MULTINUCLEAR FT-NMR USING
THE ANASAZI EFT-60 INSTRUMENT

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ABSTRACT

The purpose of this work was to demonstrate significant examples of the multinuclear NMR capabilities of the recently upgraded Anasazi EFT-60 FT-NMR at Augustana College. Instructional examples include $^{19}$F nmr spectra of NH$_4$ BF$_4$ and Na PF$_6$; $^{11}$B nmr spectra of NH$_4$ BF$_4$; $^{31}$P nmr spectra of (CH$_3$O)$_3$P, PF$_6^-$, and H$_3$PO$_2$; $^1$H spectra of (CH$_3$O)$_3$P and H$_3$PO$_2$.

Keywords

multinuclear nuclear magnetic resonance, spin-spin coupling

INTRODUCTION

Beginning in 1996 the nuclear magnetic resonance instrumentation at Augustana College has been upgraded from CW (continuous wave) to FT (Fourier transform). Initially a Hitachi Perkin Elmer R-24A NMR spectrometer was upgraded from CW to FT-NMR for $^1$H, by Anasazi Instruments, Indianapolis, IN. In 1998 another CW instrument was acquired, a Varian EM-360A NMR spectrometer. In August 1998, Anasazi Instruments upgraded this to an Anasazi EFT-60 NMR spectrometer, providing extensive multinuclear nmr capability. This includes $^1$H, $^{13}$C, $^{19}$F, and numerous other nuclei in the range of 11.26 to 25 MHz with the original $^1$H at 60.01 MHz, such as $^{31}$P, $^{11}$B, $^{29}$Si, $^{79}$Br, $^{59}$Co, and $^{23}$Na. The nuclei listed have been observed in this laboratory so far. Altogether, 42 nuclei of 34 elements fall in the observable frequency range. (Drago, 1992; Pople, 1959)

METHODS

Using the Anasazi EFT-60 FT-NMR, standard pulse sequences were used to acquire free induction decay (FID) data. Fourier transform converted the spectrum from time domain to frequency domain. (Drago, 1992). Nuclei observed include $^1$H, I=1/2, at 60.010 MHz; $^{19}$F, I=1/2, at 56.461 MHz; $^{11}$B, I=3/2, at 19.246 MHz; and $^{31}$P, I=1/2, at 24.292 MHz. Samples used were reagent grade chemicals.
RESULTS AND DISCUSSION

The $^{11}$B nmr spectrum of the BF$_4^-$ ion was run, showing the spin-spin coupling of the four $^{19}$F with the $^{11}$B nucleus.

Note that the $^{11}$B resonance is split by spin-spin coupling to the four equivalent $^{19}$F in the tetrahedral BF$_4^-$ ion. $^{19}$F has I=1/2. Expected intensities are 1:4:6:4:1 in this quintuplet. The spin-spin coupling constant was $J_{BF} = 1.2$ Hz.

Boron has two isotopes. $^{10}$B has a spin of I=3 and an abundance of 19.58%. $^{11}$B has a spin of I=3/2 and an abundance of 80.42%. Its nmr frequency is 19.246 MHz, nicely within the range of our instrument. For nuclei with I > 1/2, there is a nuclear quadrupole moment which can be a problem, in terms of broadening spectral lines. However in high symmetry environments, specifically tetrahedral or octahedral, the nuclear quadrupole moment is not a problem. So the tetrahedral BF$_4^-$ ion was an excellent case to study, as illustrated here.

The $^{19}$F nmr spectrum of NH$_4$(BF$_4$) was examined. It is expected to show a quartet of lines of equal intensity for the splitting of the $^{19}$F resonance by $^{11}$B with I=3/2, with $J_{BF} = 1.1$ Hz. $^{11}$B is the more abundant isotope. The 4 line multiplet corresponds to 2I+1 = 4. $^{10}$B, the less abundant isotope, has I=3 so that 2I+1 = 7 lines should occur in its multiplet. These were not quite resolved, and the chemical shift for $^{10}$BF$_4^-$ was slightly different than that for $^{11}$BF$_4^-$ in the $^{19}$F nmr spectrum.
A good example of a $^{31}$P nmr spectrum was that of $(\text{CH}_3\text{O})_3\text{P}$. The splitting of the $^{31}$P resonance by the nine equivalent $^1$H nuclei was expected to give a 10 line multiplet, with relative intensities 1:9:36:84:126:126:84:36:9:1. 8 lines were clearly visible, with the intensities of the first and last of the 10 lines too low to distinguish from noise. $J_m = 10.6$ Hz was the observed splitting.

The $^1$H spectrum gives $J_{PH} = 10.7$ Hz.
Hypophosphorous acid, \( \text{H}_2\text{PO}_2\) (aq) has a distinctive structure with two \( \text{P}-\text{H} \) bonds and one \( \text{O}-\text{H} \) bond. The \( ^{31}\text{P} \) nmr spectrum is a triplet, with \( J_{zz} = 573 \) Hz, a very substantial splitting.
As a final example, two nmr spectra, for \(^{31}\)P and \(^{19}\)F, were observed for NaPF\(_6\) with its octahedral PF\(_6\)\(^-\) ion. In the \(^{31}\)P spectrum, the measured coupling constant was \(J_{PF} = 714\) Hz.

In the \(^{19}\)F spectrum, the measured coupling constant was essentially the same, \(J_{PF} = 717\) Hz.

CONCLUSION

Significant examples of the multinuclear NMR capabilities of the recently upgraded Anasazi EFT-60 FT-NMR at Augustana College have been successfully demonstrated. Spectra have been observed thus far for \(^1\)H, \(^{13}\)C, \(^{19}\)F, \(^{31}\)P, \(^{11}\)B, \(^{29}\)Si, \(^{79}\)Br, \(^{59}\)Co, and \(^{23}\)Na. Altogether, 42 nuclei of 34 elements fall in the observable frequency range of 11.26 to 25 MHz along with the vicinity of 60 MHz.
LITERATURE CITED


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