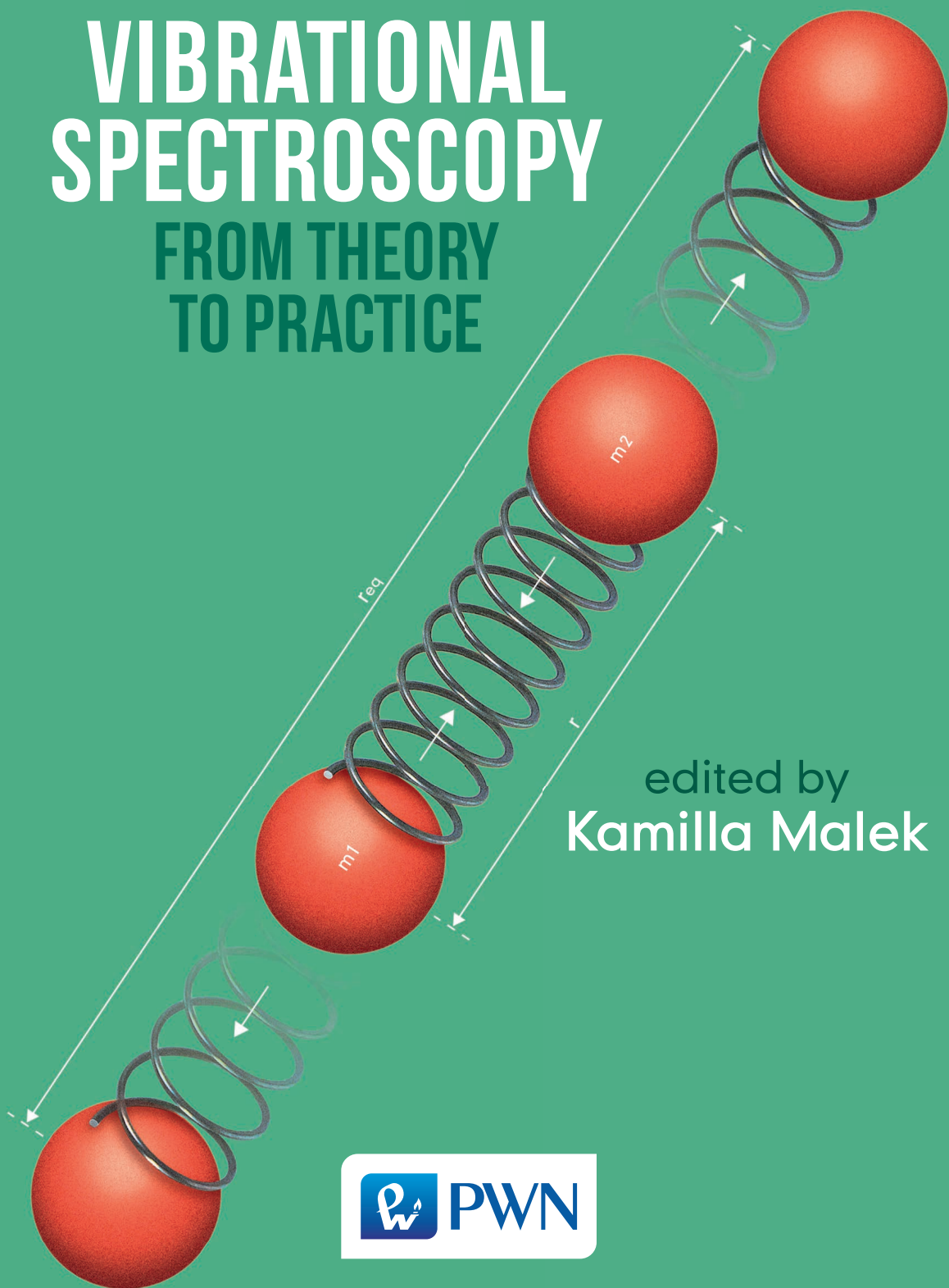# VIBRATIONAL SPECTROSCOPY

FROM THEORY TO PRACTICE

edited by
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Vibrational spectroscopy. From theory to practice
Editor Kamilla Malek

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Content

1

Fundamentals of infrared spectroscopy (FT-IR)

Kamilla Malek, Emilia Staniszewska-Ślęzak, Kamila Kochan, Katarzyna Majzner

The interaction of matter with electromagnetic radiation is fundamental in optical spectroscopy and it relies on absorption, emission and scattering of light photons. Due to such interactions one registers a spectrum consisting of bands of a given frequency, shape and intensity. As the title of this Chapter indicates infrared absorption spectroscopy results from absorption of light quantum from IR region, which matches to energy difference between vibrational levels. The IR spectrum is usually presented in a scale of wavenumbers [cm^{-1}] and can be collected in three regions of IR radiation. It should be emphasized that IR and Raman techniques (described in Chapter 2) are complementary to each other, as both relay on registration of transitions between vibrational levels, but information that they provide is complementary to each other. This can be illustrated by the rule of mutual exclusion, which states, that if a molecule has a center of symmetry, vibration active in infrared absorption spectrum is inactive in Raman and *vice versa*. The most frequently used IR region is mid-infrared radiation (MIR, *Mid InfraRed*), which covers the region of 400 – 4000 cm^{-1}. Within this IR spectrum, a region from 400 to 1500 cm^{-1}, called "fingerprint", is specific for each chemical species and this fact strictly results from characteristics of vibrational motion described by normal modes. A region of far infrared radiation (FIR, *Far InfraRed*, 50 – 400 cm^{-1}) also registers normal modes while a region above 4000 cm^{-1} (NIR, *Near InfraRed*) provides information about overtones and combination modes. The abbreviation *FT* in the name of the technique means *Fourier transform* – the mathematical operation that decomposes a function of time (a *signal*) into the function of frequency. FT-IR spectroscopy is applied for the identification and quantitative analysis of chemical compounds or their mixtures as well as the determination of physicochemical features such as molecular structure and its changes due to a stress/reaction, kinetics of reactions and intramolecular dynamics. IR spectra of a sample in any state can be collected.

1.1. Quantum description – models of the harmonic and anharmonic oscillators

Molecules consisting of nuclei and electrons, have a certain reserve of internal energy, which manifests itself in various forms of movement, e.g. vibrations. A molecule containing N atoms can perform $3N - 6$ vibrations or $3N - 5$, if it is linear. An exceptional feature of oscillations is non-zero value of their potential energy in the ground vibrational state, therefore vibrations of molecules take place in every phase and do not stop even at temperature of 0 K. As any energy in the micro-world, vibrational energy is also quantized, what means that its values are limited to certain discrete values called vibrational levels. Therefore, each chemical species adopts or donates energy only in characteristic portions called quanta. The energy of discrete vibrational levels is determined by solving the Schrödinger equation for a model of a harmonic oscillator. The eigenvalues of the vibrational Schrödinger equation for diatomic molecule are given by (Eq. 1.1):

$$E_{\text{osc}} = h\nu\left(\upsilon + \frac{1}{2}\right), \tag{1.1}$$

where: ν is frequency of the harmonic oscillator $\nu = \frac{1}{2\pi}\sqrt{\frac{f}{\mu_{\text{red}}}}$, f – force constant, μ_{red} – reduced mass $\mu_{\text{red}} = \frac{m_1 m_2}{m_1 + m_2}$, and υ – a vibrational quantum number ($\upsilon = 0, 1, 2, 3, \ldots$).

The value of the vibrational quantum number in Eq. 1.1 determines quantum nature of vibrational motion and its energy also depends on the type of the molecule since this expression includes the value of force constant and reduced mass of the chemical species.

During oscillations, potential energy reaches the maximum value at the largest deflection from the equilibrium, the potential energy curve change is illustrated by a parabola (Figure 1.1).
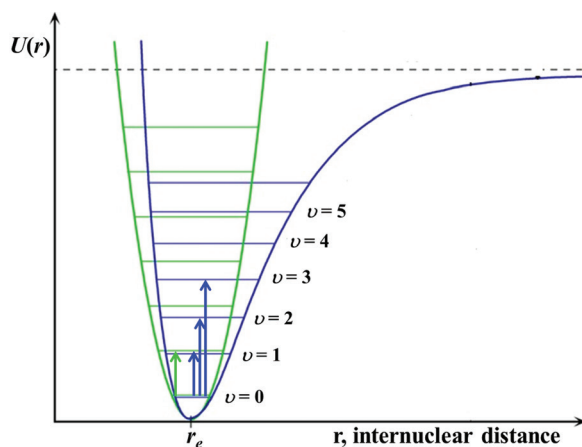
Fig. 1.1. Potential energy U curve for the models of the harmonic oscillator (green line) and of the anharmonic oscillator (blue line). Vertical arrows label allowed transitions between vibrational levels υ

Potential energy curve in Figure 1.1. shows that energy of the harmonic oscillator never reaches zero value, since the energy is ½hv for the lowest allowed vibrational level $\upsilon = 0$. The vibrational levels of the harmonic oscillator are equally separated by hv and therefore energy difference does not depend on the vibrational quantum number υ and is affected by chemical species only. Vibrational spectrum of the harmonic oscillator exhibits only one band since it represents transition for a diatomic molecule. A required condition to record the IR absorption spectrum is a change of dipole moment of a molecule during vibration, wherein the change of the vibrational level can be only $\Delta\upsilon = 1$ (a green arrow in Fig. 1.1).

The transition moment of absorption must be non-zero and is given by (1.2):

$$\mu_{nm} = \langle \Psi_n | \hat{\mu} | \psi_m \rangle \neq 0, \tag{1.2}$$

and its operator is the change of the dipole moment $\hat{\mu}$ due to transition from n to m vibrational level. This transition is called a fundamental tone. Due to the fact that the most occupied vibrational level at room temperature (according to the Boltzmann energy distribution) is $\upsilon = 0$, bands observed in IR spectrum mainly originate from transitions from $\upsilon = 0$ to $\upsilon = 1$ (the green arrow in Fig. 1.1).

The model of the harmonic oscillator is an idealized model, whereas in fact, oscillations are anharmonic, as the Hooke's law is not satisfied. In this case the potential energy curve is illustrated by the Morse curve (Fig. 1.1.B) and energy of the anharmonic oscillator is expressed by an equation 1.3:

$$E_{osc}^{anh} = hv\left(\upsilon + \tfrac{1}{2}\right) - hvx\left(\upsilon + \tfrac{1}{2}\right)^2, \tag{1.3}$$

while neighboring vibrational levels are separated by (1.4):

$$\Delta E_{osc}^{anh} = E_{\upsilon+1} - E_\upsilon = hv[1 - 2x(\upsilon + 1)], \tag{1.4}$$

where the parameter x is an anharmonic constant that describes deviation of anharmonic oscillator from the ideal harmonic model. It takes considerable values for vibrations of a high energy.

It is clear from Figure 1.1.B and equation (1.4) that the intervals between vibrational levels are not constant, but they decrease along with increasing quantum number υ. The Morse potential also shows dissociation of a bond which appears for large values of υ. In addition, the model of the anharmonic oscillator extends the selection rules. Transitions become allowed not only for $\Delta\upsilon = 1$ (fundamental tones) but also for $\Delta\upsilon = 2, 3$, …, sequentially called the first, second (etc.) overtone (blue arrows in Fig. 1.1). Their intensities are much lower than intensity of the fundamental tone.

1.2. Normal coordinates

In general, a molecule built from N atoms has $3N – 6(5)$ internal degrees of freedom. They describe oscillations, for which a concept of the normal coordinates/

vibrations/modes was introduced. A normal coordinate describes a simultaneous movement of all atoms, occurring with the same frequency and consistent in phase, although amplitude of vibration of individual atoms can be different. Vibrations do not induce translation or rotation of the molecule. Individual normal modes are orthogonal to each other, which means that their movement is mutually independent.

Extremely helpful in the analysis of IR and Raman spectra is to consider symmetry of a molecule (and therefore – its possible molecular structure) as well as its influence on spectral features. $3N – 6(5)$ normal modes of N-atomic molecules can be classified according to properties of a point group. For example, the molecule of H_2O, which belongs to the C_{2v} group, has two vibrations with A_1 and one with B_2 symmetry. The reader can get familiar with details of group theory in the literature [1].

It should be also emphasized that a number of vibrations active in IR and Raman spectra and predicted on the basis of group theory can be different from a number of bands observed in experimental spectrum. These discrepancies can result from the presence of overtones and combinatorial bands, Fermi resonance, the abolition of the degeneracy of some vibrations (due to reduction of molecular symmetry) or the presence of isomers and amorphic forms.

A helpful approach for description of vibrational spectra is to analyze them in terms of characteristic vibrations of functional groups. They occur in specific regions of a spectrum, e.g., the C-H stretching mode is observed in the region of $2850 – 3100$ cm^{-1}. Figure 1.2 shows typical vibrations for a functional group XY_2. Vibrations associated with the change of a bond length are called stretching vibrations, whereas those expressing change of the molecular angle are called deformational or bending vibrations. Another criterion arises from symmetry of vibrations (symmetric or asymmetric) or from motion in-plane and out-of-plane of a functional group (see Figure 1.2). Using tables of group frequencies, Raman and IR spectra can be described qualitatively. Each of these vibrations can be also considered in terms of principles of the group theory. Thus, the A-type vibrations are non-degenerate vibrations, symmetric to an axis of the highest multiplicity. The B-type vibrations are also non-degenerate vibrations, but anti-symmetric to an axis of the highest multiplicity. Finally, the E- and T(F)-type vibrations are vibration double and triple degenerated, respectively. Additional indexes placed with the symbol, such as 1, 2, 'i', 'g' (gerade) and 'u' (ungerade), determine the symmetry of vibrations with respect to an axis of multiplicity different than a major axis, a plane, the center of inversion, respectively.

Experimentally, the assignment of IR and Raman bands to vibrations of individual groups of atoms is also based on the isotopic shift (change of vibration frequency due to the substitution of a chosen atom by its isotope. This is supported by an assumption that the isotopic change does not alter distribution of electron density, and therefore it does not change the force constant of a molecule. Magnitude of this shift is determined by the equation 1.5:

stretching modes

symmetric

asymmetric

in-plane deformation modes

rocking

scissoring

out-of-plane deformation modes

+   **-**

twisting

+   **+**

wagging
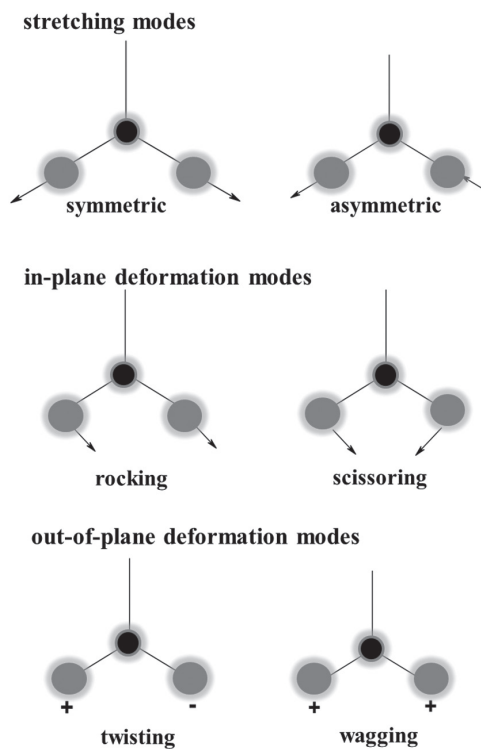
Fig. 1.2. Types of vibrations for XY_2 molecule

$$\frac{\overline{\nu}}{\nu*} = \sqrt{\frac{\mu_{\text{red}}^*}{\mu_{\text{red}}}}, \qquad (1.5)$$

where „*" corresponds to a molecule with a changed isotope.

It is also assumed that a considerable shift is only observed for bands that represent "isolated" vibrations of functional groups.

1.3. Construction of a FT-IR spectrometer

Fourier Transform IR spectrometers operate on the basis of mathematical operation called Fourier transformation. A typical spectrometer consists of a light source, an interferometer, a sample chamber and a detector.

1.3.1. Light source

A source of light in the IR spectrometer must be polychromatic infrared radiation due to the necessity of fitting its energy to transitions between vibrational levels of all the molecules. Typically, light sources are a globar (SiC) and a Nernst rod (ZrO_2 + Y_2O_3), which – when heated to high temperature – emit radiation similar

to the black body radiation. The Nerst rod emits radiation in the range from 300 to 20 000 nm (from UV to NIR), whereas the globar provides light in the range of 1 100 – 40 000 nm (NIR, MIR and FIR). The light beam from the source reaches the interferometer, then is collimated through a series of mirrors and finally directed to a sample.

Interferometer

In the Fourier Transform spectrometers, intensity of absorption is not directly recorded as a function of frequency but in a form of an interferogram, which represents relationship between a signal and time (the optical path difference). To obtain a spectrum in the frequency domain from the time domain, the interferogram is transformed by a mathematical operation called the Fourier transformation. Collection time of a spectrum is very short due to the fact that the entire spectral range is recorded simultaneously. A number of spectra registered in the time domain are averaged, and then transformed by the Fourier transformation. Advantages of the use of the interferometer in any spectrometer are as follows:

1/ Felgett's adavantage (multiplex advantage): recording all wavelengths simultaneously results in shortening data collection time and improvement of signal (S) to noise ratio (N) since $S/N \sim n^{1/2}$ (n – number of spectra). This advantage is especially important for techniques which generate weak signal (e.g. a Raman spectrometer with laser excitation in NIR region),
2/ Jacquinot's advantage: the lack of slits does not limit radiation pathway,
3/ Connes's advantage: the movement of the moving mirror is controlled optically by a He-Ne laser and this allows to achieve high precision of the wavenumber scale in a spectrum.
4/ easy change of spectral resolution.

A schematic of a typical interferometer (the Michelson interferometer) used in optical spectroscopy is illustrated in Figure 1.3. The interferometer is an element splitting the electromagnetic radiation beam and its role is similar to a grating in the monochromator. It consists of two mirrors, positioned to each other at an angle of 90°, when one of them is stationary, whereas the second mirror moves controlled by a He-Ne laser. Between the two mirrors, a beam splitter is placed at an angle of 45°. The radiation falling on the beam splitter is divided into two beams transferred to both mirrors. Then light beams are reflected on the mirrors and next they are collimated on the beam splitter. Light beams interfere to each other depending on the position of the moving mirror. If the two mirrors are located at the same distance from the beam splitter, and hence the optical path difference is zero, the highest amplification of all wavelengths is observed. In case of any different positions of the moving mirror, both beams are no longer in-phase consistent and only those wavelengths for which the interference condition is satisfied will be amplified.
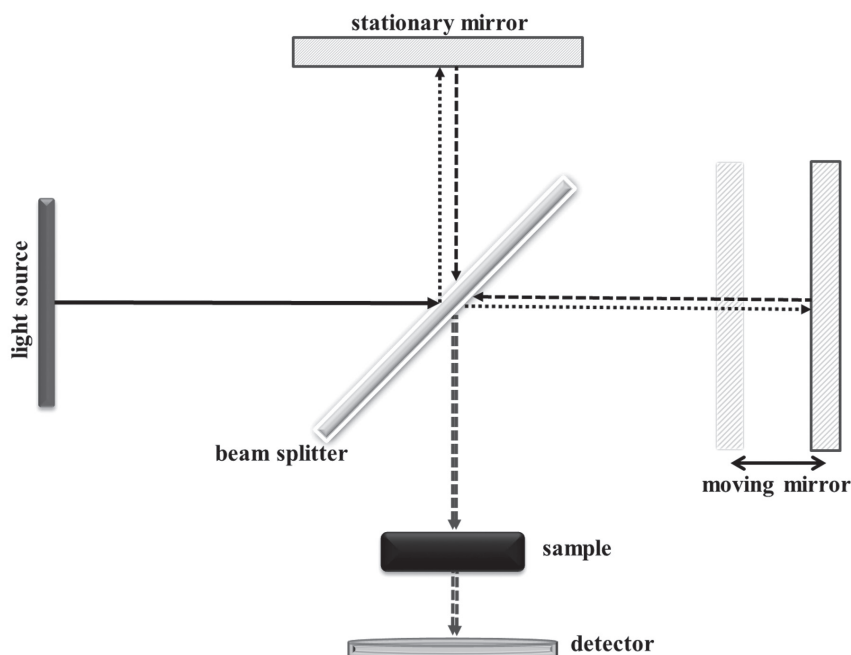
Fig. 1.3. A schematic of the Michelson interferometer along with marked pathway of beam rays

1.3.3. Sample chamber

A sample chamber of a FT-IR spectrometer is constructed specifically for each IR technique, discussed in Chapter 3.1. The chamber and the spectrometer are purged with dry air or dry nitrogen in order to remove water vapor and CO_2 present in air. Both molecules, due to the large dipole moment, generate strong bands in spectra. Water vapor shows bands at about 3500, 1630 and below 500 cm^{-1} whereas CO_2 absorbs infrared radiation at 2390 – 2280 cm^{-1} (doublet) and 672 – 665 cm^{-1}. Mostly, IR spectrometers are single beam instruments and thus collection of the empty chamber or a cuvette with solvent is required before measurement of the sample.

1.3.4. Detector

After passing through a sample, signal is analyzed by a detector, whose function is to change intensity of radiation into an electrical signal. The standard detector in FT-IR spectrometers is DLATGS (deuterated triglicyne sulfate substituted with alanine) operating in the range of 350 – 6000 cm^{-1}. This detector is a pyroelectric cell sensitive to temperature changes induced by IR radiation. In FT-IR microscope, a MCT (semiconductor – Mercury Cadmium Telluride) detector is commonly used which detects radiation in the range of 670 – 7 000 cm^{-1} (see Chapter 3.2).

References

1. Cotton F.A., *Chemical applications of group theory*, Wiley, 1990.