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Ultrahigh-Resolution Phosphorus-31 NMR

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Abstract: The feasibility of ultrahigh-resolution ^{31}P NMR on both 200- and 500-MHz (^1H resonance frequency) instruments is demonstrated. Results indicate that temperature gradients within the sample caused by proton decoupling have severely limited the resolution achieved on commercial instruments due to the larger temperature dependence of ^{31}P chemical shifts exhibited by many phosphorous-containing molecules, relative to ^{13}C chemical shifts. Conditions are described under which instrumental contributions to the observed line width of as little as 15 MHz are observed. Measurements of ^{31}P–^{13}C scalar coupling constants and ^{13}C isotope effects on ^{31}P chemical shifts are presented.

We use the term ultrahigh-resolution NMR to describe operating conditions under which the instrumental contribution to the observed line width at half-height (W_{ex}), and at other bench marks such as 0.1% of full-height, is about 1 order of magnitude smaller than typical specifications of instrument manufacturers. We have reported the development and some applications of ultrahigh-resolution ^{13}C NMR spectra on a 200-MHz instrument (50-MHz ^{13}C resonance frequency),[1-12] and we have shown that ultrahigh-resolution ^{13}C NMR is also feasible on a 500-MHz instrument.[13] The requirements for ultrahigh resolution are high digital resolution,[7] efficient ^1H decoupling,[3] mechanical stability of the spinning sample,[13] optimum sample height and position in the probe,[13] and, in particular, minimum temperature gradients within the sample.[4]

The ^{31}P chemical shifts of many phosphorus-containing molecules exhibit a larger temperature dependence[14,15] than that of ^{13}C chemical shifts.[1] We show in this report that "typical" instrumental conditions such as those suggested by manufacturers of NMR instruments have caused a severe loss of resolution in ^{31}P NMR spectra of isotropic liquid samples. The minor changes in procedure described below can yield greatly improved resolution.

Experimental Section

Proton-decoupled ^{31}P NMR spectra were recorded at 80.99 MHz on a slightly modified[2,5,7] Nicolet NT-200 NMR spectrometer equipped with a 10-mm probe from Cryomagnet Systems, Inc.[5] Proton-decoupled ^{31}P NMR spectra were also recorded at 202.46 MHz on a Bruker AM-500 spectrometer equipped with a standard Bruker 10-mm broad-band probe under conditions described elsewhere.[13] Proton decoupling on the Bruker AM-500 was accomplished using a Bruker microprogram, which provides a WALTZ-16 sequence synchronous with acquisition.

Spinning sidebands were smeared out by spinner speed modulation.[16] Line widths and relative peak positions were obtained with the use of a Lorentzian line-shape fit for all experimental points above half-height plus one more on each side of the peak. Spin-lattice relaxation times were measured essentially as described elsewhere.[2] Additional details about sample and spectral conditions are given in the figure legends.

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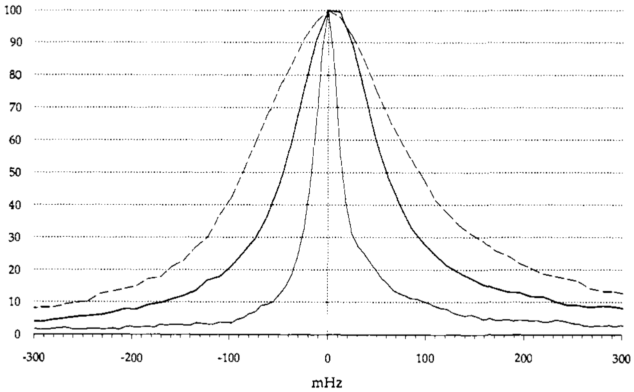

Figure 1. Single-scan ^{31}P NMR spectra of 0.05 M triphenylphosphine in acetone-d_6 recorded at 80.99 MHz and 26.5 °C, with the use of a spectral width of ±100 Hz (quadrature detection) and WALTZ-16 proton decoupling. The broadest resonance (dashed line) was obtained after adjustment of the magnetic field homogeneity on the deuterium lock, and the intermediate spectrum (thick solid line) was recorded after homogeneity was optimized on the ^{31}P free induction decay. Both spectra were obtained with the use of 16K time-domain data points, an acquisition time of 40.96 s, and a decoupler power level of 2.5 W ($\gamma H_2/2\pi$ = 3655 Hz). The narrowest spectrum (thin solid line) was recorded after homogeneity adjustment on the ^{31}P free induction decay, with the use of 32K time-domain data points, an acquisition time of 81.92 s, and a decoupler power level of 0.22 W ($\gamma H_2/2\pi$ = 1092 Hz). All three spectra were Fourier transformed after an additional "zero-filling" which yielded a final digital resolution of 6.1 mHz for the narrowest spectrum and 12.2 mHz for the other two. No digital line broadening or narrowing was applied. The variable-temperature air flow rate was 25 L/min.

Results and Discussion

Figure 1 shows proton-decoupled ^{31}P NMR spectra of 0.05 M triphenylphosphine (**1**) in acetone-d_6, recorded at 80.99 MHz (200 MHz ^{1}H resonance frequency) on the same instrument used for our ultrahigh-resolution ^{13}C NMR spectra at 50.3 MHz,[1-12] and in the same 10-mm probe,[5] under sets of conditions that yield ultrahigh-resolution ^{13}C NMR spectra.[3-5] When the WALTZ-16 decoupling power level is 2.5 W and the homogeneity adjustments are made on the deuterium lock signal, the dashed-line spectrum with a W_{ex} of 180 mHz is obtained. With the decoupler power level still at 2.5 W, but with the homogeneity adjustment made on the ^{31}P free induction decay instead of the deuterium lock, W_{ex} diminishes to 103 mHz (heavy solid line of Figure 1), which is evidence of a significant chemical shift gradient in the sample.[4] Then when the decoupler power level is brought down to 0.2 W and the sample temperature is allowed to reach a new equilibrium, W_{ex} diminishes to 31 mHz (thin solid line of Figure 1). A measurement of the spin-lattice relaxation time (T_1) yields 16 mHz for $1/\pi T_1$, which must be the lower limit for the natural line width. We conclude that the instrumental broadening is about 15 mHz when the decoupler power level is 0.2 W. Such low power is adequate for ^{31}P NMR when there are no hydrogens directly bonded to phosphorus because then the ^{31}P-^{1}H coupling constants are relatively small.[17] Otherwise it becomes necessary to develop further improvements in probe design to diminish temperature gradients.

It is more difficult to achieve ultrahigh resolution in the ^{31}P NMR spectrum of **1** than in ^{13}C NMR spectra[1-13] because the ^{31}P chemical shift in our sample of **1** changes by 0.024 ppm/°C relative to the ^{2}H resonance of the acetone-d_6 solvent, which is about 2 Hz/°C at 80.99 MHz, much larger than typical temperature effects on ^{13}C chemical shifts.[1] Typical reported temperature effects on ^{31}P chemical shifts in a variety of compounds are in the range 0.01-0.06 ppm/°C,[14] so that **1** does not exhibit an atypically large temperature dependence. Furthermore, ^{31}P relaxation times are generally long even in fairly large organophosphorus compounds,[18] so that natural line widths are small and therefore instrumental contributions can be overwhelming. It is very likely that many reported proton-decoupled ^{31}P NMR spectra have been severely broadened by temperature gradients.

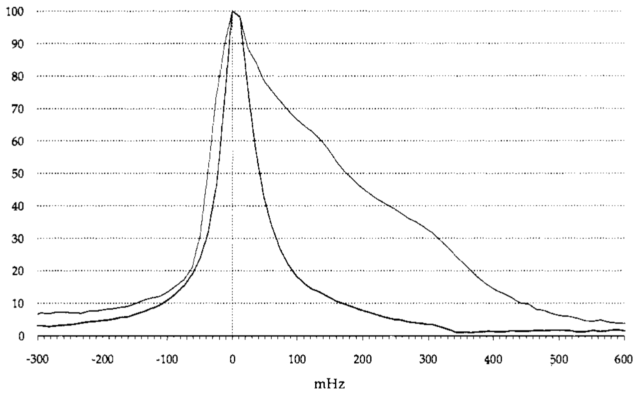

Figure 2. Single-scan ^{31}P NMR spectra of 0.05 M triphenylphosphine in acetone-d_6 recorded at 202.46 MHz and 25 °C with 8K time-domain data points, an acquisition time of 40.79 s, a spectral width of ±50.211 Hz (quadrature detection), and WALTZ-16 proton decoupling. Fourier transformation with additional 8K zero-fill time-domain data points yielded a final digital resolution of 12.3 mHz. No digital line broadening or narrowing was applied. A decoupler power level of 2.1 W ($\gamma H_2/2\pi$ = 2119 Hz) with a variable-temperature air flow rate of 5 L/min yielded the broad resonance; 0.3 W ($\gamma H_2/2\pi$ = 748 Hz) and 12 L/min gave the narrow one.

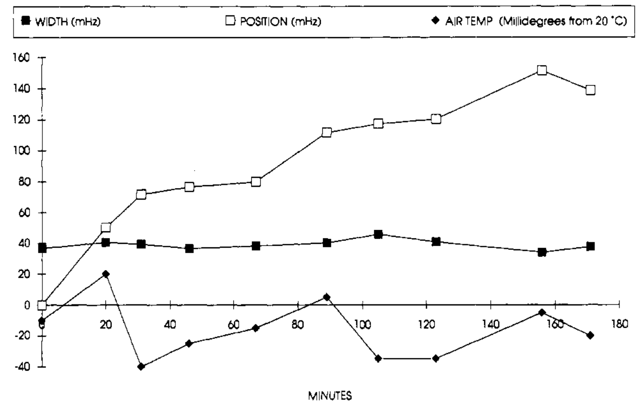

Figure 3. Fluctuations in single-scan ^{31}P NMR spectra of 0.05 M **1** in acetone-d_6 at 80.99 MHz and 26.5 °C. Line widths (solid squares) and peak position drift (open squares) are given in millihertz. Also shown is temperature drift of the prestabilized air entering the variable-temperature unit, in millidegrees relative to 20 °C (solid diamonds).

Figure 2 shows proton-decoupled ^{31}P NMR spectra of the same sample of **1** as used for Figure 1, but now recorded at 202.5 MHz on a Bruker AM-500 NMR spectrometer. The broader resonance resulted from the use of typical "standard" conditions (2-W decoupler power and about 5 L/min air flow rate for variable-temperature control). The narrower resonance was obtained when the decoupler power level was lowered to 0.3 W and the air flow was raised to about 12 L/min, the maximum feasible with the standard 10-mm probe; it has a width at half-height of 63 mHz. A T_1 measurement at 202.5 MHz yielded $1/\pi T_1$ of 16 mHz. The narrow spectrum of Figure 2 has a 47-mHz instrumental contribution to the line width at half-height, not quite ultrahigh resolution but far superior to the resolution under standard operating conditions. The achievement of genuine ultrahigh-resolution ^{31}P NMR on the 500-MHz apparatus will require improvements in temperature gradient reduction.

While ^{31}P resonances in single-scan spectra may be significantly broadened by temperature gradients in the sample as shown above,

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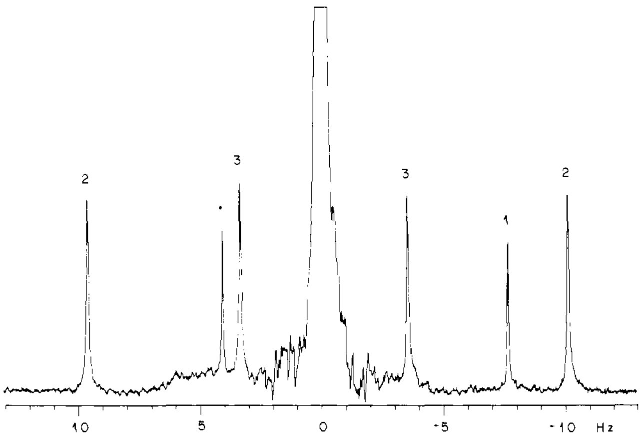

Figure 4. Proton-decoupled single-scan ^{31}P NMR spectrum of 1.0 M triphenylphosphine in acetone-d_6 recorded at 80.99 MHz and 26.5 °C, with the use of a spectral width of ±100 Hz (quadrature detection), an acquisition time of 40.96 s, 16K time–domain data points, and WALTZ-16 proton-decoupling ($\gamma H_2/2\pi = 1114$ Hz). Fourier transformation with an additional 16K zero-fill time–domain data points yielded a simulated acquisition time of 81.92 s and a final digital resolution of 12.2 mHz.

temperature fluctuations with time may degrade signal-averaged spectra. To evaluate the long-term temperature stability of our NT-200 system, we monitored W_{ex} and the peak position of **1** relative to the ^2H lock signal of acetone-d_6 along with the temperature of the prestabilized (at 20 °C) air entering the variable-temperature unit.[2] Successive single-scan ^{31}P spectra were recorded after the magnetic field homogeneity had been optimized on the ^{31}P free induction decay of **1**. The results are shown in Figure 3. The observed line width remained relatively constant, but the observed single-scan peak position fluctuated enough to undermine the ability to obtain ultrahigh resolution during long-term signal accumulation. A change in the peak position by 150 mHz (Figure 3) implies a change in the sample temperature of about 80 mdeg (see above). These results indicate the need for improved temperature stability when recording NMR spectra of ^{31}P and other nuclei with very temperature-dependent chemical shifts.

In previous reports[2,6] we demonstrated how improvements in line width and line shape can facilitate the measurement of small scalar coupling constants and secondary isotope effects on chemical shifts in samples of natural isotopic composition. Figure 4 shows a single-scan proton-decoupled ^{31}P NMR spectrum of 1.0 M **1** in acetone-d_6 processed with no digital line broadening or narrowing. The main peak is truncated at 4% of its full peak height and has a W_{ex} of about 62 mHz. The peaks labeled 1–3 correspond to $^1J_{PC}$, $^2J_{PC}$, and $^3J_{PC}$ values of 11.728, 19.733, and 6.871 Hz, respectively, in agreement with reported ones obtained from ^{13}C NMR spectra.[19] The $^2J_{PC}$ and $^3J_{PC}$ satellites are expected to have integrated intensities of 3.3% of the main peak; the experimental value is 3.2%. The $^1J_{PC}$ satellites should have 1.65% the integrated intensity of the main peak; they yield values of 1.5% (downfield) and 1.6% (upfield). The W_{ex} values are about 65 mHz for the $^1J_{PC}$ satellites but increase to about 100 mHz for the $^2J_{PC}$ and $^3J_{PC}$ satellites. These differences are probably the result of differences in the contribution from ^{31}P–^{13}C scalar relaxation and illustrate the ability of ultrahigh resolution to measure effects that would have been considered undetectable in the past. The observation of ^{31}P–^{13}C satellites also yields ^{13}C isotope effects on the ^{31}P chemical shift of **1**. With the use of the notation of Hansen,[20] the values of $^1\Delta P(C)$, $^2\Delta P(C)$, and $^3\Delta P(C)$ obtained from Figure 4 are 22.7, 3.9, and 1.8 ppb, respectively. Few $^n\Delta P(C)$ have been reported.[20]

Concluding Remarks

A diminished instrumental broadening not only improves resolution but also raises the signal-to-noise ratio per scan.[21] Perhaps this is the reason why our single-scan signal-to-noise ratio for the narrow resonance of Figure 2 (not as shown but with optimum digital line broadening) is about 840, while the manufacturer's specification for 0.05 M triphenylphosphine is 280.

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