FAST TWO-DIMENSIONAL CORRELATION SPECTROSCOPY

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Correlation spectroscopy (COSY) is one of the most powerful methods of Fourier Transform NMR, providing unequivocal evidence of scalar couplings wiithin a molecule and a measure of their magnitudes. We suggest here that a selective pulse experiment (Ψ-COSY) can be used to provide the same information more quickly through a judicious choice of one-dimensional experiments. The advantage is particularly marked when the operator already has a good idea which chemical shift correlations are important and can plan the experiment accordingly.

Instead of running a two-dimensional experiment, we simply use a shaped radiofrequency pulse to irradiate one line from each spin multiplet. Coherence is transferred to all the coupled sites in much the same way as in conventional 90^o COSY. Each selective pulse experiment gives several correlations, rather like the analogous double resonance experiment. We then compare these coherence transfer traces with the unperturbed high resolution spectrum. This gives a very direct view of the correlations and an accurate measure of the couplings, since the limiting resolution can be made very high.

If we still wish to see a two-dimensional cross-peak, this can be simply constructed by multiplying two orthogonal sections through the cross-peak taken parallel to the F_1 and F_2 axes. This assumes the amplitude transfer function for a cross-peak due to I -> S coherence transfer from a conventional 90^o COSY for a three spin system can be written

$$s(t_1, t_2) = g(t_1)\, h(t_2) \quad \text{where}$$

$$g(t_1)=\sin(2\pi\Omega_1 t_1)\sin(\pi J_{is} t_1)\cos(\pi J_{ir} t_1)\exp(-\lambda_1 t_1)$$

$$h(t_2)=\sin(2\pi\Omega_2 t_2)\sin(\pi J_{is} t_2)\cos(\pi J_{ir} t_2)\exp(-\lambda_2 t_2)$$

The cross-peak arising from S->I coherence transfer is

$$s(t_1, t_2) = h(t_1)\, g(t_2)$$

The two dimensional cross-peak signal can then be written

$$S(\omega_1, \omega_2) = G(\omega_1)\, H(\omega_2),$$

where $G(\omega_1)$ and $H(\omega_2)$ are the Fourier transforms of $g(t_1)$ and $h(t_2)$, respectively. This expression for the cross-peak signal amplitude is only true in the absence of coherence transfer echoes, which appear in the two-dimensional spectrum as tilted elliptical contours. The sections need not pass through exact resonance but should have adequate signal-to-noise and avoid extraneous resonances.

The cross-peak construction need not require two orthogonal traces taken through the cross-peak. A 90^o COSY two-dimensional spectrum has reflection symmetry about the principal diagonal, expressed mathematically in the above equations. Ψ-COSY exploits this property, deriving one trace from one cross-peak and the other fom its partner across the diagonal. The result is a very finely resolved two-dimensional cross-peak obtained in a very short time.