

CHMY 374 (2019) Experiment #1

Absorption Spectra of Molecular Iodine

Supplemental Instructions

Handouts:

1) *I2Shoemaker.pdf*: Selected portions of Experiment 42, Shoemaker et al, 5th Ed.
(We will only measure the absorption spectrum, and perform only certain parts of the analysis).

2) *FCFactors.pdf*: Authors Prof. Lee Spangler and Pat Callis

Introduction

Spectroscopic studies and analysis of the type carried out in this experiment were the earliest methods that allowed one to know bond dissociation energies.

Harmonic oscillator model. Vibrations of diatomic molecules are closely modeled as two masses connected by a harmonic spring. Photon frequencies that will be absorbed follow from the fundamental equation $\Delta E = h\nu$, where h is Planck's constant. For the **ground** state, standard notation for vibrational energies of a diatomic molecule is, when arbitrarily setting the bottom of the ground state potential energy well = 0:

$$E_{v''} = 0 + (v'' + 1/2)h\nu_e'' - (v'' + 1/2)^2 x_e'' h\nu_e'' + \text{smaller terms from higher powers of } (v'' + 1/2)$$

Notation: The subscript e denotes the value at the **equilibrium bond length**. x_e'' and x_e' are the **positive, dimensionless** anharmonicity constants for the ground and excited state respectively. These, along with the negative sign, cause the spacing between the levels to decrease with increasing vibrational energy.

Dividing by hc , where c is the speed of light in cm/s converts this to the commonly-used, useful units of wavenumbers (cm^{-1}). Why is this useful? Very widely used because everything from radio frequency light ($100 \text{ Mhz} = 0.0033 \text{ cm}^{-1}$) to far UV ($100 \text{ nm} = 100,000 \text{ cm}^{-1}$) can be easily express without using scientific notation.

The above equation in SI units then becomes the following in wavenumbers:

$$\underline{\nu_{v''}} = 0 + (v'' + 1/2)\underline{\nu_e''} - (v'' + 1/2)^2 x_e'' \underline{\nu_e''} + \text{smaller terms from higher powers of } (v'' + 1/2)$$

(The underline here means wavenumbers. The text of the Shoemaker.pdf handout uses a \sim above the ν to denote cm^{-1} .)

Similarly, for the **excited** state this becomes in cm^{-1} :

$$\underline{\nu_{v'}} = \underline{\nu_{el}} + (v' + 1/2)\underline{\nu_e'} - (v' + 1/2)^2 x_e' \underline{\nu_e'} + \text{smaller terms from higher powers of } (v' + 1/2),$$

where the first term in each equation is for purely harmonic motion, and the second is the first approximation to anharmonic behavior, which ultimately leads to bond dissociation at long bond lengths, i.e., in very high vibrational states. $\underline{\nu_{el}}$ is the "pure electronic" energy wavenumber, (corresponding to the energy difference between the potential minima of the ground and excited states. (See Fig. 1)

The Franck Principle, Condon approximation, and Franck-Condon Factors. Excitation of a diatomic molecule to its lowest excited electronic state, most often is well described by removing an electron from the highest occupied MO (HOMO) and placing it in the lowest unoccupied MO (LUMO). Usually the LUMO has one more node than the HOMO, typically causing more bonds to be more antibonding relative to the HOMO. In any case, the equilibrium bond lengths are instantly changed (a so called “vertical transition”), while the nuclei hardly move during the excitation process (a principle first articulated by James **Franck** in 1926). Initially following the electronic excitation, the excited state vibrational wavefunction of the nuclei is a non-stationary vibrational quantum state that may be described as a superposition (linear combination) of the ground state vibrational eigenstates. Also in 1926, Edward **Condon** worked out the quantum mechanics that gave the relative intensities of the vibronic transitions that contained the approximation that the electronic transition dipole moment is essentially independent of the vibrational levels involved (the **Condon approximation**), which leads to the relative absorbance of a vibronic (i.e., both electronic and vibration energies are excited) transition to be given by the *square of the overlap integral of the final state vibrational wave function with the initial ground state vibrational wave function*, now known as the “**Franck-Condon factor**”. Handout #2 indicates how the Franck-Condon factors, and thus the appearance of the spectrum will vary as a function of the bond length change upon excitation and the excited vibrational state for a single vibrational mode. This is depicted in terms of λ . (NOTE: here, λ is *not* wavelength, but a dimensionless measure of the stored harmonic spring potential energy in units of the harmonic energy level spacing, i.e., $\frac{1}{2} k\Delta r^2/h\nu$, where Δr = the change in bond length upon the “vertical excitation”. For I_2 , λ is quite large, ~ 30 . In other words, the vertical vibronic transition from the ground state will be most intense for the $v' = \sim 30$ vibrational quantum number of the excited state.

Hot bands. The figures in Handout#2 are assuming only the lowest vibrational state is populated. Boltzmann’s constant, k_B , is 0.695035 cm^{-1} , so $k_B T = 207 \text{ cm}^{-1}$ at 298 K. But, I_2 is somewhat special because of the combination of a weak bond (meaning a small force constant) and massive atoms. The vibrational “frequency” in the ground electronic state is only $\sim 200 \text{ cm}^{-1}$; therefore you can see that the relative population of the $v'' = 0, 1$, and 2 vibrational states is significantly non-zero. **Before coming to class, use the Boltzmann factor to get the quantitative numbers for the ratio of populations in the $v'' = 1$ and $v'' = 2$ states to that in the $v'' = 0$ state, assuming $v'' = 200 \text{ cm}^{-1}$ and $T = 298 \text{ K}$.**

Thus, the spectrum is therefore complicated by so called “hot bands” arising from transitions from ground state vibrational states, $v'' = 1$ and $v'' = 2$, which appear along with those from $v'' = 0$, because the Boltzmann factors are fairly large (larger than 0.1)

Experiment

Obtain the absorption spectrum from 650 to 450 nm with the highest resolution and slowest scan available. Use a 10 cm cell. *The maximum absorbance (near 530 nm) ideally should be about 0.25, and must be at least 0.1 to have accurate data.* The temperature of the cell may have to be maintained somewhat above room temperature to attain the desired absorbance, because the “vapor pressure” of the I_2 crystals is small, but like all vapor pressures, increases rapidly with increasing temperature. (Later in the semester, we will extract the ΔH^0 of sublimation from the quantitative measurement of this temperature dependence.) For this experiment, however, we only care quantitatively about the “frequencies” (cm^{-1}) of each of the many peaks in the spectrum—not how intense they are.

Data Manipulation

Plot the spectrum on a cm^{-1} (wavenumber) scale in excel (or other plotting program). (A handy fact is that $500 \text{ nm} = 20,000 \text{ cm}^{-1}$.)

With the aid of Fig. 2., identify the wavenumber values* as accurately as possible for quantum numbers (1) $v' = 18-38$ from $v'' = 0$; (2) $v' = 19-26$ from $v'' = 1$, and (3) $v' = 11-19$ from $v'' = 2$.

* Note: the correct way to record the values is to record the “band head”. This is NOT the peak but may be *estimated as the minimum on the short wavelength side* of each peak.

Analysis (we will do only a subset of what is asked in the Shoemaker et al. Handout)

It is useful to make tables in Excel in which all values with the same v'' are listed. Likewise for v' in a few cases.

1. From the wavenumbers for each transition, obtain a good number for the wavenumber difference of $v'' = 1$ and $v'' = 0$ levels of the **ground electronic state**. This is possible because there are several lines in the spectrum that have the same v' and different v'' . Their average is expected to be fairly accurate measure of $\underline{v_e''}$.
2. Obtain a rough estimate for the difference of $v'' = 2$ and $v'' = 1$ levels of the ground electronic state from the few cases with $v'' = 2$, $v'' = 1$, and 0 that have a common v' .
3. Use the **alternative analysis** procedure to construct a Birge-Sponer plot as described on p. 499 of Handout#1 using Eq. 4, and determine v'_e , and x'_e .
4. By extrapolating to the v' axis crossing ($\Delta v' = 0$) estimate the dissociation energies D_e' and D_0' from Eqs. 5 and 6. These are defined below Eq. 5 and in Fig. 1.
5. Obtain $\underline{v_e''}$, and x''_e , from the two differences you have for the ground state.
6. From Eq. 3, use the observed transition wavenumbers for $v'' = 0$, $v' = 20, 25$ and 30 to calculate values for the “pure electronic” energy wavenumber, $\underline{v_{el}}$ (corresponding to the energy difference between the potential minima of the ground and excited states. (See Fig. 1)
7. Find D_e' another way: use $\underline{v_{el}}$ and a **visual** estimate of the transition wavenumber where the spacing between bands, $\Delta v'$, goes to zero (curve becomes smooth) in your experimental spectrum (near 500 nm).

Discussion

1. Compare your results for v'_e , x'_e , v''_e , x''_e , D_e' , and D_e'' , with a “literature” source(s), which may include web sites. Cite the source in your report.

Which of the two D_e' values you determined in this experiment do you think is most accurate and why?

2. Based on your results, comment on whether Fig. 1 is a reasonably accurate representation of the potential curves.

3. Your report should contain a descriptive discussion of why the excited state vibrational frequency, anharmonicity, and D_e values are so different from those of the ground state.

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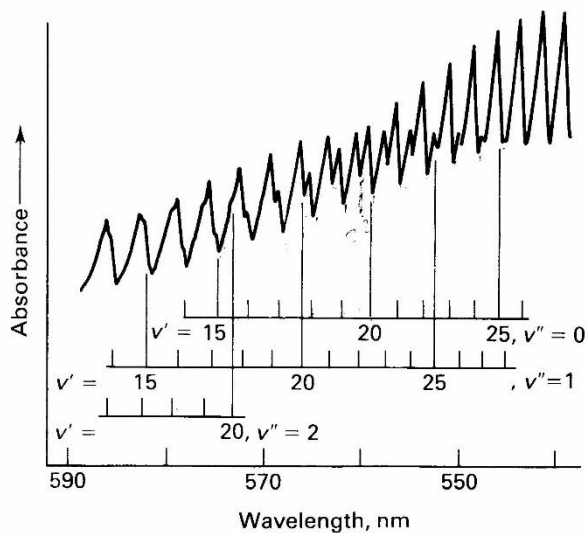


FIGURE 2

A portion of the medium-resolution spectrum of the visible $B \leftarrow X$ iodine absorption spectrum with assignments for the overlapping progressions for $v'' = 0, 1, 2$. The upper state v' values are indicated at the estimated band-head positions on the short wavelength side of each transition; the band maxima are at the top of the figure.