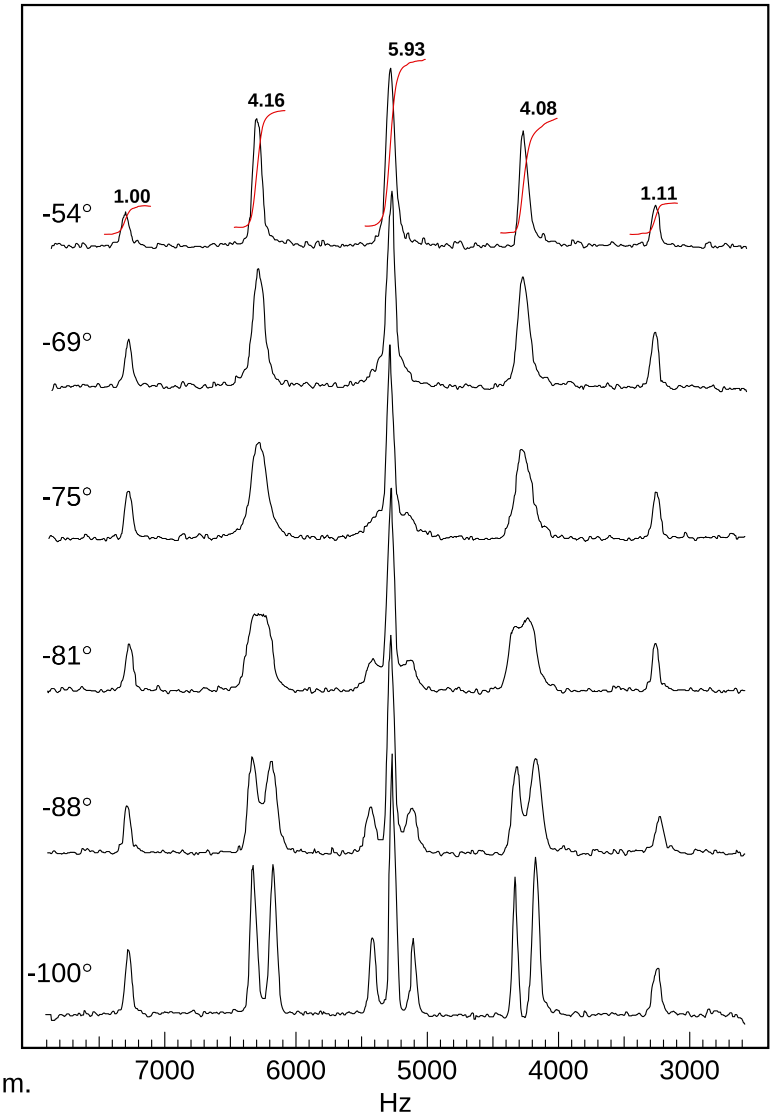
Problem R-13H ($C_2H_6F_4NP$). The variable temperature 40.5 MHz ^{31}P NMR spectrum of $(CH_3)_2N\text{-}PF_4$ is shown (Whitesides, G. M.; Mitchell, H. L. *J. Am. Chem. Soc*. **1969**, *91*, 5384).



(a) Analyze the low temperature (-100 °C) spectrum (get *J* and δ, if any). What does this tell you about the structure of $(CH_3)_2NPF_4$?

(b) Analyze the high temperature (-54 °C) spectrum.

(c) Explain briefly the process being studied here. Draw structures for $(CH_3)_2NPF_4$.

(d) Estimate the rate at one of the temperatures and calculate the free energy of activation of the process. Explain briefly.

12

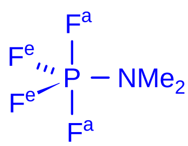
Problem R-13H ($C_2H_6F_4NP$). The variable temperature 40.5 MHz ^{31}P NMR spectrum of $(CH_3)_2N\text{-}PF_4$ is shown below (Whitesides, G. M.; Mitchell, H. L. *J. Am. Chem. Soc*. **1969**, *91*, 5384).

(a) Analyze the low temperature (-100 °C) spectrum (get J and δ, if any). What does this tell you about the structure of $(CH_3)_2NPF_4$?

Triplet of triplets, J_{PF} = 1050, 950 Hz

^{13}P is coupled to two nonequivalent pairs of fluorines - the apical and equatorial Fs are distinct (slow Berry pseudorotation)

5



An A_2M_2X system

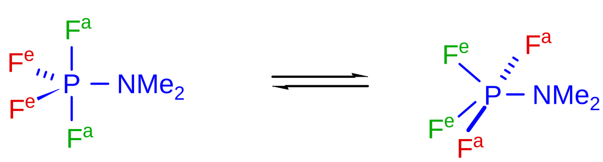
(b) Analyze the high temperature (-54 °C) spectrum.

Regular pentet, J_{PF} = 1000 Hz - the P is coupled to 4 equivalent fluorines. The two apical and two equatorial fluorines are in rapid intramolecular exchange. Intermoleculare exchange would result in loss of all P-F coupling as well, and we would see a singlet.

2

(c) Explain briefly the process being studied here. Draw structures for $(CH_3)_2NPF_4$.

3



"Berry" pseudorotation - the two axial fluorines swap with the two equatorial ones

(d) Estimate the rate at one of the temperatures and calculate the free energy of activation of the process. Explain briefly.

The two peaks at ca 6200 Hz are coalescing at -81 °C to form a peak at 6100 Hz at high temperature.

2

T_c = -81 °C, $\Delta\nu$ = 150 Hz

$$k = \frac{\pi}{\sqrt{2}}\,\nu_{AB} = 2.22\,\nu_{AB} = 333\ \mathrm{s^{-1}}$$

$$\Delta G^{\dagger} = 1.987\,T\,(23.760 + \ln(T/k_r)) = 8.9\ \mathrm{kcal/mol}$$

Note that the peaks at 5420 and 5110 Hz coalesce at higher temperature than the ones at 6200 because the speration is twice as large

Pseudorotation of Me_2NPF_4

Whitesides, Mitchell *J. Am. Chem. Soc.* **1969**, *91*, 5384