^{15}N$-^1$H Bond Length Determination in Natural Abundance by Inverse Detection in Fast-MAS Solid-State NMR Spectroscopy

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Received April 24, 2002

Sensitivity enhancement by ^{1}H inverse detection[1] is at the present time almost universally employed in heteronuclear multidimensional NMR experiments for structure determination in solutions. For solids, it was only recently demonstrated that the ^{1}H resolution enhancement achievable by fast magic-angle spinning (MAS) suffices to overcome the main limitation for inverse detection in the solid state, namely the broad ^{1}H lines.[2] Substantial gains in sensitivity were reported for a variety of ^{15}N and ^{13}C systems.[2–4] Specific pulse sequences and detection schemes providing high ^{1}H resolution allowed for large sensitivity gains also in inverse-detected static ^{2}H and ^{15}N powder spectra.[5,6] Inverse detection schemes bear particular challenges when low isotope concentrations are to be observed, because the incomplete removal of a large overhead of uncoupled ^{1}H magnetization may lead to severe spectral artifacts. In solution-state approaches, pulsed field gradients (PFGs) have emerged as the standard procedure to destroy unwanted coherences.[7] For solids, it was shown that radio frequency (RF) pulses exploiting strong dipole–dipole couplings may serve the same purpose without the need for specific spectrometer hardware.[4]

In this communication, we present two-dimensional ^{15}N$-^1$H correlation NMR experiments with ^{1}H inverse detection under fast MAS conditions on natural-abundance ^{15}N systems. PFGs or, alternatively, RF pulses ensure suppression of unwanted ^{1}H signal, and the acquisition of 2D spectra becomes feasible within experiment times of a few hours. It is shown for the first time that heteronuclear ^{1}H$-^{15}$N dipole–dipole couplings, thus bond lengths, can be faithfully extracted in natural abundance using spinning sideband patterns generated by a recently developed recoupling technique.[8] The large significance of high-precision bond length determination in solid-state NMR with respect to the characterization of hydrogen bonds has recently been highlighted.[9] In our ^{15}N$-^1$H spectra, information on (i) chemical shifts and (ii) dipole–dipole couplings/bond lengths can be accessed either individually or in a combined way using a split-t_1 approach.

The approach is based on the combination of two solid-state NMR techniques providing incoherent and subsequently coherent transfer of polarization between ^{1}H and ^{15}N (see Figure 1). Initial ^{1}H polarization is incoherently transferred to ^{15}N by a conventional cross-polarization (CP) step. At this point, to prepare for the final (inverse) detection of the weak ^{15}N signal on ^{1}H, strong remaining ^{1}H polarization is efficiently removed by either a field gradient pulse (of 100 μs duration) or by two RF pulses (of 400 μs duration and fulfilling a rotary resonance recoupling condition),[4] while the ^{15}N polarization is stored in a longitudinal state. Both dephasing techniques were found to perform almost identically. Aided by this preselection, the desired coherence transfer pathway
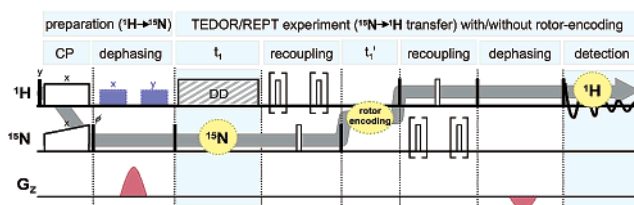
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Figure 1. Pulse sequence for ^{1}H-detected ^{15}N$-^1$H correlation NMR spectroscopy under fast MAS in the solid state. Solid and open bars represent 90° and 180° pulses, respectively. Alternative ways to suppress surplus ^{1}H magnetization are shown in red (PFGs) and blue (dephasing RF pulses).

(i.e., ^{1}H→^{15}N→^{1}H) can be selected by a four-step phase cycle and, including a final cleanup of the signal, by an overall phase cycle of 16 or 32 steps. While dephasing RF pulses are readily available on standard NMR hardware, PFGs require the installation of gradient coils at the bottom and the top of the MAS stator. Finally, the ^{15}N signal is transferred back to ^{1}H for detection using a coherent TEDOR-type[8,10] recoupling procedure, which allows the quantification of the ^{15}N$-^1$H coupling.

Two independent spectral dimensions can be inserted into this CP-TEDOR double-transfer scheme: a dipolar-decoupled (DD) ^{15}N dimension (t_1) between the two transfer blocks, and a t_1' dimension in the middle of the TEDOR sequence. While the former generates ^{15}N chemical-shift information, the latter comprises a modulation of a dipolar-ordered state by the recoupling. This "rotor-encoding" approach has been established in other homonuclear[11] and heteronuclear[8] correlation experiments. The information on the couplings can be retrieved from the t_1'-modulation of the detected signal, which is converted into a sideband pattern by Fourier transformation. These patterns sensitively depend on the product of recoupling time and dipolar coupling constant.[8]

Figure 2a shows a ^{15}N$-^1$H correlation NMR spectrum of L-histidine·HCl·H$_2$O obtained in a 2.5-mm rotor system at 30 kHz MAS. The sacrifice of signal associated with the use of small rotors, which, when applied in natural abundance, limits the technique to smaller molecules, is unfortunately unavoidable, since fast MAS is essential for an efficient and quantifiable TEDOR transfer.[8] However, only 8192 transients of the pulse sequence depicted in Figure 1 were needed to acquire the full 2D spectrum. To obtain a pure chemical-shift correlation spectrum, t_1 was incremented in steps of full rotor periods (τ_R), while rotor-encoding was omitted ($t_1' = 0$). In this way, natural-abundance ^{15}N$-^1$H correlation spectra can be recorded within 4–10 h and thus become routinely applicable for solids. The comparison of inverse-detected CP-TEDOR and the analogous ^{15}N-detected, regular 2D TEDOR experiment yielded a sensitivity gain[2] of about 6–8, as detailed in the Supporting Information.

In the spectrum shown in Figure 2a, all three expected NH correlation signals are observed when the ^{15}N$-^1$H interactions are recoupled for a duration of $2 \times 6\tau_R$ in the TEDOR step. For shorter
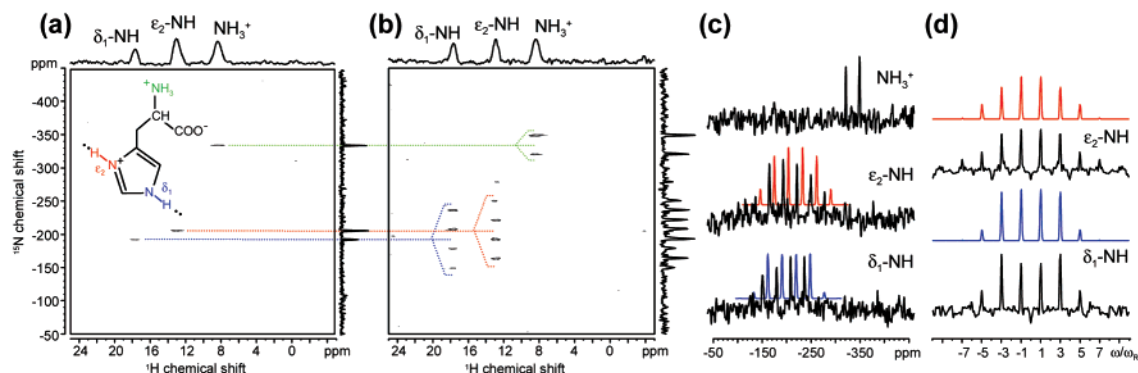
Figure 2. (a) $^{15}N-^{1}H$ correlation spectrum of L-histidine·HCl·H_2O, measured at 30 kHz MAS in a 16.4 T magnet (700 MHz ^{1}H Larmor frequency) using a recoupling time of $2\times6\tau_R$ and accumulating the signal of 8192 transients of the pulse sequence depicted in Figure 1 (with RF dephasing and $t_1' = 0$). (b) Same as in (a), but with PFG dephasing and dipolar spinning sideband patterns in the ^{15}N dimension, obtained by incrementing t_1 and t_1' simultaneously in steps of τ_R and $\tau_R/30$, respectively. (c) Slices from (b) taken along the ^{15}N dimension at the respective ^{1}H positions. (d) Pure rotor-encoded sideband patterns obtained by incrementing only t_1', while keeping $t_1 = 0$ (using RF dephasing). Calculated patterns are displayed in color above the experimental ones. The N−H dipole−dipole couplings and N−H distances determined from the patterns are given in Table 1.

Table 1. N−H Dipole−Dipole Couplings (D_{NH}) and Distances (r_{NH}) Measured from the NMR Sideband Patterns Shown in Figure 2 c,d

^{1}H signal		this work		NMR	diffraction
		$D_{NH}/2\pi$ [kHz]	r_{NH} [pm]	r_{NH} [pm]	r_{NH} [pm]
~13 ppm (ϵ_2)	(c)	9.4 ± 0.9	109 ± 4	105 ± 5	102.6 ± 0.4
	(d)	9.9 ± 0.5	107 ± 2		
~18 ppm (δ_1)	(c)	8.2 ± 0.9	114 ± 4	109 ± 5	107.0 ± 0.4
	(d)	8.85 ± 0.5	111 ± 2		

^{a} Data from previous solid-state NMR and neutron diffraction studies of L-histidine·HCl·H_2O are given for comparison.[9,12]

recoupling times ($<2\times4\tau_R$) the signal from the rapidly rotating NH_3^+ group is suppressed due to its weaker couplings. A precise quantification of the couplings is possible from spinning sideband patterns, which are introduced into the spectra by incrementing t_1' in steps of τ_R/N simultaneously with t_1 (split-t_1 approach). The integer number N determines the separation of the (odd-order only) sidebands in the spectra according to $\Delta\nu = 2\nu_R/N$, where ν_R is the MAS frequency; the spectrum shown in Figure 2b was obtained with $N = 30$. In the TEDOR step, dipolar recoupling was again applied for $2\times6\tau_R$. From the resulting sideband patterns (Figure 2c), $^{15}N-^{1}H$ couplings can be estimated in the range of $D_{NH}/2\pi >$ 2 kHz, corresponding to N−H distances of up to 180 pm. Since the signal is distributed over a pattern in the split-t_1 experiment, it requires 5 to 10 times more signal accumulations than the pure chemical-shift correlation experiment.

When the ^{15}N chemical-shift information is not required, the t_1 dimension can be skipped, and a purely rotor-encoded signal is recorded in the t_1' dimension. Figure 2d shows the sideband patterns observed for δ_1-NH and ϵ_2-NH at ~18 ppm and ~13 ppm in the ^{1}H spectrum, respectively. For signal acquisition, 20480 transients (2.5 times more than for the spectrum in Figure 2a) were used in total. The N−H distances extracted from these patterns reproduce well the results from previous investigations,[9,12] as can be inferred from Table 1. Apart from the usual overestimation of distances in NMR,[9] a further systematic error is always expected from the influence of couplings of the ^{15}N to further protons. Nonetheless, distances can reliably be extracted even when the perturbing coupling is as strong as ~30% of the dominant coupling.[8] Note that in a system with multiple protons coupled to a single ^{15}N nucleus, the technique only provides access to the dominant coupling. Two or more couplings of similar magnitude lead to destructive interference during recoupling and signal loss.[8,13]

In conclusion, we envision a wide applicability of this and related[4,6] ^{1}H inverse detection techniques, which provide dipolar-coupling and chemical-shift information in systems with ^{15}N in

natural abundance or in low isotopic concentration. In particular, the technique is valuable for investigations of N−H···N and N−H···O hydrogen bonds. With respect to biomolecules, the gain in ^{15}N sensitivity, combined with the information on $^{15}N-^{1}H$ dipolar couplings, may help to improve NMR experiments for structure determination of peptide backbones in the solid state. Further technical development, in particular the optimization of the ^{1}H RF circuit for detection, are expected to enhance the possible gain in signal sensitivity further and to promote the significance of ^{1}H-detected solid-state NMR experiments.

Supporting Information Available: Further experimental details, data on the sensitivity gain, and discussion of the error limits (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA026657X

Supporting Information

^{15}N–^{1}H Bond Length Determination in Natural Abundance by Inverse Detection in Fast-MAS Solid-State NMR Spectroscopy

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1 Experimental Details

Fig. 1 shows the pulse sequences of the ^{1}H and ^{15}N-detected TEDOR (or REPT) experiments including details on the pulse phases. The pulse sequences use REDOR (rotational-echo double-resonance) recoupling of the heteronuclear dipolar interaction under MAS by means of π pulses spaced by half a rotor period [1]. In TEDOR (transferred-echo double-resonance), which was published as an extension to REDOR [2], simultaneous $\pi/2$ pulses on both channels were introduced between two REDOR recoupling periods in order to coherently transfer magnetization from one nucleus to the other. The experiment is in principle the solid-state analogue of the solution-state INEPT experiment [3]. The acronym REPT (recoupled polarization transfer), used in our first publication [4], refers to essentially the same pulse sequence, with the difference that a t_1 dimension was introduced *between* the two central $\pi/2$ pulses, in order to achieve rotor-encoding and thus obtain sideband patterns, from which dipolar coupling constants can be extracted. Because the inverse experiment presented herein can be conducted with (split-t_1 approach) or without this rotor-encoding period, we chose to stick to the original acronym TEDOR. Details on all most relevant theoretical and experimental aspects of ^{1}H-^{13}C correlation using TEDOR/REPT pulse sequences under fast (>25 kHz) MAS can be retrieved from our two previous papers [4, 5].

In Table 1, the phase cycle for the CP-TEDOR and TEDOR 2D experiments is compiled. The phases ϕ_{1-7} are identical for the two experiments (Fig. 1a and b) and were published in [5]. For the inverse experiment, the two channels are simply interchanged, a cross polarization (CP) and a dephasing period are introduced, and one additional phase ϕ_0 and a two-step supercycle are added to the phase cycle. The phases for all other pulses are constant and noted in Fig. 1a. (XY-4)
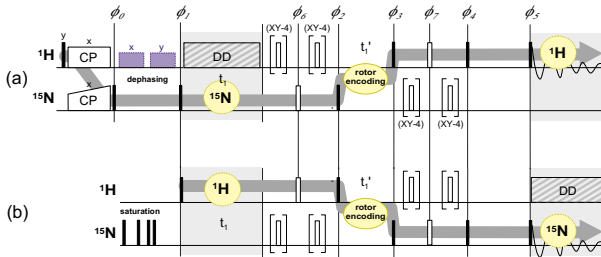
phase cycling [6] is applied to subsequent recoupling π pulses. When pulsed field gradients (PFGs) are used instead of RF dephasing, the phase cycle can be shortened by omitting the supercycle.

Magic-angle spinning of 30 kHz was applied in all cases, and RF fields of 100 kHz were used on both channels (2.5 μs $\pi/2$ pulses). The two 400 μs dephasing pulses were applied with a field of 15 kHz to fulfill the rotary resonance condition for efficient dephasing of surplus proton magnetization [7]. Alternatively, PFGs of approx. 200 and 100 G/cm were applied for a duration of 100μs in the first and second dephasing period, respectively. In the ^{15}N dimension, ^{1}H dipolar decoupling is accomplished by the TPPM scheme [8] at an RF field of 100 kHz. Dipolar decoupling of ^{1}H from ^{15}N is not strictly necessary because the ^{1}H linewidths are dominated by ^{1}H homonuclear interactions. Initial ^{15}N magnetization was created by a ramped CP [9] of 2 ms length. The matching condition was $\omega_1^N = \omega_1^H - \omega_R$, with the ramp varying from $0.9\omega_1^N$ to $1.1\omega_1^N$, where $\omega_1^H/2\pi$ was about 80 kHz. Further information on spectra processing and data analysis, in particular on the generation of the sideband patterns in Fig. 2d of the main text, are given in [5].

2 Sensitivity Gain

To determine the gain in signal-to-noise (S/N) achievable by ^{1}H-detection, we compare the ^{15}N-^{1}H CP-TEDOR scheme to a conventional ^{1}H-^{15}N TEDOR experiment. This comparison is fair in that the two experiments are equivalent as far as the quantitative and coherent recoupled transfer (TEDOR) part is concerned. The equivalence can be inferred from Fig. 1. The directly (^{15}N) detected experiment mainly differs by the *absence* of the initial CP, which represents a bottleneck for the efficiency of the inverse experiment and must be well optimized.

Both experiments were performed on L-histidine (with ^{15}N in natural abundance) under identical conditions, which means that the total number of signal accumulations was identical and fixed to 8192 transients. In the ^{1}H and ^{15}N dimension, 128 and 512 data points were acquired in steps of rotor periods, corresponding to acquisition times of 4.2 and 16.8 ms, respectively. Fig. 2 shows the ^{1}H and ^{15}N slices (direct detection in red, inverse detection in blue) taken from the 2D spectra through the ϵ_2-NH resonance at 207 ppm/12.8 ppm (^{15}N/^{1}H). Obviously, the directly detected experiment (TEDOR) did not afford any signal apparent above the noise. Consequently, from the S/N ratios a sensitivity gain of at least 6...7 can be derived for the inverse-detected experiment (CP-TEDOR) on L-histidine. A pair

Figure 1: *Pulse sequences for inverse (a) and directly detected (b) ^{15}N-^{1}H correlation experiments. Solid and open bars represent $\pi/2$ and π RF pulses, respectively. DD indicates ^{1}H dipolar decoupling. Saturation pulses in (b) remove artifacts which may potentially arise from initial ^{15}N magnetization leaking through the phase cycle.*

Table 1: *Phase cycle for the CP-TEDOR/REPT pulse sequences. ϕ_{rec} denotes the receiver phase. ϕ_0 and the second half of ϕ_{rec} are not needed for the directly detected experiment.*

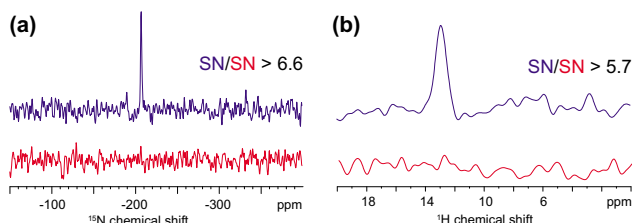|	
ϕ_0	$\{y\} \times 16 \; \{\bar{y}\} \times 16$
ϕ_1	$x\,\bar{x}\,y\,\bar{y}\,\bar{x}\,x\,\bar{y}\,y \;\; \bar{x}\,x\,\bar{y}\,y\,x\,\bar{x}\,y\,\bar{y}$
ϕ_2	$y\,\bar{y}\,\bar{x}\,x\,\bar{y}\,y\,x\,\bar{x}$
ϕ_3	$y\,y\,\bar{x}\,\bar{x}\,\bar{y}\,\bar{y}\,x\,x$
ϕ_4	$\bar{x}\,\bar{x}\,\bar{y}\,\bar{y}\,x\,x\,y\,y$
ϕ_5	$x\,x\,y\,y\,\bar{x}\,\bar{x}\,\bar{y}\,\bar{y} \;\; \bar{x}\,\bar{x}\,\bar{y}\,\bar{y}\,x\,x\,y\,y$
ϕ_6	$y\,\bar{y}\,\bar{x}\,x\,\bar{y}\,y\,x\,\bar{x}$
ϕ_7	$\bar{x}\,x\,\bar{y}\,y\,x\,\bar{x}\,y\,\bar{y}$
ϕ_{rec}	$\{y\,y\,\bar{x}\,\bar{x}\,\bar{y}\,\bar{y}\,x\,x\} \times 2$
	$\{\bar{y}\,\bar{y}\,x\,x\,y\,y\,\bar{x}\,\bar{x}\} \times 2$

Figure 2: *Slices from inverse and directly-detected ^1H-^{15}N experiments, taken along the ^{15}N dimension (a) and the ^1H dimension (b) at the ε_2-NH resonance (207 ppm/12.8 ppm) of L-histidine with ^{15}N in natural abundance (^1H dephasing by PFGs). The ^1H-detected CP-TEDOR and ^{15}N-detected TEDOR data is shown in blue and red color, respectively.*

of TEDOR/CP-TEDOR experiments was also conducted on a ^{15}N-enriched sample of imidazolium methylsufonate, where strong signal was observed in either case, and the S/N ratio of the CP-TEDOR experiment was found to be superior by a factor of approximately 8.

Our value of 6...8 for the sensitivity gain should be compared with the values of 1.6 to 3.3 (depending on the site) obtained from an inverse double-CP scheme applied to naturally abundant ^{13}C in polymers by Tycko and coworkers [7]. Assuming identical probe characteristics for ^{15}N and ^{13}C, and neglecting linewidth effects, the application of the double-CP experiment to ^{15}N could therefore be expected to lead to a $(\gamma_C/\gamma_N)^{3/2}$-fold sensitivity gain of 6 to 13. This compares reasonably well with the values obtained here using the CP-TEDOR experiment. It should be noted that the coherent transfer mechanism behind the TEDOR scheme is generally less efficient than an adiabatic CP (in particular when secondary couplings become large), but it provides quantitative results and allows precise distance determination by means of the rotor-encoding approach.

3 Experimental Errors

The error limits given in the main text rest upon the accuracy of the fitting procedure of the sideband patterns. Our fitting routine is based on numerical Fourier transformation of the analytical result for the rotor-encoding time-modulation of a heteronuclear spin pair signal [5], which is implemented into a least-squares fitting routine based on the Levenberg-Marquardt algorithm [10]. The program provides an error for each fitted variable (D_{NH} is the central one), which is derived from the covariance matrix and depends on the quality of the fit and on the accuracy of every point in the experimental input spectrum (i.e., S/N, which is an input parameter). As the spectra presented in our Communication are relatively noisy, and further adverse effects are very weak, the error limits for the derived distances can therefore be expected to be dominated by noise.

The theoretical treatments of spin dynamics under the directly detected and the new inverse experiment are identical. This is because the transverse component of the heteronuclear coherence state (depicted as the grey arrow in Fig. 1) active during recoupling changes from one nucleus to the other between the first and the second recoupling period. Therefore, all conclusions drawn from previous work for the case of REPT as applied to ^1H-^{13}C systems [5] apply equally well to the ^{15}N-^1H inverse experiment. In summary, the rotor-encoding approach (in contrast to an intensity-based strategy like normal REDOR) and the ensuing sideband analysis proved to be extremely robust towards most adverse effects like timing imperfections, flip-angle devia-

tions, CSA, and ^1H homonuclear couplings. Effects of larger multiple *heteronuclear* couplings from more remote protons to the ^{15}N nucleus of interest may lead to a considerable loss of spectral intensity, but the accuracy of spinning sideband analysis is still not seriously impeded, because the coherence-transfer process during recoupling (first one heteronucleus in the local field of the others and then vice versa during the second recoupling period) emphasizes the spin-pair character of the result.

On the down side, this means that the TEDOR/REPT approach is not suitable for configurations with multiple similar couplings (e.g. methylene groups) or when medium- and long-range distances are to be determined. Methyl groups or -NH_3^+ can, however, be studied because the multiple heteronuclear coupling tensors are identical when the moiety undergoes fast uniaxial motions. The strength of the TEDOR/REPT scheme is clearly the determination of single primary pair couplings, such as distances in direct chemical or hydrogen bonds.

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