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Magnetic Equivalence between Nuclei of Spin Greater than $\frac{1}{2}$ in Presence of Relaxation

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Both formal reasoning and numerical calculations of spectral lineshape functions confirm that magnetic equivalence between nuclei of spin greater than $\frac{1}{2}$ is generally broken in presence of relaxation. This results in a dependence of the lineshape functions on the values of *J*-couplings between the nuclei that would be equivalent in absence of relaxation. Effects of this sort may be of practical importance for systems A_nX, where the *A* nuclei are relaxed by quadrupolar interactions which are highly cross-correlated at different *A* sites. © 1997 Academic Press

The concept of magnetic equivalence, formulated in the early days of high-resolution NMR (*1*), has further given rise to a common view that *J*-couplings between equivalent nuclei are totally irrelevant. However, in the framework of the standard NMR theory (*2*) a rigorous discussion of magnetic equivalence comprises only the so called ''static limit,'' with no account for random modulations of the spin energy. Both theoretical analysis and numerical calculations reported in our previous papers (*3, 4*) showed that random nuclear exchange may in some cases cause a breakdown of the ''static'' magnetic equivalence (*3*). Namely, certain transitions that are strictly forbidden in the static limit may gain nonzero intensity due to an exchange-induced coupling to the remaining, ever-allowed transitions. It is these former transitions that can make the dynamic NMR spectra dependent on the *J*-couplings between equivalent nuclei. Similar breaking of magnetic equivalance can be effected by certain NMR relaxation mechanisms (*5*). Our previous simulations (*3, 4*) performed for nuclear exchange reveal that the equivalence breaking can cause extra problems in practical lineshape analysis. The corresponding lineshape effects are too large to be generally ignored but usually too small and too unspecific to be used for an assessment of scalar interactions within magnetically equivalent groups. Fortunately, for equivalent groups comprising two and three spin-$\frac{1}{2}$ nuclei, these additional difficulties disappear. For such groups the respective nuclear permutation symmetries, C_2 and D_3, make the offending couplings irrelevant in every instance, regardless of what sort of exchange and/or relaxation mechanism is operative (*3, 5*). This is ultimately due to the fact that for a pair of like nuclei of spin-$\frac{1}{2}$ the *J*-coupling Hamiltonian $J_{jk}\mathbf{I}_j\mathbf{I}_k$ can be expressed in terms of permutation operator interchanging nuclei *j* and *k* (*6*). The *J*-coupling between nuclei *j* and *k* is totally irrelevant when interchange of *j* and *k* is a valid symmetry operation (macroscopic symmetry operation, see (*5, 7*)) on the molecular skeleton (*3, 5*). However, for nuclei of spin greater than $\frac{1}{2}$ the *J*-coupling Hamiltonian cannot be described by a permutation operator and, accordingly, the above property does not apply. In the present contribution we briefly address the problem of magnetic equivalence between such nuclei in presence of relaxation. We consider spin systems A_n and A_nX, where $I_A > \frac{1}{2}$ and $I_X = \frac{1}{2}$, undergoing relaxation in the extreme narrowing regime.

THEORETICAL BACKGROUND

The high-resolution spin Hamiltonian of any system containing magnetically equivalent group A_n commutes with the operator of the square of the total spin of A_n, $\mathbf{F}_A^2$ (*2*). It follows that *J*-couplings within A_n can be regarded as totally irrelevant as long as the focus is only on the ''stick'' pattern of the spectrum, and the lineshape effects different than those due to field inhomogeneity are neglected. Moreover, the spectrum can be viewed as a superposition of stick spectra of independent spin isomers.

When relaxation effects are included, the system dynamics is no longer governed by the sole spin Hamiltonian but by the combined action of the latter and the Wangsness–Bloch–Redfield (WBR) relaxation matrix (*8, 9*) according to the WBR equation

$$d|\rho\rangle/dt = -i\mathbf{L}|\rho\rangle + \mathbf{R}|\rho - \rho_0\rangle, \qquad [1]$$

where $\mathbf{L} = H \times E^* - E \times H^*$ is the system super-Hamiltonian derived from the spin Hamiltonian H. Accordingly, instead of $\mathbf{F}_A^2$, the constant of motion describing magnetic equivalence in Liouville representation is the derivation su-

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peroperator of $\mathbf{F}_A^2$, $\mathbf{F}_A^{2D} = \mathbf{F}_A^2 \times E^* - E \times \mathbf{F}_A^{2*}$. Obviously, the latter must commute with $\mathbf{L}$ given that the former commutes with H but the commutativity need not automatically extend to $\mathbf{R}$. The discussion of magnetic equivalence in presence of relaxation requires thus a modified approach. As an introduction into the problem we consider a hypothetical instance where $\mathbf{F}_A^{2D}$ does commute with $\mathbf{R}$ in consequence of which the static concept of magnetic equivalence retains its full validity also in this more general contex. In order that the commutativity be ensured, the equivalent nuclei should remain such also at the microscopic level. In other words, the random interactions leading to relaxation ought to be describable in terms of the total spin of the equivalent group. This would be feasible for the familiar random-field (RF) interactions (*9*) if the fields fluctuating at individual sites of the A nuclei happened to be perfectly correlated. Such perfect correlation does not seem physically possible, perhaps except for an apparent RF mechanism deriving from spin-rotation interactions. On the other hand, the fluctuations need not be spatially isotropic. In a general (i.e., anisotropic) case, the corresponding relaxation matrix, $\mathbf{R}'_{\mathrm{RF}}$, where the prime is used to designate perfect correlation of the RF interactions, can be expressed as (see, e.g., Ref. (*7*))

$$\mathbf{R}'_{\mathrm{RF}} = -F^{\mathrm{D}}_{zA}F^{\mathrm{D}}_{zA}a - \tfrac{1}{2}(F^{\mathrm{D}}_{+A}F^{\mathrm{D}}_{-A} + F^{\mathrm{D}}_{-A}F^{\mathrm{D}}_{+A})b, \quad [2]$$

where F_{uA}, with u standing for z, $+$, and $-$, are the corresponding components of total spin of A_n, and superscript D denotes derivation superoperator; the quantities a and b are the spectral densities of the fluctuating magnetic field. The commutativity of $\mathbf{R}'_{\mathrm{RF}}$ with $\mathbf{F}_A^{2\mathrm{D}}$ is a straightforward consequence of the commutativity of $\mathbf{F}_A^2$ with each of the total spin components F_{uA}. As in the case of static equivalence, the system evolution will be described by the block of $-i\mathbf{L} + \mathbf{R}'_{\mathrm{RF}}$ concerned with eigenvalue 0 of $\mathbf{F}_A^{2\mathrm{D}}$. Because not only $\mathbf{F}_A^{2\mathrm{D}}$ but its left- and right-translation components, $\mathbf{F}_A^{2\mathrm{L}} = \mathbf{F}_A^2 \times E^*$ and $\mathbf{F}_A^{2\mathrm{R}} = E \times \mathbf{F}_A^{2*}$, commute with $-i\mathbf{L} + \mathbf{R}'_{\mathrm{RF}}$, this block will be blocked out further into independent subblocks concerned with individual eigenvalues $l^{\mathrm{L}} = l^{\mathrm{R}} \equiv l$ of the latter superoperators. These eigenvalues label individual spin isomers of A_n. The above formalism allows one to see that the static magnetic equivalence would indeed be conserved for any spin system containing group A_n provided that relaxation behavior of the latter be describable by the matrix of Eq. [2]. (Some formal problems which arise for groups composed of more than 2 nuclei (*3*) will not be considered here because they do not affect the validity of the above conclusion.)

From a formal point of view, the conservation of equivalence would be warranted when the relevant relaxation matrix could be expressed in terms of arbitrary multipoles of the total spin of A_n. However, to the author's knowledge, relaxation mechanisms involving the multipoles other than the dipole entering Eq. [2] are purely hypothetic. For the mechanisms that may be of practical significance, including the RF mechanism with imperfect correlation, $\mathbf{R}$ and $\mathbf{F}_A^{2\mathrm{D}}$ do not commute. In the following section it will be demonstrated that such a lack of commutativity means a breakdown of magnetic equivalence. The most spectacular consequence of such a breakdown is the fact that J-couplings within A_n group become spectroscopically relevant. In the present section we consider two instances where despite the lack of commutativity of $\mathbf{R}$ and $\mathbf{F}_A^{2\mathrm{D}}$ one can still speak of some sort of magnetic equivalence. In both the instances an isolated isochronous group A_n is dealt with.

First we consider such a group where at the microscopic level the relaxation interactions involve *single* nuclei and not nuclear pairs, as is in the case of dipole–dipole (DD) interactions. As was once shown by Pyper (*10*), for the former mechanisms the individual components, F_{zA} and $F_{\pm A}$, of the total spin of the system are eigenoperators of the WBR relaxation matrix concerned with eigenvalues $1/T_1$ and $1/T_2$, respectively; these eigenvalues are independent of the possible cross-correlations between the random interactions at individual nuclear sites. The operators F_{zA} and $F_{\pm A}$ are also eigenoperators, concerned with eigenvalues 0 and $\mp\omega_{0,A}$, respectively, of the static superhamiltonian $\mathbf{L}$. The latter eigenvalues are obviously independent of the J-coupling terms occurring in $\mathbf{L}$. Because the system's observables $F_{\pm A}$ describing perpendicular magnetization evolve as damped oscillations, the standard NMR spectrum of any A_n system of the above sort consists of a single Lorentzian line and is independent of the J-couplings within the system. Such situation would occur in particular for the quadrupolar (Q) relaxation mechanism which is usually the principal mechanism for nuclei of spin greater than $\frac{1}{2}$. In A_n systems matching the above relaxation pattern one can hardly distinguish independent spin isomers. For such systems the concept of magnetic equivalence has therefore a different meaning than in the static case.

When relaxation interactions engaging nuclear pairs cannot be excluded, the operators F_{zA} and $F_{\pm A}$ are no longer eigenoperators of $\mathbf{R}$ and the above inferences become invalid. Despite the fact that the most familiar mechanism of this sort, the (DD) mechanism, is marginal for nuclei of spin greater than $\frac{1}{2}$, it will be considered in order to render our discussion complete. When DD interactions are accounted for, only for an isochronous two-spin system can one speak of some sort of magnetic equivalence, provided that an additional condition is fulfilled. Namely, it is required that the WBR relaxation matrix describing the DD and other possible mechanisms operating in system A_2 be invariant under arbitrary rotations. In the extreme narrowing limit, the spherical symmetry of $\mathbf{R}$ occurs for any system, not necessarily isochronous, for which relaxation interactions involving chemical shift anisotropy (CSA) can be neglected

(as in the whole discussion, it is implied here that only spatially isotropic solvents are considered). For an isochronous system, the spherical symmetry properties are extended to the system's super-Hamiltonian referenced to the frame rotating with the resonance frequency. ω_{0A}, since in such a frame the only nonvanishing term of $\mathbf{L}$ is the (by definition, scalar) J-coupling term. A convenient basis to represent the WBR equation for an isochronous system with spherical symmetry is an operator basis comprising irreducible spherical tensor operators $T^L_{k\mu}$, where L is the tensor rank, $\mu = -L, -L+1, \ldots, L-1, L$ enumerates individual tensor components, and k is a collective label distinguishing different (orthogonal) tensors of the same rank. These tensor operators are simultaneous eigenoperators of the superoperator generating rotations about the z axis, $\mathbf{F}^D_{zA}$,

$$\mathbf{F}^D_{zA}|T^L_{k\mu}\rangle = \mu|T^L_{k\mu}\rangle, \qquad [3a]$$

and of the Casimir superoperator,

$$[F^D_{zA}F^D_{zA} + \tfrac{1}{2}(F^D_{+A}F^D_{-A} + F^D_{-A}F^D_{+A})]|T^L_{k\mu}\rangle = L(L+1)|T^L_{k\mu}\rangle. \qquad [3b]$$

By virtue of Wigner–Eckart theorem, in such a basis the blocks of $\mathbf{L}$ and $\mathbf{R}$ concerned with individual eigenvalues, μ, of $\mathbf{F}^D_{zA}$ will be blocked out further into subblocks corresponding to individual ranks L. The system observables F_{zA} and $F_{\pm A}$ constitute a tensor operator of rank 1 so that the evolution of a spherically symmetric system is confined to the subspace spanned by rank-1 tensor operators. Following the theory outlined in Refs. (*5, 11*), we give a closer description of the relevant rank-1 tensor operators for system A_2. We show that all (unnormalized) rank-1 operators which fulfill the requirements of the intrinsic permutation symmetry of A_2 can be obtained from the system observables by multiplying the latter by appropriate, mutually orthogonal tensor operators of rank 0, T^0_{k0},

$$T^1_k = \{T^0_{k0}F_{zA}, T^0_{k0}F_{+A}, T^0_{k0}F_{-A}\}, \qquad [4]$$

where $k = 1, 2, \ldots, 2I_A$. The justification for setting the number of the relevant rank-1 tensors at $2I_A$ will be given later on.

As a basis in Hilbert space of system A_2 we take the set of state vectors which are the simultaneous eigenvectors, $|lm)$, of the total spin squared, $\mathbf{F}^2_A$, and F_{zA} operators,

$$\mathbf{F}^2_A|lm) = l(l+1)|lm) \qquad [5a]$$

$$\mathbf{F}_{zA}|lm) = m|lm), \qquad [5b]$$

where $l = 0, 1, \ldots, 2I_A$ and $m = -l, -l+1, \ldots, l-1, l$. Under rotations these behave as irreducible tensors so that the kets $|lm)$ can be Clebsch–Gordan coupled with the bras $(l'm'|$ to produce the required tensor operators $T^L_{k\mu}$ (*11, 12*). It is the specificity of a symmetric two-spin system that vectors $|lm)$ are already adapted to the intrinsic permutation symmetry $S_2 \equiv C_2$: vectors concerned with the same composite spin l are all either symmetric or antisymmetric under C_2, depending on whether the symmetry index, $(-1)^{2I_A-l}$, is $+1$ or -1. Operators $T^L_{k\mu}$ of proper symmetry will be obtained only from the shift operators $|lm)(l'm'|$ where both l and l' are either even or odd. Taking this into account and considering the fact that coupling of tensors of ranks l and l' can yield tensors of ranks $L = |l-l'|, |l-l'|+1, \ldots, l+l'$, we immediately see that the number of properly symmetrized tensors T^1_k is indeed $2I_A$, as was already anticipated in the comment to Eq. [4] (it is the number of sets of the shift operators for which $l = l'$, where $l > 0$, since the operators for which $|l-l'| = 1$ are not properly symmetrized). We moreover see that the relevant rank-zero operators $T^0_{00}, T^0_{10}, \ldots, T^0_{l0}, \ldots$ are linear combinations of shift operators from the respective sets $\{|00)(00|\}, \{|1m)(1m|, m = -1, 0, 1\}, \ldots, \{|lm)(lm|, m = -l, \ldots, l\}\ldots$. There will therefore be exactly $2I_A + 1$ (orthogonal) operators T^0_{l0}, all of which will necessarily commute with F_z and $F_\pm$. Because $T^0_{00}F_u = 0$, where u stands for z and $\pm$, only the operators T^0_{l0} with $l = 1, 2, \ldots, 2I_A$ will be of use in Eq. [4], and accordingly, the rank-1 tensor operators obtained in this way will form a complete basis set in the interesting subspace. These basis operators correspond to individual spin isomers of nonzero spin. Because both F_u and T^0_{l0} commute with $\mathbf{I}_1\mathbf{I}_2$, the evolution of system's observables will be unaffected by the J-coupling. Unlike in the A_n system considered at the beginning of this section where for any n there occurs only a single Lorentzian, in the presence of a DD mechanism the spectrum of system A_2 will in general have a complex structure. It can consist of up to $2I_A$ Lorentzians centered at the same frequency but having different widths and different integral intensities. Individual spin isomers (of nonzero spin) do not evolve independently so that each of these Lorentzians describes a combination of the spin isomers. As in the preceeding case, for the system A_2 considered presently one can speak of magnetic equivalence only in a limited sense. The most important conclusion is that the NMR spectrum of such a system is independent on the J-coupling between the A nuclei.

MAGNETIC EQUIVALENCE BROKEN BY RELAXATION

Isochronous systems. For an isochronous system comprising more than two nuclei, not all of the relevant rank-1 tensor operators commute with $\mathbf{I}_k\mathbf{I}_l$. The J-couplings within the group can therefore influence the spectrum when the DD relaxation mechanism is operative. The Lorentzian lines constituting the spectrum will no longer be all centered at the same frequency. Their phases, positions as well as widths

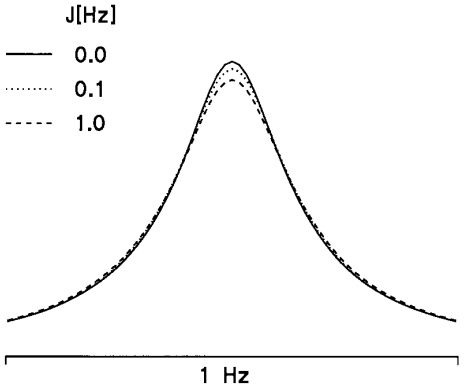

FIG. 1. Theoretical spectra of an A_2 system, with $I_A = 1$, for the displayed values of J_{AA}, in presence of DD, CSA, and cross-correlated CSA–CSA and DD–CSA relaxation mechanisms. The assumed spectral densities are 0.008, 0.032, 0.030, and 0.014 Hz, respectively; the normalization of the pertinent irreducible spherical tensor superoperators entering **R** is the same as in Ref. (*7*). The cross-correlation coefficients for CSA interactions at different nuclear sites and for DD–CSA interactions are 0.94 and 0.87, respectively.

and intensities will all be dependent on the *J*-couplings within the isochronous group. The actual structure of the spectrum will also be dependent on the magnitude of I_A and on the symmetry of the spatial arrangement of the nuclei (*5*). In order to gain some insight into the consequences of such a breakdown of magnetic equivalence, lineshape calculations of standard single-quantum spectra for systems A_3 with $I_A = 1, \frac{3}{2}$, and 2, were performed assuming that the only relaxation mechanism is the DD mechanism. The computer program used in the calculations is a mutation of our unpublished program RELAXAN to calculate WBR relaxation matrices for multispin systems according to the formalism exposed in Ref. (*7*).[1] The calculations were carried out for different input values of J_{AA}. As predicted theoretically, the calculated spectral lineshapes have proven dependent on J_{AA}. The dependence was however very weak unless high cross-correlation coefficients were assumed for random DD interactions for different nuclear pairs. (It must be added that in a three-spin system whose natural geometry is an equilateral triangle such high cross-correlations could not occur). It should be added that calculations of spectral lineshapes for the systems for which the theory of the preceeding section predicts no such dependence fully confirmed the prediction: Irrespectively of the input values of the *J*-coupling constants, the calculated lineshape functions were identical to all seven digits displayed on output.

In search of the simplest example where magnetic equivalence is broken by relaxation we considered the A_2 system, with $I_A = 1$, in the presence of DD, CSA, and cross-correlated DD–CSA mechanisms, in which instance the spherical symmetry of **R** is lost. A closer look at this prototype system seems instructive. As illustrated in Fig. 1, the calculated lineshape function of the A_2 group becomes dependent on the assumed magnitude of J_{AA}. In (anisochronous) systems *AX* cross-correlation between DD and CSA interactions can bring about asymmetry to the otherwise symmetric *A* and *X* multiplets (*13, 14*). In our case the unresolved signal becomes slightly asymmetric when J_{AA} is different from zero, and the lineshapes calculated for the values of J_{AA} of opposite signs are mirror images of each other. By virtue of the relationship referred to in the Introduction, the spectrum of a pair of isochronous spin-$\frac{1}{2}$ nuclei would in no instance be dependent on the *J*-coupling constant (*3, 5*).

A closer explanation of the effects demonstrated in Fig. 1 can be gained from a consideration of the evolution of the perpendicular magnetization in an appropriate operator basis. When rotational symmetry is lost, the evolution will no longer be confined to the subspace of rank-1 tensors of Eq. [4] but will proceed in the whole symmetry-adapted subspace of eigenoperators of F^D_{zA} concerned with eigenvalue 1. Considering the permutation symmetry properties of the vectors $|lm)$ defined in Eqs. [5a] and [5b], we see that the relevant subspace has 8 dimensions. The (orthonormal) shift operators spanning the subspace are listed in Table 1. In this operator basis the *J*-coupling super-Hamiltonian is diagonal, and its eigenvalues are equal to zero for the basis operators listed as items 1 to 6. The first four of these basis operators represent the spin isomer of composite spin $l = 2$ and the remaining two the spin isomer of $l = 1$. All of these six shift operators involve transitions that are allowed by the static magnetic equivalence symmetry since the corresponding transition amplitudes, proportional to $\mathrm{Tr}[|lm - 1)(lm|F_{+A}] = (lm|F_{+A}|lm - 1)$, are all nonvanishing. The last two items in Table 1 represent transitions that are strictly forbidden in the static limit. The pertinent (diagonal) elements of **L** in the rotating frame are $6\pi J_{AA}$ (item 7) and $-6\pi J_{AA}$ (item 8). If **R** had spherical symmetry, all off-diagonal elements of **R** between the basis operators 7 and

TABLE 1

Basis Operators Describing Evolution of Perpendicular Magnetization of System A_2, with $I_A = 1$, in Absence of Spherical Symmetry

Item	Operator
1	$\|21)(22\|$
2	$\|20)(21\|$
3	$\|2-1)(20\|$
4	$\|2-2)(2-1\|$
5	$\|10)(11\|$
6	$\|1-1)(10\|$
7	$\|2-1)(00\|$
8	$\|00)(21\|$

[1] Collaboration with Professor Adam Gryff-Keller in developing and testing the program RELAXAN is gratefully acknowledged.

8 and the basis operators 1 to 6 would vanish. The evolution of the system observables would then be confined to the subspace spanned by operators 1 to 6 and would not be affected by the *J*-coupling. Moreover, as shown in the preceeding section, by the use of the irreducible spherical basis, the subspaces spanned by operators 1 to 4 and those 5 and 6 could be reduced to one-dimensional subspaces of the irreducible operators $T^1_{21} = T^0_{20}F_{+A}$ and $T^1_{11} = T^0_{10}F_{+A}$, respectively, without any lost of information. When, as in the case considered presently, **R** lacks spherical symmetry, the off-diagonal elements of **R** between basis operators 7 and 8 and those 1 to 6 are nonvanishing, and accordingly, all eight dimensions of the symmetry-allowed, single-quantum subspace are relevant. Due to mediation of the above off-diagonal elements of **R**, the transitions that are strictly forbidden in the static limit can now borrow intensity from the remaining, ever-allowed transitions. Hence the evolution of the magnetization and, accordingly, the spectral lineshape can become dependent on the *J*-coupling between the *A* nuclei, as has been confirmed by the numerical calculations. When the value of J_{AA} assumed in the calculations is large compared to the pertinent off-diagonal elements of **R**, these elements are strongly nonsecular, and the spectrum becomes effectively insensitive to further increase of the magnitude of J_{AA}. The asymmetry of the calculated lineshape function results from the fact that in the presence of DD–CSA correlations the relaxation properties of the transitions at $\omega_{0A} \pm 6\pi J_{AA}$ are different.

A_nX Systems. In such systems already the dominating mechanisms for nuclei of spin greater than $\frac{1}{2}$, i.e., the Q mechanism, can cause breaking of magnetic equivalence. The possibility of such an effect to appear stems from the fact that none of the three reasons, discussed in the preceeding section, of at least partial conservation of equivalence could be invoked here. Namely, (i) quadrupolar relaxation matrix of group A_n does not commute with $\mathbf{F}^{2D}_A$. Moreover, (ii) in the presence of *J*-coupling between *A* and *X* neither F_{uX} nor F_{uA} are eigenoperators of the evolution superoperator. Finally, (iii) the spherical symmetry arguments employed in the discussion of equivalence in the isolated A_2 group do not pertain to the A_nX group, even when $n = 2$ (see below). In what follows it is assumed that the A_n group is relaxed only by the Q mechanism described by matrix $\mathbf{R}_Q$ and that relaxation behavior of the nucleus *X* is governed by a spherically symmetric relaxation matrix $\mathbf{R}_X$ (independent of the *A* spins), the relevant eigenvalues of which, $1/T_{1X} = 1/T_{2X}$, are much smaller than $2\pi J_{AX}$. According to these assumptions, both $\mathbf{R} = \mathbf{R}_X + \mathbf{R}_Q$ and the super-Hamiltonian describing *J*-coupling between *A* and *X* have spherical symmetry (obviously, the nonsecular components of the latter can be retained). One might thus wonder if the rejection of spherical symmetry arguments, as mentioned under point (iii) above, was not premature. However, one should remember that the desired spherical symmetry factoring of $\mathbf{R}_Q$ would be achieved only in a basis that is irreducible under rotations in the space of the sole *A* spins. On the other hand, the *A*–*X* coupling term would undergo factoring only in such spherical basis which is irreducible under rotations in the entire spin space, including both *A* and *X* spins. Because no spherical basis is simultaneously irreducible under rotations of the entire system and of its *A* part only, use of spherical bases in the following discussion would be unproductive. It would also be factitious to keep the nonsecular part of the *J*-coupling between *A* and *X*, because heteronuclear spin-locking experiments are out of scope of the present article.

First we consider the spectrum of the *A* part. Again our goal is to identify the subspace describing the system's evolution. It can be done easily by repeating the action of the relevant part, $-i(\mathbf{L}_{AX} + \mathbf{L}_A) + \mathbf{R}_Q + \mathbf{R}_X$, of the evolution superoperator on the observable $|F_{+A}\rangle$ (where $\mathbf{L}_{AX}$ and $\mathbf{L}_A$ describe the secular part of the *A*–*X* coupling and the *J*-couplings between *A* nuclei, respectively). Straightforward calculations invoking the already quoted result by Pyper (*10*) reveal that when $I_X = \frac{1}{2}$ the evolution is confined to a two-dimensional subspace spanned by the two eigenoperators of the evolution superoperator,

$$[-i(\mathbf{L}_{AX} + \mathbf{L}_A) + \mathbf{R}_Q + \mathbf{R}_X]|F_{+A}(2I_{zX} \pm E)\rangle = \left(-\frac{1}{T'_2} - \frac{1}{2T_{1X}} \pm \frac{1}{2}2\pi J_{AX}\right)|F_{+A}(2I_{zX} \pm E)\rangle. \quad [6]$$

Hence, the spectrum of the *A* nuclei will consist of two equally intense Lorentzian lines, centered at $\nu_{0A} \pm J_{AX}/2$, and having the same width at half height, equal to $1/(\pi T'_2) + 1/(2\pi T_{1X})$. The quantity T'_2 is the eigenvalue of $\mathbf{R}_Q$ concerned with F_{+A}; it is thus the perpendicular relaxation time, equal to the longitudinal relaxation time, T'_1, of the isolated group A_n. From the discussion of the preceeding section, involving isolated A_n groups relaxed by Q mechanisms, it is seen that the spectrum of part *A* will be independent of the possible cross-correlations between Q interactions at different nuclear sites. Because $\mathbf{L}_A|F_{+A}\rangle = 0$, it is evident that the spectrum is independent of the *J*-couplings within the A_n group. It must again be stressed that the above inferences are valid only in the case where *X* is a nucleus of spin $\frac{1}{2}$.

When the spectrum of part *X* is concerned, no simple analytical expressions can be derived. Nevertheless, formal considerations similar to those outlined above allow one to see that the relevant subspace contains, among others, operators of the form $|I_{+X}F^s_{zA}\rangle$, where $s = 0, 1, 2, \ldots$, which are produced from $|I_{+X}\rangle$ by repeated action of $\mathbf{L}_{AX}$. The higher powers of F_{zA} are no longer eigenvectors of $\mathbf{R}_Q$. Because $\mathbf{R}_Q$ and $\mathbf{F}^{2D}_A$ do not commute, the operators produced by the action of $\mathbf{R}_Q$ on $|I_{+X}F^s_{zA}\rangle$, which also fall into

TABLE 2
Operators in A Space Describing Evolution of Magnetization of X Part of A_2X System, with $I_A = 1$

Item	Operator
1	$\|22)(22\|$
2	$\|21)(21\|$
3	$\|20)(20\|$
4	$\|2-1)(2-1\|$
5	$\|2-2)(2-2\|$
6	$\|11)(11\|$
7	$\|10)(10\|$
8	$\|1-1)(1-1\|$
9	$\|00)(00\|$
10	$\|20)(00\|$
11	$\|00)(20\|$

the evolution subspace, will not in general commute with $\mathbf{F}_A^2$. Accordingly, the J-couplings between A nuclei may become relevant. The evolution subspace describing perpendicular magnetization of X is spanned by a complete set of orthogonal operators of the form $I_{+X}Q_{Aj}$, where Q_{Aj}, depending on the A spins only, are all such eigenoperators of F_{zA}^{D} concerned with eigenvalue zero which are adapted to the permutation (and, in fact, geometric (5)) symmetry of the system.

Equivalence breaking ought to take place already in the simplest system of the sort considered presently, i.e., when the A_n group is composed of two nuclei of spin 1, and where the system's permutation symmetry group is isomorphic with C_2. We consider this case in some detail. As the pertinent operators Q_{Aj} we again take the shift operators produced from vectors of Eq. [5]. There are 11 such operators allowed by the permutation symmetry; they are listed in Table 2. In the assumed operator basis, both $\mathbf{L}_{AX}$ and $\mathbf{L}_A$ are diagonal. The only nonzero (diagonal) matrix elements of the latter are equal to $\pm 6\pi J_{AA}$ and are concerned with items 10 and 11 of Table 2. The (diagonal) elements of $\mathbf{L}_{AX}$ are given as $2\pi J_{AX}$ times the successive eigenvalues, -2, -1, 0, 1, and 2, of F_{zA}, and the elements concerned with 0 and ± 1 eigenvalues are degenerate. In absence of relaxation, the spectrum would consist of only such lines for which the transition amplitudes, proportional to Tr Q_{Aj}, are nonvanishing. The transitions concerned with items 10 and 11 of Table 2 are strictly forbidden in the absence of relaxation (Tr Q_{A10} = Tr $Q_{A11} = 0$). In the static limit one could therefore observe only 9 lines, concerned with items 1–9 of Table 2, which would form the familiar 1:2:3:2:1 quintet because of the degeneracies. Quadrupolar relaxation couples the transitions forbidden in the static limit with the remaining transitions. Even when, as in the case considered presently, $\mathbf{R}_Q$ has spherical symmetry, the coupling can be effective. Namely, the operators Q_{A10} and Q_{A11} describing the forbidden transitions are components of rank-2 spherical tensors irreducible in the A subspace. Similarly, the subsets $\{Q_{Ai}, i = 1, \ldots, 5\}$ and $\{Q_{Aj}, j = 6, 7, 8\}$ could be unitary-transformed into the corresponding spherical subsets of which each would contain a component of a rank-2 tensor (in such a spherical basis the super-Hamiltonian $\mathbf{L}_{AX}$ would not be diagonal). There are therefore no spherical symmetry constraints on transfer of coherence between the forbidden and allowed transitions, and the lineshape function of X nucleus can in principle be dependent on J_{AA}.

Numerical calculations for A_2X system, with $I_A = 1$, show that the most pronounced dependence of the lineshape of X on J_{AA} occurs when the quadrupolar relaxation rate, T_1', becomes comparable to J_{AX}. The lineshape proves also sensitive to the assumed degree of cross-correlation of quadrupolar interactions at different sites of A nuclei. Moreover, the higher this cross-correlation, the more sensitive is the signal shape to J_{AA}. This can be rationalized in terms of microscopic symmetry factoring (5, 7) of $\mathbf{R}_Q$ which would appear in the instance of perfect cross-correlation. In such an instance, the relevant 11×11 block of $\mathbf{R}_Q$ would be blocked out further into 8×8 and 3×3 independent blocks. The latter corresponds to the three shift operators of Table 2 which are formed from vectors antisymmetric under C_2 (items 6–8). Then, the forbidden transitions, whose corresponding basis operators fall to the 8-dimensional subspace of symmetric bras and kets, could borrow intensity only from the six transitions of the same microscopic symmetry. In the case of weak cross-correlation there is no microscopic factoring and the offending transitions can in principle affect all of the remaining 9 transitions. In the latter instance the effect will be distributed more uniformly over the multiplet, and the response of the lineshape functions to varying magnitude of J_{AA} will be less pronounced.

In Fig. 2 there are shown theoretical lineshapes of a X nucleus scalar-coupled to two isochronous A nuclei. The model parameters assumed in the simulations roughly correspond to a selectively ^{15}N-substituted azide ion, $^{14}\mathrm{N}^{15}\mathrm{N}^{14}\mathrm{N}^-$, for which, due to the expected $D_{\infty h}$ symmetry of the molecule, there ought to be a substantial cross-correlation between quadrupolar interactions at the terminal sites. The lineshape variations reflecting the changes of the input values of J_{AA} are certainly nonnegligible in this case. There is a significant, monotonical decrease of the height of the central peak along with a gradual departure from zero of the value of $|J_{AA}|$. Again, when the latter becomes large compared to $\mathbf{R}_Q$, the lineshape function becomes insensitive to a further increase of $|J_{AA}|$. In such circumstances the relevant off-diagonal elements of $\mathbf{R}_Q$ are strongly nonsecular, and accordingly, the offending transitions (whose amplitudes vanish in the static limit) become effectively decoupled from the remaining transitions. In the interpretation of experimental spectra of this and similar systems one would face one more problem: The response of the calculated lineshape to a substantial departure from zero of the assumed value of J_{AA}

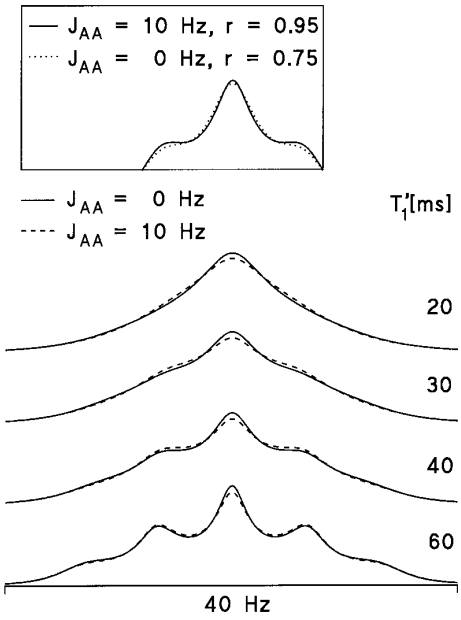

FIG. 2. A comparison between theoretical spectra of the X part of an A_2X system, with $I_A = 1$, for two input values of J_{AA}. Quadrupolar relaxation mechanism was assumed for the A nuclei. The displayed values of T_1' would be the longitudinal relaxation times of the A_2 group isolated from X. The assumed value of J_{AX} is 7 Hz. Correlation coefficient, r, of 0.95 for the cross-correlated Q interactions at different nuclear sites A is assumed. The relaxation properties of the X nucleus are accounted for in the assumed natural linewidth, $1/(\pi T_{2X})$, of 0.5 Hz. (Inset) Central parts of the X multiplet corresponding to $T_1' = 40$ ms, calculated for the indicated values of J_{AA} and r.

proves similar as the response to diminishing degree of the cross-correlation, with the value of J_{AA} being kept constant and equal to zero (see inset in Fig. 2).

CONCLUSIONS

When the whole variety of relaxation mechanisms is taken into account, the concept of magnetic equivalence lacks theoretical justification for nuclei of spin greater than $\frac{1}{2}$. However, in practice one can forget the troublesome consequences of broken magnetic equivalence unless an isochronous set of such nuclei relaxing via quadrupolar mechanism is scalar coupled to a spin-$\frac{1}{2}$ nucleus. Caution should be exercised when a nearly resolved multiplet of such a nucleus is to be dealt with, especially in an instance of high cross-correlations between the quadrupolar interactions. When the actual values of the J-coupling constants within the equivalent group are unknown but can be expected to be large compared with the quadrupolar relaxation rates, the seemingly most natural step of setting all these values to zero will usually be the most inappropriate. An independent assessment of such couplings using unsymmetric isotopomers may be indispensable when one wants to determine from the signal shape the degree of cross-correlations between the quadrupolar interactions. When isotropic media are concerned, there seem to be little chances of detecting such cross-correlations for nonisochronous quadrupolar nuclei. In the studies on molecular models containing isochronous groups of quadrupolar nuclei, one should be aware of the potential bias created by magnetic equivalence breaking.

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