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Nuclear Overhauser Effect (NOE) Enhancement of ^{11}B NMR Spectra of Borane Adducts in the Solid State

Sharon E. Ashbrook,[†] Nicholas G. Dowell,[‡] Ivan Prokes,[§] and Stephen Wimperis*,[⊥]

School of Chemistry and EaStCHEM, University of St Andrews, St Andrews KY16 9ST, United Kingdom, Institute of Neurology, University College London, London WC1N 3BG, United Kingdom, Department of Biochemistry, University of Oxford, Oxford OX1 3QU, United Kingdom, and Department of Chemistry and WestCHEM, University of Glasgow, Glasgow G12 8QQ, United Kingdom

Received February 15, 2006; E-mail: s.wimperis@chem.gla.ac.uk

The nuclear Overhauser effect (NOE) is one of the classic NMR phenomena and one of the most widely exploited.[1,2] The observation of an enhancement or a reduction in the intensity of the resonance of a spin, I, upon saturation or inversion of the resonance of a second spin, S, that lies close in space (<0.5 nm) is a key step in the NMR structure determination of both small and large molecules in solution.[3] In addition, the heteronuclear NOE is routinely used to enhance the spectra of insensitive nuclei, such as ^{13}C, in solution.[4] The NOE is generally considered to be an NMR phenomenon of spin $I = 1/2$ nuclei in solution, but here we show that a strong $^{11}B\ \{^1H\}$ NOE can be observed in the solid-state ^{11}B NMR spectra of borane adducts, yielding fractional enhancements, $f_I\{S\} = (I - I^0)/I^0$, of the magic angle spinning (MAS) NMR signal of up to 155%. This is an interesting and unusual observation as ^{11}B (spin $I = 3/2$) is a quadrupolar nucleus and the corresponding NOE is absent in solutions of the same materials.

The NOE arises as a consequence of spin-lattice relaxation driven by random modulation of the IS dipole-dipole interaction by thermal motions on the picosecond or nanosecond (or "fast") time scale ($10^{-12}-10^{-9}$ s). Such rapid motions are a general property of liquids but are less common in solids, where dynamics on the millisecond to second (or "slow") time scale ($10^{-3}-1$ s) are considered to dominate. Despite this, a heteronuclear $^{13}C\ \{^1H\}$ NOE has been observed in a number of solids, especially those containing methyl (CH_3) groups as these reorient about their C_3 axes on the fast time scale.[5] Even when fast time scale motions are present, the NOE is usually not observed in either liquids or solids if I or S is a spin $I \geq 1$ nucleus as the quadrupolar interaction is typically much stronger than the dipole-dipole one and, in this case, efficient quadrupolar spin-lattice relaxation will restore the quadrupolar nuclei to equilibrium before the IS dipole-dipole interaction has sufficient time in which to act.

The widely used steady-state $I\ \{S = {}^1H\}$ NOE experiment is not the optimal choice for solid-state NMR as it requires long periods of high-power irradiation of the ^1H nuclei, and this is not practicable on MAS NMR probeheads. Instead, here we utilize the transient NOE,[2] observing it by applying a 180° pulse to the ^1H nuclei at an interval $\tau > 0$ before the start of I spin data acquisition, as shown in Figure 1. For comparison, a spectrum without an NOE can be recorded with the same sequence by setting $\tau = 0$. Care should be taken to avoid the possibility of an inadvertent NOE by leaving a recycle interval during time averaging that is very long compared with the ^1H spin-lattice relaxation time. All the experiments described below were performed at a magnetic field strength of $B_0 = 9.4$ T (unless otherwise specified) and at $T = 300$ K.

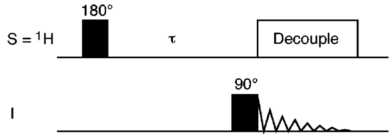

Figure 1. Pulse sequence used to measure a transient heteronuclear $I\ \{S = {}^1H\}$ NOE. In the experiments described here, the I spin is either ^{11}B, ^{13}C, or ^{31}P.

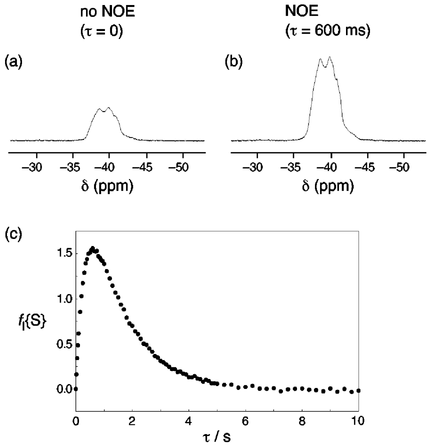

Figure 2. ^{11}B MAS NMR of borane triphenylphosphine, $BH_3{\cdot}PPh_3$. (a) Spectrum recorded without NOE enhancement. (b) Spectrum recorded with $\tau = 600$ ms in the sequence in Figure 1 and showing an NOE enhancement of $f_I\{S\} = 155\%$. (c) Fractional NOE enhancements measured as a function of the τ interval in the sequence in Figure 1.

Figure 2a shows the ^1H-decoupled ^{11}B MAS NMR spectrum of borane triphenylphosphine, $BH_3{\cdot}PPh_3$ with Ph = C_6H_5, recorded without an NOE. The ^{11}B MAS line shape is broadened by the second-order quadrupolar interaction and also shows evidence of a $^{11}B-^{31}P$ J coupling consistent with that found in solution ($^{11}B-^{31}P = 60$ Hz).[6] In contrast, Figure 2b shows the ^{11}B MAS NMR spectrum of $BH_3{\cdot}PPh_3$ recorded using the pulse sequence in Figure 1a with $\tau = 600$ ms. The heteronuclear NOE results in a fractional enhancement of the ^{11}B MAS signal by $f_I\{S\} = 155\%$. The time dependence of this transient $^{11}B\ \{^1H\}$ NOE enhancement can be followed as a function of the interval τ, and the results are shown in Figure 2c, where the characteristic biexponential form of a transient NOE can be seen.

A $^{31}P\ \{^1H\}$ NOE is also observed in $BH_3{\cdot}PPh_3$. Figure 3a shows the ^1H-decoupled ^{31}P MAS NMR spectrum recorded without an NOE, while Figure 3b shows it with a transient $^{31}P\ \{^1H\}$ NOE enhancement of $f_I\{S\} = 9\%$ obtained using the pulse sequence in Figure 1 with $\tau = 3.0$ s. The structure visible in the ^{31}P MAS line shape arises as a result of the J couplings of ^{31}P to ^{11}B (80% abundant) and ^{10}B (20% abundant).

[†] University of St Andrews.
[‡] University College London.
[§] University of Oxford.
[⊥] University of Glasgow.

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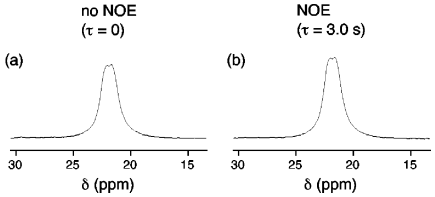

Figure 3. ^{31}P MAS NMR of $BH_3{\cdot}PPh_3$. (a) Spectrum recorded without NOE enhancement. (b) Spectrum recorded with $\tau = 3.0$ s in the sequence in Figure 1 and showing an NOE enhancement of $f_I\{S\} = 9\%$.

The most likely source of fast time scale dynamics in solid $BH_3{\cdot}PPh_3$ is the reorientation of the BH_3 group about its C_3 axis, producing a random modulation of the ^{11}B−^{1}H dipole−dipole interaction, and this hypothesis is supported by our NMR observations. The ^{11}B−^{1}H bond length is short ($r = 0.117$ nm in $BH_3{\cdot}NH_3$),[7] resulting in a strong ^{11}B−^{1}H dipole-dipole interaction and hence a large ^{11}B {^{1}H} NOE enhancement. The ^{31}P−^{1}H internuclear distance (for the ^{1}H nuclei in the BH_3 group) is much longer ($r \approx 0.25$ nm)[8] and, on account of the r^{-6} dependence of the NOE, the corresponding ^{31}P {^{1}H} NOE enhancement is much smaller. The ^{11}B {^{1}H} NOE is not destroyed by efficient quadrupolar spin-lattice relaxation as the full ^{11}B quadrupole tensor will, because of the local chemical environment, be approximately axially symmetric and oriented along the C_3 axis of the BH_3 group with the result that fast time scale reorientation about this axis gives rise to very little modulation of the ^{11}B quadrupolar interaction. [Note that the rapid reorientation means, in experimental solid-state NMR, that a line shape corresponding to a precisely axially symmetric *averaged* ^{11}B quadrupole tensor will be necessarily observed (the measured quadrupolar parameters are $e^2qQ/h = 1.2$ MHz and $\eta_Q = 0$).[6]]

For two isolated spins I and S, both with $I = 1/2$, the maximum NOE possible after a 180° inversion pulse in the fast motion limit[2] is $f_I\{S\}^{\text{trans,max}} = (2/3\sqrt{3})(\gamma_S/\gamma_I) = 0.385(\gamma_S/\gamma_I)$. With $I = {}^{11}$B and $S = {}^{1}$H, this yields $f_I\{S\}^{\text{trans,max}} = 120\%$, that is, smaller than the observed ^{11}B {^{1}H} enhancement in $BH_3{\cdot}PPh_3$. The maximum transient NOE increases, however, with the number of S spins that lie close in space to the I spin. Upon inversion of three noninteracting $S = {}^{1}$H spins, each equidistant from the $I = {}^{11}$B spin, the maximum NOE in the fast motion limit can be shown to be $f_I\{3 \times S\}^{\text{trans,max}} = 0.601(\gamma_S/\gamma_I) = 187\%$. The smaller experimental value of 155% can be attributed to enhanced ^{1}H spin-lattice relaxation by the ^{1}H−^{1}H dipolar interactions ignored in the theoretical result and probably to some quadrupolar contribution to the ^{11}B spin-lattice relaxation. Although ^{11}B has spin $I = 3/2$, the theoretical results for $I = 1/2$ quoted here are still applicable as only the $m_I = +1/2 \leftrightarrow -1/2$ transition, which behaves as a fictitious spin $I = 1/2$, is observed in the ^{11}B MAS spectrum.

Figure 4 shows the solution-state ^{1}H-decoupled ^{11}B and ^{31}P NMR spectra of $BH_3{\cdot}PPh_3$ recorded with and without ^{1}H saturation during the long recycle interval. There is a steady-state ^{31}P {^{1}H} NOE enhancement of $f_I\{S\} = 53\%$ but no measurable ^{11}B {^{1}H} NOE at all. The $BH_3{\cdot}PPh_3$ molecule will reorient randomly about all axes in solution, thus modulating the ^{11}B quadrupolar interaction and leading to efficient ^{11}B quadrupolar spin-lattice relaxation (biexponential with $T_1 \approx 20$ ms and $T_1' \approx 80$ ms) that will destroy the NOE.

We have seen transient ^{11}B {^{1}H} NOE enhancements in ^{11}B MAS spectra of other borane adducts. For example, in borane *tert*-butylamine, $BH_3{\cdot}NH_2C(CH_3)_3$, a fractional enhancement of the ^{11}B MAS NMR spectrum of $f_I\{S\} = 45\%$ was measured. The special feature of borane adducts is that the fast time scale dynamics do not modulate the ^{11}B quadrupolar interaction, and the importance of this can be seen with reference to *ortho*-carborane, $B_{10}H_{10}C_2H_2$. Although a transient ^{13}C {^{1}H} NOE enhancement of $f_I\{S\} = 63\%$ was measured in the ^{13}C MAS NMR spectrum of this solid at $B_0 = 4.7$ T, no ^{11}B {^{1}H} NOE enhancement was observed. This is because the rapid isotropic tumbling of the $B_{10}H_{10}C_2H_2$ icosahedron in the solid[9] modulates the ^{13}C−^{1}H and ^{11}B−^{1}H dipolar interactions but also modulates the ^{11}B quadrupolar interaction leading to efficient ^{11}B spin-lattice relaxation ($T_1 \approx 5$−20 ms) and hence no ^{11}B {^{1}H} NOE.

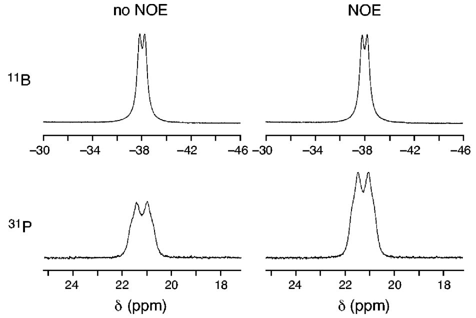

Figure 4. ^{11}B and ^{31}P NMR spectra of $BH_3{\cdot}PPh_3$ in $CDCl_3$ solution, recorded with ^{1}H-decoupling during acquisition only (no NOE) or with ^{1}H-decoupling throughout the acquisition and relaxation intervals (NOE). The ^{11}B spectrum exhibits no NOE enhancement, while the ^{31}P spectrum exhibits an enhancement of $f_I\{S\} = 53\%$.

In conclusion, the observation of a significant ^{11}B {^{1}H} NOE in solid-state ^{11}B NMR spectra of borane adducts is an intriguing result, not least because ^{11}B (spin $I = 3/2$) is a quadrupolar nucleus and the corresponding NOE is absent in solution. Although possibly restricted to a single class of compounds, the large signal enhancements shown here can be useful and are obtained with a very simple NMR experiment. More generally, one of the main applications of NMR in the future will be to the study of dynamics in solids, and this present work shows that the NOE may have a wider role to play here than has been envisaged hitherto.

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