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Stimulated Emission of Surface Plasmons at the Interface between a Silver Film and an Optically Pumped Dye Solution

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Surface plasmons (SPs) are surface-bound electromagnetic waves supported by metals, offering the possibility of strong spatial confinement of electromagnetic fields on the micro- and nanoscales. They suffer, however, from strong damping caused by internal absorption and radiation losses. Here we demonstrate amplification of SPs by stimulated emission, which marks a possible solution to this problem. We use an attenuated-total-reflection setup to detect stimulated emission of SPs at the interface between a silver film and an optically pumped dye solution acting as the amplifying medium. Clear evidence of stimulated emission is provided by an excellent agreement of the experimental observations with a theoretical analysis. Amplification of SPs can be considered analogous to photon amplification in a laser, thereby suggesting novel approaches in the field of nano-optics.

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In recent years, surface-bound electromagnetic waves guided by metals [1], so-called surface plasmons (SPs), have attracted much interest in the context of nano-optics. Their main attraction lies in the fact that they are characterized by strong enhancement and spatial confinement of the electromagnetic field [2–9]. However, they suffer from rather strong damping. Their propagation length is still sufficient to transmit them over micrometer distances and to manipulate them on the nanometer scale [10]. Nevertheless, for plasmonic signal processing in functional metallic nanostructures the strong damping of the plasmon fields is obstructive. Amplification of plasmons analogous to photon amplification in a laser could be a solution to this problem. For this, the metallic structure has to be surrounded by an active medium providing gain at the plasmon frequency. Recently, Bergman and Stockman treated such an arrangement theoretically and discussed a device analogous to the laser, which they dubbed SPASER, standing for ''surface plasmon amplification by stimulated emission of radiation'' [11].

In this Letter, as a first step toward realizing the SPASER, we demonstrate amplification of surface plasmons at the interface between a flat continuous silver film and a liquid containing organic dye molecules. Optical pumping creates a population inversion in the dye molecules, which then act to deliver energy to the plasmon field by stimulated emission. Our experiment is based on the attenuated-total-reflection (ATR) arrangement, also known as the Kretschmann-Raether configuration [1], in which the metal film is attached to a glass prism (Fig. 1). The SP at the outer metal surface is excited if *p*-polarized light is incident from the glass side at a specific angle for which the projection of the *k* vector of the photon matches the *k* vector of the SP. At this angle, the reflectance as a function of incidence angle exhibits a dip whose width and depth depend on the degree of damping that the SP experiences. A reduction of the damping caused by the presence of an amplifying medium at the film surface (in our case an ethanolic solution of either rhodamine 101 or cresyl violet) will therefore result in a characteristic modification of the reflectance curve providing a signature of stimulated SP emission.

The dye is optically pumped by a dye laser operating at $\lambda_p = 580$ nm. To couple the pump light to the dye molecules close to the silver film the pump beam is made to excite a plasmon at the metal surface [12]. The evanescent field of this plasmon, which is enhanced with respect to the incident field, ensures efficient pumping within a layer having a thickness of the order of 100 nm. This is realized

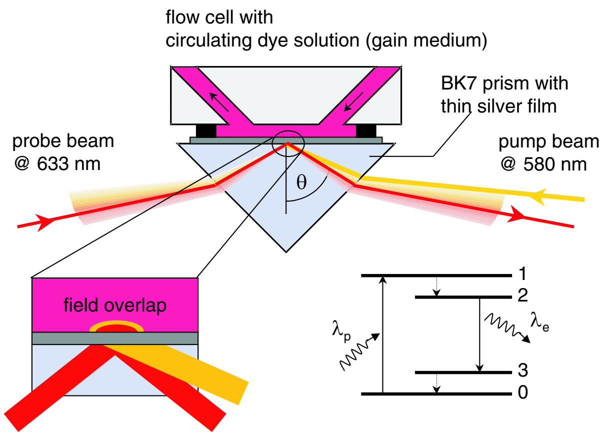

FIG. 1 (color online). Twin ATR method for SP amplification. Dye molecules, which are optically excited by the pump plasmon field, are made to coherently deliver their energy to the probe plasmon field by stimulated emission, thereby producing amplification. The signature of this process can be found in the reflected probe beam (see text). The spontaneous decay channel causes directional plasmon-coupled light emission visible as a light cone containing all colors of the dye emission spectrum. The inset shows a simplified energy level diagram of the dye molecules.

in a twin-ATR setup sketched in Fig. 1: The pump light and the light of a He Ne laser ($\lambda_e = 633$ nm) exciting the plasmon to be amplified enter the prism through opposite faces. The pump light is focussed to a $1/e^2$ radius of $w_p = 130\ \mu$m while the probe beam is more tightly focussed, so that its spot with a radius $w_e = 60\ \mu$m is completely covered by the pump focus. A flow cell through which the dye solution is circulated is attached to the side of the prism carrying the metal film. The continuous exchange of the solution at the interface is necessary for two reasons: photobleaching would otherwise lead to a loss of the gain within seconds, and the circulation also helps to reduce the heat load caused by absorption of the pump light in the metal film and in the dye. By rotating the prism by means of a goniometer the angle of incidence of the probe beam is varied while a photodiode monitors the reflected power, thereby recording the reflectance curve. An edge filter with an optical density of 10 at 580 nm prevents stray light produced by the pump beam from reaching the detector. The pump beam is delivered to the prism via a polarization preserving single-mode fiber connected to the turntable of the goniometer, so that its incidence angle always stays constant. To ensure the most efficient pump plasmon excitation, this angle was set to the reflectance minimum of the pump light. The axis of rotation is offset with respect to the symmetry plane in such a way that the probe spot remains stationary on the silver film during the rotation and, hence, the overlap with the pump focus is preserved. In the case of rhodamine 101 the prism is moved slowly in the direction normal to the plane of incidence during the measurement, so that fresh silver film is continuously moved into the focus. This keeps the problem of photochemical film deterioration to a minimum.

We treat the dye as a four-level system (see inset of Fig. 1) [13]. Optically pumping transition 0–1 transfers population to level 2. If $|E_p|$ denotes the electric-field amplitude of the pump plasmon in the dye solution and σ_p is the absorption cross section of the dye at the pump wavelength λ_p, then the pump rate experienced by a molecule in the ground state is $k_p = \varepsilon_0 n \lambda_p \sigma_p |E_p|^2/(2h)$, where $n = 1.36$ is the refractive index of the solvent, h is Planck's constant, and $\varepsilon_0 = 8.85 \times 10^{-12}$ C/(Vm). The plasmon intensity $|E_p|^2$ is enhanced with respect to the square modulus $|E_i|^2$ of the incident field in the prism by a factor up to $v \approx 35$, as calculated by an analysis of the reflection at the layered system glass-metal-liquid. In the center of the pump focus, $|E_i|^2$ can be deduced from the power P_p of the pump beam according to $|E_i|^2 = 4P_p/(\pi w_p^2 \varepsilon_0 n_G c)$, $n_G = 1.5$ being the refractive index of the prism and c the speed of light. The risk of thermal damage does not allow us to raise the pump power much above 10 mW. For $P_p = 10\,\mathrm{mW}$ and $\sigma_p = 3 \times 10^{-16}\,\mathrm{cm}^2$, one obtains a pump rate $k_p = 1 \times 10^6\ \mathrm{s}^{-1}$. The population of the upper level 2 in the steady state is determined by the ratio of the pump rate and the spontaneous decay rate k_s: $N_2 = Nk_p/(k_p + k_s)$. Here, N denotes the total number density of molecules, while N_2 is the number density of molecules in state 2. With a typical lifetime of state 2 of 3 ns we have $k_s = 3.3 \times 10^8\ \mathrm{s}^{-1}$ and thus $N_2 = 3 \times 10^{-3} N$. Transition 3–2 is now characterized by population inversion and provides gain at its transition frequency. At this frequency, the dye solution acquires an imaginary part of the dielectric constant given by

$$\varepsilon_d'' = \frac{n\lambda_e}{2\pi}(N_3 - N_2)\sigma_e, \tag{1}$$

where λ_e is the emission wavelength in vacuum, σ_e the emission cross section of the dye, and $N_3 \approx 0$ and N_2 denote the number densities of molecules in states 3 and 2. Population inversion ($N_3 < N_2$) makes ε_d'' negative, indicating gain rather than absorption. At a concentration $N = 7 \times 10^{17}\ \mathrm{cm}^{-3}$ and with $\lambda_e = 633$ nm and $\sigma_e = 3 \times 10^{-16}\ \mathrm{cm}^2$ one obtains $\varepsilon_d'' = -9 \times 10^{-6}$.

The damping of the SP is characterized by an exponential decay $e^{-\gamma x}$ of its intensity along the propagation direction. The damping constant γ contains contributions due to dissipation in the metal (γ_m) and to radiative loss (γ_r). The intrinsic damping γ_m follows from [1]

$$\gamma_m = \frac{2\pi}{\lambda_e}\frac{\varepsilon_m''}{(\varepsilon_m')^2}\left(\frac{\varepsilon_m'\varepsilon_d'}{\varepsilon_m' + \varepsilon_d'}\right)^{3/2}, \tag{2}$$

where ε_m' and ε_m'' denote the real and imaginary part, respectively, of the dielectric constant of the metal, while ε_d' is the real part of the dielectric constant of the solution (approximately given by the refractive index of the solvent: $\varepsilon_d' \approx n^2$). With the numbers from above and the dielectric constant of silver ($\varepsilon_m' = -18$, $\varepsilon_m'' = 0.7$ [14]) we obtain $\gamma_m = 6.3 \times 10^4\ \mathrm{m}^{-1}$. For the film thickness used in our experiment, the radiative damping γ_r is of the same order of magnitude. The gain provided by the dye solution reduces the damping by an amount which in analogy to Eq. (2) is given by

$$\gamma_d = \frac{2\pi}{\lambda_e}\frac{\varepsilon_d''}{(\varepsilon_d')^2}\left(\frac{\varepsilon_m'\varepsilon_d'}{\varepsilon_m' + \varepsilon_d'}\right)^{3/2}. \tag{3}$$

In our case this yields $-80\ \mathrm{m}^{-1}$, which means that the damping is only slightly reduced. Therefore, a rather small modification of the reflectance is expected.

To single out this weak effect with high sensitivity we apply a modulation scheme with phase-sensitive detection. The pump power is modulated by means of an electrooptic modulator at 27 MHz and a lock-in amplifier measures the corresponding modulation as detected by the photodiode. The main part of this signal stems from spontaneous decay of the dye molecules leading to excitation of plasmons on the silver film, whose radiative decay gives rise to directional emission of fluorescence light. This light is concentrated in a cone around the pump focus (see Fig. 1). To discriminate the small amount of light produced by stimulated emission against this fluorescence background, the probe beam is mechanically chopped at 23 Hz, which produces a small modulation at the output of the lock-in amplifier. This modulation is detected with a second lock-in amplifier, whose output signal—measured as a function of the incidence angle of the probe laser beam—directly reflects the difference between the reflectance curves in the presence and absence of the pump beam.

The choice of modulation frequency of the pump light is dictated by the need to suppress two types of background: (i) The heating produced by the power-modulated pump beam gives rise to a periodic variation of the optical constants of the heated materials. Because of the large volumetric thermal expansion of ethanol, mainly the refractive index of the dye solution is modulated. This effect makes the reflectance dip oscillate in its angular position, which produces a pronounced background signal. Above a cut-off frequency of roughly 10 Hz this signal declines as a function of modulation frequency ν, essentially following a $\nu^{-1/2}$ dependence, which gradually transforms to a ν^{-1} roll-off above 100 kHz, as shown by a theoretical analysis [15]. This behavior was verified by measurements in the frequency regime up to 1 MHz. At 100 kHz a reflectance change of no more than 2×10^{-5} was measured. (ii) Intersystem crossing transfers some of the excited dye molecules to the metastable triplet state with a lifetime τ_T of microseconds. Periodic optical pumping produces complementary modulations of the populations in the triplet and in the ground state. This may contribute to the change of the dielectric constant of the dye solution and thus represents a further source of background. Reliable numbers for the intersystem crossing rate and triplet lifetime are hardly available. A conservative estimation suggests that at low frequencies the triplet modulation may exceed the modulation of N_2 by as much as a factor of 100. However, at frequencies ν larger than $(2\pi\tau_T)^{-1}$ this modulation decreases in proportion to ν^{-1}.

By choosing a high enough modulation frequency we can suppress both background effects. As the roll-off of these signals is accompanied by a phase lag, the phase sensitivity of the detection helps to further reduce their contribution. At 27 MHz the background is expected to be well more than an order of magnitude smaller than the observed signal discussed below. On the other hand, as $2\pi \times 27$ MHz is below the spontaneous decay rate k_s, the modulation of N_2 is still fully present at this modulation frequency. Note, however, that on average an appreciable fraction of the molecules may reside in the triplet state, leading to a reduction of the effective density of molecules available for optical pumping. Unlike in a free-jet dye laser the circulation of the dye solution is ineffective in preventing this loss of gain, as the flow speed is far too low close to the metal surface.

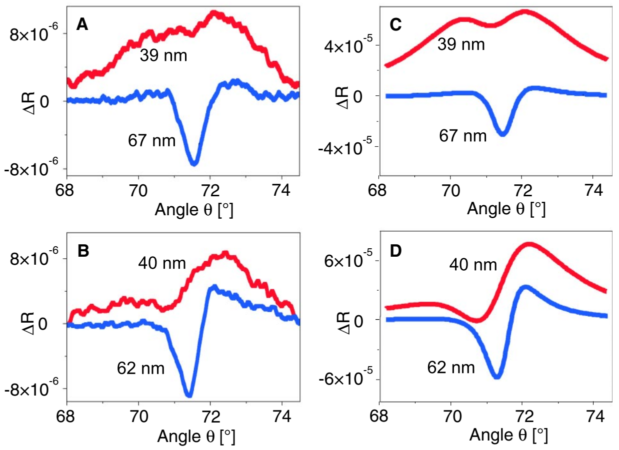

FIG. 2 (color online). Differential reflectance curves proving stimulated emission of surface plasmons for different metal film thicknesses and dyes; experiment (a), (b) and theory (c), (d). (a) and (c) refer to cresyl violet, whereas (b) and (d) depict results for rhodamine 101. The respective film thickness (measured by atomic force microscopy) is indicated for each curve. The modulation amplitude of the pump power was 10 mW root mean square (rms) for cresyl violet and 9 mW rms for rhodamine 101. The reflectance change ΔR is also given as an rms quantity. The number density of dye molecules was 7×10^{17} cm^{-3} for both dye solutions.

Figs. 2(a) and 2(b) show angular differential reflection curves obtained with the two dyes for various thicknesses of the silver film. This signal can be described theoretically in the following way: The population change ΔN_2 of level 2 leads to a change $\Delta\varepsilon_d''$ of the imaginary part of ε_d as described by Eq. (1). At the same time depletion $\Delta N_0 = -\Delta N_2$ of the ground state may contribute to $\Delta\varepsilon_d''$ if the ground state produces some absorption at λ_e. This is only a minor effect for cresyl violet and completely negligible for rhodamine 101. More importantly, both ΔN_0 and ΔN_2 produce a change $\Delta\varepsilon_d'$ of the real part of ε_d which modifies the reflectance line shape. To estimate this contribution, we calculate the spectrum of $\Delta\varepsilon_d''$ from the known absorption and fluorescence spectra of the dyes [16] and perform a Kramers-Kronig transformation to obtain $\Delta\varepsilon_d'$ at the emission wavelength. This yields $\Delta\varepsilon_d'/\Delta\varepsilon_d'' = 0.39$ for cresyl violet and $\Delta\varepsilon_d'/\Delta\varepsilon_d'' = 1.65$ for rhodamine 101.

Theoretical differential reflectance curves calculated with these numbers are depicted in Figs. 2(c) and 2(d). Absorption and emission cross sections, spontaneous decay rates and the dielectric constants of silver were taken from the literature [14,16]. For a film thickness around 40 nm the reflectance change induced by the amplifying medium is positive across the whole reflectance dip. In this case stimulated emission of SPs simply leads to an increased emission of light into the reflected probe beam due to radiative SP decay. At larger film thicknesses around 65 nm the reduced damping caused by stimulated SP emission manifests itself as a narrowing and deepening of the reflectance dip. This produces a more complicated differential line shape with both positive and negative parts. In both cases, the effect of stimulated emission is accompanied by an angular shift of the reflectance dip in accordance with $\Delta\varepsilon_d'$. The detailed signal shape therefore depends on the ratio $\Delta\varepsilon_d'/\Delta\varepsilon_d''$.

In the calculation, the following additional effects were taken into account, which affect the signal strength: (i) Refraction at the entrance face of the prism makes the beam profile elliptical with an axis ratio of 1.3. This reduces the pump intensity. (ii) The exponential decay of the pump field into the dye solution results in less efficient pumping of more distant dye molecules. The likewise exponentially decaying probe field thereby experiences an effective reduction of $\Delta\varepsilon_d$ by a factor of ~0.4. (iii) The finite size of the pump focus causes a variation of the pumping efficiency across the probe focus. Integration across the beam profiles yields a corrective factor of 0.8. (iv) As evidenced by a slightly modified reflectance dip, a thin contamination layer of photochemically deteriorated dye molecules is adsorbed to the silver film, causing extra absorption. To account for this, we assume a 1 nm thick layer whose absorption is adjusted such that the experimentally observed reflectance dip is reproduced. This layer reduces the intensity enhancement of the pump field by a factor of 0.6 to 0.8, depending on the film thickness.

The experimental curves show an excellent agreement with theory as far as the line shape is concerned. In all cases extra absorption instead of gain would lead to a distinctly different signal shape. Hence, the experimental observations provide clear evidence for stimulated SP emission. The theory predicts a reduction of the damping by $-\gamma_d \sim 10\ \mathrm{m}^{-1}$, which corresponds to a relative effect of $\sim 1.6 \times 10^{-4}$ with respect to the intrinsic damping. The measured signal levels are generally lower by a factor of 4 to 10. Two main reasons are expected to contribute to such a loss of signal: (i) An appreciable fraction of the dye molecules is trapped in the metastable triplet state, therefore not contributing to the signal. (ii) Additionally, the dye molecules closest to the metal surface are subject to an increased decay rate due to radiationless energy transfer to the metal [17]. This strongly reduces the number of molecules in level 2 in a layer approximately 20 nm thick.

In conclusion, stimulated emission of surface plasmons using optically pumped organic dye molecules as the gain medium has been realized. For future applications higher gain levels are clearly necessary. This should be feasible, since the quantum mechanical limit of the emission cross section [18], given by

$$\sigma_e = \frac{3\lambda_e^2}{2\pi}, \tag{4}$$

is many orders of magnitude higher than the values applying to even the most efficient organic dyes [19]. More efficient materials and pumping methods must be developed, including, for example, strong local field enhancement in suitable nanostructures, pumping in quantum dots, and electrical pumping in semiconductor heterostructures. The latter ones are especially promising, as they have been shown to provide gain coefficients of up to $3 \times 10^4\ \mathrm{cm}^{-1}$ [20]. This might lead to the development of novel efficient plasmon and light emitters, which holds great potential for applications in nano-optics.

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Note added in proof.—We would like to draw attention to an early proposal of a similar experiment which came to our knowledge after completion of the manuscript [21].

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