Yukihiro Ozaki · Christian Huck ·
Satoru Tsuchikawa ·
Søren Balling Engelsen *Editors*

# Near-Infrared Spectroscopy

## Theory, Spectral Analysis, Instrumentation, and Applications

Springer

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# Preface

Despite being a well-established and very mature technique, near-infrared (NIR) spectroscopy continues to demonstrate remarkable progress. New principles for instrumentation have provided cutting-edge developments within NIR imaging, handheld instruments and laser-based techniques. As with the field of data analysis in general, NIR spectral analysis and data treatments also continue to demonstrate prominent advancements that only accelerate in its scope and accomplishments. We now have instruments available that are capable of generating very high volumes of high-quality spectral data, in breath-taking speeds, perhaps even distributed over several online measurement points, and terms such as artificial intelligence, big data and deep learning are more and more commonly seen as the tools used to decipher the hidden information in the spectral data. All these advances open the pathways for the introduction of quantum chemistry to NIR spectroscopy—a decoding and understanding for modelling chemical systems based on quantum theory. It is now possible to imagine applications that use a combination of NIR spectroscopy with information and communication technology, applications that uses low-power and remote-sensing laser NIR spectroscopy, or devices incorporated in handheld instruments—maybe even embedded in our mobile phones—all of which is contributing to some artificial intelligent-assisted model to improve, for instance, food quality and safety for the individual consumer. The possibilities of NIRS technology seem to be endless!

Several textbooks and handbooks on NIR spectroscopy are currently available; they are all important books, but some of them are not up to date. We thus thought there was an increasing demand for a new state-of-the-art textbook on NIR spectroscopy. The present book, we hope, will fill the gap and find a wide audience of newcomers as well as experts to the exciting and versatile NIR spectroscopy technology. The book is intended as a go-to-book for background theory, applications and tutorial work. It consists of four major parts: Introduction and Principles, Spectral Analysis and Data Treatments, Instrumentation, and Applications. We attempted to prepare a well-balanced book with emphasis on underlying principles, spectral analysis and data treatments and at the same time cover almost all areas to which NIR spectroscopy is currently applied.

The contributors, from many countries, are all front-runners in modern vibrational spectroscopy, data analysis, instrumentation and/or applications. Another purpose of this book is making a strong bridge between molecular spectroscopists and researchers and engineers in various fields such as agriculture and food engineering, pharmaceutical engineering, polymer engineering, process engineering and biomedical sciences. We intend the book to become a valuable source for molecular spectroscopists who are interested in new applications of NIR spectroscopy and for researchers and engineers in a variety of fields who would like to study basic principles of molecular spectroscopy and NIR spectroscopy in particular.

Finally, it is our strong hope that this book will be useful for graduate science and engineering students where it can serve as inspiration as textbook for courses and seminars of graduate schools.

Last but not least, we would like to thank Dr. Shinichi Koizumi, Mr. Tony Pressler Sekar and Ms. Taeko Sato of Springer Nature, for their continuous efforts in publishing this exciting book.

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# Part I
# Introduction and Principles

# Chapter 1
# Introduction

**Yukihiro Ozaki and Christian Huck**

**Abstract** This chapter describes the introduction to NIR spectroscopy. The discovery of infrared region is mentioned first, and then, the definition of NIR region and characteristics of NIR spectroscopy are explained. Finally, the brief history of NIR spectroscopy is outlined.

**Keywords** Near-infrared · NIR · Vibrational spectroscopy · Electronic spectroscopy

## 1.1 Discovery of Infrared (IR) Region

The discovery of an invisible component beyond the red end of the solar spectrum (modern meaning-infrared (IR) region in a broad sense) is ascribed to William Herschel, a German-born British astronomer, who is famous for Herschel telescope. In 1800 one day, he investigated the effect of sunlight divided from violet to red by a prism on temperature increase. He used just sunlight, a prism, and thermometers. Figure 1.1 shows his portrait and the experimental set up he employed. He happened to find that the significant temperature increase occurred even outside of red. He thought there was a different kind of invisible radiation from visible light beyond the red end of sunlight and named this radiation "heat ray." This was really a great discovery in science, but even he could not imagine that this is light. He was 62 years old when he discovered "heat ray." Sixty-two years old in 1800 probably corresponds to today's 80 years old or so. Thus, his discovery demonstrated that even very senior scientist could have intensive serendipity.

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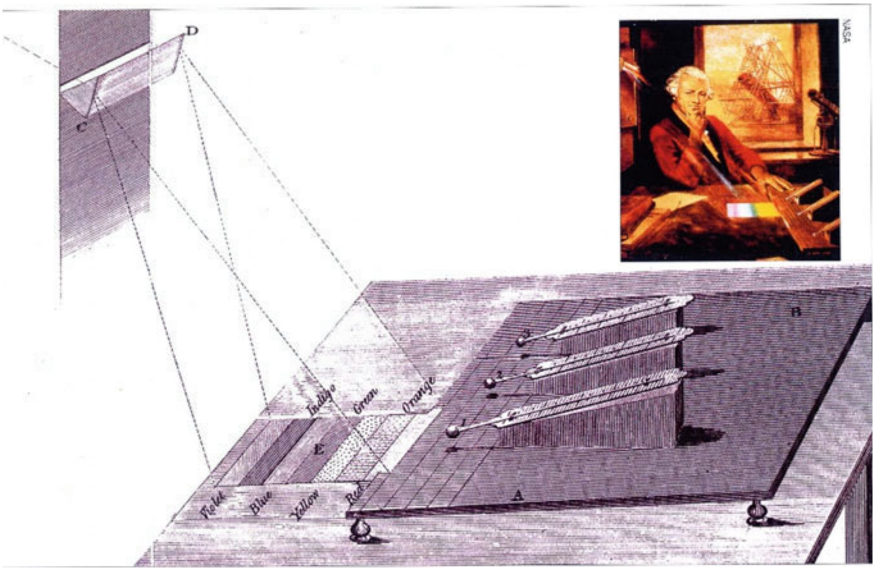

Fig. 1.1 The portrait of William Herschel and his experimental set up in 1800

Interestingly enough, just one year after the discovery of “heat ray,” Johann Ritter, a German scientist found another invisible component beyond the violet end of the solar spectrum based on an experiment of blackening of silver chloride. In this way, a new era of light was opened at the turning point from the eighteenth century to the nineteenth century. After the discovery of “heat ray,” many scientists investigated it. In 1835, it was confirmed that “heat ray” is invisible light which has longer wavelength than visible light. He named this light “infrared (IR).” Maxwell elucidated theoretically in 1864 that ultraviolet, visible, and IR light are all electromagnetic wave. In 1888, Hz proved it experimentally.

## 1.2 Introduction to NIR Spectroscopy

IR region is so wide energetically, ranging from 150 to 0.12 kJ mol$^{-1}$ (12,500–10 cm$^{-1}$). If one compares the energy of the highest wavenumber end of NIR region with that of the lowest wavenumber end of far-IR (FIR) region, one can find that the difference in the energy between the two ends is more than 1000 times. Therefore, nowadays, the IR region is divided into three regions, NIR region (12,500–4000 cm$^{-1}$; 800–2500 nm), the IR region (mid-IR; 4000–400 cm$^{-1}$; 2500–25,000 nm), and the far-IR region (FIR; 400–10 cm$^{-1}$; 25 μm-1 mm) [1–7]. NIR spectroscopy is spectroscopy in the region of 12,500–4000 cm$^{-1}$, where bands arising from electronic transitions as well as those due to overtones and combinations of normal vibrational modes are expected to appear [1–7]. Therefore, NIR spectroscopy is electronic spectroscopy as well as vibrational spectroscopy. Ultraviolet (UV)-visible (Vis) spectroscopy is electronic spectroscopy while infrared (IR) spectroscopy is vibrational spectroscopy, so that NIR spectroscopy is something special. It lies in between electronic spectroscopy region and vibrational spectroscopy region.

Figure 1.2 shows chemical structure of immobilized metal affinity chromatography (IMAC) material and NIR spectra in the region of 10,000–4000 cm$^{-1}$ of 32 kinds of IMAC materials [8]. Broad features in the 10,000–7500 cm$^{-1}$ region are due to the d-d transition of Ni coordination compound and bands in the 7500–4000 cm$^{-1}$ region arise from overtones and combinations. The spectra in Fig. 1.2 are very interesting examples, demonstrating that in the NIR region, one can observe both bands assigned to electronic transition and those originating from vibrational transitions. Most of the electronic transitions appearing in the NIR region are the d-d transitions, charge-transfer (CT) transitions, and π-π* transitions of large, or long, conjugated systems [1, 3, 7]. NIR spectroscopy involves absorption, emission, scattering, reflection, and diffuse-reflection of light [1–7].

NIR spectroscopy together with Raman, IR, and Terahertz/FIR spectroscopy forms “four sisters of vibrational spectroscopy.” Since NIR spectroscopy is concerned

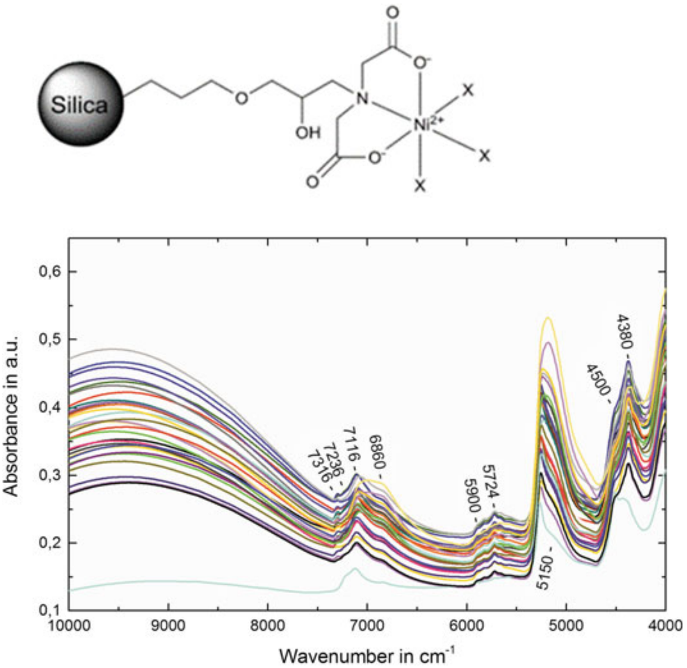

**Fig. 1.2** Chemical structure of immobilized metal affinity chromatography (IMAC) material and NIR spectra in the region of 10,000–4000 cm$^{-1}$ of 32 kinds of IMAC materials. Reproduced from Ref. [8] with permission

only with overtones and combination modes as a vibrational spectroscopy, it is very much unique compared with Raman, IR, and Terahertz/FIR spectroscopy.

The NIR region can be divided into three regions; Region I (800–1200 nm; 12,500–8500 $\text{cm}^{-1}$), Region II (1200–1800 nm; 8500–5500 $\text{cm}^{-1}$), and Region III (1800–2500 nm; 5500–4000 $\text{cm}^{-1}$) [1–7]. The boarders of the three regions are not rigorous. In Region I, bands arising from electronic transitions and those due to higher-order overtones and various types combination modes are expected to appear. Region I shows high transparency because all the bands appearing in this region are very weak, allowing biomedical applications and applications to agricultural products. Region I is the region where CCD cameras work very well, and this region is called "window of biological materials" because of high transparency to body. It has also a few more nick names: "the short-wave NIR (SWNIR) region," "near NIR (NNIR) region," or "the Herschel region."

Region II is a region for the first and second overtones of the XH ($X = C, O, N$) stretching vibrations and various types of combination modes. Region III contains mainly bands attributed to the combination modes except for the second overtone of the $C = O$ stretching vibrational mode. It shows poorer "permeability."

NIR spectroscopy, particularly vibrational NIR spectroscopy, is spectroscopy of anharmonicity [1–7]. The overtones and combination modes are the so-called forbidden transitions for a harmonic potential, yielding very weak bands. Both the frequencies and intensities of NIR bands are controlled by anharmonicity. Therefore, investigations on overtones and combination modes, anharmonicity, vibrational potential, and dipole moment function regarding NIR spectroscopy are important. However, these studies have been far behind applications of NIR spectroscopy probably because until 1990s, it was difficult to obtain accurate NIR spectra and to make reliable band assignments. It is only recent that quantum chemistry has been introduced to studies of frequencies and intensities of overtones and combination bands (Chap. 5).

The fact that bands in the NIR region are weak or very weak is what makes this region unique and markedly different from the other regions [1–7]. The reason why the NIR region is valuable in various applications is because only the NIR region serves as a highly transmitting window to radiation thanks to anharmonicity.

## 1.3 Brief History of NIR Spectroscopy

It is uncertain when NIR spectroscopy began, but there is the report that Abney and Festing measured the spectra of some simple organic compounds in the 700–1200 nm region as well as in the Vis and IR regions. In the beginning of the twentieth century, main concerns of molecular spectroscopy were UV–Vis and IR spectroscopy. It was 1920s and 30s that systematic measurements of NIR spectra were carried out. A chance came from the development of a spectrometer by Brackett. In 1930s, spectroscopists already recognized that NIR spectra arise from overtones and combination modes [9, 10]. In 1950s, NIR spectroscopy received considerable interest for hydrogen bonding studies and studies on anharmonicity [11, 12]. The development of an innovative spectrometer, Carey 14 Applied Physics in 1954, pushed NIR spectroscopy research as well as UV–Vis studies [1]. However, the development of basic studies of NIR spectroscopy was still rather slow because even development of new spectrometers was insufficient for NIR spectroscopy to observe weak NIR bands accurately, and also systematic analysis of NIR bands was very difficult. Moreover, NIR spectroscopy could not find application fields not only in basic science but also in practical applications [1–7]. Until 1960s, NIR spectroscopy was a "sleeping giant" in terms of both basic science and applications.

It was not a spectroscopist but an engineer in an agricultural field who woke up the sleeping giant. He was Karl Norris (Fig. 1.3a) of the US Department of Agriculture (USDA). Norris learnt electrical engineering as well as agricultural engineering at universities, and thus, he had good background for developing spectrometers and systems with computers. Norris was involved in a research of drying grain by use of infrared technology. He happened to find that the grain had absorbances in the NIR region. He focused on the fact that NIR spectroscopy is suitable for nondestructive analysis, and he and his colleagues tried to use NIR spectroscopy for quality assessments of agricultural products. Norris proposed to use statistical methods to build calibration models from NIR data [13, 14]. First, he employed simple linear regression and then multiple regression. His idea realized the advantages of NIR spectroscopy in practical applications. Thus, Norris is called "Father of NIR spectroscopy." Norris, Phil Williams, Fred McClure, and other engineers applied NIR spectroscopy to many applications in agriculture and then foods. Beltsville (Maryland, USA) was a place for assemblage for the bold and ambitious. Their great success partly came from the strong request of quality assessment from consumers which already started in North America from 1960s and partly from the development of spectrometers and computers.

However, many conventional spectroscopists did not accept adamantly the eccentric idea of utilizing statistical methods such as multiple regression analysis to develop calibration models of NIR data. After rather long dispute, some traditional spectroscopists started to recognize the usefulness of the statistical methods to analyze NIR spectra. Particularly, Tomas Herschfeld played a very important role in making a bridge between the spectroscopists and agricultural engineers.

Of note is that in 1960s, there was significant progress also in the applications of NIR spectroscopy to basic studies [15–17]. For examples, in 1963, Bujis and Choppin [17] measured NIR spectra of pure water and investigated water structure in relation to hydrogen bonds. Late 1960s and early 70s, a few research groups including Camille Sandorfy (Fig. 1.3b) group [16] found very interesting fact concerning with the relative intensities of free and association bands of the OH and NH stretching bands compared for the fundamentals and overtones. The relative intensity of the free band is much greater for the overtones than fundamentals. One can say Sandorfy is a pioneer in basic studies of NIR spectroscopy. He is famous particularly in the research on relation between anharmonicity and hydrogen bondings.

It is also very important to know that there is another great scientist who advanced the practical application of NIR spectroscopy. He was Frans, F. Jobsis (Fig. 1.3c),

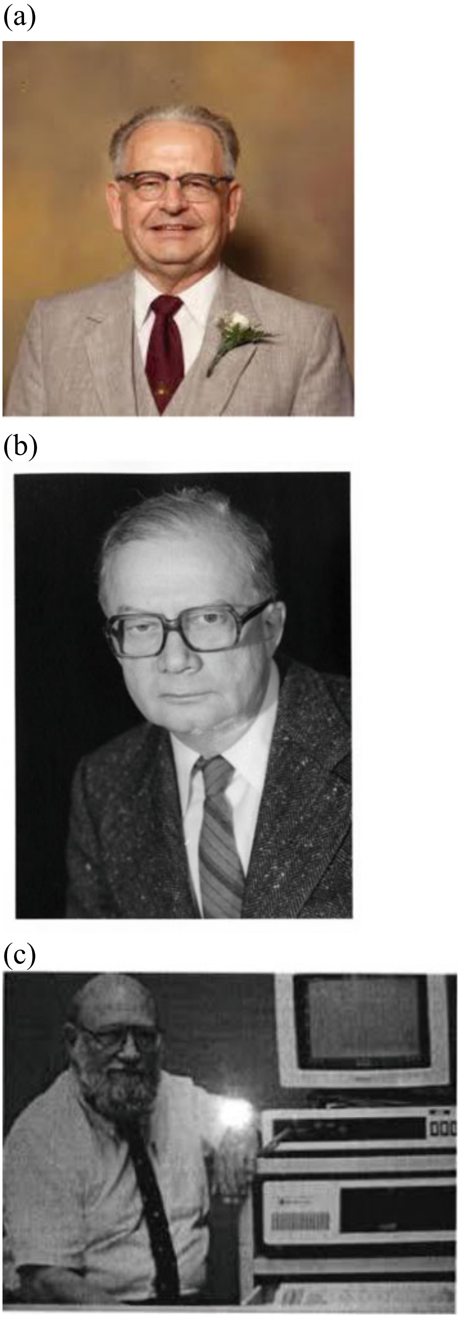

**Fig. 1.3** Portrait photos of **a** Karl H. Norris, **b** Camille Sandorfy, and **c** Frans F. Jöbsis

who carried out the in vivo monitoring of the redox behavior of cytochrome *c* oxidase (or cytochrome $aa_3$) (Chap. 20) [18]. Since his pioneering study medical application of NIR spectroscopy has shown distinctive growth as described later [19].

It is not clear when chemometrics was born, but it is clear that the use of statistical methods by Norris was one of the initiations of the development of chemometrics [1, 2, 4, 6]. Among various molecular spectroscopy, NIR spectroscopy was the first in using chemometrics. For the last half century or so, chemometrics developed NIR spectroscopy and NIR spectroscopy developed chemometrics. Nowadays, chemometrics is used in almost all kinds of spectroscopy including IR, Raman, far-infrared (FIR)/Terahertz, UV–Vis, fluorescence, and NMR spectroscopy.

In 1980s, NIR spectroscopy was used mainly for agriculture and food engineering fields, but applications to polymers and on-line analysis started in those days. After entering 1990s, application of NIR spectroscopy made remarkable progress thanks to the development of spectrometers, detectors, computers, and chemometrics. It has expanded to chemical, polymer and petroleum industries, pharmaceutical industry, biomedical sciences, environmental analysis, and even analysis of cultural resources. In the last ten years or so, development of NIR imaging and portable and handheld instruments has been a matter of big attention. Besides progresses in NIR imaging, and portable and hand-held spectrometers, those in on-line monitoring, process analysis technology (PAT), sensing for security and safety, and medical diagnosis have been particularly noted [1–6]. NIR world is stretching strongly over a huge area of science and technology.

Medical application of NIR spectroscopy is nowadays called functional NIR (fNIR) spectroscopy [20]. It uses mainly electronic NIR spectroscopy in Region 1, the region of "window of biological materials." fNIR is applied not only to medical applications but also to brain research.

Basic studies of NIR spectroscopy such as overtones, combination modes, anharmonicity, and vibrational potential, and application of NIR spectroscopy to basic science like studies of hydrogen bondings, intermolecular interactions, and solution chemistry experienced "renaissance" in the 1990s due to rapid progress in NIR spectrometers particularly FT-NIR spectrometers and spectral analysis methods like two-dimensional correlation analysis.(Chap. 13) [1, 2, 3, 5, 7] Quantum chemical calculations have realized simulations of NIR spectra not only of simple compounds but also of rather complicated molecules such as long chain fatty acids, caffeine, nucleic acid bases, and rosemaric acid (Chap. 5). They also enable one to make band assignments of NIR spectra [20]. It is noted that quantum chemical calculations are useful for both basic studies and applications of NIR spectroscopy.

NIR spectroscopy is expanding markedly to a variety of fields such as astronomy, security and safety sensing, forensic science, building site, paleocultural property science and brain science.

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# Chapter 2
# Principles and Characteristics of NIR Spectroscopy

**Yukihiro Ozaki and Yusuke Morisawa**

**Abstract** This chapter describes the principles and characteristics of NIR spectroscopy. It is divided into two subchapters, 2–1. Characteristics and advantages of NIR spectroscopy: In this subchapter some emphasis is put on the versatility of NIR spectroscopy. Some examples of NIR spectra are explained 2–2. Principles of NIR spectroscopy based on quantum mechanics: To understand principles of NIR spectroscopy, principles of IR spectroscopy are described using quantum mechanics first, and then detailed explanation about molecular vibrations-fundamentals, overtones and combinations is given. Anharmonicity is mentioned briefly.

**Keywords** Molecular vibrations · Vibrational spectroscopy · Overtones · Combinations · Anharmonicity

NIR spectroscopy has very unique characteristics and advantages in comparison with other spectroscopy like ultraviolet-visible (UV-Vis), IR, and Raman spectroscopy. Those characteristics and advantages of NIR spectroscopy all come from anharmonicity of vibrational modes. Hence, it is important to learn the characteristics and advantages of NIR spectroscopy in relation with anharmonicity, whose description needs fundamental knowledge of quantum mechanics.

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## 2.1 Characteristics and Advantages of NIR Spectroscopy

### *2.1.1 Characteristics of NIR Spectroscopy*

NIR spectroscopy is concerned with both electronic transitions and vibrational transitions [1–7]. However, as the electronic spectroscopy, it is not easy or almost meaningless to discriminate the NIR region from the visible region. The two regions are seamless in the electronic spectra. In contrast, it is quite straightforward to distingish the vibrational spectroscopy in the NIR region from that in the IR region because NIR spectroscopy deals only with bands arising from overtones and combination modes, while IR spectroscopy involves mainly bands due to fundamentals, although those originating from overtones and combinations also appear relatively weakly in the IR region.

One of the most characteristic features of NIR spectroscopy come from the fact that bands in the NIR region are weak or very weak. Both bands due to electronic transitions and those originating from vibrational transitions are weak. The overtones and combination modes arise from so-called forbidden transitions [1–7]. The reason why the NIR region is valuable from the point of applications is since only the NIR region offers as a highly transmitting window to radiation.

### *2.1.2 Characteristics of NIR Bands*

Characteristics of bands appearing in the NIR region can be summarized as follows. Here, we consider NIR vibrational bands, overtones and combinations.

(1) Bands observed in the NIR region are all due to overtones and combinations; Not only simple combination bands such as $v_1 + v_2$ but also second order and third order combination bands such as $v_1 + 2v_2$ appear. The NIR region contains many overlapping bands; NIR bands show strong multicolinearlity. Therefore, assignment of the NIR bands is generally not easy.

(2) The NIR bands become weaker and weaker as the wavelength becomes shorter since bands due to higher order overtones and the second and third order combinations appear in the shorter wavelength region. Table 2.1 tabulates the wavelength, wavenumber, and relative intensity of bands due to the fundamental, first, second, and third overtones of CH stretching mode of chloroform. It is noted that the overtone bands become weak abruptly with the increase in the order and that the third overtone bands is located in the Vis region.

(3) Most of the bands in the NIR region originate from functional groups containing a hydrogen atom (*e.g.*, OH, CH, NH). This is partly due to the fact that an anharmonic constant of an XH bond is large, and partly due to the fact that an XH stretching vibration has its fundamental in a high frequency region (3800-2800 $\mathrm{cm}^{-1}$). Hence, NIR spectroscopy is often called “an XH spectroscopic

**Table 2.1** The wavelength, wavenumber, and relative intensity of bands due to the fundamental, first, second, and third overtones of CH stretching mode of chloroform

| | Band position/nm | Band position/$\text{cm}^{-1}$ | Intensity/ $\text{cm}^2\ \text{mol}^{-1}$ |
|---|---|---|---|
| $\upsilon$ | 3290 | 3040 | 25000 |
| $2\upsilon$ | 1693 | 5907 | 1620 |
| $3\upsilon$ | 1154 | 8666 | 48 |
| $4\upsilon$ | 882 | 11338 | 1.7 |
| $5\upsilon$ | 724 | 13831 | 0.15 |

method." Besides XH vibrational bands, those arising from the second overtones of $C = O$ stretching modes appear in the NIR region. Recently, bands due to the first and second overtones of $C \equiv N$ stretching modes of acetonitrile are also observed [8]. The $C = O$ and $C \equiv N$ stretching bands are two of the most intense bands in the IR region because of their large transition dipole moments, and thus, even second overtones can be observed in the NIR region.

(4) The first overtones of XH stretching bands give a lower frequency shift upon the formation of a hydrogen bond or an inter- or intra-molecular interaction as in the cases of the corresponding fundamental bands in IR spectra. The shift of the first overtones is almost double of that for the corresponding IR bands.

(5) In the NIR region OH and NH stretching bands of monomeric and polymeric species are much better separated compared with the IR region. It is also possible to distinguish bands ascribed to terminal free OH or NH groups of the polymeric species from those due to their free OH or NH groups in the NIR region.

(6) Because of the larger anharmonicity, the first overtone bands of OH and NH stretching modes of monomeric species are much more enhanced compared with the corresponding bands of polymeric species. On the other hand, fundamental bands originating from the OH and NH stretching modes of polymeric species are much more enhanced than those of the monomeric species due to a larger charge separation of X–H ($^{\delta-}$X–H$^{\delta+}$—:Y) in a hydrogen bonding. In Fig. 4.8 you can see good example for these phenomena. In the IR spectrum a broad feature due to polymeric species is much stronger than a band originating from monometic species while in the NIR spectrum a truly opposite result is observed (Sect. 4.1.2). Therefore, one can monitor more easily the dissociation process from polymeric species into monomeric ones in the NIR region rather than in the IR region by the first overtone of the OH or NH stretching mode of the monomeric species.

Note that almost all of the above characteristics come from the fact that NIR spectroscopy is concerned with forbidden transitions within the harmonic-oscillator approximation.

### 2.1.3 Advantages of NIR Spectroscopy

Now, let us discuss the advantages of NIR spectroscopy from the point of applications [1–7]. First of all, NIR spectroscopy is a powerful non-destructive and in situ analysis method. One can explore even inside of a material using NIR spectroscopy. Second, it permits non-contact analysis, and analysis using an optical fiber. Third, it is possible to apply NIR spectroscopy to samples in various states, shapes, and thickness. As for the advantages of NIR spectroscopy for fundamental studies we discuss in Chap. 13.

One can discuss the advantages of NIR spectroscopy in comparison with IR spectroscopy.

(1) NIR spectroscopy allows in situ analysis with a sample as it originally is. While one can employ attenuated total reflection (ATR) or photoacoustic spectroscopy (PAS) for in situ analysis in IR spectroscopy, there is no other choice than NIR spectroscopy if one wishes to collect an absorption spectrum on the whole of an apple or a human head. It is also suitable for nondestructive of thick samples.
(2) In general, NIR spectroscopy is more suitable in the analysis of aqueous solutions than IR spectroscopy since the intensity of water bands is much weaker in the NIR spectrum than in the IR spectrum. ATR-IR spectroscopy permits one to examine aqueous solutions, but NIR spectroscopy can probe those in more various manners.
(3) A light-fiber probe can be set in a dangerous environment, and be remotely manipulated. This is one of the reasons why NIR spectroscopy is suitable for on-line analysis. IR Light-fibers are much less robust and more expensive.
(4) In NIR spectroscopy one can select a light path length very freely. In contrast, IR spectroscopy usually requests a cell having a very short path length. NIR spectroscopy allows one to use a 0.1-mm cell, a 1-cm cell, or even a 10-cm cell.
(5) Optical materials used in the NIR region are cheaper than those in the IR region. One can use glass cells, for example.

### 2.1.4 Versatility of NIR Spectroscopy

NIR spectroscopy holds marked versatility in many aspects. First of all, it has huge versatility in its applications [1–7]. NIR spectroscopy can be used in a laboratory, a factory, a hospital, a field and a museum, at a building site, on a road and in the atmosphere. It may be applied to solids, crystals, fibers, powders, liquids, solutions, and gases. Almost all kinds of materials, from purified samples to bulk materials, can be subjected to NIR measurements.

Another versatility in NIR spectroscopy is the versality in spectrometers and instruments. (Chap. 9) In the IR region, most of the spectrometers employed are FT spectrometers, while in the NIR region both FT spectrometers and dispersive spectrometers are employed, and dispersive spectrometers with a CCD detector play important roles in the short-wave NIR (SWNIR) region. NIR spectrometers with an acoustic optic tunable filter (AOTF) are also useful. Portable spectrometers and hand-held spectrometers are prety popular in the NIR region. Many kinds of special-purpose instruments are commercially available.

Spectral analysis gives yet another diversity of NIR spectroscopy. Compared with other spectroscopy, chemometrics is quite often used for NIR spectral analysis. Various kinds of chemometrics methods such as PCA (principal components analysis) and PLS (partial least squares) are employed extensively (Chap. 7). A variety of spectral pretreatments are employed in NIR spectroscopy, since it treats various kinds of bulk materials, which yield noise and baseline fluctuations (Sect. 4.1). Nowadays, even quantum chemical calculations are utilized in the spectral analysis in NIR spectroscopy (Sect. 5.2).

### *2.1.5 Some Examples of NIR Spectra*

To understand the characteristics of NIR spectroscopy it is important to study some examples of NIR spectra.

(a) **Water**

Figure 2.1 depicts NIR spectra of water in the region of 12000–4000 cm$^{-1}$ obtained using three kinds of cells with different path lengths (1, 0.1, and 0.01 cm). Band intensities vary markedly with the path lengths. In all the spectra an intense foot due to the fundamentals of OH stretching modes can be observed near 4000 cm$^{-1}$. Water bands become weaker and weaker stepwisely as the wavelength goes to a shorter wavelength. Two strong bands at 5235 and 6900 cm$^{-1}$ are due to the combination of H-O-H antisymmetric stretching mode ($\nu_3$) and bending mode ($\nu_2$) and that of H-O-H symmetric ($\nu_1$) and antisymmetric ($\nu_3$) stretching modes, respectively (these vibrational modes, see Fig. 2.9). These two bands are very useful for investigating

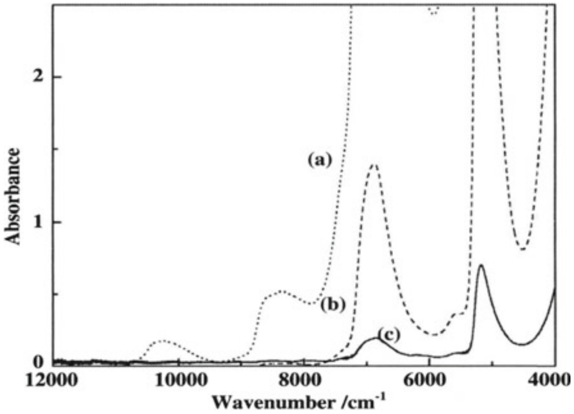


**Fig. 2.1** NIR spectra of water in the region of 12000–4000 cm$^{-1}$ obtained by three kinds of cells with different path lengths (0.01, 0.1, and 1 cm)

water structure and water contents in various materials. Bands at 10613, 8807, and 8762 $cm^{-1}$ are assigned to $2\nu_1 + \nu_3$, $\nu_1 + \nu_2 + \nu_3$, and $2\nu_1 + \nu_2$, respectively. The band at 10613 $cm^{-}$ [1] is valuable for estimating water contents in foods and materials. As you can see here, several bands attributed to the second and third order combination modes appear in the short wavelength region. More detailed analysis of water spectra will be discussed in Sect. 4.1.2.

### (b) Methanol

Figure 2.2 depicts an NIR spectrum in the 7700–3700 $cm^{-1}$ region of low concentration (0.005 M, in $CCl_4$) methanol. In this concentration it is very unlikely that methanol forms hydrogen bonds. Methanol is a very simple molecule, however, note that it gives so many bands in this region. One can easily assign a band at 7130 $cm^{-1}$ to the first overtone of the OH stretching mode of free methanol. Bands in the region of 6100–5600 $cm^{-1}$ are assigned to the first overtones of $CH_3$ symmetric and asymmetric stretching modes and their combinations. Those below 5200 $cm^{-1}$ are due to various combination modes. We need the aid of quantum chemical calculations for convincing band assignments [9]. We will discuss about the quantum chemical calculation result of methanol in Chap. 13.

### (c) Inorganic functional material-an example of electronic spectrum

Let us show one example of NIR electronic spectra. Figure 2.3a, b depict NIR diffuse-reflectance (DR) spectra in the region of 12000–4000 $cm^{-1}$ and their second-derivative spectra in the region of 10000–5000 $cm^{-1}$ of powders of high reflective green-black (HRGB; $Co_{0.5}Mg_{0.5}Fe_{0.5}Al_{1.5}O_4$) pigments, $Co_3O_4$, and α-$Fe_2O_3$, respectively [10]. The HRGB pigment developed at Toda Kogyo Co. (Hiroshima,

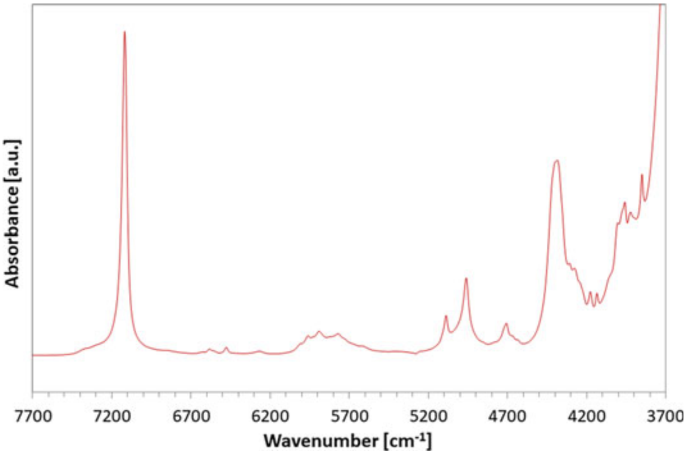
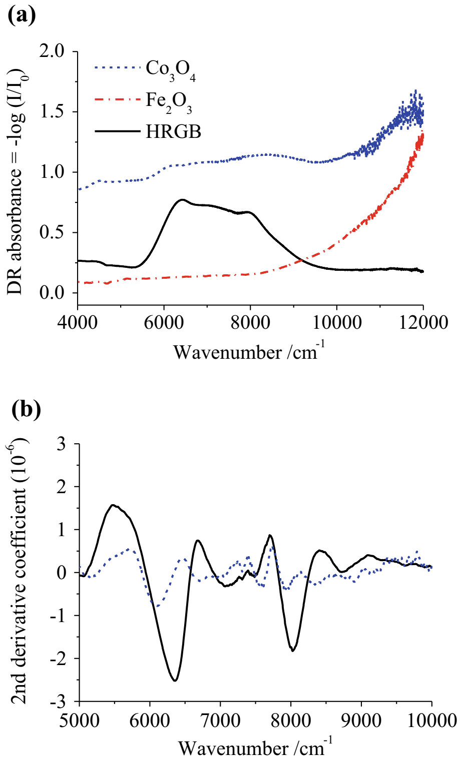


**Fig. 2.2** A NIR spectrum in the 7700–3700 $cm^{-1}$ region of low concentration (0.005 M, $CCl_4$) methanol

**Fig. 2.3** **a** NIR DR spectra of powders of HRGB, $Co_3O_4$, and α-$Fe_2O_3$ in the 12000–4000 $cm^{-1}$ region. **b** Second derivatives of the NIR DR spectra of powders of HRGB, $Co_3O_4$ and α-$Fe_2O_3$ in the 10000–5000 $cm^{-1}$ region. Reproduced from Ref. [10] with the permission



Japan) shows black color, but it absorbs little sunlight. It is noted in the second-derivative spectra that HRGB depicts bands at 6354, 7069, 7590 and 8024 $cm^{-1}$ and that $Co_3O_4$, which has a similar spinel structure to HRGB, yields those at 6094, 6713, 7569, 7951, and 8320 $cm^{-1}$. The above bands of $Co_3O_4$ are ascribed to d-d transitions, $^4A_2 \rightarrow {}^4T_1$, of Co(II) at a tetrahedral cite. A NIR DR spectrum of α-$Fe_2O_3$ gives a long tail band in the region of 12000-10000 $cm^{-1}$ due to a charge-transfer (CT) transition that has maxima at 17000 and 14000 $cm^{-1}$ [10]. HRGB shows characteristic peaks of Co(II) in spinel structure, but it does not give a tail originating from Fe(III). In this way one can explore the structure of inorganic functional materials using NIR electronic spectra.

### *2.1.6 Comparison of an NIR Spectrum with an IR Spectrum*

Whenever one studies the NIR spectrum of a sample, it is often important to compare the NIR spectrum with the corresponding IR spectrum to interpret the NIR spectrum. Figure 2.4a, b show chemical structure of poly(3-hydroxybutyrate) (PHB) and time-dependent variations in IR spectra and their second derivative spectra in the 3050–2850 $cm^{-1}$ region of a PHB film during the melt-crystallization process at 125 °C,

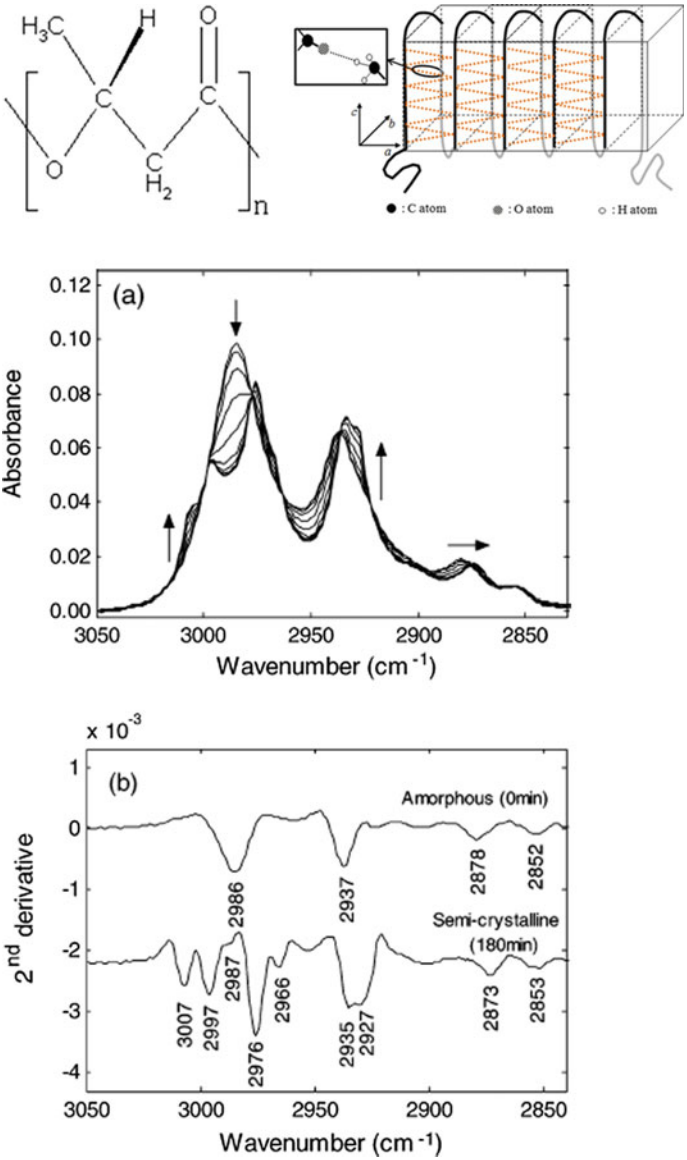


**Fig. 2.4** Chemical structure and lamellar structure of poly(3-hydroxybutyrate) (PHB). **a** Time-dependent variations in IR spectra in the 3050–2850 cm$^{-1}$ region of a PHB film during the melt-crystallization process at 125 °C. **b** Second derivative spectra of the spectra shown in **a** for 0 and 180 min. Reproduced from Ref. [11] with the permission

respectively [11]. In Fig. 2.4b the second derivative spectra for 0 and 180 min are shown. PHB is a well-known biodegradable polymer. Sato et al. [12, 13] investigated IR spectra of PHB and found that a crystalline C = O stretching band at 1723 cm$^{-1}$ shows a large downward shift by about 20 cm$^{-1}$ compared with an amorphous C = O stretching band at ~1740 cm$^{-1}$ and that a crystalline CH$_3$ asymmetric stretching band appears at an anomalously high frequency (3009 cm$^{-1}$) [12, 13]. On the basis of the IR and x-ray crystallography studies, they concluded that the CH$_3$ and C = O groups of PHB form a peculiar C–H…O = C hydrogen bonding.

Time-dependent variations in the NIR spectra in the 6050–5650 cm$^{-1}$ region of a PHB film during the melt-crystallization process at 125 °C are shown in Fig. 2.5a [11]. The second derivatives of the spectra measured at 0 and 180 min are shown in Fig. 2.5b. The second-derivative spectrum obtained at 0 min shows four amorphous bands at around 5954, 5913, 5828, and 5768 cm$^{-1}$. On the other hand, the spectrum collected at 180 min gives at least seven bands at 5973, 5952, 5917, 5900, 5811, 5757, and 5681 cm$^{-1}$ in the same region. Note that the NIR spectral changes in the 6050–5650 cm$^{-1}$ region and the corresponding IR spectral variations in the 3050–2840 cm$^{-1}$ region show significant similarities. For example, the NIR band with the highest wavenumber at 5973 cm$^{-1}$ and the corresponding IR band at 3007 cm$^{-1}$ show similar temporal variations. The former may be due to the first overtone of the latter [11].

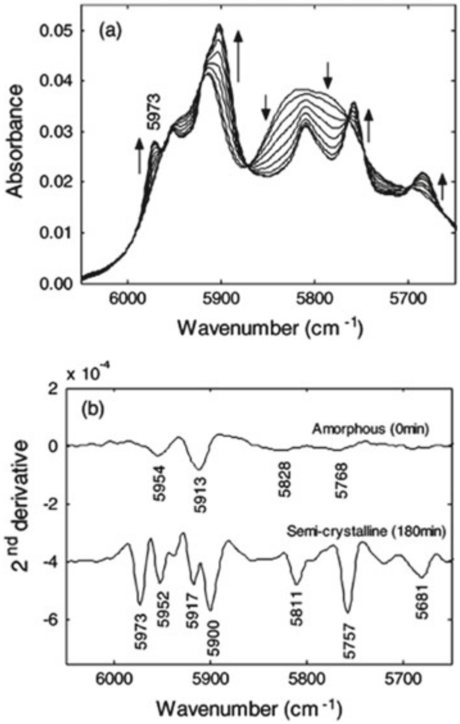


**Fig. 2.5** **a** Time-dependent variations in NIR spectra in the 6050–5650 cm$^{-1}$ region of a PHB film during the melt-crystallization process at 125 °C. **b** Second derivative spectra of the spectra shown in **a** for 0 and 180 min. Reproduced from Ref. [11] with the permission

## 2.2 Principles of NIR Spectroscopy

Before we study the principle of NIR spectroscopy we have to learn the principle of IR spectroscopy because IR spectroscopy deals with fundamentals while NIR spectroscopy treats overtones and combinations which originate from fundamentals [1, 2]. Therefore, learning the fundamentals is the base for understanding NIR spectroscopy.

### *2.2.1 Principles of IR Spectroscopy*

When a molecule is irradiated with IR light, it absorbs the light under some conditions. The energy $h\nu$ of the absorbed IR light is equal to an energy difference between a certain energy level of vibration of the molecule (having an energy $E_\mathrm{m}$) and another energy level of vibration of a molecule (having an energy $E_\mathrm{n}$). In the form of an equation,

$$hv = E_n - E_m \tag{2.1}$$

holds. This equation is known as Bohr frequency condition. In other words, absorption of IR light takes place based on a transition between energy levels of a molecular vibration. Therefore, an IR absorption spectrum is a vibrational spectrum of a molecule.

Note that satisfying Eq. (2.1) does not always mean the occurrence of IR absorption. There are transitions which are allowed by a selection rule (i.e., allowed transition) and those which are not allowed by the same rule (i.e., forbidden transition). In general, transitions with a change in the vibrational quantum number by ± 1 are allowed transitions and other transitions are forbidden transitions under harmonic approximation. This is one of selection rules of IR absorption. Another IR selection rule is a selection rule which is defined by the symmetry of a molecule [1, 2].

$$(\mu_x)_{mn} = \int_{-\infty}^{\infty} \psi_n \mu_x \psi_m \mathrm{d}Q \tag{2.2}$$

$$\mu_x = (\mu_x)_0 + \left(\frac{\partial \mu_x}{\partial Q}\right)_0 Q + \frac{1}{2}\left(\frac{\partial^2 \mu_x}{\partial Q^2}\right)_0 Q^2 + \cdots\cdots \tag{2.3}$$

$$(\mu_x)_{mn} = (\mu_x)_0 \int \psi_n \psi_m \mathrm{d}Q + \left(\frac{\partial \mu_x}{\partial Q}\right)_0 \int \psi_n Q \psi_m \mathrm{d}Q \tag{2.4}$$

The latter selection rule is a rule that IR light is absorbed when the electric dipole moment of a molecule varies as a whole in accordance with a molecular vibration.

The above two selection rules can be introduced by quantum-mechanical considerations. According to quantum mechanics, for a molecule to transit from a certain state $m$ to another state $n$ by absorbing or emitting IR light, it is necessary that the following definite integral or at least one of $(\mu_y)_{mn}$ and $(\mu_z)_{mn}$ which are expressed by a similar equation to (2.2) is not 0, where $\mu_x$ denotes an x-component of the electric dipole moment; ψ denotes the eigenfunction of the molecule in its vibrational state; and $Q$ denotes a displacement along a normal coordinate (i.e., a normal vibration expressed as a single coordinate). Now, let us consider only $(\mu_x)_{mn}$. A distribution of electrons in the ground state changes as the coordinate expressing a vibration varies, and thus, the electric dipole moment is a function of the normal coordinate $Q$. Hence, $\mu_x$ can be expanded as follows.

Expressed by a displacement of atoms during the vibration, $Q$ has a small value. This allows to omit $Q^2$ and the subsequent terms in the equation above. Substituting the terms up to $Q$ of Eq. (2.3) in Eq. (2.2), is obtained. Due to the orthogonality of the eigenfunction, the first term of this equation is 0 except when $m = n$ holds. The first term denotes the magnitude of the permanent dipole of the molecule. For the second term to have a value other than 0, both $(\partial\mu_x/\partial Q)_0 \neq 0$ and $\int \psi_n Q \psi_m dQ \neq 0$ must be satisfied. These two conditions lead to the two selection rules. The nature of the eigenfunction allows the integral to have the value other than 0 only when $n = m \pm 1$ holds. Considering $Q^2$ and the subsequent terms of Eq. (2.3) as well, we can prove that even when $n = m \pm 1$ fails to hold, $(\mu_x)_{mn}$ has a value, even though small, other than 0. The first selection rule regarding IR absorption is thus proved. The other selection rule, which is based upon the symmetry of a molecule, comes from $(\partial\mu_x/\partial Q)_0 \neq 0$. The relationship $(\partial\mu_x/\partial Q)_0 \neq 0$ indicates that IR absorption takes place only when a certain vibration changes the electric dipole moment. The vibration is **IR active** when $(\partial\mu_x/\partial Q)_0 \neq 0$ holds, but is **IR inactive** when $(\partial\mu_x/\partial Q)_0 = 0$ holds.

Most molecules are in the ground vibrational state at room temperature, and thus, a transition from the state $v'' = 0$ to the state $v'' = 1$ (first excited state) is possible. Absorption corresponding to this transition is called **the fundamental**. Although most bands which are observed in an IR absorption spectrum arise from the fundamental, in some cases, also in the IR spectrum one can observe bands which correspond to transitions from the state $v'' = 0$ to the state $v'' = 2, 3, \ldots$ They are called first, second, **overtones**. Bands due to combinations are also observed in the IR spectra. However, since overtones and combinations are forbidden with harmonic oscillator approximation, overtone and combination bands are very weak even in real molecules. Because of anharmonicity, although the intensities are weak, the forbidden bands appear.

### 2.2.2 *Molecular Vibrations*

One must learn molecular vibrations to understand all kinds of vibrational spectroscopy; IR, NIR, FIR/terahertz, and Raman spectroscopy. Vibrations of a polyatomic molecule are, in general, complex, however, according to **harmonic oscillator approximation** (i.e., an approximation on the assumption that the restoring force which restores a displacement of a nucleus from its equilibrium position complies with the Hooke's law; vibrations in harmonic oscillator approximation are called harmonic vibrations), any vibrations of the molecule are expressed as composition of simple vibrations called **normal vibrations**. Normal vibrations are vibrations of nuclei within a molecule, and in the normal vibrations, translational motions and rotational motions of the molecule as a whole are excluded. In each normal vibration, all atoms vibrate with the same frequency (**normal frequency**), and they pass through their equilibrium positions simultaneously. Generally, a molecule with $N$ atoms has $3N$–6 normal vibrations ($3N$–5 normal vibrations if the molecule is a linear molecule). Since normal vibrations are determined by the molecular structure, the atomic weight and the force constant, when these three are known, it is possible to calculate the normal frequencies and the normal modes.

#### 2.2.2.1 A Vibration of a Diatomic Molecule

Let us consider a vibration of a diatomic molecule as the simplest example of molecular vibrations. A diatomic molecule has only one normal mode ($3 \times 2-5 = 1$); it is a **stretching vibration** where the molecule stretches and contracts (Fig. 2.6a). One can delineate the stretching vibration using classic mechanics. Assuming that the nuclei are masses, $m_1$ and $m_2$, and the chemical bond is the "spring" with spring constant $k$ following the Hooke's law (Fig. 2.6b), the vibration of the molecule can be explained in accordance with classic mechanics. The classic mechanical equation of vibration of a diatomic molecule can be solved by a few methods, but here we use **a Lagrange's equation of motion**, which is equivalent to Newton's equation of motion.

We assume that the masses $m_1$ and $m_2$ deviate $\Delta x_1$ and $\Delta x_2$, respectively, from their equilibrium positions. Then, the potential energy of the system shown in Fig. 2.6b is:

$$V = \frac{1}{2}k(\Delta\chi_2 - \Delta\chi_1)^2 \tag{2.5}$$

Meanwhile, the kinetic energy of the system is:

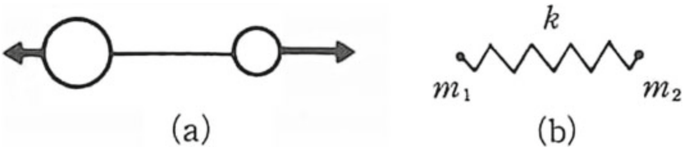


**Fig. 2.6** **a** A stretching mode of a diatomic molecule. **b** A model for a diatomic molecule (two masses combined by a spring)

$$T = \frac{1}{2}m_1\dot{\chi}_1^2 + \frac{1}{2}m_2\dot{\chi}_2^2, \quad \text{where}\left(\dot{\chi}_i = \frac{\mathrm{d}\chi_i}{\mathrm{d}t}\right). \tag{2.6}$$

Now that $V$ and $T$ are known, motions of the system can be determined by solving a Lagrange's equation of motion:

$$\frac{d}{\mathrm{d}t}\left(\frac{\partial T}{\partial \dot{\chi}_i}\right) + \frac{\partial V}{\partial \chi_i} = 0 \tag{2.7}$$

Note that Lagrange's equation of motion is more convenient in discriminating the translational motion and the vibrational motion. Before solving the Lagrange's equation of motion, let us introduce new coordinates $Q$ and $X$

$$Q = \Delta\chi_2 - \Delta\chi_1 \tag{2.8}$$

$$X = \frac{m_1\Delta\chi_1 + m_2\Delta\chi_2}{m_1 + m_2} \tag{2.9}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \ \text{(where } \mu \text{ is a reduced mass)} \tag{2.10}$$

Now, $Q$ is a coordinate regarding a displacement of a distance between the two masses, while $X$ is a coordinate regarding a displacement of the center of gravity of the system. Using $Q$ and $X$, the potential energy $V$ and the kinetic energy $T$ are written as:

$$T = \frac{1}{2}\mu\dot{Q}^2 + \frac{1}{2}(m_1 + m_2)\dot{X}^2 \tag{2.11}$$

$$V = \frac{1}{2}kQ^2 \tag{2.12}$$

We substitute $V$ and $T$ in the Lagrange's equation of motion (2.7). First, applying to the coordinate $X$ ($x_\mathrm{i} = X$), we obtain

$$\ddot{X} = 0 \tag{2.13}$$

This expresses a free translational motion which is not bounded by the potential energy. On the other hand, from the Lagrange's equation of motion regarding the coordinate $Q$ ($x_\mathrm{i} = Q$), we get

$$\mu\frac{d^2Q}{\mathrm{d}t^2} + kQ = 0 \tag{2.14}$$

From the differential equation like Eq. (2.14), we can find a solution as the follows: