guishing high and low Si/Al ratio zeolites and may be important in studies of zeolites that are chemically or physically altered.

Fluorescence Enhancement from Langmuir–Blodgett Monolayers on Silver Island Films

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Fluorescence enhancement from a Langmuir–Blodgett (LB) monolayer of a substituted phthalocyanine deposited on silver island films was observed. The competitive relaxation effect due to radiationless energy transfer from the excited molecule to the nearby metallic surface was controlled by using LB spacer layers of arachidic acid. For the phthalocyanine monolayer in direct contact with the metal islands the fluorescence is enhanced, broadened, and red-shifted relative to the fluorescence from the phthalocyanine LB films deposited onto smooth glass surfaces. With intervening spacer layers of arachidic acid the fluorescence spectrum from the phthalocyanine monolayer returns to near its unperturbed shape, but its intensity is again enhanced. The enhancement factor initially decreases from the direct contact value ($\sim$200) but then increases monotonically for increasing spacer layer thickness to a value of almost 400 for a spacer consisting of five monolayers of arachidic acid. P-polarized light consistently produces more intense enhanced fluorescence spectra by at least a factor of 2 than those produced by S-polarized light.

Introduction

In a recent communication[1] we reported the distance dependence of SERS (surface-enhanced Raman scattering) enhancement factors from Langmuir–Blodgett (LB) monolayers of tetra-*tert*-butyl metal-free phthalocyanine, $(t\text{-Bu})_4H_2Pc$, on silver and indium island films. In an independent study Cotton et al.[2] have also reported SERS distance dependence results of molecular dyes on silver island films. In both cases it was concluded that the observed SERS were due to electromagnetic enhancement. Surface-enhanced electromagnetic processes are not restricted to Raman scattering, and they include enhanced absorption, emissions (fluorescence and phosphorescence), photochemistry, and second-harmonic generation. Two extensive reviews on the general subject of surface-enhanced spectroscopy have been recently published.[3,4] Fluorescence from adsorbed molecules is generally observed as a weak signal compared with the large enhancement factors (EF) obtained for inelastic scattering. This low fluorescence intensity is apparently due to the effect of short-distance radiationless energy transfer from an excited molecule to a nearby metallic surface.[5]

A discussion of the EF in Raman scattering, resonant Raman scattering, and fluorescence from molecules on rough metal surfaces has been given by Weitz et al.[6]

According to their treatment[6] the fluorescence intensity from a molecule adsorbed on a metal surface is subject to electromagnetic field enhancements, and in addition, the fluorescence is quenched by an increased damping or nonradiative decay rate of the electronically excited molecular dipole through the metal particles. Experiments have shown that the measured fluorescence lifetimes of europium(III) thenoyltrifluoracetonate on silver island films[7] decreased some 3 orders of magnitude, while the fluorescence intensity increased approximately 5-fold. In an early report[8] the fluorescence from unsubstituted metal-free phthalocyanine on indium island films was found to increase about 30-fold.

In the present set of experiments we wanted to demonstrate that LB films could be used as spacer layers to determine the distance dependence of fluorescence enhancement/quenching from a distinct LB monolayer of chromophore near a rough metal surface. The use of LB spacer layers permitted a determination of the distance dependence of the fluorescence enhancement from a $(t\text{-Bu})_4H_2Pc$ monolayer at a Ag island film surface, without spectral interference from the arachidic acid spacer layers.

Experimental Section

Silver island films were vacuum evaporated at a rate of $\sim$0.1 nm/s onto Corning 7059 glass slides to a mass thickness of 15 nm. The glass substrates were at room temperature during deposition,

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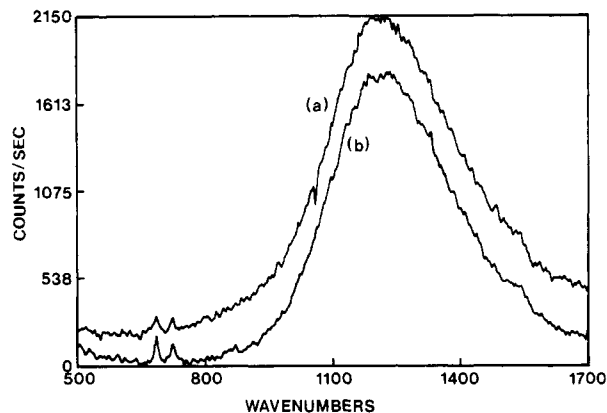(3) Moskovits, M. *Rev. Mod. Phys.* **1985**, *57*, 783.
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Figure 1. Fluorescence spectra from four LB monolayers of $(t\text{-Bu})_4H_2Pc$ on Corning 7059 glass, excited by the 647.1-nm line of a krypton laser with (a) P-polarization and (b) S-polarization.

and the background pressure was lower than 10^{-4} Pa in the VG DPUHV 12 vacuum system used. Film thicknesses were monitored by a Kronos Model QM-311 quartz crystal oscillator. Some of these substrates were then coated in a Fromherz trough[9] with LB spacer layers composed of either one, three, or five monolayers of arachidic acid. This fatty acid is known to form highly ordered monomolecular layers, which are used here to build spacer layers of well-defined thicknesses. Well-characterized[10] single monolayers of $(t\text{-Bu})_4H_2Pc$ were then transferred to the slides, with every indication of ideal LB deposition. For measurements of unenhanced or unquenched fluorescence, $(t\text{-Bu})_4H_2Pc$ mono(multi)-layer(s) were deposited onto bare 7059 glass slides.

Fluorescence spectra were measured by using a Spex 1403 double monochromator, with an 1800 lines/mm holographic grating, an electrically cooled R928 Hamamatsu photomultiplier, and photon counting electronics. The 647.1-nm line of a Spectra Physics Series 2000 krypton laser was used for spectral excitation. The wavenumber scales in the fluorescence spectra are therefore relative to this exciting wavelength.

The scattering plane and the surface of the slide (containing the monolayers) were orthogonal. The angle of incidence of the laser beam was 60°, and the observation direction formed an angle of 30° relative to the film normal. Therefore, the electric field vector of S-polarized light (transverse electric) was always parallel to the surface of the slide, while P-polarized light (transverse magnetic) had an electric field vector in the scattering plane. The fluorescence was excited with either S-polarized or P-polarized light, while the measured fluorescence spectrum was a combination of both polarizations. Any artifacts of intensity variation due to different spectrometer output for horizontal and vertical polarizations were eliminated by placing a polarization scrambler at the entrance to the spectrometer.

Results and Discussion

Figure 1 shows the unenhanced fluorescence spectra of four LB monolayers of $(t\text{-Bu})_4H_2Pc$ deposited onto Corning 7059 glass. These spectra were used as references in the study of enhanced spectra. The fluorescence spectrum excited with P-polarized light is more intense than the corresponding spectrum excited by S-polarized light with equal incident laser power. This result is in keeping with the fact that phthalocyanine (Pc) molecules in the monolayers are ordered with their molecular plane nearly perpendicular to the substrate surface.[10]

The absorption profile of the stacked $(t\text{-Bu})_4H_2Pc$ molecules in the LB film is a very symmetrical Gaussian curve when plotted on an energy scale as shown in Figure 3 of ref 10. The lower excited singlet states, which correspond to orthogonal transition moments in the molecular
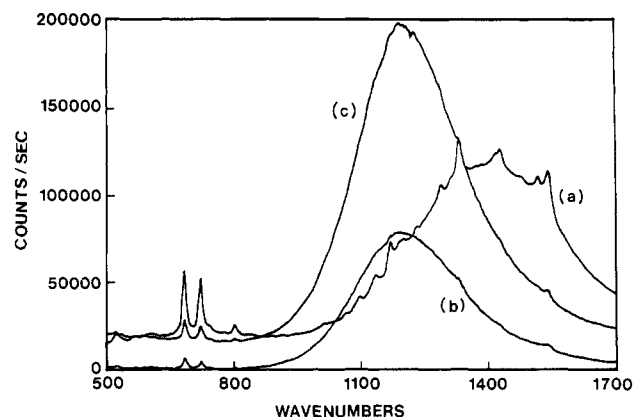
plane, [11] are nondegenerate in the free molecule; this is evidenced by two distinct absorptions in the virtually identical solution absorption spectra of unsubstituted metal-free phthalocyanine[11] and of $(t\text{-Bu})_4H_2Pc$. However, in the stacked structure[10] of the LB film, these lower excited singlets degenerate into one exciton, and the orthogonal molecular transitions become degenerate in the solid state. For Pc molecules with their molecular plane normal to the LB film surface, one would therefore expect the ratio of the P- to S-polarized absorption, for 647.1-nm laser irradiation which is in the region of the lowest singlet exciton, to be given by $A(P)/A(S) = 1 + \sin^2 \beta$, where β is the angle of refraction inside the LB film. For the molecular plane lying flat in the LB film plane, one would expect $A(P)/A(S) = \cos^2 \beta$. The greater P-polarized absorption (relative to S-polarized) for perpendicular orientation correlates with the larger fluorescence intensity for P-polarized excitation shown in Figure 1.

Figure 2 shows the enhanced fluorescence spectra of a single $(t\text{-Bu})_4H_2Pc$ monolayer on Ag island films with and without spacer layers. The spectra in Figure 1 were generated by an LB film consisting of four Pc monolayers. Spectrum a of Figure 2 was produced by P-polarized excitation with no spacer layer between the Ag islands and the $(t\text{-Bu})_4H_2Pc$ monolayer. The intensity per $(t\text{-Bu})_4H_2Pc$ monolayer in spectrum a is about 200 times greater than those of Figure 1. The strongest enhanced Raman spectrum is clearly seen on the fluorescence background in spectrum a of Figure 2.

The fluorescence intensity from P-polarized exciting light in spectrum a of Figure 2 is at least 2 times stronger than the corresponding intensity with S-polarized light. Spectra b and c of Figure 2 were excited with S- and P-polarized light, respectively, and are from a single $(t\text{-Bu})_4H_2Pc$ monolayer with a five-monolayer spacer of arachidic acid separating it from the Ag islands. Again the intensity of the P-spectrum (c) is at least twice that of the S-spectrum (b). The EF of fluorescence for P-polarized excitation with a five-monolayer spacer is almost 400 as seen by comparing the intensity of spectrum c of Figure 2 with the spectra of Figure 1.

The bandwidth of the fluorescence spectrum from the monolayer in direct contact with the silver islands is noticeably broader and red-shifted relative to the spectra with spacer layers (compare spectrum a of Figure 2 with spectra

Figure 2. Fluorescence spectra of a single LB monolayer of $(t\text{-Bu})_4H_2Pc$ on a 15-nm Ag island film from 647.1-nm krypton laser excitation with (a) no spacer layers and P-polarized excitation, (b) five spacer layers of arachidic acid and S-polarized excitation, and (c) five spacer layers of arachidic acid and P-polarized excitation.

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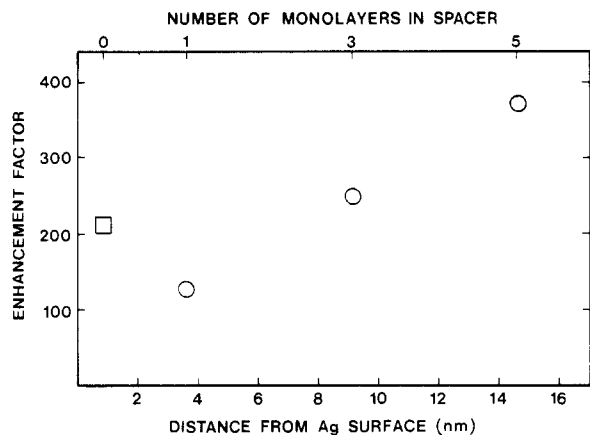
Figure 3. Experimentally measured enhancement factors of fluorescence from a $(t\text{-Bu})_4\text{H}_2\text{Pc}$ monolayer as a function of intervening spacer layer thickness on a 15-nm Ag island film. The spectra were excited by the 647.1-nm line of a krypton laser with P-polarization. The distance shown along the lower horizontal axis is from the island surface to the center of the Pc molecules;[1] along the upper horizontal axis the distance is given as the integral number of intervening arachidic acid monolayers.

b and c of the same figure). It is also broader than and red-shifted relative to the unenhanced fluorescence spectra in Figure 1. The unenhanced fluorescence spectra are virtually identical in shape with the enhanced spectra with intervening spacer layers. Both have a nearly symmetrical single peak profile similar to the very symmetrical lowest excited singlet absorption of an LB film of $(t\text{-Bu})_4\text{H}_2\text{Pc}$.[10] However, the fluorescence spectrum is considerably narrower than the absorption spectrum by about a factor of 5. One subtle difference between the unenhanced fluorescence spectra of Figure 1 and the enhanced fluorescence spectra with intervening spacer layers is that the latter are slightly blue-shifted relative to the former. The broadening of the fluorescence spectrum a in Figure 2 is in agreement with the findings of Weitz et al.[7] of a drastic decrease in fluorescence lifetime for molecules adsorbed on silver island films. To our knowledge the red-shifting of the fluorescence peak which we observe experimentally with direct contact to the Ag island films and the slight blue shift with intervening spacer layers have not been discussed theoretically in the literature in a quantitative way. However, a very small frequency shift has been predicted for an excited molecule fluorescing near a planar metal surface.[5]

Since the spectral shapes of the unenhanced fluorescence and the enhanced fluorescence with spacer layers are nearly identical, a determination of the EF as a function of the thickness of the spacer layers is in order. The fluorescence intensity and corresponding EF increase monotonically with spacer layer thickness as shown by the open circle data points in Figure 3. The EF is determined directly from the relative intensities and reaches a value of about 400 for a spacer consisting of five monolayers or arachidic acid. Each monolayer of arachidic acid has a thickness of 2.75 nm.[12] The distances in Figure 3 are calculated to the center of the Pc molecules, which are assumed to be oriented with their molecular plane perpendicular to the Ag island surfaces.[1] The EFs shown in Figure 3 are for P-polarized excitation, and in all cases the P-spectrum was stronger than the S-spectrum by approximately the same factor of 2. The monotonic increase in the EF is presumably due to decreased quenching by

the metal with increasing separation.

Model calculations have shown[13,14] that the optimum fluorescence yield does not come from a molecule directly in contact with a metal spheroid but at a certain distance above its surface. For instance, for a metal sphere the enhanced electric field decreases as $(R + d)^{-3}$, where R is the radius of the sphere and d is the distance measured from the surface to the molecule, while the radiationless decay rate decreases as d^{-3}. Therefore, for $R \gg d$ the competitive relaxation effect due to radiationless energy transfer to the metal decreases rapidly but the electric field enhancement decreases slowly. For our Ag islands the appropriate values[1] are $R \sim 40$ nm and $0 < d < 15$ nm. Consequently, one expects that the fluorescence intensity will increase with increasing separation. This is consistent with the monotonic increase in EF as given by the open circle data points in Figure 3. Ultimately, of course, the enhancement factor must decrease and return to unity for very large separations. Wokaun et al.[14] have reported the fluorescence yield of Fuchsin on Ag island films as a function of the thickness of an intervening SiO_x spacer layer. In their experiments the thickness of the dye coating was estimated from absorption measurements. It was found that for submonolayer coverage of dye a maximum fluorescence yield was obtained for a total thickness of spacer layer of ca. 2.5 nm, while above a one-monolayer coverage of dye produced a maximum fluorescence yield for a total thickness of spacer layer between 4 and 10 nm.

The EF for no intervening spacer layer is distinguished in Figure 3 as the open square data point, because of its red-shifted position and greatly altered spectral width and shape. Although the fluorescence spectrum for direct contact to the metal surface is greatly shifted and broadened, it has significantly larger intensity than the spectrum for a single spacer layer. Therefore the overall EF initially decreases on breaking contact with the metal surface before it begins to increase with the first few spacer layers. The distance dependence of the electromagnetic fluorescence enhancement is predicted to be initially monotonically increasing from zero separation.[14] No initial decrease, as we have observed, is predicted by current electromagnetic theories. If one extrapolates the enhancement factor given by the open circles in Figure 3, an enhancement factor of ~ 60 is obtained at zero separation. Therefore, one could estimate an experimentally observed "contact" enhancement of ~ 3-4. However, due to the greatly altered spectral shape, a direct numerical comparison of enhancement factors with and without intervening spacer layers should be viewed with caution. To the best of our knowledge the reason for the initial decrease in the fluorescence enhancement factor on breaking contact to the metal is not quantitatively understood at the present time. Therefore we have not attempted a quantitative comparison of our enhancement data with existing electromagnetic theories of the enhancement factor variation with distance.

P-polarized light is consistently more efficient by at least a factor of 2 than S-polarized light in producing enhanced fluorescence, with or without intervening spacer layers. However, P-polarized light is only about 10-15% more efficient in producing normal unenhanced spectra, as seen in Figure 1. The effect in unenhanced spectra can be understood by increased absorption of P-polarized light by the perpendicularly oriented Pc molecules relative to the LB film plane, as discussed above. In the case of

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enhanced fluorescence spectra, the larger efficiency difference can be simply explained in terms of the electromagnetic particle plasmon model wherein the metal island films are represented as a collection of slightly prolate hemispheroids. We have previously found[1] that a model of the Ag islands as prolate spheroids could quantitatively explain the distance dependence of the SERS EF for a (t-Bu)$_4$H$_2$Pc monolayer. In our experimental geometry S-polarized light has no electric field component perpendicular to the plane of the film, while P-polarized light does have an electric field component normal to the film's surface. Therefore, P-polarized light couples to both the axially symmetric plasma oscillations and also to the azimuthal plasma oscillations.[4,15] S-polarized light couples only to the azimuthally excited modes.[4,15] The axially symmetric plasma oscillations produce larger electromagnetic enhancements.[15] Therefore, the greater efficiency of P-polarized light in producing enhanced fluorescence can be readily understood from the spheroid model.

In conclusion, we have shown that LB films could be used as spacer layers to determine the distance dependence of fluorescence enhancement/quenching from a distinct LB monolayer of chromophore near a rough metal surface. The results reported here corroborate the theoretical predictions that in surface-enhanced luminescence there

are at least two competing processes: local field enhancement and decay by radiationless energy transfer to the metal. The competitive relaxation effect from the excited molecule to the nearby metallic surface has been mediated by using LB spacer layers of arachidic acid. For the Pc monolayer in direct contact with the Ag island film, the fluorescence intensity is enhanced by a factor of about 200 for P-polarized light. The fluorescence is also considerably broadened and red-shifted. With intervening spacer layers, the fluorescence profile is again enhanced and is nearly identical with the unenhanced spectrum except that it is slightly blue-shifted. The EF of the fluorescence initially decreases from the direct contact value. It then increases monotonically with spacer layers of one, three, and five monolayers of arachidic acid to a value of almost 400 for the five-monolayer spacer and P-polarized excitation. The initial decrease of the enhancement factor on breaking contact with the metal surface is not explained by current electromagnetic enhancement theories and needs further investigation. The EF for P-polarized incident light with or without spacer layers is consistently greater by at least a factor of 2 than the EF for S-polarization. This can be understood because only P-polarized light can excite the axially symmetric plasma oscillations of the islands, which produce a larger electromagnetic EF than the azimuthal oscillations.

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Interaction of Ni with SiO$_x$ or SiO$_2$ Formed on Si(111) and CO Adsorption Inhibition in Ni/SiO$_x$/n-Si(111) Studied by XPS and AES

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An interaction of Ni with SiO$_x$ or SiO$_2$ formed on Si(111) and CO adsorption behavior on Ni in these systems were studied with X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Binding energy (BE) of Ni 2p$_{3/2}$ and kinetic energy (KE) of Ni LMM transition shifted as a function of Ni coverage. These shifts were the same on SiO$_x$/n-Si(111), SiO$_x$/p-Si(111), and SiO$_2$/n-Si(111). However, peak to peak distance between Ni 2p$_{3/2}$ and 2p$_{1/2}$ did not change as a function of Ni coverage and was the same to Ni metal. Satellite peaks of nickel oxide were not observed. From these results, it was concluded that (1) Ni in these systems is in the metallic state and (2) charge transfer, even if it occurs, cannot be detected only by the BE shift. The coverage of Ni was estimated by decrease of Si intensity and increase of Ni intensity in conjunction with a layer by layer growth model, and they are consistent with each other within experimental error. However, decrease of oxygen intensity was too small to estimate Ni coverage. From these results, it was verified that Ni is implanted in the SiO$_x$ layer. Molecular CO adsorption was inhibited on Ni/SiO$_x$/n-Si(111) at Ni coverage below 2, although it occurred on Ni/SiO$_x$/p-Si(111) and Ni/SiO$_2$/n-Si(111) at the same Ni coverage. It was deduced that the suppression of CO adsorption is responsible for charge transfer occurring at low Ni coverage; that is, electron transfer occurs from the donor level of n-Si to the Ni d orbital and results in retardation of σ-donation from CO to Ni.

Introduction

Regulation of gas adsorption on a transition metal by using the interaction with a semiconductor has been considered significant for the modification of catalytic performance on the metal. In this sense the interaction of group VIII metals on titania and other reducible oxides has been studied.[1,2] A common feature in such systems

is the supression of H$_2$ and CO adsorption following reduction at high temperature ($\sim$800 K). This phenomenon has been termed a strong metal–support interaction (SMSI). Many studies on metal/metal oxide systems have been carried out to elucidate the cause of SMSI.[3-11] It

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