Solid-state $^{185/187}$Re NMR and GIPAW DFT study of perrhenates and Re$_2$(CO)$_{10}$: chemical shift anisotropy, NMR crystallography, and a metal–metal bond†

Cory M. Widdifield,*‡ Frédéric A. Perras and David L. Bryce*

Advances in solid-state nuclear magnetic resonance (SSNMR) methods, such as dynamic nuclear polarization (DNP), intricate pulse sequences, and increased applied magnetic fields, allow for the study of systems which even very recently would be impractical. However, SSNMR methods using certain quadrupolar probe nuclei (i.e., $I > 1/2$), such as $^{185/187}$Re remain far from fully developed due to the exceedingly strong interaction between the quadrupole moment of these nuclei and local electric field gradients (EFGs). We present a detailed high-field ($B_0 = 21.1\ T$) experimental SSNMR study on several perrhenates (KReO$_4$, AgReO$_4$, CaReO$_4$$_2$·2H$_2$O), as well as ReO$_3$ and Re$_2$(CO)$_{10}$. We propose solid ReO$_3$ as a new rhenium SSNMR chemical shift standard due to its reproducible and sharp $^{185/187}$Re NMR resonances. We show that for KReO$_4$ previously poorly understood high-order quadrupole-induced effects (HOQIE) on the satellite transitions can be used to measure the EFG tensor asymmetry (i.e., $r_{44}$) to nearly an order-of-magnitude greater precision than competing SSNMR and nuclear quadrupole resonance (NQR) approaches. Samples of AgReO$_4$ and CaReO$_4$$_2$·2H$_2$O enable us to comment on the effects of counter-ions and hydration upon Re(Ⅵ) chemical shifts. Calcium-43 and $^{185/187}$Re NMR tensor parameters allow us to conclude that two proposed crystal structures for CaReO$_4$$_2$·2H$_2$O, which would be considered as distinct, are in fact the same structure. Study of Re$_2$(CO)$_{10}$ provides insights into the effects of Re–Re bonding on the rhenium NMR tensor parameters and rhenium oxidation state on the Re chemical shift value. As overtone NQR experiments allowed us to precisely measure the $^{185/187}$Re EFG tensor of Re$_2$(CO)$_{10}$, we were able to measure rhenium chemical shift anisotropy (CSA) for the first time in a powdered sample. Experimental observations are supported by gauge-including projector augmented-wave (GIPAW) density functional theory (DFT) calculations, with NMR tensor calculations also provided for NH$_4$ReO$_4$, NaReO$_4$ and RbReO$_4$. These calculations are able to reproduce many of the experimental trends in rhenium $\delta_{iso}$ values and EFG tensor magnitudes. Using KReO$_4$ as a prototypical perrhenate-containing system, we establish a correlation between the tetrahedral shear strain parameter ($\psi$) and the nuclear electric quadrupolar coupling constant ($C_Q$), which enables the refinement of the structure of Nd$_3$ReO$_4$. Shortcomings in traditional DFT approaches, even when including relativistic effects via the zeroth-order regular approximation (ZORA), for calculating rhenium NMR tensor parameters are identified for Re$_2$(CO)$_{10}$.

Introduction

Rhenium exists in a wide range of oxidation states (−1 to +7).$^1$ Additionally, rhenium can participate in metal–metal bonding, with K$_2$Re$_2$Cl$_8$ being recognized as the first example of a compound containing a bond with an order of greater than 3.$^2$ Rhenium metal possesses very high thermal stability, and thus is a component in the alloys used to make jet engine parts.$^3$ Rhenium-containing compounds have been used as catalysts,$^4$–$^{18}$ can facilitate CO$_2$ reduction,$^{19}$–$^{23}$ and possess appealing properties for organic light-emitting diode$^{24}$,$^{25}$ and dye-sensitized solar cell$^{26}$ applications. Rhenium-containing systems also show potential as therapeutic agents,$^{27}$–$^{29}$ biomarkers,$^{30}$–$^{32}$ in vivo diagnosis,$^{33}$ single-molecule magnets,$^{34}$–$^{36}$ and in hydrogen storage applications.$^{37}$ While these attractive applications make the solid-state nuclear magnetic resonance (SSNMR) characterization of rhenium-containing compounds highly relevant, the quadrupolar nature of the two NMR-active nuclides...
(185/187Re) has significantly hampered the development of this technique to date.

All quadrupolar nuclei possess greater than one half a unit of spin angular momentum (i.e., I > 1/2). While the vast majority of routine SSNMR experiments are performed using spin 1/2 nuclei, ca. 74% of NMR-active nuclei are quadrupolar.18 As such, further development of SSNMR methods to characterize quadrupolar nuclei would benefit the chemical community. SSNMR experiments on quadrupolar nuclei can offer tremendous insights into local structure and dynamics due to the unique ability of quadrupolar nuclei (i.e., relative to I = 1/2 nuclei) to probe the electric field gradient (EFG) at the nuclear site.19 Recent examples can be found where SSNMR experiments on quadrupolar nuclei have been used to study a variety of important materials and interesting systems. For example, SSNMR experiments on the receptive 11B nucleus (I = 3/2) offered insight into the surface chemistry of double-layer capacitors,40 and a very detailed picture of short-range interactions in frustrated Lewis pairs.41 Likewise, 7Li (I = 3/2) SSNMR experiments involving spinning sideband suppression techniques were used to comment on Li+-containing batteries.42 SSNMR experiments on integer quadrupoles such as 2H and 14N (both parity even nuclei) are unable to correctly model the observed SSNMR line shapes when the QI becomes large.51 While further development of SSNMR methods for quadrupolar nuclei is important, it is also beneficial to exploit the complementary relationship between SSNMR observables and other techniques such as X-ray diffraction (XRD) measurements and quantum chemical calculations.46–48

While probing quadrupolar nuclei using SSNMR experiments is informative and widely applicable, the additional information comes with a cost, due to the quadrupolar interaction (QI) between the nuclear electric quadrupole moment (Q) of a quadrupolar nucleus and the EFG.55–56 The QI broadens the SSNMR signal, sometimes to the point that SSNMR experiments become impractical or uninformative. In addition to resolution and sensitivity issues, standard analytical line shape simulation tools (which treat the QI as a perturbation to the Zeeman eigenstates to second-order) are unable to correctly model the observed SSNMR line shapes when the QI becomes comparable to the Zeeman interaction.40,61 Until recently, this issue of line shape modeling was of little practical importance, as experimental sensitivity did not warrant the observation of SSNMR signals which were broadened to such an extreme extent. However, due to advances in magnet technology62 and sensitivity-enhancing pulse sequences,63–65 observation of SSNMR signals broadened by very large QIs is becoming increasingly common.

At present, the most dramatic examples of strongly QI-broadened SSNMR signals belong to the 185/187Re nuclides (I(185/187Re) = 5/2).66,67 In certain cases additional fine structure, due to high-order quadrupole-induced effects (HOQIE), was observed in these 185/187Re SSNMR spectra, in agreement with earlier theoretical models.68 The nuclei of the two most stable isotopes of rhenium are NMR-active, are present in high natural abundance (37.398(16)% and 62.602(16)% for 185Re and 187Re, respectively),69 and possess relatively high magnetogyric ratios (γ(185Re) = 6.1057 × 10−7 rad s−1 T−1; γ(187Re) = 6.1682 × 10−7 rad s−1 T−1).70 However, very few literature reports of 185/187Re SSNMR exist, and they are primarily restricted to very high symmetry rhenium environments and/or low temperature conditions.71–80 The dearth of 185/187Re SSNMR information is attributed to the very large Q that for both NMR-active nuclides (Q(185Re) = 2180(20) mb; Q(187Re) = 2070(20) mb).81 As such, a very small EFG can result in a rhenium QI that broadens the SSNMR powder pattern to the point that it is undetectable.

In this study, we focus on the novel information which can be obtained when analyzing 185/187Re SSNMR spectra under the conditions of a very strong QI. Due to the inconvenience of using a dilute solution standard, we present an argument for the use of a new solid standard, ReO3, and include discussion of the field- and temperature-dependence of its 185/187Re SSNMR resonances. We provide additional discussion on several high-symmetry perrenate systems (KReO4, AgReO4, Ca(ReO3)2⋅2H2O), as well as Re2(CO)10, which possesses a rhenium–rhenium bond. By precisely measuring the 185/187Re EFG tensor in Re2(CO)10, we quantify rhenium chemical shift anisotropy (CSA) for the first time in a powdered sample, and compare the present value to prior single-crystal SSNMR measurements.82 Discussions pertaining to rhenium chemical shifts as a function of the rhenium oxidation state are briefly put forth. Lastly, we comment upon the utility of modern quantum chemical approaches for calculating important rhenium NMR observables (e.g., CQ(I(185/187Re)), δiso, etc.), provide some discussion of the limitations of these quantum chemical approaches, and show that the knowledge gained in the present study can be applied to refine the neutron diffraction structure of ND4ReO4.

Experimental

1. Sample preparation
ReO3 (99.9%), KReO4 (99.9%), AgReO4 (99.995%) and Re2(CO)10 (98%) were purchased from Strem Chemicals, while Ca(ReO4)2, 2H2O was purchased from Aldrich. All were received as powders and used without modification (further details are given in the ESI† Additional experimental). All compounds are stable under normal laboratory conditions. Depending upon the experiment, the powdered samples were tightly packed into 4 mm or 7 mm outer diameter Bruker magic-angle spinning (MAS) ZrO2 rotors.

2. Solid-state 43Ca and 185/187Re NMR
Experimental data were primarily acquired at the National Ultrahigh-field NMR Facility for Solids in Ottawa, with additional experiments being performed at the University of Ottawa. The Ultrahigh-field Facility experiments used a standard bore Bruker AVANCE II spectrometer, which operates at Bo = 21.1 T (ν0(1H) ≈ 899.95 MHz; ν0(185Re) = 202.71 MHz; ν0(187Re) = 204.75 MHz; ν0(43Ca) = 60.57 MHz), and either a 4 mm Bruker HX MAS probe (185/187Re) or a 7 mm Bruker single-channel MAS probe (43Ca). Experiments performed at the University of Ottawa used a wide bore Bruker AVANCE spectrometer, which operates at Bo = 11.75 T (ν0(1H) ≈ 500.13 MHz; ν0(185Re) = 112.65 MHz;
$v_0(187\text{Re}) = 113.79\text{ MHz}$, and a 4 mm Bruker HXY MAS probe. The $^{185/187}$Re SSNMR signals were referenced to a 0.1 mol dm$^{-3}$ solution of NaReO$_4$ in D$_2$O ($\delta_{\text{iso}}(185/187\text{Re}) = 0$ ppm); however, during the course of this study it was found that the sharp rhenum SSNMR signals from solid ReO$_4$ may be used instead. The $^{43}\text{Ca}$ SSNMR signal was referenced to 2.0 mol dm$^{-3}$ CaCl$_2$(aq) ($\delta_{\text{iso}}(43\text{Ca}) = 0$ ppm). The $^{185/187}$Re pulse lengths used for experiments on AgReO$_4$, Ca(ReO$_4$)$_2$, 2H$_2$O, Re$_2$(CO)$_{10}$, and KReO$_4$ (at 21.1 T) were established using the solution reference, and include a scaling of the optimized solution pulse by $1/[I + 1/2] = 1/3$ to selectively excite the central transition ($m_I = 1/2 \leftrightarrow -1/2$; CT) of the solid. Calcium-43 pulse lengths were determined using saturated CaCl$_2$(aq) and scaled (as above) by 1/4 ($\delta^{43}\text{Ca}) = 7/2$) to be selective for the CT of the solid. Due to the extensive breadth of the $^{185/187}$Re SSNMR signals of KReO$_4$ at $B_0 = 11.75$ T, the pulse lengths were also calibrated using high- and low-frequency CT and satellite transition (ST) discontinuities of the actual KReO$_4$ sample. For further details on the frequency-dependence of the pulse lengths used to generate this $^{185/187}$Re SSNMR spectrum, see the ESI,$^\dagger$ Table S1.

For samples exhibiting a broad line shape (i.e., all solids other than ReO$_4$), the $^{185/187}$Re SSNMR signals were acquired using either Solomon (i.e., "solid") echo (i.e., $\pi/2$-$\tau_1$-$\pi/2$-$\tau_2$-acq)$^{83-85}$ or Hahn echo (i.e., $\pi/2$-$\tau_1$-$\pi/2$-acq)$^{86}$ pulse sequences. The Solomon echo experiment was preferred at $B_0 = 21.1$ T, where experimental sensitivity was not of great concern. For a given radiofrequency field strength, this sequence yields a larger uniform excitation bandwidth relative to the Hahn echo sequence. The Hahn echo sequence was preferred at $B_0 = 11.75$ T, as it is a more sensitive experiment at offsets near the transmitter frequency (although this comes at the expense of a reduced uniform excitation bandwidth). Due to the very rapid $^{185/187}$Re spin–spin relaxation in these materials, whole echo data acquisition was not used. Typical parameters for these experiments were as follows: $\pi/2$ = 0.8 to 1.5 $\mu$s; spectral window = 2 MHz; $\tau_1$ = 13.2 to 13.8 $\mu$s; recycle delay = 50 ms, and 1024 complex time-domain data points were collected per scan. The $^{43}\text{Ca}$ SSNMR data for Ca(ReO$_4$)$_2$-2H$_2$O were collected using a simple Bloch decay experiment (i.e., $\pi/2$-acq) under MAS conditions (MAS frequency of 5 kHz). Final $^{185/187}$Re SSNMR spectra were prepared using variable offset cumulative spectrum (VOCS) data acquisition methods.$^{56,87,88}$ The VOCS offsets varied from 200 to 300 kHz for Hahn and Solomon echo experiments, respectively, and were chosen in such a fashion so as to ensure that the final co-added VOCS possessed a uniform excitation profile over the region of the SSNMR signal. Depending on the compound, for each transmitter setting, between 4000 and 19 000 transients were collected, but note that for each sub-spectrum in a given VOCS, the same number of transients was collected. Each sub-spectrum was processed as usual and combined in the frequency-domain via co-addition to produce the VOCS. Due to the temperature dependence of the $^{185/187}$Re QI for these compounds, all experiments were performed at $T = 291.8(0.2)$ K, as monitored via a Bruker ‘type-T’ thermocouple and regulated using a standard Bruker variable temperature unit.

For ReO$_3$ only, it was possible under certain conditions to use a Bloch decay experiment due to its narrow $^{185/187}$Re SSNMR signals, while in other cases the Solomon echo experiment was used. Regardless of the signal acquisition method, SSNMR experiments on this material rapidly yielded high signal-to-noise ratio (S/N) spectra (e.g., at $B_0 = 21.1$ T, 16 transients with a recycle delay of 100 ms resulted in a S/N of ca. 40). Variable temperature experiments were performed on ReO$_3$ to assess the sensitivity of its rhenum $\delta_{\text{iso}}$ value to temperature. For full experimental details, see the ESI,$^\dagger$ Table S1.

3. Solid-state $^{185/187}$Re nuclear quadrupole resonance (NQR)
All experiments were carried out at the University of Ottawa using either the AVANCE spectrometer outlined above, or an AVANCE III spectrometer. NQR experiments used either 4 mm Bruker HX or HXY MAS probes, or a 7 mm Bruker HX static probe. Unless specified otherwise, all spectra were acquired using the Hahn echo pulse sequence at $T = 291.8(0.2)$ K. For single-quantum NQR experiments, short ($\leq 1.8$ $\mu$s), high-powered pulses were used as the radiofrequency transmitter was varied until a particular resonance was detected. The offset used while searching for $^{185/187}$Re NQR signals was 200 kHz. For overtone NQR experiments on Re$_2$(CO)$_{10}$, relatively long ($10$ ms), high-powered pulses were used, for reasons outlined in prior literature.$^{89}$ To acquire the $^{185/187}$Re NQR spectra for Ca(ReO$_4$)$_2$:2H$_2$O only, the VOCS data acquisition method was necessary. For further details, see the ESI,$^\dagger$ Table S1.

4. NMR/NQR line shape fitting and parameter determination
The $^{185/187}$Re SSNMR spectra were typically modeled using the ‘Quadrupolar Exact Software’ (QUEST) program, which is a numerical simulation software that treats the combined Zeeman–quadrupole Hamiltonian exactly, and includes the effects due to chemical shift anisotropy.$^{90}$ Conveniently, QUEST allows for the automatic inclusion of a $^{187}$Re site when a $^{185}$Re spectrum is calculated. Observed signals primarily correspond to the CT, although contributions from the satellite and other allowed transitions are implicitly considered in the line shape modeling in QUEST. The $^{43}$Ca MAS SSNMR spectrum was modeled using WSOLIDS.$^{91}$ Contributions to line shape broadening such as J and dipole–dipole were deemed insignificant and not considered. Uniquely for KReO$_4$, a region containing only ST signal was directly acquired. The relevant SSNMR parameters considered in these fits are outlined in the footnotes to Table 1 and 2.

To model the $^{185}$Re and $^{187}$Re NQR spectra and extract the relevant EFG tensor parameters, both QUEST and the closed-form solutions to the secular equations provided by Semin$^92$ were used and found to produce equivalent results.

5. Quantum chemical calculations
Calculations of EFG and magnetic shielding tensors were carried out using gauge-including projector augmented-wave (GIPAW) density functional theory (DFT),$^{93,94}$ as implemented in the Cambridge Serial Total Energy Package (CASTEP)$^{95-98}$ version 4.1 or 5.5. Input files were generated using the CIF2-Cell program (v. 1.2.2),$^{99}$ and all calculations used ultrasoft

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Table 1 Experimental 185/187 Re EFG tensor parameters and isotropic chemical shifts obtained via exact modeling of the quadrupole interaction

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν1(185/187 Re)/MHz</th>
<th>ν2(185/187 Re)/MHz</th>
<th>ν1(185/187 Re)/MHz</th>
<th>ν2(185/187 Re)/MHz</th>
<th>γ (185/187 Re)/MHz</th>
<th>γ (185/187 Re)/MHz</th>
<th>γ (185/187 Re)/MHz</th>
<th>ηq</th>
<th>δiso/μm</th>
<th>ppm</th>
<th>Δ/μm</th>
<th>ppm</th>
<th>Original structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>ReO3</td>
<td>28.380(0.010)</td>
<td>56.754(0.015)</td>
<td>26.860(0.010)</td>
<td>53.718(0.015)</td>
<td>189.18(0.06)</td>
<td>179.06(0.06)</td>
<td>&lt;0.003</td>
<td>-2940(8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaOReO4</td>
<td>39.811(0.007)</td>
<td>79.621(0.004)</td>
<td>37.674(0.004)</td>
<td>75.347(0.007)</td>
<td>265.40(0.03)</td>
<td>251.16(0.03)</td>
<td>&lt;0.005</td>
<td>175(50)</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Measurement errors are within parentheses and parameter definitions are as follows: C0 = eQV1/2h; ηq = |V11 − V22|/V33, where |V11| ≤ |V22| ≤ |V33|; δ12 = (δ13 + δ23 + δ33)/3, where δ13 ≤ δ23 ≤ δ11. The frequencies ν1 and ν2 correspond to the doubly-degenerate single-quantum NMR resonance frequencies, which for I = 5/2 and ηq = 0 can be defined as: ν1 = ν2 = 36 V0/20 and ν2 = 2V0 = 36 V0/10. When ηq ≠ 0, the relationships between the measured NQR frequencies and the EFG tensor parameters are more complex, but EFG tensor parameters using NQR data were determined using the procedure outlined by Semin. 158 Unless noted otherwise, SSNMR measurements were carried out at T = 298±0.2 K, and SSNMR line shape simulations were performed using QUEST. 99 While C0 may take any real value, CQ is typically measured experimentally using NQR/NSNMR. + Rhenium chemical shifts are relative to 0.1 mol dm−3 NaReO4 in D2O (δiso(185/187 Re) = 0 ppm). The measured shift position is strongly influenced by the Knight shift and T = 295 K. δ Value determined as a result of modeling a low-frequency m1 = ±1/2 ↔ ±3/2 ST. The 185/187 Re overtone NQR (m1 = ±1/2 ↔ ±5/2) transitions were measured at 65.466(0.010) and 69.162(0.010) MHz, allowing for enhanced precision in the determinations of |CQ(185/187 Re)| and ηq. Chemical shift tensor data: Ω = 150(75) ppm; k < −0.5; β = 70(20). δ From ref. 90.

Table 2 (G)PAW DFT-calculated 187 Re EFG tensor parameters and isotropic chemical shifts

| Compound | | | | | | | | Original structure |
|----------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| NaReO4   | 328.5             | 0                 | −51.7             | 63.9              | −1                | 90, 90, 180       | NaZedoszter and Range173 |
| KReO4    | 185.3             | 0                 | −68.6             | 40.5              | −1                | 90, 90, 180       | Brown et al.153 |
| AgReO4   | 254.2             | 0                 | 73.8              | 68.0              | −1                | 90, 90, 180       | Naumov et al.174 |
| RbReO4   | 187.2             | 0                 | −194.9            | 41.2              | −1                | 90, 90, 180       | Rönger and Range175 |
| ND2ReO4 (1993) | 78.8             | 0                 | −89.9             | 6.7               | −1                | 90, 90, 180       | Powell et al.154 |
| ND2ReO4 (1997-A) | 78.7             | 0                 | −43.1             | 30.1              | −1                | 90, 90, 180       | Swainson and Brown152 |
| ND2ReO4 (1997-B) | 228.3             | 0                 | −25.9             | 55.5              | −1                | 90, 90, 180       | Swainson and Brown152 |
| NH4ReO4 (refined) | 116.5             | 0                 | | | | | | Swainson and Brown152 |
| CaReO4:2H2O (1988) | 460.0             | 0.334             | −228.6            | 380.7             | −0.15             | 3.0, 49.1, 69.3   | Picard et al.149,150 |
| CaReO4:2H2O (1988) | 323.4             | 0.318             | −295.8            | 238.0             | −0.21             | 5.7, 68.1, 338.9 | Picard et al.149,150 |
| CaReO4:2H2O (1988) | 208.3             | 0.630             | −73.9             | 248.1             | −0.13             | 111.9, 89.3, 189.5 | Baur and Kassner151 |
| CaReO4:2H2O (1988) | 233.8             | 0.433             | −8.0              | 110.0             | −0.50             | 75.1, 87.2, 203.3 | Baur and Kassner151 |
| CaReO4:2H2O (1992) | 401.0             | 0.497             | −319.7            | 220.3             | 0.62              | 73.0, 48.1, 75.5 | Churchill et al.159 |
| CaReO4:2H2O (1992) | 423.1             | 0.457             | −360.1            | 404.8             | 0.87              | 37.8, 84.0, 253.4 | Churchill et al.159 |
| CaReO4:2H2O (1992) | 209.0             | 0.680             | −70.6             | 247.8             | −0.12             | 67.6, 89.2, 170.6 | Churchill et al.159 |
| CaReO4:2H2O (1992) | 215.8             | 0.434             | −11.8             | 99.9              | 0.45              | 73.7, 87.4, 207.0 | Churchill et al.159 |
| Re2(CO)10 | 695.0             | 0.409             | −440.9            | 123.5             | 0.80              | 112.0, 15.9, 163.0 | Churchill et al.159 |
| Re2(CO)10 | 651.5             | 0.166             | −417.4            | 140.5             | 0.23              | 101.9, 20.9, 282.6 | Churchill et al.159 |

A more complete disclosure of the calculated electron NQR and magnetic shielding tensor eigenvalues can be found in the ESI, Table S4. Additional parameter definitions: Ω = δ11 + δ33 and k = 3(δ23 − δ13)/2Ω. Euler angles are specified by α, β, and γ and define the orientation between the EFG tensor principal axis system (PAS) and the chemical shift tensor PAS. Further discussion on Euler angles can be found in ref. 176. While C0 may take any real value, CQ is typically measured experimentally using NQR/SSNMR and hence the calculated values are reported as |CQ|. Calculated chemical shifts have been determined from computed rhenium magnetic shielding values (i.e., δiso(μm ppm) = −0.9884α(μm ppm) − 410.7), as detailed in the ESI, Fig. S9. Labels of ‘A’ and ‘B’ denote the two distorted forms (disorder in ND2)1 proposed to be present in the structure of Swainson and Brown. Structure was refined as specified in the main text, starting from the structure of ND2ReO4 (1997-A) specified by Swainson and Brown. Prior to calculation of the NMR tensor parameters, the H atoms were optimized computationally. To map calculated νiso values to δiso values for CaReO4:2H2O, experimental ‘site I’ is assigned to computational ‘site I’, and analogously, ‘site II’ is assigned to ‘site II’. Prior to calculation of the NMR tensor parameters, the O and H atoms were optimized computationally. Prior to calculation of the NMR tensor parameters, the O and C atoms were optimized computationally.
Relativistic effects (including spin-orbit) were included under the zeroth-order regular approximation (ZORA). All-electron basis sets were used, which were quadruple-ζ in the valence (triple-ζ in the core) with polarization functions (i.e., ‘QZ4P’ according to the ADF software). A variety of commonly-available XC functionals were tested (PBE, TPSS, and PBE0), with further details provided in the ESI, † Tables S7 and S8.

Results and discussion

1. Rhenium-185/187 solid-state NMR

i. ReO₃: suggested rhenium chemical shift reference compound.

One of the first challenges encountered when performing Re SSNMR experiments is the poor sensitivity associated with the accepted chemical shift reference material. The IUPAC recommends that a 0.1 mol dm⁻³ solution containing the ReO₄⁻ group in D₂O may be taken as the primary chemical shift reference. It is unfortunate that the observation of this NMR reference signal is somewhat time-consuming (often needing several thousands of transients to be collected to obtain a modest S/N ratio). A search was thus initiated to find a convenient secondary reference material for Re NMR experiments. For reasons we outline below, ReO₃ is suggested as a suitable secondary Re NMR reference compound. To begin, this material packs in a cubic lattice and therefore the EFG at the Re nuclei is expected to be very small. As line shape broadening effects due to the quadrupolar interaction are minimized, a sharp signal should be obtained. Due to the high amount of rhenium by mass, relative to the accepted reference material, it is also expected that fewer transients would need to be acquired. As well, Re T₁ values are necessarily very small due to the large Q value associated with each Re nuclide (although not to the extent that lifetime broadening effects are of paramount significance). By coupling these advantages (i.e., fewer scans and short recycle delays), high-quality Re SSNMR spectra using ReO₃ should be obtained very rapidly, thereby minimizing the amount of NMR spectrometer time dedicated to experiments on the reference sample.

Our Re SSNMR observations using ReO₃ live up to the above expectations (see Fig. 1(a), (b), and Fig. S1 in the ESI†). A high S/N (ca. 150:1) NMR spectrum can be obtained using 256 scans at B₀ = 21.1 T, which corresponds to roughly 30 seconds of spectrometer time. The measured rhenium isotropic chemical shifts of both NMR-active rhenium nuclides at B₀ = 11.75 and at 21.1 T have been calibrated relative to the accepted primary standard as −2940(8) ppm (Table 1). The δiso value therefore appears to be field independent within the magnetic fields associated with most NMR experiments (ca. 9.4–21.1 T), and we were unable to discern any significant isotope-dependence in the measured rhenium chemical shift values. Due to the presence of delocalized conduction band electrons, we note that the measured δiso for ReO₃ is necessarily strongly shifted due to the Knight mechanism. Prior measurements of the Knight shift for ReO₃ at liquid helium temperatures establish a value of −2500(200) ppm, consistent with the conduction band electrons having 5d character. Presently, experiments were also conducted to probe the temperature-dependence of the δiso(¹⁸⁷Re) value for ReO₃, and it was found to be very...
modest for temperatures ranging from $T = 276.5$ to 306.5 K (Fig. 1c). Although the measurement errors in the position of the $^{185/187}$Re SSNMR signal are somewhat large compared to the total shift in the signal over the temperature range considered, we find that the temperature-dependence of the $\delta_{\text{iso}}$ value is $+0.24$ ppm $K^{-1}$ for near ambient temperatures. This slight sensitivity could potentially offer the side benefit of temperature calibration, as demonstrated using the halogen nuclei in $K^79\text{Br}$ and $Cs^{127}$,118,119 Finally, measurements performed on the same sample of ReO$_3$ over the course of a 1 year period produced the same chemical shift value (i.e., within the errors reported above). It is therefore believed that ReO$_3$ represents a reliable secondary chemical shift reference material that may be used in lieu of the suggested IUPAC reference material.

ii. KReO$_4$: new (and useful) high-order quadrupole-induced effects. The local rhenium environment in KReO$_4$ is a distorted tetrahedron, and as such it is similar to that of NH$_4$ReO$_4$ and NaReO$_4$, both of which have been successfully studied using rhenium SSNMR experiments.66,67 Prior rhenium NQR experiments have been performed upon KReO$_4$ and establish the following EFG tensor parameters near room temperature: $|\mathbf{Q}(^{185}\text{Re})| = 188.68$ MHz; $|\mathbf{Q}(^{187}\text{Re})| = 178.76$ MHz; and $\eta_Q < 0.02$.120 The present $^{185/187}$Re NQR measurements confirm these findings (Fig. S2, ESI† and Table 1), with the slight discrepancy between the two datasets being attributed to differences in the respective measurement temperatures. After precisely measuring the $^{185/187}$Re EFG tensor parameters, rhenium SSNMR experiments were performed at $B_0 = 11.75$ and 21.1 T (Fig. 2) to establish the isotropic rhenium chemical shift value for this compound, and to comment upon the presence of any rhenium CSA effects (something which has never been measured for $^{185/187}$Re using a powdered sample). The $^{185/187}$Re CT SSNMR spectra at both 11.75 and 21.1 T are modeled using QUEST exact QI simulation software90 with the EFG tensor parameters in Table 1, and $\delta_{\text{iso}} = 0(50)$ ppm.

While there is little evidence of HOQIE in the $^{185/187}$Re SSNMR spectrum acquired at 21.1 T, a striking observation is made at the lower applied field (i.e., $B_0 = 11.75$ T) if one includes SSNMR observations of one of the STs. Typically, for cases where the $\eta_Q$ value is nearly zero, it is well known that the CT discontinuities are of significantly higher intensity than the individual ST discontinuities. Hence, it was rather surprising to find that the discontinuities associated with the low-frequency $m_I = \pm 2 \leftrightarrow \pm 3/2$ STs were of comparable intensity to the CT discontinuities at 11.75 T. At 21.1 T, partial observation of the same ST discontinuities led to the expected result (i.e., much lower relative intensity for the ST) and hence is not discussed further. Due to this effect only being present at the lower applied field, it can be reasonably stated to be due to HOQIE. This observation is verified by QUEST simulations, and validates earlier literature predictions.68 Hence, while it is often assumed to be impractical to measure the STs for half-integer quadrupolar nuclei, in the case of a sufficiently strong QI, the critical discontinuities from the STs possess very similar intensity as the more commonly-measured CT discontinuities. With more discontinuities available for line shape fitting, it is expected that the accuracy of the extracted EFG tensor parameters could be increased. We emphasize that this finding is not limited to the $^{185/187}$Re nuclides, but would apply to any half-integer quadrupolar nucleus experiencing a strong QI (e.g., $^{35/37}$Cl, $^{69/71}$Ga, $^{73}$Ge, $^{79/81}$Br, $^{91}$Zr, $^{127}$I, etc.).

It is also noted that the above-mentioned ST discontinuities in this rather strong QI region are exceptionally sensitive to even small deviations in the $\eta_Q$ value from zero (Fig. 3). This allowed for a very precise determination of $\eta_Q(^{185/187}$Re) for KReO$_4$ (i.e., $\eta_Q < 0.003$). It is also established that SSNMR observations allow for the $\eta_Q$ value to be determined even more precisely than if only $^{185/187}$Re NQR experimental data were used (assuming a powdered sample): when using only the $^{185/187}$Re NQR data for KReO$_4$, the $\eta_Q$ value can only be constrained to $<0.02$. Proper line shape modeling of the $^{185/187}$Re ST SSNMR spectrum for KReO$_4$ under these conditions thus offers nearly an order of magnitude gain in the measurement precision for $\eta_Q$ relative to analogous NQR measurements. As the $\eta_Q$ value can offer insight into the local nuclear site symmetry,121 methods by which one can precisely measure...
its value are of interest in any area of chemical science where solid state structures are of importance.

iii. AgReO₄: the role of cation identity in determining rhenium chemical shifts.

Unsurprisingly, silver perrhenate possesses a very similar local rhenium environment compared to the other systems containing the ReO₄⁻/Co group. Prior NQR measurements at 296 K established the following QI parameters: $|C_{Q}(^{185}\text{Re})| = 265.1$ MHz; $|C_{Q}(^{187}\text{Re})| = 250.9$ MHz; and $Z_{Q} = 0.027$.¹²² This material was chosen for study to see if there was a measurable difference in the rhenium chemical shift values resulting from a change in the cationic species. While a definitive difference between the rhenium chemical shifts of NaReO₄ and KReO₄ could not be established (the former was measured in ref. 67), a silver ion might be expected to meaningfully change the SSNMR observables, as Ag⁺ is significantly more polarizable than the alkali metal ions studied earlier. Precise measurements of the $|C_{Q}(^{185/187}\text{Re})|$ and $\eta_{Q}$ values using NQR experiments (ESI† Fig. S3) largely confirm earlier NQR accounts (again after taking into consideration the slight changes in the EFG as a result of the differences in temperature between the present account and those in the literature). With the EFG tensor information established,¹⁸⁵/¹⁸⁷Re SSNMR experiments at $B_0 = 21.1$ T were used to additionally establish the isotropic rhenium chemical shift value for this compound, and we find that $\Delta_{\text{iso}}(^{185/187}\text{Re}) = 175(50)$ ppm (Fig. 4). This small positive chemical shift is in contrast with the chemical shifts which have been measured previously for NH₄ReO₄, NaReO₄, and KReO₄, all of which are indistinguishable from 0 ppm.⁶⁷ While subtle, the accuracy of this measurement is supported by several points. First, the rhenium EFG tensor parameters for AgReO₄ are known very precisely through NQR measurements and second, in the NMR regime we have employed simulation software which includes the effects of the QI exactly (as compared to perturbation theory approaches). In addition, although we have attempted to include rhenium CSA in our line shape modeling for all the perrhenates we have studied to date, we have yet to see any striking evidence of its presence in the high-symmetry ReO₄⁻ group.

The measured shift is consistent with what one would predict when replacing a given Na⁺/K⁺ counter-ion with a more polarizable Ag⁺ counter-ion. Following the model of magnetic shielding of nuclei outlined by Ramsey,¹²³–¹²⁵ and assuming that any differences in the relativistic portion of the magnetic shielding interaction as one goes from (Na/K)ReO₄ to AgReO₄ are small (as might be expected since the Fermi contact mechanism from the cationic species at the Re should be suppressed), it can be qualitatively understood that there exists an increased opportunity for ion–ion overlap in the latter case. As ion–ion overlap would be expected to lead to increased paramagnetic shielding contributions to the magnetic shielding tensor,¹²⁶,¹²⁷ and as the paramagnetic shielding mechanism nearly always leads to decreased shielding (and hence a corresponding
increase in $\delta_{\text{iso}}$, it appears that the observed differences in the chemical shifts between (Na/K)ReO$_3$ and AgReO$_4$ are consistent with the Ramsey model. In addition, GIPAW DFT quantum chemical calculations are complementary as they predict decreased magnetic shielding at the rhenium nucleus in AgReO$_4$ relative to (Na/K)ReO$_3$ (vide infra). We believe that this represents the first measurement of a rhenium chemical shift in the solid state within a set of rhenium(vi) compounds, although limited information exists from solution NMR.\textsuperscript{128}

iv. Ca(ReO$_4$)$_2$·2H$_2$O: deconvolution of multiple sites in complex $^{185/187}$Re SSNMR spectra. Calcium perrenate dihydrate presents additional aspects which should be important in future $^{185/187}$Re SSNMR studies of rhenium-containing materials. To begin, unlike the perrenate systems above, it does not pack in the $I4_1/a$ space group, and it possesses two unique local rhenium environments. As well, it should be interesting to probe the effect that hydration has upon the rhenium SSNMR parameters, something which to the best of our knowledge has not been discussed previously. Prior NQR measurements have been performed on Ca(ReO$_4$)$_2$·2H$_2$O, but they were carried out at liquid nitrogen temperatures and hence room temperature EFG tensor data do not exist for this compound.\textsuperscript{129}

The $^{185/187}$Re SSNMR spectrum that was recorded at $B_0 = 21.1$ T is complex, possessing many discontinuities and interesting spectral features (Fig. 5). This may be expected, since the $^{185}$Re and $^{187}$Re NMR signals are overlapping in the spectrum, and in addition there are two crystallographically distinct Re environments.

When taken together this would mean that the complex line shape measured by SSNMR is actually composed of four overlapped powder patterns. Attempts to fit the SSNMR data using the EFG tensor parameters measured earlier with NQR at $T = 77$ K were not fruitful, and it became clear that there was significant variation in the rhenium EFG tensor parameters between $T = 77$ K and room temperature (potentially due to the onset of H$_2$O dynamics in addition to the usual changes in lattice parameters). As such, $^{185/187}$Re NQR data were measured at room temperature for Ca(ReO$_4$)$_2$·2H$_2$O (Fig. S4 and S5, ESI?). All eight of the expected (i.e., allowed single-quantum) NQR signals were observed; however, unless additional information is known beforehand (e.g., that $\eta_0 = 0$), it is not always possible to unambiguously determine the EFG tensor parameters for multiple-site systems when $I = 5/2$ and making use of these single-quantum NQR transitions. If it is known a priori that $\eta_0 \neq 0$, one could venture into overtone NQR measurements to arrive at unambiguous EFG tensor parameters for each site, but such experiments are exceedingly insensitive or otherwise time consuming.\textsuperscript{90,130–133} Although the solution space is not extensive, to rapidly establish the set of $^{185/187}$Re EFG tensor parameters for Ca(ReO$_4$)$_2$·2H$_2$O, we undertook the intuitive, although novel, approach for a system with multiple sites,\textsuperscript{134} which simultaneously fits all the SSNMR/NQR data. In essence, the NQR data were used to begin the process with several ‘test’ solutions as to what the expected $^{185/187}$Re SSNMR spectrum would look like under the assumption that the NQR data had been assigned correctly. Predictably, all trial solutions except one yielded SSNMR spectra which did not match the experimentally observed spectrum even remotely. Only one assignment of the NQR data (Table 1) produced a simulated (via QUEST) $^{185/187}$Re SSNMR spectrum at $B_0 = 21.1$ T that was in modest agreement with the experimental spectrum. At this point, a further iterative fitting process was carried out on the NMR data alone, which allowed us to establish a final solution for both the EFG tensor parameters, as well as the isotropic chemical shifts for the two rhenium sites in Ca(ReO$_4$)$_2$·2H$_2$O. We believe that this process holds sufficient promise to analyze any multiple-site SSNMR spectrum where the QI is sufficiently strong (e.g., $^{79/81}$Br, $^{127}$I, $^{209}$Bi, etc.).

The measured isotropic chemical shift values for Ca(ReO$_4$)$_2$·2H$_2$O are rather shielded ($\delta_{\text{iso}} = -150$ (75) and $-225$ (75) ppm for the two sites) relative to the other perrenate systems studied earlier, which typically had chemical shifts equal to or greater than 0 ppm. Although we are cautious to not over-interpret this data, it is highly interesting that the direction of the shift is diamagnetic, which is analogous to that which has been observed before in the halogen SSNMR spectra of numerous halide-containing systems.\textsuperscript{135} The rationale behind this trend in the chemical shifts was noted earlier as being due to decreasing ion–ion overlap (i.e., exactly the opposite effect observed for AgReO$_4$) as a result of the water molecules being incorporated into the lattice structure of the compound. Analogous $^{43}$Ca SSNMR measurements were performed for Ca(ReO$_4$)$_2$·2H$_2$O (Fig. 5, inset). We briefly note that the measured $\delta_{\text{iso}}$($^{43}$Ca) value of $-32.6(0.4)$ ppm is shielded when compared against the
This study, 185/187Re NQR measurements have been performed also possesses a Re–Re bond. As with most of the compounds in this discussion, a Re(0) compound was chosen, which interestingly we performed 185/187Re overtone NQR measurements (Fig. 6e).† 0.642(0.02), (see Fig. S6 in the ESI, C142.06(0.06) MHz, |Z| 134.46(0.06) MHz, and ηQ = 0.642(0.02), (see Fig. S6 in the ESI,† and Table 1). In addition, we performed 185/187Re overtone NQR measurements (Fig. 6e). Briefly, for I = 5/2, these experiments involve observing the strictly forbidden ±1/2 ↔ ±5/2 NQR transitions that become weakly allowed when ηQ ≠ 0.143,144 Hence, while overtone NQR experiments are very insensitive relative to standard NQR experiments using the allowed single quantum transitions, this data enabled us to decrease the uncertainty in the measurements of |C_Q(185/187Re)| (from ±0.06 MHz to ±0.04 MHz) and ηQ (±0.002 to ±0.0008). The enhanced precision will become relevant in our attempts to measure rhenium CSA for this compound (vide infra).

Rhenium-185/187 SSNMR data have been acquired at B_0 = 21.1 T and modeled with exact theory using the EFG tensor parameters arrived at from the NQR measurements (Fig. 6f–h). To begin, the best-fit exact QI simulation requires the inclusion of a substantially negative chemical shift value, leading to the very low observed δiso value of −4400(75) ppm. Our finding is somewhat in accord with the ambitious (but relatively imprecise) work of Sheline and co-workers over 40 years ago using a single crystal of Re_{2}(CO)_{10}.82 The presently observed rhenium δiso value is also over 1400 ppm more shielded than that of ReO_{3}, where rhenium is in the +6 oxidation state (keeping in mind that for ReO_{3} there is necessarily a non-zero Knight shift term). Even if we consider only the Re(VII) and Re(0) compounds, there appears to be a relationship between the rhenium isotropic chemical shift value and the oxidation state of the Re atom. Initial line shape models which included only the EFG tensor and isotropic chemical shift parameters, while in good agreement with the experimental spectrum, did not yield a calculated 185/187Re SSNMR spectrum that exactly matched the experimental observations (Fig. 87, ESI†). Inclusion of a modest amount of rhenium CSA (Ω = 150(75) ppm; χ < −0.5) improved the agreement for essentially all the observed spectral features. Although subtle, this represents the first measurement of rhenium CSA in a powdered sample to the best of our knowledge. Earlier single crystal NMR work from Sheline and co-workers indicated a rhenium Ω value of ca. 300–500 ppm,82 but these measurements were somewhat imprecise and clearly inconsistent.

Fig. 6 Numerical QUEST simulations (a–d, and green trace in (e)), and experimental Hahn echo 187Re (e) overtone |m_i = ±1/2 ↔ ±5/2> NQR spectrum of powdered Re_{2}(CO)_{10} acquired at T = 291.8(2) K. Best fit simulation to the experimental data (e) yields |C_Q(187Re)| and ηQ values that are within experimental error of the expected positions from single-quantum NQR. The traces in (a, b) highlight the effect of small variations in the C_Q value (with ηQ = 0.6425), while the traces in (c, d) highlight the effect of small variations in the ηQ value (with |C_Q| = 134.46 MHz). Likewise, numerical QUEST simulation (f) and experimental static 185/187Re VOCS Solomon echo SSNMR spectrum (g) of Re_{2}(CO)_{10} at B_0 = 211.1 T and T = 291.8 K. In (h), a deconvolution of the two contributing signals to the total observed powder pattern in (f) is provided: the red trace corresponds to the 187Re signal, while the purple trace is due to the 185Re signal.
with our present data (in Fig. S8, ESI† we include a QUEST simulation using their NMR tensor parameters). We note that \( \Omega = 150 \) ppm is consistent with GIPAW DFT computations. Finally, we note that the best agreement was found when including \( \beta = 70(20) ^\circ \). This infers that the magnetic shielding and EFG tensor frames are non-coincident. To arrive at this value, we tracked one of the ‘horn’ discontinuities (as shown before for \(^{79/81}\text{Br} \) SSNMR of \( \text{CaBr}_2 \)),\(^{345} \) which is particularly sensitive to \( \beta \) variation. While \( \text{Re}_2(\text{CO})_{10} \) should be isostructural with \( \text{Mn}_2(\text{CO})_{10} \), when attempting to fit the rhenium data using analogous parameters from \( \text{Mn}_2(\text{CO})_{10} \) (i.e., \( \kappa = 0.95; \alpha = \beta = 90^\circ ; \gamma = 0^\circ \) with the \( \Omega \) parameter variable)\(^{146} \) we observed slightly worse agreement relative to the parameters denoted earlier.

2. Quantum chemical calculations of rhenium EFG and magnetic shielding tensors

i. General trends. Although relativistic effects play a role in determining the magnetic shielding and, to a lesser extent, the EFG tensor parameters probed by \(^{185/187}\text{Re} \) SSNMR, we note that qualitative successes of non-relativistic GIPAW DFT calculations of NMR parameters of nuclei as heavy as \(^{209}\text{Bi} \) have appeared in the literature.\(^{147} \) We do not expect exact agreement between the calculated and experimental rhenium NMR tensor parameters, but were interested to see if we could arrive at qualitative conclusions using GIPAW DFT by relating the calculated parameter values to structural features. The primary advantage of using this computational method, relative to molecular quantum chemistry approaches, is the inclusion of the translational symmetry that is present in the vast majority of crystal structures. Calculations were performed on all systems considered above in the present study (with the exception of \( \text{ReO}_3 \) which is not insulating), as well as \( \text{NH}_4\text{ReO}_4, \text{NaReO}_4, \text{and RbReO}_4 \), for which high-quality \(^{185/187}\text{Re} \) SSNMR and/or NQR data exist.\(^{56,67,148} \)

For the perrenates, using crystal structures from the literature and without performing any geometry optimizations leads to calculated \( |C_Q(187\text{Re})| \) values which are in very good agreement in some cases (e.g., \( \text{NaReO}_4, \text{KReO}_4, \text{and AgReO}_4 \) in fair agreement in others (\( \text{RbReO}_4 \)), but sometimes also in relatively poor agreement (\( \text{Ca(ReO}_4)_2 \)2H\(_2\)O and \( \text{NH}_4\text{ReO}_4 \)) (Table 2 and Fig. 7). With this in mind, a partial geometry optimization (H and O atoms) of \( \text{Ca(ReO}_4)_2 \)2H\(_2\)O leads to \( |C_Q(187\text{Re})| \) values which are in fair agreement with experiment. We note in passing that two crystal structures have been presented for \( \text{Ca(ReO}_4)_2 \)2H\(_2\)O which appear at first glance to be dissimilar despite being derived from the same diffraction data (heavy atom rmsd = 0.164 Å).\(^{149-152} \) However, we note that after performing a quantum chemical geometry optimization of the H and O atoms, the structures were nearly identical (all atom atomic rmsd = 0.012 Å). The enhanced structural agreement between this pair of geometry optimized structures is reflected in the increased similarity of the associated rhenium NMR tensor parameters with one another (Table 2). Likewise, when compared to the experimental \(^{40}\text{Ca} \) SSNMR EFG tensor and \( \delta_{iso} \) values, the (GI)PAW DFT calculated \(^{40}\text{Ca} \) SSNMR parameters for each of the original structures do not compare overly well (Table S5, ESI†).

However, very good agreement between experiment and calculation is realized after optimizing the O and H positions.

Returning to our earlier discussion, while the lack of quantitative agreement is not surprising, it is unexpected that use of the same structural building block (i.e., the \( \text{Re}_4 \) group) could lead to such disparity when comparing the agreement between experiment and calculation across all perrenate systems considered above. One might be tempted to state that dynamic processes which partially average the rhenium EFG tensor magnitudes in \( \text{Ca(ReO}_4)_2 \)2H\(_2\)O and \( \text{NH}_4\text{ReO}_4 \) are responsible for the disparity, but we will subsequently outline that this contribution is secondary relative to tetrahedral distortions of the perrenate group. When required by symmetry, it is seen that the experimentally observed \( \eta_0 \) values are reproduced by PAW DFT calculations: all of the \( \text{AReO}_4 \) systems which belong to the Scheelite class (\( A = \text{Na, K, } \text{Rb, NH}_4, \text{Ag} \)) are calculated to have \( \eta_0 = 0 \), in agreement with experiment. Calculated rhenium \( \delta_{iso} \) values are consistent with the observed chemical shift difference of ca. 4400 ppm between the \( \text{Re}(\text{vs}) \) and \( \text{Re}(0) \) systems (Fig. S9, ESI†); however, due to the errors associated with both the experimental measurements and computational limitations (as outlined above), the calculations are not reliable for distinguishing between members of the perrenate group. As shown below, very slight structural changes (order of 0.01 Å) lead to very large changes in calculated \( \delta_{iso} \) values. This is important to note, as structural displacements of this sort would be very near to the precision of the reported diffraction crystal structures.

ii. Impact of average Re–O bond distance and shear strain on rhenium NMR parameters in perrenates. To understand the somewhat erratic behavior of the calculated rhenium EFG tensor values based on similar input structures for the \( \text{Re}_4 \) systems, we sought to establish the sensitivities of the \( |C_Q(187\text{Re})| \),
δiso (via σiso), and Ω parameters to slight changes in the ReO₄⁻ group geometry. We chose KReO₄ to represent the other AReO₄ systems (i.e., A = Na, Rb, Ag, NH₄) as its structure is known from relatively recent neutron powder diffraction results.⁵¹,⁵⁵ Changes in the perrenate anion geometry were effected by modifying the average Re–O bond distances and O–Re–O bond angles about their accepted values. To begin, we note that exceptionally slight alterations in the average Re–O distance on the order of 0.01 Å produced dramatically different calculated values, especially for the value of σiso, which changes by ca. 120 ppm per 0.01 Å (Fig. 8a). While the calculated changes in the CQ values are modest relative to the chemical shift changes, it would be expected that they could serve as useful restraints for NMR crystallography approaches where structural refinements were carried out (Fig. 8b). We will return to this aspect of NMR crystallography using the rhenium NMR tensor parameters in subsequent discussions. It is also calculated that the rhenium Ω value would be relatively insensitive to changes in the average Re–O distance (Fig. S10, ESI†).

Deviations of the O–Re–O bond angles from their Platonic solid values are nicely parameterized using the shear parameter, |ψ|.⁵⁴,⁵⁵ In contrast to the moderate augmentations in |CQ(¹⁸⁷Re)| with variations in the Re–O internuclear distance, when modifying |ψ| about the accepted crystal structure value for KReO₄, we find that |CQ(¹⁸⁷Re)| is very sensitive to |ψ| (Fig. 8c). Altering |ψ| while retaining the unit cell parameters and rhenium site symmetry necessarily introduces a slight change in the average Re–O bond distances (+0.011 to −0.007 Å over the entire data range presented in Fig. 8c). Fortunately, as shown in Fig. 8b and noted above, the ¹⁸⁷Re CQ value is not particularly sensitive to Re–O variations in this range and hence much of the CQ variation comes from the alterations in the O–Re–O bond angles. While perhaps it is not surprising that the calculated |CQ(¹⁸⁷Re)| reaches a minimum absolute value when |ψ| reaches 0 (as K⁺ ions are present at other lattice sites, |CQ(¹⁸⁷Re)| should not be exactly 0), what is striking is the drastic sensitivity of the |CQ(¹⁸⁷Re)| parameter to slight changes in |ψ|. Over the range of values reported in Fig. 8c, it is important

![Fig. 8](image-url)
to note that the unique oxygen position has only been changed by ca. 0.03 Å (+0.01 to −0.02 Å) from the accepted value, but the calculated \(^{187}\text{Re}\) \(Q\) value changes by a full order of magnitude. We also find some sensitivity in the rhenium \(\Omega\) value over this range (Fig. 8d), but realize that its measurement would be very challenging and hence would not envisage this parameter to be overly useful in structural refinement endeavors. However, due to the relationship between \(|C_{Q(187\text{Re})}|\) and \(|\psi|\), coupled with the high precision that the EFG tensor can be measured for rhenium, \(|C_{Q(187\text{Re})}|\) could be used to refine chemical structures determined by diffraction measurements (vide infra).

iii. Refinement of the oxygen position in \(\text{NH}_4\text{ReO}_4\). Recall that for the majority of the AReO\(_4\) group members in the present study (A = Na, K, Rb, Ag), we found fair to good agreement between the calculated and experimental \(^{185/187}\text{Re}\) EFG tensor parameters. However, using the most recent neutron diffraction structure\(^{152}\) of ND\(_4\)ReO\(_4\) leads to calculated \(|C_{Q(187\text{Re})}|\) values that were too high by a factor of about 2 (ranging from 188 to 228 MHz) relative to experiment (110.62 MHz).\(^{67}\) While the topic of ammonium dynamics and its influence on both the lattice\(^{156}\) and the \(^{185/187}\text{Re}\) EFG parameters is well documented for both \(\text{NH}_4\text{ReO}_4\) and ND\(_4\)ReO\(_4\), the reported rhenium NQR signals as functions of temperature\(^{159-162}\) make it clear that this alone cannot reconcile our presently calculated EFG tensor values with those measured by NMR. Likewise, effects due to deuteration (i.e., going from NH\(_4\)ReO\(_4\) to ND\(_4\)ReO\(_4\)) upon the \(|C_{Q(185/187\text{Re})}|\) values have been shown to be very minor (ca. 1.3% at 297 K).\(^{163}\) In light of the profound sensitivity of the \(|C_{Q(187\text{Re})}|\) value to small distortions in the ReO\(_4^-\) tetrahedron (captured above in \(|\psi|\)), it is relevant to note the small but significant variation in the reported O-Re-O angle as a function of temperature for ND\(_4\)ReO\(_4\) (from 110.0(1)° to 110.9(1)°)\(^{152,164}\) would be expected to yield dramatic (i.e., order of magnitude) changes in \(|C_{Q(187\text{Re})}|\) rather than the modest (ca. 10–20% over the temperature range from 100 to 400 K) and continuous changes that are actually observed via NQR. Importantly, recent crystal structure accounts that used the same room temperature neutron diffraction data, and arrive at essentially the same agreement for the model fits to the data (i.e., reported \(R_{wp}\) values were 5.73% and 5.97%), yield O-Re-O angles of 110.1(2)° and 110.8(2)°.\(^{152,164}\) Clearly, there is somewhat greater uncertainty in this parameter than the diffraction-based models would lead one to believe. Recent literature reports have also found that \(R\) values from powder diffraction methods above 5% are correlated with parameter uncertainties that are larger than would be expected.\(^{165}\) Hence, while there is not a large variation between structures, the \(|C_{Q(185/187\text{Re})}|\) values, in tandem with GIPAW DFT calculations, could be used to refine the earlier structural models.

Using an adapted version of a procedure recently outlined by some of us,\(^{166}\) we allowed the oxygen atom coordinates to vary with the calculated \(|C_{Q(187\text{Re})}|\) value being the convergence parameter (Fig. 9). As a condition of the refinement, we did not allow the oxygen atom position to stray beyond the range of locations defined by the prior structure determinations using neutron diffraction data.\(^{152,164}\) As the GIPAW DFT calculations did not include relativistic effects, strict convergence criteria were not applied (i.e., once the calculated \(|C_{Q}|\) value was within 10% of the experimental value, we considered the system well-converged for the present purposes). The main goal of this endeavor was to see if it was possible to arrive at an alternate set of oxygen coordinates which simultaneously satisfy the diffraction results and reproduce the experimental \(|C_{Q(187\text{Re})}|\). Due to the sensitivity of the rhenium EFG tensor to small perturbations in the oxygen position, convergence was rapidly achieved (after three refinement steps), and all conditions outlined above were satisfied. The refined oxygen coordinates are given in the ESI,\(^{†}\) Table S6, and we note that although the position of the oxygen atom only changed by 0.007 Å, the calculated \(|C_{Q(187\text{Re})}|\) was reduced from 188 to 116 MHz. Additionally, we note that the DFT calculated system energy is lower for the presently refined structure (ESI,\(^{†}\) Table S3), relative to any of the diffraction structures, even though we did not include the system energy as a restraint in the refinement. This finding again highlights the complementary nature of diffraction, quantum chemistry, and SSNMR experiments in structure determination and refinement.

iv. Re\(_2(\text{CO})_{10}\) influence of Re–Re bond distance and modeling Re–Re interactions. As noted earlier, the presence of a Re–Re single bond in Re\(_2(\text{CO})_{10}\) allows for us to potentially comment on the influence of metal–metal interactions upon the rhenium NMR tensor parameters. Of course, probing metal–metal bonding via SSNMR, while not commonplace, is not unknown,\(^{167,168}\) but to our knowledge this is the first time such an interaction has been probed by \(^{185/187}\text{Re}\) NMR methods on a powdered sample. To begin, we note that while the GIPAW DFT calculations were able to roughly reproduce the experimental chemical shift of Re\(_2(\text{CO})_{10}\), the calculated \(|C_{Q(187\text{Re})}|\) value of 695.0 MHz is in such spectacular error when compared to the experimental measurements (\(|C_{Q(187\text{Re})}| = 134.46\) MHz) that we
thought additional discussion was warranted. As with the perrhenate species, to gain further insight we considered small structural changes about the accepted crystal structure values.\textsuperscript{169} One of the most obvious parameters to change would be the Re–Re bond distance. Indeed, while we find the calculated \( |C_Q(187\text{Re})| \) value to be sensitive to the Re–Re distance (Fig. 10), this alone does not account for the majority of the difference between the calculated and experimental values. In addition, due to most of the electron density in Re\(_2\)(CO)\(_{10}\) being associated with the Re atoms, the Re–Re distance is expected to be precisely known, while the oxygen and carbon positions perhaps are known less precisely. This is borne out by observing the reported estimated standard deviations for the O and C atoms, which are typically about 50 times larger than for the rhenium position.\textsuperscript{169} The positions of the lighter atoms in Re\(_2\)(CO)\(_{10}\) have also been noted in other studies as possessing “irregularities of an obviously random nature”.\textsuperscript{170} As such, we carried out PAW DFT geometry optimizations of the C and O atoms in Re\(_2\)(CO)\(_{10}\) while holding the Re positions fixed to their experimentally determined values. However, the agreement between experiment and calculation is not greatly enhanced (i.e., the calculated \( |C_Q(187\text{Re})| \) value is reduced only from 695.0 MHz to 651.5 MHz).

As an additional test to determine the source of the discrepancy between the experimental and calculated \( |C_Q(187\text{Re})| \) values for Re\(_2\)(CO)\(_{10}\), we carried out relativistic molecular DFT calculations using several XC functionals which are known to perform reasonably well at describing the geometries and singlet–triplet energy gaps for systems which exhibit single metal–metal bonds.\textsuperscript{172} By using this particular computational approach the translational symmetry of the crystal structure is lost, but as the intramolecular contributions to the EFG tensor are lost, we do not expect this simplification to create any critical errors in understanding or interpreting the results. Unfortunately, while the calculated results using the molecular model (Table S7, ESI) within the relativistic framework are such that the calculated \( |C_Q(187\text{Re})| \) values are significantly reduced (Table S8, ESI), it is not to the extent that the agreement between calculation and experiment could be considered anything other than poor. Even the use of large quadrupole–\( \zeta \) valence basis sets, the inclusion of spin–orbit effects, and using XC functionals beyond the GGA (i.e., meta-GGA and hybrid-GGA) did not dramatically improve the calculated rhenium EFG tensor. It is therefore clear that many commonly used DFT approaches are unable to reproduce the \( |C_Q(187\text{Re})| \) value for Re\(_2\)(CO)\(_{10}\). This very well may be due to the presence of a metal–metal bond and inherent difficulties that modern DFT methods have when dealing with this feature, but we postulate again that this may also come from small deficiencies in the reported crystal structure. As the crystal structure of Re\(_2\)(CO)\(_{10}\) has too many adjustable parameters to justify a refinement using only three NMR parameters (\( C_Q, \eta_Q \), and \( \delta_w \)), we do not attempt a refinement at present but note that reconciling this discrepancy will be of ongoing interest.

**Conclusions**

The combination of both standard as well as high-field (\( B_0 = 21.1\) T) solid-state NMR experiments with gauge-including projector augmented-wave (GIPAW) DFT calculations on a variety of rhenium-containing systems highlights the information that may be garnered by using the \( ^{185}\text{Re} \) and \( ^{187}\text{Re} \) nuclei as probes. As the \( ^{185/187}\text{Re} \) NMR signals of dilute ReO\(_4\) solutions are relatively weak, we suggest that solid ReO\(_3\) may be used as a secondary chemical shift standard since it presents narrow, stable, and strong solid-state rhenium NMR signals.

By performing experiments on KReO\(_4\) at both high and standard applied fields, we have been able to ‘tune’ the high-order quadrupole-induced effects in such a manner that they can yield EFG tensor information to unprecedented levels of precision using powdered samples. This finding is of course not limited to \(^{185/187}\text{Re} \) nuclei, and can be applied whenever the quadrupolar interaction is sufficiently large. Assuming a powdered sample, the measured error in the \( \eta_Q \) value for KReO\(_4\) (using one of the satellite transitions) is nearly one order of magnitude smaller than competing methods such as central-transition SSNMR and nuclear quadrupole resonance (NQR). Samples of AgReO\(_4\) and Ca(ReO\(_4\))\(_2\)-2H\(_2\)O have allowed us to measure for the first time chemical shift effects between Re(\( \text{VI} \)) species in the solid state. Additionally, we have shown that NQR and SSNMR experiments may yield spectra that can be fit simultaneously to accurately measure rhenium EFG and chemical shift information for the very spectrally dense Ca(ReO\(_4\))\(_2\)-2H\(_2\)O system (8 single-quantum NQR signals and 4 overlapping powder patterns in the solid-state \( ^{185/187}\text{Re} \) NMR spectrum). Rhenium-185/187 SSNMR, and in particular over-tone \( ^{185/187}\text{Re} \) NQR experiments, on Re\(_2\)(CO)\(_{10}\) allow us to measure rhenium chemical shift anisotropy for the first time.
using a powdered sample (and to greater precision than earlier studies using a single crystal sample).

GIPAW DFT calculations, despite not including relativistic effects, were found to reasonably reproduce many of the solid-state NMR observables, such as $\delta_{iso}$ [C$_{iso}$(Re)]] and $\eta_0$. In the perenhydrine systems, the extreme sensitivity of the [C$_{iso}$(Re)] value to the tetrahedral shear strain parameter, $|\psi|$, has allowed us to refine the structure of NH$_4$ReO$_4$ so that it not only agrees well with the diffraction crystal structures established earlier, but also so that the rhenum EFG tensor parameters are well reproduced. Importantly, we find that the [C$_{iso}$(Re)] parameter was much more sensitive to the refinement process than the diffraction metrics. Lastly, we have found that the EFG tensor parameters for Re$_2$(CO)$_{10}$ cannot be reproduced using several common DFT methods. This finding is not fully unexpected, as DFT sometimes struggles when calculating properties of systems containing d orbitals which are involved in metal-metal bonds.$^{172}$ Hence, the Re$_2$(CO)$_{10}$ system may provide experimental observables which can be used in future DFT calibration and benchmarking tests.

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