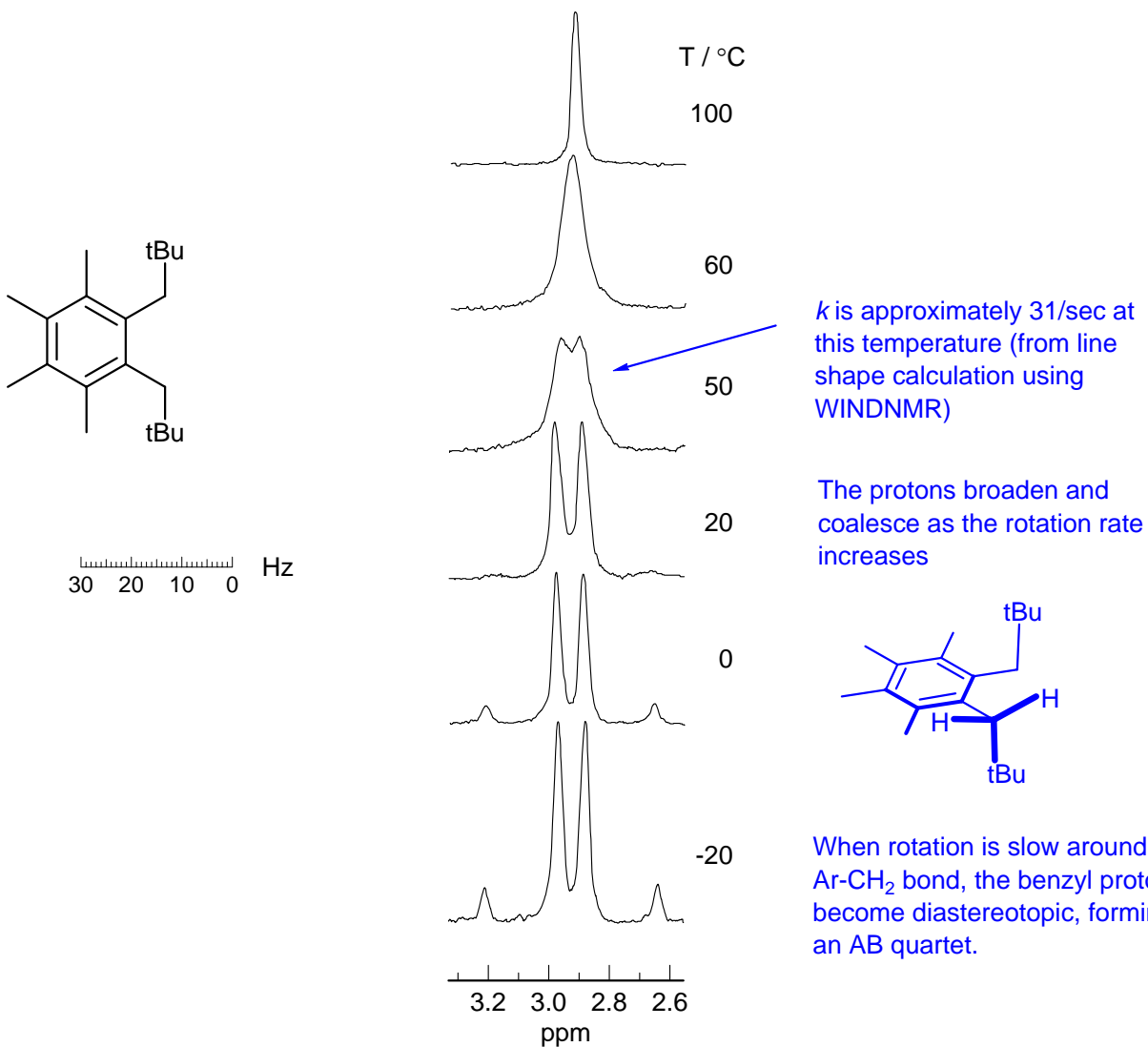# Problem Set 13 - answers

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.

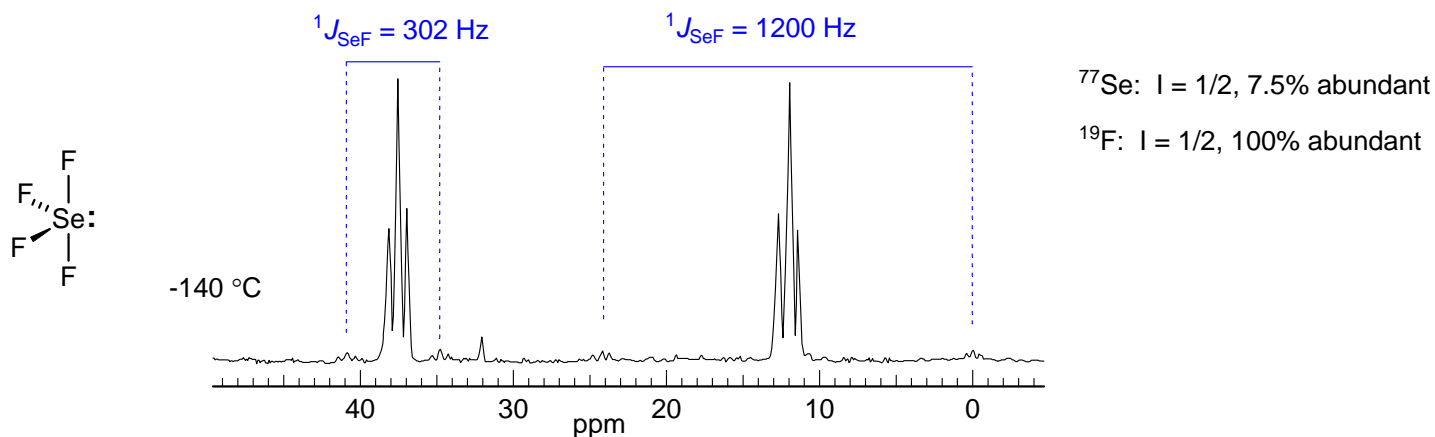What conclusion can be drawn form the observation that the +20 °C spectrum does not show the weak peaks flanking the low temperature triplets (see expansion)? (*Z. Anorg. Allg. Chem.* **1975**. *416*, 12).
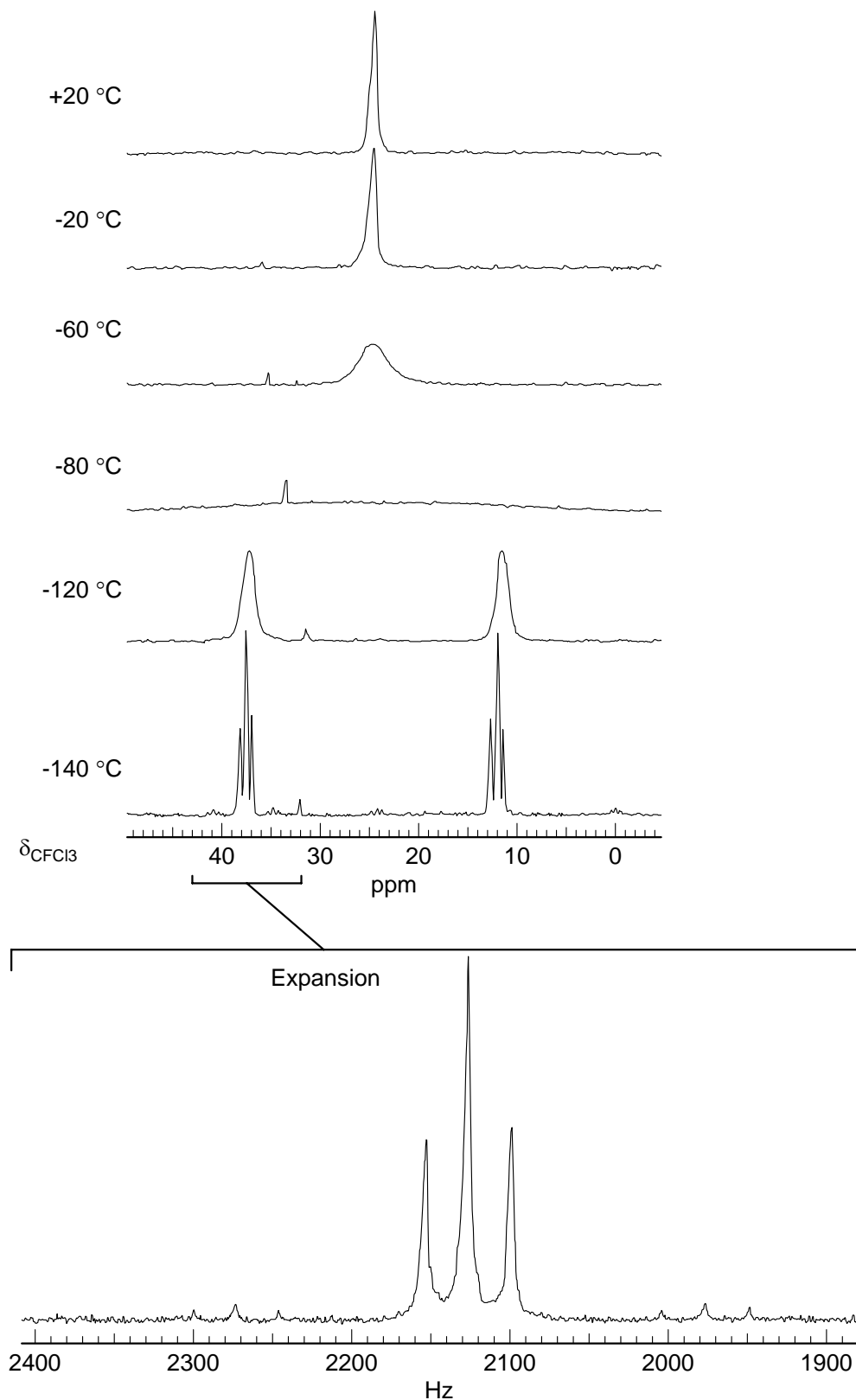
Problem R-312. Below are presented variable temperature 56.4 MHz ^{19}F NMR spectra of SeF_4. From your knowledge of structure of compounds like SF_4 and SeF_4 interpret the NMR spectra.

What conclusion can be drawn form the observation that the +20 °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 $\delta_A = 37.7$ and $\delta_X = 12.1$, $J_{AX} = 26$ Hz

$^1J_{SeF} = 302$ Hz $^1J_{SeF} = 1200$ Hz

^{77}Se: I = 1/2, 7.5% abundant

^{19}F: I = 1/2, 100% abundant

-140 °C

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

δ 37.7

$^2J_{FF} = 26$ Hz

$^1J_{SeF} = 302$ Hz
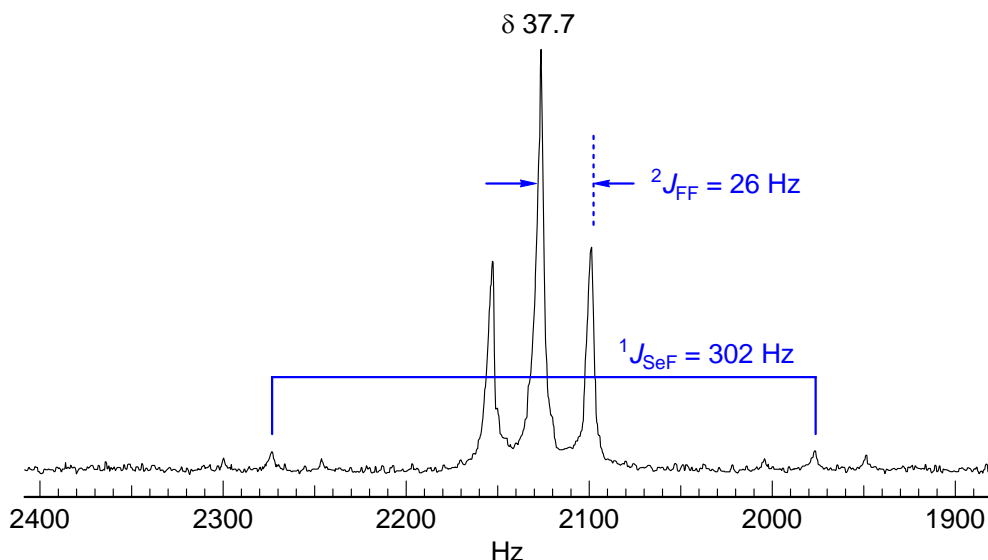
The coalescence between the two triplets is the result of equilibration between the axial and equatorial fluorines. There are two possible mechanisms - one is the "Berry pseudorotation" process where the exial and eq fluorine trade places through a square pyramidal intermediate, or an intermolecular 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 (751 Hz).

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 ($C_{63}H_{85}B_2O_{15}P_5Pt$).

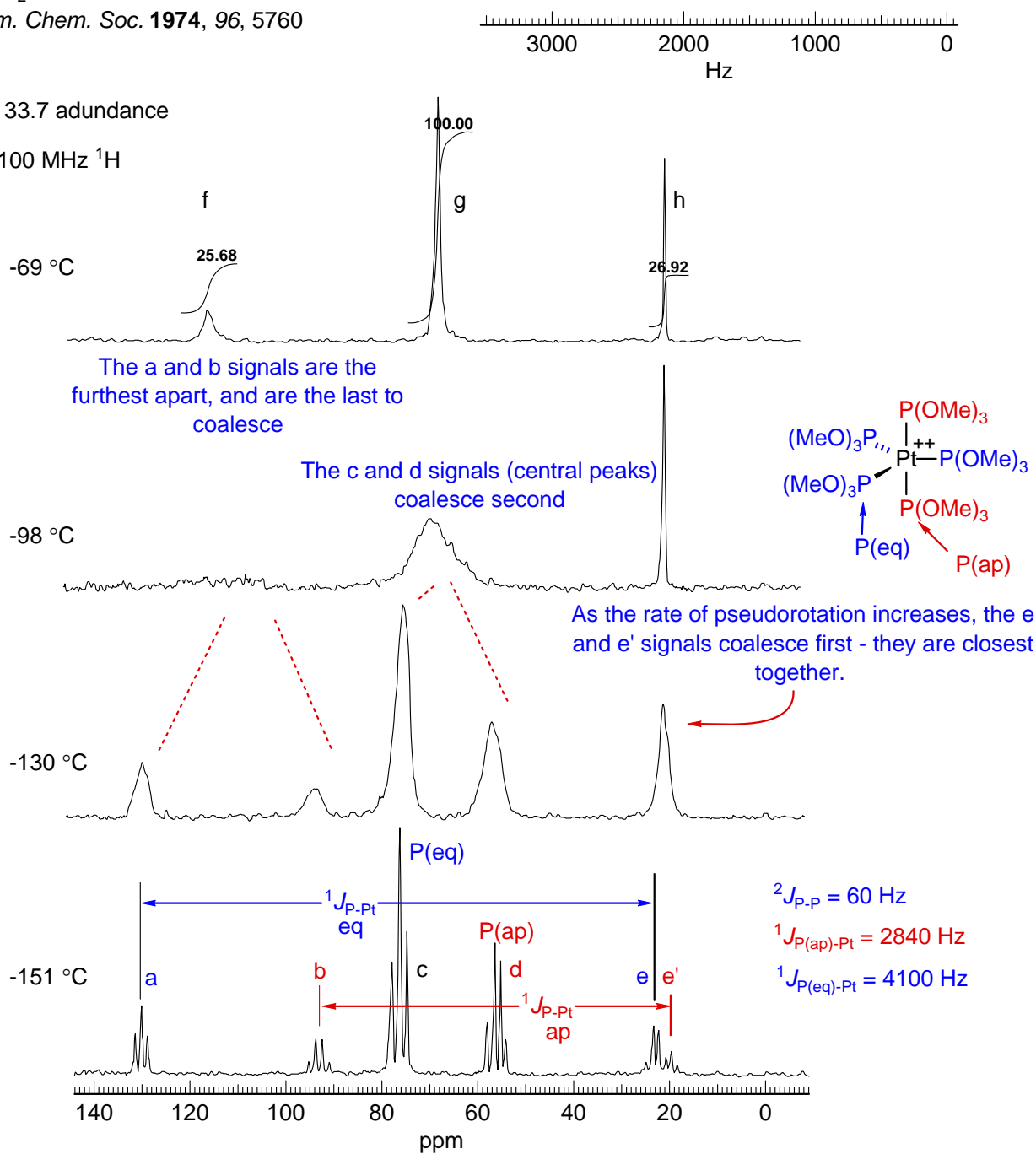Temperature dependent 36.43 MHz $\{^1H\}$ ^{31}P NMR Spectra

$Pt[P(OCH_3)_3]_5{}^{2+}$ $2B(C_6H_5)_5{}^-$
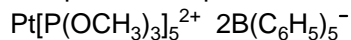
Solvent: $CHClF_2$

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

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

21.5 MHz / 100 MHz ^1H

3000   2000   1000   0
Hz

f   g   h

-69 °C   100.00   25.68   26.92

The a and b signals are the furthest apart, and are the last to coalesce

The c and d signals (central peaks) coalesce second

-98 °C

$(MeO)_3P_{,,,}$ Pt $P(OMe)_3$
$(MeO)_3P$ $P(OMe)_3$
$P(OMe)_3$
P(eq)   P(ap)

As the rate of pseudorotation increases, the e and e' signals coalesce first - they are closest together.

-130 °C

P(eq)

$^1J_{P-Pt}$ eq

P(ap)

$^2J_{P-P}$ = 60 Hz
$^1J_{P(ap)-Pt}$ = 2840 Hz
$^1J_{P(eq)-Pt}$ = 4100 Hz

-151 °C   a   b   c   d   e e'

$^1J_{P-Pt}$ ap

140   120   100   80   60   40   20   0
ppm

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).

Problem R-09P ($C_{14}H_{20}O_2S$). Spectrum (1) is a normal 400 MHz ^1H NMR spectrum of one of the isomers shown. Impurity peaks are marked with x. Spectra (2) and (3) are difference spectra, in which the normal spectrum is subtracted from the spectrum obtained by preirradiating for a few seconds at the frequency shown by the arrow ((516) 487-3794)
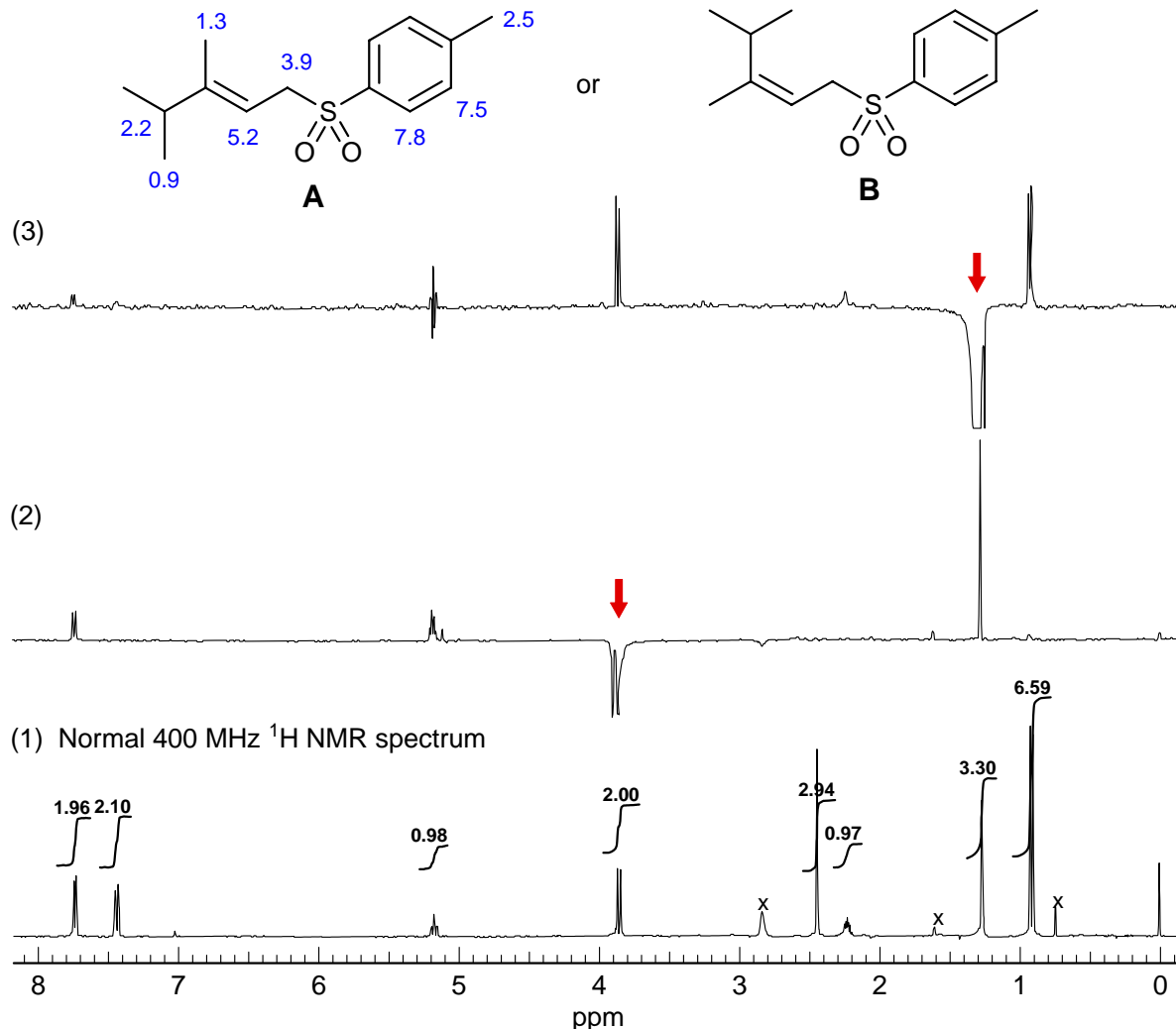
(a) What kind of experiment is being done here?

2   Proton-proton NOE difference experiment

(b) Which of the isomers is the correct structure (**A** or **B**)?_____**A** Explain briefly, but be specific.

5   Irradiation of the methyl group at δ 1.3 (spectrum 3) causes an NOE enhancement of the CH_2 doublet δ 3.9 - thus these must be cis, hence structure A. Conversely, irradiation at δ 3.9 (spectrum 2) causes NOE enhancement of the vinyl proton at δ 5.2, the ortho protons δ 7.8, and (most importantly), the methyl signal at δ 1.3, also consistent only with structure A

(c) Assign the protons by writing chemical shifts on the correct structure.

8

Problem R-09Q (C_1H_6ClN). Shown below is the 30 MHz ^1H NMR spectrum of 60% ^{15}N enriched $CH_3NH_3^+$ Cl^- in H_2O (Ogg, R. A.; Ray, J. D. *J. Chem. Phys.* **1956**, *26*, 1340).
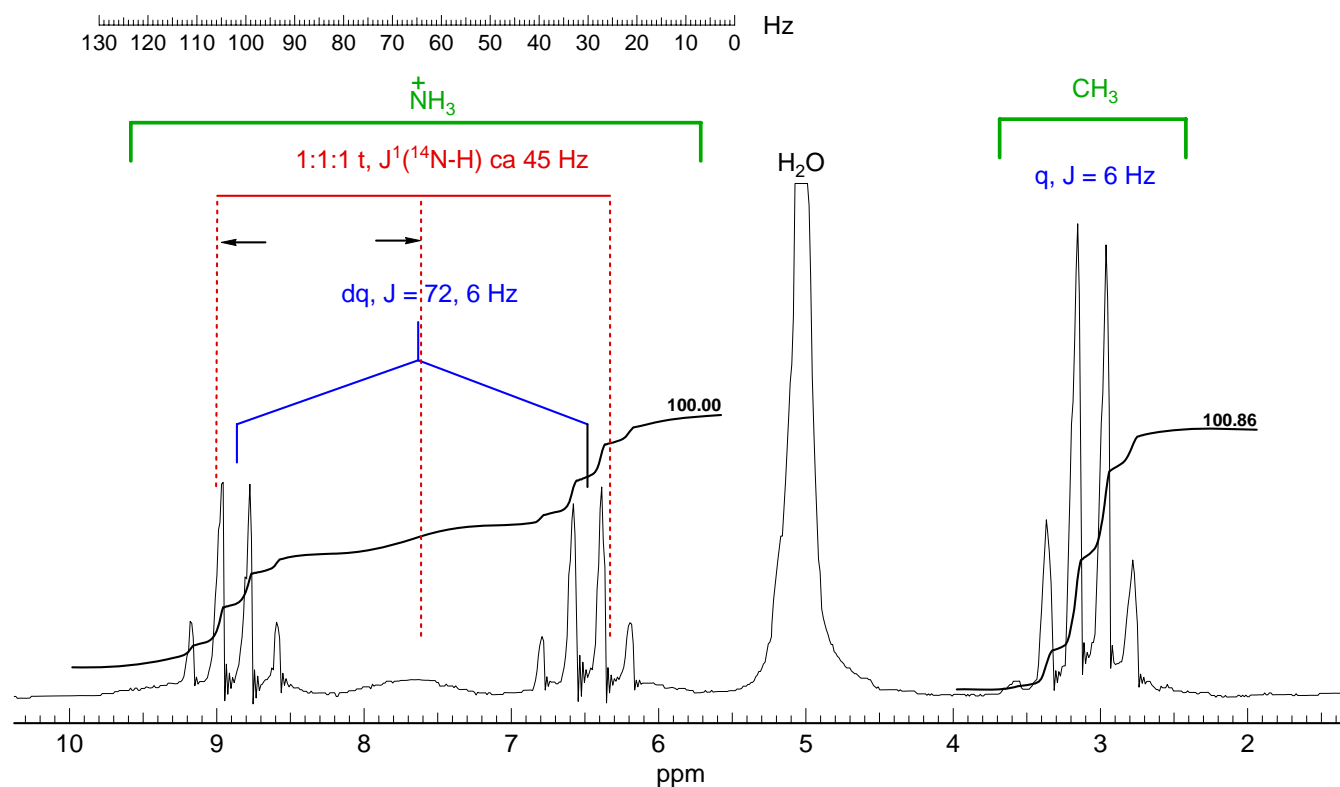
Identify all significant peaks by labelling the spectrum. Show all coupling constants in the standard format $^nJ_{x\text{-}y}$ = 00 Hz.

For the 60% ^{15}N, signals are a dq for the NH_3, and a q for the CH_3

$^1J(^{15}N\text{-}H)$ = 72 Hz.

$^3J(H\text{-}H)$ = 6 Hz.

Apparently the $^2J_{N\text{-}H}$ is too small to resolve, otherwise would see a qd for the Me group

For the 40% ^{14}N, signals are a broad 1:1:1 triplet for the NH_3. The coupling to the Me group is not resolved because T_1 relaxation of ^{14}N is fast enough to cause broadening. The quartet for the CH_3 is superimposed on the signals of the ^{15}N isotopomer.

$^1J(^{14}N\text{-}H)$ ca 45 Hz.

The ratio of $^1J(^{15}N\text{-}H)$ and $^1J(^{14}N\text{-}H)$ should be 10.13/ 7.22, i.e.predict $^1J(^{14}N\text{-}H)$ = 51 Hz if $^1J(^{15}N\text{-}H)$ = 72

Common errors: Ignoring the ^{14}N entirely; mixing up CH_3 and NH_3