Vibrational-Rotational Spectra of HCl and DCl

1   Introduction

This experiment is concerened with the the rotational fine structure of the infrared vibrational spectrum of a linear molecule such as HCl. From an interpretation of the details of this spectrum it is possible to obtain the moment of inertia of the molecule and thus the internuclear separation. In addition, the pure vibrational frequency determines a force constant that is a measure of the bond strength. By a study of DCl also, the isotope effect can be observed.

2   Theory

The simplest model of a vibrating diatomic molecule is a harmonic oscillator, for which the potential energy depends quadratically on the change in internuclear distance. The allowed energy levels of a harmonic oscillator, as calculated from quantum mechanics, are

$$E(v) = h\nu(v + \tfrac{1}{2}) \tag{1}$$

where v is the vibrational quantum number having integral values $0, 1, 2, ...$; ν is the vibrational frequency; and h is Planck's constant.

The simplest model of a rotating diatomic molecule is a rigid rotor or "dumbbell" model in which the two atoms of mass m_1 and m_2 are considered to be joined by a rigid, weightless rod. The allowed energy levels for a rigid rotor may be shown by quantum mechanics to be

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

where the rotational quantum number J may take integral values $0, 1, 2, ...$ The quantity I is the moment of inertia, which is related to the internuclear distance r and the reduced mass $\mu = m_1 m_2 / (m_1 + m_2)$ by

$$I = \mu r^2 \tag{3}$$

Since a real molecule is undergoing both rotation and vibration simultaneously, a first approximation to its energy levels $E(v, J)$ would be the sum of expressions (1) and (2). A more complete expression for the energy levels of a diatomic molecule is given below, with the levels expressed as *term values* T in cm^{-1} units rather than as energy values E in joules:

$$T(v, J) = \frac{E(v, J)}{hc} = \tilde{\nu}_e(v + \tfrac{1}{2}) - \tilde{\nu}_e x_e(v + \tfrac{1}{2})^2 + B_e J(J + 1) - D_e J^2(J + 1)^2 - \alpha_e(v + \tfrac{1}{2})J(J + 1) \tag{4}$$

where c is the speed of light in cm/s, $\tilde{\nu}_e$ is the frequency in cm^{-1} for the molecule vibrating about its equilibrium internuclear separation r_e, and

$$B_e = \frac{h}{8\pi^2 I_e c} \tag{5}$$

The first and third terms on the right hand side of Eq. (4) are the harmonic oscillator and the rigid rotor terms with r equal to r_e. The second term (involving the constant x_e) takes into account the effect of anharmonicity. Since the real potential $U(r)$ for a molecule differs from a harmonic potential U_{harm} (see
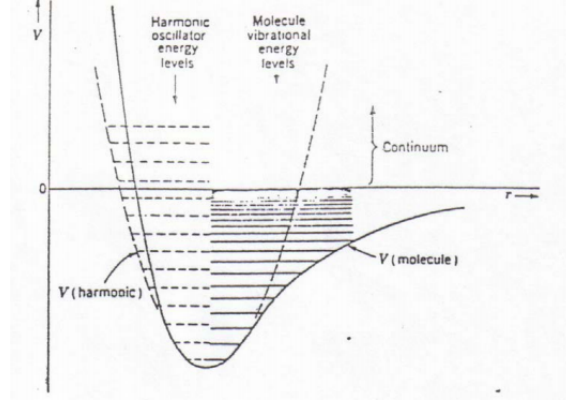
Figure 1: Schematic diagram showing potential energy U as a function of internuclear separation r for a diatomic molecule. The harmonic potential is indicated by the dashed curve. The vibrational levels are also shown.

Fig. 1), the real vibrational levels are not quite those given by Eq. (1) and a correction term is required. The fourth term (involving the constant D_e) takes into account the effect of centrifugal stretching. Since a chemical bond is not truly rigid but more like a stiff spring, it stretches somewhat when the molecule rotates. Such an effect is important only for high J values, since the constant D_e is usually very small. The last term in Eq. (4) accounts for interaction between vibration and rotation. During a vibration the internuclear distance r changes; this changes the moment of intertia and affects the rotation of the molecule. The constant α_e is also quite small, but this term should not be neglected.

Selection Rules. The harmonic oscillator, rigid rotor selection rules are $\Delta v = \pm 1$ and $\Delta J = \pm 1$; that is, infrared emission or absorption can occur only when these "allowed" transitions take place. For an anharmonic diatomic molecule, the $\Delta J = \pm 1$ selection rule is still valid, but weak transitions corresponding to $\Delta v = \pm 2, \pm 3$, etc. (overtones) can be observed. Since we are interested in the most intense absorption band (the "fundamental"), we are concerned with transitions from various J'' levels of the vibrational ground state ($v'' = 0$) to J' levels in the first excited vibrational state ($v' = 1$). From the selection rule we know that the transition must be from J'' to $J' = J'' \pm 1$. Since $\Delta E = h\nu = hc\tilde{\nu}$, the frequency $\tilde{\nu}$ (in wavenumbers) for this transition will be just $T(v', J') - T(v'', J'')$. When $\Delta J = +1$ ($J' = J'' + 1$) and $\Delta J = -1$ ($J' = J'' - 1$), we find, respectively, from Eq. (4) that

$$\tilde{\nu}_R = \tilde{\nu}_0 + (2B_e - 3\alpha_e) + (2B_e - 4\alpha_e)J'' - \alpha_e J''^2 \qquad J'' = 0, 1, 2, ... \tag{6}$$

$$\tilde{\nu}_P = \tilde{\nu}_0 - (2B_e - 2\alpha_e)J'' - \alpha_e J''^2 \qquad J'' = 0, 1, 2, ... \tag{7}$$

where the D_e term has been dropped and $\tilde{\nu}_0$, the frequency of the *forbidden* transition from $v'' = 0$, $J'' = 0$ to $v' = 1$, $J' = 0$, is

$$\tilde{\nu}_0 = \tilde{\nu}_e - 2\tilde{\nu}_e x_e \tag{8}$$

The two series of lines given in Eqs. (6) and (7) are called R and P branches, respectively. These allowed transitions are indicated on the energy-level diagram given in Fig. 2. If α_e were negligible, Eqs. (6) and (7) would predict a series of equally spaced lines with separation $2B_e$ except for a missing line at $\tilde{\nu}_0$. The effect of interaction between rotation and vibration (nonzero α_e) is to draw the lines in the R branch closer together and spread the lines in the P branch farther apart as shown for a typical spectrum in Fig. 3. For convenience let us introduce a new quantity m, where $m = J'' + 1$ for the R branch and $m = -J''$ for the P branch as shown in Fig. 3. It is now possible to replace Eqs. (6) and (7) by a single equation

$$\tilde{\nu}(m) = \tilde{\nu}_0 + (2B_e - 2\alpha_e)m - \alpha_e m^2 \tag{9}$$

where m takes all integral values and $m = 0$ yields the frequency $\tilde{\nu}_0$ of the forbidden "purely vibrational" transition. If one retains the D_e term of Eq. (4) (which assumes $D'' = D' = D_e$), Eq. (9) takes the form
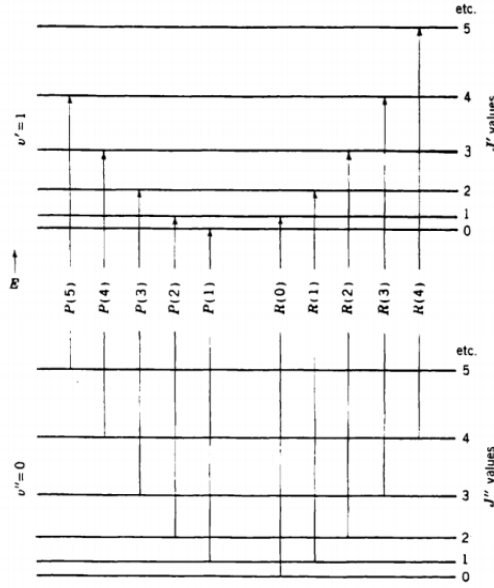
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Figure 2: Rotational energy levels for the ground vibrational state ($v'' = 0$) and the first excited vibrational state ($v' = 1$) in a diatomic molecule. The vertical arrows indicate allowed transitions in the R and P branches; numbers in parentheses index the value J'' of the lower state. Transitions in the Q branch ($\Delta J = 0$) are not shown since they are not infrared active.

$$\tilde{\nu}(m) = \tilde{\nu}_0 + (2B_e - 2\alpha_e)m - \alpha_e m^2 - 4D_e m^3 \tag{10}$$

Thus a multiple linear regression can be performed to determine $\tilde{\nu}_0$, B_e, α_e, and D_e.

   Isotope Effect. When an isotopic substitution is made in a diatomic molecule, the equilibrium bond length r_e and the force constant k are unchanged, since they depend only on the behavior of the bonding electrons. However, the reduced mass μ does change, and this will affect the rotation and vibration of the molecule. In the case of rotation, the isotope effect can be easily stated. From the definition of B_e and I, we see that

$$\frac{B_e^*}{B_e} = \frac{\mu}{\mu^*} \tag{11}$$

where an asterisk is used to distinguish one istopic molecule from another.

   For a harmonic oscillator model, the frequency $\tilde{\nu}_e$ in wavenumbers is given by

$$\tilde{\nu}_e = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{\frac{1}{2}} \tag{12}$$

which leads to the relation

$$\frac{\tilde{\nu}_e^*}{\tilde{\nu}_e} = \left(\frac{\mu}{\mu^*}\right)^{\frac{1}{2}} \tag{13}$$

The ratio $\tilde{\nu}_0^*/\tilde{\nu}_0$ differs slightly from this harmonic ratio dues to deviation of the true potential function from a quadratic form, as depicted in Fig. 1. A closer approximation to the solid curve can be had by adding cubic and higher anharmonic terms to $U(r)$, i.e.,

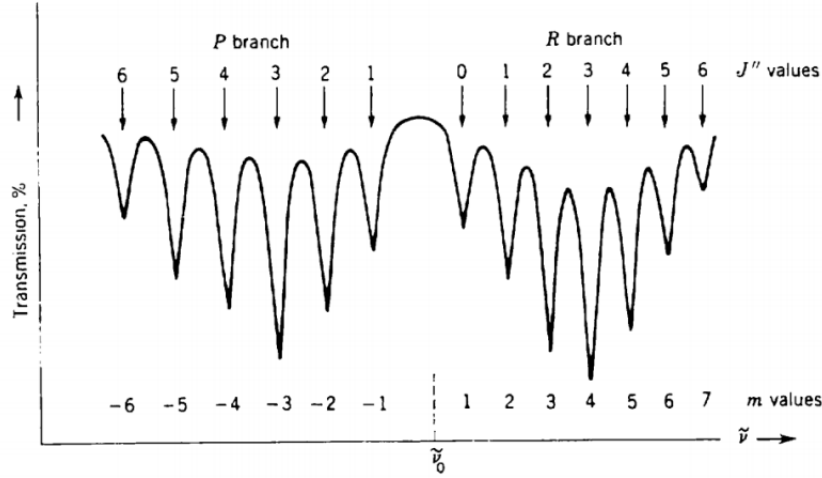$$U(r) = \frac{1}{2}k(r - r_e)^2 + c(r - r_e)^3 + d(r - r_e)^4 + ... \tag{14}$$

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Figure 3: Schematic vibrational-rotational infrared spectrum for a diatomic molecule.

Although somewhat complicated, it an be shown that the c and d terms yield, as the first correction to the energy levels, precisely the $-\tilde{\nu}_e x_e (v + \frac{1}{2})^2$ term given in Eq. (4). A similar conclusion is reached if $U(r)$ is taken to have the Morse potential form, for which $T(v) = \tilde{\nu}_e (v + \frac{1}{2}) - \tilde{\nu}_e x_e (v + \frac{1}{2})^2$. In both cases, the mass dependence of $\tilde{\nu}_e x_e$ is found to be greater than for $\tilde{\nu}_e$ and is

$$\frac{\tilde{\nu}_e^* x_e^*}{\tilde{\nu}_e x_e} = \frac{\mu}{\mu^*} \tag{15}$$

Equations (13) and (15) are useful in obtaining the $\tilde{\nu}_0^*$ counterpart of Eq. (8),

$$\tilde{\nu}_0^* = \tilde{\nu}_e^* - 2\tilde{\nu}_e^* x_e^* = \tilde{\nu}_e \left(\frac{\mu}{\mu^*} \right)^{\frac{1}{2}} - 2\tilde{\nu}_e x_e \frac{\mu}{\mu^*} \tag{16}$$

and it is seen that a measurement of $\tilde{\nu}_0$ from HCl and DCl suffices for a determination of $\tilde{\nu}_e$ and $\tilde{\nu}_e x_e$. Alternatively, of course, the latter constant can be determined from overtone vibrations ($\Delta v > 1$) of a single isotopic form. However, such overtones generally have low intensity, and the transitions may fall outside the range of many infrared instruments, so the isotopic shift method is used in the present experiment.

Since HCl gas is a mixture of $H^{35}Cl$ and $H^{37}Cl$ molecules, a chlorine isotope effect will also be present. However, the ratio of the reduced mass is only 1.0015; therefore high resolution is required to detect this effect. HCl is predominantly $H^{35}Cl$ and for this experiment, so the stronger lines in the spectra are those of $H^{35}Cl$. If deuterium is substituted for hydrogenm the ration of the reduced masses, $\mu(D^{35}Cl)/\mu(H^{35}Cl)$, is 1.946 and the isotope effect is quite large.

3   Calculations

Index the lines in the spectra with appropriate m values as shown in Fig. 3 (be sure to label your P and R branches correctly). If $^{35}Cl/^{37}Cl$ splitting is seen, index the stronger ^{35}Cl lines first. Make a table of these m values and the corresponding frequencies $\tilde{\nu}(m)$. Express the frequencies in units of cm^{-1} to the tenth of a cm^{-1}. Then list the differences between adjacent lines $\Delta\tilde{\nu}(m)$, which will be roughly $2B_e$ but should vary with m. Plot $\Delta\tilde{\nu}(m)$ against m, draw a straight line through the points, and check any points that seem out of line (note that $\Delta\tilde{\nu}(m) = \tilde{\nu}(m+1) - \tilde{\nu}(m)$, not $\tilde{\nu}(m) - \tilde{\nu}(m-1)$). Next, plot $\tilde{\nu}(m)$ against m and carry out a least-squares fit to the data with Eq. 9 to determine $\tilde{\nu}_0$, B_e, and α_e. Repeat this procedure using Eq. 10, noting that high m transmissions will be most important to determine D_e due to its m^3 dependence.

Repeat the above procedure for the ^{37}Cl lines. To distinguish these from those pertaining the ^{35}Cl, label with an asterisk as in the text.

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	$\tilde{\nu}_e$	$\tilde{\nu}_e x_e$	B_e	α_e	$D_e(\times 10^3)$	r_e (Å)	k (N/m)
H^{35}Cl	2989.74	52.05	10.5909	0.3019	0.5316	1.2746	516.3
H^{37}Cl	2987.54	51.97	10.5753	0.3012	0.5300	1.2746	

Table 1: Literature values. All figures are in cm^{-1} unless otherwise noted.

Using the $\tilde{\nu}_0$ values for H^{35}Cl and H^{37}Cl, determine $\tilde{\nu}_e$ and $\tilde{\nu}_e x_e$ for H^{35}Cl. To do this, rearrange Eq. (8) and insert into the right hand side of Eq. (16). Use the istopic masses to calculate the reduced mass ratios. These are (in atomic mass units) H = 1.007825, D = 2.104102, ^{35}Cl = 34.968853, and ^{37}Cl = 36.965903. From $\tilde{\nu}_0$ and $\tilde{\nu}_e$, calculate k (in units of N/m).

Calculate I_e, the moment of inertia, and r_e, the internuclear distance, for H^{35}Cl.

4   Discussion

Compute the ratio B_e^*/B_e cand compare with the rigid rotor prediction of Eq. (11). Compute $B_v = B_e - \alpha_e(v+\frac{1}{2})$ for the $v = 0, 1$, and 2 levels of H^{35}Cl and compute r_v for each of those levels. What is r_v and how does it change with v? Compare the ratio of of your calculated $\tilde{\nu}_0^*/\tilde{\nu}$ ratio with the ratio $(\mu/\mu^*)^{\frac{1}{2}}$ expected for the harmonic oscillator. How anharmonic is the HCl molecule, i.e., how large is x_e? Use your values of $\tilde{\nu}_e$ and $\tilde{\nu}_e x_e$ and Eq. (4) to predict the frequencies of the first overtone transition (ignore rotational terms). Compare all of your values calculated values to those in the literature. Which gives you a better estimate of the force constant, $\tilde{\nu}_0$ or $\tilde{\nu}_e$?