The Harmonic Oscillator - A Model for IR Absorption

Introduction

The harmonic oscillator is often used as a model for absorption of infrared radiation by covalently bonded molecules. This motion is as simple as the oscillations of a mass on a spring. The force required for this type of motion obeys Hooke's Law (F = kx) where x is the displacement away from equilibrium, k is the proportionality constant (called the force constant), and F is the force, usually expressed in Newtons. The restoring force to bring the mass back to equilibrium would be equal and opposite to this force.

The period for one oscillation is given by Galileo' s equation $T = 2p\sqrt{\frac{m}{k}}$. Since the frequency (ν) is the reciprocal of the period then $n = \left(\frac{1}{2p}\right)\sqrt{\frac{k}{m}}$. The m actually includes the mass of the object and the mass of the spring itself(m_m + m_s). The equation can be rearranged by inverting both sides and squaring to get the following form that is also useful for determining the constant k from frequency data.

$$\left(\frac{1}{n}\right)^2 = (2p)^2 \frac{m_m}{k} + (2p)^2 \frac{m_s}{k}$$

Plotting $(1/\nu)^2$ versus the mass on the spring should yield a straight line with slope = $(2\pi)^2/k$.

This model should be applicable to vibrational harmonic motion of molecules, such as chloroform ($CHCl_3$). If we assume that the CCl_3 group remains motionless during vibration of the C-H bond, then a force constant for the stretching and bending modes can be obtained from spectra and the change in the frequencies for isotopic substitutions such as deuterium for hydrogen can be predicted from the modeled force constants. The equation used to find the force constant k is analogous to the mass on a spring, namely

$n = \left(\frac{1}{2p}\right)\sqrt{\frac{k}{m_{eff}}}$ with m being the effective mass of the system (~ mass of the H atom)

If deuterium is substituted for H in chloroform one can calculate the new effective mass (~the mass of the deuterium atom) and use it to find the new frequency. It is also helpful to remember that IR spectra is usually reported in units of cm^{-1} ($1/\lambda$) and that $c = \lambda\nu$.

The purpose of this lab is to investigate the harmonic oscillator model using a simple mass and spring and to apply the model to predict the frequencies of deuterated chloroform.

Procedure

The Harmonic Oscillator Model

Using a simple spring system, take several masses (at least 5) and find the displacement away from the equilibrium position. Time 25 oscillations or more to find the average period.

- Find the best value of the spring constant k for the simple mass on spring system by graphing force versus extension.
- Determine the constant k using Galileo's equation. Graph $(1/\nu)^2$ versus the mass on the spring. Compare to the Hooke's Law method. Calculate the % deviation.

Application to IR spectra

- Take the IR spectra of chloroform and find the C-H stretch and C-H bend. These bands should be around 3000 cm^{-1} and 1200 cm^{-1}. Determine them as precisely as possible.
- Determine the force constant for each motion by using the Galileo equation. You will have to change wave number to frequency.
- Predict using your model (and the force constant above) the frequencies of the C-D stretch and C-D bend for deuterated chloroform.
- Take the IR spectra of deuterated chloroform and compare to your predicted values for the C- D stretch and bend. Calculate the % deviation.

References

W. B. Heuer and E. Koubek, *J. Chem. Ed.,* 74(3), 313, March 1997.

P. W. Atkins, *The Elements of Physical Chemistry,* 1st edition, 1993, pages 433-441.

P. W. Atkins, Physical Chemistry, 8th edition, 2006, pages 290-291, 979-982, 452-455.

Write-up

Use the following format for your report unless a Powerpoint presentation is required.

Harmonic Oscillator Model

1. Data tables for Hooke's Law and Galileo's equation experiments (with sample calculations)

2. Graph force vs. extension (Hooke's Law)

3. Find the best value for the spring constant from your graph using a simple propagated error analysis and the error in the slope.

4. Graph $(1/\text{frequency})^2$ vs. the mass on the spring (Galileo's equation)

5. Find the best value for the spring constant using a simple propagated error analysis and the error in the slope.

6. Compare the spring constants obtained from the 2 equations and calculate the % deviation.
% deviation $=(| k_{Hooke} - k_{Galileo}| / k_{Hooke})\ 100$

7. Conclusion – what does this prove?

Application to IR Spectra

1. Print out the IR spectra for $CHCl_3$ and $CDCl_3$. Annotate to show the C-H stretch and bend. Indicate the wave numbers for each to at least 0.1 cm^{-1}.

2. Use these wave numbers to determine the force constant "k" of these motions using the Galileo equation. Calculate and use the "reduced mass" or "effective mass" in these equations.

3. Calculate the predicted/theoretical C-D stretch and bend frequencies (in cm^{-1}) using the force constant above and the Galileo equation. Calculate and use the "reduced mass" or "effective mass" in these equations.

4. From your IR spectra calculate the % deviation for the C-D bend and stretch frequencies.
% deviation $=(| \nu_{exp} - \nu_{theoretical}| / \nu_{theoretical})\ 100$

5. Conclusion – what does this prove?