

Super-enhanced hyper-Raman scattering from dyes adsorbed on colloidal silver particles

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Hyper-Raman-scattering spectra have been measured by the standard technique for the scattering from two rhodamine dyes and a crystalline violet dye adsorbed on silver. The extremely intense spectra found are attributed, in particular, to simultaneous resonances for one- and two-photon transitions. Various mechanisms for the process are discussed. The same effects are observed at the unshifted frequency.

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Hyper-Raman scattering consists of the virtual summation of two incident photons and the scattering of a photon of a different frequency. In contrast with ordinary Raman scattering, this is a three-photon process and thus has some unusual selection rules and an exceedingly low efficiency. In particular, in several cases some transitions are seen in hyper-Raman scattering which are forbidden in both ordinary Raman scattering and infrared absorption. The hyper-Raman spectra thus furnish some new information about the substance.

An important mechanism for the sharp increase in the efficiency of hyper-Raman scattering may be the satisfaction of resonant conditions for the excitation of this scattering. We must not overlook the possibility of double resonances, if the fundamental absorption bands of the system include the frequencies corresponding to both the pump photons and the photons at twice the pump frequency. This situation apparently occurs in certain systems formed by dye molecules adsorbed on colloidal silver particles. In this case we can also expect a further enhancement of the emission by the local plasmons characteristic of these particles.

We studied rhodamine dyes and a crystalline violet dye added to a silver hydrosol prepared by the prescription of Ref. 1. The typical concentrations of the materials are 10^{-6} M. The pump light is a beam with a wavelength of 1064 nm from YAG:Nd³⁺ laser (LTI-502). The pulse repetition frequency is 10 kHz, and the peak power can be adjusted up to 10 kW. The hyper-Raman spectra are observed near the 532-nm line. Comparison spectra (i.e., spectra of ordinary Raman scattering) are excited by the second harmonic of the pump, obtained from an in-resonator lithium iodate crystal. Otherwise, the experimental conditions are the same as in Refs. 1 and 2.

Figure 1 shows parts of the hyper-Raman (a) and Raman (b) spectra of rhodamine 6G. A similar pattern was obtained for rhodamine 3B. The molecules of both these substances have a low symmetry, and for this reason spectra a and b have several lines in common. We can also clearly see some important distinctions between these spectra: different intensity distributions, different sets of lines, and slight shifts and a

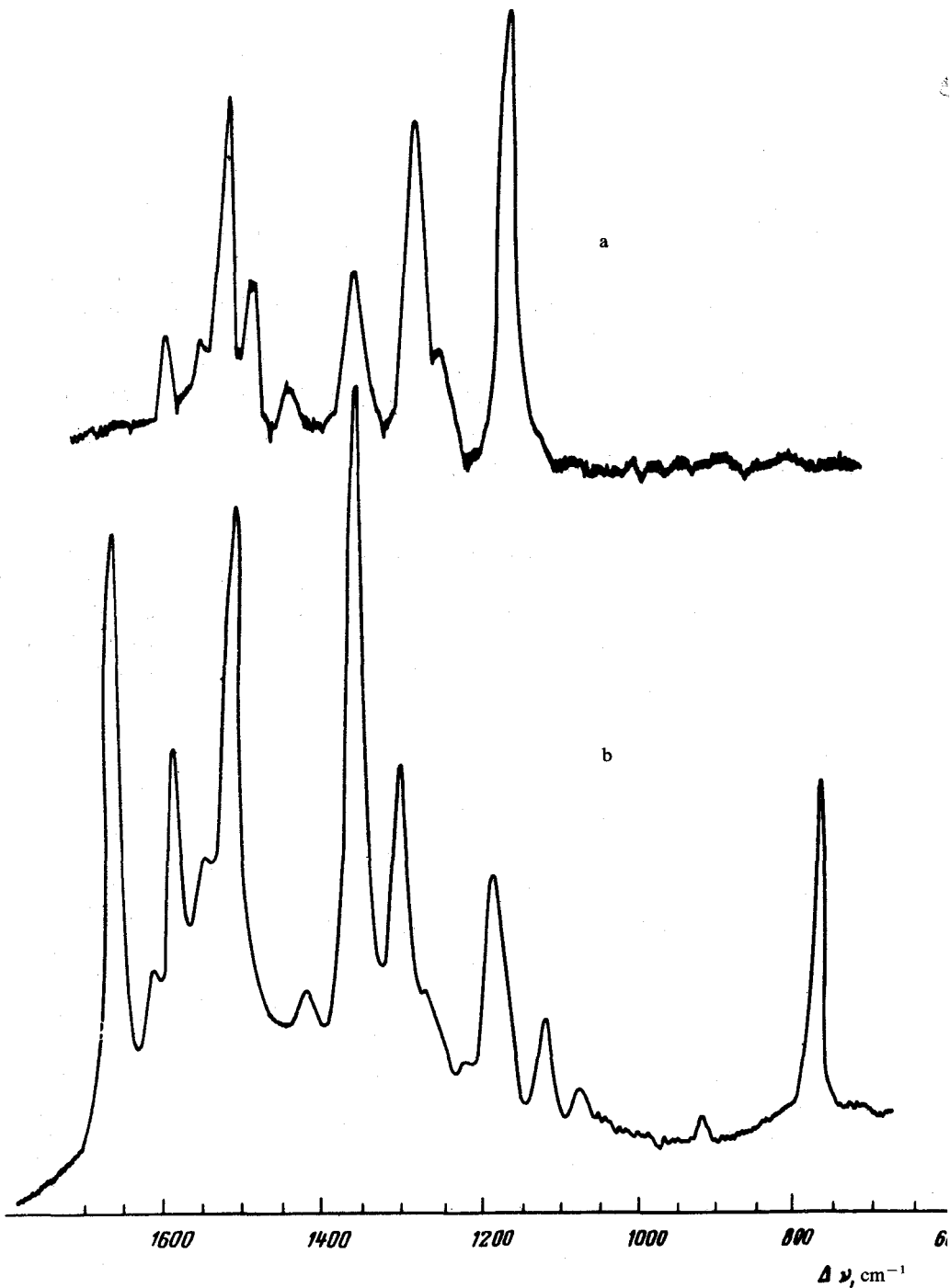


FIG. 1. a—Hyper-Raman scattering spectrum of rhodamine 6G adsorbed on silver. b—The Raman scattering spectrum of the same system. The excitation is at 1064 and 532 nm, respectively; the average power is 10 W and 100 mW, respectively; the concentrations are at 10^{-6} M and 10^{-7} M, respectively; the slits are 6 cm^{-1} wide; and $\tau = 2$ s.

broadening of some of the lines. In going from spectrum a to spectrum b, for example, we see the excitation of two intense new lines, at ~ 1670 and ~ 770 cm^{-1} , in both cases.

The crystalline violet dye is of particular interest because its molecules can formally be assigned a rather high symmetry (D_{3h}), so that we would expect to find few similarities between its hyper-Raman and Raman spectra. Experimentally, however, we find the opposite to be true: The two spectra are even more similar in this case (Fig. 2) than they are in the case of the rhodamines. It follows that in actuality the adsorbed molecules of the crystalline violet dye are essentially devoid of any symmetry elements. We can associate this result with an excursion of the benzene rings from their common plane; i.e., they rotate around $C\cdots C$ bonds in a process involving the central carbon atom.

A comparative analysis of the data on the hyper-Raman and Raman spectra of adsorbed molecules can thus provide some very important information about the actual symmetry and structural features of these molecules.

We found that the addition of even an extremely small amount of the dye to the silver hydrosol alters the absorption spectrum of the solution to different extents. The effect can be seen particularly clearly in the case of the crystalline violet dye. In Fig. 3 we see the emergence of some additional absorption, which stretches up to wavelengths near 1200 nm. Because of this new absorption, both the pump wavelength and its second harmonic lie in the absorption band, setting the stage for a double resonance in the course of the hyper-Raman scattering. The hyper-Raman cross section may increase by a factor of at least 10^5 – 10^6 .

The extremely pronounced broadening of the absorption band in the molecule-plus-metal system is apparently also due to amplification of the pump beam, the second-harmonic beam, and the hyper-Raman lines themselves by local surface plasmons in the silver particles. These processes are discussed, and their efficiencies estimated, in Refs. 3 and 4.

With regard to the nature of, and the mechanisms for, the broadening of the absorption bands, two suggestions might be offered. One is based on a shifting of the excited electronic states of the isolated molecules with surface plasmons of the metal upon the adsorption of these molecules on the metal; this process is a quite universal possibility.⁵ The other suggestion is based on the established fact that when certain substances are added to a hydrosol the metal particles coagulate, shifting the absorption of the solution toward larger wavelengths. This broadening mechanism is evidently peculiar to labile liquid systems. At this stage of the research we cannot choose between these suggestions.

In addition to studying the hyper-Raman spectra, we studied the behavior of the scattering line at the doubled frequency (532 nm) in a series of samples consisting of the pure hydrosol and the hydrosol plus various dyes. The results showed that the addition of rhodamines *B*, semi-*B*, and 110, which do not produce hyper-Raman spectra, results in an enhancement of this line (with respect to that of the pure hydrosol) by a factor of about five. The line intensities in the solutions of rhodamines 6G and 3B are amplified by a factor of up to 100. The greatest effect, however—as much as five

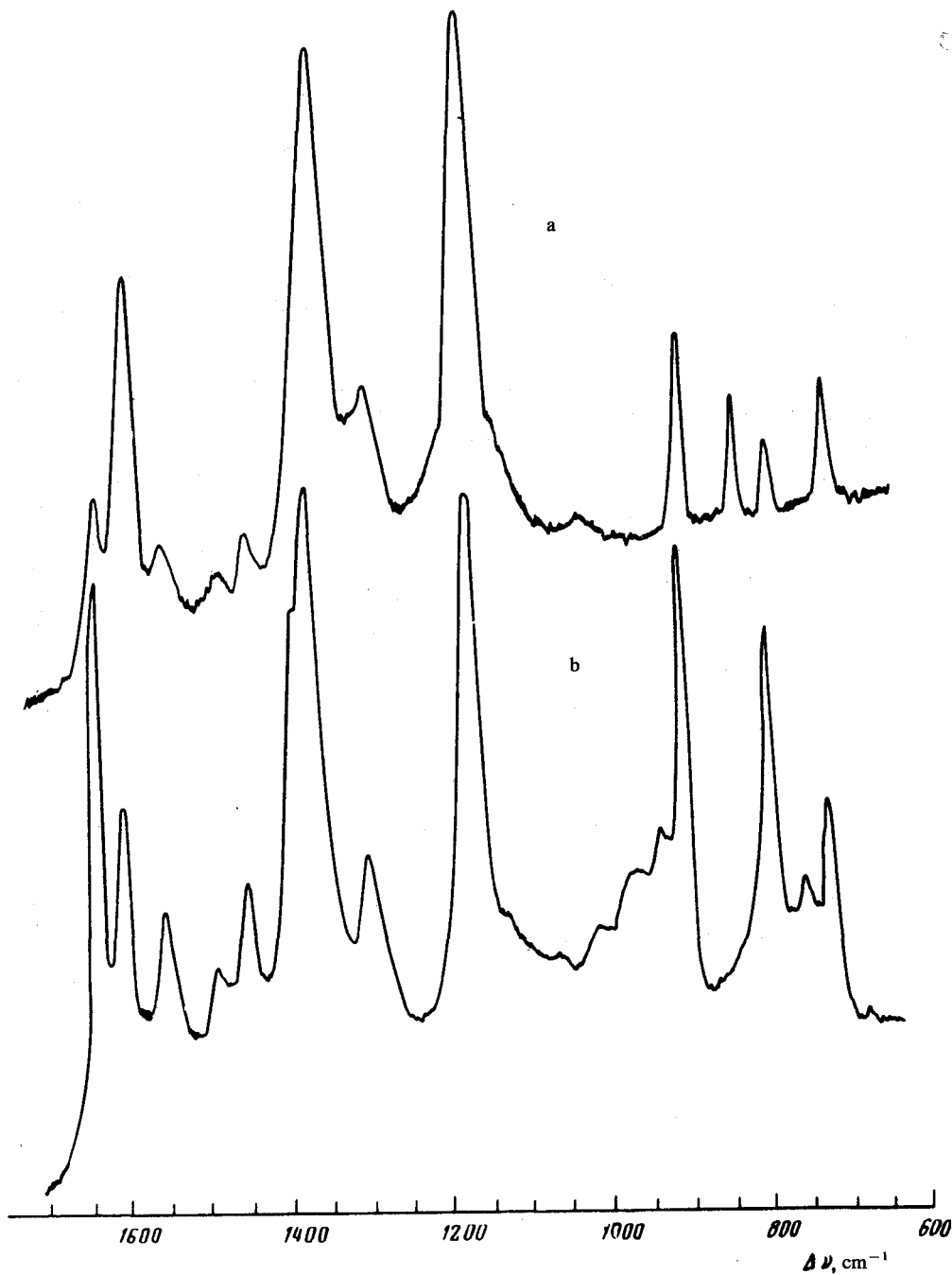


FIG. 2. a—Hyper-Raman spectrum of a crystalline violet dye adsorbed on silver. b—The Raman spectrum of the same system. The conditions are the same as in Fig. 1.

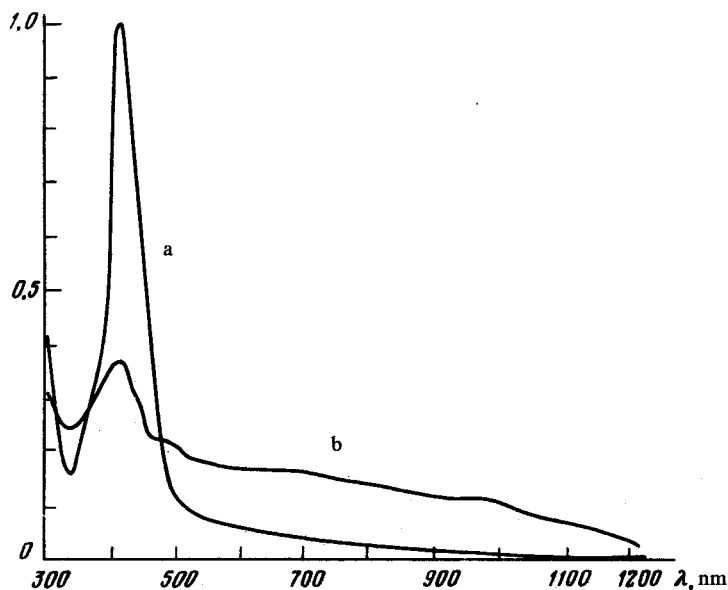


FIG. 3. Absorption spectra. a—The original silver sol. b—The sol with the crystalline violet dye adsorbed on it. $C = 10^{-6}$ M.

orders of magnitude—was observed in the experiments with the crystalline violet dye. In this case the converted light is easily seen with the naked eye. We are not surprised by the similarities in the behavior of the hyper-Raman intensity and the intensity of the 532-nm line, since the underlying processes for these two effects depend in the same way on the sharpness of the double resonances.

We note in conclusion that the number of systems which can be studied could be increased substantially by using more appropriate apparatus, e.g., multichannel detectors,^{6,7} to record the spectra.

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