DOING PHYSICS WITH PYTHON

QUANTUM MECHANICS

MOLECULAR SPECTRA

VIBRATION-ROTATION STATES: HCl MOLECULE

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Please email any corrections, suggestions, improvements, etc

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The molecule spectra for emission and absorption of diatomic molecules such as HCl depends upon the allowed transitions between vibrational-rotational energy levels.

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Vibrational analysis of the diatomic molecule HCl

Angular momentum

INTRODUCTION

Molecules emit and absorb electromagnetic radiation just like atoms. In general, the spectrum emitted by molecules can be divided into three spectral ranges which correspond to different types of quantum state transitions.

1. **Electronic spectra**: Transitions of bound electrons between different energy levels. The photons emitted or absorbed are often in the visible part of the electromagnetic spectrum.
2. **Rotation spectra**: Assume that a molecule possessed a permanent electric dipole moment. If the molecule rotates it would emit infrared or microwave radiation, or if the molecule absorbs radiation, it could set the molecule into rotation.
3. **Vibration spectra**: If the atoms in the molecule vibrate and this results in a fluctuating charge distribution then the molecule will emit radiation or when the molecule absorbs radiation it will cause the atoms to vibrate. The emission or absorption of radiation is mostly in the infrared.

The spacing of the energy levels for the vibration of molecules is greater than the spacing of the energy levels for rotation. So, the spectra for rotation-vibration are complicated and many fine emission lines or absorption lines will be observed. Typical photon energies are: rotation 10^{-5} to 10^{-3} eV (microwave) and vibration 0.2 to 2 eV (infrared).

ROTATION SPECTRA

A simple model of a molecule is to consider it to made up of a set of mass points in fixed positions (rigid rotor model). The rotational states of the molecule are characterised by its **orbital momentum quantum number *J***. The symbol J is often used by chemists, whereas physicists use the letter l $\left(J \equiv l\right)$. In the quantum world, the angular momentum is quantized and is characterized by fixed integer values including zero for the value of J $\left(J = 0, 1, 2, 3, \ldots\right)$. For diatomic molecules the line joining the atoms is an axis of symmetry and rotations perpendicular to the axis of symmetry are of significance and the moment of inertia about all such perpendicular axes will have the same value. The relationship between moment of inertia I, angular momentum L and total energy E_R of the rotating molecule (rotation frequency ω_R) are

$$L = I\,\omega_R \qquad E_R = \tfrac{1}{2} I\,\omega_R^{\,2} \quad \Rightarrow \quad E_R = \frac{L^2}{2I}$$

The quantum (wave-mechanical) value of the angular momentum L and the rotation energy $E_R(J)$ are

$$L^2 = J(J+1)\hbar^2$$

$$E_R(J) = J(J+1)\frac{\hbar^2}{2I} = J(J+1)\,B \qquad B = \frac{\hbar^2}{2I}$$

where $E_R(J)$ is the energy level for the state J and B is the **rotation constant**.

Energy of rotational transitions

A diatomic molecule such as HCl can radiate by electric dipole emission because it possesses a permanent electric dipole moment where one point mass is positive and the other negative. The selection rule for allowed transitions for electric dipole radiation is

$$\Delta J = \pm 1$$

emission, $\Delta J = -1$ and absorption $\Delta J = +1$

When a molecule is irradiated with photons of light it may absorb the radiation and undergo an energy transition. The energy of the transition must be equivalent to the energy of the photon of light absorbed

absorption

$$J \to J+1 \quad E_R(J+1) - E_R(J) = E_{photon} = h\,f \qquad \Delta J = +1$$

When the transition is from a higher energy state to a lower energy state, a photon is emitted with an energy equal to the transition energy

emission

$$J+1 \to J \quad E_R(J) - E_R(J-1) = -E_{photon} = -h\,f \qquad \Delta J = -1$$

The energy difference $\Delta E_R(J)$ between rotational levels $J \leftrightarrow J+1$ is given by:

$$\Delta E_R(J) = \left|E_R(J+1) - E_R(J)\right| = 2(J+1)B = 2(J+1)\left(\frac{\hbar^2}{2I}\right)$$

where the $\boldsymbol{J}$ in the variable $\Delta E_R(J)$ always refers to the lower energy level in the transitions $J \leftrightarrow J+1$. The parameters describing the photon absorbed or emitted are

$$E_{photon} = h\,f = \hbar\,\omega = \left|E_J - E_{J+1}\right| = 2(J+1)B = 2(J+1)\left(\frac{\hbar^2}{2I}\right)$$

$$\omega = 2(J+1)\left(\frac{\hbar}{2I}\right) \qquad f = \left(\frac{2(J+1)}{2\pi}\right)\left(\frac{\hbar}{2I}\right)$$

$$\lambda = \frac{2\pi I}{(J+1)\hbar}$$

where ω, f, λ are the frequency and wavelength of the photon absorbed or emitted.

Note: J always refers to the lowest energy level in the transitions

$J \leftrightarrow J+1$ $\qquad$ $J = 0, 1, 2, 3, \ldots.$

The first four rotational energy levels are

$$E_0 = 0 \quad E_1 = 2\left(\frac{\hbar^2}{2I}\right) \quad E_2 = 6\left(\frac{\hbar^2}{2I}\right) \quad E_3 = 12\left(\frac{\hbar^2}{2I}\right)$$

Thus, the spacing between successive adjacent energy levels are

$$\Delta E(J) = E_R(J+1) - E_R(J) = 2\left(\hbar^2 / 2I\right)(J+1) = 2B(J+1)$$

$$0 \leftrightarrow 1 \quad \Delta E(0) = 2B \qquad 1 \leftrightarrow 2 \quad \Delta E(1) = 4B \qquad 2 \leftrightarrow 3 \quad \Delta E(2) = 6B$$

Diatomic molecules

For a diatomic molecule assuming it is rigid (dimensions do not change), its moment of inertia I about its centre of mass m_u is determine by the following, where m is the mass and r is the distance from the centre of mass (centre of mass is taken as the Origin)

$$m_u = \frac{m_1 m_2}{m_1 + m_2}$$

$$m_1 r_1 = m_2 r_2$$

$$R = r_1 + r_2$$

$$r_1 = \frac{m_2 R}{m_1 + m_2} \qquad r_2 = \frac{m_1 R}{m_1 + m_2}$$

$$I = m_1 r_1^{\,2} + m_2 r_2^{\,2}$$

$$I = m_\mu R^2$$

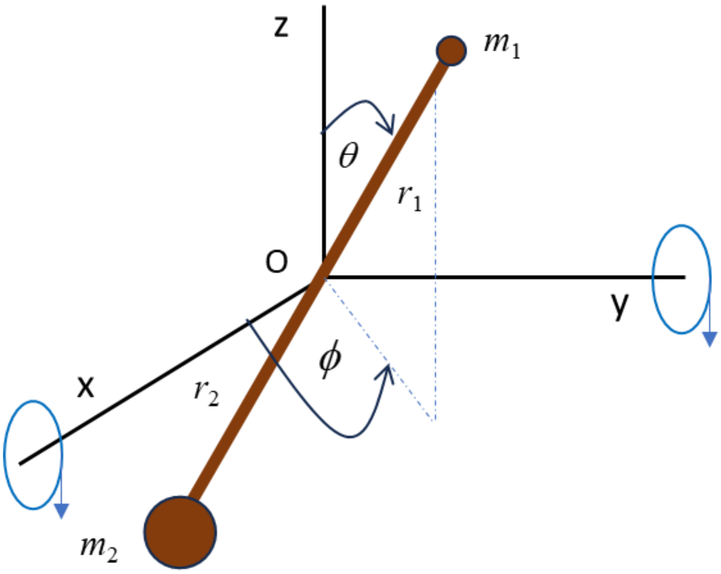

Fig. 1. The rigid rotor coordinate system. A diatomic molecule has two degrees of freedom for rotation.

The rotational energy levels for the HCl molecule are shown in figure 1. The rotational energies are given by the equation

$$E_R(J) = J(J+1)\frac{\hbar^2}{2I} = J(J+1)B$$

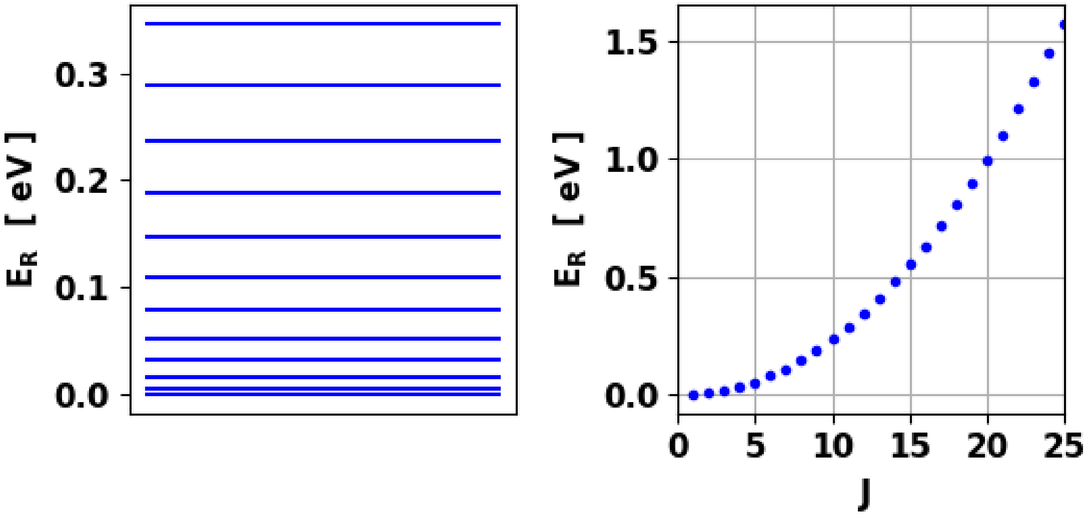

Fig. 1. The rotational energy levels for the HCl molecule (left plot: first 12 energy levels). The increase in energy E_R with the angular

momentum quantum number J is a quadratic function of J (right plot: first 25 energy levels).

Figure 2 shows the spacing between adjacent energy dE levels for transitions $\Delta J = \pm 1$

$$\Delta E(J) = E_R(J+1) - E_R(J) = 2\left(\hbar^2 / 2I\right)(J+1) = 2\,(J+1)\,B$$

The energy $dE \equiv \Delta E(J)$ is the **photon** energy that is either absorbed or emitted in the transition $J \leftrightarrow J+1$.

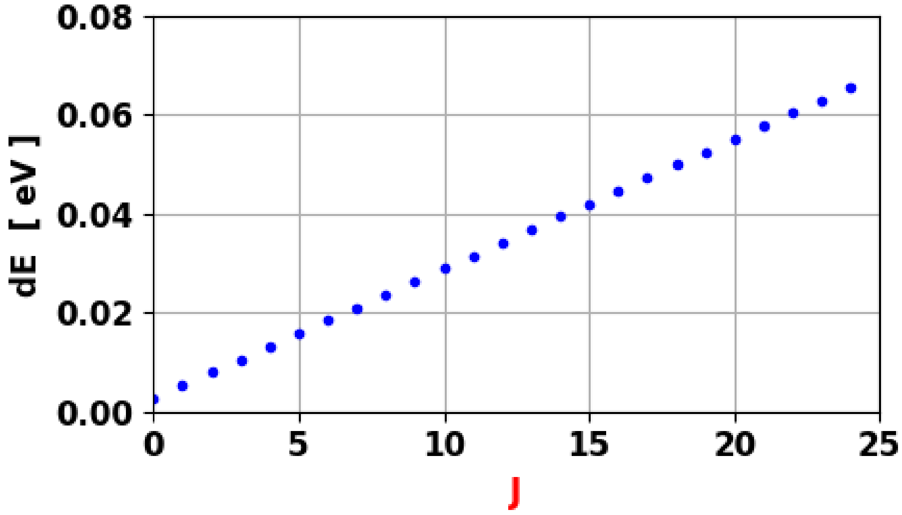

Fig. 2. Energy of emitted or absorbed photon in transitions from state $J \leftrightarrow J+1$ where J refers to the lower energy level.

All the hydrogen halides in the gases state show broad absorption lines in the microwave - far infrared. These lines are nearly equally spaced as shown by the approximately equal spacing of the blue dots in figure 2. So, our simple theory has good agreement for recorded absorption spectra.

The dependence on J for the wavelength λ, frequency f, and wave number $k = 1/\lambda$ of an emitted or absorbed photon are shown in figure 3. The linear relationship between the orbital quantum number J and the wavenumber k as shown in figure 3 is confined with experimental results.

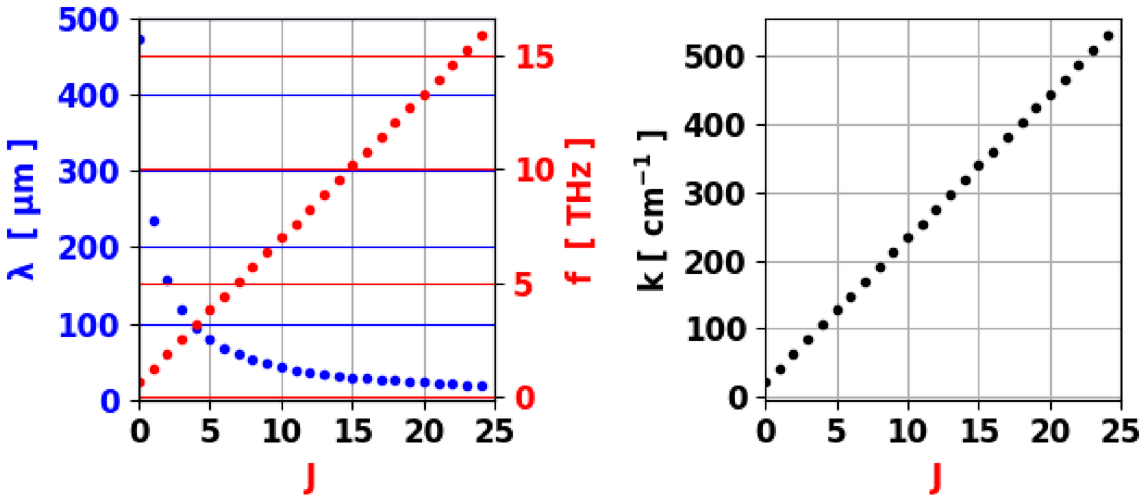

Fig. 3. Transition $J \leftrightarrow J+1$: dependence on J for the wavelength λ, frequency f, and wavenumber $k = 1/\lambda$ of the emitted or absorbed photons.

As molecules are excited to higher rotational energies they spin at a faster rate. The faster rate of spin increases the centrifugal force pushing outward on the molecules resulting in a longer average bond length which increases the moment of inertia I and thus decreasing the rotation constant B. Therefore, the addition of centrifugal distortion at higher rotational levels decreases the spacing between rotational levels. This is only a small correction which is ignored in the simulations.

VIBRATION SPECTRA

The vibration spectrum for the HCl molecule is discussed in depth in the article

Vibrations of diatomic molecules HCl: Harmonic oscillator and anharmonic oscillator (Morse potential)

The energy level diagram for the Morse potential is shown in figure 4.

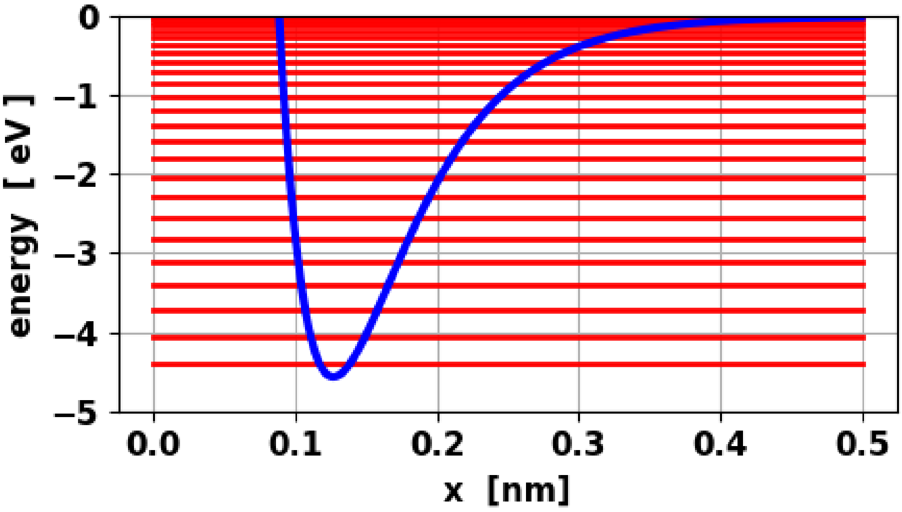

Fig. 4. Morse potential well and energy level spectrum. Note: the reduction in spacings between adjacent energy levels as the vibrational quantum number increases. Ground state $n = 0$, $n > 0$ are the excited sates. Zero-point energy, E_0 = 0.179 eV measured w.r.t. the bottom of the potential well.

The only allowed transitions are when the vibration quantum number n changes only by 1 $(\Delta n = \pm 1)$, all other transitions are forbidden for electric dipole radiation.

Selection rule for the vibrational spectra

allowed transitions $\Delta n = \pm 1$

Note: the spacing of the energy levels for vibration are about an order of magnitude greater than for the rotation energy levels.

VIBRATION-ROTATION SPECTRA

A molecule does not simply vibrate or rotate, but it is simultaneously vibrating and rotating. The total energy of a molecule is therefore the sum of the energy of vibration and rotation

$$E = E_V + E_R$$

The vibration energy E_V is found by solving the Schrodinger equation for the Morse potential by finding the eigenvalues of the Hamiltonian. The rotational energy E_R is given by

$$E_R(J) = J(J+1)\frac{\hbar^2}{2I} = J\ (J+1)B$$

and the energy of each quantum state is given by

$$E = E_V + J(J+1)\frac{\hbar^2}{2I} = E_V + J(J+1)B$$

The vibration energy is usually much larger than the rotation energy. Hence, the rotational levels belonging to each vibrational energy level from a closed spaced group. Because of the relatively small spacing between the rotational energy levels, they are said to constitute a band known as the **vibration-rotation bands**. In general, for diatomic molecules, for electric dipole radiation the selection rules for vibration and rotation apply although some there maybe violations of the rules for vibrational and rotational states

$\Delta n = \pm 1 \quad \Delta J = \pm 1$ allowed transitions

The general arrangement of the vibration-rotation levels is shown in figure 5.

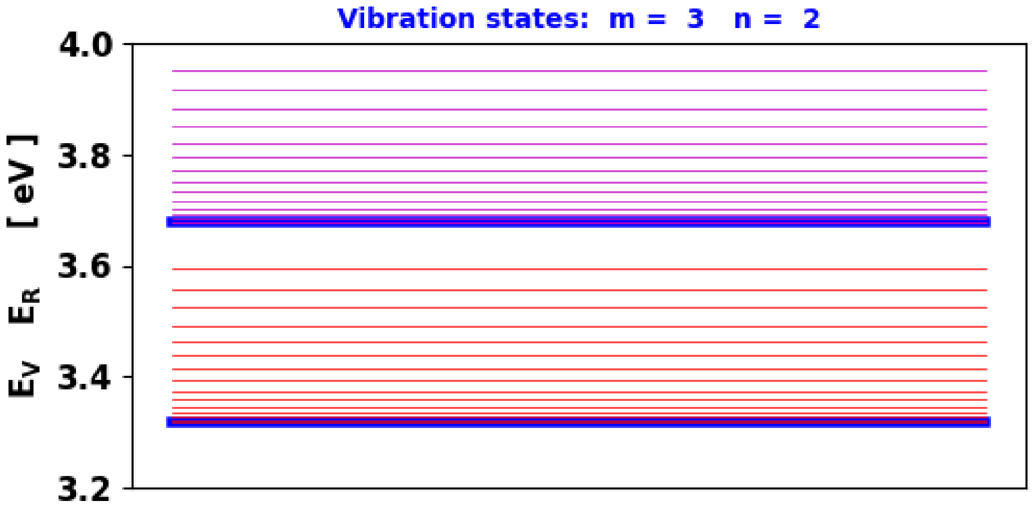

Fig. 5. Energy levels for the diatomic molecule HCl. The blue lines are the vibration states *m* = 3 and *n* = 2. The red and magenta are the energy levels for the rotational states.

The allowed transitions between states can be divided into two branches, the **R branch** and the **P branch** as the difference in energy between the $J \to J+1$ and $J+1 \to J$ transitions cause a splitting of vibrational spectra into two branches.

R branch $\Delta J = +1 \quad 0 \to 1 \quad 1 \to 2 \quad 2 \to 3 \quad \ldots$

P branch $\Delta J = -1 \quad 1 \to 0 \quad 2 \to 1 \quad 3 \to 2 \quad \ldots$

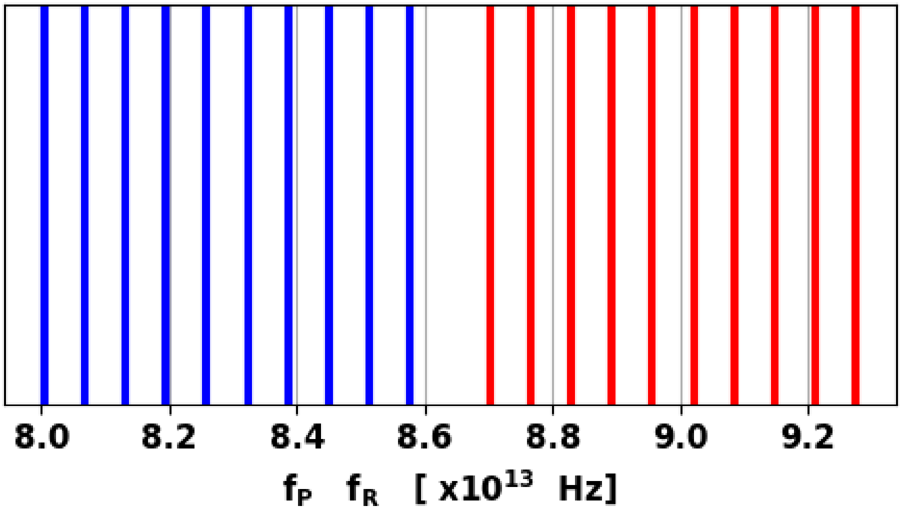

Fig. 6. Absorption or emission lines for the molecule HCl. The vibrational transition is $3 \to 2$. Vibration-rotation transitions: The lower energy transitions in blue is the P branch and the higher energy transitions in red is the R branch. Since the $\Delta J = 0$ transition is forbidden, there is no spectral line associated with the pure vibrational transition and therefore, there is a gap between the P branch and R branch. The spacing between adjacent lines for the P branch and R branch is 2*B*. Our model gives us estimates of the emission and absorption spectrum for HCl, but gives no information about the strength of the absorption lines or the radiative lifetimes of any state.

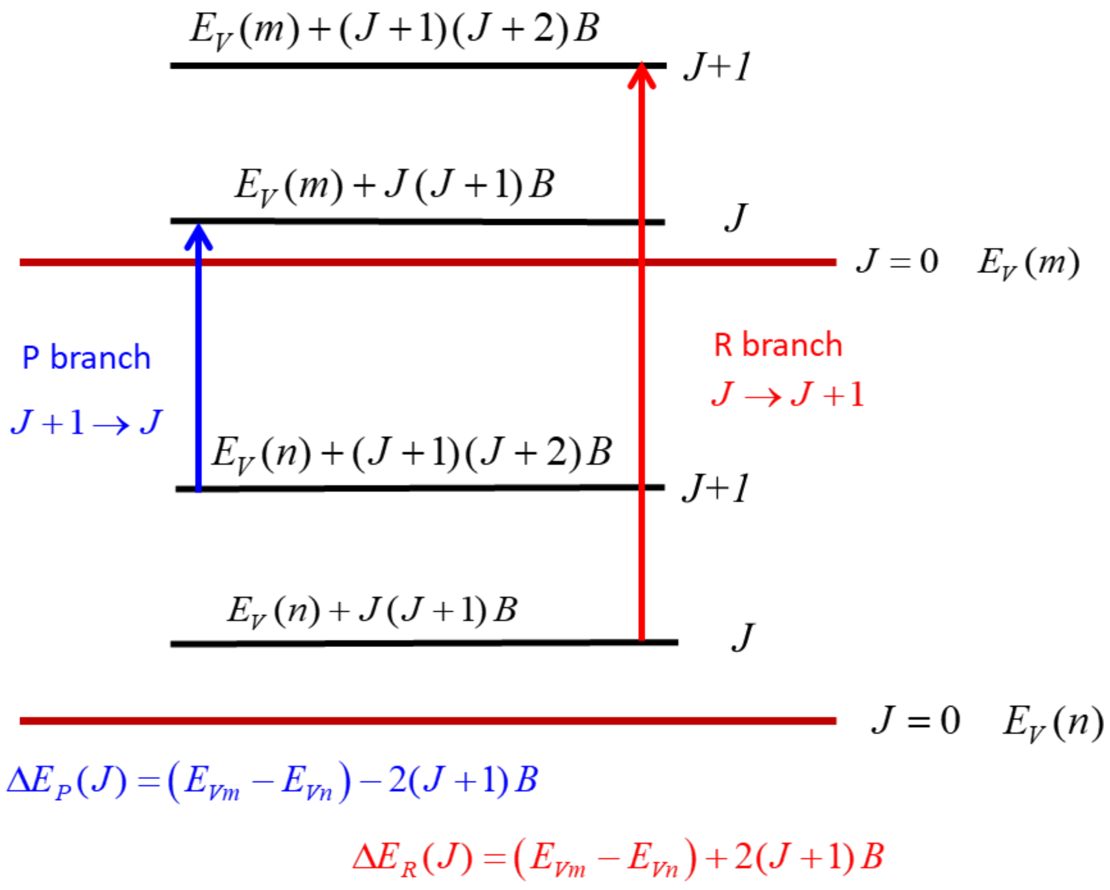

Fig. 7. Transitions between states for the P branch and the R branch.

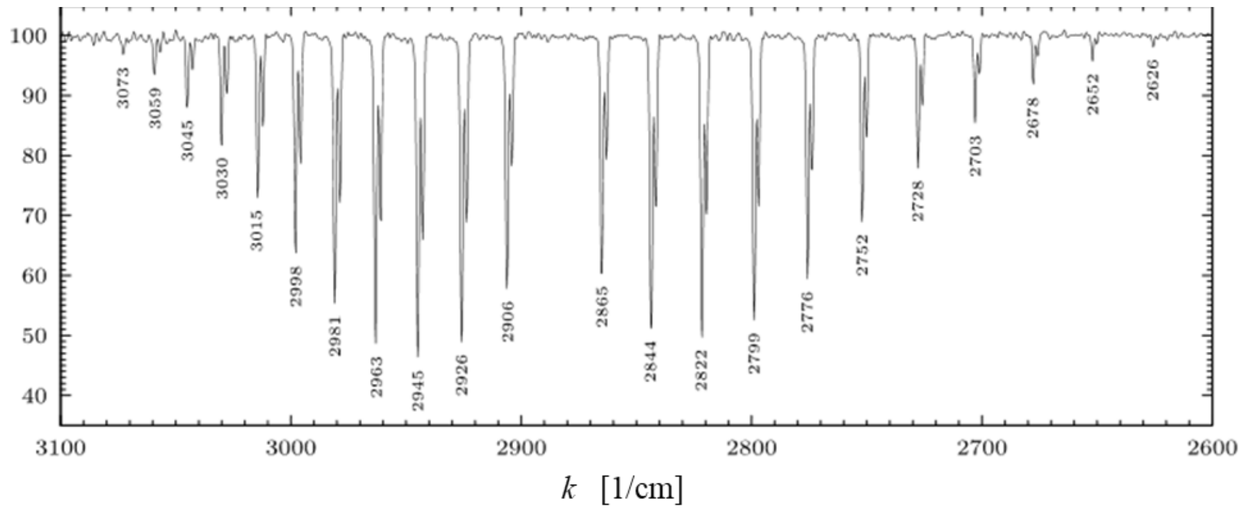

Fig. 8. Absorption spectrum for HCl. Note the double peak in the troughs. This is because a sample HCl contains two isotopes of chlorine, ^{35}C and ^{37}Cl. The slightly different masses mean different moments of inertia and slightly different energy eigenvalues.

How good is our simple model? We can compare the measured values the wavenumber *k* for the absorption lines (figure 8) with the predictions of our simple model. A comparison of the wavenumbers predicted and measured is shown in figure 9.

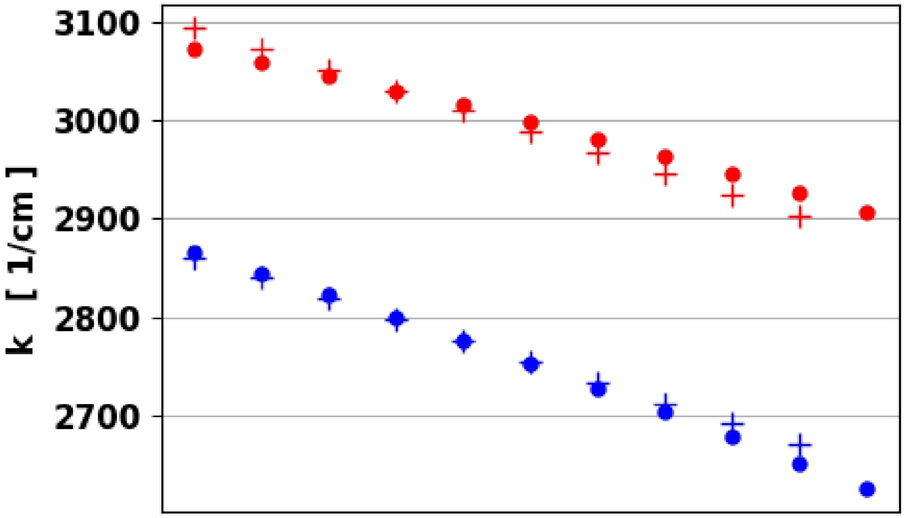

Fig. 9. The measured values of the absorption lines for the P branch and R branch (**dots**) and the model predictions (**crosses**).

Overall, we can conclude that there is an excellent agreement between the predictions from our simple model and measurements.

SCHRODINGER EQUATION:

ROTATIONAL MOTION DIATOMIC MOLECULES

The wavefunctions for the rigid rotor model are found from solving the time-independent Schrödinger Equation for the eigenvalues E_R and eigenfunction $\psi(\vec{r})$

$$\hat{H}\,\psi(\vec{r}) = E_R\;\psi(\vec{r})$$

where the Hamiltonian operator is

$$\hat{H} = \frac{-\hbar^2}{2\,m_\mu}\nabla^2 + U(\vec{r})$$

where ∇^2 is the Laplacian operator and is best expressed in spherical coordinates

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

We can simply things by making two assumptions:

- The distance between the two masses is fixed. This causes the terms in the Laplacian containing $\partial/\partial r$ to be zero.
- The orientation of the masses is completely described by θ and ϕ and in the absence of electric or magnetic fields the energy is independent of orientation. This causes the potential energy $U(\vec{r})$ portion of the Hamiltonian to be zero.

The wavefunctions $\psi(\theta,\phi)$ are customarily represented by $Y(\theta,\phi)$ and are called the **spherical harmonics**.

The Hamiltonian operator can now be given by

$$\hat{H} = \frac{-\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

The Schrödinger Equation becomes

$$\frac{-\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y(\theta,\phi) = E_R\,Y(\theta,\phi)$$

The Schrödinger equation can be solved using separation of variables.

$$Y(\theta,\phi) = \Theta(\theta)\ \Phi(\phi)$$

Azimuthal angle $\Phi(\phi)$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2$$

m is the separation constant

The solution for the azimuthal angle is

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}}\exp\left(i\,m\,\phi\right)$$

A complete rotation through 2π rad must leave the molecule in the same orientation and this can only happen if

$$m = 0,\ \pm 1, \pm 2, \pm 3,\ \ldots$$

Polar angle $\Theta(\theta)$

The quantum (wave-mechanical) value of the angular momentum L and the rotation energy $E_R(J)$ are

$$L^2 = J(J+1)\hbar^2 \quad E_R = J(J+1)\frac{\hbar^2}{2I} \quad \frac{2I\,E_R}{\hbar^2} = J(J+1)$$

where J is the rotational level, J = 0, 1, 2, 3, …

Therefore, the Schrodinger equation for the azimuthal angle is

$$\frac{d^2\Theta}{d\theta^2} + \frac{\cos\theta}{\sin\theta}\frac{d\Theta}{d\theta} + \left[J(J+1) - \frac{m^2}{\sin^2\theta}\right]\Theta = 0$$

Th solutions $\Phi_{J,m}(\theta)$ of this ODE are called the **Legendre functions** which are functions of sine and cosine terms. Solutions are only physical acceptable if J and m has the values

$$J = 0, 1, 2, 3, \ldots \qquad m = 0,\ \pm 1, \pm 2, \pm 3,\ \ldots, J$$

So, the eigenfunctions for the rotational motion of a diatomic molecule are the spherical harmonics whose values depend upon the values assigned to J and m

$$Y_{J,m}(\theta,\phi) = \Phi_{J,m}(\theta)\Phi_m(\phi)$$

and the allowed values for J and m are

$$J = 0, 1, 2, 3, \ldots \qquad m = 0,\ \pm 1, \pm 2, \pm 3,\ \ldots, J$$

where J is called the **orbital quantum number** and m the **magnetic quantum number**. (Note: $J \equiv l$)

Azimuthal angle $\Phi(\phi)$

The polar angle is $0 \le \phi \le 2\pi$ and the polar eigenfunction is

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} \exp\left(i m \phi\right)$$

The probability density is

$$\Phi^*(\phi)\ \Phi(\phi) = \frac{1}{2\pi} \qquad \text{independent of } \phi$$

and the probability of finding the orientation of the molecule in in the region from 0 to 2π is

$$probability\left(0 \le \phi \le 2\pi\right) = \int_0^{2\pi} \frac{1}{2\pi} d\phi = 1$$

So, we never can know the orientation of the molecule, we only know that there is an equal probability of finding the polar orientation of the molecule at any angle ϕ when measured.

REFERENCES

https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Spectroscopy/Rotational_Spectroscopy/Rotational_Spectroscopy_of_Diatomic_Molecules