Fluorescence properties of submonolayers of rhodamine 6G in front of a mirror

Gerard Cnossen, Karel E. Drabe, and Douwe A. Wiersma
University of Groningen, Materials Science Centre, Ultrafast Laser and Spectroscopy Laboratory, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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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 observed when the sample is close to the mirror are attributed to efficient energy transfer from the monolayer to the mirror. The experiments clearly demonstrate that both volume and surface contributions must be considered in this energy-transfer process.

INTRODUCTION

The radiative dynamics of molecules that luminesce in front of a mirror have been studied extensively during the past decades. The metal surface influences the radiative as well as the nonradiative properties of the emitting molecules. The influence of the mirror on these dynamics shows a marked distance dependence. In case of emitter–mirror distances on the order of the emitted wavelength, an oscillatory behavior of the fluorescence lifetime with distance has been found. This effect is ascribed to the interference between directly emitted waves and waves reflected from the mirror. For distances less than about 10nm 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 the case of flat silver surfaces the emission is even completely quenched.

Absorption of energy by the electrons in the metal requires momentum conservation. Three different sources can supply this momentum: (1) in the bulk—scattering by phonons, impurities, and the crystal potential; (2) scattering by the metal surface; and (3) from the spatial variation of the near-field of the excited molecule itself. Process (1) dominates at larger distances (>5 nm), for which an inverse cube distance dependence was calculated. A d−4 dependence has been derived for processes (2) and (3). These processes 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. Two different techniques have been applied. By means of infrared reflection–absorption spectroscopy information is obtained about the vibrational frequencies and bandwidths. These quantities can be studied as a function of surface coverage. The observations are explained in terms of lateral dipole–dipole and dipole–image-dipole interactions. Electron energy-loss spectroscopy has been employed to study electronic as well as infrared transitions of adsorbates on metal surfaces. In all cases a broadening of the spectral features is observed with respect to multilayer values. This is usually attributed to a reduced excited state lifetime caused by interaction between the physisorbed molecules and the metal.

For distances shorter than 1 nm chemical effects will also alter the line shape and line position. Chemical bonding to the substrate also affects the vibrational frequencies. Another effect that may occur is electron transfer from the adsorbate to the substrate.

In this paper we report on a study of the fluorescence spectra of submonolayers of rhodamine 6G (R6G) spaced by amylose–acetate ester layers from a plane aluminum mirror. Aluminum instead of silver was chosen as a substrate because the luminescence is less efficiently quenched in this case. The distance between the mirror and the R6G molecules was varied over a range of 1–6 nm by use 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 can be achieved (1 nm vs 5 nm, respectively). This is caused by the fact that only one polymer spacer layer is transferred per dipping cycle. In this way the formation of bilayers is prevented.

We found that the linewidth of the emission spectrum depends on the distance of the sample to the mirror. In addition, we observed for small distances a line broadening. We also measured the fluorescence lifetime and the apparent quantum yield of emission as a function of emitter–mirror distance. All observations can be explained assuming energy transfer from the monolayer to the mirror occurs, using existing theory.

To the best of our knowledge this is the first time that it is shown that the spectral width of a monolayer depends on the distance to a mirror.
The excitation wavelength was 488 nm.

Milli-Q water, acetone, chloroform, and hexane, purified water (milli-Q), at a temperature of 22 °C. A monolayer was transferred during every upstroke. The spacer layer consisted of amylose-acetate ester, and was made by the Langmuir-Blodgett technique at a surface pressure of 7 mN/m. The substrates were prepared by evaporation, at a pressure of 10⁻⁵ Torr, of thick aluminum layers onto Corning 7059 glass substrate. The slides were cleaned before use in chromic acid, and were rinsed ultrasonically with sure 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 fluorescence spectra, observed in the direction perpendicular to the substrate surface, were recorded using an intensified optical multichannel analyzer (Princeton Instruments). The 488 nm line of an argon-ion laser (Spectra Physics) was used as an excitation source. The photo-multiplier used was a Hamamatsu microchannel plate (R1564U-01). While the intrinsic time resolution of the detection system is 33 ps for ultrafast excitation, the actual time resolution in our experiment was 45 ps, due to the use of a mode-locked Ar⁺ laser as an excitation source.

THEORETICAL CONSIDERATIONS

For a calculation of the influence of aluminum substrates on the fluorescence lifetime of physisorbed R6G, we employ a theory developed by Persson and co-workers. In this theory the excited state lifetime for an oscillating dipole at a small distance d from the metal surface (kd<1) is

\[
T_{1,\text{NR}}^{-1}(d) \approx T_{1,\infty}^{-1}(1 + \frac{\eta}{8} (dk)^{-1}) \left[ 2 \operatorname{Im} \left( \frac{\varepsilon_m(\omega) - \varepsilon_1}{\varepsilon_m(\omega) + \varepsilon_1} \right) + 6 \varepsilon_2 \frac{\omega}{k_F d \omega_p} \right] \right]
\]

where \( T_{1,\infty} \) is the fluorescence lifetime at an infinite distance from the mirror, \( k \) is the magnitude of the wave vector 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 (\( \eta = 3/2 \) for a perpendicular dipole and \( \eta = 3/4 \) for a parallel dipole). The last two terms between square brackets contain electron-gas parameters of a typical metal. Here \( k_F \) is the Fermi wave vector, \( \omega_p \) the Fermi frequency, \( \omega_p \) the plasma frequency, and \( \varepsilon_2 \approx 1 \) (Ref. 7) is a constant which depends on the electron–gas density. The last term between square brackets is valid for the case where \( k_F \omega_p \omega_p / \omega_p \). For a derivation of Eq. (1) and a detailed discussion of the different terms in Eq. (1) we refer to the work of Persson and co-workers.

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 with the electromagnetic field of its image dipole is considered. In this theory the out-of-phase (imaginary) part of the reflected field determines the nonradiative lifetime \( T_{1,\text{NR}} \), while the in-phase (real) part affects the frequency shift \( \Delta \omega \). In deriving this term a steplike metal surface was assumed. Furthermore, a bulk metal dielectric constant is used, while surface contributions to the energy decay are neglected. In Eq. (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 behavior of the three terms between square brackets is different. For the volume scattering a \( d^{-3} \) behavior was calculated, while a \( d^{-4} \) behavior was obtained for the other two contributions. Volume contributions are expected to dominate for metal substrates in the frequency region of strong interband transitions. This expectation is indeed borne out for molecule–surface separations down to 1 nm. For nearly free-electron-like metals the \( d^{-4} \) terms are dominant at
RESULTS AND DISCUSSION

The results of fluorescence decay measurements of R6G physisorbed to aluminum substrates are given in Fig. 2, where the fluorescence lifetime is plotted as a function of the distance between the emitters and the mirror. Fluorescence decay curves could be fitted to a single exponential, in agreement with the work of Leitner et al. For molecule-surface distances shorter than ~4 nm the fluorescence decay time was found to be beyond the system response (45 ps). For these distances the fluorescence lifetime was indirectly determined from relative quantum yield measurements. The solid line in Fig. 2 is based on Eq. (1) using a metal dielectric constant \( \varepsilon_m = -39.2 + i11.77 \), \( \varepsilon_1 = 1.3 \), and \( T_{1,\omega} = 3 \text{ ns} \). Furthermore, we used \( \eta = 3/4 \) corresponding to the known parallel orientation of the R6G molecules with 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 \( k_F = 1.75 \times 10^{10} \text{ m}^{-1} \). The requirement \( k_p d > \omega_F / \omega \) is met for the whole regime of emitter-metal distances studied, justifying the expression for the last term in Eq. (1) for the smallest distance of 1 nm (\( k_p d \right )/ (\omega_F / \omega) \approx 3.2 \). The dashed line in Fig. 2 is the classical result,1 where surface contributions to the damping rate are neglected. Note that incorporation of these contributions in the calculations leads to a substantial better agreement with the 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.13 This oxide layer is formed within 2 h of exposure to air, after which it slowly grows until it reaches, after about one month, its final value of about 4 nm. This oxidation process is unavoidable due to the application of spacer layers by the Langmuir–Blodgett technique. All measurements were done within 1 h after preparation.

In addition to lifetime and quantum yield measurements we also measured the distance dependence of the fluorescence spectra for physisorbed R6G monolayers. In Fig. 3 emission spectra are shown for R6G monolayers separated by one (\( d = 2 \text{ nm} \)), respectively five (\( d = 6 \text{ nm} \)), polymer spacer layers. A broadening of the spectrum close to the mirror is observed. This broadening appears to be asymmetric due to redshift (70 cm\(^{-1}\)) that accompanies this change of line breadth. An estimate of the spectral redshift can be made by using the classical expression for the interaction between an oscillating dipole with its fictitious mirror image.1 For \( k d \ll 1 \) this yields the following equation:

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

where \( q \) is the quantum yield of emission at infinite distance from the mirror. With Eq. (2) we calculate a redshift.
of 17 cm\(^{-1}\) \((d=2 \text{ nm})\), which is substantially smaller than the observed redshift of about 70 cm\(^{-1}\) (see Fig. 3). It is clear that while the right order of magnitude for the shift is calculated quantitative agreement is not achieved. At this point it is not clear what the source of the discrepancy is.

An estimate of the line broadening can be made using Eq. (1). The effect of the reduced excited state lifetime on the homogeneous damping rate \(\Gamma_{\text{hom}}\), can be calculated from

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

where \(T_1\) is the excited state lifetime (longitudinal relaxation time), and \(T_2^*\) the pure dephasing time (transversal relaxation time).\(^{20}\) An 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 full width at half maximum (FWHM) of the fluorescence spectra, normalized with respect to the FWHM at infinite distance from the mirror, is plotted in Fig. 4. The width decreases sharply with increasing distance and remains constant for emitter-mirror distances larger than 5 nm (solid circles). Also shown are measurements for R6G physisorbed directly onto aluminum (open circles). The solid and dashed lines are based on calculations using Eqs. (1) and (3), whereby \(T_2^* = 1\ \text{ps}\) (solid line), and \(T_2^* = 100\ \text{fs}\) (dashed line).

FIG. 4. Plot of the FWHM of the emission spectrum normalized with respect to the FWHM at infinite distance from the mirror, as a function of emitter-mirror distance (solid dots). Also shown are the results of measurements for R6G physisorbed directly onto aluminum (open circles). The solid and dashed lines are based on calculations using Eqs. (1) and (3), whereby \(T_2^* = 1\ \text{ps}\) (solid line), and \(T_2^* = 100\ \text{fs}\) (dashed line).