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High-Resolution Multiple Quantum Spectra of Spin-1 Systems in the Isotropic Phase

N. Chandrakumar

Chemical Physics Lab
Central Leather Research Institute
CSIR, Adayaru, Madras 600 020, Tamil Nadu, India

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In spite of being confined to three isotopes, viz., ^2H, ^6Li, and ^{14}N, high-resolution spin-1 NMR holds the key to several chemically interesting situations. While NMR involving ^2H has been pursued for some years,[1-4] some very interesting ^6Li NMR work has been reported recently.[5-7] It is the purpose of this report to point out that unique information on molecular structure can be retrieved from the multiple quantum spectroscopy[8-10] (MQS) of spin-1 systems. We show especially that triple quantum spectroscopy would appear to be the method of choice in this context.

We have developed in the past an operator description of coherence transfer involving spin-1 and spin-$^1/_2$ systems, including spin-1 to spin-1 coherence transfer.[4,11,12] While this formalism may be directly employed to predict the multiple quantum coherence transfer processes in closed operator form, we believe that the detailed transfer between individual coherences is also of interest. Accordingly, we give below the coherence transfer function Z_{qrlu} quantifying the transfer from coherence tu to coherence qr under the action of an rf pulse. Employing the matrix elements of spin-1 operators, it can be shown that, for weakly coupled systems of N inequivalent spin-1 nuclei, the coherence transfer effected by a pulse of flip angle β along the rotating frame x-axis takes the form

$$Z_{\mathrm{qrlu}} = i^{N_s^{\mathrm{ru}}-N_s^{\mathrm{qt}}}(\cos\beta)^{N_0^{\mathrm{qt}}+N_0^{\mathrm{ru}}}[[\cos\beta + 1]/2]^{N_1^{\mathrm{qt}}+N_1^{\mathrm{ru}}}[[\cos\beta - 1]/2]^{N_d^{\mathrm{qt}}+N_d^{\mathrm{ru}}}(\sin\beta/2^{1/2})^{N_s^{\mathrm{qt}}+N_s^{\mathrm{ru}}} \quad (1)$$

Here, N_s^{ru} indicates the number of spins that must be given a one-quantum flip to convert state r to state u, and N_d^{ru} indicates the number of spins that must be given a two-quantum flip to convert state r to state u, while N_0^{qt} is the number of spins that have the same quantum number $m = 0$ in the two states q and t and N_1^{qt} is the number of spins that have the same quantum number $m \neq 0$ in the two states q and t. For every coherence tu, these numbers satisfy the relation

$$N_0^{\mathrm{tu}} + N_1^{\mathrm{tu}} + N_s^{\mathrm{tu}} + N_d^{\mathrm{tu}} = N$$

which is an expression of the fact that each state describes the orientation of all N spins in the system. A prominent difference from the case of weakly coupled spin-$^1/_2$ systems is that certain coherence transfer processes are forbidden in spin-1 systems for flip angle $\beta = \pi/2$, whereas all transfers go through for $0 < \beta < \pi$, in the case of spin-$^1/_2$.

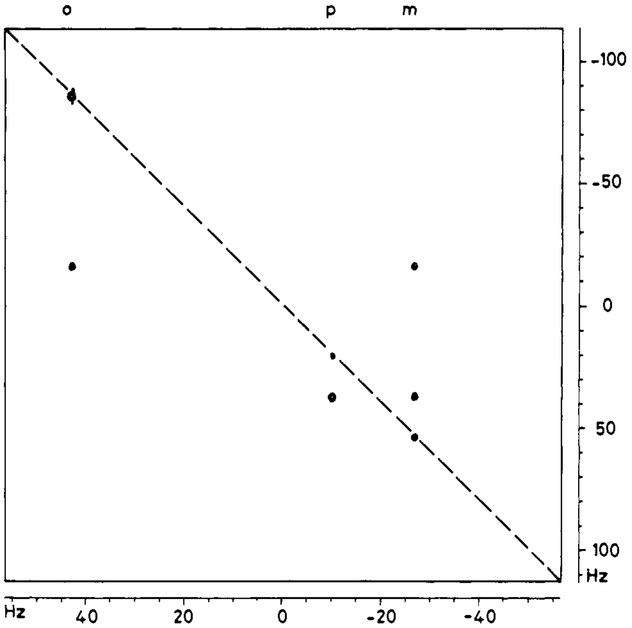

Figure 1. Two-dimensional ^2H double quantum spectrum of pyridine-d_5 at 46.073 MHz. Spectral width 113.28 Hz, 128 t_1 increments, step size being equal to the t_2 dwell. Zero-filled to 512 points in the F_1 dimension. Reconversion pulse flip angle 135°. Peaks corresponding to both one-spin and two-spin double quantum coherences are to be noted. One-spin DQCs are lone-standing and lie on the diagonal in this representation, where the Hz/cm scale on F_1 is twice the scale on F_2. Two-spin DQC peaks occur in pairs, joined by a notional tieline parallel to F_2, and are equidistant on either side of the diagonal. The experiments were performed on a Bruker MSL 300 P spectrometer with no hardware designed for high-resolution deuterium work. A 5-mm inverse probe was employed, using the X-nucleus decoupling coil for deuterium excitation and signal detection; field frequency lock was *not* employed.

It can be shown that the laboratory frame multiple quantum preparation sequence

$$(\pi/2)_{\varphi} - (\tau/2) - (\pi)_{\varphi} - (\tau/2) - (\pi/2)_{\varphi+\psi}$$

when applied to a two-spin-1 system IS results in the density matrix

$$\sigma = s_{2J}(S_xI_y + S_yI_x) + (I_z + S_z) + (c_{2J} - 1)(I_y^2S_z + I_zS_y^2) \quad (2)$$

for $\varphi = x$, $\psi = 0$, while we have for $\varphi = x$, $\psi = 90°$,

$$\sigma = s_{2J}(S_xI_z + S_zI_x) + (I_y + S_y) + (c_{2J} - 1)(I_x^2S_y + I_yS_x^2) \quad (3)$$

Here $c_{2J} = \cos 2\pi J\tau$ and $s_{2J} = \sin 2\pi J\tau$. Equation 2 displays the creation of two varieties of double quantum coherence, the first term corresponding to two-spin double quantum coherence and the third term corresponding to one-spin double quantum coherence. Both these terms survive the conventional phase cycle following evolution of the higher order coherence and its reconversion to observable signal and give rise to peaks in the two-dimensional spectrum. The one-spin double quantum coherence corresponds to the so-called type II peaks in spin-$^1/_2$ MQS.[10] Figure 1 displays a typical ^2H double quantum spectrum obtained on pyridine-d_5. It is interesting to note that reconversion of the spin-1 one-spin DQC occurs almost exclusively to the "parent" spin and not to the coupled spin. The reasons and implications of this, including the role of relaxation,[13-15] will be reported elsewhere. Unfortunately, however, this feature signifies

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that this class of peaks does not enable the direct visualization of spin connectivity.

On the other hand, eq 3 clearly demonstrates the creation of two-spin three-quantum coherence as well as combination single quantum coherences.[16,17] Figure 2 displays a typical ^{2}H triple quantum spectrum obtained on pyridine-d_5. In contrast to the double quantum spectrum, all peaks of the triple quantum spectrum directly relate to spin connectivities; each IS connectivity is reflected in fact in two sets of peaks, corresponding to frequencies (F_1, F_2) of ($2\nu_I + \nu_S$, ν) and ($2\nu_S + \nu_I$, ν), with $\nu = \nu_I$ or ν_S. In this spin system three-spin triple quantum coherence of the ortho, meta, and para deuterons is created as well, clearly reflecting directly the overall spin connectivity; this coherence is reconverted predominantly into single quantum coherence residing on the meta deuteron. These features distinguish triple quantum spectroscopy as the method of choice for spin-1 applications, in preference to zero or double quantum spectroscopy. We may add that the zero quantum spectrum exhibits of course only the two-spin peaks which reflect spin connectivity, since it is impossible, by definition, to excite one-spin zero quantum coherence, no matter what the spin quantum number.

While the spectra displayed in this work were obtained with conventional phase cycling schemes, we would point out that the efficiency of MQS both in terms of optimal use of the receiver dynamic range and in freedom from experimental artifacts would be superior with gradient controlled coherence transfer pathway selection.[18-21] Investigations of the optimum experiment design for spin-1 multiple quantum spectroscopy are in progress in our laboratory, including gradient controlled and rotating frame variants. Multiple quantum transitions effectively disperse "chemical shifts" beyond the normal range in single quantum spectra; further, spin-1 nuclei rarely give rise to resolved couplings; and finally, these systems seldom exhibit strong coupling effects: e.g., the ratio J/δ (^{2}H) at 7 T is equal to the corresponding J/δ (^{1}H) at 45.6 T! For these reasons, we believe the present experiment would prove especially fruitful.

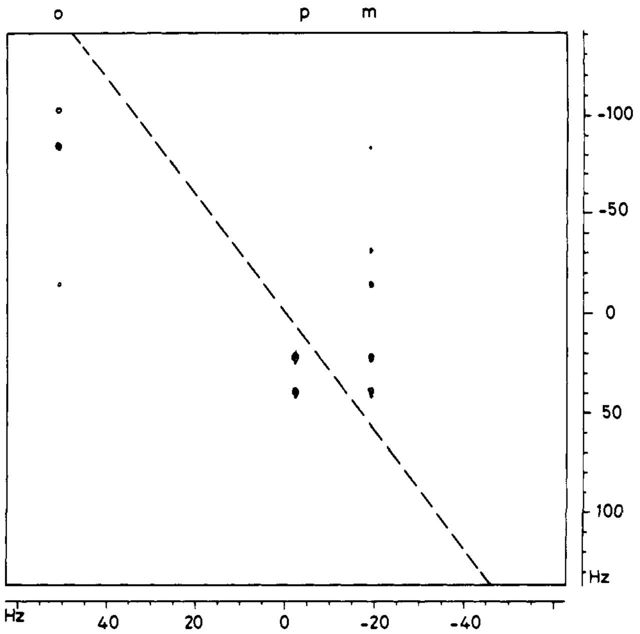

Figure 2. Two-dimensional ^{2}H triple quantum spectrum of pyridine-d_5. Spectral width 125 Hz, 128 t_1 increments, step size being equal to nine-tenths the t_2 dwell. Zero-filled to 512 points in the F_1 dimension. Reconversion pulse flip angle 135°. Both two-spin and three-spin triple quantum peaks may be noted, as also an unassigned peak at (−105.01 Hz, 52.11 Hz). The two-spin TQC peaks occur at the vertices of a notional rectangle which straddles the 1:3 skew diagonal. Note the highly asymmetric intensity distribution in the ortho–meta rectangle. The three-spin TQC peak is lone-standing.

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