EXPERIMENTAL CLASSIFICATION OF MULTI-SPIN COHERENCE UNDER THE FULL ROTATION GROUP

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The density operator of a coupled nuclear spin system often includes multi-spin coherences representing correlations between different spins. The generation and evolution of these coherences is governed by the dipole–dipole interactions between the spins and thus contains information about nuclear structure. Different multi-spin coherences may be distinguished by their behaviour under rotations. The maximum information extractable is determined by the irreducible representations of the full rotation group SO(3). By comparing the effect of rotation with various angles and rotation axes one can determine the expansion coefficients of the spin density operator in a basis of irreducible tensor operators. Experimentally, the rotation of the spins is achieved with rf pulses.

Structure and dynamics of solids manifest themselves in the dynamics of nuclear spins. Via nuclear spin–spin couplings, they determine the evolution of magnetisation and higher-order coherences. The large number of spin–spin couplings in a solid usually leads to broad spectra and makes it impossible to determine individual coupling constants from measurements on freely precessing nuclear magnetisation. The manipulation of spin Hamiltonians by application of trains of radio frequency (rf) pulses [1] allows one to convert magnetisation into higher-order spin coherences which involve correlations between a number of different spins. Most of these multi-spin coherences connect states that are separated energetically by several quanta of radiation and must therefore be studied by multiple-quantum NMR [2]. It has been shown that the measurement of multiple-quantum NMR intensities can be used to study the local structure of solid materials, especially the problem of clustering [3,4].

In multiple-quantum NMR, different multi-spin coherences are distinguished via their behaviour under rotations around the laboratory Z-axis, the direction of the static magnetic field. This corresponds to a classification of density-operator components according to the irreducible representations of the group C_∞. The motivation for this procedure is that both the initial condition and the unperturbed Hamiltonian are invariant under rotations around the z-axis. In order to create and observe multiple-quantum coherence, it is necessary to break this symmetry by the application of rf pulses along axes in the xy-plane. A single hard pulse generates transverse magnetisation, i.e. single-spin one-quantum coherence, which evolves into multi-spin single-quantum coherence under the influence of the dipole–dipole couplings. Multi-spin multiple-quantum coherence can be generated by applying a suitable train of rf pulses that converts the secular dipole–dipole Hamiltonian into an average Hamiltonian without rotational symmetry around the z-axis.

The resulting multi-spin coherences cannot be observed directly but have to be investigated via some indirect procedure. In general, the tools available for the analysis of the resulting multi-spin coherence are rf pulses. The effect of an ideal pulse on the spin system can be described as a rotation. The behaviour of the different components of the density operator under rotations depends on the number of correlated spins as well as on the coupling scheme of the various angular momenta. The most complete characterisation of multi-spin coherence that can be

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achieved by the application of rf pulses is a projection of the spin density operator onto the irreducible representations of the full rotation group SO(3), while the traditional measurement of multiple quantum intensities corresponds to a projection of the density operator onto the irreducible representations of the subgroup C_∞.

A nuclear spin system in a large magnetic field, in thermal equilibrium with the lattice, is characterised by a state of Zeeman order, with the individual nuclear spins aligned along the magnetic field. Its reduced equilibrium density operator ρ_e is proportional to I_z, the z-component of the angular momentum operator,

$$\rho_e = \sum_i I_{iz} , \tag{1}$$

with the sum running over all spins in the sample. Such a spin state does not contain any correlations between different spins and therefore does not contain information about interactions between different spins. In order to generate these correlations, it is necessary to let the system evolve under a Hamiltonian which depends on the dipole–dipole couplings and does not commute with the initial condition. The relative ease with which nuclear spin Hamiltonians can be manipulated by multiple-pulse NMR [1] provides one with a sufficient amount of freedom to generate a suitable average Hamiltonian that converts single-spin order into multi-spin coherences [5,6]. In the language of two-dimensional NMR, this step is conventionally referred to as the preparation period [7]. The resulting density operator ρ_0 can be written as

$$\rho_0 = U\rho_e U^{-1} = \sum I_{iz} I_{j+} I_{k-} \cdots , \tag{2}$$

where $U = \exp(-i\bar{H}\tau)$ is the propagator generated by the average Hamiltonian $\bar{H}$. The resulting density operator can then be subject to rotations for the purpose of analysing the multi-spin coherences generated by this "pumping" process. Since multi-spin coherences are not directly observable, however, it is necessary to convert them back into observable magnetisation. This conversion, usually referred to as the mixing process, is the inverse of the initial pumping process that generates the multi-spin coherences. The associated evolution therefore corresponds to a time reversal which can be achieved by suitably designed average Hamiltonians [5,6]. The resulting pulse sequence is represented schematically in fig. 1. The observable is most conveniently chosen to be equal to the initial condition ρ_e, thereby maximising the symmetry of the whole experiment. The signal which is finally observed becomes then

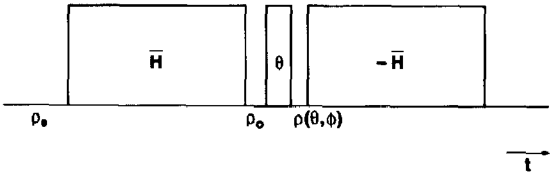

Fig. 1. Pulse sequence used to generate and analyse multi-spin coherence. The average Hamiltonian $\bar{H}$ is generated by a multiple-pulse sequence acting on the dipole–dipole Hamiltonian. A pulse with variable flip angle rotates the coherences around an axis in the xy-plane, while phase shifts of the preparation sequence are used to generate rotations around the z-axis. The mixing Hamiltonian $-\bar{H}$ is the inverse of the preparation Hamiltonian and converts the multi-spin coherences back into observable magnetisation.

$$S = \mathrm{tr}(U^{-1} R U \rho_e U^{-1} R^{-1} U \rho_e) , \tag{3}$$

where R represents the rotation applied to ρ_0. The interpretation of the experiment may be simplified by using a mixed Schrödinger–Heisenberg picture, in which the initial preparation converts the equilibrium density operator into multi-spin coherence, while the mixing acts on the observable,

$$S = \mathrm{tr}(R U \rho_e U^{-1} R^{-1} U \rho_e U^{-1}) = \mathrm{tr}(R \rho_0 R^{-1} \rho_0) . \tag{4}$$

For the present purpose it is therefore convenient to disregard the preparation and mixing procedures and consider ρ_0 as both the initial condition and observable.

The measurement of both quantum numbers of the components of irreducible tensor operators necessarily involves rotations of the system around more than one axis. One of the axes is usually chosen to be the z-axis of the laboratory frame of reference, thus allowing a straightforward determination of the magnetic quantum number m, as is routinely done in multiple-quantum NMR experiments. Such rotations of the spin system around the z-axis are most conveniently performed by shifting the phase of the multiple-pulse sequence that generates the pumping Hamiltonian. Since the equilibrium density operator as well as the unperturbed Hamiltonian are invariant under rotations around the z-axis, a phase shift by ϕ of the multiple-pulse sequence translates directly into a z-rotation of the resulting state $\rho(\phi)=\exp(-\mathrm{i}\phi I_z)\,\rho_0\,\exp(\mathrm{i}\phi I_z)$. Rotations around axes in the xy-plane can be performed directly by rf pulses. To describe the effect of the rotations, we expand the density operator in the basis of irreducible tensor operators T_{lm},

$$\rho_0=\sum_{lm} a_{lm} T_{lm}\ , \qquad (5)$$

where the additional quantum numbers required for the complete characterisation are not written explicitly. In NMR rotations are usually performed around the z-axis or around an axis in the xy-plane. We write θ for the rotation angle if the rotation axis lies in the xy-plane and ϕ if it is along the z-axis. The rotations convert the state ρ_0 into

$$\rho(\theta,\phi)=R\rho_0 R^{-1}=\sum_{lmm'} a_{lm} D^{(l)}_{m'm}(\theta,\phi)\; T_{lm'}\ , \qquad (6)$$

where $D^{(l)}$ represents a Wigner rotation matrix. The observed signal is therefore

$$\begin{aligned} S(\theta,\phi)&=\mathrm{tr}[\rho(\theta,\phi)\,\rho_0] \\ &=\sum_{ll''mm'm''} a_{lm} D^{(l)}_{m'm}(\theta,\phi)\; a_{l''m''}\ \mathrm{tr}(T_{lm'}T_{l''m''})\ . \end{aligned} \qquad (7)$$

Since $\mathrm{tr}(T_{lm}T_{l''m''})=\delta_{l,l''}\delta_{m,-m''}(-1)^m$, and the density operator is Hermitian, $a_{lm}=a^*_{l-m}(-1)^m$, this can be simplified to

$$S(\theta,\phi)=\sum_{lmm'} a_{lm} a^*_{lm'} D^{(l)}_{m'm}(\theta,\phi)\ . \qquad (8)$$

The observed signal is therefore the sum of all possible products of coefficients a_{lm}, weighted with the corresponding rotation matrix element. The measurement of m is therefore special in the sense that rotations around the z-axis do not mix the different terms. Because of the orthogonality of the $D^{(l)}_{m'm}$ [8],

$$\begin{aligned} &\int_0^{2\pi} \mathrm{d}\gamma \int_0^{\pi} \sin\beta\ \mathrm{d}\beta \int_0^{2\pi} \mathrm{d}\alpha\ D^{(l_1)}_{m_1'm_1}(\alpha\beta\gamma)\ D^{(l_2)}_{m_2'm_2}(\alpha\beta\gamma) \\ &\quad =\delta_{m_1'm_2'}\,\delta_{m_1m_2}\,\delta_{l_1l_2}\,\frac{8\pi^2}{2l_1+1}\ , \end{aligned} \qquad (9)$$

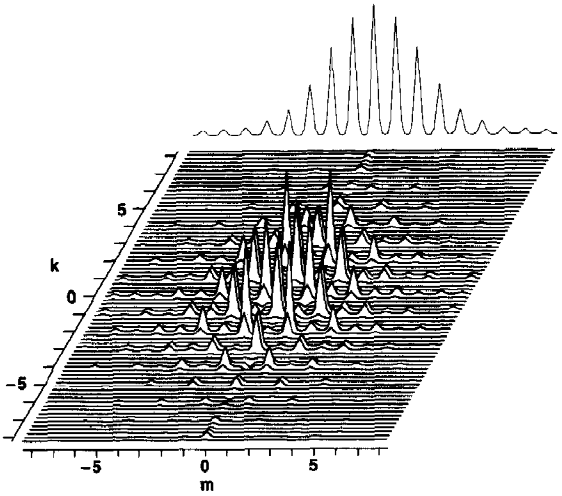

Fig. 2. Fourier transform of the observed signal as a function of phase shift ϕ and flip angle θ for a polycrystalline sample of adamantane, using a pumping time τ of 386.4 μs. The projection onto the x-axis, shown at the top, corresponds to the usual multiple-quantum spectrum.

it is in principle possible to invert eq. (8) to solve for the products $a_{lm}a^*_{lm'}$. However, since the number of individual experiments required for such a procedure grows extremely fast with l, this is hardly a practical method and more economical procedures are required.

Consider as a starting point the standard multiple-quantum NMR experiment [2], corresponding to $\theta=0$, where the pumping Hamiltonian is phase shifted systematically. Fourier transformation of the resulting signal with respect to the phase yields the amplitudes $S_m=\sum_l |a_{lm}|^2$ as a function of m. Such a spectrum is represented as the top trace in fig. 2. A rotation of the system modulates these amplitudes, according to eq. (8), as

$$S_m(\theta)=\sum_{lm'} a_{lm} a_{lm'} D^{(l)}_{m'm}(\theta)\ . \qquad (10)$$

Since the ϕ dependence of the signal has been eliminated when splitting the total signal into the contributions S_m, only θ appears as an argument in $D^{(l)}$. In general, the phases of the complex coefficients a_{lm} belonging to different transitions are independent of each other. Therefore, the terms $a_{lm}a_{lm'}$ contributing to S_m add only statistically. The number of transitions in a solid is sufficiently large that only those terms contribute noticeably to the observed signal whose coefficients a_{lm} and $a_{lm'}$ have a definite phase relation to each other, i.e. when they belong to the same transition. It is therefore possible to restrict the sum to $m'=\pm m$,

$$S_m(\theta)=\sum_l [a_{lm}a^*_{lm}D^{(l)}_{mm}(\theta) + a_{lm}a^*_{l-m}D^{(l)}_{-mm}(\theta)] . \quad (11)$$

Using the symmetry relation $a_{l-m}=a^*_{lm}(-1)^m$, we find

$$S_m(\theta)=\sum_l (R^2+I^2)d^{(l)}_{mm}(\theta) + d^{(l)}_{-mm}(\theta)[(R^2-I^2)\cos(2\alpha m) + 2RI\sin(2\alpha m)] , \quad (12)$$

where R represents the real part of the coefficients a_{lm} and I the imaginary part. α represents the phase of the rf pulse used for the θ rotation and $d^{(l)}$ represent Wigner rotation matrices for rotations around the y-axis. For the case $m'=\pm m$, the matrix elements can be calculated as

$$d^{(l)}_{mm}(\theta)=\sum_p \binom{l+m}{p}\binom{l-m}{p} \times(-1)^p 2^{-l}(1+\cos\theta)^{l-p}(1-\cos\theta)^p ,$$

$$d^{(l)}_{-mm}(\theta)=\sum_p \binom{l+m}{p}\binom{l-m}{p} \times(-1)^{l+m-p} 2^{-l}(1+\cos\theta)^{p}(1-\cos\theta)^{l-p} ,$$

$$0\leqslant p\leqslant l-|m| . \quad (13)$$

It is convenient to expand each matrix element as a Fourier series,

$$d^{(l)}_{mm}(\theta)=\sum_k b^{(l)}_{mk}\cos(k\theta) . \quad (14)$$

The coefficients $b^{(l)}_{mk}$ can be calculated from eqs. (12) and (13). Thus, if the resulting signal $S(\theta, \phi)$ is Fourier transformed and plotted as a two-dimensional spectrum, the intensities S_{mk} are given as

$$S_{mk}=\sum_l b^{(l)}_{mk}\{(R^2+I^2) + (-1)^{m+l}(1-\delta_{0,m}) \times[(R^2-I^2)\cos(2\alpha m)+2RI\sin(2\alpha m)]\} . \quad (15)$$

It is then possible to recover the coefficients a_{lm} from the experimental signal amplitudes S_{mk} via a fitting procedure.

Experiments have been performed with a polycrystalline sample of adamantane on a homebuilt spectrometer at a proton resonance frequency of 180 MHz. The pulse sequence that was used to excite multiple-quantum coherence [6] generates an average Hamiltonian

$$H=\tfrac{1}{3}\sum_{ij} d_{ij}(I_{ix}I_{jz}+I_{iz}I_{jx}) , \quad (16)$$

with d_{ij} representing the dipole–dipole coupling constant. The total duration τ of the multiple-pulse sequence was 386.4 μs. The phase of the preparation period was incremented in 32 steps from 0 to 2π in order to rotate the resulting density operator around the z-axis. Between the preparation and mixing periods, an rf pulse was applied with its flip angle incremented from 0 to 2π. For the mixing period, the pulse sequence of the preparation period was phase shifted by π, thereby inverting the average Hamiltonian.

The measured signal was stored as a two-dimensional data matrix and Fourier transformed with respect to both the phase of the preparation sequence and the flip angle of the rf pulse. The resulting spectrum is shown in fig. 2. The horizontal direction, labelled with the magnetic quantum number m, corresponds to the rotation around the z-axis, while the y-direction, labelled k, corresponds to the rotation around the x-axis. Each resonance line in the two-dimensional spectrum is defined by two frequencies or quantum numbers, m and k. The trace at the top of the figure represents the projection of the two-dimensional spectrum onto the m-axis and corresponds to the usual multiple-quantum spectrum.

A least-squares fitting procedure was used to obtain the expansion coefficients a_{lm} from the two-dimensional spectrum. The result is represented graphically in fig. 3. The left-hand side of the figure represents the real part of the expansion coefficients, $\mathrm{Re}(a_{lm})$, while the imaginary part, $\mathrm{Im}(a_{lm})$, is shown at the right-hand side. As can be seen, the coefficients are real for $l+m$ odd and purely imaginary for $l+m$ even. This is a consequence of the symmetry of initial condition and the pumping Hamiltonian.

In conclusion, we have shown that it is possible to determine experimentally the expansion coefficients

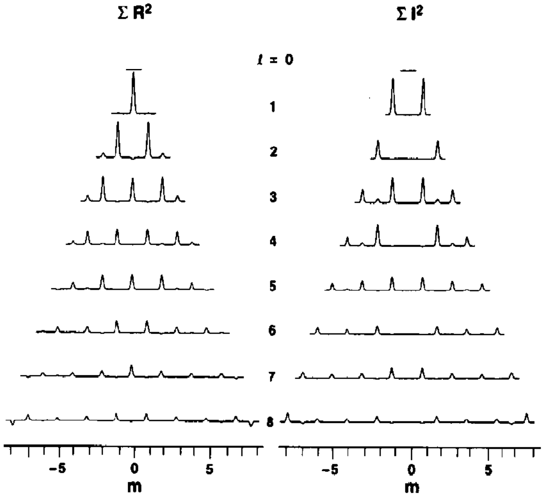

Fig. 3. Graphical representation of the expansion coefficients a_{lm} as determined from the experimental data. The data in the left-hand column correspond to the real part of the complex coefficients and the right-hand side to the imaginary part.

of the spin density operator in a basis of irreducible tensor operators. It is possible to measure not only the absolute value of the coefficients, but also the phase. The procedure represents a generalisation of multiple-quantum NMR and should improve the understanding of the dynamics of strongly coupled spin systems, which represent an interesting area at the intersection of quantum mechanics and statistical mechanics. As has been shown recently [9], the behaviour of these systems can be represented by a relatively simple "hopping model" in an *m*-quantum, *N*-spin space, a projection of the total operator space onto a two-dimensional surface. It should be possible to extend this model to include also the *l* quantum number. Applications of such measurements can be envisaged in the study of clustering where an expansion in terms of irreducible tensor operators should provide an even better measure for the size of clusters of nuclear spins than the measurement of multiple quantum intensities. The method is not restricted to solids, but may also find applications in liquid state NMR.

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