Vibrational and Rotational Analysis of Hydrogen Halides

Goals
Quantitative assessments of HBr molecular characteristics such as bond length, bond energy, etc
Spectrum of Solar Radiance

- UV: 5%
- Visible: 46%
- Near Infrared: 49%

Solar Energy Intensity [W m⁻² micrometer⁻¹]

Wavelength [micrometer]
What do things appear in different colors?

- $E = h\nu = hc/\lambda$
- For visible lights, the photon energy is within 1 to 4 eV, very comparable to transitions involving two electronic states

[Diagram showing energy levels and transitions, with labels for microwave oven and sun screen]
Vibrational and Rotational Energy

vibration

coupled

rotation

<table>
<thead>
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<th>Vibrational energy</th>
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<td>5</td>
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</table>
Infrared Spectra

• Spectral absorption peaks correspond to a transition of two vibrational-rotational states residing in the same electronic state.

• The energy (wavelength) of the peak reflects the energy difference between these two vib-rot states.

• So, what are the specific energies for the vibrational-rotational levels?
Basics of Quantum Mechanics

The hydrogen bromide (HBr) molecule has two nuclei and 36 electrons, and the coordinates of the nuclei are denoted with $\mathbf{R}$, and the coordinates of the electrons are $\mathbf{r}$. The total Hamiltonian $\mathbf{H}$ consists of the kinetic energy of all the particles plus the electrostatic interactions between the two nuclei, the electrons and the nuclei, and the electrons with other electrons. This total Hamiltonian has the form of $\mathbf{H}\Psi(\mathbf{R},\mathbf{r}) = E\Psi(\mathbf{R},\mathbf{r})$, and the eigenvalues, $E$, correspond to the electronic, vibrational, and rotational energy levels.
Born-Oppenheimer Approximation

- Max Born (December 11, 1882 – January 5, 1970) was a German physicist and mathematician. He won the 1954 Nobel Prize in Physics.
- J. Robert Oppenheimer (April 22, 1904 – February 18, 1967), American physicist, known as the “Father of the Atomic Bomb”. As a scientist, Oppenheimer is remembered most for being the chief founder of the American school of theoretical physics while at the University of California, Berkeley.
Born-Oppenheimer Approximation

Born and Oppenheimer found that the electron motions can be separated from the motion of the nuclei by writing the wavefunction, \( \Psi(R,r) = \psi(R,r)\chi(R) \), where \( \psi(R,r) \) is an electronic wavefunction, and \( \chi(R) \) is a nuclear wavefunction. With this fixed nuclei approximation we can introduce a potential energy, \( V(R) \), for nuclear motion, and we get the Central Force Hamiltonian:

\[
\left[-\frac{\hbar^2}{2m}\nabla^2 + V(R)\right]\chi(R,\theta,\phi) = E\chi(R,\theta,\phi)
\]

where spherical coordinates are used for the center-of-mass coordinates for the nuclei, and the reduced mass,

\[
\mu = \frac{m_H m_{Br}}{m_H + m_{Br}}
\]

The potential energy, \( V(R) \), is determined only by the atomic charges and the number of electrons, so it is the same for all isotopic variants for the hydrogen or bromine atoms.
Central Force problems can be further simplified by separating the angular parts \((\theta, \phi)\) of the wavefunction from the radial part \((r)\). Hence we take \(\chi(R, \theta, \phi) = R(R)S(\theta, \phi)\), and \(S(\theta, \phi) = Y_{JM}(\theta, \phi)\), where the \(Y_{JM}(\theta, \phi)\) are the Spherical Harmonics functions which are the same angular functions as are found for the hydrogen atom. In the Spherical Harmonics \(J\) assumes integer values \(0, 1, 2 \ldots\) and \(M\) is also an integer with \(-J \leq M \leq J\). There are \((2J+1)\) possible values for \(M\) for each value of \(J\).
Now the radial functions satisfy the differential equation:

$$-\frac{\hbar^2}{2\mu R^2} \frac{d}{dR} \left( R^2 \frac{dR(R)}{dR} \right) + \frac{J(J+1)\hbar^2}{2\mu R^2} R(R) + V(R)R(R) = E_{\text{rot-vib}} R(R)$$

Note that this equation does not depend on $M$ so the vibration-rotation energies do not depend on the orientation of the angular momentum. Now if we define $\phi(R) = R(R)/R$, we find

$$-\frac{\hbar^2}{2\mu} \frac{d^2 \phi(R)}{dR^2} + \frac{J(J+1)\hbar^2}{2\mu R^2} \phi(R) + V(R)\phi(R) = E_{\text{vib-rot}} \phi(R)$$
Rigid-Rotor Approximation

- We expect that the rotational energy will depend on the angular momentum \( J \), so we identify this form of energy with the second term of the previous equation:
  \[
  E_{\text{rot}} = \frac{J(J+1)-2}{2\mu R^2}
  \]

- We note that the rotational energy is zero for \( J = 0 \).

\[
\mu = \frac{m_Hm_{Br}}{m_H + m_{Br}}
\]

- \( J = 3 \)
- \( J = 2 \)
- \( J = 1 \)
- \( J = 0 \)
Rotational Energy

When there is no vibrational motion we expect the molecule to have the internuclear separation (bond length) $R = R_e$, and the rotational energy in cm$^{-1}$ or wavenumbers becomes

$$F(J) = B_e J(J + 1)$$

with

$$B_e = \frac{h}{8\pi^2 \mu R_e^2 c}$$

where $B_e$ is the Rotational Constant and $c$ is the speed of light and $h$ is the Planck’s constant. This expression for the rotational energy corresponds to the Rigid Rotor approximation.
Vibrational Energy

- We investigate the form of the vibrational energy by subtracting the term \( \frac{J(J+1)}{2\mu R^2} \phi(R) \) from the vibration-rotational Hamiltonian given above. The result is

\[
- \frac{\hbar^2}{2\mu} \frac{d^2 \phi}{dR^2} + V(R)\phi = E_{vib} \phi
\]
Harmonic Oscillator

Now if we set \( x = R - R_e \) and \( k = V''(R_e) \), and we neglect the terms with powers of \( x \) greater than 2, we have after a little manipulation the SWE

\[
-\frac{d^2 \phi(x)}{2 \mu \, dx^2} + \frac{k}{2} x^2 \phi(x) = E \phi(x)
\]

Hook’s law
Harmonic Oscillator

• The harmonic oscillator energy levels are given as \( E_{\text{vib}} = (n + \frac{1}{2})\hbar \nu \) where \( \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \) and \( \nu \) is an integer (0, 1, 2, …).

• Note that the harmonic oscillator has nonzero energy at \( \nu = 0 \). The energy for the harmonic oscillator for \( \nu = 0 \) is the zero point energy, and this zero point energy is different for different isotopic variants of a molecule.
Harmonic Oscillator

- For vibrational energies in cm$^{-1}$ or wavenumbers we have $G_v = \omega_e(v + \frac{1}{2})$ where the Vibrational Constant is
  
  $$\omega_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

  $v = 0, 1, 2, 3$
  $J = 0, 1, 2, 3$
Energy levels in the Rigid Rotor-Harmonic Oscillator Approximation

• If the rigid rotor and the harmonic oscillator approximations are combined we have the energy in wavenumbers (cm$^{-1}$) for vibration + rotation as

$$G(v) + F(J) = \omega_e(v + \frac{1}{2}) + B_e J(J + 1)$$

• We expect that this will be a good approximation for the energy levels for small $v$ and $J$, and this approximation is called the Rigid Rotor-Harmonic Oscillator or RRHO approximation.
Centrifugal Distortion Constant

However a much more accurate representation of the vibration-rotation energy levels is obtained by considering the fact that the potential energy has terms with larger powers of $x$, and that the effective internuclear separation depends on the vibrational state ($v$) of the molecule. Also the effects of centrifugal distortion can be included. The resulting expressions for $F(J)$ and $G(v)$ are the following:

$$F(J) = B_v J(J+1) - D_v J^2(J+1)^2 + \ldots$$

where $D_v$ is the centrifugal distortion constant; and $B_v = B_e - \alpha(v + \frac{1}{2})$. 
Anharmonic Corrections

\[ G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2 + \omega_e y_e (v + \frac{1}{2})^3 + \ldots \]

In this course we will neglect the centrifugal distortion and the higher terms (> 2) in the vibrational energy expression.

For purely harmonic oscillator, theoretically the molecule will never dissociate, i.e., the bond never breaks.
Vibration-Rotation Energy

Hence for a state with quantum numbers $v$ and $J$, we have the vibration-rotation energy

$$G(v) + F(J) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 + B_v J(J + 1)$$

$$= \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 + B_e J(J + 1) - \alpha J(J + 1) \left( v + \frac{1}{2} \right)$$

We see that the energy levels are determined by four parameters: $\omega_e$, $\omega_e x_e$, $B_e$, and $\alpha$, and you will determine them from the analysis of spectra.
Vibration-Rotation Spectroscopy of HBr

In the final project you will analyze the transition energies from a state with quantum numbers \( \nu'', J'' \) to another state with quantum numbers \( \nu', J' \). The transition energy in wavenumbers is given by

\[
\nu = [F'(J') + G(\nu')] - [F''(J'') + G(\nu'')] \]

where the rotational and vibrational energies are given by the above expressions.

Note that we use \( F' \) and \( F'' \) but not \( G' \) and \( G'' \). This is because \( F'(J') \) depends on \( \nu' \) and \( F''(J'') \) depends on \( \nu'' \).
Selection Rules for Rotational Transitions

• It appears that there might be many transitions from a state with \((\nu'', J'')\). However, there are actually few transitions because of Selection Rules.

• Selection Rules for Rotational Transitions:
  – There must be an oscillating dipole moment.
  – For a diatomic molecule like HBr, \(\Delta J = \pm 1\).
Selection Rules for Vibrational Transitions

• There must be an oscillating dipole moment
  – For diatomic molecules, this means the two nuclei must be different

• The value of the integral \( \int \phi_i(x) \mu(x) \phi_f(x) dx \) must be nonzero. In this equation we have the vibrational wave functions for the initial \((i)\) and final \((f)\) states and the dipole moment \((\mu)\) function for the molecule. In other words the transition dipole matrix element must be nonzero.
Selection Rules

• We find two sets of rotational transitions depending whether $\Delta J = +1$ or $\Delta J = -1$. The former type of transitions are called $R$ branch transitions, and the latter are $P$ branch transitions. Hence from $J'' = 0$ only the $R$ branch transition $R(0)$ is found, while for $J''=1$ $R(1)$ and $P(1)$ are found. The $R$ and $P$ branch transitions are labeled with the value for $J''$. 
Selection Rules for Vibrational Transitions

• For pure harmonic oscillators, we get the selection rule that $\Delta \nu = \pm 1$.

• If the molecule has mechanical anharmonicity ($V(x)$ has higher order terms) or electric anharmonicity ($\mu$ has quadratic and higher order terms), then the molecule will exhibit $\Delta \nu = \pm 2, \pm 3, \pm 4, \ldots$ transitions.

• The $\Delta \nu = \pm 1$ transitions are usually the most intense and are called \textbf{fundamental} transitions while the other transitions are weaker and are called \textbf{overtone} transitions.
Vibrational-Rotational Transitions

\( \Delta J = +1 \) \hspace{1cm} \( \Delta J = 0 \) \hspace{1cm} \( \Delta J = -1 \)

- **R-branch**
- **Q-branch**
- **P-branch**
Isotope Effects

The isotopic substituted molecules H$^{79}$Br and H$^{81}$Br have different absorption peaks because the spectroscopic constants depend on the reduced mass, $\mu$, which is different for the two molecules. In particular $\omega_e \propto \mu^{-\frac{1}{2}}$ since $k$ is the same for all isotopic variants. Similarly $B_e \propto \mu^{-1}$ since $R_e$ is the same for all isotopic variants. You are expected to find the reduced mass scaling for the spectroscopic constants $\alpha$ and $\omega_e\chi_e$. 
Data Analysis

• The expected transition energies are given by the equation: \( \nu = [F'(J') + G(v')] - [F''(J'') + G(v'')] \)

• And for \( v'' = 0 \)

\[
\begin{align*}
y &= a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4
\end{align*}
\]
Hence we can obtain the four desired spectroscopy constants by multiple regression with the independent variables given in the square brackets. \textbf{LINEST} will give all the spectroscopic constants provided data from all your group members is used. \textbf{LINEST} will also give the standard errors for each spectroscopic constant.
Bond Dissociation Energy

- If we define $\Delta G(v) = G(V+1) - G(V)$, then

$$D_0^0 = \sum_{v=0}^{v_{\text{max}}} \Delta G(v)$$
Bond Dissociation Energy

- If only the harmonic and the first anharmonic terms are used in $G(v)$, we have

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2$$

and

$$\Delta G(v) = \omega_e - 2\omega_e x_e (v+1)$$

- Now $D_0^0 = Area + \frac{\Delta G(0)}{2}$ where $Area = \frac{bh}{2} = \frac{\Delta G(0)v_{max}}{2}$

- As $v_{max} = \frac{\omega_e}{2\omega_e x_e} - 1$, $D_0^0 = \frac{\omega_e (\omega_e - 2\omega_e x_e)}{4\omega_e x_e}$

- Since $D_e^0 = D_0^0 + G(0)$, we find

$$D_e^0 = \frac{\omega_e^2}{4\omega_e x_e} - \frac{\omega_e x_e}{4}$$

- This is the Birge-Sponer expression for the Dissociation Energy.
Now the number of $v'' = 0$ HBr molecules in a given $J''$ state is given by the Boltzmann expression:

$$N_{J''} \propto (2J''+1) \exp\left(\frac{-F''(J'')}{kT}\right)$$

where $k$ has units of cm$^{-1}$K$^{-1}$. The intensity of a transition from the $J''$ state is proportional to $S(J'' \rightarrow J')N_{J'}$, where $S$ is a Honl-London Factor.
Thus for R and P branch transitions in HBr, the intensity is

\[ I(J'' \rightarrow J''+1) \propto (J''+1) \exp \left( \frac{-B_{v''}J''(J''+1)}{kT} \right) \]

\[ I(J'' \rightarrow J''-1) \propto J'' \exp \left( \frac{-B_{v''}J''(J''+1)}{kT} \right) \]

These two equations can be combined to give an expression that is valid for both R and P branch transitions:

\[ I(J'' \rightarrow J''\pm 1) \propto (J''+1) \exp \left( \frac{-B_{v''}J''(J''+1)}{kT} \right) \]

We can extract the rotational temperature, T, from a plot of

\[ \ln \left( \frac{I(\text{J}')}{\text{J}''+1} \right) \text{ vs } J''(J''+1) \]

This will be a straight line with slope \( -B_{v''}/kT \), and \( B_{v''} = B_e - \alpha (v'' + \frac{1}{2}) \).

Since the rotational constant is known, you can extract T. Error propagation must be used to determine the error in T.
Summary

- Bond length ($R_e$)
  \[ B_e = \frac{h}{8\pi^2 \mu R_e^2 c} \]

- Bond Energy ($D_e$)
  \[ D_e^0 = \frac{\omega_e^2}{4\omega_e x_e} - \frac{\omega_e x_e}{4} \]

- Experimental Temperature

Isotope effect??
FTIR Spectrometer
Fall 2010 CHEM 164A Data Analysis Lab

Textbook
Data Reduction and Error Analysis for Physical Sciences, 3rd Ed., P. R. Bevington and D. K. Robinson (optional)

Classroom
Natural Science Annex 102; Monday, 11:00 AM – 12:10 PM

Instructor
Shaowei Chen, 148 PSB, 459-5841, shaowei@ucsc.edu

Office Hours
Tuesday 10 – 11 or by appointment

Computer Lab
Ming Ong (Merrill Room 103), on Tuesday and Friday, 2:00 PM - 6:00 PM

TA
Bruce Phebus, 459-1892, bphebus@ucsc.edu

TA Office Hours
TBA

Goal:
Research in physical chemistry typically involves extraction of physicochemical properties from experimental measurements (e.g., activation energy, bond length, rate constant, etc). Thus the primary goal of this course is to learn the basic skills of data analysis by using HBr infrared spectra as an example from which the students are anticipated to estimate the values of a variety of physical/chemical parameters.

Schedule for lectures

<table>
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<tr>
<th>Date</th>
<th>Topic</th>
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<tr>
<td>September 27</td>
<td>Mean and standard deviation</td>
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<tr>
<td>October 4</td>
<td>Error propagation</td>
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<td>October 11</td>
<td>Least square fit</td>
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<td>October 18</td>
<td>Vibrational energy of molecules (Part I)</td>
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<tr>
<td>October 25</td>
<td>Vibrational energy of molecules (Part II)</td>
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<tr>
<td>November 1</td>
<td>Excel tutorial/pass out data for final report</td>
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<td>November 8</td>
<td>Lab reports clinic I</td>
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<tr>
<td>November 15</td>
<td>Lab reports clinic II</td>
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<tr>
<td>November 22</td>
<td>First drafts due</td>
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<tr>
<td>November 29</td>
<td>pick up drafts of lab reports</td>
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<tr>
<td>December 6</td>
<td>Final Reports due in my office (PSB 148) by 4:30 PM</td>
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Grade
Final report (85%); quizzes and attendance (15%)

Statistic Analysis

Experimental Background

Results and Discussion
Results and Discussion

• Work in a group of three
• Each collects raw data of one spectrum
• Share your data with your group; and each of the group will then have three sets of data
  – \((v'' = 0 \rightarrow v' = 1)\)
  – \((v'' = 0 \rightarrow v' = 2)\)
  – \((v'' = 0 \rightarrow v' = 3)\)

Which isotope exhibits higher vibrational-rotational energy, \(\text{H}^{79}\text{Br}\) or \(\text{H}^{81}\text{Br}\)?

• Estimate your errors in the raw data
Vibrational-Rotational Transitions
Procedure

• Experimental Raw Data
  – (x, y) value for each peak: \( \text{cm}^{-1} \) and intensity
  – \((J'', J')\) values for each peak

• Data Manipulation (Excel)

• Linest Fitting (Excel)

• Calculation of Molecular Parameters
  – Effects of isotope
  – Experimental Temperature
### Experimental Data

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<tr>
<th>$v'$</th>
<th>$J''$</th>
<th>$J'$</th>
<th>$v$ (cm$^{-1}$)</th>
<th>$I$</th>
<th>$v$ (cm$^{-1}$)</th>
<th>$I$</th>
<th>$x_1$</th>
<th>$x_2$</th>
<th>$x_3$</th>
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<tr>
<td>$v'' = 0$</td>
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<td>$H^{79}\text{Br}$</td>
<td></td>
<td>$H^{81}\text{Br}$</td>
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</table>

**Formula:**

$$y = \omega_{v}[v'] - \omega_{x} x_{v}(v'^2 + v') + B_{v}[J'(J'+1) - J''(J''+1)] - \alpha \left[\left(v' + \frac{1}{2}\right)J'(J'+1) - \frac{1}{2}J''(J''+1)\right]$$

**Excel:**

Excel
Summary

- Bond length ($R_e$)
- Bond Energy ($D_e$)
- Experimental Temperature

$$B_e = \frac{h}{8\pi^2 \mu R_e^2 c}$$

$$D_e^0 = \frac{\omega_e^2}{4\omega_e x_e} - \frac{\omega_e x_e}{4}$$

Isotope effect??

$R_e = 1.4145$ Å
$D_e = 366$ kJ/mol

http://www.science.uwaterloo.ca/~cchieh/cact/c120/bondel.html
Thus for R and P branch transitions in HBr, the intensity is

\[ I(J'' \rightarrow J'' + 1) \propto (J'' + 1) \exp\left(\frac{-B_v''J''(J'' + 1)}{kT}\right) \quad \text{R branch} \]

\[ I(J'' \rightarrow J'' - 1) \propto J'' \exp\left(\frac{-B_v''J''(J'' + 1)}{kT}\right) \quad \text{P branch} \]

These two equations can be combined to give an expression that is valid for both R and P branch transitions:

\[ I(J'' \rightarrow J'' \pm 1) \propto (J'' + J' + 1) \exp\left(\frac{-B_v''J''(J'' + 1)}{kT}\right) \]

We can extract the rotational temperature, T, from a plot of

\[ \ln \frac{I(J'' \rightarrow J')}{J'' + J' + 1} \text{ vs } J''(J'' + 1) \]

This will be a straight line with slope \(-B_v''/kT\)

Since the rotational constant is known, you can extract T. Error propagation must be used to determine the error in T.
Vibrational Energy

• Now we assume that $V(R_e) = 0$ and since the minimum value for $V(R)$ occurs at $R_e$, $V'(R_e) = 0$.

• If $V(R)$ is expanded in a Taylor’s series about $R_e$, we have

$$V(R) = V(R_e) + V'(R_e)(R - R_e) + \frac{V''(R_e)}{2}(R - R_e)^2 + ...$$

where the first two terms are zero.