Experiment 6: **Vibronic Absorption Spectrum of Molecular Iodine**

We have already seen that molecules can rotate and bonds can vibrate with characteristic energies, each energy being associated with a particular quantum state. Atoms and molecules also can assume many different electronic energies, each of which is associated with a particular electronic quantum state. Each electronic state corresponds to a particular electron distribution (i.e.: an arrangement of the electron(s) in certain orbitals). The electron configuration with the lowest energy is called the **ground state**, all higher energy states are called **excited states**. The potential energy experienced by the electrons in a given state is described by a potential energy curve, and the energetics of the entire system is commonly depicted using a potential energy diagram. A potential energy diagram showing the first three electronic states of molecular iodine is shown in Figure 1.
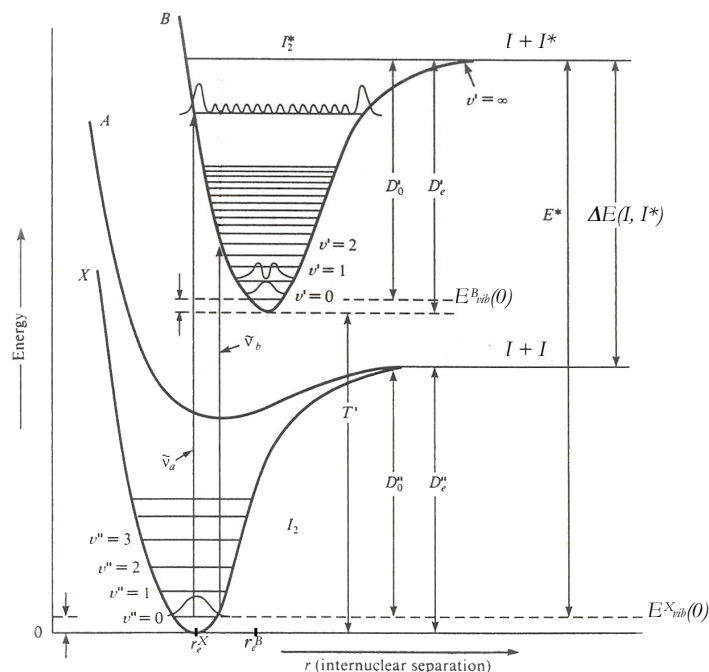

Figure 1: A potential energy diagram for I_2[1]. The curve X describes the ground electronic state, and the curves A and B describe excited electronic states. The horizontal lines within the curves indicate the vibrational energy levels within the particular electronic state.

Electronic energies can only be calculated exactly for atomic hydrogen - all other atoms and molecules require that some approximations be made in order to solve the Schrodinger wave equation (SWE). For molecules (which have several nuclei), one principle approximation is the **Born-Oppenheimer approximation**: since the electrons are much lighter than the nuclei, we assume that they can respond to nuclear motion instantaneously. This amounts to assuming that the motion of the nuclei and electrons are uncoupled. Therefore, we can choose a given arrangement of the nuclei in space (i.e.: a given internuclear distance, r, and thus a given potential energy), then solve the SWE to get the energy of the electrons at that r. This process is repeated for all possible

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[1] Adapted from Sime, R.J., *Physical Chemistry*, p. 661, Saunders College Publishing, Philadelphia (1990).

nuclear arrangements, resulting in a plot of electronic energy versus nuclear conformation (internuclear distance). The minimum of a potential energy curve occurs at the equilibrium bond length, and corresponds to the most stable nuclear conformation for that electronic configuration. In general, the equilibrium bond length is larger for excited electron configurations than for ground state electron configurations. Pictorially, this corresponds to a shift in the position of the excited state potential curve (or "well") to the right (larger internuclear distance) (see Figure 1, for example, where $r_e^X < r_e^B$).

One potential energy function that is often used to describe the potential energy experienced by the electrons in a molecule such as iodine in any "bound state"[2] is the anharmonic Morse potential:

$$U(r) = D_e \left[1 - e^{-a(r - r_e)} \right]^2 \tag{1}$$

where D_e is the well depth (i.e.: the energy from the bottom of the well to bond dissociation), and r_e is the equilibrium internuclear distance between the iodine atoms in a given bound state. The constant a is defined in terms of several fundamental molecular constants:

$$a = \overline{v}_e \left(\frac{\pi c \mu}{\hbar D_e} \right)^{1/2} \tag{2}$$

where $\overline{v}_e$ is the harmonic vibrational frequency (in cm^{-1}) of the molecule in the given electronic state, and μ is the reduced mass. The value of $\overline{v}_e$ is different in each electronic state since it depends on the stiffness of the bond, which is different in each electronic state (higher energy electronic states correspond to weaker bonds). Although the Morse potential is far more realistic than a Hooke's law (harmonic) potential, it is not the most accurate potential function available. However, the Schrodinger equation can be solved exactly with the Morse potential, which is a distinct advantage for routine calculations.

The vibrational energies, E_{vib}, that result from solution of the SWE using a Morse potential are:

$$E_{vib}(v) = \overline{v}_e \left(v + \frac{1}{2} \right) - \overline{v}_e x_e \left(v + \frac{1}{2} \right)^2 \tag{3}$$

where v is the vibrational quantum number, and the anharmonicity constant, x_e, is given by:

$$x_e = \frac{\hbar a^2}{4 \pi c \mu \overline{v}_e} = \frac{\overline{v}_e}{4 D_e} \tag{4}$$

(Notice that if we use the Morse potential, the expression for the vibrational energy is *not* an infinite series such as the expression that we used in Experiment 5.) The smallest amount of vibrational energy that the system can have is non-zero since the smallest value of v is 0, in which case:

$$E_{vib}(0) = \frac{1}{2} \overline{v}_e - \frac{1}{4} \overline{v}_e x_e \tag{5}$$

This "zero-point energy" is different for each electronic state. The total energy of any vibrational state, $E_{tot}(n,v)$, is given by the sum of electronic and vibrational energies[3]

$$E_{tot}(n,v) = T_n + \overline{\nu}_e\left(v + \frac{1}{2}\right) - \overline{\nu}_e x_e\left(v + \frac{1}{2}\right)^2 \tag{6}$$

where T_n is the energy of the nth electronic state, in cm^{-1}. In general, electronic energies are considered to be offsets from the ground state electronic energy, so that $T_1=0$. Many of these energies are shown in Figure 1 for I_2.

Electronic Transitions in Iodine

Molecular iodine is purple in color because it absorbs light in the visible (yellow) region of the electromagnetic spectrum. This absorption of light causes an electronic transition, i.e.: a transition between potential wells resulting in a change in *electron distribution* in the molecule (that is, electrons become distributed among orbitals in a different way). In general, transitions between potential wells are also accompanied by changes in vibrational energy. Such transitions are called **vibronic** transitions (vibrational and electronic).

The vibrational states in I_2 are much more closely spaced than in a molecule such as HCl. Therefore, for I_2 the first *several* vibrational states within the ground electronic state of iodine are low enough in energy to be populated even at room temperature. This means that transitions can occur from a *variety* of initial vibrational states rather than from only $v = 0$ (as for HCl). We will describe a particular vibronic transition as *(n'', v'') → (n', v')*, where double primes denote the lower energy state. Thus, absorption transitions for iodine at room temperature can be described in general as

$$\left(X, v''\right) \rightarrow \left(B, v'\right) \tag{7}$$

where X represents the ground state electronic energy well, and B represents the first accessible excited state well (these symbols come from group theory, which we will not explore). Transitions arising from vibrational levels within X where $v'' > 0$ are called "hot bands". In this experiment, we will focus on transitions only from $v''=0$, however you will need to keep in mind that hot bands can overlap or interfere with the $(X, 0) \rightarrow (B, v')$ absorptions.

The goal of this experiment is to extract values of as many molecular parameters as possible from the experimental vibronic spectrum of I_2. In order to do this, we must return to the Bohr condition:

$$E_{photon} = \Delta E_{matter} \tag{8}$$

where in this case, ΔE_{matter} corresponds to a difference in vibronic energies of I_2. As usual, this entails measuring the value(s) of E_{photon} and coming up with expressions for the values of ΔE_{matter}. For most molecules, $\Delta E_{vibronic}$ is on the order of 10^5 cm^{-1}, which is in the UV/visible region of the EM spectrum. In this region, absorption spectra are typically measured in units of wavelength. Recall

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[2] A bound state is a bonding state (versus an antibonding state), where there is a stabilization due to favorable orbital overlap. It corresponds to an electron configuration that results in a potential function that has a minimum energy, such as those in Figure 1.
[3] The contributions of translational and rotational energies to the total energy are so small relative to electronic contributions that they can be ignored for most vibronic spectra.

that E_{photon} is *inversely* proportional to λ, so wavelength measurements must be converted to some type of energy units in order to compare them to values of ΔE_{matter}.   We will work in units of wavenumbers.   Using the expression for E_{photon}:

$$E_{photon}(J) = \frac{hc}{\lambda} = hc\bar{\nu} \tag{9}$$

Dividing by hc, we find that:

$$E_{photon}(cm^{-1}) = \frac{1}{\lambda} = \bar{\nu} \tag{10}$$

To obtain expressions for ΔE_{matter}, we need the selection rules for vibronic transitions. Unlike the case of vibrational transitions *within* a single electronic state (i.e.: rovibrational spectroscopy), Δv is <u>not</u> limited to +1 for transitions *between* electronic states (vibronic spectroscopy). Rather, the selection rules for electronic transitions are based on conservation of angular momentum (which govern which electronic states can be accessed), and on the **Franck-Condon Principle** (which governs which vibrational states can be accessed).   The X $\rightarrow$ B transition is allowed according to the electronic selection rules. Thus, we must turn to the Franck-Condon principle to understand which vibronic transitions we can expect to see. This principle, also based on the fact that electrons are much lighter than nuclei, says the electron redistribution which results from an electronic transition occurs instantaneously with respect to nuclear motion. That is, the nuclei do not move *during* a transition, they only adjust *after* the absorption event is complete.   Since the internuclear distance does not change during the absorption of a photon, the transition is drawn with a vertical line on the potential energy diagram: we say that electronic transitions must be **vertical** (see for example transitions $\bar{\nu}_a$ and $\bar{\nu}_b$ in Figure 1.) Furthermore, transitions of the highest intensities occur when the **overlap** between the ground and excited state wavefunctions is largest. This means that the most intense transitions originate from the center of the $v''=0$ level (i.e.: the *equilibrium* internuclear distance).

There are two main consequences of the Franck-Condon principle for the vibronic absorption spectrum of I_2:

(1)   Because the potential wells for iodine are substantially offset along the x-axis, transitions to low-lying vibrational states, (X, 0) $\rightarrow$ (B, small v'), are <u>not</u> observed (that is, vertical transitions are not possible to small v').

(2)   For iodine, observable vertical transitions terminate at vibrational levels in the region of v'=26-50. Transitions to very large v' are not observed because the overlap between ground and excited state wavefunctions is too poor (see Figure 1).

Therefore, the Franck-Condon selection rules predict that the absorption spectrum for iodine at room temperature will primarily consists of transitions such as

$$\boxed{\left(X,0\right) \rightarrow \left(B, v' = 20, ..., 50\right)} \tag{11}$$

We expect to see also some contributions from hot bands.

The energy of the absorbed photons is given by the difference in energies between initial and final states:

$$\Delta E_{tot}(v') = E'_{tot,B}(v') - E''_{tot,X}(0) \qquad (12)$$

By convention, from this point forward we will denote the electronic state of interest using only a ' or " on E_{tot} rather than by specifying the electronic state (X or B). Using equation (6), we can therefore express ΔE_{tot} in terms of molecular constants,

$$\Delta E_{tot}(v') = T' + \overline{v}'_e\left(v' + \frac{1}{2}\right) - \overline{v}'_e x'_e\left(v' + \frac{1}{2}\right)^2 - \overline{v}''_e\left(\frac{1}{2}\right) + \overline{v}''_e x''_e\left(\frac{1}{4}\right) \qquad (13)$$

Characterization of the Excited State Well

The absorption spectrum of iodine yields information about the *excited state* (B) well rather than the ground state (X) well (notice that equation (13) depends primarily on excited state parameters). In this experiment you will characterize the excited state well by extracting values for the following excited state parameters:

- $\overline{v}'_e$ (the harmonic vibrational frequency)
- x_e' (the anharmonicity correction factor)
- D'_o (the dissociation energy)
- D'_e (the well depth)
- v_c' (the vibrational quantum number at the continuum limit)

Recall that as v' increases, the vibrational energy spacing decreases. At the upper edge of the well ($v' = v_c$'), the vibrational energy spacing decreases to 0, which means that the energies form a continuum rather than being quantized. It is at this limit that bond dissociation occurs. The energy required to dissociate the bond is actually D_o' rather than D_e' because the molecule cannot have less than the zero point energy.

As stated earlier, we can extract values for molecular parameters from a spectrum by comparing the measured energies of various spectral lines to the theoretical energies based on the solutions to the SWE (i.e.: those from equation (13)).

$$E_{photon} = \Delta E_{tot}(v') \qquad (8)$$

However, this expression creates a problem in that we don't know the value of T'. Since all of the transitions of interest originate from the <u>same</u> initial ground state, we can eliminate T' from the expression by taking the *difference* between adjacent transition energies.

$$\Delta E_{photon} = \Delta\left(\Delta E_{tot}(v')\right)$$
$$= \Delta E_{tot}(v'+1) - \Delta E_{tot}(v') \qquad (14)$$

Combining equations (13) and (14),

$$\Delta E_{photon} = \overline{v}'_e - 2\overline{v}'_e x_e(v'+1) = \Delta E_{vib} \qquad (15)$$

Since this also eliminates any ground electronic state terms, we find that the difference between adjacent transition energies is equal to the spacing between adjacent excited state vibrational energies.

Equation (15) is actually the equation for the vibrational band origin energy of the excited electronic state, with $\Delta v=1$. Recall that the band origin energy corresponds to the energy of a pure vibrational transition (no change in rotational quantum number)[4]. According to equation (15), values for $\overline{v}'_e$ and x_e' can be obtained from a plot of ΔE_{photon} versus $v'+1$. This type of plot is called a Birge-Sponer Plot, and is shown in Figure 2.[5]
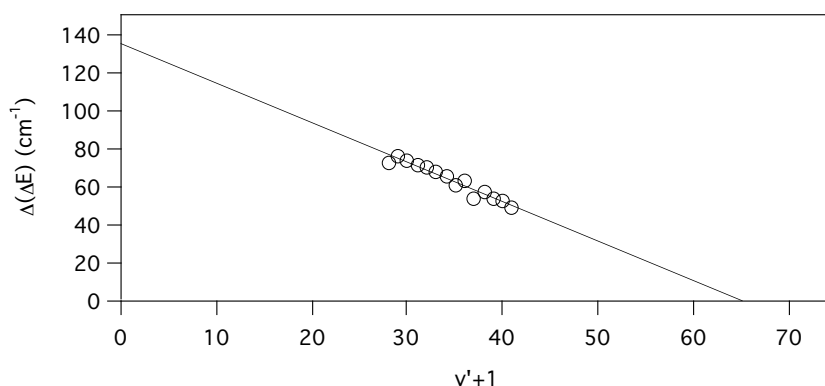

Figure 2: Sample Birge-Sponer plot for I_2.

The other excited state parameters of interest can be also obtained from the Birge-Sponer plot. The continuum limit $(v' = v_c')$ occurs when the energy gap between excited state vibrational levels is zero, i.e.: when $\Delta E_{vib}(v') = \Delta(\Delta E_{tot}(v')) = 0$. Therefore, the continuum limit vibrational quantum number (v_c') is found from extrapolation of the Birge-Sponer plot to the x-intercept. The bond dissociation energy, D_o', can be obtained from two theoretically equal methods. The first is graphical. If we view D_o' as the sum of all of the energy gaps in the potential well starting from $v' =0$, then

$$D_o' = \sum_{v'=0}^{v_c'} \Delta E_{vib}(v')$$
$$= \int_0^\infty \Delta E_{vib}(v')dv' \qquad (16)$$
$$= area\ under\ BS\ curve$$

The sum can be replaced by an integral because the energy gaps are very small. Since the energy gaps beyond v_c' are zero, the upper limit of the integral can be treated as infinity. The value of the integral in equation (16) is by definition equal to the area under the Birge-Sponer curve. This area can be calculated using the equation for a triangle and the previously determined values for $\overline{v}'_e$, x_e' and v_c'.

The second method for obtaining D_o' involves viewing the dissociation energy as a transition energy: $D_o'= E_{tot}'(v_c') - E_{tot}'(0)$ (see Figure 1). It then follows from equation (6) that

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[4] As we have seen, a *diatomic* molecule cannot undergo a pure vibrational transition – it must also experience a change in rotational quantum number. We do not consider the rotational energy here because it is such a small correction to the total energy.

[5] If second-order corrections to the anharmonicity are significant (i.e.: a Morse potential is not an adequate representation of the potential), then the Birge-Sponer plot curves downward at high values of v'.

$$D'_o = \overline{v}'_e v'_c \left(1 - x'_e \left(v'_c + 1\right)\right) \qquad (17)$$

Finally, since the excited state well depth, D_e', is larger than D_o' only by the zero-point energy,

$$D'_e = D'_o + \frac{1}{2}\overline{v}'_e - \frac{1}{4}\overline{v}'_e x'_e \qquad (18)$$

Ground State Dissociation Energies

Much of the following discussion is facilitated by referring to the potential energy diagram in Figure 1.

While the vibronic spectrum reveals information primarily on the excited state well, we can extract the values of a few ground state well parameters (D_o" and D_e") provided that we know several additional pieces of information. The characteristic vibrational frequency and anharmonicity constant of I_2 in the ground state is available from the data in Appendix C[6]. We also need the energy required to excite a single iodine atom, $\Delta E(I^*, I)$, which has been experimentally determined from atomic absorption spectroscopy[7] to be

$$\Delta E\left(I^*, I\right) = 7603.15 \; cm^{-1}$$

This energy corresponds to the energy gap between the dissociation limits of the X and B wells (see Figure 1).

The energy required to dissociate a *ground state* iodine molecule, (X,0), into an *excited* iodine atom and an unexcited iodine atom, (B, v_c'), is given the energy denoted E* in Figure 1.

$$E^* \Leftrightarrow (X, v'' = 0) \rightarrow (B, v' = v'_c) \qquad (19)$$

Therefore, we can view E* as the sum of the energy required to dissociate a ground state iodine molecule (($X,0)\rightarrow(X, v_c')$), and the energy required to excite an iodine atom, $\Delta E(I^*, I) = ((X, v_c')\rightarrow(B, v_c'))$. Therefore, the ground state dissociation energy, D_o", is equal to the difference between E* and the excitation energy of atomic iodine,

$$D''_o = E^* - \Delta E\left(I^*, I\right) \qquad (20)$$

Since $\Delta E(I^*, I)$ is known, determination of the bond dissociation energy requires only the determination of E*. The energy E* can be thought of as the energy required to undergo a transition from v"=0 to $v'=v_c$' (equation (19)). While we cannot measure this energy directly using conventional spectroscopy (the intensity is too small), we can use any observable vibronic transition to determine E*. According to equation (19),

$$E^* = E'_{tot}(v'_c) - E''_{tot}(0) \qquad (21)$$

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[6] Huber, K. P. and Herzberg, G., *Molecular Spectra and Molecular Structure IV: Constants of Diatomic Molecules*, p.332, Van Nostrand Reinhold, New York (1979). (See Appendix C)

[7] Moore, C. E., *Atomic Energy Levels, vol. III*, Circular of the National Bureau of Standards, US Government Printing Office, Washington, DC (1958).

Suppose we choose to use the transition from v''=0 to v'=27 as our observable transition. Equation (21) can then be re-written in terms of this measurable absorption energy as:

$$E^* = \left(E'(v'_e) - E'(27)\right) + \left(E'(27) - E''(0)\right) \tag{22}$$

where the first term in this expression can be expanded using equation (6) to yield an expression in terms of the known excited state constants $\overline{v}'_e$, x_e' and v_c', and the second term is the transition energy that can be obtained directly from the experimental absorption spectrum. Thus, E* can be calculated from equation (22), and D_o'' can be calculated from equation (20) and the given value of $\Delta E(I^*, I)$. The ground state well depth, D_e'', can then be calculated from D_o''.

The Look of the Spectrum: the Rotational Envelope

The rotational levels for iodine are so closely spaced that individual R and P branch transitions cannot be resolved at room temperature, even in the gas phase. Instead, we see a "rotational envelope". The shape of the rotational envelope is governed by the values of several molecular constants, which ultimately dictate whether either (if any) branch reaches a maximum energy (a band head) and folds back on itself. For iodine, the R branch reaches a band head at R(3), which is very near the band origin (see Figure 3).
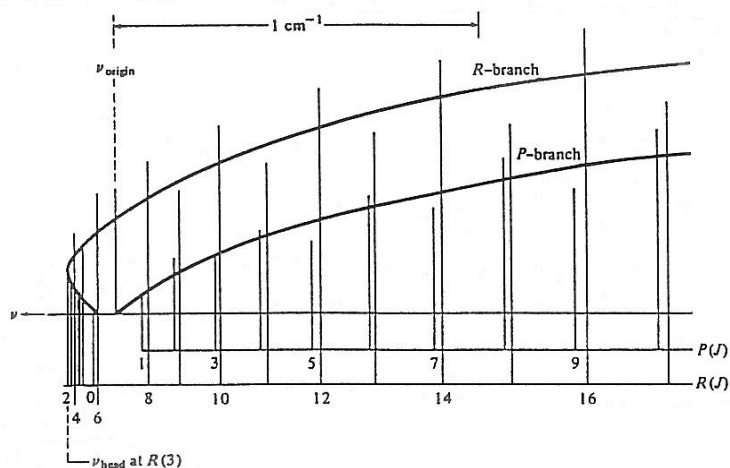
Figure 3: Band head formation in the hypothetical v''=0→v'=0 band of an I_2 X→B transition.[8] The x-axis of this diagram is transition wavelength, and the vertical lines represent the positions of the indicated R(J) or P(J) transition. The band head (R(3)) occurs at a slightly smaller transition wavelength (higher energy) than the band origin.

Note that the R(3) transition in this case is not a *rovib* transition, but a *rovibronic* transition, corresponding to a change in quantum numbers of:

(X, v''=0, J''=3) → (B, v'=0, J'=4)

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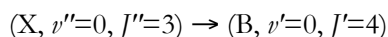
8 Steinfeld, J. I., *Molecules and Radiation*, 2nd Ed., MIT Press, Cambridge (1993).

Because the band head and band origin are so close in energy, the observed envelope looks rather like a triangle, with the high-energy (low wavelength) corner of the base being the band head (i.e.: R(3)). Since we are not interested in rotations, we would prefer to use band origin energies as our transition energies. However, it will suffice to approximate the band origin energy as the band head energy (high energy corner of the triangle), which is easier to obtain from the spectrum. A typical absorption spectrum is shown in Figure 4. Note the appearance of the first hot band at higher wavelengths ("to the red", or lower energy). You should avoid using transitions that are obscured by the hot band for your workup.
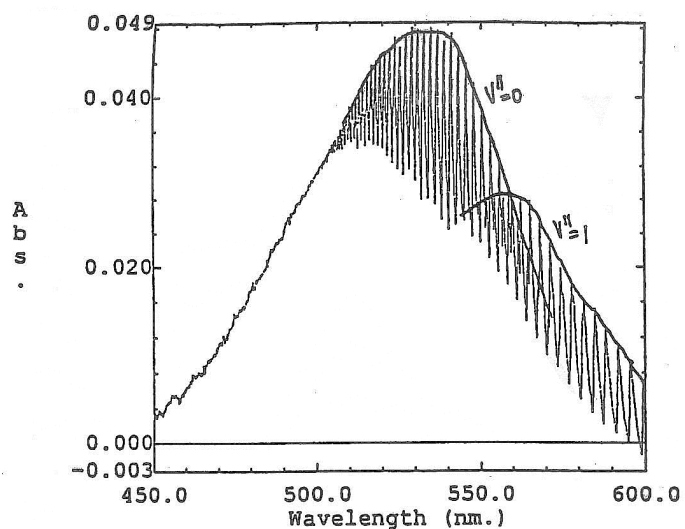

Table 1: Vibrational Quantum Numbers for selected I_2 Transitions

v'	λ (nm)
27	541
28	538
29	536

Figure 4: Vibronic absorption spectrum of I_2 vapor at ~45°C.

⇨ *Do the following in your notebook before you come to lab:*

- Derive the general expression for $\Delta E(v')$ in your notebook by first using the general case of v' and v'' as the excited and ground state quantum numbers. Once you have that expression, substitute $v''=0$ to obtain equation (13). Use the definition of the ground state electronic energy, $T_1=T''=0$.

- Derive equation (15) from equations (13) and (14).

- Derive equation (17).

- Expand the first term in equation (22) using equation (6) to yield an expression in terms of the known excited state constants $\overline{v}'_e$, x_e' and v_c'. Using ΔE_{obs} to represent the observed transition energy E'(27)-E''(0), rewrite equation (22) in terms of known values.