INEPT Experiments in Solid-State NMR

C. A. Fyfe,* K. C. Wong-Moon, Y. Huang,† and H. Grondey

Department of Chemistry, University of British Columbia 2036 Main Mall, Vancouver, BC V6T 1Z1, Canada

Received June 12, 1995

In previous work we have used homonuclear *J*-coupling based COSY and INADEQUATE experiments under MAS conditions to establish solid-state homonuclear $^{29}Si-O-^{29}Si$ connectivities in zeolites.[1] In pioneering work on heteronuclear systems, Schaefer and co-workers have introduced REDOR[2] and TEDOR[3] experiments based on the heteronuclear dipolar interaction for the measurement of internuclear heteronuclear distances, and they have applied them in the investigation of a variety of different systems.[4] It has also been shown that they can be used, as can cross-polarization, to include interactions involving quadrupolar nuclei.[5]

In the present work we show that through-bond connections involving heteronuclei can be detected using solid-state J-coupling based INEPT experiments under MAS conditions. Most importantly, these are equally applicable to quadrupolar and spin-$^1/_2$ nuclei and do not suffer from some of the limitations of dipolar-based experiments for quadrupolar nuclei.

All experiments were carried out using a Bruker MSL 400 spectrometer with a third rf channel. For the $^{27}Al \rightarrow {}^{29}Si$ and $^{23}Na \rightarrow {}^{29}Si$ experiments, a homebuilt double-tuned probe with a 14 mm Chemagnetics pencil spinner stator unit was used, and the samples were spun at 2.4 kHz. For the $^{27}Al \rightarrow {}^{31}P$ experiments, a homebuilt double-tuned probe with a 10 mm Doty Scientific supersonic stator assembly was used, and the samples were spun at 5.0 kHz. Further experimental details are given in the figure captions.

The basic pulse sequence used for I to S transfer was the standard INEPT sequence[6] with appropriate phase cycling, where maximum signal intensity for two coupled spin-$^1/_2$ nuclei is obtained when $\tau = 1/(4J)$, assuming $T_2 \gg 1/J$:

I	$(\pi/2)_x$	τ	π_x	τ	$(\pi/2)_{\pm y}$	
S			π_x		$(\pi/2)_x$	Acquire

Experiments were also carried out with the refocused INEPT experiment[7] where an additional echo sequence is added after the transfer pulses before the acquisition. We also used the closely related DEPT sequence[8] as shown below.

I	$(\pi/2)_x$	τ	π	τ	$\theta_{\pm y}$	τ
S			$(\pi/2)_x$	π		Acquire

(For maximum intensity for a pair of spin-$^1/_2$ nuclei, $\tau = 1/(2J)$ and $\theta = 90°$.)

Figure 1 shows (a) the $^{27}Al \rightarrow {}^{29}Si$ INEPT spectrum of microcline and (b) the $^{23}Na \rightarrow {}^{29}Si$ refocused INEPT spectrum of albite. The lineshapes are dispersive in Figure 1a since the magnetization is not refocused, and they are absorptive in Figure 1b since a refocused INEPT experiment is performed. In both cases, a null signal is observed when the 90° transfer pulse from the source nucleus is removed, as indicated in the figure. Two-dimensional versions of the experiments (not shown) are also successful. Since the scalar *J*-coupling operates through "bonds", i.e., by orbital overlap, bonding connectivities are obtained unambiguously. In this regard, the $^{23}Na \rightarrow {}^{29}Si$ coherence transfer of Figure 1b is of particular interest. The ^{23}Na nuclei are present in Na^+ ions, and the interaction detected by the experiment indicates a degree of orbital overlap with other atoms giving a direct confirmation and measure of the weak "bonds" often reported in X-ray diffraction derived solid-state structures. In this regard, it is worth noting that, in solution NMR spectroscopy, bonding interactions between ions in solution are not detected via *J*-couplings and, hence, are not considered. However, they are routinely detected by ESR spectroscopy when the spectra are run in poorly solvating solvents where ion association is promoted.[9]

In these experiments, we have assumed that the dipolar interactions are suppressed by the MAS at 2.4 kHz. However, the magnitudes of the *J*-couplings involved in the above experiments are relatively small compared to the line widths and are not directly observable. For this reason, we have investigated a number of systems where the *J*-coupling is clearly observable. Figure 2 shows various INEPT and related experiments on the solid triphenylphosphine trichloroaluminum complex (**1**) where the phenyl groups have been deuterated to simplify the experiment.

$$Ph_3P-AlCl_3$$
1

The ^{31}P MAS spectrum (Figure 2a) shows clearly the multiplet structure of six lines due to the *J*-coupling of the ^{31}P nucleus to the six populated energy levels of ^{27}Al. The INEPT, refocused INEPT, and DEPT experiments (Figure 2 parts b, c, and d, respectively) each show only two peaks, corresponding to coupling to only the $\pm^1/_2$ ^{27}Al energy levels. This is because the initial 90° pulse on ^{27}Al activates only coherence between these levels and it is this which is transferred to the ^{31}P nuclei. Any ^{27}Al nuclei where the $\pm^1/_2$ levels are not populated are not involved in this part of the experiment. Note that this observation is good, direct evidence that only the $\pm^1/_2$ central transition is excited, as always assumed. Since the spin system consists of single pairs of ^{31}P and ^{27}Al nuclei, there is no interaction possible between the ^{31}P nuclei and any ^{27}Al nuclei not involved in the initiating pulse. Therefore, only coupling to the $\pm^1/_2$ ^{27}Al energy levels is observed in the final spectrum. This will not be the case in more complex systems.

Further evidence of the origin of the interaction is provided by the behavior of the intensity of the detected ^{31}P signal as a function of the delays used in the INEPT experiment. The measured *J*-coupling is 268 Hz, and the maximum intensity in the INEPT experiment should be observed when the τ delay is $1/(4J) = 0.933$ ms. Figure 3a shows the intensity for the two peaks in the INEPT experiment (see Figure 2b) as a function of τ. The sinusoidal evolution of the magnetization is exactly that expected for a J-coupling mechanism. On the basis of the fact that both intensities pass through zero at $\tau = 3.75$ ms, the maxima should occur at 0.938 and 2.81 ms, while the zero points

* To whom correspondence should be addressed.
†Present address: Department of Chemistry and Biochemistry, Laurentian University, Ramsey Lake Rd., Sudbury, Ontario P3E 2C6, Canada.

(1) Fyfe, C. A.; Feng, Y.; Grondey, H.; Kokotailo, G. T.; Gies, H. *Chem. Rev.* **1991**, *91*, 1525−1543 and references therein.
(2) (a) Gullion, T.; Schaefer, J. *J. Magn. Reson.* **1989**, *81*, 196−200. (b) Pan, Y.; Gullion, T.; Schaefer, J. *J. Magn. Reson.* **1990**, *90*, 330−340.
(3) Hing, A. W.; Vega, S.; Schaefer, J. *J. Magn. Reson.* **1992**, *96*, 205−209.
(4) (a) Marshall, G. R.; Beusen, D. D.; Kociolek, K.; Redlinski, A. S.; Leplawy, M. T.; Pan, Y.; Schaefer, J. *J. Am. Chem. Soc.* **1990**, *112*, 963−966. (b) Holl, S. M.; Marshall, G. R.; Beusen, D. D.; Kociolek, K.; Redlinski, A. S.; Leplawy, M. T.; McKay, R. A.; Vega, S.; Schaefer, J. *J. Am. Chem. Soc.* **1992**, *114*, 4830−4833.
(5) (a) Fyfe, C. A.; Grondey, H.; Mueller, K. T.; Wong-Moon, K. C.; Markus, T. *J. Am. Chem. Soc.* **1992**, *114*, 5876−5878. (b) Fyfe, C. A.; Mueller, K. T.; Grondey, H.; Wong-Moon, K. C. *Chem. Phys. Lett.* **1992**, *199*, 198−204. (c) Fyfe, C. A.; Mueller, K. T.; Grondey, H.; Wong-Moon, K. C. *J. Phys. Chem.* **1993**, *97*, 13484−13495. (d) Fyfe, C. A.; Wong-Moon, K. C.; Huang, Y.; Grondey, H.; Mueller, K. T. *J. Phys. Chem.* **1995**, *99*, 8707−8716.
(6) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760−762.
(7) Pegg, D. T.; Doddrell, D. M.; Brooks, W. M.; Bendall, M. R. *J. Magn. Reson.* **1981**, *44*, 32−40.
(8) Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1982**, *48*, 323−327.
(9) (a) Carrington, A.; McLachlan, A. D. *Introduction to Magnetic Resonance*; Harper & Row: New York, 1967. (b) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance*; McGraw-Hill: New York, 1972. (c) Atherton, N. M. *Electron Spin Resonance*; Halsted Press: New York, 1973.

0002-7863/95/1517-10397$09.00/0

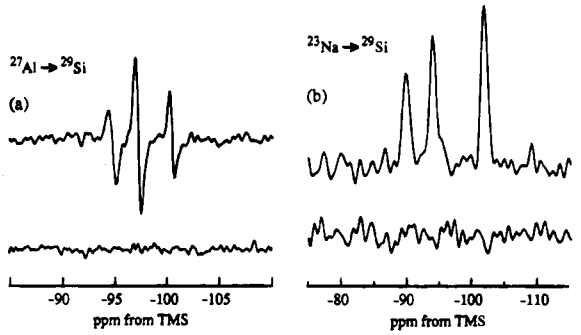

Figure 1. (a) $^{27}Al \rightarrow ^{29}Si$ INEPT spectrum of microcline, acquired using a delay of $\tau = 5$ ms. A total of 720 scans were acquired with a recycle delay of 20 s. The null experiment is shown below. (b) $^{23}Na \rightarrow ^{29}Si$ refocused INEPT spectrum of albite, acquired using delays of $\tau = 6.56$ and 6.15 ms in the first and second echo sequences, respectively. A total of 13 296 scans were acquired with a recycle delay of 5 s. The null experiment is shown below.

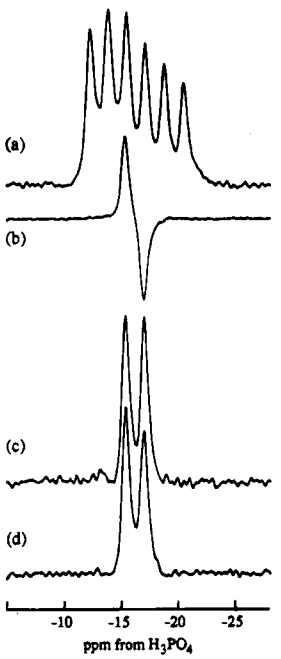

Figure 2. ^{31}P spectra of compound (**1**). (a) Simple ^{31}P MAS spectrum. (b) $^{27}Al \rightarrow ^{31}P$ INEPT spectrum, acquired using a delay of $\tau = 0.933$ ms. A total of 16 scans were acquired using a recycle delay of 5 s. (c) $^{27}Al \rightarrow ^{31}P$ refocused INEPT spectrum, acquired using delays of $\tau = 0.933$ ms in both echo sequences. A total of 16 scans were acquired using a recycle delay of 5 s. (d) $^{27}Al \rightarrow ^{31}P$ DEPT spectrum, acquired using a delay of $\tau = 1.866$ ms and a transfer pulse of $\theta = 90°$. A total of 32 scans were acquired using a recycle delay of 5 s.

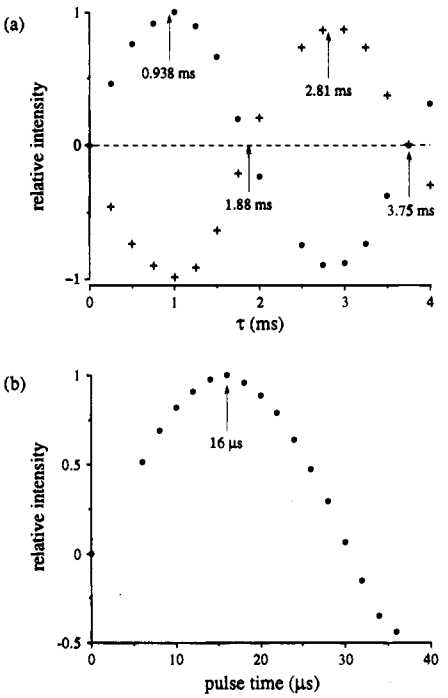

Figure 3. (a) Intensity of the upfield (●) and downfield (+) peaks in the $^{27}Al \rightarrow ^{31}P$ INEPT spectrum of compound **1** as a function of the τ delay time, with the maxima and zero points indicated by the arrows. (b) Intensity in the $^{27}Al \rightarrow ^{31}P$ DEPT spectrum of compound **1** as a function of the magnitude of the ^{27}Al transfer pulse $\theta_{\pm y}$, with the maximum at 16 μs indicated by the arrow.

should occur at 1.88 and 3.75 ms (these τ values are indicated by arrows in Figure 3a). In fact, the first maximum of 0.938 ms is very close to the expected value of $\tau = 1/(4J) = 0.933$ ms. For this system, fixing the evolution times in the INEPT experiment to be integral numbers of rotor cycles made little difference to the signal intensities and had no effect on the period of the sinusoidal intensity evolution as a function of τ.

In the DEPT experiment, the delay for maximum intensity is $\tau = 1/(2J) = 1.866$ ms as expected, indicating that the determining factor is also evolution under the influence of J-coupling. Figure 3b shows the evolution of the ^{31}P magnetization as a function of the magnitude of the ^{27}Al transfer pulse $\theta_{\pm y}$ in the DEPT sequence. The behavior is again exactly that expected, with the maximum at a pulse length of 16 μs corresponding to a pulse angle of 90°, as indicated by the arrow in Figure 3b. This behavior is strong additional evidence in favor of a J-coupling mechanism.

In summary, coherence transfer experiments based on heteronuclear J-couplings are viable in the solid state for both spin-$^1/_2$ and quadrupolar nuclei and complement current approaches based on heteronuclear dipolar couplings. They have the advantage that, because the J-coupling is not eliminated by MAS, they are very straightforward compared to the dipolar-based experiments whose success depends directly on the practical efficiency with which the averaging effect of MAS on the dipolar coupling can be reduced or eliminated. They will not yield distance information, but will give unambiguous through-bond connectivities through orbital overlap and may be of use in probing weak bonding interactions of solid-state structures. It should be possible to perform $^1H/X$ INEPT and DEPT experiments if the ^1H homonuclear dipolar interactions can be efficiently suppressed. This may be a complementary method to cross-polarization for signal enhancement and selectivity in solid-state experiments. We are exploring a range of applications for these experiments.

Acknowledgment. We acknowledge the financial assistance of the NSERC of Canada in the form of operating and equipment grants (C.A.F.), a postgraduate scholarship (K.C.W.-M.), and a postdoctoral fellowship (Y.H.). We gratefully acknowledge the assistance of Dr. M. D. Fryzuk and Mr. G. Giesbrecht in the synthesis of compound **1**.

JA951913+