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Optical properties of Rhodamine B and Rhodamine 6G on silver surfaces

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Abstract. The transmission spectra of Rhodamine B and Rhodamine 6G dyes coated on silver island films for various thickness were recorded. A strong coupling between the silver particle plasma resonance and the dye molecules is observed. The absorption of dye molecules increases when the absorption band of individual dyes and silver particles overlaps. In higher silver film thicknesses, transmission increases. The theoretical calculation using Maxwell-Garnett theory and Wang and Kerker's results qualitatively supports the observed phenomenon. A red shift in the absorption peak of dyes on silver surfaces in comparison to solution phase absorption peak indicates photobleaching.

Keywords. Transmission spectrum; antireflection coating; enhanced absorption; plasma resonance; increased transmission.

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1. Introduction

The optical properties of molecules situated close to metal surfaces are currently the subject of several investigations. Some of these are related to the adsorbed molecules on continuous films of silver (Pockrand and Swalen 1968) or problems of excitation transfer from excited molecules to the metals (Person 1978). Other related problems of current interest are motivated by the discovery of surface-enhanced Raman scattering (SERS) (Van Duyne 1979). Studies on the optical properties of organic molecules adsorbed onto metal particles were stimulated by theoretical and experimental studies on enhanced Raman scattering cross-section for absorption and luminescence (Glass *et al* 1980; Garoff *et al* 1981; Craighead and Glass 1981; Moskovits 1985). The enhanced scattering cross-section or absorption is due to the enhanced local field at the molecules which increases by the dipole field of the resonant plasma particles thus showing that surface roughness is necessary for SERS or enhanced absorption. Enhancement in absorption and luminescence is observed only on rough surfaces when the plasma peak due to particles coincides with the electronic absorption band of adsorbed molecules.

The adsorption of molecules on different surfaces shows different characters and is useful in the study of different photophysical and photochemical properties on surfaces. Dyes are fluorescent organic materials generally used as lasing medium in dye lasers. The studies of sensitizing dyes on different media and on different surfaces were reported by many workers using different experimental techniques (Ehrlich 1975; Muenter 1976; Watanabe *et al* 1977).

The aim of this paper is to study the optical properties of Rhodamine B (RhB) and Rhodamine 6G (Rh6G) on thin silver films viz enhanced absorption, antireflection character, photobleaching etc and compare our results with the available theoretical models. A comparison with solution phase spectra of RhB and Rh6G with spectra of dyes adsorbed on silver surfaces is also reported. Photoacoustic spectroscopy (Rosencwaig 1980) is used to record the transmission spectra for dye coated silver films (Rai 1987).

2. Theory

The optical transmission spectra of composite dye coated silver island films can be explained with an electromagnetic effective medium calculation (Craighead and Glass 1981) for a system of small silver particles (< wavelength of light) with thin layers of dyes (~ 1 monolayer). The effective medium theory of Maxwell Garnett (1904) is known to provide a good description of island films and composite structures. It is based on a single-particle model where particle-particle interactions are considered.

The optical properties of composite films can be described in terms of an effective wavelength-dependent dielectric constant of the film. This corresponds to a spatial average of the complex dielectric functions of the coated particles and the surrounding medium. Considering spherical particles this effective dielectric permeability $\langle \varepsilon \rangle$ is given by

$$\langle \varepsilon \rangle = \varepsilon_H \frac{(3 + 2F\alpha')}{(3 - F\alpha')}, \tag{1}$$

where ε_H is the dielectric constant of the host medium. F is the sphere volume fraction and α' is a function of the dielectric constant proportional to the polarizability of particles. For a spherical metal particle of dielectric constant ε_M coated by a material of dielectric constant ε_D, α' is given as (Van de Hulst 1957)

$$\alpha' = 3\frac{(\varepsilon_D - \varepsilon_H)(\varepsilon_M + 2\varepsilon_D) + q^3 (2\varepsilon_D + \varepsilon_H)(\varepsilon_M - \varepsilon_D)}{(\varepsilon_D + 2\varepsilon_H)(\varepsilon_M + 2\varepsilon_D) + q^3 (2\varepsilon_D - 2\varepsilon_H)(\varepsilon_M - \varepsilon_D)}, \tag{2}$$

where q is the ratio of diameter of the metal particles to that of the coated particles. For ε_M, the Drude approximation value (Craighead and Glass 1981) which is a good approximation for silver in optical range can be taken as

$$\varepsilon_M = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)} \tag{3}$$

where ω_p is the plasma frequency and τ the electron relaxation time. For RhB dye ε_D can be taken as a Lorenzian (Craighead and Glass 1981) of the form

$$\varepsilon_D = 1 + S/(\omega_0^2 - \omega^2 - 2\omega\Gamma) \tag{4}$$

where S, ω_0 and Γ are constants for the RhB dye. The effective dielectric constant can be written in terms of the coefficient of refraction n and extinction coefficient k as

$$\langle \varepsilon \rangle = n^2 - k^2 - i2nk.$$

Let

$$\langle \varepsilon \rangle = \varepsilon_1 - i\varepsilon_2.$$

Then

$$\varepsilon_1 = n^2 - k^2, \quad \varepsilon_2 = 2nk.$$

Finally the transmittance can be calculated using the following formula,

$$I = I_0 \exp[-(4\pi nkd)/\lambda], \tag{5}$$

where d is the thickness of the film and λ is the wavelength of light.

3. Experimental

In this experiment the optical transmission spectra of the thin silver films (thickness 11, 19 and 49 Å) with and without coating of RhB and Rh6G dyes of concentration 10^{-3} and 5×10^{-4} M/l were recorded. For this purpose a single beam photoacoustic spectrometer as reported elsewhere (Rai *et al* 1982) was used in which a 600 W Philips tungsten halogen lamp was used as a light source in the optical region. The light was intensity-modulated at 22·5 Hz using a chopper (EG and G, model 125A) and focused on a monochromator (CEL model F/4, 0·25 m) HM 104 with bandwidth 7 nm (2 mm). The silver films and the composite film deposited on glass plates were placed between the window of photoacoustic cell and the exit slit of the monochromator. The plane of coated films was perpendicular to the axis of propagation of light. The light coming after the transmission from film was focussed to the photoacoustic cell. A powdered carbon black was used in the photoacoustic cell to detect the transmitted light. Here the photoacoustic cell acts as a power meter. The microphone signal from the photoacoustic cell was processed using a lock-in-amplifier (EMCO, model EE201). The time constant and phase for lock-in-amplifier was kept constant at 30 s and + 5° respectively throughout the experiment.

Silver film was deposited on the glass subtrate using vacuum evaporation technique. The thickness of silver films was varied by setting a separation between the glass substrate and the boat during vacuum evaporation. The rate of deposition was kept low to get the silver island films below 60 Å thickness (Glass *et al* 1980; Garoff *et al* 1981; Craighead and Glass 1981). The thickness of silver films was determined using a quartz thickness monitor signal and a separation between glass and boat. Using this technique the silver films (thicknesses 11, 19 and 49 Å) were obtained for this experiment. Each film was coated by 10^{-3} and 5×10^{-4} M/l RhB and Rh6G dye to get different thicknesses on silver films. The dye was coated by dipping the silver film in ethanolic solution of dyes. Detailed studies (Garoff *et al* 1981) have shown that the thickness of dye layer produced in dipping technique varies linearly with the concentration of the dye solution.

The transmission spectra for each silver film were recorded with and without dye coating in the spectral range 400–800 nm. Since the power spectrum of tungsten halogen lamp was not flat, each of the transmission spectra was normalized using the power spectrum of the lamp. In the lower wavelength side the power of the halogen lamp was small resulting in a low signal-to-noise ratio. This effect was observed in all the transmission spectra reported here between 400 and 450 nm.

4. Results and discussion

The measured photoacoustic transmission spectra of 10^{-5}, 5×10^{-4} and 10^{-3} M/l RhB dye coated silver films of thicknesses 11, 19 and 49 Å are shown in figures 1 to 3. The transmission spectra of composite films in figure 1 show two dips, one at 420 nm and the other at 570 nm, whereas that for the pure silver film shows a strong dip at 450 nm which is due to plasma resonance of silver particles (Rai 1987). Usually the silver films with thickness 60 Å show a resonance absorption peak (Craighead and Glass 1981). But as the thickness of dye coating increases the dip at 570 nm (absorption) increases due to increased dye absorption. According to figure 4 the 570 nm dip can be attributed to the RhB dye absorption. The 420 nm dip occurs due to silver plasma resonance splitting, where the second split peak is suppressed due to strong absorption of RhB probably due to the thick layer of dye. The splitting of plasma resonance due to RhB coating has also been seen earlier (Glass *et al* 1980, Garoff *et al* 1981; Craighead and Glass 1981; Rai 1987).

Figure 2 shows the transmission spectra of 19 Å silver film and its composite films with an overlayer of 10^{-5}, 5×10^{-4} and 10^{-3} M/l of RhB dye. The 10^{-5} M/l dye coated silver film has three absorption dips at 430, 570 and 650 nm whereas those corresponding to 5×10^{-4} and 10^{-3} M/l RhB coating show only two peaks as in figure 1. As the dye thickness increases the 430 nm absorption dip decreases (transmission increases) whereas the dye absorption band intensity increases. Both the plasma-split peaks at 430 and 650 nm are observed only when the dye layer thickness is very small (10^{-5} M/l). The enhanced absorption is observed only at lower resonance peak at 430 nm. The peak at 650 nm is suppressed at higher thickness of

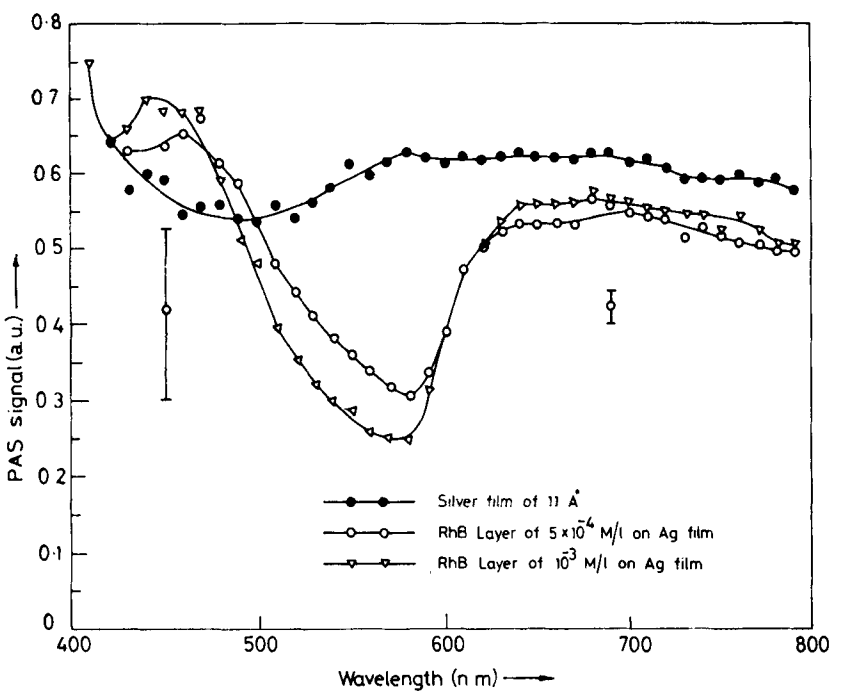

Figure 1. Transmission spectra of 11 Å silver film and composite films of 10^{-3} and 5×10^{-4} M/l RhB dye coating.

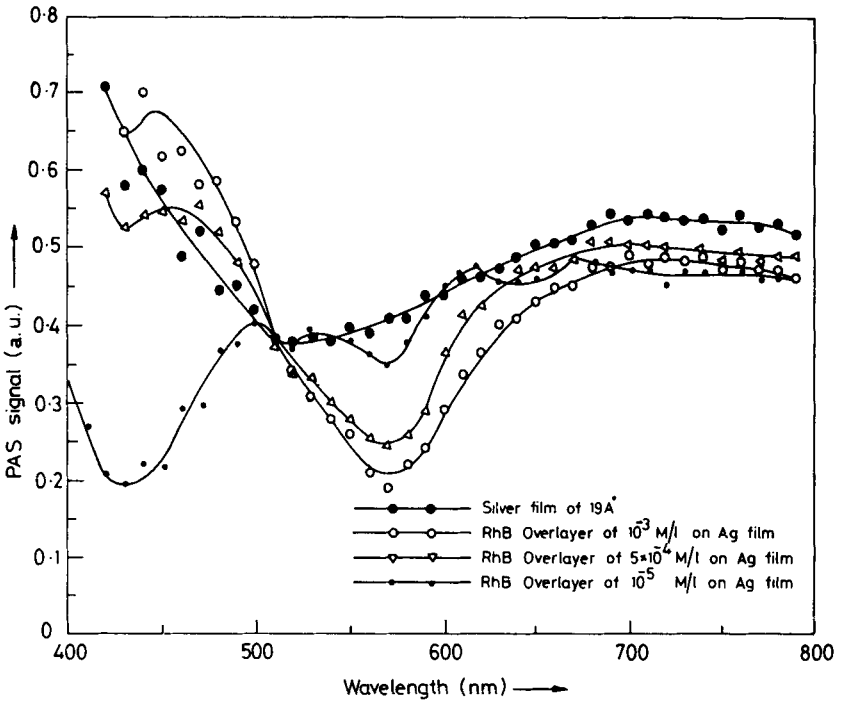

Figure 2. Transmission spectra of 19 Å silver film and composite films of 10^{-3}, 5×10^{-4} and 10^{-5} M/l RhB dye coating.

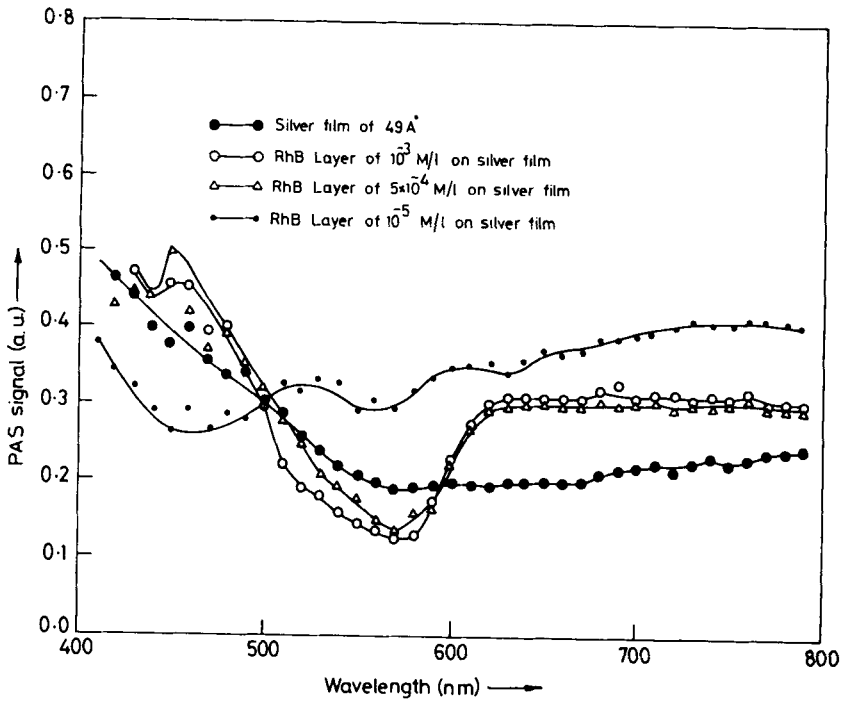

Figure 3. Transmission spectra of 49 Å silver film and composite film of 10^{-3}, 5×10^{-4} and 10^{-5} M/l RhB dye coating.

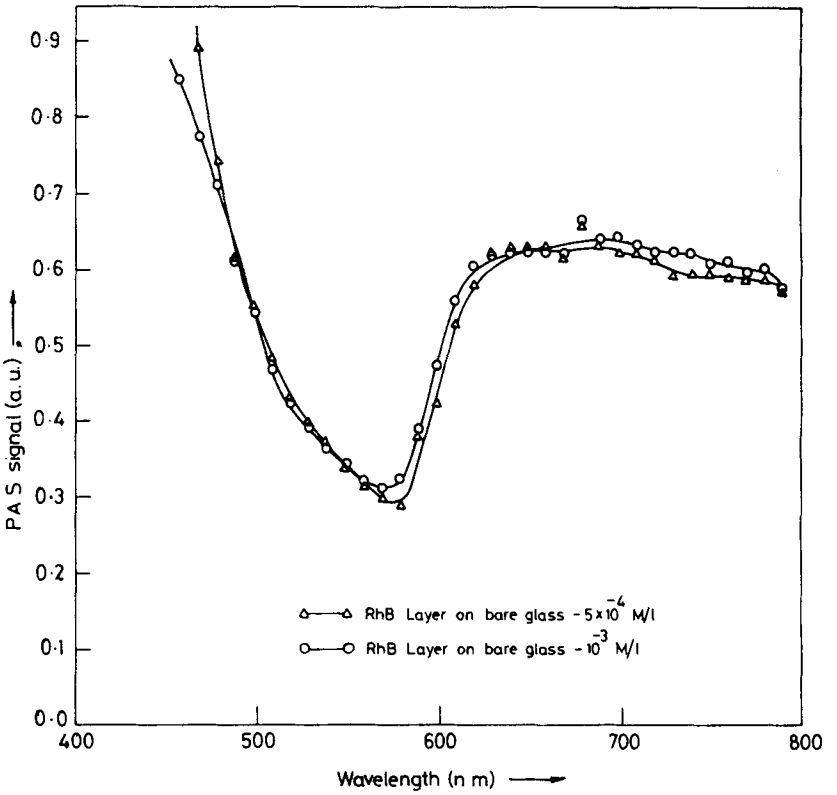

Figure 4. Transmission spectra of 10^{-3} and 5×10^{-4} M/l RhB dye on bare glass.

dye layer as in figure 1 which agrees with earlier results (Craighead and Glass 1981) except the presence of a second dye absorption peak at 570 nm. This may be due to the difference in making dye coatings. In our case dye coatings may be thicker in comparison to those of Craighead and Glass (1981) who reported that the higher wavelength-split plasma peak has smaller transmission in comparison to the lower one which is observed only with 10^{-5} M/l dye coating in our case. This is in qualitative agreement with the theoretically calculated spectra shown in figure 6. The 10^{-5} M/l RhB dye coated 49 Å silver film shows three dips at 460, 560 and 630 nm as shown in figure 3. It shows higher transmission above 500 nm in comparison to silver film, whereas this increase in transmission was absent in the earlier two composite films spectra as shown in figures 1 and 2. For 5×10^{-4} and 10^{-3} M/l dye coatings a smaller wavelength peak is observed at 440 nm and a dye absorption peak occurs at 570 nm. The third peak is absent. An increased transmission is observed here for wavelength greater than 600 nm. The rest of the properties are similar to the two earlier composite films. Comparison of these results indicates that the lower wavelength dip shifts to higher wavelength as 420, 430, 440 nm and higher wavelength third peak to lower wavelength with silver film thickness. The dye absorption (middle) peak also shows shifts towards the lower wavelength side. An overall decrease in transmission intensity is observed with increased thickness of silver films. The data show fluctuations in lower wavelength side which as mentioned earlier is due to low

power of the light source in that spectral region. In the case of 10^{-5} M/l dye coating, the spectra show greater fluctuation in data due to small absorption of dye.

The transmission spectra were calculated using equations (1) to (5). For the silver film we have taken $\omega_p = 1{\cdot}15 \times 10^{16}\,s^{-1}$, $\tau = 1 \times 10^{-15}$ s, $\varepsilon_H = 3$ and in RhB dye case $S = 5 \times 10^{31}\,s^{-2}$, $\Gamma = 2{\cdot}5 \times 10^{14}\,s^{-1}$ and $\omega_0 = 3{\cdot}2 \times 10^{15}\,s^{-1}$ as reported earlier (Craighead and Glass 1981). The transmission spectra for silver film of $F = 0{\cdot}1$ (11 Å) and $F = 0{\cdot}29$ (19 Å) having an overlayer of 1, 2 and 10 A RhB dye films are shown in figures 5 and 6. Transmission spectra of silver films have been calculated earlier (Rai 1987) where the spectra showed only one plasma resonance as shown in figures 5–6. It shifts to the higher wavelength side when the film thickness increases, and after 50 Å the peak seems to be flat. It shows that above 50 Å the silver particle distributed on the film becomes flat and the films become continuous. The plasma peak splitting is observed at 470 and 650 nm as shown in figure 5. The transmittance for increased thickness of silver film having an overlayer of 1, 2 and 10 Å RhB dye is shown in figure 6. As the thickness of the dye layer increases the transmission increases and becomes larger in comparison to the silver film in the case of 10 Å dye layer. The lower wavelength peak shift as 512, 500, 488 nm and higher wavelength peak as 625, 632 and 637 nm are observed. But as the

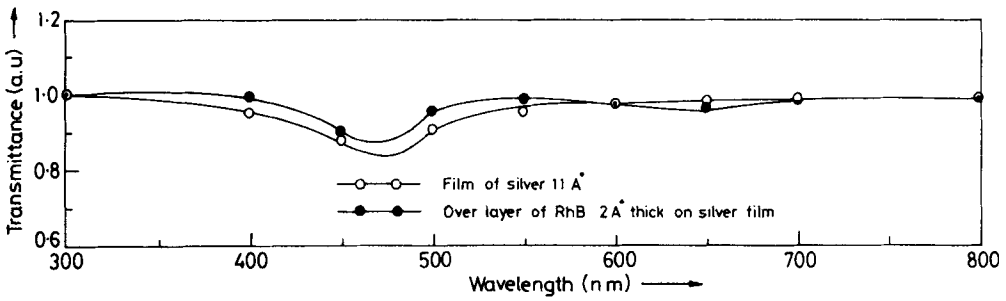

Figure 5. Theoretical calculation of transmittance for 11 Å silver film with 2 Å thick RhB dye coatings.

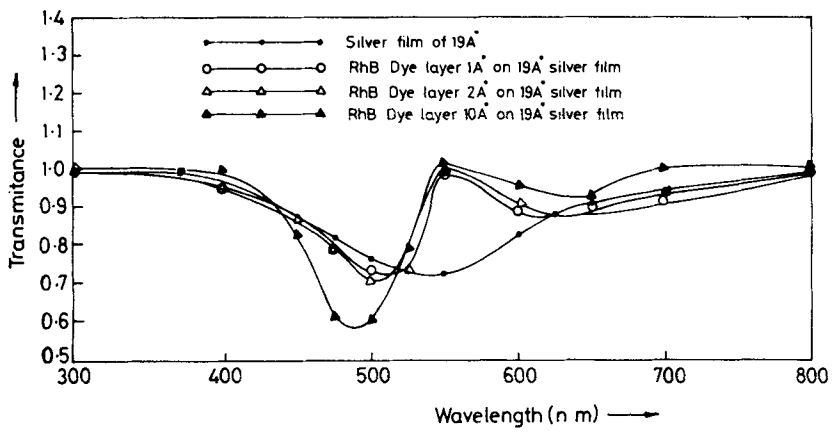

Figure 6. Theoretical calculation of transmittance for 19 Å silver film with 1, 2 and 10 Å thick RhB dye coatings.

thickness of silver film increases the lower wavelength peak shifts from 470 to 500 nm and the higher wavelength peak from 650 to 632 nm. These theoretical calculations are in good quantitative agreement with our experimental results. But the changes in transmission with thickness of dye layers in figure 6 are contrary to the observed processes. The dye absorption peak is also not observed in theoretical calculation in composite film spectra which was also not observed by earlier workers. Another discrepancy between theory and experiment is in the peak height of the lower wavelength and higher wavelength resonance peaks. Except for 19 Å silver film with an overlayer of 10^{-5} M/1 RhB dye, our experimental results are similar to theory except for the dye absorption band. The differences between the silver absorption peak in the case of 50 Å thick film reported earlier (Craighead and Glass 1981) and that with our 49 Å thick film may be due to the difference in rate and conditions of film deposition. This is because changes in optical properties of film can occur due to the rate and condition of deposition.

Increase in transmission compared to the silver film and the observation of new (middle) absorption band in this experiment have not been reported earlier. Increased transmission is observed when the refractive index of silver film becomes higher in comparison to the refractive index of dye molecules (Hollahan *et al* 1974; Ritter 1976). Such films of dye would act as anti-reflection coatings. The reflectance spectrum (Rai 1987) of silver film shows that reflectance decreases when silver was coated with dye. This phenomenon becomes dominant when the enhanced absorption, due to overlapping of silver resonance peak with dye absorption peak and absorption due to dye itself is very small. Here dye coating acts as an antireflection coating. These variations are observed due to changes in the refractive index and absorption coefficient of the composite film. A change in refractive index causes a splitting in the resonance peak whereas a change in the absorption coefficient produces damping in resonance. This is because, resonant response of a single metal particle is strongly coupled to the absorbing layers.

The above comparison of experiment and theory indicates that the Maxwell-Garnett theory is unable to explain the cause of middle peak and increased transmission. This may be due to the fact that the Maxwell-Garnet theory considers the island films to be made up of spherical particles distributed on the glass surface which need not be true. In fact as reported by other workers the silver particles may have oblate or prolate ellipsoid shape. Their optical properties not only depends on the volume fraction but on their shapes and sizes. The theory of Wang and Kerker (1981, 1982) shows the same results for silver films as the Maxwell-Garnett theory which considers silver particles as oblate in shape. The excitation cross-section with wavelength calculated for silver spheroids coated with confocal spherical shells of dyes by Wang and Kerker satisfies our experimental observation of three peaks in transmission spectra. The spectra observed for 19 Å silver film coated with 10^{-5} M/l dye and 49 Å film coated with same thickness of dye in our experiments are similar to the theoretically calculated spectra by Wang and Kerker for aspect ratios 2 and 3. Comparing the middle peak (dye absorption) on composite films with the RhB dye liquid solution spectra (Rai *et al* 1984) one sees that the peak positions shift to the higher wavelength. The same effect was observed when RhB adsorbed on Al_2O_3 powder (Rai 1988). These red shifts are observed probably due to increased triplet state absorption which may lead to the photobleaching reaction in the presence of impurity on the silver surfaces (Yamshita and Kashiwagi 1976).

Figure 7 shows transmission spectra for 10^{-3} and 5×10^{-4} M/l Rh6G coated silver film of 19 Å. These spectra show two peaks at 440 and 550 nm. It is observed that the absorption band of 10^{-3} M/l Rh6G (Rai *et al* 1984) dye coincides with 19 Å silver film plasma resonance which results in high absorption. If peaks do not coincide as in the case of 5×10^{-4} M/l an increased transmission is observed as compared to the silver film. Experimental results indicate that RhB and Rh6G both have same optical properties on silver surfaces except the peak position and absorption intensity due to different absorption cross-sections.

5. Conclusion

The present results show that dye coatings on thin silver film (< 60 Å) change the optical properties of the composite film such that the plasma resonance peak splits into two peaks. In this experiment absorption band due to dyes is also seen probably due to the higher thickness of dye compared to earlier results. The peaks of plasma resonance shift to the higher wavelength side with thickness of silver film along with increased transmission. With increased thickness of dyes, the absorption increases for the dye band and decreases for the lower resonance band along with increased transmission on the higher wavelength side first and then the transmission increases over the entire wavelength range. Theoretical calculations using the Maxwell-Garnet theory qualitatively show splitting in plasma resonance peak. But the absorption at both the

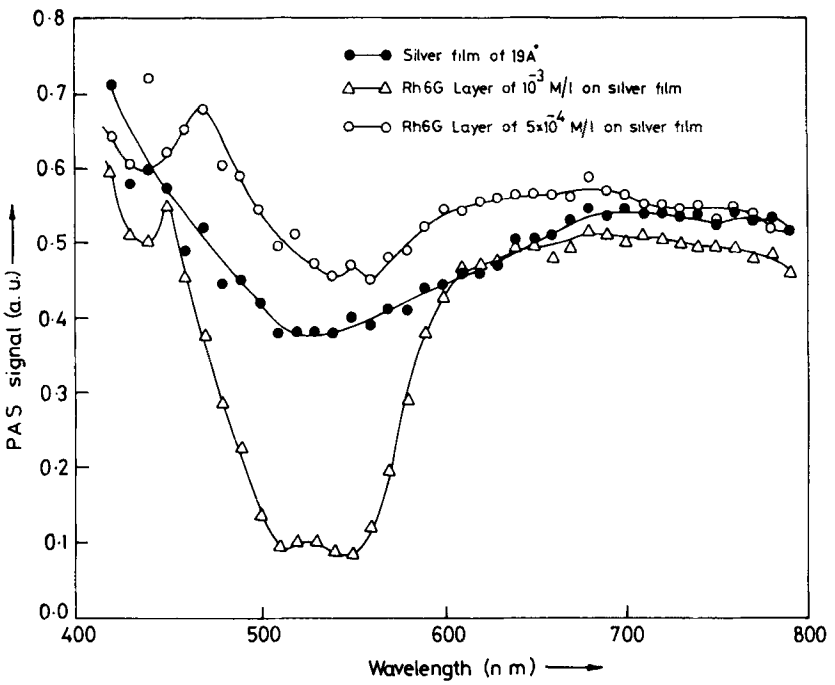

Figure 7. Transmission spectra of 19 Å silver film with composite films of 10^{-3} and 5×10^{-4} M/l Rh6G dye coating.

resonance peaks is opposite in nature compared to theoretical results with the increase in dye thickness. Comparison of the experimental results with theoretical calculations of Wang and Kerker shows better agreement compared to the Maxwell-Garnett theory, which explains the middle peak observed in our case.

The present findings support the Wang and Kerker theory. The thick RhB and Rh6G coatings have an anti-reflection character above 600 nm for silver mirror whereas thin dye coatings show anti-reflection properties for broader wavelength range in the visible region. These properties of dyes were not reported by earlier workers. The adsorption of RhB and Rh6G on silver surface enhances the photobleaching in these dyes.

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