

# 1 – Intro to Spectroscopy: Rotational and Vibrational Spectroscopy

Molecule	Rot. Spectrum?	Strong vib. spectrum?
O <sub>2</sub> (O=O)	No ( $\mu=0$ )	No ( $d\mu/dr = 0$ )
CS <sub>2</sub> (S=C=S)	No ( $\mu=0$ )	Symmetric stretch ( $\leftarrow S=C=S \rightarrow$ ): No  Antisymmetric stretch ( $\leftarrow S=C=S \leftarrow$ ): Yes  Bends* $\begin{array}{c} \uparrow \\ (\downarrow S=C=S \downarrow) \end{array}$ : Yes
HCN (HC $\equiv$ N)	Yes ( $\mu \neq 0$ ) (Actual: $\mu=2.98D$ )	Symmetric stretch ( $\leftarrow H-C \equiv N \rightarrow$ ): Yes  Antisymmetric stretch ( $\leftarrow H-C \equiv N \leftarrow$ ): Yes  Bends* $\begin{array}{c} \uparrow \\ (\downarrow H-C \equiv N \downarrow) \end{array}$ : Yes

(8 points: 1 pt for each rot. spectrum response, 1 pt for O<sub>2</sub> vib. response, 2 pts each for CS<sub>2</sub> and HCN vib. response. -1 for one incorrect CS<sub>2</sub> or HCN vib. response, -2 for two or three. It is also acceptable to draw the modes with all arrows reversed)

**Explanation:** A molecule exhibits a rotational spectrum if it has a permanent dipole moment ( $\mu \neq 0$ ). A molecule exhibits a vibrational spectrum if the vibration causes a change in the dipole moment ( $d\mu/dr \neq 0$ ). (Note that vibrational spectra can be observed even if  $\mu=0$ , so long as the vibration changes the dipole moment) (6 points: 3 for correct rotational condition, 3 for correct vib condition. May write these conditions as an explanation of each molecule, and not a separate section)

Note that in a symmetric molecule like CS<sub>2</sub>, the symmetric stretch does not change the dipole ( $d\mu/dr = 0$ ), whereas in an asymmetric molecule like HCN,  $d\mu/dr \neq 0$ . The asymmetric stretch and bend always change the dipole ( $d\mu/dr \neq 0$ ).

**Side Note:** There is actually a degeneracy in the bend motions. For linear molecules, we must have  $3N-5$  vibrational modes ( $3N$  total degrees of freedom, 3 translational modes, and 2 rotational modes). For CS<sub>2</sub> and HCN, there should be 4 vibrational modes, not 3. The fourth mode is just another bend (perpendicular to what is shown here), and is completely degenerate to the one shown above. You do **not** need to show this mode unless we ask for it.

## 2 – Rotations of Molecules (26 points)

a) From OGC (p. 831), moment of inertia ( $I$ ) is related to the allowed frequencies ( $\nu$ ) by

$$\nu = \frac{h}{8\pi^2 I} [J_f(J_f + 1) - J_i(J_i + 1)]$$

where  $J$  is the rotational quantum number. Since  $\Delta J = +1$  for absorption, set  $J_f = J_i + 1$  and solve for  $I$ :

$$I = \frac{h}{8\pi^2 \nu} [2J_i + 2] \quad (2 \text{ pts for this expression, may start here})$$

We're not actually told the quantum number (and you're not allowed to use it here anyways!). But, since the lines are successive, if line 1 corresponds to initial quantum number  $J_i$ , then line 2 corresponds to  $J_i + 1$ . First, solve our original relationship for  $J_i$ :

$$J_i = \frac{4\pi^2 \nu I}{h} - 1$$

Then, generate simultaneous equations for two successive lines:

$$\begin{aligned} J_i &= \frac{4\pi^2 \nu_i I}{h} - 1 \\ J_i + 1 &= \frac{4\pi^2 \nu_{i+1} I}{h} - 1 \end{aligned} \quad (1 \text{ pt for the simultaneous equations})$$

Solve these equations for  $J_i$ , set the resulting expressions equal to each other, and solve for  $I$ :

$$\begin{aligned} \frac{4\pi^2 \nu_i I}{h} &= \frac{4\pi^2 \nu_{i+1} I}{h} - 1 \\ I &= \frac{h}{4\pi^2 (\nu_{i+1} - \nu_i)} \end{aligned} \quad (1 \text{ pt for solving for } I)$$

Then, plug in any two consecutive frequencies:

$$I = \frac{6.62608 \times 10^{-34} \text{ J s}}{4\pi^2 (3.12 \times 10^{12} \text{ Hz} - 2.50 \times 10^{12} \text{ Hz})} = 2.7 \times 10^{-47} \text{ kg s}^2$$

(2 pts substitution, 2 pts numerical answer, -2 for either incorrect sig figs or units. **Note that we two sigfigs and not three, because the difference  $\nu_{i+1} - \nu_i$  only has two!**)

b) From OGC (p. 830),

$$I = \mu R_e^2, \text{ where } \mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}} \quad (2 \text{ pts, } -1 \text{ if student approximates } \mu = m_{Cl} \text{ because Cl is so much more massive})$$

Best method: use our expression for  $I$  from part a, then solve for  $R_e$ . This avoids propagation of rounding errors, and can lead to additional insight in the final equations. (We will still accept your answer if you directly substitute your value of  $I$  in).

$$R_e = \sqrt{\frac{h(m_H + m_{Cl})}{4\pi^2 m_H m_{Cl} (\nu_{i+1} - \nu_i)}}$$

$$R_e = \sqrt{\frac{(6.62608 \times 10^{-34} \text{ J s})(1 \text{ amu} + 35 \text{ amu}) \left( \frac{1.661 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right)}{4\pi^2 (1 \text{ amu})(35 \text{ amu}) \left( \frac{1.661 \times 10^{-27} \text{ kg}}{1 \text{ amu}} \right)^2 (0.62 \times 10^{12} \text{ Hz})}}$$

$$R_e = 1.3 \times 10^{-10} \text{ m} = 1.3 \text{ \AA}$$

(2 pts substitution, 2 pts answer, -2 for incorrect units or sig figs. -1 for using average mass ( $m_{Cl}=35.45 \text{ amu}$ ) rather than isotope mass ( $m_{Cl}=35 \text{ amu}$ ). No deduction for using  $I$  rather than the general expression)

c) From OGC p. 830,

$$E_{rot,J} = \frac{h^2}{8\pi^2 I} J(J+1) \quad (1.5 \text{ pts for equation})$$

Again, substitute your general expression for  $I$  into this equation (we will accept a direct substitution of your numerical value, although that is still a worse method)

$$E_{rot,J} = \frac{h(\nu_{i+1} - \nu_i)}{2} J(J+1)$$

Given this equation,  $\nu_{i+1} - \nu_i = 0.62 \times 10^{12} \text{ Hz}$ , and  $h = 6.62608 \times 10^{-34} \text{ J s}$ , we obtain the following:

$J$	$E_{rot,J} \text{ (J)}$
1	$4.1 \times 10^{-22}$
2	$1.2 \times 10^{-21}$
3	$2.5 \times 10^{-21}$

(1.5 pts each. No credit for any answer where sig figs are not consistent with part a)

d) We know the following equations from part a

$$J_i = \frac{4\pi^2 \nu_i I}{h} - 1, \quad I = \frac{h}{4\pi^2 (\nu_{i+1} - \nu_i)}$$

If we now substitute our equation for  $I$  into the equation for  $J$ , we get

$$J_i = \frac{\nu_i}{(\nu_{i+1} - \nu_i)} - 1.$$

Now you see a great example of why you should work with symbols as long as possible before substituting numbers. This equation is quite simple to evaluate now. You get a better feel for the relationship between variables plus you're much less likely to make a calculation error. (2 points for this equation)

Also notice that we could substitute any frequency difference as long as the frequencies represent adjacent states. The differences are the same:  $\nu_2 - \nu_1 \approx \nu_3 - \nu_2 \approx \nu_4 - \nu_3$ .

Using  $\nu_{i+1} - \nu_i = 0.62 \times 10^{12}$  Hz, we obtain

$\nu_i$ (Hz)	$J_i$	$J_f = J_i + 1$
$2.50 \times 10^{12}$	3	4
$3.12 \times 10^{12}$	4	5
$3.74 \times 10^{12}$	5	6
$4.37 \times 10^{12}$	6	7

(0.5 pts per correct  $J_i, J_f$ )

### 3 – Vibrations of Molecules (12 points)

Start with the Boltzmann distribution, (OGN, p. 605; OGC, p. 829)

$$\frac{N(E_i)}{N_0} \sim g(E_i) \exp[-E_i / k_B T], \quad [1]$$

where  $N(E_i)$  is the number of molecules occupying a given energy state,  $N_0$  is the total number of molecules,  $g(E_i)$  is the degeneracy of  $E_i$ ,  $k_B$  is the Boltzmann constant and  $T$  is absolute temperature.

In the problem statement you are given the ratio of the number of molecules in two different states. Use Equation [1] to make a ratio,

$$\frac{N(E_1)}{N(E_0)} = \frac{g(E_1)}{g(E_0)} \exp[-(E_1 - E_0) / k_B T], \quad [2]$$

where  $E_i$  is the energy related to the  $v=i$  state. (1 pt for Boltzmann eq., 1 pt for ratio)

The degeneracy for both vibrational states is  $g(E_1) = g(E_0) = 1$ . (2 points)

If you can estimate the energy difference, then the only unknown variable in Equation [2] is temperature. Calculate the energy difference using the result from quantum mechanics for vibrational energy levels, (OGN, p. 609; OGC, p. 834)

$$E_{vib,v} = h\nu \left( v + \frac{1}{2} \right), \quad [3]$$

where  $E_{vib,v}$  is the vibrational energy associated with the vibrational quantum number  $v$ ,  $h$  is Planck's constant and  $\nu$  is the oscillation frequency. (2 points)

Use Equation [3] to find the energy difference for this problem,

$$E_1 - E_0 = E_{\text{vib},1} - E_{\text{vib},0} = h\nu \left( \frac{3}{2} - \frac{1}{2} \right) = h\nu.$$

(2 points for equation or a value; but ideally, you would keep symbols.  $h\nu = 3.7 \times 10^{-21} \text{ J}$ )

Substitute this result into Equation [2] and solve for temperature,

$$\frac{N(E_1)}{N(E_0)} = \frac{g(E_1)}{g(E_0)} \exp \left[ -h\nu / k_B T \right],$$

$$T = - \frac{h\nu}{k_B} \frac{1}{\ln \left[ \frac{N(E_1) g(E_0)}{N(E_0) g(E_1)} \right]} \quad [4]$$

(2 points for correct substitution)

$$T = - \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(5.58 \times 10^{12} \text{ s}^{-1})}{1.38066 \times 10^{-23} \text{ J} / \text{K}} \frac{1}{\ln[(0.127)(1)]}$$

$$T = 1.30 \times 10^2 \text{ K}$$

(2 pts for answer, -2 for incorrect units or sig figs)

#### 4 – Intro to Spectroscopy: Beer-Lambert Law (25 points)

a) The relative absorbance of two samples (X and Y) is given by

$$\frac{A_{\lambda,Y}}{A_{\lambda,X}} = \frac{\epsilon_{\lambda,Y} \ell_Y c_Y}{\epsilon_{\lambda,X} \ell_X c_X}$$

Solve this for the ratio of molar absorptivities:

$$\frac{\epsilon_{\lambda,Y}}{\epsilon_{\lambda,X}} = \frac{A_{\lambda,Y}}{A_{\lambda,X}} \left[ \frac{(\ell_Y c_Y)^{-1}}{(\ell_X c_X)^{-1}} \right]$$

If we are making our measurements with the same cuvette, then  $\ell_Y = \ell_X$ . Since we're interested in comparing the sunscreens at the same concentration, then  $c_Y = c_X$ .

Therefore, the term in brackets is 1, and the relative molar absorptivity is equal to the relative absorbance.

$$\frac{\epsilon_{\lambda,Y}}{\epsilon_{\lambda,X}} = \frac{A_{\lambda,Y}}{A_{\lambda,X}}$$

(3 points for equation and explanation, accept any reasonable explanation that c and  $\ell$  are constant. No credit if equation is given without justification)

Using the equation above and the absorbance data in the problem set, we obtain

<i>Sunscreen concentration (g/L)</i>	<i>Relative Values of Molar Extinction Coefficients</i>	
	$\frac{\epsilon_{\lambda,SPF50}}{\epsilon_{\lambda,SPF8}}$	$\frac{\epsilon_{\lambda,SPF15}}{\epsilon_{\lambda,SPF8}}$
0.050	2.1	1.5
0.100	2.0	1.4
0.200	2.04	1.50

(0.5 pts per correct relative value, no credit for answers with incorrect sig figs)

Food for thought: If you use SPF50 instead of SPF8, you are only increasing sunscreen absorbance by a factor of two or so. Then why does SPF50 have a number that is more than six times greater than SPF8?

Answer: SPF is based on percent transmittance rather than absorbance, which brings us to the next part of the problem.

b) Start with Beer's Law,

$$A_{\lambda} = -\log_{10} \left( \frac{I_s}{I_R} \right).$$

The definition of SPF was the reciprocal of the transmittance, or  $SPF = \frac{1}{T} = \frac{I_R}{I_s}$ . Make

this substitution and solve for SPF:

$$A_{\lambda} = -\log_{10} \left( \frac{1}{SPF} \right) = \log_{10}(SPF)$$

For two given SPFs ( $SPF_1$  and  $SPF_2$ ), the relative absorbance is given by

$$\frac{A_{\lambda, SPF2}}{A_{\lambda, SPF1}} = \frac{\log_{10}(SPF_2)}{\log_{10}(SPF_1)}$$

Solve for  $A_{\lambda, SPF2}$

$$A_{\lambda, SPF2} = A_{\lambda, SPF1} \left[ \frac{\log_{10}(SPF_2)}{\log_{10}(SPF_1)} \right]$$

**(4 points for derivation of this equation, or something equivalent)**

Note: You are not required to have an identical “governing equation” because you may have substituted numbers for symbols along the way. (Whenever possible, it is good practice to derive an equation symbolically and substitute values for symbols at the end. When you have a governing equation, you can easily see the relationship between physical quantities that you might not notice if you substitute numbers earlier.)

Use Equation [3] to calculate values for absorbance for SPF50 and SPF15, using

$$A_{\lambda, SPF1} = 0.61$$

	<b><i>SPF50</i></b>	<b><i>SPF15</i></b>
SPF <sub>2</sub>	50	15
$A_{\lambda, SPF2, 0.100}$ (calculated, from Eqtn [3])	1.1	0.79
$A_{\lambda, SPF2, 0.100}$ (measured, from Table)	1.2	0.84

The calculated values are close to the measured values in the data table

**(1 pt per each calculated absorbance. No credit for answers with incorrect sig figs)**

**(1 pt for comparison of calculated and measured values)**

Note that the calculated values have two sig figs – the SPF values are whole numbers and the absorbance value has two sig figs. See the sig fig guidelines on the course website if you need further guidance.

c) Start with Beer's Law,

$$A_{\lambda} = -\log_{10}\left(\frac{I_S}{I_R}\right) = c\epsilon_{\lambda}\ell.$$

Solve for the fraction of light transmitted

$$T = \frac{I_S}{I_R} = 10^{-c\epsilon_{\lambda}\ell}$$

The sum of the transmitted fraction and the absorbed fraction must be 1, so the fraction of light that is absorbed ( $f$ ) is given as

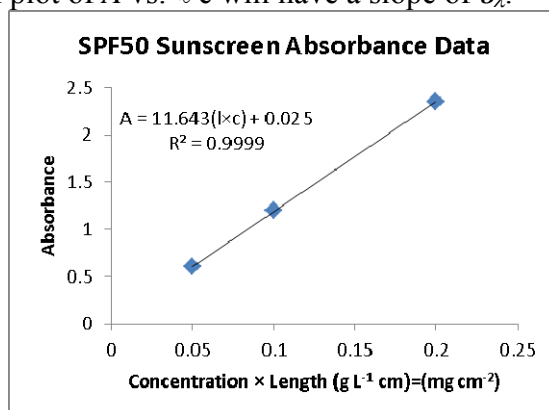
$$f = 1 - T = 1 - 10^{-c\epsilon_{\lambda}\ell}$$

(3 pts for equation)

You must first find a value for the molar extinction coefficient for SPF50,

$$A_{\lambda} = \epsilon_{\lambda}(c\ell), \text{ or } \epsilon_{\lambda} = \frac{A_{\lambda}}{c\ell}.$$

The best way to get  $\epsilon$  is to do linear regression using the left equation, i.e. use all of our data to determine  $\epsilon_{\lambda}$ . A plot of  $A$  vs.  $\ell c$  will have a slope of  $\epsilon_{\lambda}$ .



The intercept is non-zero (real data never behave like you want them to!), but the slope,  $\epsilon_{\lambda}$ , is  $11.6 \text{ cm}^2 \text{ mg}^{-1}$ . (2 pt plot, 2 pts for value, two or three sigfigs OK since this is an intermediate step)

Note: It's not really correct to consider each data point separately, but you would end up with the same answer to two sig figs. We'll be nice, and award full credit for this method, although we **did** say to use linear regression! 2 pt for table, 2 pts for final answer, two or three sigfigs OK since this is an intermediate step

Sunscreen concentration (c)	SPF50 Absorbance ( $A_{310\text{-nm}, \text{SPF50}}$ )	SPF50 molar extinction coefficient ( $\epsilon_{310\text{-nm}, \text{SPF50}}$ )
g/L	dimensionless	L/g-cm
0.050	0.60	12
0.100	1.20	12.0
0.200	2.35	11.8
Average	N/A	12



Note:  $12 \text{ L/g-cm} = 12 \text{ cm}^2/\text{mg}$

Next, use the hint:  $c\ell$  has units of mass per unit length squared – the same units as the given value of recommended sunscreen thickness. So,  $c\ell = 2 \text{ mg cm}^{-2}$  (2 points)

You now know all values for the symbols in the exponent,

$$(c\ell)\varepsilon_\lambda = \left(2 \frac{\text{mg}}{\text{cm}^2}\right) \left(12 \frac{\text{L}}{\text{g cm}}\right) \left(\frac{10^3 \text{ cm}^3}{\text{L}}\right) \left(\frac{\text{g}}{10^3 \text{ mg}}\right) = 24, \text{ so}$$
$$f = 1 - 10^{-24} = 1$$

Virtually all of the incident radiation is absorbed. (2 points for final answer)

**Side Note:**

Is this analysis reasonable? Does sunscreen really protect that well?

The molar extinction coefficient for SPF50 is about right. You could solve the problem a different way and find the molar extinction coefficient associated specifically with the active ingredients (~18wt% in sunscreen) and use sunscreen density ( $\rho \approx 1.08 \text{ g/cm}^3$ ).

You'll find the same answer. In our case we used sunscreen as our basis. In the alternative case, you use the active ingredient as your basis.

If you use SPF8 instead of SPF50, the exponent is reduced by a factor of two. (See the result in part (a).) Sounds like a lot, doesn't it? Not really though. All you did was change the fraction of *transmitted* radiation from  $10^{-24}$  to  $10^{-12}$ . That's not enough of a difference to cause a significant effect if you use sunscreen as recommended. This result is part of the reason why experts tell you to never pay a premium for SPF40 or more.

The real difference occurs during application. The industry recommends  $2 \text{ mg/cm}^2$ , which is about 20 ml to fully cover the skin of a typical adult. In practice, we rarely apply sunscreen so liberally. A study (British J. of Dermatology 144(2): 288, 2001) measured that people typically use  $0.39 \text{ mg/cm}^2$  instead of the recommend value of  $2 \text{ mg/cm}^2$ . That fact means the exponent is reduced by a factor of five. The average person using SPF8 allows ~0.4% of radiation to be transmitted, which is why people often burn even though they use sunscreen.

And we won't even talk about people who miss entire parts of their body when applying sunscreen.

**5 – Vibrational Spectroscopy: Qualitative Analysis (8 points)**

a) From the lecture notes,

$$\nu_e = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}},$$

where  $\nu_e$  is the vibrational frequency,  $k$  is the force constant, and  $\mu$  is the reduced mass. Since the reduced mass ( $\mu$ ) is the same for both H — C bonds, the force constants must be different. That means H — C = O has a smaller force constant for H — C than the typical H — C bond.

**(2 points: identify that force constant is smaller for H-C in H-C=O)**

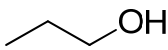
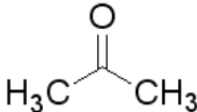
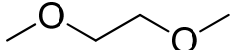
b) If H — C = O has a smaller force constant for the H — C bond, then the bond is weaker. **(3 points: identify the bond is weaker)**

c) A bond is weaker if the electron density between the atoms is lower – the oxygen atom pulls some of the electron density away from the H — C bond in H — C = O since the oxygen atom is more electronegative.

**(3 points: identify effect of electronegativity on electron density between C-H atoms.)**

**6 – IR Spectra (15 points)**

a) First, identify the unique functional group of each of the three molecules. Then, find the wavenumber range associated with each functional group.

<i>Molecule</i>			
<b>Name</b>	1-propanol	acetone	dimethyl glycol
<b>Unique functional group</b>	—OH	C=O	C—O
<b>Wavenumber range (cm<sup>-1</sup>) of functional group (lecture notes)</b>	3400–3200	1700	1260–1000

**(9 points total: 1.5 points for each answer in the six boxes)**

NOTE: No penalty if students also list C—O for 1-propanol, and no penalty if the students do/also list the combination, C—O—C, for dimethyl glycol.

b) Spectrum (A) has a large peak centered at 3400 cm<sup>-1</sup>, and thus must be the spectrum for 1-propanol. **(2 points, no credit without a justification)**

Only spectrum (B) has a prominent peak at ~1700 cm<sup>-1</sup>; therefore, spectrum (B) must be the spectrum for acetone. **(2 points, no credit without a justification)**

Spectrum (C) has a peak at 1150 cm<sup>-1</sup>, indicating the presence of a C—O bond. It does not have a peak at 3400 cm<sup>-1</sup>, meaning that the molecule does not contain an OH group. Therefore, spectrum (C) must be the spectrum for dimethyl glycol. **(2 points, no credit without a justification)**

**(Assignments may be listed in any order, not necessarily A,B,C. -2 pts for the third spectral assignment if the student simply says “since two are assigned, the third must be \_\_\_” rather than a reason based off of the spectra)**

NOTE: The values for wavenumbers listed above are approximations – students should get full credit if they list values that are similar to, but not exactly equal to, the values in the solution.

NOTE: Students may present slightly different arguments to reach the same conclusion. As long as the discussions are logical and correct, allow them as alternate solutions. Let us know about the alternate solutions so that we can add them to the published solutions.