



# Determining the relative orientation between the chemical shift anisotropy and heteronuclear dipolar tensors in static solids by SEDOR NMR



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## ABSTRACT

The measurement of the dipolar interaction between two spins provides the distance between nuclei. A better structural picture emerges when the distance is combined with the orientation of the internuclear vector in the principal axis system of the chemical shift anisotropy tensor. The SEDOR experiment is used on a static sample of alanine to show that the orientation of the vector connecting the nitrogen and carboxylate carbon nuclei can be accurately determined in the CSA PAS of the  $^{13}\text{C}$  carboxylate spin.

## 1. Introduction

Magic angle spinning nuclear magnetic resonance (MAS NMR) dipolar recoupling provides a way to obtain structural detail in a solid by determination of an internuclear distance through the measured dipolar coupling [1–3]. An enhanced structural picture emerges by finding the orientation of the internuclear vector of the coupled spin pair with respect to the principal axis system (PAS) of the chemical shift anisotropy (CSA) tensor of one of the coupled spins [4–16].

In addition to MAS NMR techniques, there are NMR methods for determining the orientation between the dipolar and chemical shift anisotropy tensors for static solids [17–21]. Stoll, Vega, and Vaughn demonstrated in 1976 a  $^1\text{H}$ - $^{13}\text{C}$  double-resonance experiment, henceforth referred to as SVV, to determine the orientation of the C–H bond with respect to the  $^{13}\text{C}$  CSA PAS [20]. In SVV, the  $^{13}\text{C}$  signal was acquired after application of a standard  $^{13}\text{C}$  spin-echo sequence of fixed duration  $\tau$ . The  $^1\text{H}$  sequence contained a multi-pulse window of length  $t_1$  and a decoupling field during the remainder of the  $\tau$  period and during  $^{13}\text{C}$  signal detection. The multi-pulse window suppressed the proton-proton dipolar interaction while maintaining a finite  $^1\text{H}$ - $^{13}\text{C}$  heteronuclear dipolar interaction. The result of SVV is that the observed  $^{13}\text{C}$  line shape is amplitude modulated by the heteronuclear  $^1\text{H}$ - $^{13}\text{C}$  dipolar interaction. Simulation of the resulting  $^1\text{H}$ -decoupled  $^{13}\text{C}$  line shape provided the desired orientation information. In some aspects, SVV is a version of the Kaplan and Hahn spin-echo double-resonance experiment (SEDOR) [22–24] modified to take into account the strong  $^1\text{H}$ - $^1\text{H}$  homonuclear dipolar interaction.

In this short paper, we revisit the SVV experiment. In particular, we show that a  $^{13}\text{C}$ - $^{15}\text{N}$  SEDOR *difference* experiment can accurately

provide the orientation of the  $^{13}\text{C}$ - $^{15}\text{N}$  internuclear vector in the PAS of the  $^{13}\text{C}$  CSA tensor. Simulations are used to show that the orientation can be determined within  $5^\circ$ . The SEDOR experiment is straightforward, especially for a pair of rare-spin nuclei, and requires only a single dipolar modulated *difference* spectrum.

## 2. Experimental details and methods

Experiments on a static sample were performed on a custom-built spectrometer using a Tecmag Redstone console and a 3.55 T magnet (proton frequency of 151.395 MHz). The NMR probe is a transmission-line design, and it incorporates a Chemagnetics 7.5 mm pencil rotor spinning assembly with a 14 mm long, 8.65 mm inner diameter, 6-turn coil made of 14-gauge tinned copper wire. Radio-frequency (rf) field strengths on the proton channel were 115 kHz for  $^1\text{H}$  decoupling and 50 kHz for  $^1\text{H}$ - $^{13}\text{C}$  cross-polarization.  $^{13}\text{C}$  and  $^{15}\text{N}$  rf field strengths were 50 kHz. The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$  power amplifiers were under active control. The  $^{13}\text{C}$  spectra were obtained with recycle delays of one second and Hartmann-Hahn cross-polarization transfer times of 0.5 ms.

The powder sample was made of a 1.0:8.4 mass ratio of L-alanine ( $^{13}\text{C}$ , 99%;  $^{15}\text{N}$ , 98%) and natural abundance L-alanine recrystallized from water. The labeled alanine was obtained from Cambridge Isotope Laboratories, Inc., and the natural abundance alanine was obtained from Acros Organics. The  $^{13}\text{C}$  spectrum of the carboxylate carbon for this sample is dominated by the chemical shift anisotropy, and the CSA parameters determined from the spectrum of our sample are an asymmetry parameter of 0.77 and an anisotropy of  $-2.71$  kHz. On our spectrometer, the edge-to-edge width of the  $^{13}\text{C}$  spectrum of the

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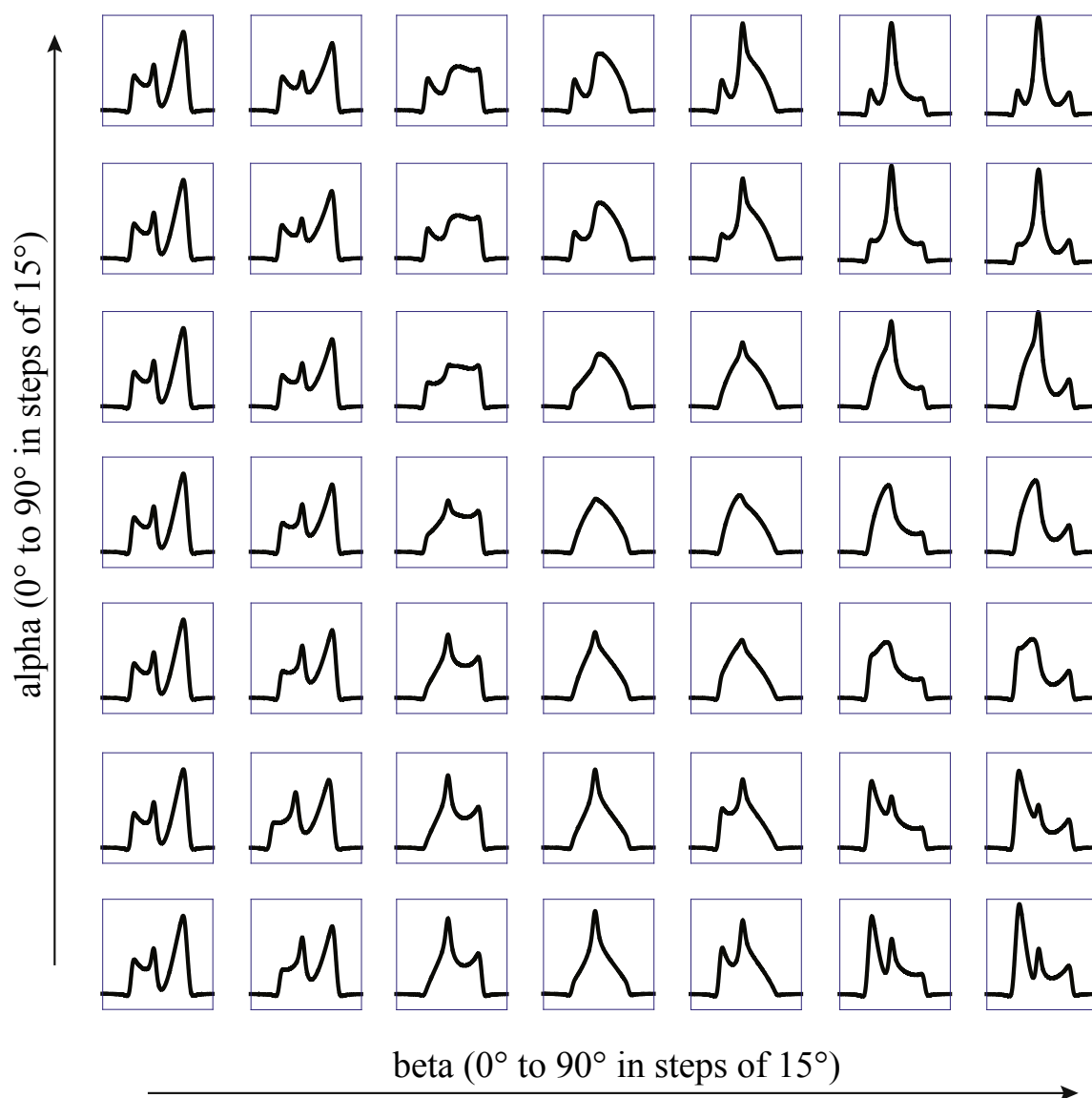


Fig. 1. Simulated *difference* spectra over the full range of Euler angles  $\alpha$  and  $\beta$  in  $15^\circ$  increments.

line shape from the carboxylate carbon is approximately 5.1 kHz. In this work, a  $^{13}\text{C}$ - $^{15}\text{N}$  dipolar coupling of 195 Hz was used for simulations; this value is intermediate between a rigid lattice calculation and a REDOR-determined value. Simulations suggest that a 6% variation in the dipolar coupling has little effect on *difference* spectrum lineshape. A 1.6 ms dipolar evolution period was used for all experiments and simulations. The experimental and simulated spectra are all shown with a spectral width of 10 kHz.

NMR simulations were performed with the SpinEvolution software package [25] using the NMR parameters described in the preceding two paragraphs and with a Lorentzian broadening of 140 Hz and a Gaussian broadening of 300 Hz.

### 3. Results and discussion

Naito et al. [26] determined and discussed the principal-axis coordinate system of the  $^{13}\text{C}$  CSA tensor of the carboxylate carbon of L-alanine using their single crystal NMR results and the neutron diffraction data of Lehmann, Koetzle, and Hamilton [27]. A coordinate system defined by the  $sp^2$  symmetry of the carboxylate carbon was described with the z-axis perpendicular to the plane defined by the positions of the carboxylate carbon nucleus and the two oxygen nuclei,

and the other two axes in this frame lie in the aforementioned plane with the x-axis parallel to C(2)–C(1) bond axis. Their experimentally determined CSA PAS differed slightly from the  $sp^2$ -defined coordinate system. For example, the angles of the direction cosines between the z-axes and x-axes differed by  $1.6^\circ$  and  $9.4^\circ$ , respectively.

Our focus is determining the orientation of the N–C(1) internuclear vector in the CSA PAS. Two Euler angles of rotation ( $\alpha$ ,  $\beta$ ) are required to bring the two respective z-axes of the CSA tensor and the  $^{13}\text{C}$ - $^{15}\text{N}$  dipolar tensor into alignment. Using the CSA PAS described by Naito et al. and the crystallographic data of Lehmann et al. the expected Euler angle pair is ( $25^\circ$ ,  $80^\circ$ ).

The  $^{13}\text{C}$ - $^{15}\text{N}$  SEDOR difference experiment is as follows. The  $^1\text{H}$  channel consists of a cross-polarization period followed by a strong decoupling field during the dipolar evolution period and during  $^{13}\text{C}$  detection. The  $^{13}\text{C}$  channel has a  $^1\text{H}$ - $^{13}\text{C}$  cross-polarization period, which is followed by a  $^{13}\text{C}$ - $^{15}\text{N}$  dipolar evolution period of length  $\tau$  containing a single  $180^\circ$  spin-echo pulse located at  $\tau/2$ . In the absence of an  $^{15}\text{N}$  pulse there is no net  $^{13}\text{C}$ - $^{15}\text{N}$  dipolar evolution during the dipolar evolution period, which yields the  $^{13}\text{C}$  control spectrum. However, when a  $^{15}\text{N}$   $180^\circ$  pulse is applied at  $\tau/2$  a net dipolar dephasing of the  $^{13}\text{C}$  spins occurs, which results in a less intense  $^{13}\text{C}$  *dephased* spectrum having a unique dipolar modulated line shape.

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