Heteronuclear Recoupling in Solid-State Magic-Angle-Spinning NMR via Overtone Irradiation

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Abstract: A heteronuclear dipolar recoupling scheme applicable to I−S spin pairs undergoing magic-angle-spinning (MAS) is introduced, based on the overtone irradiation of one of the coupled nuclei. It is shown that when I is a quadrupole, for instance 14N, irradiating this spin at a multiple of its Larmor frequency prevents the formation of MAS dipolar echoes. The ensuing S-spin signal dephasing is significant and dependent on a number of parameters, including the I−S dipolar coupling, the magnitude of I’s quadrupolar coupling, and the relative orientations between these two coupling tensors. When applied to a spin-1 nucleus, this overtone recoupling method differs from hitherto proposed recoupling strategies in that it involves only the |±1⟩ I states. Its dephasing efficiency becomes independent of first-order quadrupolar effects yet shows a high sensitivity to second-order offsets. A constant-time/variable-offset recoupling sequence thus provides a simple route to acquire, in an indirect fashion, 14N overtone spectra from rotating powders. The principles underlying this kind of S−14N experiments and different applications involving S = 13C, 59Co sites are presented.

1. Introduction

Dipole–dipole interactions between nuclear spins provide a valuable tool for probing molecular and macromolecular structures.1–3 When NMR experiments are carried out in the solid phase, such couplings can be directly measured and used to extract internuclear distances. Complications arise, however, upon attempting to determine these couplings while executing magic-angle-spinning (MAS). Throughout each rotor period, this procedure will average away all couplings that transform as second rank tensors, including the dipolar couplings. A solution to this problem is offered by double-resonance techniques.4–9 These protocols exploit the fact that dipolar Hamiltonians are given by products of spatial- and spin-dependent terms, to prevent the MAS averaging of the spatial couplings via synchronous radio frequency (rf)-driven motions of the spins. For instance, when heteronuclear I−S pairs of spin-1/2 nuclei are involved, net dipolar evolutions can be imposed on an S signal by inverting the I eigenstates with rotor-synchronized π pulses (rotational-echo double-resonance, REDOR),4–10 through continuous nutations of the I states at integer multiples of the sample spinning speed \( \omega_s \) (rotary resonance recoupling, RR).11,12

Although they are of widespread use in the spectroscopy of biological, organic, and inorganic materials, the applicability of these recoupling strategies gets compromised when quadrupolar I ≥ 1 nuclei are involved. Challenges arise in these cases from the fact that the applied rf nutation fields have to compete with much larger internal coupling frequencies stemming from the quadrupole interaction. A typical example of these complications is furnished by 14N, a 99.6% abundant I = 1 nucleus. These spins are often subject to megahertz-sized quadrupole effects which can overwhelm the nutation effects introduced by the rf irradiation. Most of the manipulations proposed for the recoupling of spin-1/2 become in these cases unachievable, or at best subject to a very different spin physics. As a result of this, quadrupole-specific recoupling strategies had to be developed for interfering with the dipolar MAS modulation.16–20 One of the most widely applicable principles available for manipulating strongly coupled quadrupolar sites in a rotor-synchronized fashion is that relying on the transfer of populations via adiabatic...
passages.\textsuperscript{21} In these experiments, which possess no close analogue in the spin-1/2 realm, changes in the \(I\) states are implemented by a continuous rf irradiation that solely becomes effective when MAS nullifies the much larger first-order quadrupolar effects. As for all crystallites this happens only a few times per rotor period, the result is an effective interference with the modulation imposed by MAS on the spatial terms of the dipolar coupling, and a net re-introduction of the latter. These are the principles underlying the continuous transfer of populations by double-resonance (TRAPDOR) recoupling strategy,\textsuperscript{16–18} as well as the recoupling by adiabatic passage double-resonance (REAPDOR) technique.\textsuperscript{19,20,22}

The present study explores an alternative for recoupling strongly coupled quadrupoles under MAS, based on irradiating these nuclei at a multiple of their Larmor frequencies. For a spin-1 like \(^{14}N\), the main consequence of implementing such a recoupling is that it becomes independent of the first-order quadrupolar interaction. Indeed, overtone irradiation at twice the Larmor frequency excites solely the usually forbidden \(|+1\rangle \leftrightarrow |–1\rangle\) transition, affected only by second-order quadrupole effects.\textsuperscript{23–27} Although such transitions violate the usual high-field NMR selection rule, they become feasible when quadrupolar couplings \(\chi_Q\) are strong enough to substantially tilt the spins’ axes of quantization. The nutation rates that are then imposed on the spins by overtone irradiation fields \(\omega_1\) are in the order of \(\omega_1\chi_Q/\omega_0\). For \(^{14}N\) \(\chi_Q/\omega_0\approx 0.1\); consequently, conventional rf irradiation strengths will produce rotary nutations in the kilohertz range, capable of effectively interfering with MAS averaging at the usual spinning rates. As is further discussed below, the time dependence that MAS induces on the first-order quadrupole coupling also splits up the overtone nutation frequencies into a sideband spectrum spaced at multiples of \(\omega_0\), that further contributes to an efficient \(I\)-\(S\) dipolar recoupling regardless of the strength of \(\chi_Q\). Throughout this study we shall refer to these phenomena as overtone rotary recoupling (ORR); the following sections introduce the basic features of these new experiments, discuss their complementary nature vis-à-vis currently available recoupling techniques, and demonstrate their potentially widespread applicability not only for measuring \(^{14}N\)-\(S\) dipolar couplings but also as simple means to acquire \(^{14}N\) overtone spectra from rotating powders.

2. Principles of Overtone-Driven Recoupling

2.1. The Overtone Excitation. Although overtone recoupling could, in principle, be applied on a variety of strongly coupled quadrupolar species, we shall restrict this analysis to the simplest \(I = 1\) case, using \(^{14}N\) as an example. To describe the details of \(^{14}N\)-\(S\) overtone recoupling, it is necessary first to discuss the basic spin dynamics occurring during overtone irradiation. Therefore, although the focus of this work will eventually become a heteronuclear spin pair on which the \(S\)-spin signal is detected, we begin centered on an \(I = 1\) spin subject to a sizable quadrupole interaction as well as to an overtone rf field. As discussed elsewhere, understanding overtone nutation requires starting from the laboratory-frame Hamiltonian,\textsuperscript{23,26,28} which for such systems will be assumed given by

\[
H_{\text{lab}} = H'_Z + H'_Q + H_{\text{rf}}
\]

\[H'_Q = -\omega_0^r J_Z \text{is the } I\text{-Zeeman interaction, and following the notation given in refs 26 and 28, quadrupole and rf interactions are written as}
\]

\[
H'_Q = \chi_Q [\sqrt{6} T_{2q}^0 d + T_{2q}^1 f - T_{-2,1} f^* + T_{2,3g}^2 + T_{-2,-2g}^2]
\]

\[
H_{\text{rf}} = 2\omega_1 (I_x \sin \theta + I_y \cos \theta) \cos(\omega_{\text{rf}} t)
\]

\[H'_Q \text{ is here given in terms of products between the irreducible spin-space spherical components } \{T_{2,3g}, T_{-2,-2g}\} \text{, and the complex functions } \{a_f, g\} \text{ depending on the asymmetry parameter } \eta_Q \text{ and on Euler angles relating quadrupolar and Zeeman principal axes systems (PASS)}. \chi_Q \text{ represents the strength of the quadrupolar interaction, given in frequency units by the standard definition } \chi_Q = \frac{e^2 q Q}{4 |I(2I - 1)|} \text{. } H_{\text{rf}} \text{ in turn is defined by an amplitude } \omega_1 \text{, an angle of coil inclination } \theta \text{ with respect to } B_0 \text{, and an oscillation frequency } \omega_{\text{rf}} \text{ in the neighborhood of } 2\omega_0^r . \text{ To reproduce overtone phenomena it is necessary to consider, at least to first order, the corrections that } H'_Q \text{ will impose on the high-field Zeeman eigenstates. For } I = 1 \text{ this entails considering the tilting matrix } \text{that diagonalizes a quadrupole-perturbed Zeeman interaction to first order in } \epsilon = \chi_Q/\omega_0^r . \text{ The Hamiltonian in this tilted frame, } H_{\text{tilt}} = T^{-1} H_{\text{lab}} T \text{, is}
\]

\[
H_{\text{tilt}} = \begin{bmatrix}
\omega_{(1)}^q + \omega_{(2)}^q - \omega_0^q & 0 & \omega_1 e(f \cos \theta + g \sin \theta) \\
0 & -2\omega_{(1)}^q & 0 \\
\omega_1 e(f^* \cos \theta + g^* \sin \theta) & 0 & \omega_{(1)}^q - \omega_{(2)}^q + \omega_0^q
\end{bmatrix}
\]

\[\text{where } \omega_{(1)}^q = \chi_Q \text{ is the usual definition for the first-order quadrupolar coupling, and } \omega_{(2)}^q = \chi_Q^2 (|f|^2 + |g|^2)/\omega_0^r \text{ is the second-order quadrupolar coupling. Within this tilted-frame approximation, the overtone rf irradiation Hamiltonian will only connect } |\pm 1\rangle \text{ eigenstates, for which the first-order quadrupole coupling } \omega_{(1)}^q \text{ acts as a mere energy shift. This, together with the unperturbed state, } |0\rangle \text{, can thus be dropped altogether from the relevant Liouville space where spin evolution takes place. A usual rotating-frame transformation } R = \exp(i\omega_1 f t) \text{ then leads to the effective spin-1/2 overtone nutation Hamiltonian}
\]

\[
H_{\text{mutation}} = (R^{-1} H_{\text{tilt}} R + |+1\rangle |+1\rangle) = \begin{bmatrix}
\Delta + \omega_{(2)}^q & \epsilon \omega_1 (f \cos \theta + g \sin \theta) \\
\epsilon \omega_1 (f^* \cos \theta + g^* \sin \theta) & -\Delta - \omega_{(2)}^q
\end{bmatrix}
\]

\[\text{where for completion we have introduced the potential of}
\]


Figure 1. Comparisons between the overtone nutation of the \( I = |+1\rangle \) quantum state (\( \rho_{1,1} \) element of \( I \)'s density matrix) under static and MAS conditions, as a function of the offset \( \Delta \) and as a function of the overtone irradiation frequency \( \tau \).

The overtone irradiation frequency (or of accounting for a chemical shift) via the offset term \( \Delta = 2\omega_0^F - \omega_{\text{irr}} \).

Equation 6 is a \( 2 \times 2 \) Hamiltonian with time-independent coefficients, and hence it enables an analytical calculation of the populations’ behavior upon rf irradiation as a function of the nutation time \( \tau \). This can in turn be used to infer basic characteristics of a heteronuclear \( I-S \) recoupling experiment, whose dipolar evolution will eventually be dictated by the time dependence of the \( I \) eigenstates. The left-hand column in Figure 1 presents the time evolution of the \( |+1\rangle \) populations that can be expected from this static Hamiltonian, calculated for typical \( I \) offset terms \( \Delta \approx 1.95 \mu s \) time increment was assumed. Notice the evolution’s sensitivity to the offset irradiation conditions, as well as the marked \( \omega_0 \) modulation observed under MAS. For \( I = |-1\rangle \), the nutation behavior can be simply derived from \( \rho_{-1,-1}(\tau) = -\rho_{1,1}(\tau) \).

The \( I = |+1\rangle \) dynamics under the action of overtone irradiation can still be calculated albeit numerically, via the time-ordered propagation of the spins’ density matrix. Assuming an initial \( \rho_0 = I \) state, this time evolution will be given by \( \rho(t) = U \rho(t) U^\dagger \), where \( U = T \exp[-if(t)H_{\text{nutation}}(t') \, dt'] \) is the propagation operator. The time dependence of the \( f \) and \( g \) functions involved in \( \omega_0^F \) and \( H_{\text{nutation}} \) can in turn be derived with the aid of Wigner rotation matrixes, which we define in this case according to the time-dependent Euler transformations

\[
\Omega(t) = \Omega_{\text{LAB}}(t) = \Omega_{\text{LAB}}(0) + \int_0^t \Omega_{\text{ROT}}(t) \, dt
\]

where a collinear sample spinning/rf coil setup fixed at the magic angle was assumed. The explicit forms taken by the \( f(t) \) and \( g(t) \) functions following these transformations are given as Supporting Information.

With the aid of these functions, the relevant Hamiltonian can be written and its effects propagated as a function of the nutation pulse length. The right-hand side of Figure 1 shows the time evolution that can then be calculated for the \( |+1\rangle \) spin eigenstate of \( I \) as a function of the overtone MAS irradiation. Comparable in both static and spinning cases are the offset-dependencies exhibited by the nutation, which only show substantial departures from the equilibrium when \( \Delta \approx -\omega_0^F \). This is because the MAS rates being considered here are approximately an order of magnitude smaller than the average \( |\omega_0^F| \), and therefore fail to introduce substantial modulations into these longitudinal couplings. Different, however, are the actual nutation profiles exhibited by static and MAS cases for the range \( \Delta \approx -\omega_0^F \) of maximum spin excitation. For static cases, the nutation behavior is made up of a complex superposition of frequencies, whereas in the spinning case a well-defined \( \omega_0 \) modulation of the nutation emerges over the complete powder. This feature has important consequences for enhancing the efficiency of dipolar MAS recoupling, and its origin can be gathered from examining the matrix elements in eq 6. On compensating \( \omega_0^F \) with a suitable irradiation offset, this nutation Hamiltonian ends up exhibiting mainly transverse components proportional to \( \omega_0^F, \omega_0^g \). In the static case \( f, g \) adopt different values depending on a crystallite’s orientation, and the powder-averaged nutation plots thus display interfering \( \{\cos(\omega_0^F t), \cos(\omega_0^g t)\} \) oscillations. When undergoing MAS, however, the \( f \) and \( g \) functions themselves acquire \( \{\pm \omega_0, \pm 2\omega_0\} \) time dependencies. The resulting overtone spin nutation curves are then composed of terms of the type \( \{\cos(\omega_0^F \cos(\theta_0)), \cos(\omega_0^F \cos(\theta_0))\} \), representing Bessel series of base \( \omega_0^F \). In terms of their frequency spectra, these nutations will thus resemble sideband-like structures that contain substantial components oscillating at \( \omega_0 \) regardless of the magnitudes of \( |f|, |g| \), i.e., regardless of a crystallite’s orientation. Hence, the basic \( \omega_0 \) modulation and relatively high coherence are displayed by the MAS overtone nutation plots, even after considering their powder integration.

2.2. Overtone Rotary Recoupling of Heteronuclear Interactions. The significant frequency components that the MAS-driven overtone nutation \( |\pm 1\rangle \) of populations display in the neighborhood of \( \omega_0 \) will enable the efficient recoupling of \( ^{14}\text{N}-S \) dipolar couplings even under fast MAS. Indeed, these \( I \) nutations will alter the evolution of the \( S-^{14}\text{N} \) coupled pairs, preventing the MAS refocusing of their mutual dipolar couplings at the end of each rotor echo. The dephasing that will then affect the \( S \)-spin signal will depend on a variety of factors including the dipolar coupling, the spinning rate, the offset of overtone irradiation, and the magnitude of the overtone nutation rate \( \omega_0^F \).
The explicit expressions then resulting for $\Delta S/S_0$ curves computed under these assumptions for typical sets of coupling values upon systematically changing the $I-S$ dipolar coupling (A), the offset of overtone irradiation (B), the relative orientation between the $I$ quadrupolar and $I-S$ dipolar tensors (C), the sample spinning rate (D), and the strength of overtone irradiation (E). These curves evidence maximum dephasing fractions $\Delta S/S_0 \approx 0.67$ developing within $t \gamma_d r_0^{6.7}$ time scales, confirming the competitiveness of this form of recoupling. It is also clear that not only the magnitude but, to a lesser extent, also the relative orientation between dipolar and quadrupolar tensors will influence the decay. The conditions for optimal dephasing also vary slightly upon changing the combination of spinning and rf nutation frequencies, with stronger $\omega_C$ fields favoring dephasing at slightly larger $\omega_C$ rates. Because of the MAS-modulated nature of the overtone rotation, however, any given $\omega_C$ rate will result in an efficient dephasing over a range of applied rf field strengths: no special rotary resonance conditions have to be met for performing this kind of experiment.

One of the most interesting applications of overtone recoupling derives from the selectivity that the heteronuclear dephasing displays to the offset of rf irradiation. To illustrate this potential, Figure 4 focuses on directly bonded model $^{13}C-^{14}N$ spin pairs and shows the dephasing fractions that for a fixed period of dephasing can be expected from the $^{13}C$ as a function of the $^{14}N$ overtone irradiation offset. The close relation between the overtone recoupling offset dependence and ideal second-order quadrupole line shapes is evidenced by these simulations. It is also illustrative to contrast this behavior with the expectations arising from the conventional recoupling of $^{14}N$, based on irradiation fields centered at $\omega_0^{17,18}$. Toward this end, Figure 5 presents, again for model $^{13}C-^{14}N$ pairs, the dephasing profiles that can be expected from constant-time ORR and TRAPDOR experiments as a function of the $^{14}N$ irradiation offset. These plots evidence the resemblance that the $\Delta S/S_0$ fractions of these two techniques have to second- and first-order...
The quadrupole patterns, respectively. When comparing the 
Comparisons between the ideal 14 N powder line shapes
Figure 4.

Figure 3. ΔS/S₀ overtone dipolar-dephasing fractions predicted for typical 13 C−14 N sets of coupled spins upon systematically changing the I−S dipolar coupling (A), the offset of overtone irradiation (B), the relative orientation between I’s quadrupolar and the I−S dipolar tensors (C), the sample spinning rate (D), and the strength of overtone irradiation (E). Unless specifically mentioned, the parameters incorporated in these simulations are χ₀/2π = 0.75 MHz, η₀ = 0, dipolar coupling = 0.8 kHz, ω₀/2π = 3.5 kHz, ω₀/2π = 60 kHz, 0 ≤ ϵ ≤ 1. Overtones irradiation offset = 72 kHz. 20° crystallite orientations together with 1.8 μs time increments were assumed for these calculations.

XY8-cycled pulse sequence (Figure 2C), whereas the single spin−

Figure 5. Comparisons between the limiting dipolar ΔS/S₀ fractions resulting as a function of the 14 N rf offset when irradiating at the Larmor (TRAPDOR) and at twice the Larmor (ORR) frequency. Calculations assumed a sequence like the one in Figure 2A for both cases; quadrupole coupling parameters were as indicated, B₀ was set at 4.7 T, and all other coupling parameters were as in Figure 4.

3. Experimental Details

To test the validity of the various features derived in the preceding paragraph, a series of double (59 Co/14 N-) and triple (1 H/13 C/14 N-) resonant experiments were carried out. All samples were analyzed at natural isotopic abundance. These included 13 C−14 N pairs in amino acids and dipetides: l-alanine (Ala), N-acetyl-l-valine (NAV), β-l-alanyl-l-valine (AlaVal), and β-l-aspartyl-l-alanine (AspAla). Also analyzed were the 59 Co−14 N complexes hexaaminecobalt(III) chloride and sodium hexanitrocobaltate(III). 14 N signals in the organic samples were acquired under TPPM 1 H-decoupling conditions and using an 14 N quadrupole patterns, respectively. When comparing the relative performance of both techniques in terms of their relative dephasing fractions expected under MAS conditions as a function of S−14 N dipolar coupling = 0.8 kHz, ω₀/2π = 37 kHz, an overtone pulse width fixed at τ = 16 rotor periods, the indicated B₀ field strengths, and various η₀ asymmetry parameter values.

14 N quadrupole patterns, respectively. When comparing the relative performance of both techniques in terms of their relative dephasing fractions, it appears that suitably tuned TRAPDOR sequences perform better than their ORR counterparts for weak quadrupoles (ε ≤ 0.1), while the opposite is the case when ε is large.

4. Results

As an example of the feasibility of carrying out ORR-based experiments, Figure 6 illustrates the dephasings exhibited by a series of 13 C and 59 Co sites proximate to 14 N’s which are undergoing overtone irradiation. Although 13 C’s are directly bonded to nitrogens, some of the 13 C resonances do not exhibit,
offsets. This procedure, in turn, involved selecting a sufficiently
large overtone rf irradiation frequency. After the 13 Co r 59 Co NMR
experiments such as those depicted in Figure 8. This offset dependence, the origin of which was alluded to earlier (Figures 4 and 5), endows the method with a selective chemical specificity that is not usually available in dipolar recoupling methods. This allowed us, for instance, to analyze the 13C dephasing in the AlaVal and AspAla dipeptides (Figure 7) solely on the basis of distances to amide nitrogens; −NH3+ groups, having smaller quadrupolar couplings, undergo ORR at significantly different irradiation offsets and thus can be considered in this recoupling analysis as if they were isotopically different species.

Besides their usefulness in setting up site-specific recoupling experiments, variable-offset/fixed-evolution-time ORR experiments provide a route to acquiring high-resolution overtone spectra from spinning powders that, at least in our experience, is considerably simpler and more sensitive than comparable direct-detection 14N overtone schemes. The meaningful overtone spectral data arising from these indirect dephasing signals can be better appreciated in Figure 9, which compares the offset dependence of several experimental ORR line shapes with the ideal overtone powders expected from 14N literature quadrupole data of NAV were fitted with dipolar couplings of 714 Hz (rN-C = 1.468 Å) and coinciding dipolar, quadrupolar tensors. The 13C and OC–N distances observed by crystallography to their respective 14N pair of L-alanine (A), for Cα–14N (B) and OC–14N (C) sites in NAV, and for 59Co–14N in sodium hexanitrocobaltate(III) (D). Rf overtone fields were in all cases set at 33 kHz. The pulse sequence in Figure 2C (ω/2π = 5 kHz) was used for the organic samples, whereas the sequence in Figure 2B (ω/2π = 6.25 kHz) was applied for the inorganic complex. The best fit for L-alanine Cα–N dephasing data matches the literature parameters: rN-C = 1.468 Å and coinciding dipolar, quadrupolar tensors. The Cα–N and OC–N data of NAV were fitted with dipolar couplings of 714 Hz (rN-C = 1.468 Å) with ξ ≈ 120°, ψ ≈ 120°, and 864 Hz (rN-C = 1.369 Å) with ξ ≈ 120°, ψ ≈ 40°. The optimal offset irradiation position for each of these samples was determined from 14N overtone experiments such as those depicted in Figure 8.

5. Discussion and Conclusions

The present study demonstrates that overtone experiments involving forbidden |+1 ↔ −1| 14N transitions can act as suitable and efficient means for dipolar recoupling under MAS. To analyze the behavior observed during these experiments and quantify their dephasing performance, a simple formalism was derived, based on an effective spin-1/2 Hamiltonian describing overtone nutation. From here the offset dependence and high recoupling efficiency of the method could be rationalized, the

Figure 6. Experimental (symbols) vs calculated (lines) ORR dephasing curves observed for the Cx–14N pair of L-alanine (A), for Cα–14N (B) and OC–14N (C) sites in NAV, and for 59Co–14N in sodium hexanitrocobaltate(III) (D). Rf overtone fields were in all cases set at 33 kHz. The pulse sequence in Figure 2C (ω/2π = 5 kHz) was used for the organic samples, whereas the sequence in Figure 2B (ω/2π = 6.25 kHz) was applied for the inorganic complex. The best fit for L-alanine Cα–N dephasing data matches the literature parameters: rN-C = 1.468 Å and coinciding dipolar, quadrupolar tensors. The Cα–N and OC–N data of NAV were fitted with dipolar couplings of 714 Hz (rN-C = 1.468 Å) with ξ ≈ 120°, ψ ≈ 120°, and 864 Hz (rN-C = 1.369 Å) with ξ ≈ 120°, ψ ≈ 40°. The optimal offset irradiation position for each of these samples was determined from 14N overtone experiments such as those depicted in Figure 8.

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(32) Lucken, E. A. C. Nuclear Quadrupole Coupling Constants; Aca-
former stemming from the large second-order quadrupole effects involved, and the latter from the periodic time dependence imposed by spinning on the transverse irradiation terms \{f, g\}. In some respects the latter aspect of overtone recoupling resembles that of certain spin-1/2 schemes such as MORE,\textsuperscript{13,14,33} which rely on amplitude-modulated rf fields for recoupling the dipolar couplings. These amplitude modulations provide a MAS dipolar recoupling scheme which is remarkably efficient and independent of rf inhomogeneities. A difference between the two classes of sequences is that, whereas in the spin-1/2 experiments \(\omega_{r}\) modulations need to be artificially introduced on the amplitude \(\omega_{s}\), in the ORR case they are natural consequences of the modulations imposed by MAS on the overtone nutation Hamiltonian.

Among the basic features found for this new form of recoupling are a conventional dependence on the \(I-S\) dipolar coupling, weak yet non-monotonic dependencies on the rf field strength and spinning rates used in the recoupling, a sensitivity with regard to the relative orientations of the tensors involved, and considerable efficiency losses as the \(\epsilon = \chi_{Q}/\omega_{0}\) ratio drops below \(\approx 0.05\). Also worth noting is the narrow-band nature of the recoupling, which allows one to discriminate the dephasing according to the quadrupole parameters of the coupled \(^{14}\text{N}\) site. Further clarification on the influences of these factors would clearly benefit from a simpler model, capable of describing ORR phenomena and their resulting dephasing curves in analytical terms. Additional theoretical and experimental work is also needed to clarify whether the combined dependence of the ORR dephasing on multiple coupling parameters, particularly on the quadrupolar coupling parameters of the irradiated nucleus, ends up being an asset or a liability for geometrical assessments.

Efforts along all these research lines are actively under way, yet it is satisfactory to note that even at this stage, experimental data show a very good agreement with the numerical predictions derived from our numerical formalism.

In addition to its structure measurement potential, one of the most promising aspects of this technique is its ability to report overtone spectra via sweeps of the irradiation recoupling field. This information arises in a fashion that is largely independent of the specific recoupling conditions, which therefore do not need to be precisely known or set, and provides reliable line shapes from the elusive realm of strongly coupled quadrupolar NMR. Given the relevance of \(^{14}\text{N}\) in a variety of synthetic and biological structures and the well-characterized correlations

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**Figure 8.** \(^{14}\text{N}\) overtone powder line shapes detected for the indicated sample sites, as deduced from the \(\Delta S/\Delta S_{0}\) dephasing fractions observed from \(^{13}\text{C}\) CPMAS and \(^{59}\text{Co}\) MAS NMR spectra. The overtone dimensions were swept in 2 kHz steps. The spinning speed was 5 kHz in all measurements, and asterisks denote spinning sidebands. Between 32 and 512 scans were collected for both \(S\) and \(S_{0}\) measurements at each overtone irradiation frequency, depending on the compound.

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**Figure 9.** Comparisons between the experimental \(^{14}\text{N}\) powder line shapes inferred from the \(\Delta S/\Delta S_{0}\) dephasing fractions (Figure 8), and best-fit powder patterns expected from ideal \(^{14}\text{N}\) overtone experiments. Simulations incorporate \(\chi_{Q}/2\pi = 0.3\) MHz and \(\eta_{0} = 0\) for \(l\)-alanine,\textsuperscript{14} \(\chi_{Q}/2\pi = 0.8\) MHz \(\eta_{0} = 0.3\) for NAV,\textsuperscript{26} and a single \(^{59}\text{Co}-^{14}\text{N}\) pair with \(\chi_{Q}/2\pi = 0.9\) MHz, \(\eta_{0} = 0.4\) for sodium hexanitrocobaltate(III). All calculations were referred with respect to the exact experimental \(2 \times \omega_{0}\) frequency, 43.596 MHz.
relating its quadrupole parameters with surrounding electronic density, this may result in a most valuable ramification of the present technique. Also intriguing is the possibility of extending this high-resolution spectroscopic approach to other strongly coupled species with spin numbers \( I \geq \frac{3}{2} \). Indeed, a number of half-integer quadrupoles (e.g., halogens, \(^{63}\text{Cu} \), etc.) can only be observed by NMR if positioned in highly symmetric environments. We are currently exploring whether overtone recoupling might help to extend this window of observation to more generic sites.

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Supporting Information Available: Explicit expressions for the various functions involved in eq 8 and needed to derive the ORR dephasing curves (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.