Fourier transforms of molecular vibrations ©

Part III: Lifetime Broadening in the Vibrational Spectrum

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Goal: The primary goals of this document, and the accompanying documents, are to gain a familiarity with standard models that describe the classical vibrations of a chemical bond and to explore the relationship between the time and frequency representations of vibrational motion. This particular document introduces students to the concept of 'Lifetime Broadening.' A damping term is added to the harmonic oscillator equation of motion (see the introductory document, FTMolVib.mcd) which causes the oscillator to lose energy as it vibrates. Consequently, each successive vibration occurs with a smaller amplitude until all the vibrational energy is lost. By altering the magnitude of the damping term, students can investigate how damping affects the vibrational spectrum.

Prerequisites: These Mathcad documents are designed to support the quantum mechanics-spectroscopy portion of a Junior-Senior level physical chemistry class. Students should have had at least one year of calculus and physics. It will be helpful if students have some knowledge of c*lassical harmonic oscillators* (the vibration of two masses connected by a Hooke's law spring). The equations describing a classical harmonic oscillator can be found in several standard physical chemistry texts [1,2]. While not necessary, it will also be helpful if students are familiar with *Fourier transform* techniques (also described in several physical chemistry texts [3,4]). This document is the third in a set of three (the introductory document being *FTMolVib.mcd* and the second document is *FTAnharm.mcd)*. This document is designed to be used in conjunction with the introductory document. These documents require Mathcad 6.0+.

Introduction: Chemical bonds can lose vibrational energy by intermolecular collisions and intramolecular vibrational energy transfer from one vibrational mode into another. Consequently, a collection of vibrationally excited molecules will eventually return to their ground state. The amount of time required for this energy relaxation to occur is called the vibrational lifetime. We can limit the vibrational lifetime of a harmonic oscillator by adding a viscous damping term to the harmonic oscillator equation of motion from document 1.

$$\frac{d^2}{dt^2}x + \frac{damp}{\mu}\cdot\frac{d}{dt}x + \frac{k}{\mu}\cdot x = 0$$

The second term in this equation of motion generates an opposing force that is proportional to the velocity (dx/dt) of the oscillator. A full description of damped mechanical oscillators (and their equations of motion) is available in many introductory differential equation texts (for example, see reference 1).

Performance Objectives for Document 3:

After completing this document, you should ....

1) be able to model a bond vibration as a damped harmonic oscillator.

2) be able to describe the phenomena called 'lifetime broadening'.

3) explain how the degree of lifetime broadening varies with the damping constant (**damp**).

Damped Harmonic Oscillator Equation of Motion:

Given below are parameters that will allow us to simulate damped harmonic vibrations in molecular chlorine, Cl_2 (the values are identical to those used in document 1).

$k := 322.7$ Spring constant in Newtons/meter

$\mu := 2.903 \cdot 10^{-26}$ Reduced mass of Cl_2 in kilograms

$damp \equiv 1 \cdot 10^{-13}$ Damping constant in kilograms/second, defined as a global variable so that it can be varied in the exercises below. Vibrational lifetimes typically range between 0.3 to 200 picoseconds for molecules dissolved in solution. The value of **damp** defined here is arbitrary (**damp**=1x10^{-13} kg/s will yield a vibrational lifetime of about 1 picosecond).

Differential equation

$$D(t,x) := \begin{bmatrix} x_1 \\ -\frac{k}{\mu} \cdot x_0 - \frac{damp}{\mu} \cdot x_1 \end{bmatrix}$$

Note that this differential equation is identical to the one defined in the introductory document, *FTMolVib.mcd*, except that it includes the viscous damping term proportional to $\mathbf{x_1}$.

$$x := \begin{pmatrix} 5\cdot 10^{-12} \\ 0 \end{pmatrix}$$

The initial amplitude (in meters) and velocity, respectively.

$$tmax := 1\cdot 10^{-}$$

The maximum time to which the equation of motion will be evaluated in seconds.

$$frequency := \frac{1}{\cdot\pi}\left(\frac{k}{\mu}\right)^{\frac{1}{2}}$$

We must specify the total number of points over which the equation with Mathcad's Runge-Kutta algorithm. The total number of points must be large enough to resolve each period of the vibration over the full time range (**tmax**
this, one can take the frequency of the oscillator (the frequency expression of an undamped harmonic oscillator is utilized here as an approximation) and multiply it by **40*tmax**
fashion, the total number of points will be great enough to allow 40 points per oscillation.

$$points := floor(40\cdot tmax\cdot frequency$$

This expression calculates the total number of points as described above, rounded down to the nearest integer value.

$$Z := rkfixed(x\ 0,\quad ,\quad -\quad)$$

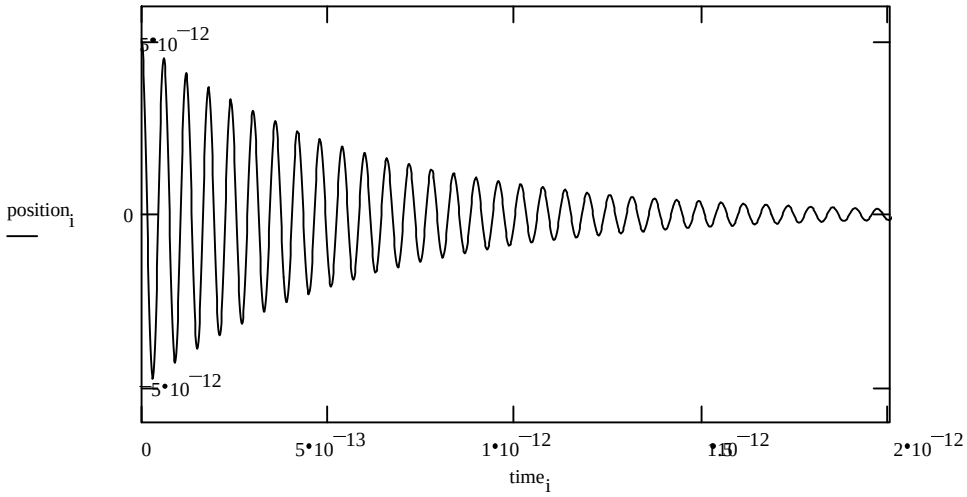
$$time := \overset{<}{Z}^{>}$$

$$position := \overset{<}{Z}^{>}$$

$$velocity := Z^{<>}$$

$$i := 0..\quad -$$

Graph 3.1: A portion of the position vector, showing the amplitude of the damped vibration as a function of time.



Exercise 3.1: Damped oscillators are classified as being *underdamped*, *overdamped*, or *critically damped*. In the *underdamped* case, the damping constant is small enough to permit vibrational motion (the oscillator can vibrate before the amplitude decays to zero). In the *overdamped* case, the damping constant is large enough to prohibit vibrational motion (the oscillator will simply decay to zero from its initial amplitude). The *critically damped* case represents the crossover between the underdamped and overdamped regimes. Repeat the above calculations using different values for the damping constant (try using values of **damp** equal to $1x10^{-14}$, $1x10^{-13}$, $1x10^{-12}$, and $1x10^{-11}$ kg/s). In each case, regenerate Graph 3.1. Which values of damp correspond to the underdamped regime? The overdamped regime? Estimate the value of **damp** that gives rise to the critically damped regime (additional calculations may be necessary).

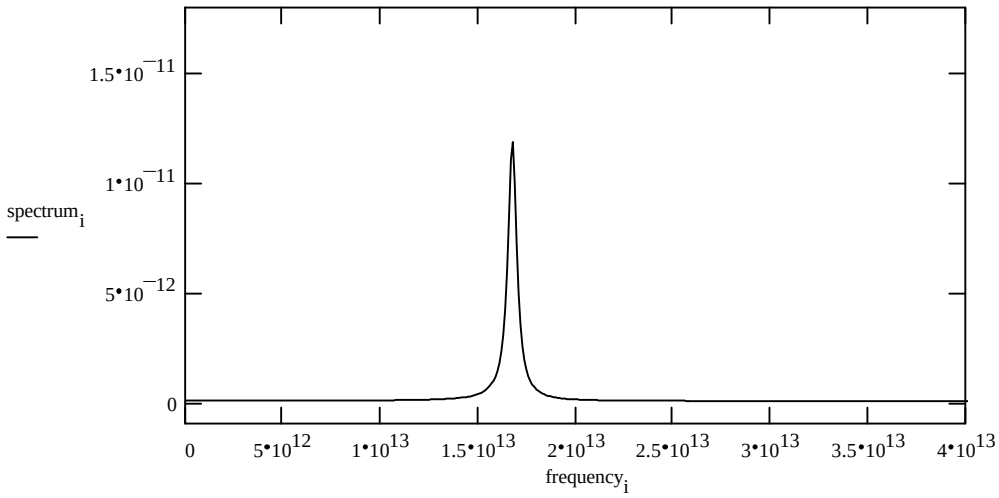
Spectrum of a Damped Harmonic Oscillator:

As was done in documents *FTMolVib.mcd* and *FTAnharmon.mcd*, we will perform a Fourier transform of the **position**$_i$ data in order to generate the frequency spectrum of the vibration.

$spectrum := Re(cfft(position))$ The Fourier transform of the damped vibration. The real part of the results are stored in the vector **spectrum.**

$frequency_i := \frac{i}{tmax}$ Defines the frequency associated with each amplitude stored in the vector **spectrum**.

Graph 3.2: Frequency Spectrum of the Damped Harmonic Vibration



An undamped harmonic vibration is characterized, in principle, by a single spectral peak that is infinitely sharp (the peak has no width). Comparing Graph 3.2 to Graph 1.3 (in document *FTMolVib.mcd*), one can see that the addition of a damping term gives rise to 'lifetime broadening'. The peak distortions that were observed in the spectra created in parts 1 and 2 are no longer present because the damping term causes the vibrational motion to stop before time=**tmax**. In other words, no truncation error will be observed in the output of the Fourier transform because the oscillations have ceased within the range of the input data.

General Exercises (part 3):

1) The degree of broadening, expressed as a frequency width ($\Delta\nu$), can be shown to be directly proportional to the magnitude of the damping constant. Regenerate graph 3.2 using values of damp equal to 0.1×10^{-13}, 0.5×10^{-13}, 1×10^{-13}, 3×10^{-13}, 1×10^{-12}, and 2.5×10^{-12} kg/s. In each case, estimate the width of the peak in graph 8 (by expanding the axes) and verify that $\Delta\nu$ is proportional to damp.

2) In exercise 1.2 (document *FTMolVib.mcd*), you were ask to determine the potential energy and kinetic energy of the harmonic oscillator at each time increment. Do the same calculations using the damped harmonic oscillator data. Graph the potential and kinetic energies on the same plot from zero to 2×10^{-13} seconds. Prepare a graph that shows how the total energy varies as a function of time for the damped harmonic oscillator. Is the total energy conserved? Explain.

Reference:

1. Miller, R. K. *Introduction to Differential Equations*; Prentice-Hall: Englewood Cliffs, NJ, 1987, pp.154-162.

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