Fourier transforms of molecular vibrations ©

Part II: The Frequency Spectrum of an Anharmonic 'Morse' Oscillator

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Goals: 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 Anharmonic 'Morse' oscillator model, which provides a more realistic descripton of bond vibrations. In particular, students can observe how the anharmonicity of the internuclear potential energy function gives rise to additional features in 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 second in a set of three (the introductory document being FTMolVib.*mcd* and the third document is *FTLifeTime.mcd)*. This document is designed to be used in conjunction with the introductory document. These documents require Mathcad 6.0+.

Introduction to Part II: The harmonic oscillator model predicts that the potential energy of a bond increases to infinity as the bond length increases. However, a real chemical bond will break when sufficiently stretched, which means that the potential energy does not increase without end. As the bond stretches, the potential energy increases to a maximum amount corresponding to the dissociation energy (**De**) of the bond. Additionally, as a real chemical bond is compressed, the internuclear repulsion causes the potential energy to rise more rapidly than a 'harmonic bond'. Overall, a plot of potential energy -vs- bond length for a real diatomic is asymmetric in shape.

Performance Objectives for Part 2:

After completing this document, you should ....

1) be able to model a bond vibration as an anharmonic Morse oscillator.

2) know how to evaluate an analytical expression for the Force exerted on any oscillator as a function bond displacement, given the potential energy function of that oscillator.

3) explain the origin of "overtone peaks" in the frequency spectrum of an anharmonic oscillator.

4) explain the origin of the 'anharmonic red-shift.'

5) explain the relationship between the magnitude of overtone peaks and the anharmonic character of the bond potential energy function.

Morse Oscillator Equation of Motion.

A simple empirical function, called the Morse function, is used here to describe the potential energy of a diatomic molecule as a function of bond length [1,2,3]. The asymmetric shape of the Morse potential energy curve is characterized by two empirical constants, the bond dissociation energy (**De**) and a constant called the Morse parameter (β). Given below are parameters that allow us to simulate 'anharmonic' vibrations in molecular iodine, I_2. Values of **De** and β for I_2 were obtained from reference 2.

$$De := 2.4 \cdot 10^{-19}$$ Dissociation energy in joules.
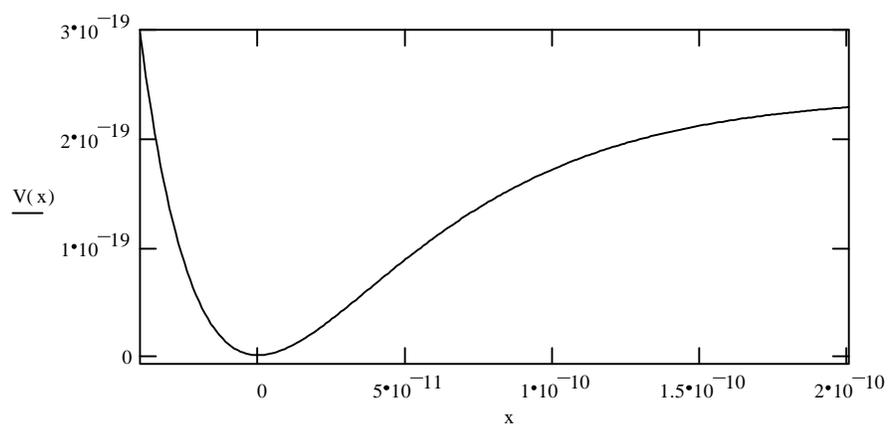
$$\beta := 1.87 \cdot 10^{10}$$ Morse parameter in m^{-1}.

$$\mu := 1.05 \cdot 10^{-25}$$ Reduced mass of I_2 in kilograms.

$$x := -4.0 \cdot 10^{-11}, -3.9 \cdot 10^{-11} .. 2 \cdot 10^{-10}$$ Range of bond displacements in meters, in increments of 0.1 picometers.

$$V(x) := De \cdot \left(1 - e^{-\beta \cdot x}\right)^2$$ **The Morse potential energy function.**

Graph 2.1: Morse potential energy

Exercise 2.1: Independently vary the values of the dissociation energy (**De**) and the Morse parameter (β). Note how each parameter affects the shape of the potential energy curve.

To simulate an anharmonic vibration, we need an equation of motion that incorporates the force that an oscillator would experience as it rocks back-and-forth within the Morse potential. We can obtain an analytical expression for this force by taking the derivative of the Morse function with respect to **x**.

$$F = -\left(\frac{d}{dx}V(x)\right) = -\left[\frac{d}{dx}De\cdot\left(1 - e^{-\beta\cdot x}\right)^2\right] = -2\cdot De\cdot\beta\cdot\left(e^{-\beta\cdot x} - e^{-2\cdot\beta\cdot x}\right)$$

<u>Question</u>: Why is a negative sign included in the derivative shown above?

Incorporating this force into Newton's second law, **F=μ d²x/dt²**, yields the following equation of motion.

$$\frac{d^2}{dt^2}x + \frac{2\cdot De\cdot\beta}{\mu}\cdot\left(e^{-\beta\cdot x} - e^{-2\cdot\beta\cdot x}\right) = 0$$

<u>Exercise 2.2</u>: Use the *Evaluate Symbolically* function of Mathcad (within the menu *Symbolic*) to determine an expression for the derivative of the Morse function V(x) with respect to x. Do you get the expression shown above?

The Morse oscillator equation of motion must be defined as a matrix within Mathcad. Following the same procedure that was used in the introductory document (*FTMolVib.mcd*), the equation of motion is defined in the matrix **D(t,x)** and a numerical solution is obtained using the *rkfixed* routine.

<u>Differential equation</u>

$$D(t,x) := \begin{bmatrix} x_1 \\ \dfrac{-2\cdot De\cdot\beta}{\mu}\cdot\left(\exp\left(-\beta\cdot x_0\right) - \exp\left(-2\cdot\beta\cdot x_0\right)\right) \end{bmatrix}$$

<---- <u>First derivative</u>: **x₁** represents the velocity at each point in time, which is unknown in our model.

<---- <u>Second derivative</u>: described by the equation-of motion, where **x₀** represents the position at each point in time

$$x := \begin{pmatrix} xinit \\ 0 \end{pmatrix}$$

Initial position and velocity. The initial position is defined as a global variable **xinit** (in units of meters) so that it can be varied in the exercises described below. The value of **xinit** given to the left is about 5x larger than the average bond displacement of diatomic iodine at room temperature. An overly large bond displacement is initially chosen in this exercise so that the oscillator moves over a large region of the potential energy curve shown in Graph 2.1. Consequently, we can observe how the vibrational spectrum is affected by the anharmonic portion of the potential energy curve.

$$xinit \equiv 5 \cdot 10^{-11}$$

$$tmax \equiv 1.2 \cdot 10^{-11}$$

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

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

We must specify the total number of points over which the numerical solution will be evaluated when solving a differential 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**). To accomplish this, one can take the frequency of the oscillator (calculated to the left) and multiply it by **40*tmax**. In this fashion, the total number of points will be great enough to allow 40 points per oscillation. The expression given to the left for calculating the frequency of a Morse oscillator is described in reference 3.

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

$$Z := rkfixed(x, 0, tmax, points - 1, D)$$

The equation-of-motion is solved by invoking Mathcad's *rkfixed* routine. The time, position, and velocity of the oscillator are stored in a 3 column matrix (Z) with a number of rows equal to **points**.
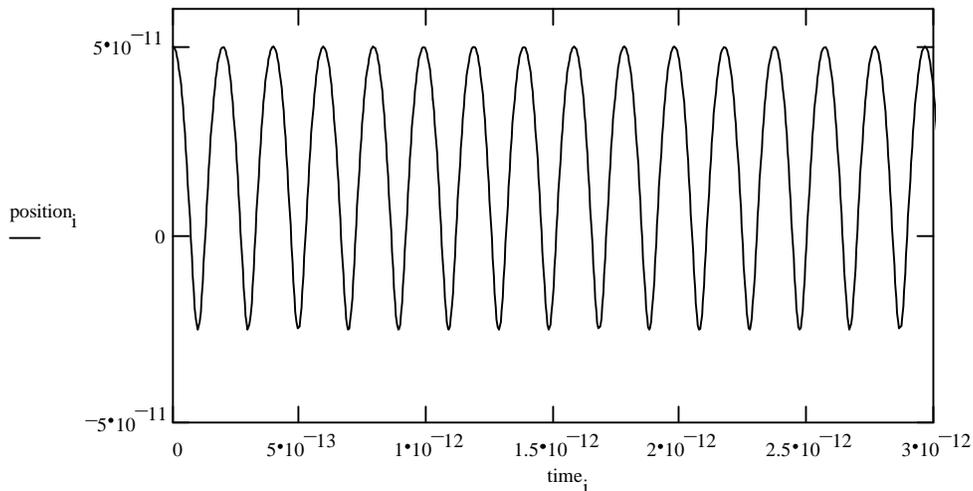
$$time := Z^{<0>}$$
$$position := Z^{<1>}$$
$$velocity := Z^{<2>}$$

These statements separate the 3 column Z matrix into time, position, and velocity vectors.

$$i := 0 .. points - 1$$

Index numbers to accompany the three vectors given above.

Graph 2.2: A portion of the position vector, showing the amplitude of the anharmonic vibration as a function of time.

position$_i$

Compare this graph to graph 1.2 (generated in the introductory document, *FTMolVib.mca*). Note that the amplitude of the vibration is asymmetric about **x=0**; the amplitude is greater when the bond stretches than when the bond compresses.

Exercise 2.3: Repeat the above calculations using different values for the initial bond displacement (try using values of **xinit** equal to 1×10^{-12}, 5×10^{-12}, 1×10^{-11}, and 5×10^{-11} meters). In each case, regenerate Graph 2.2. How does the asymmetry in Graph 2.2 vary as the initial bond displacement is increased? Explain.

Spectrum of an Anharmonic 'Morse' Oscillator.

As was done in the introductory document, *FTMolVib.mca*, we will take a Fourier transform of the **position$_i$** data to generate the frequency spectrum of this anharmonic vibration.
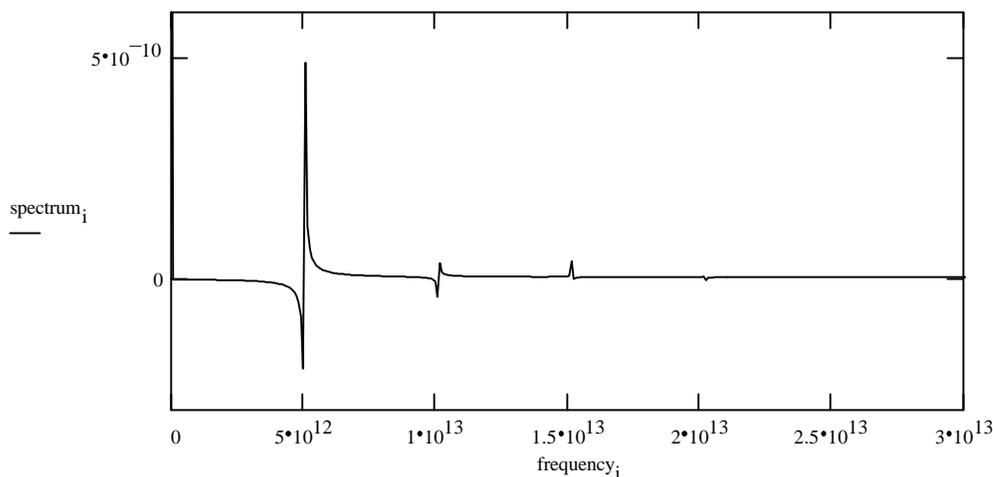
$$\text{spectrum} := \text{Re}(\text{cfft}(\text{position}))$$

This statement performs the Fourier transform, and the real part of the result is stored in the vector **spectrum**.

$$\text{frequency}_i := \frac{i}{\text{tmax}}$$

This statement defines the frequency associated with each element in vector **spectrum**.

Graph 2.4: Frequency Spectrum of the Anharmonic 'Morse' Vibration

The frequency spectrum reveals a strong peak around 5×10^{12} Hz corresponding to the fundamental vibrational frequency of the oscillator. The spectrum also reveals weak peaks at *2x*, *3x*, and *4x* the fundamental frequency. These additional peaks are called '*Overtone Bands*' and are characteristic of anharmonic motion.

The bond vibrations in real molecules are mostly harmonic when the bond displacement is small (i.e. the maximum amplitude of the vibration is small and the oscillator remains near the bottom of the potential energy well). The anharmonic nature of the potential energy well becomes more pronounced as the vibrational amplitude is increased. Consequently, the overtone bands in the vibrational frequency spectrum are more pronounced for high vibrational energy states. Also, the fundamental and overtone bands are shifted to lower frequency as a result of increased anharmonicity, a phenomenon known as an '*anharmonic red-shift*'.

General Exercises (part 2):

1) Regenerate Graph 2.4 so that it expresses the spectrum as a function of wavenumber.

2) Investigate how the spectrum of the Morse oscillator changes as the amplitude of the vibration is increased. This can be accomplished by regenerating Graph 2.4 using increasing values of the initial position **xinit** (try using the same values that were used in Exercise 2.3 above). In each case, note the number of *overtone bands* and any *anharmonic red-shifts* in Graph 2.4. Describe your observations in writing.

References:

1. Atkins, P. *Physical Chemistry*, 6th ed.; W. H. Freeman: New York, 1998, pp. 479-780.
2. McNaught, I. J. *J. Chem. Edu.***1980**, *57*, 582-584.
3. Harris, D. C.; Bertolucci, M. D. *Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy*; Dover Publications: New York, 1989, pp. 106-107, 115.