

# Absorption spectroscopy of molecular iodine

Artemis Bouzaki 10521454

University of Manchester, School of Physics and Astronomy

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The experiment was able to determine various molecular constants of the diatomic iodine molecule at room temperature through absorption spectroscopy, using a blazed grating spectrometer and a photomultiplier tube. The absorption spectrum of iodine was analysed using Birge-Sponer extrapolation. The calculated values were  $\chi'_e = (7.54 \pm 0.40) \times 10^{-3}$ ,  $D'_0 = 4,360 \pm 260 \text{ cm}^{-1}$ ,  $D''_0 = 12,492 \pm 260 \text{ cm}^{-1}$  and  $D'_e = 4,425 \pm 260 \text{ cm}^{-1}$  for the anharmonicity factor, dissociation energy of upper and lower state and depth of potential well of upper state respectively. All values where within two standard deviations from their true values.

## I. INTRODUCTION:

Spectroscopy studies the interaction of light with matter through emission and absorption. When molecules interact with light through absorption, they will absorb light at a certain wavelength by being promoted from their ground state to higher energy excited states. Each electronic transition from a ground state to an excited state is associated with numerous vibrational and rotational transitions [1]. Spectroscopy became a more accurate scientific technique during the early 1800s, when Joseph von Fraunhofer conducted experiments with a dispersive spectrometer [2]. This experiment utilised absorption spectroscopy to calculate the dissociation energy, anharmonicity factor and depth of potential well of molecular iodine at room temperature.

## II. THEORY:

According to the Born-Oppenheimer approximation the electronic, vibrational and rotational energies of a molecule are completely independent of each other and can be studied separately. The selection rule for vibrational transitions is  $\Delta\nu = \pm 1, \pm 2, \dots$  etc. where  $\nu$  is the vibrational quantum number. At room temperature, most electrons are in the electronic ground state according to the Boltzmann distribution. For iodine, we observe transitions between the ground vibrational state  $\nu'' = 0$  to excited vibrational states  $\nu' = 1, 2, 3, \dots$  etc. For notation purposes, the upper states in this report carry a single prime while the lower states carry a double prime. The vibrational changes will produce a coarse structure in the absorption spectrum and the rotational changes will produce a fine structure between the vibrational transitions [3]. In real diatomic molecules, the potential energy is more complex than that of a simple harmonic oscillator, since for larger values of displacement the molecule must dissociate. The Morse potential, which takes into consideration the molecule's anharmonicity, is a good estimate of a diatomic molecule's potential. The dissociation energy,  $D_0$ , is the energy required to break the molecule, whereas the anharmonicity, described by the

anharmonicity factor  $\chi_e$ , is the deviation of the system from being a quantum harmonic oscillator [4]. The analysis of the absorption spectrum of iodine and the calculation of the values of dissociation energy, anharmonicity factor and depth of the potential well are commonly executed using Birge-Sponer extrapolation. For the Birge-Sponer plot, all measured differences in energy between adjacent vibrational levels,  $\Delta E$  are plotted against  $\nu' + 1$ . We get that [3]

$$\Delta E = \omega'_e[1 - 2\chi'_e(\nu' + 1)] \quad (1)$$

and

$$D''_0 = E(0, 0) + D'_0 - E_{excitation}, \quad (2)$$

where  $\omega'_e$  is a constant that corresponds to the y-intercept of the Birge-Sponer curve,  $E(0, 0) = 15,730 \pm 3 \text{ cm}^{-1}$  [5] is the energy corresponding to the  $\nu'' = 0 \rightarrow \nu' = 0$  transition and  $E_{excitation} = 7,598 \text{ cm}^{-1}$  [6] is the energy required for electronic excitation. From Equation 1, the gradient of the Birge-Sponer curve is  $m = -2\chi'_e\omega'_e$ . The area under the curve corresponds to the dissociation energy of the upper state,  $D'_0$  [3]. The depth of the vibrational potential well of the upper state,  $D'_e$ , can be calculated from

$$D'_e = D'_0 + E_{ZPE}, \quad (3)$$

where  $E_{ZPE}$  is the zero-point energy of the iodine molecule and is given by [4]

$$E_{ZPE} = \frac{\omega'_e}{2} - \frac{\omega'_e\chi'_e}{4}. \quad (4)$$

## III. APPARATUS:

Light rays from a halogen bulb were collimated with a collimating lens before entering an iodine cell filled with iodine vapour. After interacting with iodine, the light was converged by a focusing lens before going into a spectrometer through an entry slit. The spectrometer utilised in this experiment was a blazed grating spectrometer, and therefore was designed to maximise efficiency in a certain diffraction order [7]. The grating generated pictures of the entry slit at different places with

varied wavelengths and it was attached to a drive motor that allowed it to revolve. The shift was measured by a gauge micrometer. In this experiment, the spectrometer was built so that the wavelength was approximately proportional to the gauge micrometre reading, although there was a slight quadratic offset [8]. The light departed the spectrometer through an exit slit that was coupled to a photomultiplier tube (PMT). The photons that entered the PMT were converted into current pulses with an amplitude proportional to the input photon's energy. An amplifier with a DC offset was used to amplify the current pulses and then an analogue-to-digital converter (ADC) converted them into a digital signal. The signal was sent to the computer, where it was processed by lab-specific software, which displayed the voltage (in  $V$ ) against the gauge micrometre reading (in  $mm$ ). The apparatus also consisted of a voltage supply for powering the PMT, which was set to  $750\text{ V}$  to minimize its dark current and noise. A schematic diagram of the apparatus is shown in Figure 1 below.

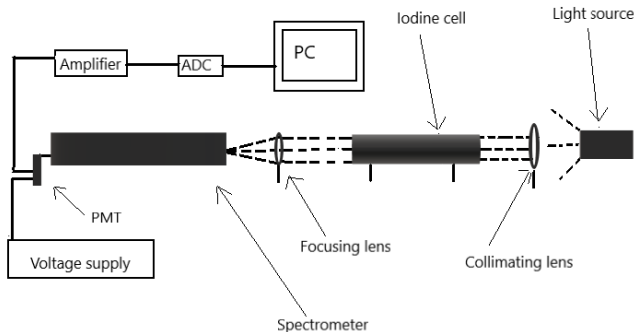


FIG. 1: An original schematic diagram of the apparatus showing the path of light leaving the halogen bulb. The absorption spectrum is produced in the PC.

#### IV. EXPERIMENTAL PROCEDURE AND RESULTS:

The source, focusing lens, iodine cell, and collimating lens were aligned with the optical axis of the entry slit to ensure that the greatest amount of light would enter the slit. The entry and exit slits were adjusted to have the same width so that the exit slit would produce an exact image of the entry slit. A narrower slit would produce better resolution, since the minimum difference in wavelength that could be resolved by the spectrometer would decrease however, the optical power available for analysis

would also decrease [7]. Adjustment was needed to find the width of the slits that produced good resolution in the spectrum but still allowed a good amount of light to enter the spectrometer. A heat gun was used to vaporize crystal iodine that was blocking light from passing through the cell. The indications on the gauge micrometer at the start and end of recording process were input manually in the software. The absorption spectrum produced for iodine at room temperature is shown Figure 2.

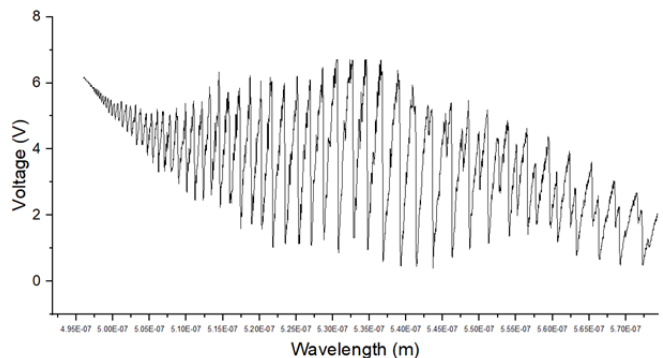


FIG. 2: Calibrated vibrational spectrum of iodine vapour at room temperature. Rotational structure is visible between vibrational transitions.

Mercury and Cadmium lamps were used to calibrate the spectrometer. For increased accuracy, the emission spectrum of Mercury was superposed with the absorption spectra of iodine using a beamsplitter that was positioned between the focusing lens and the entry slit. A Voigt function was fitted to each of the emission peaks to determine the corresponding value of the gauge micrometer reading. Through comparison of the produced emission spectra to those available in literature [9] [10], the wavelengths corresponding to those peaks were found. The wavelength was then plotted against the micrometer reading. The calibration equation for the detector used in this experiment is of the form  $\lambda = Ax^2 + Bx + C$  [8], where  $x$  is the reading of the gauge micrometer of the spectrometer. By fitting a quadratic polynomial to the data, the calibration parameters  $A$ ,  $B$  and  $C$  were determined. The uncertainty on the micrometer reading was calculated by obtaining the value of  $x$  for the same emission peak of Mercury on four separate measurements of the spectrum. This method allowed calculation of the standard deviation on  $x$  and, consequently, of the standard error. It was found that  $A = (-7.0 \pm 3.4) \times 10^{-5}$ ,  $B = (1.6 \pm 0.1) \times 10^{-5}$  and  $C = (2.9 \pm 0.1) \times 10^{-7}$ . The vibrational minimum in the absorption spectrum closest to  $\lambda = 541.2\text{ nm}$  corresponds to  $\nu' = 27$  [5]. Using this value as a reference, the corresponding vibrational quantum numbers and wavelengths for the rest of the minima were found. The energy difference between adjacent vibrational transitions was then calculated and plotted against  $\nu' + 1$  to produce a Birge-Sponer plot as shown

in Figure 3. Following Equations 1 to 4, the dissociation energy, the anharmonicity factor and the depth of the harmonic well were calculated. The error on the gauge micrometer reading was used to propagate the error on the wavelength and thus, the error on the energy difference  $\Delta E$  and the molecular constants.

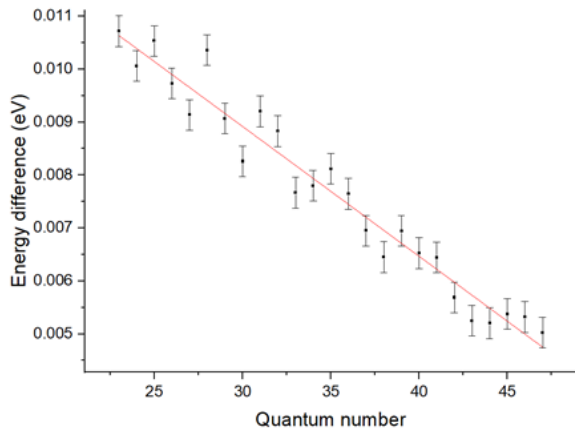


FIG. 3: Birge-Sponer plot produced for iodine vapour at room temperature with a linear fit going through the data points. The slope of this fit was  $m = (-2.5 \pm 0.1) \times 10^{-4}$  and the y-intercept was  $c = (16.3 \pm 0.4) \times 10^{-3}$ .

A summary of the values with quoted errors can be found in the following table.

	Experimental values	Literature values [5]
$\chi'_e (\times 10^{-3})$	$7.54 \pm 0.40$	$7.96 \pm 0.05$
$D''_0 (cm^{-1})$	$12,492 \pm 260$	$12,453 \pm 2$
$D'_0 (cm^{-1})$	$4,360 \pm 260$	$4,046 \pm 6$
$D'_e (cm^{-1})$	$4,425 \pm 260$	$4,112 \pm 6$

TABLE I: Table of values of the molecular constants of iodine extracted from Birge-Sponer plot compared to literature values.

## V. DISCUSSION:

The spectrum that was produced and used for analysis was of satisfactory resolution as the rotational structure between the vibrational transitions was resolved. As seen in Figure 3, the data points in the Birge-Sponer plot followed a linear trend but with a small oscillation. The procedure for determining the wavelength values at the minima was done numerous times, yielding the same findings each time. A tiny shift in the speed at which the spectrometer's rotor rotated could perhaps be one cause for the oscillation in the data points. This phenomenon would produce a slight inconsistency in the values of  $x$ , which would propagate in the energy differences, causing them to deviate from forming a straight line. This oscillation in the Birge-Sponer plot was the main reason behind the large uncertainties in  $\Delta E$ . Since the values of the molecular constants depend on the linear fitting of the Birge-Sponer, their uncertainties were larger than predicted. There was also a small systematic error coming from the human error when starting and hauling the collection procedure and from the values entered in the software, which had an error of half the resolution of the spectrometer. Those errors, however, were negligible compared to the error in  $x$  produced by the shift in the micrometer's values. The noise on the PMT was also considered to be negligible since the minima were distinguishable. Comparing the experimental values to values found in literature, we can conclude that this experiment was able to produce accurate results for the molecular constants. All of the calculated values were within two standard deviations away from their true values. This experiment would produce more accurate results if perhaps more data points were collected from the spectrum to produce a better Birge-Sponer curve. Minimizing the effect of doppler broadening caused by the random motion of the iodine molecules would also produce sharper minima which would allow for more accurate results [11]. This could be done by replacing the iodine cell with a beam of iodine molecules, minimizing the random motion.

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| <p>[1] DN Sathyanarayana. <i>Electronic absorption spectroscopy and related techniques</i>. Universities Press, 2001.</p> <p>[2] Alfred Leitner. The life and work of joseph fraunhofer (1787- 1826). <i>American Journal of Physics</i>, 43(1):59-68, 1975.</p> <p>[3] C.N. Banwell. <i>Fundamentals of Molecular Spectroscopy</i>. McGraw-Hill, 1972.</p> <p>[4] Leslie Lessinger. Morse oscillators, birge-sponer extrapolation, and the electronic absorption spectrum of i2. <i>Journal of Chemical Education</i>, 71(5):388-391, 1994.</p> <p>[5] Ian J. McNaught. The electronic spectrum of iodine revisited. <i>Journal of Chemical Education</i>, 57(2):101-105, 1980.</p> <p>[6] A G Gaydon. The determination of dissociation energies by the birge-sponer extrapolation. 58(5):525-538, 1946.</p> | <p>[7] John James. <i>Spectrograph Design Fundamentals</i>. Cambridge University Press, 2007.</p> <p>[8] Tom Waigh. The dissociation energy of the iodine molecule by absorption spectroscopy, 2019.</p> <p>[9] National Institute of Standards and Technology. Strong lines of mercury (hg).</p> <p>[10] National Institute of Standards and Technology. Strong lines of cadmium (cd).</p> <p>[11] David G Hummer. Non-coherent scattering: I. the redistribution function with doppler broadening. <i>Monthly Notices of the Royal Astronomical Society</i>, 125(1):21-37, 1962.</p> |
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