



Communication

Testing the sensitivity limits of ^{33}S NMR: An ultra-wideline study of elemental sulfur

Luke A. O'Dell, Igor L. Moudrakovski*

Steacie Institute for Molecular Sciences, National Research Council, 100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6

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ABSTRACT

Preliminary DFT investigations into the feasibility of using ^{33}S solid-state NMR to study organic and biological molecules suggest that very large ^{33}S quadrupolar coupling constants (>40 MHz) are not uncommon. We have therefore investigated the possibility of using recently developed ultra-wideline techniques to record such ^{33}S powder patterns at a high magnetic field (21.1 T). A WURST-echo sequence was used to record the spectrum from a $>99.9\%$ enriched sample of elemental sulfur, resulting in the largest ^{33}S quadrupolar coupling constant yet measured by solid-state NMR ($C_Q = 43.3$ MHz). Implications of this experiment are briefly discussed.

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Sulfur is of extreme importance in biology, chemistry, industry and materials science, being the tenth most abundant element in the universe and a ubiquitous component of biological organisms. It is therefore unfortunate that it is also a notoriously difficult element to study using nuclear magnetic resonance (NMR). ^{33}S is the only naturally occurring NMR-active isotope, and it suffers from a very low natural abundance of 0.76%. It is also quadrupolar (nuclear spin $I = 3/2$), which means that the coupling of the electric quadrupole moment of the nucleus (-67.8 mbarn) with a surrounding electric field gradient (EFG) can cause rapid relaxation in solution and significant anisotropic broadening of powder lineshapes in the solid state. Matters are made worse by its low gyromagnetic ratio of 2.06×10^7 rad T^{-1} s^{-1} , which puts it at the lower end of the NMR scale in terms of inherent signal strength. Considering each of these factors, it is perhaps not surprising that the number of published solid-state NMR studies utilizing this nucleus is so small [1–14]. However, after getting off to a very slow start during the 1980s and 1990s [1–3], ^{33}S solid-state NMR seems to be finally gaining some popularity as a useful and informative probe of the structural environment in sulfur-containing compounds [4–14]. This is mainly due to the increasing availability of high field NMR spectrometers (>14.1 T), which reduce the second order quadrupolar broadening of the central ($1/2 \leftrightarrow -1/2$) transition (CT) as well as providing an increased Zeeman polarization.

The pioneering ^{33}S solid-state NMR studies were carried out on natural abundance, model systems such as sulfides and sulfates

[1–4], which in general contain sulfur environments that are either spherically symmetric in the former case or only slightly distorted from tetrahedral symmetry in the latter. Such samples generally exhibit quadrupolar coupling constants of *ca.* 1 MHz or less, and thus have CT linewidths that are relatively narrow. These linewidths can be further reduced by magic angle spinning (MAS), which partially averages the second order quadrupolar interaction [3,4]. The first application of ^{33}S MAS NMR to non-crystalline materials was a study of isotopically enriched sulfur-doped silicate glasses of geological interest [5], in which the sulfur environments were shown to be sulfate-like by virtue of the observed chemical shifts. Since then, ^{33}S MAS NMR has been used to study mineral phases such as ettringite [7,9], tetrathiometalates [8], and other systems [6,10–14]. Other methodological improvements have also been made. MAS has been demonstrated to be useful for measuring small C_Q values *via* the satellite transitions (STs) [6], as well as for studying chemical shielding anisotropy (CSA) [8]. Signal enhancement techniques such as QCPMG [15] or population transfer experiments (which transfer polarization from the STs to the CT [16]) have been used to boost the signal and reduce experimental times significantly [9,10,12–14]. Finally, much larger C_Q values have recently been observed from transition metal disulfides [11] and potassium sulfate phases [14] using a combination of high magnetic field strengths, QCPMG enhancement and the “frequency stepping” method, in which the broad spectra are acquired in a number of separate sections whose widths are determined by the excitation bandwidth of the pulse sequence used. To date, the largest ^{33}S C_Q measured by NMR is 16.2 MHz [14], with the vast majority of investigations having been restricted to samples with C_Q values of around 2 MHz or less.

* Corresponding author.

E-mail address: Igor.Moudrakovski@nrc-cnrc.gc.ca (I.L. Moudrakovski).

Now that the utility of ^{33}S solid-state NMR in studies of inorganic materials appears to have been established, it is of interest to extend the technique to more diverse applications. We have recently been investigating the feasibility of ^{33}S NMR for studying small organic molecules, and have found that it is not unusual for ^{33}S C_Q values in organic and biological molecules to be very large indeed. For example, a preliminary DFT calculation run on the sulfur-containing amino acid L-methionine resulted in a predicted C_Q value of ca. 43 MHz for each of the two sulfur sites in the crystal structure [17]. An investigation into the detection limits of ultra-wideline methods applied to ^{33}S NMR for such large C_Q values is therefore warranted.

As a model system, and in an attempt to maximize the available NMR signal, we chose a sample of >99.9% ^{33}S -enriched sulfur ($\alpha\text{-S}_8$) [18], which is already known to exhibit a large C_Q value from a previous NQR study [19]. The spectrum, which is shown in Fig. 1a, was obtained at 21.1 T ($\nu_L(^{33}\text{S}) = 69.1$ MHz) in 18 separate pieces using a WURST-echo pulse sequence [20], which provides a much broader excitation bandwidth (ca. 800 kHz) than a regular spin-echo experiment (ca. 100 kHz), thus allowing a considerably reduced acquisition time (just over 6 h). A home-built static 4.0 mm probe was used, containing around 150 mg of sample (purchased from Trace Sciences International) packed into a thin-walled zirconia tube. Individual pieces were acquired in steps of 300 kHz with 24,000 scans per piece. The full spectrum was reconstructed from a skyline projection of these sub-spectra. The relaxation of the sulfur nuclei in this sample was observed to be very efficient, likely due to the large quadrupolar interaction as well as the network of homonuclear dipolar couplings. The short transverse relaxation time (T_2) precluded the use of the WURST-QCPMG experiment [21], allowing only a single echo to be acquired. However, the short *spin-lattice* relaxation time (T_1) permitted the use of a very short recycle delay (0.05 s). The WURST pulses [22] were 50 μs in length, had a sweep range of 1 MHz, an inter-pulse delay of 77 μs , and were applied with an RF power of $\nu_1 \approx 30$ kHz. The spectrum was referenced to the ^{33}S signal from a solution of tetramethylene sulfone in acetone, at $\delta = 367.55$ ppm with respect to CS_2 .

The simulation of the ^{33}S powder pattern in Fig. 1b shows good agreement with the experimental spectrum and allows a determination of the EFG parameters in this sample as $C_Q = 43.3 \pm 0.2$ MHz and an asymmetry parameter of $\eta_Q = 0.55 \pm 0.02$. The simulation was made using the Dmfit software [23] and neglected the effects of CSA. The reduced intensity of the low frequency discontinuity in the experimental spectrum as compared to the simulation is in fact a commonly observed phenomenon in such wideline spectra (see, for example, Fig. 3 in [14]). We note here the extremely large

experimental uncertainty associated with our reported isotropic chemical shift (500 ± 500 ppm), as well as the fact that the simulation did not allow for a meaningful experimental estimation of the CSA parameters or Euler angles (the effects of these latter parameters on the simulated lineshape were very slight). The C_Q value however, which represents an average for the four sulfur sites in this phase, corresponds to an NQR frequency of $\nu_{\text{NQR}} = 1/2C_Q(1 + \eta_Q^2/3)^{1/2} = 22.7$ MHz, which is in excellent agreement with the experimentally-determined (average) value of $\nu_{\text{NQR}} = 22.9$ MHz [19]. This is by far the largest C_Q measured by ^{33}S NMR to date. Due to the isotopically enriched and elemental nature of this sample, as well as the very high magnetic field strength used, we suggest that this represents a practical upper limit for ^{33}S C_Q values measurable using currently available solid-state NMR techniques. Precluding any similar study of a pure, enriched sulfur sample of a different phase (e.g., γ -sulfur, which is unstable [24]) or allotrope (e.g., S_6 [25]), the ^{33}S content of any other sample will be significantly diluted even if isotopically enriched. In addition, any sample with an increased T_2 , which would allow the use of QCPMG enhancement, would be likely to also feature a much longer T_1 , necessitating the use of a longer recycle delay. It is therefore highly likely that the acquisition of a spectrum from a dilute sample featuring a similar C_Q value would require a prohibitively long experimental time.

The $\alpha\text{-S}_8$ crystal structure is orthorhombic at ambient temperature and pressure, and consists of eight-member rings of sulfur atoms each featuring four crystallographically distinct sites [18] (see Fig. 2). Density functional theory calculations run on this structure using the CASTEP software [26] resulted in EFG parameters for the four distinct sites that are each very similar and agree reasonably well with our experimental values (Table 1). These calculations were done using the Materials Studio 4.3 software suite on an HP xw4400 Workstation with a single Intel Dual-Core 2.67 GHz processor and 8 GB DDR RAM. Perdew, Burke and Ernzerhof functionals were used with plane wave basis set cut-offs and Monkhorst–Pack k -space grid sizes set automatically under a “fine” basis set accuracy. The CASTEP calculations also provided values for the CSA parameters (Table 1) and the relative orientations of the EFG and CSA tensors (extracted using EFGShield [27]). The EFG tensor orientation is shown in Fig. 2 for the S2 site. The EFG tensor is oriented such that the largest component V_{33} is approximately perpendicular to the plane made by site S2 and its two neighboring sulfur atoms S1 and S3, with V_{11} pointing between these neighboring atoms. The least shielded component of the shielding tensor, σ_{11} , is tipped away from V_{33} by ca. 27° , with σ_{22} aligned very close to V_{22} in the S1–S2–S3 plane. All four sulfur sites in the crystal structure exhibit very similar EFG and shielding tensor orientations, as might be expected given the similar values for the tensor parameters and Euler angles predicted by CASTEP (Table 1).

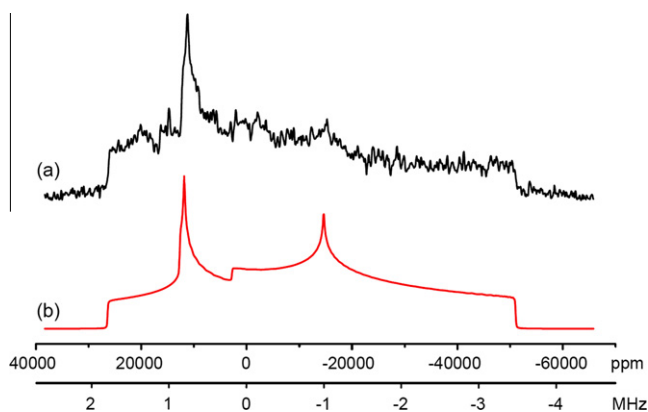


Fig. 1. (a) A ^{33}S solid-state NMR spectrum obtained from a static powder sample of ^{33}S -enriched sulfur at 21.1 T. The spectrum was reconstructed from 18 individual pieces obtained using a WURST-echo sequence. The total experiment time was 6.5 h. (b) A simulation made using parameters $C_Q = 43.3$ MHz and $\eta_Q = 0.55$.

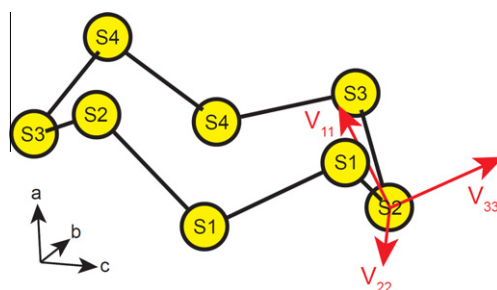


Fig. 2. The S_8 molecule as it appears in the α -phase crystal structure. The orientation of the EFG tensor for the S2 site is shown, as predicted by CASTEP. Very similar tensor orientations are observed for the other three sites.

Table 1Calculated EFG and shielding tensor parameters for the four distinct crystallographic sites in the α -S₈ structure.

Site	EFG parameters		Shielding parameters			Euler angles		
	C_Q (MHz)	η_Q	δ_{iso} (ppm)	Ω (ppm)	κ	α (deg)	β (deg)	γ (deg)
S1	40.4	0.56	72.0	641.5	−0.37	186	62	352
S2	40.4	0.55	79.9	625.4	−0.37	188	64	352
S3	40.5	0.54	78.8	614.7	−0.41	180	64	357
S4	40.3	0.55	76.2	618.5	−0.41	183	60	358
Average	40.4	0.55	76.7	625.0	−0.39	184	62	355
Experimental	43.3(2)	0.55(2)	500(500)	–	–	–	–	–

Parameter definitions are as follows: $C_Q = eQV_{33}/h$ (where eQ is the quadrupole moment of ^{33}S and h is Planck's constant), $\eta_Q = (V_{11} - V_{22})/V_{33}$, $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, $\Omega = \delta_{11} - \delta_{33}$ and $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$, where principal tensor components are ordered $|V_{33}| \geq |V_{22}| \geq |V_{11}|$ and $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. Absolute shieldings (σ) calculated by CASTEP were converted to chemical shifts (δ) using an empirical relation $\delta_{iso}(\text{ppm}) = -0.977\sigma_{iso}^{calc} + 416.4$ determined previously [14]. The Euler angles describe the orientation of the chemical shift tensor relative to the EFG tensor.

In summary, we have recorded an ultra-wideline ^{33}S NMR spectrum from an isotopically enriched sample of elemental sulfur at 21.1 T using the WURST-echo sequence and a piecewise acquisition method. We have demonstrated that very large C_Q values can in principle be measured using solid-state NMR, however, similar studies of more dilute systems will likely require experimental times that are prohibitively long. It seems probable that other experimental NMR approaches, such as the indirect detection of ^{33}S via more amenable spin-1/2 nuclei such as ^1H or ^{13}C , could provide a more realistic route to the study of sulfur in organic or bio-organic molecules.

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