

Note

# STRAFI imaging of paramagnetic solids: <sup>31</sup>P paramagnetic displacements†‡

Edward W. Randall,<sup>1\*</sup> Andrei A. Samoilenko<sup>2</sup> and Riqiang Fu<sup>3</sup>

<sup>1</sup> Department of Chemistry, Queen Mary, University of London, Mile End Road, London E1 4NS, UK

<sup>2</sup> Institute of Chemical Physics, 117977 Kosygina 4, Moscow, Russia

<sup>3</sup> Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory, 1800 East Paul Dirac Drive, Tallahassee, Florida 32310, USA

Received 15 June 2001; Revised 3 October 2001; Accepted 4 October 2001

One-dimensional stray field (STRAFI) profiles of <sup>31</sup>P in phantoms containing, variously, calcium hydroxyapatite, calcium orthophosphate and cobaltous phosphate octahydrate were obtained in a STRAFI field of 11.7 T on a 19.6 T magnet at 206 MHz. The intrinsic spatial resolution with the apatite and orthophosphate samples was about 100 μm. The profile of the image from the paramagnetic cobaltous sample was displaced to high field by 1.2 MHz. The spatial resolution for the cobalt component was degraded because of the large linewidth of ~0.6 MHz. Copyright © 2001 John Wiley & Sons, Ltd.

**KEYWORDS:** NMR; strong field gradients; STRAFI profiles; phosphorus-31; paramagnetic shifts

## INTRODUCTION

The stray-field (STRAFI) imaging method<sup>1</sup> is useful for the imaging of solid substances containing nuclei with very short spin–spin relaxation times.<sup>2</sup> Most commonly dipolar nuclei, such as <sup>1</sup>H, in solid diamagnetic compounds have been involved. The STRAFI imaging, usually in one spatial dimension, has shown its utility particularly for the study of organic polymers,<sup>1</sup> but it is more widely applicable, for example to diamagnetic crystalline hydrates and transition metal complexes, and even to paramagnetic compounds,<sup>3,4</sup> as well as to quadrupolar nuclei in solids.<sup>5–9</sup>

In the laboratory frame, the Hamiltonian describing the behaviour of nuclei of spin momentum  $I (= 1/2)$ , placed in this fringe field can be expressed as the sum of four components for diamagnetic cases: the Zeeman Hamiltonian,  $H_Z$ , the gradient Hamiltonian,  $H_G$ , and the Hamiltonians,  $H_D$ , for the nuclear–nuclear dipolar interaction,  $D$ , and  $H_J$  for the indirect interactions,  $J$ :

$$H = H_Z + H_G + H_D + H_J \quad (1)$$

The Zeeman term, including the chemical screening constant,  $\sigma$ , is

$$H_Z = \gamma B_Z(1 - \sigma)I_Z \quad (2)$$

†Dedicated to Professor Robin K. Harris on the occasion of his 65th birthday.

\*Correspondence to: E. W. Randall, Department of Chemistry, Queen Mary, University of London, Mile End Road, London E1 4NS, UK. E-mail: e.w.randall@qmw.ac.uk

‡Part of a talk given at the Special Ampère meeting on high-field magnetic resonance, Stuttgart, Germany, July 2001.

The large size of the gradient,  $G$ , which is normally of the order of 10–100 T m<sup>-1</sup>, ensures that the gradient term,  $H_G$ , dominates all other terms in the case of diamagnetic solids for spin-1/2 nuclides. The chemical shielding parameter,  $\sigma$ , and the couplings  $D$  and  $J$ , are too small to affect the STRAFI echo-trains and the image derived from them. The  $H_G$  term is so large, here 3 MHz per millimetre for protons, that it can be comparable even to the  $\gamma$ -term, so that at fixed frequency <sup>1</sup>H and <sup>19</sup>F images are brought almost into spatial conjunction and are separated by only a few millimetres.<sup>10</sup> Other similar but smaller conjunctions may be anticipated, and indeed <sup>7</sup>Li and <sup>31</sup>P profiles have been observed recently in the same STRAFI scan (E. W. Randall, A. A. Samoilenko and R. Fu, to be published) on the system used here. These ‘gamma shifts’ may be likened to chemical shift artefacts in conventional imaging.

In the case of quadrupolar nuclides we may add a quadrupolar term,  $H_Q$ , to the Hamiltonian. So far it has been only the electric quadrupole interaction,  $H_Q$ , which has been shown to affect the STRAFI echo trains, simply because the coupling,  $C_q$ , can be of the order of megahertz and can become comparable to the gradient term.<sup>5</sup>

For paramagnetic systems we may similarly add an additional term,  $H_P$ . The form of this depends on the particular case. For example, for second-order paramagnetics it can be expressed in terms of the susceptibility tensor, which in the case of first order paramagnetics becomes the  $g$ -tensor. There may also be a contact term in addition to the electron–nuclear dipolar, ‘pseudo contact,’ term.

It has been shown already that at room temperature STRAFI echo trains and profiles may be observed easily for paramagnetic solids: the linewidths are not a problem.<sup>3,4</sup> The

paramagnetic compounds investigated included a range of both transition and rare earth metal complexes. The first examples involved the  $^1\text{H}$  and  $^{19}\text{F}$  nuclides in ligands bound to the paramagnetic centers.<sup>3,4</sup> No displacements of the profiles were noted. Nuclides in the metal centres themselves have been observed also, such as  $^{51}\text{V}$ ,<sup>6</sup> and more recently  $^{59}\text{Co}$  (D. G. Gillies, J. Godward and E. W. Randall, to be published), but the studies were confined to the observation of STRAFI echoes: no STRAFI profiles were studied.

A preliminary STRAFI investigation using the Magnex magnet employed here has been published.<sup>11</sup> The nuclides reported were  $^2\text{H}$ ,  $^{23}\text{Na}$ ,  $^{27}\text{Al}$  and  $^{31}\text{P}$ , and the compounds were all diamagnetic. The study was confined to the observation of STRAFI echoes, except that in the case of  $^{27}\text{Al}$  a STRAFI profile was successfully obtained. The present work is part of a programme to investigate the prospects for  $^{31}\text{P}$  STRAFI in the imaging of solids containing phosphorus compounds such as bone.<sup>12</sup> The results reported here were serendipitous.

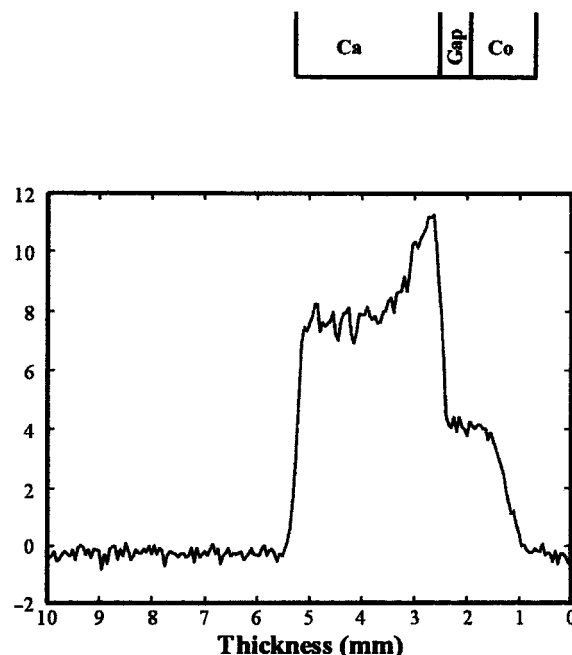
## RESULTS AND DISCUSSION

We report here the first effect of a displacement on a STRAFI projection caused by the effects of a paramagnetic centre. We shall reserve the term 'paramagnetic shift' for chemical shifts in spectroscopic experiments and use the term 'paramagnetic displacement' for the case of images. The compound responsible in each case was cobaltous phosphate octahydrate. This was employed earlier in a study of  $^{31}\text{P}$  STRAFI echo trains<sup>12</sup> due to its short  $T_1$  relaxation time (0.498 ms at a field of 5.58 T), relative to the much longer values found for diamagnetic phosphorus compounds (which are of the order of seconds), in order to eliminate saturation effects while the position of the stray-field  $^{31}\text{P}$  resonance was being found during the setting-up procedure.

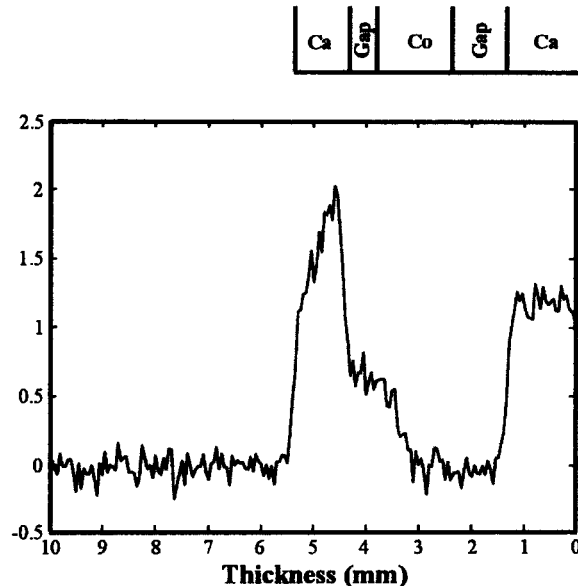
Phantom 1 consisted of a two part PMMA cylindrical tube with an internal diameter of 9 mm and a disc 500  $\mu\text{m}$  thick separating the compartments, which were filled with calcium hydroxyapatite powder on the top side and cobaltous phosphate octahydrate on the bottom. The thickness of the powdered samples was approximately 2.6 and 1.2 mm, respectively. The STRAFI profile, shown in Fig. 1, has the apatite response on the left and the cobaltous phosphate image on the right. The gap of 500  $\mu\text{m}$  between the compartments is not evident.

The spatial resolution, however, was intrinsically of the order of 100  $\mu\text{m}$ . This was attested in a profile of a phantom in which the calcium hydroxyapatite occupied *both* compartments, and the width of the gap was varied. A gap of 200  $\mu\text{m}$  was clearly resolved and the edges of the compartments in the image were sharp, spanning only about 90  $\mu\text{m}$ .

Closer examination of Fig. 1 shows that the two  $^{31}\text{P}$  images overlap indicating there is a relative displacement, which in frequency units is measured to be of the order of 1.2 MHz. It can also be seen that the right-hand edge of the image of the cobalt sample is far less sharp than the left-hand edge of the apatite signal. Since each STRAFI image is the convolution of the excitation profile and the lineshape of the sample,<sup>2</sup> the difference in sharpness is a measure of the relatively large linewidth for the paramagnetic cobalt



**Figure 1.** 1D  $^{31}\text{P}$  profile (bottom) of a phantom (top) containing from left to right calcium hydroxyapatite, a gap of 0.5 mm and cobaltous orthophosphate. The units on the vertical magnetization axis are arbitrary. The frequency was 206 MHz and the gradient strength was  $75.7 \text{ T m}^{-1}$ . Pulse duration, 10  $\mu\text{s}$ ;  $\tau = 20 \mu\text{s}$ ; and  $n = 8$  for the quadrature sequence:  $90_x - (\tau - 90_y - \tau - \text{echo} -)_n$ . Step size = 50  $\mu\text{m}$ .



**Figure 2.** 1D  $^{31}\text{P}$  profile (bottom) of a phantom (top) containing from left to right calcium hydroxyapatite, a gap of 0.5 mm, cobaltous orthophosphate, a gap of 1 mm and calcium hydroxyapatite. Other conditions as for Fig. 1.

sample. In other words, the spatial resolution is less for this compound.

Phantom 2 is similar to 1 but has an additional compartment filled with calcium phosphate, separated from the central section containing the cobalt compound by a PMMA disc of 1 mm thickness. The  $^{31}\text{P}$  profile is shown in Fig. 2.

From left to right, i.e. from the top of the sample to the bottom, the dimensions are apatite 1 mm, disc 0.5 mm, cobaltous phosphate 1.6 mm, disc 1 mm and calcium orthophosphate. The two diamagnetic calcium compounds give images with a relative displacement of about 4 mm, which is what is computed from the dimensions of the sample, but once again the image of the cobalt compound is shifted to the left in the profile. Whereas this leads to an overlap with the apatite profile as before, it gives an apparent large gap of 2 mm relative to the calcium phosphate image, whereas the spacer is only 1 mm thick. The displacement is thus about 1 mm, which in frequency terms is 1.2 MHz in this magnet. Again a feature of the profiles is the sharper edges for the diamagnetic compounds relative to the single non-overlapped edge for the cobalt compound. This difference is due to the much larger linewidth for the paramagnetic solid. We estimate this to be of the order of 0.6 MHz.

In early spectroscopic studies of cobalt phosphate octahydrate a  $^{31}\text{P}$  paramagnetic shift of 38 G in a field of 6390 G at 300 K relative to phosphoric acid was found.<sup>13</sup> Continuous-wave techniques were used and yielded derivative spectra, which were asymmetric, so that the shifts were difficult to measure: no errors were quoted and the sign of the shift was not given. This shift amounts to 5828 ppm, which at the frequency of 206 MHz used here is 1.20 MHz. The value we measured in the images agrees.

More recently, pulse-techniques have been employed for recording the spectra of such broad lines. The problem of the large bandwidth is overcome, as in FT EPR, by changing the frequency in a stepwise fashion. The response is recorded and Fourier transformed at each step so mapping the resonance: the technique called nuclear spin-echo Fourier transform mapping spectroscopy (NSEFTMS).<sup>13</sup> This method, referred to more simply as spin-echo mapping (SEM), has proved useful subsequently for  $^{31}\text{P}$  studies of paramagnetic catalysts.<sup>14,15</sup>

The STRAFI method is in fact similar to this spectroscopic work, since it deals with large bandwidths even in the case of diamagnetic samples, but differs in employing large imaging gradients. Here the pulse excites only a narrow band of resonances in a 'sensitive slice,' which is of the order of 100  $\mu\text{m}$  thick, and the spatial map is constructed by stepwise *translation* of the sample. Possibilities other than translation which have been realized are frequency sweep<sup>16</sup> and field sweep,<sup>17</sup> but for the large frequency ranges required, about 1.5 MHz/mm<sup>-1</sup> in the present instance, the translation method is the simplest. FT-STRAFI was introduced by Samoilenko and Zick<sup>18</sup> and exploited by the McDonald group,<sup>15</sup> but it has so far been confined to studies of thin samples such as films. In these cases all the sample is excited by the pulses. So far no one has combined the translation method with FT mapping but this combination could speed up the STRAFI imaging experiment.

STRAFI profiling of paramagnetic species with very broad lines could prove to be an attractive alternative to the SEM spectroscopic technique for shift and linewidth measurement. This was not the objective of this study and a proper evaluation of STRAFI from this perspective is required.

Paramagnetic displacements were not apparent in the  $^1\text{H}$  and  $^{19}\text{F}$  STRAFI profiles reported up to now.<sup>3,4</sup> We may conclude from this that the paramagnetic shifts in these cases and under the conditions employed were too small to affect the image. This is not surprising since in each case the nucleus being observed was located in the ligand, and was remote from the paramagnetic centre: too remote to give a shift substantial enough on the STRAFI scale.

## EXPERIMENTAL

The experiments were performed with a Magnex 19.6 T magnet and a Bruker model 833 console located at the National High Magnetic Field Laboratory. The field position chosen was characterized by a  $^{31}\text{P}$  resonance frequency of 206 MHz, which corresponds to 11.74 T, and a gradient of 75.7 T m<sup>-1</sup> (the largest used so far in STRAFI studies). The calibration of the tip angle was by means of the sequence  $90_x-(\tau-90_x-\tau\text{-echo-})_n$ ,<sup>19</sup> whereas the profiles were taken with the sequence  $90_x-(\tau-90_y-\tau\text{-echo-})_n$ . A pulse-duration of 10  $\mu\text{s}$  gave a tip-angle of 90° at the power used. Other conditions were  $\tau = 20 \mu\text{s}$  and  $n = 8$ . Sample translation was affected with an RRI field-mapping unit; 200 steps of 50  $\mu\text{m}$  gave a window of 10 mm.

The sample of calcium hydroxyapatite was supplied by Dr I. Abrahams, calcium orthophosphate by Hopkin & Williams and cobalt phosphate octahydrate by British Drug Houses.

## Acknowledgements

Thanks are due to Dr Alasdair Preston (at Queen Mary) for useful discussions and to Dr Bill Brey and Peter Gochev (at the NHMFL) for practical assistance.

## REFERENCES

1. Newling B, McDonald PJ. *Rep. Prog. Phys.* 1998; **61**: 1441.
2. Randall EW. In *Encyclopedia of Spectroscopy and Spectrometry*, Lindon JC (ed.) Academic Press: London, 1999; 1396–1403.
3. Randall EW, Samoilenko AA, Nunes T. *J. Magn. Reson. A* 1995; **116**: 122.
4. Randall EW. *Solid State NMR* 1997; **8**: 173.
5. Bodart P, Nunes T, Randall EW. *Appl. Magn. Reson.* 1997; **12**: 269.
6. Bodart P, Nunes T, Randall EW. *Solid State NMR* 1997; **8**: 257.
7. Gillies D, Randall EW. *J. Magn. Reson. A* 1996; **121**: 217.
8. Randall EW, Samoilenko AA, Fu R. *Solid State NMR* 1999; **14**: 173.
9. Randall EW, Nunes TG, Guillot G, Bodart PR. *Solid State NMR*, 1999; **14**: 165.
10. Randall EW, Samoilenko AA, Nunes T. *J. Magn. Reson. A* 1995; **117**: 317.
11. Samoilenko AA, Soghomonian V, Randall EW, 1997 *Annual Report*. NHMFL: Tallahassee, FL, 1998; 184.
12. Gillies DG, Newling B, Randall EW. *J. Magn. Reson.* 2001; **151**: 235.
13. Yong YY. *J. Magn. Reson. A* 1996; **119**: 22.
14. Canesson L, Boudeville Y, Tuel A. *J. Am. Chem. Soc.* 1997; **119**: 10754.
15. Tuel A, Canesson L, Volta JC. *Colloids Surf. A* 1999; **158**: 97.
16. Glover PM, McDonald PJ, Newling B. *J. Magn. Reson. A* 1997; **126**: 207.
17. Mallett MJD, Halse MR, Strange JH. *J. Magn. Reson.* 1998; **132**: 172.
18. Samoilenko AA, Zick K. In *26th Congress Ampère*, Anagnostopolous A, Milia F (eds.) Simonopolous: Athens, 1992; 40–42.
19. Randall EW. *Solid State NMR* 1997; **8**: 179.