GENERATING A SECSY SPECTRUM FROM A COSY SPECTRUM

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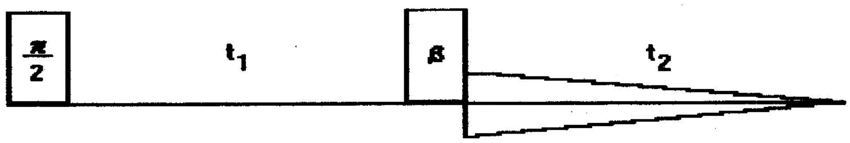
Introduction

One of the techniques that was widely used in the early days of 2D NMR was spin-echo correlated spectroscopy (SECSY).[1] This has the advantage that in cases where the difference in chemical shift between coupled spins is less than half the chemical shift range, the spectral width in the SECSY spectrum in ω_1, may be reduced. The method is now little used for a number of reasons. It does not give pure phase lineshapes (unless a z-filter is used), correlations are less obvious than in the correlated spectroscopy (COSY)[2] experiment. The total experiment time is longer but the sensitivity less than COSY for the same number of transients. Enhancement methods commonly used for COSY spectra (such as symmetrisation) cannot be used on SECSY.

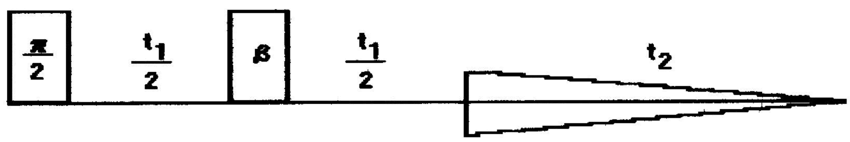
In this poster we show that both a SECSY and a Long-range COSY[3] data set can be readily generated from COSY data, obviating the need to run these experiments separately. In addition we note the potential utility of SECSY in inhomogeneous fields (e.g. in vivo) and present a method to symmetrise SECSY spectra using conventional software.

The pulse sequences for the three experiments (excluding the necessary phase cycling) are:

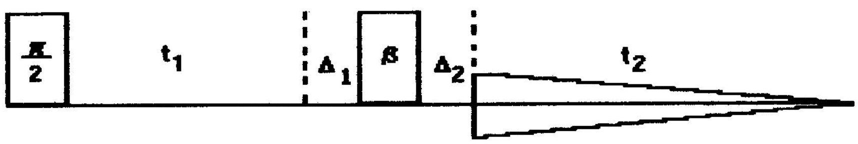
a) COSY



b) SECSY



c) Long-Range COSY



It has previously been commented upon[4] and is clear from examination of the pulse sequences, that shearing of the COSY data matrix will lead to a SECSY spectrum. The shearing is analagous to the tilting of a J-Resolved spectrum and indeed the same software may be used for both operations.

To obtain the Long-range COSY experiment the acquisition in both t_1 and t_2 is delayed by a time Δ. This may be simulated by left shifting the data in both dimensions, a process that is also readily accomplished using standard NMR software functions.

Finally, for the sake of completeness, it should be commented that a "Long-range SECSY" experiment is obtained by performing the COSY to SECSY transformation on the Long-range COSY matrix.

Clearly, in shearing or shifting the matrix, data points are discarded (from the start of the fid) and thus signal/noise is lost. This is a drawback with both the SECSY and Long-range COSY methods, but since no additional experiment has to be run this is an advantage of deriving the data sets from an existing COSY.

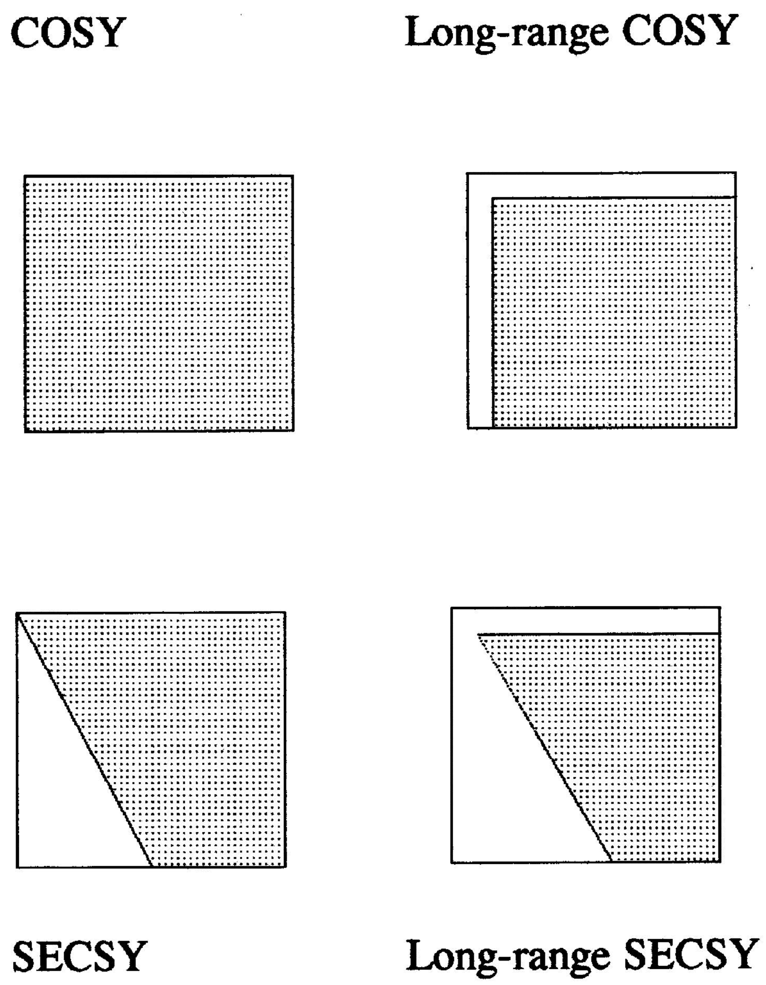


Figure 1. A pictorial representation of the relationship between COSY, SECSY and Long-range COSY (and SECSY).

For a SECSY experiment the density operator at the start of acquisition is given by:

$$\sigma(t_1,t_2=0) = \sum_{i\neq j} + \cos^2(\pi J_{ij}t_1)\sin(\omega_i t_1)\cos(\omega_i t_1)\mathbf{I}_{ix}$$
$$+ \cos(\pi J_{ij}t_1)\sin(\pi J_{ij}t_1)\sin^2(\omega_i t_1)\mathbf{I}_{iy}$$
$$+ \sin^2(\pi J_{ij}t_1)\sin(\omega_i t_1)\cos(\omega_i t_1)\mathbf{I}_{jx}$$
$$+ \sin^2(\pi J_{ij}t_1)\sin(\omega_i t_1)\cos(\omega_i t_1)\mathbf{I}_{jx}$$

Terms 1 and 2 give rise to "Diagonal" peaks (which are actually on the line $\omega_1=0$). Terms 3 and 4 give rise to the "Cross" peaks (at $\omega_2=\omega_j$, $\omega_1=\omega_i+\omega_j$). The cross peak term is a combination of $\mathbf{I}_x$ and $\mathbf{I}_y$, the resulting cross peak being in-phase but with phase-twist lineshape.

It is the in-phase signal that is the attraction of the SECSY method *in-vivo* since the broad lines of a multiplet tend to cancel if the signal is anti-phase. In certain conditions it may be possible to observe cross peaks in a SECSY spectrum but not in the corresponding COSY spectrum.

Figure 2 shows the COSY, Long-range COSY, and SECSY spectra of a simple steroid (11β-Methoxy-17α-ethynyl oestradiol) together with the SECSY and Long-range COSY spectra generated from the COSY data set.

The "simulated" SECSY spectrum has half the sweep-width in ω_1 of the actual SECSY, this is because the sampling interval is still t_1 and not $t_1/2$ as required by the pulse sequence (see diagram). Folding in ω_1 is a problem only if the differences between the chemical shifts of coupled spins is large.

A SECSY spectrum can be symmetrised if it is first tilted in the same manner as a J-resolved spectrum. The signals are then symmetrical about $\omega_1=0$. After symmetrisation the spectrum may be tilted back to the original position if desired, however the tilted spectrum is no more difficult to interpret.

Conclusion

An acceptable SECSY and Long-range COSY spectrum may be generated from a COSY data set. There is a loss of both signal-to-noise and digital resolution since the transformation process involves the discarding of data points. The method is nonetheless a time effective way to (hopefully) obtain the desired information without resort to running further experiments. In cases where the acquisition time required is long or where the sample is no longer available, this method should prove useful.

References

1) K. Nagayama, K. Wuthrich, and R.R. Ernst, *Biochem. Biophys. Res. Commun.* **90**, 305(1979).

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3) A. Bax, and R. Freeman, *J. Magn. Reson.* **44**, 542(1981).

4) R.R. Ernst, G. Bodenhausen, and A. Wokaun, In *Principles of Nuclear Magnetic Resonance in One and Two Dimensions.* p.336-340(1987).

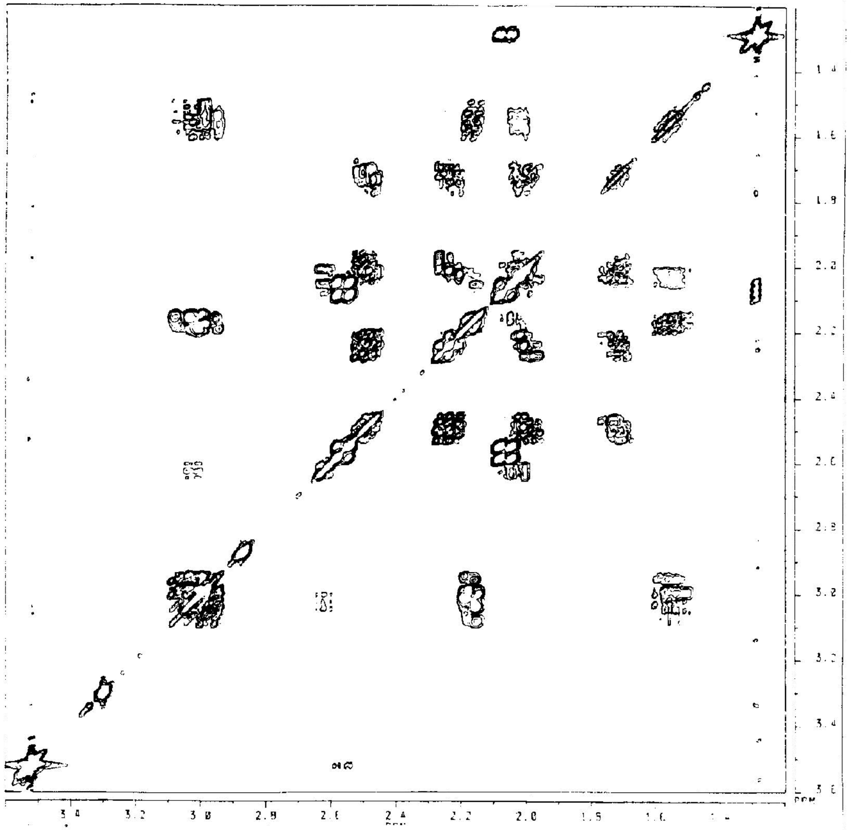

Figure 2a Original COSY spectrum

<u>Parameters</u>

2600 Hz sweep width
2048 complex points (t_2)
4 scans per increment
512 increments
2 second relaxation delay
8μs 90° pulse
sine-bell window in both dimensions

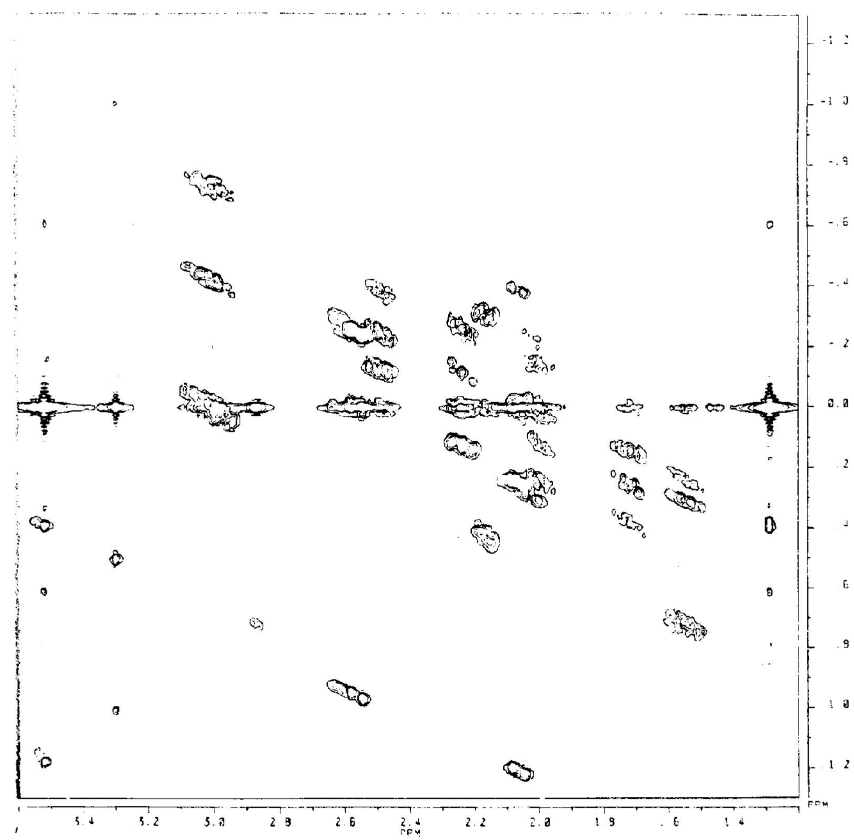

Figure 2b Original SECSY spectrum

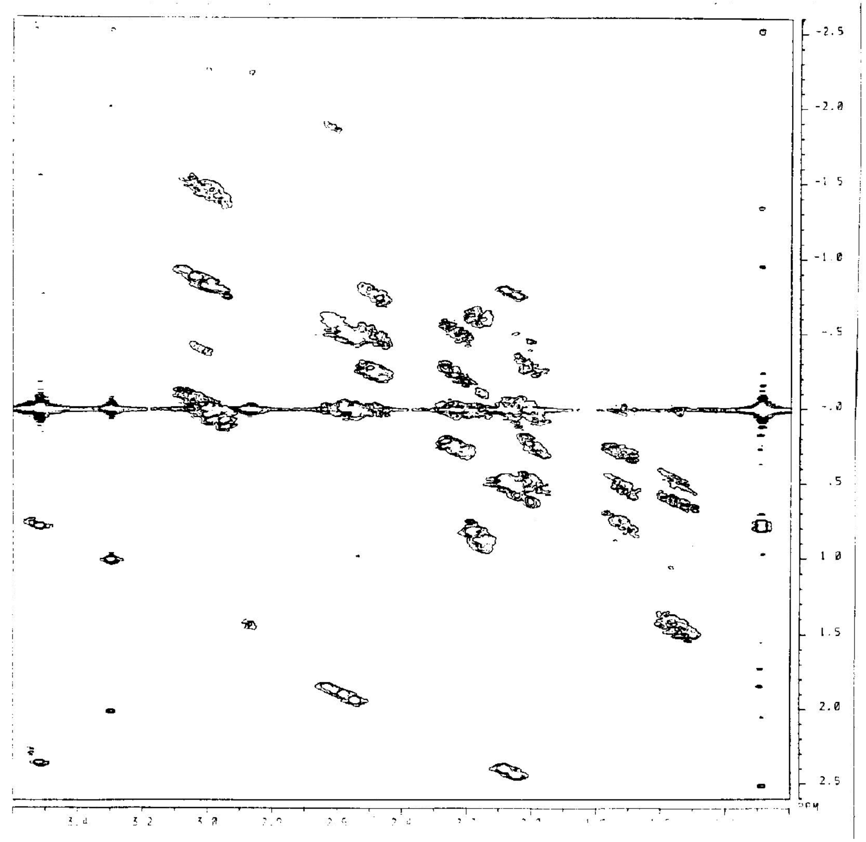

Figure 2c SECSY from COSY

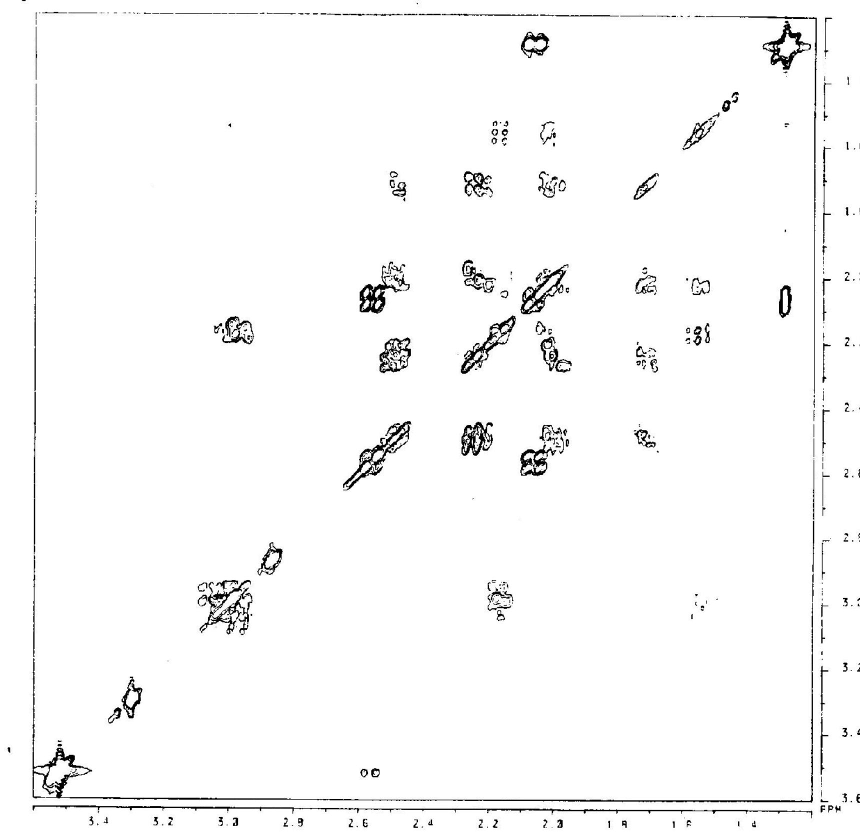

Figure 2d Long-range COSY spectrum

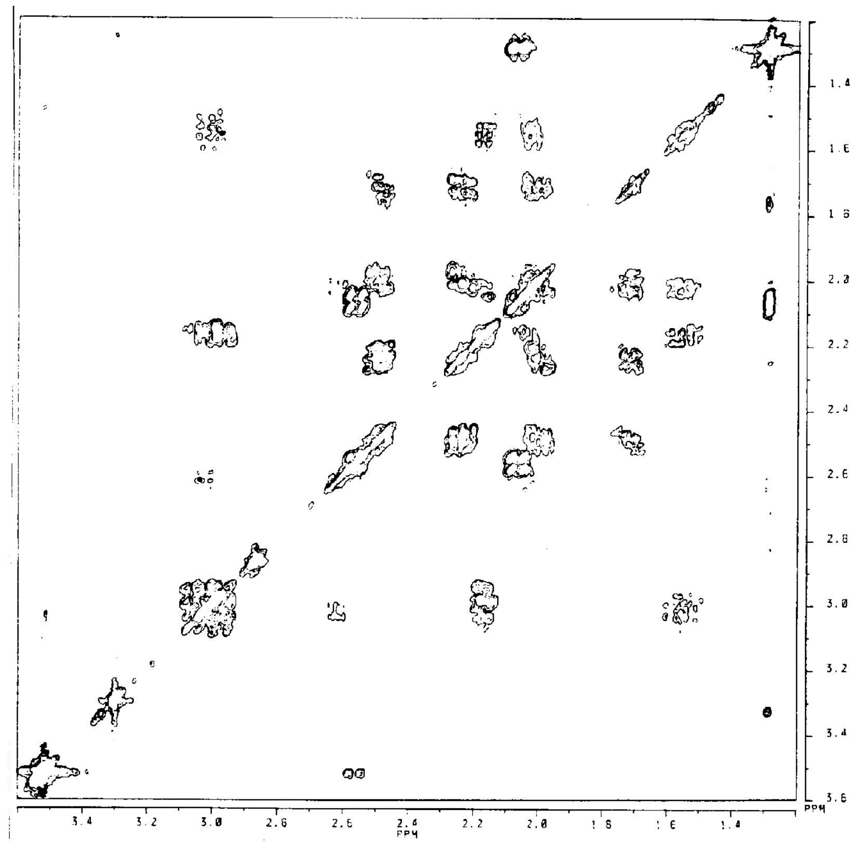

Figure 2e Long-range COSY from COSY