

Short communication

^{31}P to ^{77}Se cross polarization in $\beta\text{-P}_4\text{Se}_3$

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Abstract

Cross polarization from ^{31}P to ^{77}Se is demonstrated in $\beta\text{-P}_4\text{Se}_3$. This material, an inorganic glass, is readily synthesized from the elements and serves as a convenient sample for setting the Hartmann–Hahn condition. © 1997 Elsevier Science B.V.

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1. Introduction

Cross polarization (CP) [1,2] serves as the initial step in many solid state NMR pulse sequences. Although a variety of favorable spin-1/2 nuclei could, in principle, serve as magnetization reservoirs, the use of source nuclei other than protons for CP experiments is not widespread due to the difficulty in setting the Hartmann–Hahn matching condition. Examples include ^{19}F [3–5] and ^{31}P , the latter of which has been exploited for CP to ^{113}Cd [6,7] and to ^{29}Si [7].

In recent years the combination of ^{31}P and ^{77}Se nuclei has spurred some interest in NMR studies of inorganic solids, semiconductors, and semiconductor nanocrystals. To date, $^{31}\text{P}/^{77}\text{Se}$ double resonance studies have been limited to static SEDOR in P–Se

glasses [8] and REDOR experiments in phosphine and phosphine oxide capped CdSe semiconductor nanocrystals [9]. In particular, nanocrystals are currently the subject of much research activity [10], and their structural characterization presents considerable challenges. The motivation of the present study is to develop suitable NMR strategies for the observation of rare nuclei (^{77}Se , ^{113}Cd) within the surface layer of phosphine oxide capped CdSe nanocrystals. The ^{31}P spins associated with the capping groups are substantially closer to surface nuclei than are the protons. NMR observation would thus appear to be more favorable with CP using ^{31}P rather than ^1H as the magnetization reservoir. To the best of our knowledge, no such $^{31}\text{P}/^{77}\text{Se}$ CP experiments have been reported in the literature.

2. Materials and Methods

In this work, we report the results of CP from ^{31}P to ^{77}Se in $\beta\text{-P}_4\text{Se}_3$, which gives rise to a detectable

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CP signal after a few scans. The sample was synthesized from red phosphorus and selenium. The components were thoroughly mixed in stoichiometric amounts, sealed in a quartz ampoule and heated to 700°C for 24 h, after which the sample tube was allowed to cool to room temperature. The ampoule was opened in a glove box, where the air-sensitive, plastic-crystalline material was subsequently transferred into a 7-mm or a 4-mm rotor for the magic angle spinning (MAS) experiments. Grinding of the sample inside the glove-box proved difficult due to electrostatic charging, so some larger sample particles were introduced into the rotors, making it possible to spin the rotors at frequencies of a few kHz.

MAS spectra were obtained on a 'home-built' spectrometer operated by a Tecmag system in a Chemagnetics MAS probe at Larmor frequencies of 121.93 MHz and 57.52 MHz for ^{31}P and ^{77}Se , respectively. Compressed air was used as the drive and bearing gas (which did not lead to any noticeable sample decomposition-when the sample was removed from the rotor, it had maintained its orange color). CP experiments were performed on a CMX 500 spectrometer under non-spinning conditions with a 'home-built' MAS probe tuned to the Larmor frequencies of ^{31}P (202.45 MHz) and ^{77}Se (95.46 MHz). The Hartmann–Hahn condition was set with a radio frequency field amplitude of 27.8 kHz.

^{31}P spectra are referenced to an external standard of 85% phosphoric acid and ^{77}Se chemical shifts are reported with respect to a standard of $(\text{CH}_3)_2\text{Se}$ in CDCl_3 . A saturated solution of selenous acid was used as an external standard, with a chemical shift of 1300 ppm with respect to $(\text{CH}_3)_2\text{Se}$ [11].

3. Results and Discussion

The MAS spectra of ^{31}P and ^{77}Se in $\beta\text{-P}_4\text{Se}_3$ are shown in Fig. 1. The molecular structure of $\beta\text{-P}_4\text{Se}_3$ is shown in the inset of Fig. 1b. Peaks at the isotropic chemical shifts are marked with an asterisk. The two different phosphorus sites give rise to two ^{31}P resonances at 63 ppm and -75 ppm, respectively [12]. The ^{77}Se spectrum displays only a single resonance in accordance with the structure. Both ^{31}P and ^{77}Se spectra show spinning sidebands due to chemical shift anisotropy which was not studied in

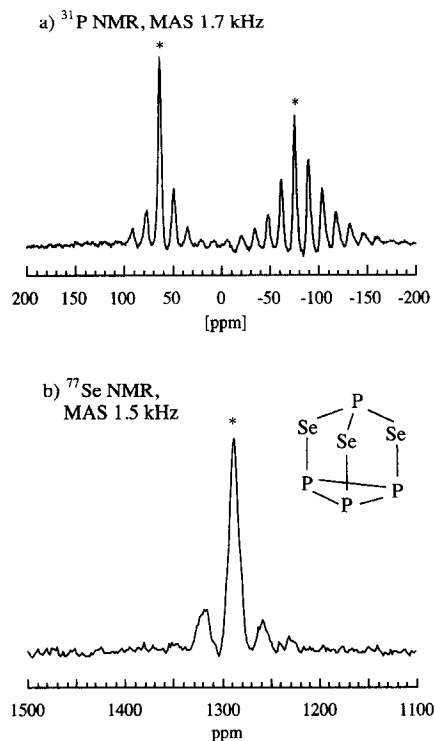


Fig. 1. (a) ^{31}P NMR MAS spectrum (1.7 kHz) at a transmitter frequency of 121.929 MHz. The spectrum was recorded with a chemical shift echo sequence ($90^\circ\text{-}\tau_1\text{-}180^\circ\text{-}\tau_2\text{-acq.}$) in order to avoid baseline distortions (16 transients, 90° pulse width $3\ \mu\text{s}$, 180° pulse width $6\ \mu\text{s}$, $\tau_1 = 50\ \mu\text{s}$, $\tau_2 = 47\ \mu\text{s}$, repetition time 3 s, sweep width 50 kHz); (b) ^{77}Se NMR MAS spectrum (1.5 kHz) at a transmitter frequency of 57.518 MHz (512 transients, single pulse excitation, pulse width $2.5\ \mu\text{s}$, receiver delay $45\ \mu\text{s}$, repetition time 300 ms). The inset in Fig. 1b shows the structure of $\beta\text{-P}_4\text{Se}_3$.

further detail. The readily available ^{31}P spectrum carries the unique signature of the target compound [12] and can be used for identification.

The upper trace in Fig. 2 shows the result of the ^{31}P to ^{77}Se CP experiment after eight transients. A conventional CP sequence with a 90° pulse on the ^{31}P spins followed by a spin locking and detection period was applied using individually adjustable radio frequency amplitude levels for all pulses. The lower trace in Fig. 2 shows the control experiment carried out under identical conditions, but with the amplitude of the 90° pulse set to zero. The duration of the contact pulse was 1 ms, but signal was also obtained at shorter and longer contact settings. A

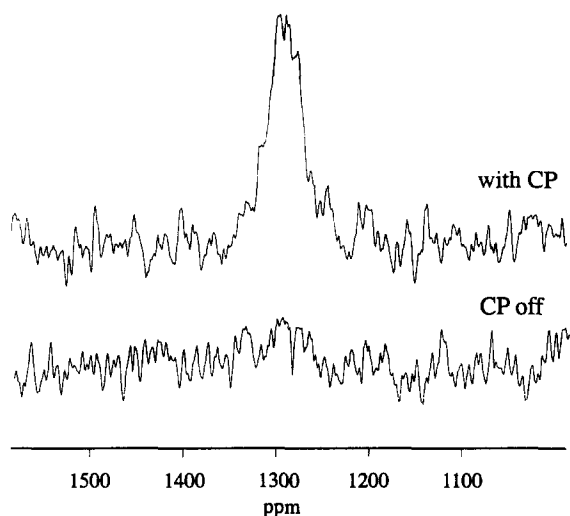


Fig. 2. ^{31}P to ^{77}Se cross polarization experiments with ^{77}Se detection under static conditions, 8 transients, repetition time 30 s. Upper trace: ^{31}P transmitter frequency 202.446 MHz, V_{pp} (to probe) 169 V for both the 90° pulse and the contact pulse, 90° pulse width 18 μs , contact pulse width 1 ms; ^{77}Se transmitter frequency 95.459 MHz, V_{pp} (to probe) 121 V. Lower trace: same conditions, but V_{pp} (to probe) 0 V for the ^{31}P 90° pulse.

further optimization of the contact pulse length was not attempted at this point due to slight probe instabilities, and the control experiment was therefore carried out before the CP experiment. The narrow CP condition demanded highly reproducible rf power levels in both channels which were achieved at a low duty cycle.

The spectra shown in Fig. 2 were obtained with a repetition delay of 30 s, although the ^{31}P spin lattice relaxation time is shorter. Under static conditions at a field of 7 T, the three basal phosphorus nuclear spins have a spin lattice relaxation time of $T_1 = 0.28 \pm 0.02$ s, whereas the single apical phosphorus has a T_1 of 1.13 ± 0.07 s. Under MAS conditions, the latter T_1 decreased (0.71 ± 0.02 s), while the former remained constant.

The ^{77}Se spin lattice relaxation time at a field of 7 T and a spinning frequency of 1.1 kHz is only 50 ms. Therefore, for the purpose of signal enhancement, averaging of ^{77}Se single-pulse acquisitions may be advantageous over CP for this sample. However, the goal of this work is to establish cross polarization from ^{31}P to ^{77}Se , and $\beta\text{-P}_4\text{Se}_3$ fulfills

this requirement. Relaxation phenomena in $\beta\text{-P}_4\text{Se}_3$ are currently being investigated in more detail.

4. Conclusion

In conclusion, we have demonstrated $^{31}\text{P}/^{77}\text{Se}$ cross polarization in an inorganic solid. The compound chosen for this study, $\beta\text{-P}_4\text{Se}_3$, can be easily synthesized from readily available starting materials and its favorable relaxation characteristics allow CP signal observation within a short time. This material therefore serves as an excellent set-up sample for optimizing the Hartmann–Hahn matching condition for such experiments.

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