Chapter 4 Solutions

1) Given $E = h\nu = 14.4$ keV, $h = 6.626*10^{-34}$ J*s and 1 eV = $1.602*10^{-19}$ J:

$1.44*10^{4}$ eV = $(6.626*10^{-34}$ J*s)/$(1.602*10^{-19}$ J*eV$^{-1}) * \nu$
$\nu = 3.48*10^{18}$ s^{-1}

where the timescale $\tau = 1/\nu$

$\tau = 1/(3.48*10^{18}$ s$^{-1}) = 2.87*10^{-19}$ s

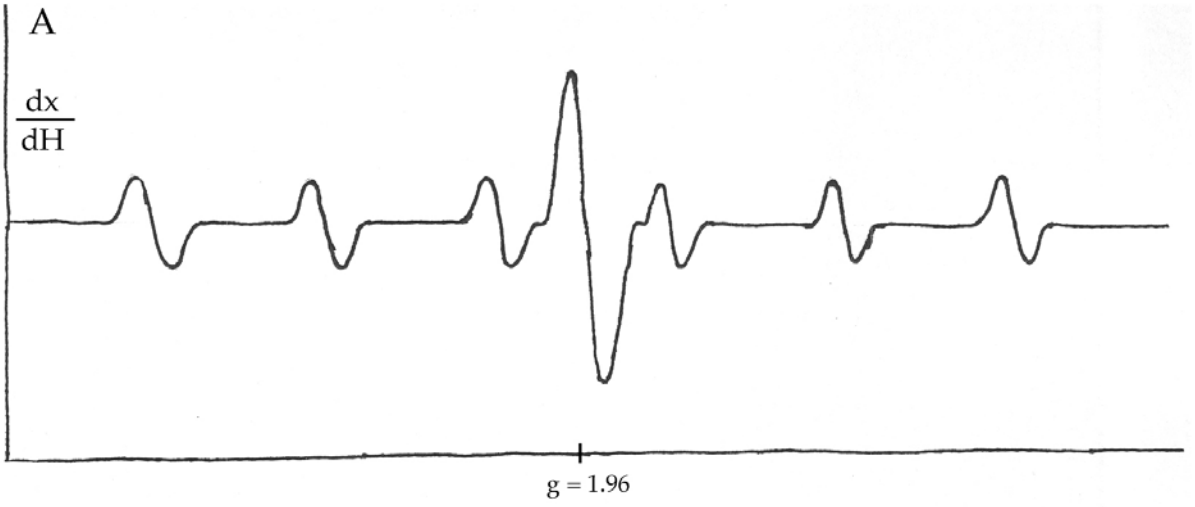
however, this is the energy of the photons released by the source. Sample iron nuclei will have different electronic environments than the source. Thus, the transition from the I = $^{1}/_{2}$ to the I = $^{3}/_{2}$ state will occur at a different energy in a sample nucleus than in a source nucleus. Moving the source with respect to the sample induces a Doppler shift that matches the energy of photons emitted by the source with the energy of the sample nuclear transition. Therefore, the timescale of the experiment depends on the difference in energy between the transitions of different sample iron nuclei. So:

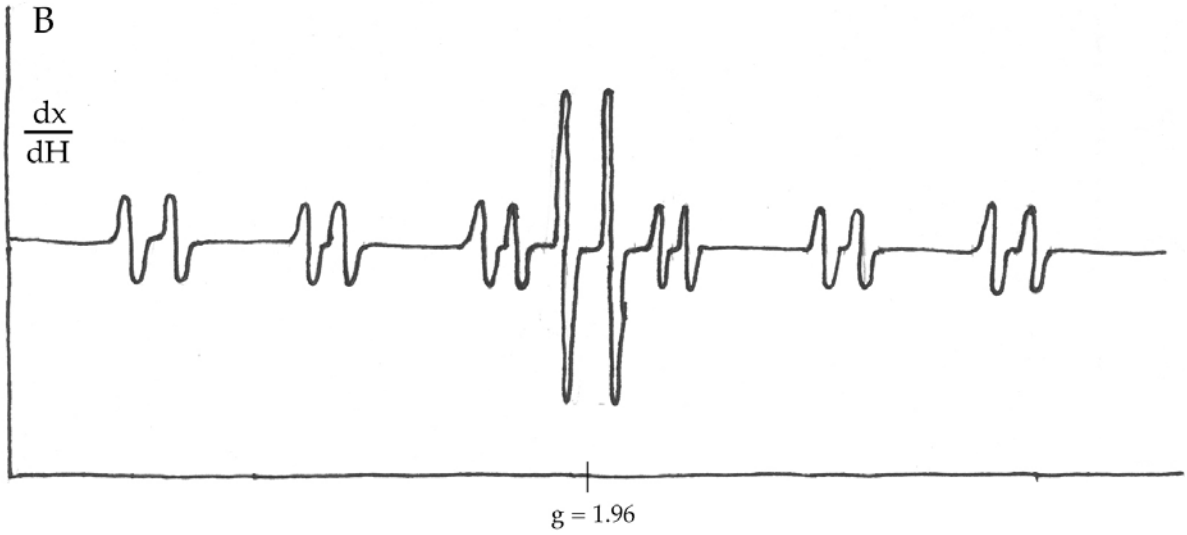
$\Delta E_s = (\nu_0/c)*E_\gamma*\cos\theta$

where des is the change in energy of a photon from the source moving relative to the sample, ν_0 is source velocity, $\cos\theta = 1$, and E_γ is energy of photon from a stationary source. If we want to resolve to peaks that are 1 mm/s apart using 14.4 keV ^{57}Fe radiation:

$\Delta E_s = (1$ mm*s^{-1} / $2.998*10^{11}$ mm*s$^{-1}) * 1.44*10^{4}$ eV = $4.80*10^{-8}$ eV
E = hν, ν = E/h = $(4.80*10^{-8}$ eV) / $[(6.626*10^{-34}$ J*s)/$(1.602*10^{-19}$ J*eV$^{-1})] = 1.16*10^{7}$ s^{-1}
$\tau = 1/\nu = 1/(1.16*10^{7}$ s$^{-1}) = 8.61*10^{-8}$ s

2) Mo(V) is d^1, which corresponds to S = $^{1}/_{2}$. Since 75% of molybdenum is not I = $^{5}/_{2}$, there will be a singlet at a g value slightly less than 2. For the 25% of molybdenum that is I = $^{5}/_{2}$, 2*I + 1 = 6, so there will be a sextet (1:1:1:1:1:1) centered at the same g value. The spacing between the sextet peaks will be $a*m_S*m_I$, where a is the hyperfine coupling constant, $m_S = \pm^{1}/_{2}$, and $m_I = \pm^{1}/_{2}$, $\pm^{3}/_{2}$, or $\pm^{5}/_{2}$. The singlet will have a peak intensity 18 times that of one of the sextet peaks (see A, next page). If $^{13}CN^-$ binds to the molybdenum end-on with the carbon, then the each peak in A will be split into a doublet centered at the same g value as before (this assumes the CN^- does not perturb the electronic environment at molybdenum) with spacing equal to $a'*m_S*m_I$, where a' is the hyperfine coupling constant between the electron and ^{13}C (see B, next page). The intensities will be unchanged. Note: intensities not to scale.


A
dx
dH
g = 1.96
H (gauss)


B
dx
dH
g = 1.96
H (gauss)

3) Co^{2+} substitution for Zn^{2+} will allow determination of the metal coordination environment (i.e. the atoms bound to the metal and the geometry at the metal).

4) Multiple answers possible. For discussions of EPR, Mössbauer, resonance Raman and EXAFS spectroscopies, see the solutions to Extra Problems 1 (3a, b, c and d, respectively).

UV-visible spectroscopy will indicate whether the copper is 1+ or 2+, since Cu(I) has no d-d transitions but Cu(II) does. Furthermore, if ligand-metal charge-transfer bands are present, the type of ligand bound to the metal can be partially determined. Given the difference in optical spectrum between Cu(I) and Cu(II), an experimentalist could follow the reaction by UV-vis to get kinetic data for the reaction.

NMR spectroscopy will provide information about the oxidation state of the copper. Cu(I) will produce a diamagnetic spectrum, whereas Cu(II) will produce broadened peaks. Along the same lines as UV-vis, an experimenter could follow the course of redox reactions by monitoring this difference. Furthermore, one could determine the structure of a protein by NMR.

A magnetic susceptometer will determine the magnetic properties of the protein as a function of temperature and reaction coordinate. This would indicate the number of unpaired electrons in the dicopper active site and the degree/nature (i.e. ferromagnetic vs. antiferromagnetic) of the coupling between each copper in the active site. An experimenter could determine the oxidation states of the copper atoms and whether the bridging ligands are strong or weak field.

Magnetic circular dichroism (MCD) will offer similar information as a magnetic susceptometer. Additionally, MCD of metalloproteins can produce spectra that are unique fingerprints of their identities.

An experimenter would gain the most information from 1) NMR of the reduced protein, 2) EPR of the oxidized protein and 3) Raman of the course of the reaction. I would expect each copper to be coordinated by histidine or carboxylate-containing residues (potentially bridging). Presumably, a dioxygen molecule would first bind end-on to one copper, then bridge between the two, before oxidizing a C-H bond.