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纳米光子学丛书

孙萌涛　王鑫鑫　宗　欢　著
Sun Mengtao　Wang Xinxin　Zong Huan

Nanoscale Photonics and Spectroscopy

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《纳米光子学丛书》
编 委 会

CONTENTS

CHAPTER 1

Introduction

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1.1 Concept of Spectroscopy

Spectroscopy is the study of the interaction between matter and electromagnetic radiation(Spectrum + copy). In 1672, Isaac Newton described an experiment in which he permitted sunlight to pass through a small hole and then through a prism(Fig. 1-1). Newton found that sunlight, which looks white to us, is actually made up of a mixture of all the colors of the rainbow.

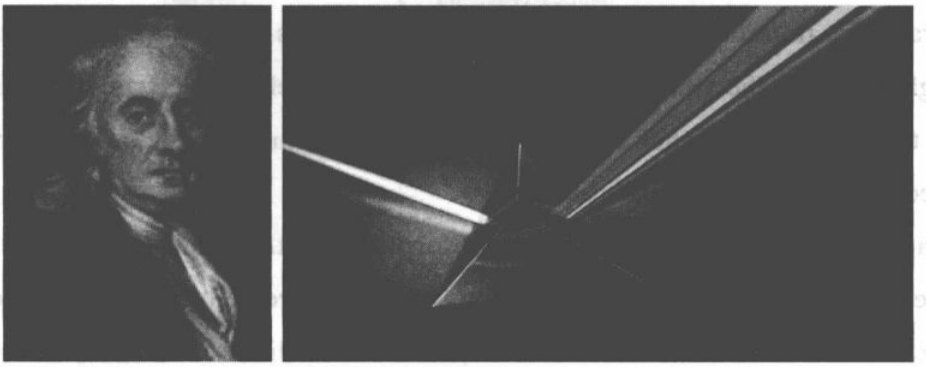

Fig. 1-1 Isaac Newton and his experiment
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In 1802, William Hyde Wollaston built an improved spectrometer that included a lens to focus the sun's spectrum on a screen(Fig. 1-2). Upon use, Wollaston realized that the colors were not spread uniformly, but instead had

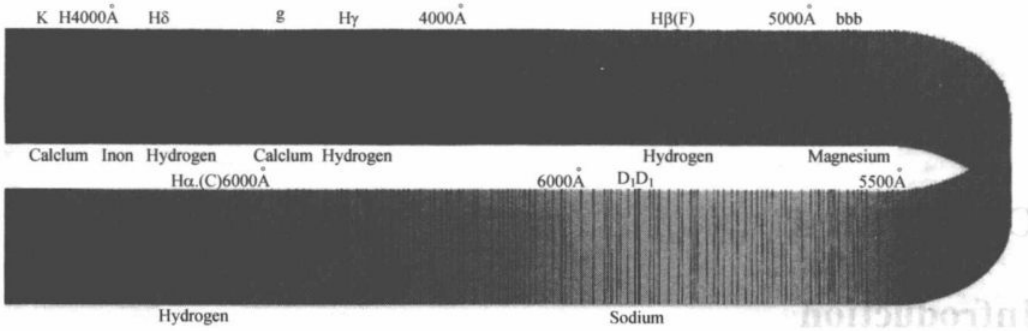

Fig. 1-2 Lines in the solar spectrum. The range illustrated is from 3900 Å to 6900 Å
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missing patches of colors, which appeared as dark bands in the spectrum. In 1815, Joseph Fraunhofer also examined the solar spectrum, and found about 600 such dark lines (missing colors), which are now known as Fraunhofer lines, or absorption lines.

Spectroscopy is the study of the interaction between matter and electromagnetic radiation. The entire electromagnetic spectrum is shown in Fig. 1-3.

In molecular spectroscopy, a Jablonski diagram (Fig. 1-4) is used to illustrate the electronic states of a molecule and the transitions between them. The states are arranged vertically by energy and grouped horizontally by spin multiplicity. Nonradiative transitions are indicated by squiggly arrows and radiative transitions by straight arrows. The vibrational ground states of each electronic state are indicated with thick lines, the higher vibrational states with thinner lines.[1] The diagram is named after Aleksander Jabłoński[2].

Radiative transitions involve the absorption, if the transition occurs to a higher energy level, or the emission, in the reverse case, of a photon. Nonradiative transitions arise through several different mechanisms, all differently labeled in the diagram. Relaxation of the excited state to its lowest vibrational level is called vibrational relaxation. This process involves the dissipation of energy from the molecule to its surroundings, and thus it cannot occur for isolated molecules. A second type of nonradiative transition is internal conversion (IC), which occurs when a vibrational state of an electronically

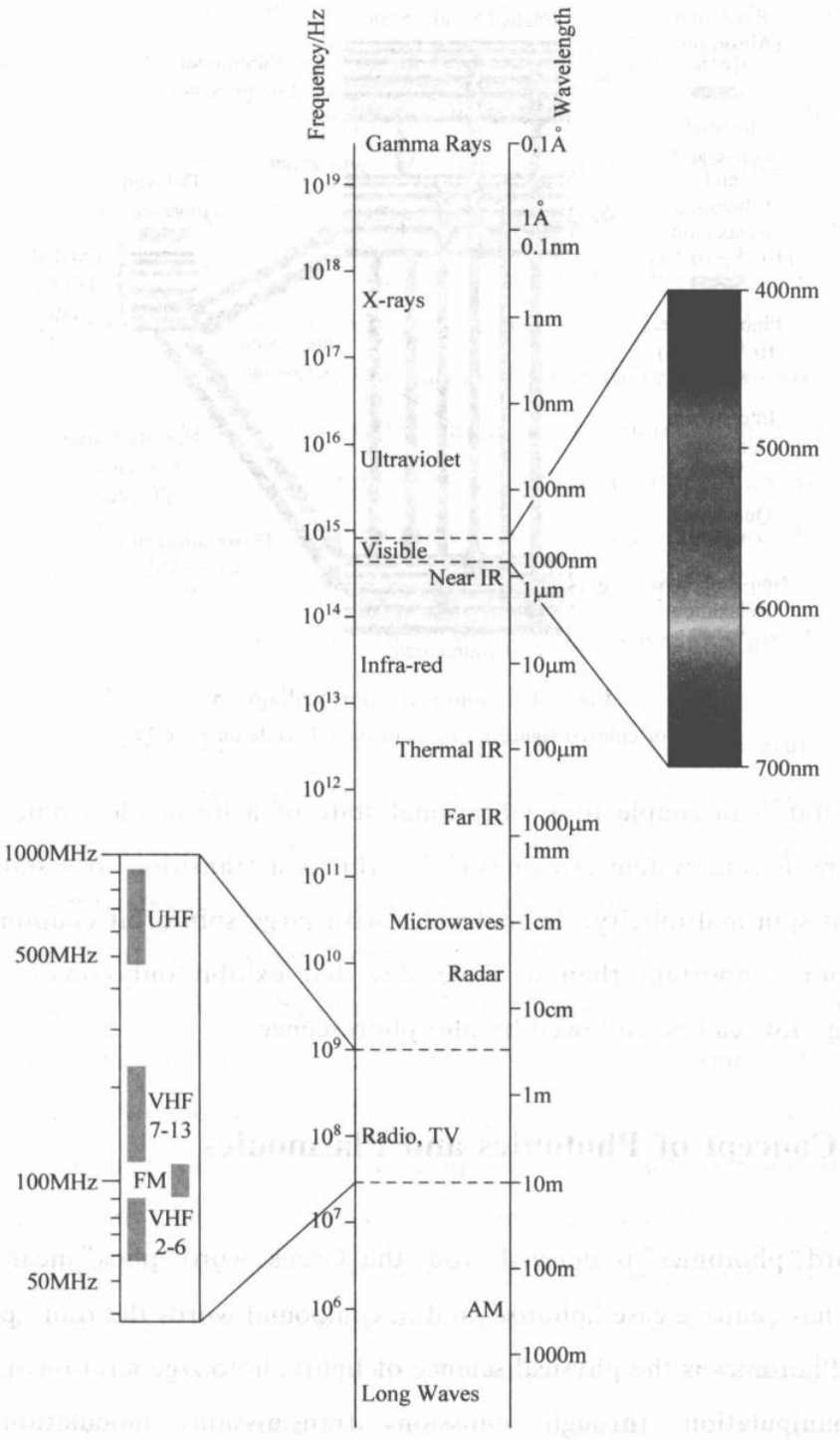

Fig. 1-3 The entire electromagnetic spectrum

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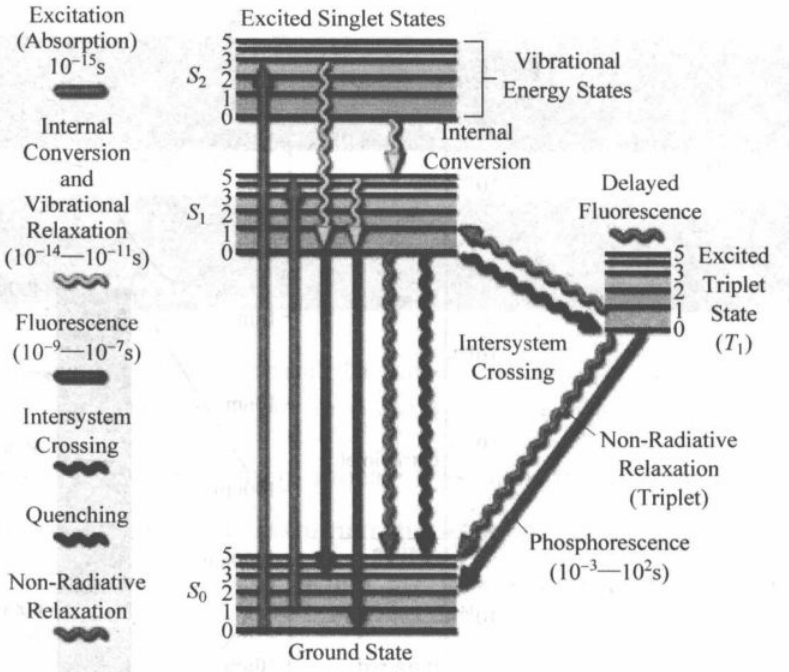

Fig. 1-4 Jablonski(energy)diagram

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excited state can couple to a vibrational state of a lower electronic state. A third type is intersystem crossing(ISC); this is a transition to a state with a different spin multiplicity. In molecules with large spin-orbit coupling, ISC is much more important than in molecules that exhibit only small spin-orbit coupling. ISC can be followed by phosphorescence.

1.2 Concept of Photonics and Plasmonics

The word "photonics" is derived from the Greek word "phos" meaning light (which has genitive case "photos" and in compound words the root "photo-" is used). Photonics is the physical science of light(photon)generation, detection, and manipulation through emission, transmission, modulation, signal processing, switching, amplification, and detection/sensing. Photonics is closely related to optics. Classical optics long preceded the discovery that light is

quantized, when Albert Einstein famously explained the photoelectric effect in 1905. Optics tools include the refracting lens, the reflecting mirror, and various optical components and instruments developed throughout the 15th to 19th centuries. Key tenets of classical optics, such as Huygens principle, developed in the 17th century, Maxwell's equations and the wave equations, developed in the 19th century, do not depend on quantum properties of light. Photonics is related to quantum optics, optomechanics, electro-optics, optoelectronics, and quantum electronics. However, each area has slightly different connotations by scientific and government communities and in the marketplace. Quantum optics often connotes fundamental research, whereas photonics is used to connote applied research and development. Photonics also relates to the emerging science of quantum information and quantum optics. The science of photonics includes investigation of the emission, transmission, amplification, detection, and modulation of light.

In photonics, metals are not usually thought of being very useful, perhaps except mirrors. In most cases, metals are strong absorbers of light, a consequence of their large free-electron density. However, in the miniaturization of photonic circuits, it is now being realized that metallic structures can provide unique ways of manipulating light at length scales smaller than the wavelength. Maxwell's equations tell us that an interface between a dielectric (e. g. silica glass) and a metal (e. g. Ag or Au) can support an surface plasmon (SP). An SP is a coherent electron oscillation that propagates along the interface together with an electromagnetic wave. These unique interface waves result from the special dispersion characteristics (dependence of dielectric constant on frequency) of metals. Similar to photonics, by means of SPs, suchresearch is referred to as plasmonics, which can be considered as optics at the nanoscale[3].

What distinguishes SPs from "regular" photons is that they have a much smaller wavelength at the same frequency. For example, a HeNe laser, whose free-space emission wavelength is 633 nm, can excite an SP at a Si/Ag interface with a wavelength of only 70 nm. When the laser frequency is tuned very close

to the SP resonance, SP wavelengths in the nanometer range can be achieved. The short-wavelength SPs enable the fabrication of nanoscale optical integrated circuits, in which light can be guided, split, filtered, and even amplified using plasmonic integrated circuits that are smaller than the optical wavelength.

SPs are easily accessible excitations in metals and semiconductors and involve a collective motion of the conduction electrons. These excitations can be exploited to manipulate electromagnetic waves at optical frequencies("light") in new ways that are unthinkable in conventional dielectric structures. The field of surface plasmon nanophotonics is rapidly developing and impacting a wide range of areas including: electronics, photonics, chemistry, biology, and medicine. SPs are coherent delocalized electron oscillations that exist at the interface between any two materials where the real part of the dielectric function changes sign across the interface(e. g. a metal-dielectric interface, such as a metal sheet in air). The existence of surface plasmons was first predicted in 1957 by Rufus Ritchie[4]. Schematic representation of an electron density wave propagating along a metal-dielectric interface can be seen from Fig. 1-5. The charge motion in a surface plasmon always creates electromagnetic fields outside(as well as inside)the metal. The charge density oscillations and associated electromagnetic fields are called SPP waves. The exponential dependence of the electromagnetic field intensity on the distance away from the interface is shown on the right in Fig. 1-5[5]. These waves can be excited very efficiently with light in the visible range of the electromagnetic spectrum.

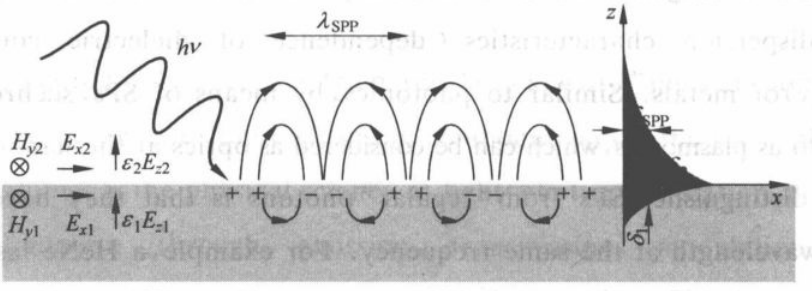

Fig. 1-5 Schematic representation of an electron density wave propagating along a metal-dielectric interface

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Surface plasmon polaritons (SPPs) are infrared (IR) or visible-frequency electromagnetic waves that travel along a metal-dielectric or metal-air interface. The term "SPP" explains that the wave involves both charge motion in the metal ("surface plasmon") and electromagnetic waves in the air or dielectric ("polariton")[6]. SPPs can be excited by electrons or photons. Excitation by electrons is created by firing electrons into the bulk of a metal. As the electrons scatter, energy is transferred into the bulk plasma. The component of the scattering vector parallel to the surface results in the formation of a SPP[7]. For a photon to excite an SPP, both must have the same frequency and momentum. However, for a given frequency, a free-space photon has less momentum than an SPP because the two have different dispersion relations. This momentum mismatch is the reason that a free-space photon from air cannot couple directly to an SPP. For the same reason, an SPP on a smooth metal surface cannot emit energy as a free-space photon into the dielectric(if the dielectric is uniform). The coupling of photons into SPPs can be achieved using a coupling medium such as a prism or grating or a defect on the metal surface to match the photon and SPP wave vectors(and thus match their momenta). The SPP is a non-radiative electromagnetic surface wave that propagates in a direction parallel to the negative permittivity/dielectric material interface.

Dispersion curve for SPPs can be seen from Fig. 1-6. At low frequency, an SPP approaches a Sommerfeld-Zenneck wave, where the dispersion relation (between frequency and wavevector) is the same as in free space. At a higher frequency, the dispersion relation bends over and reaches an asymptotic limit called the "surface plasma frequency"[8,9]. SPPs are usually shorter in wavelength than the incident light (photons). Hence, SPPs can have tighter spatial confinement and higher local field intensity. Perpendicular to the interface, they have subwavelength-scale confinement. An SPP will propagate along the interface until its energy is lost either to absorption in the metal or

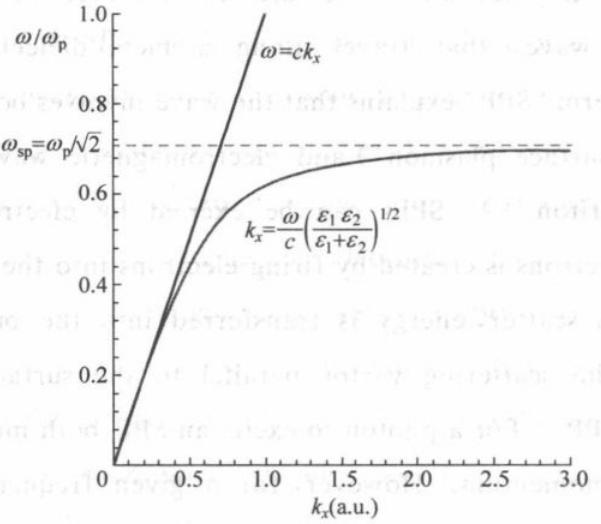

Fig. 1-6 Dispersion curve for SPPs. At low k, the surface plasmon curve (red) approaches the photon curve (blue)

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scattering into other directions (such as into free space). The k is a complex wave vector, $k_x = k'_x + ik''_x$, and in the case of a lossless SPP, it turns out that the x components are real and the z components are imaginary—the wave oscillates along the x direction and exponentially decays along the z direction.

As an SPP propagates along the surface (Fig. 1-5), it loses energy to the metal due to absorption. It can also lose energy due to scattering into free space or into other directions. The intensity of the surface plasmon decays with the square of the electric field, so at a distance x, the intensity has decreased by a factor of $\exp(2k''_x x)$. The propagation length is defined as the distance for the SPP intensity to decay by a factor of $1/e$. This condition is satisfied at a length, $L = \frac{1}{2k''_x}$ [10]. The electric field falls off evanescently perpendicular to the metal surface. At low frequencies, the SPP penetration depth into the metal is commonly approximated using the skin depth formula. In the dielectric, the field will fall off far more slowly. The decay lengths in the