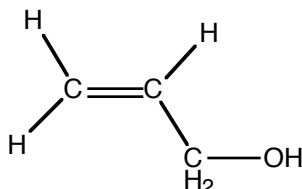
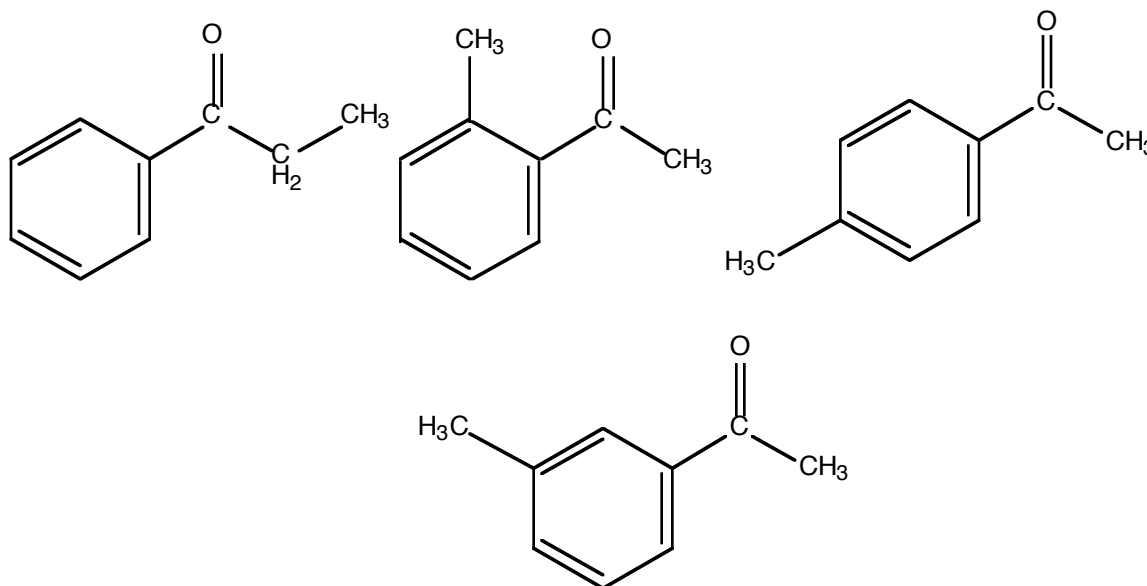


Problem Set #9
Fall 2006
SOLUTIONS

17-2. The broad band at 3400 cm^{-1} is typical of alcohols. The peak at 1650 cm^{-1} is consistent with an alkene double bond. No peak above 1700 cm^{-1} suggests the absence of a ketone or aldehyde. The molecule vinyl alcohol is consistent with this data.



17-3 The strong peak at 1700 cm^{-1} suggests that we are dealing with an aldehyde or a ketone. An aldehyde should, however, have a C-H stretch in the 2800 cm^{-1} region. We are probably dealing with a ketone. The peaks in the 1600 cm^{-1} to 1450 cm^{-1} range are consistent with an aromatic structure. The peak at 3000 cm^{-1} indicates C-H stretches attached to an aromatic system. With the formula, we find these possibilities.



In fact, the spectrum is that of *ortho*-methyl acetophenone.

17-6 Peaks in the near-IR are not as sharp as the mid-IR and hence are less susceptible to Beer's Law's deviations. In addition, the near IR region can use photoconductive detectors which are more reproducible than the thermal detectors that must be used in the mid-IR region.

17-9 The equation relating interference periods to wavelength difference is

$$b = \frac{N}{2\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)}$$

We simply substitute and solve for the path length b.

$$b = \frac{12}{2\left(\frac{1}{6.0 \mu\text{m}} - \frac{1}{12.2 \mu\text{m}}\right)} = 70.8 \mu\text{m} = 7.08 \times 10^{-3} \text{ cm}$$

18-3 It is always best to work in units that are linear in energy. Wavenumber is good, so it is best to convert the wavelengths to wavenumbers. Then to find the Stokes and anti-Stokes shifted peaks, we simply subtract or add the peak wavenumber to the excitation wavenumber. We can convert this easily back to wavelength, as requested in the problem.

$$\lambda_1 = 632.8 \text{ nm} = 6.328 \times 10^{-5} \text{ cm} \quad \lambda_2 = 488.0 \text{ nm} = 4.880 \times 10^{-5} \text{ cm}$$

$$\bar{\nu}_1 = \frac{1}{\lambda_1} = \frac{1}{6.328 \times 10^{-5} \text{ cm}} = 15803 \text{ cm}^{-1} \quad \bar{\nu}_2 = \frac{1}{\lambda_2} = \frac{1}{4.880 \times 10^{-5} \text{ cm}} = 20492 \text{ cm}^{-1}$$

Now we determine the first Stokes transition with the He:Ne laser, by first subtracting the wavenumber of the transition from the excitation wavenumber and then converting that back into a wavelength.

$$\bar{\nu}_1^{s_1} = 15803 - 218 = 15585 \text{ cm}^{-1} \quad \lambda_1^{s_1} = \frac{1}{15585 \text{ cm}^{-1}} = 641.6 \text{ nm}$$

We continue in this fashion, subtracting from the two excitation wavenumbers to obtain Stokes peaks and adding to get the anti-Stokes peaks. The complete result is as follows:

For He:Ne Laser		For Ar Ion Laser	
Stokes 5	666.1 nm	Stokes 5	507.6 nm
Stokes 4	664.8 nm	Stokes 4	506.8 nm
Stokes 3	651.7 nm	Stokes 3	499.2 nm
Stokes 2	645.6 nm	Stokes 2	495.6 nm
Stokes 1	641.6 nm	Stokes 1	493.2 nm
Rayleigh	632.8 nm	Rayleigh	488.0 nm
Anti-Stokes 1	624.2 nm	Anti-Stokes 1	482.9 nm
Anti-Stokes 2	620.5 nm	Anti-Stokes 2	480.6 nm

For He:Ne Laser		For Ar Ion Laser	
Anti-Stokes 3	614.9 nm	Anti-Stokes 3	477.3 nm
Anti-Stokes 4	603.7 nm	Anti-Stokes 4	470.5 nm
Anti-Stokes 5	602.7 nm	Anti-Stokes 5	469.9 nm

18-4 The Raman effect intensity scales with the fourth power of the excitation wavenumber. We expect the Raman peaks to be considerably more intense with the Ar ion laser. In fact, we find

$$I \propto \nu^{-4} \quad \therefore \frac{I_{Ar}}{I_{He:Ne}} = \left(\frac{20492}{15803} \right)^4 = 2.83$$

The Ar ion Raman peaks should be 2.83 times more intense. The actual measured ratio would be different because the efficiency of the grating and the efficiency of the detectors also vary with wavelength. One would have to calibrate for these differences.

18-5 The most common reason for choosing the Ar ion over the He:Ne is to avoid problems with fluorescence of the sample. With the higher energy excitation of the Ar ion source, the possibility of exciting states which will fluoresce is much greater. Other interferences arising from absorption of other components in the matrix may be a motivator for switching. One may also be interested in the lower excitation energy available from the He:Ne which can also help minimize any decomposition processes.

18-6 A Stokes line transition starts in the ground vibrational state and ends up in an excited state, which is higher than the ground state in energy by the amount of the transition. By contrast, the corresponding anti-Stokes line starts in the same excited state and ends up in the ground state. The intensity of the transition scales with the population in the starting state in each case. Hence, the anti-Stokes line should be less intense than the corresponding Stokes line and the intensity ratio is just the population ratio, as given by the Boltzmann distribution.

One needs to be sure to use the correct units. Convert the wavenumber into joules, recalling that $E = hc\nu$.

$$E_a = hc\bar{\nu}_a = (6.626 \times 10^{-34} \text{ J s}) \left(2.9979 \times 10^{10} \frac{\text{cm}}{\text{s}} \right) (218 \text{ cm}^{-1}) = 4.33 \times 10^{-21} \text{ J}$$

$$\frac{I_{as}}{I_s} = \frac{N_{upper}}{N_{ground}} = \exp\left(-\frac{4.33 \times 10^{-21} \text{ J}}{\left(1.38 \times 10^{-23} \frac{\text{J}}{\text{K}} \right) (293 \text{ K})} \right) = 0.343$$

The same calculation is used at the higher temperature, except that $T = 313 \text{ K}$ in this case.

$$\frac{I_{\text{as}}}{I_{\text{s}}} = \frac{N_{\text{upper}}}{N_{\text{ground}}} = \exp\left(-\frac{4.33 \times 10^{-21} \text{ J}}{\left(1.38 \times 10^{-23} \frac{\text{J}}{\text{K}}\right)(313 \text{ K})}\right) = 0.367$$

The other transitions are calculated similarly, giving intensity ratios as follows:

459 cm^{-1} at 293 K: 0.105

459 cm^{-1} at 313 K: 0.121

790 cm^{-1} at 293 K: 0.0206

790 cm^{-1} at 313 K: 0.0264

The anti-Stokes lines become increasingly weaker as the transition energy increases. This is reflected in this decreasing ratio.