

## EXPERIMENT 37

### Vibrational-Rotational Spectra of HCl and DCl

The infrared region of the spectrum extends from the long-wavelength end of the visible region at  $1 \mu\text{m}$  out to the microwave region at about  $1000 \mu\text{m}$ . It is common practice to specify infrared frequencies in wavenumber units:  $\tilde{\nu}(\text{cm}^{-1}) = 1/\lambda = \nu/c$ , where  $c$  is the speed of light in  $\text{cm s}^{-1}$  units. Thus this region extends from  $10,000 \text{ cm}^{-1}$  down to  $10 \text{ cm}^{-1}$ . Although considerable work is now being done in the far-infrared region below  $400 \text{ cm}^{-1}$ , the spectral range from  $4000$  to  $400 \text{ cm}^{-1}$  has received the greatest attention because the vibrational frequencies of most molecules lie in this region.

This experiment is concerned with 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.

#### THEORY

Almost all infrared work makes use of absorption techniques in which radiation from a source emitting all infrared frequencies is passed through a sample of the material to be studied. When the frequency of this radiation is the same as a vibrational frequency of the molecule, the molecule may be vibrationally excited; this results in loss of energy from the radiation and gives rise to an absorption band. The spectrum of a polyatomic molecule generally consists of several such bands arising from different vibrational motions of the molecule. This experiment involves diatomic molecules, which have only one vibrational mode.

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,<sup>1</sup> are

$$E(v) = h\nu(v + \frac{1}{2}) \quad (1)$$

where  $v$  is the vibrational quantum number having integral values  $0, 1, 2, \dots$ ;  $\nu$  is the vibrational frequency; and  $h$  is the Planck 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<sup>1</sup> to be

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

where the rotational quantum number  $J$  may take integral values  $0, 1, 2, \dots$ . 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

$$I = \mu r^2 \quad (3)$$

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<sup>2</sup> is given below.

with the levels expressed as *term values*  $T$  in  $\text{cm}^{-1}$  units rather than as energy values  $E$  in joules:

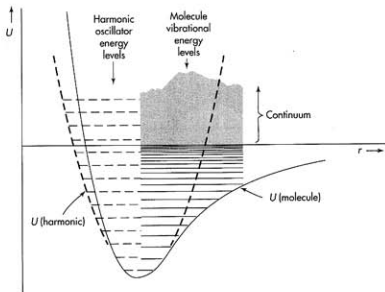
$$T(v, J) = \frac{E(v, J)}{hc} = \tilde{\nu}_e \left(v + \frac{1}{2}\right) - \tilde{\nu}_e x_e \left(v + \frac{1}{2}\right)^2 + B_e J(J+1) - D_e J^2(J+1)^2 - \alpha_e \left(v + \frac{1}{2}\right) J(J+1) \quad (4)$$

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

$$B_e = \frac{h}{8\pi^2 I_e c} \quad (5)$$

The first and third terms on the right-hand side of Eq. (4) are the harmonic-oscillator and rigid-rotor terms with  $r$  equal  $r_e$ . 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  $U_{\text{harm}}$  (see 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 inertia and affects the rotation of the molecule. The constant  $\alpha_e$  is also quite small, but this term should not be neglected.

**Selection Rules.** The harmonic-oscillator, rigid-rotor selection rules<sup>2</sup> 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 now be observed.<sup>2</sup> 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



**FIGURE 1**  
Schematic diagram showing potential energy  $U$  as a function of internuclear separation  $r$  for a diatomic molecule. The harmonic potential  $U_{\text{harm}}$  is indicated by the dashed curve. The vibrational levels are also shown

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

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

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

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

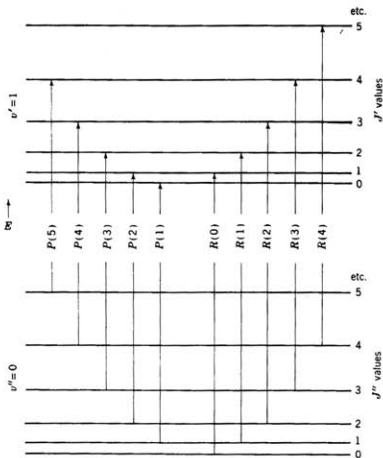
$$\tilde{\nu}_0 = \tilde{\nu}_e - 2\tilde{\nu}_e x_e \quad (8)$$

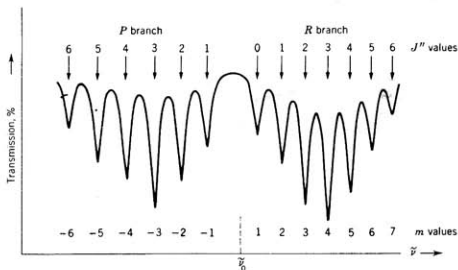
The two series of lines given in Eqs. (6) and (7) are called *R* and *P* branches, respectively. These allowed transitions are indicated on the energy-level diagram given in Fig. 2. If  $\alpha_e$  were negligible, Eqs. (6) and (7) would predict a series of equally spaced lines with separation  $2B_e$  except for a missing line at  $\tilde{\nu}_0$ . The effect of interaction between rotation and vibration (nonzero  $\alpha_e$ ) 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:

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

**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.





**FIGURE 3**  
Schematic vibrational-rotational infrared spectrum for a diatomic molecule.

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

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

Thus a multiple linear regression can be performed to determine  $\tilde{\nu}_0$ ,  $B_e$ ,  $\alpha_e$ , 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  $\mu$  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 definitions of  $B_e$  and  $I$ , we see that

$$\frac{B_e^*}{B_e} = \frac{\mu}{\mu^*} \quad (11)$$

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

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

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

which leads to the relation

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

The ratio  $\tilde{\nu}_0^*/\tilde{\nu}_0$  differs slightly from this harmonic ratio due 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  $U(r)$ , viz.,

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

Although somewhat complicated, it can be shown<sup>2,3</sup> 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 given by Eq. (9) of Exp. 39. In both cases, the mass dependence of  $\tilde{\nu}_e x_e$  is found to be greater than for  $\tilde{\nu}_e$  and is

$$\frac{\tilde{\nu}_e^* x_e^*}{\tilde{\nu}_e x_e} = \frac{\mu}{\mu^*} \quad (15)$$

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

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

and it is seen that a measurement of  $\tilde{\nu}_0$  for HCl and DCl suffices for a determination of  $\tilde{\nu}_e$  and  $\tilde{\nu}_e x_e$ . Alternatively of course the latter constants can be determined from overtone vibrations ( $\Delta v > 1$ ) of a single isotopic form (see Exp. 39). 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  $\text{H}^{35}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$  molecules, a chlorine isotope effect will also be present. However, the ratio of the reduced masses is only 1.0015: therefore high resolution is required to detect this effect. HCl is predominantly  $\text{H}^{35}\text{Cl}$ , and for this experiment we shall assume that the HCl bands obtained are those of  $\text{H}^{35}\text{Cl}$ . If deuterium is substituted for hydrogen, the ratio of the reduced masses,  $\mu(\text{D}^{35}\text{Cl})/\mu(\text{H}^{35}\text{Cl})$ , is 1.946 and the isotope effect is quite large.

**Vibrational Partition Function.**<sup>4,5</sup> The thermodynamic quantities for an ideal gas can usually be expressed as a sum of translational, rotational, and vibrational contributions (see Exp. 3). We shall consider here the heat capacity at constant volume. At room temperature and above, the translational and rotational contributions to  $C_v$  are constants that are independent of temperature. For HCl and DCl (diatomic and thus linear molecules), the molar quantities are

$$\begin{aligned} \tilde{C}_v(\text{trans}) &= \frac{3}{2}R \\ \tilde{C}_v(\text{rot}) &= R \end{aligned} \quad (17)$$

The vibrational contribution to  $\tilde{C}_v$  varies with temperature and can be calculated from the vibrational partition function  $q_{\text{vib}}$  using

$$\tilde{C}_v(\text{vib}) = R \frac{\partial}{\partial T} \left( T^2 \frac{\partial \ln q_{\text{vib}}}{\partial T} \right) \quad (18)$$

The partition function  $q_{\text{vib}}$  of HCl or DCl is well approximated by the harmonic-oscillator partition function  $q^{\text{HO}}$ . Since the energy levels of a harmonic oscillator are given by  $(v + \frac{1}{2})h\nu$ , one obtains<sup>4</sup>

$$q^{\text{HO}} = \sum_{v=0}^{\infty} \exp \left[ \frac{-(v + \frac{1}{2})h\nu}{kT} \right] = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}} \quad (19)$$

Combining Eqs. (18) and (19), we find

$$\tilde{C}_v(\text{vib}) = R \frac{u^2 e^{-u}}{(1 - e^{-u})^2} \quad (20)$$

where  $u = h\nu/kT = hc\tilde{\nu}/kT = 1.4388\tilde{\nu}/T$ .

## EXPERIMENTAL

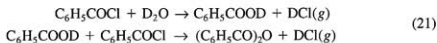
A general description of infrared instruments is given in Chapter XIX. Medium to high resolution is required for this experiment; a grating or FTIR instrument with at least  $2\text{ cm}^{-1}$  resolution is desirable. In addition grating spectrometers require careful calibration. CO and CH<sub>4</sub> are suitable gases for calibration purposes. Detailed instructions for operating the spectrometer will be given in the laboratory. Before beginning the experiment, the student should review the pertinent material. **Use the spectrometer carefully;** if in doubt ask the instructor.

The infrared gas cell is constructed from a short (usually 10-cm) length of large-diameter (4 to 5 cm) Pyrex tubing with a vacuum stopcock attached. Infrared-transparent windows are clamped against O-rings at the ends of the cell or are sealed on the ends with Glyptal resin. For studies concentrating on the region  $4000$  to  $700\text{ cm}^{-1}$ , NaCl windows will suffice. When the spectrum of interest extends down to  $\sim 400\text{ cm}^{-1}$ , KBr windows are needed. Both types of salt windows become "foggy" on prolonged exposure to a moist atmosphere and should be protected (e.g., stored in a desiccator) when not in use. In the present experiment, inert sapphire windows with transmission down to  $1600\text{ cm}^{-1}$  are particularly convenient and relatively inexpensive.

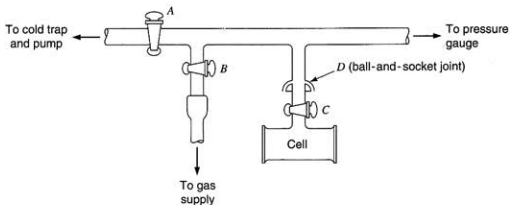
**Filling the Cell and Recording the Spectra.** An arrangement for filling the cell is given in Fig. 4. Attach the cell at *D*. With stopcock *C* open and *B* closed, open stopcock *A* and pump out the system. Make sure that the needle valve of the HCl cylinder is closed. Then open *B* and continue pumping.

Close *A* and slowly open the valve on the HCl cylinder. Fill the system to a pressure recommended by the instructor (50 to 500 Torr, depending upon the resolution of the spectrometer). Close the valve on the HCl cylinder and then close *B* and *C*. Remove the cell and take a spectrum at the highest available resolution.

**Preparation of DCl.** If DCl gas is not available in a commercial cylinder or bulb, it must be prepared in the laboratory. Deuterium chloride gas can be synthesized readily by the reaction between benzoyl chloride and heavy water:



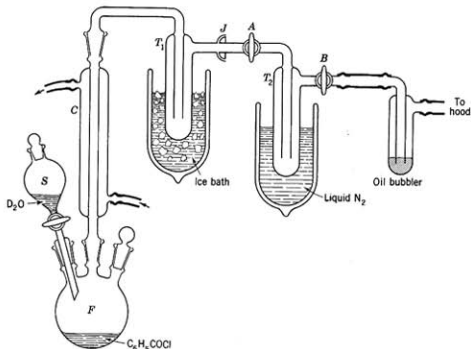
An arrangement for carrying out this reaction is shown in Fig 5; a somewhat simpler apparatus for a smaller-scale synthesis is described in Exp. 43. Approximately 2.5 mL (0.14 mol) of D<sub>2</sub>O in the separating funnel *S* is added slowly to 70 g (0.5 mol) of benzoyl



**FIGURE 4**  
Gas-handling system for filling infrared cell.

FIGURE 5

Apparatus for preparing deuterium chloride.



chloride in flask *F*. With a water-cooled reflux condenser *C* attached and either ice or Dry Ice and trichloroethylene in trap *T*<sub>1</sub>, the flask is gently heated. Stopcocks *A* and *B* are left open, and the system is swept out by allowing some DCl gas to escape through the oil bubbler into a hood. Stopcock *B* is then closed, and trap *T*<sub>2</sub> is cooled with liquid nitrogen. After 20 min remove the heat from flask *F*. Wait a few minutes, then close stopcock *A* and disconnect the ball-and-socket joint *J*. Keep trap *T*<sub>2</sub> in liquid nitrogen, and attach it to the system used to fill the cell at stopcock *B* shown in Fig. 4. After the line is pumped out, the cell can be filled by allowing the DCl in the trap to warm up slowly until the desired pressure is achieved.

A similar synthesis can be used to generate DBr from benzoyl bromide if it is desired to study DBr and HBr in addition to or as an alternative to DCl and HCl. In fact, if an equimolar mixture of the benzoyl halides is used along with D<sub>2</sub>O, which is about 95 percent D, the product mix will contain all isotopic forms with reasonable intensity ratios for an infrared scan of all four species in a single cell. Such a mixture can also be used for the determination of equilibrium constant *K*<sub>p</sub> for the H–D exchange reaction



Unfortunately, the infrared intensities do not give accurate concentrations due to pressure-broadening effects and the narrowness of the spectral lines compared to the spectral resolution. A preferable and more accurate measurement of *K*<sub>p</sub> can be made with an NMR spectrometer, as described in Exp. 43.

## CALCULATIONS

Select your best HCl and DCl spectra, and index the lines with the appropriate *m* values as shown in Fig. 3. If <sup>35</sup>Cl/<sup>37</sup>Cl splitting is seen, index the stronger <sup>35</sup>Cl lines. Make a table of these *m* values and the corresponding frequencies  $\tilde{\nu}(m)$ . Express the frequencies in

$\text{cm}^{-1}$  units to tenths of a  $\text{cm}^{-1}$  if possible. 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. Then carry out a multiple linear least-squares fit to the data with Eq. (9) to determine  $\tilde{\nu}_0$ ,  $B_e$ , and  $\alpha_e$  and their standard errors. Repeat this fitting procedure using Eq. (10), noting that high  $m$  transitions will be the most important ones in determining  $D_e$  due to its  $m^3$  dependence. Use an  $F$  test as described in Chapters III and XXI to determine if the value of  $D_e$  obtained in this second fit is significant at the 95 percent confidence level. An example of a spreadsheet calculation of this type is given in Fig. III-3. Use your values of  $\tilde{\nu}_0$  for HCl and DCl to determine  $\tilde{\nu}_e$  and  $\tilde{\nu}_e x_e$  for HCl. From  $\tilde{\nu}_e$ , calculate  $k$  for HCl.

Calculate  $I_e$ , the moment of inertia, and  $r_e$ , the internuclear distance, for both HCl and DCl. The masses (in atomic mass units) are H = 1.007825, D = 2.014102,  $^{35}\text{Cl}$  = 34.968853, and  $^{37}\text{Cl}$  = 36.965903. If HBr and DBr are examined, it is unlikely that the two nearly equal  $^{79}\text{Br}$  and  $^{81}\text{Br}$  spectral lines will be resolved, and it is appropriate to use the average atomic mass (79.904) in similar calculations. Tabulate all of your results, along with your estimates of the experimental uncertainty. Compare your results with literature values, which can be found in Ref. 2.

Using your value of  $\tilde{\nu}_0$  for HCl, calculate  $\tilde{C}_v(\text{vib})$  at 298 K and at 1000 K from Eq. (20). Compare the spectroscopic value  $\tilde{C}_v = 2.5R + \tilde{C}_v(\text{vib})$  with the experimental  $\tilde{C}_v$  value obtained from directly measured values<sup>5,6</sup> of  $\tilde{C}_p$  and the expression  $\tilde{C}_v = \tilde{C}_p - R$ :  $\tilde{C}_v = 20.80 \text{ J K}^{-1} \text{ mol}^{-1}$  at 298 K and  $23.20 \text{ J K}^{-1} \text{ mol}^{-1}$  at 1000 K.

## DISCUSSION

Compute the ratio  $B_e^*/B_e$  and compare with the rigid-rotor prediction of Eq. (11). How constant is  $r_e$  for HCl and DCl? Compute  $B_v = B_e - \alpha_e(v + \frac{1}{2})$  for the  $v = 0, 1$ , and 2 levels of HCl and DCl and from these obtain average  $r_v$  values for these levels. Comment in your report on the changes in these distances. Compare your  $\tilde{\nu}_0^*/\tilde{\nu}_0$  ratio with the ratio  $(\mu/\mu^*)^{1/2}$  expected for a 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 transitions of HCl and DCl (ignore the rotational terms). Did you see any indication of these overtones in your spectra? Do your spectra show any evidence of a  $^{35}\text{Cl}$ - $^{37}\text{Cl}$  isotope effect? Use Eq. (10) to calculate the splitting expected for this effect for several  $P$  and  $R$  branch transitions in HCl and in DCl.

**Theoretical Calculations.** A class project to calculate the physical properties of HCl using an ab initio program such as Gaussian is described in Chapter III. Compare your experimental values of  $r_e$  and  $\tilde{\nu}_e$  with values deduced from these theoretical calculations.

## SAFETY ISSUES

Lecture bottles of HCl and CO/CH<sub>4</sub> gas must be strapped or chained securely to the laboratory bench. Work on a vacuum system requires preliminary review of procedures and careful execution in order to avoid damage to the apparatus and possible injury from broken glass; in addition the liquid nitrogen used for cold traps must be handled properly (see Appendix C). Safety glasses must be worn. Benzoyl chloride, which is a potent lachrymator, and other waste chemicals must be disposed of properly.



## APPARATUS

Medium- or high-resolution infrared grating or FTIR spectrometer; gas cell with sapphire, NaCl, or KBr windows; vacuum line (with pressure gauge) for filling cell; cylinder of HCl gas with needle valve; three-neck round-bottom flask; reflux condenser; glass-stoppered dropping funnel; two traps, one with a stopcock on each arm; oil bubbler; exhaust hood; heating mantle; CO and CH<sub>4</sub> gas for calibration check (optional).

Heavy water (2.5 mL at least 95 percent D<sub>2</sub>O); benzoyl chloride (70 g); ice or Dry Ice and isopropanol; liquid nitrogen; or a 5-L flask of DCI gas (available from Cambridge Isotope Laboratories, 20 Commerce Way, Woburn, MA 01801, and other suppliers of isotopically substituted compounds).

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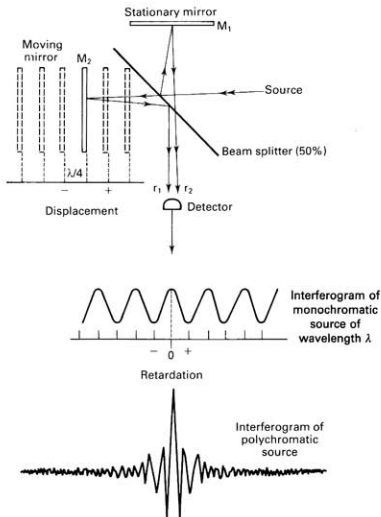
## GENERAL READING

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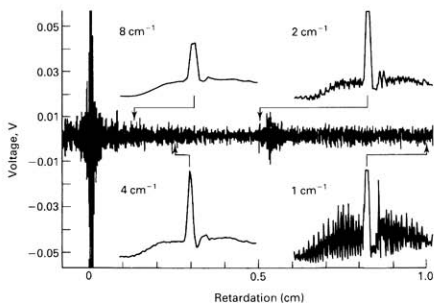
**Infrared Spectrometers.** Infrared spectroscopy is one of the most powerful tools for quantitative and qualitative identification of molecules, and this led to the early development of prism and grating spectrophotometers.<sup>32</sup> Typically, these instruments cover the region from 400 to 4000  $\text{cm}^{-1}$ , give a resolution of 1 to 4  $\text{cm}^{-1}$ , and require calibration with polystyrene films or with standard gases such as  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , or  $\text{NH}_3$ .<sup>33</sup> This allows qualitative identification of materials and the measurement of vibrational frequencies of liquids, solids, and solutions of these in various nonaqueous solvents. Solids are often sampled as a dispersion in an oil such as Nujol (i.e., in a mull) or as a suspension in KBr, prepared by pressing a powdered mixture to form a pellet. Gases are examined in a simple cell with salt windows, such as that described in Exp. 37. If vibrational-rotational information is desired, as in Exp. 37 on HCl and DCl and in Exp. 38 on acetylene, a resolution of 1  $\text{cm}^{-1}$  or better is desirable.

Descriptions of grating spectrophotometers can be found in earlier editions of this book, but such instruments have now been largely displaced by Fourier-transform infrared (FTIR) spectrometers.<sup>34,35</sup> Most FTIR instruments are based on the Michelson interferometer configuration depicted in Fig. 27. A collimated beam of light from an infrared source is divided into two halves by a beam splitter, typically KBr coated with germanium to give 50 percent reflectance. Reflections from a fixed mirror  $M_1$  and a moving mirror  $M_2$  are recombined and imaged onto a detector element that gives the net intensity. As one of the mirrors is moved, interference between the two beams occurs, which for a monochromatic source of wavelength  $\lambda$ , produces a periodic signal as depicted in the figure. The detector goes through one cycle for a mirror movement of  $\lambda/2$ , and hence the frequency  $f$  of this oscillation is given by  $f = 2\nu/\lambda = 2\nu\bar{\nu}$ , where  $\nu$  is the mirror velocity. For infrared light in the 400 to 4000  $\text{cm}^{-1}$  range (1.2 to  $12 \times 10^{13}$  Hz), a typical mirror velocity of 0.05  $\text{cm s}^{-1}$  gives  $f = 40$  to 400 Hz, well within the response time of the pyroelectric and other infrared detectors commonly used in FTIR instruments.

For a polychromatic source, the signal is a sum of such cosine waves, with all adding constructively at the zero-path-difference point where the two mirrors are equidistant from the beam splitter. At other distances, the waves interfere and the detector signal, the *interferogram*, drops rapidly as shown in the figure. The interferogram is thus a sum of cosine waves, each of which has an amplitude and frequency proportional to the source intensity at a particular infrared frequency. Recovery of this desired information is achieved by performing a Fourier transform, a process greatly aided by the use of a computer and a fast-Fourier-transform algorithm developed in recent years (Cooley-Tukey procedure).<sup>34</sup> The resolution is determined by the total mirror travel  $L$  as illustrated in Fig. 28 and is essentially  $\Delta\bar{\nu} = 1/2L$ ; commercial research instruments (Bomem and Bruker) can provide a resolution of about 0.002  $\text{cm}^{-1}$ .

**FIGURE 27**

Schematic diagram of a Michelson interferometer. The detector signal variation as a result of mirror motion is displayed for the cases of monochromatic and polychromatic sources.

**FIGURE 28**

Interferogram and transformed spectra for acetylene in the  $670$  to  $800\text{ cm}^{-1}$   $\nu_3$  bending region. The transformed spectra show the effect of retardation distance on the spectral resolution; the  $1\text{ cm}^{-1}$  case corresponds to a total mirror travel of  $0.5\text{ cm}$ . The vertical scale of the interferogram is greatly expanded; the peak-to-peak voltage at zero retardation is  $\sim 4\text{ V}$ .

**FIGURE 29**

Typical optical diagram of the Mattson series of FTIR instruments. Courtesy of Mattson Instruments, Inc.

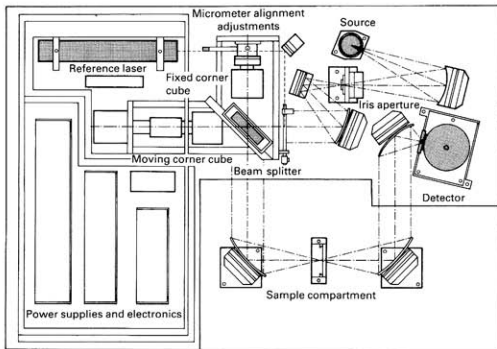


Figure 29 shows the optical configuration of a commercial FTIR instrument in which corner-cube mirror reflectors are used in place of plane mirrors. These “cat’s-eye” reflectors serve to reduce the sensitivity of the mirror alignment and make it possible to use a simpler mirror drive. The position of the mirror is determined precisely by using the fringes produced by interference of a helium–neon laser reference beam. Since the frequency of the laser is accurately known, the infrared frequencies are determined to a few hundredths of a wavenumber and routine calibration with gas standards is unnecessary. This high precision also facilitates signal averaging over many scans and comparisons between spectra. Most FTIR instruments are single-beam devices, requiring separate measurements of the source background intensity and the signal when the sample is inserted. In some commercial instruments, a double-beam capability is provided by mirrors that oscillate to redirect the beams between the sample and reference cells.

Many FTIR spectrometers offer options to extend the coverage into the far-IR and, more recently, into the near-IR and even VIS–UV regions. In general the signal-to-noise ratio is much higher for FTIR instruments than for grating spectrometers, and this allows the use of shorter scan times. This improvement is due largely to two major advantages of an FTIR over a grating instrument: higher beam intensities due to the elimination of slits, and a multiplex advantage arising from the fact that all source frequencies are monitored simultaneously. The gain in signal to noise from the latter advantage is  $N^{1/2}$ , where  $N$  is the number of resolution elements to be examined. This is particularly helpful for high-resolution studies; for a scan of  $4000\text{ cm}^{-1}$  at  $0.1\text{ cm}^{-1}$  resolution, the advantage is 200. More detail on these instrumental aspects of FTIR, on the transform process itself, and on sampling techniques can be found in Refs. 34 and 35.

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