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Nonclassical behavior of energy transfer from molecules to metal surfaces: Biacetyl($^3n\pi^*$)/Ag(111)

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The distance dependent lifetime of biacetyl separated from a Ag(111) crystal by NH₃ spacer layers ranging in thickness from 28 to 457 Å has been measured. We extended previous work, where the molecular emission was resonant with the silver interband/plasmon transition, to the case where the emission is below the interband transition. The modulation of the radiative rate is described inadequately by the classical theory for our experimental geometry. At short distances where nonradiative energy transfer to the metal is important, the classical prediction deviates from the data as well. These observations are consistent with a model in which energy is transferred to electrons localized at the metal surface but might also be explained by an inability of the classical theory to model the radiative rate properly.

INTRODUCTION

Since the first reports of the effect of metal reflecting surfaces on the lifetime of an oscillating dipole,^{1,2} this phenomenon has been the subject of considerable theoretical and experimental effort. When the dipole distance from the reflecting surface is on the order of the dipole wavelength, the radiative emission rate of the dipole is modulated by its reflected field. When the reflected field is out of phase with the dipole field, the radiative rate is decreased, and when the reflected field is in phase with the dipole field the rate is increased. At distances much less than the dipole wavelength λ , the radiative rate is still modified, and the effect of the reflected field accounts for the experimentally observed surface dipole selection rule.³ At short distances, an additional dipole-metal coupling takes place, however. For $d \ll \lambda$ the dipole nonradiatively transfers energy to the metal surface, and the dipole lifetime is reduced by many orders of magnitude.

In the 1970's, primarily through the efforts of Chance, Prock, and Silbey,⁴ significant progress was made in understanding this problem. Using an approach of Sommerfeld,⁵ Chance *et al.* (CPS) solved Maxwell's equations for the boundary conditions of a point dipole above a semi-infinite planar surface of dielectric constant $\epsilon(\omega)$, and were able to compute the lifetime of a classical dipole as a function of distance away from a metal. The CPS theory was in quantitative agreement with the extensive experimental data of Kuhn and Drexhage,^{1,2} all in the long distance regime. At short distances, CPS predicted that the lifetime of the dipole would be dramatically reduced, the nonradiative rate into the surface increasing as the inverse metal-dipole distance cubed. This prediction

was later verified experimentally, although always under circumstances where the dipole could excite interband transitions in the metal.⁶⁻⁸

The cubic distance dependence of the energy transfer rate can be understood on quite general dimensional grounds. It is well known that a standard dipole-dipole Förster energy transfer process depends inversely on the sixth power of the distance. For the case of a dipole above a metal, the energy transfer is from a point dipole to a three dimensional array of point dipoles. The rate must be integrated over a volume, hence energy transfer depends inversely on the distance cubed. The same reasoning leads one to the expectation that transfer from a dipole to a thin metal film, or to modes localized at the metal surface, scales inversely as the fourth power of the distance. The $1/d^4$ dependence for a thin film has been discussed by CPS.⁴

Recent theoretical work has suggested that for a point dipole above a metal surface, when the dipole frequency is below any interband transitions, momentum conservation forbids the transfer of energy from the dipole to the bulk of the metal, but allows transfer to the surface.¹⁰⁻¹² In this case, the energy transfer rate would scale as $1/d^4$ despite the presence of the bulk crystal. Some initial experimental work, performed only at one distance, has suggested that the selection rule is in fact operative.^{13,14}

In this work we have undertaken a systematic study of the distance dependent energy transfer rate from a dipole to a metal surface when interband transitions are not possible, and consequently in the regime where the selection rule has been predicted to operate. We have measured the lifetime of the first triplet state of biacetyl as a function of distance from Ag(111). The distance was varied by changing the thickness of an ammonia spacer layer from 28–457 Å (see Fig. 1). In the subsequent pages we first discuss, briefly, some essential experimental details.

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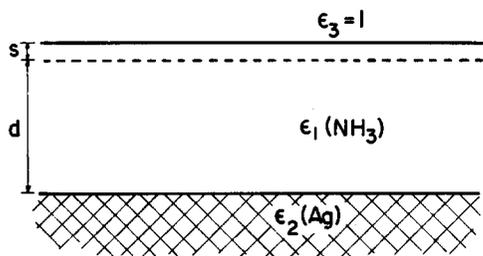


FIG. 1. In this schematic of our experimental arrangement the ϵ 's are the dielectric constants of the regions. The solid lines are the boundaries between the media and the dotted line represents the center of the biacetyl layer.

Next we describe theoretical models, classical and non-classical, for the energy transfer process. In the following sections we present our results and compare our data with these models quantitatively.

EXPERIMENTAL

Single crystals of Ag(111), 99.9995% pure, from Aremco were used in these experiments. The ultrahigh vacuum apparatus and manner of cleaning the sample have been described previously.⁸ The optical constants at $\lambda = 520$ nm (the emission wavelength of ${}^3n\pi^*$ biacetyl) for Ag and NH_3 were measured ellipsometrically [$\epsilon(\text{Ag}) = -10.16, 0.199$; $\epsilon(\text{NH}_3) = 1.716$], and were in close agreement with previously reported values.¹⁵ The spacer layer was deposited over a period of about 10 min, and the biacetyl layer was never more than 3/4 of a monolayer. Standard operating temperature was approximately 40 K.

The biacetyl used in these experiments was purchased from Aldrich and was purified by vacuum distillation until no impurities could be detected by gas chromatography with mass spectrometric detection. Subsequently, the sample was kept at 77 K, and was only exposed to red light. The biacetyl was excited by a 440 nm, 10 ns pulse from an excimer or Nd-YAG pumped dye laser system. The 520 nm phosphorescence was isolated with a 520 nm narrowband interference filter and a long pass cutoff filter. The phosphorescence was amplified and collected on a Biomation 8100 transient recorder interfaced to a PDP11-03 microcomputer.

Figure 2 shows an experimental decay curve for biacetyl/ NH_3 /Ag at a distance of 28 Å where the signal is smallest. The line through the data in Fig. 2 is the best fit to a single exponential with a lifetime of $\tau = 0.024$ ms. The data at all distances are compiled in Table I. The error in the lifetimes was computed by first finding the 95% confidence limits of the three lifetimes from 37–40 Å, all the same nominal distance, via the t test.¹⁶ Next this value was used to obtain the percentage error in the lifetime. The same percentage error was assumed for the other decays as well. If, however, a decay was particularly noisy, this error was doubled. The error in the distance measurement is less than the error introduced by the physical size of an NH_3 molecule, approximately 5 Å. Several experiments were performed with a xenon spacer layer and were in excellent agreement with NH_3 spacer lifetimes.

In order to reduce the number of adjustable parameters in the theoretical modeling of our results, we also measured the lifetime of the biacetyl at “infinite” distance from the metal, that is at distances so far from the metal that the dipole no longer interferes with itself via the metal. A spacer layer many microns thick was grown by exposing the crystal to 5×10^{-5} Torr of NH_3 for 45 min to 1 h. The value for the infinite distance lifetime, $\tau(d = \infty) = 1.98$ ms reproduced well. This value is midway between literature values for the solid state, 2.6 ms, and the gas phase, 1.6 ms.⁹

THEORY

Classical model

A rigorous classical treatment of the lifetime of an emitting molecule above a metal surface has been given by CPS⁴ and has been discussed by many authors.^{8,10–12,17–19} Here we will only mention a few features of the theory which are essential for our later discussion. In the CPS model, the metal is treated as a semi-infinite medium, characterized by its optical dielectric constant, $\epsilon(\omega, k = 0)$, and separated from the spacer layer by a sharp interface. The molecule is treated as a point dipole oscillating at the frequency of the electronic emission and oriented either parallel or perpendicular to the metal surface. The electric potential of the dipole is decomposed into wave-vector components, k , and each component interacts with the surface in exactly the same manner as a radiation field of the same frequency as the dipole. Each component is partially reflected and partially absorbed in a manner governed by the boundary conditions and the optical dielectric constant. The incident and reflected fields can be appropriately summed to give the value of the electric field at the dipole, in the presence of the metal. The imaginary part of the electric field can then be related to the perturbed lifetime of the dipole. The decomposition of the field into wave-vector components leads to a physical picture of the dipole-metal

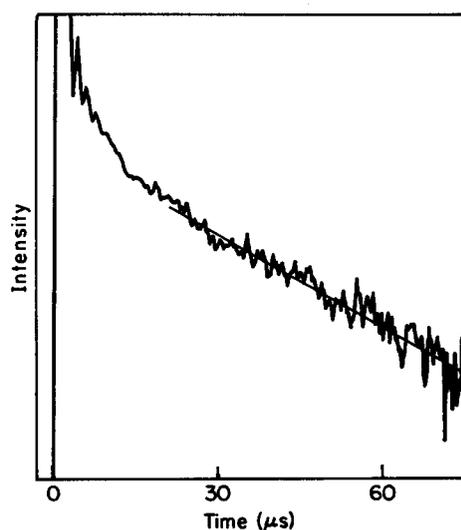


FIG. 2. This figure shows a log plot of an experimental decay curve for $d = 28$ Å with a fit (solid line) of $\tau = 0.024$ ms. The initial spike is the laser pulse convoluted with our instrument response of 1 ms.

TABLE I. Compilation of lifetime and distance data.

d (Å)	τ (ms)	λ_r (95%)	d (Å)	τ (ms)	λ_r (95%)
28	0.024	± 0.005	83	1.08	± 0.065
37	0.147	± 0.008	87	1.24	± 0.075
38	0.149	± 0.008	88	0.997	± 0.12
40	0.143	± 0.008	92	1.14	± 0.14
44	0.297	± 0.036	111	1.21	± 0.073
47	0.410	± 0.025	114	1.14	± 0.14
49	0.410	± 0.025	128	1.33	± 0.080
58	0.558	± 0.033	266	1.49	± 0.089
69	0.733	± 0.088	457	1.78	± 0.110
74	0.852	± 1.02	$> 12.5 \mu$	1.98	
77	0.825	± 0.050	$> 15.0 \mu$	1.98	

interaction. Wave-vector components less than the radiation field wave vector lead to a modification of the radiative rate by the reflected electric field. The higher wave-vector components lead to the nonradiative energy transfer to the surface through the near field of the dipole.

The classical treatment of CPS can model our experimental arrangement which actually contains a double interface as shown in Fig. 1. The expression for the total molecular decay rate is given by Eqs. (2.46)–(2.50) of Ref. 4:

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

where b_0 is the decay rate of biacetyl in the absence of the metal and q is the quantum yield of the phosphorescence. The quantity G , which represents the effect of the metal on the lifetime, is given by

$$G^{\perp} = 1 - 3/2 * \text{Im} \int_0^{\infty} [F(\hat{d}, -R_{12}^{\parallel}) * F(\hat{s}, -R_{13}^{\parallel}) / F(\hat{d} + \hat{s}, -R_{12}^{\parallel} R_{13}^{\parallel})] * (u^3/l_1) du \quad (2)$$

for dipoles oriented perpendicular to the surface and

$$G^{\parallel} = 1 - 3/4 * \text{Im} \int_0^{\infty} [F(\hat{d}, R_{12}^{\perp}) * F(\hat{s}, R_{13}^{\perp}) / F(\hat{d} + \hat{s}, -R_{12}^{\perp} R_{13}^{\perp}) + (1 - u^2) * F(\hat{d}, R_{12}^{\parallel}) * F(\hat{s}, R_{13}^{\parallel}) / F(\hat{d} + \hat{s}, -R_{12}^{\parallel} R_{13}^{\parallel})] u * du / l_1 \quad (3)$$

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

$$R_{ij}^{\perp} = (l_i - l_j) / (l_i + l_j),$$

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

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

The R_{ij} expressions are the complex Fresnel coefficients. The subscripts refer to the different regions specified in Fig. 1 and the variable u is the normalized wave vector of the dipole field. Equation (1) was evaluated numerically to compare with our data quantitatively. The details of these calculations will be discussed in a forthcoming publication.¹⁷

The classical theory, although very successful, has certain limitations, the importance of which will come to light as it is more comprehensively tested. Three obvious

limits are stated here. First, at short distances, the wave functions of the adsorbate and the metal can overlap, so that energy is nonradiatively transferred not only by the through space interaction, modeled by the classical theory, but by additional pathways as well. Next, the supposition of a sharp dielectric discontinuity at the metal/spacer interface is erroneous for two reasons. First, the wave functions of the metal electrons extend outside the plane defined by the atomic nuclei, leading to a continuous change in dielectric constant. Second, the interface cannot possibly be totally flat, but must have some small roughness components. Finally, the most serious limitation is the use of an optical (local) dielectric constant to describe the response of the medium to the dipole field. This approximation requires that two field components with the same time dependence, but with markedly different spatial properties, interact identically with the surface. In the distance regime of these experiments the first two limitations discussed above are not expected to be important; the last two could have significant effects and are discussed below.

Ford and Weber have discussed the effects of a nonlocal dielectric constant on the energy transfer rate of a molecule to a metal surface.²⁰ These authors treat the interaction in exactly the same manner as the classical theory, but use a dielectric constant which has an explicit wave-vector dependence. They use a modified Lindhard dielectric constant, a first order perturbation theory result.²¹ They conclude that nonlocal effects will not be of importance until the molecule-metal distance is less than approximately 50 Å. Their results also predict a distance dependence steeper than that of classical theory. The effects of a nonlocal dielectric constant have been discussed by other authors as well.^{11,22}

Another approximation which arises in comparing experiment to the classical theory is that of 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.²³ In this treatment Metiu solves Maxwell's equations for the case where the surface has roughness components Gaussian distributed. Other than this the assumptions of the CPS model are maintained. Metiu finds that 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.

Surface damping model

Much of the strength and predictive power of the classical theory derives from its use of a phenomenological parameter, the dielectric constant. A simple ellipsometric measurement gives us $\epsilon(\omega)$ with which we can predict the extent of the molecule-metal interaction. However, $\epsilon(\omega)$ contains much of the interesting physics we would like to know about: where does the molecular energy go initially in the metal, and by what sequence of events does it flow to the various modes of the lattice?

In recent years Persson¹⁰⁻¹² has made significant progress toward supplanting the phenomenological model of the molecule-metal interaction with a more physical model. In this model, a Fermi's golden rule calculation is considered, in which the molecule, initially in its excited state, is deexcited 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

$$1/\tau = 2\pi/\hbar \int d^3k d^3k' n_k (1 - n_{k'}) \times |\langle \mathbf{k}', n = 0 | H' | \mathbf{k}, n = 1 \rangle|^2 \delta(\epsilon_{k'} - \epsilon_k - \hbar\omega), \quad (4)$$

where $|\mathbf{k}\rangle$ is the wave function of an electron of wave vector \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 wave vector), n denotes the state of the dipole, and $H' = e\Phi(\mathbf{x}, t)$, where Φ is the potential of the dipole in the presence of the metal.

In order to obtain a meaningful nonradiative rate from this expression, it is necessary to make a number of approximations. The first approximation is to replace the time dependent dipole potential by a static potential. This approximation is considered to be valid when the electrons in the solid can respond adiabatically to the time dependent field, that is when the dipole frequency is much less than the plasma frequency of the metal. The implications of this assumption will be discussed later. Further approximations are made when considering the specific mechanisms by which energy transfer occurs.

In general, if we consider the excitation of electrons below any interband transitions, then a certain amount of momentum, far greater than the momentum of a photon of the appropriate energy, is required for momentum conservation. In the formalism developed by Persson, three possible sources of momentum are considered: (a) excitation of electron-hole pairs in the bulk, where the momentum required for the transition is supplied by the electron-electron, electron-phonon, and electron-impurity collisions, (b) electron-hole pair excitations where the required momentum is supplied by scattering against the surface potential, (c) electron-hole pair formation where the near field of the dipole provides the necessary momentum. At a distance d away from a dipole, the highest near field momentum components are on the order of \hbar/d . Thus the dipole field will not carry momentum which is a sizable fraction of the Brillouin wave vector of the metal until the dipole-metal separation is 10-30 Å. We can use this argument to disregard process (c) in our calculations.

The relative importance of processes (a) and (b) will depend on the mean free path of an electron in the solid. For an electron in the bulk to accept energy from the molecule, it must undergo a collision within a very short time after it is excited in order for momentum to be conserved. In previous experiments the molecules could excite bulk electrons by direct interband transitions.⁶⁻⁸ Below the interband transition, however, for the noble metals the 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, we would expect that the nonradiative rate would increase with the inverse dipole-metal distance to the fourth power.

The assumption that only electrons close to and traveling perpendicular to the metal surface will contribute to the energy transfer rate makes the Fermi's golden rule integration of Eq. (4) much more tractable, since the integration now only need be carried over a small fraction of the wave functions of the solid. Persson obtains a result for the energy transfer rate under these conditions:¹⁰

$$1/\tau = (|\mu|^2/4d^3\hbar)F(\omega, d), \quad (5)$$

where $|\mu|$ is the dipole transition moment and $F(\omega, d)$ depends upon the specific mechanism for energy transfer. For collisions with the surface potential Persson finds that

$$F(\omega, d) = 1.2(\omega/\omega_f)(1/k_f d), \quad (6)$$

where k_f is the Fermi wave vector, ω is the dipole frequency, and ω_f is the Fermi frequency. It is important to note that Persson's treatment excludes the effect of the dipole field interfering with itself, i.e., processes with k less than the radiation field wave vector.

RESULTS

The distance dependent lifetime was fit to both the classical model⁴ and the surface quenching model.¹⁰ The wave vector dependent dielectric constant models and the random roughness model each contain more than two adjustable parameters. The flexibility this allows the theories and the small sample of data points make comparisons to these models difficult to interpret, therefore quantitative comparisons were not performed. The data was fit to the computed values of each theory, classical and surface damping, by the Marquardt algorithm as used by Bevington.²⁴ Fits of the data were performed for two distinct cases, namely the case where both q and b_0 were varied and the case where only the quantum yield q was varied. In the latter fits the value of b_0 was determined by our measurement of the infinite distance rate, $b(d = \infty)$, using Eq. (1),

$$b^{\perp\parallel}(d = \infty) = b_0[1 - q * G^{\perp\parallel}(d = \infty)]$$

where the $G^{\perp\parallel}$ are computed by the classical model. G^{\perp} is approximately 0.52, while G^{\parallel} is approximately zero. The value of $b(d = \infty)$ differs from b_0 because the reflected field at the spacer/vacuum interface influences the radiative decay rate. The molecule is assumed to have the spacer dielectric constant. The value of chi square obtained from these fits was not normalized, but is useful for comparing between theories when fit to the same data.

In order to fit the surface damping model of Persson to the data it needed to be modified. Two obvious modifications were performed. In the first case, the long

distance value of the molecular decay rate was required to converge to our long distance measurement. The effect of the metal on the dipole radiative rate was ignored. In this limit the surface quenching mechanism is dominant. From Eqs. (5) and (6) we can write

$$\tau(d) = [(q*b_0/d^4)*4.5*10^7 + b_0]^{-1}, \quad (7)$$

where we have used the Einstein relation for the radiative rate²⁵ and $b_0 = 505 \text{ s}^{-1}$, $\omega_f = 5.48 \text{ eV}$, $k_f = 1.2*10^8 \text{ cm}^{-1}$, and d is the distance in angstroms. Second we incorporate the effect of the distance dependent radiative rate. We have added to expression (7) a term which corresponds to the distance dependent radiative rate [Eq. (2) integrated from $0 \rightarrow 1$] and obtain

$$\tau(d) = [(4.5*10^7*q*b_0/d^4 + (1-q)*b_0 + b_r(d)]^{-1}, \quad (8)$$

where

$$b_r(d) = q*b_0*[R(d)].$$

The ratio $R(d)$ was computed by numerically integrating Eq. (1) from $u = 0$ to 1 for a quantum yield q and decay rate b_0 of unity. Both Eq. (7) and (8) were fit to the data in order to demonstrate the importance of accounting for the radiative rate properly.

The measured distance dependent lifetime was fit to the classical model over the entire distance regime for which we have data (28–457 Å). The fits for parallel and perpendicular dipoles, extrapolated to cover the distances from 3 to 3000 Å, are shown in Fig. 3. In these fits, the lifetime at very large molecule–metal separations was constrained to be 1.98 ms and only the quantum yield was varied. The oscillations at large distances arise from the modulation of the dipole radiative rate by its own reflected field. The fitted value of the quantum yield, 0.47, is higher than the literature values of 0.15 in the gas phase, and 0.07 in solution, both at room temperature.⁹ We know of no measurements of q in a matrix at 40 K. If both b_0 and q are varied, the fit improves significantly between 40 and 100 Å, but not as much between 100 and 500 Å. This fit is not reasonable because the obtained values of q and b_0 are unrealistically high [$q = 0.91$, $\tau(d = \infty) = 3.9 \text{ ms}$].

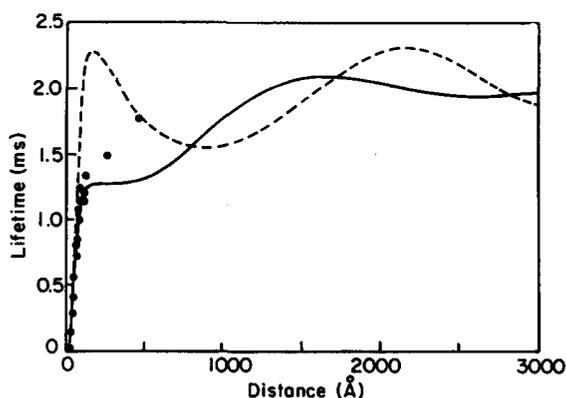


FIG. 3. This figure is a plot of our data over a wide distance range. The solid line is a best fit to classical theory with a perpendicular dipole and the dashed line is for a parallel dipole. See the text for details.

The data is not fit well by the theory in the 100–500 Å range. We have varied the modeling of the experimental geometry to try and improve the fit. The dipole orientation was varied from parallel to perpendicular with the perpendicular fits being most reasonable. According to the classical picture, the existence of the break in the experimental data at 100 Å can only be explained if the dipole orientation has a significant perpendicular component. The perpendicular fit can be substantially improved by increasing the distance between the molecule and the vacuum s in Fig. 1 to 1000 Å or more. The complete absence of a “cap” layer of NH_3 in our experiments is guaranteed, however, by the low pressure of our chamber, and has been verified ellipsometrically. As well, the CPS theory has had difficulty in fitting the data of Drexhage in this distance regime, for cases where the dipole has some perpendicular orientation and is located at a dielectric/air interface. We have varied the dipole orientation, the thickness of the cap layer, the dielectric constant of the silver substrate, and imbedded the dipole in vacuum instead of the NH_3 spacer in our attempt to model the data. We find the perpendicular dipole for the model in Fig. 1 to be the best approximation. The effects of this approximation will be dealt with in the discussion.

The behavior of the two theories in the energy transfer regime ($d \leq 130 \text{ Å}$) is shown in Fig. 4. The long dash line is the perpendicular CPS fit discussed above. As mentioned previously, when b_0 and q are both allowed to vary, the theory fits the data better, but the resultant b_0 and q values are unreasonable. When the measured value $b(d = \infty)$ is used to fix b_0 , then the resultant value of q is reasonable. In all the fits we have obtained, the CPS theory has failed to fit the lowest distance points (28–40 Å) underestimating the energy transfer rate at those distances. This observation is consistent with the predictions of the various nonclassical theories discussed earlier.

The short dash curve in Fig. 4 is a fit of the data to the surface damping model of Persson using Eq. (7). Only one variable, the quantum yield, was used in this fit. The long distance rate forces the curve to rise too sharply. The golden rule formula used by Persson gives the rate of nonradiative energy transfer from the dipole to the surface via the creation of electron-hole pairs. This model does not include the effect of the metal on the radiative rate of the dipole. When the radiative rate is treated properly as in Eq. (8), a much better fit is obtained. Equation (8) is the solid line in Fig. 4, and fits the data much better than either the classical expression or Eq. (7). The quantum yield obtained from these fits is 0.42. Since the frequency of biacetyl emission is below the silver interband transition, the dipole–metal nonradiative coupling does not dominate over the effect of the metal on the dipole radiative rate. The measured distance dependent lifetime includes both nonradiative and radiative perturbations of the excited state of the molecule and both must be treated properly.

With a quantum yield and an isolated molecular decay rate, one can use the classical theory to extract the energy transfer rate to the surface from the other rates

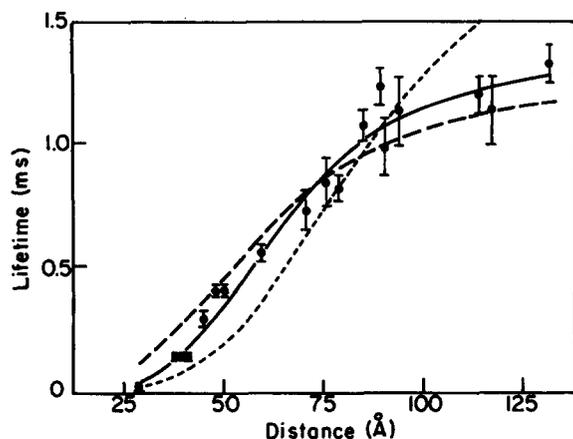


FIG. 4. Plot of data over distance regime where the surface damping mechanism is expected to dominate. The long dash line is the best fit to classical theory and the solid line is the best fit to Eq. (8). The short dash line is the best fit to the surface damping model without radiative effects added.

which contribute to the molecular decay. Using the best fit quantum yield of 0.42, we have computed the energy transfer rate from our experimental points and plotted the $\log(\tau_{et})$ vs $\log(d)$ in Fig. 5. For a pure cubic or quartic molecule-metal interaction the data would fall on a straight line of slope 3 or 4. The dashed curve in the figure corresponds to the best CPS fit of Fig. 4, and the solid curve to the Persson expression. The log-log plot of the data shows some nonlinearity which may be caused by various factors.

DISCUSSION

The classical model is unable to fit the observed lifetime over the entire distance range and gives very poor fits when the infinite distance lifetime is restricted to the measured value of 1.98 ms. The deviations at intermediate distances, $100 < d < 500 \text{ \AA}$, are especially strong and may be caused by the inability of the classical model with its macroscopic, i.e., not molecular, distance scale to describe a molecule with its dipole experiencing vacuum on one side and the NH_3 dielectric on its other side. It is plausible that this effect would be more pronounced for a perpendicular dipole which oscillates across the interface than for a parallel dipole which oscillates along the interface. Deviations from the classical model in this region for dipoles which have a significant perpendicular component and are close to the spacer-vacuum interface is evident in the fits to the data of Drexhage as well, see Figs. 7 through 12 of Ref. 4. This inability to model the radiative rate of a perpendicular dipole located at a dielectric discontinuity may be a shortcoming of the classical theory. This could have important implications for modeling of the photophysics of adsorbed species as well.

The classical perpendicular dipole model is used throughout our fits because, although not quantitatively correct, it possesses the proper qualitative features, that is, it shows a break in the curve below $\tau(d = \infty)$ instead of immediately rising above $\tau(d = \infty)$ and oscillating as

a parallel dipole would. Because the radiative rate modulation and energy transfer rate are both pronounced in our system, an improper modeling of the distance dependent radiative rate could affect our fits. For lack of a better description of the effect of the metal on the radiative rate the classical description which has been successful under many other experimental conditions was used throughout our fits.

The classical model, when fit over a more limited range, $< 130 \text{ \AA}$, shows deviations from the observed lifetime as well, although less dramatic. It appears in these fits, Fig. 4 and especially Fig. 5, that the classical model has too shallow a slope to describe the data. This type of deviation is consistent with the predictions of other models such as a nonlocal dielectric constant and the effect of small roughness features, as well as the surface damping model. The surface quenching model fits the data very well over this regime, primarily because of its steeper slope. The data may show some curvature but a more detailed study would be required to tell. This curvature could be caused by various real effects, for example an improper treatment of the radiative rate or any of the other limitations of the classical theory discussed previously.

Obviously it is difficult to distinguish between the two models, classical and surface damping, fit to the data in Figs. 4 and 5. This difficulty arises for two primary reasons. First the classical theory uses a phenomenological

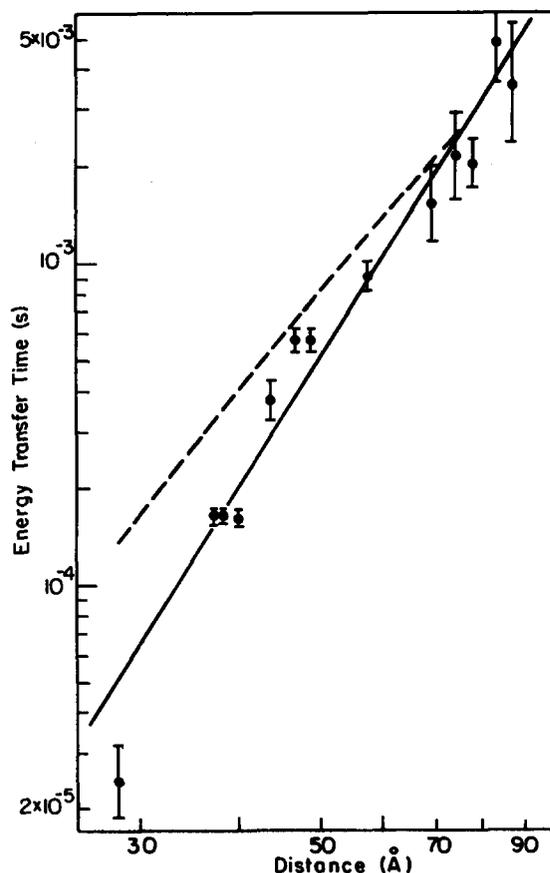


FIG. 5. Above is a log-log plot of the energy transfer rate vs distance. The dashed line is the expected classical theory behavior. The solid line is the best fit to the surface damping model. See the text for details.

parameter, the dielectric constant. This dielectric constant, which we measure experimentally, is a convolution of the bulk and surface response functions. This effect allows the classical theory to partially account for the surface quenching phenomenon. The way to distinguish between the two mechanisms is to measure the distance dependence. Since the nonradiative coupling is weak compared to other systems, the damping does not begin to dominate over the internal molecular decay mechanism until fairly close to the surface, in our case 85 Å. The near field of the dipole starts to become important at approximately 30 Å and bulk processes once again become dominant. The surface quenching mechanism may dominate over a very limited region making it difficult to observe and verify.

Even over the distance range where the surface damping should be a major decay mechanism it may not be dominant. The static potential used in the surface quenching model only penetrates the metal surface to a small extent, 2–3 Å, whereas the skin depth of an optical field at our frequency, with our measured index of refraction of silver, is approximately 260 Å. Although the dipole field may couple with the bulk less effectively than the surface, i.e., the momentum selection rule holds, there are a much larger number of electrons to couple with than expected by the Persson model. If one uses the criterion that an electron must scatter within an angstrom for momentum conservation^{10–13} and a mean free path of 1000 Å for an electron, one can compute phenomenologically the number of electrons which collide in the bulk and compare to the number which meet the above criterion at the surface. The result is that the ratio of bulk collisions to surface collisions is approximately 1:1. This simple analysis implies that mean free paths of a micron will be required for the ratio of surface to bulk collisions to rise to 10:1, implying that under all but extreme conditions bulk processes could be significant. Johnson and Christy¹⁵ report the mean free path as 430 Å for amorphous silver at room temperature. Since our sample is single crystalline and at 40 K we would expect the mean free path to be greater than 430 Å, but we cannot say without an independent measure. Even for much lower frequencies than ours, the skin depth of the dipole is 200–250 Å forcing the conclusion that, at least on silver, the electron-hole pair creation through collisions with the bulk may always be a significant contribution.

Other experiments on excited molecular electronic states of adsorbed species^{11,14} have been interpreted as agreeing with the Persson model. These experiments were performed at one distance and lifetimes extracted from electron energy loss spectra via a line shape analysis. Small changes in the distance, for example, could lead to agreement with classical predictions as well. Therefore those experiments must be interpreted and compared with the surface quenching model with extreme care, because of the sensitivity of the lifetime to the adjustable parameters remaining in the model.

In conclusion, we have studied the distance dependent lifetime of biacetyl above a Ag(111) surface. The classical

theory as developed by Chance, Prock and Silbey⁴ is unable to model the data effectively. The classical theory fails to model the distance dependent radiative rate for a perpendicular dipole at a dielectric/vacuum interface. The deviations of the classical model from our data at short distances, where the radiative rate is less important, may be caused by improper modeling of the nonradiative energy transfer from the molecule to the surface. This failure at short distances could be caused by various effects, i.e., nonlocal dielectric constant, random roughness effects, or a surface damping mechanism.

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