

Chapter 1

INTRODUCTION TO VIBRATIONAL SPECTROSCOPY

1.1. INTRODUCTION

Infrared (IR) spectrometry has changed dramatically over the past 40 years. In the 1960s, undergraduate chemistry majors would learn that the primary use of infrared spectrometry was for the structural elucidation of organic compounds. In many large research laboratories, however, the structure of complex molecules is now usually found by a combination of techniques, including two-dimensional nuclear magnetic resonance (NMR), x-ray diffraction, and mass spectrometry, with IR spectrometry playing a less dominant, although still important role. For example, U.S. pharmaceutical companies must still submit IR spectra as part of their application to the Food and Drug Administration as evidence of the putative chemical structure, and in polymer laboratories infrared spectrometry is still used as the primary instrument for the determination of molecular structure.

This is not to imply that molecular structure of simple organic molecules cannot be determined by infrared spectroscopy. In fact, the information that can be deduced from an infrared spectrum is complementary to that of other methods, and infrared spectroscopy provides valuable information that is unattainable by other methods, as is shown in the remainder of the book. More important, however, a plethora of other applications became available with the advent in 1969 of the first commercial mid-infrared Fourier transform spectrometer with better than 2 cm^{-1} resolution. These include quantitative analysis of complex mixtures, the investigation of dynamic systems, biological and biomedical spectroscopy, microspectroscopy and hyperspectral imaging, and the study of many types of interfacial phenomena. All of these applications (and many more) are described in this book. Furthermore, because of the development of such sampling techniques

as attenuated total reflection (ATR), measurement of the infrared spectra of many types of samples has become quite routine.

The impact of Fourier transform infrared (FT-IR) spectrometers was not recognized immediately. For example, in 1973, Herbert Laitinen, who was the editor of *Analytical Chemistry* at the time, made an analogy with Shakespeare's seven ages of man to define the seven ages of an analytical instrument [1]. These seven ages start with the discovery of the principles of the technique in a physicist's laboratory. After characterization and commercialization of the technique, instruments graduate from the research laboratory to routine measurements, until in their seventh age they are superseded by newer instruments with higher speed, sensitivity, specificity, or resolution. In his 1973 editorial, Laitinen used infrared spectrometry to illustrate an instrument in its seventh age. In fact, the technique was in its second childhood! Let us first consider why FT-IR spectrometers have assumed such a position of dominance for the measurement of infrared spectra.

Survey spectra in the mid-infrared region are often measured at a resolution of $\sim 4\text{ cm}^{-1}$. When such spectra between 4000 and 400 cm^{-1} are measured with a prism or grating monochromator, only one 4-cm^{-1} resolution element in the 3600-cm^{-1} -wide spectral range of interest is measured at any instant; the remaining 899 resolution elements are not. Thus, the efficiency of the measurement is only about 0.1%. It was typical for survey scans to take several minutes to measure, whereas the measurement of archival-quality spectra (measured at 1 to 2 cm^{-1} resolution) often took at least 30 minutes.

In FT-IR spectrometry, all the resolution elements are measured at all times during the measurement (the *multiplex* or *Fellgett's advantage*). In addition, more radiation can be passed between the source and the detector for each resolution element (the *throughput* or *Jacquinot's advantage*). These advantages are discussed in Chapter 7. As a result, transmission, reflection, and even emission spectra can be measured significantly faster and with higher sensitivity than ever before.

In this book we demonstrate how FT-IR spectrometry can not only be used to measure infrared spectra of the type of samples that have classically been investigated by infrared spectrometers for decades (i.e., gases, liquids, and bulk and powdered solids in milligram quantities), but that interfacial species, microsamples, and trace analytes can now be characterized routinely. Measurement times have been reduced from minutes to fractions of a second; in special cases, reactions taking place in less than a microsecond can be followed. The physical properties of materials can be correlated to the molecular structure by vibrational spectroscopy better than by any other analytical technique. It is probably true to say that during the more than three decades following Laitinen's editorial, infrared spectroscopy has entered and passed from its second childhood into its fifth age. Because of the remarkable advances made in the performance of FT-IR spectrometers, infrared spectrometry has matured to the point that it is used for the solution of a variety of problems from the research lab to the manufacturing floor, and sales of infrared spectrometers are at an all-time high.

The increased popularity of infrared spectrometry and the commercial availability of instruments that are "so simple that a child can operate them" have led to the

unexpected consequence that many operators of FT-IR spectrometers have received little or no formal training in vibrational spectroscopy. To serve these new players in the “FT-IR game” and to help give them a better appreciation of how the measurement of infrared spectra may be optimized, a brief introduction to the origin of vibrational spectra of gases, liquids, and solids is given in the remainder of this chapter. In the rest of the book, we show how FT-IR spectrometers work and how to measure the most accurate and information-rich infrared spectra from a wide variety of samples.

1.2. MOLECULAR VIBRATIONS

Infrared spectra result from transitions between quantized vibrational energy states. Molecular vibrations can range from the simple coupled motion of the two atoms of a diatomic molecule to the much more complex motion of each atom in a large polyfunctional molecule. Molecules with N atoms have $3N$ degrees of freedom, three of which represent translational motion in mutually perpendicular directions (the x , y , and z axes) and three represent rotational motion about the x , y , and z axes. The remaining $3N - 6$ degrees of freedom give the number of ways that the atoms in a nonlinear molecule can vibrate (i.e., the number of *vibrational modes*).

Each mode involves approximately harmonic displacements of the atoms from their equilibrium positions; for each mode, i , all the atoms vibrate at a certain characteristic frequency, ν_i . The potential energy, $V(r)$, of a harmonic oscillator is shown by the dashed line in Figure 1.1 as a function of the distance between the atoms, r . For any mode in which the atoms vibrate with simple harmonic motion (i.e., obeying Hooke's law), the vibrational energy states, V_{iv} , can be described

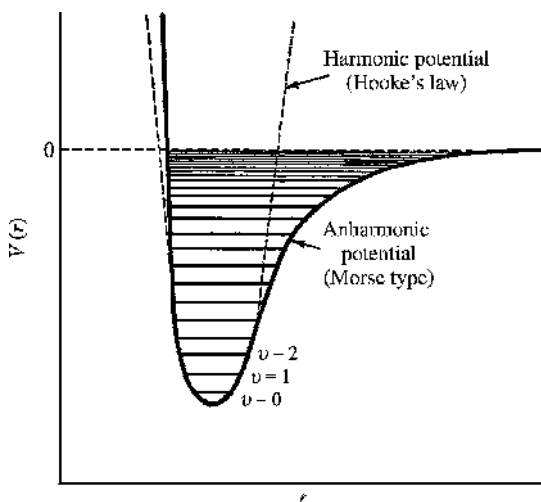


Figure 1.1. Potential energy of a diatomic molecule as a function of the atomic displacement during a vibration for a harmonic oscillator (dashed line) and an anharmonic oscillator (solid line).

by the equation

$$V_{iv} = hv_i \left(v_i + \frac{1}{2} \right) \quad (1.1)$$

where h is Planck's constant, v_i the *fundamental frequency* of the particular mode, and v_i the *vibrational quantum number* of the i th mode ($v_i = 0, 1, 2, \dots$). Note that frequency in units of hertz is usually given the symbol ν . Vibrational frequencies are often given in units of wavenumber, the number of waves per unit length. The most common unit of length is the centimeter, in which case the wavenumber has units of cm^{-1} and is given the symbol $\tilde{\nu}$ by many chemists and σ by many physicists. The energy difference for transitions between the ground state ($v_i = 0$) and the first excited state ($v_i = 1$) of most vibrational modes corresponds to the energy of radiation in the mid-infrared spectrum (400 to 4000 cm^{-1}).

The motion of the atoms during the vibration is usually described in terms of the *normal coordinate*, Q_i . The molecule is promoted to the excited state only if its dipole moment, μ , changes during the vibration [i.e., provided that $(\partial\mu/\partial Q_i) \neq 0$]. For molecules with certain elements of symmetry, some vibrational modes may be degenerate, so that more than one mode has a given vibrational frequency whereas others may be completely forbidden. Thus, because of degeneracy, the number of fundamental absorption bands able to be observed is often less than $3N - 6$. Because rotation of a linear molecule about the axis of the bond does not involve the displacement of any of the atoms, one of the rotational degrees of freedom is lost and linear molecules have an additional vibrational mode. Thus, the number of modes of a linear molecule is $3N - 5$, so that a diatomic molecule ($N = 2$) has a single vibrational mode.

The actual variation of the potential energy as a function of the displacement of the atoms from their equilibrium positions is shown as a solid line in Figure 1.1. From this curve it can be seen that Eq. 1.1 is valid only for low values of the vibrational quantum number and is not valid when v_i is large. In practice, V_{iv} must be described using an *anharmonic* (Morse-type) potential function. This behavior is shown in Figure 1.1 as a solid line, and the potential energy is given to a first approximation by the expression

$$V_{iv} = hv_i \left(v_i + \frac{1}{2} \right) + hv_i x_i \left(v_i + \frac{1}{2} \right)^2 \quad (1.2)$$

where x_i is the *anharmonicity constant*; x_i is dimensionless and typically has values between -0.001 and -0.02 , depending on the mode.

If the vibrational modes were strictly harmonic, no transitions involving changes in v_i by more than ± 1 would be allowed. The effect of anharmonicity is to relax this selection rule (i.e., to allow bands caused by $|\Delta v_i| > 1$ to become allowed). Thus, overtone ($\Delta v_i = 2, 3, \dots$) and combination ($\Delta v_i = 1$; $\Delta v_j = 1$, where j represents a different mode) bands commonly appear weakly in the mid-infrared spectrum of organic compounds along with bands due to fundamental transitions ($\Delta v_i = 1$).

For many vibrational modes, only a few atoms have large displacements and the rest of the molecule is almost stationary. The frequency of such modes is characteristic of the specific functional group in which the motion is centered and is minimally affected by the nature of the other atoms in the molecule. Thus, the observation of spectral features in a certain region of the spectrum is often indicative of a specific chemical functional group in the molecule. Extensive spectral/structure correlation tables (often known as *Colthup charts*) have been developed to allow chemists to assign one or more absorption bands in a given infrared spectrum to the vibrational mode(s) associated with a certain functional group. These tables may be found in many textbooks on the interpretation of infrared spectra. Other bands involve the significant motion of only a few atoms, yet their frequency varies from one molecule to another containing the particular functional group. These modes are useful to distinguish one molecule from another that contains similar functional groups and hence are often known as *fingerprint bands*.

Skeletal modes involve significant displacements of many of the atoms in the molecule. These bands are rarely used to indicate the presence or absence of a specific functional group but again, may be useful to distinguish between structurally similar compounds. The vibrational frequency of skeletal modes is usually quite low. As a result, they absorb long-wavelength radiation that is often below the cutoff of many mid-infrared detectors. The *far-infrared* region of the spectrum (10 to 400 cm^{-1}) is rarely used for structural elucidation but contains useful information on the vibration of heavy atoms (especially for inorganic compounds) and/or weak bonds such as hydrogen bonds.

Every molecule has slightly different vibrational modes from all other molecules (with the exception of enantiomers). Thus, the infrared spectrum of a given molecule is unique and can be used to identify that molecule. Infrared spectra give far more detailed information than simply allowing the presence or absence of certain functional groups to be recognized. In the past, many chemists had a solid understanding of how to interpret infrared spectra, but spectral interpretation is starting to become a lost art, in part because of the emergence of nuclear magnetic resonance, mass spectrometry, and x-ray diffraction for this purpose, which are easier to interpret. Although molecular orbital programs are starting to permit infrared spectra of quite complex molecules to be calculated, perfect matching of calculated and measured spectra has yet to be achieved. Today, computer-assisted comparison of the spectra of unknowns to a large number of reference spectra in a database (*spectral, or library, searching*) has become a far more popular way than manual interpretation to find the structure of a molecule from its infrared spectrum. Because of the subtle differences between the spectra of many compounds, the result of a computerized spectral search should never be assumed to give the true identity of a compound without visual comparison by the operator between the best match and the actual spectrum of the unknown.

For most pure compounds, a sample thickness of only about $10\text{ }\mu\text{m}$ is needed to yield a mid-infrared spectrum for which the bands are neither saturated (maximum transmittance less than 1%) nor so weak that they require ordinate expansion. It is often inconvenient and sometimes impossible to prepare such thin samples. In these

cases, measurement of the *near-infrared* (NIR) spectrum may prove advantageous. Overtone and combination bands are usually much weaker than the fundamental modes from which they are derived. The only exception to this “rule” is when these bands are enhanced by *Fermi resonance*, which occurs when an overtone or combination band absorbs at approximately the same frequency as that of a fundamental mode involving at least one of the same atoms. Although many overtone and combination bands absorb in the mid-infrared region, the first and second overtones ($\Delta v_i = 2$ and 3) of only the C–H, O–H, and N–H stretching vibrations, or combination bands involving these modes, are found above 4000 cm^{-1} (i.e., in the NIR region). In the last two decades, NIR spectrometry has become of tremendous importance, in large part because of the very *weakness* of these bands. For samples that are between about 0.1 and 5 mm in thickness, the NIR spectra are often much more appropriate for quantitative, and sometimes even qualitative, analysis than the corresponding mid-infrared spectra of these samples. Furthermore, samples do not have to be mounted in salt cells, sources are more intense, and NIR detectors are more sensitive than mid-infrared detectors. NIR spectra are not as easy to interpret as mid-infrared spectra, but they are very amenable to multivariate statistical analysis of the type that is now becoming common throughout analytical chemistry. Indeed, many of these algorithms were originally developed specifically for the analysis of NIR spectra.

1.3. VIBRATION–ROTATION SPECTROSCOPY

One of the greatest strengths of infrared spectrometry is that samples in all phases of matter may be studied. Infrared spectra of gases, liquids, and solids have different characteristics, and it is essential that these differences be understood if spectra of materials in each state are to be measured optimally and to yield the greatest amount of information. For example, the spectra of small molecules in the vapor phase show considerable fine structure because transitions between quantized *rotational energy* levels occur at the same time as vibrational transitions. Similar features are rarely seen in the spectra of larger molecules in the vapor phase (because the individual rotational transitions are too close together to be resolved) or any molecule in the liquid state (because collisions occur at a greater rate than the rotational frequency). The full theory of vibration–rotation spectroscopy is quite complex, and a detailed exposition of this subject is beyond the scope of this chapter, but a brief introduction to vibration–rotation spectroscopy is given below.

The simplest vibration–rotation spectra to interpret are those of diatomic molecules. The rotational energy levels of diatomic molecules are characterized by a single *rotational quantum number*, J . If the molecule is assumed to be a rigid rotor (i.e., its bond length remains constant no matter how rapidly the molecule rotates), the rotational energy is given by

$$E_J = BJ(J + 1) \quad (1.3)$$

B , called the *rotational constant*, is given by

$$B = \frac{h}{8\pi^2 I c} \quad (1.4)$$

where I is the moment of inertia of the molecule and c is the velocity of light. The selection rule for transitions between rotational energy states for linear molecules is

$$\Delta J = \pm 1 \quad (1.5)$$

so that

$$E_J - E_{J-1} = BJ(J+1) - BJ(J-1) = 2BJ \quad (1.6)$$

Thus, for a rigid rotor, the pure rotation spectrum would be comprised of a series of lines with equal spacing of $2B \text{ cm}^{-1}$. For most molecules, B is sufficiently small that the pure rotation spectrum is found in the microwave region of the spectrum; however, for light molecules such as HCl, H_2O , or CO, rotational transitions absorb in the far infrared.

Diatomic molecules, X–Y, have a single fundamental vibrational mode, of wave-number $\tilde{\nu}_0$, which is infrared active only if $X \neq Y$. For any allowed vibrational transition of a gaseous diatomic molecule, there must be a simultaneous rotational transition; that is,

$$\Delta v_i = \pm 1 \quad \text{and} \quad \Delta J = \pm 1 \quad (1.7)$$

Thus, the vibration-rotation spectrum of a rigid diatomic molecule consists of a series of equally spaced lines above and below $\tilde{\nu}_0$ that correspond to $\Delta J = +1$ and $\Delta J = -1$, respectively. The series of lines below $\tilde{\nu}_0$ ($\Delta J = -1$) is known as the *P branch* of the band, while the lines above $\tilde{\nu}_0$ ($\Delta J = +1$) are known as the *R branch*. Because $\Delta J \neq 0$, there is no absorption line at $\tilde{\nu}_0$.¹

In practice, molecules are not rigid rotors, and centrifugal forces cause the length of the bond between X and Y to increase as the angular velocity of the rotating molecule increases. The effect of centrifugal distortion is to increase the moment of inertia, decreasing the rotational constant, B , at high J . To a first approximation, the effect of centrifugal distortion is taken care of by adding a second term to Eq. 1.3:

$$E_J = BJ(J+1) - DJ^2(J+1)^2 \quad (1.8)$$

where D is the *centrifugal distortion constant*. Usually, $0.1 < B < 10 \text{ cm}^{-1}$ and $D \sim 10^{-4} \text{ cm}^{-1}$. Because of the effect of centrifugal distortion, the spacing of the lines in the P branch increases as the distance from $\tilde{\nu}_0$ increases while that of the lines in the R branch decreases.

¹There is one exception to this “rule” for diatomic molecules. The fact that nitric oxide has an unpaired electron in its ground state leads to the fact that the transition $\Delta J = 0$ is allowed.

As molecules become larger and less symmetrical, the spacing of the lines in their vibration–rotation spectra decreases and the spectra become more complex. For a linear molecule such as CO_2 , the selection rules for each mode depend on the symmetry of the vibration. The symmetric stretching mode of CO_2 (ν_1) is not active, since $(\partial\mu/\partial Q) = 0$. For the antisymmetric stretching mode (ν_3), in which the molecule remains linear throughout the vibration, the selection rules are the same as for diatomic molecules and hence the spectrum has a similar appearance (see Figure 1.2*a*). For the (degenerate) bending mode (ν_2), a vibrational transition

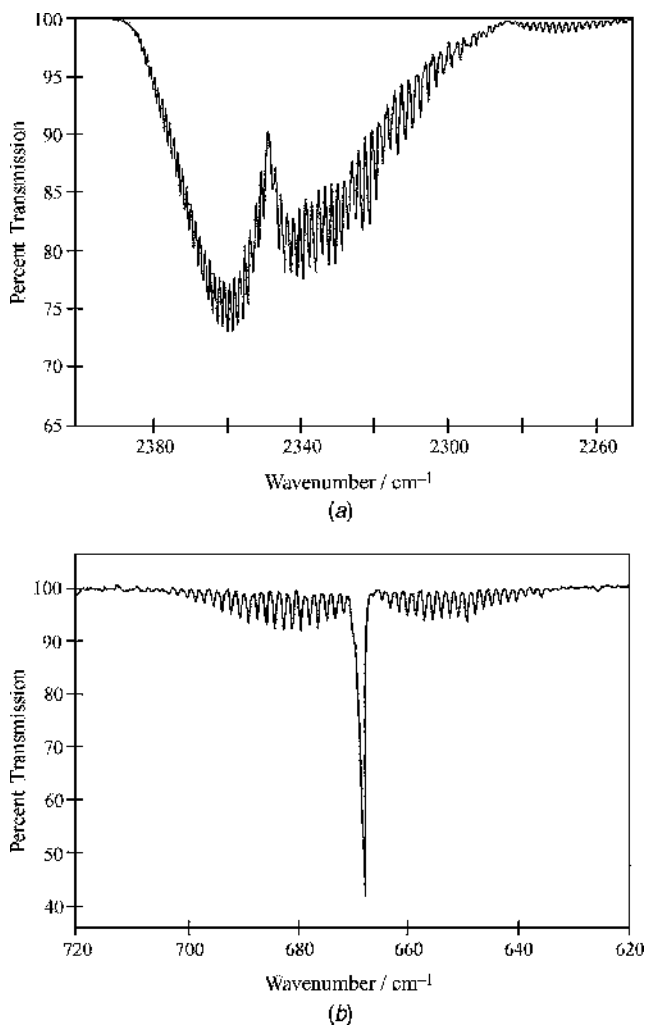


Figure 1.2. Infrared active vibration–rotation fundamental bands of carbon dioxide: (a) antisymmetric stretching mode (ν_3) for which the selection rule is $\Delta\nu_3 = \pm 1$ and $\Delta J = \pm 1$; (b) bending mode (ν_2) for which the selection rules is $\Delta\nu_2 = \pm 1$ and $\Delta J = 0, \pm 1$.

without a simultaneous change in J is permitted:

$$\Delta v_2 = \pm 1 \quad \text{and} \quad \Delta J = 0, \pm 1 \quad (1.9)$$

Thus, there is a strong line in the spectrum, known as the *Q branch*, corresponding to $\Delta J = 0$. The reason that the selection rules are different for these two modes is because different symmetry elements of the linear CO_2 molecule are lost during these two vibrations.

Linear molecules have two equal principal moments of inertia, corresponding to rotation about the center of mass about two mutually perpendicular axes, with the third principal moment equal to zero. Nonlinear molecules usually have three different moments of inertia. In this case, the vibration-rotation spectrum can be very complex, even for a simple molecule such as water. The rotational fine structure of the H-O-H bending mode of water is shown in Figure 1.3.

The two molecules whose vibration-rotation spectrum is shown in Figures 1.2 and 1.3, CO_2 and H_2O , are often encountered as interferences when mid-infrared spectra are measured (although the rotational lines in the spectrum of CO_2 are often unresolved when the spectrometer resolution is 4 cm^{-1} or poorer). In fact, it is good practice to eliminate all traces of these molecules in the beam path of an infrared spectrometer by purging the instrument with dry CO_2 -free air or pure nitrogen gas, as the bands shown in Figures 1.2 and 1.3 will often be seen in the spectra. As noted above, because collisions occur at a greater rate than the rotational frequency of molecules in the liquid state, no rotational fine structure is seen.

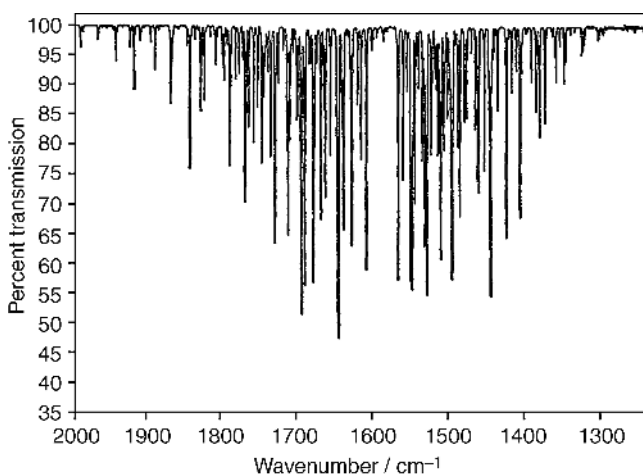


Figure 1.3. Vibration-rotation spectrum of the H-O-H bending mode of water vapor.

1.4. WIDTHS OF BANDS AND LINES IN INFRARED SPECTRA

1.4.1. Vibration–Rotation Spectra of Gases

The shape and width of individual lines in the vibration–rotation spectrum of a gas depend on the gas pressure, P . For gases at low pressure (typically, $P < 1$ torr), the shape and width of each spectral line in the width are determined by the Doppler effect (i.e., by the variation of the speed of each molecule in the direction of the beam). The shape of a Doppler-broadened line centered at wavenumber $\tilde{\nu}_0$ is Gaussian; that is, the absorbance at any wavenumber $\tilde{\nu}$ is given by

$$A(\tilde{\nu}) = A_0 \exp \left[\frac{-4 (\ln 2) (\tilde{\nu} - \tilde{\nu}_0)^2}{\gamma_D^2} \right] \quad (1.10)$$

where A_0 is the absorbance at $\tilde{\nu}_0$. γ_D is the full width at half-height (FWHH) of the band and is given by

$$\gamma_D = 2 \sqrt{\frac{2(\ln 2) kT}{m}} \frac{v}{c} \quad (1.11)$$

where k is Boltzmann's constant, T the temperature (in kelvin), v the frequency of the transition (in hertz), c the velocity of light, and m the mass of the molecule. Since m is equal to the molecular weight (in grams), M , divided by Avogadro's number, and frequency, v , is directly proportional to wavenumber, $\tilde{\nu}$, we have

$$\frac{\gamma_D}{\tilde{\nu}} = 7.16 \times 10^{-7} \sqrt{\frac{T}{M}} \quad (1.12)$$

For a line in the H–O–H bending mode of water ($M = 18 \text{ g} \cdot \text{mol}^{-1}$) at 1500 cm^{-1} , the Doppler width at room temperature (298 K) is about 0.0044 cm^{-1} . Thus, an instrument with very high resolution is needed before Doppler-broadened spectra can be measured accurately.

As the total pressure of the gas is raised above 1 torr, the mechanism of line broadening becomes more dominated by the effect of intermolecular collisions than by the Doppler effect. The shape of lines in collision-broadened spectra is Lorentzian:

$$A(\tilde{\nu}) = A_0 \frac{\gamma_C^2}{\gamma_C^2 + 4 (\tilde{\nu} - \tilde{\nu}_0)^2} \quad (1.13)$$

where γ_C , the FWHH of the collision-broadened line, is directly proportional to the pressure of the gas and increases with the polarity of each component. There are several mechanisms of collision broadening, each of which leads to a slightly different variation of the broadening coefficient with temperature, from $1/\sqrt{T}$ for hard-sphere collisions to $1/T$ for dipole–dipole interactions. For many molecules in air at ambient temperature, the collision-broadening coefficient is between 0.1 and $0.2 \text{ cm}^{-1} \cdot \text{atm}^{-1}$.

Hence for mixtures of an analyte with helium, nitrogen, or air at atmospheric pressure, γ_C of each of the rotational lines is usually between 0.1 and 0.2 cm^{-1} .

For molecules at pressures between about 1 and 100 torr, the line width is determined by both Doppler and collision broadening. In this case, the shape is given by a convolution of the shapes given by Eqs. 1.10 and 1.13; such a shape is known as a *Voigt profile*. The higher the pressure of the gas, the greater the contribution of collision broadening to the Voigt profile. Voigt profiles cannot be expressed analytically, as they result from the convolution of a Lorentzian and Gaussian shape, but the FWHH is given to a good approximation by

$$\gamma_V = \frac{\gamma_C}{2} + \sqrt{\left(\frac{\gamma_C}{2}\right)^2 + (\gamma_D)^2} \quad (1.14)$$

For large molecules, the spacing of lines in the vibration-rotation spectrum is usually less than 0.1 cm^{-1} . For such molecules in 1 atm of air or some other inert gas, the line spacing is less than γ_C , so that the lines can never be separated no matter how high the resolution of the spectrometer, and only the band contour can be measured. In this case, the higher the molecular weight of the molecule, the narrower is the band contour. Nonetheless, for most molecules, the FWHH of the band contour is at least 4 cm^{-1} . For such molecules it is rarely necessary to use a resolution much higher than 4 cm^{-1} to measure an easily recognizable spectrum, although to obtain a spectrum with minimal distortion of the rotational contour, a somewhat higher resolution should be used.

1.4.2. Spectra of Condensed-Phase Samples

Since there is no rotational fine structure in the infrared spectra of liquids, their spectra are much simpler than those of gases. To a good approximation, the shape of bands in the infrared spectra of liquids is Lorentzian (see Eq. 1.13). In practice, the far wings of bands in the spectra of liquids die out somewhat faster than would be given by Eq. 1.13. To model the behavior of bands in the spectra of liquids, bands are sometimes expressed as the sum of Lorentzian and Gaussian bands:

$$A(\tilde{\nu}) = (1 - \alpha)A_0 \frac{\gamma_L^2}{\gamma_L^2 + (\tilde{\nu} - \tilde{\nu}_0)^2} + \alpha A_0 \exp \left[\frac{-(\ln 2)(\tilde{\nu} - \tilde{\nu}_0)^2}{\gamma_G^2} \right] \quad (1.15)$$

where γ_L is the HWHH of the Lorentzian component, γ_G the HWHH of the Gaussian component (usually assumed to be the same), and α the Gaussian fraction. For many liquids, $\alpha < 0.1$. Although complicated, this form is at least analytical, unlike the Voigt profile. An even better description of bands in the spectra of liquids can be made with the use of the classical damped harmonic oscillator model, but this is beyond the scope of this chapter.

The actual widths of absorption bands in the mid-infrared spectra of liquids and solutions depend strongly on the rigidity of the part of the molecule where the

vibrational motion of the molecule is localized. For example, bands associated with aromatic groups often have widths between 2.5 and 5 cm^{-1} , whereas the FWHH of bands associated with the more flexible alkyl chains is often at least 10 cm^{-1} . Bandwidths also depend on the polarity of the solvent, with bands of a particular solute in a polar solvent usually being broader than the corresponding bands of the same molecule in a nonpolar solvent. Since water is the most polar solvent, bands of solutes in aqueous solution are usually broader than in any other solvent. When functional groups such as O—H are hydrogen bonded, the width of the stretching bands may be greater than 100 cm^{-1} . Because the widths of most absorption bands are rarely smaller than 4 cm^{-1} , it is common for survey spectra of liquids to be measured at a resolution of 4 or 8 cm^{-1} , whereas high-quality spectra for archival purposes are usually measured at a resolution of 1 or 2 cm^{-1} . Of course, measurement of a spectrum with a certain signal-to-noise ratio (SNR) takes far longer at a resolution of 1 cm^{-1} than the corresponding measurement at a resolution of 8 cm^{-1} . The “trading rules” among resolution, measurement time, and SNR are covered in some detail in Chapter 7.

Few detailed investigations into the shapes and widths of bands in the spectra of solids have been made, but the bands of solids are usually narrower than the corresponding bands of the same molecule in solution because of the restricted motion of the functional groups in the molecules. The shapes of mid-infrared absorption bands of solid compounds are often represented by Eq. 1.15, with no limitation as to the value of the Gaussian fraction, α .

Because bands in near-infrared spectra are overtones or combinations of fundamentals, the widths of these bands are typically greater than the widths of bands from which they are derived. For example, the FWHH of the first overtone of a C—H stretching band is to a first approximation twice that of the corresponding fundamental. As a result, most NIR spectra of liquids are measured at significantly lower resolution than is the corresponding mid-infrared spectrum.

1.5. QUANTITATIVE CONSIDERATIONS

1.5.1. Beer’s Law

The Bouguer–Lambert–Beer law (usually called simply *Beer’s law*) is the fundamental law of quantitative spectroscopy and is derived in all elementary textbooks on instrumental analysis. The *transmittance* of any sample at wavenumber $\tilde{\nu}$ is given by the ratio of the radiant power emerging from the rear face of the sample at that wavenumber $I(\tilde{\nu})$ to the power of the radiation at the front face of the sample, $I_0(\tilde{\nu})$. The transmittance of a pure sample of thickness b (cm) at wavenumber $\tilde{\nu}$ is given by Beer’s law as

$$T(\tilde{\nu}) = \frac{I(\tilde{\nu})}{I_0(\tilde{\nu})} = \exp[-\alpha(\tilde{\nu})b] \quad (1.16)$$

where $\alpha(\tilde{\nu})$ is the *linear absorption coefficient* (cm^{-1}) at $\tilde{\nu}$. The *absorbance* of the sample at $\tilde{\nu}$, $A(\tilde{\nu})$, is given by the base 10 logarithm of $1/T(\tilde{\nu})$:

$$A(\tilde{\nu}) = \log_{10} \frac{1}{T(\tilde{\nu})} = \frac{1}{\ln 10} \alpha(\tilde{\nu}) b \quad (1.17)$$

$(1/\ln 10)\alpha(\tilde{\nu})$ is the *absorptivity* at $\tilde{\nu}$, $a(\tilde{\nu})$.

If the sample is a mixture, the absorbance of each component, i , at concentration, c_i , is given by Beer's law as

$$\log_{10} \frac{1}{T(\tilde{\nu})} = A_i(\tilde{\nu}) = a_i(\tilde{\nu}) b c_i \quad (1.18)$$

where $a_i(\tilde{\nu})$ has the units of $(\text{concentration} \cdot \text{pathlength})^{-1}$. For N -component mixtures where more than one component absorbs at $\tilde{\nu}$, the total absorbance is given by

$$A(\tilde{\nu}) = \sum_{i=1}^N [a_i(\tilde{\nu}) b c_i] \quad (1.19)$$

Two important points should be raised. First, the absorbance, and not the transmittance, of any component is proportional to its concentration in the sample. Infrared spectra linear in absorbance are rarely measured directly. Before 1980, grating monochromators were routinely used for the measurement of infrared spectra. On these instruments, the ratio of $I(\tilde{\nu})$ and $I_0(\tilde{\nu})$ was usually measured, so the usual output of these instruments was a transmittance spectrum. Computers were interfaced to a few infrared grating spectrometers in the 1970s, so that transmittance spectra could be quickly converted to absorbance for quantitative applications. As we will see in Chapter 2, FT-IR spectrometers measure interferograms, from which a single-beam spectrum is calculated. The intensity of the single-beam spectrum, $B(\tilde{\nu})$, at any wavenumber $\tilde{\nu}$ is proportional to the power of the radiation reaching the detector. Thus, to measure the absorbance spectrum of a sample, the ratio of the single-beam spectra of the sample and background is first calculated (to yield the transmittance spectrum), which is then converted to absorbance as shown in Eq. 1.18. It should always be remembered that as the first step of many of the more popular operations in FT-IR spectrometry, including spectral subtraction, multicomponent analysis, and spectral searching, the measured spectrum should always be converted to absorbance.

Second, the effect of reflection loss at the windows of the cell has been neglected in the treatment described above. The refractive index, n , of most organic samples and windows is about 1.5, so that the reflectance of the front surface is about 4% (see Section 13.2.2). If Beer's law is to be applied accurately, the apparent absorbance caused by reflection loss (0.018 absorbance unit for windows with $n = 1.5$) should first be subtracted from the measured absorbance spectrum.

1.5.2. Optical Constants

The fundamental parameters that govern the absorption of radiation are the real and imaginary components of the complex refractive index:

$$\tilde{n}(\tilde{\nu}) = n(\tilde{\nu}) + ik(\tilde{\nu}) \quad (1.20)$$

where $\tilde{n}(\tilde{\nu})$ is the real refractive index and $k(\tilde{\nu})$ is the imaginary refractive index at $\tilde{\nu}$. $n(\tilde{\nu})$ is often simply called the *refractive index*. $k(\tilde{\nu})$ is also sometimes known as the *absorption index* and, incorrectly, as the attenuation index.

For any material, $n(\tilde{\nu})$ is determined by Snell's law. A few materials have no significant absorption in the mid- and near infrared. Those materials with low refractive index ($1.45 \leq n \leq 1.6$) are useful as windows, whereas those with high refractive index ($2.4 \leq n \leq 4.0$) are frequently used as internal reflection elements (see Chapter 15). For organic and inorganic molecules whose spectra exhibit typical absorption bands, the refractive index changes across the absorption band. A typical refractive index spectrum has the appearance shown in Figure 1.4a. This

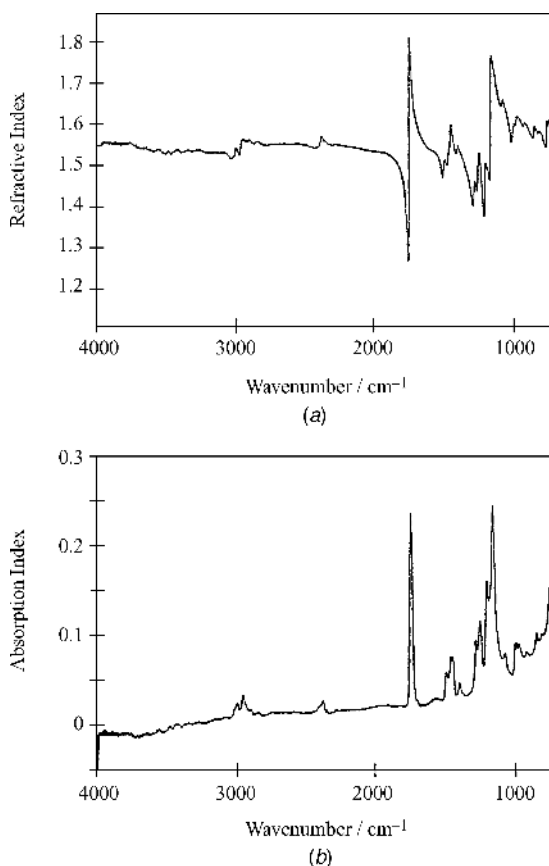


Figure 1.4. (a) Refractive index and (b) absorption index spectra of poly(methyl methacrylate).

type of variation in the refractive index across absorption bands is known as *anomalous dispersion*. Outside those regions of anomalous dispersion, n is fairly constant from the visible through the mid-infrared spectrum.

Like the real refractive index, the imaginary refractive index is also a dimensionless quantity. For pure materials, $k(\tilde{\nu})$ is given by

$$k(\tilde{\nu}) = \frac{\alpha(\tilde{\nu})}{4\pi\tilde{\nu}} \quad (1.21)$$

where $\alpha(\tilde{\nu})$ is the linear absorption coefficient defined in Eq. 1.16. A typical absorption index spectrum looks like an absorbance spectrum (see Figure 1.4b). Whereas the transmission spectrum of samples is largely determined by the value of $k(\tilde{\nu})$ for each band, both of the optical constants $n(\tilde{\nu})$ and $k(\tilde{\nu})$ control the reflection of samples, as discussed in Chapter 13.

1.6. POLARIZED RADIATION

If a beam of unpolarized electromagnetic radiation is transmitted in the z direction, the amplitudes of the components of the sinusoidally varying electric field in the x and y planes are identical. When the beam is passed through a *polarizer*, the component of the electric field in one plane is transmitted, as described in more detail in Chapter 12. For unoriented samples such as all gases and liquids and isotropic solids, the absorbance of all bands in the spectrum is independent of the orientation of the polarizer. If the molecules in a certain sample are preferentially oriented in a given direction, however, the component of the dynamic dipole moment derivative of each vibrational mode, $d\mu/dQ$, in the direction that the radiation is polarized will change as the polarizer is rotated.

Since the largest intensity of each band is observed when the beam is polarized in the direction for which the change in dipole moment for that vibrational mode is greatest, important information on the orientation of samples can be derived by installing a polarizer in the beam. For example, one of the more important applications of the use of polarized light is the measurement of the orientation of the chains in drawn or extruded polymers. A more esoteric application is the estimation of the angle at which surfactants are adsorbed on the surface of water.

Several different types of reflection spectroscopy yield more information when the radiation is polarized. For example, very thin films of molecules adsorbed on the surface of metals only absorb radiation polarized parallel to the plane of incidence. The reflection of light from bulk samples depends on the polarization of the light with respect to the plane of the sample. The effective depth into a sample that can be sensed by internal reflection spectroscopy is also different for radiation polarized perpendicular and parallel to the surface. Polarized radiation may even be used to eliminate interference fringes from the spectra of thin polymer films.

It is hoped that these few examples will give the less experienced reader an indication as to why FT-IR spectroscopy is even more popular today than when it was used primarily as a tool for structural elucidation.

1.7. RAMAN SPECTROMETRY

Raman spectrometry is an alternative, and often complementary, way to measure vibrational spectra to infrared spectrometry. In Raman spectrometry the sample is illuminated with a monochromatic beam of radiation of wavenumber $\tilde{\nu}_0$ (typically, from some type of laser). All of the photons that interact with the sample cause the potential energy of a molecule to be raised to a *virtual state* $hc\tilde{\nu}_0$ above the ground state, where c is the velocity of light. Almost immediately most molecules return to the ground state through the emission of a photon of the same wavelength as that of the incident photon. Since the energies of the incident and scattered photons are identical, this process is a form of elastic scattering often referred to as *Rayleigh scattering*. A small fraction of the incident photons drop back to the first excited vibrational state of the i th vibrational mode of the molecule, so that the energy of the scattered photon is $hc(\tilde{\nu}_0 - \tilde{\nu}_i)$ i.e., it will be observed at a wavenumber of $(\tilde{\nu}_0 - \tilde{\nu}_i)$, where $\tilde{\nu}_i$ is the wavenumber of the i th vibrational mode. Since the energies of the incident and scattered photons are different, the scattering is inelastic. This process is known as *Stokes Raman scattering*. Since a given molecule has many different vibrational modes, measurement of the spectrum from $\tilde{\nu}_0$ to $(\tilde{\nu}_0 - 4000) \text{ cm}^{-1}$ allows all Raman-active vibrational bands to be measured.

Not all molecules are in the ground vibrational state. A few molecules are in the first excited state of each vibrational mode, $v_i = 1$. Neglecting the effect of degeneracy, the Boltzmann population of molecules in the first vibrational state of the i th mode is given by

$$\frac{N_1}{N_0} = e^{-hc\tilde{\nu}_0/kT} \quad (1.22)$$

where N_1 and N_0 are the numbers of molecules in the first excited state and ground state of the i th vibrational mode, respectively. When illuminated by a laser, a few molecules in an excited vibrational state can be promoted to a virtual level, $hc(\tilde{\nu}_0 + \tilde{\nu}_i)$, and then return to the ground state, resulting in Raman bands at wavenumbers above that of the laser. This process, known as *anti-Stokes scattering*, is much weaker than Stokes scattering for bands above about 500 cm^{-1} above $\tilde{\nu}_0$ (where the Boltzmann population is less than 1%).

The intensity of bands in the Raman spectrum of a compound are governed by the change in *polarizability*, α , that occurs during the vibration. The intensity of any band in the Raman spectrum is given by the following expression:

$$I_{\text{Raman}} = KI_L(\tilde{\nu}_0 - \tilde{\nu}_i)^4 \left(\frac{d\alpha}{dQ} \right)^2 \quad (1.23)$$

where I_L is the power of the laser at the sample, $\tilde{\nu}_0 - \tilde{\nu}_i$ the wavenumber at which the band is measured, and $d\alpha/dQ_i$ the change in polarizability with the normal coordinate of the vibration. This parameter is the Raman equivalent of absorptivity and is sometimes called the Raman cross section. The constant of proportionality, K , is

dependent on the optical geometry, collection efficiency, detector sensitivity, and amplification.

Before the mid-1980s, Raman spectroscopy was often considered to be less desirable to infrared absorption spectroscopy for two reasons. First, only one in between 10^8 and 10^{10} of the incident photons undergoes Raman scattering. Thus, until about 1985, Raman spectrometry was considered to be a relatively insensitive and/or time-consuming technique. However, the advent of multiplex (usually, Fourier transform) and multichannel (monochromators with array detectors) techniques has greatly increased the sensitivity of modern Raman spectrometry. Of greater difficulty today is the fact that many compounds fluoresce when illuminated by visible lasers, such as by the radiation from an Ar^+ laser at 488 nm. For some molecules the quantum efficiency for fluorescence with 488-nm radiation can approach 100%, and it is often greater than 0.001%. Even in the latter case, the radiation emitted by luminescence far exceeds the intensity of Raman-scattered radiation. Similarly, fluorescence from a trace molecule with a quantum efficiency approaching 100% can also swamp the Raman signal.

To ameliorate the problem of fluorescence, near-infrared lasers can be used to illuminate the sample. By the use of NIR radiation, the wavelengths used to excite Raman spectra are long enough that most compounds no longer fluoresce. Two types of NIR lasers can be used to measure Raman spectra. The first is the diode laser, with the most popular emitting at ~ 785 or ~ 840 nm ($12,740$ or $11,900\text{ cm}^{-1}$, respectively). Raman spectra generated with NIR diode lasers can be measured using silicon charge-coupled device (CCD) array detectors, which cut on at about 9500 cm^{-1} , limiting the Raman spectrum to about 3240 and 2500 cm^{-1} , depending on whether a 785- or 840-nm laser is being used.

The other popular NIR laser is the Nd:YAG laser, which emits at 1064 nm ($\tilde{\nu}_0 \sim 9400\text{ cm}^{-1}$). With this laser, the problem changes from fluorescence to detection. Consider a Raman band due to a C–H stretching mode at 2950 cm^{-1} . This band must be measured at $(9400 - 2950)\text{ cm}^{-1}$ (i.e., 6450 cm^{-1}), which is well below the wavenumber at which silicon charge-coupled device (CCD) array detectors cut off. Detectors operating in this region of the spectrum are significantly less sensitive than CCDs. Furthermore, it can be seen from Eq. 1.23 that I_{Raman} is proportional to $(\tilde{\nu}_0 - \tilde{\nu}_i)^4$. Thus, a Raman band at 2950 cm^{-1} measured with a 1064-nm Nd:YAG laser would be about 55 times weaker than the same band measured with the 488-nm line of an Ar^+ laser of equal power. Since CCD array detectors do not respond at 6450 cm^{-1} , it is not surprising that Fourier transform techniques have been invoked for the measurement of weak Raman signals at such long wavelengths.

There are many reasons why scientists want to measure the Raman spectra of compounds. First, many bands that are weak in the infrared spectrum are among the strongest bands in the Raman spectrum. For example, the S–S and C=C stretching bands are often so weak as to be essentially unrecognizable in the IR spectrum but stick out like the proverbial sore thumb in a Raman spectrum. Second, some Raman bands are found at very characteristic frequencies. For instance, monosubstituted aromatic compounds, together with 1,3-disubstituted and 1,3,5-trisubstituted aromatics, have a very intense band at 1000 cm^{-1} . This band, along with the presence or absence

of other bands in the infrared and Raman spectrum, can easily identify the substitution pattern of an aromatic ring. Furthermore, samples for Raman spectrometry can be mounted in standard glass tubes, making sample handling far easier for Raman than for infrared spectrometry.

For these reasons, analytical Raman spectrometry has undergone a remarkable rebirth since about 1985. Instruments based on Fourier transform techniques and CCD array detectors are commercially available from a large number of vendors in North America, Europe, and Asia. Like infrared spectrometry, Raman spectrometry has outlived its seventh age, although whether it has matured through its second childhood yet is debatable. Nonetheless, Raman spectrometry is still a vital weapon in a vibrational spectroscopist's arsenal.

1.8. SUMMARY

In Chapters 2 to 8 we describe the theory and instrumentation needed for an appreciation of the way that Fourier transform infrared and Raman spectra are measured today. The sampling techniques for and applications of FT-Raman spectrometry are described in Chapter 18. The remaining chapters cover the techniques and applications of absorption, reflection, emission, and photoacoustic spectrometry in the mid- and near-infrared spectral regions.

REFERENCE

1. H. A. Laitinen, *Anal. Chem.* **45**, 2305 (1973).