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Infrared Spectroscopy and Its Application in Atmospheric Research

1.1 Basic Theories

Infrared (IR) spectroscopy analyzes the interaction between infrared light and a molecule. This technique applies to a molecule that can selectively absorb at certain wavelengths in the infrared region and undergo an internal transition in the vibration energy level and rotational energy level. When the photon energy is equal to the energy required for the molecular transition, which corresponds to the radiation frequency matching the dipole frequency, then the molecule will absorb the radiation and undergo an oscillation transition. One of the great advantages of IR is that it can practically analyze samples in various states.

As shown in Figure 1.1, the IR portion of the electromagnetic spectrum is divided into near-, mid-, and far-IR regions. The near-IR region, which is the highest in energy, with absorptions in the range ~14000–4000 cm^{-1} (corresponding to wavelength in the 0.7–2.5 μm), can excite overtone or harmonic vibrations. The mid-IR region, having absorptions at ~4000–400 cm^{-1} (2.5–25 μm wavelength), may be used to study the fundamental vibrations and associated rotational–vibrational structures, whereas the far-IR region that has absorptions at ~400–10 cm^{-1} (25–1000 μm wavelength) lies adjacent to the microwave region. It is the lowest in energy and is suitable for use in rotational spectroscopy.

When a chemical bond vibrates, the molecule absorbs an IR radiation. This absorption can be measured by the infrared spectrometer and be converted into a spectrum. The infrared ray was first found in 1800 by the British scientist Herschel, and in 1936, the first prism spectrometer, a single beam infrared spectrometer, was made. The double beam infrared spectrometer was later developed in 1946. In the 1960s, the second generation of infrared spectrometer using grating as dispersive element came out. In the 1970s, as the Fourier transform infrared spectrometer (FTIR) emerged, the IR spectroscopy scanning speed greatly improved. Following developments led, in the late 1970s, to laser infrared spectrometers, confocal microscopic infrared spectrometers, and so on.

The infrared spectrum, also known as molecular vibration rotation spectrum, belongs to the molecular absorption spectrum and is simply the graph plotted with the absorbed infrared light against the infrared wavelength or frequency. When a sample is irradiated with the infrared light with continuous frequency, the molecule absorbs the radiation of some frequencies. The molecular vibration or the rotation leads to a

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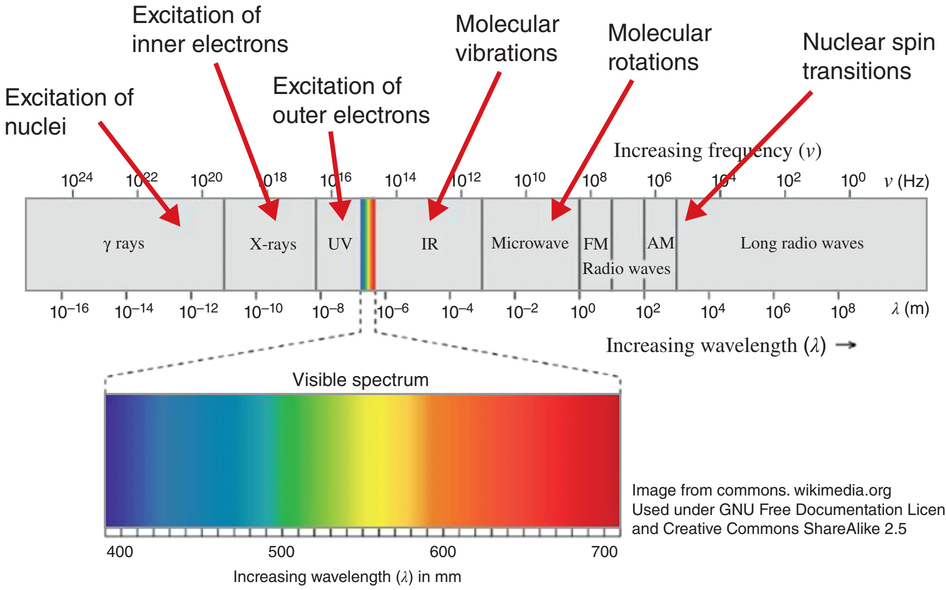

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Figure 1.1 Electromagnetic spectrum.

change in dipole moment, resulting in the vibration–rotation energy level to transit from the ground state to the excited state. The wavenumber or the wavelength curve is recorded by the transmission rate percentage ($T\%$). The infrared absorption spectrum is generally expressed by a T-λ wave curve or a T-wavenumber curve. In the infrared spectrum, the ordinate is the transmittance percentage, the abscissa is the wavelength range (μm), or the wavenumber (cm^{-1}).

All functional groups in a molecule have their own specific absorption peaks with different infrared characteristics. In different compounds, the absorption vibration of the same functional group always appears in a narrow range of wavenumbers, not on a fixed wavenumber as the specific number of waves is related to the environment in which the group is located in the molecule. The factors that cause the frequency displacement of the group are multifaceted, among which the external factors are mainly the physical state and chemical environment in which the molecule is located, such as temperature and solvent effects. For the internal factors leading to group frequency displacement, there are electric effects of substituents such as induction effect, conjugate effect, intermediate effect, dipole field effect, etc. The mechanical effects include mass effect, tension-induced bond angle effect, and vibration coupling effect, among which hydrogen bond effect and coordination effect also lead to group frequency shift. When these effects occur between molecules, they are referred to as external factors. When they are within molecules, they are referred to as internal factors.

The vibration transition probability is measured by the intensity of the infrared band, and it is related to the magnitude of the change in dipole moment upon molecular vibration. This change in dipole moment is proportional with the band intensity. Since the change in dipole moment is also related to the inherent dipole moment of the group itself, then upon molecular vibration, the stronger the polarity of the group, the greater the change in dipole moment, and the stronger the absorption band. Likewise, the higher the symmetry of the molecule, the smaller the change of dipole moment, and the weaker the absorption band. This indicates that the functional groups and constituents of a substance can be judged according to the infrared spectra.

1.1.1 Energy Level

A very important concept in spectroscopy is the Born–Oppenheimer approximation, which is the basis for understanding molecular potential energy curves. It was introduced to simplify the representation of Coulomb interactions between electrons and nuclei in a molecule by separating their motions. This approximation stands on the ground that since electrons are much lighter than the nuclei, they move so fast that they can be assumed to be moving in a field of fixed nuclei. Thus, for each relative position of the nuclei, a potential energy can be calculated relative to the position of the nuclei upon which the electronic energy parametrically depends. Figure 1.2a shows the potential energy curve of a diatomic molecule as a function of the distance between the nuclei.

When the two atoms are far away from each other, they do not feel any interaction, and the potential energy is zero. As they approach each other, however, attraction occurs between electrons and nuclei, whereas nuclei–nuclei and electron–electron repulsion occurs, giving rise to a nonattractive term. The attractive forces are prevalent at not too small distances. However, as the internuclear distance goes toward zero, the potential energy rises toward infinity, reflecting the importance of nucleus repulsion at small distances. The minimum value corresponds to the equilibrium distance between two nuclei. This value is most often referred to as the bond length, r_0. In order to dissociate the molecule, an energy corresponding to at least the dissociation energy must be used.

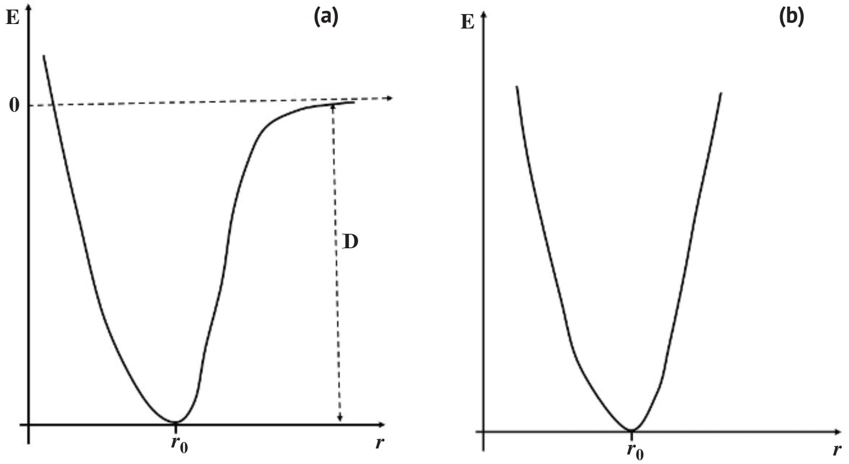


Figure 1.2 (a) Potential energy curve for a diatomic molecule. The minimum value corresponds to the bond length, and *D* is the dissociation energy. (b) Harmonic approximation of the potential energy curve.

Potential curves for diatomic molecules can be calculated accurately using a very good approximation called Morse potential, given by Equation (1.1):

$$E = D\left(1 - \exp\left(-a\frac{r - r_0}{r_0}\right)\right)^2 \tag{1.1}$$

where D is the dissociation energy, r is the distance separating the two nuclei, r_0 designates the equilibrium value, and a is a parameter which influences the width of the Morse curve.

In vibrational spectroscopy, the bottom of the potential energy curve is the most important, as will be shown below. This part of the potential energy curve can be approximated, in most cases, by a parabola described by a harmonic oscillator, given by Equation (1.2), and illustrated in Figure 1.2b. This approximation is called harmonic approximation.

$$E = \frac{1}{2}k_\mathrm{f}(r - r_0)^2 \tag{1.2}$$

where k_f is the force constant. At high potential energies, the harmonic approximation certainly performs bad as the dissociation energy goes toward infinity.

In classical view, all values for the potential energy are acceptable. However, this is not the case from quantum mechanical approach wherefrom only certain values of the potential energy are possible. Based on this approach, the values of the potential energy are given as:

$$E = hv\left(v + \frac{1}{2}\right) \tag{1.3}$$

where h is Planck's constant, and v is the quantum number taking values of positive integers (including zero). For possible values for the potential energy, the energy levels in the harmonic approximation are shown in Figure 1.3. Note that in this approximation, the energy difference between two consecutive levels is the same. This is sometimes called the distance between the levels, so that the distance is measured in energy units! The energy levels for the more realistic Morse potential are not equidistant as shown in Figure 1.3. For this potential, the distance between consecutive levels decreases with increasing quantum numbers. However, at the bottom of the Morse potential energy curve, the energy levels are nearly equidistant, consistent with the fact that the harmonic approximation is a good choice.

Quite often, the potential energy curves are not shown, but only the energy levels as illustrated for both harmonic and anharmonic potentials are shown in Figure 1.4. When the energy is given in cm^{-1} instead of Joule (or J/mol), the picture in Figure 1.4 is referred to as *term diagram*. The state with the lowest energy is the fundamental state or ground state, while other states are the excited states. When a molecule moves from one energy state to another, this process is called a *transition*. When a transition is from lower to a higher state, the energy is said to be absorbed, while for downward transitions, the energy is released or emitted. Vibrational spectroscopy deals with these transitions. Most often, these transitions are studied by examining the interaction between a molecule and an electromagnetic field, which will be discussed further. It should be noted that these transitions can also occur in other ways, for example, by exchange of energy with neutrons (inelastic neutron scattering), a technique becoming more and more important. The problem with this technique is that the neutron source is not easily accessible.

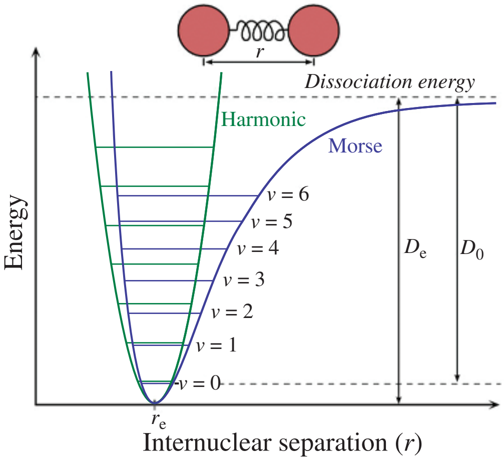


Figure 1.3 Energy levels for a Morse potential and a harmonic potential. The numbers are the vibrational quantum numbers.

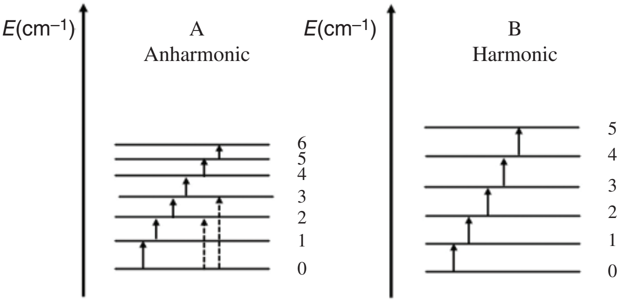


Figure 1.4 Term diagrams for (a) anharmonic and (b) harmonic potentials. The arrows drawn in full correspond to transition with $\Delta v = 1$. The broken arrows illustrate binary and ternary overtone.

The first thing to realize is that not all transitions between the levels in Figure 1.4 are possible or allowed. In the harmonic case only, changes of one in the vibrational quantum number are allowed: $\Delta v = 1$ results in *absorption*, while $\Delta v = -1$ results in *emission*. All transitions shown in Figure 1.4 correspond to absorptions. The transition from the ground state to the first excited state ($v = 1$) is known as a fundamental transition or just a fundamental.

1.1.2 Vibrational Mode

A molecular vibration takes place when some or all the atoms of a molecule are engaged in a periodic motion with the molecule remaining in constant translational and rotational motion. The frequency of such a periodic motion is called *vibration frequency* (for typical molecular vibrations, the frequencies are in the range 10^{12}–10^{14} Hz). When the molecule absorbs a quantum of energy ($E = h\nu$, where h is Planck's constant and ν is the vibration frequency), the molecular vibration is excited. The molecule absorbing one such quantum of energy in its ground state is said to undergo a fundamental transition.

The motion in a normal vibration can be approximated to a simple harmonic motion. This approximation assumes the vibrational energy to be a quadratic function (parabola) of atomic displacements, with the first overtone having twice the frequency of the fundamental. In real situations, vibrations are anharmonic, with the frequency of the first overtone being slightly lower than twice the frequency of the fundamental. The excitation of higher overtones leads to a gradual decrease of additional energy and, eventually, to the molecule as the potential energy of the molecule has become like the Morse potential. Vibrational excitation and electronic excitation (vibronic transition) can occur simultaneously, giving rise to *vibration–rotation spectra*.

Molecular vibrations involve changes in molecular bonds and angles. These can be described by displacement coordinates, as illustrated in Figure 1.5, for a nitrogen molecule. Sometimes, the notation *internal displacement coordinate* is used, or even the short notation *internal coordinate*. The latter should be avoided in order to distinguish clearly between coordinates used to describe equilibrium bond lengths (or angles) and changes in the relative nuclei positions. The displacement coordinate is given as: $\Delta r(t) = r(t) - r_0 = A_0 \cos(2\pi\nu_{NN}t)$, where ν_{NN} is the frequency for the N-N stretching vibration, and A_0 is the amplitude of the vibration. For a triple bond, the expected frequency is ~6.6×10^{13} Hz. This unit can be converted to the wavenumber unit (cm^{-1}) by dividing the frequency with the speed of light, $c = 3 \times 10^{10}$ cm s^{-1}. The displacement coordinate is also referred to as a normal coordinate, although it should be emphasized that the nuclei masses are also important for the normal coordinate. The description in terms of normal modes can be generalized to a molecule containing *N*-atoms. In this case, *3N-6* different displacements (normal) coordinates can describe the *3N-6* normal vibrations. By standard notation, these normal coordinates are called Q_1–$Q_{3N\text{-}6}$. For each of the normal coordinates, an expression as the one used for a displacement coordinate can be used: $Q = Q_0 \cos(2\pi\nu_Q t)$. The *3N-6* normal coordinates are independent of each other, so that each vibration can be described separately. Again, it is assumed that all *3N-6* frequencies are different (the nondegenerated case). For a linear molecule with *N*-atoms, *3N-5* coordinates are used. Some of these will correspond to degenerated vibrations, and less than *3N-5* vibrational frequencies are observed.

For the water molecule that contains 3 atoms, 3 × 3 − 6 = 3 vibrations are expected. These can be described by the displacement coordinates shown in Figure 1.6.

In Figure 1.6, only the motions of the hydrogen atoms are shown. The amplitudes of the nuclei depend on the atoms relative masses, and because the oxygen atom is much heavier than the hydrogen atom, hydrogen atoms are in apparent motion relative to the fixed oxygen atom. In a general description of a complex molecule, it is not trivial to find the normal modes, and quite large calculations and use of isotopic substitution are therefore necessary.

Figure 1.5 Definition of the displacement coordinate for N_2. Most often, only one set of arrows is used, and by tradition, the one showing the increase in the bond length is most often used.

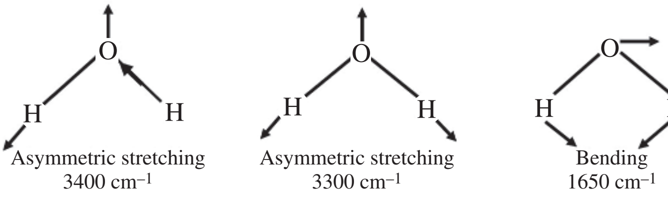


Figure 1.6 Displacement (normal) coordinates for a water molecule, together with the wavenumber for each vibration.

However, the concept of group frequency allows to understand the motion of atoms within a particular functional group. Although the real normal coordinate is not known, the main amplitudes occur for atoms within the functional group. For example, for an ester (COOR), ←C═O→ and ←C—O→ stretching modes will occur.

1.2 Infrared Spectroscopic Techniques and Principles

For a molecule to absorb an infrared radiation and produce an infrared spectrum, two conditions must be met. Condition 1 is that the energy of radiating photons is the energy required for vibration and rotation. Condition 2 is that there is a coupling between radiation and matter. When a beam of IR radiation passes through a substance, and the vibration frequency or rotation frequency of a functional group in the substance is equal to the frequency of the IR light, the energy absorbed by the molecule will transition from the original ground state vibration kinetic energy level to the higher vibration kinetic energy level. The primary aim of IR spectroscopy is to determine the molecular structure of substances according to the relative vibration between atoms and the information on molecular rotation.

The absorption peak in the IR spectrum corresponds to the vibration form of each functional group in the molecule, while the infrared spectrum of the substance is the reflection of its molecular structure. Different molecules have different infrared spectra, in such a way that the infrared spectrum is characteristic and can be used for qualitative analysis. However, since the relationship between the infrared spectrum and the structure of polyatomic molecules is complicated, it is difficult to explain in theory that the relationship between the infrared spectrum of most compounds and their structures is empirical. It is found that various functional groups, such as C—H, N—H, O—H, C—C, C═C, C═O, and the like, have their own specific infrared absorption regions. In general, the frequency of the vibration associated with a certain group is referred to as the group frequency, and the corresponding absorption peak is referred to as a characteristic absorption peak.

1.2.1 Interaction Between a Molecule and an Electromagnetic Field in Infrared Spectroscopy

Assuming that the frequency of the alternating field is too low to excite an electronic state in the molecule (with a molecular dipole moment, μ), only the electronic ground state can be considered. Performing a Taylor expansion of the molecular dipole moment in the electric field, E, leads to:

$$\mu = \mu_0 + \left(\frac{d\mu}{dE}\right)_0 E + \frac{1}{2}\left(\frac{d^2\mu}{dE^2}\right)_0 E^2 + \frac{1}{6}\left(\frac{d^3\mu}{dE^3}\right)_0 E^3 + \ldots \ldots \tag{1.4}$$

Traditionally, Equation (1.4) can be written as:

$$\mu = \mu_0 + \alpha E + \frac{1}{2}\beta E^2 + \frac{1}{6}\gamma E^3 + \cdots \cdots \tag{1.5}$$

where μ_0 is the permanent dipole moment, often referred to as μ_{mol}, α is the polarizability, and β and γ are hyperpolarizabilities.

For a diatomic molecule that has only one vibration described by the normal coordinate Q, the appearance of the IR spectrum is related to the dipole moment, μ_0, and the Taylor expansion is:

$$\mu_0 = \mu_0(0) + \left(\frac{d\mu_0}{dQ}\right)_0 \cdot Q + \frac{1}{2}\left(\frac{d^2\mu_0}{dQ^2}\right)_0 \cdot Q^2 + \cdots \cdots \tag{1.6}$$

The first term, $\mu_0(0)$, which does not depend on the molecular vibration, is the real permanent molecular dipole moment. The constant $d\mu_0/dQ$ is important for the $\Delta v = 1$ transitions (Figure 1.4), because this term must be different from zero for the transition to occur. The constant $d^2\mu_0/dQ^2$ being nonzero gives rise to transitions with $\Delta v = 2$ (binary overtones) in the infrared spectrum, and in a similar way, the next term in the Taylor expansion would give rise to ternary overtones. Note that this is the case even for a harmonic potential. For a homonuclear diatomic molecule, all terms in Equation (1.6) are zero.

For a nonlinear molecule with N-atoms, a partial differentiation regarding the *3N-6* normal coordinates can be performed. Thus, for each of the coordinates, equations that are similar to Equation (1.6) will appear. The nonlinear terms will appear differentiated by different normal coordinates for the quadratic terms in Equation (1.7).

$$\mu = \mu_0(0) + \left(\frac{d\mu_0}{dQ}\right)_0 \cdot Q \tag{1.7}$$

For example, $\delta^2\mu_0/(\delta Q_i \delta Q_j)$ leads to a combination band in the infrared spectrum with a frequency close to the value for the sum of the two fundamentals ($v_\mathrm{i} + v_\mathrm{j}$). Overtones and combination bands are usually observed a few percent below the expected values for the fundamentals. This is due to anharmonicity (see Figure 1.4). When the potential is assumed to be harmonic and higher terms than the linear in Q are omitted in the Taylor expansion of the dipole moment, we are let with the so-called double harmonic approximation. Kindly note that for a molecule (even linear) with more than two atoms, $d\mu_0/dQ$ can be different from zero, even if the permanent dipole moment, $\mu_0(0)$, is zero. Thus, for the dipole moment, it is a good approximation to include only the first linear term in Q [see Equation (1.8)].

Figure 1.7, which is the graphical expression of Equation (1.8), gives the dipole moment relative to the internuclear distance for a heteronuclear diatomic molecule. The dipole

Figure 1.7 Dipole moment as a function of intermolecular distance for a heteronuclear diatomic molecule.

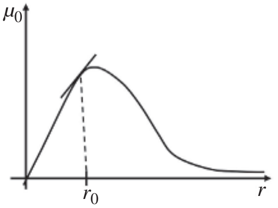
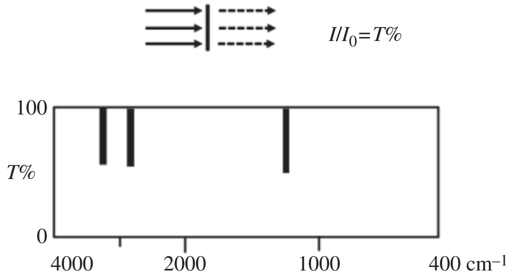


Figure 1.8 Infrared spectroscopy absorption of electromagnetic radiation and schematic illustration of IR spectrum.



moment is equal to zero in the two limiting cases with $r \to 0$ and $r \to \infty$. Equation (1.8) corresponds to approximating the curve to its slope in the proximity of the bond distance, r_0. This is a good approximation when the internuclear distance does not change too much under a vibration (Δr or Q are small). Since the lighter atoms show the largest amplitudes, hydrogen must give the upper limit. The equilibrium C—H bond distance is ~1.1 Å, and the amplitude for a C—H→ is less than 0.1 Å. This means that even in this case, the variation in bond length is less than 10%, and this variation is smaller for heavier atoms. Thus, when the curve in Figure 1.7 is rather smooth, the approximation in Equation (1.7) is fulfilled.

1.2.2 Infrared Spectra

Figure 1.8 illustrates an IR spectrum, obtained by measuring the percentage of light transmitted ($T\%$) by a sample.

This means that a nonabsorbing sample corresponds to 100% transmission. The absorption can be expressed by the Beer–Lambert law:

$$I(\overline{\nu}) = I_0(\overline{\nu})10^{-\varepsilon(\overline{\nu})cl} = I_0(\overline{\nu})10^{-D} \tag{1.8}$$

where $I_0(\overline{\nu})$ is the light intensity after travelling the cell path length l, I_0 is the initial intensity of light, ε is the molar absorption extinction coefficient, c is the molar concentration, and D is the absorbance. The transmission ($T\%$) is given as:

$$T(\%) = I/I_0 \times 100 \tag{1.9}$$

The relationship between $T(\%)$ and D is easily found as:

$$D = -\log T(\%) + 2 \tag{1.10}$$

Described by classical physics, the electromagnetic radiation is absorbed when there is a resonance with a frequency of a molecular vibration. The absorption can be expressed quantum mechanically as a transition from one energy level to another, where $\Delta v = 1$ and $\Delta E = hv$, where v is the vibrational frequency of the absorbed radiation.

1.2.3 Intensities in Infrared Spectra

The intensities in an IR spectrum are given by $(\delta\mu/\delta Q)^2$. Figure 1.9 shows the IR spectrum of water. Again, stretching vibrations seem to be stronger than the bending vibrations. However, this is not a general rule in IR. The asymmetric O—H stretch at the higher wavenumber is more intense than the symmetric stretch. The change in molecular dipole moment is not easy to relate to the electron configuration. But stretching of very polar bonds results in strong IR bands. This is in some way related to the dependence of the dipole moment upon the internuclear distance (Figure 1.7), because a high value of the dipole moment will also result in a steep slope. It is worth to note that C ≡ C and C═C stretching vibrations with symmetric substitution are completely forbidden in IR, because they do not induce any dipole moment change. With an unsymmetric substitution, the stretching becomes IR-allowed, but the dipole moment change is small and the absorption bands are weak. The same reason explains why C≡N and C═N stretching modes are weak.

The intensity is very important in the concept of group frequencies, because even when a frequency is characteristic of a functional group, it cannot be used without having also a high intensity, because a molecule with a typical "*chemical molecular weight*" contains so many bands that weak bands will be hidden.

1.2.4 Infrared Reflectance Spectroscopy

Common reflections include internal reflection, external reflection, and diffuse reflection. Reflection-based instruments include attenuated total reflection infrared spectroscopy (ATR-IRS), infrared reflection-absorption (IRRAS), diffuse reflectance infrared Fourier

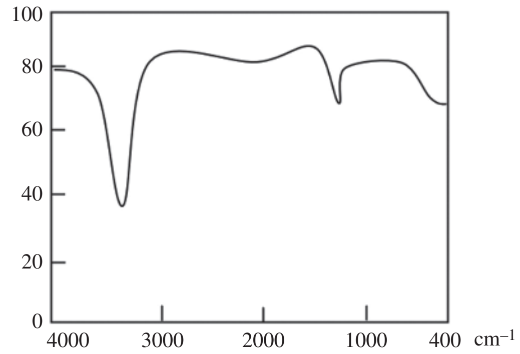


Figure 1.9 IR spectrum of liquid water at room temperature.

transform spectroscopy (DRIFTS), etc. The reflection principle is shown in Figure 1.10. These instruments can maximize the signals associated with surface active substances during the study of events occurring at the interface, especially during reaction processes.

1.2.5 Specular Reflection (Smooth Surfaces)

Specular reflection is a variant of external reflection technique. When the infrared light shines on the sample at a certain incidence angle, the reflection and refraction of light will be formed on the interface, where the reflection angle is equal to the incidence angle. If the sample, attached to the bright metal surface, is illuminated by infrared light, the light will pass through it, forming a reflection on the metal surface, and pass through the temperature production again. At this time, the outgoing light carries the sample information.

Specular reflection is usually used for infrared spectroscopy in the form of accessories, including fixed angle reflection accessories, variable angle reflection accessories, and swept angle reflection accessories. In a fixed angle, the incidence angle of the reflection attachment is fixed, usually 10°, 30°, 45°, 70°, etc. The angle of the variable angle reflection accessory can be adjusted within a certain range. Figure 1.11 shows the optical path of a specular reflection accessory with a fixed angle of 30°. This figure shows that the selection

Figure 1.10 The reflection principle of different IR instruments.

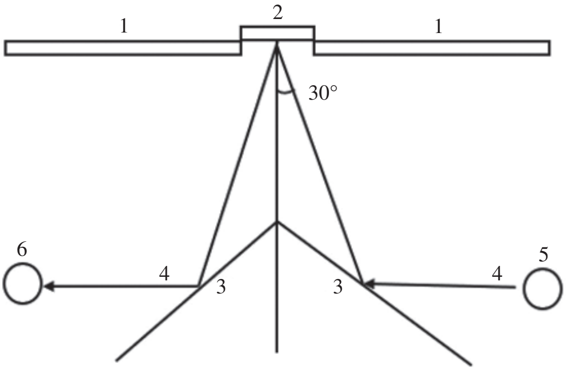


Figure 1.11 The optical path of a specular reflection accessory with a fixed angle of 30°. 1: sample support table, 2: sample, 3: reflector, 4: beam, 5: light source, 6: detector.

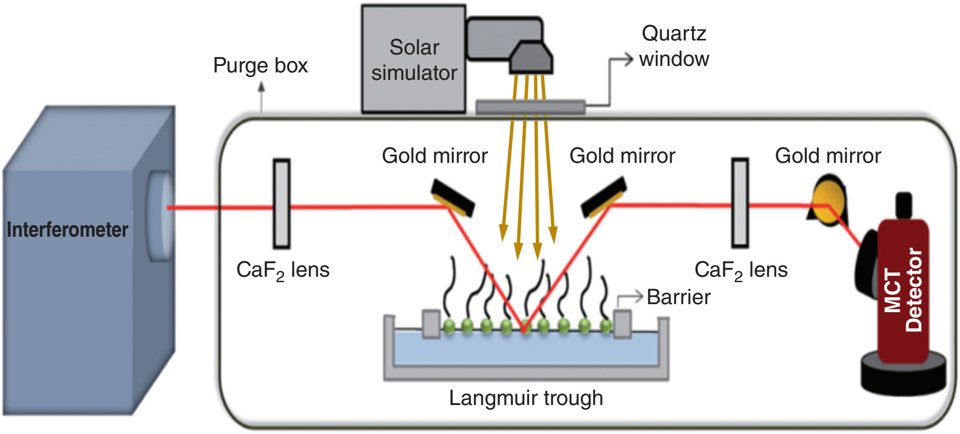


Figure 1.12 The experimental apparatus and reflection principle of IRRAS.

of incident angle is very important, as it will affect the effective path and polarization infrared response. This selection belongs to the nondestructive measurement of thin layer or monolayer, but the spectrum depends on the refractive index. IRRAS are also specular reflections, as shown in Figure 1.12.

1.2.6 Diffuse Reflection (Rough Surfaces)

Diffuse reflection occurs when light is reflected in all directions from a rough surface. Diffuse reflection is also an external reflection technique. Unlike specular reflection, this technique is mainly used on powder samples and needs to minimize specular reflection. The combination with FTIR spectroscopy is one of the most common infrared analysis methods.

DRIFTS has become one of the most popular analytical technique for *in situ* measurements of physicochemical processes occurring at gas–solid interfaces. To record the spectra of powders and rough surfaces, these surfaces are illuminated, and sufficient scattered radiation with paraboloids and ellipsoids is collected. The powder sample has the advantages of fast measurement, low repeatability of spectral data, and complex physical description of effects. DRIFTS sample preparation is done simply by placing the powder into sample cups for analysis. Highly absorbent samples must be diluted in a nonabsorbent substrate (e.g., KBr, KCl) without need to press the pellet. From a theoretical standpoint, no linear relation exists between band intensity and sample concentration. This makes quantitative analyses by the DRIFTS method to be rather complicated.

1.2.7 Attenuated Total Reflection Fourier Transform Infrared Spectroscopy

The attenuated total reflection (ATR), proposed in 1968, is a phenomenon of profound attenuation by coupling the fast decay field with surface plasmon in optics. When a light wave is incident, a monochromatic plane wave polarized in the plane of incident is fully

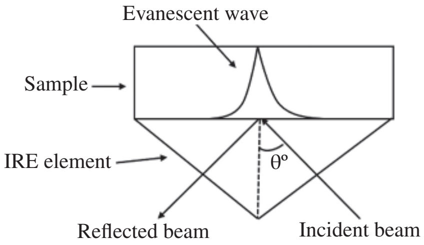


Figure 1.13 The reflection principle of single bounce ATR.

reflected at the boundary between a dense and sparse medium (Figure 1.13). The amount of fast decay field (see attenuation wave) formed in an optically phobic medium can be coupled to the surface of a metal or semiconductor to excite the surface plasmon or surface polariton resonantly. Designed based on light internal reflection principle, ATR is a versatile and nondestructive technique used to study for a large variety of materials, despite its sensitivity being ~3–4 orders of magnitude lower than the transmission. Based on the reflected signal of the sample surface, the structural information of the organic components on the sample surface can be inferred, which has the advantages of simple sample preparation, nondestructive, real-time monitoring on site, high detection sensitivity, low cost, and simple operation. The main factors affecting ATR spectra are the contact degree between the sample and the crystal, the incidence depth of infrared light, and the frequency of reflection. ATR is a very sensitive method to study the optical properties of surface or interface. Because ATR can be realized at both metal–vacuum interface and metal–dielectric interface, it has become a promising method to study surface physical phenomena.

1.2.8 Fourier Transform Infrared Spectroscopy

Three generations of infrared spectrometers have preceded the development of Fourier transform infrared spectroscopy (FTIR). The first generation, invented in the late 1950s, utilized the prism optical splitting system, with the prisms being made of NaCl. This generation of infrared spectrometer had an extremely strict requirement on the water content and particle size of the sample. Furthermore, the scan range was narrow, and the repeatability was fairly poor. This resulted in the first generation of infrared spectrometer becoming obsolete soon after its development. The second generation of infrared spectrometer was introduced in the 1960s, and it utilized gratings as the monochromator. This generation of infrared spectrometers performed much better than spectrometers with prism monochromator. Notwithstanding, they still had some weaknesses such as low sensitivity, low scan speed, and poor wavelength accuracy, which made them to quickly run out of date after the invention of the third generation of infrared spectrometers. The third generation of infrared spectrometer, namely, the FTIR spectrometer, marked the abdication of the monochromator and the prosperity of the interferometer. This replacement made infrared spectrometers to become exceptionally powerful, allowing them to be used in various applications.

The FTIR instrument mainly has five parts as shown in the schematic diagram in Figure 1.14: These are light source, interferometer, sample, detector, and computer. The light source is used to generate infrared radiation, which will go through the interferometer.

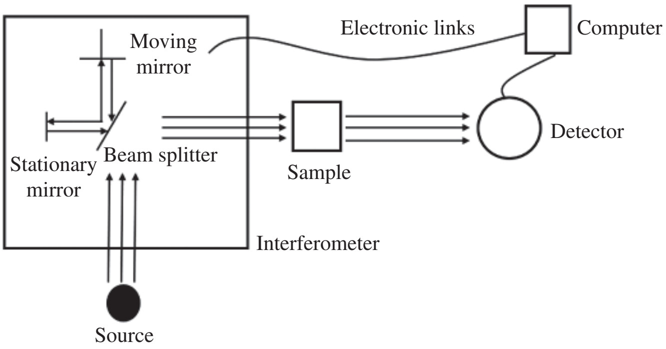


Figure 1.14 The schematic diagram of FTIR.

In the interferometer, the light passes through a beam splitter; the latter sends the former in two perpendicular directions. One beam travels to a stationary mirror and comes back to the beam splitter, while the other travels to a moving mirror. The total path length made by the mirror motion against that taken by the stationary-mirror beam is variable. When the two paths meet again at the beam splitter, they recombine, but the difference in their path lengths creates constructive and destructive interferences and forms an interferogram. The recombined beam then passes through the sample, which absorbs all characteristic wavelengths. The detector is then used to collect the radiation passing through the sample and to transmit the signal to a computer for spectral transformation and further analysis purposes. After all these processes, the infrared spectrum of the sample can be generated.

In FTIR, the radiation emitted by the light source is divided into semitranslucent and semireflective beams by the beam splitter, one of which reaches the moving mirror by transmission, and the other reaches the fixed mirror by reflection. The two different beams are reflected back to the beam splitter by the fixed mirror and the moving mirror, respectively. The moving mirror moves in a straight line at a constant speed, so that the two beams of light form a path difference and interfere after the beam splitter. The interferometer light passes through the sample cell after the beam splitter meets, reaches the detector after passing through the interferometric light containing sample information, and then processes the signal by the Fourier transform to obtain an infrared absorption spectrogram of absorbance or transmittance with the number of waves or wavelength.

FTIR spectroscopy is based on vibrations of molecules [1]. When the absorbed infrared radiation leads to a change in dipole moment, the FTIR spectrometer can measure this absorption and convert it to a spectrum. The characterization of molecular species and their titration constitute an essential part of FTIR spectroscopic analysis [2]. The major advantage of FTIR technique is that nearly all compounds exhibit characteristic peaks in the infrared spectral region, which allow for both quantitative and qualitative analyses. FTIR technique can be used for qualitative analysis because different types of bonds absorb different frequencies of infrared radiation. The FTIR quantitative analysis is based on the Beer–Lambert law, and this analytical technique is important in organic chemistry for identifying functional groups in molecules. It can also be used to confirm the identity of a pure compound or to detect the presence of specific impurities. Moreover, FTIR spectrometers can be used to investigate the mechanism of chemical reactions and the detection of unstable substances.

Since FTIR uses few optical components, neither grating nor prism splitters, it reduces the loss of light and further increases the light signal through interference, so that the radiation intensity reaching the detector is high and the signal-to-noise ratio is high. The Fourier transform processes the signal of light, avoiding the error caused by the splitting of the motor driving the grating, making the reproducibility better. According to the full band of data acquisition, the resulting spectrum is the result of multiple data acquisition averaging, and it only takes one to several seconds to complete a full data acquisition. For testing, only a very narrow frequency range is needed, and a complete data acquisition takes 10 to 20 minutes. FTIR is widely used in various fields including chemical industry, medicine, petroleum, environmental protection, geology and mining, coal, criminal investigation, gem identification, customs, and other fields [3, 4].

The FTIR spectrometer mainly differs from the dispersive IR spectrometer by the Michelson interferometer, which consists of a beam splitter and two perpendicular mirrors among which one is movable and the other is stationary. The beam splitter is designed to transmit half of the light and reflect half of it. Then, the transmitted light and the reflected light respectively strike the stationary mirror and the movable mirror. When light beams are reflected back by the mirrors, they recombine with each other at the beam splitter.

Infrared spectroscopy is an important means to analyze the structure of chemical compounds. The conventional transmission method uses tablet or film for measurement, which is difficult in testing some special samples such as those that are refractory, undissolvable, etc. In order to overcome these shortcomings, ATR infrared accessories were introduced in the early 1960s. However, the application of ATR technology in research was more limited due to the shortcomings of the performance of dispersion-type infrared spectrometers at that time. In the early 1980s, ATR technology was applied to the FTIR spectrometer, leading to ATR-FTIR. This combination makes the analysis of micro-region composition convenient and fast. The detection sensitivity can be up to several nanograms (ng), and the measurement of micro-region diameter can be up to several microns. As computer technology has developed in recent years, the nondestructive determination of nonuniform surface concave–convex bending samples has been realized, and infrared spectral images of functional groups and compounds in differential space could be obtained.

As one of the important experimental methods of infrared spectroscopy, ATR-FTIR overcomes the shortcomings of the traditional transmission method, simplifies the sample making and processing process, and greatly expands the application range of infrared spectroscopy. It has become a powerful tool and means to analyze the surface structure of substances. ATR-FTIR technology has been applied to various fields such as textile quality inspection, public security, and so on.

ATR-FTIR belongs to the category of infrared spectroscopy techniques that provide spectra with most of the characteristics of conventional FTIR. However, it also has some shortcomings relative to other infrared spectra, which are mainly manifested as: "*the quantitative analysis is not good enough, and is not suitable for analyzing trace components.*" It is an indirect analytical technique in which the calibration model used depends on the accuracy and applicability of the sample database established by the standard method. Scientists are seeking solutions to these problems, such as using lock-in amplifiers on the relevant detectors to improve the signal-to-noise ratio of the instrument, aiming to greatly reduce detection errors.

Some advantages of ATR-FTIR spectroscopy include simple sample preparation, and real-time *in-situ* tracking of nondestructive testing, which greatly expand the application field of infrared spectroscopy. The development of ATR-FTIR spectroscopy led to the improvement of instruments and the development of new application areas. At the same time, new analytical methods are being developed. To overcome the deficiency of infrared quantification, the development of a new mathematical model based on stoichiometry is expected. The application of ATR-FTIR in surface analysis, dynamics, and other aspects will continue to be a hot topic for researchers.

1.2.9 Sample Preparation Requirements of ATR-FTIR

ATR technology is suitable for the determination of solid and liquid absorption spectra. For solid samples, the tested surface is required to be smooth, so that it can be in close contact with the reflecting surface of total reflective crystal. It is, however, not suitable for the determination of porous samples and samples with rough surface. During measurements, the total reflection crystal is loaded into its fixed seat, and the sample is placed on the reflecting surface of the total reflection crystal. If the absorption peak is too strong, it can be solved by placing the sample on one side or adjusting the incident angle.

For some liquids that can be coated on the reflecting surface of the total reflective crystal, the ATR attachment of the general measurement of solid samples can be used. The liquid can be directly coated on the reflecting surface of the crystal for measurement. However, for liquids with low boiling points, or those with high boiling points that cannot form a liquid layer on the reflecting surface of the total reflective crystal, the ATR attachment with a liquid pool must be used. The penetration depth of the liquid is easily controlled by the ATR method. Compared with the transmission method, it is easier to obtain a spectrograph without saturation absorption.

During the test, it should be noted that there will be no reaction between the sample and the internal reflection crystal due to contact or other factors affecting the measurement accuracy. Therefore, the match between the test sample and the reflection crystal is obvious. There is no specific requirement on the shape, size, state, and water content of the sample, which belongs to the nondestructive measurement of the sample surface.

1.2.10 Characteristics of ATR-FTIR

i) Infrared radiation is absorbed through the interaction between the samples, which indicates that ATR spectrum has the characteristics and shapes of transmission absorption spectrum.

ii) ATR spectroscopy is a surface sampling technique, which mainly obtains the information on the sample surface layer, making it particularly suitable to observe the changes at the sample surface.

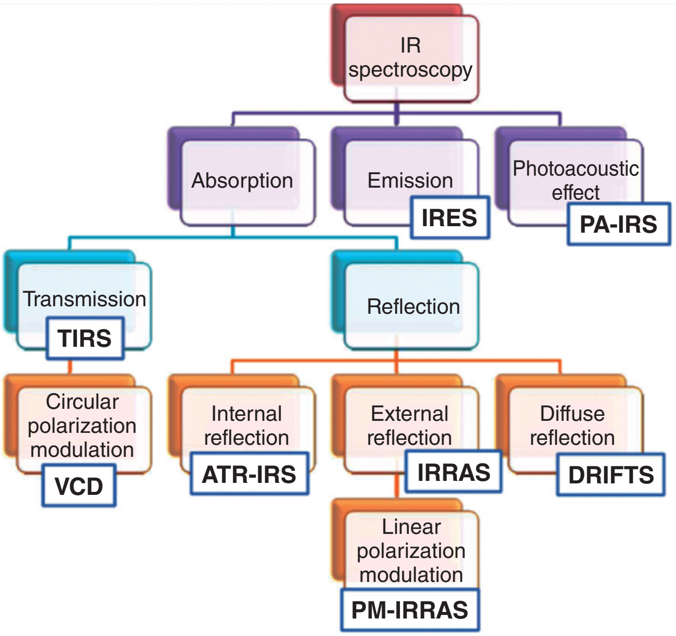
iii) It enables *in-situ*, real-time, and nondestructive measurements.

iv) Its sample preparation is simple and nondestructive, maintaining the original appearance of the sample for the determination of common transmission spectra, such as KBr tablet method.

v) The values of the electric field vector of IR radiation are different in the three orthogonal directions on the medium interface, and they are related to the incidence angle and polarization direction of the IR light.

1.3 Experimental Facility

The infrared spectrometer analyzes the chemical composition and the molecular structure of substances by using their absorption characteristics. It is usually composed of light source, monochromator, detector, and computer processing information system. According to properties of the optical splitting devices, IR spectrometers can be divided into dispersion type and interference type. For the dispersive dual-optical path optical zero-equilibrium infrared spectrophotometer, when the sample absorbs an infrared radiation of a certain frequency, the vibrational energy level of the molecule transitions, and the light of the corresponding frequency in the transmitted beam is weakened, resulting in the radiation intensity difference between the reference optical path and the sample optical path, so as to obtain the infrared spectrum of the measured sample. The classification of infrared spectroscopy techniques is shown in Figure 1.15.



TIRS: transmission infrared spectroscopy

IRES: infrared emission spectroscopy

PA-IRS: photoacoustic infrared spectroscopy

VCD: vibrational circular dichroism

ATR-IRS: attenuated total reflection infrared spectroscopy

IRRAS: infrared reflection-absorption spectroscopy

IPM-RRAS: polarization-modulation IRRAS

DRIFTS: diffuse reflectance infrared Fourier transform spectroscopy

Figure 1.15 Classification of infrared spectroscopy techniques.

1.3.1 Structural Overview of an Infrared Spectrometer

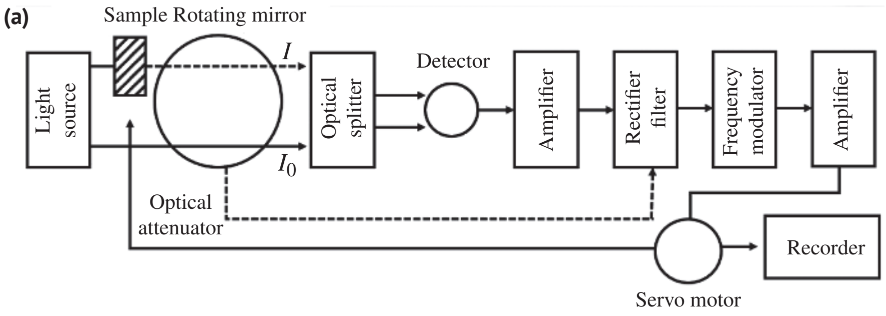
Infrared spectrometers can be divided into dispersion types and interference types.

1.3.1.1 Dispersive Infrared Spectrometer

According to the different metering methods, the dispersive infrared spectrometer (also known as dispersive infrared spectrophotometer) can be divided into optical balance type and proportional recording type. Figure 1.16a shows the optical zero-balanced structure. The optical zero-balanced instrument is used to drive the optical attenuator on the reference optical path after the detection and amplification of the modulating optical signal ($I_0 \sim I$), so that the energy of the two beams of light reaches the zero balance. At the same time, the recorder and the optical attenuator move synchronously to record the transmittance of the sample.

Figure 1.16b shows the proportion recording structure. Proportional recording instrument is to separate the modulation optical signal ($I \rightarrow$ zero $\rightarrow I_0 \rightarrow$ zero) after detection and amplification. The transmittance of a sample is obtained by measuring the ratio of two electrical signals.

A dispersive infrared spectrometer is mainly composed of a radiation source, a monochromator, and a detector. Common infrared radiation sources are inert solids that are heated electrically to promote thermal emissions of radiation in the infrared region of the electromagnetic spectrum. The monochromator is used to disperse or separate a broad spectrum of infrared radiation into individual narrow infrared frequencies. In general, dispersive spectrometers have a double-beam design with two equivalent beams from the same source passing through the sample and reference chambers as independent



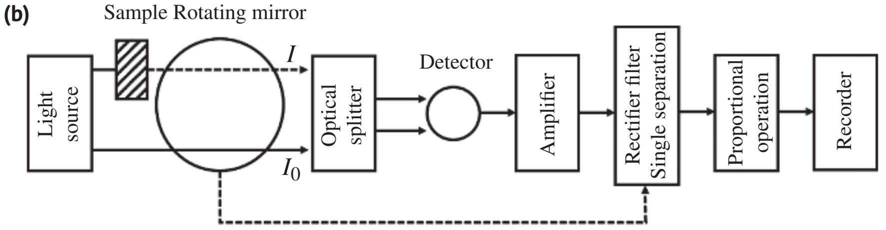


Figure 1.16 (a) The optical zero-balanced structure and (b) the proportion recording structure.

beams. Detectors convert the analog spectral output into an electrical signal. As for the mid-infrared radiation sources, they are Globar (silicon carbide), Nernst glower, and metal helix. Near-infrared region is tungsten halide lamp and ceramic-coated metal conductor. The far infrared is a mercury high-pressure lamp.

1.3.1.2 Interferometric Infrared Spectrometer

The interferometric infrared spectrometer is an FTIR that has no monochromator or slit. It is mainly composed of Michelson interferometer and computer. Figure 1.17 shows the overall working principle of the FTIR instrument.

The infrared radiation from the light source is collimated into the interferometer as a parallel beam and is modulated by the interferometer to obtain an interferometer light. The interference light passes through the sample and collects the interference light that contains spectral information to reach the detector. The interference optical signal is changed into electrical signal by the detector and amplified by the amplifier. The interference signal here is a time function, that is, the interferogram drawn by the interference signal, whose horizontal coordinate is the moving time of the moving mirror. It is difficult for people to carry out spectral analysis for the time-domain interferogram containing spectral information. Therefore, it is necessary that the interference signal enters the computer system through the analog-to-digital converter, and the Fourier transform is quickly calculated to obtain the infrared spectrum diagram (frequency domain spectrum) with wavenumber as the horizontal coordinate. It can also enter the computer through the digital-to-analog converter into the plotter for the spectrum to be drawn. This is very familiar with the infrared spectrum.

1.3.1.3 Light Source

The light source is among the key components of an infrared spectrometer. Infrared radiation energy directly affects the detection sensitivity. The ideal infrared light source should be able to test the entire infrared band, and testing the entire infrared band at present

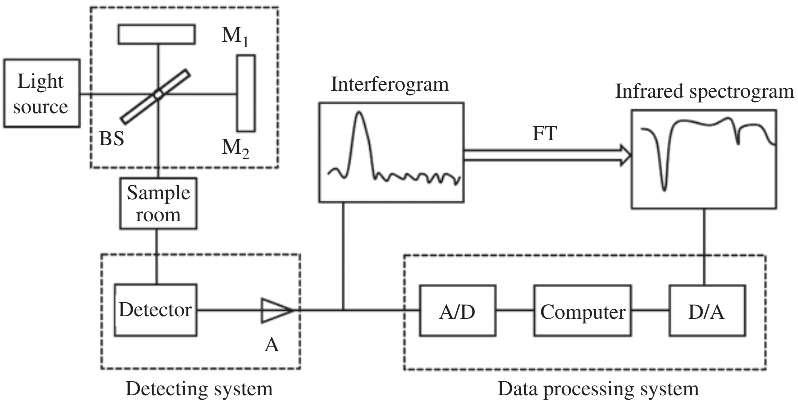


Figure 1.17 The overall working principle of the FTIR instrument.

needs at least to replace three light sources, that is, the middle-infrared, far-infrared, and near-infrared light sources, among which the most used is the middle-infrared light source. Each light source can only cover a certain band. Therefore, several light sources are usually required for infrared full-band measurement. Table 1.1 lists common light sources, while the types of infrared radiation sources are shown in Table 1.2.

At present, only one light source, mid-infrared light source, is installed in the optical platform of low-grade mid-infrared spectrometer. Two light sources are usually installed in the optical platform of high-grade FTIR spectrometer, one of which is the middle-infrared light source, and the other is the far-infrared or near-infrared light source. In a dual-light system, the switching between the two light sources is controlled by a computer.

Table 1.1 Types of common light sources.

Light source	**Used wavenumber ranges (σ/cm^{-1})**	**Main performance**
Tungsten lamp	15000–4000 (near infrared)	High energy, long life, and good stability
Halogen tungsten lamp	15000–4000 (near infrared)	High energy, long life, and good stability
Nernst stick	4000–400 (mid infrared)	Zirconia as the main body, with 15% yttrium and thorium rare earth oxides such as rod-like, working temperature 1400–2000 K. The radiation intensity is concentrated in the short wave, the emission coefficient is 0.8–0.9 at 5000–1666 cm^{-1}, and it has a long life (about 2000 h).
Silicon carbide rod	4000–400 (mid infrared)	High energy, large power, working temperature 1300–1500 K, strong thermal radiation, long service life, need to be cooled by cooling water
Wire light source	4000–400 (mid infrared)	Low power, wind cooling
Cermet rod	4000–400 (mid infrared)	High power, 1550 K, 120 mW, wind cooling, long life
EVER-GLO light	4000–400 (mid infrared)	High power, low thermal radiation, 1525 K, 150 mW, wind cooling
High-power water-cooled silicon carbon rod	400–50 (far infrared)	High power, water cooling
Cermet rod	400–50 (far infrared)	High power, water cooling
EVER-GLO light	400–50 (far infrared)	High power, wind cooling
High pressure mercury arc lamp	100–10 (far infrared)	High power, 5000 K, water cooling

Table 1.2 Different types of infrared radiation sources.

Type	Method	Material	Example of radiation source	Wavelength (μm)	Remark
Thermal radiation	Resistor heating by current flow	Tungsten	Infrared bulb	1 to 2.5	The long wavelength region is cut off by external bulb (glass). The secondary radiation is emitted through the tube.
		Nichrome Kanthal	Electric heater	2 to 5	
		Silicon carbide (siliconate)	Globar	1 to 50	Constant voltage, large current
		Ceramic	Nernst glower	1 to 50	Preheating is needed.
	Secondary heating by other power source	Metal (stainless steel, etc.)	Sheath heater	4 to 10	
		Ceramic	IRS type lamp	4 to 25	
			Radiant burner	1 to 20	Heating by gas burning
	Heating by discharge	Carbon	Carbon arc lamp	2 to 25	Causes some environmental problems such as soot.
Cold radiation	Gas discharge	Mercury Cesium Xenon	Mercury lamp Xenon lamp	0.8 to 2.5	Long wavelength region is cut off by external bulb. Secondary radiation is emitted through the tube.
Stimulated emission	Laser reaction	Carbon dioxide Gallium arsenic compounds Lead compounds	CO_2 laser InGaAsP laser PbSnTe laser	9 to 11 1.1 to 1.5 6 to 7	

1.3.1.4 Monochromator

The function of a monochromator in a dispersive infrared spectrometer is to disperse the radiation into monochromatic light. The monochromator usually refers to the part of the monochromatic light emitted from the incident slit to the exit slit, and having the same structure as the ultraviolet-visible spectrophotometer, but using a different prism material. At present, most of dispersive infrared spectrometers use sparkly grating, which can be used as filter or prism for spectral order separation. Filter adopts cut-off or passband transmission filter.

1.3.1.5 Interferometer

The interferometer, the core part of the optical system of FTIR spectrometer, determines the highest resolution and other performance indexes of the spectrometer. In the FTIR, the first thing is to change the light that is emitted by the light source into interference light through the interferometer. The interferometer is divided into various types, but its internal basic composition is the same, including three main components: moving mirror, fixed mirror, and beam splitter.

Currently, the interferometers used by FTIR mainly include air bearing interferometer, mechanical bearing interferometer, double-action mirror mechanical rotation interferometer, double-angle mirror coupling, moving mirror torsion interferometer, angular mirror Michelson interferometer, angular mirror wedge beam splitter interferometer, hanging torsion interferometer, belt mobile interferometer, etc. In recent years, the interferometer has been gradually developed and improved, and great progress has been made to simplify it by improving the utilization rate of the light, increasing the optical path difference, improving the resolution, increasing the stability of the instrument, extending the measuring band and the automatic adjustment of the interferometer, and protecting the interferometer, high-speed scanning, and stepping scanning technology.

1.3.1.6 Detector

The detector's purpose is to measure the energy of infrared light after passing through the sample. Requirements for the detector are high sensitivity, low noise, fast response speed, and wide measurement range. The commonly used detectors for dispersive infrared spectrometers are vacuum thermocouple and Goblet cell, while the commonly used detectors for FTIR spectrometers are divided into two categories: universal pyroelectric detectors and mercury cadmium telluride (MCT) detectors.

To date, general pyroelectric detectors mainly include TGS [triglycoside sulfate peptide $(NH_2CH_2COOH)_2{\cdot}H_2SO_4$], LATGS (L-alanine TGS), DLATGS (deuterated L-alanine TGS), and DTGS (deuterated TGS).

The MCT detector is made by mixing the wide-band semiconductor cadmium telluride with the semimetallic compound mercury telluride. A variety of MCT detectors with different measuring ranges and sensitivity can be obtained by changing the proportion of mixture components. There are three kinds of MCT detectors for measuring mid-infrared spectrum, namely, MCT/A (narrow-band detector), MCT/B (wide-band detector), and MCT/C (mid-band detector). The commonly used near-infrared detector is indium antimonide (InSb) detector, which has photoconductive type and photovoltaic type. Common far-infrared detectors are DTGS with polyethylene window and liquid helium-cooled resistive bolometer. The types of IR detectors are shown in Table 1.3.

Table 1.3 Types of IR detectors.

	Type		Detector	Spectral response (μm)	Operating temperature (K)	D^* (cm·Hz$^{1/2}$/w)
Thermal type	Thermocouple		Goblet cell, condenser-microphone PZT, TGS, LiTaO$_3$	Depends on window material	300	$D^*\ (\lambda, 10{,}1) = 6 \times 10^8$
	Thermopile				300	$D^*\ (\lambda, 10{,}1) = 1 \times 10^8$
	Bolometer				300	$D^*\ (\lambda, 10{,}1) = 1 \times 10^9$
	Pneumatic cell				300	$D^*\ (\lambda, 10{,}1) = 2 \times 10^8$
	Pyroelectric detector					
Quantum type	Intrinsic type	Photoconductive type	PbS	1 to 3.6	300	$D^*\ (500{,}600{,}1) = 1 \times 10^9$
			PbSe	1.5 to 5.8	300	$D^*\ (500{,}600{,}1) = 1 \times 10^8$
			LnSb	2 to 6	213	$D^*\ (500{,}1200{,}1) = 2 \times 10^9$
			HgCdTe	2 to 16	77	$D^*\ (500{,}1000{,}1) = 2 \times 10^{10}$
		Photovoltaic type	Ge	0.8 to 1.8	300	$D^*\ (\lambda p) = 1 \times 10^{11}$
			LnGaAs	0.7 to 1.7	300	$D^*\ (\lambda p) = 5 \times 10^{12}$
			Ex.LnGaAs	1.2 to 2.55	253	$D^*\ (\lambda p) = 2 \times 10^{11}$
			InAs	1 to 3.1	77	$D^*\ (500{,}1200{,}1) = 1 \times 10^{10}$
			LnSb	1 to 5.5	77	$D^*\ (500{,}1200{,}1) = 2 \times 10^{10}$
			HgCdTe	2 to 16	77	$D^*\ (500{,}1000{,}1) = 1 \times 10^{10}$
	Extrinsic type		Ge: Au	1 to 10	77	$D^*\ (500, 900, 1) = 1 \times 10^{11}$
			Ge: Hg	2 to 14	4.2	$D^*\ (500{,}900{,}1) = 8 \times 10^9$
			Ge: Cu	2 to 30	4.2	$D^*\ (500{,}900{,}1) = 5 \times 10^9$
			Ge: Zn	2 to 40	4.2	$D^*\ (500{,}900{,}1) = 5 \times 10^9$
			Si: Ga	1 to 17	4.2	$D^*\ (500{,}900{,}1) = 5 \times 10^9$
			Si: As	1 to 23	4.2	$D^*\ (500{,}900{,}1) = 5 \times 10^9$

1.3.2 Sample Preparation Techniques in Infrared Spectroscopy

Transmitted infrared spectroscopy (TIRS) carries sample information through light and is suitable for the detection of liquid and gaseous samples. For solid samples that need prior dissolution or molding in very thin films, this technique has the advantage of being more straightforward in terms of quantification than other infrared technologies. In heterogeneous catalytic reactions, TIRS is popular in field investigations, usually using extremely thin self-supporting catalyst trays, with powder samples being dispersed on a transparent grid.

1.3.2.1 Gas Sample

Gaseous samples usually use a 4 cm diameter by 10 cm long glass gas absorber with infrared windows at either end (usually potassium bromide or sodium chloride). In order to prevent air leakage, both ends of the glass tube need to be carefully polished, and the adhesive is used to combine it with the salt window. The pool body is welded with two branch pipes with piston to fill the gas sample. In general, the gas absorption tank is pumped by a vacuum pump before the sample is filled. The absorption peak intensity can be achieved by adjusting the pressure of the sample in the absorption tank (as indicated by the manometer at the absorption tank). For strongly absorbed gases (such as carbon tetrafluoride), just 666.61 Pa pressure or less is required. For weakly absorbing gases such as hydrogen chloride, 50662.50 Pa pressure or more is required, while for most gases, a pressure of 6666.10 Pa is sufficient to obtain satisfactory spectra.

When the gas sample quantity is small, small volume gas absorption tank with different cross-sectional area and taper can be used. When the component concentration of the measured body is small, a long optical path gas absorption tank (optical path specifications are 10 m, 20 m, and 50 m) can be selected, or C-FTIR can be used for direct sampling analysis. In gas determination, the following two points should be noted: (i) the absorption peak of water vapor in the mid-infrared region interferes with the determination of the sample in such a way that it must be guaranteed before injection into the absorption tank. (ii) After sample measurement, dry air should be used to thoroughly purge the absorption tank and the pipe connecting the inlet of the absorption tank. Sometimes, it is necessary to repaint the piston lubricating oil on the absorption tank so as not to pollute the next measurement results with preabsorbed samples.

Gas samples are usually taken by gas pool method with BaF_2, CaF_2, KBr, NaCl, ZnSe, and other window materials. It has the advantages of long optical path, small size, and high sensitivity, and can realize multiple reflections.

1.3.2.2 Liquid Sample

1.3.2.2.1 Liquid Cell Window Piece Material

Liquid cell window materials are divided into organic liquid window materials and window materials for testing aqueous solution. Some common window materials are provided in Table 1.4.

1.3.2.2.2 Types of Liquid Cell

Liquid pools are usually divided into three categories: removable pool, fixed thickness pool, and variable thickness pool. A detachable tank is generally used to determine the infrared

Table 1.4 Types of window materials.

Material	Useful range (cm^{-1})	Refractive index	Properties
NaCl	40000–600	1.52	Soluble in water; slightly soluble in alcohol; low cost
KBr	43500–400	1.54	Soluble in water; slightly soluble in alcohol; hygroscopic
CaF_2	77000–900	1.40	Insoluble in water; chemically resistant; mechanically strong
BaF_2	66666–800	1.45	Low water solubility; soluble in acids and NH_4Cl
CsI	42000–200	1.74	Soluble in water and alcohol; hygroscopic
ZnSe	20000–500	2.43	Soluble in strong acid

spectrum of liquid samples. The two wafers in the detachable liquid tank and the spacers between the wafers can be removed for cleaning.

Fixed thickness liquid pool refers to a liquid pool in which the thickness between two windows is fixed. A hollow gasket is sandwiched between the two windows, and the thickness of the gasket is that of the liquid pool. The fixed thickness liquid pool must have liquid inlet and outlet for the injection of the liquid to be measured and cleaning liquid pool. Figure 1.18 is a decomposition diagram of a fixed thickness liquid pool. The window and gasket of the liquid pool of fixed thickness cannot be removed for cleaning. After each sample, the pool should be thoroughly cleaned. Usually, fixed thickness pools are used only for quantitative analysis.

The thickness of the liquid film between two wafers in a variable thickness liquid pool can be changed. Variable thickness liquid pool can change the absorbance of infrared spectrum of liquid by rotating the knob and adjusting the thickness of liquid film. The cleaning of variable thickness liquid pool is easier than that of fixed thickness liquid pool, and the distance between the windows can be enlarged during cleaning.

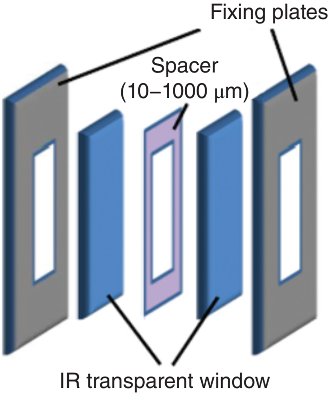


Figure 1.18 A decomposition diagram of a fixed thickness liquid pool.

1.3.2.2.3 Organic Liquid Sample

For the viscous sample, a small amount is placed in the middle of the potassium bromide wafer, with another wafer pressed, so that the sample forming a uniform film can be tested. For the liquid sample with small viscosity and good fluidity, a small glass rod can be dipped into a little liquid and placed in the middle of the potassium bromide wafer, and then another piece of potassium bromide wafer is placed. The screw of the liquid tank frame should not be tightened. When the liquid film has a thickness of 5–10 μm, the measured spectral absorbance is suitable. For volatile liquid samples, a large drop of the sample must be placed on the potassium bromide wafer, the other wafer being immediately covered, and the test be performed as soon as possible.

1.3.2.2.4 Samples of Water and Heavy Aqueous Solutions

Barium fluoride wafer is the best window material to determine the spectrum of aqueous solution samples. When the concentration of aqueous solution is above 1%, the spectrum of aqueous solution can be measured by liquid film methods. To avoid the interference of the absorption peak of water in aqueous solution to the absorption peak of the solute, the solute can be dissolved in heavy water to test the spectrum of heavy aqueous solution. The IR spectra of water and heavy water are complementary, and water or heavy water can be selected as solvent according to the need.

1.3.2.3 Solid Sample

Solid samples can exist in different forms, such as powder, granular, block, film, small hardness, high hardness, brittle, and so on. Solid sample methods for conventional transmission infrared spectroscopy include *tablet method, paste method*, and *film method*.

Tablet pressing method is a simple, easy, and commonly used sample preparation method. This method only requires diluent, agate mortar, tablet grinding tools, and tablet press. Although diluent has potassium bromide and potassium chloride (both having the same operation process), the former is commonly used. It is difficult to remove the water peak near 3400 cm^{-1} and 1640 cm^{-1} in the infrared spectrum measured by halide pressing, and these peaks are likely to interfere with the determination of crystalline water, hydroxyl, and amino groups in the sample. This shortcoming can be overcome by using *paste method*. This method is used to grind the sample and paste together in a glass mortar, so that the sample particles are evenly dispersed in the paste. The most commonly used pastes are paraffin oil (liquid paraffin) and fluorine oil. The method of grinding paraffin oil or fluorine oil with the sample is also called paraffin oil grinding or fluorine oil grinding.

The *film method* is mainly used for determining the infrared spectra of polymer materials. This method is divided into solution film making and hot-press film methods. Solution film-making method dissolves the sample in an appropriate solvent and then drops the solution on the infrared wafer (such as potassium bromide, sodium chloride, etc.), slide, or flat aluminum foil. After the solvent is completely volatilized, the film of the sample can be obtained. The best solution method is to drop the solution on potassium bromide wafers, for the film to be measured directly. The prepared solution should have a moderate concentration. If 2% solution is prepared and one to two drops of the solution are dropped, the film thickness and diameter are about 5–10 μm and 13 mm, respectively. The film prepared in this way is suitable for infrared spectroscopy. The hot-press film method can be used to hot-press thicker polymer films into thinner films, or to hot-press small samples from granular, block, or sheet polymers into films.

1.3.3 Maintenance of an Infrared Spectrometer

The infrared spectrometer provides the advantage to be able to work continuously. Nonetheless, if it has a mechanical bearing interferometer, the software design would include the sleeping mode. That is, after the instrument stops collecting spectral data, the moving mirror of the interferometer will automatically stop moving after a certain time, which can extend the service life of the interferometer. The infrared spectrometer can be stabilized soon after being turned on, and the energy of the light source can reach its maximum value within 15 minutes after being energized. The sample can be tested 30 minutes after the machine is turned on. To prolong the lifespan of the instrument, it is best to shut down after work and cut off all the power supply, so as to ensure the safety of the instrument.

In summer, when the humidity in the air is too high, if the instrument is used daily even under high humidity, the condition of the instrument will not be affected. However, a long-term no use in summer can easily damage the instrument. Therefore, in summer, even if the instrument is not in use, it should be energized at least a few hours a week to drive out the moisture off the internal components. Some infrared spectrometers are closed systems except the sample room and are equipped with dehumidifier. The frequent observation of desiccant color is necessary to timely treat and replace the desiccant failure. If the instrument is not a closed system, it is best to place a large bag of cloth silicone in the sample warehouse, and often put the silicone bag into the oven at 120°C to bake. After baking, the silicone should be cooled to room temperature before being placed in the sample bin.

Among the parts of the infrared spectrometer, the beam splitter can be most easily damaged, followed by DTGS detector. The medium infrared beam splitter is made of potassium bromide wafer, and the DTGS/KBr detector window material is also potassium bromide crystal. Therefore, the mid-infrared beam splitter and DTGS/KBr detector are the most sensitive to moisture. It is very important to ensure that the desiccant in the optical table is in an effective state. In the southern hemisphere, due to the high humidity of air, when the instrument is not working, some infrared instrument managers may like to take the beam splitter out of the optical table, store it in the dryer, and then put the beam splitter back in use to protect the beam splitter from moisture. Although this can protect the beam splitter from dampness, often taking out the beam splitter from the interferometer can easily lead to damaging the beam splitter. As collision is inevitable during taking out and loading of the beam splitter, cracks may appear on the surface of the beam splitter. Once there is a tiny crack, the light flux through the beam splitter will drop sharply, and the measurement sensitivity of the instrument will be greatly reduced. The best way is not to take out the beam splitter, but to keep the atmosphere in the optical table dry.

As the infrared microscopes should be dust proof, they should be covered with dust cover when not in use. Given that the opening of the condenser under the sample of the infrared microscope is facing upward, dust falling on the mirror of the condenser will reduce the reflectivity of the condenser. Therefore, when the infrared microscope is not operating, a piece of paper should be placed on the loading table to prevent dust from falling on the condenser mirror. When testing samples with a microscope, care should be taken not to drop samples or debris onto the condenser mirror. After using the infrared microscope for a period of time (about half a year), it is best to blow off the dust and sample fine particles above the condenser with dry N_2 gas or ear wash ball to ensure the reflectivity of the condenser.

If the interferometer uses an air bearing, the gas pushing the air bearing must be dry, dust-free, and oil-free. Compressed air provided by general nitrogen or air compressors for infrared instruments can be used. If compressed air is provided by a laboratory compressed air system, the compressor used must be an oil-free air compressor. Before compressed air enters the air bearing, it must be dried and filtered; otherwise, it will stain the air bearing and make the air bearing not work normally. The gas used to purge the optical table should also be oil-free, dry, and dust-free. When moving the infrared spectrometer remotely, the moving mirror in the interferometer should be fixed, so as not to damage the bearing due to violent vibration when moving. When using water-cooled infrared light source, in order to save water resources, circulation cooling pump should be used for water supply. Circulating water pump needs to use deionized water or distilled water into which antifreeze and biological agents have been added. Water supply hoses and interfaces should be checked regularly to prevent the aging of water pipes due to long-term use that would result in water running accidents.

1.4 Applications of Infrared Spectroscopy in Atmospheric Research

1.4.1 Qualitative and Quantitative Analysis

The sample to be tested can be made of a certain number of known or unknown substances, which both can be detected by infrared spectroscopy. If there is no standard map, it is necessary to conduct a qualitative analysis on the functional group of the infrared spectrogram, and the most likely compound is deduced according to the analysis result. If the compound is not a new substance, its infrared spectrum can be compared with the standard spectrum map. If the compound is a new substance, then spectral analysis is required. The different steps for such analysis are information collection of the compound, sample source, boiling point, melting point, refractive index, optical rotation rate, etc. Furthermore, the degree of unsaturation (Ω) should be calculated following Equation (1.11), and the molecular formula of the compound is obtained by elemental analysis (Ω).

$$\Omega = 1 + n_3 + \frac{n_2 - n_1}{2} \tag{1.11}$$

where n_1, n_2, and n_3 are numbers of hydrogen atoms, nitrogen atoms, and carbon atoms, respectively.

1.4.1.1 Verification of Known Substances

Verifying a known substance is done by comparing the infrared spectrum of the sample under test with the standard infrared spectrum of a pure substance with known molecular structure. The standard infrared spectrum of the pure substance can be tested on the used infrared instrument, and then the infrared spectrum data obtained from the test are stored on the hard disk of the computer or added to the self-built spectrum library catalog. When identification is needed, the spectrum library can be searched, or the stored standard spectrum can be called out for comparison.

Comparing two spectra relies on comparing the peak position and intensity as well as the peak widths of all absorption peaks in the spectra. If the comparison results of two spectra are completely consistent, the measured sample can be considered as known substance. If in addition to the absorption peak of the pure matter in the measured spectrum, there are additional absorption peaks, it is an indication that the measured sample contains impurities. If the two spectra are very different, then they are not the same substance.

It is very important for the quality control department of the production unit to verify the known material by using the qualitative analysis technology of the infrared spectrum. In order to ensure product quality, in addition to the verification of the final product, it is also necessary to verify the raw materials and intermediate products used in the production. In scientific research, infrared spectroscopy is a convenient method to judge whether the expected product can be obtained after processing or chemical reaction.

The verification of known matter requires standard infrared spectrum. If the standard infrared spectrum used is tested on the used infrared spectrometer, the test method and the test parameters used in the verification of known matter should be consistent with those used in the test of standard infrared spectrum. The number of samples should also be consistent. If the standard infrared spectra used are retrieved or drawn from the instrument's spectral library, or are collected from standard spectrographs or books, the sample preparation methods, test methods, and test parameters used for these standard spectrogram tests may be different from those used for verification of known substances. Therefore, extreme caution should be exercised when comparing infrared spectra. When the number of samples and the test method are different, the peaks relative intensities of the two spectra will be different. When the resolution of the test is different, the number of peaks of the two spectra will be different. For organic matter, the number of absorption peaks between the two spectra with resolutions of 4 cm^{-1} and 8 cm^{-1} is basically not different. The difference becomes significant when the resolution reaches 16 cm^{-1}. If polycrystalline isomers are present in the solid sample, it is best to use the solution method to test the infrared spectrum when performing known substance verification.

1.4.1.2 Infrared Spectroscopic Analysis of Unknown Substances

From the position of each band in the spectrum (shape and intensity of the band), it may be possible to infer the compound identity. For a mixture, while it is impossible to accurately infer its composition, the infrared spectrum can judge different functional groups contained in the mixture. The spectra of unknown mixtures can be analyzed by combining the retrieval technique of spectral database with other spectral data processing techniques. If the mixture consists of only two or three components, and the amount of each component is not very low, infrared analysis is relatively easy. However, it becomes difficult for a mixture of more than four unknown components.

The quantitative analysis of infrared spectrum consists in measuring the intensity of characteristic absorption bands and applying the Beer–Lambert law. The method is not limited by the state of the sample and can quantitatively determine gas, liquid, and solid samples, making it a widely used analytical technique. However, due to its low sensitivity, infrared analysis is not suitable for the determination of trace components.

Quantitative analysis of infrared spectra is easy for a single component system, relatively easy for two-component systems, but not easy for multicomponent systems. Especially for those homologues with similar chemical properties and structures, the quantitative analysis of multicomponent systems is very difficult. Specifically, for homologous multicomponent systems, infrared multicomponent quantitative analysis software is generally used for analysis. There are many kinds of infrared multicomponent quantitative analysis software based on different methods, such as classical least square method, partial least square method, principal component regression method, multicomponent linear regression method, etc. Various infrared instrument manufacturers are constantly developing and updating infrared multicomponent quantitative analysis software, for general as well as special analysis. Samples in both liquid and solid states can be quantitatively analyzed, and reference sample or standard sample is required. In the absence of a reference or standard sample, only a rough estimate of the content of the components in the mixture can be made. The accuracy of multicomponent quantitative analysis is low, with the error estimated at about 5%. However, the accuracy of quantitative analysis of a single component can reach about 1%.

The quantitative analysis of infrared spectrum can be performed using two methods, after a characteristic absorption peak has been found: one is based on Beale's law, and it measures the height of absorption peaks. The other, which is more accurate than the previous one, measures the peak area of the absorption peak.

1.4.2 Application in Atmospheric Processes

In a certain concentration range, the peak intensity (absorbance) in an infrared spectrum is directly proportional to the content of the measured component. However, it should be noted that the transmittance T is often used as the ordinate of infrared spectra, while the absorbance A is used for quantitative analysis. The relationship between them is $A = \log(1/T) = -1\text{og}(T)$. The methods of infrared quantitative analysis mainly include calculation method, direct comparison method, and working curve method.

For the purpose of simultaneous quantification and identification analysis, a new variant of FTIR, namely, Micro-FTIR, was developed [5]. This technique has the advantage to perform simultaneous quantification and identification of various fibers released from the washing of microfiber towels. Micro-FTIR is a prominent technique that combines an optical microscopy approach with infrared spectroscopy. By its principle (which consists in quantifying and simultaneously characterizing the fibers), Micro-FTIR optimally assesses the fiber release in the environment and simultaneously identifies their polymers. Previous studies show that Micro-FTIR data are repeatable and reliable, and they show that fibers are released in effluents even when they are washed with water only [6]. These studies indicated that, among household products, detergents were responsible for the fibers release and for the shedding, especially for small fibers, which can represent a threat for the biota and may negatively impact the environment as a whole.

FTIR spectroscopy has extensively been used as an appropriate tool to monitor the degradation of plastics due to its exquisite sensitivity to the apparition of C═O, C─O, and O─H bonds created during the degradation, as shown in Figure 1.19 [7]. FTIR and Raman spectroscopies were used to systematically characterize five kinds of bituminous coals. As the vehicle emission standards have improved recently, relevant volatile organic compounds (VOC)

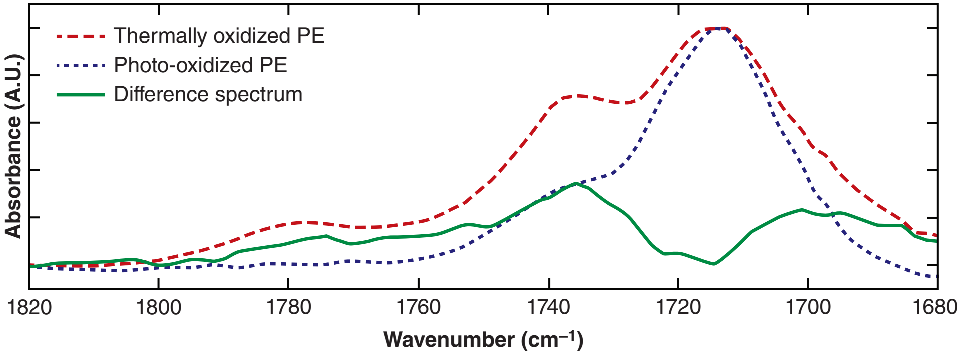


Figure 1.19 Spectroscopic differences in oxidation mechanisms. The spectra of thermally oxidized (TO_x) PE and photo-oxidized (PO_x) PE were normalized on the ketone peak at 1712 cm^{-1} and subtracted. *Source:* Reproduced from Sandt et al. [7], with permission of Elsevier.

standards changed from total hydrocarbon detection to nonmethane hydrocarbon (NMHC) detection. The rise of oxygen-containing fuels led to an increase in the measurement of nonmethane organic gas (NMOG). The method for vehicle exhaust detection that is based on portable FTIR is aimed at problems such as single component analysis, limited accuracy, and complex VOC detection process of domestic automobile exhaust analyzer. The structure of the FTIR optical system has been optimized based on a corner cube to meet anti-vibration requirements.

For atmospheric studies, there are mainly two significant and frequent FTIR spectroscopy methods: extractive measurement method and open-path measurement method.

1.4.3 Application in Extractive Measurements

Such measurements use FTIR trace gas spectroscopy that follows the following steps: extraction of a sample stream of gases from a certain location, its transportation to an IR absorption cell, and its isolation for analysis. The two major ways of extractive sampling are batch sampling [8] and continuous sampling. In the former sampling, spectra of discrete and static samples are collected, the gas cell is sealed, and then the spectrum is collected. In the latter sampling, spectra are collected while the sample gas is flowing through the cell at a controlled rate.

An important application of this method is the identification of hydrogen-bonded (X—H⋯Y, where X and Y are heteroatoms) complexes, which play a leading role in the formation of nanometer-sized aerosol particles, ultimately affecting climate and human health. If there are hydrogen-bonded complexes formed between molecules in a gas cell, FTIR spectrometer can detect the characteristics of hydrogen bond formation: X—H stretching fundamental shifts to a lower wavenumber, and the stretching transition has a pronounced intensity increase upon complexation. The O—H⋯O and O—H⋯S hydrogen bonds in the alcohol–ethylene oxide (EO) and alcohol–ethylene sulfide (ES) complexes have been investigated in the gas phase using FTIR spectroscopy. As shown in Figure 1.20, O—H⋯O and O—H⋯S hydrogen bonds exhibit similar strengths [9].

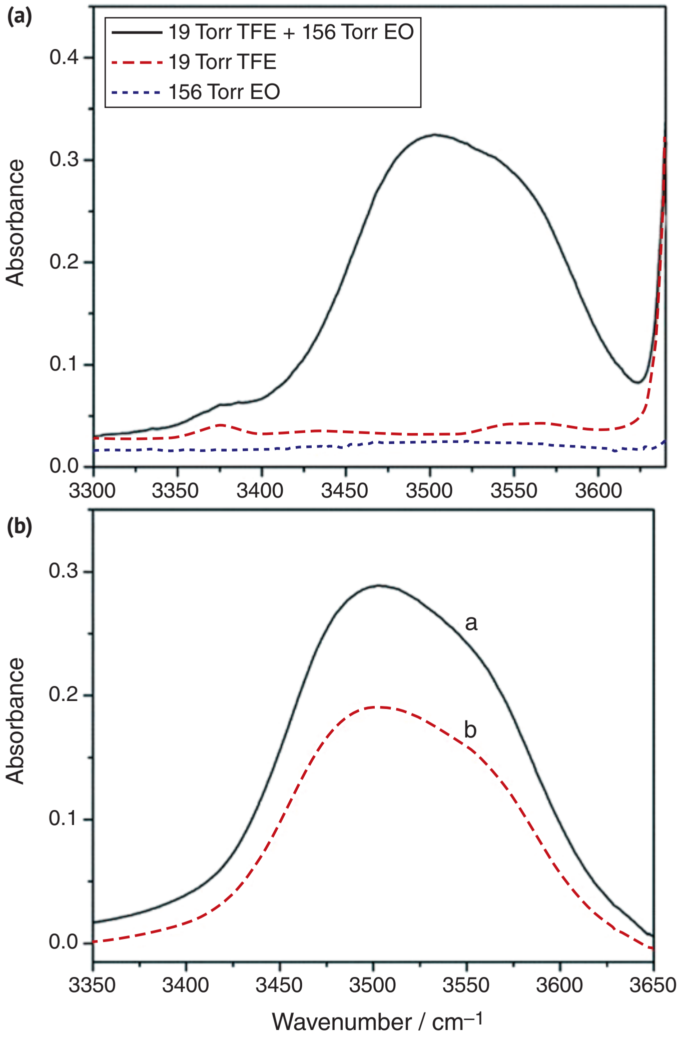


Figure 1.20 (a) Spectra of TFE, EO, and their mixture in the 3300–3640 cm^{-1} region. A 20 cm path length cell was used. (b) Spectra of the TFE–EO complex in the ν_{OH} band region. (a) 19 Torr TFE + 156 Torr EO; (b) 16 Torr TFE + 112 Torr EO. *Source:* Reproduced from Ref. [9], with permission of Royal Society of Chemistry.

1.4.4 Open-Path Fourier Transform Infrared (OP-FTIR) Spectroscopy Measurement Method

Measurements of the long-path absorption of IR radiation by gaseous air pollutants can be conducted directly in the field, near the pollution source or on an open path between an IR source and an IR spectrometer. This approach can then be used to calculate the integrated concentration over the measurement path. The measurement, which can be made without direct sampling, can be conducted in various directions. This justifies the suitability of

OP-FTIR spectroscopy for a great number of analytical tasks that cannot be performed adequately using analytical methods that are based on point sampling.

The two major ways to perform open-path measurements are the active and passive measurement techniques. The active measurement technique is an OP-FTIR technique said to be active when an artificial IR source is used for the measurement of its absorption. In the active OP-FTIR technology, a continuous beam of wideband infrared radiation is introduced into the sample to detect the absorption or the transmission spectral properties of the atmosphere.

Many organizations have been endeavoring to develop monitoring techniques to tackle the pollution caused by airborne particles from industry, vehicles, and agriculture. OP-FTIR spectroscopy has been used extensively in monitoring aerosols, which significantly influence human health and the environment [10]. For example, active OP-FTIR spectroscopy was used in a recent study to quantify the load of water droplets and solutes in the atmosphere [11]. The quantification of water load was found to be feasible for agricultural spraying systems while that of solutes was demonstrated with both nonvolatile and semivolatile solutes. The study demonstrated the potential of the OP-FTIR spectroscopy in the detection of clouds of water-based aerosols and in the quantification of water droplets and solutes at relatively low concentrations. Nevertheless, OP-FTIR spectroscopy has some limitations in quantifying airborne droplets, which are the dependence of the spectral signatures on size distribution and the noise level.

In passive measurement techniques, there is no use of any artificial IR light source as these techniques only measure the energy of IR radiation that is present in the atmosphere within the field-of-view of the instrument. These techniques are used in a variety of applications including the atmospheric monitoring of areal emission sources. A previous study showed that the passive OP-FTIR measurement technique is a flexible long-path approach to characterize large atmospheric volumes via a single rapid measurement, thereby enabling the simultaneous detection of various volatile atmospheric compounds. This study showed that passive OP-FTIR measurements can achieve robust and reliable surveys in arbitrary measurement directions, which offers a comprehensive overview. However, the use of an active open-path spectrometer is required to further improve quantitative analysis in the case of weak sources [12]. In addition, passive OP-FTIR spectroscopy has also been successfully used for the analyses of volcanic gas compositions, the measurement of atmospheric ozone concentration [13], etc.

1.4.5 Application in Interface Characterization

ATR-FTIR spectroscopy can be used to test and study the adsorption of surfactants. Its main advantage is that it can monitor the adsorption of various substances simultaneously *in situ* with a resolution of 0.1–2 s. This is difficult to achieve by other methods, such as neutron reflection, ellipsometry, reflectometry, and surface plasmon resonance.

ATR spectroscopy is a surface sampling technique, which is mainly obtained from the spectral information of the sample surface layer. A linear scanning technique developed recently using ATR-FTIR spectroscopy was used to study biofilms in different downstream positions in linear microfluidic channels [14]. The influence of a bubble during and after its disappearance was quantified by time-dependent measurements of protein and lipid groups, and through correlation between the surface spectra and the location of the bubble, the influence on certain physiochemical properties of the biointerface was demonstrated. Ustunol et al. investigated the adsorption of amino acids onto nanoparticles, aiming to provide insights into protein corona formation [15]. Their results provided pH effects on the mechanisms of more complex aqueous biomolecule–surface interactions and improved the understanding of nanoparticles effects on human exposure.

ATR-FTIR spectroscopy was used to analyze the oxidation and degradation of linear low-density polyethylene/low-density polyethylene (LLDPE/LDPE) packaging film through the combined action of abiotic and biotic treatment. As shown in Figure 1.21, the glucose-stimulated enrichment cultures (LPG) exhibit an increased peak intensity of the carbonyl group, whereas yeast extract enrichment cultures (LPYE) demonstrate an increased peak intensity of the $\mathrm{-C{=}C-}$ group. A dense biofilm layer with extracellular polymeric substances attached to the LLDPE/LDPE surface confirms microbial growth and utilization of PE material [16].

1.4.6 Application in Reaction Kinetics

One advantage of ATR-FTIR spectroscopy is that it can measure *in situ* and track in real time, which is very beneficial for the study of the kinetic process and mechanism of physical or chemical changes of certain substances.

Nur Hossain and coworkers investigated the kinetics of CO_2 reduction by using *in-situ* electrochemical ATR-FTIR spectroscopy [17]. This novel design of the *in-situ* ATR-FTIR system provided a convenient approach for direct monitoring of the formation of reactions intermediates and products when studying the mechanism and kinetics of the electrochemical reduction of CO_2 at an electrode/electrolyte interface with various potentials of the electrode. It was shown that electrochemical reduction of solvated CO_2 occurred first, followed by hydrogen evolution upon consumption of solvated CO_2 molecules. This provides a substantial ground in the system design for CO_2 efficient electrochemical reduction.

Detailed study of the adsorption–desorption kinetics of ions and molecules is important for a deeper understanding of the mobility of nutrients and pollutants in the environment. Using ATR-FTIR spectroscopy, a previous study reported the adsorption–desorption kinetics of phosphate on goethite at pH 4.5, 7.0, and 9.5 [18]. The phosphate–goethite system has emerged as a model system for testing new experimental setups and theories necessary to understand the behavior of pollutants comprising phosphinic or phosphonic moieties such as glyphosate or glufosinate. One difficulty that arises during the analysis of ATR-FTIR spectra in adsorption–desorption kinetics is the calibration of the equipment to allow the absorbance *versus* t curves to be converted into adsorption *versus* t curves. The simultaneous monitoring of the time evolution of the different surface species during adsorption and desorption at different pH highlights one of the benefits of this spectroscopy technique over traditional ones that can only quantify the total adsorption at once. This technique allows to analyze the results in terms of a simple adsorption–desorption model that takes into account the following processes: transport, attachment, detachment, and surface transformation of the adsorbed species. At a given pH, the same rate parameters could predict well the adsorption–desorption kinetics of two formed surface species

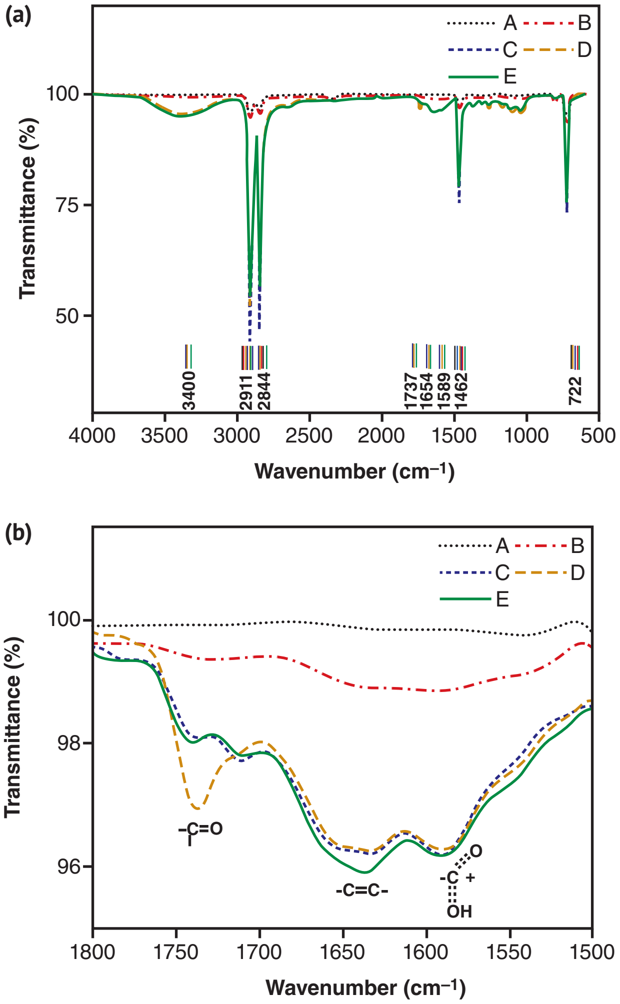


Figure 1.21 FTIR spectra for biotic treatment of naturally weathered 105 days (NW105) LLDPE/LDPE packaging film. (a) 4000 to 500 cm^{-1} and (b) 1800 to 1500 cm^{-1}. Here, A to E in the graph represent Control (virgin LLDPE/LDPE film), Natural weathering for 105 days (NW105), NW105 film exposed to LP culture, NW105 film exposed to LPG culture, and NW105 film exposed to LPYE culture, respectively. The chemical structure of the identified functional group was labeled for carbonyl group (region between 1750 and 1700 cm^{-1}), —C=C— stretching of alkenyl (vinyl) group (region between 1680 and 1620 cm^{-1}), and carboxylates (region between 1610 and 1550 cm^{-1}). *Source:* Reproduced from Jaiswal et al. [16], with permission of Elsevier.

and the corresponding adsorption isotherm, providing more insights into the dynamics of phosphate on the goethite surface. It was shown that phosphate desorption from goethite was faster at low pH than at high pH. Although this is counterintuitive, it has good practical and environmental applications.

1.4.7 Application in Environmental Analysis and Testing

ATR-FTIR spectroscopy can be used to monitor and analyze environmental pollutants. A recent study used ATR-FTIR spectroscopy to examine the differences in the surface properties of pristine and fouled ultrafiltration polyethersulfone (PES) filters with differing pore sizes [19]. The ATR spectra comprising vibration bands that are characteristic of the PES substrate and the deposited film were processed using a quantitative approach, via which the PES vibration band intensities in the presence of fouling were found to depend on both the IR radiation wavenumber and apparent thickness of the deposited layer. Using a combined approach based on batch adsorption and kinetic studies, ATR-FTIR spectroscopy, and surface complexation modeling, Huang et al. examined the effect of phthalic acid on the reductive reactivity of Fe(II) associated with goethite [20]. The ATR-FTIR spectra of the adsorbed phthalic acid in ternary mixtures indicated that outer-sphere species were the major surface species, while the formation of minor inner-sphere complexes was minor. These findings further shed light into the reaction mechanisms of surface-adsorbed Fe(II), which plays a great role in improving technologies for site remediation and risk assessment.

1.4.7.1 Chemical Identification of Microplastics

Since the 1950s, microplastic (MP) particles having diameters below <5 mm have been known to be an essential component of the Earth environment. Nowadays, they have become ubiquitous in nearly all ecosystems, from mountains to poles, as the result of an excessive plastic waste mismanagement and its loss into the environment. Exposure to MPs by inhalation and ingestion is among the current major threats to living beings and potentially global effects on Earth's ecosystems. These concerns have led to the environmental effects of MPs to be studied intensively.

In a recent study, four types of original MPs were aged under simulated solar light irradiation [21]. Several environmentally persistent free radicals were detected on the irradiated polystyrene (PS) and phenol-formaldehyde (PF) resin, which are a type of emerging contaminants. To better understand the formation of free radicals, aged PS-MP and PF-MP were characterized by a combined approach including X-ray photoelectron spectroscopy (XPS), ATR-FTIR, gel permeation chromatography (GPC), and nuclear magnetic resonance (NMR). The results suggested that the photo-oxidation process could induce more peroxide, ketone, and carboxyl groups' generation.

Shruti and coworkers used ATR-FTIR spectroscopy to identify the polymer types of atmospheric MPs in Mexico City as shown in Figure 1.22. This is useful in the detection of probable sources of MPs [22]. Only 10% of randomly chosen MPs ($n = 85$; fiber = 70; fragment = 15) in this study were chemically evaluated. The atmospheric MPs in Mexico City have five types of polymers, including polyethylene (PE), cellophane, polyamide (PA), polyethylene terephthalate (PET), and regenerated cellulose (rayon). To assess MP (<5 mm) ingestion, the gizzards of 41 emperor penguin chicks from Atka Bay colony (Dronning Maud Land, Antarctica) were dissected and analyzed for MP $> 500\ \mu m$ using ATR-FTIR spectroscopy [23]. Results indicated that MP concentrations in the local food web of the Weddell Sea and Dronning Maud Land coastal and marginal sea-ice regions are so low that no detectable biomagnification is occurring via trophic transfer.

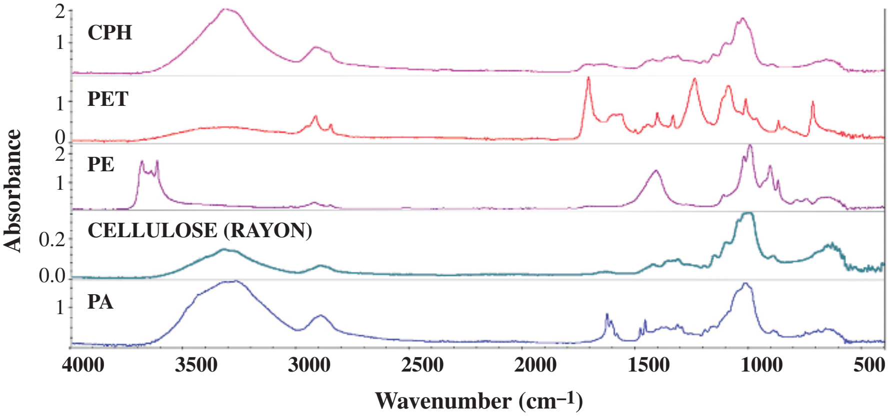


Figure 1.22 ATR-FTIR spectra of five main polymers [cellophane (CPH); polyethylene (PE); polyethylene terephthalate (PET); cellulose (rayon); and polyamide (PA)] identified in atmospheric microplastics collected from Mexico City. *Source:* Reproduced from Shruti et al. [22], with permission of Elsevier.

Plastic pollution constitutes a new form of threat to marine ecosystems. Mangroves located at estuaries worldwide are probably areas with most severe pollution that trap various plastics originated from terrestrial and nearby marine aquaculture. Among plastic debris therein as well as in the plastic garbage, expanded polystyrene has been identified as the most common. Liu et al. randomly selected two pieces of polystyrene plastics after culture with the colonies [24]. ATR-FTIR spectroscopy was used to analyze changes in the structures of polystyrene polymers with the bacterial incubation. The peaks that are characteristic of the polystyrene benzene ring (C═C stretch, 1550–1610 cm^{-1} and 1800–2000 cm^{-1}) were dampened in the bacterial-treated samples to provide evidence of ring cleavage. The decrease in the intensities of the peak characteristic of polystyrene, the appearance of a peak characteristic of a carbonyl group (C═O stretch, 1731 cm^{-1}), and that associated with the C—O stretching (1050–1250 cm^{-1}) constituted further evidence of biodegradation. The peaks at 2700–3000 cm^{-1} being broadened in all FTIR spectra of colonies' samples indicated the presence of C—H and aldehyde groups. The formation of carbonyl groups (C═O) in the oxidation pathway during polystyrene biodegradation was identified from isolates from guts of *Zophobas atratus* or *Tenebrio molitor*.

1.5 Summary

Infrared spectroscopy is mainly used to study the vibration between atoms connected by chemical bonds and the rotation of molecules, which is closely related to molecular structure. Therefore, it is an effective means to characterize molecular structures. Infrared spectroscopy is a typical environmental optical technology, which has special advantages in analyzing the physical change, chemical change, biological change, and cross change of the environment. It can monitor the change of environmental pollution at the molecular level and fine space-time structure, and deepen the understanding of the mechanism of pollution change. Combined with optical remote sensing and other technologies, infrared spectroscopy can be efficient in monitoring the spatial and temporal distribution of pollutants in a wide range or, even in global sense, in a three-dimensional space. Hence, the change law of pollution can be obtained through continuous telemetry, providing a scientific basis for pollution prevention and control.

Infrared spectroscopy detection technology is an important part of environmental optics, adopting optical and spectroscopic methods and combining it with modern scientific and technological means to obtain environmental parameters. It has the advantages of real-time, dynamic, fast, noncontact telemetry, wide monitoring range, low cost, high selectivity, trace and ultra-trace detection, and analysis sensitivity. It has the irreplaceable superiority of other conventional methods and is the development direction and leading technology of international environmental testing today.

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