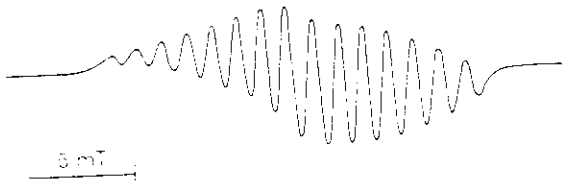
Chemistry 301 **Final Exam** **Feb. 3, 1998**

Name:

1. Sketch the shape of the EPR spectra expected for the following species, in which M has no nuclear spin (I = 0).
   a. M•
   b. MH•
   c. MH_2•
   d. MH_3•

2. Describe the ESR spectrum that you would expect to observe for Si_2H_5• in an isotropic medium.

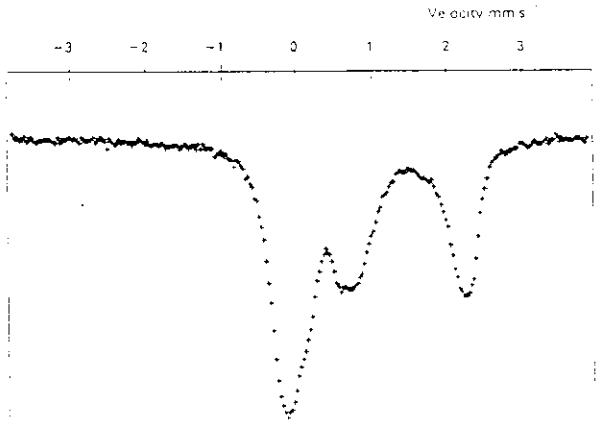
3. The ESR spectrum shown below was recorded for a solution of $[(NH_3)_5Co\text{-}O\text{-}O\text{-}Co(NH_3)_5]^{5+}$. What can you deduce from this spectrum? How might the spectrum be modified if $^{17}O_2$ was used in the preparation of the peroxo-complex?



4. $SiCl_4$ reacts with pyridine to give $SiCl_4(py)_2$, and with NMe_3 to give $SiCl_4(NMe_3)$. The pyridine ligands could be *cis* or *trans* in the first case, and the trimethylamine could occupy an axial or an equatorial position in the latter. To what extent could these various possibilities be distinguished by ^{35}Cl NQR spectroscopy?

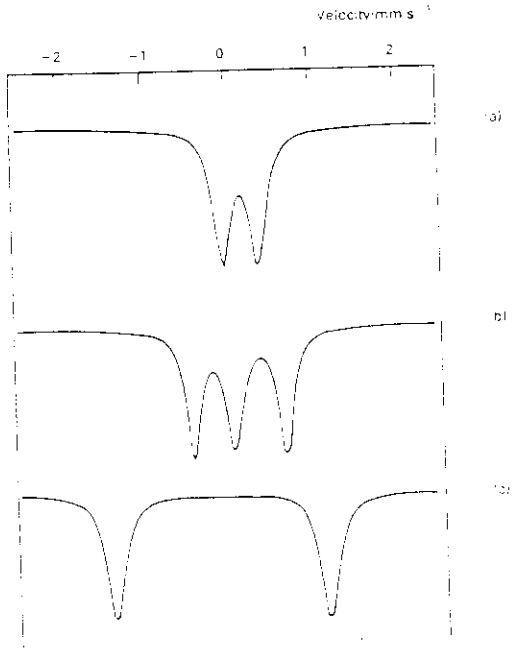
5. Reaction of CH_3COBr and $AlBr_3$ in 1:1 ratio yields a crystalline product which at low temperatures shows eight ^{79}Br nuclear quadrupole resonances. On warming the number of lines decreases. If a 1:2 reacting ratio is used, the product has seven ^{79}Br resonances. How can these observations be explained?

6. The mineral howieite, approximately $NaMn_3Fe_9Si_{12}O_{31}(OH)_{13}$, gives a Mössbauer spectrum which shows the presence of iron in two sites (see Fig. below). Analyse the spectrum, deduce the oxidation states present and derive their relative proportions.



^{57}Fe Mössbauer spectrum of the mineral howieite.

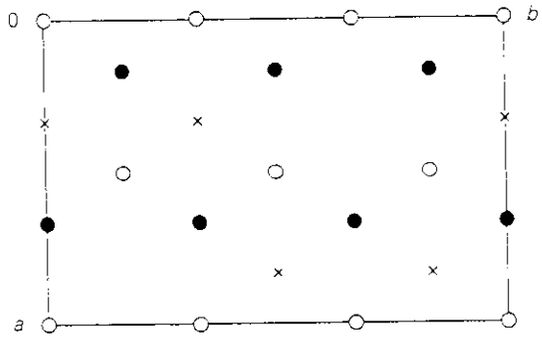
7. The three spectra shown below correspond to $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$, which have the following structures. Assign each spectrum to the appropriate structure and explain.



Simulated ^{57}Fe Mössbauer spectra for three iron carbonyls.

8. The isotopes ^{69}Ga and ^{71}Ga are 60% and 40% abundant, respectively. In a mass spectrum there is a group of ions at 69, 70, 71, 72, 73 and 74 a.m.u. with relative intensities 6:13:28:26:16:11. Calculate the relative numbers of the ions $[GaH_3]^+$, $[GaH_2]^+$, $[GaH]^+$ and $[Ga]^+$ contributing to the spectrum.

9. A projection of a portion of one unit cell of crystalline aluminum(III) chloride is shown below. The *a* (6.03Å) and *b* (10.44 Å) axes are shown; the c-axis is 17.04 Å. No atoms with other fractional z-coordinates make bonding contacts to the atoms shown. Extend the diagram along *a* and *b* to show at least two adjacent unit cells. Determine the length of the shortest Al-Cl distance and describe the coordination of the aluminum and chlorine atoms. Is the structure best described as discrete molecules, infinite chains, infinite sheets or an infinite framework?



○ Cl atoms at $z = 0$

× Al atoms at $z = 0.0833$

● Cl atoms at $z = 0.1667$