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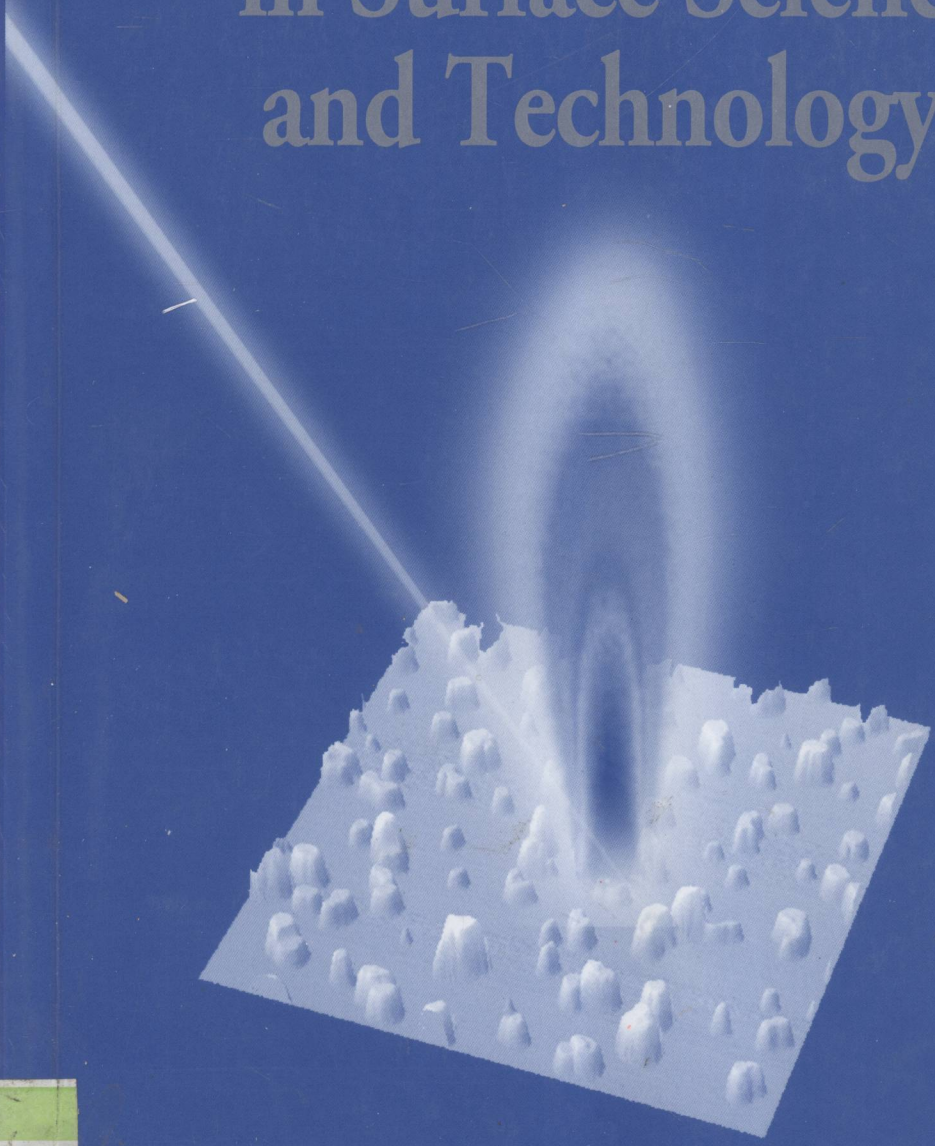

H.-G. Rubahn

LASER APPLICATIONS IN SURFACE SCIENCE AND TECHNOLOGY

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LASER APPLICATIONS IN SURFACE SCIENCE AND TECHNOLOGY

Preface

A simple experiment, which uses nothing but a commercial laser pointer and two lenses, illustrates the pecularities of the interaction of laser light with surfaces. The laser pointer is a source of coherent light, and the lenses serve to focus or to defocus it. Increasing the diameter of the laser beam by the use of lenses and irradiating a white sheet of paper results in a granular pattern with spots that appear sharply independent of spatial position. This so–called 'speckle pattern' (Dainty, 1975) is the result of scattering of coherent light from surface roughnesses. If one of the lenses is used to focus the laser beam into a tiny spot a few micrometers wide, and if this light hits a black area, then within the burn spot the strong concentration of energy results in rapid heating of the surface. Exchanging the continuous laser pointer with a pulsed laser leads to more dramatic phenomena, namely a melting of the surface and the explosive ablation of material. This kind of surface modification can be restricted to act on spatially and temporally very well defined spots. Consequently, the *materials treatment* of a solid was acknowledged as a potential area of application of laser light shortly after the experimental realisation of the laser principle in 1960 (Breech and Cross, 1962). Indeed, nowadays high–power continuous or pulsed lasers are widely used tools for drilling, marking, cutting or welding of materials. Low–power lasers are mainly used for spectroscopic or metrological applications.

In this monograph the physical aspects of laser–surface interactions are presented. These are at the heart not only of materials treatment, but also of laser spectroscopies on surfaces, which allow one to obtain important information about the electronic nature of the solid surface and of the rovibronic nature of its adsorbates. It is worth remembering that the specific surface properties (represented, for example, by the reconstruction of the atoms of the bulk lattice) are extended only a few atomic layers (of the order of a nanometer) into the bulk. On the other hand, laser light penetrates the solid much deeper. Typical values of penetration depth, given by the inverse absorption coefficient, are between 100 nanometers (metals), a few micrometers (strongly absorbing insulators) and several thousand meters (optical fibers). The laser–solid interaction, although often being accompanied by drastic modifications of the solid, therefore is not *per se*

surface–specific. Under appropriate conditions (*e.g.*, small thermal diffusion length and ultrashort pulses), however, laser–induced effects such as heating might be localized at the surface. In the case of selective surface desorption or spectroscopy of adsorbates the surface sensitivity is also evident. Finally, the laser–induced *nonlinear* polarization, which adds reflected light waves at higher harmonics to the scattered light wave at the fundamental frequency, is in the case of centrosymmetric bulk materials also intrinsically surface–sensitive and its use has become an important surface analysis method.

A thorough understanding of the pecularities of laser–surface interactions relies on a knowledge of the intrinsic properties of lasers and surfaces. Therefore, the first chapter of this monograph reminds the reader of some basics of laser and surface physics. The laser types most commonly used for the investigation of surfaces and some widespread surface–characterization methods are discussed. In addition, a few methods of surface preparation are mentioned, which have emerged only recently but have gained importance in the context of sophisticated new laser–surface treatments.

The use of laser techniques to study fundamental adsorption, desorption and diffusion processes on surfaces is discussed in Chapter 2. Important linear and nonlinear spectroscopic methods as well as the basic physical processes and some applications are explained in Chapter 3, since in the last two decades mainly *spectroscopy* with laser light has been introduced into many laboratories. Recently the development of ultrashort laser pulses has allowed one to observe directly the dynamics of electronic and vibronic surface excitation and relaxation processes. Thus Chapter 4 deals with the application of ultrashort laser pulses to surface structural, dynamic and photochemical studies. Since the methodology is fairly new, this chapter focuses on very recent experimental and theoretical findings. Possibly, some of these findings might have to be considered under a different point of view in the future, which obviously is a characteristic of active science.

The final three chapters are devoted to materials treatment, beginning in Chapter 5 with a discussion of fundamental *changes* of the plain surface induced by laser radiation, namely heating, melting and plasma generation. Here, the word 'plain' does not mean inevitably that the surface under discussion is free from adsorbates and that the discussed processes must proceed under vacuum conditions. It merely implies that the primary mechanism of interaction is not dominated by the coverage of the surface with, for example, a water film.

Structuring of the surface in terms of controlled crystallization processes, ablation of surface material, generation of periodic structures and generation of thin films is accounted for in Chapter 6.

Most of the basic mechanisms discussed in this monograph are used in laser medical applications. Here, a major field is the use of lasers in ophthalmology, which is highlighted as an example in more detail in Chapter 7.

Obviously, a rapidly expanding, innovative and important field such as the

interaction of photons with surfaces can by no means be discussed exhaustively in a single monograph. The purpose of the present book is to introduce possible laser-surface interaction mechanisms and processes and to make the reader curious to learn more about this fascinating scientific field. It is hoped that the book can provide some guidance about important new developments that one should have an eye on in the near future.

Details can be found in the literature that is extensively referenced throughout the text. In addition, recently published and more specific monographs might be consulted to fill the remaining gaps. For example, a discussion of various aspects of laser ablation processes (Miller, 1994); a compendium of articles on laser spectroscopy and photochemistry at metal surfaces (Dai and Ho, 1995); comprehensive discussions of the application of UV laser light to surfaces (Duley, 1996); a general description of recent advances in laser–tissue interactions (Niemz, 1996); an overview over laser–assisted processing on surfaces, including a most detailed discussion of ablation models (Bäuerle, 1996b); and industrial applications of lasers (Ready, 1997).

At this point I wish to thank my wife Katharina for her patience and encouragement and my colleague Frank Balzer for his indefatigable and inspired assistance as well as countless hours of extensive discussions. I am grateful also to all my other colleagues who have shared their knowledge with me. I extend special thanks to Professors E. Matthias and H.–L. Dai for constructive criticism and to Prof. J.P. Toennies for more than ten years of intellectual support at the MPI für Strömungsforschung.

Horst-Günter Rubahn

Göttingen, December 1998

Contents

1

Light and Matter

1.1 Coherent Light Sources

Lasers are sources of temporally and spatially coherent light. Compared with the light generated by a thermal lamp laser light is especially suited for applications in surface and materials science due to its coherence, intensity and due to the possibility to generate short and ultrashort pulses. In what follows we explain these properties in more detail.

Temporal and spatial coherence

Two partial waves of a light source are called *coherent* if their phase differences are constant, which leads, upon superposition, to interference phenomena. *Temporal coherence* is equivalent to the amplitudes of the emitted electromagnetic wave remaining constant over a considerably long time. This is demonstrated in Fig. 1 by comparison of the temporal evolution of the electric field amplitude emitted from a laser source and that emitted from a thermal light source.

The 'coherence length' L_c is defined as the difference in optical length that results in a phase difference between two partial waves of smaller than π; hence that difference that allows interferences to occur. The corresponding 'coherence time' $\tau_c = L_c/c$ is related to the coherence length via the speed of light c in the investigated medium.

The coherence length of thermal light behind an interference filter with spectral bandwidth of 1 Å at λ=500 nm is about 0.8 mm; that of a laser with a bandwidth of 10 MHz about 10 m. Hence the temporal coherence of a laser is several orders of magnitude higher compared with that of light generated by a thermal lamp and its light is well suited for applications which rely on interference phenomena such as optical holography.

High temporal coherence results in light that is strongly monochromatic. However, strongly monochromatic light is not necessarily highly temporally coherent since the photon statistics (and hence the amplitude fluctuations) of light from a lamp (Bose–Einstein statistics) and that from a laser (Poisson statistics) are fundamentally different. The degree of monochromasy can be

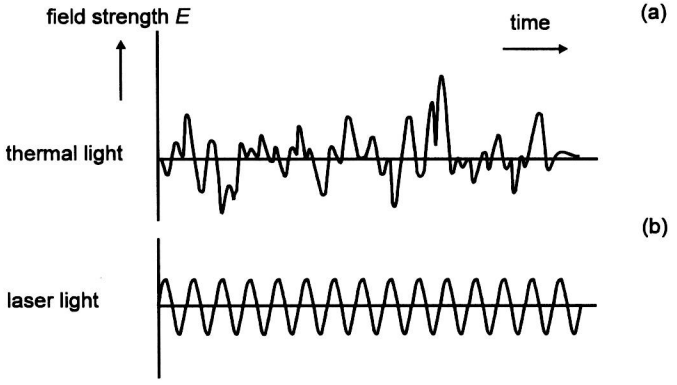

Figure 1 Temporal change of the electromagnetic field strength E for a thermal light source (a) and a laser (b).

defined via the ratio between the linewidth $\delta\nu$ and the carrier frequency ν, $\delta\nu/\nu$ ('spectral resolution') Using interference filters it is possible to obtain $\delta\nu/\nu \approx 10^{-3}$ without significant loss of intensity. The corresponding spectral range is shown in Fig. 2. An unstabilized Ar^+ laser allows us to define the wavelength and thus the energy to within 0.2 Å. A commercial, actively stabilized dye laser provides a spectral resolution of 10^{-5} Å or $\delta\nu/\nu \approx 10^{-9}$; more sophisticated systems used in basic research projects operate with linewidths in the Hz range, hence $\delta\nu/\nu \approx 10^{-15}$. This spectral resolution is comparable to that obtainable in Mößbauer spectroscopy and allows us, in principle, to determine the energies of substrate- or adsorbate-electronic states with a resolution of better than 1 μeV.

High *spatial coherence* means that laser light is parallel over a wide range. Analogously to temporal coherence light is called 'spatially coherent' if the phase difference between two partial waves is smaller than π. This condition is fulfilled for all partial waves within the Airy diffraction cone with radius a. The limiting angle for the diffraction cone of zeroth order is $\Theta_{max}=1.22\lambda/a$. It corresponds to the divergence angle of light. Laser light, which is emitted spatially coherent from an aperture with large diameter $2a$ (*e.g.*, being the outcouple mirror of the laser), has a corresponding small divergence and can be strongly focused down to the diffraction limit. Fig. 3 illustrates this behavior by showing the phase front of a light wave from a thermal source, which results from the superposition of the phase fronts of independent spherical waves (Huygen's principle). This corresponds to strong divergence. In the case of laser light the divergence is given by diffraction of the light wave at

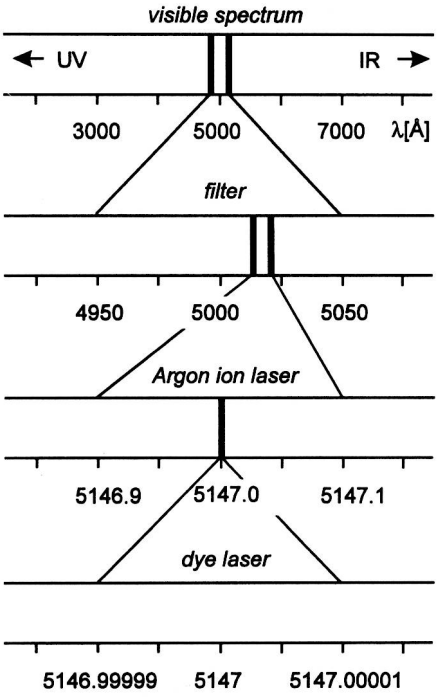

Figure 2 The monochromasy of laser light is demonstrated by comparing the spectral width (energetic uncertainty) of the emitted light from a single mode dye laser and an Ar^+ laser with that obtained by narrowing the visible spectrum with an interference filter.

the exit mirror of the laser cavity.

Due to the design of the laser resonator, laser light is emitted in most cases in the fundamental Gaussian mode $TEM_{0,0}$. Upon focusing the Gaussian beam at its waist with a thin lens of focal length f a beam waist with radius w_0^* is generated (Yariv and Yeh, 1984):

$$w_0^* = \frac{\lambda f}{\pi w_L n} \cdot \left[1 + \left(\frac{\lambda f}{\pi w_L^2 n}\right)^2\right]^{-0.5} . \tag{1.1}$$

In this equation, n is the index of refraction of the material and w_L the radius of the laser beam that hits the lens. In the near field, which is dictated by Fresnel diffraction, the beam waist increases until the beam area is twice that inside the focus (Fig. 4, 'Rayleigh-range'). This distance $s_0 = \pi\, w_0^2\, /\lambda$ defines the parallelity of laser light ($2s_0$ is usually called the 'confocal parameter') . In the far field, for $s \gg s_0$, Fraunhofer diffraction results in geometrical optics

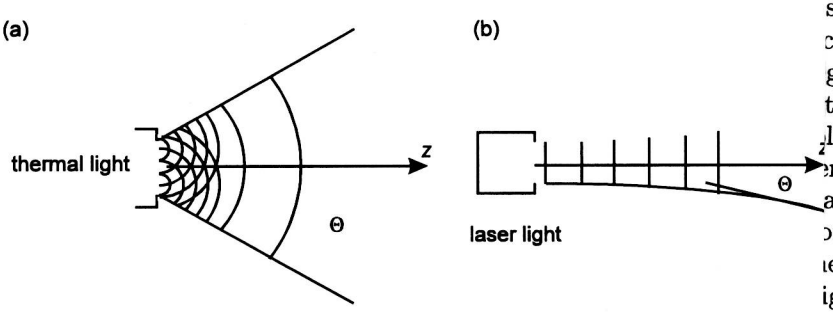

Figure 3 Divergence of light, emitted from a thermal (a) and a laser source (b). The divergence angle Θ is of the order of fractions of a mrad.

with a constant angle of divergence $\Theta \approx \lambda/\pi n w_0$.

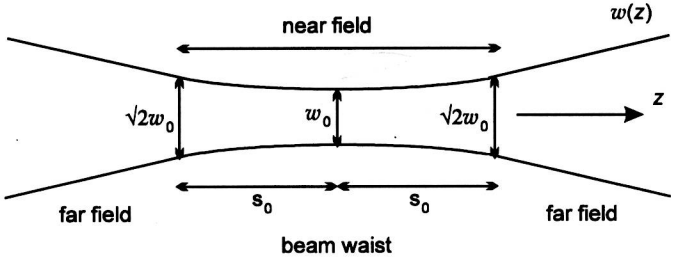

Figure 4 Focal range of a Gaussian beam ($TEM_{0,0}$–mode), propagating along the optical axis z. The Rayleigh range is denoted by s_0, the beam waist by w_0. See Eq. (1.11).

A helium–neon laser usually comes with a resonator that is construc such that the beam waist is located at the position of the outcouple mir Given an aperture of 1 mm this results in a confocal parameter of $2s_0$=2.4 and a divergence of Θ=0.7 mrad. Focusing this laser with a lens of focal len 3.5 mm would result in a focus diameter at the position of the beam wais 1.8 μm.

Intensity

Lamps rarely achieve powers of more than kilowatts. Peak power

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sers, on the other hand, easily exceed 10^5 W during continuous operation cw') or 10^{11} W during pulsed operation. These high peak powers make a gime of laser–matter interaction readily accessible, where nonlinear optical teractions occur. The 'intensity' of a light source is defined as power per lid angle. In the context of interaction with surfaces the 'irradiance' (power r area) is a more useful quantity, since it affects directly the irradiated aterial.[1] It is important to distinguish average power per area (W/cm^2) om pulsed power per area or 'fluence' (J/cm^2), i.e., the energy density, if ıe wants to estimate the influence of the laser on the surface. Since laser light ight be focused without significant losses of intensity close to the diffraction nit, average powers of 10^5 to 10^{11} W result in irradiances[2] between 10^{12} d 10^{18} or even 10^{20} W/cm^2 (Mourou, 1997). To visualize the magnitude of is irradiance one might compare it with the low irradiance of the sun (solar nstant 0.137 W/cm^2), which nevertheless results on a clear day in a well tectable heating of the skin. An irradiance of 10^{12} W/cm^2 corresponds to photon flux density of more than 10^{30} photons per square centimeter and cond. Such a flux density corresponds to a black-body temperature of about e million degrees Kelvin — a temperature which is found only under extreme nditions, such as the center of a star. Obviously, such high irradiances open a wide range of new physical phenomena including Gigagauss magnetic lds, terabar light pressures and relativistic plasmas (Perry and Mourou, 94).

For a pulsed laser with an energy of 1 mJ/pulse the number of pho- ns per pulse is $5.034{\cdot}10^{12} \cdot \lambda$ [nm] and the number of photons per second $2913{\cdot}10^{21}{\cdot}\lambda$ [nm]$/\tau$ [ns] with τ meaning the pulse length. The power P [kW] given by $939.435/\tau$ [ns], and the average power can be calculated by multi- cation with the repetition rate. Especially for the observation of nonlinear tical effects the induced electrical field strength is important, which is given a laser with beam waist w_0, which irradiates a medium with index of re- ction n, by $(245/w_0$ [cm]$) \cdot \sqrt{P[\mathrm{kW}]/n}$ [V/cm] (Birge, 1983).

Pulse generation

Light pulses might be generated from a thermal light source by a mechanical ıtter or by electrical switching of the lamp voltage. The method is limited the former case by the mechanical stability of the chopper wheel and ults in pulses of a few microseconds (μs) length. In the latter case the nimum pulse length is limited by secondary processes during the discharge

is also instructive to compare the average spectral irradiances of thermal lamps and sers. For example, at 633 nm a Xe arc lamp with 150 W electrical input power and an ea of the radiation source of 0.5 × 2.2 mm^2 provides 0.24 $Wcm^{-2}sr^{-1}nm^{-1}$, whereas He–Ne laser with 2 mW optical output power and a circular aperture of 0.63 mm ameter provides 10^8 $Wcm^{-2}sr^{-1}nm^{-1}$. The sun would have 2.2 $Wcm^{-2}sr^{-1}nm^{-1}$. onlinear interactions such as self-defocusing usually restrict the maximum obtainable radiance.

and ultimately by the electronic lifetime of the spontaneous photon emission process (nanoseconds, ns). This problem can be overcome by using light that is dominated by a stimulated emission process, i.e., by exploiting the intrinsic properties that make laser light a very special kind of light. For example, by the use of mode coupling techniques pulses with lengths of the order of femtoseconds (1 fs = 10^{-15} s) can be generated. Since light travels within, for example, 100 fs just 30 μm, those ultrashort pulses allow one to map spatially the motion of particles with extremely high spatial resolution. For example, the fragments of a molecular photodissociation process depart with a relative velocity of typically a few thousand meters per second (corresponding to the nuclear motion correlated with a vibrational frequency of 10^{12} s^{-1}). Hence a temporal delay of 100 fs between a pump pulse (which excites the molecule into a dissociating state) and a probe pulse (which checks, for example, via laser-induced fluorescence the state of the initial molecule or its fragments) corresponds to a distance of a few tenths of a nanometer (Fig. 5). This is the characteristic length scale of a typical atom–molecule or molecule–surface potential energy curve (cf. Fig. 17). The use of two laser pulses, mutually delayed by a few tens of femtoseconds, thus allows one to observe the bond breaking of a molecule or the desorption from a surface in real time.

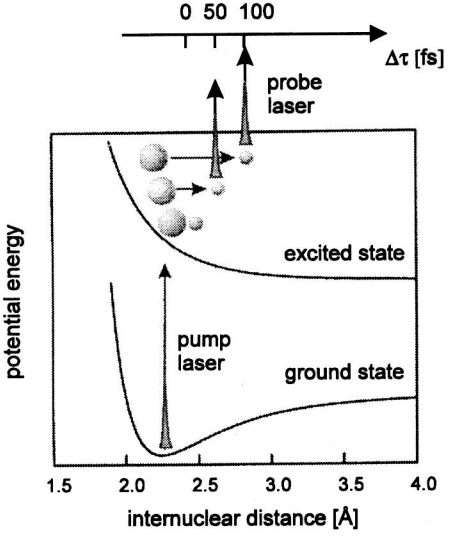

Figure 5 Laser-induced bond breaking of a molecule, which has been adsorbed on a surface. The departing fragments are probed by pulses from a second laser, which are temporally delayed by $\Delta\tau$.

Light emitted from a thermal source and laser light differ *in principle* by their *photon statistics.* Photons are bosons (even-numbered spins) and their statistics are thus described by a Bose–Einstein distribution with a mean number of photons per mode of

$$\bar{n} = \frac{\langle E \rangle}{h\nu} = \frac{1}{exp(h\nu/k_B T) - 1}. \tag{1.2}$$

Hanbury-Brown and Twiss verified these statistics experimentally 1957 by counting the number of coincidences of detecting two photons from a light beam which has been split by a beam divider into two parts (Hanbury-Brown and Twiss, 1957a; Hanbury-Brown and Twiss, 1957b). The observed Bose–Einstein distribution reveals a 'bunching' of the photons, such as is demonstrated in Fig. 6. Here, each photon that is counted as a function of time is plotted as a horizontal line. The probability of finding a photon in the case that another one has already been observed is higher than the probability of finding a photon in the case that no photon has been observed before. The corresponding probability distribution for the observation of a certain number of photons, given an average number of photons per mode, then is very broad. The variation of numbers of photons is small for small $\bar{n} \ll 1$ and is proportional to $\bar{n}$: the photons behave like classical particles, which are independent of each other. For large $\bar{n}$ the wavefield character of thermal light results in a quadratic dependence of the variation on $\bar{n}$.

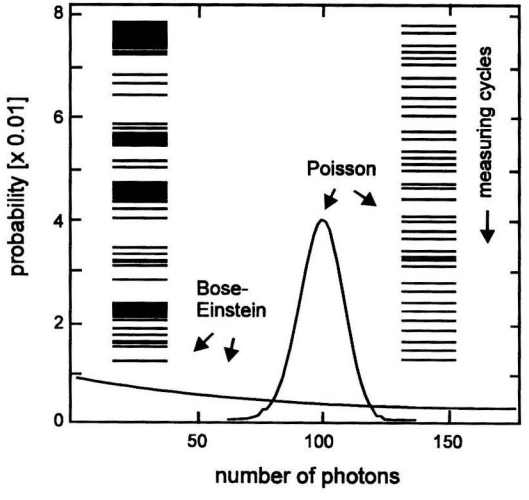

Figure 6 Bose–Einstein and Poisson distribution of observed photons as a function of time. Probability distributions are plotted as solid lines for an average number of photons per mode of $\bar{n}$ =100.

Even in the case of good spatial and temporal filtering the intensity amplitude of light is strongly fluctuating for large $\bar{n}$ (which is what one is interested in). In contrast, the light from a laser can be described by a Poisson distribution, which is the distribution found for a forced oscillator. The photons no longer 'bunch' (Fig. 6, right-hand side), and the probability distribution has a maximum at the average number of photons per mode. The mean square fluctuation is proportional to $\bar{n}$ even for large $\bar{n}$, meaning that the photons in that case too behave like independent particles ('coherent light'). Laser photons obey these statistics since they have been generated mainly by *stimulated emission* and not via spontaneous emission such as the photons of thermal light.

LASER = **L**ight **A**mplification via **S**timulated **E**mission of **R**adiation.

A LASER is based on three main elements (Fig. 7)(Schawlow and Townes, 1958; Maiman, 1960): an *energy pump* (*e.g.*, a flash lamp or an electrical plasma discharge), which irradiates the *laser-active medium* (gas, solid, liquid or plasma) and that way excites particles from the ground into high lying electronic states, from which they relax by emitting photons. A *resonator* exerts a selective feedback to the system by restricting the number of allowed eigenfrequencies (modes) that can start oscillating and by coupling the emitted photons back to the emitting particles. If the total gain per round trip of photons in the resonator exceeds the total loss, then the condition for self-excited oscillation is fulfilled and the laser starts lasing.

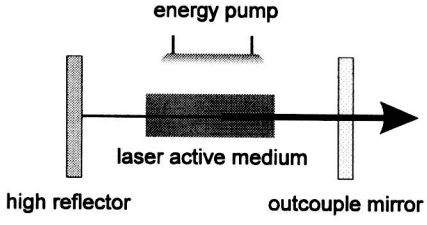

Figure 7 Fundamental constituents of a laser. High reflector and outcouple mirror build a resonator.

Let us assume for simplicity a two-level system. Since we are going to talk about large photon numbers and since we are mainly interested in processes that are stimulated by a classical radiation field it is well justified to describe the change of photon number n inside the resonator by a classical rate equation: