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NONRADIATIVE DAMPING OF MOLECULAR ELECTRONIC EXCITED STATES BY METAL SURFACES

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In this review we discuss the interaction of a molecular excited state with a smooth substrate. Both theoretical and experimental work is treated. This discussion will concentrate on the classical treatment of the interaction because of its astounding success in comparison with experiment. We do however discuss the shortcomings of the classical treatment and some recent approaches to correcting these limitations. The experimental work is considered in detail but we focus on the region close to the substrate, less than 500 Å away because the longer distance regime has been well reviewed. At the end of this article we briefly point out areas where future work is needed.

1. Introduction

Eighteen years ago a series of extremely important experiments were reported [1–3], which studied for the first time the effect of a metal on an electronically excited molecule located hundreds or thousands of ångströms away. In these experiments, the Langmuir–Blodgett monolayer assembly technique was used to create a variable thickness spacer layer on top of the metal, and a layer of the luminescent molecules was placed on top of the spacer. In this manner, the lifetime or quantum yield of the molecular excited state could be measured as a function of its distance from the metal surface. At distances on the order of the molecular emission wavelength, it was found that the excited-state lifetime oscillates as a function of distance from the surface. These observations could be explained using a simple interference model [3], in which the radiative emission rate of the molecule is modulated by its own field, which is reflected by the metal. When the reflected field is out of phase with the directly emitted field of the molecule, the radiative rate is decreased; when the reflected field is in phase, the radiative rate is increased. In the initial experimental investigations, it was also found that at distances much less than the emission wavelength, the lifetime of the molecule drops precipitously as the molecule is brought closer to the surface. While only a few points were obtained in this regime, these initial results were of great theoretical interest.

In the 1970's theoretical investigations showed that in the short distance regime the molecule nonradiatively transfers energy to the substrate [4,5]. During this period a simple, classical model for the energy transfer process was developed in great detail [4]. In this model, the molecular excited state is pictured as being a point dipole, while the solid is modeled as a medium of frequency-dependent dielectric constant $\epsilon(\omega)$. This theory predicted that the nonradiative energy transfer rate would depend on the inverse cube of the surface–molecule separation, a prediction which can be understood on general dimensional grounds. It is well known that a standard dipole–dipole Förster energy transfer rate depends inversely on the sixth power of the distance. For the case of a dipole above a metal, the problem is equivalent to one in which a point dipole transfers energy to a volume of point dipoles. The rate must be integrated over this volume and the distance dependence is thereby reduced to cubic. By the same reasoning one expects quartic distance dependence for transfer to a surface or thin film and a fifth-order dependence for transfer to a one-dimensional array. The classical theory, as well as the early experimental results, has been reviewed extensively [3,4].

Since the development of the classical theory, its predictions have been tested by many groups, using a variety of experimental configurations. In addition, many theoretical limitations of the classical theory have been discussed. It is the purpose of this review to summarize the experimental tests of the short distance predictions of the classical theory, and to lay forth the various limits in which the classical theory has been predicted to fail. We will confine ourselves to a discussion of energy transfer from molecules to flat, planar surfaces, although a variety of other interesting geometries have been studied, both experimentally [6] and theoretically [7]. Also the energy level shifts present for a molecule near a substrate is not discussed here, although both theoretical [4,8] and experimental [9] work on this effect exists. The energy transfer to flat, planar surfaces is a problem of general interest, and has been the subject of many investigations.

In this review the classical treatment of this interaction is discussed in detail. Subsequent to this discussion, various nonclassical theories which give a fuller treatment of the problem are considered. In the second section the experimental studies of this process in the short distance, or energy transfer regime are reviewed. Finally the prospects for future research in this area are discussed.

2. Theory

In the subsequent pages the classical treatment of this effect is described. The assumptions of the classical model are delineated and a qualitative understanding for the origin of energy transfer is provided. The primary classical results are presented and the limitations of the classical theory are

discussed. Secondly more recent extensions of the classical model are treated. Distinct models and the manner in which they differ from the classical model are discussed.

2.1. Classical model

After the observation of the distance dependence of the lifetime of an excited state above a metal surface, theoretical efforts were made to explain the results. Drexhage [2,3] treated the interference of the dipole with its reflected field and found good agreement with experiment at long distances, i.e. distances greater than 1000 Å. Subsequently, Kuhn [10,11] treated the interaction in a weak absorber limit and obtained much better agreement at short distances, at least qualitatively. An extension of this model, by Morawitz [12], treated the molecule quantum mechanically but the radiation field classically. Philpott [13] treated both the molecule and radiation field quantum mechanically and found good agreement with the classical treatment. Tews [14] and later Sipe [15] solved the classical problem of the damping of a point dipole by a planar metal a distance d away and obtained good agreement with experimental results. Chance, Prock and Silbey (CPS) in a series of papers [5,16–20], summarized in a classic review article [4], solved the same problem and extended their results to a much more general set of experimental configurations. The treatment of CPS is the definitive classical treatment and is discussed at length.

CPS use a purely classical description of the molecule–substrate interaction following very closely a derivation given by Sommerfeld [21] for the problem of radio-wave propagation above the earth. The molecule in the CPS description is a damped, driven harmonic oscillator. The field of this oscillator interacts through space with the metal which is described as a continuous medium of dielectric constant $\epsilon(\omega)$. The oscillator field consists of two components. One component extends infinitely away from the oscillator and obeys the dispersion relation of light ($\omega = ck$), and is called the radiation field. The other component decays rapidly away from the oscillator, and while it oscillates at the radiation field frequency, it does not obey the dispersion relation of light. This component is called the near field. CPS solve Maxwell's equations under the boundary conditions of an explicit experiment (as in fig. 1) and for an arbitrary set of interfaces. By computing the energy flux away from the oscillator they are able to obtain an expression for the decay rate of the oscillator in the presence of the metal. They find that the interference effects observed by Drexhage occur through the radiation field and at short distances energy transfer to the metal occurs through the near field.

Although CPS give a very general treatment of the problem, there are important assumptions made in their model which are not necessarily valid. First, the molecule is described as a classical oscillator and, additionally a
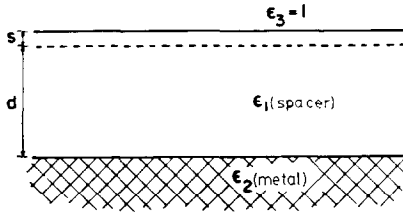
Fig. 1. In this schematic of an experimental arrangement [48] the ϵ's are the dielectric constants of the regions. The solid lines are the boundaries between the media and the dotted line represents the center of the emitting molecule. The molecule to substrate distance is d and the molecule to ambient distance is s.

point oscillator. Second, they assume that the metal is a continuous medium described by a complex dielectric constant which contains no wavevector (spatial) dependence. This assumption means that high wavevector components of the oscillator field interact with the substrate just as a radiation field does. Third, they assume that boundaries between media are infinitely sharp and planar. Fourth, they imbed the emitting dipole in a lossless medium. Despite what may appear to be very severe assumptions, the classical treatment of CPS has had extraordinary success in describing experimental observations.

CPS give various derivations of their result. For an easy separation into nonradiative and radiative rates, the energy flux treatment alluded to earlier is beneficial. For insight into the physics of the process a mechanical model similar to that given originally by Kuhn [10] is helpful. An oscillating dipole near a surface is driven by its own electric field which has been reflected from the interface. The equation of motion for the dipole is

$$\ddot{\mu} + b_0\dot{\mu} + \omega_0^2\mu = e^2 E_{\rm r}/m,$$

where μ is the dipole moment, ω_0 is the natural oscillation frequency of the undamped dipole, b_0 is the decay rate for the dipole in the absence of any interfaces, m is the effective mass of the dipole and $E_{\rm r}$ is the reflected electric field at the dipole position. The reflected field oscillates with the same complex frequency as the dipole. If one assumes a functional form

$$\mu = \mu_0 \exp\left[-{\rm i}(\omega_0 + \Delta\omega)t\right]\exp(-bt/2),$$

$$E_{\rm r} = E_0 \exp\left[-{\rm i}(\omega_0 + \Delta\omega)t\right]\exp(-bt/2)$$

and substitutes into the equation of motion, the frequency shift, $\Delta\omega$, and new decay rate, b, can be calculated [4]. CPS obtain the result

$$\Delta\omega = b_0^2/8\omega_0 + \left(e^2/2\mu_0 m\omega_0\right){\rm Re}(E_0),$$

$$b = b_0 + \left(e^2/\mu_0 m\omega_0\right){\rm Im}(E_0).$$

Therefore, it suffices to evaluate the reflected field to solve the problem.

Although CPS treat many geometries and types of oscillators, a dipole oscillator and the experimental geometry shown in fig. 1 is the simplest one amenable to experimental study. In this geometry the luminescent molecule is placed a distance d away from the substrate of dielectric constant ϵ_2, and is imbedded in the spacer layer with dielectric constant ϵ_1. The second interface is the vacuum or ambient/spacer layer interface and is located a distance s from the emitting dipole. The expression for the total molecular decay rate is given by equations 2.46–2.50 of ref. [4]

$$b^{\perp,\parallel} = b_0\left(1 - qG^{\perp,\parallel}\right),\tag{1}$$

where b_0 is the decay rate of the molecule in an unbounded medium of dielectric constant ϵ_1 and q is the quantum yield of emission. The quantity G is given by

$$G^{\perp} = 1 - \tfrac{3}{2}\, \text{Im} \int_0^\infty \frac{F\left(\hat{d}, -R_{12}^{\parallel}\right) F\left(\hat{s}, -R_{13}^{\parallel}\right)}{F\left(\hat{d} + \hat{s}, -R_{12}^{\parallel}R_{13}^{\parallel}\right)} \frac{u^3}{l_1}\,\mathrm{d}u\tag{2}$$

for dipoles oriented perpendicular to the surface and

$$G^{\parallel} = 1 - \tfrac{3}{4}\, \text{Im} \int_0^\infty \left(\frac{F\left(\hat{d}, R_{12}^{\perp}\right) F\left(\hat{s}, R_{13}^{\perp}\right)}{F\left(\hat{d} + \hat{s}, -R_{12}^{\perp}R_{13}^{\perp}\right)} \right.$$

$$\left. + \left(1 - u^2\right)\frac{F\left(\hat{d}, R_{12}^{\parallel}\right) F\left(\hat{s}, R_{13}^{\parallel}\right)}{F\left(\hat{d} + \hat{s}, -R_{12}^{\parallel}R_{13}^{\parallel}\right)} \right) \frac{u}{l_1}\,\mathrm{d}u\tag{3}$$

for dipoles oriented parallel to the surface, where $F(x, y) = 1 + y \exp(-2l_1 x)$, $\hat{d} = 2\pi n_1 d/\lambda$, $\hat{s} = 2\pi n_1 s/\lambda$ and

$$R_{ij}^{\perp} = \left(l_i - l_j\right)/\left(l_i + l_j\right), \quad R_{ij}^{\parallel} = \left(\epsilon_i l_j - \epsilon_j l_i\right)/\left(\epsilon_i l_j + \epsilon_j l_i\right),$$

$$l_j = \left(u^2 - \epsilon_j/\epsilon_1\right)^{1/2}.$$

The R_{ij} expressions are the complex Fresnel coefficients. The subscripts refer to the different regions specified in fig. 1, the ϵ_i's correspond to the dielectric constants of these regions and the variable u is the wavevector of the dipole field, normalized with respect to the wavevector of the dipole radiation field. This result has been used to describe much of the observed phenomena.

CPS give results for many more cases: the emitter can be placed in any lossless medium of dielectric constant ϵ_i with any integer number of surrounding media; the media may be birefringent; the emitter can be either an electric or a magnetic multipole oscillator of arbitrary orientation with respect to the interface. They also model the case of thin films and show explicitly the effect of the film thickness on the dipole. They have treated the experimental geometries of all experiments performed to date.

The numerical evaluation of the integral in eq. (1) must be performed with care. Poles appear on or near the real axis, corresponding to resonances discussed below, making integration along the real axis difficult. To avoid this problem numerical integration should be performed along a path through the complex plane. In our calculations Gaussian quadrature with a twenty-fourth-order Gauss–Legendre polynomial [22] was used and integration performed in small steps parallel to the real axis but in the complex plane until convergence was obtained.

As originally discussed by CPS and later by others [4,23–25] the integral in eq. (1) can be broken down into various components. The integral over wavevector components zero to one represents the radiative rate contribution to the decay rate. The integral from one to infinity represents the nonradiative rate contribution to the decay rate. The poles which appear in this range correspond to collective excitations of the substrate, such as surface plasmons. The other contributions to the energy transfer rate in this model are the "lossy surface waves", which arise because the oscillating dipole field induces electronic charge density oscillations that dissipate into the lattice. These three decay mechanisms are described in more detail below with reference to figs. 2 and 3.

The radiative rate of the dipole, as determined by integrating eq. (1) from zero to one, is identical to the interference treatment of Drexhage [2,3]. The distinction of this part of the integral from the others can be seen from a physical picture. Fig. 2a shows the radiation field of a dipole during one point
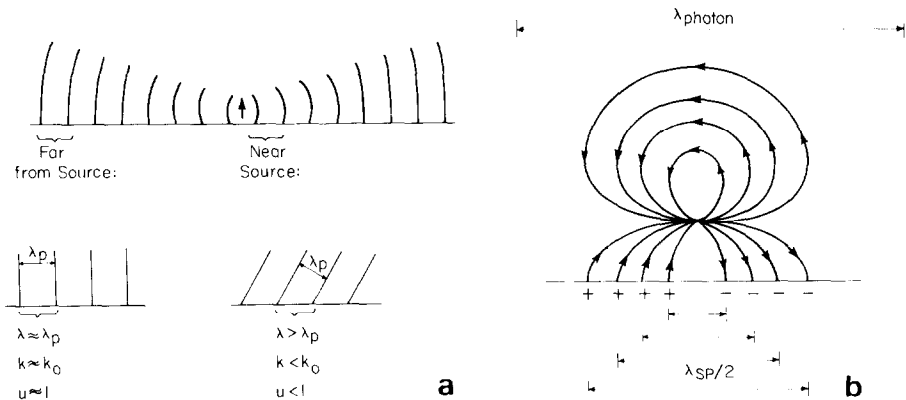
Fig. 2. The electric field lines associated with a dipole near a metal surface at one instant during its oscillation. (a) The surface charge induced by the radiation field of the dipole. The periodic charge density oscillation has wavevectors smaller than that of the radiation pattern (i.e. $k < k_{photon}$). (b) The surface charge induced by near-field components of the dipole. Here the wavevectors of the surface dipoles are greater than that of the radiation field ($k > k_{photon}$). This figure is taken from ref. [24].
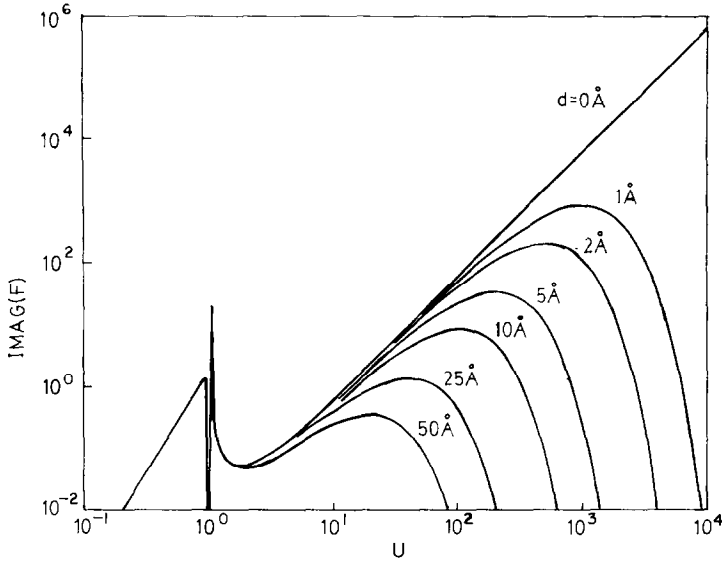
Fig. 3. The imaginary part of the energy transfer integrand versus normalized wavevector u, calculated for a perpendicular dipole emitting at 6328 Å located at various distances above a silver surface with local dielectric response (CPS model). This figure is taken from ref. [24].

in its oscillation. In this figure, each wavevector component of the dipole field initiates a surface charge density oscillation with wavevector less than or equal to the radiation field wavevector. These wavevector components of the surface charge density reradiate a field, the reflected radiation field, at an angle determined by the projection of the radiation field wavevector into the surface plane. This reflected field interferes with the field of the dipole, and this interference creates a modulation of the radiative rate with distance, as evidenced in fig. 5.

The higher wavevector components in the integration of eq. (1), which arise from the dipole near field, cause energy transfer to the substrate. These higher wavevector components of the dipole field also create charge density oscillations and if the wavevector of these oscillations matches that of the surface plasmons, the plasmons are efficiently excited. The surface plasmon dispersion relation is:

$$k_{sp} = \left[\epsilon_1\epsilon_2/(\epsilon_1 + \epsilon_2)\right]^{1/2}\omega/c.$$

In eq. (1) this resonance is characterized by a pole in the Fresnel coefficient. The surface plasmon can dissipate through collisions, or, if the experimental geometry permits, it can reradiate. Normally the radiation field and the surface plasmon are not coupled since the projection of the radiation field wavevector

onto the surface is smaller than the surface plasmon wavevector; by adjusting the index of refraction of the ambient medium the wavevectors can be matched and the surface plasmon can radiate. Weber and Eagen [26] provide an informative treatment of the conditions required for the excitation of surface plasmons and show that the distance dependence for energy transfer to surface plasmons is exponential. The properties of surface plasmons have been treated extensively both experimentally [27,28] and theoretically [29–33]. This decay mechanism can be significant and various workers have measured the surface plasmon emission intensity as a probe of the energy transfer rate.

When the charge density oscillations induced in the metal are not resonant with a collective excitation, energy transfer occurs through a different mechanism. The other excitations are referred to as "lossy surface waves", and these are short lived and do not radiate. In a quantum mechanical picture of the substrate, lossy surface waves correspond to electron–hole pair excitations in the solid with simultaneous scattering of the excited electron with phonons or impurities in the lattice. These scattering processes are required by momentum conservation, since the creation of an electron–hole pair with energy ΔE, requires momentum Δk, as determined by the band structure of the solid. As a final note we mention that in the classical theory the interaction of the near field with the substrate is assumed to be the same as that of the radiation field. In a proper picture each wavevector component of the near field would interact with the surface via a response function appropriate for that wavevector.

In fig. 3 we show a plot of the integrand from eq. (1) versus the dipole field wavevector (this plot is taken from ref. [24]). By comparing the contributions to the integral for $u = 0$ to 1, $u \cong u_{sp}$, and $u > u_{sp}$, we can see the changing importance of each of these in the energy transfer process at various distances from the surface. The plot shown is for the case of pyrazine separated from a silver surface by argon layers, and is computed for the dipole imbedded in vacuum, not the spacer layer as in fig. 1. In fig. 3 the value of the integrand near $u = 1.3$ goes through a sharp rise. This spike corresponds to an excitation of the surface plasmon and the contribution to energy transfer here is very effective. As the dipole–surface distance decreases the peak of the integrand shifts to higher values of u and the area under the integrand for $u > u_{sp}$ increases. This behavior demonstrates the increasing importance of the lossy wave mechanism at short distances.

The classical description has been and should continue to be a very powerful description of the interaction between a dipole and a substrate, although limitations are evident in the classical treatment. Many of these limitations have been pointed out by various workers and extensions of the classical model to account for these effects are discussed in the next section.

2.2. Nonclassical models

The classical theory has proven to be remarkably effective in the distance regime greater than 10 Å. It is well known, however, that the classical theory makes assumptions which lead to unphysical behaviour at very short molecule–surface separations, namely the energy transfer rate becomes infinite as the distance d approaches zero [25,34]. While only a handful of experimental investigations have been conducted in the very short distance regime [35,36] (none as a function of distance), the shortcomings of the classical theory have led theoreticians to work extensively in this area. By including the wavevector dependence of the dielectric constant, the unphysical behaviour of classical theory can be corrected [25]. Effects due to the fact that the electric field must vary continuously across the interface [34], that the response of the electrons near the surface can vary considerably from the response of bulk electrons [37,38], and that the supposedly flat surfaces used in all experiments are not necessarily flat on an atomic scale [39] have all been investigated in some detail. In addition, the effect of assuming that the molecular electronic excited state can be modeled as a point dipole has been discussed by several authors [25,35]. In this section we will present a qualitative discussion of these limitations.

An important simplifying assumption of the classical theory is that all wavevector components of the dipole near field are reflected and absorbed by the solid in a manner governed by the optical dielectric constant. This is equivalent to saying that all electromagnetic fields of the same frequency interact identically with the surface, regardless of their momentum content (spatial periodicity). The importance of this assumption is illustrated in fig. 4, taken from ref. [25]. Ford and Weber treat the energy transfer problem within the classical framework, but they substitute for the optical dielectric constant used by CPS, one which includes wavevector dependence. Fig. 4 shows the value of the energy transfer integrand versus wavevector when the nonlocal (solid line) and when the optical (dashed line) dielectric constant is used.

When an optical dielectric constant is used to describe the metal, a particular model of the solid is implicitly assumed. In this model [40,41], the positive ion cores are assumed to be smeared throughout the volume of the solid, and the electrons are confined within the solid by an infinite potential barrier. Most importantly, the electrons are assumed to have no interaction with each other. In this model, the electrons can be assumed to undergo collisions (with the lattice, impurities, or other electrons) on average with a time, τ, the relaxation time. Inclusion of the relaxation time in the model allows us to phenomenologically take into account energy dissipation by the metal.

In the more sophisticated model used by Ford and Weber [25], the positive ion cores are still assumed to be smeared out, and the electrons are still confined within the solid by an infinite barrier. However, the electron–electron
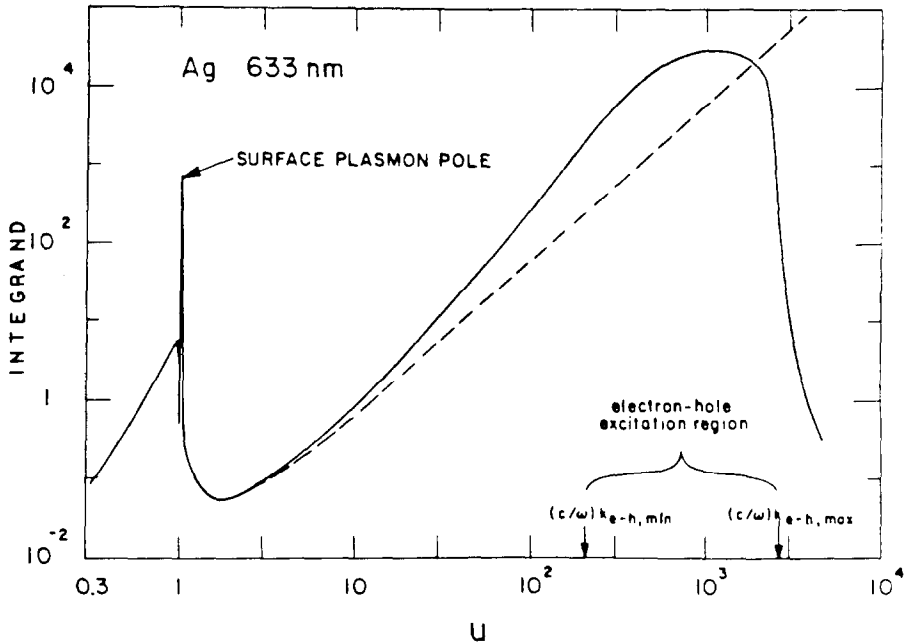
Fig. 4. The imaginary part of the energy transfer integrand versus normalized wavevector calculated for a perpendicular dipole emitting at 6328 Å located on a silver surface. The solid curve corresponds to the nonlocal model of Ford and Weber [25], and the dashed curve is for the local model [4]. This figure is taken from ref. [25].

interaction is partially taken into account. If we imagine introducing a point charge into the center of a metal with no Coulombic interactions between electrons, then the potential due to the test charge will be quite long range (it will fall off as $1/r$). If Coulombic interactions are now allowed, then the metal electrons will move in the presence of the test charge in such a way as to "screen" the test charge. In their model, Ford and Weber use a Lindhard dielectric constant [40,41] (modified to include a phenomenological relaxation time as well), in which the screening of a test charge is taken into account to first order in perturbation theory. Since the potential due to the test charge is computed as a function of distance from the charge, the inclusion of the screening is equivalent to using a wavevector-dependent dielectric constant. While in the classical model, energy dissipation by the metal was taken into account phenomenologically, here the metal absorbs energy from incident fields when electrons below the Fermi level are excited to states above it. The incident field will excite electron–hole pairs in the metal when the momentum conservation condition is satisfied [41]:

$$\left(k_F^2 + 2m\omega/h \right)^{1/2} - k_F < k < \left(k_F^2 + 2m\omega/h \right)^{1/2},$$

where k_F is the Fermi wavevector, m is the electron mass, and ω is the frequency of the incident field.

We are now in a position to understand the differences shown in fig. 4, where the energy transfer integrand is computed using a nonlocal or an optical dielectric constant. The classical theory underestimates the energy transfer rate in the range of wavevector components which can produce electron–hole pairs in the solid. The region of wavevectors where the classical theory underestimates the energy transfer rate is indicated in fig. 4 by arrows along the u axis. At much higher wavevectors, the incident fields no longer obey the momentum conservation condition for electron–hole pair excitation, and hence no energy is transferred in the nonlocal model. In the classical model there is no upper limit to wavevectors which can transfer energy to the solid, and hence as the distance between the molecule and the surface approaches zero, the energy transfer rate unphysically diverges.

When the Coulomb repulsion between the electrons in the metal is partially accounted for, the electron density of the metal is seen to change in the vicinity of the surface. Thus, by taking into account the wavevector dependence of the solid response function, an additional assumption of the classical theory can be relaxed, namely the requirement that the electric field at the interface varies discontinuously. Metiu and Maniv [34] have shown that in the treatment of Ford and Weber, the field is continuous across the interface, but the first derivative of the field is not. They provide a higher-order calculation of the wavevector dependence of the dielectric constant, in which the electric field is analytic across the interface. In both models the electrons are held in the solid by an infinite barrier and more realistic models would use a finite barrier. It is difficult to evaluate the magnitude of the effect of a nonlocal dielectric constant on the energy transfer rate, since computations of the energy transfer rate versus distance in the nonlocal case are not presented by the authors.

The fact that the electron density varies in the vicinity of the interface can lead to different response functions for the surface and bulk regions of the metal. If the energy transfer rate to the surface is substantially different from that to the bulk, then the power of the distance dependence of the energy transfer rate will be affected as well. As discussed earlier, dipole–dipole energy transfer depends on $1/d^6$. For energy transfer to a thin film or to modes localized at the solid surface, the integration is over an area, not a volume as if to bulk modes, and hence the rate depends on $1/d^4$.

We can always expect that there will be a surface ($1/d^4$) and a volume ($1/d^3$) contribution to the energy transfer rate. In order to distinguish between surface and volume effects, Persson uses a formalism quite distinct from the classical [37,38,42,43]. In this model, a Fermi's golden rule calculation is considered, in which the molecule, initially in its excited state, is de-excited while simultaneously an electron in the metal is excited to a state above the

Fermi level. The rate of energy transfer by such a process is given by:

$$1/\tau = (2\pi/\hbar) \int d^3k \; d^3k' \; n_k(1 - n_{k'}) \left| \langle \mathbf{k}', n = 0 | H' | \mathbf{k}, n = 1 \rangle \right|^2$$

$$\times \delta(\epsilon_{k'} - \epsilon_k - \hbar\omega) \tag{4}$$

where $|\mathbf{k}\rangle$ is the wavefunction of an electron of wavevector $\mathbf{k}$ in the solid, $n_k = 1$ if $k < k_F$ or 0 if $k > k_F$ and $n_{k'} = 1$ if $k' < k_F$ or 0 if $k' > k_F$ (k_F is the Fermi wavevector), n denotes the state of the dipole, and $H' = e\Phi(x, t)$, where Φ is the potential of the dipole in the presence of the metal. Persson has worked extensively on the question of whether under any particular set of circumstances the surface contributions to the damping rate would be expected to dominate over the volume contribution. Below the interband transition in the noble metals the relaxation time (mean free time between collisions) is very long so that bulk electrons will be forbidden by momentum conservation from accepting the dipole energy. Only electrons close to the surface will undergo surface collisions soon enough after excitation for momentum to be conserved. Hence, for a dipole in the frequency regime $2\pi/\tau < \omega < \omega_p$ above a noble metal, the nonradiative rate would be expected to increase with the inverse dipole–metal distance to the fourth power. Persson predicts that this effect will be strong in the distance range of 20–100 Å. An important limitation of the treatments presented by Persson is that they do not include effects due to the radiation field.

Independent of how the electron density in the solid changes near the interface, is the question of whether or not the surface is flat. The classical theory assumes a planar interface, the experimentally unobtainable ideal. The effects of small random roughness, where the roughness features are below experimental detection limits, has been treated by Metiu [39]. In this treatment Metiu solves Maxwell's equations for the case where the surface has roughness components Gaussian distributed. The effects of small random roughness are important for distances less than 50 Å when the roughness components are on the order of 20 Å. They also find that the observed lifetime will fall more quickly with distance than expected classically.

While all of our attention so far has focused on shortcomings of the classical description of the solid, the classical picture of the molecular electronic excited state is also wanting. In the classical theory the molecule is treated as a point dipole, a picture which will no longer be applicable at very short (< 10 Å) distances from the surface. Ford and Weber [25] account for this effect in their work by treating the molecule as a sphere of radius r. They derive a general formulation for the charge density of the molecule using a multipole expansion, although computations are only performed for a dipole of radius r. This treatment will break down for small molecule–surface separations, and higher multipoles would be required. Maniv and Metiu [34] have found that adding

higher-order multipoles is not efficient, since the expansion does not converge rapidly. Maniv and Metiu used two approaches to the problem: in one, the molecule was represented by a collection of charges, suitably located in space to emulate the field of the molecule. In the other, each bond of the molecule was represented as an oscillating dipole. Computations of the expected dis-
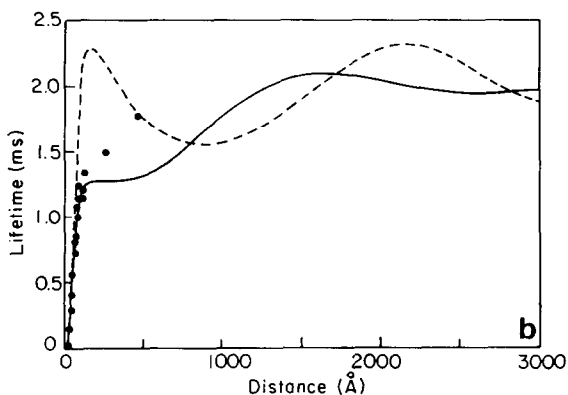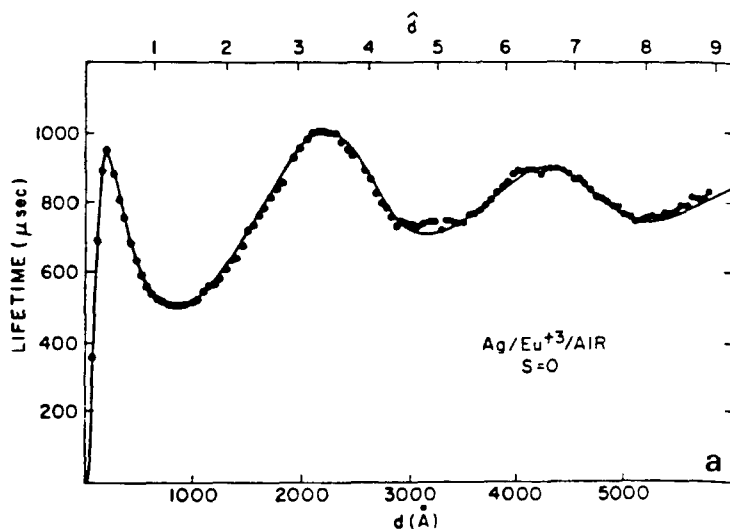

Fig. 5. Lifetime versus distance plots for two systems. (a) This figure from ref. [17] is a best fit of the classical model to the data of Drexhage et al. [1–3]. The system is Eu^{3+} separated from a silver film by fatty acid layers. The emission frequency of the ion is 6120 Å, and the dipole is assumed to be isotropically oriented. (b) This figure from ref. [53] is a best fit to the classical model for biacetyl separated from a silver (111) surface by ammonia spacer layers. The dashed line is the best fit to a parallel dipole, and the solid line to a perpendicular dipole. Biacetyl emission was detected at 5200 Å.

tance-dependent lifetimes have not been performed using these models and these authors do not predict the effects of a more realistic charge density on the excited-state lifetime.

3. Experimental studies

In fig. 5 we show data from two experimental studies. The first figure, 5a, shows the data of Drexhage in the long distance regime, where the classical theory has been found to work very well. The second figure, 5b, is from a more recent experiment which probes the short distance regime. These figures show the oscillations of the lifetime with distance for molecule–surface separations on the order of the emission wavelength. At very short distances, the lifetime drops rapidly due to nonradiative energy transfer to the surface. In order to test the applicability of the classical theory in the energy transfer regime, the distance scale in the second plot needs to be greatly expanded (see ref. [53]).

Experiments which probe the dipole–substrate interaction in the energy transfer regime, < 500 Å, are discussed. The experiments are divided into three arbitrary sections: those where the energy transfer to surface plasmons was the focus, those where only the total energy transfer rate was treated, and those where attempts were made to measure the effects of energy transfer directly on the surface. In table 1 the available data on energy transfer are compiled. The nature and type of substrate, spacer layer and emitting species are all provided. The type of measurement and number of data points are provided as well. The distance range studied is also specified and in parentheses the distance resolution. Finally it is noted whether the results agree with classical theory or not.

Most workers measure emission intensities and obtain a relative quantum yield, a procedure with certain pitfalls. The angular distribution of the radiation changes with distance as well as the quantum yield. This angular distribution arises from interference effects via the metal [3]. Another variable which must be accounted for in quantum yield measurements is the number of species which are excited by the incident light. The population will change because of standing wave effects at the surface. In those cases where these effects were properly considered, they were found to have a noticeable affect on the results [44]. Measurements of the excited-state lifetime are insensitive to these effects.

Four groups have tried to study the energy transfer to surface plasmons. Hansma and Metiu have studied various metallic films and invoke energy transfer to surface plasmons to explain their results [44,45]. The other groups have conducted experiments in which initially excited molecules transfer energy to the substrate, exciting both lossy waves and surface plasmons. The surface plasmons then radiate and the plasmon emission intensity is monitored

Table 1
Compilation of available data on the distance dependent energy transfer rate from electronically excited states to solid surfaces

Substrate (thickness)	Spacer	Molecular emitting species	Measured quantity	Distance range [a] (Å)	Number of points	Fit to classical model	Reference
Al film	Fatty acid	Anthracene singlet exciton	Molecular emission intensity	27–130	12	See text	Vaubel et al. [48]
Au film (300 Å)	Fatty acid	Anthracene singlet exciton	Molecular emission intensity	20–100	16	Yes	Kurczewska and Bässler [49]
Au film (10 Å)	Fatty acid	Dye molecule	Molecular emission lifetime	25–300 [b]	5	Yes	Inacker and Kuhn [54]
Al film	Fatty acid	Dye molecule	Photocurrent	27–133 [b]	4	Yes	Killesreiter [55]
Ag film (750 Å)	–	R-6G in ethanol	SP intensity	<1000	–	See text	Weber et al. [26]
Ag film (550 Å)	Fatty acid	Dye molecule	SP intensity	27–241 [b]	5	Yes	Pockrand et al. [44]
Ag film (80 Å)	N_2	N atom $^2D-^4S$	Atomic emission lifetime	30–3000 (30)	5	Yes	Adams et al. [45,46]
Ag film (600 Å)	N_2	N atom $^2D-^4S$	Atomic emission lifetime	30–3000 (30)	7	Yes	Adams et al. [45,46]
K film (400 Å)	N_2	N atom $^2D-^4S$	Atomic emission lifetime	30–3000 (30)	8	Yes	Adams et al. [45,46]

Table 1 (continued)

Substrate (thickness)	Spacer	Molecular emitting species	Measured quantity	Distance range [a] (Å)	Number of points	Fit to classical model	Reference
K film (1200 Å)	N_2	N atom $^2D-^4S$	Atomic emission lifetime	30–3000 (30)	7	Yes	Adams et al. [45,46]
Na film (500 Å)	N_2	N atom $^2D-^4S$	Atomic emission lifetime	30–3000 (30)	7	Yes	Adams et al. [45,46]
Na film (1000 Å)	N_2	N atom $^2D-^4S$	Atomic emission lifetime	30–3000 (30)	8	Yes	Adams et al. [45,46]
Ni(111)	Ar	Pyrazine ($^3n\pi^*$)	Molecular emission intensity	7.5–100 (5)	6	Yes	Campion et al. [52]
Ag film	–	Tb^{3+} complex in ethanol	SP decay time	<600	–	See text	Eagen et al. [26b]
Au film (550 Å)	Fatty acid	Dye	SP intensity	27–295 [b]	6	Yes	Pockrand et al. [44]
Ag film	Fatty acid	Dye	SP intensity	27–295 [b]	6	Yes	Pockrand et al. [44]
Ag(111)	Pyrazine	Pyrazine ($^1B_{2u}$)	EELS lineshape	3–6	2	No	Avouris and Demuth [35]
Ag(111)	Ar	Pyrazine ($^3n\pi^*$)	Molecular emission lifetime	10–400 (5)	14	Yes	Whitmore et al. [24]
Ag film	Ar	Pyrazine ($^3n\pi^*$)	Molecular emission lifetime	35–210 (20)	14	No	Rossetti and Brus [51]

Table 1 (continued)

Substrate (thickness)	Spacer	Molecular emitting species	Measured quantity	Distance range [a] (Å)	Number of points	Fit to classical model	Reference
Au film	Ar	Pyrazine ($^3n\pi^*$)	Molecular emission lifetime	35–210 (20)	10	Yes	Rossetti and Brus [51]
Al(111)		N_2 ($C^3\Pi$)	EELS lineshape	1–5	2	No	Avouris et al. [36]
GaAs	LiF	Tetracene	Molecular emission intensity	25–2000 (50)	64	See text	Hayashi et al. [56]
p-Si	LiF	Tetracene	Molecular emission intensity	25–2000 (50)	41	See text	Hayashi et al. [56]
n-Si	LiF	Tetracene	Molecular emission intensity	25–2000 (50)	30	See text	Hayashi et al. [56]
p, n-Si	LiF	Tetracene	Molecular emission intensity	25–2000 (50)	52	See text	Hayashi et al. [56]
GaAs(110)	NH_3	Pyrazine ($^3n\pi^*$)	Molecular emission lifetime	20–430 (5)	9	Yes	Whitmore et al. [57]
Ag(111)	NH_3	Biacetyl ($^3n\pi^*$)	Molecular emission lifetime	28–457 (5)	22	No	Alivisatos et al. [53]

[a] Distance resolution in these experiments is given in parentheses.
[b] In these experiments the distances were confined to multiples of 27 Å.

as a function molecule–surface separation. These studies show that surface plasmon excitation is definitely a decay mechanism for the excited state. Its importance in comparison to the lossy wave mechanism is less clear and will depend greatly on whether the surface plasmons are resonantly or nonresonantly excited.

The observation of surface plasmon emission shows clearly that molecular excited states transfer energy to surface plasmon modes. Weber and Eagen [26] conducted experiments with an attenuated total reflection (ATR) prism where the silvered part of the prism was immersed in a solution of ethanol containing rhodamine-6G. This experiment resembled the ones described in the previous paragraph, except that the fluorescer in these experiments was not excited directly. An ion laser was used to excite surface plasmons in the silver film, and these plasmons nonradiatively excited the rhodamine-6G in solution. The rhodamine-6G was located at a wide variety of distances from the surface, and it could diffuse through the solution as well. Therefore, these authors were not able to conclude much about the validity of the classical picture, other than there is definitely coupling to surface plasmons. Lukosz and Meier [47] performed ATR experiments as well, but in the Otto arrangement [27,28] and measured the lifetime of the emitting species at three different distances. They saw a decrease in lifetime with distance by a factor of five but they only had 100 Å resolution and were unable to conclude much about the distance dependence predicted by classical theory. Möbius et al. [44] have performed a set of ATR experiments, in the Kretschmann configuration, where a monolayer of emitter is separated from the metal film by a fatty acid layer. They probed the angular distribution of the intensity of the emitted cone of surface plasmon radiation and integrated to obtain a relative quantum yield. They also corrected for standing wave effects. In the interpretation of their data these authors assumed that on the distance scale less than 180 Å the energy transfer rate to surface plasmons is a slowly varying function of distance. They found qualitative agreement with classical theory and found that at close distances, < 150 Å, the lossy surface wave mechanism dominates. Support for this conclusion comes from the fact that the plasmon emission intensity sharply decreased at shorter distances. Surface plasmon excitation is expected to increase with shorter distance separation, and hence the emission intensity would rise if lossy wave damping were not dominant. The validity of the assumption that surface plasmon excitation is relatively flat with distance could be checked with the same experimental configuration, by monitoring both the molecular and the surface plasmon emission.

Metiu and Hansma [45,46] have studied energy transfer to sodium, potassium, and silver films of various thicknesses (see table 1). These workers grew N_2 films of variable thickness on top of the substrates. An electron beam was used to dissociate N_2 into excited N atoms, which luminesced (only N_2 within 30 Å of the vacuum interface was excited in this manner). The decay time of

the excited N atoms was measured as a function of distance. They found good agreement with the classical theory under all conditions. They saw quite different distance dependences for different films and film thickness. They argued that the dependence of the emission efficiency on film type and thickness arises from the shift in the position of the surface plasmon resonance with respect to the molecular emission energy. The conclusions from the experiments performed by these four groups are that surface plasmon excitation is definitely a significant, observable, effect when the emitting species is close to resonance with the surface plasmon. However, when nonresonant or close to the surface, < 100 Å, other decay processes dominate.

Now we discuss energy transfer measurements in the short distance regime, 7–300 Å. Two groups have performed studies on thick metal films, > 100 Å, which are expected to behave as bulk metals. The first studies of energy transfer were by Vaubel et al. [48]. They measured the decay of the singlet exciton of an anthracene crystal spaced from an aluminum film by a fatty acid layer. An oxide layer may have been present on the aluminum surface [49], and when taken into account gives good agreement with CPS theory. A subsequent set of experiments by the same group [49] using a gold instead of aluminum film gives excellent agreement with classical theory. It is not clear whether these workers accounted for angular interference or standing wave effects. Rossetti and Brus [50,51] have studied excited-state quenching on silver and gold. They measured the distance-dependent lifetime of a phosphorescer, $^3n\pi^*$ pyrazine, spaced from a metal film by argon spacers. The emitter layer consisted of a 20 Å thick mixture which was one part pyrazine and 20 parts argon. Their results on gold films show excellent agreement with the classical treatment of CPS. On silver they find a d^3 distance dependence, but the data disagrees with the double interface model of CPS. This disagreement has not been resolved. The deviations from the classical theory are to shorter lifetimes than predicted and might be explained by limitations of the classical theory discussed previously.

Our group has performed a series of energy transfer experiments on well characterized single-crystalline substrates [24,52,53]. An initial set of experiments was performed by measuring the phosphorescence intensity of $^3n\pi^*$ pyrazine spaced from Ni(111) by argon spacer layers. A cubic distance dependence for the yield was found. The interference effects alluded to earlier were not accounted for in these experiments. All subsequent experiments were performed with lifetime measurements only. Specifically, we have studied energy transfer to Ag(111) for both pyrazine, which could excite the metal interband transition, and biacetyl which is below the interband transition. The pyrazine studies were the first lifetime measurements with sufficient distance resolution to evaluate the validity of the classical theory in the energy transfer regime. Agreement was found within experimental error, which would imply that the deviations seen by Rosetti and Brus could be caused by differences in

the two substrates. For biacetyl we have observed deviations from the classical behaviour. These deviations are small but could be interpreted either as a breakdown of the bulk versus surface descriptions of the dielectric constant or as a breakdown of the boundary conditions at the interfaces. This latter experiment implies that the surface damping mechanism proposed by Persson is not dominant.

Finally studies on very thin metal films have been reported by two groups. Kuhn [54] has investigated the distance dependence of the energy transfer from the singlet and triplet states of the same dye molecule to an approximately 10 Å thick gold layer, using fatty acid spacer layers. For the triplet state lifetime measurements were performed and for the singlet states emission intensities were measured. In this study he finds good agreement with d^4 distance dependence which is adequately described classically. This d^4 dependence can be understood on the dimensional grounds discussed earlier. Killesreiter [55] has also investigated the effects of energy transfer to semi-transparent Al films for a dye molecule separated from the film by fatty acid spacer layers. In these experiments the dye layer could also transfer to a chloranil single crystal in contact with another aluminum film and the photoconductivity of this photo-cell was measured as the dye to aluminum film distance was varied. Killesreiter found good agreement with Kuhn's model. Interference effects may not be important, because these very thin films are relatively transparent.

There have been two reports of energy transfer to semiconductors which explicitly test the distance dependence of the classical theory. The report by Hayashi et al. [56] concludes that the energy transfer rate does not increase below 100 Å. This effect could be caused by the thickness of the fluorescent layer (50 Å). These authors measure emission intensities and do not account for interference effects. The other report, by our group, for the phosporescence lifetime of pyrazine above GaAs [57] shows reasonable agreement with classi-cal expectations. This work implies that the dominant decay mechanism is the transfer of energy to interband electron–hole excitations of the semiconductor through the high wavevector components of the dipole field. Future investiga-tions on semiconducting materials are necessary to assess the validity of the classical model and should be of great interest.

Finally we discuss two experiments performed by Avouris et al. for species directly on the substrate [42,35,36]. These experiments are of great importance, since they are the only ones in which the molecules are in contact with the metal, the situation in which the classical theory is most likely to fail. Electron energy loss studies were performed for electronically excited states of sub-monolayer coverages of $N_2(^3\Pi_u)$ on Al(111) and pyrazine ($^1B_{2u}$) on Ag(111). In these studies a lineshape analysis is used to extract information about the lifetime of the excited electronic state. In the pyrazine experiments the spec-trum which is obtained after background corrections is assumed to be homoge-neously broadened. These workers justify this assumption on the grounds that

experiments on clean, annealed, single-crystal surfaces minimize site inhomogeneities. They find a lifetime broadening of 100 meV in contrast to the classical prediction of 590 meV. The studies on N_2 are similar to those of pyrazine but inhomogeneous broadening, caused by orientational disorder, is accounted for and background corrections are less important. They extract a lifetime of 5×10^{-15} s as compared to the classical prediction of 5×10^{-14} s and attribute this to the surface quenching model of Persson [37]. In both of these studies radiative effects on the dipole have been ignored and measurements made at one distance coupled with variability in other parameters makes comparison to classical theory difficult. This group also finds a frequency shift which is in disagreement with classical predictions.

4. Conclusions

The experimental work performed to date shows good agreement with classical predictions. Although deviations in the short distance regime (< 100 Å) have been reported [36,51,53], they are less than an order of magnitude. Theoretical efforts have accelerated beyond the experimental work in this field, and there are many predictions that substantial deviations from the classical theory should be observed at distances < 50 Å. This region should be investigated by experiments which are able to distinguish between the various processes which are predicted theoretically. As a rule of thumb, we expect the lifetime of an electronically excited state to be reduced by a factor of 10^6 when at the surface of a metal, as implied by theoretical treatments and experimental extrapolation. This would make time-resolved experiments on adsorbed species where the molecular emission rate is observed extremely difficult, but feasible.

Although extensive studies, both experimental and theoretical, have been performed on metals, little work has appeared for semiconductors. Two experimental reports [56,57] imply that the classical model of energy transfer may work well, at least in the longer distance regime. The wide variety of electronic states available in semiconductors, however, make us expect new behaviour, especially at short distances (< 50 Å). More theoretical studies on energy transfer to semiconductors for small molecule–surface separations are needed.

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