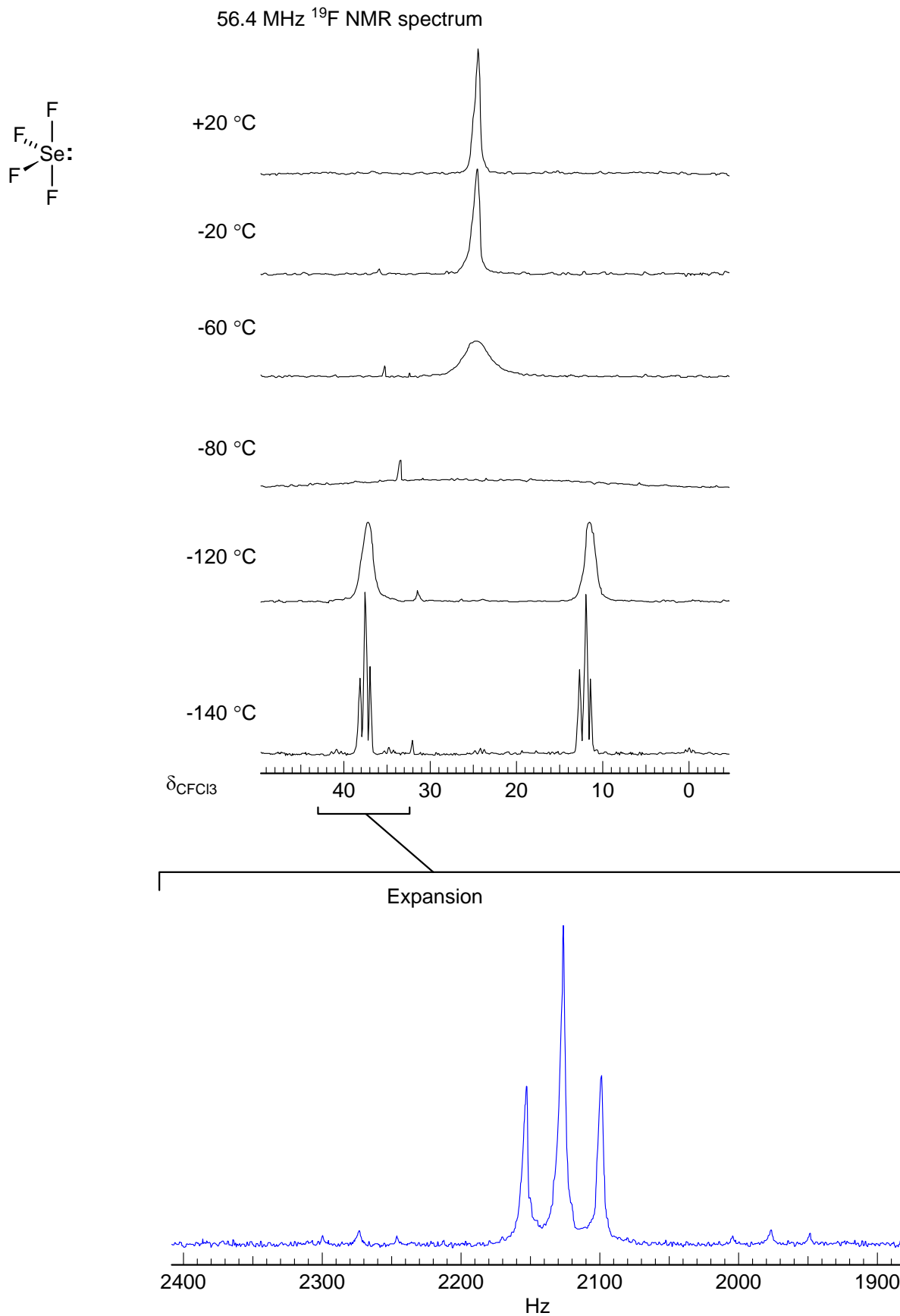


**Problem R-312.** Below are presented variable temperature 56.4 MHz  $^{19}\text{F}$  NMR spectra of  $\text{SeF}_4$ . From your knowledge of structure of compounds like  $\text{SF}_4$  and  $\text{SeF}_4$  interpret the NMR spectra.

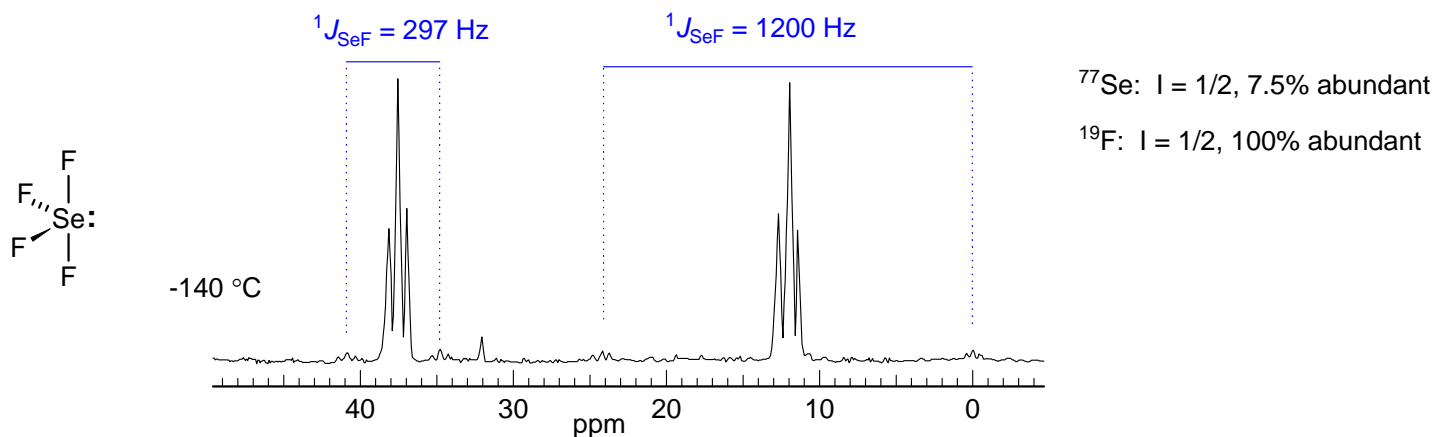
What conclusion can be drawn from the observation that the  $+20\text{ }^\circ\text{C}$  spectrum does not show the weak peaks flanking the low temperature triplets (see expansion)? (*Z. Anorg. Allg. Chem.* **1975**, 416, 12).



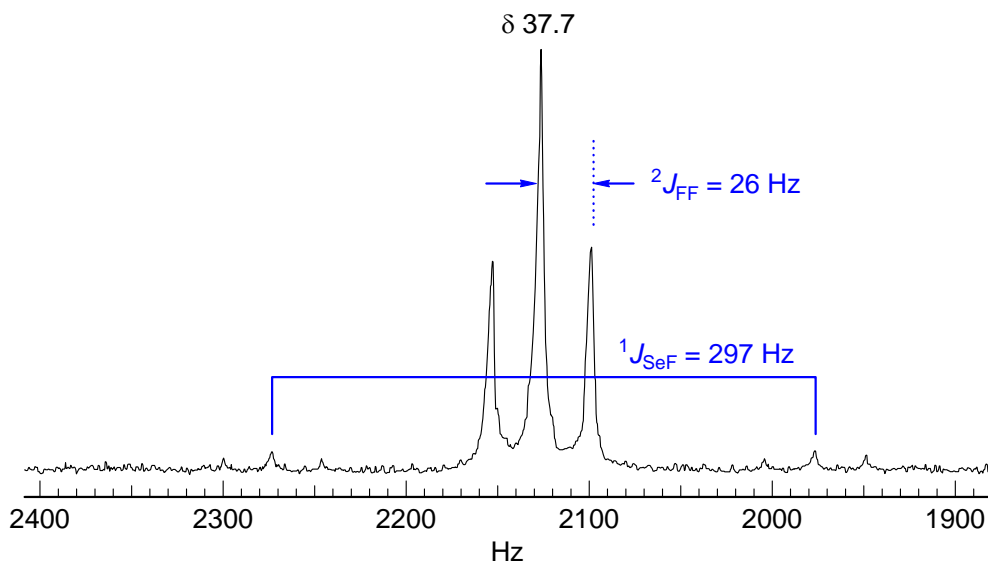
**Problem R-312.** Below are presented variable temperature 56.4 MHz  $^{19}\text{F}$  NMR spectra of  $\text{SeF}_4$ . From your knowledge of structure of compounds like  $\text{SF}_4$  and  $\text{SeF}_4$  interpret the NMR spectra.

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  $-140^\circ\text{C}$  the molecule is static on the NMR time scale (slow Berry pseudorotation), giving an  $\text{A}_2\text{X}_2$  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  $^{77}\text{Se}$  satellites on the  $^{19}\text{F}$  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  $^{77}\text{Se}$  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  $^{77}\text{Se}$  satellites on the fluorine NMR peak. Their separation would be the average of the two low-temperature  $J$  values.