

# FTIR

Chem 61

Unit 3 HWK  
(not graded)

Skog 7-22

Remember that the Michelson interferometer down 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.)

$$f = 2 \frac{v_M}{c} \nu \quad \text{and} \quad c = \nu \lambda \quad \Rightarrow \quad f = 2 \frac{v_M}{\lambda}$$

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

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

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

(d)  $f = 2 \left( \frac{1.25 \text{ cm s}^{-1}}{20 \text{ } \mu\text{m}} \right) \left( \frac{10^4 \text{ } \mu\text{m}}{\cancel{\mu\text{m}}} \right) = \boxed{1.2 \times 10^3 \text{ Hz}}$

Skooog 7-23

Chem 61  
Unit 3 HWK

P. 2

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:

$$\Delta\bar{\nu} = \frac{1}{\delta}$$

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

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

$$\Delta\bar{\nu} \equiv |\bar{\nu}_2 - \bar{\nu}_1| = \left| \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right| = \frac{1}{\delta} \quad (\text{N.B. } \Delta\bar{\nu} \neq \frac{1}{\Delta\lambda} !!)$$

$$\text{so } \delta = \left| \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right|^{-1}$$

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

$$(b) \quad \delta = \left| \frac{1}{2.500} - \frac{1}{2.501} \right|^{-1} \mu\text{m} \left( \frac{\text{cm}}{10^4 \mu\text{m}} \right) = 0.6252 \text{ cm} \Rightarrow \boxed{\frac{\delta}{2} = 0.3126 \text{ cm}}$$

Skoog 16-8

Chem 61  
Unit 3 HWK  
p. 3

FTIR advantages include Fellgett's (better resolution and signal/noise for the same scan range),  
Jacquinot's (light throughput to detector), Connes'  
(wave number accuracy due to use of He-Ne laser),  
and shorter scanning time.

Skoog 16-12

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

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

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

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

$$= \left[ \frac{10}{1} \left( \frac{4}{5} \right) \right]^2$$

$$n_j = 1600$$

# NMR

Skoog 19-6

$$I = \frac{5}{2} \Rightarrow \boxed{m_I = -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}, +\frac{5}{2}} \quad \text{p. 4}$$

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

(b)  $^{13}\text{C}$   $\gamma = 6.73 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1} \Rightarrow \boxed{\nu_p = 2.6 \times 10^7 \text{ Hz}}$

(c)  $^{19}\text{F}$   $\gamma = 2.52 \times 10^8 \text{ rad T}^{-1} \text{ s}^{-1} \Rightarrow \boxed{\nu_p = 9.6 \times 10^7 \text{ Hz}}$

(d)  $^{31}\text{P}$   $\gamma = 1.08 \times 10^8 \text{ rad T}^{-1} \text{ s}^{-1} \Rightarrow \boxed{\nu_p = 4.1 \times 10^7 \text{ Hz}}$

Skoog 19-9

$$\frac{N_j}{N_c} = e^{-\Delta E/kT} = e^{-\frac{\gamma B_0 h}{2\pi kT}}$$

$$= \exp \left[ \frac{-(6.7283 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}) (2.4 \text{ T}) (6.626 \times 10^{-34} \text{ J s})}{2\pi \text{ rad} (1.38 \times 10^{-23} \text{ J K}^{-1}) (298 \text{ K})} \right]$$

$$= \boxed{0.999996}$$

Skog 19-10

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 <sup>random</sup> spin-spin dephasing and  $\vec{B}_0$  inhomogeneities.

See notes for more detail

Skog 19-11

See notes.

X-Ray Spectrometry

Skog 12-2

Use data in Table 12.1 and the equation

$$eV_0 = \frac{hc}{\lambda_0}, \text{ where } V_0 \text{ is the minimum tube}$$

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:

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

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

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

$$\lambda_0 = \frac{12398}{V}$$

	$K_{\beta}$ (V)	$L_{\beta}$ (V)
(a) U	$1.12 \times 10^5$	$1.72 \times 10^4$
(b) K	$3.59 \times 10^3$	no line
(c) Rb	$1.50 \times 10^4$	$1.75 \times 10^3$
(d) W	$6.74 \times 10^4$	$9.67 \times 10^3$

Skoog 12-3

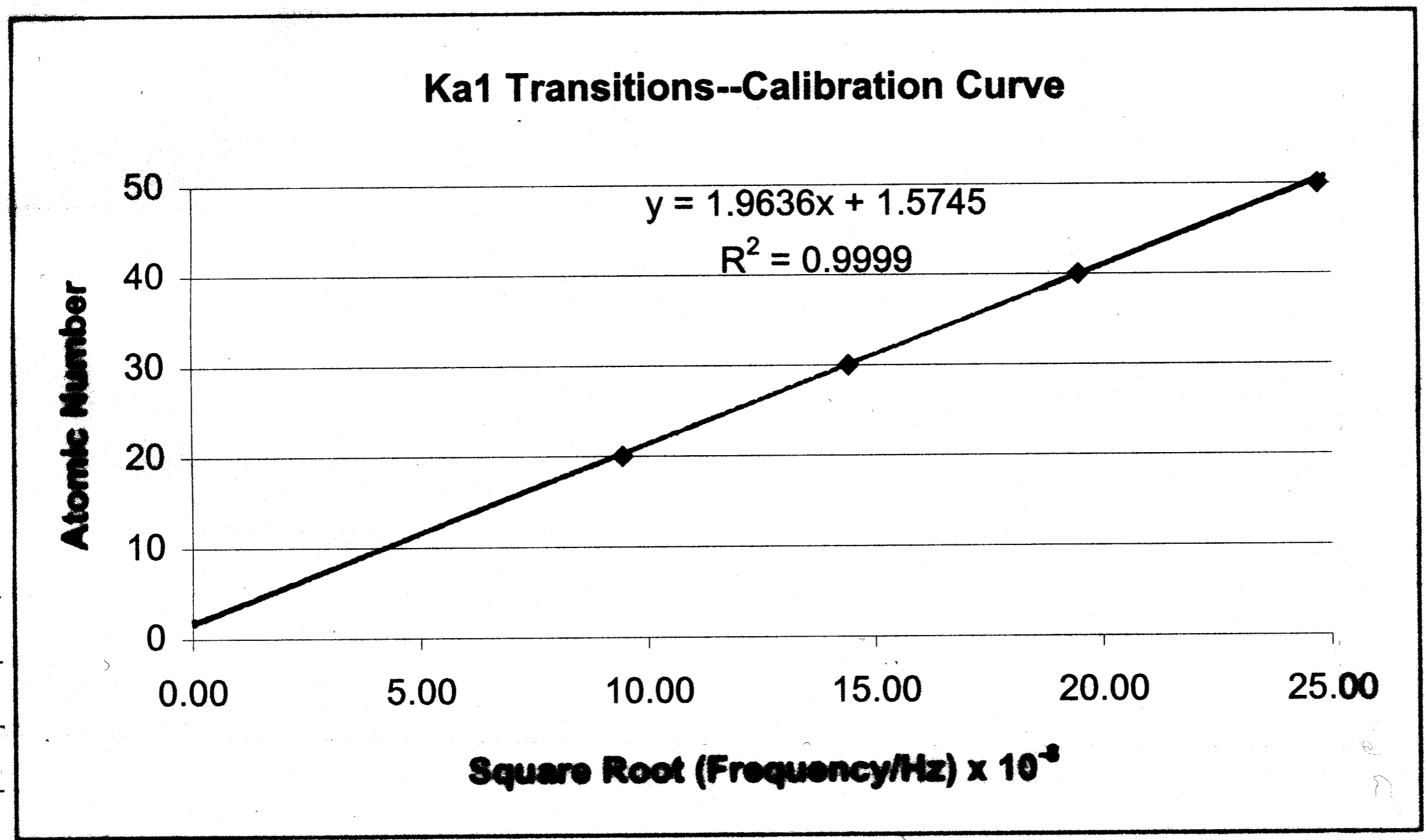
We use the data to generate a linear plot of atomic number (Z) vs. the square root of the frequency ( $\sqrt{\nu}$ ) for the  $K_{\alpha 1}$  transition. (ie  $2p \rightarrow 1s$ )

Note:  $c = \lambda \nu \Rightarrow \nu = c/\lambda \Rightarrow \sqrt{\nu} = \sqrt{c/\lambda}$

so, for example, for the  $K_{\alpha 1}$  line of Ca,

$$\sqrt{\nu} = \sqrt{\frac{2.998 \times 10^8 \text{ m s}^{-1}}{3.36 \times 10^{-10} \text{ m}}} = 9.45 \times 10^8 \text{ Hz}$$

Wavelength (Å)	Sqrt(Freq/Hz) x 10 <sup>8</sup>	Z	Element
3.36	9.45	20	Ca
1.44	14.43	30	Zn
0.79	19.48	40	Zr
0.49	24.74	50	Sn



Note that  $y = Z$  and  $x = \sqrt{\nu} \times 10^{-8}$ .

$$\text{So } Z = 1.9636 \times 10^{-8} \sqrt{\nu} + 1.5745$$

$$\Rightarrow \sqrt{\nu} = \frac{Z - 1.5745}{1.9636 \times 10^{-8}} \quad [1]$$

$$\text{Also, } c = \lambda \nu \Rightarrow \lambda = c/\nu. \quad [2]$$

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

Z	Element	Sqrt (Freq/Hz)	Wavelength (Å)
23	V	1091133632	2.52
28	Ni	1345767977	1.66
34	Se	1651329191	1.10
35	Br	1702256060	1.03
48	Cd	2364305358	0.54
51	Sb	2517085965	0.47

## Skooog 12.9

Wavelength selection in X-ray spectroscopy is effected by a crystal which diffracts the radiation incident upon it according to Bragg's Law:

$$n\lambda = 2d\sin\theta$$

$$\Rightarrow \sin\theta = \frac{n\lambda}{2d} \Rightarrow \theta = \text{Arcsin}\left(\frac{\lambda}{2d}\right) \quad \text{in 1st order}$$

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

$$2\theta = 2 \text{Arcsin}\left(\frac{\lambda}{2d}\right)$$

Table 12-3 provides values of  $d$  for typical crystals.

Sample calculation: To detect the  $K_{\alpha}$  line of Fe ( $1.76 \text{ \AA}$ ) with topaz ( $d = 1.356 \text{ \AA}$ ),

$$2\theta = 2 \text{Arcsin}\left(\frac{1.76 \text{ \AA}}{2(1.356 \text{ \AA})}\right) = 80.9^{\circ}$$

	Fe ( $1.76 \text{ \AA}$ )	Se ( $0.992 \text{ \AA}$ )	Ag ( $0.497 \text{ \AA}$ )
(a) Topaz ( $1.356 \text{ \AA}$ )	$80.9^{\circ}$	$42.9^{\circ}$	$21.1^{\circ}$
(b) LiF ( $2.014 \text{ \AA}$ )	$51.8^{\circ}$	$28.5^{\circ}$	$14.2^{\circ}$
(c) NaCl ( $2.820 \text{ \AA}$ )	$36.4^{\circ}$	$20.3^{\circ}$	$10.1^{\circ}$