The Iodine Spectrum Revisited

R. B. Snadden

Heriot–Watt University, Riccarton, Edinburgh EH14 4AS, Scotland

An excellent undergraduate experiment in molecular spectroscopy involves the study of the absorption spectrum of iodine vapor in the visible region.[1] The normal procedure focuses attention on lines originating at the lowest vibrational level of the ground electronic state. The convergence of vibrational levels in the upper excited electronic state then permits a complete analysis to be made of the iodine molecule in its excited state with values being obtained for the fundamental oscillation frequency, the force constant of the bond (k), the anharmonicity constant (x), and the dissociation energy (D_0).

While this is in itself of considerable interest, similar data for the iodine molecule in its ground electronic state is of even greater interest but cannot be obtained following the above procedure without additional information being made available. The normal method for obtaining such data is to excite the iodine molecule with monochromatic radiation and analyze the resulting fluorescence spectrum.[2,3] However, handling an emission spectrum is complicated both experimentally and analytically.

This paper outlines an alternative procedure for analyzing the ground electronic state of the iodine molecule by using information provided by "hot" bands, observed in the absorption spectrum of iodine vapor.

The band spectrum of iodine vapor in the visible region of the spectrum as obtained by a spectrograph is shown in Figure 1.

The spectrum arises because iodine molecules absorb "visible" photons and are thereby promoted from the ground electronic state to an upper excited state. From about 500 to 545 nm the spectrum is uncomplicated and lines within this region are known to originate from the $v = 0$ vibrational level in the ground electronic state to all values of v in the upper excited electronic state.

Beyond 545 nm the spectrum becomes more complicated due to the appearance of "hot" bands, that is, bands originating from $v = 1$ and $v = 2$ in the ground electronic state. Because of this complication the standard undergraduate experiment focuses attention on the spectral region 500 to 545 nm. Treatment of the results within this region can lead to the complete analysis of the iodine molecule in its excited state. Such an analysis requires information additional to that provided by the actual spectrum.

However, if attention is concentrated on the "hot" bands, the ground state properties of the iodine molecule can be obtained without recourse to any additional data. If a spectroscope is used it is very difficult to "unscramble" the lines originating from $v = 0$, $v = 1$, and $v = 2$. The use of a spectrograph improves things slightly but greatly increases the time spent on the experiment. However, modern spectrophotometers of high resolution can now be obtained at relatively little cost. Using one such instrument (Shimadzu UV 240), an iodine spectrum can be obtained of such clarity that no difficulties arise in the identification of the hot bands because we can now employ line intensities to "unscramble" the data as is made clear in Figure 2.

Thus the series of lines from 500 to 543.2 nm originate at $v = 0$; their intensities are clearly seen to diminish beyond 543.2 nm. A new band begins to appear at 545 nm and increases in intensity up to about 563 nm beyond which it decreases. This new band, absorbing at higher wavelengths
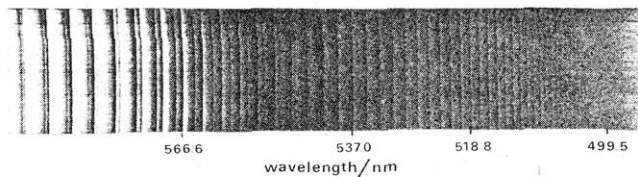

Figure 1. Band spectrum of iodine vapor in the visible region (adapted from Barnard, A. K.; Mansell, A. L. *Fundamentals of Physical Chemistry*; McGraw–Hill: London, 1966; p 87).
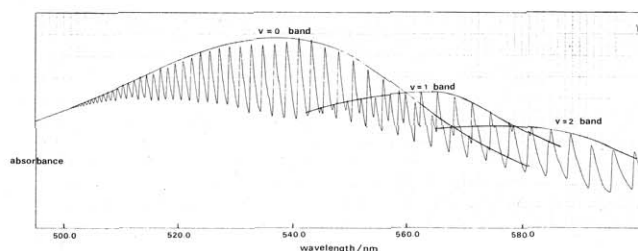

Figure 2. The use of line intensities to "unscramble" the spectrum.

and hence corresponding to transitions of lower energy, is the "hot" band originating at $v = 1$. Finally a further "hot" band, corresponding to still lower energies and originating at $v = 2$, makes its appearance at about 569 nm.

Transitions responsible for the three bands are shown in Figure 3. Comparison of the information in Figures 4(a) and 4(b) shows that

$$\bar{\nu}_{0,0} - \bar{\nu}_{0,1} = \bar{\nu}_{1,0} - \bar{\nu}_{1,1} = \bar{\nu}_{2,0} - \bar{\nu}_{2,1}, \text{ etc.} = X$$

Each of the above differences represents the energy difference (expressed as a wave number) between the vibrational levels $v = 0$ and $v = 1$ in the ground electronic state.

Now the pattern of allowed vibrational energy levels given by the Schrodinger equation for the Morse potential energy function is approximately

$$E_v = h\omega(v + \tfrac{1}{2}) - xh\omega(v + \tfrac{1}{2})^2$$

where ω = oscillating frequency in hertz. The energy difference between the $v = 0$ and $v = 1$ states is therefore

$$E_1 - E_0 = \Delta E_{1,0} = h\omega(1 - 2x)$$
$$= hc\bar{\omega}(1 - 2x)$$

Expressing this energy difference in spectroscopic units of cm^{-1} gives

$$\Delta E_{1,0}/hc = \bar{\omega}(1 - 2x)$$
$$\therefore X = \bar{\omega}(1 - 2x) \tag{1}$$

[1] Levitt, B. P., Ed. *Findlay's Practical Physical Chemistry*, 9th ed.; Longman: London, 1973; p 183.

[2] Verma, R. D. *J. Chem. Phys.* **1960**, *32*, 738.

[3] Shoemaker, D. P.; Garland, C. W.; Steinfield, J. I. *Experiments in Physical Chemistry*, 3rd ed.; McGraw–Hill: London, 1974; p 474.

Wave Numbers of "Lines" in the Iodine Spectrum

"Lines" originating at $v = 0$		"Lines" originating at $v = 1$		"Lines" originating at $v = 2$		$\Delta\bar{\nu}_{1,0}/\text{cm}^{-1}$	$\Delta\bar{\nu}_{2,1}/\text{cm}^{-1}$
"Line" No.	$\bar{\nu}/\text{cm}^{-1}$	"Line" No.	$\bar{\nu}/\text{cm}^{-1}$	"Line" No.	$\bar{\nu}/\text{cm}^{-1}$		
1	18559.7	16	18350.7			209.0	
2	18484.5	17	18275.2			209.3	
3	18408.3	18	18195.4			212.9	
4	18330.5	19	18115.1			215.4	
5	18246.5	20	18029.7			216.8	
6	18162.0	21	17948.0			214.0	
7	18075.8	22	17863.9			211.9	
8	17987.6	23	17777.7	31	17569.6	209.9	208.1
9	17898.2	24	17688.9	32	17477.1	209.3	211.8
10	17810.2	25	17598.2	33	17387.1	212.0	211.1
11	17717.9	26	17504.3	34	17292.4	213.6	211.9
12	17621.9	27	17407.0	35	17196.9	214.9	210.1
13	17524.2	28	17309.6	36	17098.4	214.6	211.2
14	17425.3	29	17211.7	37	16999.2	213.6	212.5
15	17323.5	30	17108.6	38	16985.8	214.9	212.8
						Mean = 212.8	Mean = 211.2
						$\therefore X = 213.8\ \text{cm}^{-1}$	$\therefore Y = 211.2\ \text{cm}^{-1}$

Similarly, comparison of the information in Figures 4(b) and 4(c) yields

$$\bar{\nu}_{0,1} - \bar{\nu}_{0,2} = \bar{\nu}_{1,1} - \bar{\nu}_{1,2} = \bar{\nu}_{2,1} - \bar{\nu}_{2,2}, \text{ etc.} = Y$$

Here each of the above expressions represents the energy difference between the vibrational levels $v = 1$ and $v = 2$ in the ground electronic state.

$$\therefore E_2 - E_1 = \Delta E_{2,1} = h\omega(1 - 4x) = hc\bar{\omega}(1 - 4x)$$

$$\therefore \Delta E_{2,1}/hc = \bar{\omega}(1 - 4x)$$

$$\therefore Y = \bar{\omega}(1 - 4x) \tag{2}$$

Knowing X and Y, eqs 1 and 2 can be solved simultaneously to obtain values of $\bar{\omega}$ and x. The determination of the force constant of the bond (k) and the dissociation energy (D_0) follow for they are related to $\bar{\omega}$ and x by the equations

$$k = 4\pi^2\bar{\omega}^2c^2\mu$$

$$D_0 = \frac{hc\bar{\omega}(1 - 2x)}{4x} \approx \frac{hc\bar{\omega}}{4x}$$

where μ = reduced mass.

Returning now to the actual iodine spectrum. The problem is to match a particular line originating at $v = 0$ and terminating at v' with a line originating at $v = 1$ and terminating at the *same* v'; similarly for lines originating at $v = 1$ and $v = 2$. For this purpose each of the lines is identified by a serial number. Lines originating at $v = 0$, $v = 1$, and $v = 2$ are identified respectively by the numbers 1–15, 16–30, and 31–38 (Fig. 4). The wave numbers of the lines are tabulated in the table such that matching data are aligned horizontally.

From the table, the energy difference (in cm⁻¹) between the $v = 0$ and $v = 1$ vibrational levels of the ground electronic state is seen to fluctuate about a mean of 212.8 cm⁻¹. Hence from eq 1

$$212.8 = \bar{\omega}(1 - 2x) = \bar{\omega} - 2x\bar{\omega} \tag{3}$$

That this is the only correct match can be confirmed by obtaining diagonal values of $\Delta\bar{\nu}$ from the table. Such values do not fluctuate about a mean but either steadily increase or decrease.

Similarly the energy difference (in cm⁻¹) between the $v = 1$ and $v = 2$ vibrational levels of the ground electronic state fluctuates about a mean of 211.2 cm⁻¹. Hence from eq 2

$$211.2 = \bar{\omega}(1 - 4x) \tag{4}$$

Equations 3 and 4 can now be solved simultaneously to obtain values of $\bar{\omega}$ and x equal to 214.4 cm⁻¹ and 0.0037, respectively. These compare favorably with literature values
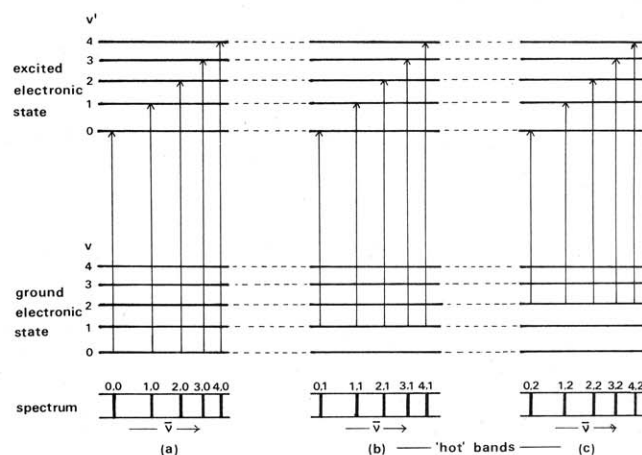

Figure 3. Transitions responsible for the three bands observed in the iodine spectrum.
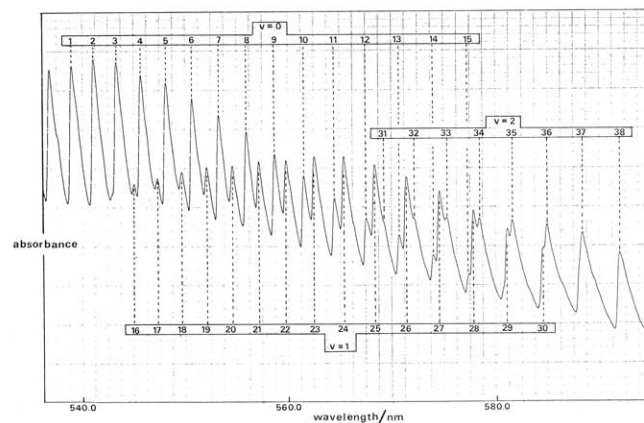

Figure 4. Allocation of serial numbers to identify lines.

of 214.50 cm⁻¹ and 0.0029, respectively.[2] The force constant and the dissociation energy can then be calculated to be 172 N m⁻¹ and 173 kJ mol⁻¹. This latter result is about 15% higher than the literature value. The main reason for the discrepancy is that the Schrödinger equation for the allowed levels contains only one anharmonicity constant. In fact a more precise expression requires cubic, quartic, ... terms in $(v - \frac{1}{2})$ with additional anharmonicity constants y, z, ...

These terms become important at large values of v and hence in the determination of dissociation energy.

As a final exercise the student can justify the existence of "hot" bands by determining the relative populations (N) at room temperature (293 K) in the $v = 0$, $v = 1$, and $v = 2$ states from the calculated spacings. Thus the spacing between the $v = 0$ and $v = 1$ levels is 212.8 cm^{-1}. From the Boltzmann distribution

$$\frac{N_{v=1}}{N_{v=0}} = \exp\left[-\frac{\Delta E}{kT}\right] = \exp\left[-\frac{\Delta Ehc}{hc \cdot kT}\right] = \exp\left[-\frac{Xhc}{kT}\right]$$

$$= 0.35$$

Similarly the spacing between the $v = 1$ and $v = 2$ levels is 211.2 cm^{-1}.

$$\therefore \frac{N_{v=2}}{N_{v=1}} = 0.35$$

$$\therefore N_{v=0}:N_{v=1}:N_{v=2} = 1:0.35:0.12$$

that is, the population of the $v = 1$ and $v = 2$ states are significant.

In summary, using *all* the information provided by the absorption spectrum for iodine vapor it is possible to determine important parameters of the iodine molecule in its ground electronic state without employing any extraneous data. The loss of accuracy inherent in this method is acceptable and is more than compensated for by the experimental simplicity.