Fourier Transform Infrared Spectrometry

Second Edition

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PREFACE

The advances in the field of Fourier transform infrared (FT-IR) spectrometry in the past 20 years have been quite remarkable. FT-IR spectrometers are installed in just about every analytical chemistry laboratory in the developed world. Actually, we sometimes wonder why so many people still refer to these instruments as FT-IR spectrometers, or more colloquially simply as FTIRs, rather than simply as infrared spectrometers, since almost all mid-infrared spectra are measured with these instruments. We note that scientists who use nuclear magnetic resonance, the other technique that has been revolutionized by the introduction of Fourier transform techniques, no longer talk about FT-NMR, as continuous-wave instruments (e.g., grating monochromators) are a distant memory. Nonetheless, practitioners of infrared spectrometry seem to want to recall the era of grating monochromators, even though the vast majority has never seen one!

This book is the second edition of a volume that was published in 1986. In the past 20 years, an enormous body of work has been published in which the key measurements have been made on FT-IR spectrometers. When we started to write this new edition, it was not our intention to give a compendium of all these applications. Instead, we have tried to give a description of the theory and instrumentation of FT-IR spectrometry as it stands today. Even with this limitation, the material has taken 23 chapters to cover, and we know that a number of topics has been omitted. We ask all our many friends whose work is not referenced in this book for their understanding and forgiveness. All we can say is that had we reviewed all the important and elegant experiments that have been done over the past 20 years, the book would have rivaled the size of the 4000-page-long *Handbook of Vibrational Spectroscopy* that one of us recently coedited. Instead, what we have tried to do is to provide users of FT-IR spectrometers with a reasonably detailed description of how their instruments work and the types of experiments that can be performed even on the less expensive instruments.

At this point we should note that the way that infrared spectroscopy is applied has changed dramatically over the past 20 or 30 years. Whereas infrared spectrometry once played an important role in the structural elucidation of new organic compounds, this task is now largely accomplished by NMR, mass spectrometry and x-ray crystallography. Why, then, is the popularity of infrared spectrometry at an all-time high? The answer is in part to be found in the versatility of this technique and in part in the relatively low cost of the instrumentation. The number of applications for which a careful measurement of the infrared spectrum will yield important qualitative, quantitative, and/or kinetic information is limited only by the imagination of the user. In the book we have attempted to summarize the types of experiments that can be carried out on FT-IR spectrometers. For most of them, we do not go into great detail. There are a few measurements, however, such as the treatment of dynamic linear dichroism spectra by two-dimensional correlation, where we felt that a more detailed description was needed if it is to be understood by the average reader.

We have attempted to use the correct nomenclature throughout the book. Regrettably, few spectroscopists use correct terminology in their papers and reports. Correct usage for spectroscopic terms has been defined beautifully by John Bertie in a glossary at the end of the *Handbook of Vibrational Spectroscopy*, and we use his recommendations in a consistent manner. The book is largely about the measurement of spectra: hence the title "Fourier Transform Infrared Spectro*metry*."[1] Throughout the book we have tried to use the term *wavenumber* when we refer to the abscissa scale of a spectrum in cm^{-1}, using the term *frequency* only when referring to the modulation of a signal in hertz. We note that *curve fitting* and *deconvolution* are often (incorrectly) used interchangeably and we have tried to use the terms correctly. We would also note that the verb from which (*de*)*convolution* is derived is (*de*)*convolve* (as in *revolve/revolution* and *evolve/evolution*). Both of us wish to demonstrate that the five years we each spent learning Latin in high school was not misspent!

Measured or measurable parameters end in the suffix -*ance* (e.g., transmittance, absorbance, reflectance). A spectrum that is plotted with one of these parameters as the *y*-axis can validly be referred to as a *transmittance*, *absorbance*, or *reflectance* spectrum; otherwise, it should be referred to as a *transmission*, *absorption*, or *reflection* spectrum. We particularly note how reflection spectroscopy has fallen into this misuse. Unfortunately, *diffuse reflectance spectroscopy* and *attenuated total reflectance* (ATR) *spectroscopy* are now part of many spectroscopists' lexicon. Pedagogy has held sway, however, and we have attempted to use the correct terminology throughout the book. One of us (P.R.G) particularly regrets the poor usage of the term *diffuse reflectance spectroscopy* in his early papers on this subject. He regrets even more that he coined the term *DRIFT* for this technique, as *drift* has all the wrong connotations for any spectroscopic measurement. Shortly after the first papers on DRIFT were published, Bob Hannah of PerkinElmer showed that diffuse reflection infrared spectra could be measured easily on grating spectrometers and coined the acronym *DRUIDS* (diffuse reflection using infrared dispersive spectrometry!). We hope that neither Bob nor Peter is forced to live in acronym hell as result of their transgressions on this planet!

We would also like to note the reason for the hyphen between FT and IR throughout the book. This is to distinguish *Fourier transform infrared spectrometry* from *frustrated total internal reflection*; FTIR is now an infrequently used term for

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[1] The etymology of the term *spectrometry* is clear, but the meaning of *spectroscopy* is less so as spectra are no longer measured with spectroscopes. In this book we use *spectrometry* to mean the measurement of spectra and *spectroscopy* to mean the science of obtaining qualitative and quantitative information from spectra.

ATR, but nevertheless, this usage was introduced before FT-IR spectrometers became popular.

Finally, we would like to thank the many people who have either supplied material for the various chapters in this book or proofread the work in one of its several drafts. In particular, we would like to thank Richard Jackson, Bruce Chase, Larry Nafie, Rina Dukor, John Chalmers, Milan Milosevic, Neil Everall, and Roger Jones, as well as the members of our research groups, for their comments. We gratefully acknowledge the patience and good grace of the six (count ‘em!) Wiley editors who have tried to extract the manuscript from us. Finally, our wives, Marie and Leslie, deserve our unending gratitude for putting up with us over the many years that it has taken to assemble the material for this book.

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 $2\,\mathrm{cm}^{-1}$ 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

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Fourier Transform Infrared Spectrometry, Second Edition, by Peter R. Griffiths and James A. de Haseth

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 $\sim 4\,\mathrm{cm}^{-1}$. When such spectra between 4000 and $400\,\mathrm{cm}^{-1}$ 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 $2\,\mathrm{cm}^{-1}$ 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

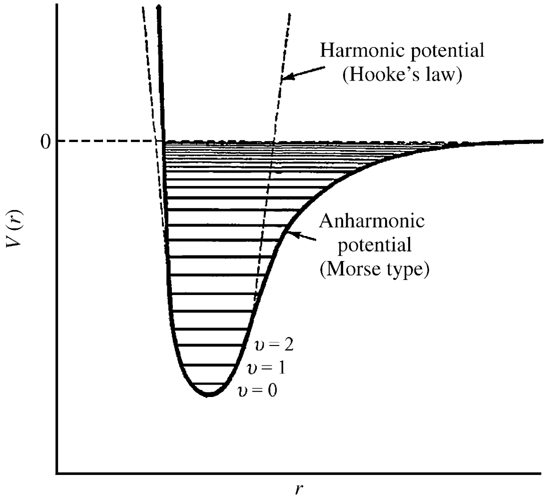

Figure 1.1. Potential energy of a diatomic molecule as a function of the atomic displacement during a vibration for a harmonic oscillator (dashed line) and an anharmonic oscillator (solid line).

by the equation

$$V_{iv} = h\nu_i\left(v_i + \frac{1}{2}\right) \tag{1.1}$$

where h is Planck's constant, ν_i the *fundamental frequency* of the particular mode, and v_i the *vibrational quantum number* of the *i*th mode $(v_i = 0, 1, 2, \ldots)$. 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

$$V_{iv} = h\nu_i\left(v_i + \frac{1}{2}\right) + h\nu_i x_i\left(v_i + \frac{1}{2}\right)^2 \tag{1.2}$$

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 $(\Delta v_i = 2, 3, \ldots)$ 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 spectra/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 μm 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

$$E_J = BJ(J+1) \tag{1.3}$$

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

$$B = \frac{h}{8\pi^2 Ic} \tag{1.4}$$

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

$$\Delta J = \pm 1 \tag{1.5}$$

so that

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

Thus, for a rigid rotor, the pure rotation spectrum would be comprised of a series of lines with equal spacing of $2B$ 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 wavenumber $\tilde{\nu}_0$, 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,

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

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:

$$E_J = BJ(J+1) - DJ^2(J+1)^2 \tag{1.8}$$

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.

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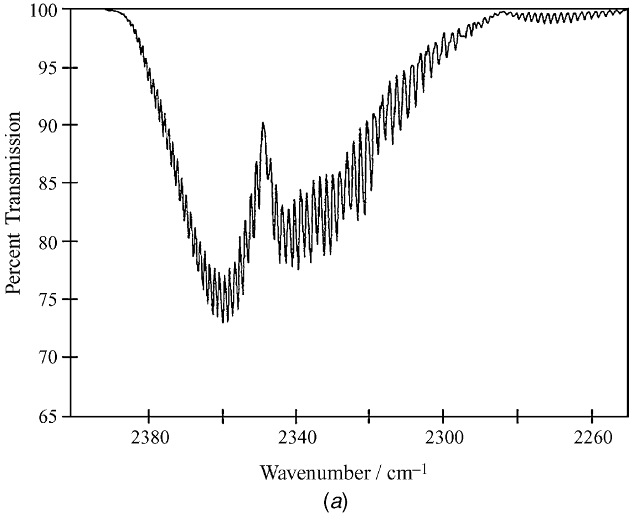
[1] There is one exception to this "rule" for diatomic molecules. The fact that nitric oxide has an unpaired electron in its ground state leads to the fact that the transition $\Delta J = 0$ is allowed.

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



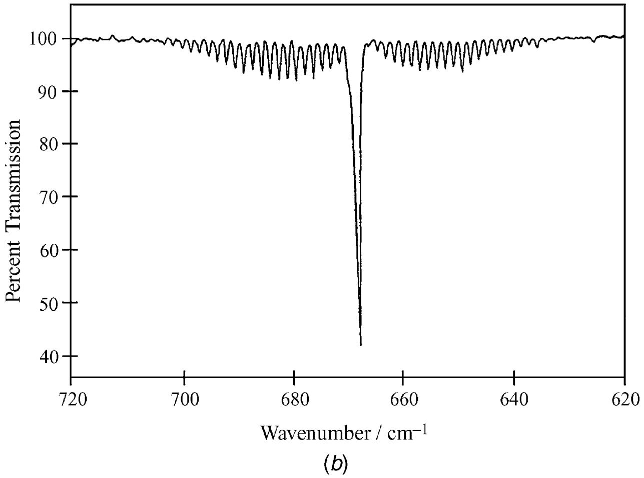


Figure 1.2. Infrared active vibration–rotation fundamental bands of carbon dioxide: (*a*) antisymmetric stretching mode (ν_3) for which the selection rule is $\Delta\nu_3 = \pm1$ and $\Delta J = \pm1$; (*b*) bending mode (ν_2) for which the selection rules is $\Delta\nu_2 = \pm1$ and $\Delta J = 0, \pm1$.

without a simultaneous change in J is permitted:

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

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.

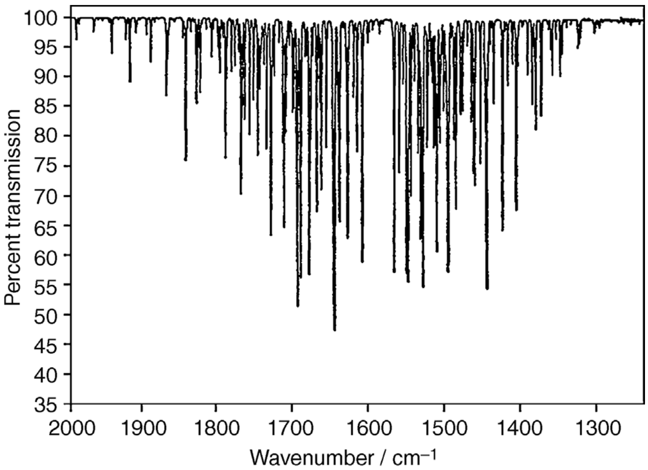


Figure 1.3. Vibration–rotation spectrum of the H–O–H bending mode of water vapor.

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

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

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

$$\gamma_D = 2\sqrt{\frac{2(\ln 2)\,kT}{m}}\frac{\nu}{c} \tag{1.11}$$

where k is Boltzmann's constant, T the temperature (in kelvin), ν 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, ν, is directly proportional to wavenumber, $\tilde{\nu}$, we have

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

For a line in the H–O–H bending mode of water ($M = 18$ g · 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:

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

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 cm^{-1} · atm^{-1}.