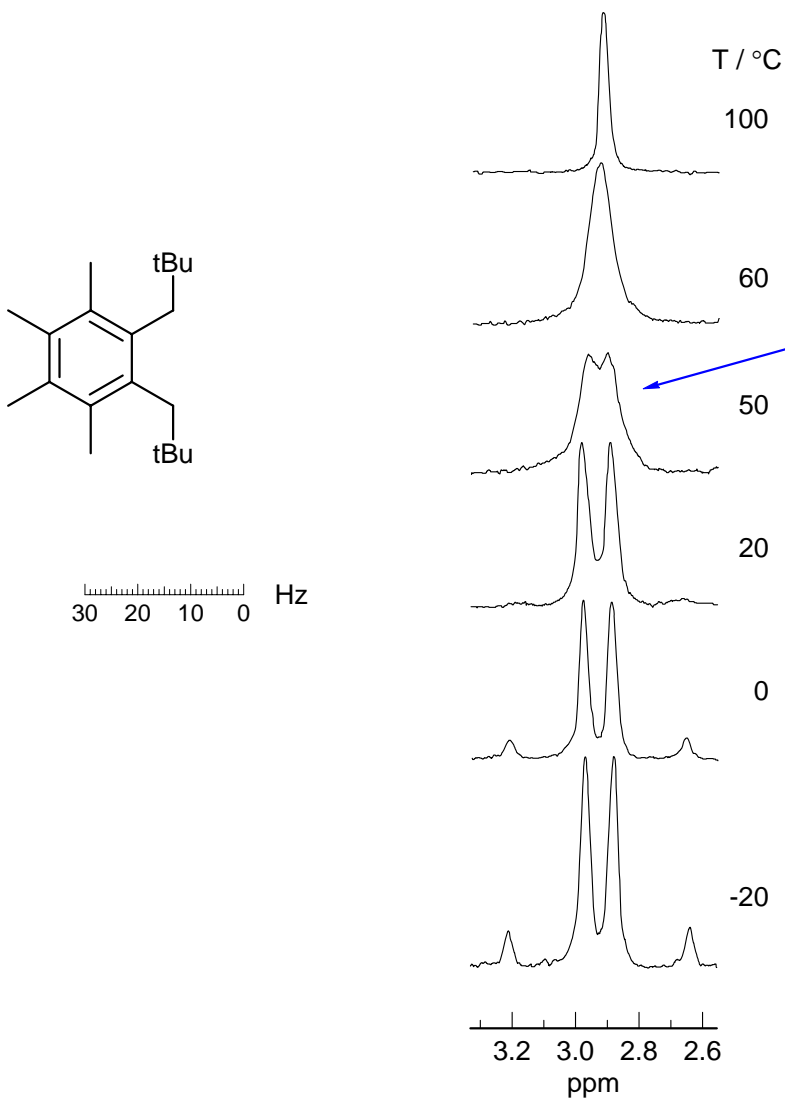


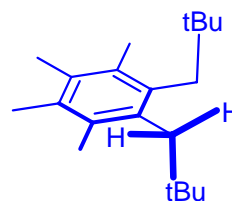
Problem Set 13 - answers

Problem R-03N ($C_{20}H_{34}$): Interpret the 60 MHz variable temperature 1H NMR spectrum of 1,2-dineopentyl-3,4,5,6-tetramethylbenzene in CCl_4 . Source: Dix, D. T.; Fraenkel, G.; Karnes, H. A.; Newman, M. S. *Tetrahedron Lett.* **1966**, 517



k is approximately 31/sec at this temperature (from line shape calculation using WINDNMR)

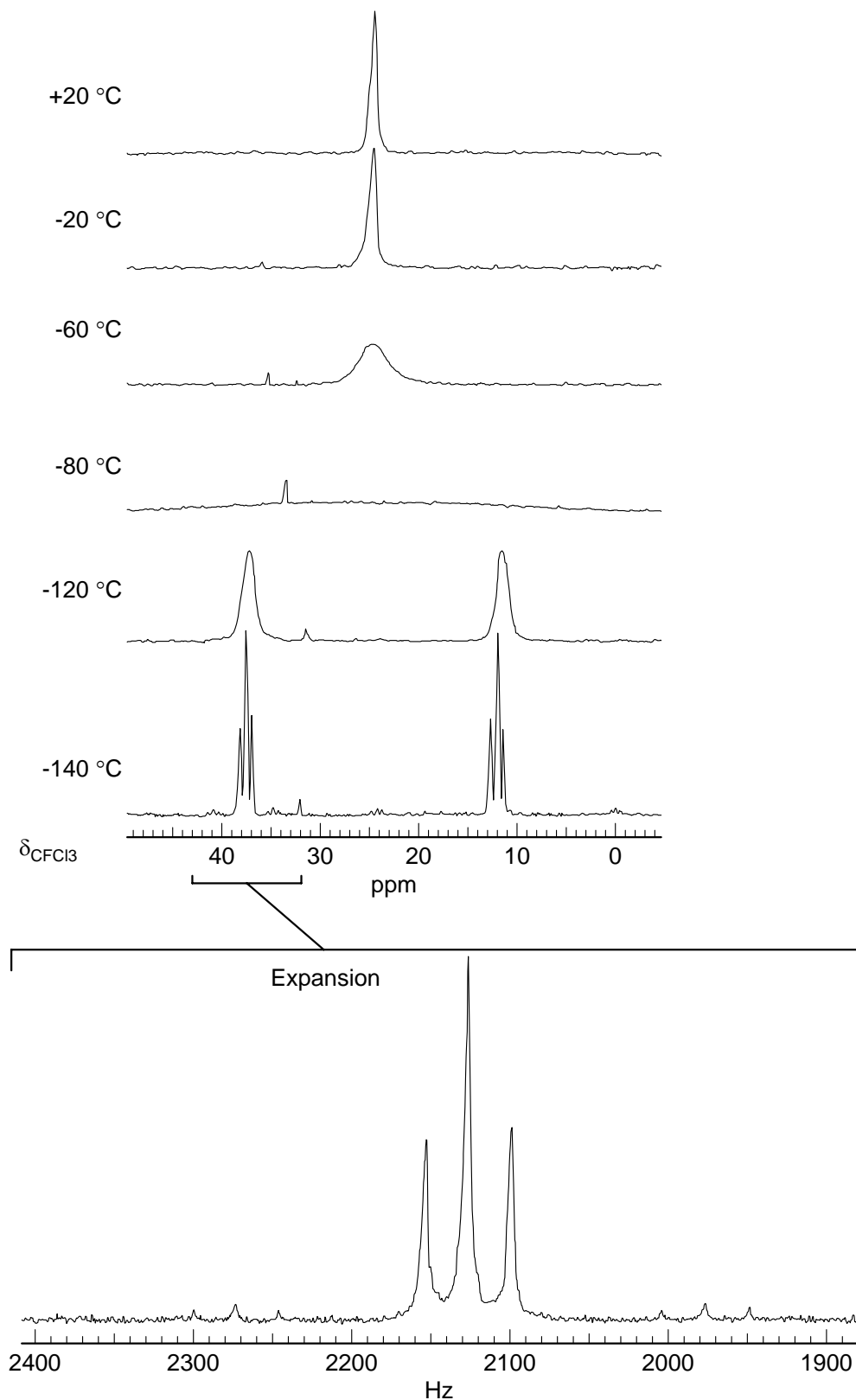
The protons broaden and coalesce as the rotation rate increases



When rotation is slow around the Ar- CH_2 bond, the benzyl protons become diastereotopic, forming an AB quartet.

Problem R-312. Below are presented variable temperature 56.4 MHz ^{19}F NMR spectra of SeF_4 . From your knowledge of structure of compounds like SF_4 and SeF_4 interpret the NMR spectra.

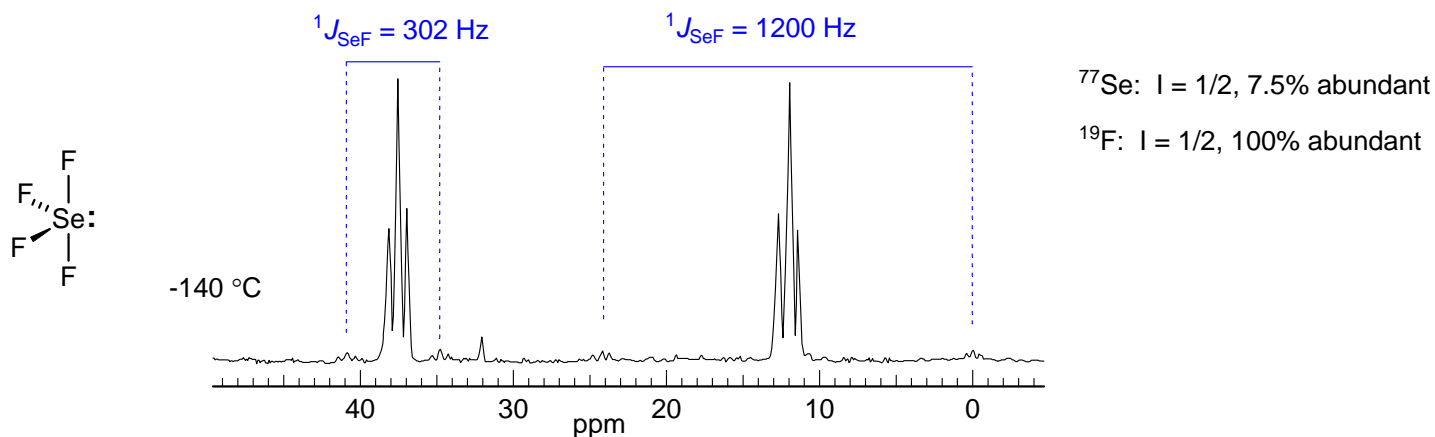
What conclusion can be drawn from the observation that the $+20^\circ\text{C}$ spectrum does not show the weak peaks flanking the low temperature triplets (see expansion)? (*Z. Anorg. Allg. Chem.* **1975**, 416, 12).



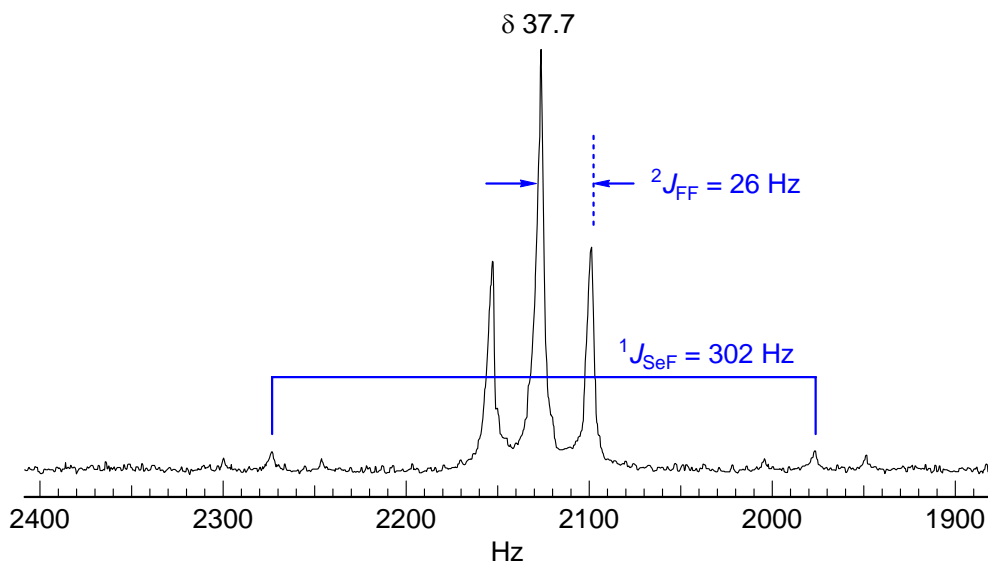
Problem R-312. Below are presented variable temperature 56.4 MHz ^{19}F NMR spectra of SeF_4 . From your knowledge of structure of compounds like SF_4 and SeF_4 interpret the NMR spectra.

What conclusion can be drawn from the observation that the $+20^\circ\text{C}$ spectrum does not show the weak peaks flanking the low temperature triplets (see expansion)? (*Z. Anorg. Allg. Chem.* **1975**, 416, 12).

Problem R-312. This type of hypervalent molecule has trigonal bipyramidal structure, with one site unoccupied. At -140°C the molecule is static on the NMR time scale (slow Berry pseudorotation), giving an A_2X_2 pattern consisting of two triplets, with $\delta_{\text{A}} = 37.7$ and $\delta_{\text{X}} = 12.1$, $J_{\text{AX}} = 26$ Hz



The small triplets are ^{77}Se satellites on the ^{19}F signals due to the 7.5% abundance of the spin 1/2 selenium isotope



The coalescence between the two triplets is the result of equilibration between the axial and equatorial fluorines. There are two possible mechanisms - one is the "Berry pseudorotation" process where the axial and eq fluorine trade places through a square pyramidal intermediate, or an intermolecular exchange of fluorines, which would also average the two shifts.

The absence of ^{77}Se satellites in the high-temperature spectrum means that the exchange must be intermolecular (fluorine transfer between molecules), which would cause loss of Se-F coupling in addition to averaging of the chemical shifts. A Berry pseudorotation mechanism would retain the Se-F coupling, and the final coalesced singlet would have singlet ^{77}Se satellites on the fluorine NMR peak. Their separation would be the average of the two low-temperature J values.

Problem R-99P ($C_{63}H_{85}B_2O_{15}P_5Pt$). This problem requires you to interpret the 36.43 MHz ^{31}P variable temperature NMR spectra of a platinum phosphite complex $Pt[P(OCH_3)_3]_5^{++} 2BPh_4^-$. The spectrum was taken with proton decoupling.

(a) Analyze the low temperature (-151 °C) spectrum. Explain the origin of each of the marked peaks a to e with reference to the structure of the compound. Report coupling constants. Use the form $^nJ_{X-Y} = 00.0$ Hz. In your drawings, feel free to use "P" for the $P(OCH_3)_3$ group. Hint: make sure you consider the NMR active isotope(s) of platinum.

Peak a:

Peak b:

Peak c:

Peak d:

Peak e:

(b) What molecular process is responsible for the changes in the NMR spectrum as a function of temperature? Is it intra- or intermolecular? Explain how you know.

(c) For the spectra at -98 °C and -69 °C, explain why peak f is broad and peak h is relatively sharp (at still higher temperature both f and h become sharp).

Problem R-99P ($C_{63}H_{85}B_2O_{15}P_5Pt$).

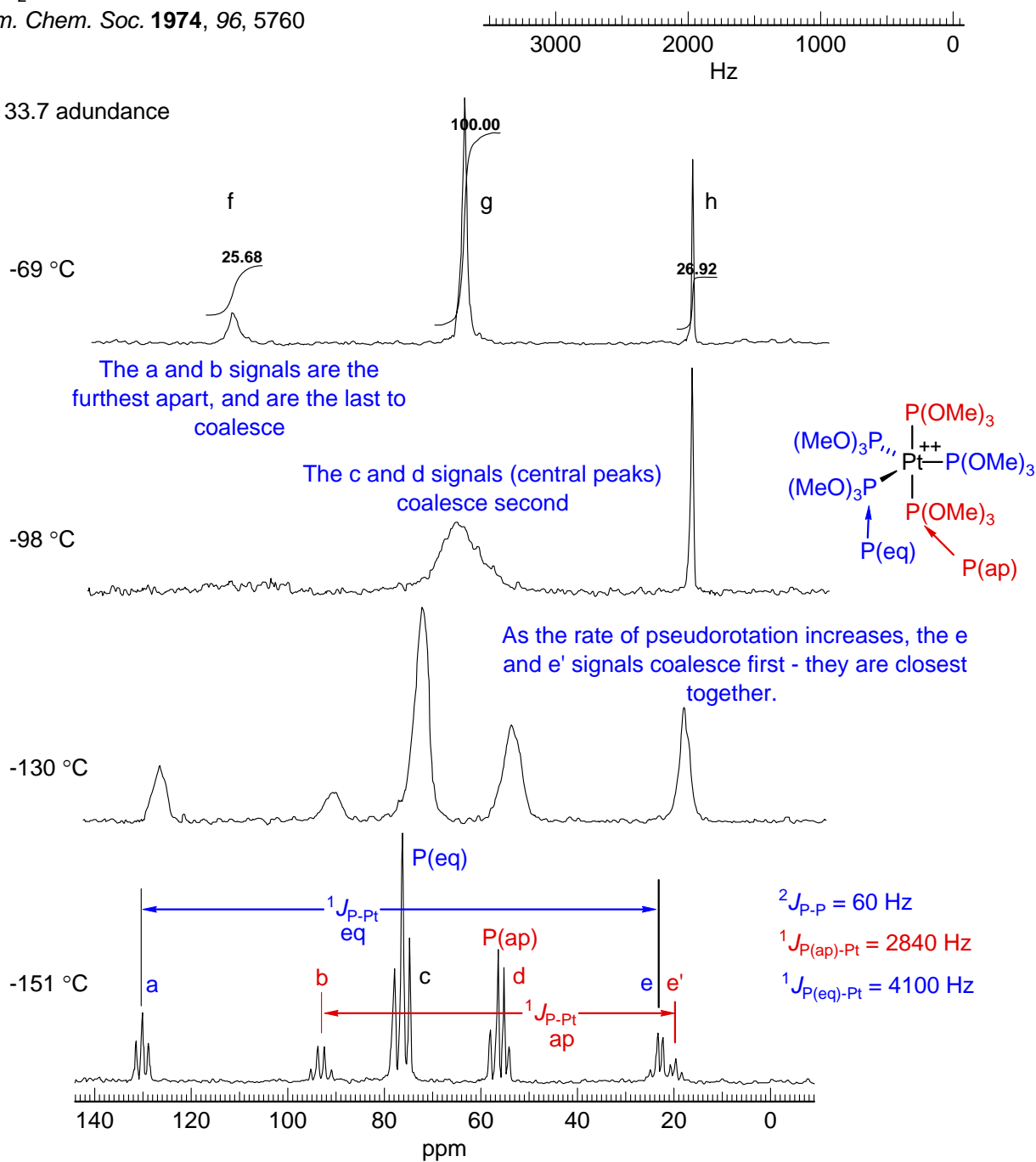
Temperature dependent 36.43 MHz $\{^1H\}$ ^{31}P NMR Spectra

$Pt[P(OCH_3)_3]_5^{2+} 2B(C_6H_5)_5^-$

Solvent: $CHClF_2$

(Source: *J. Am. Chem. Soc.* **1974**, 96, 5760)

^{195}Pt I = 1/2, 33.7 abundance



In the low-temperature spectrum there are distinct ^{31}P signals for the apical and equatorial P - the apical a triplet, the equatorial a quartet due to P-P coupling. Each one has ^{195}Pt satellites, which are also triplets and quartets. The e and e' signals are quite close, and coupled to each other, so there is a lot of leaning, much less for the a and b signals (also coupled to each other) since they are far apart. The fact that the e and e' signals coalesce with each other to form h, and the a and b signals to form f, proves that the sign of the PtP coupling constant is the same for the apical and equatorial P (not surprising).