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Modification of spontaneous emission lifetimes in the presence of corrugated metallic surfaces

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We report the results of measurements of the spontaneous emission lifetime of a Eu^{3+} complex in the presence of a nearby metal surface. The excited-state lifetime of the ions are measured as a function of their separation from both planar and periodically corrugated metallic surfaces. Several corrugated silver surfaces were used, each having a different combination of pitch and amplitude. No significant difference is found between data obtained for ions situated above a planar silver surface and those above corrugated surfaces that have pitches greater than the emission wavelength. However, for surfaces with a pitch less than the emission wavelength, differences are seen, and are shown to increase with increasing corrugation amplitude. Possible explanations for the observed differences are given, including a discussion of the role of surface plasmon polariton modes on corrugated metallic surfaces. [S0163-1829(99)05511-3]

I. INTRODUCTION

The fluorescence properties of an emitter are controlled not only by the electronic wave functions of the emitter, but also by the local optical environment, a point first noted by Purcell.[1] In particular the emission of energy in the form of a photon requires the surrounding structure to support a photon mode. The strength of the coupling between the emitter and the photon mode depends on the density of such modes at the emission frequency, a concept we refer to as photonic mode density (PMD). Boundary conditions imposed on the electromagnetic field by the local structure, notably reflecting and absorbing surfaces, may modify the local photonic mode density, thereby changing the probability of spontaneous emission. Although much work has been carried out on fluorescence near metallic interfaces, relatively little experimental work has been reported in cases where the reflecting surfaces posses periodic texture on the scale of the wavelength of the light.

In the 1970s an elegant series of experiments were performed by Drexhage *et al.*[2] in which a technique of sequentially stacking inert organic monolayers was used to separate a monolayer of fluorescing molecules from a metal surface. By adjusting the number of inert spacer monolayers, the separation between the emitter and the metal surface could be controlled to within a few nm. The excited state lifetime and the radiation pattern were measured as a function of the separation. It was found that the emission was dictated by an interference condition between direct and reflected fields, giving rise to oscillations in the excited-state lifetime and striking features in the radiation pattern from the emitting layer. Further, when the separation was small (less than 10 nm) the excited-state lifetime was found to reduce monotonically to zero, see Fig. 1. These features were successfully modeled by Chance, Prock, and Silbey,[3] who described the emitting ions as forced, damped, oscillating electric dipoles.

The oscillations in the excited state lifetime with distance are the result of the phase of the reflected field at the dipole site changing as the separation was varied. When the reflected field is in phase with the source field, emission is enhanced, thus reducing the lifetime; when it is out of phase the emission is suppressed. The reduction in the excited-state lifetime in the small separation regime was identified with the excitation of surface plasmon polaritons (SPP's) at the metal surface. The SPP modes have wavevectors greater than that of light of the same frequency. Consequently, coupling between the emitters and SPP modes takes place via the high wave vector, near-field components of the dipole field (these are the evanescent components of the dipole field). At still smaller separations a further reduction in the excited-state lifetime was observed, arising from coupling between the emitter and lossy modes of the metal (e.g., electron hole pair excitation) as shown by Pockrand, Brillante, and Möbius.[4]

We have recently reported how the thickness of a metal film affects the emission from ions situated nearby.[5] As the thickness of the metal film is reduced the fields associated with the emitter can penetrate the metal to excite SPP modes on the far side of the metal film. This introduces an extra decay route with the consequence that the excited state lifetime may be reduced still further in the small emitter/metal

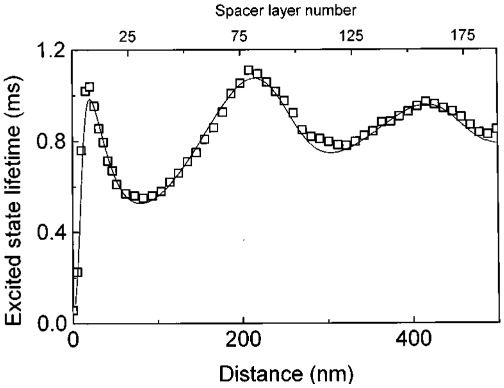

FIG. 1. The excited state lifetime of Eu^{3+} ions situated above an infinite planar silver mirror as a function of emitter/metal distance. The open squares are experimental data points, the size of which indicates the error in the value. The solid line is a theoretically derived curve in which the experimentally derived values of the silver parameters, the dielectric constant for the spacer layers (22-triconsenoic acid) and thickness were used. The quantum efficiency was adjusted to obtain the best fit (and is equal to 0.7 ± 0.05).

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separation regime. The experimental results were compared to the theory of Chance, Prock, and Silbey[3] and excellent agreement was obtained. Furthermore, at larger emitter/metal separations, the metal film thickness may also affect the oscillations in the excited-state lifetime. This was attributed to the lower reflectivity of the thin metal film resulting in a modification of the interference condition.

The channels by which the emitter may loose its energy may be summarized as follows. The emitter may decay via the production of radiation, or it may decay nonradiatively to produce SPP modes or lossy modes in the metal as described above. The density of modes associated with both radiation and SPP's depends on the specific sample geometry and composition. The local photonic mode density thus comprises components due to radiation and SPP modes. We have discussed above the fact that both of these components may be changed, the first by altering the emitter/metal separation, the second by, for example, reducing the thickness of the metal layer. It is interesting to ask how the spontaneous emission may be further modified if the metal surface is periodically corrugated rather than planar. In this case the translational symmetry of the system is broken and new factors may come into play.

(i) Breaking the translational symmetry of the plane allows nonradiative modes, such as SPP's, and if present, waveguide modes, to couple to radiation by scattering from surface structure. Bragg vectors associated with periodicities in the surface profile may provide the momentum required to couple such nonradiative modes and photons.[6]

(ii) Scattering of surface modes by the corrugation may give rise to band gaps in the propagation of SPP modes on the surface.[7] If the emission frequency of the emitter lies in the band gap then this decay route may be blocked, if on the other hand the emission frequency lies at the band edge the SPP decay route may be enhanced.[8] For a singly corrugated surface the dispersion of the SPP modes and the nature of any band gap depends on the direction of propagation of the mode on the surface.[9] This makes quantifying the effect of a corrugation on the probability of the emitter decaying via the SPP channel difficult, a point we will come back to later.

(iii) Surface modes such as SPP's may become localized in the presence of appropriate surface structure. Localization leads to dramatic enhancements in the local photonic mode density associated with them.[10]

(iv) All emitter sites within a sample are no longer equivalent; some emitters may be in a trough, others at a peak of the corrugation profile. These different sites will have different photonic mode densities associated with them.

(v) Corrugating the surface may reduce the reflectivity as seen by the emitters since some light may be scattered into diffracted orders rather than reflected specularly.

Nonradiative SPP modes that are initially excited by the decay of a nearby emitter may scatter to produce photons, as demonstrated by Knoll, Philpott, and Swalen.[11] They used the LB technique pioneered by Kuhn and Drexhage[2] to separate a monolayer of dye molecules from a corrugated silver surface, i.e., a metallic grating. By examining the polarization, wavelength, and intensity dependence of the emission as a function of emission angle, they were able to show that the majority of the radiated power was produced via the SPP decay channel for dye films ~10–15 nm from the metal surface. Adams *et al.*[12] measured the emission from N_2 films deposited on silver, for films up to 2000 nm thick. In contrast to the work of Knoll, Philport, and Swalen the films used by Adams *et al.* were thick enough to support waveguide modes, as well as SPP's; both types of mode were clearly seen in the measured radiation patterns, features that had been predicted by Aravind, Hood, and Metiu.[13]

With careful control of the corrugation used in such experiments, a band gap in the propagation of SPP modes may be produced. The band gap arises when the pitch of the corrugation provides just the required momentum to backscatter the SPP mode. The two counter propagating SPP modes set up a standing wave and, owing to the different surface charge and field distributions associated with the two standing wave solutions, a band gap is opened up.[14] Thus the SPP decay channel may be turned off.

By examining the intensity of emission from a laser dye spun down on top of a corrugated silver surface, Kitson, Barnes, and Sambles[15] recently demonstrated blocking of the SPP decay channel with this technique. The radiation pattern arising from emission of a spun film of DCM laser dye was measured as a function of the emission angle (both polar and azimuthal angles). Since the spun film was directly in contact with the metal the fluorescence was heavily quenched by decay to SPP modes at the metal surface. They showed that by suitably corrugating the surface the energy lost to the SPP modes could be recovered as radiation. To conserve momentum this coupling only occurred at well-defined angles dictated by the pitch of the corrugation. They also showed the existence of energy band gaps in the dispersion of the SPP modes that arose due to the coupling between propagating and counter propagating SPP modes via the periodic surface. If the emission energy of the dye coincided with the band gap no excitation of SPP modes was possible, giving rise to a decrease in the fluorescence intensity at angles corresponding to the gap region.

For the single corrugation used, SPP propagation was only blocked over a small range of directions centered on the normal to the corrugation groves. This matter is developed further in the discussion and has been reported elsewhere.[9] To block SPP propagation in all directions and, therefore, to turn off the SPP decay route at the emission frequency completely, a surface that is periodically modulated in at least two directions is required. Kitson, Barnes, and Sambles[16] demonstrated that a hexagonally textured surface could indeed be used to produce such a complete SPP band gap.

The work mentioned above has concentrated on radiation patterns produced in the presence of corrugated surfaces. For a given emitter/metal separation, differences between radiation patterns in the presence of planar and corrugated surfaces arise due to the coupling of nonradiative guided modes and radiation by Bragg scattering. Such measurements do not address the question of whether corrugated surfaces also change the photonic mode density; to answer this question requires the measurement of spontaneous emission lifetimes. Considerable theoretical effort has been devoted to this last problem. In a series of papers, Leung and co-workers[17–22] considered the effect of corrugated metal surfaces on fluorescent emission from nearby molecules. Several of their papers have in particular dealt with the issue of the decay rate of an excited molecule above a corrugated metal surface.[17,18,22] Several assumptions were made, notably, that the depth/pitch ratios for the corrugations are very small (weak modulation) so that first-order perturbation theory may be applied. Their theory predicts morphology-dependent resonances that cause significant changes in the decay rate compared to the decay rate in the presence of a planar surface. Indeed, the predicted changes, often an order of magnitude, seem quite remarkable for the very weak corrugations considered. It is with these considerations in mind that the present experimental investigation has been undertaken.

Our study involves repeating the experiments of Drexhage *et al.*[2] using substrates with a variety of geometries. We have therefore measured the spontaneous emission lifetime as a function of emitter/metal separation both for planar silver metal surfaces and for a variety of corrugated silver surfaces. By comparing data for different samples we are able to examine how surface corrugation modifies the spontaneous emission lifetime and thus say something about the associated photonic mode density.

II. EXPERIMENT

Substrates were made from flat, polished silica slides. They were first cleaned and exposed to hexamethyldisilazane (HMDS) to render their surface hydrophobic. A silver film 200 nm thick was deposited onto one side by thermal evaporation so forming the metallic mirror. A Langmuir-Blodgett (LB) spacer film was then deposited onto the silver film as a sequence of monolayers, followed by a monolayer of an organic complex containing a Eu^{3+} ion. 22-tricosenoic acid was chosen for the spacer film because of the relative ease with which it may be deposited and because of its transparency at the emission wavelength of the Eu^{3+} ions. It was deposited at a surface pressure of 30 mNm^{-1} at 25 °C with *Y*-type deposition (subphase purity of 18 $M\Omega cm^{-1}$ and pH of 5.5).

The Europium complex (hexadecyl pryidinium tetrakis 1-3 diphenyl 1-3 propanedione europium III) consisted of a symmetrical arrangement of four bidentate ligands and a long hydrophobic hydrocarbon chain, the latter to aid LB film forming properties. However, a stable floating monolayer of this material could not be produced, despite trying a range of subphase pH and temperature. Furthermore, even at modest surface pressures (greater than 10 mNm^{-1}) the floating monolayer collapsed forming bilayer regions and crystallites. Normal deposition onto a glass slide at pressures greater than 25 mNm^{-1} produced very poor quality LB films consisting of a large number of defects and crystallites. Attempting to deposit at lower surface pressures simply resulted in no transfer of material to the substrate. To overcome this problem the europium complex was deposited at a surface pressure of 5 mNm^{-1} thus avoiding film collapse, the substrate being lowered through the film horizontally. By depositing different numbers of acid bilayers, 16 different spacer-layer thicknesses could be deposited onto one substrate.

The corrugated samples were produced by exposing a thin photoresist film to an interference pattern. After development, the substrate was ion etched to transfer the pattern from the photoresist to the glass substrate. However, it was found that as the pitch of the corrugations decreased the amplitude of the etched corrugations in the substrate decreased dramatically. Reproducible short pitch corrugations were therefore produced using an alternative technique. Replica corrugated samples were formed from a hardened photoresist master. Heated (120 °C) Perspex pieces were contacted onto the master, removed and cooled to produce a replica surface. A large planar region was present on the replica samples and used as a control region to compare with both silica polished planar samples and theory.

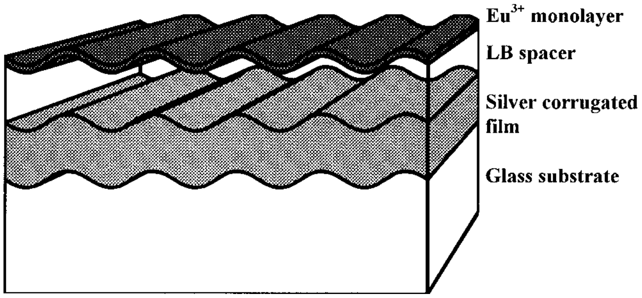

FIG. 2. The corrugated sample structure consisting of four layers. The first is a 10-mm-thick glass disk with an etched corrugated relief profile on one surface. The glass is coated with a 200-nm-thick silver film. Spacer layers of 22-tricosenoic acid are deposited via the LB technique, and finally via the same technique, a single monolayer of a europium complex was added.

Depositing high-quality LB films onto corrugated samples also presented problems. Depositing 22-tricosenoic in the usual way often resulted in films that contained a large number of defects. This was alleviated by ensuring that the corrugations were perpendicular to the water surface. The deposition speed was also decreased from 1 to 0.1 $mm\,s^{-1}$. The europium complex was deposited satisfactorily using the horizontal transfer technique described above. The sample geometry used is shown in Fig. 2.

The europium complex was excited with a 5-ns pulse from a nitrogen laser at a wavelength of 337 nm. This pump source excited the bidentate ligand of the complex, from which energy is transferred to the europium ion. Emission from the ion was centered at 614 nm, the emission spectrum of an LB film containing the europium complex is shown in Fig. 3. The emission was collected by a lens and passed through a spectrometer set to pass 614 nm with a bandwidth set to 10 nm. A cooled (−30 °C) photomultiplier was used to detect the emerging light. The photomultiplier was connected to a multichannel scalar averager (Stanford SR340), which was operated in photon counting mode and was triggered by a pulse from a photodiode that sampled part of the pump beam. The overall temporal resolution was 5 ns. An example of such data is shown in Fig. 3, showing the fluorescence decay of the europium complex in the absence of a metallic mirror. (The lifetime of the europium complex powder was measured to be 0.93 ms.)

Excited-state lifetimes were determined by fitting a single exponential decay, with an offset, to the experimental data. This was done using statistical weighting of the data of the form $1/y$ where y is the data value. The χ-squared difference per data point between the fitted function and the experimental data was typically unity. A minority of data sets were found to be better fit by a biexponential decay. The short-lifetime component was always significantly weaker than the

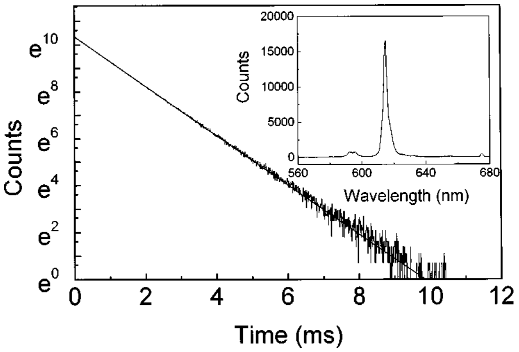

FIG. 3. The time evolution of the fluorescence from a monolayer of the europium complex that is deposited onto a silica glass slide via the LB technique. The fluorescence was collected at 614 nm. The solid line is a single exponential fit of the form given in the text and gives an excited state lifetime of 0.93 ms for the material. The inset shows the fluorescence intensity as a function of wavelength for a sample of europium chelate (Hexadecyl pyridinium tetrakis 1-3 diphenyl 1-3 propandione europium III). The emission at 614 nm is electric dipole in nature and accounts for 90% of the total emitted light.

long-lifetime component and showed no oscillatory dependence on ion-mirror separation. Consequently for these data the long lifetime is the one recorded here.

The relative permittivity of the metal films used, together with the corrugation profiles were determined by obtaining angle-dependent reflectivity data. Theoretical models of the reflectivity were the fit to the data, the relative permittivity and corrugation profile being fitting parameters. The theoretical model for the reflectivity calculations used a coordinate transformation technique initially introduced by Chandezon, Dupuis, and Cornet.[23] Details of the experimental arrangement and fitting procedures have been given elsewhere.[24,25]

III. RESULTS

The dependence of the excited state lifetime for Eu^{3+} ions above a planar silver film on the emitter/metal separation is shown in Fig. 1. The expected oscillations in the excited state lifetime are seen, due to the interference between direct and reflected emission. The quenching at small separations noted in the introduction is clearly present. Also shown in Fig. 1 is a numerically calculated line based on the theory of Chance, Prock, and Silbey.[3] The calculation uses the relative permittivity of the LB spacer layer and the relative permittivity of the silver film, both of which were derived from reflectivity measurements described above. For the purposes of modeling, the europium complex monolayer was assumed to have the same optical properties as the 22-tricosenoic acid.[5,26] Emission was assumed to be purely electric dipole in nature and the dipole orientation assumed to be effectively isotropic, i.e. the dipole moment sampled all spatial directions on a time scale much faster than the spontaneous emission lifetime. Further, the emission was taken to be monochromatic at 614 nm. The only adjustable parameter in the model was thus the quantum efficiency of the transition and the best fit to the experimental data was obtained when the quantum efficiency equaled 0.7±0.05, in good agreement with Chance, Prock, and Silbey.[3] Further details of the calculations are given in Refs. 3, 5, and 26.

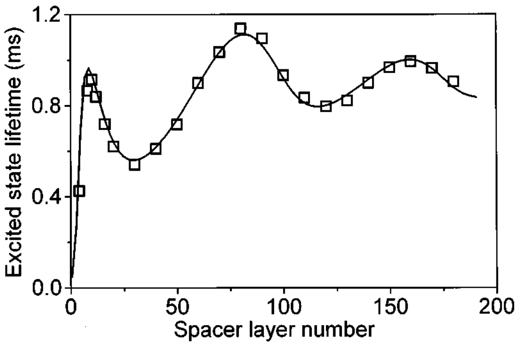

FIG. 4. The excited-state lifetime of a monolayer of the europium complex situated above a corrugated silver surface of pitch 1075 nm and amplitude 39 nm as a function of distance. The solid line is a theoretically modeled curve for a *planar* surface in which the experimentally derived values of the silver parameters, the dielectric constant for the spacer layers (22-triconsenoic acid) and thickness were used. The quantum efficiency was equal to 0.7 ±0.05. It should be noted that there is little or no difference between corrugated and planar surfaces.

Figure 4 shows how the excited-state lifetime depends upon the distance from a 1074.8×0.1 nm pitch corrugated surface of amplitude 39.8±0.1 nm. Also shown is the theoretical dependence for a *planar* surface based upon the experimentally determined silver parameters for this particular film. Clearly there is very little difference between planar and corrugated regions.

Figure 5 shows how the excited state lifetime depends upon the distance from a 800.7±0.1 nm pitch corrugated surface of amplitude 18.9±0.1 nm. Again, the theoretical dependence for a planar surface is shown for comparison, based upon the experimentally determined silver parameters. Here too there is very little difference. These two results suggest that provided the pitch is larger than the emission wavelength and the amplitude of the surface modulation is small, there is little affect on the excited-state lifetime. We

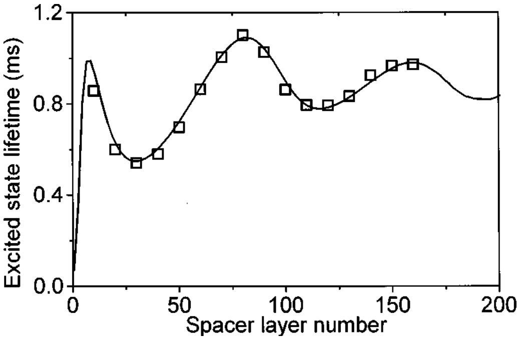

FIG. 5. The excited-state lifetime of a monolayer of the europium complex situated above a corrugated silver surface of pitch 801 nm and amplitude 19 nm as a function of distance. The solid line is a theoretically modeled curve for a *planar* surface in which the experimentally derived values of the silver parameters, the dielectric constant for the spacer layers (22-triconsenoic acid) and thickness were used. The quantum efficiency was equal to 0.7 ±0.05. It should be noted that there is little or no difference between corrugated and planar surfaces.

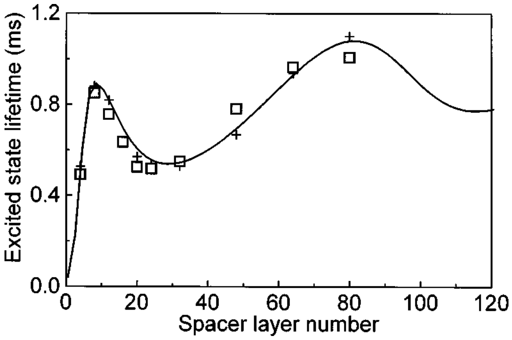

FIG. 6. The excited-state lifetime of a monolayer of the europium complex situated above a corrugated silver surface of pitch 408 nm and amplitude 30 nm as a function of distance. The solid line is a theoretically modeled curve for a *planar* surface in which the experimentally derived values of the silver parameters, the dielectric constant for the spacer layers (22-triconsenoic acid) and thickness were used. The quantum efficiency was equal to 0.7 ±0.05. It should be noted that there is a difference between planar and corrugated regions at a distance of 48 and 80 spacer layers.

thus infer that there is little change in the local photonic mode density, probably because such surfaces perturb the reflected field only slightly and also produce little change in the density of SPP modes on the surface.

Figures 6 and 7 show the separation dependence of the excited-state lifetime for Eu^{3+} ions situated above 407.7 ±0.1 nm pitch surfaces of amplitudes 30±1 and 68 ±4 nm, respectively. Clearly there is now a difference in the separation dependence of the excited-state lifetime, both between the corrugated surfaces and the planar surface, and between the two different corrugated surfaces. The most noticeable change is a reduction in the amplitude of the oscillations of lifetime with separation. There is also a significant reduction in lifetime for the smallest values of *d* measured, possibly related to a change in the PMD associated with the SPP mode. A discussion of these and other matters is given in the next section.

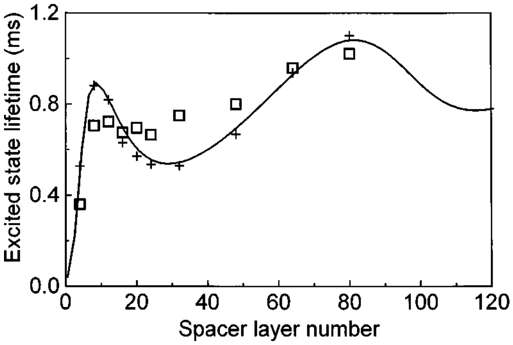

FIG. 7. The excited-state lifetime of a monolayer of the europium complex situated above a corrugated silver surface of pitch 408 nm and amplitude 68±4 nm as a function of distance. The solid line is a theoretically modeled curve for a *planar* surface in which the experimentally derived values of the silver parameters, the dielectric constant for the spacer layers (22-triconsenoic acid) and thickness were used. The quantum efficiency was equal to 0.7 ±0.05. It should be noted that there is now a significant difference between planar and corrugated regions for most of the spacer-layer regions.

Before moving to that discussion we should note that it was not possible to identify whether molecules with different lateral position with reference to the corrugation experienced different decay rates. Different sites, if they have different lifetimes, will produce a multiexponential fluorescence decay curve. Since some data were nonexponential on the planar regions, we are unable to infer whether different sites have different lifetimes. A site-selective excitation (or collection) technique would be needed to investigate this aspect further.

IV. DISCUSSION

As discussed in the introduction, the excited-state lifetime of an emitter above a planar metal surface is determined by two conditions, that of interference between direct and reflected fields, and coupling to the SPP mode. A corrugated surface may be expected to modify both conditions.

Firstly, the interference condition may be modified since the far field of the dipole may be diffracted by the periodic surface modulation. This process is likely to reduce the reflected field at the site of the emitter since diffracted fields are unlikely to have the same phase as specularly reflected ones. Assuming diffraction reduces the reflected field, and therefore reduces the modulation of the photonic mode density, we would expect the amplitude of the lifetime oscillations to be reduced.

Secondly, periodic corrugation of the surface leads to the existence of energy gaps in the SPP dispersion.[7,9] Bragg scattering from this periodic modulation couples propagating and counter propagating SPP modes to produce two standing wave solutions. The two solutions have different field profiles and different surface charge densities associated with them. Consequently the two standing wave solutions have different energies, but the same wave vector. The high-energy solution has field extrema at the corrugation troughs whilst the low-energy solution has field maxima at the corrugation peaks.[14]

For SPP modes propagating perpendicular to the corrugation grooves a band gap arises when the following relationship is satisfied,

$$k_{\mathrm{SPP}}=G/2, \tag{1}$$

where **G** is the corrugation vector equal to 2π/corrugation pitch, and k_{SPP} is the SPP wave vector. For SPP modes propagating in the plane of the surface at an angle φ (the azimuthal angle) to the corrugation Bragg vector **G**, the condition for a band gap is[9]

$$k_{\mathrm{SPP}}=\frac{G}{2\cos\varphi}. \tag{2}$$

Thus for a given corrugation pitch and SPP wave vector (i.e., given corrugation sample and an SPP mode with a frequency equal to the emission frequency of the Eu^{3+} ions) the gap will occur at some value of the angle φ. (Note, this will only be true provided $k_{\mathrm{SPP}}>G/2$.) The width of the gap depends upon the corrugation amplitude.[14] The azimuthal angle range over which SPP propagation is forbidden depends upon the position of the upper and lower band edges, see Fig. 8, and hence is determined by the corrugation pitch and amplitude, details are given in Ref. 9. The effect of the spacer layer is to

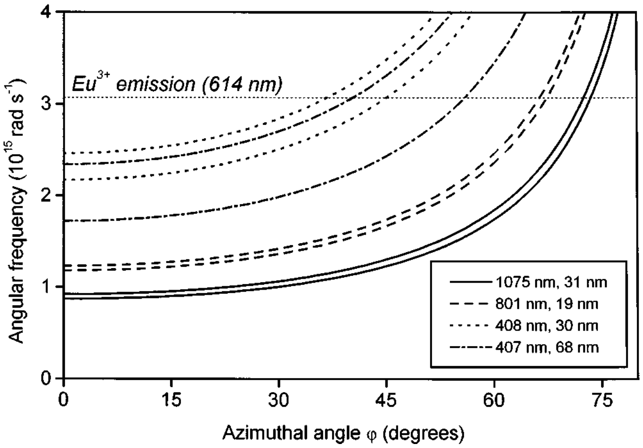

FIG. 8. A schematic of the theoretically derived azimuthal angle dependence of the SPP band gap for the different gratings used (in the model the effect of the spacer layers on the SPP dispersion was ignored). For each grating the position of the upper and lower band edges are shown as a function of the azimuthal propagation angle ϕ. Note that the band edges increase in energy as the azimuthal angle of propagation is increased. There is only a narrow angle range over which the propagation of SPP's are forbidden at the emission frequency (equivalent to 614 nm); for the 1075- and 801-nm gratings this angle range is ~1% of the total angle range indicating that for these gratings the SPP band gap will have little effect of the excited-state lifetime of the europium complex.

increase the wave vector of the SPP mode and thus shift the band gap to higher azimuthal angles for a given emission frequency. The total angle range over which SPP propagation is forbidden can be calculated for the case of zero spacer layer thickness,[9] and is given in Fig. 8 for the different gratings used. While ignoring the spacer layer cannot be an accurate calculation for the samples studied, it does give an indication of the extent of the SPP band gap. The effect of a spacer layer will be to increase the wave vector of the SPP mode of a given frequency. Thus the frequency at which an SPP band gap occurs will be reduced with respect to a similar corrugation and no spacer layer. The result of this will be a reduction in the angle range over which the gap is effective as the spacer layer thickness is increased.

We can see in Fig. 8 that for the first two corrugation samples (pitches of 1075 and 801 nm), the fraction of angles over which a band gap exists is small, ~1%. Hence we expect little change in the excited-state lifetime in the small separation regime ($\leqslant 10$ spacer layers) of these two samples, where SPP coupling dominates the decay of the emitters.[11] However, for the 400-nm pitch samples the extent of the gap is significant, ~20%. One would expect that the presence of a gap would reduce the PMD and thus increase the excited-state lifetime. This is however the opposite of what is observed in Figs. 6 and 7.

At present two possible explanations can be put forward for this unexpected result. Firstly, at the edge of the gap the PMD associated with the SPP modes is enhanced.[8] If this enhancement of states at the band edge more than offsets the lack of states within the band gap, then we would expect the excited-state lifetime to be reduced. A more detailed theoretical analysis in which the spacer layer is included and the density of SPP states evaluated is clearly needed. Secondly, it may be possible for the near field of the dipole to scatter from the corrugation. In this way components of the dipole field that previously could not participate in dissipating power, notably the evanescent or near-field components, could scatter from the corrugation thus allowing coupling of the emitters to both radiation modes and the SPP mode. Whether such diffraction from the corrugation requires the near field of the emitter to be scattered by the periodic modulation, or is more simply scattered by a nearby feature (trough, peak) in the surface profile, is unclear.

There is currently little theoretical work in the literature that can be easily compared with the experimental results reported above. The theories that are published, such as those of Arias Aravind, and Metia[27] and those of Leung and co-workers[17–22] are not expected to work for deep corrugations and/or small surface-emitter separations, the later causing problems due to the need to consider high wave vector components of the dipole nearfield. These limitations are unfortunate since the data presented above show that this is just the regime where changes in the excited state lifetime are seen.

Further experiments are clearly needed. In particular, experiments such as those reported above, but for shorter pitch corrugations are required. If the pitch is short enough the far field of the emitter cannot be diffracted, scattering of the near field might then be more easily examined, perhaps by measuring the radiation pattern from such samples. Experiments such as these are currently under way.

V. SUMMARY

The excited state lifetime of Eu^{3+} ions has been determined as a function of their separation from corrugated silver surfaces. Five samples were studied. The first was planar and provided a reference to compare with the results from nonplanar surfaces. The four remaining samples were corrugated, each having a different combination of pitch and amplitude. For the two longer pitch corrugations (1075 and 801 nm) the separation dependence of the excited-state lifetime was found to be indistinguishable from that due to a planar surface. For the two shorter pitch corrugations (408 nm) significant differences in the separation dependence of the excited-state lifetime were observed, a stronger effect being seen for the deeper corrugation. The reduction in the oscillations has been tentatively attributed to diffraction of the dipole far field. Further, the quenching of the fluorescence in the small separation regime, where coupling to SPP's is expected to dominate, was found to be increased. The possibility that the increased quenching is due to changes in the photonic mode density associated with SPP band gaps has been discussed, but further experimental and theoretical work is urgently required to help us understand the mechanisms involved.

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