Remember that the Michelson interferometer **modulates** the intrinsic frequency of light sent into it. (Also remember that it doubles the frequency of the light since constructive interference occurs if the movable mirror is \( \frac{1}{2} \lambda \) closer or further to the beamsplitter than the fixed mirror.)

\[
f = \frac{2 \nu m}{c} \nu \quad \text{and} \quad c = \nu \lambda \quad \Rightarrow \quad f = \frac{2 \nu m}{\lambda}
\]

so... (a) \( f = 2 \left( \frac{1.25 \text{ cm s}^{-1}}{300 \text{ mm}} \right) \left( \frac{10^9 \text{ mm}}{m} \right) \left( \frac{m}{10^2 \text{ cm}} \right) = 8.33 \times 10^4 \text{ Hz} \)

(b) \( f = 2 \left( \frac{1.25 \text{ cm s}^{-1}}{700 \text{ mm}} \right) \left( \frac{10^7 \text{ mm}}{\text{cm}} \right) = 3.57 \times 10^4 \text{ Hz} \)

(c) \( f = 2 \left( \frac{1.25 \text{ cm s}^{-1}}{7.5 \text{ mm}} \right) \left( \frac{10^6 \text{ mm}}{m} \right) \left( \frac{m}{10^2 \text{ cm}} \right) = 3.3 \times 10^3 \text{ Hz} \)

(d) \( f = 2 \left( \frac{1.25 \text{ cm s}^{-1}}{20 \text{ mm}} \right) \left( \frac{10^4 \text{ mm}}{\text{cm}} \right) = 1.2 \times 10^3 \text{ Hz} \)
We derived in class that in pure time-domain spectroscopy, the resolution improves (that is, \( \Delta \nu \) gets smaller) as the signal collection time increases:

\[ \Delta \nu = \frac{1}{t} \]

We then argued by analogy that a similar relation holds for the interferograms obtained in FTIR:

\[ \Delta \nu = \frac{1}{\delta} \]

where \( \frac{\delta}{2} \) is the length of the Michelson interferometer mirror driven (similar reasoning as in 7-22).

Re-express this in terms of wavelength (since that's what's given to us):

\[ \Delta \nu = \left| \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right| = \frac{1}{\delta} \quad (\text{n.b. } \Delta \nu \neq \frac{1}{\Delta \lambda} \text{!!}) \]

So \( \delta = \left| \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right|^{-1} \)

\[(a) \quad \delta = \left| \frac{1}{20.34} - \frac{1}{20.35} \right|^{-1} \, \mu \text{m} \left( \frac{\text{cm}}{10^4 \mu \text{m}} \right) = 4.139 \text{ cm} \Rightarrow \frac{\delta}{2} = 2.070 \text{ cm} \]

\[(b) \quad \delta = \left| \frac{1}{2.500} - \frac{1}{2.501} \right|^{-1} \, \mu \text{m} \left( \frac{\text{cm}}{10^4 \mu \text{m}} \right) = 0.6252 \text{ cm} \Rightarrow \frac{\delta}{2} = 0.3126 \text{ cm} \]
FTIR advantages include Fellgett's (better resolution and signal/noise for the same scan range), Jacquiot's (light throughput to detector), Connes' (wavenumber accuracy due to use of He-Ne laser), and shorter scanning time.

First, find the S/N of one scan of the peak in question:

\[
\left( \frac{S}{N} \right)_i = \left( \frac{S}{N} \right)_0 \sqrt{n_i} \implies \left( \frac{S}{N} \right)_0 = \frac{(S/N)_i}{\sqrt{n_i}} = \frac{5/1}{\sqrt{16}} = \frac{5}{4}
\]

Now find the number of scans for the desired S/N of 50:1

\[
\left( \frac{S}{N} \right)_j = \left( \frac{S}{N} \right)_0 \sqrt{n_j} \implies n_j = \left[ \frac{(S/N)_j}{(S/N)_0} \right]^2 = \left( \frac{50/1}{5/4} \right)^2
\]

\[
= \left[ \frac{10}{1} \times \frac{4}{5} \right]^2
\]

\[
= 1600
\]

\[n_j = 1600\]
NMR

Skoog 19-6

\[ I = \frac{5}{2} \Rightarrow \{ \frac{5}{2}, \frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \} \]

6 possible states

Skoog 19-7

The absorption (that is, the precessional/Larmor) frequency is given by

\[ \nu_p = \frac{\gamma B_0}{2\pi} \]

so for...

(a) \(^1H\)

\[ \nu_p = \left( \frac{2.6752 \times 10^8 \text{ rad T}^{-1} \text{ s}^{-1}}{2\pi \text{ rad}} \right) (2.4 \text{ T}) = 1.0 \times 10^8 \text{ Hz} \]

(b) \(^{13}C\)

\[ \nu = 6.73 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1} \Rightarrow \nu_p = 2.6 \times 10^7 \text{ Hz} \]

(c) \(^{19}F\)

\[ \nu = 2.52 \times 10^8 \text{ rad T}^{-1} \text{ s}^{-1} \Rightarrow \nu_p = 9.6 \times 10^7 \text{ Hz} \]

(d) \(^{21}P\)

\[ \nu = 1.08 \times 10^8 \text{ rad T}^{-1} \text{ s}^{-1} \Rightarrow \nu_p = 4.1 \times 10^7 \text{ Hz} \]

Skoog 19-9

\[
\frac{N_j}{N_c} = e^{-\frac{\Delta E}{kT}} = e^{-\frac{\pi B_0 h}{2\pi kT}} = e^{\exp \left[ \frac{-6.7283 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}}{2\pi \text{ rad} (1.38 \times 10^{-23} \text{ J K}^{-1}) (298 \text{ K})} \right]}
\]

= 0.9999996
Longitudinal relaxation: The return of magnetization along the z-axis (that is, parallel to the constant \( \vec{B}_0 \)) to its equilibrium value.

Transverse relaxation: The decay of magnetization in the xy plane (that is, perpendicular to \( \vec{B}_0 \)) due to spin-spin dephasing and \( \vec{B}_0 \) in inhomogeneities.

See notes for more detail.
Use data in Table 12.1 and the equation

\[ eV_0 = \frac{hc}{\lambda_0} \]

where \( V_0 \) is the minimum take voltage. This equation assumes that all the KE of a given e\(^-\) is transferred to an atom and used to dislodge the given core e\(^-\).

Sample calc for the K\(_\beta\) line of U:

\[ V_0 = \frac{hc}{e\lambda_0} = \frac{\left(6.626 \times 10^{-34} \text{ J s}\right) \left(2.998 \times 10^8 \text{ m/s}\right)}{\left(1.602 \times 10^{-19} \text{ C}\right) \left(0.111 \times 10^{-10} \text{ m}^3\right)} \left(\frac{1 \text{ V}}{8 \cdot 10^3 \text{ C}^2}\right) \]

\[ V_0 = 1.12 \times 10^5 \text{ V} \]

Note that instead of substituting in the constants explicitly, we can use the Duane-Hunt law:

\[ \lambda_0 = \frac{12398}{V} \]

\[ \begin{array}{ccc}
(a) \ U & 1.12 \times 10^5 & 1.72 \times 10^4 \\
(b) \ K & 3.59 \times 10^3 & \text{no line} \\
(c) \ Rb & 1.50 \times 10^4 & 1.75 \times 10^3 \\
(d) \ W & 6.74 \times 10^4 & 9.67 \times 10^3 \\
\end{array} \]
We use the data to generate a linear plot of atomic number (Z) vs. the square root of the frequency (\( \sqrt{\nu} \)) for the Ka\(_1\) transition (ie 2p \(-\rightarrow\) 1s).

Note: \( c = \lambda \nu \Rightarrow \nu = \frac{c}{\lambda} \Rightarrow \sqrt{\nu} = \sqrt{\frac{c}{\lambda}} \)

So, for example, for the Ka\(_1\) line of Ca,

\[
\sqrt{\nu} = \sqrt{\frac{2.998 \times 10^8 \text{ m/s}}{3.36 \times 10^{-10} \text{ m}}} = 9.45 \times 10^8 \text{ Hz}
\]

<table>
<thead>
<tr>
<th>Wavelength (Å)</th>
<th>Sqrt(Freq/Hz) x 10(^8)</th>
<th>Z</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.36</td>
<td>9.45</td>
<td>20</td>
<td>Ca</td>
</tr>
<tr>
<td>1.44</td>
<td>14.43</td>
<td>30</td>
<td>Zn</td>
</tr>
<tr>
<td>0.79</td>
<td>19.48</td>
<td>40</td>
<td>Zr</td>
</tr>
<tr>
<td>0.49</td>
<td>24.74</td>
<td>50</td>
<td>Sn</td>
</tr>
</tbody>
</table>

Ka\(_1\) Transitions--Calibration Curve

\[
y = 1.9636x + 1.5745 \\
R^2 = 0.9999
\]
Note that \( y = z \) and \( x = \sqrt{v} \times 10^{-8} \).

So \( z = 1.9636 \times 10^{-8} \sqrt{v} + 1.5745 \)

\[ \Rightarrow \sqrt{v} = \frac{z - 1.5745}{1.9636 \times 10^{-8}} \quad [1] \]

Also, \( c = \lambda v \Rightarrow \lambda = \frac{c}{v} \). \quad [2]

With [1] and [2], we can predict the \( K_{\alpha} \) wavelengths (in \( \text{Å} \)) for the other elements:

<table>
<thead>
<tr>
<th>Z</th>
<th>Element</th>
<th>Sqrt (Freq/Hz)</th>
<th>Wavelength (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>V</td>
<td>1091133632</td>
<td>2.52</td>
</tr>
<tr>
<td>28</td>
<td>Ni</td>
<td>1345767977</td>
<td>1.66</td>
</tr>
<tr>
<td>34</td>
<td>Se</td>
<td>1651329191</td>
<td>1.10</td>
</tr>
<tr>
<td>35</td>
<td>Br</td>
<td>1702256060</td>
<td>1.03</td>
</tr>
<tr>
<td>48</td>
<td>Cd</td>
<td>2364305358</td>
<td>0.54</td>
</tr>
<tr>
<td>51</td>
<td>Sb</td>
<td>2517085965</td>
<td>0.47</td>
</tr>
</tbody>
</table>
Wavelength selection in X-ray spectroscopy is effected by a crystal which diffracts the radiation incident upon it according to Bragg's Law:
\[ n \lambda = 2 d \sin \theta \]

\[ \Rightarrow \sin \theta = \frac{n \lambda}{2d} \Rightarrow \theta = \arcsin \left( \frac{\lambda}{2d} \right) \text{ in 1st order} \]

Note also that for a crystal tilt of \( \theta \) with respect to the incident radiation, the detector must be oriented at \( 2\theta \):

\[ 2\theta = 2 \arcsin \left( \frac{\lambda}{2d} \right) \]

Table 12-3 provides values of \( d \) for typical crystals.

Sample calculation: To detect the Ka line of Fe (1.76 Å) with topaz (\( d = 1.356 \) Å),

\[ 2\theta = 2 \arcsin \left( \frac{1.76}{2 \times 1.356} \right) = 80.9^\circ \]

<table>
<thead>
<tr>
<th></th>
<th>Fe (1.76 Å)</th>
<th>Se (0.992 Å)</th>
<th>Ag (0.497 Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Topz (1.356 Å)</td>
<td>80.9°</td>
<td>42.9°</td>
</tr>
<tr>
<td>(b)</td>
<td>LiF (2.014 Å)</td>
<td>51.8°</td>
<td>28.5°</td>
</tr>
<tr>
<td>(c)</td>
<td>NaCl (2.820 Å)</td>
<td>36.4°</td>
<td>20.3°</td>
</tr>
</tbody>
</table>