Chapter 2
Principles and Characteristics of NIR Spectroscopy

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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 distinguish 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 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/cm^{-1}	Intensity/ cm^2 mol^{-1}
υ	3290	3040	25000
2υ	1693	5907	1620
3υ	1154	8666	48
4υ	882	11338	1.7
5υ	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 (v_3) and bending mode (v_2) and that of H-O-H symmetric (v_1) and antisymmetric (v_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)
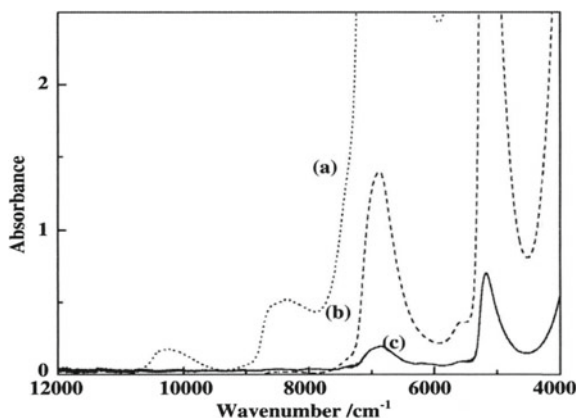
water structure and water contents in various materials. Bands at 10613, 8807, and 8762 cm^{-1} are assigned to $2v_1 + v_3$, $v_1 + v_2 + v_3$, and $2v_1 + v_2$, respectively. The band at 10613 cm$^-$ [1] is valuable for estimating water contents in foods and materials. As you can see here, several 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$_3$O$_4$, and α-Fe$_2$O$_3$, respectively [10]. The HRGB pigment developed at Toda Kogyo Co. (Hiroshima,
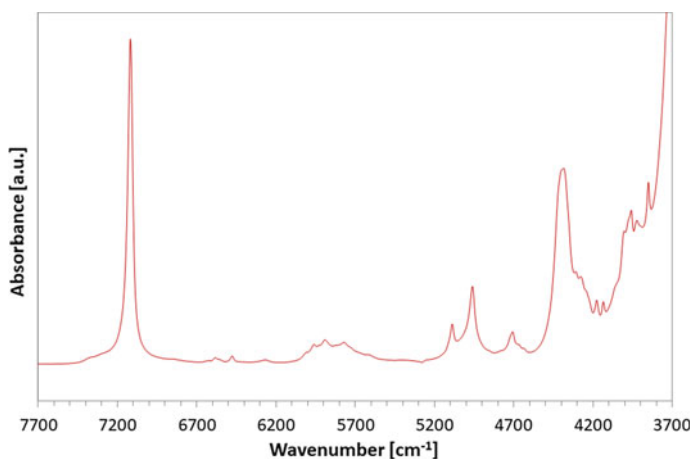
**Fig. 2.2** A NIR spectrum in the 7700–3700 cm^{-1} region of low concentration (0.005 M, CCl$_4$) methanol
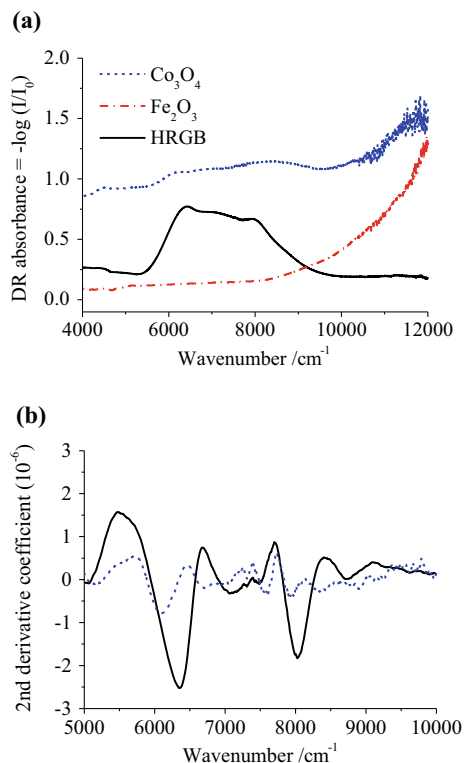
Japan) shows black color, but it absorbs little sunlight. It is noted in the second-derivative spectra that HRGB depicts bands at 6354, 7069, 7590 and 8024 cm^{-1} and that Co_3O_4, which has a similar spinel structure to HRGB, yields those at 6094, 6713, 7569, 7951, and 8320 cm^{-1}. The above bands 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,
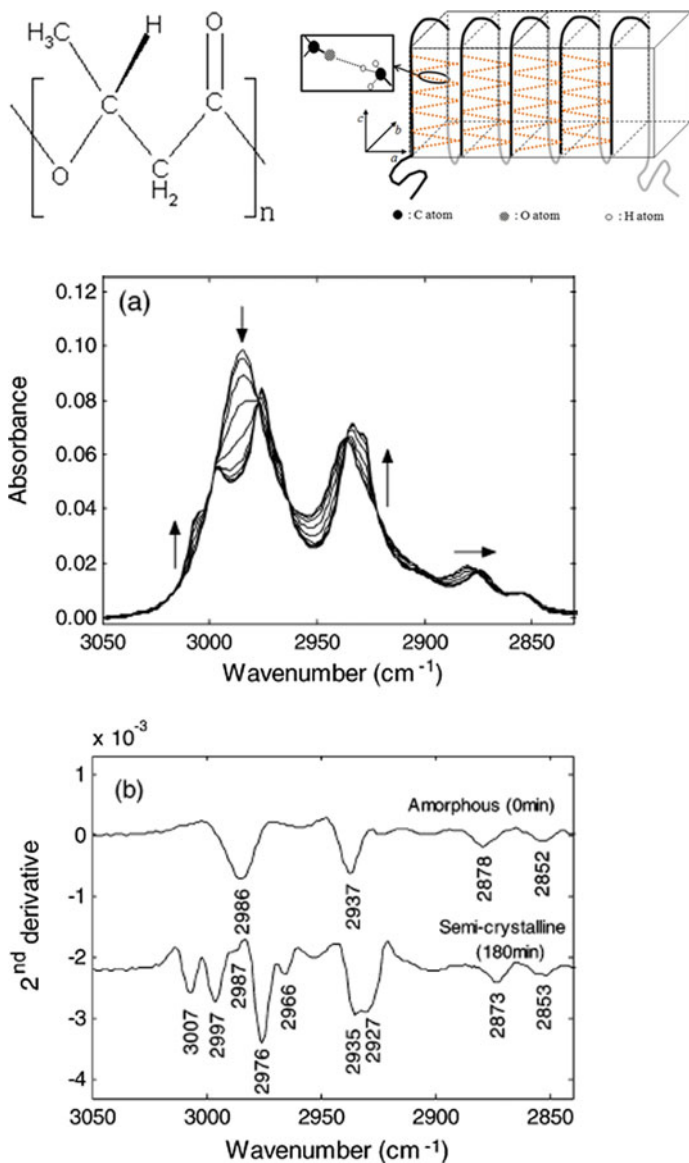
Fig. 2.4 Chemical structure and lamellar structure of poly(3-hydroxybutyrate) (PHB). **a** Time-dependent variations in IR spectra in the 3050–2850 cm^{-1} region of a PHB film during the melt-crystallization process at 125 °C. **b** Second derivative spectra of the spectra shown in **a** for 0 and 180 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 $\sim$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
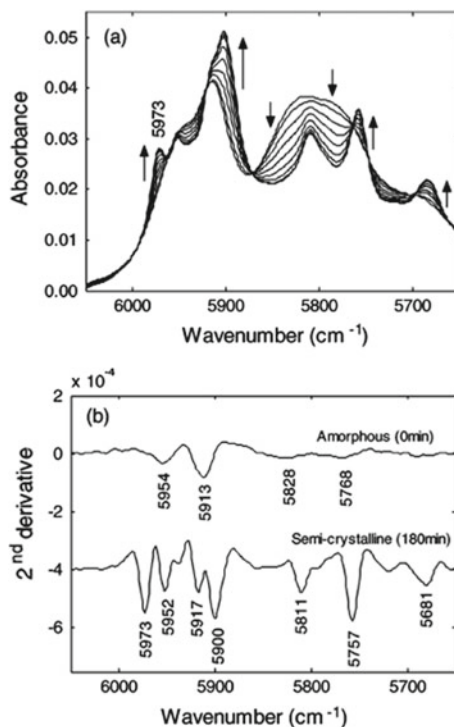
2.2   Principles of NIR Spectroscopy

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_m) and another energy level of vibration of a molecule (having an energy E_n). In the form of an equation,

$$h\nu = E_n - E_m \tag{2.1}$$

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 μ_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, μ_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 $\int \psi_n Q \psi_m d Q \neq 0$ 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.
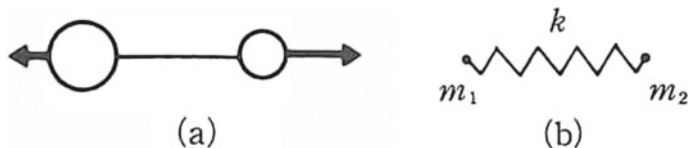
2.2.2.1 A Vibration of a Diatomic Molecule

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 Δx_1 and Δx_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 ($x_i = X$), 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 ($x_i = Q$), we get

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

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

$$Q = Q_\circ \cos 2\pi \nu t \tag{2.15}$$

Equation (2.15) implies that the system illustrated in Fig. 2.6b has a simple harmonic motion with the frequency ν and the amplitude Q_0. Substituting Eq. (2.15) in Eq. (2.14),

$$\left(-4\pi^2 \mu \nu^2 + k\right)Q = 0 \tag{2.16}$$

Finally, we get the frequency of the spring as:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{2.17}$$

The frequency of the spring corresponds to that of the molecular vibration, and the spring constant parallels to the force constant of the chemical bond, and hence, it can be seen from Eq. (2.17) that the frequency of the molecular vibration is proportional to the square root of the force constant and inversely proportional to the square root of the reduced mass of the atoms. It can be seen from Eq. (2.17) that the stronger a chemical bond is and the smaller the masses of atoms are, the larger the stretching frequency of a molecule is. H_2, which has small masses of atoms and relatively small force constant, gives the highest frequency among the all diatomic molecules (4160 cm^{-1}). The frequency of a vibrational more higher than 4000 cm^{-1} is only this one by H_2. This band is not IR active but Raman active, so that it cannot be observed in an IR spectrum. As a result, all bands due to all fundamentals appear below 4000 cm^{-1} in the IR spectra. This is the reason why 4000 cm^{-1} is the border between IR and NIR regions.

2.2.2.2 Quantum Mechanical Treatment of a Vibration of a Diatomic Molecule

Energy levels of vibrations of diatomic molecules can be described using quantum mechanics. In quantum mechanics, the first step is to write down a Schrödinger's equation, $\hat{H}\Psi = E\Psi$. The second step is to solve the equation to calculate an eigen value and an eigen function. In terms of classic mechanics, the total energy H of a vibration of a diatomic molecules is the sum of a kinetic energy $1/2\mu \, \dot{Q}^2$ (Eq. 2.11) and a potential energy $(1/2)k \, Q^2$ (Eq. 2.12),

$$H = T + V = \frac{1}{2}\left(\mu\dot{Q}^2 + kQ^2\right) \tag{2.18}$$

Replacing $\dot{Q}$ with an operator $-ih/2\pi \cdot \text{d/d} \, Q, \hat{H}$ is calculated as:

$$\widehat{H} = -\frac{h^2}{8\pi^2\mu}\frac{d^2}{dQ^2} + \frac{1}{2}kQ^2 \tag{2.19}$$

Now, we got Hamiltonian. Substituting this in $\hat{H}\Psi = E\Psi$ and processing the formula, a Schrödinger equation on harmonic oscillator of a diatomic molecule is obtained.

$$\frac{d^2\psi}{dQ^2} + \frac{8\pi^2\mu}{h^2}\left(E - \frac{1}{2}kQ^2\right)\psi = 0 \tag{2.20}$$

It is not easy to solve this differential equation, but one can do it rigorously. As how to solve this equation is described in detail in a number of textbooks, we will explain only results. Formula 2.20 yields a solution only to the following eigen value E_v:

$$E_v = \left(v + \frac{1}{2}\right)h\nu \tag{2.21}$$

where v is a quantum number of a vibration ($v= 0, 1, 2,…$). It can be seen from Eq. 2.21 that under the harmonic oscillator approximation, the energies take discreet values and their spacings are equal. Figure 2.7 shows the energy levels of vibration of a diatomic molecule. It is noted that the lowest vibrational energy is not 0 but $E_0 = 1/2\, h\nu$. E_0 is called zero point energy. Energies have discrete values; $E_1 = 3/2\, h\nu$, $E_2 = 5/2\, h\nu$, $E_3 = 7/2\, h\nu$,…, and an energy difference between adjacent energy levels is always $h\nu$.

An eigen function to each value of E_v is expressed as:
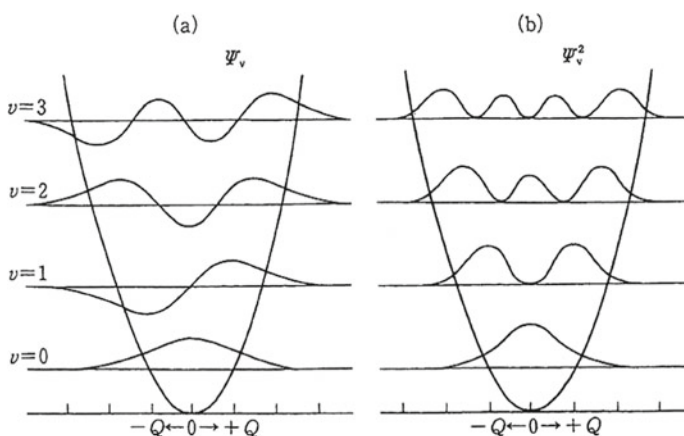
Fig. 2.7 Potential energy curve for a harmonic oscillator and allowed energy levels. **a** wave functions and **b** probability density functions of the harmonic oscillator

$$\psi_\upsilon = N_\upsilon H_\upsilon(\sqrt{\alpha}Q)\exp\left(-\frac{\alpha Q^2}{2}\right) \tag{2.22}$$

where N_υ denotes a normalization constant, H_υ is a Hermite polynomial, and $\alpha = \frac{2\pi\sqrt{\mu k}}{h}$

Wave functions to $\upsilon = 0$, 1, and 2 are as follows.

$$\psi_0 = (\alpha/\pi)^{1/4}\exp\left(-\alpha Q^2/2\right)$$
$$\psi_1 = (\alpha/\pi)^{1/4}(2\alpha)^{1/2}Q\exp\left(-\alpha Q^2/2\right)$$
$$\psi_2 = (\alpha/\pi)^{1/4}\left(1/\sqrt{2}\right)(2\alpha Q^2 - 1)\exp\left(-\alpha Q^2/2\right) \tag{2.23}$$

These formulas clearly show that a wave function of harmonic oscillator is an even function when a quantum number is an even number but is an odd function when a quantum number is an odd number. Figure 2.7 shows a potential energy, (a) wave functions, Ψ_υ, (b) probability density function, Ψ_υ^2 and energy eigen values, E_υ, of the harmonic oscillator.

2.2.2.3   Vibrations of Polyatomic Molecules

As examples of vibrations of polyatomic molecules let us consider normal vibrations of carbon oxide and water; these molecules are examples of linear and non-linear triatomic molecules, respectively. CO_2 has $3 \times 3 - 5 = 4$ normal vibrations. Figure 2.8 exhibits its four normal modes in CO_2, 1, 2, 3a and 3b. The normal vibrations 1 and 2 are vibrations where two CO bonds stretch and contract in phase (1) and out of phase (2), respectively, called **symmetric** and **anti-symmetric stretching vibrations**. Meanwhile, the vibrations 3a and 3b are both vibrations that the angle of OCO changes and called **bending vibrations**. While the vibrations 3a and 3b are independent of each other, energies required for the vibrations are principally equal

Fig. 2.8 Normal modes in CO_2. (+ and − denote vibrations going upward and downward, respectively, in the direction perpendicular to the paper plane). 1, symmetric stretching vibration. 2, antisymmetric stretching vibration. 3a, 3b, degenerate bending vibrations
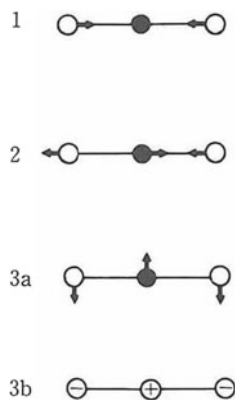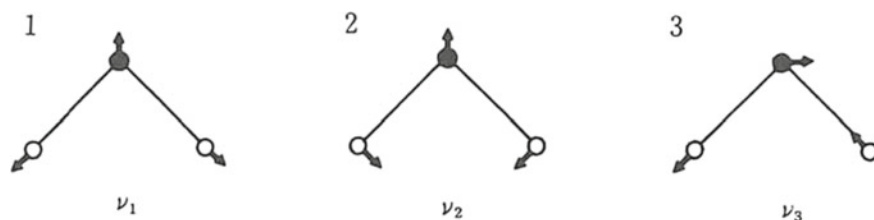
Fig. 2.9 Normal modes of vibration of water. 1: symmetric stretching vibration (v_1). 2: bending vibration (v_2). 3: antisymmetric stretching vibration (v_3)

to each other, only with planes of the vibrations differing 90 degrees from each other. That is, the two vibrations, 3a and 3b, have exactly the same energy. Such vibrations which have principally the same energy are called **degenerate vibrations.**

To know whether the normal vibrations 1, 2, 3a and 3b are IR active or not, we have to examine a change in the electric dipole moment at an equilibrium position $(\partial \mu_x / \partial Q)_0$. In the normal vibration 1, the electric dipole moment is always 0. Hence, the normal vibration 1 is IR inactive. Conversely, the electric dipole moment largely changes in the normal vibration 2, and thus, it is IR active. In a similar manner, the normal vibrations 3a and 3b accompany a change in the electric dipole moment, and therefore, are IR active. By the way, with respect to a molecule such as a CO_2 molecule which has the center of symmetry, a general rule holds true that an IR active vibration is a Raman inactive and a Raman active vibration is IR inactive. This rule is called **the mutual exclusion rule**.

Water, being a nonlinear triatomic molecule, has three normal vibrations as shown in Fig. 2.9. Normal vibrations, 1, 2, and 3 (v_1, v_2, and v_3) are named symmetric stretching, bending, and antisymmetric stretching modes. The normal vibrations 1 and 3 have different frequencies from each other, because of different $H_1 \ldots H_2$ interactions between the two vibrations. The three modes are all IR active but their first overtones are inactive. One can understand if overtones and combinations are active or inactive based on group theory. Bands due to their first overtones are very weak in NIR spectra, being almost impossible to be identified. Bands due to water observed in the NIR region are all due to combinations such as $v_1 + v_3$ and $v_2 + v_3$ (Fig. 2.1).

Both in the cases of CO_2 and H_2O molecules, the frequencies of stretching vibrations are larger than that of a bending vibration. This indicates that the stretching vibrations require larger energies than the bending vibration.

2.2.2.4   Group Frequencies

In general, **group frequencies** are useful to consider vibrations of a polyatomic molecule. Group frequencies are vibrations of functional groups such as C = O stretching vibration of a carbonyl group, stretching vibration of an OH group, and symmetric and antisymmetric vibrations of a CH_2 group. The concept of group

frequencies hold truth when certain normal vibrations are determined substantially by movements of two or more atoms (atomic group). Group frequencies play prominent roles in analysis of IR and Raman spectra. And even for NIR spectroscopy the idea of group frequency is useful 1–7 For example, NIR spectra show bands due to the overtones and combinations of CH_2 and CH_3 groups.

Next, let us consider vibrations of atomic groups. Figure 2.10 displays six vibrational modes of an AX_2 group (e.g., CH_2, NH_2). Of the six, two vibration modes are stretching vibrations, one being symmetric stretching vibration and the other antisymmetric stretching vibration. The remaining four are bending vibrations, i.e., **scissoring, rocking, wagging**, and **twisting vibrations**. Among the four bending vibrations, scissoring and rocking vibrations are bending vibrations in the plane of CH_2 (**in-plane vibrations**), while wagging and twisting vibrations are vibrations which displace vertically to the plane of CH_2 (**out-of-plane vibrations**).

The idea of group frequencies is beneficial ever for a very complex molecule such as a protein and a polymer. Let us consider normal vibrations of an amide group as an example. Normal vibrations of an amide group have been calculated in detail, taking *N*-methylacetamide (Fig. 2.11) as a model of the amide group. Considering a methyl group as one atom, *N*-methylacetamide is a six-atom molecule, and hence, has twelve normal vibrations ($3 \times 6\text{-}6 = 12$). Of the twelve, the normal vibrations shown in Fig. 2.11 are amides I, II and III modes which are key vibrations for studying the structure of proteins and nylons. As clearly seen in Fig. 2.11, the amide I has a strong
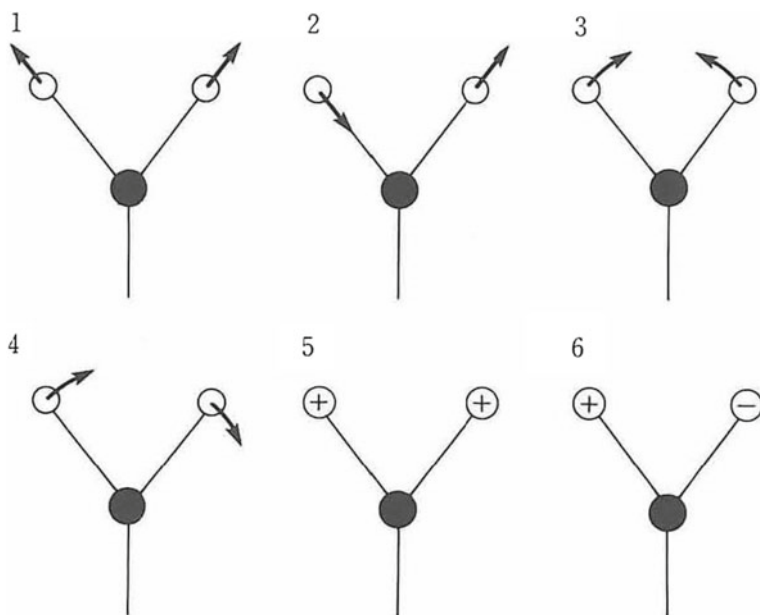
Fig. 2.10 Vibrations of AX_2 group. 1: symmetric stretching vibration. 2: antisymmetric stretching vibration. 3: scissoring vibration. 4: rocking vibration. 5: wagging vibration. 6: twisting vibration
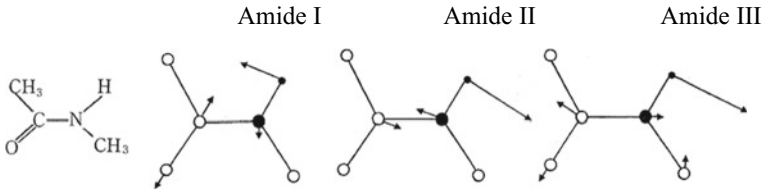
Fig. 2.11 Three normal vibrations of N-methylacetamide which is a model of an amide group

characteristic of $C = O$ stretching vibration. Meanwhile, the amides II and III are coupling modes of C-N stretching vibrations and N-H in-plane bending vibrations. Of the three, the amides I and II appear strongly in IR spectra, and in Raman spectra the amide I and III appear intense. The amide I, II and III bands of proteins are found generally in the regions of 1690-1620 cm^{-1}, 1590-1510 cm^{-1} and 1320–1210 cm^{-1}, respectively. These modes are known to sensitively reflect secondary structures of polyaminoacids, peptides, and proteins. In NIR spectra bands due to the overtones and combinations of amide modes such as the combination of NH stretching mode and Amide II appear.

2.2.2.5 Quantum Mechanical Treatment of Vibrations of Polyatomic Molecules

Now, let us study vibrations of polyatomic molecules using quantum mechanics. A kinetic energy T and a positional energy V are expressed as:
    Therefore, a total energy H is:

$$T = \frac{1}{2} \sum_{i=1}^{n} \dot{Q}_i^2 \tag{2.24}$$

$$V = \frac{1}{2} \sum_{i=1}^{n} \lambda_i Q_i^2 \tag{2.25}$$

Therefore, a total energy H is:

$$H = T + V = \frac{1}{2} \sum_{i=1}^{n} \dot{Q}_i^2 + \frac{1}{2} \sum_{i=1}^{n} \lambda_i Q_i^2 \tag{2.26}$$

Replacing $\dot{Q}$ with $-ih/2\pi \cdot d/d\, Q$ again and calculating $\hat{H}$, we can obtain a Schrodinger equation of vibrations of polyatomic molecules.

$$-\frac{h^2}{8\pi^2} \sum_{i=1}^{n} \frac{\partial^2 \psi}{\partial Q_i^2} + \frac{1}{2} \sum_{i=1}^{n} \lambda_i Q_i^2 \psi = E\psi \tag{2.27}$$

As normal vibrations are independent of each other, the above formula can be separated into n wave equations, respectively, corresponding to the respective normal vibrations, an eigen value E_v is expressed as the sum of eigen values E_i of the respective normal vibrations, and an eigen function ψ_v is given as a product of eigen functions ψ_i representing the respective normal vibrations. Since Formula 2.27 has the same style as Formula 2.20, the eigen value E_i is also the same as Formula 2.21.

$$E_i = \left(v_i + \frac{1}{2} \right) h v_i \tag{2.28}$$

Therefore, a total of vibrational energies whose frequencies are $v_1, v_2, \ldots, v_n$ is:

$$E_v = E_1 + E_2 + \cdots\cdots E_n = \left(v_1 + \frac{1}{2} \right) h v_1$$
$$+ \left(v_2 + \frac{1}{2} \right) h v_2 + \cdots\cdots + \left(v_n + \frac{1}{2} \right) h v_n \tag{2.29}$$

The lowest ground state of water can be represented as (0,0,0), and (1, 0, 0), (0, 1, 0), and (0, 0, 1) denote fundamental states where v_1, v_2, and v_3, respectively, have a quantum number of 1. Transitions between the lowest ground state and the fundamental levels are called **fundamentals**. Next, (2, 0, 0), (0, 2, 0), and (0, 0, 2) represent states where v_1, v_2, and v_3 have a quantum number of 2, respectively, and are called **overtone levels**. (3, 0, 0)… are also overtone levels. **Overtones** are transitions between the lowest ground state and these overtone levels. Combination mode levels are levels, such as (1, 0, 1) and (0, 1, 1), where two or more normal vibrations are excited. Transitions between the lowest ground state and the combination mode levels are called **combination modes**.

2.2.3 Anharmonicity

Until now, we have treated molecular vibrations as a harmonic oscillator. However, in reality, the harmonic oscillator model is not a good model for molecular vibrations except for the vicinity of the bottom of a potential energy curve. If the harmonic oscillator model were correct, molecules should never dissociate no matter how large the amplitude is (Fig. 2.7). Therefore, it is necessary to consider a potential energy function $V(Q)$ (Q denotes an inter-nuclear distance) which more accurately expresses vibrations of molecules. In accordance with our instinct, $V(Q)$ must be such a function which rapidly increases when $Q < <0$ but gradually comes close to a dissociation energy, De, where $Q \gg \varrho_e$ (ϱ_e is an equilibrium distance) holds. As a function which satisfies this condition, a Morse's function expressed as below is well-known:

Fig. 2.12 Morse's function
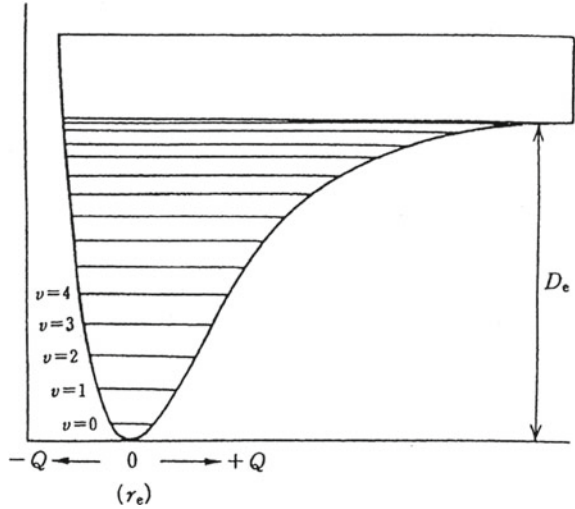
$$V(\varrho) = D_e\big[1 - \exp\{-a(\varrho - \varrho_e)\}\big]^2 \tag{2.30}$$

In Formula 2.30, ϱ is an inter-nuclear distance and a is a constant. This function was proposed by P. M. Morse in 1929. Figure 2.12 deliniates the Morse's function. Assuming that $Q(= \varrho - \varrho_e)$ is always small and expanding $V(\varrho)$ by a Taylor's series into a polynomial with respect to Q in the vicinity of ϱ_e,

$$V(\varrho) = V(\varrho_e) + \left(\frac{\partial V}{\partial \varrho}\right)_{\varrho_e} Q + \frac{1}{2}\left(\frac{\partial^2 V}{\partial \varrho^2}\right)_{\varrho_e} Q^2 + \frac{1}{6}\left(\frac{\partial^3 V}{\partial \varrho^3}\right)_{\varrho_e} Q^3$$
$$+ \frac{1}{24}\left(\frac{\partial^4 V}{\partial \varrho^4}\right)_{\varrho_e} Q^4 + \cdots\cdots \tag{2.31}$$

As the first term on the right-hand side is a constant term, this term is regarded 0. With respect to the second term as well, since V is extremely small to ϱ_e, the second term is also regarded 0. Now, ignoring the fourth and the higher-order terms and applying $(\partial^2 V/\partial Q^2)_{\varrho_e} = k$, the following formula holds:

$$V(\varrho) = \frac{1}{2}kQ^2 \tag{2.32}$$

In other words, the Morse's function is equivalent to a function which expresses harmonic oscillator approximation in the region close to the equilibrium inter-nuclear distance ϱ_e (Second derivative on Formula 2.30 provides $k = 2a^2 D_e$).

A potential energy V is generally expressed as:

$$V = k_2 Q^2 + k_3 Q^3 + k_4 Q^4 + \cdots\cdots \tag{2.33}$$

The high-order terms such as Q^3 and Q^4 are called **anharmonic terms**. Calculating an eigen value E'_v considering up to the Q^3-term, we obtain,

$$E'_v = \left(v + \frac{1}{2}\right)h\nu_e - \left(v + \frac{1}{2}\right)^2 h\nu_e \chi_e \tag{2.34}$$

where $\nu_a = a/\pi\sqrt{D_e/2\pi}$. The symbol χ_e is a constant called an **anharmonic constant**. One can estimate the degree of anharmonicity from the value of this constant. Table 2.2 summarizes the values of anharmonic constants for several diatomic molecules. The constant χ_e becomes large for a molecule with a hydrogen atom which has a light mass while it is much smaller for molecules which do not have a hydrogen atom (Table 2.2). Since the anharmonic constant χ_e holds the following relationship with respect to a, D_e, etc., one can calculate the shape of a Morse's function and a dissociation energy of the molecules, etc.

$$\chi_e = \frac{h\nu_e}{4D_e} = \frac{ha}{4\pi\sqrt{2\mu D_e}} \tag{2.35}$$

From Formula 2.34, it is possible to calculate an energy difference, ΔE_v, between energy levels of vibrational quantum numbers v and $v + 1$.

$$\Delta E_{(v \to v+1)} = h\nu_e - 2h\nu_e x_e(v + 1) \tag{2.36}$$

Formula 2.36 indicates that the larger v is, the smaller ΔE_v is (Fig. 2.12) and the larger x_e is, the smaller ΔE_v is. In this formula, a transition $v = 0 \to 1$ is:

Table 2.2 Values of anharmonic constant for several diatomic molecules

Molecule	Anharmonic constant
H_2	0.02685
D_2	0.02055
HF	0.02176
HCl	0.01741
HBr	0.01706
HI	0.01720
N_2	0.006122
O_2	0.007639
Cl_2	0.007081
I_2	0.002857
NO	0.007337

$$\Delta E_{(0\rightarrow 1)} = h\nu_e - 2h\nu_e x_e = h\nu_e(1 - 2x_e) \tag{2.37}$$

Thus, $\Delta E_\upsilon = h\nu_e$ does not hold. For the IR, NIR, and Raman spectra, we always use a frequency in a unit of cm^{-1} as $\tilde{\nu} = \nu/c$. The value $\tilde{\nu}_{obs} = \Delta \tilde{E}_{(0\rightarrow \upsilon)}$ (which is an observed value in the unit of cm^{-1}) is obtained as

$$\tilde{\nu}_{obs} = \Delta \tilde{E}_{(0\rightarrow \upsilon)} = \tilde{\nu}_e \upsilon - \chi_e \tilde{\nu}_e \upsilon(\upsilon + 1) = \tilde{\nu}_e \upsilon[1 - \chi_e(\upsilon + 1)] \tag{2.38}$$

We will now describe a method of calculating ν_e from $\tilde{\nu}_{obs}$. HCl yields a strong band at 2886 cm^{-1} due to a fundamental ($\upsilon = 0$ to 1) and a weak band at 5668 cm^{-1} due to a first overtone ($\upsilon = 0$ to 2). From these observed values one can calculate an absorption wavenumber ν_e and an anharmonic constant χ_e.

With respect to $\upsilon = 0\rightarrow 1$ and $\upsilon = 0\rightarrow 2$,

$$\Delta \tilde{E}_{\upsilon(0-1)} = \tilde{\nu}_e(1 - 2x_e)$$
$$\Delta \tilde{E}_{\upsilon(0-2)} = 2\tilde{\nu}_e(1 - 3x_e) \tag{2.39}$$

Therefore,

$$2886\text{cm}^{-1} = \tilde{\nu}_e(1 - 2x_e)$$
$$5668\text{cm}^{-1} = 2\tilde{\nu}_e(1 - 3x_e) \tag{2.40}$$

Solving these simultaneous equations, we obtain $\chi_e = 0.0174$ and $\tilde{\nu}_e = 2990\,\text{cm}^{-1}$. We must consider $\tilde{\nu}_e$ to discuss the strength of a chemical bond, because considering $\tilde{\nu}_{obs}$ is not enough for this purpose.

2.2.4 Overtones and Combination Modes

It is anharmonicity that permits overtones and combination modes to be observed. Let us consider selection rules of IR spectroscopy once more. This time, we will consider anharmonicity on a dipole moment.

$$\mu_x = (\mu_x)_0 + \left(\frac{\partial \mu_x}{\partial Q}\right)_0 Q + \frac{1}{2}\left(\frac{\partial^2 \mu_x}{\partial Q^2}\right)_0 Q^2 + \cdots\cdots \tag{2.41}$$

$$(\mu_x)_{nm} = (\mu_x)_0 \int \psi_n \psi_m dQ + \left(\frac{\partial \mu_x}{\partial Q}\right)_0 \int \psi_n Q \psi_m dQ$$
$$+ \frac{1}{2}\left(\frac{\partial \mu_x^2}{\partial Q^2}\right)_0 \int \psi_n Q^2 \psi_m dQ + \cdots\cdots \tag{2.42}$$

The third term of Formula 2.42 has a value other than 0 when $(\partial^2 \mu_x / \partial Q^2) \neq 0$ and $\int \psi_n Q^2 \psi_m d Q \neq 0$ both hold. The latter integral has a value other than 0 when $\upsilon' = \upsilon$ and $\upsilon \pm 2$. Therefore, even a first overtone is not forbidden any more if we include the term of Q^2. Similarly, second, third… overtones are not forbidden any more as we take higher-order terms into consideration. However, the intensities of these overtones are far weaker than those of fundamentals. The frequencies of first, second, third… overtones are smaller than double, triple, quadruple of the frequencies of fundamentals, respectively, as already described. This is because the differences between the vibrational energy levels become narrower as the quantum number υ increases, as clearly depicted in Fig. 2.12 and indicated by Formula 2.36. Anharmonicity excludes combination modes as well from those forbidden in a similar manner. The intensities of combination bands are also weak.

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