

## Spectral-Spatial E.S.R. Imaging of Portions of Spectra of Paramagnetic Metals

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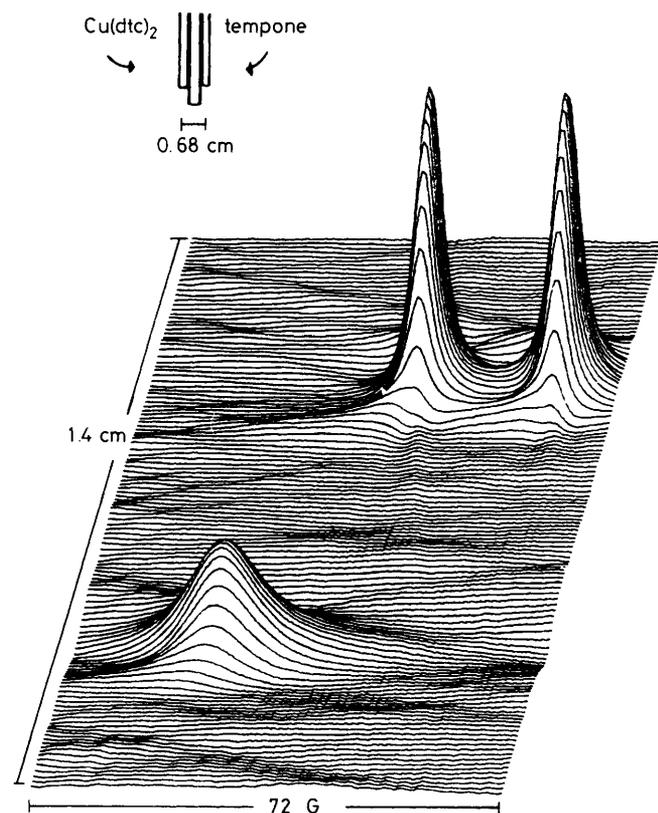
Spectral-spatial e.s.r. imaging has been performed with a maximum gradient of  $400 \text{ G cm}^{-1}$  ( $G = 10^{-4} \text{ T}$ ) and a spectral window that includes only a portion of the hyperfine-split spectra of paramagnetic metal complexes; this result removes a previously perceived barrier to e.s.r. imaging of species with multi-line spectra.

Until recently it was believed that hyperfine splittings and  $g$ -value anisotropies would severely limit the applicability of e.s.r. imaging.<sup>1</sup> Most examples of imaging of species that exhibit multiline e.s.r. spectra, or mixtures of more than one radical species, have carefully selected one isolated hyperfine line.<sup>1,2</sup> Further, these experiments avoided use of magnetic field gradients that would cause overlap of the selected line with other hyperfine lines. This placed severe restrictions on the type of spectra that could be imaged. Since spatial resolution is increased by the use of high gradients, limitations on maximum gradient restricted the resolution that could be achieved for complex spectra.

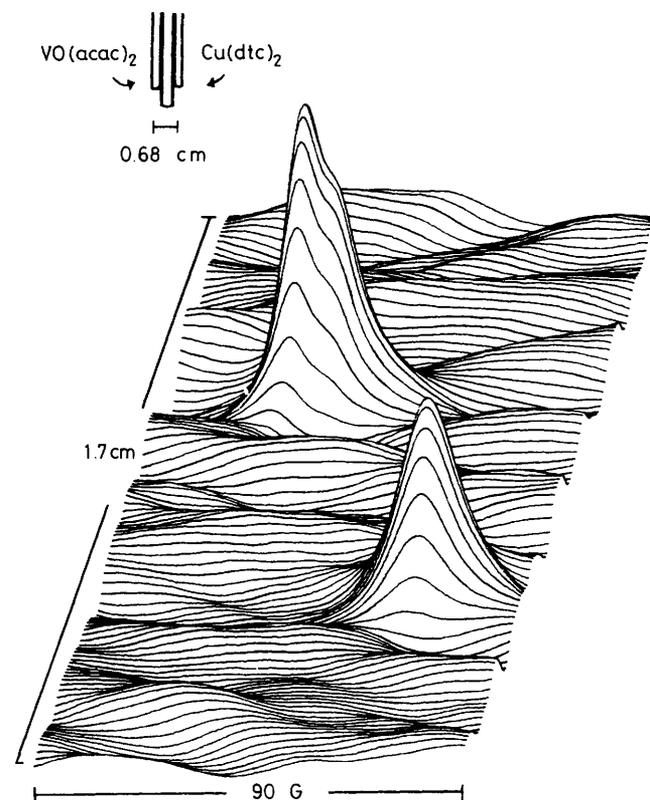
Recently we demonstrated two-dimensional spectral-spatial e.s.r. images with the full hyperfine-split spectra of multiple

species along one axis and spatial distribution along the other axis.<sup>3</sup> This technique eliminated the restriction to isolated lines, but still appeared to require that all spectral components be included in each spectrum used to construct the image. In spectral-spatial imaging, e.s.r. spectra are recorded at a series of magnetic field gradients. Each gradient corresponds to an angle  $\alpha$  in the spectral-spatial plane. The magnetic field sweep at each angle equals  $\sqrt{2} \Delta H (\cos \alpha)^{-1}$ , where  $\Delta H$  is the length of the magnetic field axis in the resulting image. The length of the spatial axis in the resulting image,  $L$ , is equal to  $\tan(\alpha_{\text{max}}) \Delta H / \text{maximum gradient}$ . Since  $L$  is proportional to  $\Delta H$ , a spectral-spatial image that encompassed the full spectrum for a metal with large hyperfine splitting would give a very large value of  $L$  and unacceptably low spatial resolution of the image.

Here we demonstrate that even this limitation on e.s.r. imaging can be overcome. Figure 1 shows a two-dimensional spectral-spatial image of a sample composed of two 0.3 cm OD tubes supported on a 0.4 cm OD tube to give a centre-to-centre separation of 0.68 cm between the two tubes.



**Figure 1.** The two-dimensional spectral-spatial e.s.r. image of a sample composed of a tube of  $\text{Cu}(\text{dte})_2$  solution and a tube of  $^{15}\text{N}$ -tempone solution. The image was obtained on a Varian E-9 X-band spectrometer with gradient coils that produce a maximum magnetic field gradient of  $400 \text{ G cm}^{-1}$  ( $4 \text{ T m}^{-1}$ ). Spectra were obtained with 100 kHz modulation frequency, 0.2 G modulation amplitude, and 8 mW microwave power. The image was reconstructed from 60 experimental projections and 4 'missing' projections with the iterative algorithm described in ref. 4. The image is displayed on a  $128 \times 128$  grid.



**Figure 2.** The two-dimensional spectral-spatial e.s.r. image of two tubes containing  $\text{VO}(\text{acac})_2$  and  $\text{Cu}(\text{dte})_2$ . The experimental conditions and image reconstruction were the same as for Figure 1, except that the modulation amplitude was 1.0 G.

One tube contained a solution of copper(II)bis(diethyldithiocarbamate)  $\text{Cu}(\text{dtc})_2$ , (5 mm in toluene), and the other tube contained  $^{15}\text{N}$ -tempone (4-oxo-2,2,6,6-tetramethylpiperidin-1-oxyl) (2 mm in air-saturated toluene). A horizontal slice through the image gives the e.s.r. spectrum at a point along the spatial axis. A vertical slice through the image gives the spatial distribution of the e.s.r. signal intensity at a particular value of magnetic field. The value of  $\Delta H$ , 72 G ( $G = 10^{-4}\text{ T}$ ), was selected to include one hyperfine line from the four-line copper spectrum and the tempone spectrum. The magnetic field sweeps used for data collection ranged from 102 to 834 G, so the narrowest sweeps encompassed only one copper line and the widest sweeps encompassed the complete four-line copper spectrum. Even so, the reconstructed image contains only one of the copper lines and the two nitroxyl lines. The image accurately reflects the fact that the broad copper line is spatially removed from the two-line nitroxyl spectrum by 0.68 cm and there are relatively few artifacts in the image.

Figure 2 shows a 2-dimensional spectral-spatial image obtained with a sample composed of two tubes containing solutions of vanadyl acetylacetonate,  $\text{VO}(\text{acac})_2$ , and  $\text{Cu}(\text{dtc})_2$ , which have 8- and 4-line spectra, respectively. The spectral window chosen for the image,  $\Delta H$ , included only the highest-field copper line ( $m_I = -\frac{3}{2}$ ) and the vanadyl  $M_I = -\frac{1}{2}$  line. The magnetic field sweeps used to obtain the image varied from 127 to 1040 G. Consequently, as the gradient was increased, additional lines that were not in the chosen window were included in the spectra. The resulting image shows the

spatial resolution of the copper and vanadyl lines and the isotope splitting ( $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ ) is partially resolved on the copper line. The large number of lines outside the selected window causes more baseline artifacts in Figure 2 than in Figure 1. Techniques are being explored to remove the artifacts.

This result opens the field of e.s.r. imaging to a much wider range of samples with multiline spectra than heretofore anticipated.

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