

Chapter 1

Lab 2: IR spectroscopy of HCl gas

The aim of the lab is to determine the bond length, dissociation energy, and the fundamental frequencies/wavenumbers of a heteronuclear diatomic molecule (HCl) using its rovibrational spectrum in the IR region. We will also determine correction terms beyond the simplest rigid-rotor/harmonic-oscillator description in order to improve agreement with experiment.

1.1 Theory

Spectroscopy is based on the fact that electromagnetic radiation can be emitted or absorbed when atoms, molecules, or ions undergo transitions between different energy states. These energy changes can be associated with electronic motion (UV/Vis), vibrational motion (IR), or rotational motion (microwave), depending on the energy scale.

In this lab, you will investigate the absorption spectrum of gaseous hydrogen chloride (HCl) in the IR region. IR absorption increases the vibrational energy of the molecule. Because rotational and vibrational motion are coupled, a vibrational transition is typically accompanied by a change in rotational state, and the resulting spectrum is called a *rotation-vibration (rovibrational)* spectrum. Only molecules with a (permanent or vibration-induced) dipole moment can give such IR spectra.

Rigid rotor (rotation)

In the rigid rotor model one assumes that the molecule is completely stiff, i.e. the bond length does not change during rotation. The rotational energy levels are

$$E_J = \frac{\hbar^2}{8\pi^2 I} J(J+1), \quad (1.1)$$

where $\hbar = 6.626 \times 10^{-34}$ Js is Planck's constant, $J = 0, 1, 2, \dots$ is the rotational quantum number, and

$$I = \mu r^2 \quad (1.2)$$

is the moment of inertia. Here r is the bond length and μ is the reduced mass:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (\text{diatomic molecule}). \quad (1.3)$$

Because experimental IR spectra are plotted versus wavenumber (cm^{-1}), the rotational constant is usually expressed as a wavenumber:

$$\tilde{B} = \frac{\hbar}{8\pi^2 c I}, \quad (\text{SI unit: } \text{m}^{-1}; \text{ spectra often use } \text{cm}^{-1}). \quad (1.4)$$

The rotational energy can then be written as

$$E_J = hc\tilde{B}J(J + 1). \quad (1.5)$$

Note that the energy separation between rotational levels increases with J since the term is proportional to $J(J + 1)$ (Eq. 1.1); the corresponding allowed rotational transitions are shown in Fig. 1.1.



Figure 1.1: Allowed rotational transitions for a rigid diatomic molecule.

Harmonic oscillator (vibration)

The simplest model for vibrational motion is the harmonic oscillator (“mass on a spring”). The potential energy is

$$V(x) = \frac{1}{2}kx^2, \quad (1.6)$$

where $x = R - R_e$ is the displacement from the equilibrium bond length R_e and k is the force constant. Solving the Schrödinger equation gives vibrational energies

$$E_v = \hbar\omega \left(v + \frac{1}{2}\right), \quad (1.7)$$

where $v = 0, 1, 2, \dots$ is the vibrational quantum number and

$$\omega = \sqrt{\frac{k}{\mu}} \quad (1.8)$$

is the vibrational angular frequency. In the harmonic model, the spacing between neighboring vibrational levels is constant; the corresponding allowed vibrational transitions are shown in Fig. 1.2.

Rovibration and corrections (anharmonicity + vibration–rotation coupling)

In practice, vibrational and rotational motion occur simultaneously. As a starting point we treat the molecule as a harmonic oscillator (vibration) combined with a rigid rotor (rotation), so that the total energy is the sum

$$E_{v,J} = E_v + E_J = \hbar\omega \left(v + \frac{1}{2}\right) + hc\tilde{B}J(J + 1), \quad v, J = 0, 1, 2, \dots \quad (1.9)$$

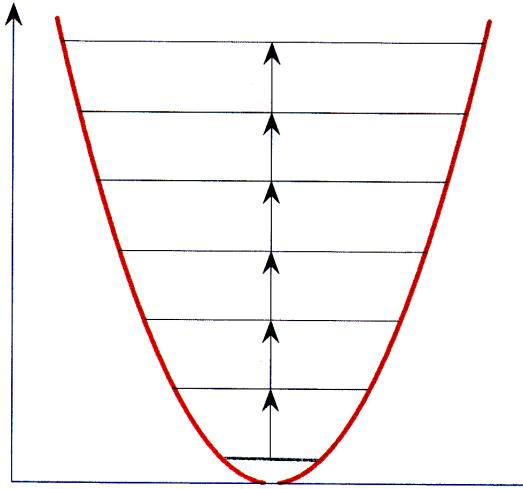


Figure 1.2: Allowed vibrational transitions for a harmonic oscillator.

The model (1.9) is approximate. Two important real-molecule effects are:

- **Anharmonicity:** the bond is not a perfect spring. At higher v the vibrational level spacing decreases, and ultimately the bond can dissociate as shown in Fig. 1.3.
- **Vibration–rotation coupling:** the average bond length is slightly larger in higher vibrational states, which increases the moment of inertia $I = \mu r^2$ and therefore decreases the rotational constant.

A common first improvement beyond the harmonic-oscillator/rigid-rotor model is to (i) include the leading anharmonic correction to the vibrational energy and (ii) allow the rotational constant to depend on the vibrational state v :

$$E_{v,J} \approx hc \left[\tilde{\omega}_e \left(v + \frac{1}{2} \right) - \tilde{\omega}_e x_e \left(v + \frac{1}{2} \right)^2 \right] + hc \tilde{B}_v J(J+1), \quad (1.10)$$

Here a tilde denotes a wavenumber, i.e. $\tilde{\omega} = \omega/(2\pi c)$ (typically reported in cm^{-1}), and the subscript e refers to values defined at the equilibrium geometry. $\tilde{\omega}_e$ is the harmonic vibrational constant, x_e is the (dimensionless) anharmonicity constant, and the product $\tilde{\omega}_e x_e$ sets the size of the first anharmonic correction. The decrease of the rotational constant with increasing v (due to a slightly larger average bond length in higher vibrational states) is often modeled as

$$\tilde{B}_v = \tilde{B}_e - \alpha_e \left(v + \frac{1}{2} \right), \quad (1.11)$$

where \tilde{B}_e is the rotational constant at the equilibrium bond length and α_e (cm^{-1}) is the vibration–rotation coupling constant.

Anharmonicity also implies that the potential flattens at large bond distances and the molecule can eventually reach a continuum of dissociated states. In that picture D_0 (introduced later) measures the depth from the bottom of the well to the lowest dissociation limit. The anharmonic level spacing contracts with increasing v , hinting at the finite number of bound levels and the possibility of bond breaking.

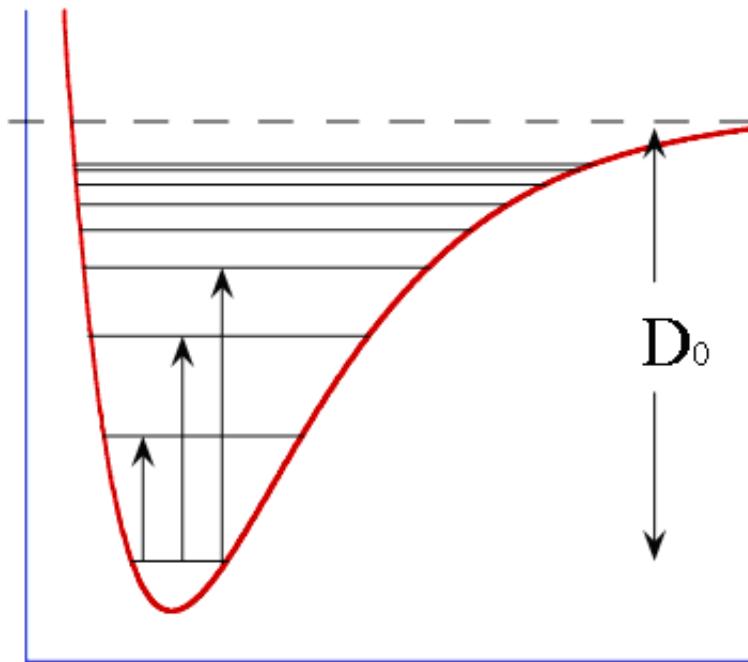


Figure 1.3: Anharmonic oscillator (Morse-like). Higher v states lie closer together and the bond can dissociate (D_0).

Selection rules and branch structure

For IR rovibrational spectroscopy of a heteronuclear diatomic molecule, the dominant (fundamental) band follows

$$\Delta v = \pm 1, \quad \Delta J = \pm 1. \quad (1.12)$$

The $\Delta J = \pm 1$ rule produces two sets (branches) of lines:

- **R branch:** $\Delta J = +1$
- **P branch:** $\Delta J = -1$

A Q branch would correspond to $\Delta J = 0$, but it is not observed here in the simple diatomic rovibrational electric-dipole picture.

In real spectra, line intensities reflect the Boltzmann population of the lower rotational levels: at room temperature most HCl molecules occupy low J values, so lines near the band origin are strongest and weaken at higher $|m|$. Population factors and the negative c coefficient (see below) together make the branch envelopes appear smooth and gently tapered.

Anharmonicity allows overtones with

$$\Delta v = \pm 1, \pm 2, \pm 3, \dots \quad (1.13)$$

but these are much weaker than the fundamental.

Line positions for the fundamental band

We focus on the fundamental rovibrational band, i.e. the transition from the ground vibrational state to the first excited state ($v'' = 0 \rightarrow v' = 1$). For this band, the observed transition wavenumbers can be written as

$$\tilde{\nu}_R = \tilde{\omega}_0 + (\tilde{B}_1 + \tilde{B}_0)(J'' + 1) + (\tilde{B}_1 - \tilde{B}_0)(J'' + 1)^2 \quad (J'' = 0, 1, 2, \dots) \quad (1.14)$$

for the R branch ($\Delta J = +1$, with $J' = J'' + 1$), and

$$\tilde{\nu}_P = \tilde{\omega}_0 - (\tilde{B}_1 + \tilde{B}_0)(J' + 1) + (\tilde{B}_1 - \tilde{B}_0)(J' + 1)^2 \quad (J' = 0, 1, 2, \dots) \quad (1.15)$$

for the P branch ($\Delta J = -1$, with $J'' = J' + 1$). Introducing $m = J'' + 1$ for R ($m = +1, +2, \dots$) and $m = -J'$ for P ($m = -1, -2, \dots$) combines both cases into

$$\tilde{\nu}_{R,P}(m) = \tilde{\omega}_0 + (\tilde{B}_1 + \tilde{B}_0)m + (\tilde{B}_1 - \tilde{B}_0)m^2, \quad (1.16)$$

where $\tilde{B}_0 \equiv \tilde{B}_{v=0}$ and $\tilde{B}_1 \equiv \tilde{B}_{v=1}$ are the rotational constants in the lower and upper vibrational states, respectively, and $m = \pm 1, \pm 2, \pm 3, \dots$. Positive m correspond to the R branch and negative m to the P branch. Because $\tilde{B}_1 < \tilde{B}_0$, the coefficient $(\tilde{B}_1 - \tilde{B}_0)$ is negative, so the line spacing decreases slightly as $|m|$ increases.

Only transitions that satisfy both $\Delta v = \pm 1$ and $\Delta J = \pm 1$ are observed here; the full set of formally allowed transitions is narrowed by these selection rules and by dipole constraints.

1.2 Preparation

1. With the selection rules in mind: what molecular vibrations can be studied using IR spectroscopy? Which diatomic molecules can be studied?
2. Describe limitations of the harmonic oscillator model for IR vibrations. Describe a more realistic model introduced in this course.
3. Describe limitations of the rigid rotor model for rotation. Which more realistic correction do you know?
4. Discuss the selection rules for rotation–vibration spectroscopy and the meaning of the P and R branches.
5. How is the rotational constant obtained from a rovibrational spectrum?
6. Derive an expression for the bond distance r as a function of the rotational constant using Eqs. 1.2 and 1.4.

1.3 Instructions

In a full experiment, one fills a gas cuvette with HCl vapor and records an IR spectrum. **HCl is highly corrosive.**

For this lab session: a recorded IR spectrum will be **provided** for analysis.

Data analysis roadmap (read this first)

You will fit the provided line positions to Eq. 1.16 by using m as the x-variable. Use the conventions:

$$\begin{aligned} R(J'') : \quad m &= J'' + 1 \quad (J'' = 0, 1, 2, \dots) \\ P(J'') : \quad m &= -J'' \quad (J'' = 1, 2, 3, \dots) \end{aligned}$$

Fit $\tilde{\nu}$ versus m to $y = a + bx + cx^2$, then identify

$$a = \tilde{\omega}_0, \quad b = \tilde{B}_1 + \tilde{B}_0, \quad c = \tilde{B}_1 - \tilde{B}_0. \quad (1.17)$$

Hence,

$$\tilde{B}_1 = \frac{b+c}{2}, \quad \tilde{B}_0 = \frac{b-c}{2}, \quad \alpha_e = \tilde{B}_0 - \tilde{B}_1. \quad (1.18)$$

Unit note: If you use SI values of h , c , and μ in the bond-length expression, convert \tilde{B} from cm^{-1} to m^{-1} via $\tilde{B}(\text{m}^{-1}) = 100 \tilde{B}(\text{cm}^{-1})$.

Data analysis tasks

- Identify the absorption peaks for the R and P branches and make a table like Table 1.1. Identify as many peaks as you can.

Question: Why is each line within both branches split into two lines? *Hint: consider isotopes ($H^{35}\text{Cl}$ and $H^{37}\text{Cl}$) and the reduced mass.*

Table 1.1: Example table for assigned line positions (fill in your measured wavenumbers).

m	Peak	cm^{-1}	m	Peak	cm^{-1}
+10	R(9)		-1	P(1)	
+9	R(8)		-2	P(2)	
+8	R(7)		-3	P(3)	
+7	R(6)		-4	P(4)	
+6	R(5)		-5	P(5)	
+5	R(4)		-6	P(6)	
+4	R(3)		-7	P(7)	
+3	R(2)		-8	P(8)	
+2	R(1)		-9	P(9)	
+1	R(0)		-10	P(10)	

- Using *Excel* (e.g. a 2nd-order polynomial trendline), *Python* (e.g. `numpy.polyfit`), or any other fitting tool, fit your data to

$$y = a + bx + cx^2, \quad (1.19)$$

where $x = m$ and $y = \tilde{\nu}$ (cm^{-1}). From this fit, a , b , and c correspond to $\tilde{\omega}_0$, $(\tilde{B}_1 + \tilde{B}_0)$, and $(\tilde{B}_1 - \tilde{B}_0)$, respectively.

3. From your results, calculate \tilde{B}_0 and \tilde{B}_1 . Also calculate the coupling constant

$$\alpha_e = \tilde{B}_0 - \tilde{B}_1. \quad (1.20)$$

From the rotational constants and Eq. 1.4, calculate r_0 and r_1 . Discuss the difference between r_0 and r_1 . What does this difference mean physically?

4. For the first overtone band, an analogous expression to Eq. 1.16 leads to

$$\tilde{\omega}'_0 = 2\tilde{\omega}_e(1 - 3x_e). \quad (1.21)$$

We can rewrite the two relations as

$$\tilde{\omega}_e = \frac{\tilde{\omega}_0}{(1 - 2x_e)}, \quad (1.22)$$

and

$$\tilde{\omega}_e = \frac{\tilde{\omega}'_0}{2(1 - 3x_e)}. \quad (1.23)$$

Setting Eqs. 1.22 and 1.23 equal gives

$$\frac{\tilde{\omega}_0}{1 - 2x_e} = \frac{\tilde{\omega}'_0}{2(1 - 3x_e)}. \quad (1.24)$$

Cross-multiplying and rearranging yields

$$2\tilde{\omega}_0(1 - 3x_e) = \tilde{\omega}'_0(1 - 2x_e), \quad (1.25)$$

which can be regrouped to

$$\tilde{\omega}'_0 - 2\tilde{\omega}_0 = x_e(2\tilde{\omega}'_0 - 6\tilde{\omega}_0). \quad (1.26)$$

Solving for x_e gives

$$x_e = \frac{\tilde{\omega}'_0 - 2\tilde{\omega}_0}{2\tilde{\omega}'_0 - 6\tilde{\omega}_0}. \quad (1.27)$$

A literature value $\tilde{\omega}'_0 = 5668 \text{ cm}^{-1}$ has been reported for H³⁵Cl. Using this value and your experimental $\tilde{\omega}_0$, calculate x_e (Eq. 1.27) and then $\tilde{\omega}_e$ (Eqs. 1.22–1.23).

5. The dissociation energy D_0 can be estimated from

$$D_0 = \frac{hc\tilde{\omega}_e}{4x_e} - \frac{1}{2}hc\tilde{\omega}_e \left(1 - \frac{1}{2}x_e\right). \quad (1.28)$$

Calculate D_0 in kJ for HCl using your result from the previous task. Compare your result with the value given in Atkins (Table 43.1, p. 954).

FTIR spectrum (reference)

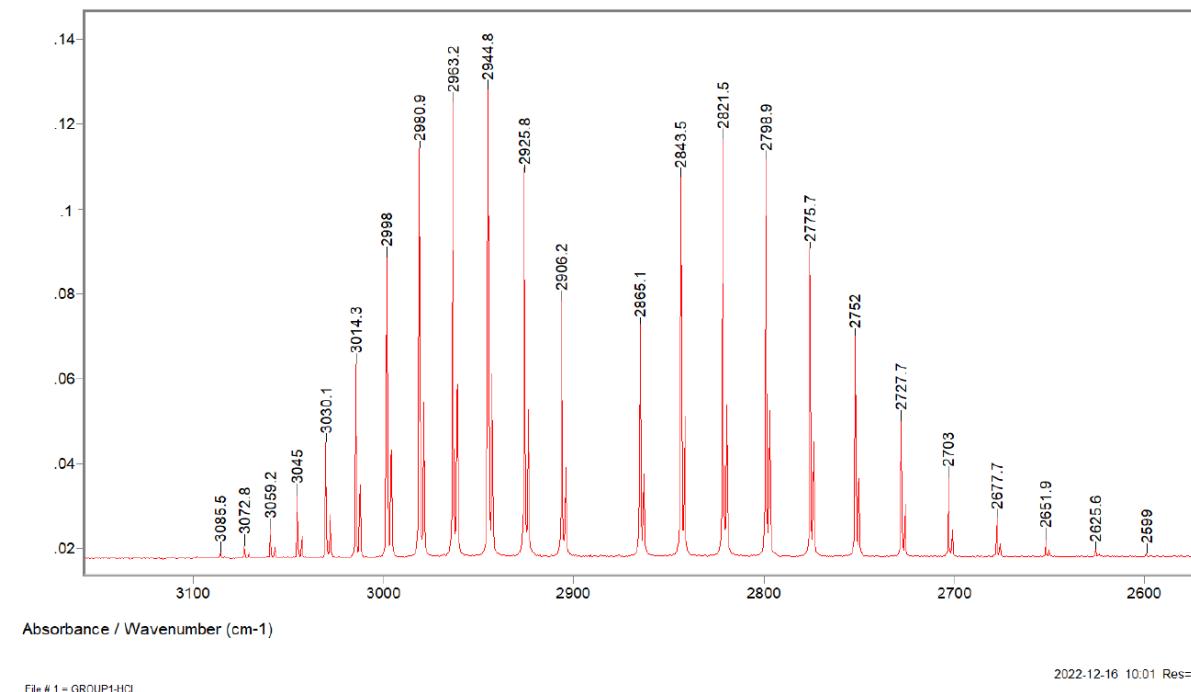


Figure 1.4: HCl FTIR reference spectrum.