

LAB #4: SPECTRUM AND DISSOCIATION ENERGIES OF I₂
(This lab is largely adapted from the Hope College Chem 346 lab manual.)

Abstract

The electronic spectrum of I₂ is recorded using UV-Vis spectroscopy. The vibrational fine structure is analyzed using an anharmonic model and the bond dissociation energy of I₂ is determined.

Related Reading

McQuarrie and Simon, *Physical Chemistry: A Molecular Approach*, Sections 13-6 and 13-7.

Background

The purple color of iodine vapor is due to the absorption of green, yellow, and red light by an electronic transition, B ← X. Superimposed on this electronic transition are vibrational transitions originating from thermally populated levels v'' = 0, 1, 2. This vibronic spectrum of iodine can be analyzed for a wealth of molecular parameters, including vibrational constants and dissociation energies of each electronic state.

The vibrational and electronic parameters

$$\tilde{\nu}_e'', \tilde{\chi}_e''\tilde{\nu}_e'', \tilde{D}_e'', \tilde{D}_0'', \tilde{\nu}_e', \tilde{\chi}_e'\tilde{\nu}_e', \tilde{D}_e', \tilde{D}_0', E^*, \tilde{T}_e', \text{ and } E(\text{I}^*)$$

are defined in the vibronic energy level diagram for iodine (see Figure 1 – attached- or McQuarrie and Simon, Ch 13). It is a tribute to the power of spectroscopy that all of these parameters can be determined from the analysis of the iodine visible absorption spectrum.

Energy Level Expressions. Each vibronic energy level of iodine can be written as a sum of electronic and vibrational energy

$$\tilde{E}'(v') = \tilde{T}_e' + \tilde{\nu}_e'(v' + \frac{1}{2}) - \tilde{\nu}_e'\tilde{\chi}_e'(v' + \frac{1}{2})^2$$

and

$$\tilde{E}''(v'') = \tilde{T}_e'' + \tilde{\nu}_e''(v'' + \frac{1}{2}) - \tilde{\nu}_e''\tilde{\chi}_e''(v'' + \frac{1}{2})^2$$

where single prime (') and the double prime (") characters refer to the upper and lower levels, respectively, and the units of E, T, $\tilde{\nu}_e'$, and $\tilde{\nu}_e''$ are assumed to be wavenumbers.

B State Vibrational Frequency (Birge-Sponer Plot). It is useful to consider the differences between transition wavenumbers; i.e., the spacing between adjacent (e.g., v' and v' + 1) peaks in the spectrum.

$$\Delta\tilde{\nu}(v') = \tilde{\nu}(v' + 1) - \tilde{\nu}(v') = \tilde{\nu}_e' - 2\tilde{\nu}_e'\tilde{\chi}_e'(v' + 1)$$

A plot of $\Delta\tilde{\nu}(v')$ against (v' + 1) will allow the determination of the upper level vibrational frequency $\tilde{\nu}_e'$ from the intercept and the upper level anharmonicity $\tilde{\chi}_e'\tilde{\nu}_e'$ from the slope. Such a plot is called a Birge-Sponer plot.

B State Dissociation Energy. Note that the area under the Birge-Sponer plot equals the dissociation energy \tilde{D}'_0 which is related to the equilibrium dissociation energy \tilde{D}'_e by the zero point energy

$$\tilde{D}'_e = D'_0 + \frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{\nu}'_e\tilde{x}'_e$$

Convergence Limit. The convergence limit E^* is obscured as the band structure becomes continuous. However, it may be estimated from the sum of the highest observed transition energy to the highest observed excited vibrational level b plus an estimate of the remaining dissociation energy A' from the Birge-Sponer plot

$$E^* = \tilde{\nu}(v' = b) + A'$$

X State Vibrational Frequency. The spacing between adjacent vibrational energy levels $\Delta\tilde{\nu}(v'' = 0)$ and $\Delta\tilde{\nu}(v'' = 1)$ can be determined from a Deslandres Table (see below).

These two values can be used to create two equations:

$$\Delta\tilde{\nu}(v'') = \tilde{\nu}''_e - 2\tilde{\nu}''_e\tilde{x}''_e(v'' + 1)$$

in which $v'' = 0$ and $v'' = 1$. These two equations can be solved for the two unknowns $\tilde{\nu}''_e$ and $\tilde{x}''_e\tilde{\nu}''_e$. Alternatively, an emission spectrum could be acquired, providing many v'' points for fitting (this is what we would have done with the laser system).

X State Dissociation Energy. $D''_0 + E(I^*) = E^*$ (see the energy level diagram) so the dissociation energy can be found from previously determined parameters as

$$D''_0 = E^* - E(I^*)$$

where the energy of the excited iodine atom $E(I^*)$ is known from atomic spectroscopy to be 7603.15 cm^{-1} (Moore, C.E., "Atomic Energy Levels," vol. III, 1958). As before, the equilibrium dissociation energy can be found by adding the zero point energy

$$\tilde{D}''_e = D''_0 + \frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{\nu}''_e\tilde{x}''_e$$

B State Electronic Energy. Finally, the electronic energy of the B state can be found using previously determined parameters

$$\tilde{T}'_e = D''_e + E(I^*) - D'_e$$

Deslandres Table. In the above analysis, it is extremely useful to organize your data (transition wavenumbers) into a Deslandres table, which assists in determining energy differences between adjacent levels $\Delta\tilde{\nu}$ that are used. A spreadsheet is set up with column levels for $v''=0,1,2$ and row labels for $v'=10,11,12,\dots,60$. A difference between adjacent transition wavenumbers $\Delta\tilde{\nu}$ is calculated, yielding $\Delta\tilde{\nu}(v'')$ between the columns and $\Delta\tilde{\nu}(v')$ between the rows. These $\Delta\tilde{\nu}$ values are then averaged and used in the preceding analysis for constructing the Birge-Sponer plot and determining the X state vibrational frequencies.

Procedure:

In the Lab:

1. Place a few crystals of iodine in a 1 cm cuvette (if not already prepared).
2. Set-up the Cary UV-Vis... Log into the computer (Instrumental Class, password: che380) and run the Scan program (in folder Cary Uv-Vis). After the Scan program has loaded, turn on the Cary spectrophotometer. Wait for the Cary to initialize (it is initialized when the Abs and Wavelength displays in the upper corners of the screen are active).
3. In the set-up dialog box, set the following:

Cary tab:	Cary tab:
X Mode	Scan Controls
Mode: Nanometers	Ave time(s): 1
Start: 600	Data Interval (nm): 0.1
Stop: 500	
Y Mode	Options Tab:
Mode: Abs	SBW (nm): 0.2
Ymin: 0	Beam Mode: Double
Y max: 0.1	Source/Detector: VIS
4. Place the reference cell in the back sample holder of the UV/Vis.
5. Heat the cuvette gently until you can see I_{2(g)}.
6. Place the sample cell in the front sample holder of the UV/Vis and click start.
7. For the Save As location, find the C:\Chem372 directory and use your initials and sample as the filename, e.g, AMN-Iodine.
8. When finished, print a copy of the entire spectrum. Then label the peaks. Zoom in on the spectrum (by changing the x-axes) until you can resolve all of the numbers. Print this series of spectra.
9. When finished, clean up any mess. If you are the last group, turn off the Cary and log off of the computer.

Safety and Other Concerns: Do not add too much I₂ to the cuvette and don't overheat the cuvette.

Analysis:

Assign each of the peaks to a transition between vibrational quantum numbers, $v' \leftarrow v''$. In many spectra the so-called "0-0 transition" is easily identifiable. In the case of iodine, however, the bond length of the upper potential energy surface is so much larger than the ground electronic state that the intensity of the 0-0 band is vanishingly small. Quantum mechanically, the Franck-Condon factor which governs vibronic transition intensities is practically zero because of small overlap between the shifted harmonic oscillator vibrational wavefunctions of the $v''=0$ and $v'=0$ states. Thus, a starting place is required to assign the peaks properly. The table below gives the assignments of several transitions originating from each of the lowest three vibrational levels of the ground electronic state. In the area of overlapping bands, the smoothly changing intensities must be used to determine the ground vibrational state of each band (see class handout). Write the assignment of each transition on the spectrum.

Selected I₂ Transition Wavelengths

v'	v''	λ / nm	v'	v''	λ / nm	v'	v''	λ / nm
27	0	541.2	18	1	571.6	13	2	595.7
28	0	539.0	19	1	568.6	14	2	592.0
29	0	536.9	20	1	565.6	15	2	588.5

Once the spectrum is assigned, construct a Deslandres table using Excel or other spreadsheet program. (See file 'Deslandres Table.pdf'). Note that all entries are in wavenumbers (cm⁻¹) not nanometers. The Deslandres table contains both spectral transition data and differences between vibrational energy levels (again refer to class handout).

Prepare a Birge-Sponer plot. Fit the slope and intercept of the Birge-Sponer plot to analyze the data. From the Deslandres table, Birge-Sponer plot and the background material above, find $\tilde{\nu}_e''$, $\tilde{x}_e''\tilde{\nu}_e''$, \tilde{D}_e'' , \tilde{D}_0'' , $\tilde{\nu}_e'$, $\tilde{x}_e'\tilde{\nu}_e'$, \tilde{D}_e' , \tilde{D}_0' , E*, and \tilde{T}_e' (Hint: start in the order discussed in the background material and use the information in each section for direction on how to determine those molecular constants.)

Lab Report

This lab report will have the style of a communication to a major chemistry journal. Please see 'How to Write a Communication/Letter' on the course website.

References

Dr. Smith's site: http://www.gustavus.edu/academics/chem/pchem/quantum_lab.html

SOU Chem445 site: <http://www.sou.edu/chem/ch445/iodine.htm>

Hope College: Chemistry 346 Lab Manual, 2002

Also see references listed on these sites and your textbook.