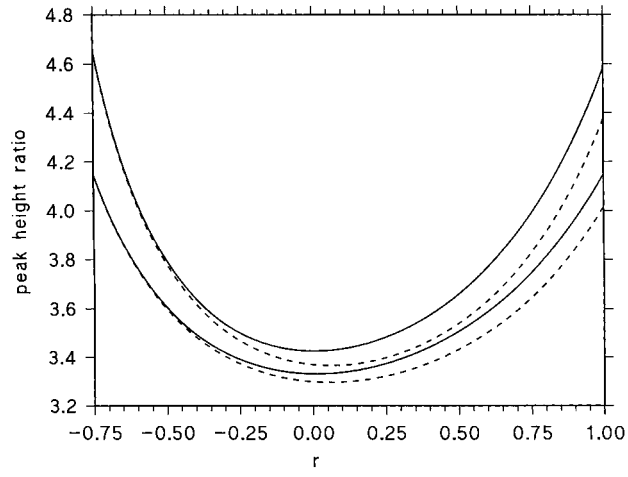

FIG. 1. Theoretical dependences on the quadrupolar cross-correlation factor of the height ratios of the central and outer components in the *A* pentet in the AX_2 spin system, calculated with (solid lines) and without taking into account the impact of the coherences with broken magnetic equivalence on the lineshape. The calculations were performed for $J_{AX} = 21.5$ Hz, and the extraneous line broadening $w/\pi = 0.52$ Hz. The solid curves were calculated assuming $J_{XX} = 0.24$ Hz; for the top and bottom pairs of curve, the values of $j = (1/20T_{1Q})$ are 0.434 and 0.217 rad s^{-1}, respectively.

Inspection of Fig. 1 reveals that for the system mentioned above the neglect of the coherences with broken magnetic equivalence may impose a systematic bias on the assessment of r based on the lineshape parameter h_c/h_o. This is clearly seen

if we compare the maximum difference between the corresponding values of h_c/h_o, calculated with and without taking into account the latter coherences, with the range of variations of this parameter in the displayed range of r. (Although the maximum difference generally occurs for r approaching 1, it is an adequate measure of the effect discussed since for r values above 0.5 both the curves go nearly parallel to each other.) For the top pair of curves, the maximum difference amounts to about 13% of the whole variability range, and it is increased to about 18% when the parameter h_c/h_o is calculated assuming $J_{XX} = 0$. For the bottom pair, the corresponding figures are 12 and 20%. The latter value is close to an upper limit of the discrepancies between the peak height ratios calculated in these two ways. For the sake of transparency, the h_c/h_o curves calculated assuming $J_{XX} = 0$ are not shown in Fig. 1. Because even minor changes in the values of J_{XX} can lead to such significant variations of the course of the h_c/h_o curves, in order to get an unbiased estimate of r from the peak height ratio in resolved spectra a very precise knowledge of the magnitude of J_{XX} may be required.

It can also be seen from the displayed curves that when the true value of J_{XX} is comparable with the quadrupolar relaxation rate, the assessments based on the approximate theory will generally deliver overestimated values of $|r|$. A similar conclusion can be drawn regarding the use of the approximate lineshape equations in iterative analysis of the resolved spectra. Only in the instances where the true value of r falls below -0.3, does the approximate approach become essentially equivalent to the exact approach, which was already anticipated from the form of the pertinent off-diagonal matrix elements in Eq. [4a].

The tendency to overestimate $|r|$ we also observed in our studies on 2,1,3-benzoselenadiazole (*4*), where we analyzed unresolved ^{77}Se spectra, obtained under conditions of moderate quadrupolar relaxation rates of the equivalent ^{14}N nuclei, using the complete BWR lineshape equation. For example, for the experiment at 393 K, an iterative lineshape fit, performed with an assumed (i.e., not optimized) large value for J_{NN}, which amounts to a neglect of the coherences with broken magnetic equivalence, delivered for r the value of 0.52 ± 0.02 while for $|J_{NN}| < 5$ Hz, which is a realistic assumption, the corresponding estimate was 0.10 ± 0.21. The latter value is in good agreement with the prediction based on both quantum chemical calculations of the relevant electic field gradient tensors and the assumption of isotropic reorientation. Generally, knowledge of the value of the coupling constant between the equivalent quadrupolar nuclei is a prerequisite for an unbiased assessment of the quadrupolar cross-correlation factor. In the limit of slow quadrupolar relaxation, use of the convenient, closed-form lineshape formulas of Ref. (*5*) must be restricted to cases in which the frequency gap between the equivalence-conserving and equivalence-breaking coherences (controlled by the magnitude of J coupling between the equivalent nuclei) is large compared to the quadrupolar relaxation rate and/or to such cases where it is a priori known that the value of r is strongly negative.

ACKNOWLEDGMENT

We are grateful to Professor L. G. Werbelow for insightful comments.

REFERENCES

1. S. Szymański, *J. Magn. Reson.* **127,** 199 (1997).
2. R. K. Wangsness and F. Bloch, *Phys. Rev.* **89,** 728 (1953); F. Bloch, *Phys. Rev.* **102,** 204 (1956); *Phys. Rev.* **105,** 1206 (1957).
3. A. G. Redfield, *Adv. Magn. Reson.* **1,** 1 (1965).
4. P. Bernatowicz, O. Bjørlo, E. H. Mørkved, and S. Szymański, *J. Magn. Reson.* **145,** 152 (2000).
5. G. Werbelow, G. A. Morris, P. Kumar, and J. Kowalewski, *J. Magn. Reson.* **140,** 1 (1999).
6. S. Szymański, A. M. Gryff-Keller, and G. Binsch, *J. Magn. Reson.* **68,** 399 (1986).
7. G. Werbelow, *in* "Encyclopedia on Nuclear Magnetic Resonance" (D. M. Grant and R. K. Harris, Eds.), p. 4092, Wiley, Chichester (1996).
8. S. Szymański and A. Gryff-Keller, *J. Magn. Reson.* **16,** 182 (1974).
9. H. Günther, "NMR Spectroscopy: An Introduction," Chap. 4, Wiley, Chichester (1980).
10. D. Canet, *Concepts Magn. Reson.* **10,** 291 (1998).