Vibrational-Rotational Spectrum of HCl

Introduction

In this experiment, we will measure the infrared (IR) vibrational-rotational spectrum of gas phase hydrogen chloride (HCl) molecules. The infrared region of the spectrum extends from 700 nm (the long-wavelength end of the visible region) to 1000 µm (the beginning of the microwave region). In terms of wavenumbers, the infrared region is located between 10-14000 cm⁻¹. The instrument used in this experiment, an FTIR spectrometer, can obtain IR spectra in the range 400-4000 cm⁻¹, the region where most vibrational transitions in molecules are observed.

While polyatomic molecules have many vibrations and therefore have infrared spectra that are often difficult to analyze, the absorption spectrum of a diatomic molecule such as HCl has a relatively simple appearance. Transitions are generally observed only between the two lowest energy vibrational states (ν'=1 ← ν''=0, where we use the usual convention of labeling the quantum numbers for the higher energy state with a single prime and the quantum numbers for the lower energy state with a double prime). In the present experiment the measurements have sufficient resolution to pick out transitions between individual rotational levels between the two vibrational states, and to even distinguish between peaks from ¹H³⁵Cl and ¹H³⁷Cl. Because of this, we can analyze the spectrum to obtain high precision values for the rotational and vibrational constants for both isotopic forms of hydrogen chloride.

Theory [1]

To a first approximation the vibrational and rotational energy for a diatomic molecule can be treated independently, so that

$$E_{\text{total}} = E_{\text{vib}} + E_{\text{rot}}$$

where $E_{\text{vib}}$ is the vibrational energy and $E_{\text{rot}}$ is the rotational energy. The $\sim$ symbol above the symbol $E$ ($\tilde{E}$) is used to indicate when energy is given in units of wavenumbers (cm⁻¹). Recall that the energy of a photon of light is

$$E(J) = h\nu = \frac{hc}{\lambda} = \tilde{E}(\text{cm}^{-1})$$

where $\nu$ and $\lambda$ are the frequency and wavelength for light, $c$ is the speed of light, and $h$ is Planck’s constant. Therefore, the conversion factor between energy in Joules and energy in cm⁻¹ is

$$E(J) = hc \tilde{E}(\text{cm}^{-1}) = (1.9864 \times 10^{-23} \text{ J/cm}^{-1}) \tilde{E}(\text{cm}^{-1})$$

Wavenumbers is a convenient unit for spectroscopy, since transitions in the infrared, visible, and near UV region of the spectrum fall between 10-50000 cm⁻¹ (or between $2 \times 10^{-22}$ J/molecule and $1 \times 10^{-18}$ J/molecule)

To a first approximation the rotational and vibrational energy levels for a diatomic molecule can be found using the Rigid Rotor (RR) model for rotation and the Harmonic Oscillator (HO) model for vibration. Solving the appropriate Schrodinger equations for these models gives the following results for allowed values for energy:

**Rotation (RR model)**

$$E_{\text{rot}} = J(J+1)B_e$$

where the rotational constant, $B_e$, is given by the expression

$$B_e \text{ (in cm}^{-1}\text{)} = \frac{h}{8\pi^2 c \mu_e r_e^2}$$

where the reduced mass for a diatomic molecule AB is
\[ \mu_{AB} = \mu = \frac{m_A m_B}{m_A + m_B} \] (6)

and where \( r_e \) is the equilibrium bond distance for the molecule. \( J \), the rotational quantum number, can take on any non-negative value, and so \( J = 0, 1, 2, \ldots \). There is a second quantum number, \( M_J \), whose allowed values are \( M_J = 0, \pm 1, \pm 2, \ldots, \pm J \). The rotational energy for a diatomic molecule does not depend on the value for \( M_J \), but \( M_J \) is indirectly responsible for the observed variations in the intensity of peaks appearing in the infrared spectrum. This is because for a particular value of \( J \), there will be \( 2J + 1 \) possible values for \( M_J \) (technically, we say that the degeneracy of the rotational energy levels is \( g_J = 2J + 1 \)). Note that the quantum numbers \( J \) and \( M_J \) for rotation are similar to the quantum numbers \( \ell \) and \( m_\ell \), the orbital quantum numbers for the electron in a hydrogen atom, and \( s \) and \( m_s \), the quantum numbers for electron spin. This is not a coincidence, but is due to each of these sets of quantum numbers being associated with an angular momentum.

**Vibration (HO model)**

\[ \tilde{E}_{\text{vib}} = (v + \frac{1}{2}) \omega_v \quad v = 0, 1, 2, \ldots \] (7)

where the vibrational constant, \( \omega_v \), is given by the expression

\[ \omega_v \text{ (in cm}^{-1}\text{)} = \left(\frac{1}{2\pi c}\right) \left(\frac{k}{\mu}\right)^{1/2} \] (8)

where \( k \) is the force constant for the molecule (MKS units N/m).

From the equations for the rotational constant (\( B_e \)) and vibrational constant (\( \omega_v \)) it is clear that spectroscopic measurements on diatomic molecules can provide useful information about the molecules. In particular, the equilibrium bond distance (\( r_e \)) for a diatomic molecule can be found from the value for \( B_e \), while the force constant for the bond (a measure of the strength of the bond) can be found from the value for \( \omega_v \).

In the RRHO (rigid rotor+harmonic oscillator) model of a diatomic molecule, the sum of the rotational and vibrational energy is given in terms of two quantum numbers, \( v \) and \( J \). By combining eq 4 and eq 7, we get

\[ \tilde{E}_{\text{total}}(v,J) = (v + \frac{1}{2}) \omega_v + J (J + 1) B_e \] (9)

For diatomic molecules it is usually the case that \( \omega_v \gg B_e \). The pattern of energy levels commonly observed for diatomic molecules is given in Figure 1.

**Selection rules**

Based on the above discussion we would expect molecules could absorb light at any wavelength with an energy equal to the difference in energy between two vibrational-rotational energy levels. This is in fact not what is observed. Instead, only a few of the transitions satisfying conservation of energy are actually seen. This is because there are restrictions, called selection rules, that govern the possible changes that can occur for the vibrational and rotational quantum numbers when a molecule absorbs (or emits) light.

For a heteronuclear diatomic molecule such as HCl, the selection rules most commonly seen are

for \( v \): \( \Delta v = \pm 1 \) \hspace{1cm} (10)

for \( J \): \( \Delta J = \pm 1 \) \hspace{1cm} (11)

Since we are interested in light absorption in this experiment, and since the spacing between adjacent vibrational energy levels is much larger than that for adjacent rotational energy levels, the only vibrational transitions observed for HCl are those with \( \Delta v = +1 \). But since at room temperature and at equilibrium over 99.9% of the HCl molecules
are in their ground (lowest energy) vibrational state, the only vibrational transition observed in the infrared spectrum of HCl is $v'=1 \leftarrow v''=0$.

Figure 1. Diagram indicating the energy levels for a diatomic molecule (RRHO model). Rotational states with $v = 0$ are in blue, while rotational states with $v = 1$ are in red. The gap in the energy scale is to indicate that the separation between the $v = 0$ and $v = 1$ rotational energy levels is much larger than that given in the figure. The allowed P-branch and R-branch are also indicated.

Because $\hat{E}_{\text{vib}} \gg \hat{E}_{\text{rot}}$, when a molecule moves from $v''=0$ to $v'=1$, the rotational quantum number $J$ can either increase by 1 or decrease by 1. This gives rise to two families of transitions:

$\Delta v = 1, \Delta J = -1$ P-branch transitions \hfill(12)

$\Delta v = 1, \Delta J = +1$ R-branch transitions \hfill(13)

These two sets of transitions are shown in Figure 1.

Equation 9 can be used to predict the energies at which the P-branch and R-branch transitions take place. The general formula for the difference in energy ($\Delta \hat{E}$) between the initial and final state of a diatomic molecule in the RRHO model is

$$\Delta \hat{E} = \hat{E}(v',J') - \hat{E}(v'',J'')$$ \hfill (14)
For allowed transitions, and recalling that almost all of the HCl molecules are in the $v''=0$ state, we may say

$$v''=0 \quad v'=1 \quad J' = J'' - 1 \quad \text{P-branch transition} \quad (15)$$

$$J' = J'' + 1 \quad \text{R-branch transition} \quad (16)$$

Substitution of eq 9 for the total (vibrational + rotational) energy into eq 14, and making use of the restrictions for allowed transitions from the selection rules (eq 15 and 16) one can derive, after a bit of algebra, the energies at which P-branch and R-branch transitions will occur.

- **P-branch**
  $$\hat{E}_P(J'') = \omega_b - 2J'' B_e$$  
  (17)

- **R-branch**
  $$\hat{E}_R(J'') = \omega_b + 2(J'' + 1) B_e$$  
  (18)

Note that the P-branch and R-branch transitions are labeled by the rotational quantum number for the initial rotational state, $J''$. So, for example, $P(2)$ is the transition $v'=1, J'=1 \leftrightarrow v''=0, J''=2$, while $R(4)$ is the transition $v'=1, J'=5 \leftrightarrow v''=0, J''=4$. The P-branch transitions will be $P(1), P(2), P(3), \ldots$, while the R-branch transitions will be $R(0), R(1), R(2), \ldots$ There is no $P(0)$ transition, since this would require $J'=-1$, which is not a possible value for the rotational quantum number.

The above model makes the following predictions for the appearance of the infrared spectrum of HCl:

1) There should be a series of P-branch transition of decreasing energy. The separation between adjacent peaks in the P-branch transitions should be equal to $2B_e$.

2) There should be a series of R-branch transitions of increasing energy. The separation between adjacent peaks in the R-branch transitions should be equal to $2B_e$.

3) There will be a central gap in the spectrum between the highest energy P-branch transition, $P(1)$ and the lowest energy R-branch transition, $R(0)$, equal to $4B_e$.

Examination of the infrared spectrum of HCl given in Figure 2 shows that the above predictions are qualitatively correct. However, it is clear from the figure that the spacing between adjacent peaks in the spectrum is not constant. In addition, it can be seen that each peak is actually a pair of two closely spaced peaks.

There are several reason for the differences between the observed and predicted spectra:

1) A real molecule is not a harmonic oscillator. Instead, the location of the vibrational energy levels is lower than that predicted by the HO model, with the differences between the real molecule and the HO prediction becoming larger as the quantum number $v$ increases.

2) A real molecule is not a rigid rotor. Instead, the location of the rotational energy levels is lower than that predicted by the RR model, with the differences between the real molecule and the RR predictions becoming larger as the quantum number $J$ increases.

3) The value for the rotational constant $B$ is different for molecules with different values for the vibrational quantum number $v$. This is a violation of the assumption that we can cleanly separate the total energy of the molecule into a vibrational and a rotational term, and represents a form of interaction between rotation and vibration in the molecule.

4) Because the values for the rotational constant $B_e$ and the vibrational constant $\omega_b$ depend on the reduced mass of the molecule, the values for $B_e$ and $\omega_b$ will be slightly different for the molecules $^{1}\text{H}^{35}\text{Cl}$ and $^{1}\text{H}^{37}\text{Cl}$. This results in two closely spaced peaks appearing for each allowed transition. Since natural abundance chlorine is $\sim 75\%$...
\(^{35}\text{Cl}\) and \(\sim 25\% \ {^{37}\text{Cl}}\), the more intense peak (at higher energy) is for \(^{1}\text{H}^{35}\text{Cl}\), and the less intense peak (at lower energy) is for \(^{1}\text{H}^{37}\text{Cl}\).

Various methods have been developed to account for the differences between real diatomic molecules and the RRHO model. The most common method to account for these differences (a method not, however, usually used by spectroscopists who do high resolution laser spectroscopy on diatomic molecules [2]) is the following:

\[
\hat{E}_{\text{vib}} = (v + \frac{1}{2}) \alpha_e - (v + \frac{1}{2})^2 \alpha_e \chi_e
\]  

(19)

\[
\hat{E}_{\text{tot}} = J (J + 1) B_v - J^2 (J + 1)^2 D_e
\]  

(20)

\[
B_v = B_e - (v + \frac{1}{2}) \alpha_e
\]  

(21)

where \(\alpha_e \chi_e\) is a constant [3] that corrects for flaws in the harmonic oscillator model for the molecule and \(D_e\) is a constant that corrects for flaws in the rigid rotor model for the molecule. To account for differences in the value for the rotational constant for different vibrational states of the molecule, \(B_e\) in the equation for rotational energy (eq 20) is replaced by \(B_v\). \(B_0\) is the value for the rotational constant for molecules in the \(v = 0\) state, \(B_1\) is the value for molecules in the \(v = 1\) state, and so forth. Equation 21 is used to find the value for \(B_v\) for molecules in different vibrational states. Equations 19 and 20 are power series expansions for the vibrational and rotational energy of a molecule, in powers of \((v + \frac{1}{2})\) for the vibrational energy and in powers of \(J (J + 1)\) for the rotational energy. This is similar to what is done when the equation of state for a real gas is written as a virial equation in powers of \(p\) or \(1/V\).

If we follow the same method previously used to find values for the locations of the P-branch and R-branch transitions, but use eq 19 and 20 for the vibrational and rotational energy instead of eq 5 and 7, we get (after a considerable amount of straightforward but tedious algebra) the following modified values for the energies at which the P-branch and R-branch transitions occur:
\begin{align}
\text{P-branch} & \quad \hat{E}_p(J'') = \omega_0 - 2 (B_e - \alpha_e) J'' - \alpha_e J''^2 + 4D_e J''^3 \quad (22) \\
\text{R-branch} & \quad \hat{E}_r(J'') = \omega_0 + 2 (B_e - \alpha_e) (J'' + 1) - \alpha_e (J'' + 1)^2 - 4D_e (J'' + 1)^3 \quad (23)
\end{align}

where \( \omega_0 = \omega_e - 2 \alpha_e x_e \). By introducing a new variable \( m \), defined as

\[
m = -J'' \quad \text{(for P-branch transitions)} \quad (24)
\]

\[
m = J'' + 1 \quad \text{(for R-branch transitions)} \quad (25)
\]

eq 22 and 23 can be combined into a single expression for the energy at which transitions take place in HCl.

\[
\hat{E}(m) = \omega_0 + (2B_e - 2\alpha_e) m - \alpha_e m^2 - 4 D_e m^3 \quad (26)
\]

**IT IS THIS EQUATION (EQ 26) THAT SHOULD BE USED TO ANALYZE THE DATA FOR THE HCl SPECTRUM.**

**Experimental**

The infrared gas cell is constructed from a short length of a large diameter glass tube with NaCl salt windows, which are transparent to infrared light with \( \hat{E} > 600. \text{cm}^{-1} \). A vacuum tight seal is made by carefully compressing the windows against the O-rings at either end of the cell. Note that the windows are fragile, and are susceptible to moisture, and so the faces of the windows should never be touched. When not in use, the gas cell should be kept in a desiccator to protect the windows.

The gas cell is first evacuated with a vacuum pump, and a background spectrum is run on the FTIR spectrometer with the cell empty. A gas handling system similar to the one in the lab is shown in Figure 3. Initially stopcocks A, B, and C should all be closed. The gas cell is attached to the gas handling system at D. Stopcock C is opened. To pump out air from the gas cell, open stopcock A to the vacuum pump. After the cell has been evacuated, stopcocks A, B, and C are closed, and the gas cell removed from the gas handling system.

After running a background spectrum, the gas cell is reconnected to the gas handling system. After pumping out the gas cell, stopcock A is closed, and stopcock B is slowly opened to fill the gas cell with approximately 100 torr of HCl [4]. A mercury manometer attached to the gas handling system can be used to monitor pressure. After the gas cell has been filled with HCl, stopcocks A, B, and C are closed. The gas cell can now be removed from the gas handling system, and the sample spectrum run on the FTIR spectrometer.
After running the sample spectrum, the gas cell should again be attached to the gas handling system. The HCl should be pumped out of the gas cell. After closing stopcocks A, B, and C, the gas cell can be removed and stored in a desiccator.

Details on how to run the background and sample spectra are given in the instrument manual. Usually the spectra will be run by your instructor or an instrument technician. The spectrum should be run over the region 2500-3200 cm\(^{-1}\) at the highest resolution setting. The peak pick option can be used to find the location of P-branch and R-branch transitions. Note spectra are usually given in terms of %T (percent transmission) rather than absorbance. Since it is the location of the peaks that is important, use of %T is the preferred method to display the data.

**Calculations and Lab Report**

A sample HCl spectrum is given in Figure 2, indicating the P-branch and R-branch transitions and giving an assignment for the first few peaks in each branch. You can use this as a guide for carrying out your own assignment of the HCl spectrum.

1) Create two tables of peak assignments for the observed transitions, one for transitions in \(^1\)H\(^{35}\)Cl and the other for transitions in \(^1\)H\(^{37}\)Cl. Relative to the central gap in the spectrum, the P-branch transitions will occur at lower energies (in order P(1), P(2), P(3), …), while the R-branch transitions will occur at higher energies (in order R(0), R(1), R(2), …). Figure 2 can be used as a guide for assigning the P-branch and R-branch transitions. Only assign transitions that you are sure are from the HCl spectrum. Note that for each pair of peaks, the higher intensity and higher energy peak is from \(^1\)H\(^{35}\)Cl, while the lower intensity and lower energy peak is from \(^1\)H\(^{37}\)Cl.

2) Using eq 24 and 25 and your peak assignments, give the value for \(m\) for each peak in the spectrum.

3) Fit your data to a third order polynomial. This can be done on EXCEL. Also use EXCEL to plot the data (plot \(\tilde{E}(m)\) vs \(m\)). The fitting should be done separately for the \(^1\)H\(^{35}\)Cl and \(^1\)H\(^{37}\)Cl data.

4) By comparing the values for the constants in the polynomial fit eq 26, you can find the experimental values for \(\omega_0\), \(B_e\), \(\alpha_e\), and \(D_e\). You should have two sets of constants – one set for the \(^1\)H\(^{35}\)Cl data and one set for the \(^1\)H\(^{37}\)Cl data.

5) Compare your experimental values for \(\omega_0\), \(B_e\), \(\alpha_e\), and \(D_e\) to the values given at the NIST website for the ground (X) electronic state of \(^1\)H\(^{35}\)Cl. Comment on the level of agreement (or disagreement) between your values and the NIST values. Note that you will have to use the information on the NIST website and the definition for \(\omega_0\) following eq 23 to find the literature value for \(\omega_0\). The NIST website is located at

https://webbook.nist.gov/chemistry/name-ser/

6) Literature values for the constants \(\omega_0\), \(B_e\), \(\alpha_e\), and \(D_e\) for \(^1\)H\(^{37}\)Cl are not given at the NIST website. However, based on eq 5 and 8 for the rotational and vibrational constants for a diatomic molecule, the following relationships should hold for these constants

\[
(\omega_0^*/\omega_0) = (\mu/\mu^*)^{1/2}
\]

and

\[
(B_e^*/B_e) = (\mu/\mu^*)
\]

where the * is used to indicate the \(^1\)H\(^{37}\)Cl isotope. Note that the relationship in eq 27 is really for \(\omega_0\), and not \(\omega_0\), but the difference between these is small, and so eq 27 is still expected to apply. In finding the reduced mass for \(^1\)H\(^{35}\)Cl and \(^1\)H\(^{37}\)Cl the following values for atomic mass can be used [5]

\[
m(^1\text{H}) = 1.007825 \text{ amu} \quad m(^{35}\text{Cl}) = 34.968853 \text{ amu} \quad m(^{37}\text{Cl}) = 36.965903 \text{ amu}
\]
7) Your report should contain a discussion of the degree of agreement between the constants you find for \(^1\)H\(^{35}\)Cl and those given at the NIST website, and how well the values for \(\omega_0\) and \(B_e\) predicted for \(^1\)H\(^{37}\)Cl compare to those found experimentally. You do not need to give confidence limits for your experimental values for \(\omega_0\), \(B_e\), \(\alpha_e\), and \(D_e\).

References

1. Discussions of the rigid rotor model for rotation in a diatomic molecule and the harmonic oscillator model for vibration in a diatomic molecule are given in P. W. Atkins, J. de Paula Physical Chemistry, Tenth Edition, (Freeman, New York, 2014). This reference also contains a good general discussion the selection rules for vibrational-rotational transitions.

2. For high resolution spectroscopy of diatomic molecules an alternative method for fitting spectral data, first given by Dunham, is generally used (Dunham, J. L. (1932). The energy levels of a rotating vibrator. Phys. Rev. 41, 721-731.) The constants found by Dunham’s method can be related to the constants in eq 19, 20, and 21.

3. \(\omega_0x_e\) is now generally treated as a single constant.

4. Using high pressures of HCl makes it easier to find the positions of weaker peaks of the spectrum, but distorts the shape of the most intense peaks and so leads to errors in their location. Using low pressures of HCl reduces the number of peaks observed in the spectrum.

5. A convenient source for high precision mass values for isotopes is at the NIST website

https://physics.nist.gov/cgi-bin/Compositions/stand_alone.pl

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The absorption spectrum of iodine vapor

Introduction

To a good first approximation the total energy of a molecule \( \text{E}_{\text{total}} \) is given by the expression

\[
\text{E}_{\text{total}} = \text{E}_{\text{trans}} + \text{E}_{\text{rot}} + \text{E}_{\text{vib}} + \text{E}_{\text{elec}} \tag{1}
\]

where \( \text{E}_{\text{trans}} \), \( \text{E}_{\text{rot}} \), \( \text{E}_{\text{vib}} \), and \( \text{E}_{\text{elec}} \) 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 \( \text{E}_{\text{trans}} < \text{E}_{\text{rot}} < \text{E}_{\text{vib}} < \text{E}_{\text{elec}} \). 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 \( \text{I}_2 \) 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

\[
\begin{align*}
\text{E}''(v'') &= \omega_e''(v''+\frac{1}{2}) - \omega_xe''(v''+\frac{1}{2})^2 \quad \text{(ground state)} \tag{2} \\
\text{E}'(v') &= T_e' + \omega_e'(v'+\frac{1}{2}) - \omega_xe'(v'+\frac{1}{2})^2 \quad \text{(excited state)} \tag{3}
\end{align*}
\]

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. \( \omega_e \) and \( \omega_xe \) 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 \( v' \leftrightarrow v'' \), with the quantum number for the higher energy state appearing first. The direction of the arrow indicates whether the transition is light absorption (\( \leftrightarrow \)) or light emission (\( \rightarrow \)). Starting with eqs 2 and 3, the following equation can be found for the energy at which \( v' \leftrightarrow v'' \) transitions will occur

\[
\Delta E = \text{E}(v') - \text{E}(v'') = T_e' + \left[ \omega_e'(v'+\frac{1}{2}) - \omega_xe'(v'+\frac{1}{2})^2 \right] - \left[ \omega_e''(v''+\frac{1}{2}) - \omega_xe''(v''+\frac{1}{2})^2 \right] \tag{4}
\]
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

\[
\Delta E = \left[ T_e - \frac{\omega_{e''}}{2} + \omega_x(v'+1/2) - \omega_x v''(v'+1/2)^2 \right] + \frac{\omega_x}{4} \tag{5}
\]

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

\[
\Delta E = a_0 + a_1 x + a_2 x^2 \tag{6}
\]

gives (based on eq 5)

\[
a_0 = \left[ T_e - \frac{\omega_{e''}}{2} + \frac{\omega_x}{4} \right] \tag{7}
a_1 = \omega_x' \tag{8}
\]
\[
a_2 = -\omega_x x'' \tag{9}
\]

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 \( \omega_{e''} \) and \( \omega_x x'' \), 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 I$_2$. 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' $\leftarrow$ v'' is, to a first approximation, proportional to the Franck-Condon factor [5] for the transition, given by the expression

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

where the term on the right hand side of eq 10 is called the Franck-Condon factor. 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' $\approx$ 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 distomic molecules, I$_2$ 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 and approximation and Boltzmann distribution, the relative population of molecules in excited vibrational states is given by the expression

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

where $\omega$ 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 I$_2$, at T = 20. °C and T = 50. °C. Unlike CO, I$_2$ has a large number of 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>
<thead>
<tr>
<th>Molecule</th>
<th>Rel. population</th>
<th>T = 20. °C</th>
<th>T = 50. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>$P_{1}/P_0$</td>
<td>2.3 x 10^{-5}</td>
<td>6.3 x 10^{-5}</td>
</tr>
<tr>
<td></td>
<td>$P_{2}/P_0$</td>
<td>5.6 x 10^{-10}</td>
<td>40.2 x 10^{-10}</td>
</tr>
<tr>
<td>I$_2$</td>
<td>$P_{1}/P_0$</td>
<td>0.349</td>
<td>0.385</td>
</tr>
<tr>
<td></td>
<td>$P_{2}/P_0$</td>
<td>0.122</td>
<td>0.148</td>
</tr>
</tbody>
</table>

Calculations use $k = 0.69503$ cm$^3$/K, $\omega$(CO) = 2170. cm$^{-1}$, and $\omega$(I$_2$) = 214.5 cm$^{-1}$.

**Experimental**

The visible absorption spectrum of I$_2$ 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

<table>
<thead>
<tr>
<th>Spectral bandwidth (resolution)</th>
<th>0.20 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Averaging time</td>
<td>1 second</td>
</tr>
<tr>
<td>Data interval</td>
<td>0.25 nm/point</td>
</tr>
</tbody>
</table>

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.

![Absorption spectrum of I₂ vapor](image)

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 \(v' = 25, 26, 27, \ldots\). Successive peaks at lower energies (longer wavelengths) are also in order, and can be assigned \(v'' = 22, 21, 20, \ldots\).

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. 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

\[
\Delta E = \frac{1}{\lambda}.
\]  

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

4) Fit your peak locations to a quadratic function using eq 6. Remember that \(y = \Delta E\), and \(x = v' + \frac{1}{2}\), 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 \(T'_e\), \(\omega_{x'}\), and \(\omega_{x''}\), 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 \(\omega_{y}''\) and \(\omega_{x''}\) 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 $T_e'$, $\omega_e'$, and $\omega_x'e'$. 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 $\nu_e$ and $\nu_ex_e$ instead of $\omega_e$ and $\omega_xx_e$ 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 $\omega_xx_e$ 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 $\omega_e''$ and $\omega_xx_e''$ are labeled with the prefix X, and those for the excited electronic state (T' $e'$, $\omega'e'$, and $\omega_xx'e'$) are labeled with the prefix B.

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

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