origin energies. Be sure to avoid using regions of the spectrum that are contaminated by hot bands. Print full-scale and expanded scale versions of the I_2 spectrum. Mark and label the v"=0 and v"=1 envelopes on your full-scale spectrum (see Figure 4). Label the expanded scale spectrum with excited state vibrational quantum numbers using the values in Table 1 as a starting point.

Working up the Data: Results and Calculations

You will be using a combination of Excel and Igor Pro to work up your data, extract all necessary molecular parameters, and produce a potential energy diagram. By now you should have a good enough feel for working in Igor that you do not need specific directions to do every operation. A few new bits of programming are introduced here. Be sure to keep a good notebook and comment your code well so that others can understand what you are doing. Your procedure window and command window should be part of your report, as appendices.

The extraction of molecular parameters is most easily done in Excel. Be sure that all columns are labeled with column headings, and that you make careful use of absolute and relative addressing as appropriate (see the Appendix A if you need a refresher).

- Open up an Excel spreadsheet, and enter values for the band origin wavelengths and excited state vibrational quantum numbers that you obtained from your experimental spectrum.

- In a new column, convert the transition wavelengths to wavenumbers. Recall that transition energies correspond to a *difference* in energies of matter, so that these are now values of $E_{photon}=\Delta E_{tot}(v')$, in units of cm^{-1}. In your notebook, show how you are converting wavelengths to transition energies (i.e.: give an example and show all unit conversions).

- To create the Birge-Sponer plot, you will need columns of ΔE_{photon} and $(v'+1)$ (see equation 15). Pay careful attention to how you line up values of ΔE_{photon} and $(v'+1)$.

- Create a Birge-Sponer plot that shows the best fit line, *extrapolated to both x- and y-intercepts*. Display the fit equation on the plot.

The remaining calculations should be done in your notebook:

- Calculate values of D_o' using <u>both</u> the graphical and mathematical methods.
- Calculate a value for D_e'.
- Use your derived expression for equation (22) to calculate a value for E*.
- Using the lieterature values of $\Delta E(I^*, I)$, $\overline{\nu}_e''$, and x_e'', calculate values for D_o" and D_e".
- Calculate values of a" and a' using equation (2) and your experimental molecular parameters. Be sure to pay careful attention to the units!
- Calculate a value for T"=T_2, the electronic energy of the B state.
- Create a table in your notebook that contains all of the calculated molecular parameters. Group ground state parameters separately from excited state parameters.

The final step is to use Igor to create a potential energy diagram from your data. You will need one extra set of information - the literature[8] values for the ground and excited state internuclear distances, which are **r_e" = 2.665 Å** and **r_e' = 3.0276 Å**.

The Morse potential functions require several molecular constants. As for the HCl simulation, the best way to handle constants in a function or macro is to declare them as global variables. Copy your **NewConstants** macro from your HCl simulation into the Procedure window of your new experiment. You will need to modify the macro to input values for the molecular constants D_e", D_e', a", a', r_e", r_e', and T'. Use the ending X for ground state parameter variable names, and B for excited state parameter names (for example, D_e" would be **DeX**). After you run your macro, test it by running entering **Print "reX=", reX** in the Command window. Igor should respond in the History area with **reX = 2.665**.

Now that all of the molecular constants are available, you can write the functions that will calculate values of the Morse potential. I suggest that you write two functions, **UX(r)**, and **UB(r)**, although there are ways to combine these two calculations into one function (you may experiment if you like). Your functions should return a value for the potential energy at a given value of r (internuclear distance). Be sure to thoroughly comment your code.

At this point you should be able to ask Igor to calculate a single value of the potential for any internuclear distance that you want. To test your code, enter the following text in the Command window:

    print UX(2.665)

Igor should return a value of **0**. (Why?!) Test your UB(r) function by typing:

    print UB(3.0276)

Igor should *not* return a value of **0**. (Why?!) Document in your notebook the value that you expect should be returned, and check that your function is operating correctly.

Now you need to calculate U(r) for many values of r (try r=1.25 to 9.00 è), for both the ground and excited states. This will require a macro containing a loop structure. The skeleton of my macro looks like this (the macro does not need any input variables):

```
Macro PotentialWells()
    variable r,i
    r=1.25
    i=0
    do
        {things to be done for this r}
        r+=0.01
    while (r<=9)
End
```

where **i** is a dummy variable that will index the waves that will hold the values of UX(r), UB(r) and r. You will need to create three waves to hold the values of UX(r), UB(r) and r (calculate how many points will be required so that you can make a wave of the right size). You cannot reuse function or variable names, so come up with something else descriptive (I used **MorseX, MorseB** and **rValue** as my wave names). Append these new waves to a new table so that you can see what is going on as you program and test your code.

Your job is now to fill in the **{things to be done for this r}** part. The things to be done include the following:

• keep track of the values of r that are used to calculate the X and B potentials (that way you

will be able to plot the Morse potential values versus r.) One way to do this is to use a line of code inside the loop like:

    rValue[i]=r

where i is an index to the wave rValue. For example, when i=0, rValue[0] is equal to 1.25.

- calculate values of UX(r) and UB(r)

- assign values to all three waves within the loop. Index all three waves with the dummy variable i.

- increment the value of i within the loop so that each calculation is stored in a new location in each wave.

You may come ask questions if you get stuck, but don't wait until the last minute!! When you think you have the macro working,

- Check the calculation for UX(1.25) using Igor, then:

⇨ Check the calculation for UX(1.25) in your notebook.

Once you have gotten your PotentialWells macro to work, you are ready to make your potential energy diagram. Plot MorseX and MorseB versus rValue. Thoroughly label your diagram. Don't forget to include units with the axes labels.

Wrapping it Up

Your report should include a title, abstract, notebook pages, and short discussion, as well as the following printouts:

- Two copies of your Excel spreadsheet, one with numbers (this should be in the <u>body</u> of the report, with the final results in your notebook), one with formulas (an appendix) - be sure to print column and row heading with each one.

- Your Birge-Sponer plot, with a figure number and title (this should be in the <u>body</u> of the report, with the final results in your notebook)

- Your potential energy diagram with a figure number and title (this should be in the <u>body</u> of the report, with the final results in your notebook)

- your Data table from your Igor session (an appendix)

- your Procedure window (an appendix)

- your Command window (an appendix)

In your notebook, make a table (numbered and titled) of the all of the molecular constants that you determined (*do not forget to include units*). Include literature values of all constants, and specific references to the sources of those values (see Huber & Herzberg[6], Steinfeld[8], and McNaught[10,]).

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[10] McNaught, I. J., "The Electronic Spectrum of Iodine Revisited", *J. Chem. Educ.*, <u>57</u>, 101 (1980).

For your discussion, briefly compare your experimental dissociation energies with literature values (Appendix C). Then pick one of the following aspects of the experiment to discuss in as much depth as you can.

- Discuss the two limits of the vibronic band (the low wavelength end where there is no structure, and the high wavelength end where the band disappears) in terms of their physical meanings and connection to experimentally obtained molecular constants. Compare the $v''=0$ and $v''=1$ bands. How does the offset of the potential wells affect all of these spectral features?

- Discuss the differences between the molecular constants for the ground and excited state wells. Give a physical explanation based on your understanding of chemistry in each comparison. Using the data in Appendix C, calculate the values of B_0' and B_0'' and compare these results.

- Calculate the value of R(3) and the band origin energy for the $0 \rightarrow 0$ vibronic transition. Determine the value of J* for the $0 \rightarrow 27$ vibronic transition, and determine the band origin energy and band head energy for that transition. How significant is the error in approximating the band origin energy as a band head energy?

Be as specific as possible, using numerical examples to support your ideas. You can use your Igor session to calculate lots of interesting pieces of information that arise from the details of the potential energy diagram if you are so inspired.

Additional General References

P. W. Atkins, *Quanta*, 2nd Ed., Oxford University Press, Oxford (1991) (see *Born-Oppenheimer approximation*, *Colour*, *Electronic spectra*, *Franck-Condon principle*, *Progression*, *Vibronic transition*.)