

The absorption spectrum of iodine vapor

Introduction

To a good first approximation the total energy of a molecule (E_{total}) is given by the expression

$$E_{\text{total}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}} \quad (1)$$

where E_{trans} , E_{rot} , E_{vib} , and E_{elec} are the translational, rotational, vibrational, and electronic energies of the molecule. Translational energy represents the kinetic energy due to the motion of the center of mass of a molecule through space, and can be separated from the other types of molecular energy, which collectively are called the internal energy of the molecule. Because there are interactions among the different types of internal energies (particularly between rotational and vibrational energy) eq 1 is only approximately correct, but it represents a good starting point in describing the total energy of a molecule.

It is usually the case that $E_{\text{trans}} < E_{\text{rot}} < E_{\text{vib}} < E_{\text{elec}}$. As a consequence, when a molecule absorbs a photon in the visible or ultraviolet region of the spectrum (corresponding to photon energies sufficient to change the electronic state of a molecule), and when both the initial and final electronic states of the molecule are bound with respect to dissociation, there is sufficient energy to also cause vibrational and rotational transitions in the molecule to occur. In this case, vibrational and rotational structure is expected to be observed in the absorption spectrum of the molecule. It is difficult to observe rotational structure in the electronic absorption of a molecule [1], but vibrational structure can often be observed, even in low resolution absorption measurements.

Electronic absorption spectrum of molecular iodine

The potential energy curves for the ground ($X^1\Sigma_g^+$) and one of the bound excited electronic states ($B^3\Pi_{0u}^+$) of the molecule I_2 are shown in Figure 1 [2]. It is convenient to choose zero energy for a molecule as the minimum in the ground electronic state potential energy curve, as shown in Figure 1. The electronic transition between these two states is spin forbidden, but the spin selection rule is less exact for diatomic molecules composed of atoms in the lower rows of the periodic table, and so an absorption spectrum corresponding to this electronic transition is observed in the visible region of the spectrum. Vibrational structure in the spectrum is observed even at low resolution.

If we ignore rotational energy, then the energy, in units of wavenumbers (cm^{-1}), for a molecule in a particular vibrational energy level in the ground and excited states are

$$E''(v'') = \omega_e''(v''+1/2) - \omega_e x_e''(v''+1/2)^2 \quad (\text{ground state}) \quad (2)$$

$$E'(v') = T_e' + \omega_e'(v'+1/2) - \omega_e x_e'(v'+1/2)^2 \quad (\text{excited state}) \quad (3)$$

In the above expressions for energy we have followed the usual convention of labelling the higher energy state with a single prime (') and the lower energy state with a double prime (''). T_e' is the energy at the minimum in the potential energy curve for the excited state, measured relative to the minimum in the ground electronic state. ω_e and $\omega_e x_e$ are the vibrational constants (harmonic term and first anharmonic correction term) for each electronic state [3].

A transition between a particular vibrational state v' in the upper electronic state and a vibrational state v'' in the lower electronic state is written as $v' \leftarrow v''$, with the quantum number for the higher energy state appearing first. The direction of the arrow indicates whether the transition is light absorption (\leftarrow) or light emission (\rightarrow). Starting with eqs 2 and 3, the following equation can be found for the energy at which $v' \leftarrow v''$ transitions will occur

$$\begin{aligned} \Delta E &= E(v') - E(v'') \\ &= T_e' + [\omega_e'(v'+1/2) - \omega_e x_e'(v'+1/2)^2] - [\omega_e''(v''+1/2) - \omega_e x_e''(v''+1/2)^2] \end{aligned} \quad (4)$$

In the present experiment we limit our analysis to absorption transitions beginning in the $v'' = 0$ vibrational state of the lower electronic state. In that case, rearrangement of eq 4 gives

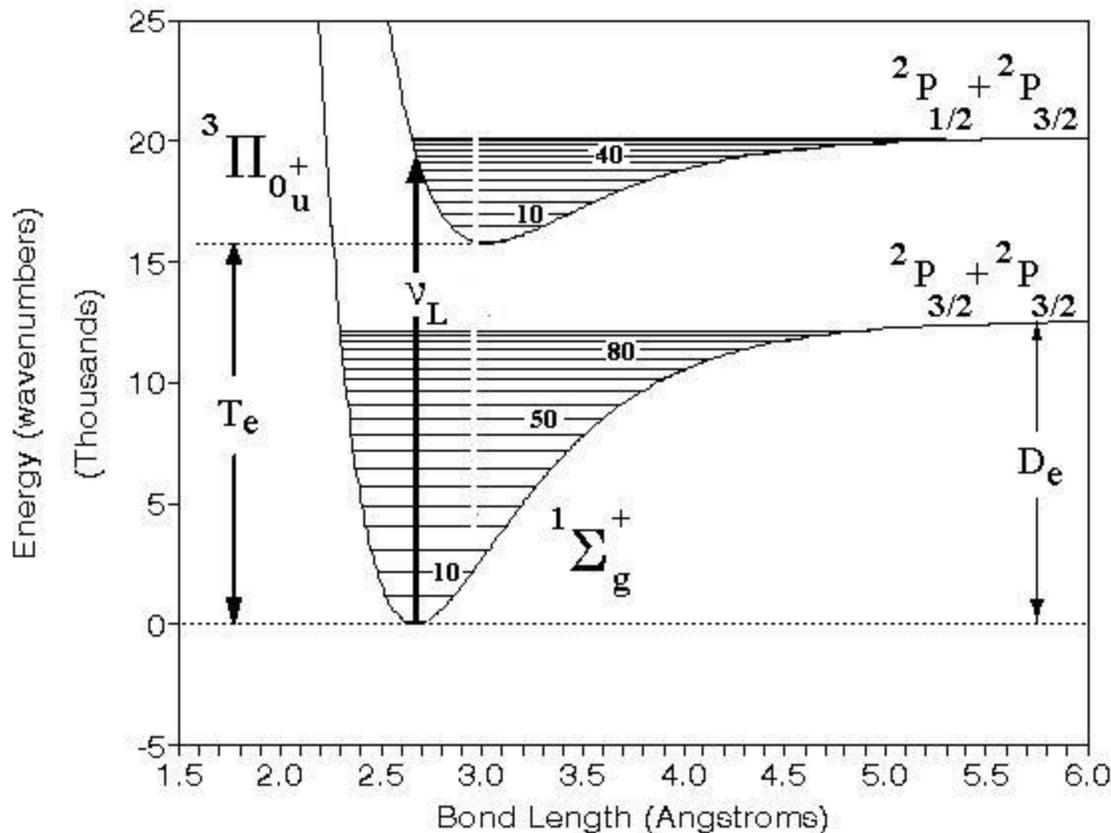


Figure 1. Potential energy curves for the $X^1\Sigma_g^+$ and $B^3\Pi_{0u}^+$ states of I_2 . Note: 1 Angstrom = 0.1 nm.

$$\Delta E = [T_e' - (\omega_e''/2) + (\omega_e x_e''/4)] + \omega_e'(v'+1/2) - \omega_e x_e'(v'+1/2)^2 \quad (5)$$

Note that eq 5 is quadratic in powers of $(v'+1/2)$. If we define $x = v'+1/2$, we can then plot ΔE vs x . A fit of experimental absorption data for a series of transitions $v' \leftarrow v'' = 0$ to a quadratic equation of the form

$$\Delta E = a_0 + a_1 x + a_2 x^2 \quad (6)$$

gives (based on eq 5)

$$a_0 = [T_e' - (\omega_e''/2) + (\omega_e x_e''/4)] \quad (7)$$

$$a_1 = \omega_e' \quad (8)$$

$$a_2 = -\omega_e x_e' \quad (9)$$

The vibrational constants for the upper electronic state are found directly using the best fit values for a_1 and a_2 . The value for T_e' can be found from the best fit value for a_0 and the known values for ω_e'' and $\omega_e x_e''$, obtained using Raman spectroscopy and available at the NIST website [4].

There are two additional complicating factors in the analysis of the absorption spectrum of I₂. First, not all of the transitions from v''=0 in the ground electronic state to the different v' vibrational states in the upper electronic state are actually observed. The intensity of any particular transition v' ← v'' is, to a first approximation, proportional to the Franck-Condon factor [5] for the transition, given by the expression

$$I(v',v''=0) \sim \left| \int_0^\infty \psi_{v'}(r) \psi_{v''=0}(r) dr \right|^2 \quad (10)$$

where the term on the right hand side of eq 10 is called the Franck-Condon factor. The transitions are often called “vertical transitions” in this context because the definition of the Franck-Condon factor is founded on the notion (expressed classically) that the nuclei do not change position during the transition between electronic surfaces. The Franck-Condon factors change in a regular manner, first increasing in size and then decreasing in size, and so the peaks observed for a particular value for v'' also increase and decrease continuously.

Examination of Figure 1 shows that the largest values for the Franck-Condon factors for molecules with v''=0 occur for v' ≅ 35, and that the Franck-Condon factors for v' < 15 are so small that these transitions cannot be seen in the spectrum.

A second complicating factor arises because there are a sufficient number of molecules with v''=1 and v''=2 that transitions originating in these two initial vibrational states overlap with the v''=0 transitions, as seen in Figure 2. Unlike most diatomic molecules, I₂ has a significant population of molecules in the higher vibrational states in the ground electronic state, due to the unusually large mass of the I atoms, which results in a small value for the vibrational constant for the molecule. At equilibrium, using the harmonic oscillator approximation and Boltzmann distribution, the relative population of molecules in excited vibrational states is given by the expression

$$\frac{P_{v''}}{P_0} = \exp(-v''\omega/kT) \quad (11)$$

where ω is the vibrational constant for the molecule, T is temperature, and k is the Boltzmann constant. Because measurements of the absorption spectrum of iodine are usually carried out at temperatures above room temperature (to increase the partial pressure of iodine in the gas phase) the problem of overlapping transitions from molecules with different initial values of v'' is even greater than would occur in room temperature absorption measurements.

Table 1 shows the relative populations of molecules with v''=1 and v''=2 for CO (a typical diatomic molecule) and I₂, at T = 20. °C and T = 50. °C. Unlike CO, I₂ has a large number of molecules in the v''=1 and v''=2 vibrational states, which explains why transitions originating in those states are observed in the spectrum in Figure 2.

Table 1. Relative populations of molecules in v''=1 and v''=2 for CO and I₂ at T = 20. °C and T = 50. °C.

Molecule	Rel. population	T = 20. °C	T = 50. °C
CO	P ₁ /P ₀	2.3 x 10 ⁻⁵	6.3 x 10 ⁻⁵
	P ₂ /P ₀	5.6 x 10 ⁻¹⁰	40.2 x 10 ⁻¹⁰
I ₂	P ₁ /P ₀	0.349	0.385
	P ₂ /P ₀	0.122	0.148

Calculations use k = 0.69503 cm⁻¹/K, ω(CO) = 2170. cm⁻¹, and ω(I₂) = 214.5 cm⁻¹.

Experimental

The visible absorption spectrum of I₂ will be taken on the Cary-100 UV-visible spectrophotometer or similar instrument. The highest resolution of the instrument should be used instead of the default settings to increase the precision in the location of the peaks in the spectrum. Using high resolution decreases the intensity of light passing

through the sample, and so increases the noise in the measurement, and so a long averaging time should be used to reduce the level of noise in the spectrum. The following settings can be used as a starting point, and modified, if necessary, to improve the quality of the spectrum

Spectral bandwidth (resolution): 0.20 nm
Averaging time: 1 second

Data interval: 0.25 nm/point

The peaks in the spectrum lie in the range 500-650 nm. With the above settings, the scan rate for acquiring a spectrum is 15 nm/min, and so it will take 10 minutes to do the measurement.

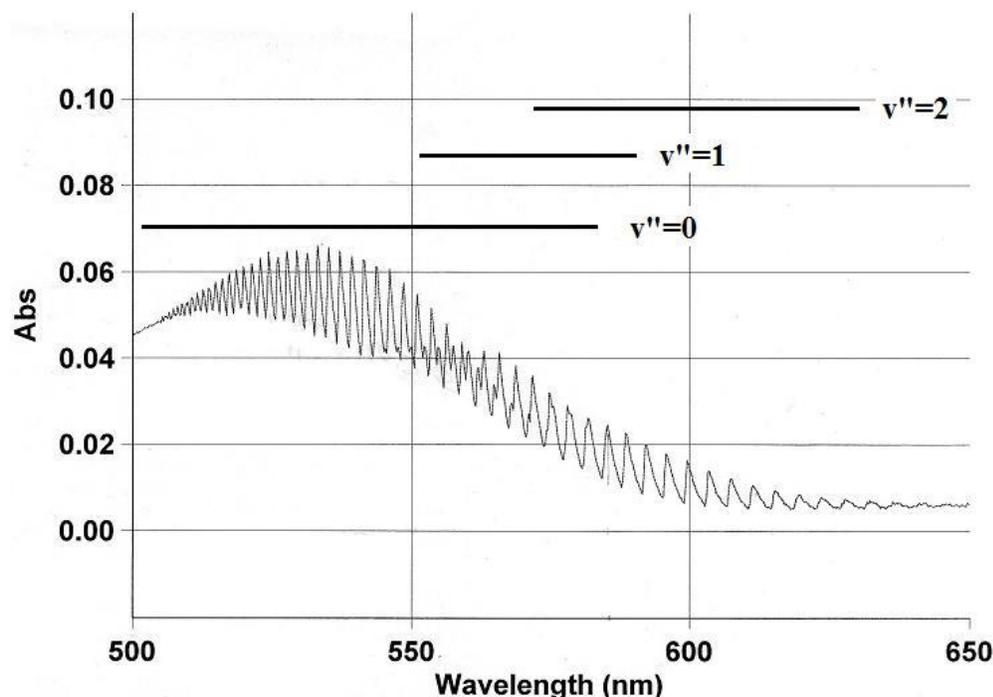


Figure 2. Absorption spectrum of I₂ vapor. The sample was I₂ vapor above solid iodine, in a capped 1 cm cuvette. T = 50. °C, SBW = 0.20 nm, averaging time = 1. s.

Before beginning the measurements, the instrument should be allowed to warm up for at least 10 minutes. The cell holder for the instrument should be set to a temperature of 50. °C. Prior to taking the absorption spectrum a baseline spectrum should be obtained using an empty cuvette in the reference and sample cell holders. Since the only information being used in the measurements is the location of the peaks in the spectrum, a baseline spectrum is not strictly necessary, but it acts to center the spectrum at zero absorbance.

After taking the baseline spectrum the empty cuvette in the sample cell should be replaced with a capped cuvette containing a small amount of solid iodine. The cuvette should be allowed to warm up for at least five minutes to allow the temperature of the cuvette (and iodine) to reach the temperature set for the cell holder. Sublimation of the iodine will produce a partial pressure of iodine vapor in the gas phase.

After the solid and gas phase iodine has achieved equilibrium the spectrum can be taken. The absorbance scale should be chosen to contain the absorbances observed for the vapor (- 0.02 to + 0.10 can be used as an initial choice). The peak peak feature of the instrument should be used to find locations of peaks in the spectrum. An initial value for the peak threshold of 0.050 can be used.

After an initial absorption spectrum has been measured, the instrument settings can be varied and additional spectra taken to improve the quality of the data. Note that if the spectral bandwidth, data interval, or averaging times are changed a new baseline spectrum will need to be run.

The final result from the measurements should be a high quality absorption spectrum with the locations of the peaks clearly identified.

Assignment of the peaks in the spectrum

The one remaining difficulty is in assigning peaks in the spectrum of I_2 to specific transitions between vibrational levels in the ground and excited electronic states. In cases where the $v'=0 \leftarrow v''=0$ transition is not observed this is usually not an easy thing to do. We therefore give the assignment for two transitions to use as a starting point to assign other peaks in the spectrum. The peak appearing at approximately 551. nm is due to the transition $v'=23 \leftarrow v''=0$ (labeled 23,0). The next peak, which appears at approximately 548. nm, is due to the transition $v'=24 \leftarrow v''=0$ (labeled 24,0). Successive peaks at higher energies (shorter wavelengths) are in order, and can be assigned to $v' = 25, 26, 27, \dots$. Successive peaks at lower energies (longer wavelengths) are also in order, and can be assigned $v' = 22, 21, 20, \dots$

In the region where there is overlap between peaks from states with $v''=0$ and $v''=1$ it is more difficult to identify the peaks corresponding to $v''=0$. This is because overlap between transitions from different initial vibrational states results in double peaks, or sometimes shoulders on the side of a peak. One guide to assigning peaks in the overlap region is to use the fact that the spacing between adjacent peaks changes slowly and so to a first approximation is constant. Therefore, if you know the location of two peaks in the spectrum, that information can be used to predict the approximate location of peaks at longer or shorter wavelengths, and so extend the assignment of the spectrum. Another guide to assigning peaks is to note that, as one moves from short to long wavelength, the $v''=1$ peak first appears as a barely visible shoulder next to a $v''=0$ peak. The $v''=1$ shoulder gradually increases in size from peak to peak until one has a double peak. Eventually, the $v''=1$ portion of the double peak becomes larger than the $v''=0$ portion, and later yet, the $v''=0$ portion becomes a mere shoulder and eventually disappears. At even longer wavelength, one can observe the gradual replacement of $v''=1$ peaks by $v''=2$ peaks. In summary, in the region corresponding to wavelengths less than 550. nm, all peaks can be attributed to transitions from $v''=0$, since in this region overlap with peaks from $v'' = 1$ or 2 is weak and so not observed. For wavelengths longer than 550 nm it is more difficult to assign peaks to the $(v',0)$ progression, but careful analysis should make it possible to identify at least a few additional peaks out to about 560. nm.

It is possible to assign peaks in the spectrum to transitions from $v''=1$ and $v''=2$, which would allow additional analysis of the absorption data, including finding the values for the vibrational constants in the ground electronic state, but this will not be done in the present experiment.

The data analysis should be done as follows:

- 1) Assign the peaks for the (23,0) and (24,0) transitions, as discussed above.
- 2) Use the assignment of these peaks to assign other peaks in the spectrum. Assign only peaks originating in the $v''=0$ vibrational state in the ground electronic state of the molecule. In the region of overlap, assign as many peaks as possible while being careful not to assign peaks where the assignment might be in error
- 3) Convert peak locations for all assigned peaks from wavelength to energy. Give the energies for the peak locations in cm^{-1} . Recall that energy in wavenumber can be found by the expression

$$\Delta E = 1/\lambda \tag{12}$$

where λ is given in units of cm. So, for example, if $\lambda = 400.00$ nm then $\Delta E = 20000. \text{cm}^{-1}$.

- 4) Fit your peak locations to a quadratic function using eq 6. Remember that $y = \Delta E$, and $x = v'+1/2$, where v' is the vibrational quantum number in the upper electronic state of I_2 .

- 5) Use eq 7, 8, and 9 to find experimental values for T_e' , ω_e' , and $\omega_e x_e'$, the energy of the upper electronic state (relative to the minimum in the ground state potential energy curve), and the vibrational constants for the upper

electronic state. Note that you will need to go to the NIST website (given below) to find the values for ω_e'' and $\omega_e x_e''$ required to use eq 7 to find T_e' .

6) Compare your results for the upper electronic state ($B^3\Pi_{0u^+}$) constants to those given at the NIST website for I_2 . (<http://webbook.nist.gov/chemistry/form-ser.html>).

Lab Report

Your laboratory report should include the following:

1) The details and results of your data analysis, including your final values for T_e' , ω_e' , and $\omega_e x_e'$. Be sure to show explicitly how you assign the $v''=0$ component of any double peaks or peaks with shoulders. You do not have to find confidence limits for the values you obtain for the molecular constants.

2) A comparison of your molecular constants for the $B^3\Pi_{0u^+}$ state to those found in the literature (NIST website).

References

1. One way to circumvent this difficulty is to use a laser to excite a transition from a specific initial vibrational-rotational state in the ground electronic state of a molecule to a specific final vibrational-rotational state in an excited bound upper electronic state. Cooling of the molecules (to reduce the population of excited states and minimize Doppler broadening of spectral lines), monitoring of fluorescence from excited molecules, and a variety of other techniques (often involving the use of multiple lasers) have been used since the early 1970s to obtain high resolution spectra of molecules.

2. The symbols used to label the electronic states of a diatomic molecule communicate information about the spin and symmetry properties of the state, as discussed in Section 13.A.1 (pp. 533-535) of P. W. Atkins, J. de Paula Physical Chemistry, Tenth Edition, (Freeman, New York, 2014).

3. Atkins and de Paula, pp. 506-508. Higher order corrections to the expression for energy can be given when justified by the quality of experimental data. Note that some books use v_e and $v_e x_e$ instead of ω_e and $\omega_e x_e$ for the constants in the expression for vibrational energy, or other related expressions (as is true for Atkins and de Paula). When high resolution data are available, there are alternative expressions that are used for the combined vibrational and rotational energy of a diatomic molecule (see, for example, P. F. Bernath, Spectra of Atoms and Molecules, (Oxford University Press, New York, 1995)), pp. 206-208. Finally, remember that $\omega_e x_e$ is a single constant, and that it is written as it is for historical reasons.

4. The NIST website is <http://webbook.nist.gov/chemistry/form-ser.html>. The constants for the ground electronic state (ω_e'' and $\omega_e x_e''$) are labeled with the prefix X, and those for the excited electronic state (T_e' , ω_e' , and $\omega_e x_e'$) are labeled with the prefix B.

5. Atkins and de Paula, pp. 536-538.

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