

The Dissociation Energy of Halogen Gases

Purpose: This lab uses the vibrational fine structure of electronic absorption spectra to determine the dissociation energy of I₂ and Br₂ by Birge-Sponer extrapolation.

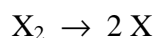
Introduction

The strengths of chemical bonds are some of the most fundamental concepts in chemistry. The experimental measures of the strength of chemical bonds include bond dissociation energies, bond force constants, and bond lengths. Table 1 lists these parameters for some diatomic molecules.

Table 1. Bond characteristics for some diatomic molecules.

	B ₂	C ₂	N ₂	O ₂	F ₂	CN	CO
D ₀ , kJ/mol	289	602	941	494	151	787	1070
Bond length, Å	1.59	1.24	1.10	1.21	1.44	1.18	1.13
k (N/m)	350	930	2240	1140	450	1580	1860
<i>Predicted bond order</i>	1	2	3	2	1		

D₀ is the dissociation or bond energy and corresponds to the process



The bond order predicted using molecular orbital theory is also given in Table 1. The data from Table 1 is plotted in Figure 1. The correlation of the bond dissociation energy and force constants and the molecular orbital theory predictions for the bond order allow us to validate molecular orbital theory. This correlation helps us to understand the nature of the chemical bond and the electronic structure of molecules.

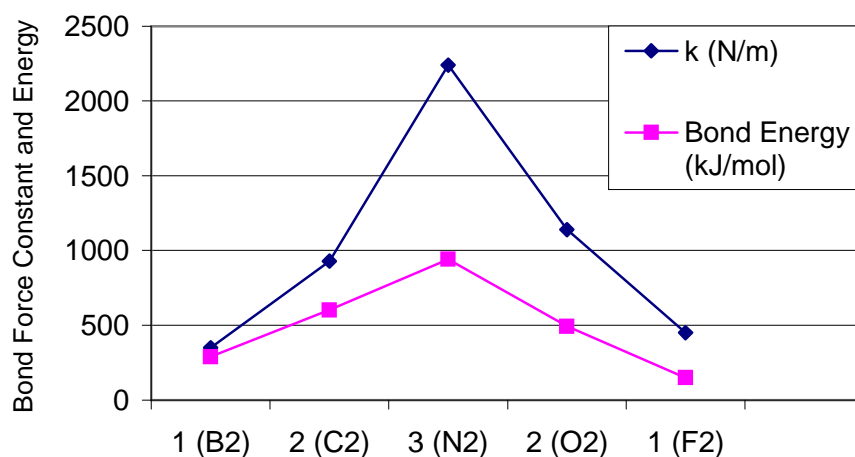


Figure 1: Bond Force Constant and Energy verses predicted Bond Order¹.

The vibrational force constant of a molecule can be determined using IR or Raman spectroscopy. The bond dissociation energy is best-determined using Birge-Sponer extrapolation, either from the vibrational spectrum or from vibrational fine structure in the electronic absorbance spectrum of the molecule. In this exercise, the electronic absorbance spectrum of I_2 and Br_2 will be used as the basis for the Birge-Sponer extrapolation and the results will be compared to the values in Table 1.

Vibrational Spectroscopy and Anharmonicity

Before we deal with electronic absorption spectra, first we need to review some concepts from vibrational spectroscopy. Figure 2 shows the vibration fundamental, $\nu: 1 \leftarrow 0$, and the vibrational overtones, $\nu: 2, 3, \dots \leftarrow 0$ for an anharmonic oscillator, where ν is the vibration quantum number. The overtone transitions are not allowed for a harmonic oscillator, but are weakly allowed for an anharmonic oscillator.

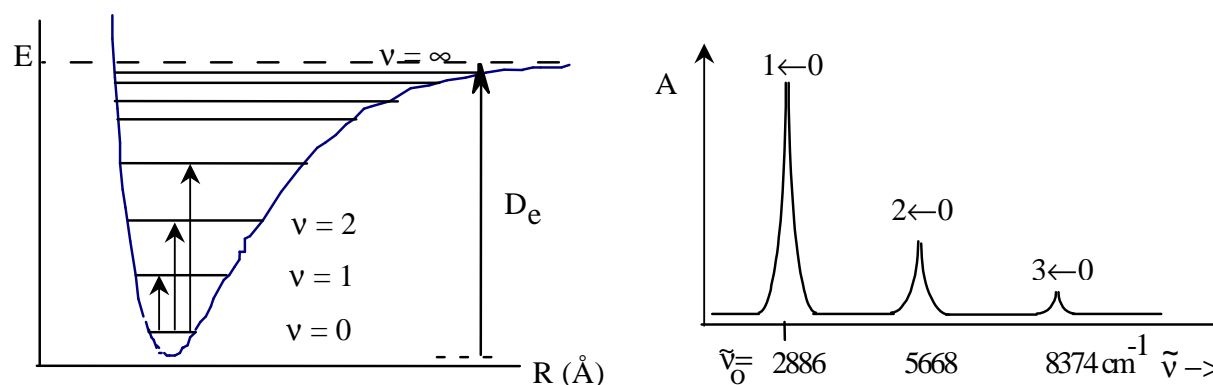


Figure 2: Energy level diagram and spectrum for an anharmonic oscillator.

For an anharmonic oscillator, the energy of the vibrational levels can be expanded in a power series:

$$E_{\nu} = h\nu_e (\nu + 1/2) - \chi_e h\nu_e (\nu + 1/2)^2 + \chi_e h\nu_e (\nu + 1/2)^3 + \dots \quad 1.$$

Most molecules can be adequately approximated by the first two terms. χ_e is the anharmonicity.

$$E_{\nu} = h\nu_e (\nu + 1/2) - \chi_e h\nu_e (\nu + 1/2)^2 \quad 2.$$

The transition energies are given by the differences:

$$E_{\nu+1} - E_{\nu} = h\nu_e (\nu + 1 + 1/2) - \chi_e h\nu_e (\nu + 1 + 1/2)^2 - h\nu_e (\nu + 1/2) + \chi_e h\nu_e (\nu + 1/2)^2 \quad 3.$$

$$\Delta E = h\nu_e - \chi_e h\nu_e 2(\nu + 1) \quad \Delta\tilde{G} = \tilde{\nu}_e - \tilde{\nu}_e \chi_e 2(\nu + 1) \quad 4.$$

where ΔE is the transition energy in joules and $\Delta\tilde{G}$ is the transition energy in cm^{-1} , wavenumber units. The spacing between the successive overtone peaks gets smaller with increasing ν , because

of the anharmonicity. The bond dissociation energy is D_0 and is related to the energy at the bottom of the potential energy curve, D_e , by taking into account the zero point vibrational energy.

$$D_e = D_0 + \frac{1}{2} h\nu_e - \frac{1}{4} \chi_e h\nu_e \quad \tilde{D}_e = \tilde{D}_0 + \frac{1}{2} \tilde{\nu}_e - \frac{1}{4} \tilde{\nu}_e \chi_e \quad \text{in cm}^{-1} \quad 5.$$

D_0 is the experimental bond dissociation energy and D_e is the bond energy that you get from quantum mechanical calculations.

Electronic Absorption Spectra

The energy level diagram and corresponding spectrum for a diatomic molecule is shown in Figure 3. The example values given are for the oxygen molecule. Each peak in the spectrum represents a transition starting at the ground vibrational state of the ground electronic state with an initial vibration quantum number of zero. The ground state of oxygen molecules dissociates into two ground state oxygen atoms. The ground state of the oxygen molecule is $^3\Sigma_g$, and the ground state of the oxygen atom is 3P . The $^3\Sigma_g$ and 3P are called term symbols, which are concise nicknames for the electronic states of atoms and molecules. The excited electronic state of oxygen dissociates into a ground state and an excited state atom, with corresponding term symbols of 3P and 1D .

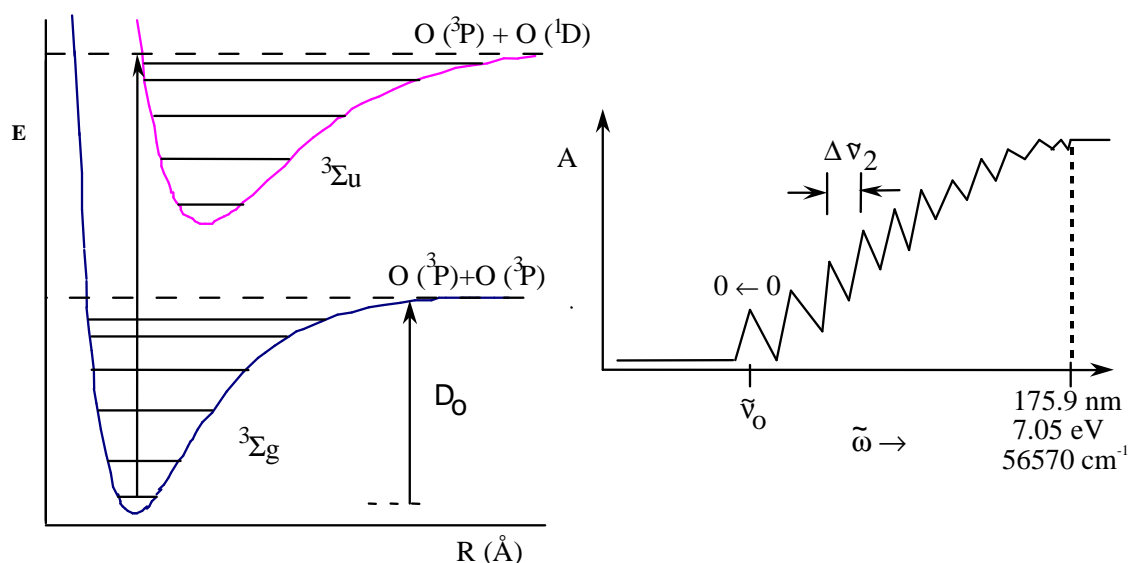


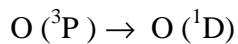
Figure 3: Energy level diagram and electronic spectrum for O_2 .

The various peaks in the absorbance spectrum are caused by transitions to different vibrational levels of the excited electronic state. In other words, the vibrational transitions are “going along for the ride” with the electronic transition. The first transition corresponds to the transition from the lowest energy vibrational state of the ground electronic state to the lowest energy vibrational state of the excited electronic state, $\tilde{\nu}_0$. This state is therefore labeled $0 \leftarrow 0$. The next peak corresponds to the $1 \leftarrow 0$ transition, the third, $2 \leftarrow 0$, etc. Physically, these higher energy peaks correspond to the production of a molecule that is in an electronic excited state and also an excited vibrational state. The vibrational fine structure in the absorbance spectrum corresponds to the vibrational spacings in the excited state of the molecule, not the ground state as in vibrational spectroscopy. The vibrational fine structure converges to a limit that is the sum of the

dissociation energy of the ground state of the molecule and the atomic excitation energy, ΔE^{atomic} .

$$\Delta E_{\text{converge}} = D_0 + \Delta E^{\text{atomic}} = \tilde{\nu}_0 + \sum_{i=0}^{\infty} \Delta \tilde{\nu}_i \quad 6.$$

Here, $\Delta \tilde{\nu}_i$ is the difference in energy between two successive transitions. The first difference is numbered $i=0$. The sum extends over all successive differences up to the convergence limit. The atomic excitation energy, ΔE^{atomic} , corresponds to the process $X \rightarrow X^*$. For O atoms $\Delta E^{\text{atomic}}=1.97$ eV and corresponds to the atomic excitation:



The vibrational energy of the excited state is also given by Equation 2. The effect of anharmonicity is once again to cause successive transitions to be closer together. The convergence limit corresponds to the dissociation of the **excited state** molecule, D_0^* . Figure 4 is a simplified diagram that shows the important molecular and atomic energy terms.

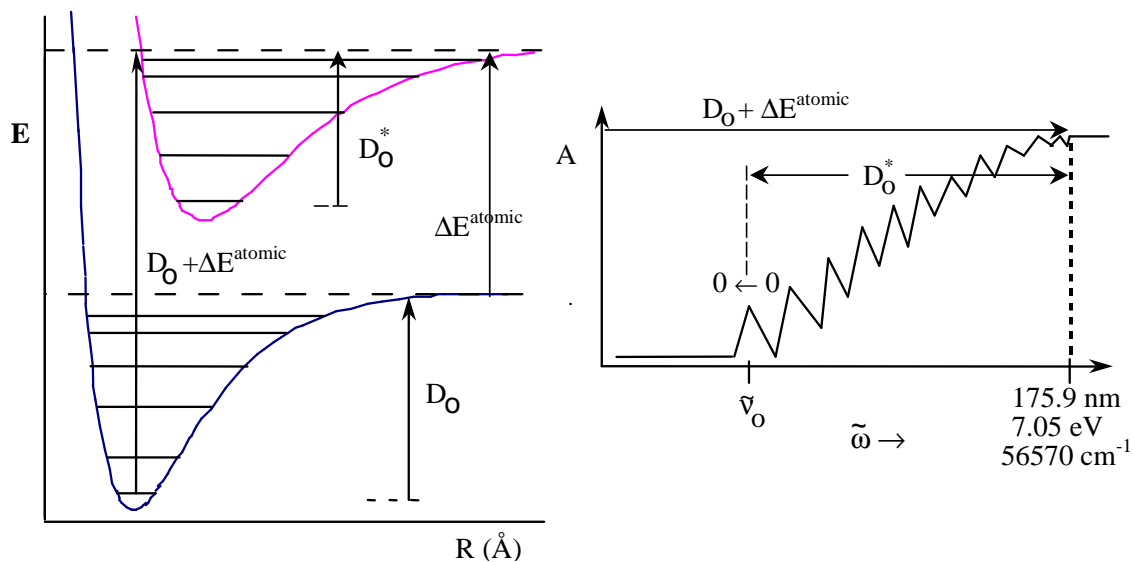


Figure 4: Molecular and atomic energy terms for electronic absorption spectroscopy.

Above the convergence limit, absorption is continuous because the absorbing molecule has dissociated into fragments that can have variable kinetic energies. Convergence limits are especially valuable in determining bond energies. For O_2 , solving equation 6 for the bond dissociation energy of the ground state gives:

$$D_0 = \Delta E_{\text{converge}} - \Delta E^{\text{atomic}} = 7.05 - 1.97 \text{ eV} = 5.08 \text{ eV}$$

ΔE^{atomic} must be determined by a separate experiment, or simply looked up in the literature.

The convergence limit is often difficult to read directly from the spectrum, because of noise in the spectrum. For a quick determination, reading the convergence limit is fine. However, for

careful determinations it is best to extrapolate the vibrational spacings to find the convergence limit. This extrapolation procedure is called a Birge-Sponer extrapolation.

Birge-Sponer Extrapolation

If both the ground electronic state and the excited electronic state have vibrational levels that can be expressed by equation 2 and if the molecule starts in the $\nu=0$ vibrational state, then the transition energy is:

$$E_{\nu}^* - E_0 = E^* + h\nu_e^* (\nu + 1/2) - \chi_e^* h\nu_e^* (\nu + 1/2)^2 - E_0 \quad 7.$$

Here, E_0 is the electronic energy of the ground state with $\nu = 0$, E^* is the electronic energy of the excited state at the minimum in the potential energy well, ν is the excited state vibrational quantum number, χ_e^* is the anharmonicity for the excited state, and ν_e^* is the fundamental vibration frequency of the excited electronic state. The energy difference between two adjacent spectral lines is:

$$\Delta E = E_{\nu+1}^* - E_{\nu}^* = h\nu_e^*(\nu + 1 + 1/2) - \chi_e^* h\nu_e^* (\nu + 1 + 1/2)^2 - h\nu_e^*(\nu + 1/2) + \chi_e^* h\nu_e^* (\nu + 1/2)^2 \quad 8.$$

The first and third term on the right simplify to give just $h\nu_e^*$. Grouping the factor of $1/2$ with ν simplifies the algebra:

$$\Delta E = h\nu_e^* - \chi_e^* h\nu_e^* [(\nu + 1/2) + 1]^2 + \chi_e^* h\nu_e^* (\nu + 1/2)^2 \quad 9.$$

Expanding the square and canceling terms gives:

$$\begin{aligned} \Delta E &= h\nu_e^* - \chi_e^* h\nu_e^* [(\nu + 1/2)^2 + 2(\nu + 1/2) + 1] + \chi_e^* h\nu_e^* (\nu + 1/2)^2 \quad 10. \\ &= h\nu_e^* - \chi_e^* h\nu_e^* (2\nu + 2) \end{aligned}$$

Examples of such differences are shown in Figure 3 for $\nu = 0, 1, 2$. Converting to wavenumbers gives:

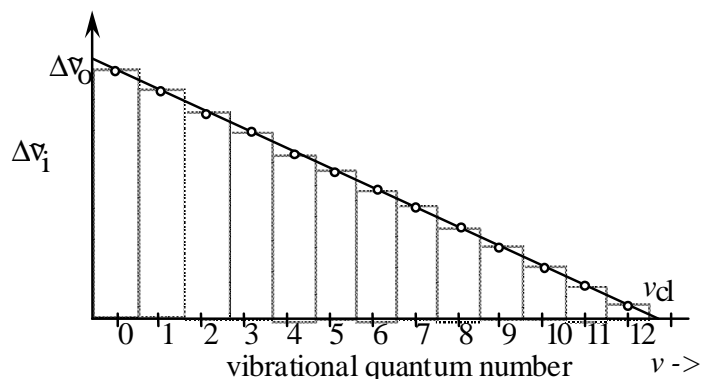
$$\Delta\tilde{\nu}_i = \frac{\Delta E}{hc} = \tilde{\nu}_e^* - \chi_e^* \tilde{\nu}_e^* (2\nu + 2) \quad 11.$$

Here $i = \nu$, the vibrational quantum number of the lower transition. Equation 11 is in straight line form:

$$\Delta\tilde{\nu}_i = (\tilde{\nu}_e^* - 2\chi_e^* \tilde{\nu}_e^*) - 2\chi_e^* \tilde{\nu}_e^* \nu \quad 12.$$

$$\Delta\tilde{\nu}_i = a - b \nu \quad 13.$$

With slope = $b = -2\chi_e^* \tilde{\nu}_e^*$ and y intercept = $a = (\tilde{\nu}_e^* - 2\chi_e^* \tilde{\nu}_e^*)$. The convergence limit has been reached when $\Delta\tilde{\nu}_i = 0$. In other words, if the excited state vibrational energies are well approximated using just the first anharmonicity, then the spacing between successive vibrational lines extrapolates linearly to the convergence limit. $\Delta\tilde{\nu}_i = 0$, corresponds to the x intercept. We call the vibrational quantum number at the convergence limit ν_{cl} . Also note that, using Equation 4, $a = (\tilde{\nu}_e^* - 2\chi_e^* \tilde{\nu}_e^*) = \Delta\tilde{\nu}_0$, which is the first vibrational spacing. This plot is shown in Figure 5.



Notice that if we draw in a rectangle for each point, where the width of each rectangle = 1 and the height of each rectangle = $\Delta\tilde{\nu}_i$, that the area of each rectangle = $(\Delta\tilde{\nu}_i)(1)$. Then completing the sum in Equation 6 is the same as the area of the triangle constructed from all the rectangles.

Figure 5. Birge-Sponer extrapolation.

Substituting the area into Equation 6 gives:

$$D_0 + \Delta E^{\text{atomic}} = \tilde{\nu}_0 + \text{area} \quad 14.$$

From the formula for the area of a triangle of $\frac{1}{2}$ (base)(height) we can easily calculate:

$$\text{area} = \frac{1}{2} \Delta\tilde{\nu}_0 \nu_{cl} \quad 15.$$

Peak Intensities: The O_2 example shown in Figure 3 is characteristic of a transition in which the equilibrium bond length in the excited state is much greater than the ground state. Such a case is actually rare. For many molecules the equilibrium bond lengths are about the same in both the ground state and the excited state. For small changes in bond length, the spectrum appears as in Figure 6. In these cases, the convergence limit cannot be read directly from the spectrum, and the Birge-Sponer extrapolation is the only way to calculate the energy at the convergence limit.

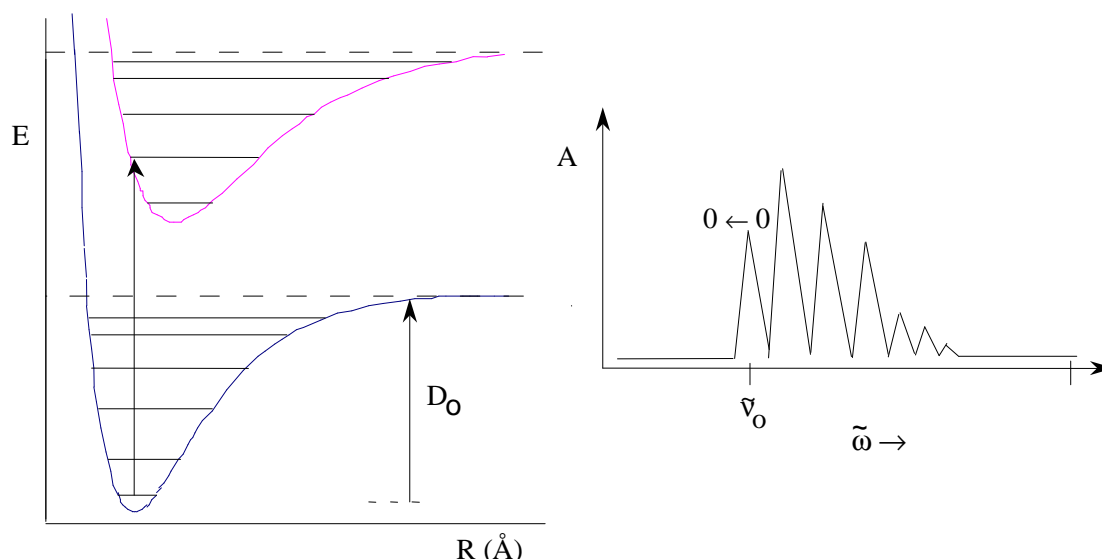


Figure 6: Spectrum when the equilibrium bond lengths are similar in the ground and excited electronic states.

Why does the shape of the spectrum change? In the ground vibrational state, the molecule has an internuclear distance near the center of the vibrational well, while in excited vibrational states the molecule is most probably at a distance near either extreme of the vibration. On electronic excitation, according to the Franck-Condon principle, the internuclear distance does not change. The transition is therefore represented by a vertical line from the middle of the ground state vibrational energy level to the extreme of an excited-state vibrational level. In Figure 3, because of the shift of the excited electronic state to large internuclear distance (i.e., to the right), the most probable transitions end at vibration levels above the dissociation energy. Therefore the wavelength of maximum absorption is in the continuum, and the convergence limit can be determined by inspection. In other words, the increase in equilibrium bond length increases the probability that an electronic transition will cause dissociation of the molecule. On the other hand, if the two electronic states have similar equilibrium bond lengths, as in Figure 6, the most probable transition will be to a vibrational state that will not dissociate. In this case the probability of dissociation is slight, and to locate the convergence limit an extrapolation technique is required.

Hot Bands

At room temperature, almost all molecules are in their ground vibrational state. However, a few molecules are in excited vibrational states. The number of molecules in state j compared with state i is given by the Boltzman distribution:

$$\frac{n_j}{n_i} = e^{-\Delta E/RT} \quad 16.$$

where ΔE is the energy difference between the two states. This ratio is usually quite small for stretching vibrations where ΔE is large, so almost all molecules are in their ground vibrational state at room temperature. For weak bonds, however, ΔE is small and many molecules are found in the excited state. Equation 16 also shows that the number of vibrationally excited molecules increases with temperature.

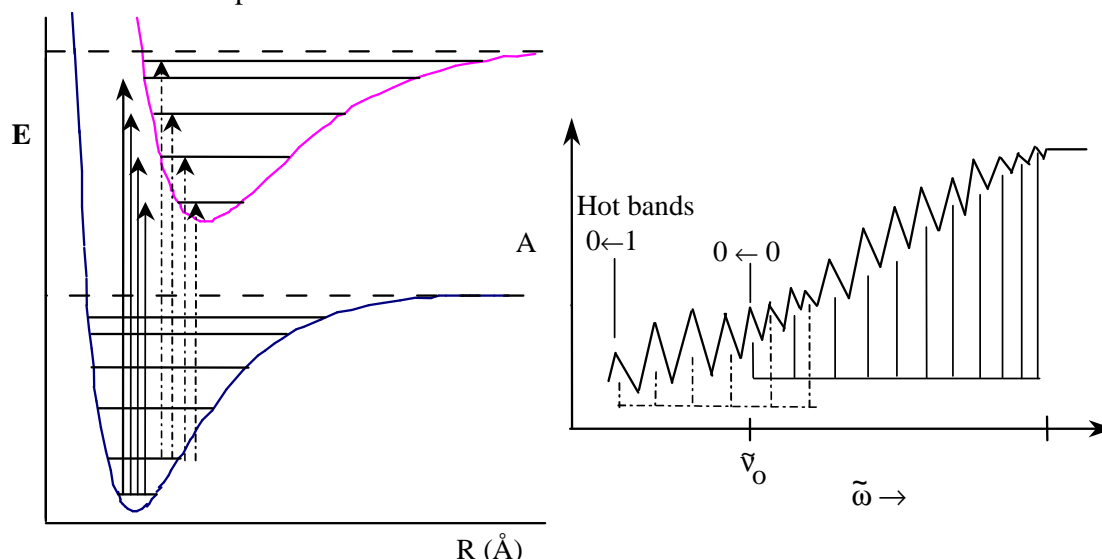


Figure 7: Hot bands, $\nu \leftarrow 1$, appear as a second series of peaks at smaller energies than the normal $\nu \leftarrow 0$ transitions. The hot bands are shown with dashed lines.

For iodine the observed electronic absorption spectrum consists of two series of peaks², Figure 7. One series starts from the ground vibrational state of the ground electronic state as expected. A second series, shown with dashed lines, starts from the first excited vibrational state of the ground electronic state. The second series is less intense than the first because fewer molecules are in the first excited vibrational state, as given by the Boltzman distribution. Transitions that start from excited vibrational states are called hot bands, because of the effect of increased temperature on the Boltzmann distribution.

Procedure

Equipment

10-cm stoppered gas cell
plastic pipette
Perkin Elmer UV/Visible 200 Spectrophotometer
Bromine liquid and solid iodine.

Caution: Bromine liquid is very corrosive. Wear gloves. Contact with bromine can cause burns that leave sensitive areas on your skin for decades. Halogen vapors are toxic and cause burns, also.

On the spectrophotometer, turn on the visible lamp only. Adjust the lamp selector mirror for the visible range. Adjust the slit width to the minimum, 0.2 nm, to obtain the best resolution. Start with the Response at fast. Calibrate the instrument by selecting the %T scale. Then block the sample beam and adjust the output to 0 using the 0%T knob. Remove the beam block and adjust the output to 100% using the 100%T/0 ABS knob. Then switch to the 0-2A scale so that the instrument output is in absorbance. Choose the slowest scan rate by selecting the 30 nm/min setting and checking the gears in the right-hand side of the monochromator (the right-hand side cover is held on magnetically). The big gear should be on top. Set the data acquisition rate to 0.5 sec per sample. This combination will allow you to read the peak wavelengths accurately.

Using the plastic pipette, withdraw some bromine vapor from a bottle of liquid bromine. Only withdraw vapor; do not touch the liquid. Dealing only with the vapor greatly decreases the hazards involved in this experiment. Transfer the vapor to a 10-cm cell and stopper quickly. Place the cell in the UV/Visible spectrophotometer. Scan the spectrum by hand first to determine if the absorbance remains less than 1.0. You should scan in the range of roughly 450-650 nm. Take the spectrum. Check with the instructor to determine if your spectra have sufficient readability.

Use air to flush out the 10-cm cell. Place just a few crystals of iodine in the cell, stopper, and warm the cell with your hands or gently with a hot air gun. Be careful not to touch the cell windows. Repeat the above procedure to obtain the spectrum. You should scan in the range of roughly of 400-650 nm. When finished, tap the cell to remove the iodine crystals and leave the cell open in the hood. No washing is necessary.

Calculations and Report

Carefully read the wavelengths of the peaks. Convert the wavelengths to wavenumbers. Each peak is assigned an arbitrary quantum number. Assign $\nu=0$ for your lowest wavenumber peak and then number the rest sequentially. For iodine, choose the lowest wavenumber peak so as to avoid the hot-band series. For bromine start with the lowest wavenumber peak that has good signal-to-noise. Find the successive differences between the wavenumbers of the peaks and plot these differences versus ν of the lower wavenumber peak. Use linear least squares to find the slope and intercept of the line and then calculate the x-intercept by setting $y = \Delta\tilde{\nu}_i = 0$. Use Equations 13-15 to calculate the dissociation energy for Br_2 and I_2 . The atomic excitation energy is $7599. \text{ cm}^{-1}$ for iodine atoms and $3860. \text{ cm}^{-1}$ for bromine atoms.² Calculate the uncertainties in these energies using the uncertainties in the fit values. Compare your dissociation energies with the literature values and with the values in Table 1.

Report the anharmonicities, in the form $\chi_e^* \tilde{\nu}_e^*$ in cm^{-1} using Eqs. 12-13. These anharmonicities are for the vibrations in the excited state. How anharmonic is the excited state? In other words, is the anharmonicity, $\chi_e^* \tilde{\nu}_e^*$, a significant fraction of the fundamental vibration frequency? To answer this question, note the following information. First, remember that the observed fundamental vibration frequency for a pure vibrational transition is $\tilde{\nu}_o = \tilde{\nu}_e - 2\chi_e \tilde{\nu}_e$. So to answer about the extent of the anharmonicity, we compare the fundamental vibration frequency for the pure vibrational transition, $\tilde{\nu}_e^*$, with $\chi_e^* \tilde{\nu}_e^*$. For this experiment, we don't get a value for $\tilde{\nu}_e^*$ for the excited state, since we don't resolve the first $\nu = 0$ transition. Instead, we will use the fundamental vibration frequencies of the ground state to get a rough guess for the fundamental vibration frequency of the excited state. The fundamental vibration frequency, $\tilde{\nu}_e$, for Br_2 is 325.32 cm^{-1} and I_2 is 214.50 cm^{-1} in the ground states, from Raman spectroscopy. The excited state fundamental vibration frequencies will be smaller. However, for comparison purposes with the excited state anharmonicity, assume that the fundamental vibration frequencies for the excited state and ground state are similar.

1. Does anharmonicity play an important role in observed experimental vibration frequency of these molecules, why?
2. Redraw Figure 1, but include your results and CN and CO. How well do your results fit to the trend in Figure 1? Explain any deviations in terms of periodic trends for the atoms. [The plot is easily constructed using the number of valence electrons as the horizontal axis. The predicted bond orders can be added to the horizontal axis later by hand.]
3. How would increased temperature affect the spectrum?
4. For iodine the observed spectrum consists of two series of peaks.² One series, starting from the first excited vibrational state, is in the red to green regions of the spectrum. The other, starting from the ground vibrational state, is in the green and violet region. Explain why the series starting from the ground state is in a higher frequency region than the other.
5. Explain why the peaks come closer to each other near the convergence limit.
6. Is the equilibrium bond length of the electronically excited iodine molecule the same as that of the ground state? Explain. Answer the same question for bromine.

References:

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2. H. W. Salzberg, J. I. Morrow, S. R. Cohen, M. E. Green, *Physical Chemistry Laboratory*, Macmillan, New York, N. Y., 1978. Experiment 37.
3. K.P. Huber and G. Herzberg, "Molecular Spectra and Molecular Structure, v. 4, Constants of diatomic molecules," Van Nostrand, Toronto, Canada, 1945.