Vibrational-Rotational Spectra of HCl

Introduction

In this experiment, we measure the infrared (IR) vibrational spectrum of a linear diatomic HCl molecule in the gas phase with rotational resolution, i.e., with the rotational fine structure. The IR range of the spectrum extends from 1 μm (the long-wavelength end of the visible region) to 1000 μm in the microwave region. In terms of wavenumbers, this corresponds to 10,000 cm^{-1} to 10 cm^{-1}. We will use the FTIR spectrometer, which employs the absorption technique; radiation from the source emitting IR frequencies (4000-400 cm^{-1}) is passed through sample, a cell filled with the gaseous HCl. When the radiation frequency matches a vibrational frequency of the molecule, the molecule may become vibrationally excited by absorbing this radiation. Then, energy is lost from the radiation and this results in an absorption band. The FTIR spectrometer records absorption bands with high resolution, with a best resolution of 0.5 cm^{-1}. Whereas the spectrum of a polyatomic molecule contains multiple absorption bands corresponding to different vibrational motions, a diatomic molecule, such as HCl, has only one vibrational mode (bond stretching). In the meantime, high resolution of the spectrometer allows us to observe excitations from and to various rotational states of the HCl molecule thus providing the rotational resolution.

<u>Theory</u>

In the first approximation, energy levels of HCl can be described in terms of the Rigid Rotor – Harmonic Oscillator (RRHO) model. Here, the allowed energy levels of a harmonic oscillator are

$$E(v) = h\nu\left(v + \frac{1}{2}\right) \tag{1}$$

where v is the vibrational quantum number (0, 1, 2, …); ν is the vibrational frequency; and h is the Planck constant. The allowed energy levels of a rigid rotor are expressed as

$$E(J) = \frac{h^2}{8\pi^2 I} J(J + 1) \tag{2}$$

where J is the rotational quantum number (0, 1, 2, …), I is the moment of inertia, $I = \mu r^2$, with r being the internuclear distance, and μ - the reduced mass, $\mu = m_1 m_2/(m_1 + m_2)$.

In the RRHO model, the total energy of the molecule is simply a sum of the vibrational (harmonic oscillator) and rotational (rigid rotor) energies. However, a more accurate expression includes additional terms, such as deviation from the harmonic oscillator behavior (anharmonicity), deviation from the rigid rotor behavior, and coupling between the rotational motions. Conversion of energy to the units of wavenumbers ($1/\alpha$, in cm^{-1}) gives the expression of molecular energy levels as *term values* T depending on the vibrational quantum number v and the rotational quantum number J:

$$T(v,J) = \omega_e\left(v + \frac{1}{2}\right) - \omega_e x_e\left(v + \frac{1}{2}\right)^2 + B_e J(J + 1) - D_e J^2(J + 1)^2 - \alpha_e\left(v + \frac{1}{2}\right)J(J + 1) \tag{3}$$

The first and third term in Eq. (4) come from the RRHO model. Here, the rotational constant B_e is defined as

$$B_e = \frac{h}{8\pi^2 I_e c} \tag{4}$$

where I_e is the moment of inertia corresponding to the equilibrium internuclear distance r_e and c is the speed of light in cm s^{-1}. The second term accounts for anharmonicity, i.e., the deviation of the potential energy of the diatomic molecules from harmonic behavior. The fourth term (involving the constant D_e) describes the effect of centrifugal stretching, i.e., a change of the internuclear distance during rotation of the molecule. This effect is significant only for very fast rotation corresponding to high values of J and hence, D_e is usually very small. The fifth term in Eq. (4) accounts for coupling between vibration and rotation originating from the fact that during a vibration the internuclear

distance r changes thus changing the moment of inertia and hence the rotational energy. Even though the constant α_e is quite small, this term should not be neglected.

Absorption of a photon of light (an IR photon in this experiment) occurs only when the wavenumber of the photon ($\tilde{\nu} = 1/\lambda$) matches the difference between the final and initial term values, $T_f(v_f,J_f) - T_i(v_i,J_i)$. Upon this absorption, the molecule gets excited from the initial rotational-vibrationl (rovibrational) state to the final rovibrational state. Therefore, the absorption peaks observed in IR spectra correspond to various rovibrational term differences. However, not all transitions are allowed by quantum mechanics and hence not the whole variety of term differences needs to be considered when the IR spectrum is analysed. Allowed transitions are determined by the selection rules. The RRHO slection rules are $\Delta v = \pm 1$, $\Delta J = 0, \pm 1$, but for most diatomics, including HCl, $\Delta J = 0$ is not allowed. For an anharmonic diatomic molecule the $\Delta J = (0), \pm 1$ selction rule remains valid, but weak transition to $\Delta v = \pm 2, \pm 3$, etc., called overtones may be observed. In this experiment, we will observe only the most intense absorption band (called "fundamental") corresponding to $\Delta v = +1$ from the vibrational quantum number $v'' = 0$ to the vibrational quantum number $v' = 1$ – here and below double prime denotes the initial (ground) state and prime denotes the final (excited) state. In the meantime, as a result of a transition, the rotational quantum number can either increase by 1, $\Delta J = +1$ ($J' = J'' + 1$), or decrease by 1, $\Delta J = -1$ ($J' = J'' - 1$). These two cases give rise to two different branches in the absorption band, the R branch and the P branch (see Figure 1). The Q branch corresponding to $\Delta J = 0$ ($J' = J''$) is forbidden for most diatomic molecules, including HCl (but it is allowed for NO, for example; see a physical chemistry text such as Aktins and de Paula to learn why).

Figure 1, Origin of the P, Q, and R branches in rovibrational spectra (adopted from Wikipedia)
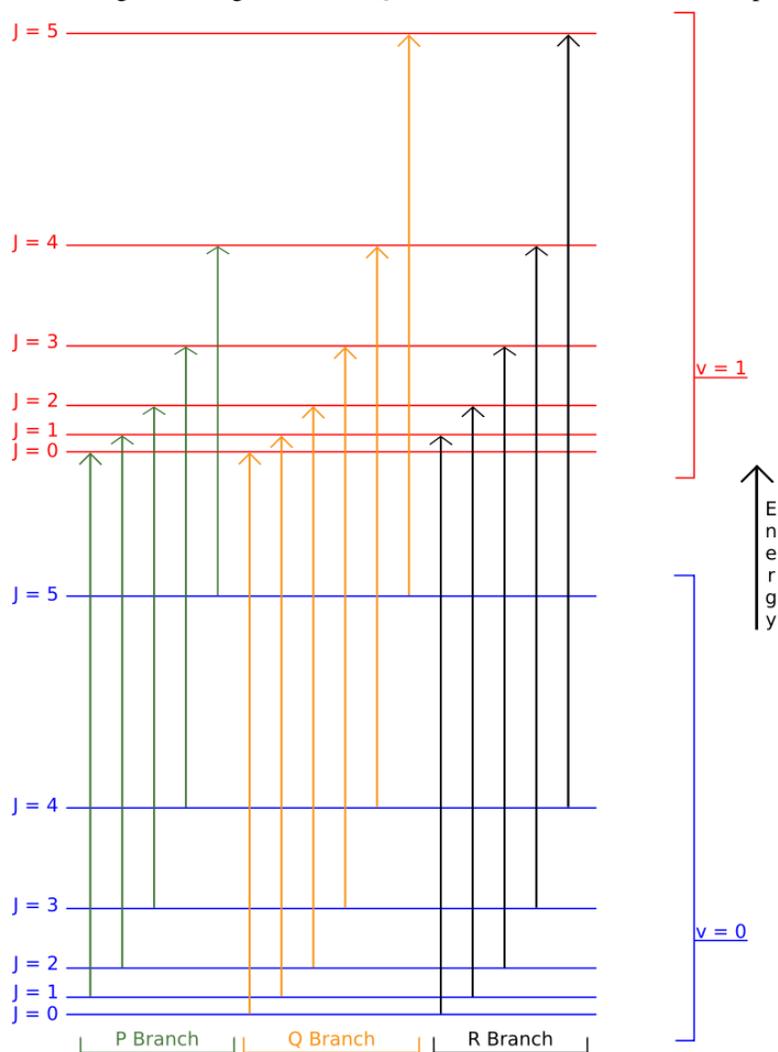
The expressions for the wavenumbers of the absorption peaks in the R and and P branches can be then derived as the following:

$$\check{v}_R = T(v=1, J'=J''+1) - T(v=0, J'=J'') = \omega_0 + (2B_e - 3\alpha_e) + (2B_e - 4\alpha_e)J'' - \alpha_e J''^2$$

$$J'' = 0, 1, 2, \ldots \quad (5)$$

$$\check{v}_P = T(v=1, J'=J''-1) - T(v=0, J'=J'') = \omega_0 - (2B_e - 2\alpha_e)J'' - \alpha_e J''^2$$

$$J'' = 1, 2, 3, \ldots \quad (6)$$

Here, the D_e term was dropped and ω_0 is the wavenumber of the forbidden transition from the Q branch:

$$\omega_0 = \omega_e - 2\omega_e x_e \quad (7)$$

The two equations (5) and (6) can be combined into one if we introduce a new variable $m = J'' + 1$ for the R branch and $m = -J''$ for the P branch:

$$\check{v}(m) = \omega_0 + (2B_e - 2\alpha_e)m - \alpha_e m^2 \quad (8)$$

If we keep the D_e term in Eq. (3) and assume that the centrifugal distortion is identical in the ground and excited vibrational states, we get

$$\check{v}(m) = \omega_0 + (2B_e - 2\alpha_e)m - \alpha_e m^2 - 4D_e m^3 \quad (9)$$

Equation (9) will be used in the analysis of the infrared red spectrum of HCl to derive constants of this diatomic molecule, including the fundamental vibrational frequency ω_0, rotational constant B_e (and hence the moment of inertia I_e and the internuclear distance r_e), the centrifugal distortion constant D_e, and the vibrational-rotational coupling constant α_e.

Experimental

The infrared gas cell is constructed from a short-length large-diameter tubing with salt (NaCl) windows, which are transparent to the IR light. The windows are clamped against the O-rings and are sealed with resin. The cell is first evacuated with a vacuum pump and used to run the background on the spectrometer. A gas-handling system is shown in Figure 2. The cell is attached at D. When stopcock C open and B closed, open stopcock A and pump out the system. The needle valve of the HCl cylinder needs to be closed. Then, open B and continue pumping. After the pumping out is completed, the pump is switched of, stopcocks A, B, and C are closed, and the cell can be disconnected from the system. After running the background on the spectrometer, the cell is reconnected, the system is pumped out again and then, the cell is filled with the HCl gas from a cylinder to a pressure of about 100 Torr. To fill the cell, close A and slowly open the valve on the HCl cylinder. When the system is filled to the recommended pressure, close the valve on the HCl cyclinder, then close B and C. Remove the cell and take the spectrum at the highest available resolution (0.5 cm⁻¹).

Figure 2. Gas-handling system for filling infrared cell.
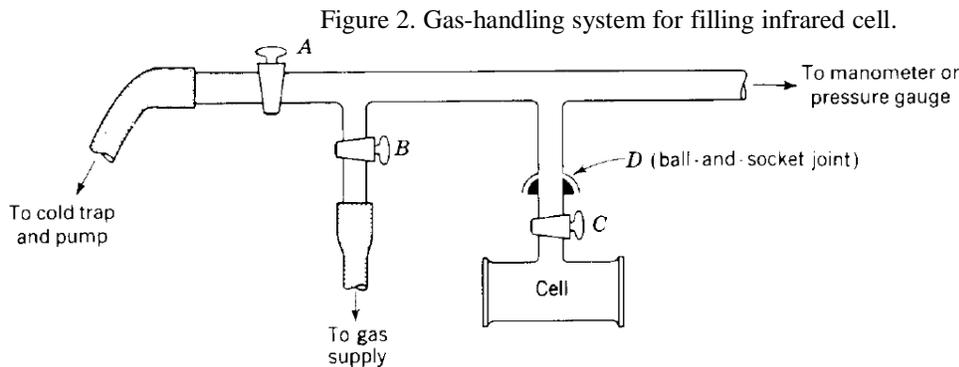
Calculations and Lab Report

A sample HCl spectrum is given below, 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.

Figure 3. Infrared spectrum of HCl
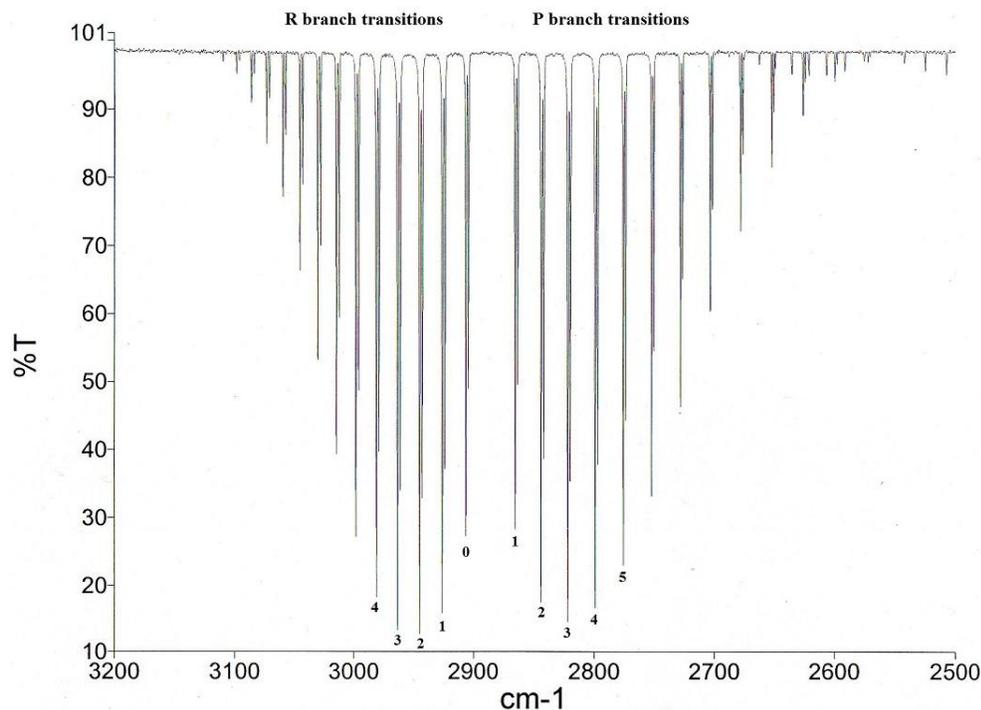
(1) Create a table that associates peak frequencies (in cm^{-1}) with values of m for each isotopomer. Each table will have peak assignments and peak locations - one table for the $^1H^{35}Cl$ molecules and the other table for the $^1H^{37}Cl$ molecules. Because the reduced masses of these two isotopic forms of the HCl molecule are close to one another, you will observe pairs of peaks in your spectrum. For each pair of peaks, the higher intensity (and higher energy) peak belongs to the $^1H^{35}Cl$ molecules (^{35}Cl natural abundance is ~ 75%) and the lower intensity (and lower energy) peak belongs to the $^1H^{37}Cl$ molecules (^{37}Cl natural abundance is ~ 25%). Please list the peaks in each table in order from lowest energy to highest energy

It is useful to recall that the set of peaks at lower energies than the central gap in the spectrum are the P branch transitions ($\Delta J = -1$ peaks) and the set of peaks at higher energies than the central gap are the R branch transitions ($\Delta J = +1$ peaks). The two peaks on either side of the central gap are the P_1 peak (lower energy side) and R_0 peak (higher energy). Moving away from the central gap, the peak numbering increases by one as you move from peak to peak (P_1, P_2, P_3, ... as you move to lower energies than the central gap, and R_0, R_1, R_2, ...as you move to higher energies than the central gap).

Your tables should have include the values for m for each peak ($m = J'' + 1$ for the R branch and $m = -J''$ for the P branch). So, for example, $m = -3$ for the P_3 transition, and $m = 5$ for the R_4 transition. By defining this new label for the peaks, this allows us to do a single fit to all of the peaks, both the P branch and the R branch transitions.

(2) Fit the data in each table to a third-order polynomial to determine the spectroscopic constants. The equation to which the peak locations will be fit is Eq. (9), where $\tilde{\nu}(m)$ is the peak location in units of cm^{-1}. Note that ω_0, B_e, α_e, and D_e will also have units of cm^{-1}. Since Eq. (9) is a cubic equation in m, the "best fit" values for ω_0, B_e, α_e, and D_e. can be found by comparing the coefficients of the fit to the coefficents of the powers of m in Eq. (9). Note

that the D_e value is expected to be small. Use the value of B_e to calculate the moment of inertia I_e and the internulcear distance r_e.

(3) For the $^1H^{35}Cl$ isotopomer, you should compare your values for ω_0, B_e, r_e, α_e, and D_e to the values listed at the NIST website (http://webbook.nist.gov/chemistry/form-ser.html). You will have to calculate a value for ω_0 using Eq. (7), $\omega_0 = \omega_e - 2\omega_e x_e$, where ω_e and $\omega_e x_e$ are taken from the NIST website.

(4) You should also calculate predicted values for the $^1H^{37}Cl$ constants ω_0 and B_e using the relationships

$$(\omega_0*/\omega_0) = (\mu/\mu*)^{1/2} \tag{10}$$

and

$$(B_e*/B_e) = (\mu/\mu*) \tag{11}$$

where the "*" indicates values for the $^1H^{37}Cl$ molecules, and μ, the reduced mass. Values for the masses of ^1H, ^{35}Cl, and ^{37}Cl are the following (in atomic mass units): $^1H = 1.007825$, $^{35}Cl = 34.968853$, $^{37}Cl = 36.965903$. Note that Eq. (10) really applies to ω_e, but it should be approximately correct for ω_0.

(5) Your report should contain a discussion of the degree of agreement between the constants you find for $^1H^{35}Cl$ and those given at the NIST website, and how well the values for ω_0 and B_e predicted for $^1H^{37}Cl$ compare to those found experimentally. You do not need to give confidence limits for your experimental values for ω_0, B_e, or α_e.

References

Atkins, P. W. and J. de Paula Physical Chemistry, 10th Edition. New York: W. H. Freeman, 2014.
Garland, C. W., J. W. Nibler, D. P. Shoemaker Experiments in Physical Chemistry, 8th Edition. New York: McGraw-Hill, 2009.

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