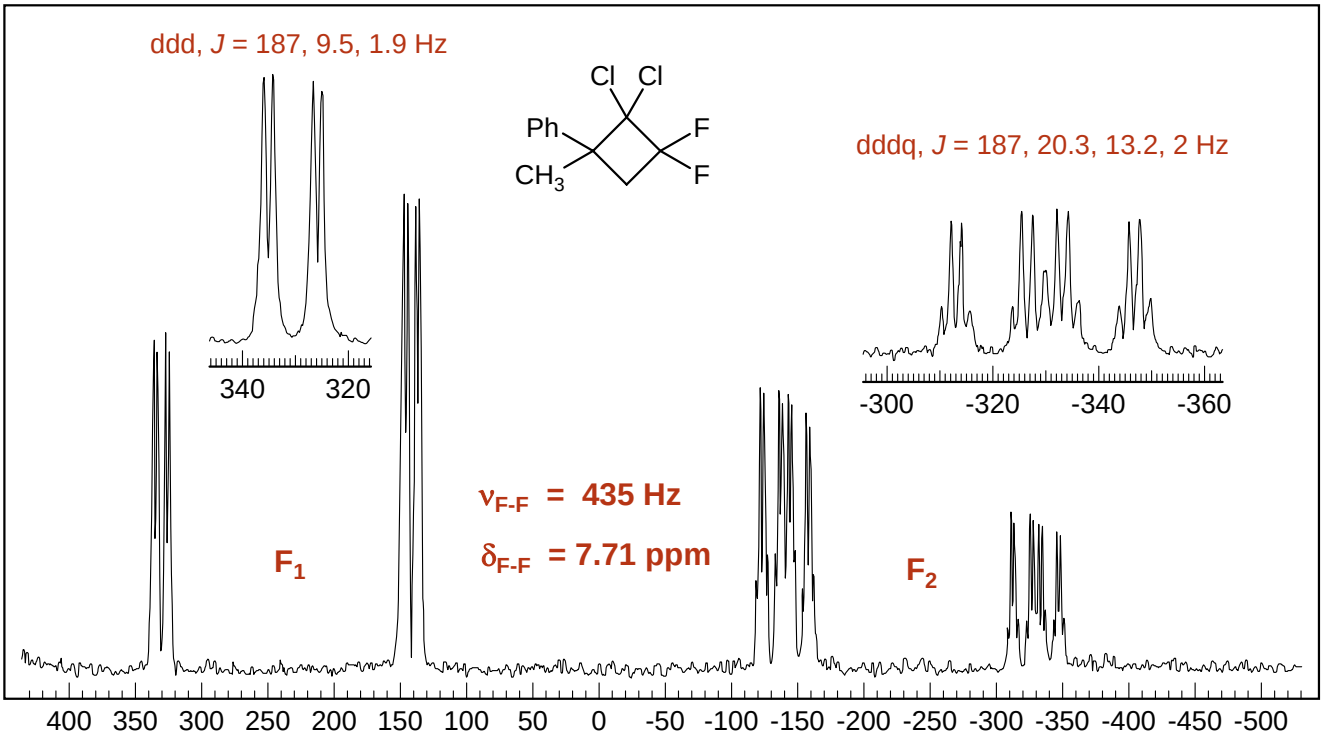
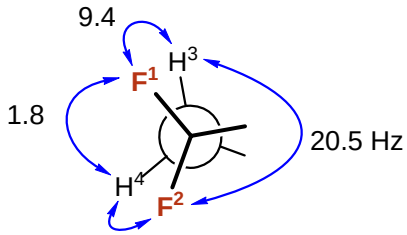
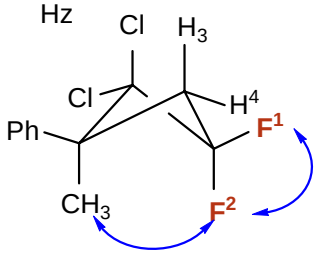
Problem Set 11 - Partial Answers

Problem R-310 ($C_{11}H_{10}Cl_2F_2$). Interpret the 56.4 MHz ^{19}F NMR spectrum below (CCl_4 solvent). Determine the chemical shifts of the fluorines, and estimate the various coupling constants. Consider conformations of the cyclobutane ring (*J. Am. Chem. Soc.* **1962**, *84*, 2935).





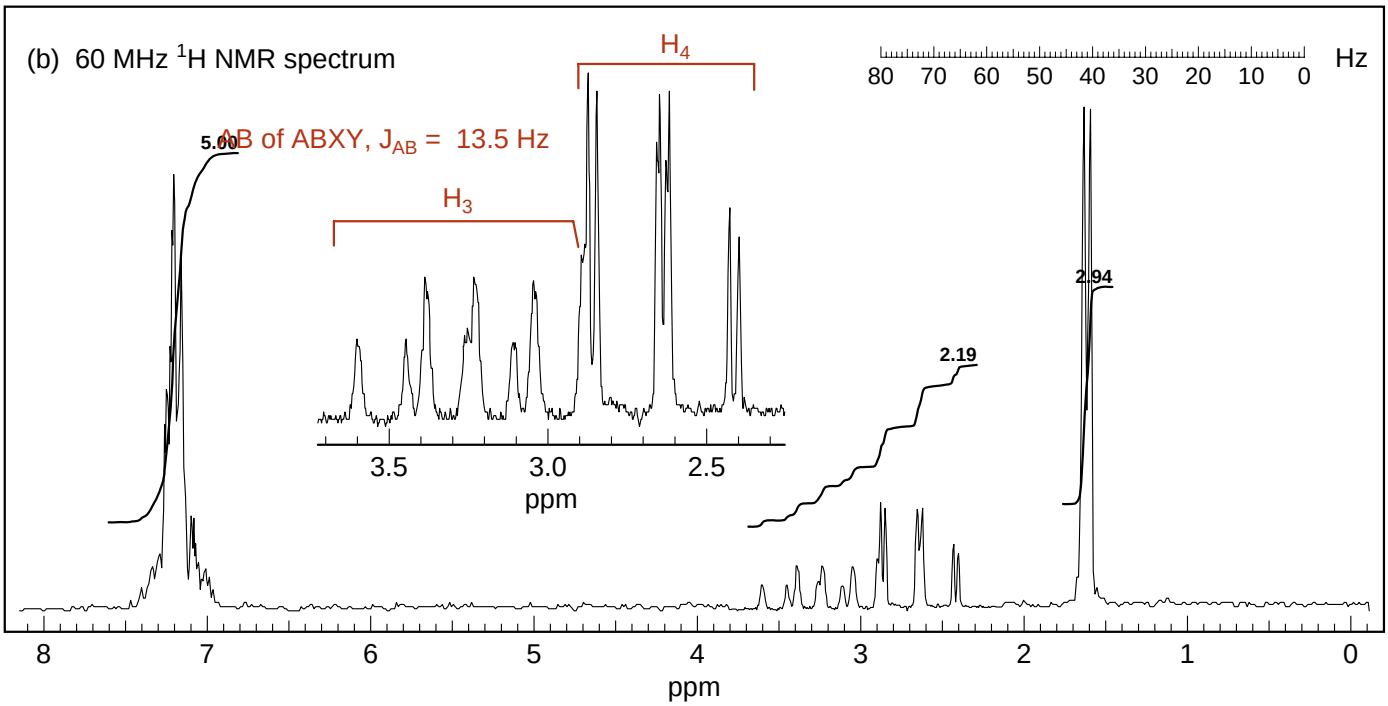
$^3J_{F\text{-}H}$ = 13.7 Hz



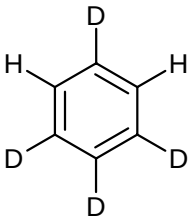
$^2J_{F\text{-}F}$ = 187 Hz

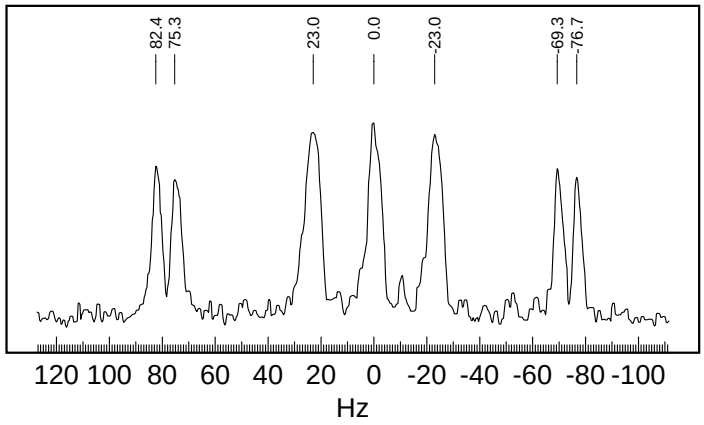
$^5J_{F\text{-}H}$ = 2 Hz

Sca



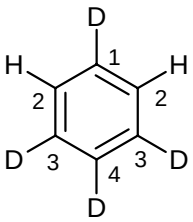
Problem R-311 ($C_6H_3D_3$). Assign the peaks in the ^{13}C NMR spectrum below. The spectrum is not ^{1}H decoupled. Estimate the coupling constants (*J. Am. Chem. Soc.* **1967**, *88*, 2967).

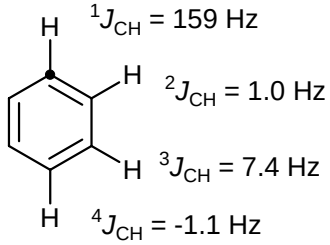




ANSWER

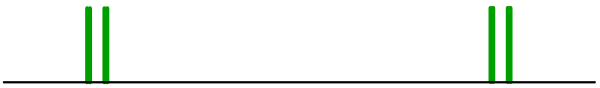
There are four kinds of carbons in this molecule



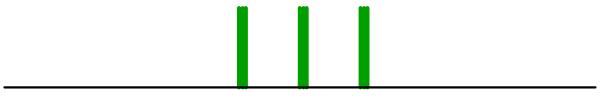


1: The only significant coupling is $^{1}J_{CD}$ = 23 Hz. The $^{2}J_{CH}$ will be 1 Hz, too small to resolve

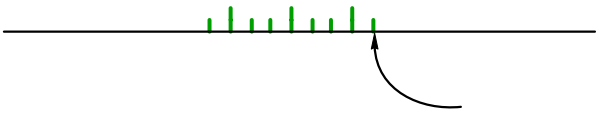
2: This carbon will be a double intensity dd, with $^{1}J_{CH}$ = 159 Hz and $^{3}J_{CH}$ = 7 Hz. There will also be a $^{2}J_{CD}$ of about 1Hz, too small to resolve



3: Carbon 3 will be a double intensity 1:1:1 triplet of 1:1:1 triplets, $^{1}J_{CD}$ = 23 Hz and $^{3}J_{CD}$ = 1 Hz

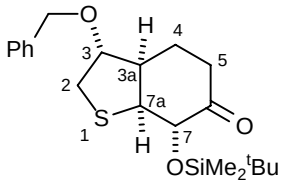


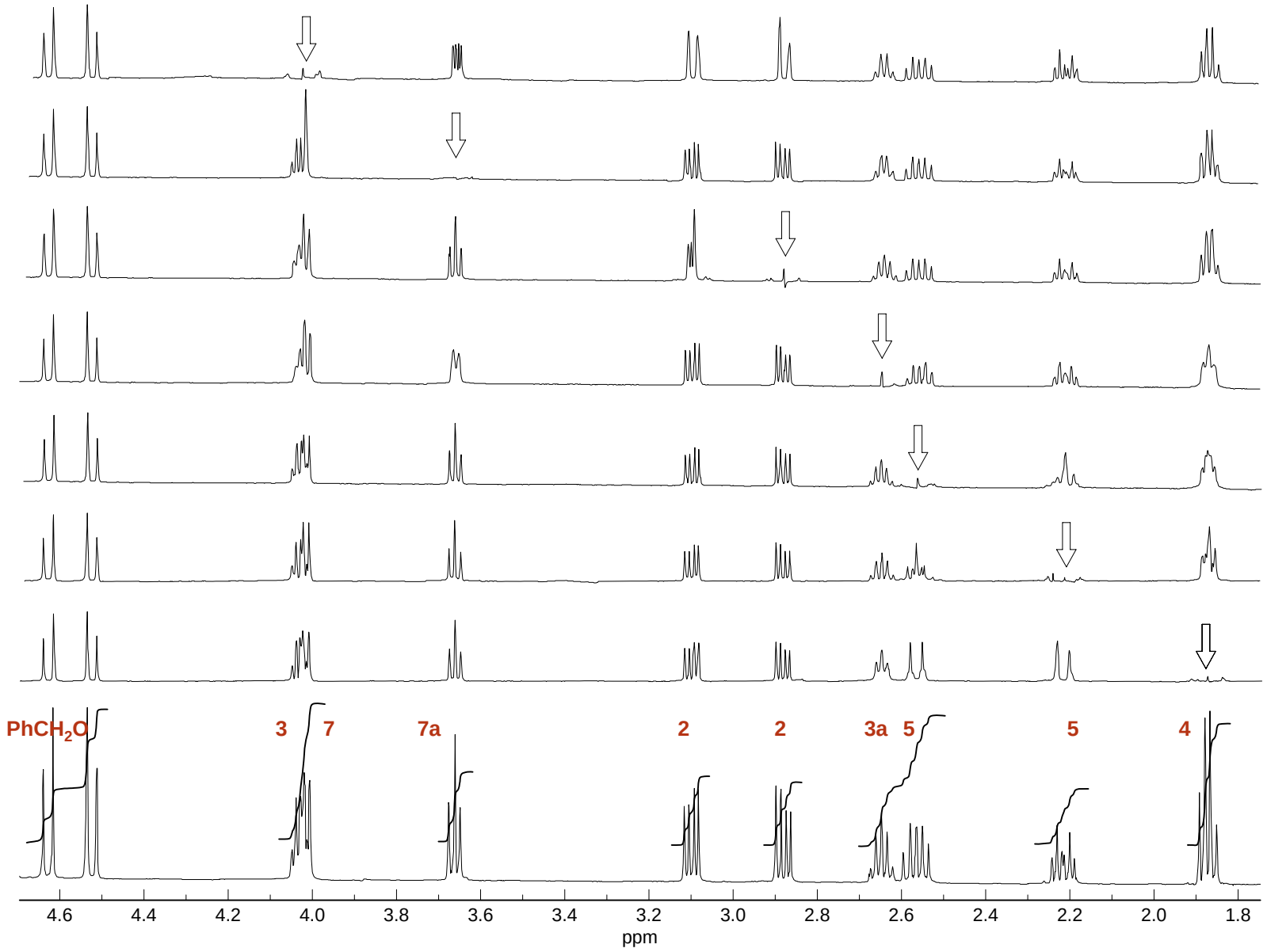
4: Carbon 4 will be a 1:1:1 triplet of 1:2:1 triplets, $^{1}J_{CD}$ = 23 Hz and $^{3}J_{CH}$ = 7 Hz the outer lines of the triplets are too small to be visible



These outer triplet peaks will be approximately 1/16 of the intensity of the superimposed central peaks, hence not detectable at this signal to noise

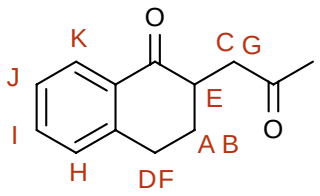
Problem R-28C ($C_{21}H_{32}O_3SSi$). Use the 500 MHz ($CDCl_3$) homonuclear decoupled spectra below to assign the protons of the compound shown. Source: Mark Matulenko/Burke



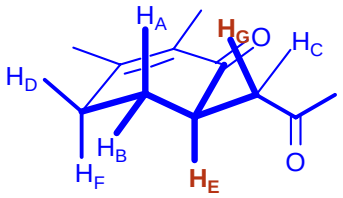


Problem R-28D ($C_{13}H_{14}O_2$)
500 MHz ^{1}H NMR in $CDCl_3$
Source: Wilds/C. Fry (C82)

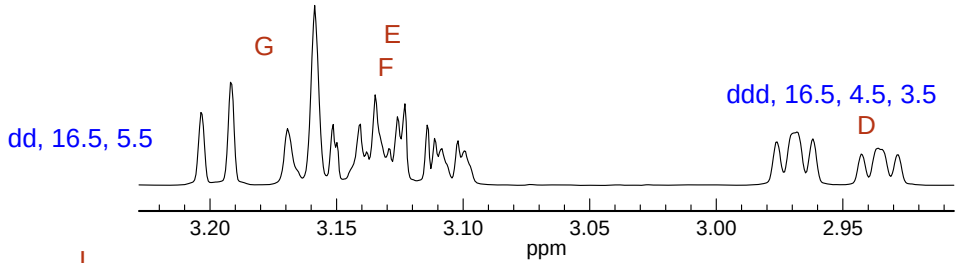
Assign all protons in this spectrum, using the 500 MHz ^{1}H NMR spectrum, and the 300 MHz COSY spectrum. The 300 MHz ^{1}H spectrum is also provided. Explain specifically why some of the peaks are more complicated in the 300 compared to the 500 MHz spectrum. Draw a conformation, and label with chemical shifts.

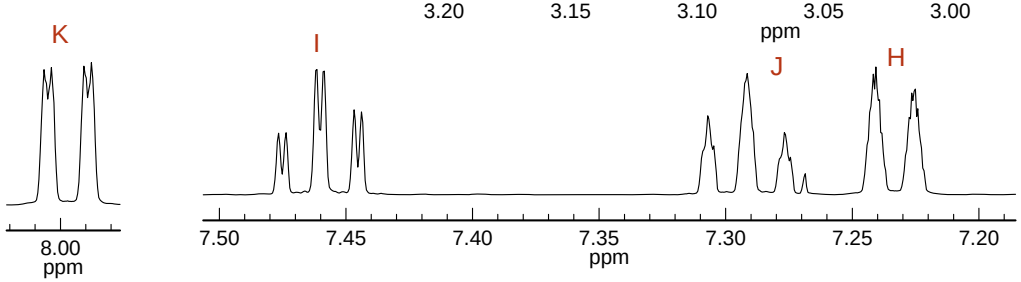


Answer



The protons G and E are very close in chemical shift, and are coupled to each other. This leads to virtual coupling effects, with H_C, H_A and H_B (all of which are coupled to H_E/H_G) showing complications. The "virtual coupling" effects are particularly pronounced because the coupling between H_G/H_C and H_E/H_C have different signs.





A	B	C
13 (AB)	13 (BA)	16.5 (CG)
13 (AF)	4.5 (BF)	5.5 (CE)
13 (AE)	4.5 (BE)	
4.5 (AD)	3.4 (BD)	

D	E	F	G
16.5 (DF)	13 (AE)	16.5 (DF)	16.5 (GC)
4.5 (DA)	4.5 (BE)	13 (AF)	5.5 (GE)
3.5 (DB)	5.5 (CE)	4.5 (BF)	
	5.5 (GE)		

E and F are badly overlapped, hard to confirm the coupling