

COMMUNICATIONS

Small Crystals and Small Coils in Variable-Temperature Single-Crystal NMR

Thomas Vosegaard,¹ Preben Daugaard, Eigil Hald, and Hans J. Jakobsen

Instrument Centre for Solid State NMR Spectroscopy, Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

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Time savings by a factor of between 20 and 30 in the acquisition of multinuclear single-crystal (SC) NMR spectra have been obtained for submillimeter-size (0.01 to 0.03 mm³) single crystals when compared to recent results for ³¹P and ⁸⁷Rb SC NMR. This gain in sensitivity is achieved by optimizing the filling factor using the smallest possible rf coil (2.0 mm inner diameter) for the specific SC probe design. Furthermore, this small coil is particularly useful for variable-temperature SC NMR studies. A probe design for such studies is presented and demonstrated experimentally. © 2000

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Great efforts to improve the efficiency and precision in the acquisition and analysis of single-crystal (SC) NMR spectra have been exercised in our laboratory during the past few years. Important advances with respect to instrumentation as well as software for the spectral analysis have been achieved (1, 2). These have proven their usefulness in a number of applications to quadrupolar nuclei (3). Generally, however, widespread applications of multinuclear SC NMR to problems in chemical research have been hampered by the poor filling factor of the coil in SC NMR probes. The reason is that commercial as well as homebuilt probes are designed to accommodate not only the single crystal but also the much larger goniometer (e.g., the standard three-face cube) inside the rf coil. To improve the sensitivity of SC NMR spectroscopy we recently constructed a SC probe of a new and untraditional design (4). In this probe the complete goniometer has been moved outside the rf coil, since this allows the use of a smaller coil in order to increase the filling factor. For this design the crystal is mounted at the end of a thin glass pin. During rotation of the goniometer this glass pin traverses the surface of a cone with the crystal positioned at the tip of the cone. Using a coil of 3.8 mm i.d. the gain in sensitivity was demonstrated by the recording of a ³¹P–{¹H} cross-polarization (CP) NMR spectrum at 14.1 T for a 0.25 × 0.5 × 0.7 mm = 0.088 mm³ crystal of (NH₄)₂HPO₄ in just 9 min (S/N = 23:1). To our knowledge this represents the optimum signal-to-noise response obtained

for the smallest crystal so far from a fully automated SC NMR probe (4). In addition to the immediate gain in filling factor, this design invites additional modifications in relation to the performance of SC NMR experiments. These concern modifications for (i) variable-temperature (VT) SC NMR studies and for (ii) optimization of the filling factor for tiny crystals; i.e., what is the lower limit inner diameter of the coil considering the precision and constraints of this new SC NMR method? In this communication we demonstrate the results achieved by these modifications of the probe.

The modification of the original SC NMR probe design for VT experiments and with a small diameter coil is illustrated by the photograph in Fig. 1. A stream of temperature-controlled hot/cold air is taken to the top of the probe through a glass dewar and guided directly onto the crystal/coil through a short tube of Torlon (polyamide-imide, Amoco). On the opposite side and next to the coil, a thermocouple measures the actual temperature of the air stream around the crystal. This is a simpler VT setup for SC NMR than the corresponding setup for the usual three-face cube goniometer design. Most importantly, during the course of our first VT NMR investigations of single crystals it appeared that cleavage of even fairly small crystals along definite lattice planes may be a general problem in such studies. For large crystals, especially, the tensions within the crystal for a given temperature variation become increasingly high. Although this observation came somewhat unexpectedly to us, it appears to be a common problem encountered in VT SC X-ray diffraction studies. In SC NMR it calls for the use of the smallest possible crystals in order to reduce the lattice tensions during VT (*vide infra*). Thus, this challenge goes hand in hand with the optimization of the rf coil i.d. for best signal-to-noise.

The optimization of the rf coil to the smallest possible inner diameter, i.e., optimum filling factor, depends highly on the top angle chosen for the cone traversed by the glass pin holding the crystals. As discussed elsewhere this angle is related to the precision of the parameters determined employing this new SC NMR probe technology (4); i.e., for a decrease in the cone angle the precision of the parameters decreases, and for a

¹ Current address: Centre de Recherches sur les Matériaux à Haute Température, CNRS, 45071 Orléans Cedex 2, France

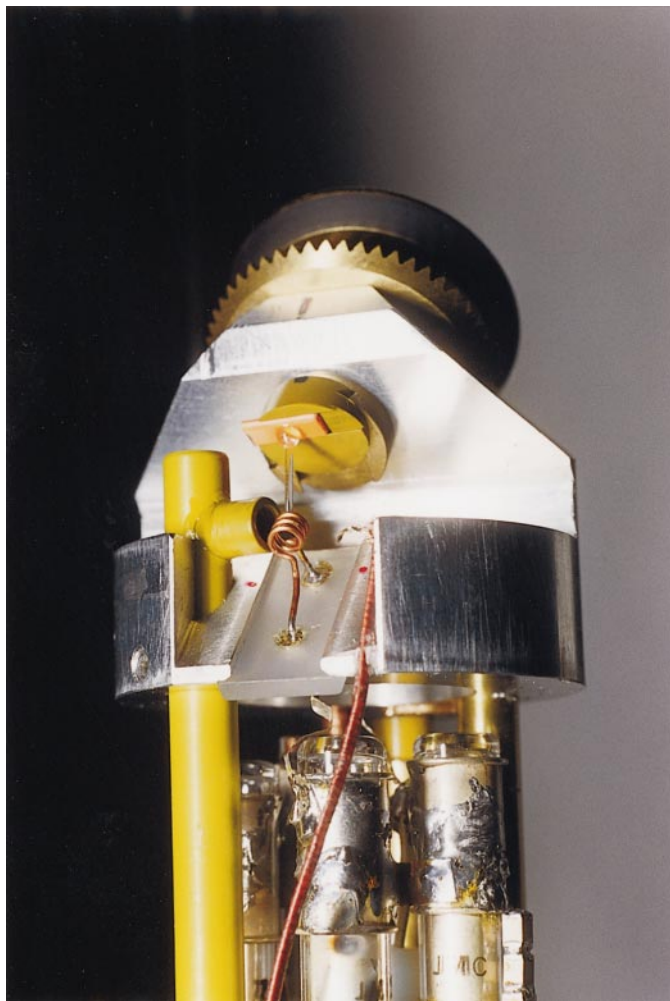


FIG. 1. Single-crystal variable-temperature NMR probe equipped with an optimized three-turn 2 mm inner diameter rf coil for studies of submillimeter crystals (see text).

vanishing angle this SC probe technology does not provide the information necessary to determine all the parameters describing the tensorial interaction(s). Thus, a compromise must be made between the minimum coil i.d. and the precision of the determined parameters. We have chosen not to slacken on the precision of the method and we stick to the half cone top angle $\phi = 19.4^\circ$ used earlier (4). With this concept we arrive at an optimum three-turn coil of inner diameter 2 mm (coil length equal to 2.4 mm) as shown in Fig. 1. Using this coil for the probe we show that a further time saving by a factor of about 30, as compared to our earlier results, can be achieved for even smaller crystals. This is shown by the recording of a ^{31}P CP NMR spectrum for a crystal of size 0.032 mm^3 of $(\text{NH}_4)_2\text{HPO}_4$, i.e., approximately one-third the volume of the crystal used earlier (4). The resulting spectrum appears to demonstrate by far the highest sensitivity achieved in SC NMR, and gives great promises for the use of tiny crystals in this experimental method. This is further demonstrated by the ^{87}Rb NMR spectrum for a crystal of size 0.019 mm^3 of $\text{RbZn}_2(\text{HPO}_4)\text{PO}_4$.

NMR experiments were performed at 242.9 (^{31}P), 196.3 (^{87}Rb), and 144.1 (^{59}Co) MHz on a Varian INOVA 600 (14.1 T) spectrometer. The two-axis goniometer single-crystal probe recently described (4) was equipped with a three-turn 2.0 and 3.8 mm i.d. coil, respectively, for the two different crystal sizes of the samples used to illustrate the improved performance and time saving.

^{31}P CP NMR spectra of similar S/N ratio for two different-sized single crystals of $(\text{NH}_4)_2\text{HPO}_4$, recorded using two different rf-coil diameters, are illustrated in Figs. 2a and 2b. The spectrum of the 0.088 mm^3 crystal (Fig. 2a), employing the original 3.8 mm i.d. coil and 512 scans, is identical to that shown elsewhere to illustrate the performance of our new SC probe design (4). For the approximately one-third smaller crystal of size 0.032 mm^3 , the spectrum in Fig. 2b, recorded for the smaller rf-coil of 2.0 mm i.d. and only 128 scans, shows that a time saving by a factor of approximately 30 is obtained for the small crystal using a small coil (2.0 mm i.d.) as compared to the standard 3.8 mm i.d. coil.

To further illustrate the time saving that can be achieved in SC NMR of small crystals using small coils, Figs. 2c and 2d show the results of ^{87}Rb single-pulse experiments for two crystals of $\text{RbZn}_2(\text{HPO}_4)\text{PO}_4$ with ^1H decoupling. The two spectra in Figs. 2c and 2d exhibit about the same S/N ratio. However, the spectrum in Fig. 2c is that of a 0.048 mm^3 crystal (3.8 mm i.d. coil and 8192 scans), whereas that in Fig. 2d is for a 0.015 mm^3 crystal (2.0 mm i.d. coil and 4096 scans). Again these spectra demonstrate that a considerable time saving, in

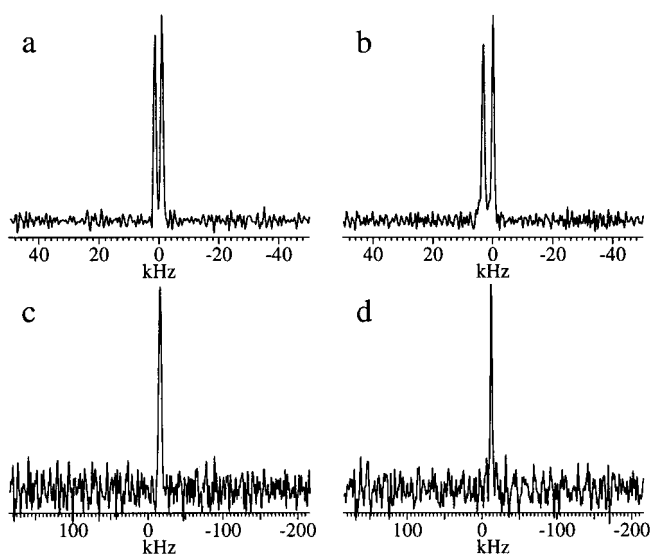


FIG. 2. (a) and (b) 242.9 MHz ^{31}P CP NMR spectra (proton decoupled) of two different small crystals of $(\text{NH}_4)_2\text{HPO}_4$. (a) Crystal size $0.25 \times 0.5 \times 0.7\text{ mm} = 0.088\text{ mm}^3$, rf coil of 3.8 mm i.d., and 512 scans in 9 min. (b) Crystal size $0.2 \times 0.4 \times 0.4\text{ mm} = 0.032\text{ mm}^3$, rf coil of 2.0 mm i.d., and 128 scans in 2 min. (c) and (d) 196.3 MHz ^{87}Rb NMR spectra (proton decoupled) of two different small crystals of $\text{RbZn}_2(\text{HPO}_4)\text{PO}_4$. (c) Crystal size $0.05 \times 0.38 \times 2.5\text{ mm} = 0.048\text{ mm}^3$, rf coil of 3.8 mm i.d., and 8192 scans in 55 min. (d) Crystal size $0.05 \times 0.20 \times 1.5\text{ mm} = 0.015\text{ mm}^3$, rf coil of 2.0 mm i.d., and 4096 scans in 27 min.

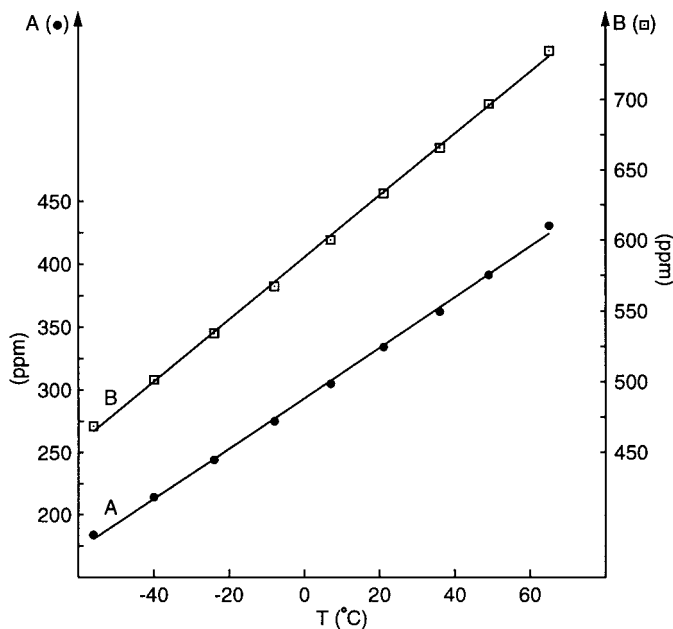


FIG. 3. Graph illustrating the temperature dependencies for the ^{59}Co resonance positions (the two central transitions) observed for the two magnetic nonequivalent ^{59}Co sites in a single crystal (0.02 mm^3) of $\text{Co}(\text{acac})_3$ with an arbitrary orientation. The reference point for the ppm scale has been arbitrarily chosen.

this case by a factor of 20, can be achieved in SC NMR of tiny crystals by using the optimized small i.d. for the rf coil.

As an illustration of the VT performance of the probe we have investigated the temperature dependence of the ^{59}Co ($I = 7/2$) resonances for a small single crystal ($\sim 0.02\text{ mm}^3$) of cobalt(III) trisacetylacetonate, $\text{Co}(\text{acac})_3$. ^{59}Co chemical shifts in solution studies are generally known to be extremely sensitive to variation in temperature. Similar evidence has been obtained from powder ^{59}Co VT MAS NMR studies in our lab of cobalt complexes, e.g., for $\text{K}_3\text{Co}(\text{CN})_6$ the temperature coefficient exceeds $1\text{ ppm}/^\circ\text{C}$. The ^{59}Co NMR spectrum for the single crystal of $\text{Co}(\text{acac})_3$ appears as two sets of seven-line spectra in accordance with its crystal structure (5) which indicates two sets of magnetic nonequivalent nuclei within the asymmetric unit. The linewidths of the resonances for the two central transitions ($-1/2 \leftrightarrow +1/2$) in the ^1H decoupled spectra at 14.1 T are approximately 400 Hz, i.e., about 2.8 ppm. The temperature dependence of the resonance positions for the two central transitions from about -60°C to $+65^\circ\text{C}$ is illustrated in Fig. 3. It is observed that the two magnetic nonequivalent ^{59}Co sites exhibit very large but slightly different temperature coefficients, $2.01\text{ ppm}/^\circ\text{C}$ (line A) and $2.20\text{ ppm}/^\circ\text{C}$ (line B), for the particular orientation of the single crystal. To our knowledge these temperature coefficients are by far the largest temperature-dependent shifts reported in multinuclear solid state NMR; they are currently being dealt with in more detail. We note that for single crystals of about three times larger volume, we observe cleavages of the crystals during the VT studies. This is evidenced by the sudden observation of, for example, a dou-

bling of the number of resonances with an arbitrary intensity ratio which may show up at the high or low end of the temperature range. Furthermore, in removing the crystal from the goniometer after the experiment it falls apart into two or more pieces. To reduce the tension within the crystal the use of a small crystal and therefore of the smallest possible coil, as employed in Fig. 3, is recommended for VT SC NMR experiments.

Finally, since single-crystal NMR is usually regarded the standard technique for determination of the absolute orientation (i.e., within the molecular or crystal frame) of the tensor for one or more NMR interactions, the present optimizations for tiny crystals will allow more widespread applications of this technique. Recently there has been an increasing interest in ^{31}P SC NMR studies of crystals, which are of biological interest (6, 7). These have a size in the range from 0.12 to 0.25 mm^3 and obviously require much longer accumulation time than used here because of the dilution of the ^{31}P nuclei. It is believed that our new SC NMR probe design employing the optimized small i.d. coil with its improved sensitivity will further stimulate applications of SC NMR in biological research since even smaller crystals than those used earlier (6, 7) may be applicable.

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