Topical review
Fluorescence near interfaces: the role of photonic mode density

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Abstract. A review of fluorescence near interfaces is presented. Recent work that examines the role of photonic mode density in this process is surveyed and the underlying concepts discussed. The review includes an examination of the role of surface and waveguide modes, as well as non-radiative decay. The importance of textured surfaces in providing large changes in photonic mode density and in coupling non-radiative modes to radiation is highlighted. Indications are given for future areas of research and on how photonic mode density may influence optical processes other than fluorescence.

1. Scope

An interface may alter the way an excited molecule loses energy through fluorescence in two ways. Firstly, by modifying the boundary conditions of the electromagnetic field, it may alter both the radiative decay rate and the spatial distribution of the emitted radiation. Secondly, the excited molecule may lose its energy to the interface via non-radiative energy transfer. It is the purpose of this review to examine the concepts, to elucidate the underlying physics and to discuss recent results and current problems. Particular emphasis will be placed on work carried out in the last decade, on anticipating future directions and in assessing the relevance of the subject to other areas of science. Several excellent review articles were produced on fluorescence near interfaces in the 1980s [1–3]. It is not the purpose of the present article to duplicate that work, rather to concentrate on what has happened since then. However, we shall need to cover similar background physics, and the state of the field at the time of these reviews will be summarized where required to provide a foundation for the present discussion.

The review is divided up into a further seven sections. Section 2 sets out the basic concepts involved and discusses briefly the areas to be dealt with in later sections. Section 3 develops the concepts in more detail by discussing the classic experiment in this area, a study of how the fluorescence lifetime of a molecule in front of a metallic mirror depends on the distance between the molecule and mirror. This section also includes the development of an appropriate theoetical framework that assists greatly in understanding the phenomena under investigation. In section 4 we consider the different routes by which the energy of the excited molecule may be dissipated, concentrating on the role of surface and waveguide modes as decay routes. Although not directly dependent on photonic mode density (PMD), non-radiative decay often competes with radiative decay and

this is also discussed. Frequency shifts associated with changes in PMD are discussed in section 5, whilst the influence of nonplanar interfaces including islands, periodic corrugations and surface roughness are dealt with in section 6. Sections 2–6 are concerned with the effect of PMD on spontaneous emission; however, there are many other optical processes that may also be affected. Since these processes are providing much of the interest for future research, section 7 provides a link between the discussion of PMD and fluorescence and these other processes. Section 8 summarizes the review and areas for future work.

2.   The basic concept

Fluorescence is an example of the spontaneous emission process. Here the emitter is an atom, molecule or ion (henceforth simply referred to as either molecule or emitter) and is initially assumed to be in an excited state. Spontaneous emission results in the emitter decaying to a lower-energy stage, a photon taking away the energy of excitation. In fact, the emitted energy need not necessarily be in the form of a photon; it could, for example, be a waveguide mode, a subject that we shall discuss further in section 4. Spontaneous emission is an archetypal quantum-mechanical process; we can say nothing about when a particular spontaneous emission event will occur; rather we may merely predict the probability of decay for an ensemble of emitters. It is surprising, therefore, when one first discovers that the process of spontaneous emission is not entirely intrinsic but is subject to external influence.

The probability of spontaneous emission is given by Fermi's [4] golden rule as

$$\Gamma_{ij} \propto |M_{ij}|^2 \rho(\nu_{ij}). \tag{1}$$

Γ_{ij} is the rate for the transition between the excited state i and lower-energy state j; M_{ij} is a matrix element that connects the excited and lower energy levels and is determined by the wavefunctions associated with those levels; $\rho(\nu_{ij})$ is the density of the optical field at the transition frequency, hereafter referred to as the photonic mode density (PMD), and will be discussed below. This control of the decay rate through PMD was first pointed out (at radio frequencies) by Purcell [5] in 1946.

How may an interface modify the spontaneous emission rate? Can this be accomplished through the first term M_{ij} in equation (1)? Put another way, can an interface modify the wavefunction of the emitter? Provided that the emitter and the interface are close enough, the wavefunction can be perturbed by the interface. Typically, the emitter and an atom that makes up the interface will need to be nearest neighbours (in the solid or liquid state). For this to happen their separation will be that characteristic of the wave function, approximately 1 Å. Whilst this type of modification is very important, it is not the subject of the present review. We are concerned with the second term $\rho(\nu_{ij})$, the PMD at the transition frequency. Through this term the interface may modify the spontaneous emission process, its importance in part arising from the characteristic separation of molecule and interface over which it is effective, the wavelength of the emission.

There are two main ways to view the PMD: firstly, as vacuum fluctuations, which is an essentially quantum-mechanical viewpoint; secondly, via the ability of the structure surrounding the emitter to support the emitted photon (electromagnetic mode), which is an essentially classical viewpoint. Interestingly,

these two viewpoints do not provide explanations in different limiting regimes, as one might have expected from the correspondence principle. Rather, they have more the character of complementary explanations, providing the same quantitative answers when applied to the same problem. In fact, this is not so surprising, the quantum treatment of light is only really different from the classical treatment in its predictions on the statistical nature (i.e. temporal behaviour) of the optical field [6]. We shall predominantly be concerned with the classical viewpoint, which will be explored in some detail below.

2.1. *The classical viewpoint*

Consider an emitter residing in an enclosed volume whose inner surface is a perfect reflector. If the emitter decays, it will excite the electromagnetic field within the enclosed volume. Since this energy cannot be radiated away, it may well subsequently cause the re-excitation of the emitter (assuming the latter to be a simple two-level system), whereupon the whole process can start over again. This is a bad picture; we cannot talk of *an emitter* and *a cavity* in isolation as we are unable to make independent measurements on them since they are hidden from us by the perfectly reflecting walls. Rather, we must consider a new hybrid system of *cavity* + *emitter* and think of the excitation energy as an attribute of this new system.

If the cavity is small enough, $\lambda_{ij}/2$ or less, then no electromagnetic mode may be supported within it at the transition frequency ν_{ij}, owing to destructive interference of successive reflections from the cavity boundaries. The emitter is unable to emit and the surrounding structure is unable to support a mode. In this case, we say that the PMD at the emission frequency is very low and spontaneous emission is inhibited.

If we relax the condition on the boundary and allow it to transmit a small fraction, then we can make measurements. We may see the energy oscillate between two states, emitter excited and cavity mode empty $\leftrightarrow$ emitter in low-energy state and cavity populated by one photon; these are the so-called Rabi oscillations. In fact, if the resonant exchange of energy between cavity and emitter is of greater probability than that of transmission through the boundary, then the allowed frequencies of the cavity will be split (Rabi splitting) owing to the strong coupling of the cavity and the emitter.

The cavity discussed above is idealized and is of little practical value. There are, however, many other structures that may be used to alter the PMD at the site of an emitter, and the single interface is much the simplest of these. A great deal of work has been carried out on more complex structures specifically designed to afford control over PMD, particularly the photonic solid [7] and the microcavity [8]. The practical importance of such structures, especially in controlling the spontaneous emission of light in light-emitting diodes and lasers, is well established [9, 10].

Whilst, in general, the simple interface provides a weaker modification of PMD, it is nonetheless of great interest. The reasons for this are as follows.

(*a*) Many optical processes take place near interfaces, a topical example being the use of near-field optical microscopy to study single molecules.

(*b*) Interfaces play a vital role in both forming and determining the properties of microcavities.

(*c*) New opportunities in controlling PMD are being explored by texturing interfaces on the scale of the wavelength of the emission, important both on its own and because photonic solids are bounded by such interfaces and may well govern the behaviour of such systems.

The single interface, with a few adaptations, especially texturing, is the focus of this topical review.

3. The planar interface

The modification of spontaneous emission produced by a planar interface is of the same origin as that occurring in the idealized spherical cavity considered above. The field reflected by the interface interferes with the emitter. If the reflected field is in phase, the PMD at the emitter site will be high, resulting in the dipole being driven harder; consequently the emission will be enhanced. If the reflected field is out of phase, emission will be inhibited. Quantum-mechanically we must add up all the different ways in which spontaneous emission may take place. The presence of the interface provides additional paths involving reflection from the surface and it is the inclusion of these additional paths that produces the modification. This is perhaps the simplest example of the area of physics known as cavity quantum electrodynamics (QED).

Fluorescence in the presence of a planar surface provided the first experimental demonstration that the spontaneous emission rate could be modified by changing the local photonic mode density. Pioneering experiments were carried out by Drexhage and coworkers [10–13] in the 1960s and are summarized in [14]. Before examining in detail the results of this type of investigation and how they are interpreted, it is worth anticipating what may happen as the distance between the emitter and the surface is varied.

The classical approach considers the emitter to be a forced damped dipole oscillator for the following reasons: it is *forced* in that the field reflected by the boundary provides a driving term in the behaviour of the dipole; it is *damped* because the oscillator radiates power; it is an *electric dipole* because many atomic or molecular transitions that produce light are electric dipole in nature. We take account of the effect of the surface by determining the field at the site of the dipole that arises owing to reflection from the surface. In so doing, we must consider both the amplitude and the phase of the reflected field. The retardation effects that occur owing to the finite round-trip involved in going from the dipole, to the surface and back again, must also be included.

We are now in a position to predict the change in spontaneous emission rate as a function of the separation between the emitter and the surface. Two effects can be expected. Firstly, the spontaneous emission rate should oscillate as the distance is increased, since the phase of the reflected field changes with distance. Secondly, as the distance increases, the strength of the oscillation will decrease, owing to the point source nature of the dipole emitter. (The radiation field of the dipole weakens with increasing distance from it; thus the strength of the reflected field will also fall.) Results of an experiment involving a highly reflecting surface are shown in figure 1.

These data (figure 1), produced recently [15], directly confirms the original results of Drexhage [14]. There are three important features.
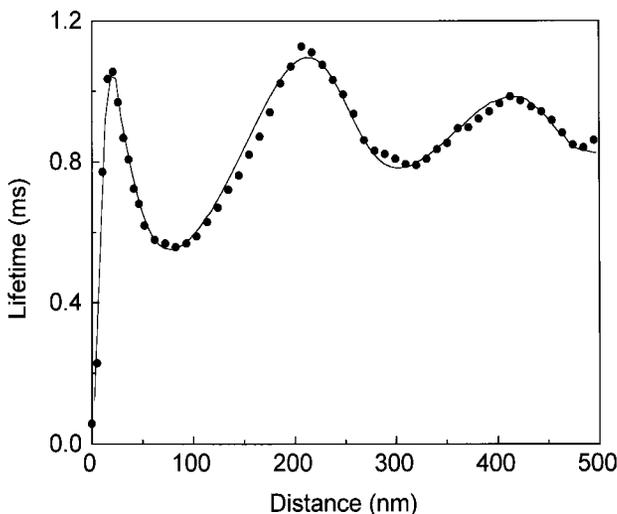
Figure 1. Lifetime of Eu^{3+} ions in front of a Ag mirror as a function of separation between the Eu^{3+} ions and the mirror. Note particularly the oscillations due to the changing PMD and the quenching of the emission for very small separations. The details of the structure used are shown in figure 6; the figure is taken from [15]. The solid curve is a theoretical fit, details of which are given in the text. The dielectric constant of the LB film spacer layer (figure 6) was 2.49, and that of the Ag $-16 + 0.4i$.

  (i) The expected oscillation is clear.
 (ii) The oscillation is damped, as expected.
(iii) The spontaneous emission is strongly quenched for small emitter–surface separations.

We did not anticipate feature (iii), which is due to direct coupling between the dipole field and surface plasmon polaritons (SPPs). SPPs are non-radiative modes of the metal–dielectric interface and are discussed in detail in section 4. There are many details of the sample structure that influence the form of the distance dependence of the spontaneous emission lifetime. These will be introduced as required to develop a conceptual picture and detailed theoretical treatment.

First of all, there is an important feature that we have so far neglected and that might be supposed to produce the quenching of the emission in the small-separation regime, namely the orientation of the dipole with respect to the surface. The relevance of dipole orientation can be seen by considering the reflecting surface to produce an image dipole (figure 2). When the surface molecule separation d is small, a dipole that is parallel to the surface tends to be cancelled out by its image, whilst one that is perpendicular to the surface is enhanced. Assuming the mirror to be perfect, the variation in spontaneous emission rate with d is predicted (on the basis of the theory given in the next section) to be as shown in figure 3. In the experiment, involving Eu^{3+} ions above a Ag mirror, the dipole moment of the Eu^{3+} ion is free to rotate rapidly within the spontaneous emission lifetime; the dipole thus samples all orientations during the emission lifetime and so takes an appropriate average value. From figure 3 we see that including the effect of different dipole orientations in insufficient to explain the data of figure 1.

Parallel   Perpendicular
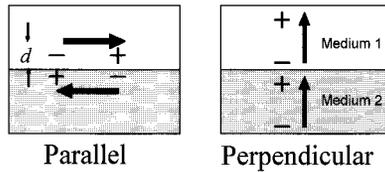
Figure 2.   The effect of an image dipole on the net dipole strength when the dipole is
near a good reflector. When the dipole moment is parallel to the interface the image
acts to cancel the source, reducing the dipole strength; the strength of the
perpendicular dipole is increased by the effect of the image.
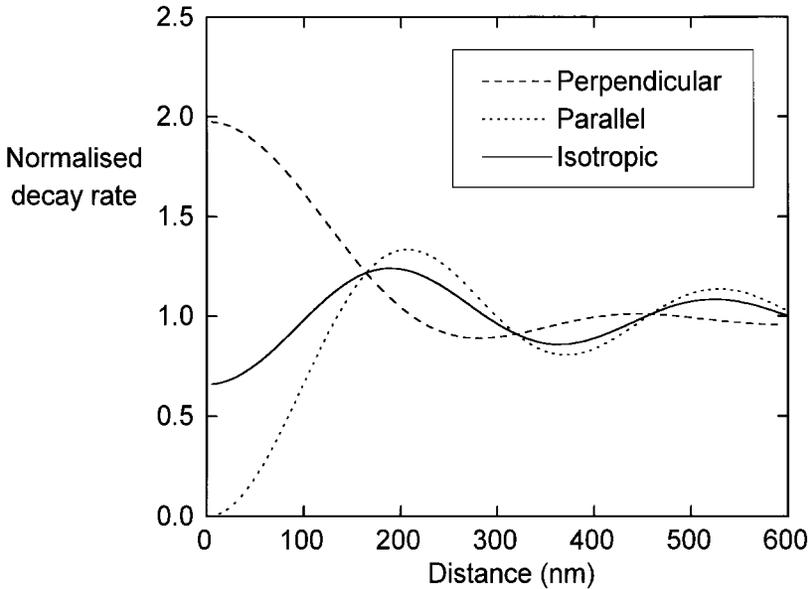
Figure 3.   Calculated decay rates for dipole emitters of different orientation in front of a
perfect mirror. As is suggested by figure 2, the decay rate of the perpendicular
dipole is doubled and the decay of the parallel dipole completely inhibited when
adjacent to the mirror. The effect on a dipole emitter that is averaged over all
directions is also shown and, importantly, is insufficient to account for the
quenching seen in figure 1.

Whilst these considerations do not explain the quenching in figure 1, they do
highlight the need to take account of dipole orientation.

3.1. *Theoretical model*

At this point we examine an appropriate theoretical model that allows us to
develop considerable phsical insight. The data in figure 1 was initially modelled as
an interference phenomenon in which the emitter is assumed to emit into the far
field both directly and by reflection from the surface [16]. This method allows the
radiation pattern, that is the radiation distribution in the far field, to be evaluated,
but it fails to account for the quenching at small separations. The reason for this is
that the approach did not include the effect of the SPP mode. The mode was added

in artificially to the interference method [16], but this was not a very satisfactory solution.

A more comprehensive treatment that overcame this limitation was given by Chance, Prock and Silbey (CPS) [2] in 1978. Here the SPP mode arises naturally through use of the full optical response of the surface, that is the complex dielectric permittivity of the metal. Many workers have developed equivalent approaches based on the same concept. (The equivalence of the classical model and a full quantum-mechanical calculation has been established by Yeung and Gustafson [17].) The details of such theories will not concern us here, since they are thoroughly treated in the literature and compared by Sipe [18]. Rather, we shall discuss the outline of the approach adopted by Sipe [18], an approach that, conceptually, appears to be the most straightforward to the present author.

3.1.1. *Building blocks of the model*. The key requirement is to develop an expression for the dipole field reflected back to the dipole position by the surface. This is done using the following conceptual steps.

   (1) Expand the dipole field as a summation of plane waves, the plane waves characterized by having different wave-vectors (momenta) in the plane of the surface.
   (2) Evaluate the reflection coefficient (both amplitude and phase) for each of these wave-vector components, taking account of the distance between the dipole and the surface and the refractive index of the intervening material.
   (3) Sum these reflected fields to find the net reflected field.
   (4) Combine the reflected field with the source field of the dipole to deduce the spontaneous emission rate (lifetime).
   (5) Do the above for the two orthogonal dipole orientations.

3.1.2. *Approximations in the model*. There are many assumptions made in using such a model. They are as follows.

   (i) The point dipole approxmation is used; the size of the dipole is small compared with both the wavelength λ and the dipole–surface separation d.
   (ii) The planar approximation is employed, that is the interface involved is flat.
   (iii) The transition between the media on either side of the interface is infinitely sharp.
   (iv) The substrate is a continuous medium whose optical properties at a given frequency may be completely described by a macroscopic dielectric permittivity ε. There is therefore no wave-vector-dependent response, that is no spatial dispersion.
   (v) The dipole is embedded in a loss-free medium (any non-radiative decay of the emitter is handled solely through the use of a phenomenological quantum efficiency).
   (vi) None of the media exhibits gain at the emission wavelength.

Despite these approximations, the model has wide validity. We shall have cause later to look at the limits imposed by these approximations and to examine how some of them may be overcome.

3.2. *Details of the model*

As discussed above, we consider the emission to take the form of a forced damped harmonic oscillation [2, 19]. The equation of motion for the electronic dipole moment p is thus

$$\frac{\mathrm{d}^2 p}{\mathrm{d}t^2} + \omega_0^2 p = \frac{e^2}{m} E_\mathrm{r} - b_0 \frac{\mathrm{d}p}{\mathrm{d}t}, \tag{2}$$

where ω_0 is the resonant angular frequency in the absence of all damping, m is the effective mass, e the electric charge, E_r is the reflected field at the dipole position and b_0 is the damping constant (inverse lifetime) in the absence of the reflecting structure. The reflected field does work on the dipole and they oscillate with the same complex frequency $\Omega = \omega - ib/2$, that is

$$p = p_0 \exp\left(-i\Omega t\right) = p_0 \exp\left[-\left(\frac{i\omega + b}{2}\right)t\right], \tag{3}$$

$$E_\mathrm{r} = E_0 \exp\left(-i\Omega t\right), \tag{4}$$

where ω and b are the frequency and damping rate respectively in the presence of the mirror. Substituting equations (3) and (4) into equation (2) and equating real and imaginary components, and noting that $\Delta\omega = \omega - \omega_0 \ll \omega, \omega_0$ we find that

$$\frac{b}{b_0} = 1 + \frac{e^2}{m\omega p_0 b_0} \mathrm{Im}\left(E_0\right), \tag{5}$$

$$\Delta\omega \approx \frac{b^2}{8\omega} - \frac{bb_0}{4\omega_0} - \frac{e^2}{2m\omega_0 p_0} \mathrm{Re}\left(E_0\right). \tag{6}$$

We see from equations (5) and (6) that the normalized damping rate and frequency shift are related to the out-of-phase and the in-phase components respectively of the reflected field. The frequency shift is, in general, quite small and will be discussed further in section 5. The change to the damping rate is dictated by the reflected field. Calculating the reflected field has been the focus of many reports; most make use of a Green function approach, often involving an expansion of the dipole field in terms of plane waves [19] (and references therein). We shall not follow through the development that leads to the reflected field, we are here only interested in the result. Any dipole orientation may be considered as a combination of perpendicular (subscript $\perp$) and parallel (subscript $\parallel$) dipole components. The decay rates for these two orientations are found to be [2]

$$b_{\perp,\parallel} = b_0(1 - qz_{\perp,\parallel}), \tag{7}$$

where q is the radiative quantum efficiency of the emitter in the material in which the dipole resides. The parameters $z_\perp$ and $z_\parallel$ are given by

$$z_\perp = 1 - \tfrac{3}{2} \mathrm{Im} \int_0^\infty \frac{u^3}{l_1} (1 - r_{1,2}^\mathrm{p}) \exp\left(-i\beta\right) \mathrm{d}u \tag{8}$$

$$z_\parallel = 1 - \tfrac{3}{4} \mathrm{Im} \int_0^\infty \frac{u}{l_1} [(1 + r_{1,2}^\mathrm{s}) - (1 - u^2)(1 + r_{1,2}^\mathrm{p})] \exp\left(-i\beta\right) \mathrm{d}u \tag{9}$$

Several parameters need explaining here. The integration variable u is the

component of the wave-vector (of the dipole field) in the plane of the interface, normalized with respect to the far-field wave-vector k_1 of the dipole radiation field in medium 1; thus $u = k_x/k_1$. The parameter l_1 is given by $l_1 = -i(1 - u^2)^{1/2}$ and is related to the component of the wave-vector perpendicular to the interface. The phase angle β is the phase due to retardation, that is the phase change incurred in the round trip from the emitter, to the interface and back. The coefficients $r^p_{1,2}$ and $r^s_{1,2}$ are the Fresnel reflection coefficients for p- and s-polarized light respectively at the interface, evaluated as a function of u. Since the latter may range over all positive values between 0 and infinity, the reflection coefficients have to be calculated for both real and complex angles of incidence. These correspond to incident waves that are propagating and evanescent respectively; we shall see the importance of the latter soon. We note that, when a multilayer structure capable of supporting guided modes is present, the perpendicular dipole will couple to only transverse magnetic (TM) polarized modes since $z\perp$ involves only $r^p_{1,2}$. A dipole of any other orientation will be able to couple to transverse electric (TE) and TM modes, if present, since $z\|$ contains both $r^p_{1,2}$ and $r^s_{1,2}$.

Equation (7), together with equations (8) and (9), provides a particularly convenient formulation of the problem. The decay rates can be evaluated simply from a knowledge of the reflection coefficients of the interface between the upper half-space (1) and the substrate (2). These in turn are derived from the dielectric permittivities ε_1 and ε_2 (which may be complex where necessary) and may be expressed as

$$r^p_{1,2} = \frac{l_2\varepsilon_1 - l_1\varepsilon_2}{l_2\varepsilon_2 + l_1\varepsilon_2}, \quad r^s_{1,2} = \frac{l_1 - l_2}{l_1 + l_2}. \tag{10}$$

The coefficient l_2 is defined in a similar way to l_1 above. Note that it is possible to have different formulae from those given in equation (10) for the Fresnel coefficients (for example [1]), the differences being simple sign changes. They differ because different authors choose to draw different diagrams relating the vector components of **E** and **B** associated with the incident and reflected waves respectively. Provided that the appropriate vector diagrams are kept in mind when evaluating reflection coefficients, all approaches are equivalent.

An important aspect of this technique is that it does not require us to calculate the modal properties of the structure under investigation. Further, by making straightforward modifications to equations (8) and (9) the system under study can be extended to include multilayers below and above the dipole, a matrix method being used to calculate the reflection coefficients for the multilayers [2].

For the data presented in figure 1 we assumed that the dipole orientation was isotropic, by which we mean a dipole whose moment rotates and samples all directions in space in a time much faster than the fluorescence lifetime. In this case, the decay rate b_{iso} is given by

$$b_{iso} = \tfrac{2}{3}b_\| + \tfrac{1}{3}b_\perp. \tag{11}$$

Before exploring the physics represented by the above equations (7)–(11), it is useful to consider in more detail the nature of the dipole field. The important aspect for the present study is the near field, a zone that extends roughly a distance of λ from the dipole. The field due to the dipole is shown schematically in figure 4. The near field is seen to contain components with a large range of wave-vectors k. Components with $k > k_1$ do not propagate into the far field; they are evanescent in
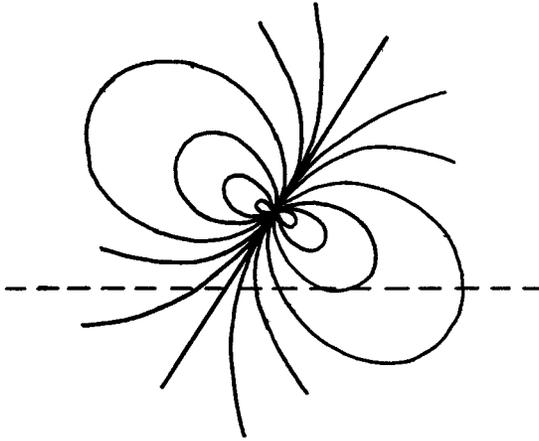
Figure 4.   Electric field lines of an electric dipole in the near-field regime. The broken
       line indicates a plane through the near field representing a nearby interface. Note
       that at the interface the dipole field contains many different wave-vector
       components. (Note also that the presence of a substrate will modify this field
       distribution.)

nature. Importantly, for a dipole located near to a planar surface, a wide range of k_x exists (k_x being the wave-vector in the plane of the surface). Thus the dipole can couple to modes having in plane momenta greater than k_1, such as SPPs, modes that are not accessible to incident plane waves.

Equations (7)–(11) allow us to calculate the fluorescence lifetime of an arbitrarily oriented dipole emitter. Before comparing this theory with the experimental data in figure 1, it is worth using it to examine where the power of the dipole is dissipated, that is the different decay routes that are available and their relative importance. In fact, this is the real value of the theoretical framework described above and can be done by examining the integrands in equations (8) and (9). We start by examining the integrand for the case of an emitter located in free space above a metallic mirror. The integrand is plotted in figure 5 for a range of emitter interface distances d.

There are three key features to note, delineated by different intervals of u in the plot.

(i)   The region $0 \leqslant u \leqslant 1$ represents coupling of the emitter to radiation in the far field, the value of u dictating the direction of emission.

(ii) The sharp spike at $u \approx 1.06$ represents coupling to the SPP mode at the metal interface. As we shall see below, the SPP mode is non-radiative, that is $u > 1$, so that coupling to it can only occur via the near field of the dipole; decay of the emitter to this mode is also therefore non-radiative. Note too that coupling to this mode increases as the separation d decreases. This is due to the evanescent nature of the field associated with the SPP mode (section 4.1).

(iii) At still smaller separations a broad feature in the region $u \gg 1$ develops, increasing in strength rapidly as d falls. This additional non-radiative decay route represents coupling of the emitter to what have been called 'lossy surface waves' [1]. The non-radiative decay arises because the
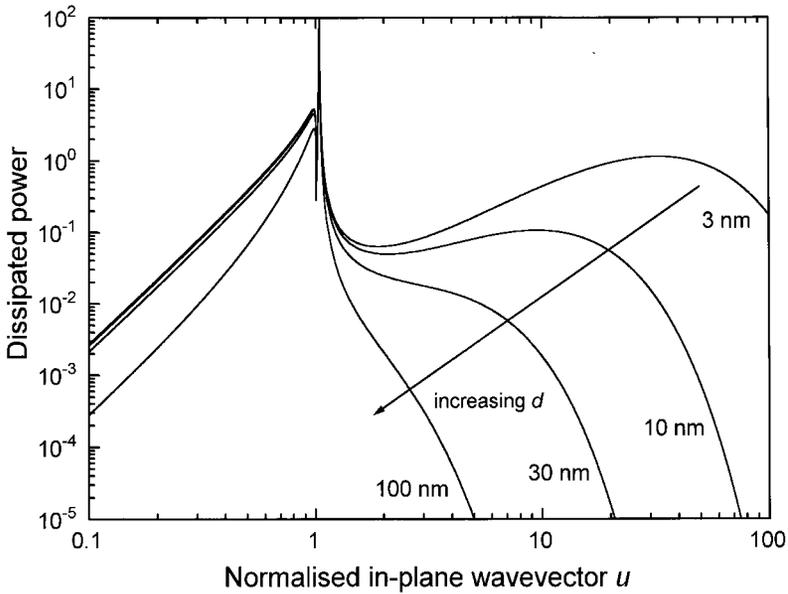
Figure 5. The integrand of equation (7) (for an isotropic distribution of dipole orientations) as a function of the normalized in-plane wave-vector u. The figure shows the power dissipated by the emitter for a range of emitter–surface separations, as indicated. Note that, as the distance between the emitter and the surface increase, the coupling to the lossy surface waves, $u \gg 1$, drops dramatically. The system consists of an emitter having a wavelength of emission 614 nm, immersed in vacuum and positioned above a Ag surface. The dielectric constant of the Ag is $-16 + 0.6i$.

oscillating near field of the dipole induces electronic charge density oscillations (e.g. excitation of electron–hole pairs) that dissipate through scattering in the substrate. We note that, when the emitter surface separation is very small, $d \leqslant \lambda/50$, the applicability of our model based on a simple dielectric permittivity to account for the response of the substrate (approximation (iv) in section 3.3) fails. Further details of this problem and ways to overcome it are examined in sections 4.4 and 4.5.

To summarize, those wave-vector components of the integration that lie between zero and one represent coupling of the emitter to radiation; those components between one and infinity represent energy transfer to the substrate. Before looking in more detail at the role of PMD in the different decay mechanisms, we extend our picture to include a type of structure that is very common experimentally and is shown in figure 6. Rather than having two semi-infinite media separated by an interface, our substrate is coated with a thin spacer layer, the emitters generally comprising the top surface of the space. Inclusion of this spacer layer enables the separation to be controlled by altering the thickness of the spacer layer. Care and appropriate techniques are required to ensure uniform layers of well controlled thickness, to within a nanometre or better. Examples include the Langmuir–Blodgett (LB) technique of depositing organic multilayers and molecular-beam epitaxy. Our single interface theoretical model is easily adapted to include the extra reflected field produced by the top surface of the spacer layer, as described above. The importance of including this interface, even
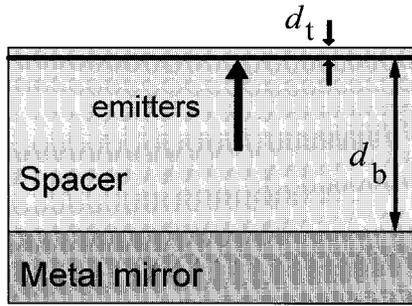
Figure 6.   Schematic diagram of the experimental arrangement used by Drexhage [14]
       and many others. The emitters are maintained at a specified distance from the
       mirror substrate by a spacer layer, often being embedded in the spacer as shown.
       For the theoretical curve shown in figure 1, a value of 1.3 nm was used for d_t.

when the emitting molecules comprise the top monolayer of the spacer, is
demonstrated by the fact that the fit of theory to experimental data shown in
figure 1 cannot be achieved without it.

Another feature of the spacer layer is that if sufficiently thick it may support
waveguide modes. Again, examination of the integrand of equations (7) helps to
show this (figure 7). The figure shows the integrand for a structure that supports a
SPP mode and one TE-waveguide mode. Coupling to these modes is represented
by the poles of the integrand at $u \approx 0.7$ and $u \approx 1.05$ respectively. Note how the
different dipole orientations have different coupling strengths to the various
modes. Once again, the physical model detailed above allows us to build a physical
understanding about the different decay mechanisms.

It is our task now to examine the role of PMD on the different decay
mechanisms that we have been discussing. We start by examining in more detail
the coupling between the emitter and SPP modes.

4.   Decay mechanisms

The decay of the excited molecule may take place in one of two ways:
radiatively with the emission of light into the far field, and non-radiatively to
guided and/or lossy waves. The probability of these two routes depends on the
details of the system. Changes in PMD act principally to alter the radiative decay
but in so doing also alter the probability that decay may take place non-radiatively.
In addition, where changes in the PMD are due to periodically textured interfaces,
changes to the PMD may allow coupling of non-radiative guided modes to
radiation. The latter aspect is the subject of section 6; here we concentrate on
changes in PMD near planar interfaces.

4.1. *Coupling between the emitter and surface plasmon polariton modes*

Many excellent reviews of SPP modes are available in the literature [20, 21].
SPPs comprise the coupled oscillation of an electromagnetic field and surface
charges at a metal–dielectric interface. This coupling increases the momentum
(wave-vector) of the mode when compared with a free-space photon of the same
frequency. The dispersion relation of the SPP mode at the interface between a
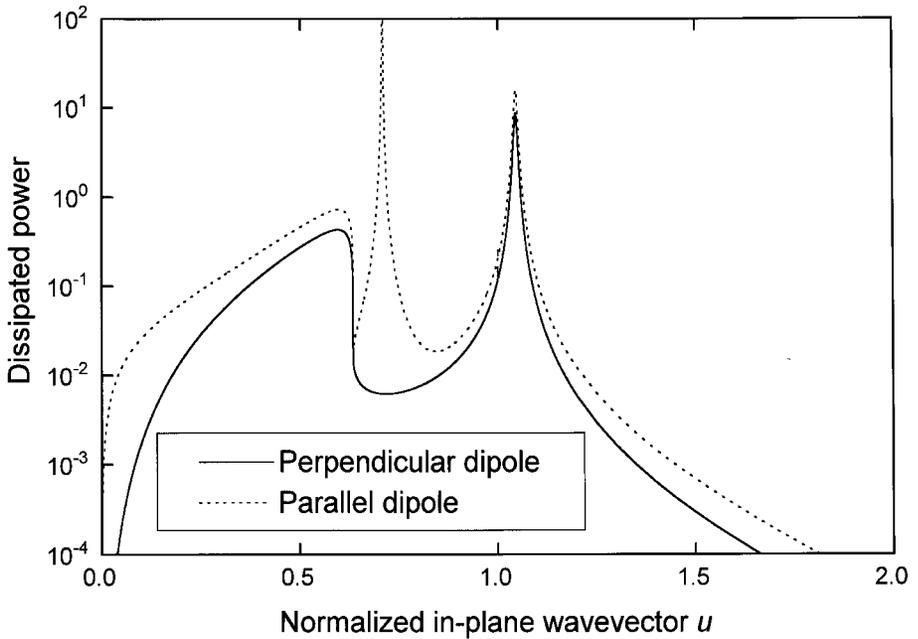
Figure 7. The dissipated power as a function of u for the system shown in figure 6. The feature at $u = 1.1$ is the SPP mode, and that at $u = 0.7$ the first TE waveguide mode. Note the different couplings of the two dipole orientations. The in-plane waveguide wave-vector is now normalized with respect to propagation in the LB spacer layer so that the critical value of u above which radiation cannot propagate into the far field in 0.63. The dielectric constant of the Ag was taken as $-17.6 + 0.6i$, and that of the (LB) spacer layer 2.49; the distances d_b and d_t were 140 nm and 1.3 nm respectively.

dielectric of relative permittivity ε_1 and a metal of complex relative permittivity ε_2 is given by [20]

$$k_x = \frac{\omega}{c}\left(\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1 + \varepsilon_2}\right)^{1/2}. \tag{12}$$

Note that, assuming a simple Drude-type model for the metal, there is an upper asymptotic frequency $\omega_{SPP} = \omega_p/(1 + \varepsilon_2)^{1/2}$, where ω_p is the bulk plasmon frequency of the metal. The wave-vector (momentum) of the mode is in the plane of the interface and is always greater than that of a free photon in medium 1; it is therefore non-radiative. Note too that the fields associated with the SPP mode decay exponentially away from the interface.

The non-radiative nature of the SPP mode means that decay of energy from the excited molecule into this channel cannot be directly observed, a feature common to all non-radiative decay routes. How, then, it is possible to distinguish contributions due to different non-radiative decay channels? For the SPP mode this is relatively straightforward. Momentum-matching techniques such as prism and grating coupling may be used to couple SPPs to photons [20]. The characteristic polarization and direction of the photons coupled out in this way may then be used to establish their origin as SPPs. It was with just such a technique (in fact, prism coupling) that Weber and Eagen [22] were able to demonstrate that a

significant fraction of excited molecules adjacent to a metal surface decay to give SPPs.

In an elegant experiment, Pockrand *et al.* [23] used similar techniques to determine the distance dependence of the coupling between the emitters and SPPs. They found a maximum coupling distance of approximately 20 nm (for emission in the visible). Knobloch *et al.* [24] also observed an optimum coupling distance for SPPs, using grating coupling to scatter SPPs into photons, thus allowing the SPP decay channel to be monitored. Here, we are temporarily considering a nonplanar sample structure since Knobloch *et al.* [24] used a corrugated surface simply to facilitate coupling of the SPPs to photons. The effect of the grating, and surface texturing in general will be considered fully in section 6.

In view of the exponential decay of the fields associated with the SPP mode away from the surface, it is somewhat surprising to find that the coupling between the emitter and the SPP mode is maximal for a small but finite separation of the emitter and surface. This is a consequence of the competition for this decay channel with lossy surface waves. As the separation is reduced, this latter decay route rapidly dominates. This is shown in figure 8, where the contributions to radiation, SPPs and lossy waves are calculated as functions of separation, using the model developed above.

It is worth noting at this stage that, unless decay to non-radiative modes can be recovered in some way (e.g. the grating and prism coupling of SPP modes mentioned above), it represents an effective decrease in the radiative quantum yields of the emitter. When the emitter is sufficiently far from the substrate that coupling to non-radiative modes is negligible, then the variation in PMD with distance does not alter the radiative quantum yield. Rather such changes alter the spatial distribution and rate at which the radiation is produced [2].

An interesting issue raised by CPS was the transfer of energy from an excited molecule to a thin metal film. Thin here means optically thin, that is capable of transmitting at least a small fraction of light incident on it. In this situation, a SPP mode may be supported on both metal surfaces. If the metal film is thin enough, an emitter on one side may couple to SPP modes on both metal surfaces. In this way, the excitation energy is transferred across a thin metal film. By using corrugated metal films, Gruhlke and Hall [25] were able to observe the light outcoupled by the corrugation from SPPs on one surface of the metal that were excited by molecules adjacent to the opposite side. Amos and Barnes [15] investigated the effect of this extra SPP mode on the decay kinetics of the excited molecule. They found that PMD was altered in two ways: firstly, by the presence of the new SPP decay channel and, secondly, by the reduced reflectivity of the thin metal film (when compared with optically thick films).

SPP modes play a very significant role in modifying the PMD near a metal surface. Their important contribution to surface enhanced Raman scattering is well known (see section 7.1). Even stronger changes in PMD occur for nonplanar metal surfaces and are discussed below (section 6).

4.2. *Coupling between the emitter and waveguide modes*

Let us return to reconsider the experimental arrangement originally examined by Drexhage (figure 6). The emitter was spaced from a metallic substrate by organic LB monolayers. By varying the number of LB layers, the emitter surface separation could be varied in a controlled way. We have seen above that, for small
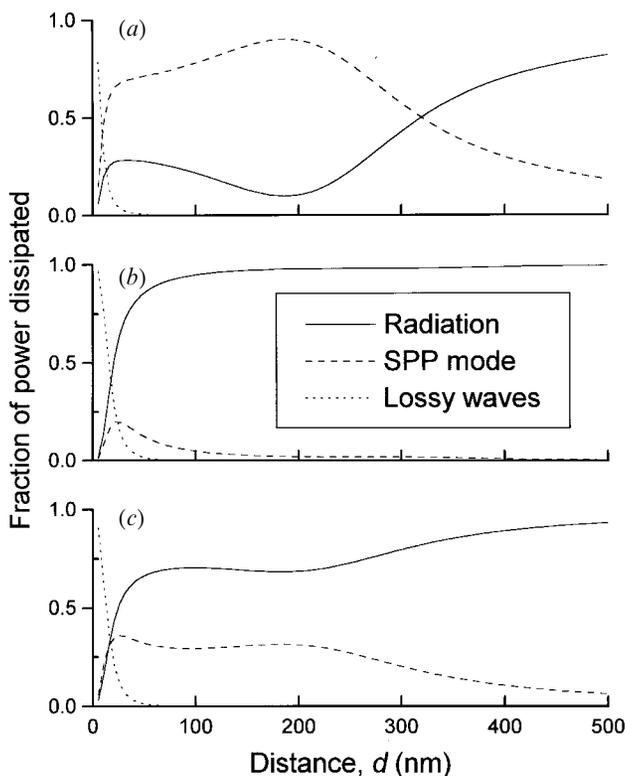
Figure 8. The calculated fraction of power dissipated by an emitter in vacuum above a Ag mirror (details as in figure 5) to the different decay mechanisms: (*a*) for a perpendicular dipole orientation; (*b*) for a parallel orientation; (*c*) for an isotropic combination.

separations and no spacer, a significant fraction of molecules couple to the SPP mode (figure 8). This is still true when a spacer layer is present, although the nature of the SPP modes is somewhat modified by the spacer layer, particularly through an increase in k_{SPP} as the thickness of the spacer increases (see figure 10 below). Further, as the thickness of the spacer increases, it is eventually able to support a waveguide mode.

The waveguide mode, like the SPP, is a resonant optical mode of the system and may provide a new decay route for the excited molecule. This was shown in figure 7 where the integrand of equation (7) was plotted for a spacer layer sufficiently thick to support one waveguide mode. As the thickness of the layer is increased, further waveguide modes may be supported by the structure, adding still more decay channels. Figure 9 shows the calculated fraction of power dissipated into these different decay routes evaluated in analogous way to the data of figure 8.

Interestingly, the appearance of a waveguide mode as the spacer thickness increases does not appear to produce a discontinuous change in the decay rate. In figure 1, no discontinuous changes are seen at those values of *d* where waveguide modes cut on, about 100 nm and 220 nm (figure 9). It appears as though coupling to a waveguide mode occurs at the expense of coupling to radiation (and other
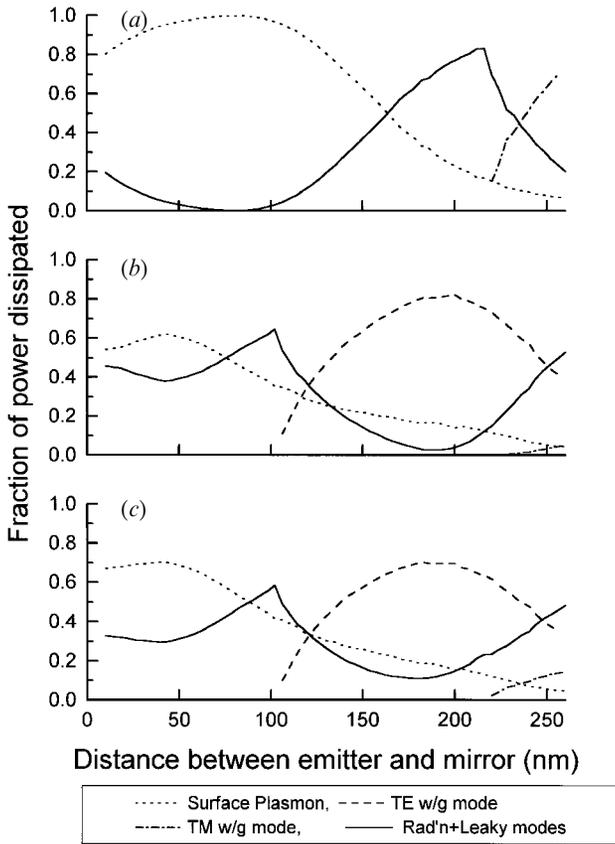
Figure 9. As figure 8 except that now a spacer layer of dielectric constant 2.49 lies between the emitter and the Ag; the emitters are also covered by 1.3 nm of the same dielectric. Note particularly how the appearance of the TE waveguide mode computes with decay to radiation. Further details are given in the text.

waveguide modes if present); this matter is the subject of an ongoing investigation [26, 27].

The importance of the coupling between excited molecules and waveguide modes for sensing applications has been highlighted by Holland and Hall [28]. In particular, they found that, by careful choice of spacer layer thickness and the use of surface corrugation to allow the outcoupling of waveguide modes, significant enhancements in detection efficiency could be obtained.

Examination of plots such as that in figure 7 for different values of d show that the waveguide modes do not suddenly disappear below their cut-off thickness. Rather, they become much broader and less strong, they are weakly (leaky) guided modes. This can be more clearly seen in figure 10 where the integrand of equation (7) is shown as a function of both d and u. This allows us to build up a picture of the development of the coupling between the excited molecule and the modes of the system as the thickness of the spacer layer is increased. The modes become leaky when their u value falls below 0.63 (the critical value of u for guiding in the dielectric layer). As a consequence of their leaky nature these modes radiate, the angle of the emerging radiation being dictated by their u value.
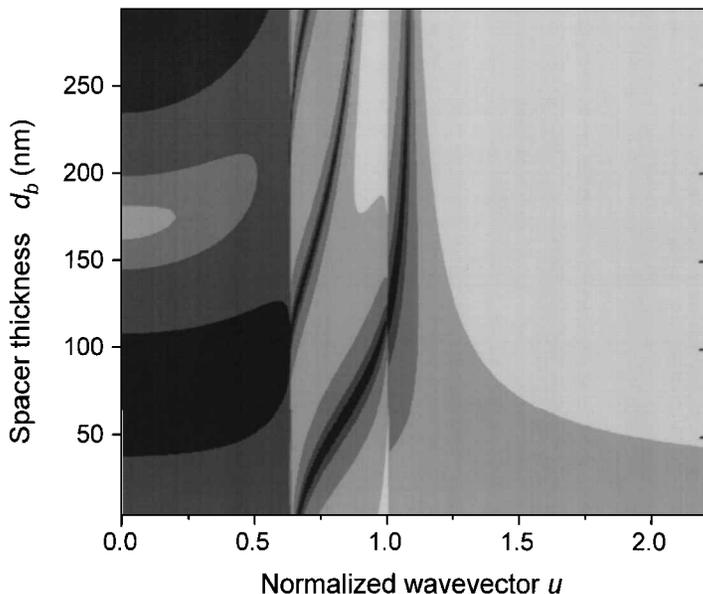
Figure 10. The integrand of equation (7) for an isotropic distribution of dipole orientations as a function of spacer layer thickness and normalized in-place wavevector. An overlayer of 1.3 nm thickness is again used. The emission wavelength is 614 nm; the Ag has a dielectric constant of $-17.6 + 0.6i$ and that of the spacer is 2.49. The 'glitch' at $u = 1.0$ is the critical value for propagation in the spacer layer. The figure thus shows the coupling to the various modes with increasing spacer layer thickness. Note how the radiation and leaky modes for u below 0.63 match the guided modes, $u > 0.63$.

4.3. *Coupling between the emitter and radiation* (*radiation patterns*)

As mentioned above, the presence of an interface in the vicinity of a radiating dipole alters the spatial radiation pattern of the dipole. The simple picture shown in figure 11 indicates the origin of this modification. Radiation into a particular direction may now occur via two different paths: one direct and the other by reflection from the surface. This is a classic interference situation; the radiation pattern in the far field is given by the sum of the field due to both paths, account being taken of their relative phase and amplitude.

Three distinct cases may be identified (figure 11). In the first, the dipole moment is perpendicular to the surface. In the other two, the dipole moment is parallel to the surface; the second case has the dipole moment also in the plane of emission, while in the third it is perpendicular to the plane of emission. Any particular dipole orientation can be represented as a weighted sum of these three cases. Note that for emission into the plane of the diagram cases 1 and 2 give p-polarized radiation, and case 3 gives s-polarized radiation.

The phase and amplitude of the reflected field are determined by use of the Fresnel reflection coefficients. Once again, great care needs to be exercised in evaluating these coefficients since the phase change that takes place on reflection is vital in calculating the interference condition, and thus the radiation pattern.

Many workers have concentrated on the case of molecules adsorbed directly onto the surface; there is thus no geometric phase change to be considered [29]. An

Case 1   Case 2   Case 3
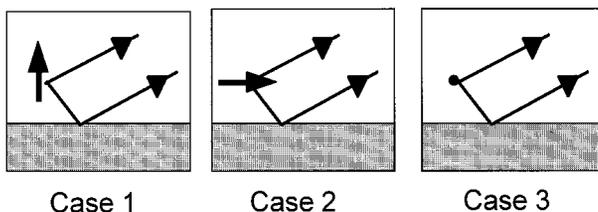
Figure 11.   Interference between direct and reflected waves may be used to calculate radiation patterns. Three different dipole orientations must be considered: case 1, dipole perpendicular to interface; case 2, dipole parallel to interface and in place of emission; case 3, dipole parallel to interface but normal to plane of emission.

examination of radiation patterns in this regime has been used to investigate the orientation of anthracene molecules on Ag, and their re-orientation on heating [30]. Ishibasi *et al.* [31] used the same technique to investigate the orientation of tetraphenylporphine molecules on Ag, Au, Cu and Al substrates, finding them to be coplanar with the surface in the case of Ag, Au and Cu, and obliquely oriented in the case of Al.

Drexhage [14] investigated the radiation patterns from emitters spaced from the surface using the LB technique employed to study the lifetime (section 3 above). Thus, phase changes due to the interface *and* due to the finite distance (the geometric or retardation phase) have to be taken into account. In this case, inclusion of birefringence in the LB film was invoked to explain the mismatch between experiment and theory. The examination of radiation patterns has also been used to study the orientation of molecules near interfaces in biophysical systems. The aim of such investigations range from general studies concerning model membranes of cells to the molecular basis of muscle contraction [32].

4.4. *Non-radiative decay*

When the molecule is less than about $\lambda/4$ from the surface a strong distance-dependent quenching sets in. The non-radiative decay processes involve the transfer of energy from the excited dipole to the substrate. If we assume that transfer takes place to a dipole within the substrate, for example excitation of an electron–hole pair, then the transfer will be dipole–dipole in nature. For the small separations under consideration the dipole field is dominated by the near field, the strength of which falls as d^{-3}. The standard Förster [33] model for dipole–dipole energy transfer has a d^{-6} dependence of the transfer rate because it involves the distance dependence of the near field of both the donor and the acceptor of the energy. If the acceptor takes the form of a line of dipoles rather than a point dipole, integration over all possible transfer sites yields a d^{-5} dependence. Similarly, a sheet of acceptors (a surface) yields a d^{-4} dependence, whilst transfer to the bulk shows a d^{-3} dependence. Quenching of fluorescence at small distances is clearly seen in the data in figure 1, although the detailed distance dependence cannot be evaluated from that figure because of the limited spatial sampling of the data.

That the classical theory also predicts this quenching (figure 1) implies that the quenching mechanism is simply described by the dielectric constant of the substrate material. However, as the separation between the molecule and the surface is reduced, this simple description fails. So, too, does the approximation

that the interface has no width, that is that the dielectric response of the system is discontinuous at the interface.

There are three main categories of quenching mechanism, all involving the excitation of an electron–hole pair, that is an exciton, via the near field of the dipole. Persson and co-workers [34–37] have carried out detailed theoretical investigations in this area. In the transfer of energy from molecule to exciton, momentum as well as energy must be conserved [37]. The three quenching mechanisms differ in the source of the momentum required to ensure conservation; they are as follows.

Process A arises from the bulk; the excitation energy of the molecule is absorbed by the creation of an exciton in the bulk of the substrate. Momentum is conserved in this process by scattering from electronic impurities and phonons (intraband) and from the crystal potential (interband) scattering.

Process B arises from the surface; the excitation energy is absorbed by the creation of an exciton at the surface of the substrate. Momentum is conserved here by scattering from the surface potential.

Process C arises from the spatial variation in the near field; when the molecule is very close to the surface, then high-wave-vector components in the near field of the dipole may provide the required momentum directly.

We have already noted that process A is accounted for in the classical picture. The addition of process B to the model requires the inclusion of a continuously varying dielectric function to cope with the interface. This is discussed further in section 4.5, where the surface region is treated as a selvedge, a region with properties different from the bulk that is able to account for non-local effects, the build up of surface charge, etc. Inclusion of process C requires us to consider non-local effects. These occur when the wave-vector of the near field is of order or less than some characteristic length scale l. When the field varies on a length scale shorter than l, that is $k_x l < 1$, the response of an electron at one time and place will depend on its velocity. In turn, the electron's velocity depends on the forces acting on it at an earlier time and in another place (hence the expressions, non-local response and spatial dispersion, both of which are used to describe this regime). Thus the length scale l is the range over which the electron phase is retained and this is determined by the mean free path associated with defect, impurity, phonon and electron scattering. The dielectric constant in this non-local regime is no longer a constant but is wave-vector dependent.

How can we assess the relative importance of the three processes (A, B and C above) for a given system? To some extent this can be achieved by measuring the distance dependence of the decay rates for the different mechanisms. For process A the decay rate is proportional to d^{-3}, whilst for processes B and C it is proportional to d^{-4} [35, 37].

Experiments investigating the distance dependence of the decay rate in this near regime have been numerous. Process C has been verified by inelastic electron scattering [38]. We should be able to ascertain the relative importance of processes A compared to B + C by investigating the distance dependence of the lifetime. It is natural to ask: what is the distance regime over which one should one look? This depends on the ratio of l to d, that is of the electron mean free path to the molecule surface separation. For a noble metal and a frequency of $\omega/\omega_P \approx \frac{1}{2}$, $l \approx 400$ Å so that, in the distance regime 10 Å $< d <$ 200 Å, processes B (and possibly C) are expected to dominate [36]. Conversely, a short mean free path (e.g. Ni) would

result in the bulk term, process A, dominating. Results obtained with Ni substrates by Campion *et al.* [39] do indeed indicate the dominance of process A. The following section details the results of experimental investigations into this distance regime. The lower limit (about 10 Å) is set by the need to maintain the validity of the approximations that the dipole is small compared with its separation from the surface, and that wavefunction overlap with the surface should be avoided.

4.4.1. *The intermediate-distance regime* (10 < d < 200 Å) (*for metallic substrates*). Many experimental investigations have been undertaken. The results of those up to 1985 were analysed and discussed in a review article by Waldeck *et al.* [3]. Here, we discuss a few pertinent investigations from pre-1985 together with more recent results. We start by noting that caution needs to be exercised in interpreting relevant experimental results for four principal reasons.

(i) Where experimental data of the fluorescence decay are not presented, it is usually not possible to judge how well those data fit the single-exponential decay that all the models assume.

(ii) The thickness of space layers in this thickness regime are not easy to measure.

(iii) Distance dependences other than those expected might arise from a distribution of distances being present, for example with rough spacer layers, rather than the single distance assumed. This was the cause of much activity in the early 1980s when Rossetti and Brus [40] reported lifetime measurements for pyrazine ($\lambda_{fl} = 410$ nm) above Ag that were distance independent! This turned out to be because the sample structure was not the structure that was assumed; the emitters responsible for the measured emission were always at the same distance from the substrate. Although this problem was quickly dealt with [41, 42], it sparked off activity that helped to elucidate the nature of non-radiative transfer of energy to surfaces.

(iv) It is often possible for several distance dependences to fit the data equally well, owing to the limited range of d over which measurements are usually taken, and the limits of experimental uncertainty in individual data points, some causes of which are mentioned above.

As Waldeck *et al.* [3] pointed out, most experiments, such as those by Whitmore *et al.* [43] and Daffersthofer *et al.* [44], have confirmed the validity of the classical model and have shown a d^{-3} dependence. As discussed above, for many systems (e.g. pyrazine above Ag mentioned in (iii) above) this is not unexpected since the electron scattering at the emission frequency is strong enough to ensure that decay via bulk modes dominates. To ensure that bulk modes *do not* dominate and thus to see the effect of surface damping, that is a d^{-4} dependence, one needs to change either the substrate or the emission frequency (or both) so that electron scattering is reduced. Lowering the frequency into the infrared may easily satisfy this criteria so that it is not surprising that investigations of vibrational relaxation [38] show up this dependence.

Where energy transfer is possible to both bulk and surface modes, that is processes A and B present, a distance dependence between d^{-3} and d^{-4} might be expected. Such a dependence was found by Alivisatos *et al.* [45] for the decay of

biacetyl above Ag(111) $\left(\lambda_{fl} \approx 520\,\text{nm}\right)$. More recent work has claimed agreement with the classical model $\left(d^{-3}\right)$ for a similar system, tetraphenylporphyryrin above Au $\left(\lambda_{fl} \approx 650\,\text{nm}\right)$ [46]. From the arguments outlined above, one might have expected a distance dependence lying somewhere between d^{-3} and d^{-4}. In fact, examination of the data presented by Sato *et al.* [46] shows the fit to d^{-3} to be far from perfect, the absence of error bars on the experimental data making it difficult to judge the degree of discrepancy.

This area of the subject is really of secondary interest since it involves the non-radiative loss of energy by the excited state. There is much physics buried here: the nature of realistic models for the spatial dispersion of the substrate, the nature and properties of the surface region (see also section 4.5) and the inclusion of surface roughness. It is, however, very important to recognize the existence of these decay channels, to be aware of the limitations of the classical model in taking account of them, and to understand in what situations they may play an important role. After all, they act as competing mechanisms to the fluorescence in which we are interested. Conversely, their effect on the fluorescence may, as we have seen above, by used to provide important information on these processes.

4.5. *The selvedge treatment of the interface*

The non-local response of the surface of the substrate mentioned above can be thought of as providing an additional layer in the system at the boundary between the two media. The properties of this layer, often referred to as the selvedge region, are different from either of the two adjoining semi-infinite media and may incorporate such aspects as impurities or dopants on the surface, and surface defects. That the surface of a conducting material should have different properties to the bulk is not surprising since impurities etc., and, more fundamentally, the presence of the interface will lead to a build-up of charge that will partially screen the bulk of the conductor.

The presence of this additional layer is to produce a change in the reflectivity (and transmission) of the interface. A particularly fruitful way to undertake such calculations is to develop modified Fresnel reflection coefficients. The details of such modifications depend on the microscopic model adopted for the electronic response of the conductor. Several theoretical treatments have been given, based on the modified Fresnel coefficient approach [47–50]. Note that an extra layer is *not* introduced; rather the reflection coefficient of the surface is modified to take account of a surface layer. Such treatments predict the existence of additional plasma frequencies and lead to the idea of extra poles in attenuated total reflectivity (ATR) measurements (commonly undertaken in measuring the reflectivity of metal surfaces [20]) associated with the accompanying additional surface plasmons.

The simplest case considers the addition of one new plasma frequency, and thus one new feature of ATR-type measurements is expected. Lang *et al.* [51] claimed to have experimental evidence for such an additional feature in the ATR spectrum of a thin Al/Ag bilayer. The new mode was associated with the Ag–air interface, the Al being used to control the surface roughness of the Ag. The features were seen in those films suspected of having greater surface roughness. The new feature occurred as an extra dip in frequency-dependent ATR measurements, near the bulk Ag plasmon frequency. Fitting their theory to the experi-

mental data, these workers found that their new feature indicated a selvedge region of about 1.5 nm thickness.

Balzer *et al.* [52] have measured the fluorescence lifetime (inferred from fluorescence linewidths in an elegant two-photon technique) and frequency of Na atoms near (2–4 nm) to Au and Pt surfaces, organic monolayers being used as the spacers. In this distance regime, they found considerable disagreement between their data and simple CPS-type classical theory. In particular, they measured lifetimes that were a factor of two smaller than theoretically predicted and found a distance dependence closer to d^{-4} than d^{-3}. The measured frequency shifts were found to be approximately two orders of magnitude smaller than expected on the basis of CPS theory (see section 5).

Inclusion of roughness, modelled as a small sphere, and a non-local dielectric function based on a hydrodynamical model of the metals reduced the disagreement between experiment and theory but were perhaps too crude to allow a good match. Recently, the same group has re-analysed their data using a model that incor-porates a selvedge region. Assuming that this region introduced just one extra surface plasmon mode, they were able to fit simultaneously both the lifetime and the frequency shift data, a thickness of 0.1–0.2 nm being found for the selvedge region. The agreement between experiment and theory was much improved; in particular, the two-orders-of-magnitude difference between experiment and theory for the frequency shift was largely removed. Questions still remain; for example, the theoretical frequency shift now decreases rapidly with increasing distance between Na atom and surface whilst the experimental values are relatively constant. Further work is still required: in particular, more experimental data are needed that probes both the lifetime and the frequency shift in this intermediate distance regime. Comparison with more realistic models is also required, for example including the space-layer–air interface. Investigations with well defined corrugations rather than surface roughness may also prove fruitful.

4.6. *Fluorescence near semiconducting interfaces*

In contrast with the study of electronically excited molecules above metals, surprisingly little effort has been devoted to the photophysical properties of molecules above semiconductors. We have seen above how the excitation energy of the molecule may be transferred to a metal. That transfer is well accounted for by a dipole–dipole-type interaction between the molecule and the unbound electrons of the metal, the latter dominating the dielectric response of the metal. For insulating materials and semiconductors, the dielectric response is usually governed by the behaviour of bound electrons. It is not immediately clear that the use of the energy transfer model based on the same classical model of the dielectric response should be as successful as it has been when applied to metals. In particular, does the rate of transfer depend on d^{-3} in the quenching regime?

Although some experimental and theoretical work has been undertaken, the situation is still not clear. Hayashi *et al.* [53] examined fluorescence from thin layers of tetracene $\lambda_{\mathrm{fl}} = 580\,\mathrm{nm})$, spaced from Si and GaAs by LiF layers. They examined the quenching regime with spacer layer thicknesses of $20\,\text{Å} < d < 400\,\text{Å}$ and claimed an exponential distance dependence of the transfer rate to Si. For GaAs they found the rate to be independent of d for $d < 100\,\text{Å}$. However, these rates were inferred from fluorescence intensity data. As noted above, such a

method is inappropriate since the radiation pattern changes quite dramatically as the spacer layer thickness is changed.

Whitmore *et al.* [54] studied fluorescence from pyrazine $(\lambda_{fl} = 380\,\text{nm})$ above GaAs(110) using ammonia as the spacer layer. They measured the lifetimes of the molecules directly and found that the dependence followed the classical d^{-3} in the quenched regime, with the possibility of a slightly faster dependence in the $20\,\text{Å} < d < 100\,\text{Å}$ range. Alivisatos *et al.* [55] examined the lifetimes of pyrene $(\lambda_{fl} = 390\,\text{nm})$ above Si(111), Xe being used for the spacer layer. Their investigation of the distance dependence of the transfer to the Si substrate was somewhat inconclusive, there being, in addition to energy transfer to the Si, significant transfer of energy between molecules in the pyrene layer. Brandstätter *et al.* [56] claimed that there was no energy transfer to the Si substrate in their study of cyanine $(\lambda_{fl} = 440\,\text{nm})$ above Si. However, this claim was based solely on fluorescence intensity measurements, the relevant data being confined to a small corner of one of their graphs.

In a more recent study, Sluch *et al.* [57] investigated fluorescence from palmitic acid $(\lambda_{fl} = 450\,\text{nm})$ above Si, LB layers of tricosenoic acid being used as spacers. They claimed their data to show a d^{-3} dependence of the lifetime for $100\,\text{Å} < d < 300\,\text{Å}$ but found that for $30\,\text{Å} < d < 80\,\text{Å}$ the distance dependence was slower than this, in contrast with the faster dependence found by Whitmore *et al.* [54]. This contrast was not noted by Sluch *et al.*

Transfer of excitation energy from an excited molecule to a semiconductor thus remains an area requiring further attention; in particular the nature of the energy transfer process for $10\,\text{Å} < d < 100\,\text{Å}$ needs to be clarified.

4.7. *Fluorescence near dielectric interfaces*

Our discussion so far has been dominated by consideration of substrates that are good reflectors, namely metals and semiconductors, whose bandgap is less than the excitation energy. However, the concepts and theoretical model that we have developed are just as applicable to materials that give weaker reflections, such as glass and liquids.

There are two principal consequences of having dielectric substrates rather than good reflectors, such as metals.

(i) The reflected field at the site of the emitter will be weaker, thus reducing interference effects on the decay rate and radiation pattern. This was well shown by Drexhage *et al.* [14] who undertook measurements similar to those of figure 1 but with a simple glass slide as the substrate. The change in the radiation pattern has been calculated by, among others, Sipe *et al.* [58].

(ii) The near field of the emitter will, when d is less than λ_{ij} from the interface, sample the dielectric properties of the substrate. The refractive index in which the emitter is embedded is therefore a mixture of the two media.

Thus far, we have not considered the important role played by the refractive index surrounding the emitter on the PMD. As the refractive index rises, the wavelength falls; the volume into which an optical mode may be confined is therefore reduced, so increasing the PMD. A simple consideration in which the wavelength in a dielectric of index n goes from λ_{ij} to λ_{ij}/n indicates that the modal volume, and thus the PMD, should be proportional to n^3. This simplistic view

neglects the fact that the host surrounding the emitter further modifies the electromagnetic field through dielectric and local field effects. These further complications have been extensively investigated and are nicely reviewed by Barnett *et al.* [59].

This dependence on refractive index was reported by Rikken [60] who looked at the emission from Eu^{3+} in liquids of different refractive indices. Their results matched theoretical models, provided that local field corrections were taken into account. Snoeks *et al.* [61] studied the lifetime of Er^{3+} ions embedded just beneath the surface of a glass slide. The found the lifetime to depend on the refractive index of the liquid that covered the surface of the slide. Again, good agreement between experiment and theory was found. Evaporated films containing Eu^{3+} were used by Lukosz and Kunz [62] to examine the effect on the lifetime of proximity to a glass superstrate, brought into optical contact with the evaporated film by mechanical means. This experimental arrangement allowed the distance between a fixed set of emitters and the interface of interest to be varied and enabled them to show that the changes induced in the decay rate by the superstrate were reversible. Liberherr *et al.* [63] deposited dye molecules onto glass substates of different refractive indices. They were able to show that the measured variation in lifetime for substrates of different refractive indices were in fair agreement with calculations based on the theoretical model outlined above. Additionally, the lifetime data were used to evaluate the quantum efficiency of the emission, a technologically important parameter. These workers also looked at the way that the radiation patterns were altered by substrates of different refractive indices. In a rather different study, of emission from electron–hole recombination in a thin slab of GaAs on substrates of different refractive index, Yablonovitch *et al.* [64] demonstrated the importance of the PMD on either side of the slab. Higher-refractive-index substrates had higher mode densities which, owing to their close proximity to the emitters, were able to increase the decay rate significantly.

In investigating the lifetime of emission from molecules deposited as very thin films, roughly a monolayer or less, care has to be taken in interpreting the quenching of the emission lifetime. This is because many systems show either intermolecular energy transfer that often leads to energy being trapped and lost at impurity sites, etc., or coverage-dependent effects (low density, submonolayer films consisting of isolated molecules, monolayer and thicker films having sufficient number densities to allow the formation of dimers, excimers, etc.), thus changing entirely the nature of the emitter. Both of these effects were examined by Haynes *et al.* [65] and have been reported by many others, for example Puech *et al.* [66].

Crackel and Struve [67], motivated by the possibility of enhancing the wavelength range of photodetectors by coating their surface with dyes, examined the non-radiative decay of the dye cresyl violet above TiO_2. For this wide-bandgap substrate, Crackel and Struve found a quenching of the lifetime by about 50% on changing the separation from 500 to 100 Å. A control experiment using silica as the substrate showed only a 10% variation in lifetime over the same distance range. The mechanism of the non-radiative decay to the TiO_2 was not identified. In a similar experiment, Shu *et al.* [68] measured the distance dependence of the emission intensity of Eu^{3+} ions above an indium tin oxide surface. They found that this commercially important transparent conductor produced a tenfold quenching of the fluorescence when the spacer thickness was reduced from 100 to 2 nm.

The primary interests in this area are thus to examine and exploit the control of emission from within a thin layer by altering the PMD in the surrounding media and to identify the mechanisms of non-radiative decay to dielectric and semiconductor substrates.

A more exotic choice of substrate is the phase conjugate mirror, discussed by Agarwal [69] and Milonni *et al.* [70]. As might be anticipated, the field reflected by a phase conjugate mirror acts to cancel the original field. Should such a mirror have unit reflectivity, then complete inhibition of spontaneous emission would be expected.

5. Frequency shifts

Whilst the out-of-phase component of the reflected field alters the decay rate, the in-phase component changes the resonant frequency of the emitter. Just as the new decay rate is a property of the emitter–surface system, so too is the new frequency, as given by equation (6) (the width also increases [71]). We should note that the frequency shift given by equation (6) is based on a classical harmonic oscillator model. Although such a model provides a starting point for discussing frequency shifts and gives us an intuitive way to see how they arise, it is not necessarily a very realistic model. Barton [72] has given a detailed critisicm of such a model and highlighted its inconsistency with quantum mechanics; the reader is referred to that work for more details.

For most emitters in the visible, the decay rate b is sufficiently small compared with the transition frequency ω that the first two terms in equation (6) may be ignored [71]. The frequency shift may then be written as [50]

$$\Delta\omega_\perp \propto -\frac{3}{4\pi_0}\mathrm{Re}\,(E_0).\qquad(13)$$

The frequency shift will thus be easier to measure if the lifetime is short. In the experiments involving Eu^{3+} spaced by one LB monolayer (about 2.5 nm) from a Ag surface a frequency shift of the order of megahertz is expected. However, if the emitting state has a lifetime of 1 ns rather than the 1 ms of Eu^{3+}, one would expect a shift of the order of gigahertz rather than megahertz. Using Na atoms with a lifetime of the order of picoseconds and an elegant two-photon technique, Balzer *et al.* [52] were able to measure frequency shifts of the order of gigahertz. The measured frequency shifts could not be accounted for by the classical model, equation (6), the two differeing by a factor of 100. Wylie and Sipe [73] considered a quantum-mechanical linear-response model [73] that included a selvedge region at the surface of the metal. They obtained theoretical values of the same order as those measured, although the theoretically predicted variation in frequency shift with separation d was not observed. It would seem that a more sophisticated model and further measurements are required, especially to allow the effects of surface roughness to be accounted for. Therefore, it might be useful to undertake measurements for a variety of well controlled surface morphologies.

Holland and Hall [74] examined the frequency shift not of atoms or molecules but of the resonant frequency of small metal islands separated from a metallic surface. Such artificial dipole oscillators have both a large dipole moment and a very short natural lifetime. Together with the small difference in frequency between the resonant frequency of the islands and the asymptotic SPP frequency
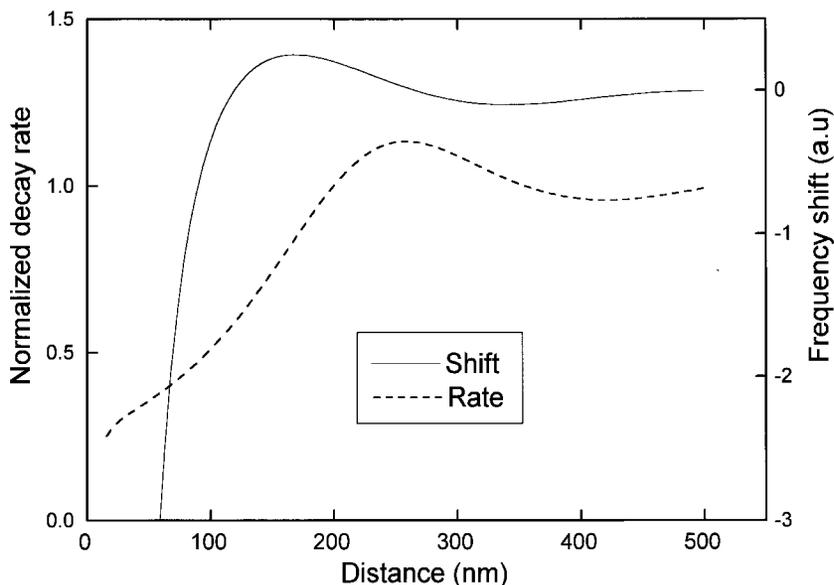
Figure 12.   Calculated frequency shift and decay rate for a perpendicular dipole
(emitting at 614 nm) above a Ag mirror of dielectric constant $-16 + 0.6i$ (a.u.,
arbitrary units). Note the initial red shift followed by a small blue shift as the
distance between the emitter and the surface increases. Details of the calculation are
described in the text.

this meant that the expected frequency shifts were of the order of 10%. By varying
the separation of the islands from the metal film, Holland and Hall were able to
observe the frequency shift by measuring the wavelength-dependent specular
reflectivity of their structures. For small separations they found a red shift, and
for larger separations a blue shift. Using a model based on the classical approach
adopted above, and illustrated in figure 12, they were well able to account for their
data. Since the classical theory includes only the interaction between the dipole
and the surface, this result suggests that, for the films examined, any interaction
between islands was negligible. In fact, the measured red shift at small separations
was less than expected, a fact which these workers attributed to the poor quality of
the thin (less than 20 nm) spacer layers. For island films in which the islands are
much closer packed, electromagnetic interactions between islands are important.
Frequency shifts for such systems have been measured and modelled, assuming
the islands to form a film with an effective dielectric function [75]. Island films are
discussed further in section 6.3.

From the above, we see that there has been relatively little work concerning the
frequency shifts have also been seen in the emission of a Ru complex coated on
Ag island films. Using a combination of different types of luminescence measure-
ment, Garoff et al. [76] found evidence for frequency shifts, although the sample
fabrication technique did not allow the distance dependence to be properly
evaluated.

From the above, we see that there has been relatively little work concerning the
frequency shift of emission close to a mirror, in contrast with the situation in
microcavities [77]. This is because, in general, the frequency shifts are small and
the experiments often not easy. However, more work needs to be done on looking
at frequency shifts above surfaces with well characterized morphology.

6. Nonplanar interfaces

If we relax the requirement that the interface in our system is planar, three new factors may come into play.

(i) Breaking the translational symmetry of the plane allows non-radiative modes, such as SPPs and waveguide modes, to couple to radiation by scattering from surface structure. Bragg vectors associated with periodicities in the surface profile may provide the missing momentum required to couple non-radiative modes and photons.

(ii) In many of the nonplanar structures the surface modes may become localized. This leads to dramatic enhancements in the local PMD associated with them.

(iii) Fabrication techniques that lead to a singular value of the emitter surface separation d in the case of a planar sample may now produce samples with a range of d, complicating the interpretation of results obtained from them.

In terms of changes to the PMD and its manipulation via surface morphology and/or composition, it is the ability of nonplanar surfaces to support localized modes that is most important. In particular, very significant increases in PMD can be achieved with metallic structures possessing features with small radii of curvature. The localized SPP modes associated with such features are at the heart of surface enhanced Raman scattering (section 7.1).

Just as important as changing the PMD is the role that nonplanar surfaces play in coupling non-radiative modes to radiation. This is vital in allowing us to access the high PMD that nonplanar structures may possess. The competition between non-radiative decay to SPPs and to lossy surface waves (section 4.4) provides a clear example. Coupling between an emitter and the SPP modes of an underlying metallic substrate is a non-radiative loss route for a planar structure, despite the high PMD associated with the SPP mode (section 4.2). The possibility of scattering from surface features allows the SPP to be coupled to radiation, so that this decay mechanism is no longer non-radiative and, owing to the high PMD associated with the SPP mode, the radiative yield is likely to reach a peak when the power lost by the emitter to the SPP mode is greatest.

The high PMD associated with modes such as SPs means that they may successfully compete with internal non-radiative decay of the emitter, via the emission of phonons into the material immediately adjacent to the emitter. In this way, the radiative quantum yield of low-quantum-efficiency emission may be overcome [78], something that may be of importance in such applications as microlasers where non-radiative decay may be the limiting factor in obtaining lasing on some transitions [79].

A further important feature of nonplanar interfaces is that it makes the model developed in section 3 inappropriate; new models need constructing, as discussed below.

6.1. *Corrugated surfaces*

The effect of surface morphology on the emission of nearby molecules has been investigated extensively, but the study of this area is still far from complete. We start by considering the effect of periodically corrugating the surface on radiation

patterns. As mentioned above, one of the most important effects is for the corrugation to couple non-radiative modes such as SPPs to radiation. The radiation pattern of the emitted light will generally comprise lobes due to SPPs and waveguide modes. These would not be present in the absence of the corrugation since, as discussed above, they have in-plane wave-vectors that are too large to be supported in the air.

The role of surface corrugation in scattering the non-radiative SPP excited by the decay of a nearby emitter into photons was first demonstrated by Knoll *et al*. [80]. They used the LB technique pioneered by Kuhn and Drexhage to separate a monolayer of dye molecules from a corrugated Ag surface, that is a metallic grating. By examining the polarization, wavelength and intensity dependences 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 about 10–15 nm from the metal surface. This is as expected from figure 8. Adams *et al*. [81] measured the emission from N_2 films up to 2000 nm thick deposited on Ag. In contrast with the work of Knoll *et al*., the films used by Adams *et al*. were thick enough to support waveguide modes, as well as SPPs; both types of mode were clearly seen in the measured radiation patterns, features that had been predicted by Aravind *et al*. [82] on the basis of small-amplitude corrugation theories. Agarwal and Kunasz [83] showed theoretically that under appropriate circumstances, notably when the emission frequency is close to the asymptotic surface plasmon frequency, non-local effects in the dielectric response of the metal (section 4.4) can lead to changes in the angular position of the lobes of the radiation pattern.

With careful control of the corrugation used in such experiments, a bandgap in the propagation of SPP modes may be produced. The bandgap arises when the pitch of the corrugation provides just the required momentum to back-scatter the SPP mode. The two counter-propagating SPP modes set up a standing wave and, owing to the different surface charges and field distributions associated with the two standing-wave solutions, a bandgap is opened up. Thus the SPP decay channel may be turned off. Examining the intensity of emission from a laser dye spun down on top of a Ag grating, Kitson *et al*. [84] recently demonstrated blocking of the SPP decay channel with this technique. For the single corrugation used, SPPs of a given frequency are only blocked from propagating in the direction normal to the corrugation groves (in fact, the detailed angular dependence is slightly more complicated than this [85]). To block SPP propagation in all directions and therefore to turn off the SPP decay route at the emission frequency completely requires a surface that is periodically modulated in at least two directions. Kitson *et al*. [86] demonstrated that a hexagonally textured surface could, indeed, be used to produce such a complete SPP bandgap.

These developments mark a new stage in controlling the PMD near metallic surfaces, since it is now possible to manipulate the PMD associated with the SPP mode. The effect of single corrugations on fluorescence [84] and surface-enhanced Raman scattering (SERS) [24] have already been demonstrated. An obvious next step will be to verify that the absence of such modes will alter the decay rate, as one would expect.

There are still many interesting questions to be answered concerning fluorescent emission close to textured surfaces; they become increasingly important with the use of near-field optical microscopy [87]. One such question concerns the

control of other types of surface mode, for example the surface exciton polaritons associated with absorbing media, by PMD.

At this stage, it is useful to review the considerable theoretical work that has been undertaken on modifications to the decay rate and emission frequency in the presence of corrugated surfaces. In a series of papers, Leung and co-workers [88–93] considered the effect of corrugated metal surfaces on fluorescent emission from nearby molecules. Several of their papers in particular have dealt with the issue of the decay rate of an excited molecule above a corrugated metal surface [88, 89, 93]. Several assumptions were made, notably that the depth-to-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. Indeed, the predicted changes, often an order of magnitude, seem quite remarkable for the very weak corrugations considered.

Only very recently have any experimental data become available on decay rate modifications in the presence of a corrugated surface. New results from the present author's laboratory, taken by R. M. Amos, concern the distance dependence of the lifetime of Eu^{3+} ions above corregulated Ag surfaces. The lifetime data are shown in figure 13, together with the results for the planar surface for comparison.

The most noticeable difference is a reduction in the amplitude of the oscillations of lifetime with distance, perhaps owing to an effective reduction in the reflectivity of the corrugated surface when compared with a planar surface. There is also a significant reduction in lifetime for the smallest values of d measured, possibly resulting from a change in the PMD associated with the SPP mode. It was not possible to identify whether molecules with different lateral positions with respect to the corrugation experience different decay rates. A site-selective excitation (or collection) technique would be needed to investigate this. The effects of depth and pitch and whether a single corrugation or more than one are present are all interesting areas for future research.
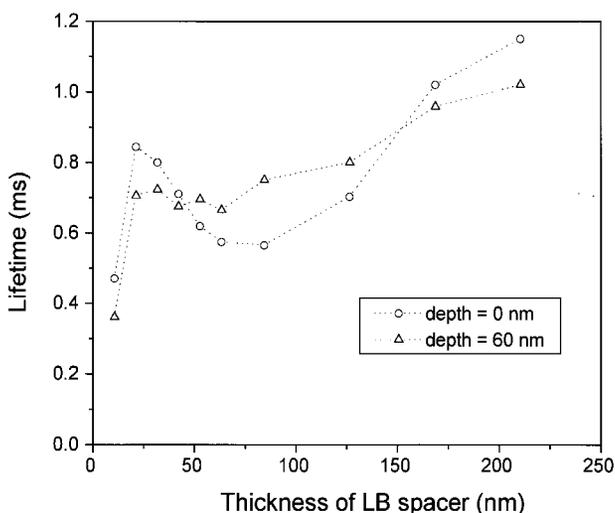
Figure 13.   Lifetime of Eu^{3+} in front of a Ag surface for a flat surface and a corrugated surface. The pitch of the corrugation was 407 nm; other details are as figure 1.

The theories of Arias *et al*. [94] and those of Leung *et al*. [90] are not expected to work for deep gratings and/or small surface–emitter separations, the latter causing problems because of the need to consider high-wave-vector components of the dipole field. These limitations are unfortunate since this is just the regime where things become interesting; it is not clear what the effect of the corrugation on the radiation pattern will be. Principal among the unanswered questions is: will the evanescent components of the dipole field be scattered by the corrugation? Since the evanescent field is of limited extent, it is not clear whether it will 'see' the periodicity of the surface; more work in this area is urgently needed.

6.2. *Surface roughness and small particles*

Many important surface processes are based on the presence of surface roughness, for example the surface-enhanced Raman effect (section 7.1). Although an understanding of the mechanism involved is more easily found by examining surfaces with periodic texture (section 6.1), in this section we simply review the work most directly concerned with surface roughness.

One may consider a rough surface to be multicorrugated, with the rough surface represented as a sum of periodic surface corregulations with appropriate weightings. Such a surface will enable coupling between non-radiative modes and radiation. Often the surface will contain surface features with considerably greater surface curvature than that found in corrugated surfaces. Thus, as will the islandized films discussed below, it is the localized modes of such structures and the PMD associated with them that provides the most important difference between these and planar systems. Small particles are included in this discussion since many theoretical models of surface roughness are based on considering the surface to consist of a collection of small particles.

The importance of the high PMD associated with localized modes of small particles in enhancing the quenching of fluorescence was evaluated theoretically by Gersten and Nitzan [95]. They assumed that the separation between molecule and surface was sufficiently small that retardation effects could be ignored. The same workers also examined the effect of such localized modes on the transfer of energy between molecules via the dipole–dipole interaction [96, 97]. They found that, when the frequency of the transfer was similar to that of the particle resonance, there were significant increases in the transfer rate. Pineda and Ronis [98] also examined theoretically the quenching of fluorescence by metal particles and, by taking account of electromagnetic particle–particle interactions, predicted that the resonant frequency of the molecule–particle system would split. Liver *et al*. [99] considered the interaction between an excited molecule and a cluster of dielectric particles. They found that the cluster geometry was important in determining the decay rate and quantum yield of the emission. Ruppin [100] has calculated the distance dependence of the decay rate of a molecule near a small metal sphere for separations in the range appropriate to the data figures 1 and 13. Ruppin found that the primary effect of the change of geometry from planar to small sphere was to reduce the reflectivity, thus washing out the oscillations of decay rate that occur as the molecule surface distance is varied.

Balzer *et al*. [52] have recently performed experiments on Na atoms above rough Au and Pt surfaces and have measured both their decay rate and their frequency shift. They found that, in order to fit theory to their experimental data, they had to invoke a selvedge region (section 4.5).

Surfaces showing microscopic roughness also affect radiation patterns. The roughness providing the coupling of non-radiative SPP and waveguide modes to radiation. They also result in a scrambling of the information on dipole orientation, information that for planar surfaces can be found by looking at the polarized radiation patterns [101]. This is to be expected since, when the surface is rough, polarization is no longer well defined.

Another possibility is that of coupling energy between an excited molecule and the whispering gallery modes, or Mie resonances, of dielectric particles [102]. The modes of such particles can exhibit very large Q so that the PMD associated with them can be larger than anything so far considered [103]. Discussion of this topic is outside the scope of this article but clearly forms a natural extension of the concepts under discussion.

6.3. *Islandized films*

Nonplanar interfaces may also be formed by varying the composition of a thin layer, rather than just the morphology of the surface. Many metals will naturally form films of metallic islands in approximately the 10–100 nm range when evaporated under suitable conditions. Although such samples usually possess nonplanar morphology, it is their mixed composition that is of primary interest to us here, since it both provides the source of scattering to couple non-radiative modes with radiation *and* results in the existence of localized modes.

The frequency of the localized modes depends on both the size and the shape of the islands. In general, the techniques used to form islandized films produce irregular arrays of islands with a range of sizes and shapes. Careful control may limit this range, thus providing substrates with reasonably well defined localized frequencies. Some work has been undertaken on periodically arrayed dots of well controlled dimensions using lithographic techniques [104]. The coupling between SPP modes and radiation via scattering from islands, has been demonstrated by many workers (for example [105, 106]). Wokaun *et al.* [107] showed how the luminescence yield peaked as a function of separation between emitter and metal substrate (section 4.2). Garoff *et al.* [76] reported a series of time-resolved, spectral and intensity measurements of fluorescence from adsorbates on Ag and Au island films, demonstrating the importance of measuring several parameters to build up a good picture of the role of PMD in this process.

Kummerlen *et al.* [78] showed how the effective quantum yield from low-quantum-efficiency emitters could be enhanced by extracting their energy via the SPP route. Enhancements of the order of 500 in luminescence intensity, due largely to localized SPP resonances, have been reported by Aroca *et al.* [108]. These workers also found that the yield, rather than decreasing as the distance d fell below the optimum value, actually went back up again. However, this was based on one data point and was for an adsorbed layer rather than a layer on a very thin spacer; consequently, it is difficult to read very much into this last result.

Ritchie *et al.* [104] looked at Ag islands on an Al rather than a glass substrate. They found two localized SPP frequencies and attributed them to oscillations along and across their (roughly) elliptical Ag islands. They demonstrated the role of the islands in increasing the radiative yield, by investigating the yield as a function of island number density. In an interesting alternative to the usual fabrication techniques, Ghumanov *et al.* [109] used colloidal metal films as their substrate. They found that the fluorescence intensity was highest for emitters

adsorbed directly onto the metal particles, contrary to what would have been expected from the arguments presented above. These workers attributed this to a proposed population of emitters located between the colloidal metal particles, thus experiencing a high PMD without being significantly quenched by the metal. Interestingly the colloidal particles used in this work were formed in such a way that they did not aggregate; rather they maintained a separation of the order of 10 nm, their diameter being about 40 nm. They did not find any splitting of the resonant SPP frequencies associated with the colloidal particles, indicating that strong coupling between SPP modes on adjacent particles was not taking place. This remains an area in which further research to look for coupling effects needs to be undertaken. The importance of using colloidal particles in fluorescence-based sensors is now established, so that this work is of technological as well as scientific interest [110]. Note that much of the modelling undertaken to look at the PMD associated with island films has been based on the analysis of ellipsoidal particles by Gersten and Nitzan [95–97].

6.4. *Near–field optical microscopy*

The PMD is at the heart of near-field optical microscopy, a technique that allows the optical study of many structures on scales down to atomic dimensions. Active control over the distance between the emitter and a metallic surface, a metal-coated optical probe, is easily undertaken and has been used by Pagnot *et al*. [111] for just such an experiment. The convex nature of the metallic surface meant that the oscillations in decay rate with increasing emitter–surface separation were largely washed out, as expected (section 6.2).

Perhaps in this area, more than any other area discussed so far, control and understanding of local PMD will be of benefit to researchers in many different disciplines as near-field optical techniques become commonplace in characterization and control at the molecular level. Of crucial importance in interpreting the data acquired in such experiments is the role played by the tip. The tip not only measures the local PMD but, to a considerable extent, also determines it. Significantly, the sensitivity of near-field techniques has allowed optical processes associated with single molecules to be investigated [112–114]. Thus, the question of how the tip influences processes such as fluorescence lifetimes is crucial; our understanding in this area is still being developed [115, 116].

7. Other optical processes

This review concerns the effect of PMD on spontaneous emission. Together with the absorption of light, spontaneous emission is possibly the most studied and best understood optical process. However, it is not the only optical process that depends on PMD; there are many others. Of particular importance has been SERS, a process that relies on the significant changes in PMD associated with the localized SPP modes of small metallic particles. This and other processes are briefly reviewed below. Their importance lies in the fact that they are involved in many physical and chemical reactions and processes.

7.1. *Surface-enhanced Raman scattering*

The (SERS) effect has perhaps been the most widely studied of all surface optical phenomena. It is important in the context of our discussion on the role of

PMD near surfaces, since PMD is one of two factors that causes the enhancement in the SERS effect. In Raman scattering, a pump photon is incident on a molecule and is scattered by it; in the process, some of the energy of the photon is lost, the energy being used to excite a vibrational (Raman) mode of the molecule.

In the SERS effect the molecule resides on a rough metallic surface. Enhancement occurs in two ways. The first, is electromagnetic, that is PMD based. The roughness causes localized SPP modes which have high local field (PMD) enhancements. Further, the incident pump light couples via surface roughness to SPP modes, the enhanced fields of which interact with the molecule. Similarly, the scattered photon emerges from the molecule via the excitation of another SPP mode, again providing an enhancement. The second enhancement mechanism is chemical in origin and is due to the way that the bond between the molecule and the surface produces a strong vibrational (Raman) mode in the adsorbate–substrate system via a charge-transfer intermediate state. Many reviews of the SERS effect have been published, a particularly comprehensive and recent review being that by Otto *et al*. [117].

We wish here to concentrate only on the role of the PMD in the SERS effect. Its importance is most clearly seen when, instead of a rough surface, a surface with more well defined morphology is used. Knoll *et al*. [118] used a grating to control the coupling of the scattered light from SPP modes; the role of the SPP mode was made very clear by studying the strength of the SERS signal in the vicinity of a SPP band gap.

One may think of the metallic surface as providing antennae that couple to the molecule, thus acting as large aerials. The role of the grating as antennae was demonstrated by Baltog *et al*. [119], who showed that there exists an optimum groove depth for the grating, a depth at which the corrugations best act as antennae. Still greater enhancements may be obtained by using islandized or colloidal metals as the substrate; this is due, once again, to the very high PMD associated with the localized SPP resonances of such structures [120]. Indeed, enhancements have become high enough to allow the detection of single molecules using the SERS effect [121].

SERS is an example of the very strong modifications that can be imposed upon optical processes by changes in the PMD that arise from surface morphology.

7.2. *Energy transfer*

The transfer of energy is of fundamental importance in many areas of science, from photosynthesis to the quenching of luminescence in laser materials. One common mechanism for such transfer is the resonant dipole–dipole interaction (RDDI). In this process an excited molecule (the donor) interacts with an unexcited molecule (the acceptor) through the exchange of virtual photons, resulting in the transfer of energy from donor to acceptor. Thus, as for the case of spontaneous emission discussed above, the PMD may be expected to play an important role in this interaction. This can easily be seen in the picture where we consider the images produced by the surface of the dipoles involved, assuming the dipoles to be very close to the surface. If both dipoles (donor and acceptor) are perpendicular to the interface, then the dipole moment will effectively be doubled when the images are taken into acount (see figure 2). Consequently the RDDI process will effectively be enhanced. Conversely, if the dipoles lie in the plane

of the surface, then the effective moment will be decreased, suppressing the interaction.

The reasoning outlined above on the role of the interface on excitation energy transfer was given recently by Cho and Silbey [122]. We must beware of carrying the concept of image dipoles too far. The virtual photons involved in the RDDI are associated with the near field of the dipoles and are thus evanescent in character. Attention has focused recently on this aspect in opposing theoretical predictions [123, 124] and is not yet resolved.

Much of the experimental work undertaken on excitation energy transfer via the RDDI in the vicinity of an interface has not involved time-resolved measurements and thus has not been able to give much information on the effect of the substrate interface (for example Yonezawa *et al.* [125]). More often, the RDDI has been studied for donor–acceptor systems close to an interface, with the purpose of looking at excitation energy transfer in restricted geometries, that is two dimensional rather than three-dimensional, [126, 127].

Interest in the role of PMD in the RDDI has heightened recently, with new theoretical work in relation to microcavities [123, 124], and in relation to photonic solids [128, 129]. These results have been significant, in that they have predicted very strong modification of the transfer rate in such environments. However, the single surface is an important practical system, for example in catalysis and sensors, as well as in studies on the conformation of deoxyribonucleic acid on surfaces [130]. Whilst the modification of the transfer rate for the single surface may not be as dramatic as for the systems described above, significant effects may still be expected through changes in the quantum yield of the RDDI process. Here one envisages that a change in the PMD brought about by an interface may, for example, block the fluorescent decay of the donor, thus increasing the likelihood that the excitation energy eventually reaches the acceptor. Conversely, enhancing the probability that the donor will fluoresce will decrease the likelihood that the acceptor is excited.

As far as the present author is aware, the only experimental work to have been undertaken in this area [131] has not shed any light on the role of PMD variations near an interface on the RDDI. This area is one in which new experimental work is urgently needed; indeed, many possibilities are open for trial including using SPP modes as mediators of the RDDI process near metallic surfaces [132].

7.3. *van der Waals interactions at surfaces*

Just as spontaneous emission may be modified by the presence of an interface, so too may the van der Waals (vdW) interaction between two neutral polarizable molecules. Recall the origin of the vdW interaction [133]. One of the two molecules absorbs a virtual photon and thus acquires a temporary dipole moment, oscillating at the photon frequency. This oscillating dipole in turn induces an oscillating dipole moment in the second molecule. The average value of the dipole–dipole interaction energy is the vdW energy. Since the vdW interaction is dipole–dipole in character, a change in the PMD is likely to alter the interaction, just as it did for excitation energy transfer in the previous section. This has been demonstrated in experiments where a cavity rather than a single surface is used to modify the PMD [134]. The simple argument given above showing how a consideration of image dipoles modifies the dipole–dipole interaction applies equally here. Depending on the alignment of the dipole moments, the vdW interaction can be either

enhanced or suppressed. A more detailed analysis of how a single interface (and cavity) modifies the vdW interaction has been given by Cho and Silbey [135].

Even more recently, experiments to measure directly the strength of the vdW force between an atom and a dielectric substrate have been undertaken. Rb atoms were directed towards an evanescent wave atomic mirror, the intensity of the evanescent wave being adjusted to balance the vdW force and the inertia of the incident atom [136]. So far, the results have not been sufficient to distinguish between an electrostatic or QED model of the vdW interaction.

The nature of the interface is very important and has been theoretically investigated by Fichet *et al.* [137]; for example, a good reflector such as a metal will provide strong image dipoles. Additionally, when the substrate is metallic, further alterations have been predicted. If the molecule has an energy level that is resonant with the asymptotic surface plasmon frequency, then the SPP mode, rather than photons, may act as the intermediary for the vdW interaction. Metiu [138] examined this possibility and found that, in this case, the interaction was oscillatory with molecular separation and had an unusually long range. These findings required the inclusion of spatial dispersion.

Whilst a great deal of work has been undertaken on the theory of vdW interactions, experimental work, such as that of Landragin *et al.* [136] on the role of PMD, is only just beginning.

In the above sections we have seen how the PMD may affect processes other than simple absorption and emission. Our choice was by no means exhaustive; many others exist. Two-photon excited fluorescence was studied by Kano and Kawata [139], the PMD associated with SPP modes being used to enhance the process, whilst Atksipetrov *et al.* [140] investigated the dependence of second-harmonic generation at an interface on the local PMD. We might expect PMD to play a significant role in up-and-down conversion and co-operative effects, such as subradiance and superradiance [141]. Controlling the light–matter interaction and processes dependent on it will surely be the focus of much future work.

8. Summary

We have seen that interfaces can have a marked effect on the fluorescence of nearby molecules. The emission rate, the spatial distribution of the emitted radiation, and the apparent quantum yield of the emission, may all be altered. We have discussed in detail the role of surface and thin-film waveguide modes in modifying the emission by acting as non-radiative decay channels. The importance of energy transfer to non-optical modes of the substrate, predominantly the free and bound charges, was also discussed, owing to its importance as a competing mechanism for the decay of excited molecules. Particular emphasis was placed on looking at non-planar interfaces, both because they allow much greater changes in PMD and because they allow energy that would otherwise be lost to non-radiative optical modes to be recovered.

After 30 years or more, research in this area continues unabated. This reflects the underlying importance of the way changes in PMD at surfaces are manifested, from photochemistry to near-field optical microscopy. It seems very likely that this situation will continue. We have discussed some of the areas future research may develop. The use of interfaces possessing periodic texture is really only beginning; much more needs to be done to understand and to exploit the relationship between

surface texture and PMD. In particular, the interaction between periodic texturing and the near field of the emitter remains an open subject for both experimental and theoretical development. Localized modes associated with islands or other structures are also likely to become more important, particularly as fabrication techniques improve. Islands and the like may act as antennae for emitters, greatly increasing their coupling to radiation. Will it be possible to produce structures that show coherent effects between such antennae? The experimental investigation of optical processes other than spontaneous emission near interfaces, and their dependence on PMD is another largely unexplored area. It is hoped that this review will stimulate new ideas and lead to new research.

Acknowledgments

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