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Flip angle dependence in two-dimensional multiple quantum coherence NMR spectroscopy

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Abstract. The multiple-quantum pathway description developed earlier for two-dimensional single-quantum correlation spectroscopy (COSY), is generalized and applied to the two-dimensional multiple-quantum transitions (2D MQT) spectroscopy. The connectivity classes of COSY are also generalized to MQT spectroscopy. The pathway description allows a straightforward method of computation of the flip angle dependence of the intensity of various peaks in two-dimensional correlation spectroscopy. It is shown that a variation of flip angle allows distinction between various classes and types of transitions, as well as optimization of experiment for selective detection of certain classes of peaks in 2D spectroscopy.

Keywords. Nuclear magnetic resonance; two-dimensional multiple quantum coherence; flip angle.

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1. Introduction

Multiple quantum coherence spectroscopy has become an important tool in the hands of NMR experimentalists in recent years. These coherences can be easily excited by pulsed methods and are indirectly detected by coherence transfer to observable single quantum transitions (Hatanaka *et al* 1975; Hatanaka and Hashi 1975; Vega *et al* 1976; Vega and Pines 1977; Stoll *et al* 1977; Drobny *et al* 1979; Warren *et al* 1979, 1980a, b; Warren and Pines 1981a, b; Tang and Pines 1980; Weitekamp *et al* 1981, 1982; Sinton and Pines 1980). Two-dimensional methods form a natural choice for such techniques (Aue *et al* 1976; Wokaun and Ernst 1977, 1978, 1979; Maudsley *et al* 1978; Müller 1979; Müller and Ernst 1979; Bodenhausen 1981; Bax 1982; Brunner *et al* 1980; Minoretti *et al* 1980; Bax *et al* 1980a, b; Freeman *et al* 1981; Jaffe *et al* 1982; Bain and Brownstein 1982; Bodenhausen *et al* 1980; Bax *et al* 1980c). It has been demonstrated that the information content of two-dimensional (2D) experiments can be greatly enhanced by variation of the flip angle of the pulse used for the coherence transfer. In particular it has been demonstrated that the flip angle variation leads to identification of related peaks (Mareci and Freeman 1983), sign of coupling constants (Hore *et al* 1983; Bax and Freeman 1981) and characterization of coupling networks (Braunschweiler *et al* 1983). Recently there have been several approaches to study the coherence transfer process (Bain 1984; Ernst 1984; Bodenhausen *et al* 1984).

We have developed a multiple quantum pathway description for studying the flip angle dependence of transitions in single quantum to single quantum 2D correlation spectroscopy (COSY) (Albert Thomas *et al* 1983) which is generalized in this paper to include multiple quantum to single quantum correlation spectroscopy (MQT). Such a multiple quantum pathway description allows computation of flip angle dependence in a straightforward manner.

Using such a description it is possible to enhance the information content of 2D experiments by varying the flip angle of the coherence transfer pulse. In the MQT spectroscopy the transitions involving the observed spin are separated from those not involving them and connectivity classes are identified. In COSY experiments this leads to a complete identification of connected transitions. We have further generalized the connectivity classes of COSY to MQT spectroscopy and their flip angle dependence has been studied using the pathway description. The pathway description is given in §2, the type and connectivity classes are discussed in §3 and the optimization of the flip angle is discussed in §4.

2. Pathway descriptions

The basic algorithm for excitation and detection of multiple quantum coherences using 2D NMR spectroscopy is shown in figure 1. The signal intensity in such an experiment is calculated using the density matrix approach and is given by (Aue *et al* 1976; Bax 1982; Albert Thomas and Anil Kumar 1984),

$$Z_{abcd} \propto (F_x)_{ab} [P_y(\alpha)]^{-1}_{bc} (\sigma^\circ)_{cd} [P_y(\alpha)]_{da}, \quad (1)$$

where $(\sigma^\circ)_{cd}$ represents the multiple quantum coherence; the operator F_x is the detection operator and $[P_y(\alpha)]$ the propagator associated with the mixing pulse of angle α along the y axis. The coherence cd evolves during t_1 with its characteristic frequency ω_{dc} and is transferred to the single quantum coherence ab detected during t_2 with frequency ω_{ab}.

Equation (1) can be represented pictorially in an energy level diagram by a closed pathway (figure 2a). The single quantum transition ab (shown with thick arrow) detects the multiple quantum coherence cd (also shown with thick arrow), *via* the pathway b to c and d to a. The pathways bd and ca on the other hand correlate the coherence σ°_{dc}, which has a frequency $(-\omega_{dc})$ in the ω_1 domain, to ab. Often it is useful to distinguish the $\pm\omega_1$ quadrants and therefore both these pathways will be considered in all subsequent analysis.

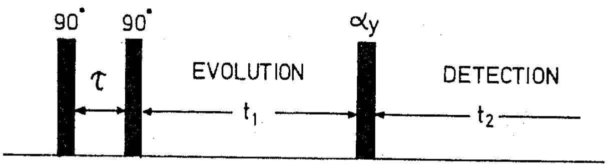

Figure 1. The first 90° pulse applied to the spin system in equilibrium creates single quantum coherences which are transferred to multiple quantum coherences by the second 90° pulse applied after a short time $\tau(\tau < T_1, T_2)$. The coherences evolve during time t_1 and are transferred by the pulse of angle α into single quantum transitions detected during t_2. A complete set of data $(s(t_1, t_2))$ is collected as a function of t_1 and t_2. Double Fourier transformation with respect to t_1 and t_2 yields a 2D MQT spectrum, $S(\omega_1, \omega_2)$, with the ω_1 axis containing all the multiple quantum coherences and ω_2 axis containing the correlated single quantum transitions. While this algorithm also contains single quantum to single quantum correlation information, a simpler two-pulse sequence, in which the first 90° pulse is absent, is used for COSY (Aue *et al* 1976).

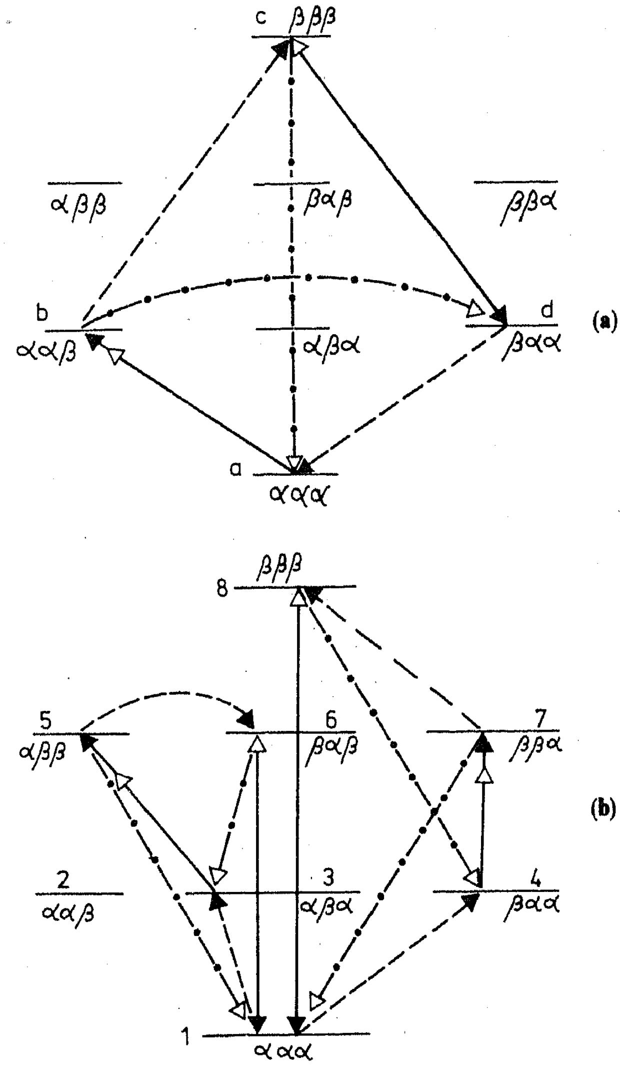

Figure 2. Schematic energy level diagrams of a weakly coupled three spin half nuclei forming a spin system of the type AMX. **a.** The multiple quantum coherence *cd* is detected *via* the single quantum transition *ab*. The pathways are constructed by following the detected single quantum transition and from the top of the SQT to either the top or the bottom of the MQT, following the MQT and returning back to the bottom of SQT (These two paths are respectively shown with dashed lines with filled arrows and by dash-dot lines with open arrows). **b.** Shows the paths required for detection of TQ (AMX) coherence $1 \to 8$ *via* the SQT(M) $4 \to 7$ and the paths required for detection of the DQ (AX) coherence $1 \to 6$ *via* the SQT(X) $3 \to 5$.

The operator $P_y(\alpha)$ can be expressed for a system of N coupled spin 1/2 nuclei as (Anil Kumar 1978),

$$P_y(\alpha) = \prod_{j=1}^{N} [\cos(\alpha/2)\mathbf{1} + 2i \sin(\alpha/2) I_y(j)],$$

$$= \sum_{n=0}^{N} \cos^{N-n}(\alpha/2) \sin^{n}(\alpha/2) (I'_y)^n, \qquad (2)$$

where $$(I'_y)^n = \sum_{p}^{N} \left[\prod_{j=1}^{n} \{I'_y(j)\} \right],$$

where $I'_y(j) = 2i\,I_y(j)$ and Σ_p^N means sum over the product of spin operators over all possible permutations of the $I'_y(j)$ spin operators. For example if $N = 4$ and $n = 2$,

$$\sum_p^N \left[\prod_{j=1}^{n} \{I'_y(j)\} \right] = I'_y(1)\,I'_y(2) + I'_y(1)\,I'_y(3) + I'_y(1)\,I'_y(4) + I'_y(2)\,I'_y(3) + I'_y(2)\,I'_y(4) + I'_y(3)\,I'_y(4). \tag{3}$$

The intensity of a 2D correlated peak with frequency coordinates ω_{ab} and ω_{dc} is governed by the sum of the powers of the I'_y operators required to complete the pathway. If the order of I'_y operators required to complete the pathway is $(I'_y)^n \times (I'_y)^{n'} = (I'_y)^m$ where $m = n + n'$, the following rules hold for weakly coupled spin systems.

(a) The intensity of a peak is proportional to

$$(\cos(\alpha/2))^{2N-m}(\sin(\alpha/2))^m. \tag{4}$$

(b) For even order coherences detected *via* single quantum transitions the value of m will be odd and *vice versa*.

(c) The order n of any path bc is given by the number of spins flipping in the path bc. For example the path $\alpha\beta\alpha \rightarrow \alpha\beta\beta$ is a $n = 1$ path while the path $\alpha\beta\alpha \rightarrow \beta\alpha\beta$ is a $n = 3$ path although both these paths involve single quantum transitions. A path involving a zero quantum transition has a minimum n of order 2. A $n = 0$ path is possible only for $b = c$.

(d) The sign of intensity is given by $(-1)^{n+l+l'}$, where l and l' are the number of spins lowering their states in the two paths and n is the order of the first path starting from the top of the single-quantum transition of w_2 domain.

These rules are required to calculate the flip angle dependance of any peak in a 2D correlated experiment. Figure 2a shows that in a three-coupled spin system AMX, the pathway connecting the double quantum coherence cd to the single quantum transition ab involves one $n = 1$ path and one $n = 2$ path, yielding $m = 3$ and an intensity of $\cos^3(\alpha/2)\sin^3(\alpha/2)$. On the other hand coherence dc observed *via* ab involves one $n = 3$ and the other $n = 2$ path, yielding an intensity of $\cos(\alpha/2)\sin^5(\alpha/2)$. In figure 2b, the triple quantum coherence $1 \rightarrow 8$ detected *via* single quantum coherence $4 \rightarrow 7$ requires two $n = 1$ paths in one quadrant and two $n = 2$ paths in the other, yielding $\cos^4(\alpha/2)\sin^2(\alpha/2)$ and $\cos^2(\alpha/2)\sin^4(\alpha/2)$ respectively for peaks in $+\omega_1$ and $-\omega_1$ quadrants. In case of double quantum coherence $1 \rightarrow 6$ detected *via* the single quantum transition $3 \rightarrow 5$ the paths are $n = 2$ and $n = 1$ yielding $m = 3$ in one quadrant. In the other quadrant the paths are $n = 2$ and $n = 1$ or 3 yielding $m = 3$ or 5 depending upon whether the path $3 \rightarrow 6$ involves flipping of 1 or 3 spins. In the present example the path involves flipping of 3 spins ($n = 3$) yielding $m = 5$.

For higher order spin systems, such as AMPX, the above pathway description similarly allows computation of the flip angle dependence of MQT, in a straightforward manner.

3. Type and connectivity of transitions

Using the pathway description given in §2 the flip angle dependence of intensities in the 2D correlated (MQT and COSY) spectroscopy have been calculated and relations between various multiple (including single) quantum coherences of ω_1 domain observed *via* the single quantum transitions of ω_2, have been obtained. In order to facilitate the above discussion the connectivity definitions of COSY given by Aue *et al* (1976), are generalized to include the MQ coherences, in the following manner.

3.1 *Types of transitions*

Transitions in 2D correlated spectra can be classified into (i) parallel (l), (ii) progressive (p), (iii) regressive (r) and (iv) mixed (pr) (contains mixture of progressive and regressive only) types.

In the 2D MQ spectra all the four types are possible while only the first three are possible in the 2D COSY spectra. The parallel types are generalized to include peaks in which a MQ coherence is transferred to a participating spin. The progressive, regressive and mixed types are those MQ coherences which are transferred to a non-participating spin and the mixed type appears with both progressive and regressive character.

In addition to the above classification, it is necessary, in the MQT, to specify the order of MQ coherence (δ) and the number of spins involved in that coherence (γ). The following notations completely specify peaks in the 2D correlated spectra.

$$\gamma s\delta Q[SlN]\text{—parallel type,}$$

$$\gamma s\delta Q[SpN]\text{—progressive type,}$$

$$\gamma s\delta Q[SrN]\text{—regressive type,}$$

$$\gamma s\delta Q[S(\varepsilon p\eta r)N]\text{—mixed type.}$$

The above notations are read as, γ-spin-δ-quantum coherence observed *via* a SlN type transition, where S is the effective number of spins changing their spin states in the

Table 1. Type of connectivity of some of the multiple quantum coherences of AMPX detected *via* single quantum transitions, in 2D correlated spectroscopy.

Transitions			
MQ in ω_1 , SQ in ω_2	Notation*	Type**	Connectivity
$(\alpha\alpha\alpha\alpha \to \beta\beta\beta\alpha), (\alpha\alpha\alpha\alpha \to \beta\alpha\alpha\alpha)$	$AMP(X_+), A(M_+P_+X_+)$	$3s3Q[3l4]$	C
$(\alpha\alpha\alpha\alpha \to \beta\beta\beta\alpha), (\alpha\alpha\beta\alpha \to \beta\alpha\beta\alpha)$	$AMP(X_+), A(M_+P_-X_+)$	$3s3Q[3l4]$	U
$(\alpha\alpha\alpha\alpha \to \beta\beta\beta\alpha), (\alpha\alpha\alpha\beta \to \beta\alpha\alpha\beta)$	$AMP(X_+), A(M_+P_+X_-)$	$3s3Q[4l4]$	U
$(\alpha\alpha\alpha\alpha \to \beta\beta\beta\alpha), (\alpha\alpha\alpha\alpha \to \alpha\alpha\alpha\beta)$	$AMP(X_+), X(A_+M_+P_+)$	$3s3Q[4r4]$	C
$(\alpha\alpha\alpha\alpha \to \beta\beta\beta\alpha), (\beta\beta\beta\alpha \to \beta\beta\beta\beta)$	$AMP(X_+), X(A_-M_-P_-)$	$3s3Q[4p4]$	C
$(\alpha\alpha\alpha\alpha \to \beta\beta\beta\alpha), (\alpha\alpha\beta\alpha \to \alpha\alpha\beta\beta)$	$AMP(X_+), X(A_+M_+P_-)$	$3s3Q[4(1p2r)4]$	U
$(\alpha\alpha\alpha\alpha \to \beta\beta\beta\alpha), (\alpha\beta\beta\alpha \to \alpha\beta\beta\beta)$	$AMP(X_+), X(A_+M_-P_-)$	$3s3Q[4(2p1r)4]$	U
$(\alpha\alpha\beta\beta \to \beta\alpha\alpha\alpha), (\alpha\alpha\alpha\alpha \to \beta\alpha\alpha\alpha)$	$APX(M_+), A(M_+P_+X_+)$	$3s1Q[3l4]$	C
$(\alpha\alpha\alpha\alpha \to \alpha\alpha\beta\beta), (\alpha\alpha\beta\alpha \to \beta\alpha\beta\alpha)$	$PX(A_+M_+), A(M_+P_-X_+)$	$2s2Q[3(1p1r)4]$	U
$(\alpha\alpha\alpha\alpha \to \alpha\alpha\beta\beta), (\alpha\beta\beta\alpha \to \beta\beta\beta\alpha)$	$PX(A_+M_+), A(M_-P_-X_+)$	$2s2Q[4(1p1r)4]$	U
$(\alpha\alpha\alpha\alpha \to \alpha\alpha\beta\beta), (\alpha\beta\alpha\beta \to \alpha\beta\alpha\alpha)$	$PX(A_+M_+), X(A_+M_-P_+)$	$2s2Q[3l4]$	U
$(\alpha\beta\alpha\beta \to \alpha\alpha\beta\beta), (\alpha\beta\alpha\beta \to \alpha\beta\alpha\alpha)$	$MP(A_+X_-), X(A_+M_-P_+)$	$2s0Q[3(1p1r)4]$	C

* The spins involved in the transitions are indicated outside the bracket, while those not involved are indicated inside the bracket along with their spin states (Aue *et al* 1976); ** $l \equiv$ spin flipping in SQ transition is also involved in the MQ coherence; $p, r, pr \equiv$ Different spins flip in MQ and SQ coherences. For example let the SQ coherence be an X transition and MQ be AMP 3-spin-3 quantum coherence. Those of A, M, or P spins which appear with polarization identical to X within the brackets are regressive and those A, M, or P which appear with polarization opposite to X within the brackets are progressive; example $AMP(X_+)$, $X(A_+M_-P_+)$ is a $3s3Q[4(1p2r)4]$ type;
C = Connected; U = Unconnected.

two transitions constituting a peak in the 2D spectrum and N is the total number of spins in the system. Some examples in table 1 explain the above notations.

With these notations the intensity formulae given for COSY by Aue *et al* (1976) are generalized, to include the MQ coherences, in the following manner.

The parallel type (l) peaks have intensity, in one of the quadrants of ω_1, proportional to:

$$(\sin(\alpha/2)^{2S-\gamma+1}(\cos(\alpha/2))^{2N-(2S-\gamma+1)}, \tag{5}$$

and in the other quadrant, proportional to:

$$(\sin(\alpha/2))^{2S-\gamma-1}(\cos(\alpha/2))^{2N-(2S-\gamma-1)}. \tag{6}$$

The progressive, regressive and mixed type (p, r, pr) peaks have intensity proportional to:

$$(\sin(\alpha/2))^{2S-\gamma-1}(\cos(\alpha/2))^{2N-(2S-\gamma-1)}, \tag{7}$$

in both the quadrants of ω_1.

3.2 *Connectivity rules*

Using the pathway description of §2, and the above classification, the following connectivity rules are obtained in correlated spectroscopy of weakly-coupled non-symmetrical spin systems.

(i) Whenever a particular peak has identical absolute intensity in the $+\omega_1$ and $-\omega_1$, quadrants, (which is reflected by the identical m values in the $\pm\omega_1$ quadrants) then that peak represents a coherence transfer to a non-participating spin and is of type p, r or pr. For example DQ (AX) coherences detected *via* a M single quantum transition have $m = 3$ in both the quadrants in an AMX spin system. In COSY every cross peak between different spins is of type p or r and has identical intensity in $\pm\omega_1$ quadrants.

The p, r and pr type peaks can further be distinguished, depending on the S value; (a) when $\gamma = (N-1)$, S can only take a value equal to N. All such coherences within the same order have the same flip angle dependence. Connectivity of transitions in such cases plays no role in the intensities. (b) When $\gamma < (N-1)$, S can take values $\gamma+1$, $\gamma+2, \ldots N$. In COSY ($\gamma = 1$) all transitions of this class which have $S = \gamma+1$ are connected. Thus the connected p, r, transitions of COSY follow the lowest total order pathway (sum of m values in $\pm\omega_1$ quadrants) (Albert Thomas *et al* 1983). For MQT ($\gamma > 1$) however, while all connected transitions follow the lowest total order pathway there are some unconnected transitions which also follow the lowest total order pathway.

(ii) The peaks which do not have identical intensity in $\pm\omega_1$ quadrants, are of l type, and can also be further distinguished depending on the S value. (a) when $\gamma = N$, S can only take a value equal to N. This case represents the highest quantum peaks and peaks such as 3-spin-1QT in a three-spin-system, 4-spin-2QT or 4-spin-0QT in a four-spin-system etc. Each of such coherences has the same flip angle dependence to all SQTs along ω_2, which may be different for a different coherence along ω_1 of the same order. The connectivity of transitions plays no role in these cases as well. (b) when $\gamma < N$, S takes values $\gamma, \gamma+1, \ldots N$. When $\gamma = 1$, *i.e.*, in the COSY spectrum all diagonal peaks have $S = 1$ and follow total pathway of lowest order. All other l type peaks in COSY (auto peaks) have $S > 1$, and represent unconnected transitions. When $\gamma > 1$ *i.e.* in the MQT spectrum, peaks for which $S = \gamma$ include all connected transitions and some unconnected transitions in higher order spin systems. For example in the AMX case, the DQ (AX) coherences seen on A have two 2/3 type peaks both of which are connected to the concerned DQ coherence while in the AMPX case TQ (AMP) seen on A have four 3/4 type peaks, only 2 of which are connected.

Thus, in general in 2D correlated spectroscopy peaks arising from connected transitions follow a total pathway of lower order.

From the above rules it is clear that a variation of flip angle of the coherence transfer pulse, enables one to distinguish the various classes of transitions in MQT and COSY spectroscopy. In particular, in the COSY spectra the connectivity of transitions can be established by such a variation.

4. Optimization of the flip angle

Pathways involving higher order paths are attenuated in intensity as the flip angle α is reduced below 90°, (equation (4)), while they are enhanced for an increase of the flip angle above 90°. It is thus possible to selectively enhance and distinguish types of transitions by a variation of the flip angle. Depending on the type of information desired the flip angle can be optimized for maximum information, both in 2D COSY spectra and 2D MQT spectra.

4.1 *MQT*

Figure 3 shows schematically the flip angle dependence of triple-quantum (TQ), double-quantum (DQ), zero-quantum (ZQ) and three-spin-one-quantum (TSQ) coherences, in a 2D correlated spectrum of an AMX spin system. Clearly seen in this spectrum are the connectivity features outlined in §3, *viz*; the transitions between non-participating spins have identical intensities in the $\pm\omega_1$ quadrants and the participating spin transitions have the total order of pathway lower if they share a common energy level between ω_1 and ω_2 domains. The intensities of these peaks have flip angle dependence given by $\sin^m(\alpha/2)\cos^{6-m}(\alpha/2)$; where m is the order of the pathway. The functional form of $\sin^m(\alpha/2)\cos^{6-m}(\alpha/2)$ for $m = 0$ to 6 is plotted in figure 4. It is noted that (i) all transitions have equal intensities for $\alpha = 90°$ and (ii) $\sin(\alpha/2)\cos^5(\alpha/2)$ has its maximum at $\alpha = 45°$ with the value approximately twice that for $\alpha = 90°$. DQ and ZQ coherences transferred to a connected single quantum coherence of a participating spin have intensities proportional to $\sin(\alpha/2)\cos^5(\alpha/2)$. These can thus be either enhanced in intensity in one of the ω_1 quadrants by use of $\alpha = 45°$ or selectively detected by using $\alpha = 15°$. For $\alpha = 15°$ all other MQTs have much lower intensity and the concerned DQ and ZQ have intensities approximately same as for $\alpha = 90°$. (iii) As a corollary, the unconnected DQ and ZQ coherences of participating spins can be enhanced in intensity by using $\alpha = 135°$ or selectively detected by using $\alpha = 165°$.

4.2 *COSY*

The flip angle dependence in the COSY spectrum of AMX spin systems is given in figure 5. It is seen that all cross peaks between different spins have identical intensity in the $\pm\omega_1$ quadrants while the auto and diagonal peaks have different intensities in the two quadrants. Further it is seen that use of a flip angle greater than 90° enhances unconnected cross peaks between different spins. Simultaneously however, auto peaks

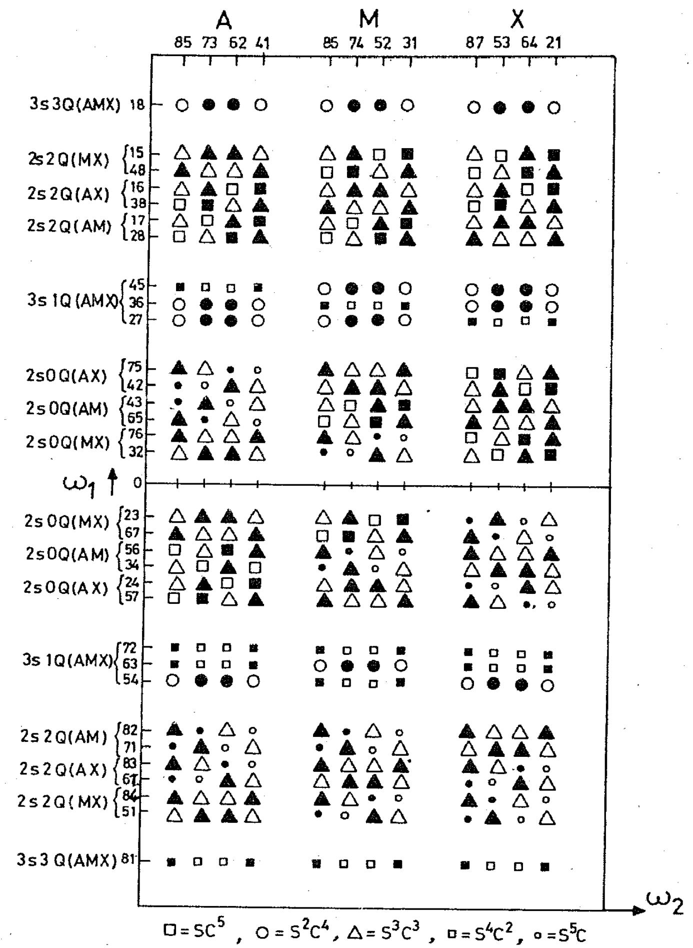

Figure 3. Schematic 2D multiple quantum spectrum of an AMX spin system for a mixing pulse of angle α. This figure contains all coherences except $1s1Q$ coherences. $S = \sin(\alpha/2)$, $C = \cos(\alpha/2)$ (Filled symbols represent negative intensity).

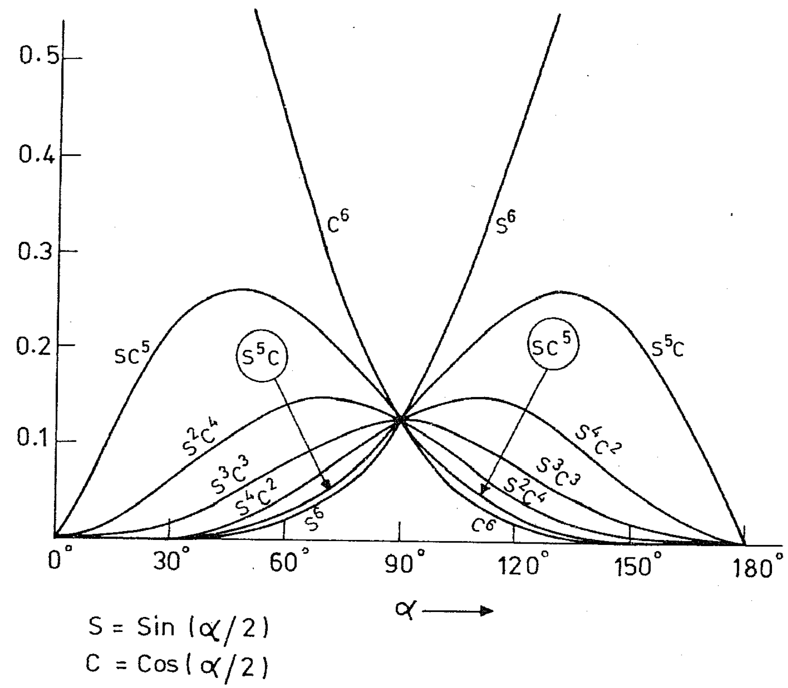

Figure 4. Plot of $\sin^m(\alpha/2)\cos^{6-m}(\alpha/2)$ for $m = 0, 1, \ldots 6$, *as a function of* α.

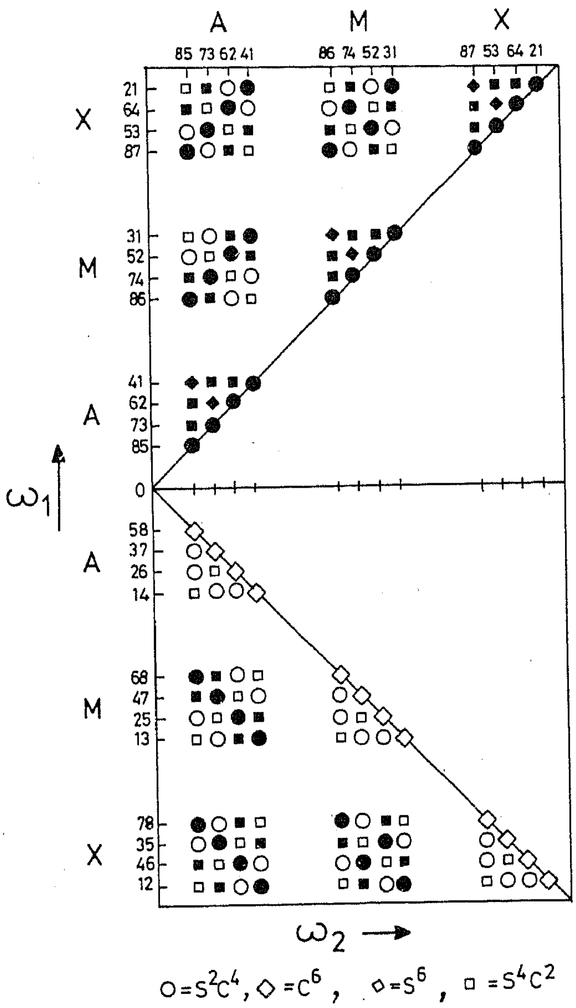

Figure 5. Schematic 2D COSY spectrum of an AMX spin system for a mixing pulse of angle α. Notation for symbols same as in figure 3. Symmetric half of the spectrum is not drawn.

of type 3/3 are enhanced in both the quadrants with auto peaks of type 2/3 enhanced only in one of the quadrants. The diagonal peaks are reduced significantly in both the quadrants. It is seen that an optimum flip angle of 130° yields a COSY spectrum with maximum contrast between the reduced diagonal peaks and the unconnected cross peaks. The intensity distribution for $\alpha = 150°$ is shown in figure 6. It is clear that such a spectrum has the desired information of cross peaks with much less chance of cancellation of cross peak intensities due to poor spectral or digital resolution, compared to an experiment with $\alpha = 90°$. This complements the SUPER COSY method suggested recently (Anil Kumar *et al* 1984).

5. Conclusions

The pathway description provides a straightforward method of computing flip angle dependence of various multiple quantum coherences in the 2D MQT and the 2D COSY spectroscopy. Using this flip angle dependence it is possible to distinguish various connectivity classes of the coherences detected *via* the single quantum transitions.

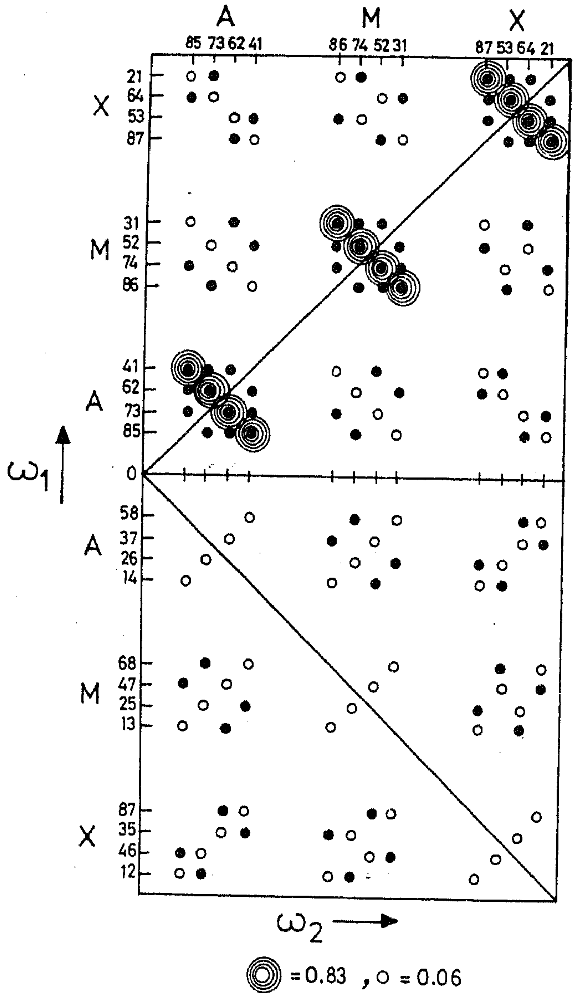

Figure 6. Schematic 2D COSY spectrum of an AMX spin system for a mixing pulse of angle $\alpha = 150°$. The diagonal peaks are reduced in intensity in both quadrants and are absent. The negative ω_1 quadrant has all peaks of the same absolute intensity, which are of value approximately half that for $\alpha = 90°$ (Filled inner circles indicate negative intensity).

Monitoring the amplitudes of peaks in the $\pm\omega_1$ quadrants allows distinction between coherence transfer between participating spins and non-participating spins. It is shown that, in general, transfer of a multiple quantum coherence to a connected single quantum transition takes place *via* a lower order pathway. The intensity of such transitions can be enhanced compared to others, by the use of a flip angle of the coherence transfer pulse lower than 90°. In COSY spectroscopy, all the connected transitions take lower order paths compared to unconnected transitions and can be exclusively detected by the use of a low flip angle. On the other hand, use of a large flip angle $\alpha = 150°$ allows selective detection of only unconnected transitions and elimination of diagonal peaks.

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