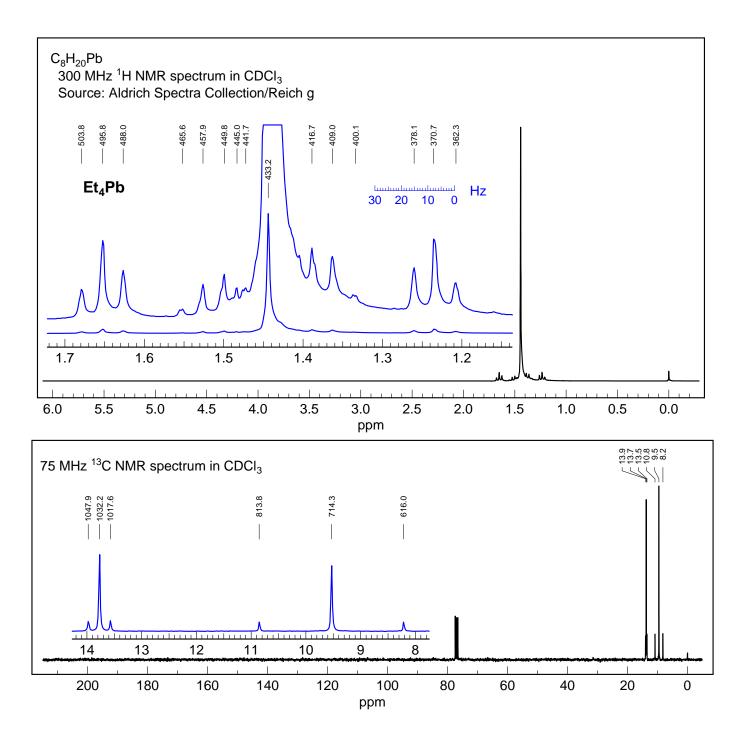
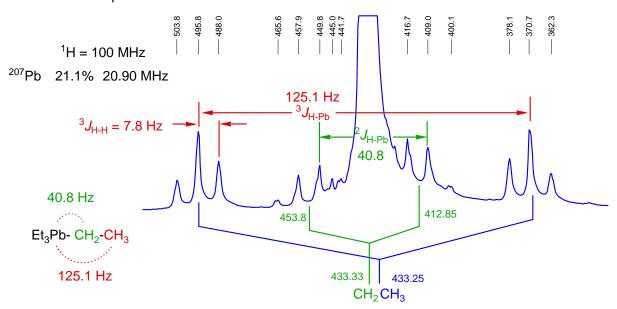
**Exercise**: Determine all available couplings ( $J_{HH}$ ,  $J_{HPb}$ ,  $J_{CPb}$ ), and measure the chemical shift difference between the CH<sub>3</sub> and CH<sub>2</sub> protons (the CH<sub>3</sub> and CH<sub>2</sub> protons of the A<sub>3</sub>B<sub>2</sub> system are too close together to resolve in the central peak).



## **Answer**

Lead has one spin 1/2 isotope, <sup>207</sup>Pb, which is 21.1% abundant (so satellites are easily seen). The central peak is a singlet due to the superposition of the CH<sub>3</sub> and CH<sub>2</sub> signals, providing almost no structural information. The satellites are readily identified, and allow analysis of the coupling and shifts.

**Problem R-21M** C<sub>8</sub>H<sub>20</sub>Pb 300 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> Source: Aldrich Spectra Collection/Reich



Although the central peaks for the  $\mathrm{CH}_2$  and  $\mathrm{CH}_3$  protons are almost superimposed so that neither the chemical shift nor the coupling between them can be measured, the satellites are well separated. Thus the chemical shift difference between  $\mathrm{CH}_2$  and  $\mathrm{CH}_3$  protons is the difference between the centers of the two sets of satellites, about 0.1 Hz. Of course, such a small effect could also be an isotope shift.

It is interesting to note that the NMR spectrum pf Et<sub>4</sub>Pb at 300 MHz shown here looks identical to the one at 40 MHz (Narasimhan, Rogers) this is because the chemical shift between the protons is almost 0, and all of the line separations are governed by coupling constants which are field independent.

The <sup>13</sup>C NMR spectrum:

