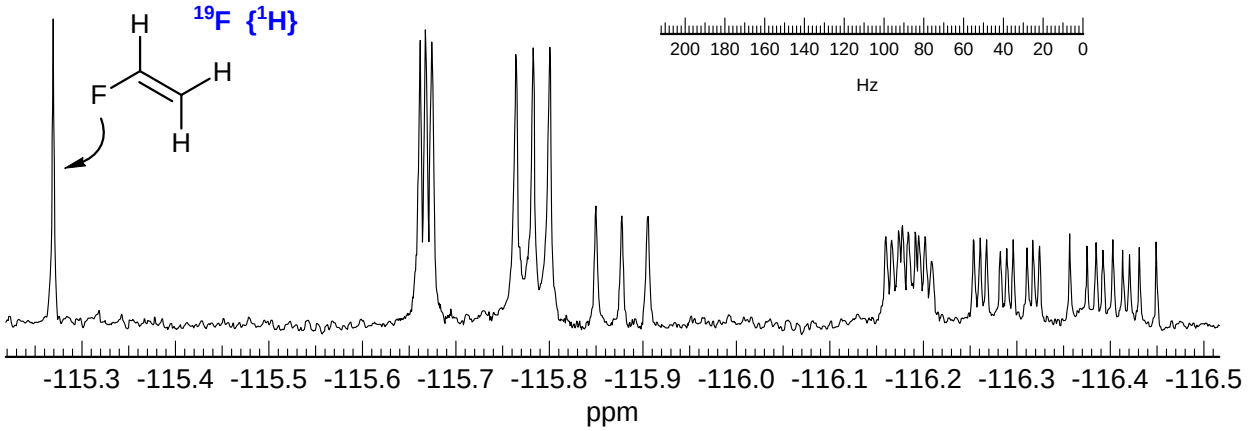
20

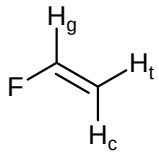
Problem R-10N. Below is a proton decoupled 470.4 MHz ^{19}F NMR spectrum of vinyl fluoride and several deuterated isotopomers. Analyze the spectrum. (Morton *J. Am. Chem. Soc.* **1992**, *114*, 7127)



(a) Draw below the compounds which give the signals between -115.9 and -115.6 ppm. Report couplings and chemical shifts. Briefly explain your assignments.

(b) Draw below the compounds which give the signals between -116.5 and -116.1 ppm. Report couplings and chemical shifts.

(c) From the information collected above calculate the gem, trans and cis F-H couplings of vinyl fluoride. Show your work.



$^{2}J_{F\text{-}Hg}$ = _____ Hz

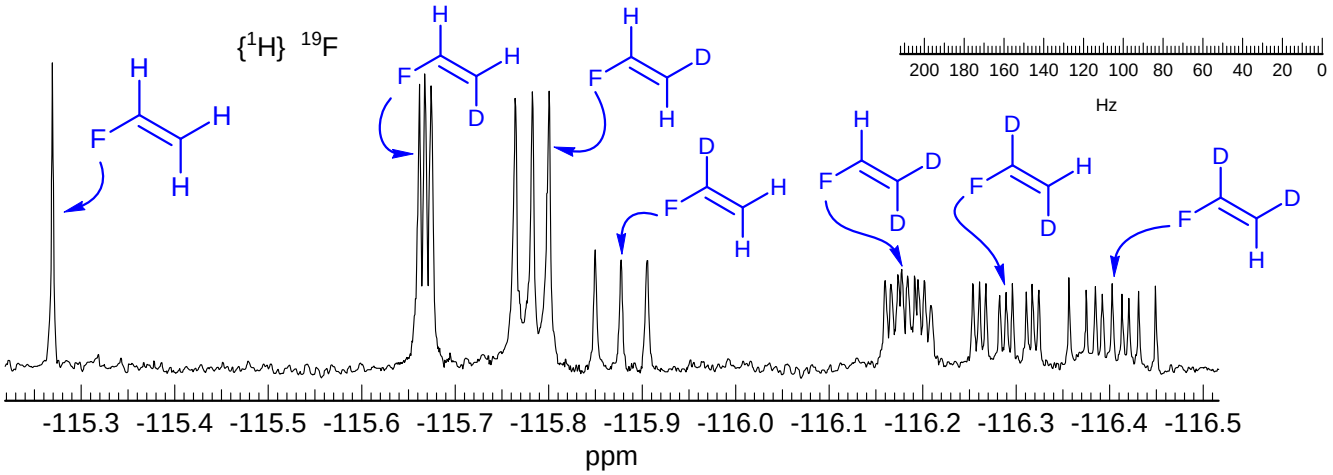
$^{3}J_{F\text{-}Ht}$ = _____ Hz

$^{3}J_{F\text{-}Hc}$ = _____ Hz

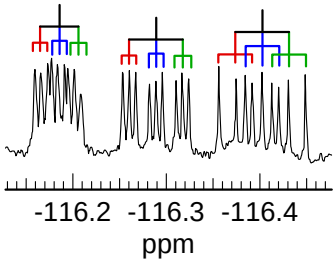
(d) Estimate the ^{19}F chemical shift of the trideutero isotopomer.

20

Problem R-10N. Below is a proton decoupled 470.4 MHz ^{19}F NMR spectrum of vinyl fluoride and several deuterated isotopomers. Analyze the spectrum. (Morton *J. Am. Chem. Soc.* **1992**, *114*, 7127)



(a) Draw below the compounds which give the signals between -115.9 and -115.6 ppm. Report couplings and chemical shifts. Briefly explain your assignments.



These are the mono-deuterated vinyl fluorides

δ -115.67 1:1:1 t, $^3J_{FD}$ = 2.9 Hz, smallest J and smallest Δδ (0.40 ppm), F/D cis

δ -115.78 1:1:1 t, $^3J_{FD}$ = 8.5 Hz, $J_{trans} > J_{cis}$, medium Δδ (0.51 ppm), F/D trans

10

δ -115.88 1:1:1 t, $^2J_{FD}$ = 13.2 Hz, 2-bond will be largest Δδ (0.61 ppm), F/D gem

Assignment of the two largest couplings (trans and gem) is not simple - after all, in alkenes $^2J_{HH}$ is the smallest of the three couplings. It is the size of the deuterium isotope shift that allows a firm assignment (2-bond shift > *trans* 3-bond > *cis* 3-bond)

(b) Draw below the compounds which give the signals between -116.5 and -116.1 ppm. Report couplings and chemical shifts.

These are the di-deuterated vinyl fluorides

δ -116.18 1:1:1 t of 1:1:1 t, $^3J_{FD}$ = 8.5 (trans), 3 (cis) Hz, two smallest *J* and Δδ

δ -116.29 1:1:1 t of 1:1:1 t, $^2J_{FD}$ = 13, $^3J_{FD}$ (cis) = 3 Hz

δ -116.40 1:1:1 t of 1:1:1 t, $^2J_{FD}$ = 13, $^3J_{FD}$(trans) = 8.5 Hz, two largest *J* and Δδ

6

(c) From the information collected above calculate the *cis*, *trans* and *gem* F-H couplings of vinyl fluoride. Show your work.

$^2J_{F\text{-}Hg}$ = 86.0 Hz 13.2 x 6.515 = 86.0

$^3J_{F\text{-}Ht}$ = 55.4 Hz 8.4 x 6.515 = 55.4

4

$^3J_{F\text{-}Hc}$ = 18.9 Hz 2.9 x 6.515 = 18.9

$\frac{\gamma_H}{\gamma_D} = \frac{100}{15.35} = 6.515$

(d) Estimate the ^{19}F chemical shift of the trideutero isotopomer.

δ_{gem} = 115.88-115.27 = 0.61

δ_{cis} = 115.67-115.27 = 0.40

δ_{trans} = 115.78-115.27 = 0.51

116.18 + 0.61 = 116.79

116.40 + 0.40 = 116.80

116.29 + 0.51 = 116.80

We are assuming the isotope shifts are additive, which is nearly correct.