

## ABSORPTION SPECTRUM OF IODINE

### 1. Purpose

This experiment involves the measurement and analysis of the spectrum of  $I_2$  vapour. Since the text book describes both absorption and emission spectra (S&G, 5th ed., Expt 42, 6th ed., Expt 40, 7<sup>th</sup> and 8th ed., Expt 39) be sure that you read and understand Ref. 1 before starting the experiment.

### 2. Safety

Organic solvents must be discarded to the proper waste solvent container. Wear eye protection at all times in the laboratory.

### 3. Data collection

The Cary 17-OLIS spectrophotometer is used for this experiment. This must be used only under the supervision of an instructor or the appropriate technician.

Place a small crystal of solid  $I_2$  into a 10 cm UV/Vis cell (careful not to touch the end windows), place the cell in the spectrophotometer, set the sample thermostat to 45 C and wait for about ½ hour for the temperature to equilibrate before beginning. Record the spectrum from 650 nm to 500 nm, with the following settings: 1200 increments, 50 reads/datum, and bandwidth at 0.05 nm. It may be desirable to do a quicker scan first to be sure that everything is working properly. In order to be able to transport the data for later manipulation with a convenient program of your choice, the spectrum has to be saved in ASCII format; position the mouse cursor in the graph area, then right click to bring up the export menu window.

Once your data have been collected, shut the circulating water bath and discard the  $I_2$  crystal in the waste solvent carboy. Rinse the cell with some dichloromethane then some acetone and let it dry.

### 4. Calculations

Identify the various Franck-Condon progressions in your spectrum. Convert wavelengths to wavenumber ( $cm^{-1}$ ) and construct a Deslandres table based on your experimental data. Extrapolate your data to determine the dissociation limit.

The 0-0 transition is not observable for I<sub>2</sub>. Use the literature value of 15598 cm<sup>-1</sup> for this transition and calculate the upper state dissociation energy of I<sub>2</sub>.

The upper (<sup>3</sup>Π<sub>ou</sub><sup>+</sup>) state of I<sub>2</sub> dissociates into a ground state (<sup>2</sup>P<sub>3/2</sub>) and an excited (<sup>2</sup>P<sub>1/2</sub>) I atom. Look up the atomic excitation energy and use this with your upper state dissociation energy to calculate the ground state dissociation energy for I<sub>2</sub>.

Compile your data to construct Birge-Spooener plots (plot of Δω(ν') versus ν' and Δω(ν'') versus ν'' to obtain the ground and excited state vibrational and anharmonicity parameters\*: ω<sub>e</sub>', ω<sub>e</sub>'x<sub>e</sub>', ω<sub>e</sub>'', ω<sub>e</sub>''x<sub>e</sub>''. Compare the results of your analysis with that obtained from a multiple linear regression fit as suggested in reference 4. This fit can be performed with the help of the spreadsheet I2FIT.XLS available from some of the computers in the Pchem. Lab or from the course web site. From the same site download, fill in and submit with your report the MS-Excel file Iodine\_results.XLS. Answer the questions in S&G. Present a table comparing your results with accepted literature data and comment on the discrepancies (if any).

When handing in your report, submit an electronic version of your raw data (peak position) as an email attachment.

## 5. References

- J.L. Hollenberg, *J. Chem. Educ.* **47**, 2 (1970)†.  
G. Herzberg, *Molecular Spectra and Molecular structure*, 2nd ed., Van Nostrand, N.Y.(1950).  
C.N. Banwell, "*Molecular Spectroscopy*", Ch. 6.  
I.J. McNaught, *J. Chem. Educ.* **57**, 101 (1980).

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\* Some references (in particular S&G) use the symbol  $\tilde{\nu}$  instead of  $\omega$  to designate frequency expressed as wavenumber.

†Careful with this reference as some of the molecular constants have been misprinted and also the labeling of one graph is wrong. You will have to check with the original paper by J.D. Verma, *J. Chem. Phys.* **32**, 738 (1960).