

# Chapter 1

## The Energy and Geometrical Structure of Molecules

When a molecule absorbs light, it gains energy and reaches a state called an excited state. With visible or ultraviolet (UV) light, the electrons in the molecule are excited, and with infrared (IR) light, the molecular vibration is excited. When a molecule absorbs microwave, its molecular rotation is excited. This chapter seeks to explain that a molecule has discrete energy levels, by looking at three familiar examples; the color of dye molecules, the IR emission from the Earth detected by observation satellites, and microwaves arriving from space. We will also learn that we can calculate the distances among atoms within a molecule based on the scattering patterns of high energy electron beams, and that the precise geometrical structures of molecules can be determined by molecular spectroscopy and gas electron diffraction.

### Summaries

#### *1.1 Absorption and Emission of Light by Dye Molecules*

Here we learn that various organic compounds absorb and emit light with specific wavelengths, and that all molecules have discrete energy levels. We will reach the understanding that we can use quantum theory to estimate the size of a molecule by looking at the wavelengths of the light that it absorbs.

#### *1.2 Infrared Radiation from the Earth*

We will see that a spectrum of the IR emitted from the Earth, as recorded by an observation satellite, gives us information on the vibrational motion of the molecules in the air. We will thus learn that a molecule has discrete energy levels associated with its vibrational motion.

#### *1.3 Microwaves Arriving from Outer Space*

We learn that the spectrum of electric waves arriving from space contains signals reflecting the variety of molecules in outer space, and that a molecule has discrete energy levels associated with its rotational motion.

#### *1.4 The Hierarchical Structure of Molecular Energy Levels*

We learn that exciting the vibrational motion of a molecule requires a photon with 100 to 1000 times the energy as that required for exciting its rotational motion, and that exciting the motion of the electrons within a molecule requires a photon with 10 to 100 times the energy as that required for exciting the vibrational motion of this molecule.

### 1.5 The Diffraction of Electron Beams and Molecular Structures

When molecules are irradiated with an electron beam accelerated to a high speed, interference fringes appear in the scattering pattern of the electron beam. By examining this phenomenon, we will reach an understanding of the wave nature of electrons. Then, we will learn that the geometrical structure of a molecule can be determined from its interference fringes.

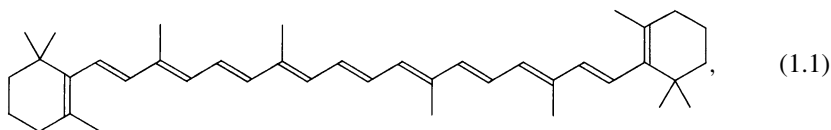
### 1.6 Methods of Molecular Structure Determination

We will learn how we can obtain information about molecular structures from the electronic spectra, vibrational spectra, rotational spectra, and gas-phase electron diffraction, in this final section.

## 1.1 Absorption and Emission of Light by Dye Molecules

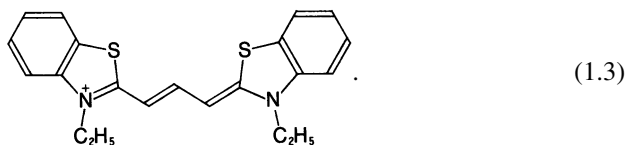
Objects surrounding us in our everyday lives have various colors. The reason we can see these different colors is because, of the light shining on each object, be it sunlight or the light from a lamp, certain wavelengths are efficiently absorbed by it while the others are reflected.

For example, there are a multitude of colors characterizing flowers of different plants. These are all due to a kind of organic compound called dyes. Examples of dyes include such groups of chemical compounds as the carotenoid dye and the flavonoid dye. An example of a carotenoid is the  $\beta$ -carotene, which is responsible for the red color found in carrots. The  $\beta$ -carotene is shown in the structural formula (1.1) in the form of a bond-line formula, where the vertices represent the locations of carbon atoms and all hydrogen atoms are omitted. An example of a flavonoid dye, the flavonol, is given by the structural formula (1.2). This dye gives a yellow color.



Another group of dye is the one called the cyanine dye, which is used as a sensitizing dye for color photographs. For example, this is one type of cyanine dye called the

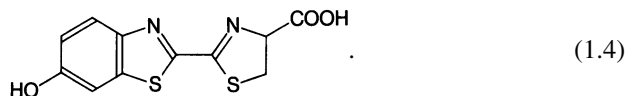
thiacarbocyanine:



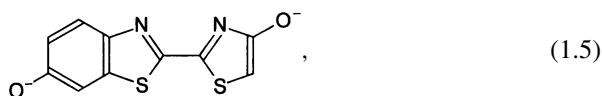
This compound absorbs yellow-green light in methanol solutions. By adding another adjacent pair of a double bond and a single bond to the middle section of the molecule, lengthening the chain-like structure by one unit, we can make the compound absorb red light instead. When we shorten the chain by one unit, on the other hand, the compound starts to absorb blue light. Thus, this material allows us to design dyes with different absorption wavelengths.

These compounds absorb light of each their own specific wavelengths, from which they take the energy to be excited to a state where the electrons in each molecule are excited, that is, an electronically excited state. Most molecules then lose their energy by a radiationless process, in which no light emission occurs.

Aside from these cases where objects reflect light, we can also sense colors when objects themselves emit light, whose respective wavelengths, when they are within the visible region, are perceived by our eyes as different colors. A familiar example of this is the light emission of fireflies. In the body of a firefly is a kind of compound called the luciferin, which is described as



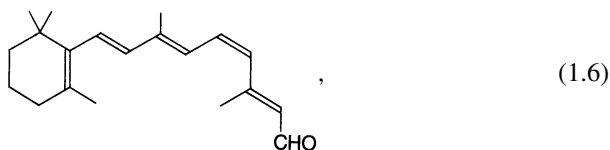
When this compound is oxidized inside the body, the oxyluciferin, described as

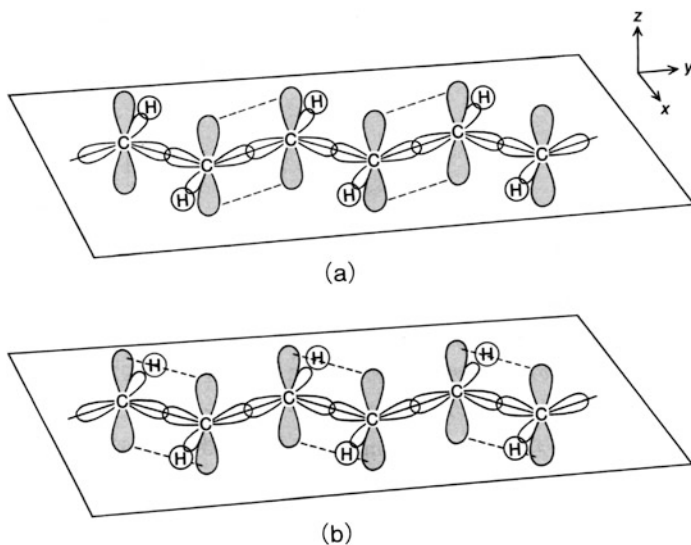


is produced in its electronically excited state. This type of electronically excited state is what is known as a “singlet state,” and emits light, thereby reverting to a singlet electronic ground state. The wavelength of this light lies in the region of yellowish green, which causes our perception of this color in the light of a firefly.

As shown in the above examples, molecules can be excited from a low energy level to a high energy level by photoabsorption, or brought down from a high energy level to a low energy level through the process of photoemission.

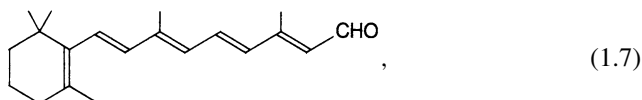
In the retina of our eyes, there is a visual substance called rhodopsin. When light is perceived, one of its constituents called the 11-cis-retinal, represented as



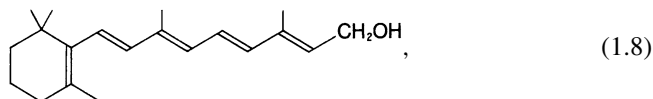


**Fig. 1.1** Schematic illustration of a  $\pi$ -conjugated chain

absorbs the light. This 11-cis-retinal is known to be photoisomerized into the all-trans-retinal,



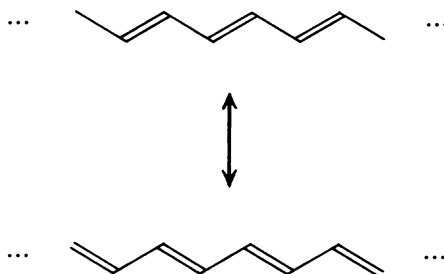
through this photoabsorption process. Incidentally, vitamin A, shown as



is an alcohol form of the retinal, and the  $\beta$ -carotene, as previously depicted, can be regarded as a compound consisting of two vitamin A molecules or of two retinals. In fact, inside our bodies,  $\beta$ -carotene is broken down by our metabolisms to produce vitamin A.

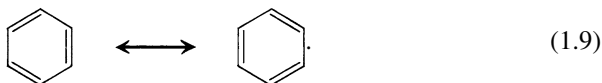
The dye molecules and biological molecules discussed here all have a common structure, namely a chain of double bonds alternating with single bonds, which usually consist of carbon atoms. In the moiety of a carbon chain or a benzene ring, the carbon atoms form a type of electron orbital called the  $sp^2$  hybridized orbital, which aligns the  $\sigma$  bonds onto the  $x$ - $y$  plane. The  $p_z$  orbital, which does not participate in the hybridization, stands perpendicular to the plane, and forms alternating  $\pi$  bonds, as illustrated by the dashed lines in Fig. 1.1a. It seems also likely, however, that these  $\pi$  bonds between carbon atoms may be shifted onto their neighbors, so that the representation can be regarded as Fig. 1.1b. These dual possibilities are schematically expressed as line-bond figures in Fig. 1.2.

**Fig. 1.2** A  $\pi$ -conjugated chain in a bond-line formula



It is a known fact that a  $\pi$  bond accommodates two electrons, which must be localized in the region between those specific carbon atoms. However, when the  $\pi$  bond shifts to the adjacent pair of carbon atoms, as shown in Fig. 1.2, the electrons initially localized in the first  $\pi$  bond transfer to the region of the second pair of atoms and are localized as their  $\pi$  electrons. From the point of view of each  $\pi$  electron, then, what this means is that the chain of  $\pi$  bonds allows it to be delocalized over the whole region of this chain. Such a molecular chain made up of  $\pi$  bonds is called a conjugated system of  $\pi$  bonds, or a  $\pi$ -conjugated chain. The word “conjugate” comes from the two Latin words, “con” (two or together) and “jugate” (join).

We have just looked at an example of a  $\pi$ -conjugated system that comes in the form of a chain, to understand its structure. However, benzene, of course, also forms a  $\pi$ -conjugated system. In this case, we can visualize the  $\pi$ -electrons as delocalizing throughout the benzene ring, as they shift between two Kekulé structural formulae,



The example of the cyanine dye tells us that, by extending the region through which the electrons can move around, we can lengthen the photoabsorption wavelength of the molecule. This also means that, conversely, by measuring the photoabsorption wavelength of a molecule, we can gain information about its length and size, or more generally about its molecular structure.

Let us now overview the relationship between the optical wavelength and energy of light. Using the Planck constant  $h$  ( $= 6.62606876 \times 10^{-34}$  J s) and the optical frequency  $\nu$ , the energy of the light,  $\varepsilon$ , is given by

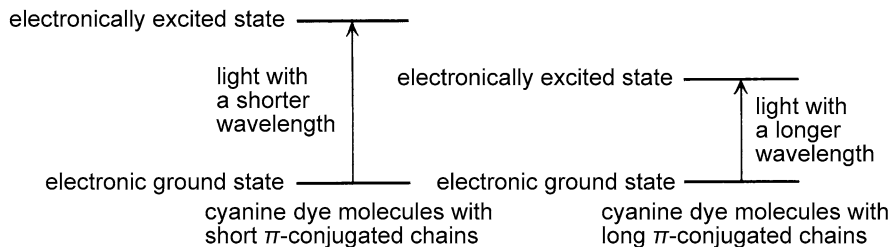
$$\varepsilon = h\nu. \quad (1.10)$$

This can be interpreted as the energy of a photon whose frequency is  $\nu$ . Using the velocity of the light,  $c$  ( $= 2.99792458 \times 10^8$  m s $^{-1}$ ), the optical wavelength  $\lambda$  is related to  $\nu$  by

$$c = \lambda\nu, \quad (1.11)$$

so that we can write

$$\varepsilon = h\nu = hc \cdot \frac{1}{\lambda}. \quad (1.12)$$



**Fig. 1.3** The relationship between the length of a  $\pi$ -conjugated chain and its absorption wavelength

This signifies that the energy of light is proportional to the  $\nu$ , or to  $\frac{1}{\lambda}$  the reciprocal of the wavelength.

Therefore, we can understand from the fact that a cyanine dye with a short  $\pi$ -conjugated chain absorbs light with short wavelengths that the energy  $\frac{hc}{\lambda}$  of the photon that it absorbs is larger than that absorbed by a cyanine dye with a longer  $\pi$ -conjugated chain, and that this causes the shorter-chain molecule to be excited to an electronically excited state of higher energy, as illustrated in Fig. 1.3.

For an accurate understanding of the relationship between the eigenenergy and size of a molecule, we need to describe the electron motion within the  $\pi$ -conjugated chain in terms of quantum theory. Let us for example determine the length of the  $\pi$ -conjugated chain of  $\beta$ -carotene, using the wavelength of the light that it absorbs.

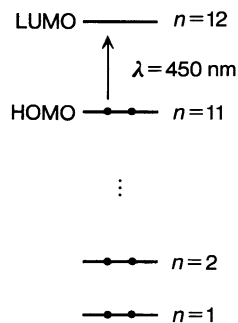
According to quantum theory, the energy levels for a particle of mass  $m$  which moves within a box-type potential of length  $L$  are given by

$$E_n = \frac{h^2}{8mL^2} n^2, \quad (1.13)$$

where  $n$  is an integer whose magnitude is not less than 1. With  $\beta$ -carotene, we can regard the  $\pi$ -conjugated chain as a one-dimensional box into which all electrons are confined. In such a case, as the particle in question is an electron, we can substitute the mass of an electron,  $m_e = 9.10938188 \times 10^{-31}$  kg, for  $m$  in Eq. (1.13). As the  $\pi$ -conjugated chain is composed of 11  $\pi$  bonds, each of which is composed of two electrons, a total of 22  $\pi$  electrons exist in the  $\pi$ -conjugated chain. Designating the levels by  $n = 1, 2, \dots$  and their respective energies by  $E_1, E_2, \dots$ , and mapping them in sequence from the bottom as shown in Fig. 1.4, we can use the knowledge that each level holds two electrons, one with an upward electron spin and the other with a downward spin, to infer that eleven levels, denoted as  $n = 1, 2, \dots, 11$ , are required to contain all of the  $\pi$  electrons. The level denoted by  $n = 11$  here is called the Highest Occupied Molecular Orbital, or HOMO. The numbers designating such discrete energy levels are called quantum numbers.

When light is absorbed, one of the electrons occupying the  $n = 11$  level of  $\beta$ -carotene is excited to the  $n = 12$  level, which is called the Lowest Unoccupied Molecular Orbital, or LUMO. Thus the energy  $h\nu$  of the absorbed photon is equal to the difference between  $E_{11}$  and  $E_{12}$ . The wavelength at which light absorption by

**Fig. 1.4** Excitation from HOMO to LUMO induced by the photoabsorption of  $\beta$ -carotene



$\beta$ -carotene reaches its maximum is known to be  $\lambda = 450$  nm. Using this wavelength, we can obtain  $L$ , the length of the  $\pi$ -conjugated chain for  $\beta$ -carotene.

First, the energy of the absorbed photon can be described as

$$h\nu = \frac{hc}{\lambda}. \quad (1.14)$$

The energy difference between the two levels is derived from Eq. (1.13) as

$$E_{12} - E_{11} = \frac{h^2}{8m_e L^2} (12^2 - 11^2) = \frac{23h^2}{8m_e L^2}. \quad (1.15)$$

As these two energies become equal at  $\lambda = 450$  nm, we can write

$$\frac{23h^2}{8m_e L^2} = \frac{hc}{\lambda}, \quad (1.16)$$

which allows us to derive the length of the  $\pi$ -conjugated chain,  $L$ , as

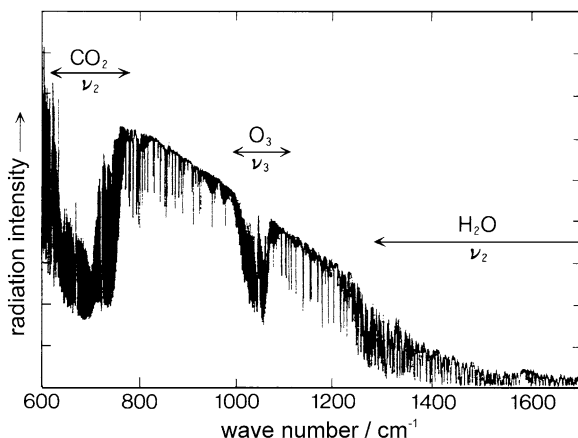
$$L = \sqrt{\frac{23h\lambda}{8m_e c}}. \quad (1.17)$$

By substituting the values for  $h$ ,  $m_e$ , and  $c$ , as well as  $\lambda = 450 \times 10^{-9}$  m, into this equation, we obtain  $L = 1.77 \times 10^{-9}$  m = 17.7 Å. When we use the standard bond lengths for a C–C bond and a C=C bond instead, the length of the  $\pi$ -conjugated chain of  $\beta$ -carotene is estimated to be approximately 25 Å. Comparing these two values, we can see that the estimation of 17.7 Å, obtained from the box-type potential model, is reasonably good.

## 1.2 Infrared Radiation from the Earth

Infrared light is electromagnetic radiation whose wavelength ranges from 1 to 100  $\mu$ m. Of the range of electromagnetic waves that is categorized as light, what

**Fig. 1.5** Infrared radiation spectrum of the Earth observed by the IMG (Interferometric Monitor for Greenhouse gases) mounted on ADEOS (the Advanced Earth Observing Satellite)



we call infrared light, or the infrared beam, belongs to the region of the longest wavelengths. Electromagnetic waves with longer wavelengths than infrared light are categorized as microwave (whose wavelength range is from 1 mm to 1 m), and are commonly classified as electric waves rather than light. Electromagnetic waves in the wavelength range of 100  $\mu\text{m}$  to 1 mm are called far-infrared light, or terahertz (THz) waves.

When an electric heater glows red, it emits electromagnetic radiation covering a wide range of wavelengths from visible light centering around the red color to infrared light. Our very perception of its warmth is caused by the skin tissue on the surface of our bodies absorbing such electromagnetic radiation and thus being excited, their energy then to be converted into heat and cause a rise in temperature on our body surface.

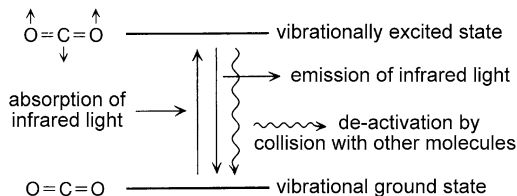
Emission and absorption of infrared light are ubiquitous events. It is also something that happens on the global scale, as the Earth's surface constantly emits infrared light and the air both absorbs it and emits it. In this sense, we can say that the emission and absorption of infrared light is an important factor governing the global environment.

Today, satellites equipped with infrared detectors have been sent into orbit around the Earth to investigate the global atmospheric environment, and they monitor light in the infrared wavelength region emitted from the surface of the Earth. The spectrum shown in Fig. 1.5 gives an example of measurements performed by a satellite sent into orbit at the altitude of 800 km. The term "spectrum" is applied to a diagram which plots the transmittance or emission intensity of light, along the ordinate, as a function of its wavelength or wave number, a reciprocal of the wavelength, along the abscissa. In the case of this figure, the ordinate represents the radiation intensity of the infrared light.

Before we discuss this figure in depth, let us explain the idea of wave numbers, which here are plotted on the abscissa. A wave number is defined as the reciprocal



**Fig. 1.6** Absorption and emission of infrared light by a CO<sub>2</sub> molecule



of a wavelength of light, as

$$\tilde{\nu} = \frac{1}{\lambda}, \quad (1.18)$$

and is usually expressed in the unit of  $\text{cm}^{-1}$ . In other words, a wave number describes how many periods of waves there are in 1 cm of light waves. Thus from Eqs. (1.12) and (1.18), we can write the energy of light as

$$\varepsilon = hc\tilde{\nu}. \quad (1.19)$$

The unit  $\text{cm}^{-1}$  used for wave numbers is called the reciprocal centimeter, or simply the centimeter-minus-one. In the past, the symbol K has been used, pronounced as “kayser,” but this unit is no longer in use today.

When the wavelength of light is  $5 \mu\text{m}$ , for example, the corresponding wave number is derived as

$$\tilde{\nu} = \frac{1}{5 \times 10^{-6} \text{ m}} = \frac{1}{5 \times 10^{-4} \text{ cm}} = 2000 \text{ cm}^{-1}.$$

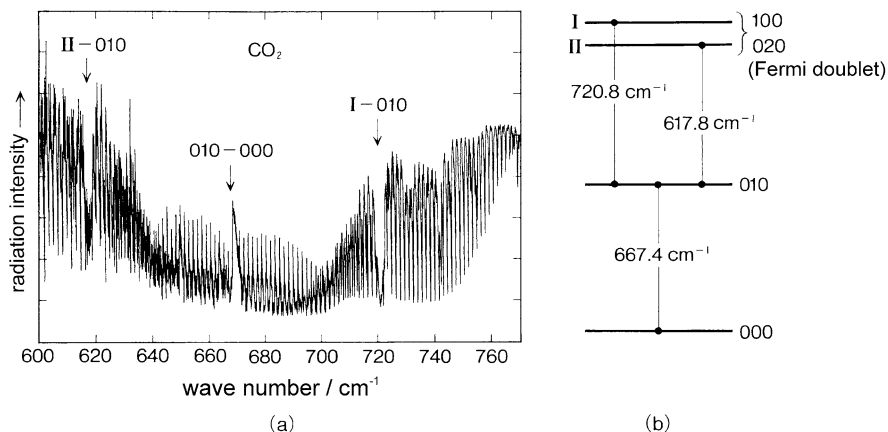
This value can be easily converted into the energy of the light, by multiplying it by  $hc$ . For green light with the wavelength of  $500 \text{ nm}$ , the wave number is calculated as

$$\tilde{\nu} = \frac{1}{500 \times 10^{-9} \text{ m}} = \frac{1}{5 \times 10^{-5} \text{ cm}} = 20000 \text{ cm}^{-1}.$$

Thus we see that a photon of visible light whose wavelength is  $500 \text{ nm} = 0.5 \mu\text{m}$  has ten times the energy of a photon of infrared light with the wavelength of  $5 \mu\text{m}$ .

One thing that we notice in Fig. 1.5 is that the radiation intensity of the observed light gradually decreases as the wave number increases, or the infrared light emitted from the Earth becomes weaker the shorter its wavelength. This pattern of the radiation intensity corresponds to the intensity distribution of black body radiation at  $295 \text{ K}$ , indicating that the surface temperature of the Earth is  $295 \text{ K}$ . Now, what merits our attention is that there are three dips in this spectrum, appearing at around  $700$ ,  $1040$ , and  $1600 \text{ cm}^{-1}$ . These dips in intensity are known to be caused by the carbon dioxide (CO<sub>2</sub>), ozone (O<sub>3</sub>), and water (H<sub>2</sub>O) molecules in the atmosphere, as they each absorb infrared light of specific wavelengths.

In the case of CO<sub>2</sub>, for example, we know that a molecule absorbs infrared light of around  $667 \text{ cm}^{-1}$  and vibrates in what is called a bending vibration mode (the  $\nu_2$



**Fig. 1.7** (a) Magnified view of Fig. 1.5 around the area of the  $\nu_2$ -mode absorption band for  $\text{CO}_2$ ; (b) Relationship between the observed transitions and energy levels; The three digit numbers such as 010 given in the figure signify the vibrational quantum numbers for the symmetric stretching vibration, the bending vibration, and the anti-symmetric stretching vibration, respectively, from left to right

mode), where its skeletal structure bends back and forth. This means that, by absorbing this infrared light,  $\text{CO}_2$  is excited to its vibrationally excited state, as schematically shown in Fig. 1.6. The energy gained by the infrared photoabsorption may be lost from the vibrationally excited molecule through a photo emission process, or it may be converted into kinetic energy when the  $\text{CO}_2$  molecule collides with another molecule in the atmosphere. It is also possible for a vibrationally excited molecule to receive energy through a collision with another molecule and be excited to a state with even higher vibrational energy. Of the infrared light emitted by vibrationally excited  $\text{CO}_2$  molecules, most is absorbed again by other  $\text{CO}_2$  molecules in the atmosphere.

As has been described, molecules in the atmosphere such as  $\text{CO}_2$  continuously repeat the cycle of absorption and emission of infrared light, as well as collide with each other randomly, which induce excitation and de-excitation. As a consequence, radiation equilibrium and thermal equilibrium are both achieved at any given time. Another significance of the atmosphere containing infrared-absorbing molecules is that the infrared light emitted from the surface of the Earth becomes trapped by these molecules and thus less likely to escape into outer space. It follows, therefore, that if the concentration of molecules in the atmosphere that absorb infrared light at a higher efficiency increases, then more infrared light is trapped in the atmosphere, causing the atmospheric temperature to rise. This is what we commonly call the greenhouse effect.

Taking into consideration the above discussion, we cannot regard the observed emission spectrum of infrared light shown in Fig. 1.5 as a simple result of the molecules in the atmosphere absorbing the infrared light emitted by the Earth. This point becomes clearer when we look at Fig. 1.7(a), which gives us a magnified view

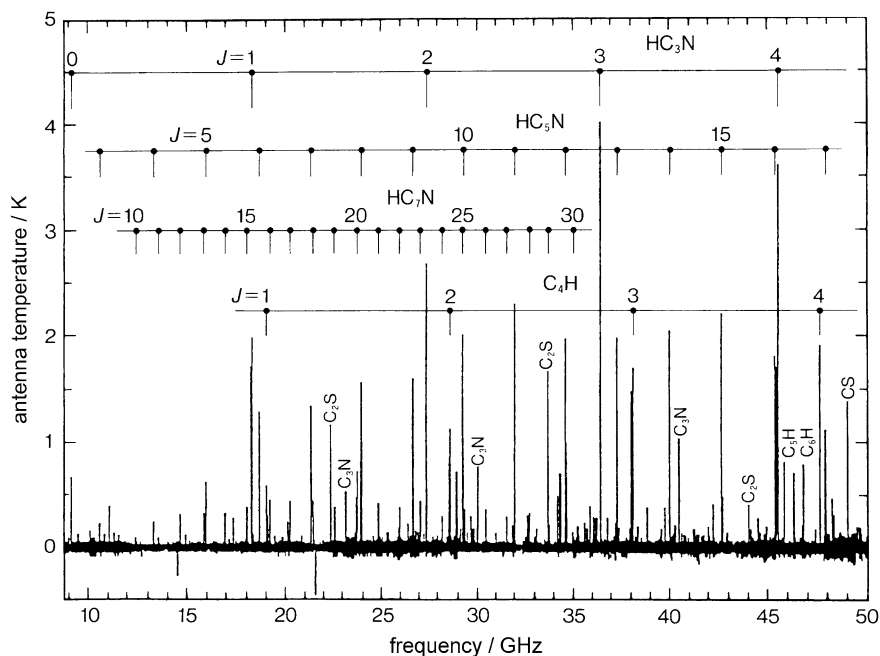
of the spectral region surrounding  $667\text{ cm}^{-1}$  in Fig. 1.5. In the center of Fig. 1.7(a) around  $667\text{ cm}^{-1}$ , we see a thick, intense peak protruding upward. This peak indicates that we have observed infrared light being emitted from  $\text{CO}_2$  molecules as they change their state from the state in which bending vibration is excited to the state in which it is not. The two thick downward peaks seen on both sides of this upward peak, on the other hand, at around  $618\text{ cm}^{-1}$  and  $721\text{ cm}^{-1}$ , correspond to the infrared absorption that occurs when molecules in the bending excited state are further excited to the two levels with higher vibrational energies. As illustrated in Fig. 1.7(b), these two states are formed as a mixture of the state in which the bending vibration is doubly excited and the state in which the two  $\text{C}=\text{O}$  bonds stretch and shrink in phase, through a mechanism called Fermi resonance. These two adjacent levels produced by Fermi resonance are referred to as the Fermi doublet.

Let us see why, then, the peak at  $667\text{ cm}^{-1}$  is observed as an emission peak, and the two peaks on the sides of it as absorption peaks. With  $\text{CO}_2$ , its photoabsorption efficiency for infrared light around  $667\text{ cm}^{-1}$  is extremely large, so that this range of infrared light emitted from the surface of the Earth is almost entirely trapped by the atmosphere as it propagates through the troposphere (0 to 20 km) and the stratosphere (15 to 50 km). This results in the infrared light emitted from  $\text{CO}_2$  molecules around the top of the stratosphere (at altitudes exceeding 30 km) emerging in the observation as an emission peak. On both sides of this, on the other hand, there are areas where the absorption efficiencies of  $\text{CO}_2$  are not so large, which is where the two peaks originating from the Fermi doublet are observed. Thus the spectral profile of the infrared light absorbed by the atmosphere near the surface of the Earth is maintained until it reaches the satellite, and this causes the two peaks to appear as absorption peaks.

In Fig. 1.7(a), we can also observe sharp, spike-like peaks on both sides of the peak at  $667\text{ cm}^{-1}$ , as well as on both sides of the two Fermi-doublet peaks. These peaks can be attributed to the rotational structure of  $\text{CO}_2$  molecules, which appears in the spectrum thanks to the wavelength resolution of this spectral measurement being as high as  $0.05\text{ cm}^{-1}$ .

As we will learn in Sect. 3.6, such a type of spectrum is called a vibration-rotation spectrum. The thick central peak is referred to as the Q-branch ( $\Delta J = 0$ ), the succession of sharp peaks on the side of it with higher wave numbers as the R-branch ( $\Delta J = 1$ ), and the succession of sharp peaks on the other side, where the wave numbers are low, as the P-branch ( $\Delta J = -1$ ). The  $J$  used in the parentheses ( ) here is called a rotational quantum number, which will be further discussed in Chap. 3, Rotating Molecules.

An important lesson that we can draw from the spectrum in Fig. 1.5 is that each molecular species, such as  $\text{CO}_2$ ,  $\text{O}_3$ , or  $\text{H}_2\text{O}$ , has a specific set of vibrationally excited levels with its own designated energies. The dip appearing in this spectrum around  $1040\text{ cm}^{-1}$  is ascribed to a vibrational motion of  $\text{O}_3$  called the anti-symmetric vibrational motion (the  $\nu_3$  mode), and the broad dip around  $1600\text{ cm}^{-1}$  to the bending vibration (the  $\nu_2$  mode) of  $\text{H}_2\text{O}$ . These facts show that the energy of molecular vibration takes only discrete values, and that these values are intrinsic to the respective molecular species. In Chap. 2, Vibrating Molecules, we will discover



**Fig. 1.8** The spectrum of the Taurus Dark Cloud observed at the Nobeyama Astronomical Observatory. The vertical axis represents the emission intensity, as converted into temperature.  $J$  stands for the rotational quantum number. For instance,  $J = 3$  signifies the microwave radiation that accompanies a transition from the level of  $J = 4$  to the level of  $J = 3$

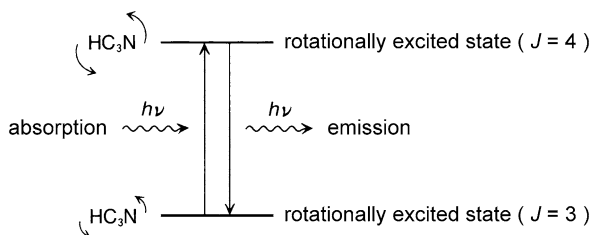
why the energy of molecular vibration takes discrete values by looking at the issue from the perspective of quantum theory.

### 1.3 Microwaves Arriving from Outer Space

In the field of radio astronomy, scientists study celestial bodies and interstellar substances by detecting electric waves in the region spanning microwaves and radio waves, or those with wavelengths from 1 mm to 30 m, which reach the Earth from outer space. Figure 1.8 shows the overall spectrum obtained by pointing a radio telescope toward the dark nebula in the constellation Taurus called TMC-1 (the Taurus Molecular Cloud 1). As annotated in the figure, the sharp peaks record microwaves radiated from mainly linear molecules, such as  $\text{HC}_3\text{N}$  ( $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ ),  $\text{HC}_5\text{N}$  ( $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ ), and  $\text{HC}_7\text{N}$  ( $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ ). Observations of such spectra have made it clear that many kinds of molecular species exist in interstellar spaces.

An important thing to note here is that each molecular species radiates microwaves of specific frequencies. We should also pay attention to the fact that peaks

**Fig. 1.9** Absorption and emission of microwave by  $\text{HC}_3\text{N}$



belonging to the same molecular species are spaced at regular intervals in terms of frequency. For instance, the strongest peak observed in Fig. 1.8 is the transition of  $\text{HC}_3\text{N}$ , assigned as  $J = 3$ , and its frequency is roughly

$$\nu = 36.4 \text{ GHz} = 36.4 \times 10^9 \text{ s}^{-1},$$

its wavelength

$$\lambda = \frac{c}{\nu} = 0.824 \text{ cm}.$$

Expressed in terms of wave numbers, this becomes

$$\tilde{\nu} = \frac{1}{\lambda} = 1.21 \text{ cm}^{-1}.$$

The energy of this microwave is about 1000 times smaller than the vibrational level energies discussed in Sect. 1.2.

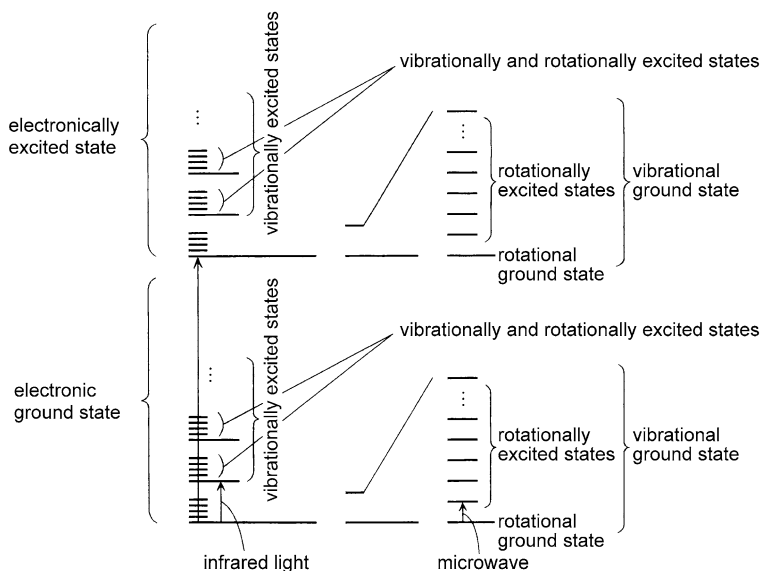
In fact, what causes this microwave radiation is the change of the state of the molecules from their rotationally excited state ( $J = 4$ ) to a rotationally less excited state ( $J = 3$ ), as illustrated in Fig. 1.9 (where  $J$  is the rotational quantum number). This shows us that the energy produced by the rotational motion of a molecule always takes a discrete value, as was the case with the vibrational motion.

We can also see from Fig. 1.8 that the intervals between adjacent peaks are narrower the longer the molecules, which hints to us that observing the energy gaps between rotational levels can lead to the determination of molecular structures. These intervals between adjacent peaks are in fact nearly equal to twice the values of what is called the rotational constants of the molecules. A rotational constant, in turn, is known to be inversely proportional to the moment of inertia of each molecule.

Therefore, by observing a rotational spectrum, we can calculate the moment of inertia of the molecule, and determine the structure of the molecule. In Chap. 3, Rotating Molecules, we examine this rotational motion of molecules from the standpoint of quantum theory, and discuss discrete energy levels and molecular structures.

## 1.4 The Hierarchical Structure of Molecular Energy Levels

As we have seen, we can irradiate molecules with light of specific wavelengths to excite them to a higher energy level. Such levels are classified into three types:



**Fig. 1.10** The hierarchical structure of the energy levels of molecules

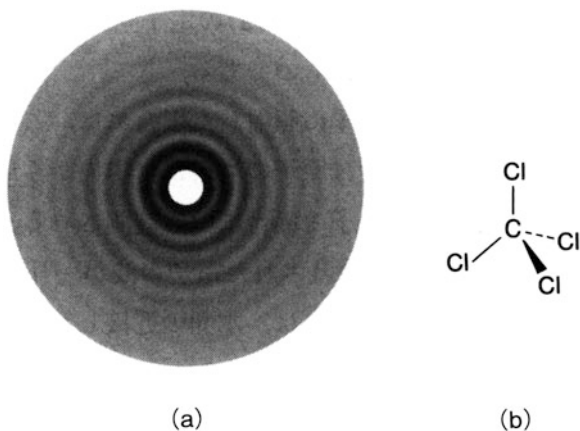
the level of the electronically excited state, that of the vibrationally excited state, and that of the rotationally excited state.

To excite a molecule to its electronically excited state, what is used is light in the visible or ultraviolet region, and the energy of its photons is  $5 \times 10^4$  to  $1 \times 10^5 \text{ cm}^{-1}$  in most cases. To excite a molecule to its vibrationally excited state, light in the infrared region is used, and the energy of its photons is usually  $4 \times 10^3$  to  $1 \times 10^2 \text{ cm}^{-1}$ . For the rotationally excited state, microwave is used, and the energy of its photon tends to be 2 to  $0.5 \text{ cm}^{-1}$ . This relationship found in the energy levels of molecules is illustrated in Fig. 1.10. What this shows is the hierarchical nature of energy levels, which is a characteristic feature of molecules, as they have three different types of excited states, electronic, vibrational, and rotational.

We will examine molecular vibration and molecular rotation in depth, from the point of quantum theory, in Chaps. 2 and 3, respectively. As will be discussed in Chap. 3, molecular vibration and rotation can occur simultaneously. This molecular state corresponds to the state in which both vibration and rotation are excited, as shown in Fig. 1.10. As we will learn in Chap. 3, we can determine the geometrical structure of a molecule from the energy of its rotational level. We can also determine molecular structures from rotational structures observed in vibrational spectra.

Another powerful method for determining the structures of molecules is the electron diffraction method. Chapter 4, Scattering Electrons, is concerned with grasping the principles of this method through a discussion based on the quantum theory of electron scattering. Let us briefly take a look at this electron diffraction method in the next section.

**Fig. 1.11** An electron diffraction photograph (a) and the molecular structure of carbon tetrachloride ( $\text{CCl}_4$ ) (b)



## 1.5 The Diffraction of Electron Beams and Molecular Structures

An experiment performed by Davidsson, Germer, Kikuchi, and Thompson in the late 1920s revealed that a diffraction image can be observed when we irradiate an accelerated electron beam onto a solid target such as metallic foil. This is a well-known case of the electron being shown to have the property of a wave. The wavelength of this electron is expressed as

$$\lambda = \frac{h}{m_e v}, \quad (1.20)$$

where  $m_e$  stands for the mass of the electron and  $v$  for the speed of the electron. When we view particles as waves, such as in this case, these waves are called matter waves or de Broglie waves. With electron beams, increasing the accelerating voltage causes the speed  $v$  to increase and the wavelength  $\lambda$  to decrease.

Due to such wave-like properties of electrons, we can observe highly interesting phenomena when we irradiate molecules in the gas phase with an electron beam. In an electron diffraction experiment, we accelerate electrons to around 10 to 60 keV and irradiate the gas target with them to record the scattered electrons on a photographic plate. Figure 1.11(a) shows one such electron diffraction photograph of carbon tetrachloride ( $\text{CCl}_4$ ).

A point worth noting in this photograph is that we can observe in it a clear repetition of concentric rings formed by the dark and light shades of gray, which spread from the central area to the circumference. These characteristic patterns are called halos, taking its name from a term that originally refers to the ring of light often observed around the Sun or the Moon. When we observe such patterns of electron scattering, the density of electrons around the center becomes very high, with the number of scattered electrons rapidly decreasing as the distance from the center increases. Therefore, in order to obtain clearer halos we use a method called the rotating sector method, which reduces the number of electrons to reach the photo-

graphic plate the closer they are to the center. The electron diffraction photograph shown in Fig. 1.11(a) is taken using such a rotating sector.

When we irradiate an electron beam onto a group of atoms, on the other hand, we do not observe any halos. What we see in the case of atoms is a monotonic decline in the intensity of the scattered electron beam from the center outward. Halos are observed only with molecules because they are the result of the two scattered electron waves caused by each pair of atoms within each molecule interfering with each other. This situation can be compared to the way in which two sets of ripples interfere with one another on a water surface when we simultaneously throw in two stones at adjacent spots. Obviously, molecules in the gas phase point in various directions in space, with no spatially fixed alignment. However, as we will discuss in detail in Chap. 4, Scattering Electrons, when all of the interference patterns of the electrons scattered by the randomly oriented molecules add up together, what emerges is a pattern of halos such as the one shown in Fig. 1.11(a).

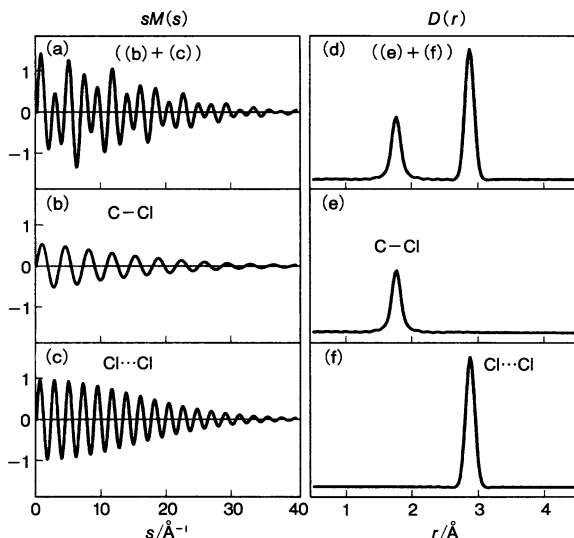
Let us then first consider a case where electrons are scattered by a triatomic molecule ABC, which can be, for example, a  $\text{SO}_2$  or  $\text{OCS}$  molecule. The electrons form an interference pattern as they are scattered by atoms A and B, while at the same time they form another interference pattern as they are scattered by atoms B and C, and yet another as they are scattered by atoms A and C, even though this last pair of atoms are not directly linked by a chemical bond. Halos created by triatomic molecules are thus observed as a sum of these three types of interference patterns. In the case of carbon tetrachloride, too, we can look at the creation of the halos in a similar vein. A carbon tetrachloride molecule is known to have a regular tetrahedral structure as schematized in Fig. 1.11(b). There are four sets of atom pairs between the C atom and the Cl atoms to be found in this molecule, and these are all equivalent. Thus when electrons reach a carbon tetrachloride molecule as a wave, they are scattered by these four atom pairs to produce the same interference pattern. At the same time, there are six combinations of two Cl atoms to be found, none of them chemically bound, and all of these can be considered to give the same interference pattern, too. Therefore, the halos to be observed are created as a sum of these two types of interference patterns.

To explain this in more detail, we will now turn to some simulations of the molecular scattering curve which take the scattering degree of the electron as the vertical axis, and a variable  $s$ , called the scattering parameter, as the horizontal axis. We can assume that the scattering parameter is proportional to the distance of the point on the photographic plate where electrons hit as measured from the center of the circle shown in Fig. 1.11(a) in the direction of the radius. Now, the effect of the interference caused by the four sets of combinations between a C atom and a Cl atom can be represented by the molecular scattering curve shown in Fig. 1.12(b). This expresses a sine function with a specific period, whose amplitude decreases as  $s$  increases. When we Fourier transform this function, we can see that it consists of one component, as shown in Fig. 1.12(e).

This type of figure is called a radial distribution curve, and its horizontal axis represents the internuclear distance between the two atoms within the molecule. Thus, we can calculate the internuclear distance between the C atom and each of



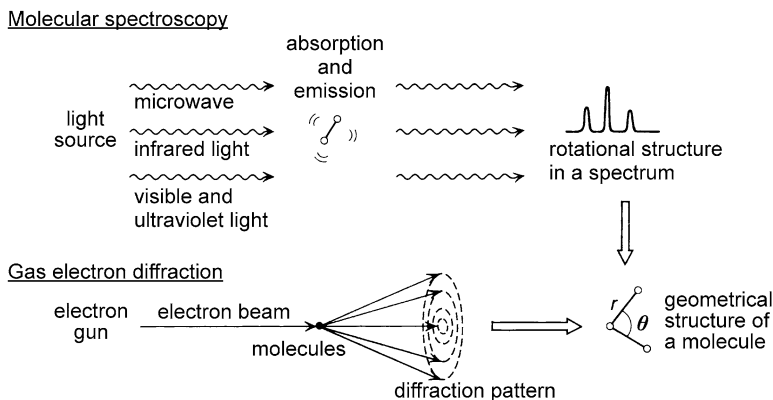
**Fig. 1.12** A simulated molecular scattering curve ( $sM(s)$ ) (a) and radial distribution curve ( $D(r)$ ) (d) for  $\text{CCl}_4$ . The contribution of each type of atom pair in  $sM(s)$  is given in (b) and (c) and that in  $D(r)$  is given in (e) and (f)



the Cl atoms from the molecular scattering curve. Turning next to the interference effect caused by the six non-bonded atom pairs between two Cl atoms, we obtain a molecular scattering curve as shown in Fig. 1.12(c). When we Fourier transform this function, we can obtain the radial distribution curve shown in Fig. 1.12(f). When we compare Figs. 1.12(b) and 1.12(c), we see that the interval between adjacent dark shades in halos is smaller for the atom pair with the longer internuclear distance.

What we have discussed so far are the results of simulation. In reality, the interference pattern created by the four pairs of the C and Cl atoms and the one created by the six pairs between Cl atoms are observed at once, superimposed upon each other. Therefore the overall interference pattern observed as a molecular scattering curve will be as shown in Fig. 1.12(a), which is the sum of Figs. 1.12(b) and 1.12(c). We can in fact explain the dark and light shades constituting the halos in Fig. 1.11(a) by the interference pattern of Fig. 1.12(a). When we Fourier transform this molecular scattering curve, we obtain a radial distribution curve that has two peaks, as shown in Fig. 1.12(d). Needless to say, the positions of these two peaks reflect the internuclear distances of the C-Cl bond and of the non-bonded atom pair  $\text{Cl}\cdots\text{Cl}$ . By synthesizing the interference patterns using these internuclear distances as variables so that they reproduce the observed interference patterns in the actual photograph, we obtain  $r(\text{Cl}-\text{Cl}) = 1.767 \text{ \AA}$  and  $r(\text{Cl}\cdots\text{Cl}) = 2.888 \text{ \AA}$ .

So far we have used the word “internuclear distance” to express the distance between two atoms, but sometimes this distance is called the “interatomic distance.” In many cases these two terms are used interchangeably, but when we discuss molecular geometry in this textbook, we are not taking into account the positions of the electron in each atom, so it would be more appropriate to use the term “internuclear distance.” It is for this reason that we adopt this terminology throughout this book, whether we are talking about molecular structures determined by molecular spectroscopy or those calculated by the electron diffraction method.



**Fig. 1.13** Methods of determination of the geometrical structure of molecules using molecular spectroscopy and gas electron diffraction

As we have briefly shown in this section, it is possible to determine the geometrical structure of molecules by using the phenomenon where electron beams are scattered by molecules. In Chap. 4, Scattering Electrons, we will examine the scattering process from the point of view of quantum mechanics, to better understand the meaning of the molecular structures determined from electron diffraction images that are obtained through scattering. One issue that will be discussed, for instance, is the fact that the peaks shown in Fig. 1.12(d) have a width, which points to a certain distribution range that must be present in internuclear distances. Does this then mean that the structure of molecules is fluctuating? Such questions will be answered when we learn the quantum mechanics of the vibrational motion of molecules in Chap. 2, Vibrating Molecules.

Finally, when we fully recognize the different meanings of the molecular structures determined by the electron diffraction method and those determined by the method discussed in Chap. 3, Rotating Molecules, we will have reached a fundamental understanding concerning the nature of the motion and geometrical structure of molecules as they exist in the microscopic universe governed by the law of quantum mechanics.

## 1.6 Methods of Molecular Structure Determination

The way in which the methods discussed so far contribute to the determination of molecular structures is shown schematically in Fig. 1.13, and as a flow chart in Fig. 1.14. In molecular spectroscopy, we obtain the energies of discrete levels of a molecule by taking advantage of the absorption and emission of light observed in molecules. To determine the geometrical structure of a molecule, we mainly look for the energy level associated with its rotational motion, so that we can calculate the moment of inertia for the molecule. Once we have the moment of inertia, we

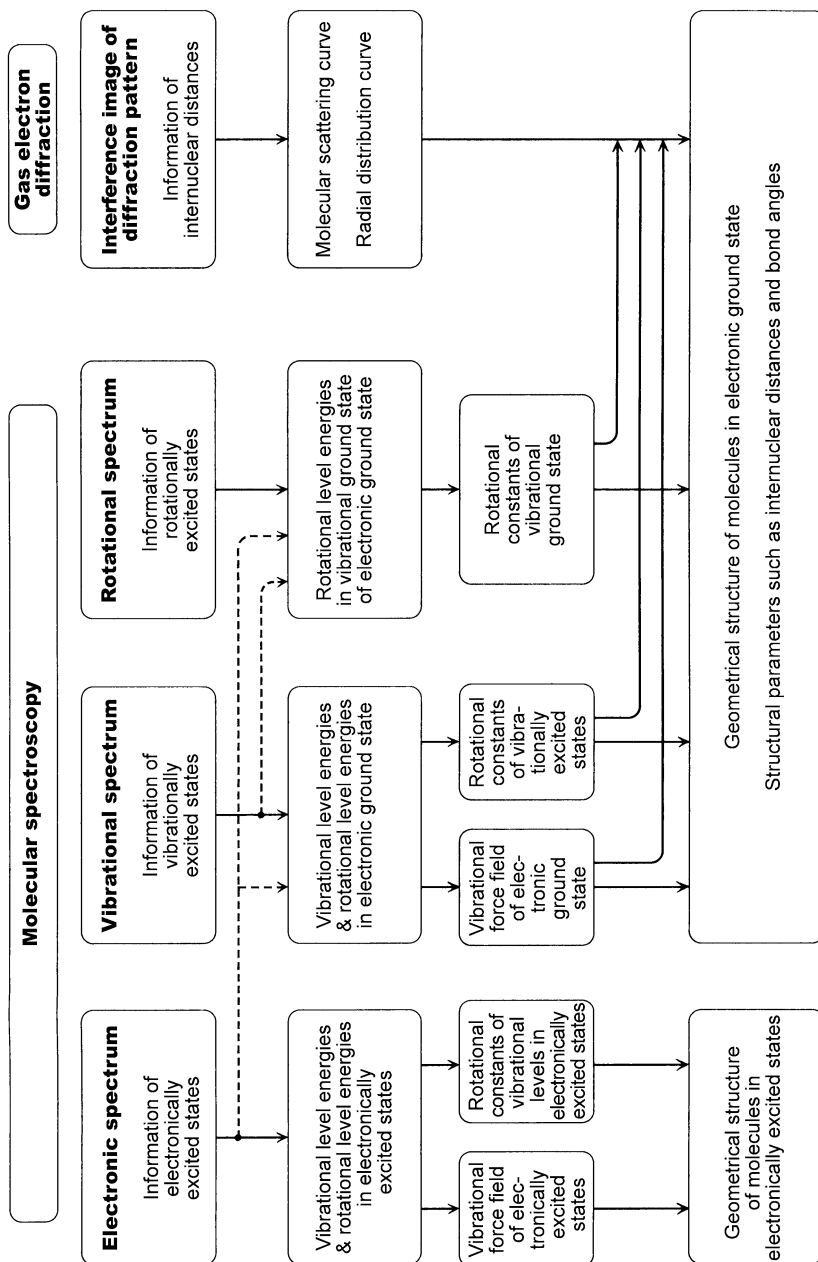


Fig. 1.14 Flow chart for the determination of geometrical structures of molecules

can determine the distances between the atoms that compose the molecule, or the internuclear distances. We can also determine the molecular structure of a molecule at its electronic ground state or its electronically excited state by observing the rotational structure of its absorption and emission spectra of the electronic transition in the visible and ultraviolet regions. An alternative to these spectroscopic methods is the electron diffraction method discussed in Sect. 1.5. When molecules are in the gas phase, their geometrical structures have been determined through rotational structures observed in the molecular spectroscopic method as well as through electron diffraction images obtained by the electron diffraction method.

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