

# Vibronic Spectra of Diatomic Molecules and the Birge-Sponer Extrapolation ©

George M. Shalhoub  
Department of Chemistry  
LaSalle University  
Philadelphia, PA 19141

and

Theresa Julia Zielinski  
Department of Chemistry,  
Medical Technology, and Physics  
Monmouth University  
West Long Branch, NJ 07764-1898

shalhoub@lasalle.edu

tzielins@monmouth.edu

© Copyright George M. Shalhoub and Theresa Julia Zielinski 1997. All rights reserved. You are welcome to use this document in your own classes. Commercial use is not allowed without the permission of the authors .

## Goal

The goal of this document is to examine the potential energy curves for both the ground and excited states of a diatomic molecule and to examine the electronic transition between these two states. This will set the stage for a Birge-Sponer determination of the dissociation energies,  $D_0$  and  $D_e$ , of the excited state from experimental UV-visible spectral data.

## Prerequisites

This document is appropriate for use by students in the Junior-Senior level physical chemistry classes. To use this document you should have had at least a year of calculus and some prior experience with using Mathcad in physical chemistry. This document is one of a suite of five. The other four are MorsePotential.mcd, FranckCondonBackground.mcd, FranckCondonComputation.mcd, and IodineSpectrum.mcd. Each document can be used alone but you will derive the greatest benefits from your studies by using them together. Furthermore you should be familiar with the features of a UV-vis spectrum for diatomic molecules and the relationship between electronic and vibrational energy levels for the ground and excited states of molecules. **To use this document toggle live symbolic and optimize to the 'on' position in the Math Menu. This document illustrates using some of the symbolic mathematics features of Mathcad.**

## Performance Objectives

At the end of this exercise you will be able to:

1. explain the relationship between the potential energy curves for excited and ground states in a molecule;
2. explain the significance of each parameter in the Morse potential with respect to the shape of the Morse potential function and the properties of the molecule;
3. use a Birge-Sponer plot to determine the dissociation energy of the molecule;
4. derive a relationship between  $D_e$  and  $\omega$ .

## Introduction

A major emphasis in upper level chemistry courses is spectroscopy. This prompts us to ask, what information can we obtain from the vibronic (vibration-electronic) spectrum of a molecule? An answer is possible if we assume a model for the potential energy of the vibrating molecule. Consider a diatomic molecule. If one were only interested in the equilibrium bond length of the molecule the simple harmonic oscillator would be adequate to represent the diatomic molecule potential energy. However, the simple harmonic oscillator model does not account for the fact that, given sufficient energy, bonds can be broken. To account for the dissociation of molecules

the Morse potential,  $V(r) := D_e \left[ 1 - e^{-\beta \cdot (r - R)} \right]^2$ , is one of the simplest potential

functions we can use. To use the Morse function to compute the potential energy of a diatomic molecule like iodine or bromine as a function of internuclear separation  $r$ , we need the equilibrium bond length  $R$ , the dissociation energy  $D_e$ , and the Morse parameter  $\beta$ .

The Morse potential, like the harmonic oscillator potential is only an approximation for a diatomic molecule. One sees this by comparing the experimental, harmonic and Morse potentials for the  $H_2$  molecule (see Figure 7.1 p 259 in Berry, Rice, and Ross). The harmonic potential is clearly the least adequate. It gives agreement only at the very bottom of the potential well where the curvature can be used to determine the force constant for a bond. The Morse potential fits better over a wider range of internuclear distances but it fails at larger values of  $r$ . London dispersion forces become important at larger distances. These cause a change in the experimental potential that results in a more rapid approach to the dissociation limit compared to that predicted by the Morse potential. A comparison of the experimental and Morse potential curves for  $I_2$  can also be found in Barrow p 241 and Verma (1963).

In this document we will examine some of the properties of the Morse potential function. We will also derive the equations needed to create a Birge-Sponer plot that will be used to extract the parameters needed to prepare a Morse potential curve for the excited state of a molecule.

## Part 1. Exploring the Morse Potential.

In this section we will examine the Morse potential in detail. You are to work through the questions presented here and record your answers in your notebook. The accompanying MorsePotential.mcd document provides complementary practice with the Morse potential.

**Question 1.** Identify  $D_e$  and distinguish it from  $D_0$ . Locate a source for values of  $D_e$ , the dissociation energy of a diatomic molecule, and  $R$ , the equilibrium bond length of a diatomic molecule.  $\beta$  is the third parameter used in the Morse potential. How could you obtain  $\beta$  ?

As an example we will prepare the Morse potential plot for the two lowest electronic states of iodine and graph them below. These graphs assume that the Morse Potential is a valid representation for the potential energy of a bond as a function of internuclear distance.

### Setting up the parameters for the Morse potential plots.

$$\text{pm} := 10^{-12} \cdot \text{m} *$$

define a picometer  
(note the use of units)

[the red \* indicates that optimize  
in the Math menu is toggled to  
the 'on' position.]

$$i := 0 .. 500$$

$$r_i := (.5 + i) \cdot \text{pm} *$$

Here we set up the Index for graphing the function.  
Note how the index is used to define a range for r.  
Remember that the Morse potential is a function of r.

### Here we summarize the Morse parameters for the ground and excited states of iodine.

#### Excited B state parameters ( sub e)

#### Ground X state parameters ( sub g)

$$D_{e_e} := 4911 \cdot \text{cm}^{-1} *$$

dissociation energy

$$D_{e_g} := 18941 \cdot \text{cm}^{-1} *$$

$$\beta_e := 1.535 \cdot 10^{10} \cdot \text{m}^{-1} *$$

Morse " $\beta$ "

$$\beta_g := 1.517 \cdot 10^{10} \cdot \text{m}^{-1} *$$

$$R_e := 3.105 \cdot 10^{-10} \cdot \text{m} *$$

bond length

$$R_g := 2.66 \cdot 10^{-10} \cdot \text{m} *$$

These parameters were obtained from Herzberg (1939) and Harmony (1972).

Examine the data for the two states. We have deliberately used different units for the two states. Mathcad will use appropriate units in all subsequent calculations, i.e. the conversions will be done automatically.

#### A Note on Units:

1/cm is not formally a unit of energy in spectroscopy though it is widely used as one. The 1/cm is the unit often used for wavenumber. To convert from 1/cm to energy you multiply by a factor of  $hc$  ( $h$  = Planck's constant, and  $c$  = velocity of light in vacuum). It is useful to commit this conversion to memory.

### Morse potential functions for each state

#### Excited state function (EB)

$$EB_i := D_e \cdot e^{-\beta_e \cdot (r_i - R_e)^2} + 15642 \cdot \text{cm}^{-1} *$$

#### Ground state function (EX)

$$EX_i := D_e \cdot e^{-\beta_g \cdot (r_i - R_g)^2} *$$

**Question 2.** Examine the Morse function for both the excited state and ground state. What is the difference between these two functions? Explain.

If the Schrodinger equation is solved using the Morse potential the energy (in  $\text{cm}^{-1}$ ) is given by the equation (1)

$$G(v) := \left[ \left( v + \frac{1}{2} \right) \cdot \omega_e - \left( v + \frac{1}{2} \right)^2 \cdot \omega_e \chi_e \right] \text{e} \quad (1)$$

where  $v$  is the vibrational quantum number,  $\omega_e$  is the vibrational constant, and  $\omega_e \chi_e$  is the anharmonicity constant. In this document  $\omega_e \chi_e$  is the same as  $\omega_e \chi_e$  seen in physical chemistry texts and the literature. Values for these parameters for many diatomic molecules can be found in most physical chemistry text books. **Care must be taken with the units used in this equation.**

In equation (2)  $G(v'')$  is the expression for the energy of a vibrational level in the ground state of the  $I_2$  molecule. The vibrational levels for the ground state are identified by the quantum numbers  $v''$ .

$$G(v'') := \left( v'' + \frac{1}{2} \right) \cdot 215 \cdot \text{cm}^{-1} - \left( v'' + \frac{1}{2} \right)^2 \cdot 0.61 \cdot \text{cm}^{-1} * \quad (2)$$

**Question 3.** Verify the values and units for the vibrational constant and anharmonicity constant used in equation (2).

To the right we see the plot of the Morse potential for the ground and excited states along with the energy of one of the vibrational levels in the ground state.

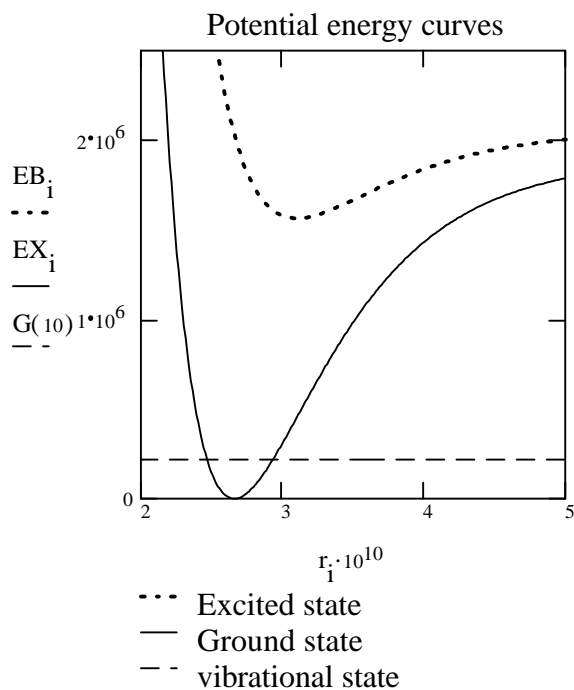
**Question 4.** Why are the depths different for the ground and excited state curves?

What Morse parameter causes this difference?

Why are the curvatures different for the ground and excited state curves? What Morse parameters cause this difference?

Hint: What is the relationship between curvature and the second derivative of a function?

**Question 5.** The tenth vibrational energy level is shown on the graph ( $G(10)$ ). Graphically estimate the approximate quantum number,  $v''$ , needed to dissociate the ground state molecule? What would be this value in the excited state?



## Part 2. Derivation of the Birge-Sponer Equations

As we read in Part I, solving the Schrodinger equation using a Morse potential energy function gives equation (1) for the energy of each vibrational state

$$G(v) := \left[ \left( v + \frac{1}{2} \right) \cdot \omega_e - \left( v + \frac{1}{2} \right)^2 \cdot \omega_e x_e \right] \text{ cm}^{-1} \quad (1)$$

where  $v$  is the quantum number identifying the vibrational energy level,  $\omega_e$  is the fundamental vibrational energy in  $\text{cm}^{-1}$  and  $\omega_e x_e$  is the anharmonicity correction. Using  $v'$  to designate the vibrational energy levels of the excited state we find that the difference between two adjacent vibrational levels in the excited electronic state is:

$$\Delta G(v') := \omega_e - 2 \cdot \omega_e x_e \cdot (v' + 1) \text{ cm}^{-1} \quad (3)$$

and therefore a graph of  $\Delta G(v')$  vs.  $v'+1$  should be a straight line with slope of  $-2\omega_e x_e$  and intercept of  $\omega_e$ . (See the derivation of equation 3 below.) Such a graph is called a Birge-Sponer Plot. Obviously it is easy to extract the fundamental vibrational frequency and anharmonicity constant from such a graph. **Explain how you would extract the fundamental vibrational frequency and anharmonicity constant from the graph.**

Soon we will demonstrate that the area under the Birge-Sponer Plot is the excited state dissociation energy of the molecule,  $D_e$ . A qualitative argument can be made by looking at the vibrational levels associated with a Morse potential energy function. If you consider any excited state energy gap,  $\Delta G(v')$ , and add these gaps, you reach the top of the curve, i.e., the dissociation energy. Recall that  $D_e$  is the dissociation energy from the bottom of the potential well.

**Question 6.** On a piece of paper, sketch a Morse curve for the ground state and label the first few vibrational states. Obtain a relationship between  $D_0$ , the dissociation energy from the ground vibrational state, and  $D_e$ , the dissociation energy from the bottom of the curve. Draw the Morse curve for the excited state on the same page and label the first few vibrational states.

**Question 7.** Compute the energies of the vibrational states that you drew and labeled in question 6. How do the energy levels vary as the quantum numbers  $v'$  and  $v''$  increase? Explain what would happen at large vibrational quantum numbers near the dissociation limit?

**Question 8.** Compute  $\Delta E$  for several electronic transitions that involve  $v'' \rightarrow v'$  where  $v''$  and  $v'$  have the same value. Repeat the calculation when  $v''$  and  $v'$  are different. How do the  $\Delta E$  values compare to each other? Are they very close, the same, etc.? What resolution instrument would be required to distinguish the transitions experimentally? What would you observe in the spectrum as the resolution of the instrument decreases?

To demonstrate that the sum of  $\Delta G(v')$  is the dissociation energy, first calculate the maximum vibrational quantum number at dissociation. As the molecule approaches dissociation, the vibrational energies converge, so  $\Delta G(v') \rightarrow 0$ . For the excited state we write  $G(v')$  as

$$G(v') := \left[ \left( v' + \frac{1}{2} \right) \cdot \omega_e - \left( v' + \frac{1}{2} \right)^2 \cdot \omega_e x_e \right] *$$

**be sure that optimize is toggled 'on'**

Note: The prime symbol is just under the tilde ~ symbol on the key board.

We can use the expression for  $G(v')$  to find the difference between two neighboring energy levels  $\Delta G(v')$ . Here we write the difference as the average of the differences between  $G(v')$  and the state on either side of  $G(v')$ . We solved symbolically in place by using the symbolic equal sign (ctrl period) key sequence.

Define  $\Delta G$

Note that we are using the mean of two states.

See Straughan & Walker, pg 108.

$$\Delta G(v') := \frac{1}{2} \cdot (G(v'+1) - G(v'-1)) *$$
 (4)

**Exercise: Verify equation 4.**

Calculate  $\Delta G$

$$\Delta G(v') \rightarrow \blacksquare$$

Paste a copy of the expression for  $\Delta G(v')$  here below.

$$\frac{1}{2} \cdot \left( v' + \frac{3}{2} \right) \cdot \omega_e - \frac{1}{2} \cdot \left( v' + \frac{3}{2} \right)^2 \cdot \omega_e x_e - \frac{1}{2} \cdot \left( v' - \frac{1}{2} \right) \cdot \omega_e + \frac{1}{2} \cdot \left( v' - \frac{1}{2} \right)^2 \cdot \omega_e x_e$$

$$\omega_e - 2 \cdot \omega_e x_e \cdot v' - \omega_e x_e \quad (5)$$

Simplify the expression for  $\Delta G(v')$  by highlighting the whole expression with a blue selection box and using Simplify from the Symbolic drop down menu. The result is shown in (5). **Show that the expression shown in (3) is the same as that shown in (5).**

$$\frac{1}{2} \cdot \frac{(\omega_e - \omega_e x_e)}{\omega_e x_e} \quad (6)$$

The difference between energy levels converges to zero at the dissociation limit. When we set (5) equal to zero and solve for  $v'$  we obtain  $v_{\max}$ , the vibrational quantum number at the dissociation limit. Here we found  $v'$  (result is in (6)) by using the solve for variable option in the symbolic drop down menu after highlighting the  $v'$  in (5). Copy and paste was used to create (7) from (6).

$$v_{\max} := \frac{1}{2} \cdot \frac{(\omega_e - \omega_e x_e)}{\omega_e x_e} * \quad (7)$$

We use this expression to calculate the maximum value of the vibrational quantum number for the oscillator, i.e. the value for the vibrational quantum number where dissociation occurs. In this document we will use (6) as the upper limit in the integration to find  $D_0$ .

Draw a Morse potential function with a number of vibrational levels in it. Use this graph to convince yourself that if we sum over all  $\Delta G$  within the curve we will have the dissociation energy, measured from the ground vibrational state. If we have small  $\Delta G$  then the sum becomes an integral from  $v' = 0$  to  $v' - v_{\max}$ .

**Integrate  $\Delta G(v')$  over  $v'$  to obtain the area under the curve.**

$$\int_0^{\frac{1}{2} \cdot \frac{(\omega_e - \omega_e x_e)}{\omega_e x_e}} \Delta G(v') dv' \Rightarrow \frac{-1}{(12 \cdot \omega_e x_e)} \cdot (4 \cdot \omega_e x_e^2 - 3 \cdot \omega_e^2 + 6 \cdot \omega_e \cdot \omega_e x_e) + \frac{7}{12} \cdot \omega_e x_e \quad (8)$$

$$\frac{-1}{(12 \cdot \omega_e x_e)} \cdot (-3 \cdot \omega_e^2 + 6 \cdot \omega_e \cdot \omega_e x_e + 4 \cdot \omega_e x_e^2) + \frac{7}{12} \cdot \omega_e x_e$$

The value of the integral, shown here to the left, simplifies to yield (9).

$$\frac{1}{4} \cdot \frac{(\omega_e^2 - 2 \cdot \omega_e \cdot \omega_e x_e + \omega_e x_e^2)}{\omega_e x_e} \quad (9)$$

**note:** you may also highlight one of the terms in the expression for the integral and use the collect on terms option in the symbolic drop down menu to do the simplification for you.

Recall we are determining  $D_e$  and  $D_0$  for the excited state. What we have in (9) is  $D_0$ . To obtain  $D_e$  we need to add in the zero point energy,  $G(0)$ . Since we have already defined the expression for  $G(v')$  all we need do is use it. Add  $G(0)$  to expression (9).

$$\frac{1}{4} \frac{(\omega_e^2 - 2 \cdot \omega_e \cdot \omega_e \chi_e + \omega_e \chi_e^2)}{\omega_e \chi_e} + G(0) \Rightarrow \frac{1}{4} \frac{(\omega_e^2 - 2 \cdot \omega_e \cdot \omega_e \chi_e + \omega_e \chi_e^2)}{\omega_e \chi_e} + \frac{1}{2} \cdot \omega_e - \frac{1}{4} \cdot \omega_e \chi_e$$

$$\frac{1}{4} \frac{(\omega_e^2 - 2 \cdot \omega_e \cdot \omega_e \chi_e + \omega_e \chi_e^2)}{\omega_e \chi_e} + \frac{1}{2} \cdot \omega_e - \frac{1}{4} \cdot \omega_e \chi_e \quad \text{Copy and paste result.}$$

$$\frac{1}{4} \frac{\omega_e^2}{\omega_e \chi_e} \quad (10) \quad \text{Simplify to obtain (8) which is } D_e, \text{ the dissociation energy from the bottom of the potential well. This expression is exact for a Morse potential.}$$

$$D_e := \frac{1}{4} \frac{\omega_e^2}{\omega_e \chi_e} \quad \text{The final desired result.} *$$

Application of these equations to experimental data is given in the document IodineSpectrum.mcd. The examination of units in the Morse potential is found in the MorsePotential.mcd document.

## References:

1. Sime, R. J., "Physical Chemistry, Methods, Techniques, and Experiments", Saunders College: Philadelphia, 1990; pp 660-668.
2. Snadden, R.B., "The Iodine Spectrum Revisited", J. Chem. Educ. 1987, 64, pp 919-1921.
3. D'alterio, R, Mattson, R., Harris, R., "Potential Curves for the  $I_2$  Molecule: An Undergraduate Physical Chemistry Experiment", J. Chem. Educ. 1974, 51, pp 282-284.
4. Lessinger, L., "Morse Oscillators, Birge-Sponer Extrapolation, and the Electronic Absorption Spectrum of  $I_2$ ", J. Chem. Educ. 1994, 71, pp 388-391.
5. McNaught, I. J., "The Electronic Spectrum of Iodine Revisited", J. Chem. Educ. 1980, 57, pp 101-105.
6. Berry, R. S., Rice, S. A., and Ross, J., "Physical Chemistry", John Wiley & Sons: New York, 1980, p 259.
7. Barrow, G. M., "Introduction to Molecular Spectroscopy", McGraw Hill: New York, 1962, p 241.
8. Verma, R. D., "Ultraviolet Spectrum of the Iodine Molecule", J. Chem. Phys. 1960, 32, pp 738-749.
9. Herzberg, G., "Molecular Spectra and Molecular Structure I. Diatomic Molecules", Prentice-Hall: New York, 1939, p 400.
10. Harmony, "Introduction to Molecular Energies and Spectra", HRW: New York, 1972, pp 461-464.
11. Straughan, B. P. & Walker, S., "Spectroscopy" v. 3, Chapman & Hall: London, 1976, p 108.