ENHANCEMENT OF THE LUMINESCENCE OF RHODAMINE 6G IN A COLLOIDAL SOLUTION OF SILVER

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An enhancement of the luminescence and absorption of rhodamine 6G in a colloidal water solution of silver has been found. The enhancement coefficient has been investigated as a function of the optical properties of the colloidal solution, the exciting wavelength, and the thickness of the solution. Electronic resonances in the metal particles are discussed as a possible mechanism of enhancement.

Enhanced Raman scattering and luminescence by molecules near the rough surface of a noble metal have attracted increasing attention in the spectroscopy of surfaces and separation boundaries in recent years. Giant Raman scattering has been extensively investigated but luminescence enhancement has attracted relatively less attention. This is probably due to the commonly held view that the luminescence of molecules lying near the surface of a metal is "suppressed" by the radiationless transfer of energy from the molecules to the metal. This effect is particularly well defined when the molecule is absorbed directly on the surface of the metal. However, the electrodynamic enhancement of inelastic scattering of radiation ensures that the effective electromagnetic field can be significantly amplified if the frequencies of the exciting and radiated electromagnetic fields lie in the range containing the electronic resonance frequencies of the metallic particles [1]. Such particles may be looked upon as "resonance amplifiers" of the exciting and radiated fields. This means that, under certain definite conditions that depend on the structural properties and the dimensions of the metallic particles, the concentration of the solution, and the relative disposition of the frequencies, the "suppression" of the luminescence by the metal may actually be replaced by significant amplification. An order of magnitude estimate of the absorption efficiency of dye molecules [2] suggests that the luminescence produced in a water colloidal solution of silver can be stronger by a factor of about 2 than in a water solution. The luminescence enhancement effect has been investigated using models such as island films of silver and gold [3] and solutions of silver salts [4]. Experimental results obtained so far are in approximate agreement with existing theory, but the mechanism responsible for the enhancement is not entirely clear. The colloidal water solution of silver is a convenient model for investigating the phenomenon. The metallic particles in this solution are almost regular spheroids, so that the system is particularly suitable for comparison with the theoretical model of isolated solid particles [1].

Experimental method. We have investigated the absorption and luminescence by the dye rhodamine 6G in a colloidal water solution of silver, prepared by sputtering in a dc arc [5]. The silver electrodes were placed in distilled water containing the surface active material (SAM) triton X-100, which prevents

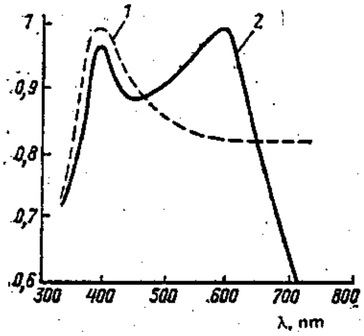

Fig. 1

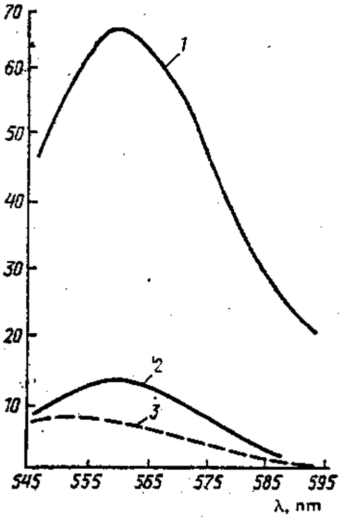

Fig. 2

Fig. 1. Normalized absorption spectra of a colloidal water solution of silver. 1) Colloid No. 1; 2) colloid No. 2.

Fig. 2. Luminescence spectra of rhodamine 6G in colloidal solutions of silver: curve 1) No. 2; curve 2) No. 1; curve 3) in water. The intensity is given in arbitrary units.

the sedimentation of the particles as a result of coalescence. A dc voltage of 110 V was applied to the cylindrical electrodes (about 2 mm in diameter) with pointed ends. The electrodes were slowly brought together and then separated, producing an electric arc with a current of 4-6 A. The fusing of the two electrodes was prevented by giving the lower electrode the positive polarity. The separation between the ends of the electrodes was gradually reduced during the sputtering process. A brown or gray-green cloud consisting of the sputtered metal was formed around the arc. The larger metallic particles fell out of the arc and produced a sediment. The colloidal solution formed in this way was filtered several times.

The colloidal solution of silver (colloid No. 1) obtained after filtration was yellow and had a broad absorption band with a maximum at 385 nm (curve 1, Fig. 1). This shape of the spectrum is typical for colloidal silver with approximately spherical particles of a few tens of nanometer in diameter. After about to or three days, the color of the colloidal solution changes to blue-gray after passing through a red phase (colloid No. 2). The spectrum of colloid No. 2 has a second absorption band at 585 nm (curve 2, Fig. 1). This second band is due to the aggregation of silver particles with the formation of pearl-string type structures [6].

The absorption spectra were measured with the Specord UV VIS spectrophotometer and the luminescence spectra with the HITACHI MPF-4 spectrofluorimeter.

The colloidal and water solutions of rhodamine 6G were prepared from a water solution of rhodamine 6G with a concentration of 10^{-4} mol/l and the silver colloid or water in a proportion ensuring that the solution had a concentration of between $0.9 \cdot 10^{-6}$ and $2 \cdot 10^{-5}$ M (for example, 0.1 ml of the solution of rhodamine 6G per 1 ml of the colloid or water). The degree of association of the

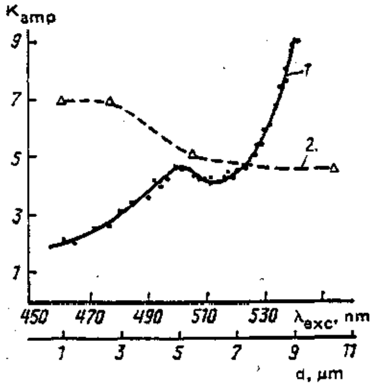

Fig. 3

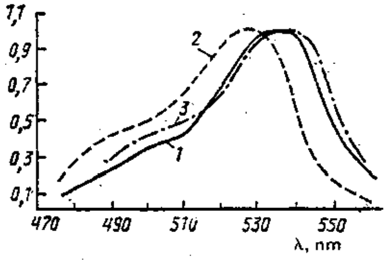

Fig. 4

Fig. 3. Luminescence amplification coefficient as a function of the exciting wavelength λ_{exc} (1) for d = 2.5 μm and as a function of the thickness d of the layer of the solution (2) for λ_{exc} = 535 nm ($C = 2 \cdot 10^{-5}$ mol/l; colloid No. 2).

Fig. 4. Normalized absorption spectra of rhodamine 6G in a colloidal solution of silver (1), in water (2), and in water containing the SIM (3). The concentration of the rhodamine 6G solution was $C = 2 \cdot 10^{-5}$ mol/l.

rhodamine 6G molecules can be regarded as negligible in such weak solutions.

Experimental results. The colloidal and water solutions of rhodamine 6G were held in quartz cells of thickness d = 2.5 μm and were exposed to radiation of wavelength λ_{exc} = 535 nm. Resulting luminescence spectra are shown in Fig. 2. It is clear that the spectral density of the luminescence emitted by the colloidal solution is much higher throughout the spectrum, and its maximum is shifted toward longer wavelengths by $\Delta\lambda \approx 10$ nm. Significantly, a considerable amplification of the luminescence was observed for colloid No. 2 (curve 1): the amplification coefficient $K_{amp} = I_{coll}/I_{water}$ at the maximum of the luminescence band at the above excitation wavelength was equal to 7. When colloid No. 1 was employed, the amplification effect observed under comparable conditions was very much lower (about 30-40%), but the maximum of the luminescence band was shifted by the same amount, i.e., 10 nm (curve 2).

The amplification coefficient K_{amp} is very dependent on the excitation wavelength. This is illustrated by curve 1 in Fig. 3, which was obtained in a cell of thickness d = 2.5 μm, using the solution of rhodamine 6G in colloid No. 2. It is clear that the dependence of K_{amp} on the exciting wavelength is not monotonic and shows the most rapid increase when the exciting wavelength approaches the midpoint of the long-wave absorption band of colloid No. 2 (540 nm).

We note that the amplification coefficient K_{amp} is also a function of the thickness of the layer of the solution, i.e., the thickness d of the cell (curve 2, Fig. 3). Curve 2 was obtained for a solution of rhodamine 6G in colloid No. 2 under excitation with 535 nm radiation. In all these experiments, the shift of the maximum of the luminescence band, Δλ, remained constant when either the exciting wavelength or the layer thickness was varied.

In addition to the above variations in the luminescence parameters of rhodamine 6G in colloidal solutions, there were parallel changes in absorption spectra. The absorption band was found to shift toward longer wavelengths by $\Delta\lambda \approx 10$ nm for both colloidal solutions of rhodamine 6G (Nos. 1 and 2), and this was accompanied by an increase in absorption (the amplification coefficients of both absorption and luminescence were practically the same). Figure 4 shows the normalized absorption spectrum of rhodamine 6G in the colloidal solution of silver (curve 1). This illustrates the variation in the shape and position of the absorption band relative to the spectrum recorded for the water solution (curve 2).

Discussion. The above result can be interpreted in terms of existing ideas on electrodynamic amplification (amplification of the effective field near a metallic particle) and the molecular mechanism (change in the molecular polarizability when a molecule is adsorbed on the surface of the particle).

The molecular mechanism is thought to be unlikely in our case. Actually, the introduction of the SAM triton X-100 into the colloidal solution prevents the direct interaction between the rhodamine 6G molecules and the metal surface (this is indicated by the fact that the shift of the absorption and luminescence spectra of rhodamine 6G in the colloidal solution is independent of the properties of the colloid). The shift $\Delta\lambda \approx 10$ nm observed in all cases can be related to the interaction between the rhodamine 6G molecule and the SAM molecule. This is confirmed by control measurements or by the addition of SAM to the water solution of rhodamine 6G producing a similar shift of the spectrum (curve 3, Fig. 4).

Comparative analysis of the absorption spectra of colloids No. 1 and No. 2 and the absorption and luminescence spectra of rhodamine 6G in colloidal solutions shows that the electrodynamic amplification mechanism predominates under our experimental conditions. The observed absorption spectra of the colloidal solution (Fig. 1) correspond to the excitation of electronic resonances in the metallic particles: the short-wave band is due to resonances in approximately spherical particles and the long-wave band is due to resonances in elongated particles and filament-type aggregations. Comparison of Figs. 1, 2, and 4 shows that, in the case of colloid No. 1 (curve 1, Fig. 1), the absorption and luminescence bands of rhodamine 6G are only slightly overlapped by the electronic resonance band. This luminescence amplification coefficient is therefore low in this region. In the case of colloid No. 2 (curve 2, Fig. 1), the absorption and luminescence bands of rhodamine 6G are completely overlapped by the long-wave electronic resonance band. Here, the luminescence is substantially amplified and the amplification coefficient increases rapidly as the exciting wavelength approaches the center of the long-wave part of the electronic resonances. The dependence of the amplification coefficient on the exciting wavelength (curve 1, Fig. 3) has a small peak at 500 nm which may be associated with the nonuniform nature of the absorption of the colloidal solution of rhodamine 6G in the range 495-510 nm (curve 1, Fig. 4). This peak is difficult to interpret because of a lack of the necessary data.

The amplification coefficient K_{amp} is also a function of the thickness of the layer of the solution (curve 3, Fig. 3). This is probably due to considerable reduction in the exciting intensity as light propagates through the colloidal solution (as compared with the water solution). When the layer thickness is less than the optical path length in the colloidal solution (the optical path length is the distance in which the intensity falls by a factor of e as a result of absorption), the amplification effect becomes slight.

CONCLUSIONS

Our results show that the intensity of luminescence emitted by the dye molecules near the surface of small metallic particles in solution can be amplified by almost an order of magnitude as compared with the luminescence in the water solution. Electronic resonances in the metallic particles play a significant part in the amplification mechanism, but the situation is not fully understood and requires further investigation. The effect is promising from the point of view of practical applications: the magnitude of the amplification coefficient, and the shape and position of the absorption and emission bands, can be used to extract information about the properties and structure of inhomogeneous metallic surfaces and about the change in the properties of molecules that are near metal surfaces or are adsorbed on them. These problems are of interest not only to physicists, but also to chemists concerned with, for example, heterogeneous catalysis (in which metallic particles act as catalysts) or adsorption on silver electrodes with randomly rough surfaces.

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