Molecular Spectroscopy Lab
Student Handout

Week 1: Introduction to Potential Energy Curves and Iodine

In this section, you should become reacquainted with the harmonic oscillator and the Morse potential. We will be using a Mathcad exercise written by T. J. Zielinski to help set up the calculations and explore how the parameters affect the shape of the Morse Potential. All textbook citations refer to the text: Physical Chemistry: Thermodynamics, Structure, and Change, 10th ed. © 2014, Atkins and de Paula.

BACKGROUND
Complete this section BEFORE you come to lab. All work should be completed in your lab notebook.

1. Read Chapter 8, Section B (Harmonic Oscillator) in your text.
2. Write the function for the energy levels of the harmonic oscillator. Then, show $E_{\upsilon+1} - E_{\upsilon} = \hbar\omega$.
3. Discuss the importance of the previous relationship. When dealing with a harmonic oscillator, will the size of the spacing ever change based on the value of υ and $\upsilon+1$? Will a diatomic bond ever break? Discuss the strengths and weaknesses of this model.
4. Sketch the shape of the harmonic oscillator potential energy surface on a plot with displacement (x) on the x-axis, and energy on the y-axis. What does "displacement" mean? Make sure you understand that this is NOT the length of the bond!! The sketch should include the first five allowed energy levels with their quantum numbers labeled.
5. Figure 8B.7 in your text shows probability densities for the first 5 states and $\upsilon = 18$. The most likely displacement for the $\upsilon = 0$ state is x = 0, meaning that in this state, the bond length is most likely to be the equilibrium bond length or R_e. Describe, based on the probability densities, how the most likely displacement changes as you increase the energy level.

A. Read Chapter 12 Section D.1 in your text. This section introduces vibrational motion of a diatomic molecule and how the shape of the vibrational potential energy curve relates to the force constant, k_f.

1. Take a moment to really think about how the value of the force constant relates to the bond stiffness and the shape of the potential well. If needed, look back at your physics text and reread the sections on springs. Write in your notebook what happens to the potential well shape when k_f increases or decreases.
2. This subsection also introduces "terms" which are a common way to see energies expressed in spectroscopy. You can convert energies in joules to terms in wavenumbers (cm^{-1}) by dividing the energy by ($h * c$), taking care to deal with units appropriately. (Note that this is NOT $\hbar$!) Work an example of this conversion in your notebook by converting 564.4kJ/mol to cm^{-1}. It is also common in spectroscopy to report light in wavenumbers rather than wavelengths which is a simple reciprocal relationship. (As long as you handle the units carefully!) Convert 532 nm to cm^{-1}.
3. The equation for harmonic oscillator vibrational energy levels is:
$$E_{\upsilon} = \hbar\omega(\upsilon + 1/2), \qquad \upsilon = 0,1,2,\dots$$
Write this equation in your notebook and list the units for each term.

4. This equation can also be written using vibrational terms, $\tilde{G}(v)$, where $E_v = hc\tilde{G}(v)$. The vibrational term is then:
$$\tilde{G}(v) = \tilde{v}(v + 1/2), \qquad v = 0,1,2,\ldots$$
Write this equation in your notebook and list the units for each term. Derive the mathematical relationship between $\tilde{v}$ and ω.

5. The force constant for HCl is 516 N m^{-1}. Calculate $\tilde{v}$ and ω for HCl.

B. Read Chapter 12 Section D.3(a) in your text. This section introduces anharmonicity and the Morse potential.

1. Write the function for the Morse potential. Define and provide units for each term.

2. Recall that valence bond theory describes covalent bonds through orbital overlap. (You may want to look back at Chapter 10A if this is foggy.) Discuss in your notebook (in words and sketches) how Coulomb's Law dictates the shape of the potential well. Describe the relative magnitudes of the attractive and repulsive forces between the atoms at large distances apart, very small distances apart, and at the distance R_e. Note how much better the Morse potential does at modelling the potential energy curve associated with VBT.

3. Two of the new variables introduced are D_0, and D_e (both in units of Joules). The wavenumber versions of these constants are $\tilde{D}_0$ and $\tilde{D}_e$ (both in cm^{-1}). Note that these are related in the same way as discussed above:
$$D_0 = hc\tilde{D}_0 \text{ and } D_e = hc\tilde{D}_e$$
D_0, and D_e are easy to confuse! Define what they are physically. Note which one is larger? Give a mathematical expression for how they are related.

4. The Morse potential is exactly solvable when used in the vibrational motion Shrödinger equation with solutions that lead to quantized vibrational terms of the form:
$$\tilde{G}(v) = \tilde{v}(v + 1/2) - \chi_e\tilde{v}(v + 1/2)^2, \qquad v = 0,1,2,\ldots,v_{max}$$
These terms are no longer equally spaced as they were in the harmonic oscillator model. What happens to the spacing as you increase the level? Another significant difference is that there is a maximum value for the quantum number. Why? Is that more or less realistic than the harmonic oscillator model? If you stretch a bond beyond the displacement defined by v_{max}, will there be a bond?

The following exercises should be completed with your lab group of 3 or 4 people. Although you will be working as a team, make sure to record the data and results in your individual notebooks as you go.

A. Warm-Up Excercises
   1. Discuss among your group your answers to the Background Exercises. Do not change the answers that are recorded in your notebooks, but record any calculation fixes, or any additional information you learn from the discussion before you move on to today's procedure.
B. Explore the Morse potential using Mathcad.
   1. Work through MorsePotential.mcd, (*The Mathcad worksheet provided to you, and much of the content below is a modified version of a published work by Theresa Julia Zielinski, 1997*) This document helps you set up a calculation in Mathcad for computing a Morse potential energy curve. The original worksheet contains parameters for HCl as an example. As you work through the following exercises, refer to the HCl example to copy and paste functions and constants that you need.
   2. Modify the original Mathcad worksheet so that you can view the plot as you adjust β systematically. (Use HCl as a guide for a reasonable start value.) Record the effect of β on the shape of the curve. Write the mathematical expression for β in terms of the force constant k_f. Does the curvature of the Morse potential change with k_f in the same way that the harmonic oscillator potential does?
   3. Modify the original Mathcad worksheet so that you can view the plot as you adjust the equilibrium bond length systematically. (Use HCl as a guide for a reasonable start value.) Record the effect of R_e on the shape of the curve.
   4. Starting with the original Mathcad worksheet, replot the Morse potential for HCl as E(R) vs. R (where R is the bond length). What is the advantage of each plot?
   5. Replot the data using eV units for energy.
C. Plot a Morse potential curve for the ground electronic state (X-state) of I_2.
   1. Modify the worksheet you completed in Exercise 3 above to plot the Morse potential E(R) vs. R for I_2. You will need to look up constants for this!
   2. Calculate the first 3 vibrational energy terms for this state.
   3. Calculate v_{max} for this state.
D. Plot a Morse potential curve for the excited electronic state (B-state) of I_2.
   1. In all of your plots so far, you should have noticed that the bottom of the well rests on the x-axis where the potential energy is zero. That is because each plot referenced a diatomic molecule in the ground electronic state where we have defined the electronic energy E_{el} to be zero. When the diatomic molecule is in a higher bound electronic state, that extra energy (E_{el}) is added to the vibrational energy as a constant.

$$E(R) = E_{el} + D_e\left(1 - e^{-\beta(R-R_e)}\right)^2$$

Look up the relevant constants for the excited (B-state) of I_2. Plot the Morse potential E(R) vs. R. (Note: You will want the results of Exercise C again, so make sure to copy and paste rather than overwrite your work.

2. Record how this curve compares to the plot of the ground state. How does the equilibrium bond lengths of the ground and excited state compare? Would you expect that this same trend would apply to all diatomic molecules? Also discuss what you notice about the shapes of the curves.
3. Calculate the first 5 vibrational energy terms for this state, as well as the $v = 20, 30,$ and $40,$ levels.
4. Calculate v_{max} for this state.

E. Plot an overlay of the Morse potential curves showing the ground and excited electronic states of I_2.
   1. Make this one count! You will want to include this in your final write-up for the lab, so make sure you finish with a "figure-quality" plot with Titles and Axes defined.
   2. Scale this figure to fit a page in your notebook and print it. Affix it to a blank page in your notebook.

Both of these curves represent bound states of molecular iodine as is evident from their shapes. They will each have their own values for vibrational constants, and bond energy (both D_0 and D_e), so it is important to distinguish which electronic state we are talking about. It is common in spectroscopy for this to be done using primes to indicate constants for the excited state (for example, χ_e', or D_0') and double primes to indicate constants that correspond to the ground electronic state (for example, χ_e'', or D_0''). The same notation is used to indicate ground and excited state vibrational quantum numbers.

You should note that the asymptote of each electronic state (the point in the curve where the bond has dissociated) occurs at different points on the energy scale. (Note the y-values at large x-values are very different for the two curves.) This means that the products of the dissociation (although they must both be two iodine atoms) have different amounts of energy. The "ground" or lowest electronic state of I_2 will dissociate into two iodine atoms both in their lowest electronic energies. The excited electronic state of I_2 dissociates into one iodine atom in the lowest electronic energy, and one in an excited electronic state.

   3. Add the following items to the figure: (Do your best to keep it neat, but you can estimate the actual positions by eye or with a ruler.)
      - Draw a vertical line between the curves at a large enough x-value that both curves are horizontal. Subtract to get the value of this energy difference. The energy required to excite atomic iodine, I, is 7602.97 cm^{-1}. This should reinforce the identities of the products of dissociation for each curve.
      - Add horizontal lines depicting the first 3 vibrational levels of the ground state.
      - Add horizontal lines depicting the vibrational levels you calculated in Exercise D.
      - Add a vertical arrow from the $v'' = 0$ to the $v' = 20$ level of the excited state. Calculate the wavelength of light associated with that transition.

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Week 2: Collect Iodine Absorption Spectrum, and Construct Linear Birge-Sponer Extrapolation Plot

In this section, you will begin by collecting the absorption spectrum for molecular iodine (I_2). You should assign as many peaks as possible and construct a linear Birge-Sponer plot from your data. Determine the vibrational spectroscopic constants for the excited state of iodine (the B-State) as well as D_0 for the ground state.

BACKGROUND

Complete this section BEFORE you come to lab. All work should be completed in your lab notebook.

    A. You will be handling solid I_2 in the lab. Look up and list safety measures that should be followed in order to do this safely.

    B. You will be collecting an absorption spectra in lab this week. You should arrive familiar with the Beer-Lambert Law. Your book has a section in Chapter 12 (Section A1c.) about the Beer-Lambert Law if you need a refresher, but you may prefer to look at a different source.

        1. In the context of collecting an absorption spectrum, what is the definition of a "blank"? Why is it important to use a blank in an absorption measurement?

        2. Write a physical description of molecular iodine (I_2). I am simply talking about color, phase, and other noticeable physical properties. Look up pictures and information if needed. Based on this, what color of light do you expect it to absorb? Provide a 150 -200 nm range of wavelengths where you would expect to observe absorption for iodine. Explain why you chose this range.

        3. Look back at the plot you generated at the end of lab last time. The last exercise had you calculate the wavelength of a transition between the ground vibrational state ($v'' = 0$) of the ground electronic state and the 20th vibrational state ($v' = 20$) of the excited electronic state. How does that answer compare to the 100 nm range of wavelengths that you predict will be absorbed by iodine?

        4. For comparison, calculate the wavelength of light associated with a transition between the $v' = 0$ and $v' = 1$ states within the ground electronic state. This wavelength falls into which region of the electromagnetic spectrum?

    C. Read Chapter 13, Section 1c (Electronic Spectra: Vibrational Structure) in your text.

        1. Define the Franck-Condon principle. Explain its relationship/similarities to the Born-Oppenheimer approximation.

We always draw vertical arrows on the potential energy plots to denote excitation (absorption) or relaxation (emission) The significance of this is easy to take for granted as it seems like the tidiest way to indicate a transition on the plot. The vertical transition is important as it illustrates the Franck-Condon principle as the change in energy (y-axis) occurs without nuclear movement (x-axis).

        2. Quantum mechanically speaking, the Franck-Condon principle says that the nuclear wavefunction is the same both before and after the transition. So, the transition that is most likely to take place is one in which the wavefunction of the excited state is the most similar to that of the ground state. This can be mathematically described through the equation below called the Franck-Condon factor:

$$|S(v_f, v_i)|^2 = \left(\int \psi_{v,f}^* \psi_{v,i} d\tau_n \right)^2$$

When the overlap is significant (meaning that the two wavefunctions look similar if overlayed), this value will be larger and the transition intensity will be large on the spectrum. If the two wavefunctions were identical (which is a hypothetical, and just to imagine the largest overlap) what would the value of this integral be?

3. Using the figure you produced of the potentials of the two relevant states of I_2, give a range of 5 vertical transitions from the $v'' = 0$ vibration to vibrational levels in the excited electronic state that you feel will correspond to the strongest absorptions. *It is common to write a transition as* $v'' = 0 \rightarrow v' = 25$ *indicating that the transition originated at the* $v = 0$ *vibration of the ground electronic state, and ended at the* $v = 25$ *vibration of the excited electronic state.* Look back at the shape of the wavefunctions for the vibrational levels of a harmonic oscillator as a hint.

4. Do you expect to see an absorption peak associated with the transition between the ground vibrational states of the two electronic states? Why or why not?

5. Hot bands are transitions that originate from a $v > 0$ vibrational level of the ground electronic state to any vibrational level of the excited electronic state. Sketch the shape of the wavefunction of the $v = 0$ and 1 states of a harmonic oscillator. How do you think the transition of maximum absorbance will change based on what you drew?

D. Your text only refers to a Birge-Sponer plot in reference to vibrational spectra. The spectrum we are collecting of I_2 is an electronic spectra with vibrational structure. Therefore, the explanation in your text is a bit different, but the basic idea is the same. The material is found in Chapter 12 D, Section 3b in your text.

The basic idea behind the Birge-Sponer plot is that the sum of all of the vibrational spacings in an electronic state will equal D_0 or the energy needed to break the bond if the molecule starts in the ground vibrational state ($v = 0$). Because some of these transitions are usually absent in the data due to poor Franck-Condon factors, it is sometimes simpler to plot the data and extrapolate. If the spacings of the states are plotted against the lower state plus ½, the plot should be linear if the potential curves are well described as Morse potentials. The bond energy is the area under the line.

1. Work through the data given in Example 12D.2 on page 508, then work Self-Test 12D.4

The following exercises should be completed with your lab group of 3 or 4 people. Although you will be working as a team, make sure to record the data and results in your individual notebooks.

A. Warm-Up Excercises

    1. Discuss among your group your answers to the Background Exercises. Do not change the answers that are recorded in your notebooks, but record any calculation fixes, or any additional information you learn from the discussion before you move on to today's procedure.

    2. Based on your observations of iodine, come to an agreement as a group of a good wavelength range for the absorption spectrum of iodine. This range should be about 100 to 150 nm wide.

B. Iodine Spectrum Collection

    1. The absorption spectrum of iodine is quite simple using our Cary UV-vis instrument. Instructions for applying background subtraction and data saving are located in the manual next to the spectrometer.

    2. We will collect the spectrum at a warm temperature (50°C) so that the concentration of iodine vapor is sufficient to collect a nice spectrum. You will need to allow enough time for the cuvette's temperature to equilibrate before beginning the collection. Five to ten minutes should be sufficient for both the blank and the sample.

    3. Slow and steady is the name of the game with this spectrum! You will need to adjust the step setting to the smallest possible for the spectrometer. Adjust the averaging to a reasonable level so that the spectrum takes no longer than 15-20 minutes to collect. Before collecting a slow spectrum, you may want to check the range that you chose using a quick scan.

C. Assignments of Band heads

    1. Use the data provided in class to help you in assigning the spectral peaks. Be especially careful in the hotband region of the spectrum. Rather than the peaks, we will assign the valley on the low wavelength side of each peak. This is nearest the band-head region of each vibrational band.

    2. For transitions FROM the $v'' = 0$ vibrational level: Create a spreadsheet to organize your band head values with the vibrational level of the upper electronic state.

    3. Do the same for transitions FROM the $v'' = 1$ and 2 vibrational levels. There will be fewer of these, but they are still useful.

D. Construct a Birge-Sponer plot for I_2

    1. Complete the portion of the lab handout titled: Theoretical Background of Birge-Sponer Extrapolation (attached to the end of this handout) with your lab partners.

    2. Construct a linear Birge-Sponer extrapolation for I_2 using the method outlined in the handout.

    3. Determine values (with units) for $\tilde{D}_0$, $\tilde{D}_e$, ω_e, and $\omega_e\chi_e$ for the excited state. (These will all be seen with primes to denote that they are associated with the excited state ($\tilde{D}_0'$).

    4. Determine the value of $\tilde{D}_0''$ (the bond energy of the ground state) using the excitation energy of I*.

    5. Compare your values to literature values. Provide references for these values.

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Week 3: Exploring the Morse Potential: Is it a good model?

In this section, you will examine your data for the iodine spectroscopy and discuss whether the Morse potential is an adequate model for this system. You will then use spectroscopic data for bromine monoxide to construct a Birge-Sponer plot for this molecule, and compare the bond energy determined from the plot with the accepted literature value.

BACKGROUND

Complete this section BEFORE you come to lab. All work should be completed in your lab notebook.

A. Find a reference other than your text that discusses another model (other than Morse or the Harmonic Oscillator) for a vibrational potential curve.
    1. Describe that model in words and by writing the functional form of the potential energy. Looking at the functional form, describe any similarities or differences you note when this function is compared to the Morse potential?
    2. When reading about this potential, record the noted advantages over Morse that the model claims.
B. When you walk into lab today, you MUST have the calculations done from the week before. Make sure that you have a printout of the Birge-Sponer plot for I_2 in your notebook along with the linear fit function and R^2 value. You must also have your vibrational constants and bond energies recorded and have comparison values from the literature.

A. Warm-Up Excercises

1. The Birge-Sponer plot that you made for I_2 is for the vibrational spacings of the excited state. Therefore, your analysis of the data is only relevant to the shape of the excited state potential well. Our Birge-Sponer extrapolation is based on the Morse potential. Consequently, the linearity of your plot is a measure of how well the Morse potential models the excited state potential well of I_2. Discuss among your group members how your plot looks. Is the linear model appropriate? Can you tell based on the noise in your data? If you see apparent curvature, is it apparent near the bottom or top of the well?

2. Each lab group should present their data to each other for comparison. How does your data compare to the other lab groups' data? Are there noticeable features on the plots? Curvature? Can you tell due to the noise?

3. Discuss with the class and your instructor the strengths and weaknesses of the Morse potential.

B. Absorption Spectrum of BrO

1. You are about to look at absorption spectral data for another diatomic molecule, BrO. (The data was taken from: Wilmouth, Hanisco, Donahue, and Anderson, *J. Phys. Chem.* **1999**, 103, 8935-8945.) The absorption peaks are found in the UV-Vis region from 280 nm to 380 nm. If you make connections with the I_2 system, what type of transitions do you expect in this region? Predict the shape of the spectra. Do you expect a broad peak, or multiple sharp peaks? Why?

2. Based on your prediction of its spectrum, sketch potential energy curve(s) and a few representative transitions that you expect to see. (No units are necessary, don't look up any constants for this molecule. Use what you know about I_2 to help. You don't know much about the molecule, but we should still expect the potentials and vibrational levels to work the same way.)

3. The data for the absorption spectrum for bromine monoxide (BrO) has been provided for you in the file BrO.xls. First look at the image containing the absorption spectrum. Is this what you expected to see? Discuss how this spectrum compares to the one you collected for I_2. Based on the transitions that are labeled on the BrO spectrum, would you guess that the equilibrium bond lengths of the ground and excited states of BrO are more or less similar than those of I_2?

C. Bond Dissociation Energy of BrO

1. The Excel file you are given also contains very high resolution band head data for transitions $v'' = 0 \rightarrow v'$ that are labeled with the appropriate v'. Construct a Birge-Sponer plot for BrO. Using a linear fit, determine the value for $\widetilde{D}_0'$.

2. Look closely at your plot. Does the data seem linear? Do you think a different fitting method would be better? If so, try some other fits, and include the equations, and R^2 values of the fits you try.

3. Leave the best non-linear fit on your plot with the linear fit. Use it to determine a value for $\widetilde{D}_0'$.

4. Based on your plot, how do the spacings compare to the Morse potential? Does it seem that the spacings converge more or less quickly than the Morse potential predicts? What does it tell you about how the Morse potential describes BrO?

D. LeRoy-Bernstein Extrapolation

Although it is common for the vibrational energy spacings to exhibit curvature towards the x-axis causing the actual bond energy to be less than the linear extrapolation predicts, it is actually also possible for the opposite to happen. It has been shown that in the cases of the Cl_2, I_2, Br_2, O_2, and ClO, that the extrapolation will have a positive curvature at only high levels of v. This is due to "long-range attractive interactions." That means that near the dissociation limit when the two atoms are pulled so far apart to be almost dissociated they show more attraction than is predicted by the Morse potential. One consequence is that higher vibrational levels exist than what we predict with Morse, and the bond energy is larger than the Morse potential predicts. So at atomic displacements that are so large the Morse potential says there should be no more interaction, these atoms hang on to each other a little longer. Based on the examples of where this

LeRoy and Bernstein predict that this curvature will occur only near the dissociation limit, so the curvature is not expected to be seen unless the vibrational levels recorded are very near the dissociation limit. This theory predicts that there should be a linear relationship between $(\Delta G_{v+1/2})^{(\tilde{n}-2)/(\tilde{n}+2)}$ versus $v + 1/2$. In the case of BrO, the authors expect that the value of $\tilde{n}$ is equal to 5 which indicates quadrapole-quadrapole attractive interactions between the Br and O atoms as they dissociate. This means that near dissociation, the plot of the spacing raised to the 3/7 power, $(\Delta G_{v+1/2})^{3/7}$ versus $v + 1/2$ is a line. Using the last 5 vibrational spacings, this analysis has been done for you. (You are so welcome!) The extra spacings from this analysis are also in the BrO.xls spreadsheet.

5. Use the extra spacings to calculate the upper prediction for D_0. (A simple way to do this is to add the extra spacings to the value of the highest recorded transition, 34909.4cm^{-1}.)
6. Compare the value of v_{max} from this extrapolation to the value predicted by your best fit curved extrapolation.
7. The accepted literature value for the bond dissociation energy of the excited state of BrO is ####. Comment on the extrapolations and their "correctness" based on this value.

E. Wrap-Up

One of the major goals of this project is to convince you to take a critical approach to using models. That doesn't mean that using models is bad and should be avoided! However, as scientists who use models and approximations to explain very complex phenomena, we need to remember that models have strengths and weaknesses. Use them with care! Also, we should understand that when a model "fails" it really provides us with useful information to dig deeper into the chemistry that drives the process we are modelling. We obviously incorrectly assumed something about the modelled system. Often, the issue is that something that was assumed to be negligible was actually important. Whether the model "works well" or not, we should always walk away pondering theories about why the model did or didn't work. Before you leave today, discuss with your group some of the strengths of the Morse potential. Based on the BrO data, predict how the excited well compares to the Morse potential at several regions along the displacement.

References