

## INTRODUCTION

Not all bonds are the same. Tables of bond energies are actually averages taken over many molecules. For example, C-C single bonds vary in strength from compound to compound. This experiment involves measuring trends in bond energies for different carbon-oxygen bonds and probing what causes those variations.

IR spectroscopy can be used as an identification tool. It can also be used to probe trends in bonding across a series of compounds that have a similar bond in common. Infrared absorptions occur when a molecule absorbs a photon of light. This light is used to promote the molecule into an excited vibrational state. The energy of the vibration is usually associated with a particular bond or pair of bonds. Most important IR absorptions lead to increased bond stretching motions in a molecule. The bond stretching motion acts like a spring, stretching and contracting at some frequency,  $\nu$ . The spectrum is usually measured in terms of frequency in units of "wavenumbers," which is the reciprocal of the wavelength of absorbed light, in cm.

$$\text{Wavenumber: } \tilde{\nu}(\text{cm}^{-1}) = \frac{1}{\lambda (\text{cm})}$$

The spring motion follows Hooke's Law:

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \mu \text{ is the reduced mass: } \mu = \frac{m_1 \times m_2}{m_1 + m_2}$$

The  $m$  values are the masses of the bonded atoms (from the periodic table, converted to kg/atom). The force constant,  $k$ , is proportional to the bond strength of the vibrating bond. This force constant,  $k$ , is the target of our measurements in this experiment. An increase in  $k$  indicates an increase in bond strength, and can therefore be used as a probe of things that affect bonding in molecules.

### Example Calculation of k

A carbon-nitrogen triple bond has an IR stretching absorption at  $2245 \text{ cm}^{-1}$ .

$$m1(\text{C}) = \frac{12 \times 10^{-3} \text{ kg}}{\text{mol}} \times \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ atoms}} = 1.99 \times 10^{-26} \text{ kg/atom}$$

$$m2(\text{N}) = \frac{14 \times 10^{-3} \text{ kg}}{\text{mol}} \times \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ atoms}} = 2.33 \times 10^{-26} \text{ kg/atom}$$

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2} = \frac{1.99 \times 10^{-26} \times 2.33 \times 10^{-26}}{1.99 \times 10^{-26} + 2.33 \times 10^{-26}} = 1.07 \times 10^{-26}$$

$$2245 \text{ cm}^{-1} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi \times 2.998 \times 10^{10} \text{ cm}} \sqrt{\frac{k}{1.07 \times 10^{-26}}}$$

$$4.24 \times 10^{14} = \sqrt{\frac{k}{1.07 \times 10^{-26}}}$$

$$k = 1920 \text{ N/m}$$

## Exercise 1.

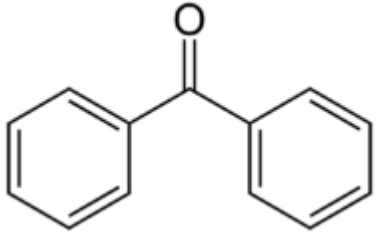
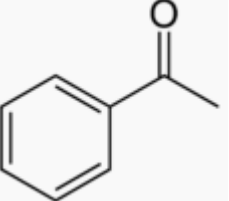
Analysis of the effects of *conjugation* and ring strain in organic systems on C=O (carbonyl) bonding.

When a molecular structure has pi-bonding atoms near one another, they can form resonance structures that make the molecule as a whole more stable. This experiment probes the effect of conjugation on the strength of a carbonyl (C=O) bond in a series of molecules.

### MEASUREMENTS:

Obtain the IR spectra of the molecules: benzophenone and acetophenone.

Record the C=O stretching frequency and calculate the force constant,  $k$ . The C=O stretching band is the largest one between 1500-1800  $\text{cm}^{-1}$ .

Compound	Structure	$\nu_{\text{CO}}, \text{cm}^{-1}$	Force constant, $k$
benzophenone			
acetophenone			

Answer the following questions:

### Question 1:

Rank the compounds in order of increasing conjugation (by inspecting the structures):

\_\_\_\_\_ < \_\_\_\_\_

### Question 2:

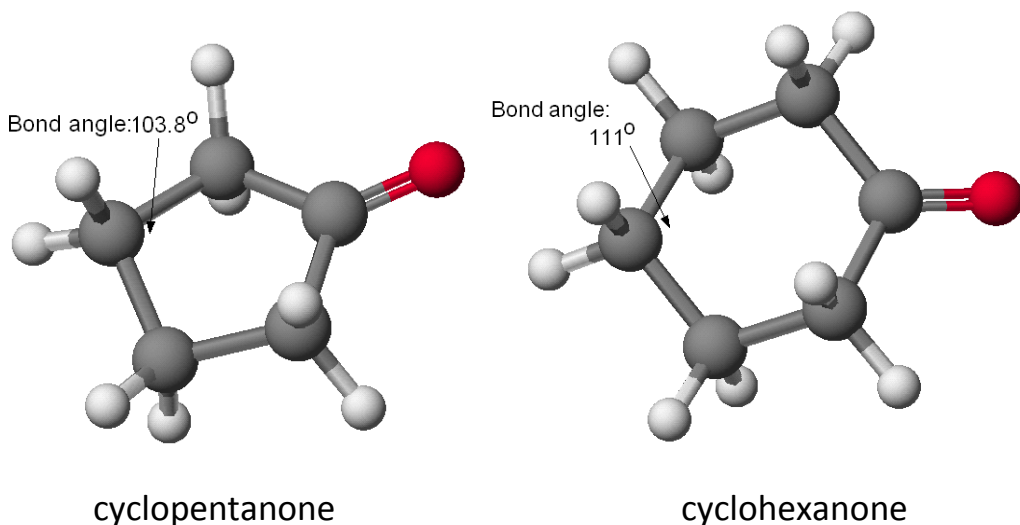
What effect does conjugation around the C=O group have on the strength of the C=O bond?

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## Exercise 2.

Analysis of the effects of ring strain on the strength of C=O carbonyl bonding.

The structures of three cyclic ketones are given here.



The ring structure does not allow the C-C-C bonds to assume their preferred bond angles. This causes the molecule as a whole to become less stable, and is known as "ring strain." Measure the IR spectra of these two compounds and determine the effect of increased ring strain on the C=O bond strength.

Compound	Bond angle	$\nu_{\text{CO}}$ , $\text{cm}^{-1}$	Force constant, k
cyclopentanone			
cyclohexanone			

### Question 1.

Rank the compounds in order of increasing ring strain?

\_\_\_\_\_ < \_\_\_\_\_

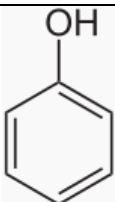
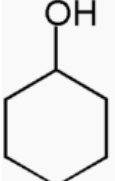

### Question 2.

What is the effect of increasing ring strain on the C=O bond strength?

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### Exercise 3.

Analysis of the effects of conjugation and strain in organic systems on C-O single bond strengths.

Compound	Structure	$\nu_{\text{CO}}, \text{cm}^{-1}$	Force constant, k
phenol			
cyclohexanol			
n-amyl alcohol = 1-pentanol			

$\nu_{\text{CO}}$  = largest IR band between 1000-1300  $\text{cm}^{-1}$  is the one.

Measure the IR spectra of the compounds above. The C-O (single bond) stretching frequency is the largest observed between 1000 – 1500  $\text{cm}^{-1}$ .

#### Question 1.

Which two of these compounds are useful for comparing conjugation in these systems?

#### Question 2.

Does increased conjugation increase or decrease the C-O bond strength?

#### Question 3.

Which two of these compounds are useful for comparing angle strain in these systems?

#### Question 4.

Does increased strain increase or decrease the C-O bond strength?

#### Exercise 4.

Analysis of bonding of carbon monoxide to metal atoms.

Many metals in low oxidation states bond to one or more CO molecules. These are called metal carbonyl compounds. The bonding involves the CO molecule donating electron density into a d-orbital on the metal, and the metal donating electron density into a pi orbital between the C and O atoms. This experiment is used to answer the question:

Does the metal donate electron density into a CO pi bonding orbital, or into a CO pi antibonding orbital?

Measurements:

Obtain the IR spectrum of  $W(CO)_6$ .

Compound	Charge on metal	$\nu_{CO}$ , $cm^{-1}$	Force constant, k
$W(CO)_6$			
$Co(CO)_4^-$		1890	
$Fe(CO)_4^{2-}$		1790	
Free CO	----	2143	

#### Question 1.

Does bonding to the metal increase or decrease the strength of the CO bond? Compare the force constants of free CO and that of CO in  $W(CO)_6$ .

#### Question 2.

Which does this indicate?

The metal donates electrons into a CO pi bonding orbital.

The metal donates electrons into a CO pi antibonding orbital.

#### Question 3.

Explain the trend in CO force constants going from  $W(CO)_6$  to  $Co(CO)_4^-$  to  $Fe(CO)_4^{2-}$ .

#### Question 4.

Another series of compounds are of the type:  $L-Ni(CO)_3$ , where the additional ligand, L, is varied. The following data are obtained. Does this make sense based on your conclusions above? Explain.

Compound, L	$\nu_{CO}$ , $cm^{-1}$
$P(CH_3)_3$	2064
$P(OCH_3)_3$	2080
$PF_3$	2111