Supporting Information for:

A Natural Abundance $^{33}$S Solid-State NMR Study of Layered Transition Metal Disulfides at Ultrahigh Magnetic Field

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Table S1: Experimental and calculated $^{33}$S NMR parameters. Page S2
Table S2: Detailed experimental conditions for $^{33}$S NMR. Page S3
Experimental Section Page S4-S6
Figure S1: Structure of (a) 2H-MoS$_2$ / WS$_2$ and (b) 1T-ZrS$_2$ / TiS$_2$ / TaS$_2$. Page S7
Figure S2: $^{33}$S static frequency-stepped acquisition QCPMG spectra of 2H-MoS$_2$ at 21.1 T. Page S8
Figure S3: $^{33}$S static frequency-stepped acquisition QCPMG spectra of 2H-WS$_2$ at 21.1 T. Page S9
Figure S4: $^{33}$S NMR spectra of 1T-TiS$_2$ at 21.1 and 9.4 T. Page S10
Figure S5: $^{33}$S static NMR spectra of 1T-TaS$_2$ at 21.1 T. Page S11
Figure S6: Powder XRD patterns of the metal disulfides Page S12-13
### Table S1. Experimental and calculated $^{33}$S NMR parameters.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>$C_Q$ (MHz)$^a$</th>
<th>$\eta_Q$$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H-MoS$_2$</td>
<td>experimental</td>
<td>9.3 (8)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>calculated$^c$</td>
<td>7.53</td>
<td>0</td>
</tr>
<tr>
<td>2H-WS$_2$</td>
<td>experimental</td>
<td>7.9 (5)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>calculated</td>
<td>6.66</td>
<td>0</td>
</tr>
<tr>
<td>1T-ZrS$_2$</td>
<td>experimental</td>
<td>0.5 (5)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>calculated</td>
<td>0.54</td>
<td>0</td>
</tr>
<tr>
<td>1T-TiS$_2$</td>
<td>experimental</td>
<td>1.8 (5)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>calculated</td>
<td>1.08</td>
<td>0</td>
</tr>
<tr>
<td>1T-TaS$_2$</td>
<td>experimental</td>
<td>4.5 (5)</td>
<td>0.50 (10)</td>
</tr>
<tr>
<td></td>
<td>calculated</td>
<td>3.85</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$ $C_Q = eQV_{ZZ}/h$;  
$^b$ $\eta_Q = (V_{xx} - V_{yy})/V_{ZZ}$ where $|V_{ZZ}| \geq |V_{yy}| \geq |V_{xx}|$. $\eta_Q$ was set to 0 for all the metal disulfides due to the $C_3$ site symmetry; $^c$ see experimental section for more details of the calculations.
Table S2. Detailed experimental conditions for $^{33}$S NMR.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type of experiment</th>
<th>$B_0$ (T)</th>
<th>$90^\circ$ pulse length (µs)</th>
<th>SW (kHz)</th>
<th>recycle delay (s)</th>
<th>$\tau_a$ (µs)</th>
<th>$\tau_1$ (µs)</th>
<th>$\tau_2$ (µs)</th>
<th>$\tau_3$ (µs)</th>
<th>$\tau_4$ (µs)</th>
<th># scans</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H-MoS$_2$</td>
<td>static QCPMG</td>
<td>21.1</td>
<td>5</td>
<td>500</td>
<td>5</td>
<td>200</td>
<td>64</td>
<td>29</td>
<td>30</td>
<td>30</td>
<td>7 x 3600</td>
</tr>
<tr>
<td>2H-WS$_2$</td>
<td>static QCPMG</td>
<td>21.1</td>
<td>10</td>
<td>500</td>
<td>5</td>
<td>250</td>
<td>128</td>
<td>29</td>
<td>30</td>
<td>30</td>
<td>8 x 3600</td>
</tr>
<tr>
<td>1T-ZrS$_2$</td>
<td>static Hahn-echo</td>
<td>21.1</td>
<td>5</td>
<td>100</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 pulse MAS at 6 kHz</td>
<td>21.1</td>
<td>4</td>
<td>100</td>
<td>10$^a$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>9850</td>
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<td>1T-TiS$_2$</td>
<td>static QCPMG</td>
<td>9.4</td>
<td>3</td>
<td>100</td>
<td>3</td>
<td>1000</td>
<td>19</td>
<td>25</td>
<td>26</td>
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<td>27</td>
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<tr>
<td></td>
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<td>21.1</td>
<td>5</td>
<td>200</td>
<td>3</td>
<td>1000</td>
<td>64</td>
<td>29</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>static Hahn-echo</td>
<td>21.1</td>
<td>5</td>
<td>200</td>
<td>10$^a$</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>Hahn-echo MAS at 6 kHz</td>
<td>21.1</td>
<td>5</td>
<td>200</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>1T-TaS$_2$</td>
<td>static QCPMG</td>
<td>21.1</td>
<td>5</td>
<td>250</td>
<td>1</td>
<td>250</td>
<td>128</td>
<td>29</td>
<td>30</td>
<td>30</td>
<td>8 x 4096</td>
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<tr>
<td></td>
<td>static Hahn-echo</td>
<td>21.1</td>
<td>5</td>
<td>250</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>58827</td>
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</table>

$^a$ The recycle delay of 3 seconds was sufficient for almost complete relaxation.
Experimental Section:

**Materials.** The samples of MoS$_2$, WS$_2$, ZrS$_2$, TiS$_2$ and TaS$_2$ were purchased from STREM Chemicals, Inc. and used as received. The identity, purity and crystallinity of the samples were confirmed by powder X-ray diffraction (see Figure S6).

**Powder X-ray diffraction.** Powder X-ray diffraction patterns were recorded on a Rigaku diffractometer equipped with a graphite monochromator using Co K$_\alpha$ radiation ($\lambda = 1.7902$ Å). The step size used was 0.02° and scan range was from 5 - 65° ($2\theta$) with a rate of 10°/minute.

**Solid-state NMR spectroscopy.**

a. **Experiments at 21.1 T.** Solid-state $^{33}$S NMR experiments were performed on a 900 MHz Bruker Avance II spectrometer at the National Ultrahigh-field NMR Facility for Solids in Ottawa, Canada, operating at a frequency of 69.05 MHz. A 7.0 mm single channel Bruker MAS probe was used for both static and MAS experiments. The samples were ground into a fine powder and then packed into 7.0 mm o.d. Bruker zirconia rotors. For MoS$_2$ and WS$_2$, the samples were first pressed into pallets under hydraulic pressure and then packed in the rotor to fit in more than double amount of the sample. Experimental setup, pulse calibration and referencing were done using either 1M Cs$_2$SO$_4$ solution ($\delta_{so} = 333$ ppm) or solid CaS ($\delta_{so} = -28.5$ ppm), both can act as a secondary standard to neat CS$_2$ at 0.0 ppm. $^{33}$S static NMR spectra were collected using the conventional quadrupolar Carr-Purcell-Meiboom-Gill (QCPMG) pulse sequence, while a single pulse or a rotor-synchronized Hahn-echo pulse experiment was carried out to acquire MAS spectra. The Hahn-echo pulse sequence has the form $(\pi/2) - \tau - (\pi) - \tau - \text{acq}$, where $\tau$ represents inter-pulse delays of 20 - 50 µs. For QCPMG, the frequency-stepped
technique was used when the breadth of the CT spectra exceeded the pulse width excitation profile. The sub-spectra with different frequency offsets were co-added in frequency scale (Hertz). The resulting spectrum was then treated and referenced as a single spectrum. The spectrometer conditions used are summarized in Table S2. Since the samples have no protons, proton-decoupling was not applied.

b. Experiments at 9.4 T. $^{33}$S SSNMR experiments were also carried out on a Varian InfinityPlus spectrometer with an Oxford 9.4 T wide-bore magnet, operating at resonance frequency of 30.65 MHz. A Varian/Chemagnetics 7.5 mm HXY MAS probe was used. The samples were ground into fine powders and packed into 7.5 mm o.d. zirconia rotors. Experimental setup, pulse calibration and referencing were done using either 1M Cs$_2$SO$_4$ solution ($\delta_{\text{iso}} = 333$ ppm) or solid CaS ($\delta_{\text{iso}} = -28.5$ ppm), both acting as secondary standard to neat CS$_2$ at 0.0 ppm. $^{33}$S static NMR spectra were collected using the QCPMG pulse sequence (see Table S2 for details).

NMR spectral simulations. All NMR parameters including $C_Q$, $\eta_Q$, $\delta_{\text{iso}}$, $\Omega$, and $\kappa$ were determined by analytical simulations of NMR spectra using the WSOLIDS$^1$ simulation package. The experimental error for each measured parameter was determined by visual comparison of experimental spectra with simulations. The parameter of concern was varied bidirectionally starting from the best fit value and all other parameters were kept constant, until noticeable differences between the spectra were observed.

Theoretical calculations. First-principles (ab initio) calculations based on plane wave-pseudo potential Density Functional Theory were conducted using CASTEP (version 4.3)$^2$, program setup by the Materials Studio graphical user interface, running on a single CPU. The NMR module$^{4,6}$ was used to calculate the $^{33}$S EFG and CSA tensors.
The gauge-including projector augmented-wave (GIPAW) method which uses pseudo potentials and plane wave basis sets to describe three dimensional lattices in crystalline materials was utilized. Unit cell parameters and atomic coordinates were taken from corresponding crystal structures.\textsuperscript{7-11} The Generalized Gradient Approximation (GGA) with Perdew, Burke and Ernzerhof (PBE) functional was used for all the calculations.\textsuperscript{12, 13} The principal components of the EFG tensor ($V_{XX}$, $V_{YY}$, $V_{ZZ}$) were converted to quadrupole coupling constant $C_Q$ and asymmetry parameter $\eta_Q$ according to the following definition: $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$; $C_Q$ (in Hz) = $(eV_{ZZ}Q/h) \times 9.71736 \times 10^{21}$ V·m$^{-2}$; $\eta_Q = (V_{XX} - V_{YY})/V_{ZZ}$, where $e$ is the electric charge; $Q$ is the nuclear quadrupole moment [$Q^{(33}\text{S}) = -0.0678$ barn]\textsuperscript{14}.

References:

Figure S1. Structure of (a) 2H-MoS$_2$ / WS$_2$ and (b) 1T-ZrS$_2$ / TiS$_2$ / TaS$_2$

Different views of MS$_2$: 1) view down c axis, 2) metal coordination site, 3) unit cell, 4) view down b axis, 5) packing of layered MS$_2$. 

(a) 

1) 

2) 

3) 

4) 

5) 

(b) 

1) 

2) 

3) 

4) 

5)
Figure S2. $^{33}$S static frequency-stepped acquisition QCPMG spectra of 2H-MoS$_2$ at 21.1 T.

7 pieces for qcpmg (5 hours each)
Figure S3. $^{33}$S static frequency-stepped acquisition QCPMG spectra of 2H-WS$_2$ at 21.1 T.

8 pieces for qcpmg (3 hours each)
Figure S4. a) $^{33}$S NMR spectra of 1T-TiS$_2$ at 21.1 T. b) $^{33}$S static QCPMG spectra of 1T-TiS$_2$ at 9.4 T.
Figure S5. $^{33}$S static NMR spectra of 1T-TaS$_2$ at 21.1 T.
**Figure S6. Powder XRD patterns of MS₂**

- **Powder XRD of 2H-MoS₂**
  - 2theta vs. a.u.
  - Peaks at specific 2theta values

- **Powder XRD of 2H-WS₂**
  - 2theta vs. a.u.
  - Peaks at specific 2theta values
Powder XRD of 1T-ZrS$_2$

Powder XRD of 1T-TiS$_2$

Powder XRD of 1T-TaS$_2$