Chapter 1

Introduction

Intramolecular motion includes translation and rotation between molecules，relative vibration between atoms，electronic transitions，and nuclear spin transitions. Every sport has a certain energy level. Except for translation，the energy levels of other motions are all quantized，that is，a certain motion has a ground state，one or more excited states，and transitions from ground to excited state，and the energy absorbed is the difference between the two energy levels instead of the random ones.

Translational motion does not produce a spectrum，and the translational kinetic energy is the smallest among various molecular motion energies. The energy when a molecule rotates around its center of gravity is called rotational energy，and the energy that an atom has when it leaves its equilibrium position to vibrate is called vibrational energy. The energy required for the spin transition of the nucleus is only greater than the translational kinetic one，but less than that of other molecules. Therefore，we can divide the energy of molecules into several parts，namely，the vibration energy (E_v)，the rotational energy (E_r) and the electronic energy (E_e)，and the energy required for the electronic transition is the largest among the above-mentioned transitions：

$$\Delta E_e \gg \Delta E_v \gg \Delta E_r. \tag{1-1}$$

The schematic diagram of molecular energy levels is shown in Fig. 1-1，in which E_r represents rotational energy. If arranged according to wavelength or wave number，the signal of the light intensity change absorbed by a certain

movement inside the molecule or the scattered light signal generated after the absorption of light is recorded to obtain various spectra, so the light of different energy can act on the sample molecule. The corresponding molecular motion is caused to obtain different spectra. The spectra obtained by our analysis can be made judgments on the structure of the molecule, the content of the components and the chemical environment of the group.
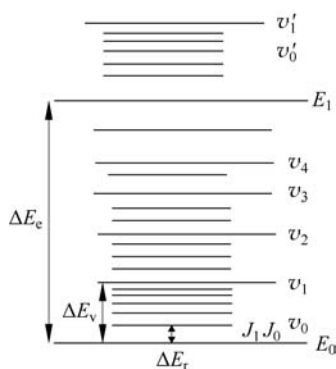

Fig. 1-1   Schematic diagram of molecular energy levels

The plasmon is a kind of quantized charge density wave, which is the elementary excitation of the collective oscillation of electrons in a solid with respect to the background of real positive charges of ions. In the early 1950s, David Pines first proposed plasma oscillation[1-2]. In 1957, Ritchie calculated and found that when a fast electron passed through a metal film, a new collective electron oscillation mode was excited[3]. In 1960, Stern and Ferrell defined this mode as surface plasmons (SPs)[4]. In 1977, surface-enhanced Raman scattering (SERS) phenomenon based on the enhancement effect of SPs in the electromagnetic field[5] had been resolved by Van Duyne. Subsequently, other phenomena such as surface-enhanced fluorescence were gradually discovered. At present, the research based on SPs has penetrated into many disciplines and has become an interdisciplinary subject integrating physics, chemistry, materials, etc., called SP photonics. Enhanced spectroscopy technology based on SP photonics is one of the hottest fields in the world. It is

not only widely used in ultra-sensitive spectral detection，but also in biochemical sensing，information dissemination and processing，and new energy sources. All the above frontier issues have great application potential.

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Chapter 2

Molecular Spectroscopy

Molecular spectroscopy is a method used to study molecular motion and its interaction with light，or it can be said to use light and electromagnetic waves to study molecular motion. It can be seen that the connotation of molecular spectroscopy includes two parts，one is the nature of light and the movement of molecules，and the other is the interaction between them. We can divide the motions of molecules into electronic motion，molecular vibration and rotational motion. Therefore，molecular spectroscopy mainly contains three spectroscopy kinds of：concerning electronic，vibration and rotation，respectively，according to different research objects.

2.1　Ultraviolet-visible（UV-vis）Absorption Spectroscopy

2.1.1　Principles and characteristics of UV-vis absorption spectroscopy

The absorption spectroscopy produced by molecules absorbing electromagnetic waves in the ultraviolet-visible region from 200 nm to 800 nm is called UV-vis absorption spectroscopy. The UV-vis absorption spectroscopy is related to electronic transitions. Taking a molecule composed of two different atoms，A and B，for example，the state of electrons in the molecule can be described by molecular orbital theory. The molecular orbital also is regarded as a linear combination of the corresponding atomic orbitals. For the

σ bond of $A - B$, the linear combination of the atomic orbital of A and the atomic orbital of B can form two different molecular orbitals. A molecular orbital with low energy is a bonded molecular orbital, which is formed by the addition of the atomic orbitals of A and B, and is called the σ molecular orbital. The other molecular orbital with high energy and empty anti-bond molecular orbital is formed by subtracting the atomic orbitals of A and B, and is called σ^* molecular orbital. The two electrons that make up the bond are in the low-energy σ molecular orbital, which is the ground state of the $A - B$ molecule, and its corresponding energy is E_1. The molecule may also be in a high-energy state, where one electron is in the σ molecular orbital, and the other electron is in the σ^* molecular orbital. The molecule is usually in the ground state, but when the molecule is irradiated by ultraviolet light, and the energy of the ultraviolet (UV) light ($E = h\nu$) is the difference in energy between ground state and high energy state ($E_2 - E_1$), energy transfer may occur, so that the electron transitions from E_1 to E_2 (Fig. 2-1).
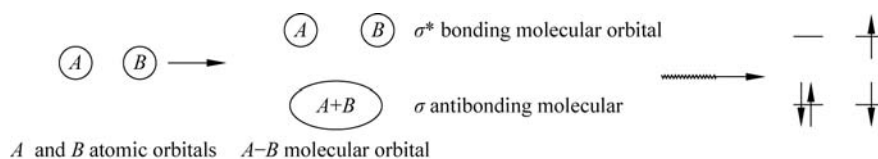

Fig. 2-1　Schematic diagram of valence electron transition

In the UV-vis spectroscopy, the intensity of peak obeys Lambert Beer's law[1]

$$A = -\lg T = \lg \frac{I_0}{I} = \varepsilon c l , \qquad (2\text{-}1)$$

where A is the absorbance; I and I_0 the transmitted and the incident light intensities, respectively; ε the molar absorption coefficient (L/(mol · cm)); l the optical path length, and c the substance concentration (mol/L). UV-vis absorption spectroscopy is one of the earliest physical approaches applied to the identification of organic structures, and it is also a fast and simple analytical method commonly used in chemical analysis.

2.1.2 Detection and application of UV-vis absorption spectroscopy

Nanoparticles（NPs）usually refer to particles with a size for $1\sim100$ nm. The physical and chemical properties of NPs are very different from bulk materials. NPs have many applications in physics，one of them is plasma oscillation connected to their shape and size. Silver NPs（AgNP）have unique electrical，optical and thermal properties，and are widely used in catalysts and photonics，and play important roles in water purification，medicine，and flexible electronics[2-5]. Therefore，how to synthesize AgNPs and study their properties is significant. Alim-Al-Razy used Turkevich chemical method to synthesize AgNPs of different sizes. First，silver nitrate（$AgNO_3$）and trihydrate citrate（$C_6H_5O_7Na_{3.2}H_2O$）are synthesized into colloidal solutions of silver NPs，and then dark glass bottles wrapped in aluminum foil are used to store these solutions in order to isolate the sun light and air. The colors of the solution produced by the different citrate concentrations are different，that is to say，the sizes of the AgNP are altered. By changing the amounts of the two raw materials，NPs of different sizes can be obtained.

After the colloidal solutions are synthesized，they are analyzed by UV-vis spectroscopy. Using the controlled variable method：at first，keep the concentration of $C_6H_5O_7Na_{3.2}H_2O$ unchanged，adjust the quality of $AgNO_3$，observe and compare the UV-vis diagram（Fig.2-2），and then，keep the amount of $AgNO_3$ unchanged，whereas adapt the concentration of $C_6H_5O_7Na_{3.2}H_2O$，finally，observe the spectrum again（Fig.2-3）. From the figure，we can get more information about the particle size. As shown in Fig.2-2 and Table 2-1，we can find that with the increase of the amount of $AgNO_3$ in the range of $1\sim$ 3 mm，the larger the size of the NP obtained，when increasing to 5 mm at this time，the smaller the particle size than that at 1 mm.

Table 2-1 Peak value and estimated particle size when trisodium citrate was kept constant

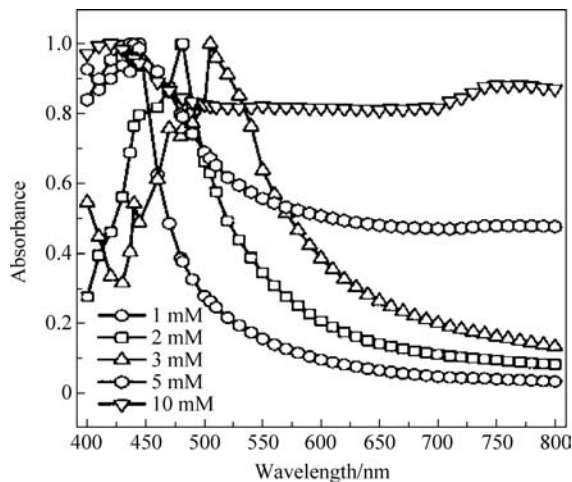| 3% trisodium citrate	1 mM	2 mM	3 mM	5 mM	10 mM
Peak value/nm	444.5	481.5	505	436.5	420
Particle size/nm[10]	70	95	110	65	50

Fig. 2-2   UV-vis spectroscopy of AgNP with it's different molarity,
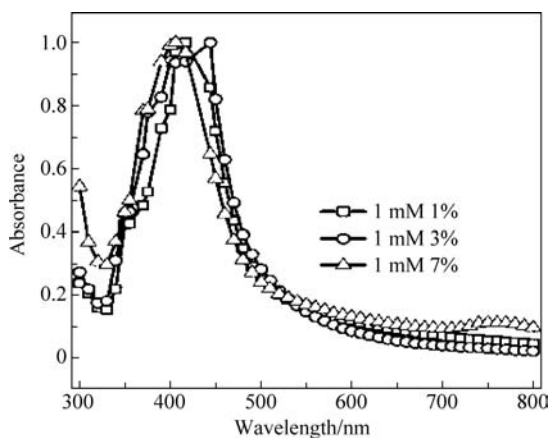when concentration of Trisodium citrate was 3%

Fig. 2-3   UV-vis spectroscopy of AgNP with different concentration of AgNP,
when molarity of $AgNO_3$ was 1 mM

By observing Fig. 2-3 and Table 2-2, we find that when the concentration of $AgNO_3$ increases to 3%, the particle size no longer increases with its increase again, but starts to decrease instead. And compared with the above figure, when the concentration of $AgNO_3$ is 1 mM, the size of the synthesized particles is smaller. By comparison, when the concentration of $C_6H_5O_7Na_{3.2}H_2O$ is 3%, the

size of the NPs obtained is larger，which means that the aggregation is stronger.

Table 2-2   Peak value and estimated particle size when silver nitrate was kept constant

1 mM AgNO₃	1%	3%	7%
Peak value/nm	417	444	406
Particle size/nm[10]	48	70	30

It can be seen that UV-vis absorption spectroscopy can be applied in the field of nanoparticle synthesis，and can successfully reveal how the size of NPs changes with changes in raw materials[6].

As nanotechnology continues to mature，the exploration of the optical properties of carbon nanotubes has become more and more extensive. A series of comprehensive studies on single-walled carbon nanotubes（SWNT）plasma absorption have been carried out using UV-vis absorption spectroscopy. The authors using complementary experiments and theoretical methods have linked the relationship between the energy absorbed by the plasma and the diameter of the nanotubes，so it is feasible to use UV-vis absorption spectroscopy to observe the diameter of carbon nanotubes. We are used an UV-vis spectrophotometer to record the absorption spectroscopy in the range of 190～550 nm，as shown in Fig. 2-4. The figure highlights the great difference in plasmon
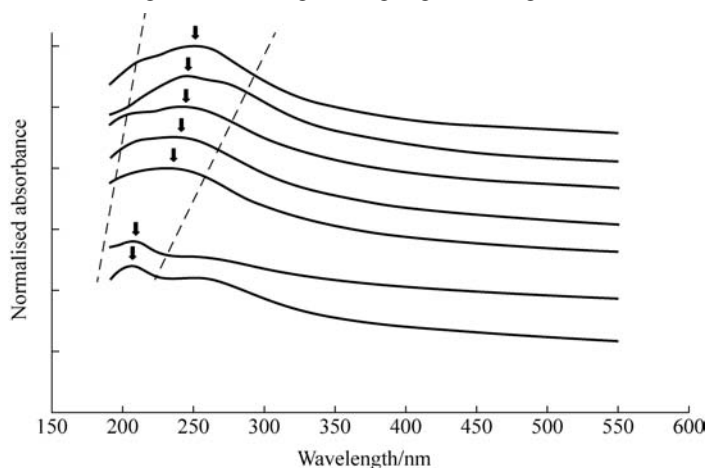

Fig.2-4   UV-vis absorbance spectra of single-walled carbon nanotube suspensions in water

absorption in different carbon nanotubes. This study can establish a certain relationship between the diameter of the nanotube and the plasmon energy. We can estimate the average diameter of SWNT by ultraviolet-visible absorption spectroscopy[7].

2.1.3　Introduction to one-photon absorption

One-photon absorption（OPA）can be rewritten as 1-photon absorption（1PA），or single-photon absorption. It means a process of transitioning from a lower energy state such as the ground to a higher one by an atom absorbing a photon，which is a linear optical phenomenon. In other words，if the molecules are irradiated with light，and the intensity of the absorbed light is proportional to the first power of the incident light intensity，it is OPA phenomenon.

When the transition from the ground state to the excited occurs，combining time-dependent density functional theory[8-11]，and quantum mechanics，we can get the strength of the transition oscillator formula

$$f_{kg} = \frac{2\omega_{kg}}{3} \sum_i \mid \mu_i^{kg} \mid^2 , \qquad (2\text{-}2)$$

where ω represents the energy required for the transition and μ the electric dipole moment operator. Following with the Gaussian broadening formula，we can further obtain the OPA spectrum calculation expression

$$G(\omega) = \frac{1}{c\sqrt{2\pi}} e^{-\frac{(\omega-\omega_i)^2}{2c^2}} , \qquad (2\text{-}3)$$

where $c = \dfrac{\text{FWHM}}{2\sqrt{2\ln 2}}$，$\omega$ is the abscissa of the spectrum[12].

When exploring the interaction between light and matter，charge transfer（CT）is one of the things we have to study. It can be used in the design of optoelectronic devices，solar cells，materials science，and biology. Photoinduced CT exists in many systems[13-22]. Among them，the electron transition of the donor-acceptor is the most special. Under the excitation of light，the donor is responsible for providing electrons，and the acceptor will receive them. Since the mobility of π electrons is

relatively strong and the binding rate is poor, if the donor and acceptor can be connected through π electrons, molecules with stronger charge transfer effects can be designed[23]. Mu et al. combined OPA and two-photon absorption visualization to study the charge transfer characteristics of the donor-bridge-acceptor system. The specific details will be expanded in the next section.

2.1.4   Introduction to two-photon absorption（TPA）

TPA refers to the phenomenon that an atom or molecule absorbs two photons at the same time and transitions to a higher energy level. In the case, energy difference between the energy levels is exactly equal to the total energy of the absorbed photons. TPA requires two photons to react with the molecule together, so this process causes the probability of TPA to occur much smaller （the probability is proportional to the square of the light intensity）, and it belongs to the range of non-linear optics. Since the energy required in the TPA process is halved, the penetration capability of TPA is improved compared to OPA. The discussion about TPA can be traced back to Maria Goppert-Meyer's doctoral thesis in 1931[24], but the laser had not yet been invented at that time, so it was difficult to achieve the light intensity required for TPA. The actual experiment was not realized until 1961[25].

Unlike OPA, TPA is a non-linear process, and the whole process of transition from the ground state to the final excited state can be divided into two situations, one is a two-state model, that is, a direct transition from the ground to the final excited state, the other is three-state[26]. The model first transitions from the ground state to the intermediate excited , then from the intermediate to the final excited, which means that it is a two-step. And the selection of the intermediate state is not unique. For example, when the electron transitions from the ground（S_0）to the third excited state（S_3）, the intermediate can be selected from the first excited（S_1）or the second excited（S_2）. So how do we determine the strength of TPA? The TPA cross section is the key to solving this problem. This cross-section is a physical quantity related to the transition