Causality of surface plasmon polariton emission processes

G. Isfort and K. Schierbaum
Heinrich-Heine Universität Düsseldorf, Institut für Physik der kondensierten Materie, Abteilung für Materialwissenschaft, Germany

D. Zerulla*
University College Dublin, UCD, Physics, Belfield, Dublin 4, Ireland
(Received 17 November 2005; published 26 January 2006)

Fundamental physical quantum phenomena, such as surface plasmon polaritons (SPP's), require specific conditions as described in their dispersion relation for excitation by photons. These conditions exactly define the **k** vector of the incident photons as well as the elastically reemitted, outbound photons that follow from the decay of the plasmon. Our conclusion demonstrates that these requisites are indeed fulfilled even on the introduction of an inelastic, wavelength-shifting process like fluorescence emission to the system. Such a process is established by placing fluorescent molecules into the strong evanescent field of the SPP. The analysis of the outbound photons shows an angular behavior, which can only be explained if the fluorescent photons also satisfy SPP conditions. This behavior enables the development of a model for the chronology and causality of surface plasmon polariton deexcitation mechanisms.

DOI: 10.1103/PhysRevB.73.033408 PACS number(s): 73.20.Mf, 78.66.−w, 42.82.Gw

I. INTRODUCTION

Surface plasmon polaritons (SPP's) play an important role in a multitude of applications such as surface-enhanced Raman scattering (SERS) and surface plasmon resonance (SPR).[1,2] It is therefore expected that a fundamental understanding of the mechanisms and chronology of SPP excitations and deexcitations will unlock novel perspectives and methodologies—e.g., ultrasensitive detectors required for biotechnology.[3,4] The dispersion relation of SPP's dictates the conditions under which they are excited. Specifically, their excitation is not possible by direct irradiation of photons on the thin metal film but requires special optical configurations, such as those initially proposed by Raether and Kretschmann[5] and Otto.[6] Their common property is that the photons approach from an optically denser medium, before impinging on the metal in an attenuated total reflection (ATR) setup.[5,6] In this paper we will exclusively use the Kretschmann configuration (see Fig. 1). For SPP's excited at thin, smooth metal surfaces, the excitation of an SPP according to its dispersion relation is given by the equation (see Ref. 7)

$$k_x = \frac{\omega}{c}\sqrt{\frac{\epsilon_1+\epsilon_2}{\epsilon_1\epsilon_2}} = \frac{\omega}{c}\sqrt{\epsilon_0}\sin(\alpha), \qquad (1)$$

where ϵ_i is the optical constant of medium i (see Fig. 1). Using Fresnel equations by the matrix formalism from the optical constants at a given wavelength, the reflectivity and field enhancement of the SPP for a multilayered system (which consists of the prism substrate ϵ_0, metal film ϵ_1, sample molecules ϵ_2, and additional layers such as a passivating layer) can be calculated.[8] Following the creation of the SPP, its consequential decay may occur by the emission of photons under equivalent conditions. More precisely, the photons have identical wavelengths and after reflection they proceed with the same angle with respect to the metal surface. Due to scattering processes in the metal layer (e.g., surface roughness or impurities), the emitted photons partially lose their spatial coherence, but the angle with respect to the surface is conserved. This leads to the so-called ATR ring which is shown in Fig. 2. The intensity of the displayed ATR ring depends strongly on the roughness of the surface, the quality of which has been additionally controlled by atomic force measurements (AFM).[9] In connection to this publication[9] an interesting property of the emitted light in the ATR cone was discovered—namely, its polarization dependence—the results of which can be found in Ref. 10. Consequently, this paper will investigate the causality and time dependence of interactions between an SPP and those molecules, which have been introduced into its enhanced evanescent electromagnetic field, thus resulting in a wavelength-shifted reemission of photons.

II. MEASUREMENTS

In order to investigate the resonant coupling of plasmon polaritons, excited by an ATR optical configuration, and fluorescent molecules in the near field, the first concern is to investigate the spatial dependence of the spectral emission of the chosen fluorescent dye. Rhodamin 6G was used as dye for the experiments due to its high stability and because it is a strong emitter with a broad spectral emission. Prior to the

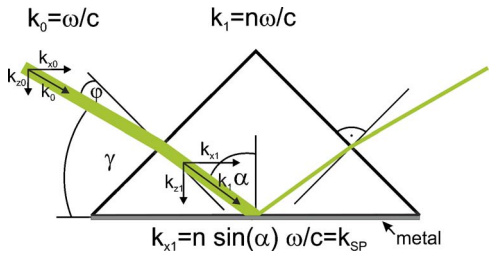

FIG. 1. (Color online) The ATR-SPP setup (Kretschmann type). Note the differences in definition between angles α, γ, and φ.

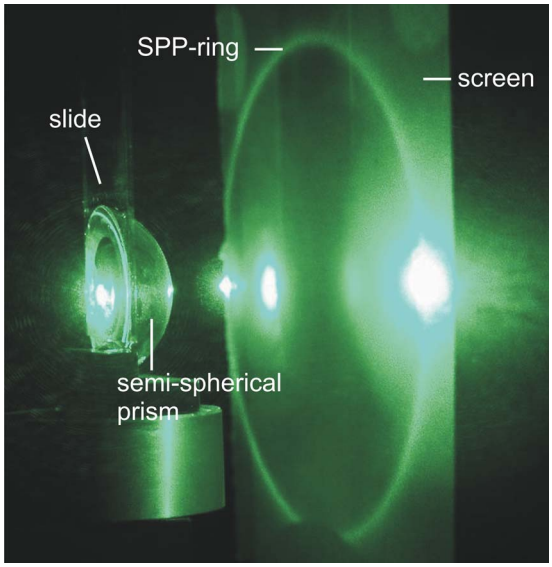

FIG. 2. (Color online) The ATR-SPP setup (Kretschmann type). Plasmon excitation at 514.5 nm on an evaporated silver film. The ATR SPP cone is projected onto a screen and is visible as a bright circle. The "spots" are a result of the unscattered strong laser light and its partial reflections, while the brightness of the circle in respect to the spots is a measure of the silver surface roughness. For the sake of illustrating the phenomenon an untypical rough silver film and a semispherical prism were used.

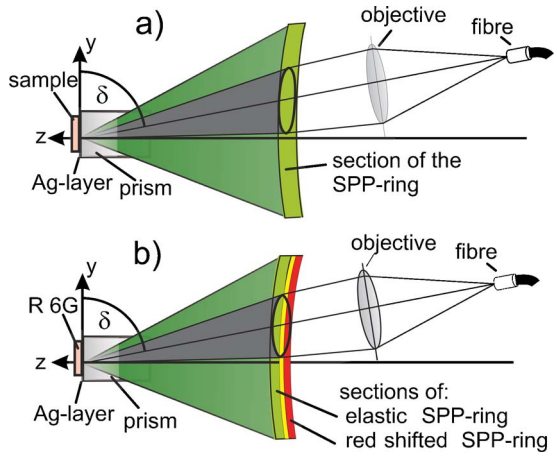

FIG. 3. (Color online) (a) Sketch for the detection of elastically scattered photons within the ATR cone. (b) Sketch of the wavelengths distribution and its detection within the ATR cone.

SPP experiments the spatial dependence of the dissolved dye excited at 514.5 nm was tested. The outcome proved that the spectral emission is isotropic after subtraction of the elastically scattered background. Following this first experiment, the setup was transformed into a Kretschmann-type ATR setup. In order to prevent quenching, charge-transfer reactions, and so-called SERS first-layer (hot-spot) effects, the thin silver layer (thickness 50 nm) was passivated with a hexadecanethiol self-assembling monolayer. This monolayer is stable, dense, and well ordered so that the rhodamin molecules are effectively blocked from reaching the Ag surface.[11,12] Optimized parameters for the excitation of the SPP prevented the laser photons from reaching the dye molecules directly; rather, excitation occurred through the excited plasmon. Following the excitation of the dye via the SPP an intense fluorescent signal was detected and analyzed, showing that the strong evanescent field of the SPP was the source of the excitation of the dye.

The investigations focused mainly on the angular distribution of the emitted fluorescence photons. In a simple model, one would expect that the SPP decays radiatively followed by photon absorption via the dye molecules. The response would be a redshifted fluorescent emission. Assuming that no coupling between the excitation and emission processes of the photons occurs, the emission would be of an isotropic nature.

However, if a coupling via the evanescent field were postulated, the angular intensity distribution would predict maxima at the same angles as the SPP photon emission—i.e., similar to forward and backward scattering. In particular, this distribution is expected to be independent of the emitted (redshifted) wavelength but to have its maximum for an angle, which would still be valid for the SPP excitation with the 514.5-nm laser photons.

Nevertheless, the physical measurements show a different behavior. The angular distributions of the emitted photons are sharply defined and depend on the respective emitted wavelength. The case for the simple ATR cone is shown in Fig. 3(a) while the results of the fluorescent emission are displayed in Fig. 3(b). In order to quantify the results in a more precise way, interference filters have been used to investigate spectral parts of the broad rhodamin 6G emission. The filters have maximum transmissions for redshifted wavelengths of 534.7 nm (shift 752 cm^{-1}) and 583.9 nm (shift 2330 cm^{-1}). Together with the elastically Rayleigh-scattered light at 514.5 nm (shift 0 cm^{-1}), three different wavelengths were chosen to illustrate the following facts:

According to these conditions the relative change in azimuth for the maximum of the shifted emission at 752 cm^{-1} is $1.5° \pm 0.5°$ with respect to the Rayleigh-scattered light. For the shifted emission at 2330 cm^{-1} the deviation is $3.7° \pm 0.5°$ with respect to the Rayleigh-scattered photons. The changes in azimuth for the three wavelengths are shown in Fig. 4.

The energy spacings are not uniform for the three used filters. Also, it is reasonable to compare the measured results with simulations of the excitation of an SPR for the three wavelengths (see Fig. 5). The simulations show that the angle with respect to the surface normal is decreased for longer wavelengths, as shown in the measurements. The relative shifts are $\Delta\alpha_{1,2}=0.7°$ and $\Delta\alpha_{2,3}=0.9°$, respectively.

For comparison with the experimental data one also has to take the dispersive properties of the ATR prism into account and to transform the internal ATR angle α (within the prism) into the external angle φ or γ by means of applying simple ray optics and geometrical considerations according to the optical constants $\epsilon(\lambda)$: $\varphi=\arcsin[\sqrt{\epsilon_{prism}(\lambda)}\sin(\alpha-45°)]$.[13] The results of this transformation are shown in Table I. The changes in azimuth according to calculations are now 1.3° (for 752 cm^{-1}) and 3.1° (for 2330 cm^{-1}) both with respect to the Rayleigh-scattered photons. This is in very good agreement with the recorded measurements, especially if one takes into account that surface plasmon resonance is extremely

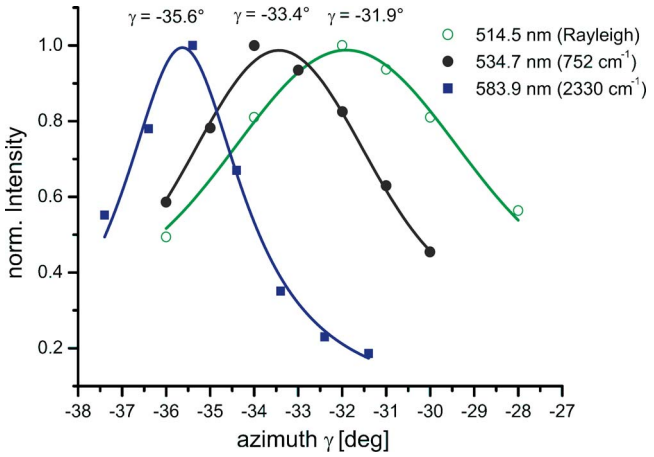

FIG. 4. (Color online) Measured angular dependence of the fluorescent emission with respect to its wavelength.

sensitive to changes in thickness as well as reactions involving sulphur and oxygen with the silver layer.

While the transformation from internal angles α to external angles φ already contains the refraction of the photons at the prism-air interface, all remaining effects (besides the SPP) connected to the total reflection at the prism-metal interface and its evanescent field have been so far neglected. The total internal reflection from the rear facet of the prism causes a small but measurable displacement of the light. A comprehensive analysis of this phenomenon, which is known as the Goos-Hänchen effect, can be carried out by decomposition of the incident beam into its plane-wave spectrum,

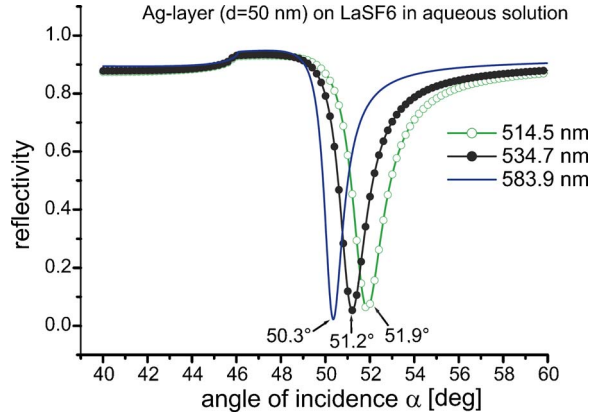

FIG. 5. (Color online) Calculation of the SPP excitation with respect to the angle α for the selected three wavelengths.

TABLE I. Results of the ATR-SPP calculations and their transformation into external azimuth angles in comparison to the measurements.

cm^{-1}	α_{calc}	φ_{calc}	γ_{calc}	γ_{meas}	$\Delta\gamma_{calc}$	$\Delta\gamma_{meas}$
0	51.9°	12.9°	32.1°	31.9°	—	—
752	51.2°	11.6°	33.4°	33.4°	1.3°	1.5°
2330	50.3°	9.8°	35.2°	35.6°	3.1°	3.7°

computation of the Fresnel reflection coefficients for each such plane wave, and superposition of the reflected plane waves.[14–17] The Goos-Hänchen effect is a direct consequence of the evanescent field. The resulting effect is of the order of the chosen wavelength and is a pure displacement and not a change in angle.[17] For this reason this effect can be neglected. This is still true if the light undergoes a change in wavelengths within the evanescent field as happens here due to the fluorescence. Emile *et al.* showed that even a second-harmonic generation process in a nonlinear medium does not change the angle of reflection[18] and even investigations of this effect with surface plasmons have been carried out.[19,20] These experiments produced positive or negative lateral optical beam displacements but again no change in angle was observed.

As a consequence, the measured and simulated azimuth angles can only be derived by applying the SPP dispersion relation for the different reemitted wavelengths.

III. CONCLUSION

The fluorescent emission, excited in the near field of the evanescent SPP field, remains a coherent process and therefore obeys the new conditions for the excitation of the plasmons as a result of the changed wavelength. By doing this it allows us to determine the causality of the underlying mechanisms of the entire process. It is shown experimentally that depending on the wavelength of the incident photons there is exactly one angle of incidence which will excite an SPP. This SPP has a strong, evanescent field. Instead of releasing a photon that is subsequently absorbed by a molecule, the SPP field directly interacts with the molecule in the near field, thereby maintaining its SPP character. The process might generate the equivalence of a fluorescent photon which still follows the SPP conditions in combination with the properties of its evanescent field. The fluorescent photons are then coherently emitted in wavelength dependent azimuth angles on the prism side of the metal film, in accordance with the SPP conditions.

*Electronic address: dominic.zerulla@ucd.ie

[1] K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. R. Dasari, and M. S. Feld, Phys. Rev. Lett. **78**, 1667 (1997).
[2] A. P. Hibbins, B. R. Evans, and J. R. Sambles, Science **308**, 670 (2005).
[3] J.-N. Lin and C. J. Wilson, U.S. Patent No. 5,776,785 (1998).
[4] J. Malicka, I. Gryczynski, and J. R. Lakowicz, J. Biomol. Screening **9**, 208 (2004).
[5] E. Kretschmann and H. Raether, Z. Naturforsch. A **23**, 2135 (1968).
[6] A. Otto, Z. Phys. **216**, 398 (1968).
[7] H. Raether, *Surface Plasmons* (Springer Verlag, Berlin, 1988), Vol. 111.
[8] C. E. Reed, J. Giergiel, J. C. Hemminger, and S. Ushioda, Phys.

Rev. B **36**, 4990 (1987).
[9] G. Isfort, Ph.D. thesis, Universität Düsseldorf, 2005.
[10] D. Zerulla, G. Isfort, and K. Schierbaum (unpublished).
[11] D. Zerulla, I. Uhlig, R. Szargan, and T. Chasse, Surf. Sci. **402-404**, 604 (1998).
[12] D. Zerulla and T. Chasse, Langmuir **18**, 5392 (2002).
[13] E. D. Palik, *Handbook of Optical Properties of Solids* (Academic Press, Orlande, FL, 1985).
[14] F. Goos and H. Hänchen, Ann. Phys. **1**, 333 (1947).
[15] H. K. V. Lotsch, Optik (Stuttgart) **32**, 299 (1971).
[16] H. K. V. Lotsch, Optik (Stuttgart) **32**, 116 (1970).
[17] F. Bretenaker, A. Le Floch, and L. Dutriaux, Phys. Rev. Lett. **68**, 931 (1992).
[18] O. Emile, T. Galstyan, A. Le Floch, and F. Bretenaker, Phys. Rev. Lett. **75**, 1511 (1995).
[19] C. Bonnet, D. Chauvat, O. Emile, F. Bretenacker, and A. Le Floch, Opt. Lett. **26**, 666 (2001).
[20] X. Yin, L. Hesselink, Z. Liu, N. Fang, and X. Zhang, Appl. Phys. Lett. **85**, 372 (2004).