CHAPTER 5

Fluorescence properties of rhodamine 6G physisorbed to aluminum

5.1 Abstract

5.2 Introduction

5.3 Experimental

5.4 Results and Discussion

References
5.1 Abstract

Fluorescence properties of submonolayers of rhodamine 6G have been measured as a function of distance to an aluminum mirror. For distances less than 5 nm (spacer layers of 1 nm thickness were used) a broadening of the emission spectrum is observed. The fluorescence lifetime has been measured for distances up to 6 nm. The broadening of the fluorescence spectra and the shortening of the lifetime is attributed to efficient energy-transfer to the aluminum substrate. Good agreement with theory is found if volume and surface contributions are included in the energy transfer rate.

5.2 Introduction

The radiative behaviour of luminescing molecules in front of metal surfaces has been studied extensively during the past decades [1–3]. The metal surface influences the radiative as well as the nonradiative properties of emitting molecules. The influence of the mirror shows a marked distance dependence. In case of emitter–mirror distances on the order of the emitted wavelength, an oscillatory behaviour of the fluorescence lifetime with distance is found [2]. This effect is ascribed to the interference between directly emitted waves and partially reflected waves from the mirror. For distances less than about 10 nm the lifetime of the excited state is dominated by radiationless energy transfer to the metal substrate. The excited molecule interacts through the near-field with the electron gas of the metal and the excitation energy is dissipated through various scattering processes into the bulk. A reduction of the excited state lifetime by several orders of magnitude is observed. In case of flat silver surfaces the emission is even completely trapped, and no fluorescence is observable [4].

Absorption of energy by metal electrons requires momentum conservation. Three different sources of momentum can be distinguished [5,6,7]: (A) in the
bulk: scattering by phonons, impurities, and the crystal potential; (B) scattering by the metal surface; (C) from the spatial variation of the near-field of the excited molecule itself. Process (A) dominates at larger distances (>~5 nm), for which an inverse cube distance dependence is calculated. A $d^{-4}$ dependence is estimated for processes (B) and (C), which are expected to dominate for small molecule-metal distances (<~5 nm).

A considerable amount of work has been devoted to line shape studies of physisorbed molecules [5,8]. Two different techniques have been applied. By means of infrared reflection-absorption spectroscopy information is obtained about the vibrational frequencies and bandwidths, which are studied as a function of surface coverage [8,9]. The observations are explained in terms of lateral dipole-dipole and dipole-image-dipole interactions [10]. Electron energy-loss spectroscopy has been used to study electronic as well as infrared transitions of adsorbates on metal surfaces [5,11]. In all cases a broadening of the energy levels is observed with respect to multilayer values, which is usually attributed to the reduced excited state lifetime [5,8,11].

For distances shorter than 1 nm chemical effects will also alter the lineshape and line position [3,5]. The chemical bonding to the substrate affects the vibrational frequencies. In addition electron transfer from the adsorbate to the substrate may occur [3,5].

In this chapter we study fluorescence spectra of submonolayers of rhodamine 6G (R6G) spaced by amylose-acetate ester layers from plane aluminum mirrors. Aluminum was chosen because the luminescence is less efficiently quenched compared to, for example, a silver surface. The distance between the mirror and the R6G molecules was varied over a range of 1–6 nm by the application of transparent polymer layers of 1 nm thickness. The advantage of using polymer spacer layers instead of conventional fatty acid monolayers is that a higher spatial resolution is achieved (1 nm versus 5 nm, respectively), caused by the fact that only one polymer spacer layer is transferred per dipping cycle through which the formation of bilayers is prevented [2,12].

We found that the width of the emitted spectrum depends on the distance to the mirror. For small distances a broadening was observed. In addition we measured the fluorescence lifetime and the apparent quantum yield of emission as
Fluorescence properties of rhodamine 6G physisorbed to aluminum

a function of emitter–mirror distance. All observations are explained in terms
of energy transfer theory, for which acceptable agreement with experimental data
is found.

To our knowledge no reports have yet appeared in which the lineshape
broadening could be detected via fluorescence emission, and in which the
broadening was measured as a function of emitter–metal distance.

5.3 Experimental

R6G was obtained from Lambda-Physik, and was used without further
purification. R6G monolayers were prepared by the dipping technique. The dipping
proceeded at a rate of 0.25 mm/s from a 5·10−5 M ethanolic solution. As is
evident from the absorption spectrum (Fig. 5.1), no sign of aggregation is
observed [13].

The substrates were prepared by evaporation, at a pressure of 10−5 Torr, of
thick aluminum layers onto Corning 7059 microscope slides. The slides were
cleaned before use in chromic acid, and were rinsed ultrasonically with milli–Q
water, acetone, chloroform, and hexane.

The spacer layer consisted of amylose-acetate ester, and was applied by the
Langmuir–Blodgett technique at a surface pressure of 7 mN/m [12]. The subphase
was highly purified water (milli–Q), at a temperature of 22 °C. A monolayer was
transferred during every upstroke.

Fluorescence spectra were recorded by means of an intensified optical
multichannel analyzer (Princeton Instruments), in the direction perpendicular to
the substrate surface. The 488 nm line of an argon–ion laser (Spectra Physics)
was used as excitation source.

Fluorescence decays of R6G monolayers were measured using a time correlated
single photon-counting system. A cavity-dumped mode-locked Argon–ion laser
(Coherent, Inc.) operating at a repetition rate of 94 kHz (514.5 nm) was used as
excitation source. The photomultiplier used was a Hamamatsu microchannel plate
(R1564U–01). The time resolution of the detection system is 33 ps, but due to
the rather long pulse duration of the Ar⁺-laser the time resolution after

57
deconvolution was 45 ps.

Figure 5.1: Absorption (solid curve) and fluorescence (dashed curve) spectra of submonolayers of rhodamine 6G on a Corning 7059 glass substrate. Excitation wavelength: 488 nm.

5.4 Results and Discussion

For the calculation of the influence of aluminum substrates on the fluorescence lifetime of physisorbed R6G, we use the theory developed by Persson et al. [5,6,7]. In this theory the excited state lifetime for an oscillating dipole at small distances $d$ from the metal surface ($kd \ll 1$) is given by:

$$T_{1,m}(d) \approx T_{1,\infty}\left\{1 + \frac{\eta}{8}(dk)^{-3}\left[2\text{Im}\left(\frac{\varepsilon_m(\omega) - \varepsilon_1}{\varepsilon_m(\omega) + \varepsilon_1}\right) + 6\xi \frac{1}{k_F d} \frac{\omega}{\omega_p} + 18 \frac{\omega_F \omega}{\omega_p \omega_p k_F d}\right]\right\},$$

(5.1)
where $T_{1,\infty}$ is the fluorescence lifetime at infinite distance from the mirror, $k$ is the magnitude of the wavevector at the emitted frequency $\omega$, $\varepsilon_m(\omega)$ is the (complex) metal dielectric constant, $\varepsilon_1$ is the dielectric constant of the medium in which the dipole is embedded, and $\eta$ is an orientational parameter ($\eta = \frac{3}{2}$ for a perpendicular dipole and $\eta = \frac{3}{4}$ for a parallel dipole). Some typical metallic electron gas parameters are contained in the last two terms between square brackets, where $k_F$ is the Fermi wavevector, $\omega_F$ the Fermi frequency, $\omega_p$ the plasma frequency, and $\xi \approx 1$ [7] is a constant which depends on the electron gas density. The last term between square brackets is valid for the limiting case $k_F d \gg \omega_F / \omega$. For a complete derivation and discussion of the different terms in Eq.(5.1) we refer to the work of Persson et al. [5,6,7].

The three terms between square brackets signify the different sources of momentum, as mentioned in the introduction. The first term represents the bulk contribution to the damping rate, and is identical to the classical result where the interaction of the transition dipole of the molecule with the electromagnetic field of its image dipole in the mirror is considered [1]. In this classical theory the out-of-phase (imaginary) part of the reflected field determines the non–radiative lifetime $T_{1,nr1}$, while the in-phase (real) part of the reflected field affects the frequency shift $\Delta \omega$. In the derivation a steplike metal surface was assumed. Furthermore, a bulk metal dielectric constant is used, neglecting surface contributions to the energy decay. In Eq.(5.1), however, surface contributions are accounted for by the second term between square brackets, where the required momentum is supplied by the surface potential. In the last term momentum originates from the spatial variation of the near-field of the dipole. The distance behaviour of the three terms between square brackets is different. For the volume scattering a $d^{-3}$ behaviour is calculated, while a $d^{-4}$ behaviour is computed for the other two contributions. Volume contributions are expected to dominate for metallic substrates in the frequency region of strong interband transitions, where indeed an inverse cube distance dependence is found for molecule–surface separations down to 1 nm [3,14]. For nearly free-electron like metals the $d^{-4}$ terms are dominant at small molecule–surface separations ($d \leq 5$ nm), and a fluorescence lifetime is calculated which is about 10 times shorter than one would estimate on ground of bulk
scattering contributions only.

Figure 5.2: Fluorescence lifetime as a function of emitter–metal distance (closed circular points). The solid line results from the calculation according to Eq.(5.1), the dashed curve results in case only bulk contributions to the energy transfer rate are incorporated.

The results of fluorescence decay measurements of R6G physisorbed to aluminum substrates are given in Fig.5.2. The fluorescence lifetime is plotted against the distance to the mirror. Fluorescence decay curves could be fitted to a single exponential, in agreement with the work of Leitner et al. [15]. For molecule–surface distances shorter than ≈4 nm the fluorescence decay time was shorter than the time resolution of the measuring system (45 ps). For these distances the fluorescence lifetime was determined from quantum yield measurements. The solid line in Fig.5.2 is based on Eq.(5.1) using a metal dielectric constant \( \varepsilon_m = -39.2 + i11.77 \) [16], \( \varepsilon_1 = 1.3 \), and \( T_{1,\infty} = 3 \text{ ns} \), and \( \eta = 3/4 \) corresponding to the known parallel orientation of the R6G molecules with
Fluorescence properties of rhodamine 6G physisorbed to aluminum

respect to the substrate surface [17]. Furthermore, we used \( \omega = 3.3 \times 10^{15} \) rad/s, \( \omega_p = 2.39 \times 10^{16} \) rad/s, \( \omega_F = 1.7774 \times 10^{16} \) rad/s, and \( k_F = 1.75 \times 10^{10} \) m\(^{-1}\) [18]. The requirement \( k_F d > \omega_F/\omega \) is met for the whole regime of emitter-metal distances studied, justifying the expression for the last term in Eq.(5.1) (for the smallest distance of 1 nm \( (k_F d)/(\omega_F/\omega) \approx 3.2 \)). The dashed line in Fig.5.2 is the classical result [1], where surface contributions to the damping rate are neglected. Incorporation of the surface scattering contributions gives a better agreement with experimental data.

In estimating the distance of the emitting layer from the metal surface we presume a native oxide layer of 1 nm thickness to be present at the metal surface [19]. This oxide layer is formed within two hours of exposure to air, and continues to grow very slowly and reaches its final value of about 4 nm after one month. Oxidation is unavoidably due to the application of spacer layers by the Langmuir-Blodgett technique. All measurements were done within one hour after preparation.

In addition to lifetime and quantum yield measurements we measured the distance dependence of the fluorescence spectra for physisorbed R6G monolayers. In Fig.5.3 emission spectra are shown for R6G monolayers separated by one \((d=2 \text{ nm})\), respectively five \((d=6 \text{ nm})\) polymer spacer layers. An asymmetric broadening of about 200 cm\(^{-1}\) for the spectrum close to the mirror is observed. The asymmetric broadening is accompanied by a small red shift of the emission maximum of about 50 cm\(^{-1}\). An estimate of the spectral red-shift can be made on ground of the classical interaction of an oscillating dipole with its fictitious mirror image [1], which gives \((kd \ll 1)\):

\[
\Delta \omega = \omega(d) - \omega(\infty) = -\frac{\eta}{8} (dk)^{-3} T_{1,n} \text{Re}\left( \frac{\varepsilon_m(\omega) - \varepsilon_1}{\varepsilon_m(\omega) + \varepsilon_1} \right),
\]

where \( q \) is the quantum yield of emission at infinite distance from the mirror. On basis of Eq.(5.2) we calculate a red-shift of 17 cm\(^{-1}\) \((d=2 \text{ nm})\), which is smaller than the observed red shift of about 50 cm\(^{-1}\) (see Fig.5.3). Though the right order of magnitude is calculated, the calculated value is a factor of three off from the experimental value.
Figure 5.3: Fluorescence spectra of Rhodamine 6G submonolayers separated from the aluminum surface by one \((d=2\,\text{nm},\ \text{solid\ line})\) respectively five spacer layers \((d=6\,\text{nm},\ \text{dashed\ line})\). Excitation wavelength: 488 nm.

An estimate of the line broadening can be made on ground of Eq.(5.1). The effect of the reduced excited state lifetime on the homogeneous damping rate \(\Gamma_{\text{hom}}\) can be calculated from [20]:

\[
\Gamma_{\text{hom}} = (2T_1)^{-1} + (T_2^*)^{-1},
\]

where \(T_1\) is the excited state lifetime (longitudinal relaxation time), and \(T_2^*\) the pure dephasing time (transversal relaxation time) [20]. Any effect of the reduced excited state lifetime on the homogeneous linewidth can be expected if \(T_1\) becomes comparable to \(T_2^*\).

The distance dependence of the width (FWHM) of the fluorescence spectra, normalized with respect to the FWHM at infinite distance from the mirror, is
Fluorescence properties of rhodamine 6G physisorbed to aluminum

Plotted in Fig. 5.4. The width decreases sharply with increasing distance and remains constant for emitter–mirror distances larger than 5 nm (closed circles). Also shown are measurements of the FWHM for R6G physisorbed directly onto aluminum surfaces (open circles). The distance dependence of the normalized FWHM is calculated according to Eq. (5.3) using the expression of Eq. (5.1) for $T_1$, where we assume the pure dephasing rate and the inhomogeneous broadening to be independent of emitter–metal distance. The solid line in Fig. 5.4 is the result.

Figure 5.4: Plot of the FWHM normalized with respect to the FWHM at infinite distance from the mirror, as a function of emitter–mirror distance (closed circles). Open circles are results of measurements of the FWHM for R6G physisorbed directly onto aluminum. Also shown are the results of calculations based on Eqs. (5.1) and (5.3), using $T_2^* = 1$ ps (solid line), and $T_2^* = 100$ fs (dashed line).

Of the above calculations where $T_2^*$ was set to 1 ps. For directly adsorbed R6G agreement with theory is obtained if a pure dephasing time 100 fs was used.
Chapter 5

(dashed line in Fig. 5.4). The thickness of the oxide layer, which is known to be about 1 nm as argued above, is 1 nm in these calculations.

The difference in pure dephasing times found for R6G directly adsorbed to aluminum and for R6G physisorbed to polymer spacer layers must be attributed to the difference in chemical environment. Incoherent fluctuations in the electric field of conduction electrons as felt by directly adsorbed dye molecules may be a cause for the reduction in dephasing time found.

The estimated pure dephasing time of 1 ps for the polymer-spaced dye monolayers is an order of magnitude longer than the value found for molecules dissolved in, for example, (three dimensional) polymer matrices [21]. However, the value is still orders of magnitude smaller than found for molecules in the gas-phase [20]. The reduced dimensions of our samples is probably the main cause for the long dephasing time found compared to dye molecules dissolved in (three dimensional) polymer matrices.

The excited state lifetime of 200 fs we calculate for a distance of 1 nm from the aluminum surface is of the same order of magnitude as the lifetime estimated by Avouris et al. [11], who studied the $1^1B_{2u} \rightarrow 1^1A_1$ transition of pyrazine physisorbed to a Ag(111) surface.

In summary, we studied the fluorescence properties of submonolayers of R6G as a function of distance to the aluminum substrate. A shortening of the fluorescence lifetime and a reduction of the emission quantum yield by several orders of magnitude ($\approx 10^4$) was observed. Also a broadening and red-shift of the emission spectra was observed. The dependence on distance of these results was measured in steps of 1 nm, allowing a detailed test of the distance dependence of the quenching of emission by the aluminum substrate. From the distance dependence of the broadening of the spectra we derive a pure dephasing time of 100 fs for directly adsorbed R6G molecules, and a pure dephasing time of 1 ps for the polymer spaced R6G monolayers. All observations agree favourably with theory, if bulk and surface contributions to the scattering of excited metal electrons are incorporated.
Fluorescence properties of rhodamine 6G physisorbed to aluminum

References

[18] N.W. Ashcroft and N.D. Mermin in Solid State Physics (Saunders College,

